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Crystal Growth Technology

From Fundamentals and Simulation to Large-scale Production



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Polar bismuth zinc borate, Bi₂ZnB₂O₇, point symmetry group mm2, grown from high temperature solution using Top Seeded Solution Growth (TSSG) method. (Source: M. Burianek and M. Mühlberg; Institute of Crystallography, University of Cologne) All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

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Preface

This volume deals with the technologies of crystal fabrication, crystal characterization and crystal machining. As such it will be of interest to all scientists, engineers and students who are engaged in this wide field of technology. High-quality crystals form the basis of many industries, including telecommunications, information technology, energy technology (both energy saving and renewable energy), lasers and a wide variety of detectors of various parts of the electromagnetic spectrum.

Of the approximately 20,000 tons of crystals produced annually the largest fraction consists of semiconductors such as silicon, gallium arsenide, indium phosphides, germanium, group-III nitrides, cadmium telluride and cadmium mercury telluride. Other large fractions include optical and scintillator crystals and crystals for the watch and jewellery industries.

For most applications these crystals must be machined, i.e. sliced, lapped, polished, etched or surface treated in various ways. These processes are critical to the economic use of these crystals as they are a strong driver of yields of usable material. Improvements are always sought in these various areas for a particular crystal.

This book contains 19 selected reviews from the 'Third International Workshop on Crystal Growth Technology' held in Beatenberg, Switzerland between 10–18 September, 2005. The first in the series 'First International School on Crystal growth Technology' was also in Beatenberg between 5–14 September 1998, while the second in the series was held between 24–29 August 2000 in Mount Zao Resort, Japan. The latter generated a book of 29 selected reviews that was published in 2003 by Wiley, UK entitled 'Crystal Growth Technology' edited by Hans J. Scheel and Tsuguo Fukuda.

Part 1 covers general aspects of crystal growth technology, including thermodynamics, phase diagrams, defects and thermophysical properties of melts. In Part 2 the emphasis is on theoretical modeling of the thermal and liquid/gaseous flows in the growth of both elemental and compound semiconductors, e.g. silicon and gallium arsenide, respectively. Part 3 discusses the growth of several compound semiconductors in more detail. These include gallium arsenide, cadmium mercury telluride and gallium indium antimonide. There is also a chapter on the importance of X-ray

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characterization in these materials. Part 4 covers the growth and applications of a range of halide and oxide crystals, including those grown by the Verneuil technique, which is recognized as the key technology from which most other types of bulk crystal growth are derived. The subject of crystal growth in the energy industries, including energy saving and energy sources is detailed in Part 5. The final section of the book, Part 6, describes the current situation in both crystal slicing and slice machining.

The editors would like to thank all the contributors for their valuable reviews and the sponsors of IWCGT-3. Furthermore, the editors gratefully acknowledge the patience and hard work of the following at Wiley-VCH: Martin Ottmar, Andreas Sendtko, Waltraud Wüst, Nele Denzau and Maike Petersen.

The editors hope that the book will contribute to the scientific development of crystal growth technologies and to the education of future generations of crystal growth engineers and scientists.

Beatenberg, Switzerland and Southampton, UK	Hans J. Scheel
October 2007	Peter Capper

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Ioffe Physical Technical Institute Russian Academy of Sciences Polytechnicheskaya 26 St.-Petersburg 194021 Russia Part I General Aspects of Crystal Growth Technology

Phase Diagrams for Crystal Growth

Manfred Mühlberg

1.1 Introduction

1

The operating abilities of a large part of modern technological hardware (electronic and optic devices, control and operating systems, watches, etc.) is based on active and/or passive crystalline core pieces. For various applications the crystalline state is required to be polycrystalline (ceramics), multigrained (solar cells), crystalline designed (thin film sequences) or single crystalline (semiconductor and NLO devices, CaF₂ lenses, prisms, etc.). The dimension of the crystallites and crystals covers a wide range from <nm> (nanocrystallites) and < μ m> (ceramics, thin-film arrangements) up to <*mm*> and <*cm*> scales (electronics, optics), in special cases up to <m> scale (silicon single crystals, natural ice and quartz crystals).

This chapter is only focused on the growth conditions of so-called single crystals in the dimension of <mm> and <cm> scale. The fabrication of such single crystals is normally connected with the well-established growth methods named after Bridgman, Czochralski, Verneuil or zone melting, top seeded solution growth (TSSG), recrystallization techniques, etc. All these methods can be described by the following definition of crystal growth:

- 1. In growing single crystals, one is primarily concerned with obtaining a crystal of predetermined size with a high degree of structural perfection and a well-determined chemical composition.
- 2. Growth of a single crystal requires the nucleation, subsequent growth, eventual termination of the process and, finally, removal of the crystal from the apparatus.
- 3. The transition into the solid/crystalline state can be realized from the vapor phase, liquids or a polycrystalline solid phase. Liquid phases are melts or high- or low-temperature solutions. The growth from liquid phases plays the most important role.
- 4. Each step of the growth process is affected by controlling the experimental parameters pressure *p*, temperature *T*, and concentration (of components) *x_i*.

3

4 1 Phase Diagrams for Crystal Growth

Paragraphs (1) and (2) are primarily determined by the growth method and optimized technological parameters. Paragraphs (3) and (4) are correlated with some thermodynamic terms: phases, pressure, temperature, and concentration. In a pictorial representation crystal growth means to start in a $p - T - x_i$ phase space at any point p_0 , T_0 , $x_i^{(0)}$. By default, the final point of the growth process is fixed at the normal atmospheric pressure, room temperature and a desired crystal composition. One (i), in some cases two (ii) challenges must be overcome between the starting and final point in the phase space.

- i. A phase transition (of first order) is necessary for the transfer into the solid/crystalline state. They are denoted as sublimation, solidification, precipitation, recrystallization, etc.
- ii. Additionally, one or more phase transitions may exist in the solidified material between the starting and final point. The kinds of solid/solid phase transitions are very varied (Rao and Rao [1]), and the structural quality of the grown crystal is strongly influenced by the type of these phase transitions. Ferroelectric compounds play an important role in several technical applications. For this reason, ferroelectric phase transitions, classified as phase transition of second order, are of special interest in crystal growth. The most important materials undergoing ferroelectric phase transitions are members of the perovskite group (LiNbO₃, BaTiO₃, KNbO₃) and the tetragonal tungsten bronzes (strontium barium niobate (SBN), calcium barium niobate (CBN), potassium lithium niobate (KLN), and potassium titanyl phosphate (KTP =KTiOPO₄).

Phase diagrams represent all these transitions. Consequently, the determination, knowledge and understanding of phase diagrams are one of the essential preconditions for selection and basic application of the growth method and the growth process.

1.2

Thermodynamics and Phase Diagrams

Phase diagrams are the reflection of thermodynamic laws and rules between different phases in the $p - T - x_i$ phase space. The general thermodynamic background is given in textbooks (e.g. [2, 3]). There are also some distinguished overviews (e.g. [4]) and collections of selected phase diagrams (e.g. [5]). The aim of this chapter is to give an overview and understanding of phase diagrams with the dedicated focus to crystal growth. The basic thermodynamic functions and variables are seen as prerequisite and are not included in this chapter (see Chap. 2).

As mentioned above, the crystallization process is a phase transition of first order characterized by a jump of the latent (transition) heat, volume and several physical and chemical properties like heat conductivities, densities etc. The latent heat $\Delta H_{\rm tr}$ must be considered as the first important parameter.

Kind of transformation	Heat of transformation $\Delta H_{tr} [kJ/mole]$	Entropy of transformation $\Delta S_{tr}[\frac{J}{K \cdot mole}]$
solid/solid		
first order	1-(5)	<10
solid/liquid	10 (metals)	10
	10–100 comp.	10-50
liquid/vapor	10-100 (elem.)	10
	> 100 (comp.)	pprox 80

 Table 1.1 Typical values for the heat and entropy of transformation.

In particular, some growth processes from the melt have relatively high growth rates, being influenced by release of the heat of fusion. There are the following relationships between the different kinds of latent heat (legend: s/s – solid/solid; fus – fusion; vap – vapor; sub – sublimation):

$$\Delta H_{\rm s/s} < \Delta H_{\rm fus} < \Delta H_{\rm vap}; \ \Delta H_{\rm sub} = \Delta H_{\rm fus} + \Delta H_{\rm vap}; \ \Delta H_{\rm fus} << \Delta H_{\rm sub}$$
(1.1)

Table 1.1 shows typical values being valid for the heats and entropies of transformation. The latent heats cover a range of two orders of magnitude, and we will see later the distinctive consequences on the kind and appearance of phase diagrams.

1.2.1 One-component Systems

The second important thermodynamic function is the Gibbs free energy G describing the convertible energy amount between two phases. In an equilibrium state between two phases in a one-component system one can write the following approach for the change of the free energy

$$dG_{\rm phase1} = dG_{\rm phase2} \tag{1.2}$$

$$(V_{p2} - V_{p1})dp - (S_{p2} - S_{p1})dT = 0$$
(1.3)

Considering:

$$(S_{p2} - S_{p1}) = \frac{\Delta H_{tr}}{T}; \, \mathrm{d}V\mathrm{d}p - \Delta H_{tr}\frac{\mathrm{d}T}{T} = 0 \tag{1.4}$$

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{\Delta H_{\mathrm{tr}}}{T \cdot \Delta V} \text{ and/or } \frac{\mathrm{d}T}{\mathrm{d}p} = \frac{T \cdot \Delta V}{\Delta H_{\mathrm{tr}}}$$
(1.5)

Equations (1.5), also called the *Clausius–Clapeyron* (CC) equations, describe the temperature dependence of the vapor pressure and the dependence of the vapor pressure on the (melting) temperature, respectively. The consequences can be seen

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Fig. 1.1 Ideal (top left) and real (SiO₂ [2], top right) one-component system. DTA plot of the α - β quartz phase transition.

at a simple one-component phase diagram, which can be articulated completely by the CC equation.

For a solid/liquid phase transition the steepness of dp/dT can be greater or less than zero caused by a positive or negative volume difference between the two phases. In most cases, these differences are positive, i.e. the volume of the liquid phase is greater than the volume of the solid state (see top left image in Fig. 1.1). Furthermore, ΔV is very small for solid/liquid and solid/solid transitions, and the pressure dependence on the melting point is also very small, typically in the range of 10^{-3} K/bar. Additionally, a differential thermal analysis (DTA) plot of the well-known $\alpha \leftrightarrow \beta$ quartz transition is given in the top right picture of Fig. 1.1. The plot displays a heat effect for this transition being typical for phase transitions of first order. On the other side, the $\alpha \leftrightarrow \beta$ quartz transition can be specified using the Landau theory by a typical phase transition of second order. The rotation δ of the SiO₂ tetrahedrons between 16 °C (at room temperature) and 0 °C (at 573 °C) is the order parameter and satisfies the classical rule $\delta \sim (T - T_{tr})^{1/2}$. Table 1.2 shows some examples for a positive and/or negative slope of the solid/liquid transition.

^d π/dp(K/bar)	$s\leftrightarrows$	s ↔ l	l ↔ v
Ag		$+4 \times 10^{-3}$	
H ₂ O		$-8 imes10^{-3}$	28.01
CdSe		$-0.2 imes 10^{-3}$	
HgTe		$+4.5 \times 10^{-3}$	
$\alpha \leftrightarrow \beta$ Quartz	0.021		
α = Quartz. \leftrightarrow Tridymite	0.620		

Table 1.2 Slope of dT/dp for the types of phase transitions: solid/solid, solid/liquid and liquid/vapor.

For transitions from a condensed phase into the vapor phase (the vapor phase is assumed to be perfect: $V_v - V_{cond} \approx V_v = R \cdot T/p$) the solution of the CC equation results in

$$p = p_0 \cdot \exp\left(\frac{\Delta H_{\rm tr}}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \tag{1.6}$$

The one-component system can be easily expanded by Raoult's and van't Hoff's laws if it is diluted. These laws describe that a low solute composition x_B reduces the freezing point of a solid phase and the partial pressure over a liquid phase (see Fig. 1.2).

Raoult's law:
$$p_{\rm s} = (1 - x_{\rm B}) \cdot p_{0(\rm A)}$$
 (1.7)

van't Hoff equations:

boiling point elevation :
$$\frac{\Delta T}{T_{\rm v}} = x_{\rm B} \cdot \frac{RT_{\rm v}}{\Delta H_{\rm v}}$$
 (1.8)

freezing point depression :
$$\frac{\Delta T}{T_{\rm m}} = -x_{\rm B} \cdot \frac{RT_{\rm m}}{\Delta H_{\rm f}}$$
 (1.9)

Equation (1.9) is useful to derive solubility curves from limited solubility data.

1.2.2 Multicomponent Systems

For a multicomponent system Eqs. (1.2) and (1.3) can be primary extended by a term describing the composition influence of the participated components $x_{A,B,C,...}$. The thermodynamic activity of any component (e. g. A) is expressed by the chemical potential $\mu_A{}^i = \mu_A{}^{i(0)} + R \cdot T \ln x_A{}^{(i)}$; *i* corresponds to solid or liquid or vapor. The chemical potential can be understood in terms of the Gibbs free energy per mole of substance, and it demonstrates the decreasing influence of a pure element or a compound in a diluted system. If any pure component is diluted then the term $R \cdot T \ln x_A{}^{(i)}$ will always take values lower than zero (note, that only an ideal solution behavior is considered by the mole fraction x_A . For real cases the so-called activity

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Fig. 1.2 Extension of a one-component system by adding a solute; $p_s - va$ -por pressure over a dilute solution; $p_{o(A)} - vapor$ pressure of the pure solvent A; $x_B \Delta$ mole fraction of an impurity; T_v , $T_m -$

boiling point, melting point; $\Delta T = T - T_v$; $\Delta T = T - T_m$ – absolute boiling point elevation or freezing point depression; ΔH_v , ΔH_f – heat of vaporization, heat of fusion.



Fig. 1.3 The chemical potential of a pure component is reduced in a binary system; it is also a function of temperature; μ_A^0 is the chemical potential of the pure compound A.

 $a_A = f_A \cdot x_A$ must be used. The activity coefficient f_A collects all deviations from an ideal solution behavior). Figure 1.3 shows the reducing influence in a diluted solution as a function of the temperature.

Accepting that all processes have to be discussed in a $p - T - x_i$ phase space, Eq. (1.10) describes the complete change d*G* of the free energy of a multicomponent system.

$$dG = Vdp - \underbrace{SdT + \sum_{i=1}^{n} \mu_i dx_i}_{T-x_i \text{ phase diagrams}} + d\gamma_{\text{surf}} + (..) d\varepsilon_{\text{elast}}$$
(1.10)

For many processes the vapor pressure can be neglected and also the last two terms must only be considered for small particles (surface influence) or nucleation inside of a solid phase (elastic strain). They can be neglected for any bulk growth processes from the liquid or vapor phase. These assumptions are the basis for the presentation of the technical important T - x phase diagrams. Equation (1.10) is reduced for the case of a two-component system A–B to

$$dG = Vdp - SdT + x_A d\mu_A + x_B d\mu_B$$
(1.11)

Using the chemical potential as the "partial molar Gibbs free energy" in Eq. (1.12) and accepting that many processes are running at a nearly constant pressure (p = const.; dp = 0) one can rewrite Eq. (1.12) to Eq. (1.13) for a two component system A–B in solid(s)/liquid(l) equilibrium

$$d\overline{G}_{A}^{s} = d\overline{G}_{A}^{1} \quad d\overline{G}_{A} = \frac{dG}{dx_{A}}$$
(1.12)

$$-(\overline{S}_{A}^{s} - \overline{S}_{A}^{1})dT + RT \cdot d\ln \frac{x_{A}^{s}}{x_{A}^{1}} = 0$$
(1.13)

Replacing $-(\overline{S}_{A}^{s} - \overline{S}_{A}^{1})$ by $\frac{\Delta H_{fus}}{T}$ and integrating Eq. (1.13) gives the final expression for an ideal binary phase diagram of a solid solution system A–B. This equation is also indicated as the van Laar equation for a two-component system A–B [3].

$$ln\frac{x_{\rm A}^{\rm s}}{x_{\rm A}^{\rm l}} - ln\frac{x_{\rm B}^{\rm s}}{x_{\rm B}^{\rm l}} = \frac{\Delta H_{\rm A}}{RT} \left(1 - \frac{T}{T_{\rm A}}\right) - \frac{\Delta H_{\rm B}}{RT} \left(1 - \frac{T}{T_{\rm B}}\right)$$
(1.14)

The van Laar equation is only determined by the two melting points T_A , T_B and the heats of fusion ΔH_A , ΔH_B of the end members A and B. Their influence on the shape of a solid solution system can easily be shown on a PC if the equation is converted in parametric functions [Eqs. (1.15) and (1.16)] and calculated by any data and function plotting utility (e.g. Gnuplot [6], see Fig. 1.4).

Equations (1.15) and (1.16) illustrate the parametric function for the solidus and liquidus curve

$$x_{\rm B}^{\rm s} = \frac{\exp\left\{\frac{\Delta H_{\rm A}}{R}\left(\frac{1}{T} - \frac{1}{T_{\rm A}}\right)\right\} - 1}{\exp\left\{\frac{\Delta H_{\rm A}}{R}\left(\frac{1}{T} - \frac{1}{T_{\rm A}}\right) - \frac{\Delta H_{\rm B}}{R}\left(\frac{1}{T} - \frac{1}{T_{\rm B}}\right)\right\} - 1}$$
(1.15)





Fig. 1.4 Application of the van Laar equation to a solid/liquid and a solid(α)/solid(β) with random, but typical values.

$$x_{\rm B}^{\rm l} = \frac{\exp\left\{\frac{\Delta H_{\rm A}}{R}\left(\frac{1}{T} - \frac{1}{T_{\rm A}}\right)\right\} - 1}{\exp\left\{\frac{\Delta H_{\rm A}}{R}\left(\frac{1}{T} - \frac{1}{T_{\rm A}}\right)\right\} - \exp\left\{\frac{\Delta H_{\rm B}}{R}\left(\frac{1}{T} - \frac{1}{T_{\rm B}}\right)\right\}}$$
(1.16)

Examples for a binary complete solid solution system for the a) solid \Leftrightarrow liquid transition: (with $\Delta H^{f}{}_{A} = \Delta H^{f}{}_{B} = 50 \text{ kJ/mole}$, and for melting points: $T_{A} = 1000 \text{ K}$; $T_{B} = 1400 \text{ K}$) and for b) $\alpha \leftrightarrow \beta$ phase transition: (with $\Delta H^{tr}{}_{A} = \Delta H^{tr}{}_{B} = 1.5 \text{ kJ/mole}$ transition temperatures: $T_{A} = 500 \text{ K}$; $T_{B} = 900 \text{ K}$) are given in Fig. 1.4.

It can be seen in Fig. 1.5 that the higher the heats of fusion the broader the width between the liquidus and solidus lines of an ideal system. Furthermore, the difference between the heats of fusion determines the asymmetric shape of the phase diagram. In Section 1.3.1 the consequences of the shape of the solid solution phase diagrams on the segregation behavior in normal freezing growth processes will be discussed.

The extension to real cases and eutectic systems can be carried out in an analogous manner and is described by Kubaschewski and Alcock [7].

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Fig. 1.5 Influence of the heat of fusion on the design of solid solution phase diagrams; calculated by Eqs. (1.15) and (1.16).

1.2.3 Gibbs Phase Rule and Phase Diagrams

The main key for the understanding of phase diagrams is the phase rule of William Gibbs (1876)

$$P + F = C + 2$$
 (1.17)

where *P* is the number of phases, *C* is the number of components in the system, and *F* is the number of freedom, or variance. The definition for the combined terms are: *P* – any part of a system that is physically homogeneous within itself and bounded by a surface; component *C* – smallest number of independently variable chemical constituents and degree of freedom – smallest number of intensive variables (e.g. *p*, *T*, *x*_i of components in each phase) that must be specified to completely describe the state of the system.

Phase diagrams are the graphical representations of the phase rule, and they are classified by the number of components as follows: one-, two-, three-, ... component systems. On the other side, the phase rule is the most important tool for verifying phase diagrams. If pressure is omitted as a variable, the number of variables in a system is two: temperature and composition. The phase rule reduces to F = C - P + 1 and in this form is referred to as the condensed phase rule or phase rule for condensed systems. As an example, let us discuss the application of the phase rule on a simple three-component system A–B–C with one compound BC.

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Fig. 1.6 Application of the Gibbs phase rule on three special points in a simple three-component system. The phase diagram was taken from [2].

If at least one phase exists then there is a four-dimensional phase space determined by the variables: p, T, x_A , x_B . As an illustration, we have to reduce the dimension of the phase space. In the first step a constant pressure is assumed and the phase space is reduced to a trihedral prism with the coordinates T, x_A , x_B . Normally, the projection onto this trihedral prism is used for printing processes. Figure 1.6 and the legend give the explanation for the relationship between the number of phases and the number of freedom.

```
P = 1 \rightarrow F = 4 \ p, T, x_A, x_B \text{ phase space}
P = 1 \rightarrow F = 3 \ T, x_A, x_B \text{ phase space, if } p = \text{const.}
P = 2 \rightarrow F = 2 \ BC_{\text{sol.}} + \text{melt}(\oplus)
P = 3 \rightarrow F = 1 \ (A + BC)_{\text{sol.}} + \text{melt}(O)
P = 4 \rightarrow F = 1 \ (A + B + BC)_{\text{sol.}} + \text{melt}(\Delta)
```

There are several violations of the phase rule resulting in incorrect description of phase relationships. Instructive examples of such thermodynamically impossible



Fig. 1.7 Fictive binary phase diagram with several violations, after Okamoto und Massalski [8].

situations were given by Okamoto and Massalski [8] expressed by a fictive binary phase diagram (points A–T in Fig. 1.7).

1.3 Phase Diagrams vs. Crystal Growth from Liquid Phases

This section will describe some special problems, violations and handicaps of crystal growth associated with different types of phase diagrams. Growth of bulk crystals from the liquid state plays a dominant role for many technical applications and also in basic research. For this reason, the section is focused on growth processes from the melt, from high-temperature solutions and from aqueous solutions. The variable *pressure* cannot be neglected, but it is accepted to have little influence for many material systems, also at elevated temperature.

Figure 1.8 in combination with Table 1.3 shows basic types of binary phase diagrams being responsible for the mentioned growth processes. Some material systems will be selected and discussed in more detail.

Only one type has the identical composition of the melt and the solid crystalline phase at a congruent melting composition/point. This point corresponds to a distribution coefficient $k_0 = 1$, and it is the best condition for growth from a liquid phase. An equilibrium between the solid and liquid phase in all other cases is characterized by a composition difference and consequently the existence of

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Fig. 1.8 Important phase diagram types being relevant for crystal growth from the melt and from solution.

Table	1.3	The	four	main	types	of th	e liquid	/solid	transition
being	im	porta	nt fo	r crys	tal gro	wth.			

Solid-solution system	Congruent melting	 Incongruent melting nonstoich. melt HT – solutions 	 Eutectic system phase transition T_m lowering pressure lowering
Bridgman method Czochralski method (Si,Ge) (Hg,Cd)Te (Sr,Ba)NB ₂ O ₆ segregation!!	Czochralski method Bridgman method GaAs, InP LiNbO ₃ , SrTiO ₃ garnets (e.g. YAG) preferable	TSSG, THM solution growth KNbO ₃ KTiOPO ₄ (KTP) garnet (YIG) inclusions!!	TSSG, THM solution growth BaTiO ₃ β – BaB ₂ O ₄ (BBO) inclusions!!

distribution coefficients not equal to unity. Segregation of the components and capture of solvent are the main problems for growth from solutions. Inclusions are a form of growth instability that in the case of growth from melts can be prevented by high purity and by an appropriate temperature gradient at the growth front defined by the constitutional supercooling criterion. In growth from solutions, inclusions of solvent can be prevented by applying a growth rate below the maximum stable growth rate that can be derived from the phase diagram (concentration, solubility curve) as discussed in Chapter 6 of Elwell and Scheel [9]. Forced convection along the growth interface reduces the diffusion boundary layer, and thus allows to increase stable growth rates. Furthermore, the seeding of the growth process is complicated in these cases. The precise knowledge of the liquidus curve is required in order to avoid either spontaneous crystallization or dissolving of the seed crystal. For this reason, any crystal growth laboratory should closely cooperate with a laboratory for thermal analysis. Also, the reinvestigation of known and published phase diagrams is necessary in many cases. Figure 1.9 shows an example of considerable differences between published data and the reinvestigated phase diagram.



Fig. 1.9 Phase diagrams of the Bi-rich side of the system $Bi_2O_3-B_2O_3$. Original data were taken by Levin and Mc-Daniel [10]. *This work* means the paper of Burianek and Muehlberg [11]. The intention of this investigation was to find suitable conditions for

growth of the sillenite-type $Bi_{24}B_2O_{39}$. The precise composition of this sillenite was revised in a subsequent paper to be $Bi_{24,5}BO_{38,25}$ [12]. See text for further details of the crystal growth of this compound.

1.3.1 Solid-solution Systems

Segregation is always included in crystal growth of solid solution systems from the melt. The Bridgman and (in parts) the Czochalski method are termed *normal freezing* methods, i.e. the whole melt volume will be transferred into the solid state. In this well-arranged case the distribution function is described by the so-called Pfann/Scheil equation. A complete mixing of the melt at each time is assumed to exist for the derivation of this equation

$$x_{\rm s} = k_{\rm o} \cdot x_{\rm o} \, \left(1 - \frac{z}{L}\right)^{k_{\rm o} - 1} \tag{1.18}$$

with x_s – crystal composition, x_o – starting melt composition, k_o – (nearly equilibrium) distribution coefficient, z – current axial position, L – total length of the crystal.

The distribution situation for $k_o < 1$ and $k_o >$ should be known and is given in textbooks with respect to crystal growth. A nearly complete mixing at reduced growth velocities can be realized in many growth processes and the simplified conditions were very well reflected by Eq. (1.18).

A common problem in growth of solid solution crystals are striations, i.e. growth bands with varying concentrations. Striations are caused by temperature fluctuations, not by hydrodynamic fluctuations in a system of homogeneous temperature (Scheel and Swendsen [13], Scheel [14]). For the example of $KTa_{1-x}Nb_xO_3$



Fig. 1.10 Axial distribution in a $Hg_{1-x}Cd_xTe$ crystal grown by the Bridgman method; $x_o = 25$ mole fraction CdTe, $\nu = 0.33$ mm/h, total length *L* of the crystal: 85 mm.

(KTN) Rytz and Scheel [15] have derived from the phase diagram the theoretical requirements of precise temperature control and forced convection to homogenize the high-temperature solution in order to achieve striation-free KTN crystals.

Considerable deviations from the ideal behavior expressed by Eq. (1.18) can be seen in growth of the complete solid solution system (Hg,Cd)Te. This system shows a remarkable separation between the solidus and liquidus curve [16]. Figure 1.10 shows the axial segregation curve for a Bridgman-grown Hg_{1-x}Cd_xTe crystal. The curve can be classified into three parts: a) the first-to-freeze region has an abnormal course caused by spontaneous crystallization of the undercooled tip region in the ampoule. If low axial temperature gradients \approx 10 K/cm and very pure (semiconducting) materials are used then an undercooling of several centimeter is developed followed by a breaking down, abnormal segregation curve and a multigrained tip region [17]. b) + c) $k_0 \approx 3$ and $k_0 \approx 2$ region: because the splitting up of the liquidus and solidus curve, the values for k_0 are not constant during the entire growth process.

1.3.2

Materials with a Congruently Melting Composition

A materials system with a congruently melting composition is particularly suitable for crystal growth from the melt. Thus, only elements (e.g. silicon) or compounds with a congruently melting composition can be grown as large crystals for important technical applications. Note that for thermodynamic reasons, the exact congruently melting composition of compounds is not identical with its stoichiometric composition. There are deviations within the stability regions between nearly 0 and about 2 mole fraction. Figure 1.11 shows the simple binary phase diagram Pb–Te. PbTe crystallizing in the sodium chloride structure is the only



Fig. 1.11 Phase diagram of the binary system Pb–Te and stability region of PbTe (left). Te precipitations in PbTe made visible by transmission electron microscopy (right) [19].

compound in this system. The stability region of PbTe covers the stoichiometric line and has been well investigated by Hall effect measurements of annealed and quenched samples. Deviations up to $10^{19} \,\mathrm{cm^{-3}}$ can be easily detected because this level is about three orders of magnitude higher than the impurity level of the used 6N materials (impurity level corresponds to about $10^{16} \,\mathrm{cm^{-3}}$). All stability regions show a retrograde solubility. The retrograde solubility is responsible for formation of precipitates during the cooling process of a grown crystal. The right image in Fig. 1.11 shows small Te precipitations in PbTe detected by transmission electron microscopy and identified by electron diffraction and Moiré fringes.

An excellent introduction into the thermochemistry of nonstoichiometric compounds was given by Albers and Haas [18].

1.3.3 Materials with an Incongruently Melting Composition

A distinctive feature in crystal growth of these materials is the composition difference between the liquid and solid phase, especially at the growing interface. The two right phase diagram types in Fig. 1.8 describe the crystal growth from high- or low-temperature solutions or from nonstoichiometric melts. Growth processes are characterized by a slow lowering of the temperature in order to force the crystallization. The mentioned phase diagram types in Fig. 1.8 allow growth of materials with incongruently melting compositions and materials with a solid/solid phase transition. Furthermore, the application of a suitable solvent or nonstoichiometric composition is capable of reducing a high growth temperature or pressure, so that growth close to thermal equilibrium may yield crystals with a high structural perfection. As am example, SrTiO₃ can be mentioned that has been grown from the melt (Verneuil method), by top-seeded solution growth (TSSG), and at the lowest temperature from a Sr-Li-borate flux (Scheel *et al.* [20]). The measured dislocation densities of $10^6 - 10^7$, $10^1 - 10^2$, and $0 - 10^2$ cm⁻², respectively,

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demonstrate the improved structural perfection at decreasing growth temperature. Adverse aspects are the low growth rate (\approx grams per day) and the low crystal yield, especially if the slope $\frac{\Delta T}{\Delta x}$ of the liquidus curve is large. Concerning the solvent, there are several requirements (see also Chapter 3 of Elwell and Scheel [9]): high solubility of the component of interest, no (or low) chemical reactivity between material and solvent, low vapor pressure, minor differences in heat conductivity between the material and the solvent, easily removed after the growth process, high purity, and low toxicity. In growth from high-temperature solutions the so-called *top-seeded solution growth* (TSSG) method is widely used. Figure 1.12 shows three examples of single crystals grown by the TSSG method. Note the well-defined crystallographic equilibrium faces. As mentioned above, only a limited part of a solution can be transferred into the solid state depending on the phase diagram. It is shown from Fig. 1.13 that the growth is practicable in the range $\Delta x_0 = x_e - x_0$. The obtainable crystal size V_{cr} is a function of the steepness of the liquidus curve and the inserted solution charge V_{ch} . The relative crystal yield described





(a)







Fig. 1.12 Three examples for crystal growth from solution: Boron-sillenite $Bi_{24}B_2O_{39}$ (PSG: 23) [15] (top left), $Bi_2ZnB_2O_7$ (PSG: *mm2*) [unpublished], $Bi_2Ga_4O_9$ (PSG: *mmm*) [22] (bottom).



Fig. 1.13 Phase diagram of an incongruently melting compound x_c and representation of the limited yield of crystal size at growth from solution.

by the ratio $\left(\frac{V_{cr}}{V_{ch}}\right)^*$ can be estimated by a balance equation (see right image in Fig. 1.13)

$$(x_{\rm o} - x_{\rm c}) \cdot \left(\frac{V_{\rm cr}}{V_{\rm ch}}\right)^* = (x_{\rm e} - x_{\rm o}) \cdot \left[1 - \left(\frac{V_{\rm cr}}{V_{\rm ch}}\right)^*\right]$$
(1.19)

to be:

$$\left(\frac{V_{\rm cr}}{V_{\rm ch}}\right)^* \approx \frac{x_{\rm e} - x_{\rm o}}{x_{\rm e} - x_{\rm c}} = \frac{\Delta x_{\rm o}}{x_{\rm e} - x_{\rm c}}$$
(1.20)

An estimation of the relative crystal size is based on the corresponding phase diagrams. Using these equations the yields $\left(\frac{V_{cr}}{V_{ch}}\right)^*$ represent for KNbO₃ 94%, for BaTiO₃ 18% and for Bi₂Al₄O₉ 7% (!). Crystal growth of ZnSe from a SnSe solution zone by the traveling heater method (THM) is an example of using a suitable solvent [23], see Fig. 1.14. ZnSe is a high-melting semiconducting compound with a melting point at about 1525 °C. Since the application of silica ampoules is limited up to about 1200 $^{\circ}$ C, the solvent for ZnSe should be an end member of a eutectic system with a eutectic line clearly below 1200 °C. SnSe melts at about 900 °C and the eutectic line is at about 850 °C. If no detailed data are available then the rule of Kordes [24] may be helpful for proposing an approximate phase diagram. This rule states in a eutectic system that the higher the difference between the melting temperatures of the end members the narrower the eutectic composition is located at the end member with the lowest melting temperature. Figure 1.15 shows a simple eutectic system, and on the right side some examples for the validity of the rule of Kordes if a linear relationship of this rule is fitted. The rule is very well fulfilled by the quasibinary system ZnSe–SnSe (see Fig. 1.15, left). Assuming that two components form a eutectic system and the melting points are known than the eutectic composition can be estimated on the basis of the rule of Kordes. Knowing these three points, the approximate path of the liquidus lines can be found.





Fig. 1.14 The quasibinary phase diagram SnSe–ZnSe and the setup for the traveling heater method (THM). ZnSe single crystal grown by THM and using SnSe as solvent (top right).

1.3.4 Materials with Solid-Solid Phase Transitions

Solid/solid phase transitions restrict the possibilities of successful crystal growth. Depending on the types of phase transitions additional structural defects will be involved in the grown ingot during the cooling process. A phase transition handicap can be avoided if there exists a liquidus line at lower temperatures than the transition temperature. Such a case is demonstrated in the right image of Fig. 1.8. An example is BaTiO₃ showing a congruent melting point at 1618 °C [25]. At 1460 °C there is a phase transition from hexagonal to cubic BaTiO₃.



Fig. 1.15 Simple eutectic system and some examples for the validity of the rule of Kordes.

Successful growth is possible by the TSSG method using a mixture containing an excess of TiO₂. Furthermore, the cubic phase (PSG: *m3m*) is transformed into the ferroelectric tetragonal phase (PSG: *4mm*) at about 120 °C. Additional phase transitions into a orthorhombic (*mm2*) and rhombohedral (*3m*) phase will take place at 9 °C and -90 °C, respectively. Ferroelectric phase transitions are correlated with the formation of domain structures obeying the laws of group theory. Some examples of ferroelectric phase transitions are given in the left image of Fig. 1.16. In many cases the phase transitions "are accepted" by the grown crystal. Single-domain material can be formed by applying a high voltage electric field in such cases like BaTiO₃, KNbO₃ and the ferroelectric tungsten bronzes SBN and CBN. A special situation is given for LiNbO₃. Single-domain LiNbO₃ is produced by applying an electric field during the growth process because the phase transition $\overline{3m} \rightarrow 3m$ is several degrees below the melting temperature.

Cracking or distortion occurs if the thermal expansion is strongly influenced by the phase transition. The bottom left image of Fig. 1.16 shows the anomalous thermal expansion in the [001] and [*hk*0] direction of the tetragonal calcium barium niobate. This material undergoes a ferroelectric phase transition of the type $4/m \ mm \longrightarrow 4mm$ and formation of 180° domain structure. Potassium lithium niobate shows the same transition type characterized by cracking along (*hk*0) faces (see Fig. 1.16, right).

1.3.5 Growth from Aqueous Solution

The widely used crystal growth from aqueous solutions can be described in the same manner as growth from high-temperature solutions. Figure 1.17 shows a common phase diagram of a system H_2O -anhydrous salt. It must be pointed out that in many cases salt compounds exist with different water content in the crystalline structure. Salts with a water content are regarded as discrete *peritectic melting compounds*. Based on the phase diagram type of Fig. 1.17 these compounds




Fig. 1.16 Some ferroelectric compounds and their phase transition types and temperatures. Different thermal expansion of calcium barium niobate in [hk0] and [001] direction. Cracking along (hk0) faces in potassium lithium niobate caused by crossing the phase transition temperature at about 460°C.

can only be grown within a limited temperature region. The higher the growth temperature the lower the water content in the salt. For this reason, only a limited number of compounds can be obtained as anhydrous salt. The right image in Fig. 1.17 shows solubility curves of several salts. It can be seen that in the case of NaI the access to the anhydrous salt is only possible at a temperature higher than about 65 °C. Convenient growth conditions are given if there is a moderate slope dT/dx. Unfortunately, sodium chloride as the most common salt on earth shows a very steep dependence dT/dx, and it is difficult to grow large crystals.



Fig. 1.17 Fictive phase diagram of a system H_2O -salt with several compounds salt $\cdot n H_2O$ (left). Real solubility curves of some salts (right).

1.3.6 No Correlation to Phase Diagrams: Anisotropic Growth

Phase diagrams have only a thermodynamic background, but actual crystal growth is also influenced by crystallographic characteristics, by kinetics, and by technological parameters of the growth method. Materials with a cubic symmetry show isotropic physical properties. Consequently, cubic crystals take an isometric shape and grow with small differences in unequal [hkl] directions as long as crystals are grown in stable growth conditions. Otherwise, unstable growth may lead to dendrites, to platelet growth by the leading-edge growth mechanism (Scheel and Niedermann [26]), or to needles and whiskers. All noncubic materials are characterized by a more or less pronounced anisotropic growth behavior. In all other crystal systems the habit is intermediate between two singularities referred to as plate and needle shaped (see Fig. 1.18). This means that crystals can be elongated parallel to a symmetry dominated axis, e.g. the *c*-axis in the tetragonal, hexagonal and trigonal system or the *b*-axis in the monoclinic system. On the other side, in the case of plate-shaped growth the influence of the symmetry dominated axis is extremely suppressed.

An additional aspect of anisotropic growth is related to crystals with polar structures. In particular, crystals with the point symmetry groups *2*, *3*, *3m*, *4*, *4mm*, *6*, *6mm* can show a ratio in growth velocities along the polar axis up to 10(!).

1.4 Conclusions

Phase diagrams are the complete or partial graphical description of the existence of an element or a compound in the pressure–temperature–composition $(p-T-x_i)$ space. The validity of nearly equilibrium conditions are assumed. The knowledge



Fig. 1.18 The three basic types of growth behaviors and typical examples.

and understanding of phase diagrams are the most important condition both for the selection of the growth principle and the adjusting of several technological parameters. For this reason there are several phase diagram collections and software programs for calculation of phase relationships.

Many published phase diagrams have errors and/or inaccurate data. The thermal analysis (differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetry (TG)) in combination with phase analysis by X-ray diffraction are the main methods for the investigation of phase diagrams in the periphery of a crystal growth lab. Special measurement methods (e.g. Bourdon manometer) are needed for phase analysis if any gaseous state must be considered. Furthermore, the thermomechanical analysis (TMA) is a very sensitive method for detection and characterization of solid/solid phase transitions.

The Gibbs phase rule is the most important tool for checking the correctness of determined phase relations. There are also some additional useful rules like the rule of Kordes for selection of applicable phase diagrams.

In all cases of crystal growth from solution, the precise knowledge of the liquidus curve is necessary because inserting a seed crystal into the solution requires conditions close to the thermal equilibrium. Finally, phase transitions of first, second or higher order can influence successful growth and must be considered in (re)investigations of phase-diagram studies. Note that only a thermodynamic background is reflected by phase diagrams. Actual growth conditions can be markedly influenced by crystallographic characteristics, by kinetics and by technological parameters. More or less anisotropic growth behavior must be expected in materials with lower crystal symmetry.

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2.1 Introduction

In the preface to the "Book of Lecture Notes" to the "3rd International Workshop on Crystal Growth Technology" it is stated that "crystal technology is not widely recognized, there is no curriculum or chair at a technical university for this complex and multidisciplinary field, despite the wish of industries to hire crystal technology engineers and scientists, instead of expensive long-year in-house education and training of scientists with little or no background in crystal technology." This book will contribute to fill this gap.

Crystal growth can be understood as the central part of crystal technology. "Crystal growth" or "crystal production processes" is different from "industrial crystallization". The latter is a unit operation in chemical technology, the aim of which is mostly to separate or purify solids, producing them as crystalline powders. In contrast, crystal production processes are intended to grow single crystals with properties and dimensions that make them usable as individuals for technical purposes. Crystalline solids of highest purity and most perfect structure show typical solid-state effects most distinctly. The desired solid-state property is frequently already achieved and usable in thin crystalline layers; only sometimes large bulk crystals are needed. Growth of epitaxial layers must also be considered as a crystal production process. Consequently, neither volume nor mass is the criterion for "crystal production". The term "crystal production process" shall be used for the growth of crystal individuals of any size or dimensionality that are used for technical products and that are produced according to industrial standards. "Industrial standards" means reproducibility, purity, yield, economy, accordance with certified standards, and so on. The aim of crystal production processes is to produce crystalline solid material not only of a certain chemical composition, modification and purity, but also of high structural perfection and with desired dimensions.

Thermodynamics is one of the pillars of many scientific and technical disciplines, including crystal growth or crystal technology. The question arises if there is a special "thermodynamics of crystal growth"?

The answer is on the one hand "No", because the laws of thermodynamics and the formal apparatus used are universal. On the other hand, one can also answer "Yes", because a special "thermodynamics of crystal-growth technology" can be identified when considering some topics of special importance or characteristics for crystal growth:

- Any crystal-growth process is a phase transition, the final product of which is a crystalline solid.
- Phase diagrams are an important tool in crystal growth.
- Any crystal-growth process leads from a less-ordered to a highly ordered (i.e. lowest entropy) solid phase.
- At least in the nucleation and initial growth phase, surfaces/interfaces play an important role.
- Crystal growth is sustained by intentionally maintaining a deviation from equilibrium (i.e. supersaturation) that provides the driving force for crystal growth.
- The equilibrium shape of crystals may be determined by thermodynamics.
- Point defects largely determine technically important crystal properties and their concentration is largely governed by thermodynamics.

Any crystal-growth system comprises at least two phases, one of which is the crystal, a highly ordered regular solid, while the other one, the "growth medium", "feeding phase", or "nutrient phase", is a less-ordered vapor, liquid or solid. The transition or conversion of matter from the starting phase, characterized by its own set of constant intensive properties, into the final crystalline state is not only a chemical conversion of material and/or a change in the degree of order but it is also associated with the exchange of energy, sometimes also with work, between the different phases of the system and/or with its surroundings. Thermodynamics is that branch of science that deals with the relationships between changes of the macroscopic properties of a system (the state of the system) and heat, work, and other forms of energy that cause or accompany these changes. The word "thermodynamics" is derived from the Greek words "thermos" for "warm, hot" and "dynamis" for "power".

Classical thermodynamics is a macroscopic science, i.e. it is not applicable to systems of molecular or atomic size. It deals with the average changes that occur among large numbers of atoms or molecules and not with the detailed changes that occur in a single molecule, atom or ion.

Classical or *equilibrium thermodynamics* deals with systems in equilibrium. A crystal is in equilibrium with its surroundings when in a certain time interval the number of building blocks that become part of the crystal is equal to the number of growth units that are leaving the crystal. Thus, on a macroscopic scale, in an equilibrium situation the mass of a crystal remains unchanged in time. Consequently, the term crystal *growth* implies inherently that, as long as the crystal increases in mass, equilibrium is not prevailing.

In contrast to sustaining an equilibrium state, crystal growth by human interference is achieved by continuous, intentional distortion of equilibration. "The art of growing crystals is the ability to maintain the supersaturation region, which is metastable from a thermodynamic point of view, over such long periods of time as they are required for the built-up of single crystals" [1]. "A situation is intentionally created where higher than equilibrium pressures drive the system to produce the ... solid desired. The maximum quantity of ... solid that can be produced is simply the amount (the supersaturation) that would establish equilibrium, and is, thus, fundamentally limited by thermodynamics ..." [2].

So, one can ask if equilibrium thermodynamics is applicable at all for crystal-growth processes. The answer is mostly "yes", because most crystal-growth processes need only slight deviations from thermodynamic equilibrium in order to proceed and thermodynamics tells at least whether a certain process is feasible or not. In order to control the crystal-growth process one must know the equilibrium state and how far one is away from it. Equilibrium thermodynamics computations can

- identify or predict the state of equilibrium of a system that initially is not in equilibrium,
- provide the magnitude of driving force for the formation of crystals,
- provide the amount of work or the flow of heat either required or released to accomplish a specified change of state of a system, or, alternatively, predict the change in thermodynamic state that occurs for given heat or work flows,
- reveal usable synthesis paths and conditions,
- identify chemical species occurring in the system, their concentrations and reactions,
- provide the extent of existence regions of phases that are stable under given conditions,
- show the effect of changes in the process variables,
- provide concentrations of species that enter into expressions for the growth kinetics.

This list could be prolonged.

This contribution concentrates on selected topics of classical thermodynamics that appear to be of primary relevance to crystal growth. Besides other topics, phase diagrams and the Gibbs' phase rule are almost completely omitted because they will be dealt with in another contribution. Also, the thermodynamics of point defects had to be ignored for space reasons.

Classical thermodynamics of crystal growth is closely related to chemical and metallurgical thermodynamics. There are numerous excellent textbooks on physical chemistry and on chemical and metallurgical thermodynamics. Different people have different preferences. The author of this contribution grew up with a number

of textbooks and basic papers cited in the list of references [3-14]. Probably, there will be some coincidence with these presentations, but this appears to be unavoidable and should be apologized for.

2.2

Recapitulation of Some Basic Concepts

Although it can be supposed that any crystal grower is familiar with the fundamentals of thermodynamics, some basic concepts shall be recapitulated. The selection is of course subjective, it is, however, based on the experience from teaching students. In this short excursion inevitably some concepts will be simplified to make them "handy". For a more stringent treatment, the reader is advised to consult one of the numerous textbooks available, e.g. reference [3].

The thermodynamic quantity of central importance for crystal growth is the Gibbs free energy *G*. (In German the Gibbs free energy is commonly called "free enthalpy".) It is *defined* as

$$G \equiv H - TS \tag{2.1}$$

where H is the enthalpy (see below), T is the absolute temperature, and S is the entropy. Differentiation gives

$$dG = dH - TdS - SdT$$
(2.2)

The enthalpy H is defined as

$$H \equiv U + PV \tag{2.3}$$

and in differential form as

$$dH = dU + PdV + VdP \tag{2.4}$$

P and *V* are the pressure and the volume, respectively.

For condensed phases (solids and liquids) the *PV* term is usually very small in comparison to *U*, that is $H \approx U$.

When heat is absorbed in a constant-pressure process by a closed system that can do PV work only this energy supply is used for increasing the internal energy of the system and for doing work w that is given up from the system by increasing its volume against the surroundings:

$$dq = dU - dw = dU + PdV$$
(2.5)

or

$$\mathrm{d}U = \mathrm{d}q - P\mathrm{d}V \tag{2.6}$$

In this equation the heat flow d*q* is related to the entropy change d*S* by

$$dq = TdS \tag{2.7}$$

Substitution of Eq. (2.6) into Eq. (2.4) and of Eq. (2.7) into Eq. (2.6) gives

$$dH = dq - PdV + PdV + VdP = TdS + VdP$$
(2.8)

Now, substitution of the latter expression for the free energy into Eq. (2.2) for the change in free energy leads to

$$dG = VdP - SdT \tag{2.9}$$

This is the change in free energy that a closed system of fixed size and composition, i.e. a system containing a fixed number of moles of one component only, experiences.

Returning to Eq. (2.1), the Gibbs free energy combines the enthalpy H and the entropy S in one quantity. Each of the two terms reflects an important tendency that, however, counteract when a crystal is grown:

Crystallization is a phase change proceeding usually from a less-dense state to a denser one. The highest density of the solid, in comparison with the same material in its gaseous or liquid state, mirrors the fact that in a solid the constituting atoms or molecules have the largest number of nearest neighbors and are closest to each other. For all kinds of chemical (or physical) bonding, energy is released when the building blocks approach each other up to their equilibrium distances. In this process the latent heat of crystallization, ΔH_{cryst} , is released, i.e. the enthalpy change associated with crystallization has a negative sign and will consequently reduce the free energy of the system.

On the other hand, the crystalline state is that of highest order. The higher the degree of order, the lower is the entropy. In a statistical interpretation the entropy is expressed by

$$S = k \ln \Omega \tag{2.10}$$

where Ω is the number of distinguishable microstates for a system of fixed composition, volume and internal energy. The more perfect the solid is, the lower is the number of distinguishable microstates. The perfect crystal has the lowest entropy. The second law of thermodynamics says that spontaneous processes proceed always in the way that the entropy increases. But this holds only for isolated systems without exchange of matter or energy with its surroundings. In crystal growth, however, we are nearly exclusively dealing with closed (not isolated) systems, where no matter, but energy can be exchanged with its surroundings.

The deciding quantity for a process to take place or not is the change in Gibbs free energy *G*. The necessary criterion for any phase transition is

$$\Delta G = G_2 - G_1 < 0 \tag{2.11}$$

i.e. the free energy of the system in its final state is lower than that in its initial one. G_1 and G_2 are the free energies of the initial and the final states, respectively. Any transformation that results in a decrease in free energy is possible. The transformation needs not go directly to the stable equilibrium state but can pass through a whole series of intermediate metastable states.

Crystals grow as long as the free energy of the system decreases with crystal formation. From the definition of the Gibbs free energy, the entropy term counteracts against crystallization, because in any case $\Delta S_{\text{cryst}} = (S_{(\text{cryst})} - S_{(\alpha)}) < 0$, where α denotes a phase different from the crystalline one. Therefore, by crystallization the term $-T\Delta S_{\text{cryst}}$ becomes positive, thus leading to an increase in free energy. This is compensated by the exothermic nature of crystallization, i.e. $\Delta H_{\text{cryst}} =$ $(H_{(\text{cryst})} - H_{(\alpha)}) < 0$, the release of enthalpy, when the building blocks combine to form a crystal. Thus, the state with the highest stability will be that with the best compromise between low enthalpy and high entropy. At low temperatures solid phases are most stable since they have the strongest atomic binding and therefore the lowest internal energy (enthalpy). The gain in energy is eventually the reason why a solid is formed as a crystal and not in amorphous form.

At high temperatures, however, the -TS term dominates and phases with more freedom of atom movement, liquids and gases, become most stable.

Extending these considerations to multicomponent systems and systems with a large surface to volume ratio, the free energy must be expressed as a function of pressure P, temperature T, mole number n and surface area A:

$$G = f(P, T, n_i, n_j, \dots, A)$$
 (2.12)

or in differential form

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,\dots,A} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,\dots,A} dT + \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\dots,A} dn_i + \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_i,\dots,A} dn_j + \dots + \left(\frac{\partial G}{\partial A}\right)_{P,T,n_i,n_j,\dots} dA$$
(2.13)

The contribution of the surface/interface can be neglected in most cases. However, it plays an important role when the bulk volume of the crystalline phase is small. This is the case in the initial phase of crystal formation or when a thin (epitaxial) crystalline layer is formed. In the latter case besides the energy of free or unstrained interfaces the elastic strain imposed by coherent intergrowth with the substrate of different lattice constant also provides a contribution to the total energy balance that can not be neglected.

 n_i , n_j , n_k are the numbers of moles of the species i, j, k, ... present in the system. If the mole numbers of the various species remain constant during the process and the contribution of surfaces and interfaces can be neglected, then Eq. (2.13) simplifies to

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,\dots,A} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,\dots,A} dT$$
(2.14)

A comparison between Eqs. (2.14) and (2.9) shows the meanings of the partial derivatives:

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,\dots,A} = V \tag{2.15}$$

and

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,\dots,A} = -S \tag{2.16}$$

The physical meaning of the derivative of free energy with respect to the surface/interface area is a surface free energy or surface tension, commonly denoted by γ_{if} or σ :

$$\left(\frac{\partial G}{\partial A}\right)_{P,T,n_i,n_j,\dots} = \sigma \tag{2.17}$$

Actually, if surface/interface effects have to be taken into account one has frequently to consider several interfaces, between solid and liquid or between solid and vapor, and so on.

If surface/interface contributions can be neglected, than from Eqs. (2.14, 2.15) and (2.16) Eq. (2.13) can be written as

$$dG = VdP - SdT + \sum_{i=1}^{i=k} \left(\frac{dG}{\partial n_i}\right)_{P,T,n_j,\dots} dn_i$$
(2.18)

 $\sum_{i=1}^{i=k} \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\ldots} dn_i \text{ is the sum of contributions to the change of the total free}$ energy caused by changes in the number of moles of the different species $i \dots k_i$ keeping constant P, T and n_i , where n_i is the number of moles of every species other than the *i*th species.

 $\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\dots}$ is the partial molar free enthalpy of species *i* in the multicomponent system. It is called the chemical potential of the species *i* and designated as μ_i :

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\dots} = \overline{G_i} \equiv \mu_i \tag{2.19}$$

The partial molar free energy of a component *i* is equal to the change in the total free energy of the system when one mole of the component i is added to such a volume of the mixture that its composition remains unchanged.

Even for a one-phase, one-component system (molten Si, e.g.) the concept of the chemical potential can be applied. $\overline{G_i}$ should be the molar free energy of pure *i* at the temperature T and the pressure P of the system. The free energy is an extensive quantity, hence the total free energy of a one-component, one-phase system is

$$G = n_i \overline{G_i}(T, P) \tag{2.20}$$

While the free energy G is an extensive variable, the chemical potential, as the ratio between two extensive quantities, is an intensive property.

With the abbreviated writing Eq. (2.18) becomes

$$dG = VdP - SdT + \sum_{i} \mu_{i} dn_{i}$$
(2.21)

This equation is known as the *fundamental equation of chemical thermodynamics*. It can also be considered as the *fundamental equation of the thermodynamics of crystal growth*. It is applied for both (physical) phase and (chemical) reaction equilibria.

Since the state function *G* is a function of *P*,*T*,*n*_{*i*}, *n*_{*j*},... its partial derivative $\left(\frac{\partial G}{\partial n_i}\right)$ is also a function of these variables:

$$\mu_i = \mu_i(P, T, n_i, n_j, \ldots)$$
(2.22)

Equation (2.21) refers to a one-phase system. If the system consists of several phases, its total free energy is the sum of the free energies G^{α} of each of its constituting phases:

$$G = \sum_{\alpha} G^{\alpha}$$
 and $dG = \sum_{\alpha} dG^{\alpha}$ (2.23)

 $\alpha,\,\beta,\,\gamma$ are symbols for the different phases. Correspondingly, for a multiphase system Eq. (2.21) becomes

$$dG = \sum_{\alpha} V^{\alpha} dP - \sum_{\alpha} S^{\alpha} dT + \sum_{\alpha} \sum_{i} \mu_{i}^{\alpha} dn_{i}^{\alpha}$$
(2.24)

where V^{α} and S^{α} are the volume and the entropy of phase α , μ_i^{α} is the chemical potential, and n_i^{α} is the number of moles of component *i* in phase α . Since *V* and *S* are extensive quantities, the sums of the volumes and the entropies of the different phases constitute the total values of the system under consideration. Hence, for a multiphase system in mechanical and thermal equilibrium, which can do *PV* work only, the fundamental equation (2.21) becomes

$$dG = VdP - SdT + \sum_{\alpha} \sum_{i} \mu_{i}^{\alpha} dn_{i}^{\alpha}$$
(2.25)

Now, the chemical potential shall be expressed in practical quantities that are measurable experimental variables.

Remember that the pressure dependence of the free energy (Eq. (2.15)) is

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,\dots,A} = V \tag{2.15}$$

Furthermore, we have

$$\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_j,\dots} = \overline{V}_i \tag{2.26}$$

 $\overline{V_i}$ is the partial molar free volume of the component *i* in a mixture. Its meaning is analogous to that given above for the partial molar free energy, the chemical potential. Combination of Eqs. (2.15) and (2.26) provides

$$\left(\frac{\partial^2 G}{\partial P \partial n_i}\right)_{T,n_j,\dots} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j,\dots} = \overline{V}_i \text{ or } d\mu_i = \overline{V}_i dP$$
(2.27)

In an ideal gas mixture the partial molar volume $\overline{V_i}$ of a component *i* is the same as the molar volume of an ideal pure gas that obeys the ideal gas law, PV = RT. This leads to

$$d\mu_i = RTd\ln P_i \tag{2.28}$$

For a component in an ideal mixture of condensed phases, Dalton's law

$$P_i = x_i P_{\text{tot}} \tag{2.29}$$

can be used to substitute the less convenient partial pressure P_i by the mole fraction x_i of component *i*. Thus, at a total pressure $P_{tot} = 1$ bar the chemical potential of a component *i* in an ideal mixture is defined as

$$d\mu_i = RT d\ln x_i \tag{2.30}$$

In an ideal mixture the interactions between the atoms or molecules of all the constituents are energetically equal. This is an idealization that is useful for the general understanding, but only seldom fulfilled. Nevertheless, frequently proportionality between the size of a certain quantity and the concentration, as for example given by Eq. (2.30) for the chemical potential, does exist. A useful approach for preserving the general form of the proportionality to the concentration but taking into account deviations from the ideal behavior is the substitution of the concentration by the "activity", i.e. an "operative concentration".

The activity a_i is given as the product of an activity coefficient γ_i and the concentration x_i :

$$a_i = \gamma_i x_i \tag{2.31}$$

The activity coefficient can be found as an empirical, experimentally determined factor. However, there exist numerous more or less sophisticated theoretical models and expressions. We will come back to this point later in the section on solution growth.

Thus, we have now two expressions for the chemical potential of a component *i* in an ideal mixture

$$d\mu_{i(\text{ideal})} = RTd\ln x_i \tag{2.30}$$

and in a nonideal mixture

 $d\mu_{i(real)} = RTd\ln(\gamma_i x_i) = RTd\ln a_i$ (2.32)

This reads in integrated form as

$$\mu_i = \mu_i^{\rm o} + RT \ln x_i \tag{2.33}$$

and

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{2.34}$$

The integration constant μ_i° , the so-called chemical standard potential, is the partial molar free energy at a pressure *P* = 1 bar, temperature *T* and at an activity of unity. In an ideal mixture the activity coefficient is unity, so that the aforementioned definition holds for both real and ideal mixtures.

Now we can combine the results so far briefly deduced into one equation for the free energy of a system, only omitting the surface/interface contribution:

$$dG = VdP - SdT + \sum_{\alpha} \sum_{i} RTd\ln a_{i}^{\alpha}$$
(2.35)

Enthalpy, entropy and the Gibbs free energy are temperature dependent. The temperature coefficient of the enthalpy is the molar heat capacity (or specific heat if it is not related to one mole, but to a mass). The molar heat capacity is the quantity of heat (in Joules) required to raise the temperature of one mole of the substance by one degree Kelvin. In crystal growth usually one needs its value at constant pressure. It is denoted by C_p and is given by

$$C_{\rm p} = \left(\frac{\partial H}{\partial T}\right)_{\rm p} \tag{2.36}$$

The variation of *H* with *T* can then be calculated by integrating Eq. (2.36), i.e.

$$H(T) = H_{298}^{o} + \int_{298}^{T} C_{p} dT$$
(2.37)

In considering phase transformations or chemical reactions, only *changes* in thermodynamic functions are of interest. Consequently, *H* can be measured relative to any reference level. This is usually done by *defining* $H_{298}^{o} = 0$ for a pure element in its most stable modification at 298 K (25 °C). For a compound, H_{298}^{o} is taken as the standard heat of formation of one mole of this compound from its elemental constituents in their standard states.

The variation of entropy with temperature can also be expressed using the specific heat capacity C_P . From classical thermodynamics

$$\frac{C_{\rm p}}{T} = \left(\frac{\partial S}{\partial T}\right)_{\rm p} \tag{2.38}$$

Taking the entropy at zero Kelvin as zero $(3^{rd}$ law of thermodynamics), Eq. (2.38) can be integrated to give

$$S = \int_0^T \frac{C_p}{T} dT$$
(2.39)

Finally, the variation of *G* with temperature is given by temperature dependent functions of the enthalpy, entropy and specific heat changes:

$$\Delta G = \Delta H_{298}^{0} + \int_{298}^{T} \Delta C_{\rm p} \mathrm{d}T - T \Delta S_{298}^{0} - T \int_{298}^{T} \frac{\Delta C_{\rm p}}{T} \mathrm{d}T$$
(2.40)

The heat capacity itself is also a function of temperature.

2.3

Relationships Between Thermodynamics and Kinetics

Classical thermodynamics can not answer the question how fast a system will respond to a change in constraints. This means that chemical kinetics, the *speed* of

heat or mass transfer, and fluid dynamics are beyond the scope of a thermodynamic treatment of crystal growth. Thermodynamic quantities and equations do not contain time and lengths as dimensions (with the exception of force and energy in SI units). Nevertheless, there are close links between thermodynamics and kinetics.

As discussed by Jackson [5], the rate of crystallization is the product of four terms:

$$r = a \cdot v^+ \cdot f \cdot u_k \tag{2.41}$$

with

a – a distance related to the atomic or molecular diameter of the growth unit

 $\upsilon^+~$ – the rate at which atoms join the crystal at active growth sites on the surface

f – the fraction of interface sites that are active growth sites

 u_k – the local free energy (or chemical potential) difference between the two phases.

This equation shows the link between kinetic (r) and thermodynamic quantities (u_k). The fourth term in the above equation is given by

$$u_k = 1 - \exp\left(\frac{\Delta G}{kT}\right) \tag{2.42}$$

where the difference in the Gibbs free energy

$$\Delta G = \Delta V \Delta P - \Delta S \Delta T \tag{2.43}$$

can be expressed in different ways, each of which is most appropriate for the crystal-growth process under consideration. The pressure and temperature differences are the deviations from the equilibrium values when two phases coexist, $\Delta P = P_{eq} - P$ and $\Delta T = T_m - T$. Then the change in free energy can be expressed as

$$\Delta G = -\Delta S \Delta T = -\frac{\Delta H_{\rm m} \Delta T}{T_{\rm m}} \quad \text{for melt growth at constant pressure}$$
(2.44)

$$\Delta G = \Delta V \Delta P = RT \frac{\Delta P}{P} \quad \text{for vapor growth at constant temperature}$$
(2.45)

and

$$\Delta G = RT \ln \frac{a_i}{a_{i,eq}}$$
 for solution growth at constant pressure and temperature

(2.46)

 $a_{i,eq}$ is the equilibrium activity of component *i*.

It shall also be remembered that the first derivation of the law of mass action by Guldberg and Waage was based on a kinetic approach. They obtained the equilibrium constant, a thermodynamic quantity, as the ratio of the rate constants, i.e. kinetic quantities, for the forward and back reactions.

Another link between thermodynamics and kinetics arises from the fact that most expressions for the rate of crystal growth contain concentrations (or gradients

thereof). These concentrations are frequently determined from thermodynamic computations.

In liquid phase epitaxial growth of compound semiconductor layers, the growth rate depends on the slope of the liquidus line and on the supercooling ΔT at the time of the initial contact between substrate and growth solution. This is another example that illustrates that the growth kinetics is determined by thermodynamic phase relations.

Thus, although it is correct that thermodynamics does not deal with time-dependent quantities, kinetics uses thermodynamic quantities, thus strong links between kinetics and thermodynamics exist.

2.4

Thermodynamics of Melt Growth

2.4.1

General Considerations

Melt growth is the formation of a crystalline solid from a liquid phase that has essentially the same composition as the solid. If the composition of the liquid shows a larger deviation from that of the solid one deals with solution growth. Fundamentals of thermodynamics of melt growth can be found, e.g. in [15].

Whenever possible, crystals should be grown from melt. The main reason is that mass transport is not required. The two most important, most widely applicable techniques of melt growth are the Czochralski technique and the Bridgman technique, both with a number of special variants.

The melting point T_m of a solid is the temperature at which solid and liquid are in equilibrium at a given pressure *P*. The normal melting point of a solid is its melting point at *P* = 1 bar. For a one-component system, once the temperature is chosen, the pressure is fixed, and vice versa.

At the melting temperature $T_{\rm m}$ discontinuous changes occur in entropy $S_{\rm (s)}$, volume $V_{\rm (s)}$ and the enthalpy $H_{\rm (s)}$ of the solid, the typical characteristics of a first-order phase transition.

At all temperatures the liquid has a higher enthalpy (internal energy) than the solid. Therefore, upon crystallization latent heat is released (i.e. solidification from a melt is an exothermic process), the amount of which is equal to the heat of melting, but with opposite sign:

$$\Delta H_{\rm cryst} = -\Delta H_{\rm m} = H_{\rm (s)} - H_{\rm (l)} \tag{2.47}$$

Therefore at low temperatures $G^{L} > G^{S}$.

On the other hand, the melt is the less-ordered state, i.e. it has higher entropy than the crystalline solid. Therefore crystallization, including crystallization from the melt, is connected with a decrease in entropy

$$\Delta S_{\text{cryst}} = S_{(\text{s})} - S_{(\text{l})} \tag{2.48}$$

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It has already been mentioned that (a) the entropy values are generally positive quantities, and (b) $S_{(g)} > S_{(l)} > S_{(s)}$. Consequently, the Gibbs free energy of the liquid decreases more rapidly with increasing temperature than that of the solid, since $\frac{\partial G}{\partial T} = -S$ (Eq. (2.16)). For temperatures up to $T_{\rm m}$ the solid phase has the lower free energy and is therefore the stable equilibrium phase, whereas above $T_{\rm m}$ the liquid phase has the lower free energy and is the energy and is the equilibrium state of the system. At the melting (or fusion) point $T_{\rm m}$, where melt and crystal are coexisting in equilibrium, the Gibbs free energies of the crystal and that of the melt are equal:

$$\Delta G_{\rm m}(T_{\rm m}) = G_{\rm (s)}(T_{\rm m}) - G_{\rm (l)}(T_{\rm m}) = 0 \tag{2.49}$$

$$\Delta G_{\rm m}(T_{\rm m}) = (H_{\rm (s)}(T_{\rm m}) - T_{\rm m}S_{\rm (s)}(T_{\rm m})) - (H_{\rm (l)}(T_{\rm m}) - T_{\rm m}S_{\rm (l)}(T_{\rm m})) = 0$$
(2.50)

$$\Delta G_{\rm m}(T_{\rm m}) = (H_{\rm (s)}(T_{\rm m}) - H_{\rm (l)}(T_{\rm m})) - T_{\rm m}(S_{\rm (s)}(T_{\rm m}) - S_{\rm (l)}(T_{\rm m})) = 0$$
(2.51)

$$\Delta G_{\rm m}(T_{\rm m}) = \Delta H_{\rm m}(T_{\rm m}) - T_{\rm m} \Delta S_{\rm m}(T_{\rm m}) = 0 \tag{2.52}$$

$$\Delta H_{\rm m}(T_{\rm m}) = T_{\rm m} \Delta S_{\rm m}(T_{\rm m}) \tag{2.53}$$

The last relationship shows that the temperature of melting, $T_{\rm m}$, is an intrinsic macroscopic property of a solid that is proportional to its latent enthalpy of melting, which is an expression of the bond strength. Furthermore, Eq. (2.53) shows that the enthalpy of melting is proportional to the entropy change that is associated with the process of melting.

Gersten and Smith [13] compare the enthalpy of melting of a substance with its cohesive energy. The cohesive (or binding) energy of a solid, ΔH_c , is the enthalpy change that is associated with the isothermal transformation of the solid into isolated atoms (for metallic and covalently bound crystals), ions (for ionic crystals) or molecules (for molecular crystals). For a metal or a molecular crystal, for example, it is equivalent to the heat of sublimation. Interestingly, the ratio between the enthalpy of melting and the cohesion energy is relatively constant, $\Delta H_{\rm m}/\Delta H_{\rm c} \approx$ 0.03 - 0.07. There are, however, exceptions: For silicon, single crystals of which are grown in greater quantity than any other material and nearly exclusively from the melt, the ratio is considerably higher (0.111), and for SiO₂ (only the α -quartz polytype of which is of industrial interest that, however, can not be grown from the melt) the ratio is about an order of magnitude lower (≈ 0.005) than for most other materials. The reason is that melting of Si is associated with a significant change of bonding (from covalent to metallic), while the nature of the chemical bonds in SiO₂ is not very much different in the liquid and the solid phases. Furthermore, the data show that only a few per cent of the total energy necessary for evaporation is required for the transition from one condensed phase (the solid) into the other condensed phase. Most energy is already stored in the liquid state.

Finally, some consequences of the application of Gibbs' famous phase rule will be considered for crystal growth from the melt.

At the melting temperature T_m the crystal usually coexists with the melt and a vapor, i.e. there are three phases (p = 3). If we consider a one-component system,

such as elemental silicon or a congruently melting and evaporating compound, we get from the phase rule

$$f = c_{\text{ind}} - p + 2 = 1 - 3 + 2 = 0 \tag{2.54}$$

where f is the variance or degree of freedom, p is the number of coexisting phases, and c_{ind} is the number of *independent* components.

Thus, at the melting point no variance is left, the system is completely determined. If a crystal is grown from two independent components, $c_{ind} = 2$, one degree of freedom is left.

The consequences will be discussed for a two-component system of industrial relevance. Up to now, a great percentage of GaAs is industrially grown by the LEC (liquid encapsulated Czochralski) technique. In this growth method the almost stoichiometric melt is covered by molten boron oxide in order to prevent the evaporation of arsenic from the melt. Thus, we have below the covering B₂O₃ melt only two phases, solid and liquid. Once the composition of the melt is selected, the temperature, as another degree of freedom, is still variable, without distortion of equilibrium. In the upper region, upside of the B₂O₃ barrier, the GaAs crystal is in contact with the vapor phase, a liquid is not present. However, the grown crystal decomposes incongruently. But without a separate arsenic source we do not have two independent components: All the arsenic in the vapor stems from the decomposition of the solid GaAs, i.e. the mass balance is $n_{\text{Ga}} = 4n_{\text{As}_4} + 2n_{\text{As}_2}$. This is an additional constraint, reducing the number of independent components and consequently also the number of degrees of freedom. If we choose the temperature, the corresponding equilibrium pressure is fixed. On the other hand, in the so called VCz (vapor pressure controlled Czochralski growth) variant of this technique, an independent separate arsenic source communicates with the free gas space. Thus, the arsenic pressure in this gas space can be adjusted via the temperature of the separate arsenic source. In this case one has one component more, thus also increasing the variance of the system. Now the temperature becomes an adjustable variable. It can be lowered, thus reducing thermal gradients that cause the generation of crystal defects. Commonly, the dislocation density of VCz-GaAs is about one order of magnitude lower than that of standard LEC material.

2.4.2

Freezing-Point Depression

Freezing-point depression is a phenomenon that is closely related to both melt and solution growth. For a chemist the determination of the melting point of a substance is a proof of its purity. The purer a substance is the higher its melting point. If the material contains some impurity or solvent, its melting point is lowered. The freezing-point depression is the same phenomenon that determines the shape of a multicomponent phase diagram.

In the following, the solvent (the majority component) *A* is the material that shall be crystallized, and the minority component *B*, the solute is, e.g. an impurity. (Commonly, in crystal growth from solution, the minority component *B* is the

material to become a crystal.) If the temperature of a solution composed of the solvent *A* and the solute *B* is lowered, the pure solvent *A* begins to separate out as a solid at a temperature $T_{\rm f}$. This freezing temperature is lower than the melting point of the pure solvent, $T_{\rm m}^*$. In any crystal-growth process from a liquid phase, either melt or solution, one is encountered with this phenomenon of freezing-point depression of the solvent.

An intimately related phenomenon is the elevation of the boiling point of a solvent *A* caused by the addition of a solute *B*. Boiling occurs at a temperature at which the total vapor pressure of the liquid phase equals that of the surrounding atmosphere. Addition of an involatile solute *B* lowers the vapor pressure of the solvent *A*. Hence, the vapor pressure of the surroundings is reached only at a higher temperature and the boiling point of a solution is higher than that of the pure solvent.

The freezing-point depression, $\Delta T = T_m^* - T_f$, can be estimated as follows.

The freezing point $T_{\rm f}$ is the temperature at which pure solid $A_{\rm (s)}$ coexists with a liquid mixture that is concentrated in this component. At equilibrium the chemical potential of A is the same in both phases:

$$\mu_{A_{(f)}}^{*}(T_{f}, P) = \mu_{A_{(f)}}^{*}(T_{f}, P) + RT_{f} \ln \gamma_{A} x_{A}$$
(2.55)

Under normal conditions the pressure $P = P^{\circ} = 1$ bar. It will be fixed at this value and will therefore no longer be indicated throughout the following considerations. γ_A is the activity coefficient of $A_{(1)}$ in the mixed liquid phase, and x_A is the mole fraction of A in the solution. The star is the indication of a pure substance. For simplicity we will consider a very diluted binary solution, i.e. $x_B < < x_A$ and $\gamma_A \approx 1$. Then we can use the mole fractions instead of the activities. For a binary solution $x_A + x_B = 1$.

The difference between the chemical potentials of *A* in the liquid and in its pure solid state is just the change in the free energy associated with the transition from the liquid to the solid state, the free energy of fusion $\Delta \overline{G}_{\text{fus},A}(T_{\text{f}})$:

$$\mu_{A_{(l)}}^{*}(T_{\rm f}) - \mu_{A_{({\rm s})}}^{*} = \Delta \overline{G}_{{\rm fus},A}(T_{\rm f})$$
(2.56)

Consequently, Eq. (2.55) can be written as

$$RT_{\rm f} \ln x_A = RT \ln(1 - x_B) = \mu^*_{A_{\rm (s)}}(T_{\rm f}) - \mu^*_{A_{\rm (l)}}(T_{\rm f}) = -\Delta \overline{G}_{{\rm fus},A}(T_{\rm f})$$
(2.57)

From the definition of the free energy we have

$$\Delta \overline{G}_{\text{fus},A}(T_{\text{f}}) = \Delta \overline{H}_{\text{fus},A}(T_{\text{f}}) - T_{\text{f}} \Delta \overline{S}_{\text{fus},A}(T_{\text{f}})$$
(2.58)

If *A* freezes as a supercooled liquid at a temperature T_f below its normal freezing point T_m^* , when it is a pure substance, the isothermal freezing $A_{(l)}$ (T_f) $\rightarrow A_{(s)}$ (T_f) at T_f is an irreversible transition and for such a process $\Delta S \neq \Delta H/T$ and $\Delta G \neq 0$. Therefore, the irreversible process $A_{(l)}(T_f) \rightarrow A_{(s)}(T_f)$ at T_f must be replaced by a process starting from the same initial and leading to the identical final state, but consisting of a number of reversible steps:

 $A_{(l)}$ (T_{f}) $\rightarrow A_{(l)}$ (T_{f}^{*}) $\rightarrow A_{(s)}$ (T_{f}^{*}) $\rightarrow A_{(s)}$ (T_{f}). Using the common equations for the temperature dependencies of the enthalpy and the entropy, the enthalpy and entropy data in Eq. (2.58) can be replaced by

$$\Delta \overline{H}_{\text{fus},A}(T_{\text{f}}) = \Delta \overline{H}_{\text{fus},A}(T_{\text{m}}^{*}) + \int_{T_{\text{m}}^{*}}^{T_{\text{f}}} \Delta \overline{C}_{\text{p},A} dT$$
(2.59)

and

$$\Delta \overline{S}_{\text{fus},A}(T_{\text{f}}) = \frac{\Delta \overline{H}_{\text{fus},A}(T_{\text{m}}^{*})}{T_{\text{m}}^{*}} + \int_{T_{\text{m}}^{*}}^{T_{\text{f}}} \Delta \overline{C}_{\text{p},A} \frac{\mathrm{d}T}{T}$$
(2.60)

where

$$\Delta \overline{C}_{p,A} = C_{p,A_{(l)}}(T) - \overline{C}_{p,A_{(s)}}(T)$$
(2.61)

For the molar heat capacities the data at the freezing point of pure *A* can be used, and they can be taken as independent of temperature.

Now, combination of these equations leads to

$$\ln x_A = -\frac{\Delta H_{\text{fus},A}(T_{\text{m}}^*)}{R} \left[\frac{T_{\text{m}}^* - T_{\text{f}}}{T_{\text{m}}^* T_{\text{f}}} \right] - \frac{1}{RT_{\text{f}}} \int_{T_{\text{m}}^*}^{T_{\text{f}}} \Delta \overline{C}_{\text{p}} dT + \frac{1}{R} \int_{T_{\text{m}}^*}^{T_{\text{f}}} \frac{\Delta \overline{C}_{\text{p}}}{T} dT$$
(2.62)

and, after integration and taking out the heat capacities, to

$$\ln x_A = -\frac{\Delta H_{\text{fus},A}(T_{\text{m}}^*)}{R} \left[\frac{T_{\text{m}}^* - T_{\text{f}}}{T_{\text{m}}^* T_{\text{f}}} \right] - \frac{\Delta \overline{C}_{\text{p}}}{R} \left[1 - \frac{T_{\text{m}}^*}{T_{\text{f}}} + \ln\left(\frac{T_{\text{m}}^*}{T_{\text{f}}}\right) \right]$$
(2.63)

Two further assumptions can be made:

For very dilute solutes, when the mole fraction of *B* is very small, i.e. $x_B \ll 1$, we have

$$\ln x_A = \ln(1 - x_B) \approx -x_B \tag{2.64}$$

In this case, the temperature interval between the freezing points of the pure substance *A*, $T_{m,A}^*$, and that of *A* in solution, T_f , can also be expected to be small.

For this restricted temperature interval we can also consider the enthalpy and the entropy of fusion to be independent of temperature.

Under these conditions, Eq. (2.63) simplifies to

$$x_{B} = \left\{\frac{\Delta \overline{H}_{\text{fus},A}(T_{\text{m},A}^{*})}{R}\right\} \left\{\frac{1}{T_{\text{f}}} - \frac{1}{T_{\text{m},A}^{*}}\right\} = \left\{\frac{\Delta \overline{H}_{\text{fus},A}(T_{\text{m},A}^{*})}{R}\right\} \left\{\frac{T_{\text{m},A}^{*} - T_{\text{f}}}{T_{\text{f}}T_{\text{m},A}^{*}}\right\} (2.65)$$

 $T_{\rm f}$ and $T_{{\rm m},A}^* \approx (T_{{\rm m},A}^*)^2$. Finally, $T_{{\rm m},A}^* - T_{\rm f}$ is the freezing-point depression $\Delta T_{\rm f}$ and we arrive at the final expression

$$\Delta T_{\rm f} = \frac{\left(RT_{\rm m,A}^*\right)^2}{\Delta \overline{H}_{\rm fus,A}} x_B \tag{2.66}$$

For dilute mixed solutes this equation becomes

$$\Delta T = T_{m,A}^* - T_f = \frac{R(T_m^*)^2}{\Delta H_{\text{fus}}(T_{m,A}^*)} \sum_{i=B}^J x_i$$
(2.67)

with the sum extending over all solute species.

2.5 Thermodynamics of Solution Growth

2.5.1 General Considerations

Industrial mass crystallization is essentially solution growth. It is estimated that about 75% of all solid products of the chemical and pharmaceutical industries are crystals. Also, most natural crystals are the product of solution growth.

On the other hand, artificial individual single crystals of a certain minimum size are not so frequently grown from solution because the growth rate is usually rather low. In growth from the melt the particle density of the material to be grown is nearly the same in both the crystalline and the liquid phases, mass transport is not required. In contrast, the rate of solution growth is frequently determined by slow diffusion processes in the solvent. Furthermore, there is the danger that solvent inclusions can be found in the grown crystal. Nevertheless, solution growth is an important technology also for the industrial growth of bulk single crystals and of epitaxial layers, e.g. quartz crystals and liquid phase epitaxy of III-V compounds for light-emitting diodes (LEDs).

For a thermodynamic analysis of solution growth precise information about the final products and the starting material is needed. The end product is a pure, stoichiometrically well-defined solid in its crystalline state, while the initial state is usually a homogeneous solution of the constituent(s) of the crystal to be formed in a solvent. Thus, for a thermodynamic treatment of solution growth, the difference between values of the characteristic thermodynamic data for the crystal on the one hand and for its constituents in the feeding solution on the other hand are required. The difficulties lie in the precise knowledge of the nature of the dissolved particles and an adequate description of the solution. Frequently, one does not know in detail the nature of the growth solution. Particles that eventually form the crystal can be ionized, they are probably solvated and/or associated in solution, they show different kinds of attractive or repulsive interactions with solvent or solute particles.

Crystallization from solution may be associated with a chemical reaction between different constituents in the solution, or it may be a physical process without chemical reaction.

The two most important aspects for solution growth are a) the absolute solubility of a material to be crystallized, and b) the temperature dependence of the solubility.

Concerning the absolute solubility, care must be taken about the concentration measures – molarity, molality, mole fractions, frequently also masses per volume or the weight fraction are in common use. Hence, it is sometimes difficult to know what is really meant, when a solubility between 10% and 60% is considered to be suitable for crystal growth. For the selection of an appropriate solvent the old Latin sentence "similis similibus solvuntur" holds, i.e. the solubility of a certain material is high in a solvent of close chemical similarity. "Chemical similarity" refers to the nature of chemical bonding. Therefore, from a practical point of view, five classes of solvents can be distinguished:

- water and related polar liquids,
- nonpolar molecular liquids,
- salt melts,
- metals with low melting points and low vapor pressures, and
- liquids in a supercritical state.

For any of these solvents industrial crystal-growth processes exist. The general aspects of growth from high-temperature solutions are discussed by Elwell and Scheel [16], while the thermodynamics of low-temperature solution growth is extensively discussed by Rodríguez-Clemente [17]. An interesting, relatively new development is the "rapid growth technique", by which large KDP (potassium dihydrogen phosphate)-type crystals are grown. Hundreds of such crystals with dimensions exceeding 50 cm in all three dimensions are needed for Pockels cells and frequency conversion in the nuclear fusion projects ongoing in the USA and in France [18, 19]. Growing such KDP crystals by conventional techniques from solution, where growth rates are in the order of 1-2 mm/d, would require more than two years. Additionally, at the low supersaturations used in conventional growth, impurities in the starting salt generate a "dead zone", in which the growth rate is zero in certain directions [19]. Zaitseva and coworkers showed that KDP solutions can be stable against spontaneous nucleation for induction time periods of months at undercoolings of up to 30 °C and during continuous cooling, supersaturations of up to 100-130% can be reached. Such a wide metastability Ostwald-Miers region shows that thermodynamics can frequently provide only a guide for the principal behavior while the actual crystal growth is determined by kinetic effects.

The most basic approach to the thermodynamics of crystal growth from solution can again be easily derived from the fundamental equilibrium condition

$$G_{i(cr)} = G_{i(sol)} \tag{2.68}$$

for the coexistence of pure crystalline *i* and the substance *i* in solution.

The differential free energies of *i* in both phases can be expressed as

$$V_{i(cr)}dp - S_{i(cr)}dT = V_{i(sol)}dp - S_{i(sol)}dT + RTd\ln a_i$$
(2.69)

or

$$RTd \ln a_i = (V_{i(cr)} - V_{i(sol)})dp - (S_{i(cr)} - S_{i(sol)})dT$$
(2.70)

For the pressure dependence of the solubility under isothermal conditions (dT = 0) one easily obtains from this equation

$$\left(\frac{\mathrm{d}\ln a_{i(\mathrm{sol})}}{\mathrm{d}p}\right)_{T} = \frac{\left(V_{i(\mathrm{cr})} - V_{i(\mathrm{sol})}\right)}{RT}$$
(2.71)

The pressure dependence of the solubility is determined by the difference between the molar volumes of the solute *i* in the crystalline state and in the solution.

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In both cases one is dealing with condensed phases (in contrast, e.g., to the solubility of a gas in a solution), and therefore the volume difference is small. Therefore, the dependence of the solubility on pressure is usually very small. The reason for the application of an external pressure is therefore not to change the solubility of the solute, instead it is to suppress the evaporation of the solvent, to increase its existence region as a liquid or to prevent the evaporation of volatile constituents from the melt. This also holds true for hydrothermal crystal growth. The necessity of high pressure is only due to the high vapor pressure of the solvent at high temperatures, with the exceptions of diamond and GaN.

The temperature dependence of the solubility is obtained from the same equilibrium condition. At constant pressure (dP = 0) one gets

$$\left(\frac{\mathrm{d}\ln a_{i(\mathrm{sol})}}{\mathrm{d}T}\right)_{P} = \frac{1}{RT} \cdot \left(S_{i(\mathrm{sol})} - S_{i(\mathrm{cr})}\right)$$
(2.72)

The difference in the entropies of the solute i in solution and in its crystalline state can be replaced by

$$\Delta S_i = \frac{\Delta H_{\rm diss}}{T} \tag{2.73}$$

where ΔH_{diss} is the enthalpy change connected with the dissolution of crystalline *i*:

$$\Delta H_{\rm diss} = H_{i(\rm sol)} - H_{i(\rm cr)} \tag{2.74}$$

In this way, the temperature coefficient of the solubility is obtained as

$$\frac{\mathrm{d}\ln a_i}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{diss}}}{RT^2} \tag{2.75}$$

This is the well-known van't Hoff equation. The enthalpy of dissolution (commonly denoted as "heat of dissolution") of a substance, ΔH_{diss} , is the change in enthalpy that is associated with the dissolution of this substance in a certain amount of the solvent. The heat of dissolution in infinite dilution is the amount of heat that is released or has to be added, when one mole of a certain substance is dissolved in an infinite amount of the solvent. Under such conditions the interaction between the dissolved particles can be ignored.

Equation (2.75) shows that the sign of the temperature coefficient of the solubility is determined by the sign of the heat of solution. As a rule, the solubility increases with temperature. In this cases ΔH_{diss} is positive, i.e. energy has to be supplied in order to dissolve a material, or $H_{i(\text{sol})} > H_{i(\text{cr})}$. There are, however, also numerous examples for a retrograde solubility, i.e. increasing solubility with decreasing temperature. Frequently, a reversal of the temperature dependence of solubility is observed when a larger temperature range is considered. As an example, the solubility of GaPO₄ in concentrated phosphoric acid shall be mentioned.

From the experimentally determined enthalpies of solution the enthalpies of formation of the different sorts of particles in solution can be determined – provided one knows the kind of particles that exist in solution. For example, the enthalpy

of formation of common salt in solution is the sum of the standard enthalpy of formation of NaCl and the enthalpy of dissolution:

$$\begin{split} & 1/2\mathrm{Na}_{(\mathrm{s})} + 1/2\mathrm{Cl}_{2(\mathrm{g})} \rightarrow \mathrm{NaCl}_{(\mathrm{s})} \qquad \Delta H^{\mathrm{o}}_{\mathrm{f},298} \\ & \frac{\mathrm{NaCl}_{(\mathrm{s})} \rightarrow \mathrm{NaCl}_{(\mathrm{diss})}}{1/2\mathrm{Na}_{(\mathrm{s})} + 1/2\mathrm{Cl}_{2(\mathrm{g})} \rightarrow \mathrm{NaCl}_{(\mathrm{diss})}} \qquad \Delta H_{\mathrm{diss}} \end{split}$$

The enthalpy of formation of an ionic compound can be obtained as the sum of the heats of formation of the corresponding ions in solution. Thus, the enthalpy of formation $\Delta_{\rm f} H_{\rm (diss)}$ of NaCl_(diss) in solution is the sum of the enthalpies of formation of the ions Na⁺_(diss) and Cl⁻_(diss). Usually, it is easy to determine the heat of solution experimentally. The difficulty is how this value is shared between the two kinds of ions. This problem is solved by defining a reference value. The standard enthalpy of formation of $H^+_{\rm (diss)}$ is defined to be zero at any temperature:

$$1/2H_{2(g)} \rightarrow H^+_{(diss)} \qquad \Delta H^o_f = 0$$

With one value fixed, the enthalpy of formation of a next dissolved ion can be determined. For example, from $\Delta H_{\text{diss},\text{HCl}} = -167.16 \,\text{kJ/mole}$ for HCl one gets $\Delta H^{\text{o}}_{\text{f},\text{Cl}^-_{(\text{diss})}} = -167.16 \,\text{kJ/mole}$ for chloride ions. Combining this value with the heat of dissolution of NaCl_(diss) provides a value for $\Delta H^{\text{o}}_{\text{f},\text{Na}^+_{(\text{diss})}}$, and so on.

The dissolution of a crystal can be considered as a sequence of single steps. For thermodynamic considerations only the final and the initial state are important, intermediate states and the path from the initial to the final state are of no importance. According to Hess's law the heat of a desired reaction can be obtained by combining the heats of several intermediate reactions. For example, the process of dissolution of an ionic compound *AB* can be considered as a sequence of

- melting of the pure crystalline substance AB,
- mixing of two liquid phases (molten solute *AB* and solvent *C*),
- dissociation of $AB_{(l)}$ into the ions $A^{\nu z_+}$ und $B^{\nu z_-}$,
- solvation of these ions.

Thus, the total enthalpy of dissolution is

$$\Delta H_{\rm diss} = \Delta H_{\rm melting} + \Delta H_{\rm mix} + \Delta H_{\rm dissoc} + \Delta H_{\rm solv} \tag{2.76}$$

Without dissociation the enthalpy of dissolution is reduced to

$$\Delta H_{\rm diss} = \Delta H_{\rm melting} + \Delta H_{\rm mix} \tag{2.77}$$

For an ideal solution, the enthalpy of mixing is zero, thus simplifying this equation to $\Delta H_{\text{diss}} = \Delta H_{\text{melting}}$. In this case also the activity can be replaced by the mole fraction x_i . In the case of dissolution without dissociation the mole fraction

of the dissolved substance *AB* is x_{AB} . Coming back now to Eq. (2.74), integration between the limits "pure crystalline substance *AB*", ($x_{AB} = 1$, $T = T^*_{\text{melting},AB}$), and "dissolved *AB*", ($x = x_{AB}$, T = T), leads to the exact expression

$$RT \ln \gamma_{AB} x_{AB} = \Delta \overline{H}_{\text{melting},AB} \left(\frac{1}{T_{\text{melting},AB}^*} - \frac{1}{T} \right)$$
$$-\Delta \overline{c}_{\text{p,melting},AB} \left(\frac{T - T_{\text{melting},AB}^*}{T} - \ln \frac{T}{T_{\text{melting},AB}^*} \right)$$
(2.78)

which even contains the temperature dependence of the heat of melting.

With the approximation $\gamma \rightarrow 1$ and neglecting the second term on the right-hand side of the above equation one obtains

$$R \ln x_{AB} \approx \Delta \overline{H}_{\text{melting},AB} \left(\frac{1}{T_{\text{melting},AB}^*} - \frac{1}{T} \right)$$
 (2.79)

or

$$\ln a_{AB} = \ln(\gamma_{AB} \cdot x_{AB}) = A' - \frac{\Delta H_{\text{melting}}}{RT}$$
(2.80)

and

$$a_{AB} = A \cdot \exp\left(-\frac{\Delta H_{\text{melting}}}{RT}\right) \tag{2.81}$$

with a constant A.

This is frequently a good approximation for the temperature dependence of the solubility of two organic substances.

2.5.2

Solution Growth from Metallic Solvents: Liquid Phase Epitaxy (LPE) of III-V Compounds

Solution growth from metallic solvents is common industrial practice in the liquid phase epitaxy of phosphides, arsenides and antimonides of the group III elements. Also, a number of other epitaxial layers of compound semiconductor materials and even silicon are grown from metallic solutions. Here, knowledge of the temperature–composition–pressure relationships as represented in the equilibrium phase diagrams is of fundamental importance for determining the appropriate liquid solution compositions and growth temperatures, for designing the growth apparatus, and for controlling the properties of the epitaxial layers, such as composition of mixed-crystal layers and gradients therein, deviations from stoichiometry, vacancy concentrations, and other properties.

The T - x phase diagrams of the binary III-V systems are characterized by the presence of only one nearly stoichiometric, congruently melting solid phase. The very small deviations from the exact 1:1 stoichiometry of the solid compound will be neglected for the present treatment, although they play a deciding role in

the material quality. Owing to the strong bonding, the binary compounds have high melting temperatures, much higher than those of the constituting elements. The eutectics on the metallic side are generally degenerate. The liquidus curve is parabolic around the melting temperature of the solid compound, with a large radius of curvature. This shape of the liquidus curve together with the large heats of fusion and the higher density of the liquid phase than that of the solid indicate that the compounds can be assumed to be completely dissociated into their constituents upon fusion or dissolution.

The LPE growth of a III-V compound usually takes place on the group III metal-rich side of the liquidus curve at temperatures far below the melting point of the compound. The group III metal serves as the solvent for the group V element as solute. For practical purposes, the liquidus curve in a limited growth region can be rather well represented by a simple expression of the form

$$x_{\rm V} = A \exp(-B/kT_{\rm l}) \tag{2.82}$$

with

A, B – constants (cf. Eq. (2.81)!)

 $x_{\rm V}$ – atom fraction of the group V element in the group III-metal-based solution

 T_1 – liquidus temperature,

k – Boltzmann constant.

The liquidus curves of the III-V systems can be described by means of an equation derived by Vieland [20].

The basic equilibrium condition for a reaction

$$AB_{(s)} = A_{(l)} + B_{(l)}$$

is

$$\mu_{AB_{(s)}}^{\circ}(T) = \mu_{A_{(l)}}^{\circ} + RT \ln a_{A(l)} + \mu_{B_{(l)}}^{\circ} + RT \ln a_{B(l)}$$
(2.83)

with the standard chemical potentials μ_i^{o} and the activities a_i^l of the components *A* and *B* in the liquid phase.

Choosing a melt of stoichiometric 1:1 composition as the standard state, one obtains

$$\mu_{i(\text{st.l.})}(T) = \mu_{i(\text{l})}^{\circ} + RT \ln a_{i(\text{st.l.})} \quad \text{or} \quad \mu_{i(\text{l})}^{\circ} = \mu_{i(\text{st.l.})}(T) - RT \ln a_{i(\text{st.l.})}$$
(2.84)

Substitution of Eq. (2.84) into Eq. (2.83) yields

$$\mu_{AB(l)}^{o}(T) = \mu_{A(\text{st.l.})}(T) - RT \ln a_{A(\text{st.l.})} + RT \ln_{A(l)} + \mu_{B(\text{st.l.})}(T) - RT \ln a_{B(\text{st.l.})} + RT \ln a_{B(l)}$$
(2.85)

or

$$\mu_{AB(l)}^{o}(T) = \mu_{A(\text{st.l.})}(T) + \mu_{B(\text{st.l.})}(T) + RT \ln \frac{a_{A(l)}a_{B(l)}}{a_{A(\text{st.l.})}a_{B(\text{st.l.})}}$$
(2.86)

The difference in the chemical potentials of the pure compound *AB* and its constituents in a stoichiometric melt corresponds to the free energy of fusion $\Delta G_{\text{fus}}(T)$:

$$(\mu_{A(\text{st.l.})} + \mu_{B(\text{st.l.})}) - \mu_{AB(\text{s})}^{o}(T) = \Delta G_{\text{fus}}(T) = RT \ln \frac{a_{A(\text{st.l.})}a_{B(\text{st.l.})}}{a_{A(\text{l})}a_{B(\text{l})}}$$
(2.87)

The derivative of the free energy of fusion with respect to temperature gives the negative entropy of fusion:

$$\left(\frac{\partial \Delta G_{\rm fus}}{\partial T}\right) = -\Delta S_{\rm fus} \tag{2.88}$$

Integration between the temperature of fusion of the pure compound, T_f , where the free energy of fusion is zero, and any temperature T gives

$$\Delta G_{\rm fus}(T) = \Delta G_{\rm fus}(T_{\rm f}) - \Delta S_{\rm fus}(T - T_{\rm f}) = 0 + \Delta S_{\rm fus}(T_{\rm f} - T)$$
(2.89)

From Eqs. (2.89) and (2.87) follows that

$$\Delta \overline{S}_{\text{fus}}(T_{\text{f}} - T) = RT \ln \frac{a_{A(\text{st.l.})} a_{B(\text{st.l.})}}{a_{A(\text{l})} a_{B(\text{l})}}$$
(2.90)

The activity is the product of the atomic fraction x_i and the activity coefficient γ_i , i.e. $a_i = \gamma_i x_i$. Furthermore, in the stoichiometric binary melt one has $x_{A(l)} = x_{B(l)} = 1/2$. Substitution into Eq. (2.90) leads to

$$\Delta \overline{S}_{\text{fus}}(T_{\text{f}} - T) = RT \ln \frac{\frac{1}{2} \times \frac{1}{2}}{x_{A(l)} x_{B(l)}} + RT \ln \frac{\gamma_{A(\text{st.l.})} \gamma_{B(\text{st.l.})}}{\gamma_{A(l)} \gamma_{B(l)}}$$
(2.91)

or

$$\ln \frac{\gamma_{A(\text{st.l.})}\gamma_{B(\text{st.l.})}}{\gamma_{A(l)}\gamma_{B(l)}} - \ln(4x_{A(l)}x_{B(l)}) = \frac{\Delta \overline{S}_{\text{fus}}}{R} \left(\frac{T_{\text{f}}}{T} - 1\right)$$
(2.92)

This is one form of Vieland's equation, derived neglecting the difference between the heat capacities of the solid and the liquid phases and assuming a mean entropy of fusion for the temperature interval considered.

2.5.3 Ideal and Nonideal Solutions, Activity Coefficients

The activity coefficients in Vieland's equation account for deviations from ideality in the properties of solutions. For solutions with ideal behavior, for brevity "ideal solutions", they have a value of unity. For solutions with nonideal behavior ("nonideal solutions") there exist numerous models for the calculation of activity coefficients, physically more or less grounded and more or less sophisticated.

At first, an ideal solution will be considered. Characteristic of an ideal solution is that the interaction energies ε_{ij} between the different particles *A* and *B* in the solution are equal, i.e.

$$\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB} \tag{2.93}$$

Thus, the formation of an ideal solution is not associated with any net change in the enthalpy, i.e. the enthalpy of mixing is zero, $\Delta H_{\text{mix}}^{\text{id}} = 0$. Nevertheless, a change in the free energy occurs by mixing formerly isolated components, which is, however, solely due to the increase in entropy. Thus, for an ideal solution

$$\Delta G_{\rm mix}^{\rm id} = -T\Delta S_{\rm mix}^{\rm id} \tag{2.94}$$

Generally, the molar free energy of mixing is the sum of the changes in the individual partial molar free energies for each of the *i* components multiplied by their respective mole fractions. It is remembered that the partial molar free energy is the same as the chemical potential μ_i .

$$\Delta G_{\rm mix} = \sum x_i \Delta \mu_i \tag{2.95}$$

The chemical potential of a constituent in an ideal solution is given by Eq. (2.33), $\mu_i = \mu_i^{o} + RT \ln x_i$, and the difference in the chemical potentials of this component, being either constituent of a solution or a pure substance, is

$$\Delta \mu_{i} = (\mu_{i}^{o} + RT \ln x_{i}) - \mu_{i}^{o} = RT \ln x_{i}$$
(2.96)

A comparison between Eqs. (2.95) and (2.96) shows that

$$\Delta G_{\min}^{\mathrm{id}} = RT \sum_{i} x_{i} \ln x_{i} = -T \Delta S_{\min}^{\mathrm{id}}$$
(2.97)

which leads to

$$\Delta S_{\min}^{id} = -R \sum_{i} x_i \ln x_i \tag{2.98}$$

or, for a binary solution, to

$$\Delta S_{\rm mix}^{\rm id} = -R[x_A \ln x_A + (1 - x_A) \ln(1 - x_A)]$$
(2.99)

From a statistical approach, leading to the same result, the ideal entropy of mixing is also designated as the configurational entropy ΔS_c .

Differentiation of Eq. (2.99) shows that $\Delta S_{\text{mix}}^{\text{id}}$ has its maximum at $x_A = 1/2$, about which it is symmetrically disposed. Correspondingly, from Eq. (2.97), the free energy of mixing has its minimum also at the equimolar composition and decreases with increasing temperature.

For solutions with nonideal behavior, the energies of the three different types of bonding between nearest neighbors in the solution, ε_{AA} , ε_{BB} and ε_{AB} , differ from each other, resulting in a nonzero enthalpy of mixing. The entropy of mixing can, but needs not necessarily, be conserved as for an ideal solution.

One of the simplest and most widely used models for the thermodynamic characterization of a nonideal solution is the so-called "simple solution model". In this model the excess free energy of mixing, accounting for deviations from the ideal entropy of mixing, is taken as an expression that is proportional to the product of the mole fractions of the constituents,

$$\Delta G_{\text{mix}}^{\text{exc}} = (\Delta H_{\text{mix}} - T\Delta S_{\text{mix}}^{\text{ecx}}) x_i (1 - x_i)$$
(2.100)

A special variant is the "regular solution model". Here, the entropy of mixing is supposed to be just the ideal entropy of mixing, $\Delta S_{\text{mix}}^{\text{rs}} = -R[x_A \ln x_A + (1 - x_A) \ln(1 - x_A)]$. In contrast, the enthalpy of mixing is different from zero and is expressed by

$$\Delta H_{\rm mix}^{\rm rs} = \Omega x_A x_B \tag{2.101}$$

The proportionality constant Ω is called the interaction energy. It is

$$\Omega = zN_A \left[\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right]$$
(2.102)

with z – the number of nearest neighbors, N_A – Avogadro's constant and the term in brackets is the difference between the bond energy of an A – B pair and the mean of the A – A and B – B bond energies.

It is easily seen that $\Omega = 0$ if the bond energies are all equal (as for an ideal solution). The interaction parameter is determined by fitting to experimentally measured liquidus and solidus curves.

Again, the excess free energy of mixing has a minimum symmetrical about $x_A = x_B = 1/2$. It becomes deeper the stronger the interaction between *A* and *B* particles in the solution.

The activity coefficients are now related to this interaction energy by

 $RT\ln\gamma_i = (1 - x_i)^2\Omega \tag{2.103}$

Solutions in which the data can be fitted well enough to a constant value of the interaction parameter are classified as "strictly regular". A better fit can be obtained by a temperature-dependent interaction parameter of the form

$$\Omega = a - bT \tag{2.104}$$

This resembles immediately on the general form of the excess free energy of mixing

$$\Delta G_{\rm mix}^{\rm exc} = \Delta H_{\rm mix}^{\rm exc} - T S_{\rm mix}^{\rm exc} \tag{2.105}$$

Using the general form of Eq. (2.104) of the interaction parameter, a number of special cases and solution models with special designations can be distinguished. They are listed in Table 2.1.

For ternary and still more complex systems, the general approaches are the same. But for these systems, not only must the relations for the liquid phase be modified, but also those for the solid phase. A comprehensive review on phase equilibria in ternary III-V systems has been written by Panish and Ilegems [21]. A useful semiempirical expression for the calculation of the solid-solution interaction parameter, based on the difference in the lattice constants of the binary constituent compounds, has been developed by Stringfellow [22].

While the entropy of mixing is always positive, the enthalpy of mixing may have either a positive or a negative sign, depending on the values for the two energy terms in the above expression for the interaction parameter. Thus, while

 $\Delta G_{\rm mix}^{\rm exc} = (\Delta H_{\rm mix} - TS_{\rm mix}^{\rm exc})x(1-x)$ $\Delta G_{\rm mix}^{\rm exc} = (a - bT)x(1 - x)$ Simple solution $\Delta G_{\rm mix}^{\rm exc} = \Omega x (1-x)$ Ω physical meaning special case $\Delta H_{\rm mix} = a$, $\Delta S_{\rm mix}^{\rm exc} = 0$ strictly regular а athermal -bT $\Delta H_{\text{mix}} = 0, \ \Delta S_{\text{mix}}^{\text{exc}} = b$ $\Delta H_{\text{mix}} = a, \ \Delta S_{\text{mix}}^{\text{exc}} = b$ quasiregular a - bT

Table 2.1 Classes of "Simple Solutions".

the generation of entropy by mixing always favors the formation of a mixture, the enthalpy change associated with mixing of two (or more) components can either enhance or prevent the formation of a solution. If the interaction energy between A and B species is weak, a homogeneous solution, either a liquid or a solid one, tends to separate into two phases.

2.5.4

Phase Diagram of a Two-Component Ideal System

Under the heading of solution growth also the analytical description of the phase diagram of a two-component ideal system can be treated. If we do not start the solidification from a binary liquid solution with a 1:1 composition, the term "solution growth" appears to be justifiable.

Both the liquid and the solid phases are supposed to form homogeneous solutions.

The phase diagram of a binary system is a plot of the melting or solidification temperatures, resp., as a function of composition. While a pure substance melts at a fixed temperature, the melting temperature of a binary solid solution shifts over a range of temperatures. This is the same phenomenon that one observes as freezing-point depression. In the melting range, components A and B in the solid phase are in chemical equilibrium with A and B in the coexisting liquid phase. Chemical equilibrium means that the chemical potential of a certain component *i* is the same in both phases:

$$\mu_{A_{(1)}} = \mu_{A_{(s)}} \text{ and } \mu_{B_{(1)}} = \mu_{B_{(s)}} \tag{2.106}$$

Assuming the A - B solutions as ideal in both the solid and the liquid phases, the chemical potentials are

$$\mu_{A_{(l)}}^{o} + RT \ln x_{A_{(l)}} = \mu_{A_{(s)}}^{o} + RT \ln x_{A_{(s)}}$$
(2.107)

and

$$\mu_{B_{(l)}}^{o} + RT \ln x_{B_{(l)}} = \mu_{B_{(s)}}^{o} + RT \ln x_{B_{(s)}}$$
(2.108)

The expressions (2.107) and (2.108) can be rearranged to

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$$\ln\left(\frac{x_{A_{(s)}}}{x_{A_{(l)}}}\right) = \frac{\mu^{\circ}_{A_{(l)}} - \mu^{\circ}_{A_{(s)}}}{RT}$$
(2.109)

and

$$\ln\left(\frac{x_{B_{(s)}}}{x_{B_{(l)}}}\right) = \frac{\mu_{B_{(l)}}^{o} - \mu_{B_{(s)}}^{o}}{RT}$$
(2.110)

These expressions contain the differences between the Gibbs free energies of the liquid and the solid phases in their pure standard states, i.e. these are the free energies of melting of the pure substances. They are, however, needed for temperatures other than $T_{m,i}^*$, the equilibrium melting points of the pure substances. An approximate equation can be obtained in the following way.

The temperature coefficient of the Gibbs free energy in general form is $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$ (Eq. (2.16)).

Here, the Gibbs free energy of melting is considered, consequently also the entropy of melting. For component i this can be substituted by

$$\Delta \overline{S}_{\mathrm{m},i}(T_{\mathrm{f}}) = \frac{\Delta \overline{H}_{\mathrm{m},i}(T_{\mathrm{m},i}^{*})}{T_{\mathrm{m},i}^{*}} + \int_{T_{\mathrm{m}}^{*}}^{T_{\mathrm{f}}} \Delta \overline{C}_{\mathrm{p},i} \frac{\mathrm{d}T}{T}$$
(2.111)

where

$$\Delta \overline{C}_{\mathbf{p},i} = C_{\mathbf{p},i_{(1)}}(T) - \overline{C}_{\mathbf{p},i_{(s)}}(T)$$
(2.112)

In most cases, the enthalpy and the entropy of fusion can be taken as independent of temperature and the terms containing the molar heat capacities disappear. Thus,

$$\left(\frac{\partial \Delta G_{\mathrm{m},i}}{\partial T}\right)_{P} = -\frac{\Delta \overline{H}_{\mathrm{m},i}(T^{*}_{\mathrm{m},i})}{T^{*}_{\mathrm{m},i}}$$
(2.113)

Both sides of this equation can be integrated between $T^*_{m,i}$ and a temperature *T* below the melting temperature of the pure substance:

$$\int_{\Delta G_{m,i}(T^*_{m,i})}^{\Delta G_{m,i}(T)} d\Delta G_{m,i} = -\frac{\Delta \overline{H}_{m,i}}{T^*_{m,i}} \int_{T^*_{m,i}}^T dT$$
(2.114)

At the melting temperature of the pure substance *i* the chemical potentials of *i* in the liquid and solid states are equal, and consequently $\Delta G_{m,i}(T_{m,i}^*) = 0$.

Following the path in the section on the freezing-point depression, the difference between the chemical standard potentials in the liquid and the solid state is given by

$$\mu_{i(l)}^{\circ} - \mu_{i(s)}^{\circ} = \Delta \overline{H}_{m,i} \left(1 - \frac{T}{T_{m,i}^*} \right)$$
(2.115)

where $\Delta \overline{H}_{m,i}$ is the heat of melting, *T* is the varying temperature of fusion of the solution, and $T^*_{m,i}$ is the melting temperature of the pure substance *i*. Substitution into the above expressions (2.109) and (2.110) gives

$$\ln\left(\frac{x_{A(s)}}{x_{A(l)}}\right) = \frac{\Delta \overline{H}_{m,A}}{RT} \left(1 - \frac{T}{T_{m,A}^*}\right)$$
(2.116)

and

$$\ln\left(\frac{x_{B(s)}}{x_{B(l)}}\right) = \frac{\Delta \overline{H}_{m,B}}{RT} \left(1 - \frac{T}{T_{m,B}^*}\right)$$
(2.117)

With these expressions, the mole fractions $x_{B_{(1)}}$ and $x_{B_{(s)}}$, respectively, can now be computed as a function of the temperature *T*. Expressions [2.116] and [2.117], respectively, are also the expressions for the equilibrium distribution coefficients.

In each phase the sum of the mole fractions of all components is equal to unity, $x_{A(s)} + x_{B(s)} = 1$ and $x_{A(l)} + x_{B(l)} = 1$.

These relations can be combined with Eqs. (2.116) or (2.117), and one gets after some algebraic manipulation

$$x_{A(l)} = \frac{1 - \exp[(\Delta H_{m,B}/RT)(1 - T/T_{m,B}^*)]}{\exp[(\Delta H_{m,A}/RT)(1 - T/T_{m,A}^*)] - \exp[(\Delta H_{m,B}/RT)(1 - T/T_{m,B}^*)]}$$
(2.118)

or the analogous expression for the mole fraction of *B* in the liquid phase.

The mole fraction in the solid can then easily be obtained from the rearranged Eq. (2.116)

$$x_{A(s)} = x_{A(l)} \exp\left[\frac{\Delta \overline{H}_{m,A}}{RT} \left(1 - \frac{T}{T_{m,A}^*}\right)\right]$$
(2.119)

In this way, the complete solidus and liquidus curves of the binary phase diagram can be calculated. The only data required are the melting temperatures of the pure substances, $T^*_{m,A}$ and $T^*_{m,B}$, and the corresponding heats of fusion, $\Delta \overline{H}_{m,A}$ and $\Delta \overline{H}_{m,B}$, respectively.

2.6

Thermodynamics of Crystal Growth from the Vapor

2.6.1 General Considerations

Growth from the vapor is the preferred phase transition for the production of thin epitaxial layers, while growth of bulk crystals from the vapor is rather the exception, only applied if unavoidable. An example is the growth of semiconductor-grade SiC by the so-called modified Lely method (MLM), a sublimation technique. The physical reason for the avoidance of vapor growth techniques for bulk crystals is the huge difference in the particle densities between the two states of aggregation.

In vapor growth, the formation of a crystal is the result of a phase transition $gas \rightarrow solid$. The constituents of the crystal to be grown are fed into the deposition

zone of the reactor via the vapor phase. Vapor-growth techniques can be classified into physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods. The characteristic of the physical methods is the transition of a source material into the vapor phase by evaporation or sputtering, the transport of this material through a concentration or temperature gradient, and its condensation on the growing surface. In PVD processes, the character of the vapor is preferably beam-like, and the mean free path length of vapor species is larger than the distance between source and substrate surface.

CVD processes can be characterized as the formation of a crystal (mostly a crystalline layer) as the result of a chemical reaction involving one or more reagent gas(es) containing constituents of the material to be deposited. The mean free path of the vapor phase species is shorter than the distance between inlet into the reaction chamber and substrate surface.

Consequently, PVD processes usually proceed under high-vacuum conditions ($P < 10^{-1}$ Pa), while CVD processes usually take place at atmospheric or only slightly reduced pressure (10^5 Pa $\ge P \ge 10^2$ Pa).

The borders between the two classes of vapor phase growth techniques are not sharp. Even in the processes generally considered as typical physical vapor deposition processes, in most cases chemical reactions take place. The most striking example is molecular beam epitaxy (MBE).

PVD plays a minor role in the growth of single crystals. This is mainly due to the incongruent evaporation of the source materials leading to deviations in stoichiometry and lower crystallographic perfection. In order to maintain the beam-like characteristics of the material flux, high or ultrahigh vacuum is required, thus inherently a low material density in the vapor phase exists, resulting in low growth rates.

The most widely used methods of chemical vapor deposition are chemical synthesis processes performed in open-flow systems. Here the constituents of the crystal to be grown are transported as volatile chemical compounds, mostly independent from each other in the case of a crystalline compound, into the deposition zone, where they decompose and/or react with each other. In most cases appropriate gaseous compounds are available that also exist at room temperature. Sometimes, however, appropriate feed gas compounds are stable only at high temperatures and must therefore be synthesized only within the reactor (GaCl_(g) is a typical example). In these methods, a continuous supply of feed gases into the deposition zone can be provided. The feed gases can also be transported by means of an inert carrier gas, whose flow can be easily controlled. Thus, in open-flow systems, changes in the gas supply can easily be realized in any desired manner, and the sources are inexhaustive.

In chemical transport processes, the source material and the crystal to be grown are – in contrast to chemical synthesis processes – identical. In a source zone, the starting material is converted into one or more volatile chemical compound(s) by a chemical reaction with a transporting agent. The volatile material is transported by a carrier gas or a pressure difference into the spatially separated deposition region where the thermodynamic conditions favor the reaction in the opposite direction.

Also combinations between transport and synthesis methods are possible. The disadvantage of transport processes is that impurities of the source material are in most cases also incorporated into the deposited material, and that a presynthesis of the substance to be grown in crystalline form is required. Furthermore, deliberate doping is difficult.

The advantages of vapor growth methods can be summarized as follows:

- Crystallization proceeds at temperatures much below the melting point.
- The lack of a liquid phase increases the variance of the system (cf. Gibbs' phase rule!).
- Also "difficult" materials, impossible to obtain by other methods (for example, owing to large differences in the segregation coefficients of the constituents of an alloy) can be synthesized.
- Mixed crystal composition and dopant concentration can be held constant or changed in almost any desired manner during growth.
- Generally, the source materials for the synthesis process can be provided with high purity.
- The thickness of crystalline layers to be deposited can be controlled with an accuracy of one atomic monolayer.
- The crystalline material generally shows good surface morphology, high purity, good crystallographic perfection and uniform layer thickness, if required.
- Owing to the high supersaturation achievable in most CVD processes, they are well suited for heteroepitaxial deposition. Meltback, or substrate dissolution, frequently posing problems in the presence of a liquid phase, does not occur.
- Chemical vapor deposition in open-flow systems is well suited for scaling up to industrial requirements of mass production.

2.6.2

Thermodynamics of Physical Vapor Growth

Most physical methods include the thermal evaporation of a starting material. For good control of such a process knowledge of the temperature dependence of the vapor pressure is an important prerequisite. Vapor pressures, melting and boiling points, and their associated energies have been thoroughly selected, evaluated and tabulated for 81 elements by Honig and Kramer [23]. This compilation is a reliable source still today. The vapor pressures P are tabulated as a function of the absolute temperature T in terms of the general equation

$$\log_{10} P = AT^{-1} + B\log_{10} T + CT + DT^2 + E$$
(2.120)

where A, B, C, D, E are coefficients characteristic of the element. In most cases, only A and E are used.

Especially in the two-term presentation the thermodynamic background for this equation is easily recognized.

Considering a one-component system, the condition for liquid \leftrightarrow vapor equilibrium is

$$(V_{(g)} - V_{(l)})dP - (S_{(g)} - S_{(l)})dT = 0$$
(2.121)

This gives

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{(S_{\rm (g)} - S_{\rm (l)})}{(V_{\rm (g)} - V_{\rm (l)})} \tag{2.122}$$

and with

$$\Delta S = \frac{\Delta H}{T} \tag{2.123}$$

one arrives at Clapeyron's equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{T(V_{\mathrm{g}} - V_{\mathrm{l}})} \tag{2.124}$$

with ΔH the latent heat of vaporization (or sublimation, for the evaporation of a solid). Clapeyron's equation is the general expression for the temperature dependence of the vapor pressure of a condensed phase. More frequently used is the so-called Clausius-Clapeyron equation. It is obtained from the Clapeyron equation with two approximations:

- 1. The molar volume of the liquid is neglected in comparison to the molar volume in the vapor phase: $V_{(g)} - V_{(l)} \approx V_{(g)}$.
- 2. The vapor phase is assumed to behave as an ideal gas: $V_{(g)} \approx \frac{RT}{P}$.

With these two approximations Clapeyron's equation becomes

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{vap}}P}{RT^2} \quad \text{or} \quad \frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{vap}}}{RT^2} \tag{2.125}$$

Integration gives

$$P(T) = P_{\rm o} \exp -\left(\frac{\Delta H_{\rm vap}}{RT}\right)$$
(2.126)

This is the well-known Clausius-Clapeyron equation, which explains the origin of the above-mentioned constants A and E in the compilation of the vapor-pressure data.

By coupling with kinetic aspects, one can extend these considerations to nonequilibrium conditions, such as evaporation into a vacuum. This is a situation that frequently prevails in industrial crystal production.
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For a one-component system the evaporation can be written as a chemical reaction

$$A_{(\mathrm{s})} \leftrightarrow A_{(\mathrm{g})}$$

The corresponding law-of-mass-action expression is

$$\frac{a_{A_{\rm (g)}}}{a_{A_{\rm (s)}}} = \frac{P_A^{\rm eq}}{1} = K(T) = \exp -\left(\frac{\Delta G_{\rm r}^{\rm o}}{RT}\right)$$
(2.127)

with P_A^{eq} – equilibrium vapor pressure of A.

Thus, the equilibrium pressure can be calculated from the standard free energy of reaction ΔG_r^0 . This can be found from tabulated thermochemical standard data:

$$\Delta G_{\rm r}^{\rm o} = G_{A_{\rm (g)}}^{\rm o} - G_{A_{\rm (s)}}^{\rm o} \tag{2.128}$$

Now, from kinetic gas theory, the particle flux condensing on a standard area per unit time is

$$J_{\rm cond} = P^{\rm eq}(T)/\sqrt{2\pi m k_{\rm B} T}$$
(2.129)

if equilibrium is established, i.e. when the flux density of evaporating particles is the same as that of condensing particles, $J_{\text{vap}} = J_{\text{cond}}$.

This leads to

$$J_{\rm vap}(T) = \frac{P^{\rm eq}(T)}{\sqrt{2\pi m k_{\rm B} T}} = \frac{1}{\sqrt{2\pi m k_{\rm B} T}} \exp\left(-\frac{\Delta G_{\rm r}^{\rm o}}{RT}\right)$$
(2.130)

Again, this shows how thermodynamic and kinetic approaches can be coupled; eventually permitting the assessment of nonequilibrium situations, in this case the evaporation into a vacuum.

We will remember the kinetic approach from Jackson [5], discussed in Section 2.3. Jackson's approach was

$$r = a \cdot \upsilon^+ \cdot f \cdot u_k \tag{2.41}$$

where

a a distance related to the atomic or molecular diameter of the growth unit

 v^+ the rate at which atoms join the crystal at active growth sites on the surface

f the fraction of interface sites that are active growth sites, and

 u_k the local free energy (or chemical potential) difference between the two phases. In a kinetic approach the thermal activation of surface atoms out of their surface potential wells must be considered:

$$J_{\rm vap}(T) = n_{\rm s}(T) f_{\rm vib} \exp\left(-\frac{\Delta G_{\rm des}}{k_{\rm B}T}\right)$$
(2.131)

This can be compared with the expression (2.41) given above.

Considering solid \leftrightarrow vapour equilibria in binary systems with compound formation, for many systems the evaporation can best be characterized by a chemical reaction

$$nAB_{(s)} \leftrightarrow nA_{(g)} + B_{n(g)}$$

$$K_{p}(T) = P_{A}^{n}P_{B_{n}}$$
(2.132)

The activity of the pure solid is unity. The equilibrium constant can be calculated from tabulated standard data:

$$\ln K = -\frac{\Delta G^{\circ}}{RT} \quad \text{and} \quad \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
(2.133)

The total pressure is the sum of the two partial pressures, $P_{\text{tot}} = P_A + P_{B_n}$, with the only constraint that the product of the two partial pressures must stay constant.

At any temperature there is a minimum total pressure that can be obtained from either of the two conditions

$$\frac{\partial P_{\text{tot,min}}}{\partial P_A} = 0 \tag{2.134}$$

and

$$\frac{\partial P_{\text{tot,min}}}{\partial P_{B_n}} = 0 \tag{2.135}$$

This gives

$$P_{A,\min} = nP_{B_n,\min} = n^{\frac{n}{n+1}} K_p^{\frac{1}{n+1}}$$
(2.136)

The sum of these two partial pressures provides the minimum pressure at the point where the stoichiometric solid melts.

2.6.3

Thermodynamics of Chemical Reactions

Epitaxial layers of compound semiconductors are most frequently grown by chemical synthesis reactions. Thermodynamics can predict whether a reaction is feasible at all for the generation of crystalline solid from the vapor phase. It can, furthermore, predict the effect of variations in the experimentally controllable variables, such as input partial pressures and temperature on the yield of the reaction or the composition of solid solutions.

Let us consider the following generic chemical reaction:

 $aA + bB \Leftrightarrow cC + dD$

where *a*, *b*, *c* and *d* are the stoichiometric coefficients.

The change in free energy associated with this reaction is

$$\Delta G = cG_C + dG_D - aG_A - bG_B \tag{2.137}$$

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The free energy of any of the individual reactant or product species *i* is given by

$$G_i = G_i^0 + RT \ln a_i \tag{2.138}$$

 G_i° is the standard free energy of the species *i*, *R* is the universal gas constant, *T* the absolute temperature, and *a_i* is the activity of *i*, an effective concentration. "Standard free energy" refers to the free energy of the species in a standard state. For solids this is usually the pure form of that modification of the compound or element that is the stable one at pressure *P* = 1 bar and at temperature *T*. These data can obtained from tabulated standard data,

$$G_i^{\rm o} = H_i^{\rm o} - TS_i^{\rm o} \tag{2.139}$$

The standard enthalpies and entropies are tabulated in books or computerized data bases as H_{298}^{o} and S_{298}^{o} . They can easily be calculated for other temperatures.

The activities are usually given as product of the actual concentration c_i and an activity coefficient γ_i . The preferred concentration measure is, for convenience, the mole fraction or atom fraction x_i , which is obtained from the total number of moles (or atoms, respectively) of the constituents of the system:

$$x_i = \frac{n_i}{n_A + n_B + n_C + \dots}$$
(2.140)

Thus, $a_i = \gamma_i x_i$. Vapor phases are mostly considered as ideal gas mixtures and partial pressures are used instead of concentrations. They are defined in the same manner as in Eq. (2.140), the mole numbers, however, are replaced by the respective pressures.

Combination of these equations gives

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} = \Delta G^{\circ} + RT \ln \frac{x_C^c x_D^d}{x_A^a x_B^b} + RT \ln \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$$
(2.141)

with the standard free energy of reaction

$$\Delta G^{\circ} = cG_C^{\circ} + dG_D^{\circ} - aG_A^{\circ} - bG_B^{\circ}$$

$$\tag{2.142}$$

For a system in equilibrium $\Delta G = 0$, and all activity values are the equilibrium ones. Thus

$$0 = \Delta G^{\circ} + RT \ln \frac{a_{C_{(eq)}}^{c} a_{D_{(eq)}}^{d}}{a_{A_{(eq)}}^{a} a_{B_{(eq)}}^{b}} = \Delta G^{\circ} + RT \ln K_{eq}$$
(2.143)

The law of mass action equilibrium constant K_{eq} can be calculated from the thermodynamic standard data of all reactants and products involved:

$$\ln K_{\rm eq} = -\frac{\Delta G^{\rm o}}{RT} \tag{2.144}$$

For a situation where chemical equilibrium is still not established, one gets from Eqs. (2.141) and (2.144)

$$\Delta G = \Delta G^{o} + RT \ln \frac{a_{C}^{c} a_{D}^{d}}{a_{A}^{a} a_{B}^{b}} = -RT \ln K_{eq} + RT \ln \frac{a_{C}^{c} a_{D}^{d}}{a_{A}^{a} a_{B}^{b}}$$
$$= RT \ln \frac{\left(a_{C}/a_{C_{(eq)}}\right)^{c} \left(a_{D}/a_{D_{(eq)}}\right)^{d}}{\left(a_{A}/a_{A_{(eq)}}\right)^{a} \left(a_{B}/a_{B_{(eq)}}\right)^{b}}$$
(2.145)

In this equation, each term $(a_i/a_{i_{(eq)}})$ represents a supersaturation of the species *i*, if it is larger than unity, and an undersaturation if it is less than unity. If the numerator in Eq. (2.145) is smaller than the counter, ΔG is negative and the reaction will proceed spontaneously to the right-hand side of the reaction equation. The driving force for the reaction is the possible decrease in free energy as long as the argument to the logarithm is smaller than unity.

It has already been mentioned that from a thermodynamic point of view the art of crystal growth consists in maintaining a permanent state of deviation from equilibrium over long time periods.

Usually, one wants to grow crystals with supersaturations not too high, because the kinetics also follows laws with potentials of the concentrations (or activities). Thus, high supersaturations result in high growth rates and rearrangement of wrongly positioned building units is hardly possible. Another way to react against supersaturations that are too high is that nuclei do not increase in size so quickly, instead of this the frequency of formation of nuclei is increased in an undesirable measure.

Summarizing, crystals should be grown with supersaturations that are not too high, or, in other words, under conditions where the activities of the reactant species are not too far from their equilibrium values. Under such conditions $\Delta G \approx \Delta G^{\circ}$ and the standard free reaction energy provides the information on the feasibility of a chemical reaction for the crystal formation.

Ohring [9] points to another important aspect: "... also many of the data are the result of measurement, some values are inferred from various connecting thermodynamic laws and relationships. In this way a consistent set of thermodynamic data for a very large number of materials has been generated. Thus, even though the vapor pressure of tungsten at room temperature cannot directly be measured, its value is nevertheless 'known'. It should be borne in mind, that the data refer to equilibrium conditions only, and that many reactions are subject to overriding kinetic limitations despite otherwise favorable thermodynamic indications."

2.6.4

Thermodynamics of Chemical Vapor Deposition - Transport Methods

Chemical transport reactions were introduced in 1925 by van Arkel and de Boer for the purification of zirconium. Zirconium metal reacted with iodine forming the

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volatile zirconium tetraiodide. This was transported into a hotter region, where the back reaction takes place. Analogous reactions are still in widespread use.

Another example for a transport reaction is the deposition of crystalline $GaAs_{(s)}$ via transport with $HCl_{(g)}$:

$$4GaAs_{(s)} + 4HCl_{(g)} \iff 4GaCl_{(g)} + As_{4(g)} + 2H_{2(g)}$$

At higher temperatures the reaction proceeds predominantly to the right, while the back reaction prevails at lower temperature.

The direction of transport with respect to the temperature depends on the sign of the enthalpy of reaction $\Delta_r H_T^o$, according to the van't Hoff equation

$$\frac{d\ln K_{\rm p}}{dT} = \frac{\Delta_{\rm r} H_T^{\rm o}}{RT^2} \tag{2.146}$$

For an efficient transport the following conditions must be fulfilled:

- The equilibrium constant of the reaction must not be extreme (because forward and back reaction are needed); as a rule of thumb it should be of the order of unity.
- The magnitude of the enthalpy of reaction Δ_rH^o_T should not be too small; otherwise very large temperature gradients would be required.

2.6.5

Thermodynamics of Chemical Vapor Deposition – Synthesis Methods

In contrast to transport methods the term "synthesis methods" is used here for chemical reactions where the crystalline final product has a chemical composition different from that of the source material. Thus, the deposition of a silicon epitaxial layer by thermal decomposition of silane will also be denoted as "synthesis" method, although it is a decomposition – commonly considered as the opposite to synthesis.

For a thermodynamic treatment of crystal formation by chemical synthesis processes the following suppositions approach will be chosen:

- Source region and deposition region are considered separately.
- Thermodynamic equilibrium is established in both the zones independently.
- In the source region those chemical species are generated that eventually enter the deposition zone.
- The partial pressures of the species entering the deposition region correspond to their equilibrium values in the source region.
- The equilibrium partial pressures in the deposition region are established according to the conditions (temperature, presence of the crystalline final product) in this region.

The driving force for growth is the nonequilibrium situation in the deposition region that is built up either by the changed growth environment (temperature different from that in the source region) or by bringing together different vapor phase species that have been fed into this region separately and can now react with each other.

Equilibrium in the deposition region is established by either extraction or addition of gaseous species under formation (or dissolution, resp.) of solid material.

A fruitful approach to the thermodynamic treatment of chemical vapor deposition has been developed by Sirtl *et al.* and Ban *et al.* for the technologically important epitaxial deposition of Si from tetrachlorosilane and hydrogen [24, 25]. Hurle and Mullin developed a related concept for the deposition of III-V compound mixed-crystal layers [26]. The general approach consists in the numerical solution of a set of equations that is obtained from the law-of-mass-action expressions for all the independent chemical reactions between the different chemical species present in the deposition region and the conditions for the conservation of masses. Following Hurle and Mullin [26], the deposition of epitaxial layers of $GaAs_{1-x}P_x$, as applied in LED production, is used as an example.

The above-mentioned assumptions are specified as follows:

- The deposition region is considered to be a pseudoequilibrium region, i.e. the nonequilibrium input gas mixture converts rapidly into an equilibrium one with establishment of thermodynamic equilibrium between all coupled reactions.
- All vapor species obey the ideal gas law.
- At the liquid Ga source, complete conversion of the incoming HCl gas into GaCl takes place. Consequently, all HCl in the deposition region stems from the formation of the solid.
- The nine gaseous species that must be taken into account are H₂, HCl, GaCl, PH₃, P₄, P₂, AsH₃, As₄, and As₂.

Under these presumptions one has six independent chemical reaction equations:

 $2GaCl + 1/2As_4 + H_2 \iff 2GaAs_{(ss)} + 2HCl$ $2GaCl + 1/2P_4 + H_2 \iff 2GaP_{(ss)} + 2HCl$ $As_4 \iff 2As_2$ $AsH_3 \iff 1/2As_2 + 3/2H_2$ $P_4 \iff 2P_2$ $PH_3 \iff 1/2P_2 + 3/2H_2$

Another independent equation is the expression for the total pressure p_{tot} , which is the sum of the partial pressures of the different chemical species present in the

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system:

$$p_{tot} = p_{H_2} + p_{GaCl} + p_{HCl} + p_{As_4} + p_{As_2} + p_{AsH_3} + p_{p_4} + p_{p_2} + p_{PH_3}$$

The total pressure is in an open-flow system, as is common for industrial processes, 1 bar and equal throughout the system. Two other independent equations are obtained from the introduction of two variables whose values are constant throughout the deposition process. One is the input ratio of the Cl- and H-bearing species

$$q_1 = \frac{n_{\rm Cl}}{n_{\rm H}} = \frac{p_{\rm HCl} + p_{\rm GaCl}}{p_{\rm HCl} + 2p_{\rm H_2} + 3p_{\rm AsH_3} + 3p_{\rm PH_3}} = q_1^{\rm o}$$

while the other one is the ratio of the Ga-bearing and As- or P-bearing species to the number of H-bearing species:

$$q_{2} = \frac{n_{\text{Ga}} - (n_{\text{As}} + n_{\text{p}})}{n_{\text{H}}}$$
$$= \frac{p_{\text{GaCl}} - (p_{\text{AsH}_{3}} + p_{\text{PH}_{3}} + 4p_{\text{As}_{4}} + 2p_{\text{As}_{2}} + 4p_{\text{p}_{4}} + 2p_{\text{p}_{2}})}{p_{\text{HCl}} + 2p_{\text{H}_{2}} + 3p_{\text{AsH}_{3}} + p_{\text{PH}_{3}}} = q_{2}^{\text{o}}$$

 n_i is the number of moles of atomic species *i*, which is obtained from the perfect gas law as $n_i = m_i/M_i = p_i V/RT$ with the mass m_i and the molecular weight M_i . Using a quotient causes the common factor V/RT, which contains the volume *V* and the temperature *T* of the reactor, to cancel out.

The superscript ° denotes the input ratio. It remains constant, i.e. $q = q^{\circ}$ throughout the process. q_1 remains constant because neither Cl nor H are incorporated into the solid phase, accordingly q_2 remains constant because the sum of the As and P atoms entering the solid is equal to the number of Ga atoms in the growing mixed crystal, thus the number Ga atoms lost from the vapor phase by formation of the crystalline layer equals the sum of the arsenic and phosphorous atoms lost from the vapor phase.

For the chemical reaction equations given above the corresponding law-of-mass-action expressions can be written down. The equilibrium constants can be calculated from the thermodynamic standard data.

A problem is the activity coefficients in the solid mixed crystal phase, for which, however, different models are available, as discussed in Section 2.5.3.

Now we have nine independent equations for nine unknowns (the partial pressures). The equilibrium partial pressures of all of the species are obtained as solutions to this system of equations.

These are related to the input partial pressures p_i^0 (experimental variables) via

$$p_{AsH_3}^{o} = p_{AsH_3} + 4p_{As_4} + 2p_{As_2} + (1 - x)p_{HCl}$$
$$p_{PH_3}^{o} = p_{PH_3} + 4p_{P_4} + 2p_{P_2} + xp_{HCl}$$

The HCl terms account for the arsenic and phosphorous transferred into the solid. *x* is the mole fraction of GaP in the solid solution $GaAs_{1-x}P_x$.

In this principal way the composition of mixed crystals can be calculated as a function of the experimental growth variables p_{tot} , T, q_1^o , q_2^o for all systems and growth methods, including MOCVD. Today, such calculations are easily performed by computer programs. The correspondence between calculations and experiment is usually quite good, even for methods where it is not immediately expected, e.g., MBE that is said to operate far from equilibrium.

2.7 Solid-Solid Equilibria

Many solids occur in different crystal structures that from a thermodynamic point of view are distinct phases. Transitions from one solid phase into another one obey the same laws as do solid—liquid phase changes, for example. Most solid–solid phase transitions occur at high temperatures and pressures, far from normal ambient conditions, so the modification of many materials we observe is only one of many possible structures. Sometimes, phase transitions in the solid state prevent the applicability of an otherwise desirable crystal-growth method. As an example, it should be remembered that the solidification of a silica melt leads to the cristobalite modification of SiO₂ and not to the desired α -quartz modification.

The appearance of different solid phases with increasing temperature up to melting is the rule rather than the exception. In the reverse direction, during cooling, usually a high-temperature modification is frozen-in, i.e. the modification that is thermodynamically stable at room temperature is not obtained for kinetic reasons.

Also, solid \rightarrow solid transitions are a consequence of free-energy minimization, just as is the melting process. It has been discussed several times already that at constant pressure the free energy changes with temperature as $\left(\frac{\partial G}{\partial T}\right)_{\rm p} = -S$. Since the entropy is always positive, the free energy of any phase decreases with increasing temperature. If a substance is heated that can occur in two modifications in the solid state before melting, phase stability is inferred from the three Gibbs free-energy curves (for the liquid and the two solid phases). The entropy of the liquid phase is generally higher than that of any solid phase, therefore the slope of the $G_{(1)}(T)$ curve is steeper than that of both the $G_{(s1)}(T)$ and the $G_{(s2)}(T)$ curves. The slope of the $G_{(s)}(T)$ curve is less steep for the solid phase with the lower entropy than the corresponding one for the solid phase with the larger entropy. On the other hand, the free energy of the phase with the highest degree of order is lowest at the lowest temperatures, because the enthalpy contribution to the free energy is dominant at the lower temperature. The point where two curves intersect is the phase-transition temperature. The phase with the lower enthalpy, but larger entropy remains stable up to the melting temperature, where the $\Delta G(T)$ curve of the liquid phase intersects that of the solid.

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A solid–solid equilibrium of special interest is the graphite \rightarrow diamond transition. Diamond has a structure of higher symmetry than that of graphite, which is also reflected in the densities ρ of the two modifications ($\rho_d = 3.513 \text{ g/cm}^3$, $\rho_g = 2.266 \text{ g/cm}^3$). Consequently, diamond has a molar entropy that is lower than that of graphite ($S_{\text{diamond}} = 2.360 \text{ J/(mole K)}$, $S_{\text{graphite}} = 5.742 \text{ J/(mole K)}$), the difference being $\Delta S_{d-g} = -3.382 \text{ J/(mole K)}$. At room temperature, the free energy difference between the two phases is

$$\Delta G_{d-g} = \Delta H_{d-g} - T \Delta S_{d-g} = (1828 - 0) - [300 \times (-3.382)] = 2843 \text{ J/mole}$$
(2.147)

At normal pressures it remains positive up to the melting point of graphite, $T_{\rm m} \approx$ 4765 K. Thus, graphite is the thermodynamically stable form and diamond exists only due to the extremely slow transformation kinetics.

Natural diamonds, metastable in our common world, were created deep in the Earth's mantle under higher pressure. The partial differential of the free energy with respect to pressure is

$$\left(\frac{\partial \Delta G_{\rm d-g}}{\partial P}\right)_T = \Delta V_{\rm d-g} \tag{2.148}$$

Integration between atmospheric pressure (10⁵ Pa) and the pressure $P_{d/g}$, at which both forms can coexist, gives

$$\Delta G_{d-g}(P_{d/g}) - \Delta G_{d-g}(10^5) = \Delta V_{d-g}(P_{d/g} - 10^5)$$
(2.149)

The difference between the molar volumes can be calculated from the density data, given above,

$$\Delta V_{\rm d-g} = \frac{12.011}{3.513} - \frac{12.011}{2.266} = 3.419 - 5.301 = -1.882 \,\rm{cm}^3/mole$$

Assuming the compressibilities of the two allotropes are the same, this difference can be considered as independent from the pressure.

Now, the transformation from graphite to diamond can occur when the free energies of the two phases are the same, i.e. when ΔG_{d-g} ($P_{d/g}$) = 0. From Eq. (2.149) we get

$$\begin{split} \Delta G_{d-g}(P_{d/g}) &- \Delta G_{d-g}(10^5) = \Delta V_{d-g}(P_{d/g} - 10^5) \\ 0 &- 2843 = -1.88 \times 10^{-6} (P_{d/g} - 10^5) \\ P_{d/g} &= \frac{-2843}{-1.88 \times 10^{-6}} + 10^5 = 1.512 \times 10^9 \text{ Pa} = 1.512 \times 10^4 \text{ bar} = 15.12 \text{ kbar} \end{split}$$

From this thermodynamic analysis the transformation from graphite to diamond can be expected to proceed at a pressure of about 15 kbar.

2.8 Thermodynamics of Nucleation and Interfaces

A building unit in the surface of a liquid or a solid phase has a different surrounding from a particle inside the volume. On average, a particle within the volume has the same kind of neighbors more or less symmetrically placed around it. The particle is on a site where its energy is minimized because it is only on this position. Any change in its environment would increase its energy. The bonding vectors directing from an interface particle to its neighbors show an asymmetric distribution. The total differential of the Gibbs free energy, *G*, is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\mu_i,n_j,\dots,A} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\mu_i,n_j,\dots,A} dP + \sum_{i=1}^{i=k} \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\dots,A} dn_i + \left(\frac{\partial G}{\partial A}\right)_{T,P,n_i,n_j,\dots} dA$$
(2.13)

or, substituting the partial derivatives in this expression by the variables so far discussed,

$$dG = -SdT + VdP + \sum_{i=1}^{i=k} \mu_i dn_i + \gamma dA$$
(2.150)

 n_i is the mole number of the *i*th constituent, μ_i is its chemical potential, γ is the free energy per unit area of surface (sometimes also designated by σ), and *A* is the surface area. Frequently, γ is also called surface tension. Surface energies of condensed phases have values between 0.2 to 3 J/m², most typically about 1 J/m². With increasing temperature, they decrease slightly.

Let us estimate the contribution of the interface formation to the total change in free energy associated with the crystallization of one mole of a certain substance in compact form. Considering only orders of magnitude, one mole corresponds typically to a volume of $10-30 \text{ cm}^3$. This gives a surface area in the order of a few cm² or some 10^{-4} m^2 . With a specific surface energy of 1 J/cm^2 , the interface contribution to the free energy is numerically the same. The molar volume contribution to the free energy is in the order of one kJ to tens of kJ. Thus, the surface contribution to the total change in free energy is about seven (or more) orders of magnitude smaller than the volume term and can be ignored for macroscopic dimensions.

Now, let us consider an epitaxial layer of a few monolayer thickness on a substrate with 2" diameter. The volume of such a layer is in the order of 10^{-6} cm³, corresponding to a mole number in the order of 10^{-7} . The interface area amounts to a few 10^{-3} m². Thus, the volume contribution is in the order of a few tens or hundreds of Joule, and the interface energy is about four orders of magnitude lower.

For an isothermal, isobaric system of unchanging size and composition, $\gamma dA = w$ is the reversible work required to incrementally create additional surface. The energy of a surface can be altered by a change in either γ or A. Changes in the

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specific surface energy can be caused by changes in the arrangement of the surface atoms (surface reconstruction), as is observed on the substrate surface during heating in MBE growth. It can also be altered by strain exerted by the intergrowth of two materials with nonmatching lattice parameters, or, e.g., by the formation of an oxide layer.

Interface energies are of importance when a new phase is emerging. In crystal-growth practice one is predominantly concerned with heterogeneous nucleation because commonly a substrate or a seed crystal is required in order to force the growth in a specified crystallographic direction and to lower the supersaturation required for crystallization to occur.

When a nucleus of a crystalline film F is formed from atoms leaving a nutrient phase N and depositing onto a substrate S, volume of F and two new interfaces, those between the film and the nutrient and the film and the substrate, are formed, while the area of another one, that between the substrate and the nutrient, diminishes. Consequently, the associated total change in free energy is given by

$$\Delta G = a_3 r^3 \Delta G_{\rm V} + a_1 r^2 \gamma_{\rm fn} + a_2 r^2 \gamma_{\rm fs} - a_2 r^2 \gamma_{\rm sn}$$
(2.151)

The superscripts refer to the different interfaces. *r* is a mean dimension, and the *a*'s are factors accounting for the nucleus geometry. Assuming the nucleus shape to be a spherical cap with the curved surface area a_1r^2 , the projected circular area a_2r^2 on the substrate and the volume a_3r^3 , these factors are $a_3 = \frac{\pi}{3}(2 - 3\cos\theta + \cos^3\theta)$, $a_1 = 2\pi(1 - \cos\theta)$, and $a_2 = \pi \sin^2\theta$, and θ is the contact or wetting angle.

Formation of new volume leads to the release of energy, thus also decreasing the free energy, while the creation of new surfaces requires energy. At very small dimensions the creation of interfaces is the dominant contribution, while the counteraction of volume formation determines the total free-energy change when the nucleus grows further. Thus, it can be expected that the dependence of the free energy on the nucleus dimension passes through a maximum. Differentiation of Eq. (2.151), setting this to zero and resolving for *r* gives a critical dimension *r*_{crit}, on both sides of which the free energy ΔG decreases. Thus, nuclei with dimensions smaller than *r*_{crit} tend to dissolve, while surpassing this value leads to further stabilization. The critical radius is

$$r_{\rm crit} = \frac{-2(a_1\gamma_{\rm fn} + a_2\gamma_{\rm fs} - a_2\gamma_{\rm sn})}{3a_3\Delta G_{\rm V}}$$
(2.152)

Substituting this back into the expression (2.151) for the free energy, gives

$$\Delta G_{\rm crit} = \frac{4(a_1 \gamma_{\rm fn} + a_2 \gamma_{\rm fs} - a_2 \gamma_{\rm sn})^3}{27 a_3^2 \Delta G_{\rm V}^2}$$
(2.153)

Substituting the geometrical constants by the corresponding expressions with the wetting angle θ and rearranging leads to

$$\Delta G_{\rm crit} = \frac{16\pi (\gamma_{\rm fn})^3}{3(\Delta G_{\rm V})^2} \left\{ \frac{2 - 3\cos\theta + \cos^3\theta}{4} \right\}$$
(2.154)

In this expression, the bracketed term accounts for the interaction of the nucleus with the substrate. In the case of maximum wetting ($\theta = 0$), the term in brackets

becomes zero, i.e. there is no barrier to nucleation at all. At the other extreme, complete dewetting ($\theta = 180^{\circ}$), the term in brackets becomes unity, and the free energy change associated with the formation of a nucleus with the critical diameter, $r_{\rm crit}$, is equal to that for homogeneous nucleation.

In a similar manner, other contributions to the change in free energy can be taken into account. An important case is the strain energy that is stored in an epitaxial layer when the lattice constants of the free-standing substrate and layer materials do not agree. It can be assumed that a nucleus of the layer material is elastically strained throughout, while the bulky substrate crystal remains rigid. The free energy of a strained material is higher than that of the material in its relaxed form. This can be taken into account in Eq. (2.151) by adding a strain-related contribution $a_3r^3\Delta G_s$ to the volume term of the free energy change. Eq. (2.154) takes the form

$$\Delta G_{\rm crit} = \frac{4(a_1\gamma_{\rm fn} + a_2\gamma_{\rm fs} - a_2\gamma_{\rm sn})^3}{27a_3^2(\Delta G_{\rm V} + \Delta G_{\rm s})^2}$$
(2.155)

 $\Delta G_{\rm V}$ is negative, while $\Delta G_{\rm s}$ has a positive sign. Thus, strain leads to an increase in $\Delta G_{\rm crit}$, the energy barrier to nucleation increases.

In other cases, impurities on the substrate surface or electrical charges can also alter the free-energy change associated with the heterogeneous nucleation.

Coupling thermodynamics with elasticity theory enables the derivation of an explanation for the change in the growth mechanisms of epitaxial layers and the critical layer thickness can be estimated, at which the transition from a flat layer-by-layer growth to rough surfaces formed by the growth of independent three-dimensional islands occurs. This has been worked out by Wessels [27]. The following considerations are based on his paper. For didactic reasons they will be simplified by restricting the discussion to normal stresses and strains and using scalars in a mean-field approximation instead of tensors.

Three classical growth modes can be distinguished. These are the two-dimensional layer-by-layer growth (Frank–van der Merwe mechanism), the growth of three-dimensional isolated islands (Volmer–Weber mechanism) and the combined mechanism of initial layer growth, switching after a few layers into the growth of isolated islands (Stranski–Krastanov mode). For energetic reasons the layer growth proceeds two-dimensionally in its first stage. If there is a lattice mismatch between substrate and layer materials, the film of one or only a few atomic layers thickness is elastically strained. The lattice mismatch strain f, or simply misfit, is defined as

$$f = \frac{|a_{0(f)} - a_{0(s)}|}{a_{0(s)}}$$
(2.156)

where $a_{0(f)}$ and $a_{0(s)}$ are the lattice parameters of the unstrained film and substrate materials, respectively. The substrate remains in a relaxed state, i.e. it preserves its unstrained lattice constant $a_{0(s)}$, while the epitaxial layer is deformed and stores a certain amount of free strain energy ΔG_s . From elasticity theory, this energy can be expressed as

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$$\Delta G_{\rm s} = \frac{1}{2} Y \varepsilon^2 \tag{2.157}$$

where *Y* is Young's modulus and ε is the strain. The strain is the deformation caused by a stress σ . The latter corresponds to a pressure, i.e. a force *F*, exerted onto an area *A*, $\sigma = \frac{F}{A}$. The strain is expressed as a relative change in length, $\varepsilon = \frac{\Delta l}{l_0}$. In an elastic regime, strain and stress are linearly proportional and coupled via *Y* as the proportionality constant, i.e. $\sigma = Y\varepsilon$. Now coming back to the morphological stability of a strained layer, it can be supposed that only a limited amount of elastic energy can be stored in the deformed epitaxial material. If this amount is exceeded it becomes favorable when the two-dimensional layer growth breaks down and is replaced by the three-dimensional growth of independent, unstrained islands. The nucleation of a hemispherical island (not a spherical cap) with radius *r* on top of a strained epitaxial layer is associated with a net change in free energy

$$\Delta G = \frac{2\pi r^3}{3} \Delta G_{\rm V} + \pi r^2 \gamma + \pi r^2 h \Delta G_{\rm s}$$
(2.158)

with the volume free energy of the island ΔG_V , the interfacial energy between island and intermediate layer γ , and the contribution ΔG_s , that accounts for the strain energy between the island and the epilayer. The strain-related term ΔG_s is taken as the difference between the free energies per unit volume of the epitaxial layer after the island nucleation $(\frac{1}{2}Y\epsilon^2)$ and prior to it $(\frac{1}{2}Yf^2)$. ϵ is the mean misfit in the strained film, f the misfit between the unstrained materials. Therefore,

$$\Delta G_{\rm s} = \frac{1}{2} Y \pi r^2 h(\epsilon^2 - f^2) \tag{2.159}$$

Again, a critical nucleus radius can be defined, where the free strain energy reaches a maximum. Smaller islands will disappear, while those with larger diameters will stabilize. The critical radius can be determined from the condition that $d\Delta G/dr = 0$. One obtains

$$r_{\rm crit} = -\frac{\left[\gamma - \frac{1}{2}Yh(\epsilon^2 - f^2)\right]}{\Delta G_{\rm V}}$$
(2.160)

The transition from the two-dimensional layer-by-layer growth (Frank–van der Merwe mode) to the formation of three-dimensional islands on top of the flat layer (Stranski–Krastanov mode) takes place when $r_{\text{crit}} = 0$. This gives a critical layer thickness for the onset of surface roughening

$$h_{\rm crit} = \frac{2\gamma}{(\epsilon^2 - f^2)Y} \tag{2.161}$$

The model predicts that the critical thickness for island formation depends inversely on the square of the misfit. For the growth of strained InGaAs layers on a GaAs substrate Wessels estimates that the transition to the Stranski–Krastanov mechanism occurs when $h_{\rm crit} \times f^2 > 1.8 \times 10^{-10}$ [cm].

2.9 Summary

Equilibrium thermodynamics is one of the pillars of the science of single-crystal growth. Despite of a close proximity to "chemical thermodynamics" and "metallurgical thermodynamics", one can also identify a "thermodynamics of crystal growth". It comprises the thermodynamic treatment of a number of topics that are of specific importance for crystal growth. Single crystals can be and are grown by pure physical processes and by chemical reactions. The final product is in any case a solid with a crystalline arrangement of its building units. The nutrient phase, however can be a vapor, a liquid or a solid in another state of order. Today, a single crystal can no longer be considered as a bulky solid formed by a highly translational symmetric arrangement of atoms. Even the growth of two-dimensional and one-dimensional crystalline arrangements of atoms is now industrial practice. Thus, the thermodynamics of the growth of single crystals has numerous facets. The point in common is the final product of any of these processes, the single-crystalline material. In this brief review, the principles of equilibrium thermodynamics are outlined that are useful and characteristic for any phase transition the final product of which is a crystal. The structure of this review is given by the nature of the phase transition that is used to grow a crystal.

Equilibrium thermodynamics provides a useful guideline at least for any crystal-growth process, being a physical phase transition or a chemical reaction leading to single-crystalline structures. Astonishingly, it turns out that it provides useful, and frequently highly accurate results, even for processes that are operated with high supersaturations, usually considered as far from equilibrium, such as MOCVD or MBE. Any crystal-growth process that is based on science rather than on art, needs a sound understanding of the thermodynamic background.

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Thermodynamics, Origin, and Control of Defects

Peter Rudolph

3

3.1 Introduction

The quality of single crystals and devices made therefrom are very sensitively influenced by structural and atomistic deficiencies generated during the crystal-growth process. It is the chief task of the crystal grower to determine the conditions for minimization or even prevention of defects. This chapter gives an overview of the important defect types and their origins. The main thermodynamic principles are considered as the driving force of defect generation. Results of modeling and technologies of *in-situ* control are presented. Strong emphasis is given to semiconductor crystal growth from melts since it is from this class of materials that most has been first learned, the resulting knowledge then having been applied to other classes of material. Historical aspects of the development of defect understanding in crystal growth were recently summarized by Hurle and Rudolph [1]. Mullin outlined the defect control in the course of melt growth progress of III-V compounds [2].

The discussed defects are treated in the classical manner: 0-, 1-, 2- and 3-dimensional ones, i.e. point defects, dislocations, grain boundaries and second-phase inclusions. It will be shown which problems are still to be solved, even from a technological point of view. There is insufficient space in this chapter to consider some special defect phenomena, such as twinning and microinhomogeneities (striations). However, the reader can find very instructive papers dealing with these issues by Hurle [3] and Scheel [4], respectively. The consequences of faceting and morphological instability for dopant redistributions are outlined in Ref. [1].

Today, most of the important defect-forming mechanisms have become well understood. That is not to say that all defects can be avoided. Even the intrinsic point defects and their agglomerations, like precipitates, are bound up with deviations from stoichiometry, which is still not exactly controlled during standard growth processes. Furthermore, during the production of semiconductor compounds it is not yet possible to reduce the thermal stresses to a sufficiently low level to avoid completely dislocation multiplication. Also, the rearrangements of dislocations in characteristic bundles, lineages and cell structures, leading to mechanical and

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physical parameter inhomogeneities, are not yet understood in detail and, therefore, still not controllable. This chapter will contribute to a better understanding of the interaction between growth conditions and defect genesis to take well-calculated steps towards optimized defect engineering.

3.2 Native Point Defects

According to thermodynamics, at all temperatures above absolute zero, equilibrium concentrations of vacancies, self-interstitials and, in the case of compound crystals, antisite defects will exist. This is because point defects increase the configurational entropy leading to a decrease in the free Gibbs potential of a crystal. Considering the interplay between ordering (enthalpic) and disordering (entropic) forces it is not possible to grow an absolutely perfect but only an "optimal" crystal. The entropic contribution to the defect concentration varies exponentially with temperature. Thus, in thermodynamic equilibrium the crystal perfection is limited by incorporation of a given native point-defect concentration *n*, having the generalized form [5]

$$n = N \exp(-E_{\rm d}/kT) \tag{3.1}$$

with *N* the total number of possible sites, *k* the Boltzmann constant, *T* the absolute temperature and $E_d = E_{form} + E_{vib} + E_s$ the defect-formation energy (between 1 and 4 eV) consisting of the formation (E_{form}), vibration (E_{vib}) and entropic (E_s) terms. In consequence, a phase extent with deviation from stoichiometry δ will exist in each AB compound. Assuming a conservative system with defect balance the value δ can be expressed in concentrations of the native point defects in each sublattice as [6]

$$\delta = \delta A - \delta B = \{ [A_i] - [V_A] + 2[A_B] - 2[B_A] \} - \{ [B_i] - [V_B] + 2[B_A] - 2[A_B] \} (3.2)$$

with [A_i], [B_i], [V_A], [V_B], [A_B] and [B_A] the interstitial, vacancy and antisite contents, respectively. In simple words, by using Eq. (3.1) for each defect type in Eq. (3.2) the maximum equilibrium defect solubility in a given AB crystal at each temperature becomes identical with the solidus curves in the phase diagram. As can be concluded from Eq. (3.1) the existence region widens with increasing temperature or, vice versa, in a cooling crystal the solidus curves take a retrograde course. Hence, due to the limitation of diffusion and annihilation rates a certain fraction of high-temperature defects freezes in during the cooling process of as-grown crystals and can exceed the equilibrium concentration at room temperature markedly. In standard-grown compound semiconductor crystals the real intrinsic point-defect concentration yields at room temperature between 10^{15} and 10^{17} cm⁻³. This is about 7–9 orders of magnitude higher than the calculated values in thermodynamic equilibrium (if E_d is assumed to be 1-2 eV).

Today, there is a huge number of theoretical and experimental papers dealing with point defects in semiconductor crystals. Excellent reviews include those by Dornberger [7], Falster and Voronkov [8] for silicon, Wenzl *et al.* [9] and Hurle [10] for GaAs, and Neumark [11] for II-VI compounds, for example. From these it follows that numerous former questions could be solved during recent years due to the continuously improved control of crystal quality as well as progressing numerical ab-initio defect studies. Thus, experimental facts and theoretical interpretations have been improved markedly. However, as can be also deduced from the literature, there are still some open problems. This is particularly true in compound materials. Such processes as defect-incorporation kinetics, interaction dynamics between the sublattice deficiencies and complex-formation mechanisms, especially with foreign atoms, are not yet totally understood. The most serious drawback, however, is the limitations of the current analytical techniques. The quantitative analysis of intrinsic defect contents below 10¹⁷ cm⁻³ begins to fail [1, 12]. As a result, the width and shape of the compound existence region versus stoichiometry and the solidus course in the phase diagram, being essential information for the crystal grower, are not yet known exactly. For instance, it is still not yet clear whether the phase extent of GaAs is located completely on the arsenic-rich side or not [12]. Consequently, ab-initio theoretical treatments by computer modeling have come to the fore [9, 10, 13].

In the present chapter a complete treatment of point-defect details in as-grown and annealed crystals is not possible. For this the author refers to the above-mentioned reviews with numerous related references therein. Here, only selected examples, showing their sensitive correlation to the crystallization conditions, will be touched upon.

First, the kinetics of defect formation at propagating melt/solid interfaces will be discussed. At the beginning one has to clarify whether the front moves by atomically rough or smooth morphology. Common semiconductor materials, with their covalent bonding, show at the melting point a Jackson factor α [14] around 2, i.e. the crystallographic binding structure along the crystallizing plane determines whether the front is microscopically flat or rough. Semiconductors with diamond, zincblende and wurtzite structures grow from the melt along most directions by the atomically rough mode. They tend to form atomically smooth interfaces only on their most close-packed (i.e. {111}) planes. On atomically rough interfaces atoms can be added singly without the need for nucleation, i.e. at very low chemical potential difference between solid and liquid phases. As a result, possible defect sites are added to the crystal under quasiequilibrium conditions too. In contrast, for atomically smooth planes much higher supercooling is required in order to initiate 2D nucleation followed by layer-by-layer growth. In such a case, vacancies, interstitials and foreign atoms, possibly delivered by the adjacent liquid boundary layer, can be overgrown very rapidly and, hence incorporated in metastable states if their diffusion rate back to the melt is not high enough. This situation is demonstrated by the sketch in Fig. 3.1. According to Chernov [15] an equilibrium defect incorporation takes only place when the lateral step rate $R_{\rm st}$ fulfils the inequality

$$R_{\rm st} < D_{\rm IF}/h \tag{3.3}$$

with D_{IF} the interface diffusion coefficient and h the step height. For instance, in silicon the diffusion coefficient for vacancies and interstitials near the melting point

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Fig. 3.1 Sketch of intrinsic point-defect kinetics of an AB compound at atomically flat melt/solid interface propagating by a step-growth mechanism (R_{st} – lateral step-growth rate).

is $D_{\rm s} \approx D_{\rm IF} \approx 5 \times 10^{-4} \,{\rm cm}^2 \,{\rm s}^{-1}$ [16] and the height of a characteristic double-step is $h \approx 10^{-7}$ cm. These result in a required equilibrium rate of $R_{\rm st} < 5 \times 10^3$ cm s⁻¹. The actual step growth velocity along dislocation-free {111} silicon planes can be estimated by the relation $R_{\rm st} = \beta_i \,\Delta T$ with β_i the kinetic step coefficient (50 cm s⁻¹ K⁻¹ [17]) and ΔT the supercooling, which has been determined at growing {111} facets to be ≤ 7 K [18]. Hence, the step flow rate becomes $R_{\rm st} = 350$ cm s⁻¹ at most. That is one order of magnitude lower than the allowed value in Eq. (3.3). Hence, in this case the point-defect incorporation proceeds to equilibrium.

The above consideration assumes that vacancies and interstitials are already generated in the adjacent liquid boundary layer. Indeed, the fluid phase should deliver sufficient deficiencies due to its structural instability and disordered character. However, as recent molecular dynamics (MD) simulations have demonstrated, between the liquid and crystal surface a characteristic transition region of several atomic layers does exist within which the thermal motion of the atoms decreases and the structure approaches the crystalline one [17]. In fact, as was ascertained by high-resolution in-situ transmission electron microscopy the {111} solid/liquid interface of Si has already a well-ordered transition layer on the atomic scale, which is compatible with a defect-free 1×1 Si-{111} surface [19]. It can be assumed that the presence of such an ordered transition region should stabilize the growth kinetics against incorporation of an excess of deficiencies. After Motooka et al.'s [20] MD simulations point defects are formed directly at the interface due to the density misfit between the liquid and solid phases. Finally, according to the thermodynamic principle a balancing selection procedure takes place in the solid boundary layer ensuring the thermodynamic defect equilibrium (see Eq. (3.1)) and electroneutrality, the more if the defects are ionized. The configurational entropy is responsible for generation of a marked fraction of defects at high temperatures. Even Frenkel defects, releasing vacancy-interstitial pairs, can be produced very easily due to the enhanced thermal oscillations of atoms. At the same time, however, the high probability of defect annihilation has to be considered too [8].

For silicon crystals at high temperature it is accepted that vacancies and interstitials are simultaneously present and that they can recombine very rapidly. Ultimately, the ratio between them within the cooled crystal is determined by the relation of the atomistic transport processes (convection, diffusion, thermodiffusion) and the applied growth parameters (temperature gradient, pulling velocity). Principally, the numbers of Peclet Pe = RL/D(T), Damköhler Da = $C_{eq}(T)L^2/D(T)$ and Soret $S_T = D_T/D(T)$, which compare the convection, recombination and thermodiffusion with Fickian diffusion, respectively, are somewhat enhanced in Si for vacancies compared with interstitials [7] (R - growth rate, L - characteristic length, C_{eq} - equilibrium concentration, D_T - coefficient of thermodiffusion, D(T) – coefficient of Fickian diffusion of vacancies and interstitials, respectively). Today, a good understanding of the native point-defect dynamics has been obtained and described for this material by fairly sophisticated modeling and experimental confirmation. Generally, at the melting point the concentration of vacancies and interstitials is in equilibrium and amounts to $10^{14} - 10^{15}$ cm⁻³. But at high pulling rates the flux of vacancies dominates that of self-interstitials leading to their excess and condensation during cooldown in the form of octahedral microvoids. On the other hand, at low pulling rates or high temperature gradients interstitials are in excess forming a network of dislocation loops. In between, a defect-free region is obtained that is bounded by a ring of oxidation-induced stacking faults (OSF). The balance between the number of vacancies and interstitials is the controlling factor. The growth of quasi-defect-free crystals can be obtained by keeping the growth conditions within the defect-free regime, which is approximately $\pm 10\%$ around the critical ratio $(R/G)_{cr} = 1.34 \times 10^{-3} \text{ cm}^2 \text{ K}^{-1} \text{ min}^{-1}$, where R is the growth rate and G the temperature gradient at the interface (Fig. 3.2). In practice, such a small tolerance permits only very low pulling velocities of about 0.5 mm min⁻¹.





interstitial recombination, 1-4 – increasing R/G ratios as a function of the crystal radius r deviating from the ideal $(R/G)_{cr}$ ratio (adapted from Dornberger *et al.* [22]).

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Therefore, Falster and Voronkov [21] proposed conditions for *in-situ* outdiffusion of interstitials. In this case, the crystals are pulled under interstitial-rich conditions and maintained at high temperatures for extended times. However, extended cooling times with very low cooling rates are required to enable defect diffusion from the crystal core to the periphery. Hence, more practicable measures seem to be to use a maximum pulling rate with fast cooling followed by a wafer annealing process or the deposition of a thin Si layer onto the unannealed wafer surface covering the vacancy-induced defects [22]. This combines a maximum pull rate and fast cooling with a relatively low-cost treatment.

The situation in III-V [10] and II-VI compounds [23] is more complicated and less studied. The equilibrium point-defect concentrations at the melting point tend to be much higher than in Si. After Hurle's calculations [6, 10] in GaAs the concentrations of the principal native point defects yield at the melting temperature about $10^{17}-10^{19}$ cm⁻³ for [V_{Ga}], [Ga_i] and [As_i], [V_{As}], respectively. This is comparable to or even greater than the intrinsic carrier concentrations. Due to their isolated and, usually, electrically charged states they can influence the Fermi-level position. This results in a complex interaction between electrically active dopants and the native point defects [6], which can exist in more than one charge state. In highly n-doped GaAs the important gallium vacancy VGa even converts to a triply charged acceptor V_{Ga}³⁻. Against this, the arsenic interstitial As_i seems to be not ionized during the melt growth process. In standard Te-rich CdTe the Cd vacancy, V_{Cd}, and Cd interstitial, Cd_i, are the prevailing point defects at high temperatures [24]. They exist in singly and doubly charged states as acceptors V_{Cd}^{1-,2-} and donors Cd_i^{1+,2+}, respectively. Of most note, however, is the appearance of antisites due to the double sublattice situation. In GaAs, the As_{Ga} antisite is well known and characterized to be a very stable deep donor named EL2 with the charged state EL2⁺, which is fundamentally connected with the semi-insulating (SI) properties of undoped crystals. In state-of-the-art melt-growth technology the Fermi level is pinned at the midgap by compensation of EL2⁺ with the likewise very stable shallow acceptor C_{As}^{-} (more details are given in the reviews [6, 10, 25]). It is established that As_{Ga} would appear not at the growth temperature but forms rather during the cooling process. In material grown from a near-congruent composition, i.e. slightly As-rich melt, the much higher As_i content than V_{Ga} concentration removes the $[V_{Ga}]$ by producing As_{Ga} as soon as the lowering temperature produces supersaturation [10]. A nearly identical mechanism takes place in CdTe. In cooling Te-saturated samples the antisite Te_{Cd} does form and may become important as singly and doubly ionized midgap donors $Te_{Cd}^{1+,2+}$ responsible for compensation of the shallow native acceptor V_{Cd}^{1-,2-}. Unfortunately, here, the situation is not as comfortable as in GaAs where the antisite donor holds a stable deep midgap position. In CdTe, the V_{Cd} acts as the dominant defect, whereas the Te_{Cd} antisite behaves quite unstably. On the Cd-rich side the singly and doubly ionized Cd interstitial $Cd_i^{1+,2+}$ and Te vacancies $V_{Te}^{1+,2+}$ dominate as donors, whereas the Cd_{Te} antisite is thought to be an electrically inactive defect [24, 26]. There have been efforts to obtain undoped SI CdTe by *in-situ* control of stoichiometry during the melt growth [27] or by postgrowth annealing in Cd saturated atmosphere [28]. However, until now all growth techniques have failed to ensure a stable intrinsic state of high reproducibility. Compensation doping with impurities having energy levels near the midgap or forming complexes with native defects creating deep levels, such as Cl, Sn, Ge or V, for example, is more promising [29].

The high-temperature incorporation, diffusion and annihilation mechanisms of the native point defects in semiconductor compounds are not nearly as well understood as in silicon. There are still no detailed studies demonstrating the correlation between temperature gradient at the growing interface, crystallization rate and content of the given intrinsic defect types. Of course, one reason is the presence of dislocations acting as effective getters (see Section [3.4]) that makes it difficult to study the point-defect dynamics in its pure form. But, there is one additional specific parameter to be considered in multicomponent materials the stoichiometry. Deviations from it control the prevailing type of intrinsic point defects [10, 24, 26], their interaction efficiency with dopants [10, 30] and, hence, the electrical properties very sensitively. As is obvious from theoretical calculations and annealing studies [9, 24, 28] stoichiometric growth conditions should guarantee a minimum of native defect concentration. This follows from the C(P) – Brouwer diagrams (C – concentration of ionized defects, P – partial vapor pressure) of the II-VIs where the existence regions are extended on both sides from the stoichiometric composition. Against this, the situation in III-Vs is not so obvious because the phase extents are shifted towards an excess of one of the components [12]. As a result, marked deviations from stoichiometry in the melt are necessary to obtain the stoichiometric solid composition and, hence, decreasing native defect contents. From the thermochemical modeling of Jurisch and Wenzl [31] the VGa concentration decreases considerably only at melt mole fractions lower than $x_{\rm L} \approx$ 0.42 (8% Ga excess!) being consistent with their calculated phase extent located on the As-rich side. The same tendency is obtained by Nishizawa and Oyama [41] who found by annealing experiments a minimum of the lattice constant, ascribed to interstitials (As_i), at As partial pressures between 0.1 and 0.3 bar corresponding to melt-growth experiments with mole fractions $x_L < 0.40$. The author's team detected in GaAs crystals Ga vacancies by positron annihilation. Their content decreases from 2 × 10¹⁶ cm⁻³ at $x_L \approx 0.5$ to 5 × 10¹⁵ cm⁻³ at $x_L \approx 0.475$ [32].

In general, there are numerous papers investigating the physical parameters of III-V and II-VI semiconductors versus the melt composition from which they are grown. The *in situ* control of near-stoichiometric growth by applying a temperature-fixed vapor source of the volatile component at the horizontal Bridgman (HB) method without covering of the melt [33] has been well known for a long time. In this technique there is a direct contact of the vapor phase with the crystallizing melt–solid phase region that guarantees near phase equilibrium conditions during the whole growth run. However, the technical limitation of the HB for scaled-up production of crystals with diameters larger than 3 inch is commonly known. Also, the VB and VGF techniques were introduced by using an extra source for the vapor-phase control [34]. Rudolph [35] pointed out that there is a certain difference of the acting phase relation compared to HB that results from the missing contact of the crystallization front with the controlling vapor phase. A

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transport transient of the species through the melt and diffusion boundary layer has to be considered. As was estimated theoretically, a somewhat higher source temperature needs to be established for stoichiometric growth compared to HB. At present for VB and VGF, being obviously the most favorable melt-growth techniques for semiconductor compounds, this problem is not yet solved on the industrial scale. The continuously decreasing height of the melt column during the normal-freezing process would require a well-controlled source temperature program being well fitted with the growth rate. As a result, the stoichiometry is tuned in cut wafers by postgrowth annealing if it is required for a given application (see, e.g., Oda *et al.* [36]).

At present, the above-mentioned complexity of the native-defect analysis prevents precise knowledge about the real point-defect situation in such crystals from being obtained. Relatively well measurable is the As_{Ga} (EL2) antisite content in SI GaAs. Concentrations down to 10^{15} cm⁻³ are detectable by using local vibrational mode (LVM) IR spectroscopy. As was shown, the As_{Ga} content reduces to values below 10^{16} cm⁻³ in crystals grown under nearly stoichiometric conditions, i.e. from Ga-rich melts [37, 38]. GaAs crystals with lowered antisite concentration are of interest for production of radiation detectors with high carrier lifetime, which is affected by deep level EL2 trapping [38].

The *in situ* control of stoichiometry in the Czochralski growth of semiconductor compounds is much less used. For this, a modified technique without boric oxide encapsulant is required to influence the melt composition by the partial pressure of the volatile element. For the first time, Baldwin *et al.* [39] applied a separately heated As source in a GaAs Czochralski container to control the As partial pressure over an uncovered melt. During the 1980s the hot-wall Czochralski (HWC) technique with As source was advanced by Nishizawa and coworkers to analyze the variations of the physical parameters and dislocation density in GaAs and GaP crystals as functions of the melt composition (see e.g. [40, 41]). During recent years also in the author's laboratory the *in situ* control of stoichiometry in GaAs by Czochralski growth has been under intensive investigation. For this, the vapor-pressure-controlled Czochralski (VCz) technique [42] without boric oxide encapsulation is used (Fig. 3.3). The mole fraction of the melt is controlled in the range of $0.45 \le x_L \le 0.50$ by partial arsenic pressures between 0.02-2.1 MPa adjusted via the temperature of the As-source from 540 to 650° C. More experimental details are described elsewhere [43].

Today, it is not yet exactly clarified which melt composition meets the stoichiometric solid composition in GaAs. This is due to the still uncertain location of the homogeneity region versus stoichiometry. Hurle mentioned a mole fraction of $x_{\rm L} = 0.483$ being in equilibrium with stoichiometry [10]. Concerning newer calculations, the solid GaAs phase crosses the stoichiometry in the phase diagram at lower $x_{\rm L}$ values (<0.40) [13] or is even completely located on the As-rich side [31, 44]. Further investigations are underway.

In general, the Czochralski growth of SI GaAs crystals from Ga-rich melt proves to be a big technological challenge. As was mentioned above, under near-stoichiometric growth conditions the concentration of the deep-level donor EL2 falls below 10^{16} cm⁻³. Therefore, the concentrations of the compensating shallow acceptor carbon and residual impurities must be reduced drastically in



Czochralski (VCz) method without boric oxide encapsulation in order to control the melt composition and, hence, the solid stoichiometry of GaAs crystals by the partial

Fig. 3.3 Principle of vapor-pressure-controlled arsenic pressure. The carbon concentration is controlled by flowing CO gas communicating with the inner growth chamber (adapted from Rudolph and Kiessling [46]).

order to meet the precondition $[EL2] > [C] + (N_{\Sigma A} - N_{\Sigma D}) > 0$ with $N_{\Sigma A,D}$ the total concentrations of acceptors (A) and donors (D) shallower than EL2. In our VCz experiments, first a proper in situ carbon control down to 1×10^{15} cm⁻³ was adjusted. This was solved by CO gas streaming communicating with the inner VCz chamber (see Fig. 3.3). Furthermore, only highly purified chamber internals were used to minimize the residual impurity content (note no impurity gettering by the B_2O_3 encapsulant takes place as in the LEC method). Additionally, the growth rate and temperature gradient were chosen undercritically in order to prevent morphological instability and Ga-inclusion incorporation in growth from Ga-rich melts. Considering all these technological measures perfect near-stoichiometric SI GaAs single crystals with electrical resistivity $3 \times 10^8 \Omega$ cm have been grown successfully. EL2 and carbon concentrations of 8.0×10^{15} and 6.3×10^{15} cm⁻³ were obtained, respectively. More information about the intrinsic and extrinsic point defect situation in such crystals with drastically reduced B, O and H contents are given elsewhere [32, 45, 46].

3.3 Dislocations

Contrary to native point defects, dislocations are not in thermodynamic equilibrium and, hence, in principle are preventable. However, at present only silicon

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and germanium standard crystals can be grown dislocation-free. This is because in compound crystals the situation is complicated by a much higher intrinsic point-defect content (Section [3.2]) and lower critical resolved shear stress ($\tau_{CRSS} \approx 0.5$ MPa at T_m instead of ~10 MPa in Si) encouraging dislocation climb and glide, respectively. There exist numerous reliable methods to analyze dislocations such as i) high-resolution transmission electron microscopy (HRTEM), ii) X-ray Lang topography, enabling Burgers vector analysis, ii) laser scattering tomography (LST), ascertaining the spatial dislocation courses, and iii) fully automatized etch pit density (EPD) mapping, for example. Even high-temperature synchrotron X-ray and transmission electron imaging techniques make it possible to study the dislocation kinetics at the crystallization front *in situ* (see e.g. [19, 47]). As a result, the knowledge about dislocation types and their mobility in correlation with the growth conditions as well as their interaction with dopants is today well developed and a huge number of related papers are available. For the III-V compounds, a comprehensive summary was published by Sumino and Yonenaga [48], for example.

Principally, for growing crystals a differentiation between the terms "generation" and "multiplication" of dislocations is recommended even more carefully than has been done in the literature so far. The formation of new dislocations within an ideal dislocation-free crystal is under normal growth conditions nearly impossible. Stresses of the order of the material strength limit $\tau \approx 10^{-2} - 10^{-1}$ G (G – shear modulus, $\approx 10-70$ GPa) would be required, being much higher than that usually obtained in standard growth processes (around 10 MPa at most) [53]. Such values are not even high enough to penetrate Shockley partials in zincblende structures from microscopically stepped crystal surfaces that requires stresses of ~ 100 MPa at least [49]. Dislocations can be generated in the form of Frank loops due to collapsing vacancy agglomerations, interstitial disks and interface misfits between foreign-phase inclusions and matrix. The possibility of such origins is enhanced in nonstoichiometric material (see Section [3.5]). The majority of dislocations in as-grown crystals are, however, originated by climb- and glide-assisted elongation (bowing out) and multiplication (dissociation, crossglide) of primary existing faults grown-in from the seed crystal.

It is well established that the dislocation density and distribution in crystals are primarily due to the thermoplastic relaxation of thermally induced stress [50, 51, 53]. Therefore, the content of dislocations is determined by the time- and space-dependent stress level during growth that is related to the temperature field in the growing crystal and cooling-down procedure. The higher the temperature field nonlinearities (correlating with second derivative of the temperature gradient and crystal radius), the higher the mechanical stress. Due to the difficulties of measurements, global numerical simulation is of increasing importance for heat flow, thermomechanical stress and dislocation-density analysis. The modern way estimates the local dislocation density from the constitutive law of Alexander and Haasen linking the relation between plastic shear rate and movement and density of dislocations (Orowan equation) with the applied stress in the course of the cooling procedure of the crystal [51, 52]. As was emphasized by Völkl in his review [53] the plastic relaxation varies due to time-dependent experimental conditions and



Fig. 3.4 Calculated residual elastic stress τ_{el} and plastic deformation ϵ_{pl} along a elastoplastic crystal (InP) using the Alexander–Haasen model. The τ_o curve shows the elastic stress course in a purely elastic body. The relaxation of elastic stress,

identically with the onset of plastic deformation, i.e. dislocation multiplication, is shifted away from the interface with increasing growth rate 1 cm h^{-1} (1), 2 cm h^{-1} (2), and 20 cm h^{-1} (3) (adapted from Völkl [53]).

due to continuously acting dislocation dynamics. Therefore, the driving force for dislocation multiplication is given by the actual value of the elastic strain and not by the total deformation (Fig. 3.4). Thus, one has to consider that the often published von Mises contours, calculated along growing crystal cuts and cross sections, reflect snapshots of the unrelaxed thermoelastic stress only. Certainly, they are usable for estimation of the dislocation density at the growing interface but not within the cooling crystal volume where the majority of the elastic strain is already relaxed by plastic deformation. Note, changing stress situations can appear during the growth run like in LEC case when the crystal emerges from the liquid encapsulant towards the streaming gas atmosphere submitting a thermoelastic shock, for example.

Recently, Pendurti *et al.* [54] reported the global numeric modeling of the nonstationary elastic stress and related dislocation development in growing LEC InP crystals by implying the history of the thermal field in the furnace and crystal as well as the convection in the melt and vapor phase. Figure 3.5 shows their calculated elastic stress history and related dislocation density evolution in various crystal points. As the elastic stress alternates, the dislocation-density increases stepwise accordingly. The authors found that the gas convection has a significant effect on the total dislocation density – a quite important fact that was not yet considered so far. This is the right direction to go in the future.

As was estimated in Ref. [25] only very small isotherm deviations from linearity of 1-2 K are enough to reach the critical resolved shear stress (CRSS) for dislocation multiplication in GaAs crystals at high temperatures (~ 0.5 MPa). In the production of compound semiconductor crystals of diameters 100 and 150 mm it has been not been possible to reduce the thermal inhomogeneities and the related thermal-induced stress to a sufficiently low level at all process phases in



Fig. 3.5 The history of elastic stress and dislocation density at the edge (1) and in the center (2) of a 2-inch InP crystal growing from the melt under a 20-mm thick B_2O_3 layer (right) calculated by a broadened

Alexander–Haasen model with gas Grashof number 10⁸, melt Grashof number 10⁶ and rotational Reynolds number 500 (adapted from Pendurti *et al.* [54]).

order to avoid dislocation multiplication. The highest-temperature nonlinearities and, hence, related thermal stress values, increasing very sensitively with diameter, appear in LEC crystals. Today, in such undoped 4- and 6-inch GaAs crystals the mean dislocation densities are $(5-7) \times 10^4$ and $(1-2) \times 10^5$ cm⁻², respectively. Such values are increasingly problematic as the demand of high-quality wafers for epitaxial device processes is increasing. The situation can be improved by Czochralski growth in low thermal gradients. In 6-inch SI VCz crystals of more than 20 cm length, grown at the IKZ Berlin (see sketch in Fig. 3.3), the average etch pit densities (EPD) along the <110> and <100> directions can be reduced down to $(1.8-2.6) \times 10^4$ and $(2-3) \times 10^4$ cm⁻², respectively. Minimum values of $(6-8) \times 10^4$ cm⁻², respectively. 10^3 cm⁻² were ascertained near the r/2 region (r – wafer radius). In 4-inch VCz crystals a somewhat lower average EPD of $(5-10) \times 10^3$ cm⁻² was found [55]. The best EPD results, however, can be obtained by the VGF method, matured on the industrial scale since the mid-1990s as the most promising growth variant for compound semiconductor crystals. The decisive technological measure proved to be the maintenance of a uniaxial heat flow through the growing crystal during the whole growth run by proper control of the cooling rate between a top and bottom heater flanked by a booster heater to avoid radial heat outflow [56]. In undoped GaAs VGF crystals with diameters between 3- and 6-inch dislocation densities in the range from 500 to 5000 cm⁻² have been reported [57, 58]. Müller et al. [59] succeeded in the growth of Si-doped 4-inch GaAs crystals with the lowest EPD of 31 cm⁻² by optimized VGF.

It is noteworthy that the distribution of very low dislocation densities below $200 \,\mathrm{cm}^{-2}$ turns out to be inhomogeneous. As was observed by Birkmann *et al.* [60] in such (100)-oriented VGF wafers the residual dislocations are accumulated cross-like along the <100> directions. Furthermore, they no longer lie within the main <110>{111} glide system, as is characteristic for GaAs crystals with higher EPD. Instead of the typical stress-induced 60° dislocations other dislocation types dominate. Within the cross they belong to the (010)1/2[101] system [60, 61]. There arise two important questions having not yet complete answers up to now. Do these dislocations still originate from the seed crystal and how are they arranged along the <100> directions? Why do they leave the mean glide plane? Obviously, the second phenomenon is related to the rapidly decreased elastic strain in VGF crystals being no longer high enough for plastic shear by dislocation glide. Under such conditions the dislocation mobility by diffusion-controlled creep, i.e. point-defect-assisted climb, should be responsible for dislocation mobility. Concerning the first fact it is conceivable that the residual dislocations are connected with the pronounced joint of the $\{111\}$ facets along the <100> directions in the crystal cone. In fact, looking carefully on an as-grown VGF crystal cone the border between the {111} facets is not planar but rather they are interlocked with each other. Such a mechanism seems to be kinetically quite uncontrollable and, probably, able to generate dislocations by lattice misfits between the meeting Ga and As facets [61]. Such an explanation would favor the growth with a flat bottom from a seed of the same diameter [62, 63] in order to maintain the rotational symmetry without pronounced facetting. Is this the future technology, coupled with minimized thermal stress and in situ control of stoichiometry, towards dislocation-free compound semiconductor crystal growth of large diameters?

Generally, for a dislocation-free growth of GaAs (and further compounds) with large diameters the proper combination of the following conditions seems to be required: i) use of dislocation-free seed crystals, probably, with the same diameter as the crystal to be grown, ii) strongly uniaxial heat flow with very small temperature gradients, i.e. nearly flat isotherms at all stages of the growth process, iii) omit the boric oxide encapsulant, the presence of which introduces markedly thermomechanical stresses at the crystal periphery and, perhaps, its replacement by a detached growth mode, iv) *in situ* stoichiometry control by an arsenic source in order to reduce the intrinsic point-defect content that promotes high-temperature dislocation multiplication by climb. Currently, VB/VGF (probably also VCz without boric oxide encapsulant) is the most suitable method to meet these demands in total. However, what contribution to the dislocation generation will arise from boundaries between facets and rough areas at the crystal surface is not yet known exactly.

3.4 Dislocation Cells and Grain Boundaries

One of the characteristic structural features in semiconductor compounds, which is not yet completely clarified, is the patterning of dislocations into a cellular



Fig. 3.6 Cellular dislocation patterns in undoped GaAs crystals revealed by (a) KOH etching of a 4-inch wafer [42], (b) LST analysis with integrated depth 2 mm [64], and (b) X-ray synchrotron topography [65] (reproduced by permission of Maney Publishing (a), Elsevier (b) and Wiley-VCH (c)).

network. Figure 3.6(a) shows such cells in a 4-inch GaAs wafer, revealed by a standard etching process. The cell structure can be analyzed in more detail by laser scattering tomography (LST) that takes advantage of dislocation decoration by precipitates of the excess component in the case of nonstoichiometric crystals [64] (Fig. 3.6(b)), or by high-resolution X-ray synchrotron topography (ST) [65] (Fig. 3.6(c)). The cells are of globular-like shape consisting of walls with high dislocation density separated by interiors of markedly dislocation-reduced or even dislocation-free material. Their size decreases with increasing average dislocation density yielding diameters of 1–2 mm at a dislocation density of $\leq 10^4$ cm⁻² and of about 500 μ m at a density of 10⁵ cm⁻². Such patterns are also well known from as-grown crystalline metals (e.g. Fe, Al, Ni, Mo), metallic alloys (e.g. Fe-Si, Ti₃Al, Cu-Mn) and dielectric crystals (e.g. LiF, CaF2, SrTiO3, quartz) independent of which growth or postgrowth deformation method was applied [66]. However, some differing morphological details are noteworthy. For instance, in Mo, Cu-Mn and GaAs the cell interiors are nearly free of dislocations and the walls are fuzzy-like of a certain thickness consisting of many tangled dislocations (see Fig. 3.6(c)). It is noteworthy that the tilt angle between cells in high-quality GaAs standard crystals is not more than about 10 arcsec. Compared to those in CdTe, PbTe and CaF₂ the cell walls are very thin, of the order of one dislocation row, reminiscent of classical low-angle grain boundaries. In these crystals the matrix shows mostly individual dislocations that can occasionally form a subcell structure [66]. Finally, there are

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crystals where cell structures are not well distinguishable in the as-grown state as in InP [61, 66] or even missing if special dopants are added, like Si to GaAs or Se to CdTe [66]. Until now the reasons for such varying cell genesis are not yet finally clarified. Some possible origins will be discussed below.

As is well known, the dislocation rearrangement into cell networks is due to external or internal stresses in the course of plastic relaxation. Cell patterning is studied best in metals under external load, but also in postdeformed elemental and compound semiconductor crystals. Today, there is a huge number of papers dealing with this aspect, especially in the field of metal physics and mechanics. Reviews on fundamentals are given by Kubin [67], Amodeo and Ghoniem [68] and Zaiser [69], for example. For growing crystals, however, there is not yet a detailed knowledge about the genesis of dislocation dynamics (DD) at high temperatures. In all probability cellular substructures are due to the acting internal thermomechanical stress field. It can be assumed that the cell formation is coupled with dynamic polygonization behind the growing interface where the plastic relaxation by dislocation multiplication takes place. There is a well-confirmed in situ observation on thin crystallizing and remelting Al plates by Grange et al. [47]. They observed, by real-time synchrotron X-ray topography the appearance of the cellular dislocation structure due to the thermally induced strain within the region some millimeters behind the melt-solid phase boundary.

Note that not all types of patterning can be attributed to DD that takes place within the crystal volume. As is well known in the case of morphological instability of a fluid–solid phase boundary, induced by constitutional supercooling, their former planar shape changes into a characteristic cellular profile (see review of Billia and Trivedi [70], for example). As a result, a lamellar-like structure with longitudinally extended walls is formed. However, their distinction from dislocation patterning is sometimes not trivial, even when cross-sectional crystal wafers are investigated. The best way to distinguish between them is the application of analytical methods with 3D imaging like LST [64] revealing the globular cell morphology, being typical of dislocation patterning. Moreover, as is well known, dislocation cells may disappear completely if certain dopants are added, like In to GaAs or Se to CdTe although their presence should even promote constitutional supercooling.

In general, inhomogeneous dislocation distributions in the form of cellular substructures impair the crystal quality. Whereas the interior is of a constant lattice orientation, across the dislocation-rich walls a discontinuous orientation change arises. As a result, optical inhomogeneities appear, for example. Across semi-insulating {100} GaAs wafers a mesoscopic resistivity variation is observed due to the accumulation of As_{Ga} antisite defects (EL2) within the cell walls [71]. Subgrain boundaries also impede the electron transport in $Cd_{1-x}Zn_xTe$ radiation detectors [72]. Hence, the crystal grower is usually striving to determine proper measures to prevent dislocation patterning (see below) or reduce the accompanying compositional inhomogeneities by postgrowth annealing at least. However, there is a certain interest in crystals with mosaic structure too. For instance, crystal diffraction lenses for nuclear astrophysics show an improved reflection power when crystals with mosaicity of 20–50 arcsec (e.g. $Ge_{1-x}Si_x$) are used [73]. Furthermore,



Fig. 3.7 Cell diameter *d* vs. dislocation density ρ and dislocation spacing $\rho^{-1/2}$ (compiled from different GaAs crystals grown by various methods) [66]. For comparison the results of mechanical deformation experiments on α -iron crystals, representing the typical correlation in metals [78, 79], are added (reproduced by permission of Wiley-VCH).

in nanocrystalline materials the controlled reduction of grain size to the nanometer scale leads to many interesting new properties including a great increase in strength [74]. Therefore, the further development of knowledge about collective dislocation interactions in growing crystals is of general practical relevance for both targets – suppressing and provoking cellularity.

Recently, a systematic analysis of the origins and genesis of cell formation during the growth of compound semiconductor crystals, especially GaAs, was started by Rudolph *et al.* [75–77]. First, the relation between the stored dislocation density ρ and the cell size (diameter) *d* has been determined. To deduce the 3D cell diameters from the 2D etch pit images, obtained on cut wafers, a stereological analyzing method was used as described in ref. [77]. Figure 3.7 shows this correlation taken from own experimental data and literature. For the samples with EPD > 2 × 10⁴ cm⁻² nearly the same correlation as in deformed metals [78] has been found, i.e.

$$d \approx K \rho^{-1/2} \tag{3.4}$$

with the factor of proportionality $K \approx 10 - 20$. This is surprising if one considers the marked differences between dislocation densities and cell dimensions in as-grown GaAs crystals and those in metals under load. The result shows that Holt's scaling relation [78] is fulfilled over a wide range of materials and dislocation densities. At dislocation densities below 10^4 cm⁻², however, the cells begin to dissociate and, hence, a larger scatter is obtained.

Furthermore, the relation between acting stress and cell dimension was investigated. From postgrowth deformation experiments on numerous metals and dielectrics a universal relation between cell diameter and shear stress τ is known [79]

$$d = \alpha \ K \ G \ b \ \tau^{-1}$$

(3.5)

with α another proportionality factor, *G* the Young's modulus and *b* the Burgers vector. The analysis of this correlation in the case of growing crystals is more difficult due to the still impracticable nature of *in situ* measurement of the acting thermomechanical stress values. As was pointed out in Section [3.3] only the elastic term is responsible for dislocation movement and, thus, for the collective dislocation rearrangement in cells. Considering that the subgrain generation is initiated shortly after the onset of plastic deformation [80] it can be assumed that the cell-formation process takes place immediately behind the growing interface (see, e.g., ref. [47]) and is completed in the course of plastic relaxation. Thus, the frontal elastic strain acting immediately after the propagating phase boundary can be taken as the driving force. This stress value is today readily calculable by global modeling (see, e.g., refs. [53, 54] and Fig. 3.4). Therefore, the author's team used the calculated frontal thermoelastic shear stresses of growth situations being identical with the real growth positions of each crystal where the EPD distributions and cell-size measurements were taken from [77]. The obtained correlation between d and τ^{-1} in the form of Eq. (3.5) d = K' (Gb / τ) with $K' = \alpha K$ is shown in Fig. 3.8. For comparison, the results from deformed metals as well as the slopes for NaCl and LiF are included [79, 81]. As can be seen, for cell sizes smaller than 700 µm and calculated stresses larger than about 1 MPa the functional slope is similar to those of deformed materials. Independent of the growth conditions, it was found that d is inversely proportional to τ^{-1} . Obviously, in this region





comparison with the data of postdeformed GaAs [66], InP [83] and metals [78]. The slopes for some post-deformed dielectrics [81] and the mean dependence with K = 23 after Raj and Pharr [79] are added (reproduced by permission of Wiley-VCH).

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dislocation glide is the prevailing driving force for cell formation, due to the fact that the stress is larger than the critical resolved shear stress. In the case of larger cell dimensions the trend changes, showing only a very slight slope $d \sim \tau^{-0.25}$. In these regions, a resolved shear stress $\tau < 1$ MPa was calculated. One can suppose that for such very low thermomechanical stress, even below the critical resolved shear stress ($\tau_{CRSS} \approx 0.5$ MPa), glide-driven plastic relaxation can no longer be the prevailing driving force for cell formation. Other cell-structuring mechanisms must become dominant, like point-defect-controlled creep. This is in accordance with the above-described observation that the residual dislocations in low-EPD GaAs VGF crystals no longer lie within the basal glide system (Section [3.3]).

Compared to GaAs in InP crystals, often a missing cell structure is reported even if the dislocation density exceeds 10^5 cm^{-2} [66]. Obviously, under standard LEC growth conditions in undoped as-grown InP crystals the cell formation is much more restrained [82]. Only at markedly higher stresses over 20 MPa, as was applied in postgrowth deformation experiments [83], also in InP crystals does a cellular dislocation network with *d* between 2 and 10 µm appear.

In both undoped as-grown CdTe and PbTe crystals the presence of cellular structures is obvious. Mean cell dimensions in the range of $100 - 200 \,\mu\text{m}$ at EPD of 5×10^4 and 2×10^4 cm⁻², respectively, have been detected in CdTe crystals grown in axial temperature gradients > 20 K cm⁻¹ [35]. However, the characteristic features differ from those in GaAs. The matrix contains numerous isolated dislocations and much sharper cell walls are formed, consisting of only one row of dislocation pits. Durose and Russell [84] and Sabinina et al. [85] investigated the cell-wall structure in vapor- and melt-grown CdTe samples by transmission electron microscopy and observed that the dislocations that constitute the boundaries are nearly all parallel and most have the same Burgers vector (see Fig. 3.1 in ref. [84]). Such behavior is well known from the standard type of polygonized low-angle grain boundaries containing only the excess dislocations of similar Burgers vector after the annihilation process is completed. In fact, the DD contributes in CdTe and PbTe crystals much more effectively to substructure ripening than in GaAs. Also, the larger disorientation angle between the neighbouring cells refers to a typical polygonized grain-boundary structure. Tilt angles of 60-120 arcsec and even 18 arcmin were reported for melt- and vapor-grown CdTe crystals, respectively. Higher disorientation angles in the range of 2-30 arcmin, in some cases even up to 3°, have been ascertained in PbTe crystals. Such a feature is also characteristic of dielectric materials like CaF2 and NaCl [86, 87]. It is obvious that in these crystals we have to deal with typical well-ripened grain boundaries, i.e. primary subboundaries, which are often superimposed by cellular structure and secondary subboundaries formed previously [87]. The scheme in Fig. 3.9 shows the possible stages of dislocation patterning during crystal growth beginning from cell formation towards a ripened small-angle (primary) grain-boundary structure. In their dependence on the dislocation mobility (highest in CdTe, PbTe), the intrinsic point-defect content (lowest in InP), the stacking-fault energy (lowest in InP, CdTe) the ripening time and frozen-in level are, however, different in various materials.



Fig. 3.9 Schematic demonstrating the different types and ripening stages of dislocation substructures that may develop from an initial uniform dislocation distribution. Some materials with typical related patterns, observed after crystallization, are added.

To date, there exists no commonly accepted approach towards a complete theoretical understanding of the genesis of dislocation patterning. A number of theories have been proposed to account for the stress dependence of the subgrain size. It is usually thought that the decreasing cell dimension with increasing stress is due to cell splitting in the course of increasing stress, leading to progressive construction of new walls [88]. Newer papers favor a stochastic dynamics of the entire dislocation ensemble (e.g. [69, 80]). Until now, however, the question is whether the cell patterning is driven energetically or by a self-organizing process in the frameworks of equilibrium or nonequilibrium thermodynamics, respectively. There are well-known facts to be stated for energy-related processes. In the classical sense, the driving force for subgrain formation is the reduction in strain energy resulting from the clustering (i.e. mutual field screening) of dislocations in cell and subgrain boundaries, whereas it is important to note that for the formation of cells with globular morphology beside dislocation glide even spatial mechanisms like climb and cross-glide are absolutely required [89]. Even under very low elastic stress ($\tau/G < 5 \times 10^{-5}$), as in the case of VGF growth, the diffusion-controlled creep can play the dominant role. However, the process of plasticity cannot be explained exclusively by equilibrium thermodynamics due to the presence of typical preconditions for irreversibility, such as stress and temperature gradients during the growth process. Hence, a growing crystal can be treated as a thermodynamically open system with continuous import and export of entropy. As a result, a rate of entropy is produced within the crystal evoking self-ordered patterning of the stored

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dislocations. Much more fundamental coworking between crystal growers and theoretical physicists is required to clarify this still open problem.

What possible in situ steps to prevent dislocation patterning are there? First, independently of the materials used, the cell formation can be reduced very effectively by doping. No cell structuring was observed in GaAs doped with In or Si at concentrations $> 10^{18}$ cm⁻³. Such an effect is due to the impurity gettering at the dislocation core rising with temperature because of the increasing diffusion rate. In consequence, the yield stress is enhanced by dislocation locking. Jiminez-Melendo et al. [90] observed a decrease in the stacking fault energy when GaAs was doped with In. They explained this effect by Suzuki segregation or direct interaction between solute atoms and stacking faults making cross-slip events more unlikely. No low-angle grains were found in $CdTe_{1-x}Se_x$ and $Pb_{1-x}Sn_xTe$ crystals when solution hardening by mixing components Se (x > 0.4) and Sn (x > 0.15) was provided, respectively. However, there is the well-known drawback of segregation when dopants are added to the melt. On the one hand, there is the danger of morphological interface instability by constitutional supercooling and, thus, low growth rates or high temperature gradients are required for its prevention. On the other hand, for device applications doped and mixed crystals cannot always replace undoped and binary material because of the sensitivity of physical parameter verification on adding foreign atoms.

Obviously, the best way to exclude dislocation patterning is the reduction of the dislocation density by minimization of the thermomechanical stress. In undoped GaAs it was observed that at ρ values $< 5 \times 10^{-3}$ cm⁻² the cell structure began to disappear. However, for compound crystals with larger diameters over 100 mm the attainment of such low dislocation densities is not yet solved empirically when hardening dopants are not added. Hence, the current efforts are directed to homogenization of the thermal field in the growing crystals in order to reduce the dislocation multiplication and their mobility by minimizing the thermomechanical stress.

Another important way to prevent cell patterning is the minimization of the intrinsic point-defect content by *in situ* control of stoichiometry during growth. The stoichiometry can be regulated by the partial pressure of the volatile component over the melt applying an extra heated source within the growth chamber (see also Section [3.2]). Recently, the author's team demonstrated by using the VCz arrangement without boric oxide encapsulant that the cellular structure dissolves when the GaAs crystal grows from the proper-controlled Ga-rich melt composition [32, 75].

3.5

Second-Phase Particles

The presence of second-phase particles in as-grown crystals named COPs (crystal-originated particles), markedly affecting the optical and electronic bulk quality but also the surface perfection of epiready substrates, is one of the most-studied harmful defect types in compound semiconductor crystals. They are present in II-VIs (e.g. [35, 91]), III-Vs (e.g. [92, 93]) and IV-VIs (e.g. [94]). As is explained



Fig. 3.10 Sketch representing the different inclusion incorporation and precipitation mechanisms during crystal growth from melt. Two images showing a Ga inclusion with traveling Ga-rich solvent trail [43] and As precipitates [93] in GaAs crystals (reproduced by permission of Elsevier).

in detail in Ref. [35] it is important to distinguish between two different foreign particle formation mechanisms – i) precipitation and ii) inclusion incorporation. A schematic sketch of origins of both processes is given in Fig. 3.10. Their relations to the phase diagram are demonstrated in Fig. 3.11.

Precipitates are formed due to the retrograde solubility of native point defects in nonstoichiometric solid compositions. As the as-grown crystal cools the solidus is crossed and nucleation of the second phase takes place. Probably, Ostwald ripening has to be considered. Favored sites of precipitate ripening are dislocations, as has been concluded from IR laser scattering tomography (Refs. [64, 93], for example). Average precipitate densities of about 10⁸ cm⁻³ and up to 10¹² cm⁻³ have been found in GaAs [92] and CdTe [35], respectively. Typical sizes between 10–100 nm have been determined for As precipitates in GaAs [95] and Te precipitates in CdTe [96]. Half-empty precipitates have been found by transmission electron microscopy (TEM) in GaAs [97] and CdTe [98], probably, caused by vacancy condensation in one of the sublattices accompanied by conglomeration of excess atoms of the opposite sublattice.

In CdTe, both tellurium and cadmium precipitates have been found (e.g. [91, 99]). This depends on the melt composition from which the crystal was grown (Te- or Cd-rich, respectively). According to the CdTe phase diagram their density can be effectively minimized at growth under near-stoichiometric conditions (as is sketched in Fig. 3.11) [35]. Contrary to this, in melt-grown GaAs crystals only As precipitates were observed. Fornari *et al.* [95] found a correlation between the As precipitate size and deviation from stoichiometry. Whereas at the stoichiometric


Fig. 3.11 Nonstoichiometry-related effects of second phase particle formation in a growing compound crystal AB explained by a sketched phase diagram with elongated phase extent. The segregation evokes the rejection and, hence, enrichment of excess component at the interface that may lead

to inclusion incorporation. Homogeneous (matrix) and heterogeneous (decoration) precipitations take place due to second phase nucleation at the retrograde slope of the solidus curves, probably, with following Oswald ripening.

melt composition ($x_L = 0.5$) the diameter is about 120 nm, from Ga-rich melts As precipitates of 40 nm diameter form even when the mole fraction is markedly Ga-enriched ($x_L = 0.425$). Sonnenberg and Altmann [100] reported similar results in material grown from markedly Ga-rich melts ($x_L \approx 0.444$). These authors underlined that according to their Raman scattering spectra all the precipitates found are always of arsenic. This would to be in accordance with a GaAs existence region located completely on the As-rich side [31, 44].

There are two effective ways to minimize the precipitation concentration – i) *in situ* control of the stoichiometric crystal composition, as already described in Section [3.2], and ii) postgrowth annealing under controlled partial pressure. As was demonstrated by Rudolph and Kiessling [46], on applying the VCz growth of GaAs without boric oxide encapsulant, melt compositions less than or around a mole fraction of $x_L \approx 0.45$ yield near-stoichiometric crystals essentially without precipitation, which is in good agreement with the value predicted by Hurle [10]. Oda *et al.* [36] developed a multiple postgrowth wafer-annealing technology for semi-insulating GaAs. Highly uniform substrates with markedly decreased arsenic precipitate density were obtained. Postgrowth wafer annealing was also successfully used by other authors for InP, GaP, CdTe and ZnSe wafers.

In contrast to precipitates, *inclusions* are formed by capture of melt-solution droplets, gas bubbles or foreign particles from the diffusion boundary layer adjacent to the growing interface and enriched by the rejected excess component. Preferred sites are re-entrant angles of grain boundaries and twins crossing the interface. Dinger and Fowler [101] found lineages made of tellurium along the growth direction of CdTe crystals grown from Te-rich melt. They attributed this phenomenon to the enhanced cellular growth caused by constitutional supercooling. The inclusions are concentrated in the interlamella notches (Fig. 3.10). Typical inclusion diameters are $1-2\,\mu$ m, but sizes up to 30 μ m have been also observed in HB and VB CdTe crystals grown without a Cd source [35, 91]. Their axial distribution increases slightly with an increase of the excess component by segregation. Melt-solution inclusions due to nonstoichiometric melt compositions show a specific crystallization genesis within the already solidified matrix [91]. Mostly, they are embedded in a negative polyhedron formed by adjacent zincblende {111} planes.

An inclusion can be also captured at a nearly flat interface by an overgrowth or embedding mechanism as discussed by Chernov [15]. He estimated a critical interface rate R_{cr} for inclusion or gas bubble incorporation depending on the particle (bubble) radius r_{in} , interface energy α and dynamical viscosity of the melt η as

$$R_{\rm cr} \le (0.11B/\eta r_{\rm in}) (\alpha/Br_{\rm in})^{1/3}$$
(3.6)

with *B* a constant ($\sim 10^{-17}$ cm² kg s⁻²). For instance, in the growth of GaAs from the melt with $\eta = 2.8 \times 10^{-5}$ kg cm⁻¹s⁻¹ a solid spherical foreign particle with $r_{\rm in} = 1.5 \times 10^{-3}$ cm and $\alpha = 0.19$ kg s⁻² would be rejected from the propagating interface if its normal rate $R_{\rm n}$ is < 2 mm h⁻¹. After Chernov [102], the hydrostatic pressing force of gaseous bubbles towards the interface plane is lower than solid particles. Hence, the prevention of incorporation of arsenic microbubbles of the same radius would require the consideration of a somewhat enhanced critical velocity of about 8 mm h⁻¹.

In summary, two technological measures against inclusion incorporation are of importance – i) growth from nearly stoichiometric melts and vapor phases, i.e. at the congruent melting or vaporization point in case of melt or vapor growth, respectively, and ii) the choice of undercritical growth velocities. Furthermore, accelerated crucible rotation techniques [102, 103], control by ultrasonic [104, 105] or nonsteady magnetic fields [106] can be assumed as effective additional steps to disassemble phase boundary layers in future melt-growth processes.

3.6 Summary and Outlook

Over the half century of the development of semiconductor technology, most of the important defect-forming mechanisms and their control have become well understood. This is not to say that all defect origins can be clearly described and even avoided. For instance, point-defect-incorporation kinetics, interaction dynamics between the sublattice deficiencies and complex-formation mechanisms of native defects, especially with foreign atoms, are not yet understood completely. The most serious drawback, however, is the limitations of the current analytical techniques that begin to fail below intrinsic defect contents of 10^{17} cm⁻³. This important field needs to develop urgently for the future progress. Of high technological importance

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for mastering of the point-defect situation in semiconductor compounds is the *in situ* control of stoichiometry during the growth. There are quite successful laboratory results both for vertical Bridgman growth and the Czochralski technique but the large industrial scale is not yet matured.

Due to the relatively poor thermal conductivity and low yield stresses of III-V and II-VI compounds, as compared with Ge and Si, it is not possible to reduce the thermal stresses to a sufficiently low level to avoid dislocation multiplication. However, recent developments in vertical gradient freeze techniques have produced a marked reduction of dislocation density in undoped GaAs and InP. In VGF growth the establishment of a uniaxial heat flow has led to minimum dislocation densities below 10^3 cm^{-2} and 10^2 cm^{-2} in 4-inch undoped and Si-doped GaAs crystals, respectively.

A characteristic phenomenon in nearly all as-grown crystals is the rearrangement of the stored dislocations into cellular networks and low-angle grain boundaries, which are based on dynamical polygonization. The cell dimension is indirectly proportional to the dislocation density and the acting elastic shear stress – a correlation that is not yet exactly clarified. Both dislocation glide and climb are responsible formation mechanisms. However, the process of plasticity cannot be explained exclusively by equilibrium thermodynamics due to the presence of typical preconditions for irreversibility such as temperature and stress gradients during the growth process leading to dissipative structuring by self-organization. Steps to avoid such patterns are drastic reduction of thermomechanical stress, codoping, and stoichiometric growth conditions.

Two types of three-dimensional defects, still present in as-grown crystals, which impair the device qualities are precipitates and inclusions. Whereas precipitates are formed due to the retrograde solubility of native point defects in nonstoichiometric solid compositions while the crystal is cooling down, inclusions are formed by capture of micromelt/solution droplets, gas bubbles or foreign particles from the diffusion boundary layer adjacent to the growing interface. Precipitates can be reduced by near-stoichiometric growth conditions or postgrowth annealing. To avoid inclusions, conditions of morphological stability of the growing interface, undercritical growth rates, accelerated crucible rotation, ultrasonic vibration or alternating magnetic fields are effective possibilities.

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Thermophysical Properties of Molten Silicon

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4.1 Introduction

Modern society features information processing on a large scale and is supported by information technologies, which require high-speed data processing and high-speed data transmission. From the viewpoint of materials science and engineering, this is supported by high-quality semiconductor crystals, produced from high-temperature melt processes, such as the Czochralski, the floating zone, Bridgman processes, and so on. In order to understand and control these high-temperature processes, computer modeling is one of the superior tools available. This shows us the physics of these processes and how to improve processes and products, as shown in Fig. 4.1 [1]. This has been made possible thanks to the year-by-year improvements in computer performance, and even turbulence flow can now be handled. In modeling equations for continuity, momentum, energy and the Maxwell equation are solved simultaneously. In order to calculate temperature, flow and pressure fields of a high-temperature process, the thermophysical properties of the molten state in particular are indispensable. A survey was carried out on the required thermophysical properties for silicon crystal growth processes and on thermophysical properties actually employed in modeling in Japan: see Fig. 4.2 and Table 4.1 [2–4]. Table 4.1 shows thermophysical properties employed in 44 papers. The scatter of the data is rather large; particularly for the temperature coefficient of surface tension, the difference is one order of magnitude. Historically, Glazov et al. [5] reviewed thermophysical properties of molten semiconductors not only for molten silicon but also for other compound molten semiconductors. However, modern society requires the development of new measurement techniques and improvements in the accuracy and precision of data. Iida and Guthrie [6] overviewed thermophysical properties of molten metals and methods for measurements; this is a good textbook for thermophysical property measurement of high-temperature melts.

Figure 4.2 shows that thermal conductivity, specific heat capacity and surface tension are urgently required. Although thermal conductivity is required to calculate heat balance at the solid/liquid interface during crystal growth and is important to

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Fig. 4.1 Numerical simulation of silicon single crystal growth [1].



Fig. 4.2 Importance of thermophysical properties of molten silicon (increasing from 0 to 5) required for numerical modeling of crystal growth processes [2].

estimate crystal growth rate, the data are less reliable, except for thermal diffusivity data measured by a laser flash method; Yamamoto *et al.* [7] measured thermal diffusivity of molten silicon for the first time. Thermal conductivity λ is estimated from thermal diffusivity κ Eq. (4.1), where C_p^{mass} and ρ are isobaric mass heat capacity and density, respectively; uncertainty of measurement not only due to thermal diffusivity but also due to C_p^{mass} and ρ is transferred into that of thermal conductivity

Thermophysical properties	Value
Melt	
Melting temperature	1680–1685
Heat of fusion [kJ/kg]	1410-1800
Density [kg/m ³]	2.420-2.570
Thermal expansion coefficient [1/K]	$1.14 imes 10^{-4} - 1.5 imes 10^{-4}$
Specific heat [J/(kg K)]	911-1059
Specific heat [J/(mol K)]	25.6-29.7
Emissivity [-]	0.05-0.64
Thermal conductivity [W/(m K)]	42.9-67.0
Thermal diffusivity [m ² /s]	2.13×10^{-5} - 2.65×10^{-5}
Surface tension [N/m]	0.72-0.7426
Temperature coefficient of surface tension	$- 7 \times 10^{-5}$ to -4.3×10^{-4}
[N/(m K)]	
Diffusion constant (O) $[m^2/s]$	2.8×10^{-8} and 5×10^{-8}
Diffusion constant (B, P) $[m^2/s]$	3×10^{-8} for B, 3.4×10^{-8} and 5×10^{-8} for P
Viscosity [kg/(m s)]	$7 imes 10^{-4} - 8.6 imes 10^{-4}$
Electrical conductivity [S/m]	$1.2 imes 10^{6} - 3.8 imes 10^{6}$
Crystal	
Density [kg/m ³]	2300-2530
Thermal conductivity [W/(m K)]	22, 27.2, 98.89–9.43 × $10^{-2}T$ + 2.89 × $10-5T^2$, 96017 $T^{-1.149}$, 22 × (4.495–7.222(T/T_m) + 3.728(T/T_m) ²), 22(T_m/T), 75.0($T/300$) ^{-0.32} exp(- 5.3 × $10^{-4}(T-300)$)
Specific heat [J/(kg K)]	900-1060
Emissivity [–]	$0.55-0.75, 0.46 \times 1.39$ if $T/T_{\rm m} < 0.593,$
Electrical conductivity [S/m]	$4.3 \times 10^4 - 5.8 \times 10^4$

Table 4.1 Thermophysical properties of silicon actually employed in 44 papers.

 $\lambda = C_{\rm p}^{\rm mass} \cdot \rho \cdot \kappa \tag{4.1}$

That is why an accurate value of the specific heat capacity is required. On the other hand, thermal conductivity has been estimated from electrical conductivity assuming the Wiedemann–Franz law, as shown in Eq. (4.2), because the semiconductor is considered to be metallic in its molten state [8],

 $\lambda/\chi = L \cdot T \tag{4.2}$

where χ is electrical conductivity. *L* and *T* are the Lorenz number ($L = 2.445 \times 10^{-8}$ /W Ω K⁻²) and temperature, respectively. The temperature dependence of surface tension is indispensable to estimate the Marangoni flow of molten silicon, which appears at the melt surface.

Containerless processing techniques have been developed to a great extent for space experiments; i.e. these are electromagnetic [9], electrostatic [10], aerodynamic [11] and aero-acoustic levitations [12]. Containerless processing assures measurements of thermophysical properties of molten semiconductors; usually it

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is very difficult to measure thermophysical properties of molten semiconductors, because they have high melting temperatures, and are chemically reactive and opaque in the visible region. This is why there are no appropriate crucible and sensor materials; moreover, optical techniques cannot be applied. Measurement of thermophysical properties under undercooled conditions opens up a new field of science and technology, because previously it had been almost impossible to measure thermophysical properties under such conditions. Use of microgravity conditions also enables precise measurement of thermophysical properties of high-temperature melts, particularly transport properties, because buoyancy flow can be suppressed; measurement of diffusion constants by Frohberg *et al.* [13] explicitly revealed the effectiveness of microgravity conditions for thermophysical property measurements.

In this chapter, thermophysical properties of molten semiconductors are reviewed, including measurement techniques, particularly for molten silicon.

4.2 Density and Volumetric Thermal Expansion Coefficient

Density is one of the most basic thermophysical properties. As shown in Eq. (4.3), the temperature derivative of density corresponds to the volumetric thermal expansion coefficient β , which corresponds to the driving force for thermogravitational convection.

$$\beta = -(1/\rho)d\rho/dT \tag{4.3}$$

For molten silicon, density is measured either by the maximum bubble pressure, sessile drop, levitation, Archimedean or pycnometer method. Mukai and Yuan [14] evaluated density and thermal expansion coefficient of molten silicon precisely. Figure 4.3 shows the principle of the improved sessile drop method, where the volume of a droplet is obtained from its recorded shape. The density, ρ , is calculated dividing mass *M* by the volume *V*, as follows,

$$\rho = M/V \tag{4.4}$$

In order to avoid changes in the size of projected images and to obtain the correct shape, a parallel back light is used for illumination. X-rays can be also used. Light emission from the droplet surface causes error in the process of shape determination, although the outline of the droplet can be determined without illumination. When the levitation technique is used, density can be measured by measuring the volume of a levitated droplet and dividing the mass of a specimen by its volume, as shown in Fig. 4.4 [15]. This method assures measurement even under undercooled conditions, because there is no nucleation center for undercooled melts. The Archimedean method measures buoyancy acting on the bob inserted into molten materials. Figure 4.5 shows a measurement device for the Archimedean method. If two bobs are used, the effect of surface tension is eliminated [16].



Fig. 4.3 Modified sessile drop method [14].



Fig. 4.4 Shape of a levitated droplet revealed by back light illumination [15].

Figure 4.6 shows reported density values of molten silicon [5, 14, 15, 17–23]. Density lies between 2.52 and 2.58×10^3 kg·m⁻³ at the melting temperature and shows a high level of agreement within $\pm 1.6\%$, regardless of the measurement method. Density shows less scatter compared with other thermophysical properties, whereas the temperature coefficient of density shows a rather large degree of scatter compared to that for density, as shown in Table 4.2. The temperature dependence of density measured using an electrostatic levitator appears to follow a quadratic function, whereas density measured by other methods shows a linear relationship against temperature. Although the existence of anomalies of thermophysical properties just above the melting temperature had been reported by the Kimura Meta Melt Project [16, 24, 25] as shown in Fig. 4.7, this was not confirmed in other measurements in the wide temperature range including the undercooled condition, i.e.



Fig. 4.5 Bobs for measuring density of molten silicon [16].



Fig. 4.6 Density of molten silicon as a function of temperature [5, 14, 15, 17-23].

use of a levitation technique. In Fig. 4.6 density data with anomalous behavior are omitted. Mukai and Yuan [14] discussed precisely the effect of boron concentration on density; as long as the concentration level is as low as that actually employed. The effect of oxygen partial pressure of an ambient atmosphere on density was also precisely investigated; the oxygen partial pressure does not affect density.



Fig. 4.7 Density anomaly of molten silicon [25].

Method	ρ(Mg m ⁻³)	β (10 ⁻⁴ × K ⁻¹)	Investigators and Reference
Maximum bubble pressure	2.52	1.40	Lucas [22]
Archimedean	2.52	1.38	Glazov et al. [5]
Modified Sessile Drop	2.52	1.29	Mukai and Yuan [14]
Pycnometer	2.56	1.03	Sato <i>et al.</i> [23]
Electromagnetic levitation	2.52	1.40	Langen et al. [17]
Electromagnetic levitation	2.58	0.78	Higuchi et al. [18]
Electrostatic levitation	2.53	0.66	Rhim <i>et al.</i> [19]
Electrostatic levitation	2.58	0.66	Ohsaka <i>et al</i> . [20]
Electrostatic levitation	2.58	0.62	Rhim and Ohsaka [21]
Electrostatic levitation	2.58	0.72	Zhou <i>et al.</i> [15]

Table 4.2 The density of silicon ρ and the thermal expansion coefficient β at the melting temperature.

At present, the levitation technique is considered as the most elegant method for density measurement, because it assures measurement under undercooled conditions. The method of determining the shape of a droplet has been much improved with developments in image-processing techniques; in the early days, droplet shape was determined by extracting averaged outlines over 200 pictures using a Legendre polynomial. Although the melt surface oscillates in electromagnetic levitation, it has been assumed that the droplet shape is axisymmetric. Besides oscillation of five

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modes, i.e. $m = 0, \pm 1$ and ± 2 , droplets also rotate. Recently, images have been processed taking account of the effect of rotation, so that the uncertainty of calculated density can be minimized [26]. Application of a static magnetic field suppresses surface oscillation and also improves measurement accuracy. Use of backlight illumination reduces error introduced during the shape-definition process: see Fig. 4.4.

The density of molten silicon is closely related to the structure of molten silicon. A structural study was carried out by observing the structure factor S(Q) and the radial distribution function using synchrotron radiation at Spring-8, Japan, for molten silicon, including undercooled conditions. The first nearest-neighbor coordination number and interatomic distance were about 5 and 0.248 nm, respectively; they showed no dependence on temperature in the range of 1900–1550 K (Figs. 4.8(a) and (b)) [18, 27, 28]. These experimental results show that the short-range order based on tetrahedral bonds of molten silicon does not change with the degree of undercooling but that medium-range order changes with the degree of undercooling.

4.3

Isobaric Molar Heat Capacity

Isobaric molar heat capacity is also one of the most basic thermophysical properties. For molten silicon, the isobaric molar heat capacity has been measured by drop calorimetry [29–31]; 24.7 J/mol K [29], 29.2 + 25.0 \times 10⁻⁴T J/mol K [30] and 28.7 J/mol K [31]. The 27.0 J/mol K reported by NIST-JANAF [32] is the average of data measured by Olette [29] and Kantor et al. [30], as shown in Fig. 4.9. Sung et al. [33] measured the isobaric molar heat capacity as follows: $C_p = 3R + 4.8$ $\times 10^{-4}T + 4.157 \times 10^{5}T^{-2} - 1.002 \times 10^{-7}T^{2}$ J/mol K, where R is the gas constant. They measured the ratio of molar heat capacity to total hemispherical emissivity C_p/ε_T by electrostatic levitation and calculated the total hemispherical emissivity ε_T using the C_p value reported by Iida and Guthrie [6]. This ε_T was used to calculate C_p using the above C_p/ε_T ratio. Fukuyama's group developed a novel method to measure molar heat capacity using a novel AC noncontact calorimetry method that employed the levitation technique; molar heat capacity $C_{\rm p}$, total hemispherical emissivity $\varepsilon_{\rm T}$ and thermal conductivity λ are measured simultaneously using a combination of electromagnetic levitation and application of a strong magnetic field [34-37]. They applied a noncontact AC calorimetry, which was originally developed by Wunderlich and Fecht for a solid specimen [38], to a molten specimen. The measurement facility is shown in Fig. 4.10. A molten silicon droplet was heated by a sinusoidally modulated semiconductor laser beam (wavelength: 808 nm) with a modulation frequency of ω from the top of the specimen. The isobaric molar heat capacity C_p was obtained by measuring the amplitude of the temperature oscillation $\Delta T_{AC,l}$ at the bottom of the droplet (see Fig. 4.11), under conditions in which heat conductance by conduction is greater than that of radiation; this means that the relationship between the relaxation time for conduction τ_c and that for radiation τ_r must satisfy the following condition:

$$\omega^2 \tau_r^2 >> 1 >> \omega^2 \tau_c^2$$
(4.5)



Fig. 4.8 (a) Coordination number of molten silicon compared with previous data. (b) Radial distribution functions of molten silicon [18, 27, 28].

When the amplitude of the temperature oscillation is measured at the bottom, this is written as:

$$\Delta T_{\rm AC,l} = \frac{S_{\rm h} A M_{\rm Si} P_0}{\omega m C_{\rm p}} \left\{ 1 + \frac{1}{\omega^2 \tau_{\rm r}^2} + \omega^2 \tau_{\rm c}^2 \right\}^{-1/2}$$
(4.6)

$$f = \left\{ 1 + \frac{1}{\omega^2 \tau_{\rm r}^2} + \omega^2 \tau_{\rm c}^2 \right\}^{-1/2}$$
(4.7)

Here, S_h is a fraction of the area of the sample where the laser beam is irradiated, A is the total area of the sample, P_0 is laser power. M_{Si} and m are molecular weight of the silicon and mass of silicon specimen. f is defined as a calibration factor.



Fig. 4.9 Molar heat capacity of molten silicon as a function of temperature [29-33, 35].



Fig. 4.10 Noncontact AC calorimetry using electromagnetic levitation superimposed with static magnetic field for simultaneous measurements of isobaric molar heat capacity, total hemispherical emissivity and thermal conductivity [34, 35].

A plot of the product of ω and $\Delta T_{AC,I}$ as a function of frequency ω shows the maximum value at a certain frequency. Using this maximum $\omega \Delta T_{AC,I}$ value, the isobaric molar heat capacity C_p is obtained using Eqs. (4.6) and (4.7), because this condition satisfies $f \approx 1$. The isobaric molar heat capacity measured by this method is $28.2 \pm 3.3/J$ mol⁻¹K⁻¹ [1750–2050 K].

The heat of fusion at the melting temperature was reported to be 50.7×10^3 J/mol [29].



Fig. 4.11 Principle for measuring isobaric molar heat capacity, total hemispherical emissivity and thermal conductivity [34].

4.4 Emissivity

Emissivity is a thermophysical property related to optical energy transfer. The normal spectral emissivity is used for noncontact temperature measurement and the total hemispherical emissivity is used for estimating the energy transmitted from the melt surface by radiation.

4.4.1 Normal Spectral Emissivity

The normal spectral emissivity ε_N was measured by Lange and Schenck at 650 nm for the first time [39]. Since then, over ten measurements have been reported [40–50], as shown in Fig. 4.12. Shvarev *et al.* [40] reported that thermal emission from molten silicon can be explained by Drude's free-electron model. Pulse lasers have been used to melt silicon. This method has advantages, in that measurement can be carried out in a very short time and a furnace is not required [42–44]. However, it is difficult to measure the sample temperature accurately as long as laser heating is employed. Recently, measurements using a cold crucible or levitator have been attempted; these techniques assure measurement conditions without optical contamination, because there is no crucible wall at high temperature, which causes disturbing emission and reflection [47–50].

Kawamura *et al.* [50] successfully measured the normal spectral emissivity over a wavelength range between 550 and 1600 nm using an electromagnetic levitation technique, which assures measurements for molten silicon in undercooled conditions from 1553 to 1797 K, as shown in Fig. 4.13.





Fig. 4.12 Normal spectral emissivity of molten silicon at the melting point [39-50].



Fig. 4.13 Normal spectral emissivity measured at various wavelengths using levitation [50].

4.4.2

Total Hemispherical Emissivity

The total hemispherical emissivity was measured using electromagnetic levitation by observing a relaxation time τ_1 of the cooling curve due to radiation of molten silicon with a heat capacity of C_s , as shown in Fig. 4.11 and Eqs. (4.8)–(4.10) [51],

$$T_0 + \Delta T_{\rm DC} = \exp(-t/\tau_1) \tag{4.8}$$

$$\varepsilon_{\rm T} = C_{\rm p} m / (16\pi r^2 M_{\rm Si} \,\sigma_{\rm SB} \,\tau_1 \,T^3) \tag{4.9}$$

$$C_{\rm p}/C_{\rm s} = M_{\rm Si}/M \tag{4.10}$$

where $T_0 + \Delta T_{DC}$ and T_0 are the temperature of the sample before and after cooling, *t* is the time, *r* is the sample radius, σ_{SB} is the Stefan–Boltzmann constant:

 $\sigma_{SB} = 5.6705 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$. C_s and M_{Si} are sample heat capacity and mass of 1 mole of silicon, respectively: $\epsilon_T = 0.23 \pm 0.03$ at 1750–1950 K.

The total hemispherical emissivity is also obtained by measuring the relation between the phase shift ϕ and frequency ω . The phase shift ϕ is obtained using the following equation.

$$\phi = \tan^{-1} \left(\frac{\Delta T_{\rm md}^{\rm out}}{\Delta T_{\rm md}^{\rm in}} \right) \tag{4.11}$$

Here, $\Delta T_{\rm md}^{\rm in}$ and $\Delta T_{\rm md}^{\rm out}$ are the in-phase and out-of-phase components of the modulation temperature amplitude $\Delta T_{\rm md}$, respectively, and are obtained by numerically solving Eqs. (4.12) and (4.13) with parameters of ε_T and thermal conductivity λ under boundary conditions, Eqs. (4.14)–(4.19) [35, 36].

$$\lambda \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial (\Delta T_{\rm md}^{\rm in})}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial (\Delta T_{\rm md}^{\rm in})}{\partial \theta} \right) \right] - \rho C_{\rm p}^{\rm mass} \ \omega \Delta T_{\rm md}^{\rm out} = 0$$
(4.12)

$$\lambda \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial (\Delta T_{\rm md}^{\rm out})}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial (\Delta T_{\rm md}^{\rm out})}{\partial \theta} \right) \right] - \rho C_{\rm p}^{\rm mass} \ \omega \Delta T_{\rm md}^{\rm in} = 0$$
(4.13)

At the droplet surface irradiated by the laser:

$$-\lambda \frac{\partial (\Delta T_{\rm md}^{\rm in})}{\partial n} = 4\sigma_{\rm SB} \,\varepsilon_{\rm T} \, T_0^3 \,\Delta T_{\rm md}^{\rm in} \, \frac{2\alpha P_0}{\pi r_{\rm laser}^2} \, \exp\left[-\frac{2 \, R_{\rm s}^2 \,\sin^2 \,\theta}{r_{\rm laser}^2}\right] (-n \cdot e_{\rm laser})$$

$$(4.14)$$

$$-\lambda \frac{\partial (\Delta T_{\rm md}^{\rm out})}{\partial n} = 4\sigma_{\rm SB} \,\varepsilon_{\rm T} \, T_0^3 \,\Delta \, T_{\rm md}^{\rm out} \tag{4.15}$$

At the droplet surface without the light source:

$$-\lambda \frac{\partial (\Delta T_{\rm md}^{\rm in})}{\partial n} = 4\sigma_{\rm SB} \ \varepsilon_{\rm T} \ T_0^3 \ \Delta \ T_{\rm md}^{\rm in}$$
(4.16)

$$-\lambda \frac{\partial (\Delta T_{\rm md}^{\rm out})}{\partial n} = 4\sigma_{\rm SB} \,\varepsilon_{\rm T} \, T_0^3 \,\Delta \, T_{\rm md}^{\rm out} \tag{4.17}$$

At the centerline:

$$-\frac{\partial(\Delta T_{\rm md}^{\rm in})}{\partial\theta} = 0 \tag{4.18}$$



Fig. 4.14 Total hemispherical emissivity of molten silicon as a function of temperature [21, 33, 34].

$$-\frac{\partial(\Delta T_{\rm md}^{\rm out})}{\partial\theta} = 0 \tag{4.19}$$

Here, ρ and $C_{\rm p}^{\rm mass}$ are the density and the isobaric mass heat capacity. *n*, $r_{\rm laser}$, e_{laser} and σ_{SB} are the normal distance from the droplet surface, e^{-2} radius of laser beam, unit vector pointing out the incident direction of laser beam, and the Stefan-Boltzmann constant, respectively. r and θ are the spherical coordinates. Such a set of equations, Eqs. (4.12) to (4.19), is derived by simplifying the unsteady-state heat-conduction equation accompanied by radiative heat transfer to the ambient, under the assumptions that the temperature response is at the stationary modulation state, and that both average temperature and modulation amplitude are much less than the initial temperature T_0 just before laser heating. A nonlinear least square curve fit is applied to show the $\phi-\omega$ relation with parameters ϵ_T and $\lambda,$ so that ϵ_T and λ can be found that can reproduce the experimentally observed $\phi - \omega$ relation. The total hemispherical emissivity for molten silicon determined by this method was 0.25 ± 0.03 [T = 1750-1950 K]. Since the total hemispherical emissivity is obtained simultaneously with thermal conductivity, whose measurement requires application of magnetic field, hemispherical emissivity is plotted for various magnetic fields, although total hemispherical emissivity does not depend on magnetic field, as shown in Fig. 4.14.

Rhim and Ohsaka [21] measured the ratio of the isobaric molar heat capacity to the total hemispherical emissivity, C_p/ε_T , observing a cooling curve within an electrostatic levitator and obtained $\varepsilon_T = 0.18$ using the C_p of 25.6 J/mol K at the melting temperature. Sung *et al.* [33] obtained total hemispherical emissivity using the method mentioned in Section 4.3, as follows: ε_T (*T*) = 0.267 - 5.615 × 10⁻⁵*T* + 9.133 × 10⁻⁹*T*²: see Fig. 4.14.

4.5 Thermal Conductivity

Thermal conductivity is one of the most demanding thermophysical properties but difficult to obtain experimentally, because on Earth thermogravitational convection exerts a major effect on heat transfer and it is almost impossible to suppress this effect. There are four methods to obtain the thermal conductivity of molten silicon. Historically, thermal conductivity has been estimated from the measurement of electrical conductivity χ and applying the Wiedemann–Franz law, as shown in Eq. (4.2) [5, 8, 52, 53]. Thermal diffusivity was measured also by a laser flash method [7, 24, 54] and is converted into thermal conductivity using density ρ and mass heat capacity C_p^{mass} . Although transient hot-wire and hot-disk methods assure direct measurement of thermal conductivity, an insulating coating must be applied to prohibit electric current leakage from the wire to the melt, as well as corrosion of the wire by the melt [55, 56]. The Insulating coating causes measurement error so that the measured thermal conductivity can be smaller than the correct value. Furthermore, insulating coating becomes difficult with increasing melt temperature.

Application of noncontact AC calorimetry using electromagnetic levitation under a strong DC magnetic field enables direct measurement of thermal conductivity; melt flow is suppressed and heat transfer is controlled only by conduction within a droplet, so that a droplet behaves as if it were solid [35, 36]. Furthermore, measurements are free from the sensor insulation coating. The thermal conductivity can be obtained from the $\phi-\omega$ relation simultaneously with total hemispherical emissivity ϵ_T , as described in Section 4.3.

As shown in Fig. 4.15, thermal conductivity of molten silicon was successfully measured using noncontact AC calorimetry [35]. Figure 4.15 also shows other reported thermal conductivity data for the purposes of comparison. With magnetic fields above 2T, the effect of convection is suppressed. This is supported by numerical calculations for a levitated silicon melt flow in the electromagnetic levitator superimposed with a strong static magnetic field [37]. Calculated results show that the melt flow within the droplet was almost suppressed, whereas a weak Marangoni flow due to coil heating remains. However, this effect is too small to affect the heat transfer within the sample. This suggests that heat flow is controlled by conduction. Therefore, noncontact AC calorimetry can be used for the measurement of thermal conductivity of molten materials. The thermal conductivity of molten silicon at the melting temperature was $\lambda = 62 \pm 3$ W m⁻¹ K⁻¹.

4.6 Surface Tension

Surface tension and its temperature coefficient are indispensable to describe surface-tension-driven flow at the silicon melt surface during crystal growth. The existence of the surface-tension-driven flow, i.e. the Marangoni flow, of molten



Fig. 4.15 Thermal conductivity, directly measured in various magnetic fields between 0.5 and 4T [35] and estimated from thermal diffusivity and electrical conductivity [5, 7, 8, 24, 52–56].

silicon was confirmed through crystal growth experiment under microgravity conditions [57]. The driving force for Marangoni flow is a shear force due to the surface-tension difference at the melt surface. Both the temperature distribution at the melt surface and the temperature coefficient of surface tension contribute to this mechanism. In 1989, Keene [58] reviewed surface tension and the temperature coefficient, and categorized surface tension σ and its temperature coefficient ∂ $\sigma/\partial T$ into two groups, as shown in Fig. 4.16 [58–79]. Except for data in (Refs. [78, 79]) one group shows low surface tension at the melting temperature, i.e. $\sigma = 700$ -750×10^{-3} N/m and small absolute values of temperature coefficient $\|-\partial\sigma/\partial T\|$ $= 0.05 - 0.15 \times 10^{-3}$ N/K m. The other group shows rather high surface tension and large absolute values of temperature coefficient, i.e. $\sigma = 800 \times 10^{-3}$ N/m and $\|-\partial\sigma/\partial T\| = 0.2 - 0.3 \,\mathrm{mN/K}$ m. Such an extensive scattering of data is reflected in the temperature coefficient of surface tension used for simulation, as shown in Table 4.1. Keene suggested that lower surface tension and its temperature coefficient are affected by oxygen, and that attention must be paid to oxygen, i.e. the surfactant for the high-temperature melts. He also recommended use of the levitation technique to avoid contamination problems introduced from the crucible wall or the substrate, because surface tension is sensitive to contamination, whereas surface tension was conventionally measured using the sessile drop method, the maximum bubble pressure method and the ring method, which employs such jigs. Chung et al. [78] introduced a unique method to measure surface tension, i.e. the dynamic hanging-drop method.

Przyborowski *et al.* [79] applied the levitation technique for the first time to measure the surface tension of molten silicon and reported a high level of surface tension at the melting temperature and a steep temperature dependence as $\sigma = 783.5-0.65(T-1410)$ mN/m. The rather large absolute value of temperature



Fig. 4.16 Surface tension of molten silicon [58-79].

coefficient of -0.65×10^{-3} N/K-m is attributed to the use of the levitation technique, which is free from the crucible wall, as well as the use of pure Ar gas. In the course of preparatory research into microgravity experiments for the Marangoni flow of molten silicon, Mukai *et al.* [80] measured surface tension and its temperature coefficient as a function of both temperature and oxygen partial pressure of an ambient atmosphere using the sessile drop method with a substrate made of p-BN, which can withstand molten silicon, as shown in Figs. 4.17(a) and (b). The oxygen partial pressure dependence of the Marangoni flow velocity for molten silicon observed under microgravity conditions [81] was well explained by taking account of the oxygen partial pressure dependence of the temperature coefficient of surface tension.

Huang *et al.* [82] measured the surface tension of molten silicon also as a function of oxygen partial pressure. However, there was a magnitude difference of over ten-fold in the oxygen partial pressure between Mukai's measurement and Huang's measurement. This discrepancy was clearly explained by the Ratto–Ricci–Arato model [83], which was validated by Azami and Hibiya [84]. In this model, chemical equilibrium and transport of oxygen to and from the silicon melt surface are included. The oxygen partial pressure at the silicon melt surface, $P_{O_2}^{\text{surface}}$, is lower than that introduced into a container $P_{O_2}^{\text{inlet}}$, because SiO has a high vapor pressure and oxygen can be taken away as SiO from the melt surface. As shown in Eq. (4.20), the oxygen partial pressure at the container inlet, as follows:



Fig. 4.17 Surface tension (a) and its temperature coefficient (b) of molten silicon as a function of oxygen partial pressure of an ambient atmosphere for various temperatures [80].

$$P_{O_2}^{\text{inlet}} = P_{O_2}^{\text{surface}} + P_{\text{Si}}^{\text{saturation}} \sum_{j=\text{reaction}}^{\text{SiO,SiO_2}} \alpha_j K_j \frac{(1+\text{Pe})}{(1+\text{Pe}/\Psi_j)} P_{O_2}^{\text{surface}^{\alpha_j}}$$
(4.20)

In this model, two kinds of chemical equilibria are considered, as follows:

$$Si + \alpha_j O_2 = SiO_{2\alpha}, \quad \alpha_{SiO} = 1/2, \ \alpha_{SiO2} = 1.0,$$

$$\begin{split} & \text{for}\, j=1, \;\; \text{Si}(l)+1/2O_2(g) \rightarrow \, \text{SiO}(g) \text{ and } \alpha_1=1/2, \\ & \text{and}\; \text{for}\, j=2, \;\; \text{Si}(l)+O_2(g) \rightarrow \, \text{SiO}_2(s) \text{ and } \alpha_2=1. \end{split}$$

Here, K_j is the equilibrium constant for the *j*th reaction, Ψ_j is the dimensionless diffusion constant of oxygen, and Pe, the Peclet number, is defined as the ratio of flow to diffusion of oxygen.

4.7 Diffusion Constant

Data on diffusion constants of impurity atoms are important to calculate incorporation of dopant impurities in silicon crystals, which control the electronic properties of silicon. However, there are fewer data on impurity diffusion constants except for that reported by Turovskii [85], Kodera [86], Shashkov and Gurevich [87], Gnesin and Raichenko [88], and Keller and Mühlbauer [89]. In the Landholt-Börnstein data book, Mühlbauer recalculated reported data using the kinematic viscosity of molten silicon ($\nu = 3.5 \times 10^{-7} \text{ m}^2/\text{s}$) [91]. Diffusion constants reported are tabulated in Table 4.3.

Besides these impurities, the diffusion constant for oxygen in Si melt is required for calculating oxygen transport during crystal growth, because oxygen concentration and its distribution must be carefully controlled in bulk Si crystals. Oxygen in silicon wafers has two important roles, as outlined below. Slippage formation during heat treatment in the LSI (large-scale integration) process is prohibited due to the impurity hardening effect; i.e. interstitial oxygen can be an energetic barrier for dislocations to propagate. Oxygen in the interstitial site can precipitate as SiO₂ during heat treatment due to the temperature dependence of oxygen solubility in a silicon crystal as a solid solution. At the interface between 100-nm size SiO₂ crystals and silicon matrix, heavy metals such as Fe, Ni and Cu, which adversely affect device quality, can be mopped up – otherwise known as the gettering effect.

Iwanaga *et al.* [92] tried to measure the diffusion constant of oxygen in molten silicon using an electrochemical method. Figure 4.18 shows a schematic measurement facility, which consists of a furnace, crucible, solid-state oxygen sensor made of ZrO₂-11%CaO, and electrodes. Due to dissolution of SiO₂ glass settled in the Si melt, oxygen is transported from the SiO₂ glass surface to the solid-state electrolyte. If the change of the electromotive force due to oxygen concentration difference is measured as a function of time, the rate of the change corresponds to the diffusion process of oxygen in the silicon melt, where transport of oxygen by convection is neglected. The diffusion constant *D* was obtained from the curve fitting of electromotive-force data by analytically solving the diffusion equation with suitable boundary conditions. The value of *D* obtained was 1.1×10^{-8} m²/s at 1753 K. On the other hand, the diffusion constant obtained by the conventional long capillary method was 1.21×10^{-8} m²/s at 1753 K [92]. The diffusion constant

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	$D(m^2 s^{-1})$	Ref. ^a
В	$\begin{array}{c} 2.4 \times 10^{-8} \\ 1.8 \times 10^{-8} \\ 3.3 \times 10^{-8} \end{array}$	[86] [91] [87]
Al	$\begin{array}{l} 7.0 \times 10^{-8} \\ 5.3 \times 10^{-8} \\ 2.3 \times 10^{-8} \end{array}$	[86] [91] [85]
Ga	$\begin{array}{l} 4.8 \times 10^{-8} \\ 3.6 \times 10^{-8} \\ 6.6 \times 10^{-8} \end{array}$	[86] [91] [87]
In	$6.9 imes 10^{-8}$ $5.2 imes 10^{-8}$ $1.7 imes 10^{-8}$	[86] [91] [87]
T1	$7.8 imes 10^{-8}$ $5.9 imes 10^{-8}$	[89] [91]
С	$\begin{array}{l} 2.0\times 10^{-8}\\ 1.5\times 10^{-8}\\ 4.8\times 10^{-8}\end{array}$	[90] [91] [88]
Р	$\begin{array}{l} 5.1\times 10^{-8}\\ 3.9\times 10^{-8}\\ 2.3\times 10^{-8}\\ 2.7\times 10^{-8}\end{array}$	[86] [91] [85] [87]
0	$1.1 imes 10^{-8} \ 4 imes 10^{-8}$	[92] [93]

Table 4.3 Impurity Diffusion Constants in Molten Silicon D.

a Data of [91] were calculated from either from Refs. [86, 89] or [90] using a kinematic viscosity value of $\nu = 3.5 \times 10^{-7} \text{ m}^2/\text{s}.$

of oxygen estimated by molecular dynamics simulation was $4 \times 10^{-8} \text{ m}^2/\text{s}$ [93]. These data are of the same order as that experimentally measured.

Using microgravity conditions, diffusion constants of molten tin and lead were measured successfully [13, 94]; diffusion constants were reported to be proportional to the square of the absolute temperature, as follows:

 $D = AT^2 \tag{4.21}$

However, for molten semiconductors, particularly for molten silicon, the temperature dependence of diffusion constants has not been made clear. The measurement of the diffusion constant under microgravity was a driving force to improve the measurement techniques; development of diffusion cells made of ceramics, application of a shear cell technique, and so on [94]. Application of a strong static magnetic field could also be effective in suppressing convection on Earth [95]. The diffusion



Fig. 4.18 Measurement cell for diffusion constant of oxygen in molten silicon [92].

constant for silicon melt, i.e. diffusion constants for self-diffusion and impurities, could be measured precisely using up-to-date techniques in the near future.

4.8 Viscosity

Viscosity is one of the most important properties to describe mass flow within the melt. For low Prandlt number fluids, such as molten metals and semiconductors with low viscosity, the oscillating cup method has been employed, as shown in Fig. 4.19, because this is one of the most appropriate methods for melts with low viscosity [5, 96–98]. Sato *et al.* [98] measured the viscosity of molten silicon carefully using the oscillating cup method. As shown in Fig. 4.20, measurements were carried out using crucibles made of various materials, i.e. graphite, silicon carbide, alumina, silicon nitride, boron nitride, silica glass, 8 mol%-YSZ, and it was found that the crucible material does not affect viscosity measured using this method. They measured viscosity under undercooled conditions of \sim 30 K, even though measurements were carried out using crucibles. Recommended viscosity is as follows:

$$\log \eta / m Pa \cdot s = -0.727 + 819/T \tag{4.22}$$

$$E_{\rm n} = 15.7 \, \rm kJ \, mol^{-1}$$
 (4.23)

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Fig. 4.19 Viscosity measurement facility: oscillating-cup method [98].

Viscosity can also be measured by levitation, by observing a damping constant Γ of oscillation of a droplet; Γ is defined as the reciprocal decay time of oscillation from an initial amplitude to that of 1/e, as shown in Fig. 4.21 [99] and,

$$\Gamma = (20 \ \pi/3)(R \ \eta/M) \tag{4.24}$$

Zhou et al. [15] measured the viscosity of molten silicon using electrostatic levitation across a wide temperature range, including undercooled conditions of \sim 50 K, as follows, $\eta = 0.5572 - 5.39(10^{-4}(T - T_m) \text{ mPa s} (1635 \text{ K} < T < 1845 \text{ K})$, where T_m = 1687 K; see Fig. 4.20. This value is slightly smaller than that recommended by Sato et al. shown in Eqs. (4.22) and (4.23). Both Sato et al. and Zhou et al. measured viscosity successfully under the various conditions, including the undercooled condition; anomalies of viscosity, such as those reported by Kimura and Terashima [24], were not observed. Although viscosity can be measured using electrostatic levitation under normal gravity conditions on Earth, it is almost impossible to measure it using electromagnetic levitation on Earth. In the case of electromagnetic levitation, a positioning coil, which levitates a droplet, introduces strong flow within the droplet and the surface oscillation does not decay on earth. However, under microgravity conditions decrement of oscillation can be observed, because only a small amount of electric current is required for a positioning coil. Measurement of viscosity of metallic melts was performed under microgravity on-board the Space Shuttle [100].



Fig. 4.20 Viscosity of molten silicon. Sato *et al.* repeatedly measured viscosity to see the effect of crucible materials [5, 15, 96–98].

Viscosity is also available by measuring the half-width value of oscillation $\Delta v_{1/2}$ under microgravity, as shown by [101].

$$\Delta v_{1/2} = (\sqrt{3} \Gamma)/\pi \tag{4.25}$$

4.9 Electrical Conductivity

Electrical conductivity is used for the calculation of melt flow under a magnetic field. Electrical conductivity is also used to estimate thermal conductivity assuming the Wiedemann–Franz law, as shown in Eq. (4.2). Glazov *et al.* [5], Schnyders and Zytveld [52], and Sasaki *et al.* [8] measured electrical conductivity using a four-probe method. Figure 4.22 shows a typical measurement cell for the four-probe method, where resistivity, which is the inverse of electrical conductivity, is measured [8].



Fig. 4.21 Damping of surface oscillation in an electrostatic levitator after electrical excitation for a molten sample measured by the diameter-sensing system [101].



Fig. 4.22 Cell made of BN for measurement of electrical resistivity (conductivity) [8].

Sasaki *et al.* [8] reported an electrical conductivity of $\chi = 1.39 \times 10^6$ S/m. ($T_m < T < 1900$ K).

Recently, an electrical conductivity measurement has been carried out using electromagnetic levitation, by observing the impedance changes in the coil [102]. This new method was applied in microgravity for the first time by analyzing housekeeping data for the electromagnetic levitation facility, TEMPUS. Since then continuous efforts have been made to apply this technique, even on the ground.

This proposal of a new technique will assure measurement of electrical conductivity under undercooled conditions.

4.10 Sensitivity Analysis

Although each thermophysical property is necessary and important for numerical modeling, not all thermophysical properties need to be measured with the same degree of certainty; priority for the improvement of measurement techniques should be given depending on the influence of the thermophysical property in question on the numerically obtained results. The Tsukada group performed global numerical simulation for CZ silicon crystal growth [103]; the criteria for the sensitivity analysis were the nondimensional crystal pulling rate, i.e. the Peclet number Pe, and the deflection of the melt/crystal interface Δz , where the positive value means concave to the melt, and the negative value convex to the melt. Distribution of stream functions and isotherms within the melt were also investigated. The properties examined were the temperature coefficient of surface tension, viscosity, thermal conductivity, the thermal expansion coefficient and total hemispherical emissivity of the melt ε_m , and the thermal conductivity and emissivity of the crystal. As shown in Figs. 4.23(a) and (b), the position of the melt/crystal interface, i.e. Δz is sensitive to the total hemispherical emissivity of the molten sate. The effects of variation of thermophysical properties on Pe and Δz are quantitatively characterized using the following equations, where the change in Pe and Δz is characterized against 1% change of a certain thermophysical property X:

$$S_X^{\rm Pe} = \frac{({\rm dPe}/{\rm dX}) X_{\rm av}}{100}$$
(4.26)

$$S_X^{\Delta z} = \frac{\left(\mathrm{d}\Delta z/\mathrm{d}X\right)X_{\mathrm{av}}}{100} \tag{4.27}$$

As shown in Table 4.4, it was clarified that, for thermophysical properties of molten state, Pe and Δz are sensitive to emissivity; for thermophysical properties of solid state, Pe is sensitive to thermal conductivity and Δz is sensitive to emissivity.

4.11 Recommended Thermophysical Property Data for Silicon System

Table 4.5 summarizes the thermophysical properties of molten and solid silicon recommended for use in numerical modeling. Multiple data are evaluated from the viewpoint of reliability of measurement technique and collated.



Fig. 4.23 Example of sensitivity analysis; the effect of the total hemispherical emissivity of silicon melt was examined. Note that crystal/melt interfaces depend on emissivity; a) $\epsilon_m = 0.20$, b) $\epsilon_m = 0.50$ [103].

Table 4.4 Sensitivity analysis [103].

Properties X	S_X^{Pe}	$S_X^{\Delta z}$
(a) Melt		
Temperature coefficient of surface tension Viscosity Thermal conductivity Thermal expansion coefficient Total hemispherical emissivity	$\begin{array}{l} 9.47 \times 10^{-5} \\ 1.96 \times 10^{-5} \\ 1.00 \times 10^{-4} \\ 3.25 \times 10^{-5} \\ 5.61 \times 10^{-4} \end{array}$	$\begin{array}{l} 5.70 \times 10^{-4} \\ 3.48 \times 10^{-5} \\ 2.59 \times 10^{-4} \\ 3.66 \times 10^{-5} \\ 1.33 \times 10^{-3} \end{array}$
(b) Crystal Thermal conductivity Total hemispherical emissivity	$3.21 imes 10^{-4}$ $2.28 imes 10^{-4}$	$4.69 imes 10^{-4}$ $4.92 imes 10^{-4}$

4.12 Summary

Thermophysical properties of molten silicon were reviewed, because thermophysical properties are indispensable for numerical modeling. It is important to supply recent data and some evaluations of numerical modeling in the present chapter. Since materials processing experiments started to be carried out in space, microgravity conditions have been considered to be promising for thermophysical property measurements, because buoyancy-driven flow can be suppressed and high-temperature melts can be sustained under containerless conditions. This allows for conditions in which heat can be transferred only by conduction and radiation contamination from the crucible wall can be suppressed, when droplet is levitated without crucible. Even on Earth, great efforts have been made to apply containerless levitation techniques to thermophysical property measurements and materials processing. Many thermophysical properties have been attempted to be measured using levitation on Earth. In particular, superposition of a static magnetic field to electromagnetic levitation could suppress internal flow within a levitated droplet and unnecessary oscillation due to a nonaxisymmetric distribution of the magnetic field prepared by a coil. This has allowed accurate measurement of the thermal conductivity of metallic melts and improved the certainty of density measurements. This is very much a spin-off of space materials-processing experiments. Due to the introduction of levitation techniques, almost all thermophysical properties of molten silicon can be measured under undercooled conditions. This technique can be applied to measurements of other melts, such as molten metals, alloys and compound semiconductors as well. One thermophysical property that cannot currently be measured by levitation is a diffusion constant, because the suppression of mass transport is more difficult than that of heat transfer; the existence of a free surface and a small amount of temperature inhomogeneity causes the Marangoni flow, which is sufficiently small for thermal conductivity measurement but affects the diffusion constant measurements [37]. Because

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 Table 4.5 Recommended thermophysical propertiess.

Melt		Ref.
Density ρ [kg/m³]	2560	[23]
Thermal expansion coefficient β [1/K]	1.03×10^{-4}	[23]
Isobaric molar heat capacity C _p [J/(mol K)]	$28.2 \pm 3.3 \ (1750 - 2050 \ \text{K})$	[34]
Normal spectral emissivity $\epsilon_N \; [-]$	0.231 (at 650 nm), 0.223 (at 800 nm), 0.217 (at 970 nm), 0.194 (at 1550 nm)	[50]
Total hemispherical emissivity ϵ_T [–]	$0.25 \pm 0.03~(1750 - 1950~{ m K})$	[35]
Thermal conductivity λ [W/(m K)]	62 ± 3 (at m.p.)	[35]
Surface tension σ [mN/m]	831 – 29.5 ln (1 + 3.88 × $10^{10} Po_2^{1/2}$) at 1693 K	[80]
	814 – 30.1 ln (1 + 3.06 × $10^{10} Po_2^{1/2}$) at 1723 K	
	$793 - 30.6 \ln (1 + 2.47 \times 10^{10} \text{Po}_2^{1/2})$ at 1753 K	
	$774 - 31.0 \ln (1 + 1.01 \times 10^{10} \text{ Pos}^{1/2})$ at 1773 K	
Temperature coefficient of surface tension	$-0.90 + 0.370 \ln(1 + 6.62 \times 10^{10} \text{ Pos}^{1/2})$	
∂ σ/∂ T [N/(m K)]	$-0.387 \ln (1 + 8.22 \times 10^9 P_{02}^{1/2})$	[80]
	$(1693 \text{ K} < T < 1773 \text{ K}, Po_2 < Po_2^{\text{sat}})$	
Diffusion constant (B) $[m^2/s]$	1.8×10^{-8}	[91]
Diffusion constant (P) $[m^2/s]$	3.9×10^{-8}	[91]
Diffusion constant (O) $[m^2/s]$	$2.5 imes 10^{-8}$	[92, 93] ^a
Viscosity η [mPa s]	$\log \eta = -0.727 + 819/T$, $E_{\eta} = 15.7 \text{ kJ/mo1}$	[98]
Electrical conductivity χ	1.39×10^6 S/m. ($T_{ m m} < T < 1900$ K)	[8]
Heat of fusion [I/mol]	50.7×10^{3}	[29]
Crystal		[=-]
Density [kg/m ³]	2330	[5]
Thermal conductivity [W/(m K)]	22	[104]
Specific heat []/(kg K)]	1037	[30]
Spectral emissivity at 0.65 μ m [–]	0.46	[105]
Electrical conductivity [S/m]	$5 imes 10^4$	[5, 106] ^b

 $^a2.5\times 10^{-8}\,m^2/s$ is an average of data reported in Refs. [92] and [93].

 $^{b}5\times10^{4}$ S/m is calculated from average resistivity reported in Refs. [5] and [106].

electromagnetic levitation is only applicable to electrically conductive materials, electrostatic levitation is a powerful tool for thermophysical property measurements of insulating materials, such as molten ceramics and glass. Therefore, electromagnetic levitation and electrostatic levitation are able to complement each other.
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Part II Simulation of Industrial Growth Processes

5 Yield Improvement and Defect Control in Bridgman-Type Crystal Growth with the Aid of Thermal Modeling

Jochen Friedrich

5.1 Introduction

The state-of-the-art of industrial bulk growth of important crystal materials has achieved quite impressive dimensions of the crystals. It is obvious from Table 5.1 that vertical Bridgman and vertical gradient freeze crystal-growth configurations (called the Bridgman-type configuration throughout this chapter) play a very important role among the various industrial crystal-growth techniques.

In general, Bridgman-type crystal-growth configurations consist of a furnace with several cylindrical side heaters. For crystals to be grown with diameters larger than 75 mm (3") a bottom and top heater are preferably used in addition to the side heaters in order to establish an axial heat flux inside the crystal, i.e. low radial temperature gradients [1, 2]. This means that the heater setup should provide ideally a constant (negative) gradient parallel to the growth direction (see Fig. 5.1). The single-crystal seed is positioned in the lower end of the crucible. The polycrystalline feed is melted and then directionally solidified by a controlled shifting of the temperature profile relative to the crucible from the seed to the top end, which means anti-parallel to the direction of gravity. This shifting can be achieved by three means:

- moving the crucible relative to the fixed furnace (Bridgman-Stockbarger method);
- ii. moving the furnace relative to the fixed crucible;
- iii. without any mechanical movement only by a shifting of the temperature profile by a controlled change of the heating powers of the furnace (Tammann-Stober or gradient freeze method).

Methods (i) and (ii) are called, in the literature, "vertical Bridgman (VB)", and method (iii) vertical gradient freeze (VGF); (i), (ii) and (iii) are called Bridgman-type.

These methods have several advantages compared to the Czochralski technique. Crystals can be grown in a cylindrical shape without any diameter control and

Table 5.1 Maximum Crystal Diameters Achieved byState-of-the-Art Industrial Crystals and Growth Processes:Cz = Czochralski-Type, B = Bridgman-Type, * Multicrystallinefor Photovoltaics.

Crystal	Si	Si*	GaAs	InP	CdZnTe	CaF ₂	Al ₂ O ₃
Growth method Diameter in mm Reference	Cz 300	B 680 × 680 [12]	Cz, B 200 [7, 8]	B 150 [9, 10]	B 75 [11]	B 400 [14]	B 500 [15]

under stable hydrodynamic conditions. The temperature gradients in the growing crystal are usually significantly smaller than in Czochralski configurations. This is of great importance as the crystal can be grown under conditions of considerably lower thermal stress, which results in a much lower density of structural defects, especially dislocations (EPD).

However, a crucial problem of Bridgman-type crystal growth is the possibility of a strong interaction between the growing crystal and the crucible wall. The interaction can create crystal imperfections like dislocations, twinning or polycrystal formation, which limits the yield and hence the industrial applicability. The occurrence of these imperfections cannot be observed *in situ* during the growth process. Therefore, it is not possible to correct the failure by a remelting as it is typically performed in Czochralski growth.

Nevertheless, there is an increasing industrial interest in the use of Bridgman-type growth configurations because of the less-expensive equipment and the fact that the structural perfection of the single crystals is higher than that of crystals produced by Czochralski methods. The latter is mainly due to lower thermal stress that causes dislocations.



Fig. 5.1 Schematic principle of (a) the vertical gradient freeze method and (b) the vertical Bridgman method.

An important breakthrough was achieved in the late 1980s when the vertical gradient freeze (VGF) technique was developed [3, 4]. In the following period it was possible to improve the crystal-growth conditions continuously with respect to decreased thermal stress, especially by a rigorous application of modeling and process-simulation tools [5, 6].

Nowadays, Bridgman-type crystal-growth configurations are mainly applied for the industrial production of compound semiconductors like high-quality GaAs [7, 8] and InP single crystals [9, 10], which are used as substrates for optoelectronic applications and in communication technology, CdZnTe crystals [11] used for infrared and X-ray detectors, but also for multicrystalline silicon [12] for photovoltaic applications. In the field of metallurgy, directional solidification is used to produce single-crystalline nickel-based superalloys for turbine blades [13]. A variety of oxide and fluoride crystals are also grown by Bridgman-type methods for high-value applications. For example, CaF₂ crystals with diameters up to 400 mm [14] are used as lenses for the deep-ultraviolet wavelength range in the semiconductor lithography technology. Another example is the growth of large sapphire crystals are grown by a modified VGF technique, the so-called heat exchanger method (HEM). The original characteristic of HEM is that a gas-cooled heat exchanger is placed below the seed crystal.

An interesting feature was developed to avoid the crystal crucible interaction in Bridgman-type crystal growth by a dewetting process [16]. In this so-called detached solidification a small gap is formed between the growing crystal and the crucible wall. The formation and stability of such a gap depends on the wetting conditions between the melt and the crucible material, the contact angle, the growth angle and external forces (especially a certain gas pressure difference between the gap in the vicinity of the solid/liquid interface and the gas cavity above the melt). The experimental results achieved so far for semiconductors demonstrate that the structural perfection of the crystals can be improved when the dewetting effect is used [17]. However, there remains still a lot of research to be done until this technology can be transferred into an industrial production.

5.2 Principles of Thermal Modeling

5.2.1 Introduction

Virtual crystal growth, i.e. numerical simulation of the heat- and mass-transport processes has become a standard tool for the development and optimization of academic and industrial crystal-growth processes [5, 18, 19]. This holds especially for the optimization of Bridgman-type crystal-growth configurations. A typical crystal growth setup implies a vast variety of coupled and interacting physicochemical processes, which have all to be taken into account as accurately as possible to

provide reliable and useful numerical predictions. In general, heat transport by conduction, radiation and convection (including turbulent flows), species transport, and thermal stress are the common important phenomena, but also some special aspects like the application of magnetic fields or defect formation have to be considered. The reader is referred to the corresponding reviews e.g. [20, 21].

A prerequisite for a successful application of numerical modeling with respect to a better control of defect formation and hence an improved yield of the whole crystal-growth process is the availability of accurate models that were validated by using experimental data. Furthermore, the models have to be implemented in efficient and user-friendly software tools that are equipped with an *easy to learn* and *easy to use* graphical user interface.

The approach of modeling currently most often applied is a so-called *global model*. It uses geometric representation of the whole growth equipment that can often be assumed as axisymmetric. It is frequently based on a CAD drawing of the crystal-growth facility. The CAD drawings have to be modified during a preprocessing step to delete details that are negligible for simulation and eventually to add modifications. The different geometrical regions of the crystal-growth equipment setup are assigned with material properties such as thermal conductivity (including its temperature dependence), emissivity, etc. Of particular importance is the precise knowledge of the material data that sometimes is a problem.

In the step of mesh generation, a suitable geometrical mesh is generated on which the discretized governing equations are solved in algebraic form. The width of the mesh must be adapted to the equations that should be solved in this region. It should be fine enough to describe precisely the considered physical phenomena, but not too fine because then the numerical performance becomes worse by increasing the computing time unnecessarily.

Very frequently, an unstructured triangulated mesh is used that has been proven to be very powerful in terms of automation of the preprocessing and in terms of solving inverse problems [22, 23], but less efficient for the treatment of convective phenomena [24]. In order to overcome this problem and also to solve convection phenomena in complex geometries the use of a hybrid mesh seems to be very powerful [24]. Such a hybrid mesh consists of an unstructured grid and a block-structured grid. The latter has proven to be very effective for the solution of convection-dominated problems that occur, for example, in Czochralski configurations [25] or in Bridgman-type processes that are carried out under high gas pressure conditions [26]. However, the disadvantage of using a block-structured grid is the conditional degree of automation of the preprocessing and the decreasing convergence rate for very complex geometries [24].

After the grid generation the boundary conditions, initial conditions, the properties of the heaters (e.g. heating power) and of control points as well as growth parameters such as crystal rotation, gas pressure, etc., and numerical parameters have to be defined.

After the completion of the preprocessing the numerical calculation is started. Depending on hardware and on the physical and numerical model the solution of the problem may take minutes, hours or even weeks. Finally, the calculated numerical results are visualized, analyzed and evaluated for improving the process or for comparison to experimental results.

5.2.2 3D Modeling

In most cases, Bridgman-type crystal-growth configurations can be modeled by using an axisymmetric representation of the geometry. Of course any phenomena that are not axisymmetric can only be described by a 3D model. In particular, the solidification of multicrystalline silicon in rectangular molds requires a 3D global thermal model of the whole facility. A 3D approach is necessary in order to calculate the heat transport at the edges of the crucible, which can influence the shape of the solid/liquid interface and therefore, for example, the thermal stress in the grown silicon. In a few cases, such fully 3D global calculations allowed the geometry of the crystal-growth equipment to be simplified [e.g. 27].

Frequently, partial 3D models are applied, which consist typically of (crucible) melt and crystal. Such models are useful to perform basic studies on convection and crystallographic phenomena (facets, stress, strain, dislocations, glide planes, etc.). In [28] it was shown that a small tilt of the ampoule relative to gravity can have a significant influence on the flow pattern and the flow velocities. Lan and Tu [29] presented 3D simulations for the growth of YAG crystals, in which facet formation is coupled to heat flow and segregation.

5.2.3 Quasisteady-state Approach

In the field of global modeling of different growth configurations, most frequently the quasi-steady-state approach (QSS) is applied, which means that the time derivative in the governing equations is set to zero ($\delta/\delta t = 0$) [30]. This is justified in many cases according to Table 5.2 because usually the typical time scale for a temperature change through a geometrical variation of the system τ_{system} , i.e. by the growing crystal, is much larger than the time scale for a temperature change by conduction $\tau_{conduction}$ or convection $\tau_{convection}$. Furthermore, the QSS approach has been proven to be in good agreement with the results obtained by fully time-dependent calculations carried out for the growth of GaAs crystals by the VGF technique [31].

However, the application of the QQS approach requires the specification of the growth rate R as an important input parameter for solving the Stefan problem and for predicting the interface shape. Especially for Bridgman configurations it must be carefully analyzed whether it can be assumed that the growth rate R is equal to the translation rate of the crucible relative to the furnace $R_{\text{translation}}$. Often this is not the case as shown in Fig. 5.2. Here, global thermal simulations are performed for the growth of CdZnTe crystals. In this study, crystal growth is achieved by shifting the furnace relative to the crucible with a constant translation $R_{\text{translation}}$. The growth rate R, which is defined as the movement of the position

Table 5.2 Comparison of the Different Time Scales for Different Materials and Growth Techniques for Typical Crystal Dimensions L (Radius), Growth Rates R, and Axial Temperature Gradients in the Crystal G: Cz = Czochralski-Type, B = Bridgman-Type,

EFG = Edge-Defined Film-Fed Growth. The Time Scales are Defined as Follows According to [30]: $\tau_{system} = L/R$; $\tau_{conduction} = L^2/\kappa^2$; $\tau_{convection} = L^2/(g^*G^*L^4)^{0.5}$ with Thermal Diffusivity κ , and Gravity g.

Material	Method	<i>L</i> in mm	<i>R</i> in mm/h	G in K/cm	$\tau_{conduction}/\tau_{system}$	$\tau_{convection}/\tau_{system}$
Si	Cz	150	36	50	5.9E-02	1.4E-05
	В	300	10	5	5.4E-02	3.9E-06
	EFG	1	900	300	9.8E-03	1.7E-04
GaAs	В	50	2	5	3.8E-03	5.9E-07
	Cz	80	10	70	2.9E-02	7.9E-07
CdTe	В	30	1	10	5.4E-03	7.5E-08
AlSi	В	4	360	10	1.6E-01	9.6E-05
Al_2O_3	Cz	50	5	20	2.6E-02	1.8E-06
CaF ₂	В	200	1	2	1.2E-03	5.0E-07



Fig. 5.2 Ratio between the simulated actual growth rate R_{growth} and the translation rate $R_{\text{translation}}$ versus normalized crystal length for the Bridgman growth of CdZnTe for two different crystal diameters. The translation rate of the ampoule $R_{\text{translation}}$ relative to furnace is constant and was used as input parameter in the QSS simulations.

of the solid/liquid interface at the crystal axis for the different time steps, differs significantly from the translation rate $R_{\text{translation}}$.

Therefore, the growth rate *R* must be known prior to the numerical simulation from experiments. Otherwise, a sensitivity analysis has to be performed in which the influence of the growth rate *R* on the temperature field and on the shape of the s/l interface is analyzed. Such a sensitivity analysis for the growth of CaF_2 crystals by the VGF technique is shown in Fig. 5.3 [32]. It is obvious that for the considered



Fig. 5.3 Simulated shapes and positions of the solid/liquid interface in the VGF growth of CaF₂ (diameter 150 mm) for the same furnace boundary conditions. $R_{\text{growth}} = 0 \text{ mm/h}$ (no latent heat) $R_{\text{growth}} = 0.8 \text{ mm/h}$ (with realistic latent heat) [32].

growth configuration a small variation of the growth rate *R* results in a significant change of the position and shape of the s/l interface.

5.2.4 Melt and Gas Convection

In the past, the study of convective flows was mainly focused on large Czochralski melts. However, with the increasing dimensions of Bridgman-type growth configurations it seems to be necessary to consider also the influence of convection on the heat and especially species transport during directional solidification. The origin of convective flows in so-called "hydrodynamically stable" growth configurations (bottom seeding) are radial temperature gradients that lead to a bending of the solid/liquid interface and thus to buoyant convection [33]. A typical flow velocity *V* can be estimated for such configurations by using [33]:

$$V = \sqrt{g * \beta * G_m * \Delta x * (L/2)} \tag{5.1}$$

with crucible diameter *L*, axial temperature gradient G_m in the melt close to the solid/liquid interface, bending Δx of the solid/liquid interface, gravity *g* and volumetric expansion coefficient of the melt β .

A thermal Peclet number Pe can be defined by using the flow velocity V and the interface bending Δx :

$$Pe = \frac{V * \Delta x}{\kappa}$$
(5.2)

with κ the thermal diffusivity of the melt.

Table 5.3 shows the resulting values of the Pe-numbers for various materials grown in Bridgman-type configurations (with bottom seeding) industrial relevant dimensions and typical growth parameters.

Table 5.3 Estimation of the Peclet Number Pe According Eqs. (4.1) and (4.2) for Various Materials and Diameters of Bridgman-Type Growth Configurations with Bottom Seeding and Typical Parameters: $G_m = 3 \text{ K/cm}, \Delta x = 5 \text{ mm}, \beta = 10^{-4} \text{ K}^{-1}.$

Material	Si	Ge	InP	GaAs	Sapphire	CaF ₂
Diameter <i>L</i> in cm	70	20	10	15	20	40
Pe number	4.30	3.37	4.29	7.30	23.33	140

The Pe number in Table 5.3 is in the order of one for all Bridgman-type growth configurations of semiconductors. This means convection should have only a minor influence on the thermal field [34]. Therefore, for a qualitative optimization of a Bridgman-type semiconductor crystal-growth process it is sufficient to take into account only conduction and radiation in global simulations. However, for a precise quantitative description of the heat transport and especially species transport convective flows should not be neglected. For example, a better agreement between the measured and computed interface shape has been achieved for the VGF growth of GaAs crystals with 3" diameter when melt convection was considered [35].

Furthermore, Table 5.3 shows that $Pe \gg 1$ in the case of the growth of large CaF_2 crystals by a Bridgman-type setup. This means that the convective heat transport has a major influence on the position and on the shape of the solid/liquid interface, even if the flow rate seems to be relatively low. As shown in Fig. 5.4, convection causes a less pronounced bending of the solid/liquid interface [32]. Therefore, convection has to be taken into account in global thermal models for the Bridgman-type growth of crystalline materials with low thermal conductivity of the melt.

Finally, it must be noted that melt convection has definitely to be taken into account when segregation phenomena are investigated. In this case, the solutal Peclet number has to be considered $Pe_s = V^* \Delta X/D$ (D = diffusion coefficient). Pe_s is a measure for the influence of convection on the species transport. Pe_s is typically one to two orders of magnitude larger than the thermal Peclet number Pe [34]. Therefore, the flows that are present during growth in the vicinity of the solid/liquid interface have a much stronger influence on the distribution of dopants and impurities compared to diffusion. It is well known that in poorly mixed systems the melt flow can result in strong compositional nonuniformities. For example, in Fig. 5.5 the simulated nitrogen distribution in a silicon melt is plotted for different flow velocities in the melt under conditions of directional solidification from the bottom. It is obvious that the observed pileup of the nitrogen concentration in front of the solid/liquid interface (top) correlates directly with the location of eddy flow cells in the melt.

In addition to melt convection, the convective heat transport in the gas atmosphere can be of importance, too. The importance of gas convection on the heat transport can be estimated by considering the Nusselt number, Nu, giving the ratio



Fig. 5.4 Simulated convective flow rates (top) and shapes of the solid/liquid interface (bottom) during the growth of CaF_2 crystals (150 mm diameter) by a Bridgman-type method. V_{max} = maximum flow rate in the upper melt region; V_{s-1} = flow rate in the "vicinity" of the solid/liquid interface, i.e. 1 mm above the interface at half of the melt radius [32].

of convective and conductive heat transport. Nu is related to the Grashof number Gr giving the ratio of convective to viscous flow by $Nu = A^*Gr^{1/4}$ with the prefactor A close to 1 for gases [26, 34]. For an ideal gas Gr_{gas} depends on the square of the absolute pressure p according to:

$$Gr_{gas} = \frac{g * \Delta T * L^3 * M^2 * p^2}{T_{abs}^3 * R^2 * \mu^2}$$
(5.3)

with gravity *g*, characteristic temperature difference ΔT , characteristic length *L*, molecular weight *M*, absolute pressure *p*, mean temperature T_{abs} , universal gas constant *R* and viscosity μ .

Now, the influence of convective gas flow on the heat transfer can be estimated for Bridgman-type crystal-growth processes carried out under high gas pressure conditions such as the growth of GaAs (3–7 bar) InP (30–40 bar) and GaP (~80 bar). Assuming a temperature difference ΔT between the water-cooled vessel and the outer thermal insulation of the heaters of 100 K and a distance *L* of more than 5 cm one obtains for a gas pressure p > 1 bar from Eq. (5.3) a Grashof number Gr > 1000 and a Nusselt number Nu \gg 1.

This means that gas convection has to be considered in numerical simulations. The simplest model is to introduce an effective thermal conductivity for the gas by

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Fig. 5.5 Numerically computed nitrogen distribution (left) and flow pattern (right) during directional solidification of a silicon melt with dimension of $68 \times 55 \times 14 \text{ cm}^3$ for a concave, planar and convex interface obtained by applying different thermal boundary

conditions: Due to the recirculation in front of the interface poorly mixed ranges result (e.g. top and middle). Therefore, a local accumulation of the dopant is observed.

which convective heat transfer can be accounted for indirectly. The specific value of the effective thermal conductivity has to be adjusted by fitting the numerical results with experimental data for each specific setup. Although this engineering approach can lead to a good correlation of the thermal field and measured temperature data it can also fail for a quantitative simulation of other data like heater powers. Such a problem was recently described for the VGF growth of InP crystals where the shape and position of the grown interface was well described by the model, but totally failed for the heating powers [10]. A more precise approach is to compute gas convection directly by solving the Navier–Stokes equation including an appropriate turbulence model. However, this increases the numerical efforts considerably and one needs efficient numerical methods using a combination of block-structured and unstructured meshes.

5.2.5

Radiative Heat Transfer with Participating Media

When only fully opaque or fully transparent materials are involved in the crystal growth set up the radiative heat transport between all surfaces of all inner furnace parts has to be considered. In this case the computation is usually based on Lambert's law (grey diffusive radiation) and the determination of the so-called view factors between the surfaces [36]. However, in crystal-growth configurations that contain optically semitransparent materials like SiO₂ parts, boric oxide encapsulant and especially semitransparent ("optical") crystals the above-mentioned model of radiative heat transfer is not sufficient. In these cases of participating media the radiative heat transfer within the material can have a strong influence on the temperature distribution. In certain cases it can strongly influence the shape of the solid/liquid interface. Therefore, the selection of an appropriate model is of great importance for a precise simulation of the position and shape of the solid/liquid interface and hence the thermal stress. In the selection of the model it is important to consider the phenomena by which the participating medium is interacting with thermal radiation, such as absorption, reflection, refraction, volume emission, and scattering. Such so-called semitransparent material behaves quite differently from opaque and completely transparent ones (where the radiation travels unaffected through the material).

Several models with increasing complexity and numerical efforts are in use. The range of application of these models can be estimated by using the dimensionless parameter *D*. The optical thickness $D = a^*r$ is one important parameter for the radiative heat transfer. *D* is defined as the product between the extinction coefficient *a* and the typical length of the radiative path like the radius *r*. The other important parameter is the conduction–radiation interaction parameter or Stark number N_r , which is defined as [36]:

$$N_{\rm r} = \frac{k * a}{4 * \sigma * T^3} \tag{5.4}$$

where *T* is the mean temperature of the semitransparent material, σ the Stefan–Boltzmann constant, and *k* the thermal conductivity.

Several models and approximations exist in dependence on the optical thickness D and the interaction parameter N_r .

 $D \ll 1$; $N_r \rightarrow 0$ For optically thin materials ($D \ll 1$) the medium has such a low extinction coefficient that the intensity of the radiation is not changed by absorption, emission, or scattering within the medium. In such cases, the material can be treated as a fully transparent material. Then, it is sufficient to calculate the

radiative heat transfer between the surfaces surrounding the crystal and the melt by using the classical view-factor method, i.e. the material is not participating.

 $D \gg 1$; $N_r \rightarrow infinity$ For optically thick materials ($D \gg 1$) the treatment of the internal radiation can be significantly simplified. In such cases, the so-called Rosseland diffusion approximation [36] can be applied that takes into account the enhancement of the heat transfer through radiation by using an effective thermal conductivity k_{eff} ;

$$k_{\rm eff} = k_{\rm m} + \frac{16 * n^2 * \sigma * T^3}{3 * a_r}$$
(5.5)

where $k_{\rm m}$ is the contribution due to conduction and the second term is due to radiation; n is the refractive index, σ the Stefan–Boltzmann constant, *T* temperature and $a_{\rm r}$ the Rosseland mean absorption coefficient, which can be obtained by averaging the spectral dependence of *a* [36]. The diffusion approximation merges into the limiting case of an opaque medium for infinite absorption coefficient.

Intermediate Cases (0.01 < D < 100) For growth of optical crystals such as sapphire, BGO, YAG, fluorides, the material is neither transparent ($D \ll 1$) nor optically very thick ($D \gg 1$) in the whole infrared spectrum. Therefore, more complex models have to be applied in order to compute the radiative heat transport in such materials. Three kinds of models are frequently used:

Discrete Ordinates Model The discrete ordinates method is capable of resolving the nonisotropic directional characteristics of radiative heat transfer by subdividing the directional space into discrete solid angles. After preselecting a set of representative discrete directions the radiative-transfer equations as well as the corresponding boundary conditions can be written as a set of equations for each direction, which is then solved. However, the equations for each direction depend on each other if scattering and reflection is considered.

P-n Radiation Model The P-n model (method of spherical harmonics) transforms the equations of radiative transfer into a set of partial differential equations that are simultaneously solved. Usually, low-order approximations, i.e. P-1, P-3 are used in which the angular dependence of the real radiation field is reduced to spherical functions. The low-order approximations are only accurate in optically thick media.

Monte Carlo Methods / Ray-tracing Methods Monte Carlo methods are well suited to the thermal radiation problems since the energy travels in photons, having a straight path before interacting with matter. The principle of the Monte Carlo / ray-tracing method is to trace the history of a statistically meaningful number of photons from their point of emission to their point of absorption.

n-Band In addition, it has to be considered that the optical properties depend on the wavelength λ . This can be taken into account by dividing the spectrum



Fig. 5.6 Influence of the optical thickness D on the solid/liquid interface. Simulation of radiative heat transfer was done by a ray-tracing method [37] for a typical VGF growth setup. The temperature difference between the isotherms is 10 K.

into bands. Within each of these bands the radiative properties are assumed to be constant.

Details about the principle and the numerical treatment of these methods can be found elsewhere [36].

The sensitivity of the position and shape of the solid/liquid interface on the optical thickness *D*, i.e. on the absorption coefficient of the crystal and melt for a typical VGF configuration are illustrated in Fig. 5.6 [37]. In these global simulations performed by using a ray-tracing method the absorption coefficient was assumed to be independent of the wavelength. It is obvious that the smaller the optical thickness *D*, i.e. the smaller the absorption coefficient, the smaller the temperature gradient in the melt and crystal for given heater powers. Therefore, it is necessary for highly transparent materials, e.g. to construct an efficient heat sink under the crucible in order to establish a temperature gradient in the vicinity of the solid/liquid interface allowing a controlled growth.

5.2.6 Modeling of Defect Formation

One of the primary objectives of a crystal grower is to avoid the formation of crystal defects like dislocations, twins, low-angle grain boundaries and precipitates of point defects that are deleterious for applications. Among these structural defects dislocations are very crucial as they are the origin for the formation of further defects like dislocation clusters or (low-angle and large-angle) grain boundaries.

In addition, they can directly reduce the performance of optoelectronic devices because they act as recombination centers.

Dislocations are generated in the crystal because of plastic deformation. During the growth process, stress is generated as a result of an inhomogeneous temperature field in the growing crystal. This can cause the generation and the movement of dislocations. The dynamics of the formation and movement of dislocations is a physically complex process. Therefore, the numerical treatment requires also a tremendous effort. This is why in most cases the von Mises stress σ_{vm} is used only for optimizing growth configurations with respect to low dislocation densities. The von Mises stress σ_{vm} is an important scalar that is obtained from the distinct stress components. For optimization, the growth conditions are adjusted by modifications of growth parameters or the growth configuration in order to achieve small absolute values of the von Mises stress close to the solid/liquid interface. Fortunately, it has been confirmed that this pragmatic engineering approach helps to optimize various crystal-growth processes [5-7, 10]. For example, Fig. 5.7 shows the maximum value of the von Mises stress versus process time during growth of CdZnTe crystals (75 mm diameter) obtained from global thermal modeling. At the end of this process a strong increase of the von Mises stress is observed. This correlates qualitatively with experimental observation of cracks in the upper part of the crystal [38].

A quantitative comparison between calculated and measured dislocation densities can only be performed when more sophisticated models are used. A popular model for the description of the generation of dislocations by plastic deformation is the Alexander–Haasen model [39]. Völkl and Müller [40] used the Alexander–Haasen



Fig. 5.7 Numerically calculated axial temperature gradient in the vicinity of the phase boundary (open symbols) and maximum von Mises stress (full symbols) as a function of the position of the ampoule tip relative to

the furnace. The temperature gradient as well as the von Mises stress are normalized to the value at the beginning of the growth processes.



Fig. 5.8 Radial distribution of the dislocation density for the growth of GaAs by vapor-controlled Czochralski (VCZ) method with 6" and 3" diameter by the VGF method with 3" diameter and for the growth of InP by the VGF method with 2" diameter in a

flat-bottom crucible and a conical crucible. Left: measured values; right: values obtained from numerical simulation by calculating the temperature field and afterwards the dislocation density based on the Alexander-Haasen model [41].

model to simulate the dislocation formation in InP crystals during liquid encapsulated Czochralski growth. The growing crystal is treated as to be continuously moving through a time-dependent thermal field. The generated time-dependent thermal stress acts on each volume element of the crystal and deforms it continuously plastically. An integration over the full growth period results in a locally varying length of dislocation lines in the whole crystal, which can be transformed into a number of dislocation lines intersecting a unit area to arrive at the usual characterization measurement of etch pit density (EPD).

Recently, this approach of Völkl and Müller [40] was further developed and a quantitative comparison of the computed and measured dislocation densities was carried out for various semiconductor crystals grown by different growth methods [41]. It is obvious from Fig. 5.8 that the calculated dislocation density is always of the same order of magnitude as the measured one and that the lateral distribution is similar. However, it is not clear whether the deviation between the numerical and experimental data is due to deviations of the calculated thermal field including the shape of the solid/liquid interface or whether it is caused by simplifications of the dislocation model, which neglects, for example, the annihilation of dislocations [41].

Regardless of the progress that was made in recent years, modeling of dislocation formation is still a challenging topic especially if one wants to take into account all relevant physical mechanisms acting during the formation of dislocations and considering their interaction, which can result in further defects like dislocation clusters, dislocation networks and low-angle boundaries. For this purpose, it is also necessary to utilize models and methods other than the Alexander–Haasen model. Nevertheless, it can be assumed that crystal-growth engineers will also use in the future the von-Mises stress as measure to optimize crystal-growth processes with respect to low dislocation densities.

5.2.7

Inverse Modeling

The main driving force for using thermal modeling is to support the crystal grower in finding process parameters that allow him to grow the crystal under such growth conditions where the formation of crystal defects can be controlled in the desired way and the grown crystal has the required properties. The requirement on the control of defect formation can be translated into the requirement on certain growth conditions, i.e. a certain temperature and stress field if this correlation is precisely known. Therefore, the objective of thermal modeling is to predict which heater temperatures for a given setup have to be adjusted in order to achieve a certain temperature field inside the crystal.

This can be achieved manually by running so-called forward simulations, in which the heating powers are input data and the corresponding temperature fields are calculated. Then, the user has to change the heating powers manually by trial and error until the desired temperature field is achieved.

The better approach is that the model is able to calculate the inverse problem. This means the user can define the temperature in an arbitrary number of points and the model calculates automatically the corresponding heater temperatures, respectively heating powers, in order to achieve the desired temperatures. This is the so-called inverse simulation [42, 43]. The numerical treatment and typical applications of the inverse-simulation strategy can be found in [42, 43]. Today, the inverse-modeling approach is a necessary feature for an efficient process optimization. By using more advanced mathematical methods it is possible to apply the inverse-modeling approach for even more complex tasks than only adjusting the heating powers. In [19, 44] it has been demonstrated that, for example, the automatic optimization of geometrical problems like the positioning of the heaters or the design of heat shields and the automatic selection of materials for certain furnace parts like the crucible support in the VGF method is possible.

5.3 Verification of Numerical Models

5.3.1 General Strategy

The utility and benefits of modeling of crystal-growth processes depends strongly on the reliability of the simulation results. Therefore, the procedure for the development and validation of a global thermal model of a growth facility should ideally consist of the following steps, which are summarized in Fig. 5.9.

The first step is to build the model based on an original, but simplified CAD drawing of the real growth equipment and on a set of reliable material data. The second step is to perform a systematic sensitivity analysis. The sensitivity analysis consists of pure numerical parametric studies. It has the objective to identify



Fig. 5.9 The strategy for validation of global thermal modeling.

to which parameter changes, e.g. mesh size, view factor accuracy, geometrical simplifications the model is sensitive. In particular, a systematic variation of all material properties is needed because, in general, not all material properties (especially the emissivities) are really known. Having the parameters identified to which the model is sensitive the third step is to validate the model against experimental data obtained in so-called model experiments (see Section 5.3.2). This means to adjust material properties and to modify geometrical details within reasonable ranges in order to achieve the required accuracy with respect to a quantitative agreement of experimental and numerical results. If the required accuracy is obtained, the model is validated and can be used for optimization of the growth process.

5.3.2 Model Experiments

For validation, so-called model experiments have to be performed under welldefined and well-documented conditions [5]. They are designed to provide quantitative data (e.g. temperatures) related to important phases of the growth process. They should come as close as possible to the real growth setup and growth conditions, but should not have the necessity to grow a high-quality crystal.

A proper and frequently used concept of experimental validation is the use of thermocouples in dummy crystals or inside the melt and crystal that allows for an *in-situ* measurement of temperature distributions along certain positions (e.g. crystal/crucible axis) at various time steps of the growth process. However,

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Fig. 5.10 Simulation of temperature distributions (left) and axial temperature profiles (right) in a VGF configuration for the growth of CaF_2 crystals with a central axial thermocouple in a coaxial tube (a) and without (b) [17].

it is very important to consider the influence of this thermocouple also in the numerical simulation. Otherwise, the results of experiment and simulation can differ considerably and may not be comparable. This situation is illustrated in Fig. 5.10. Figure 5.10 shows the computed temperature field during growth of CaF_2 crystals with 6" diameter [32]. In order to measure the temperature *in situ* in the melt and the crystal a protection tube containing the thermocouple has to be inserted that alters significantly the thermal field. The deviation between the temperatures without and with thermocouple at the symmetry axis is up to 20 K.

In addition to the temperature measurements, a second kind of model experiments provides data about the position and shape of the solid/liquid interface for various growth steps. Therefore, suitable methods of interface demarcation have to be applied in the experiments such as the usage of heat pulses. Figure 5.11 shows the measured and computed positions of the solid/liquid interface at the symmetry axis during growth of InP with 2" diameter. The deviation of the growth velocity is less than 10% indicating a good correlation of the thermal field between experiment and simulation [45]. Although a satisfactory accuracy of the thermal field is observed in the melt–crystal–crucible region, the computed heating powers deviate strongly from the measured values for the considered case, because gas convection was not directly taken into account [10].

Figure 5.12 shows a comparison of the measured and calculated bending of the solid/liquid interface during the VGF growth of CaF_2 crystals (150 mm diameter) [32]. In the experiments, the shape of the solid/liquid interface was measured by mechanical means. In the simulation the radiative heat transfer in CaF_2 , melt



Fig. 5.11 Experimental and simulated positions of the solid/liquid interface during VGF growth of 2" InP crystals on the crucible axis versus growth time. The experimental interface demarcation (doping striations) was achieved by short-term pulses of the heater power. The corresponding growth rates are evaluated from the slopes of the curves.



Fig. 5.12 Simulated (open symbols) and measured (full symbols) bending of the solid/liquid interface during VGF growth of a CaF_2 crystal (150 mm diameter) [32].

convection and the real growth rate was considered. In both, experiment and simulation, the interface shape is concave in the bottom part of the grown crystal, becomes convex in the middle part and again concave in the top part. This good correlation between experiment and simulation can only be achieved if the radiative heat transfer in CaF₂, the convective heat transport in the melt, and a realistic growth rate are considered in the QSS thermal model [32].

5.4

Yield Enhancement by Defect Control

In the following, typical tasks in the field of optimization of Bridgman-type crystal-growth processes are presented where both, thermal modeling and experimental analysis, contribute.

5.4.1 Control of the Shape of the Melting Isotherm

The control of the shape of the solid/liquid interface during the whole growth process is, in general, and not only for Bridgman-type crystal-growth processes, of great importance for several reasons:

- removal of latent heat from the center to the periphery;
- control of the growth mode (facetted or nonfacetted);
- avoidance of the formation of all kinds of defects that are related to thermal stress (curvature of solid/liquid interface) especially dislocations and low-angle boundaries;
- avoidance of the extension of defects occurring at the periphery (e.g. spurious nuclei, dislocation clusters) into the crystal volume.

Especially in Bridgman-type growth configurations it is often the objective to obtain a flat solid/liquid interface during the whole crystal-growth process by growing the crystal in a linear temperature field under low thermal stress conditions. Under the assumptions that the radial heat flux into the crucible can be neglected, the density in the melt and in the crystal are the same, and convective heat transfer can be neglected, an one-dimensional consideration of the heat flux balance at the solid/liquid interface during growth of a crystal results that heat flux density through the melt Q_{melt} plus the heat release by the latent heat at the interface Q_{latent} must be equal to the heat flux density in the crystal $Q_{crystal}$. This approach leads to the definition of the parameter ΔQ :

$$\Delta Q = \frac{Q_{\text{melt}} + Q_{\text{latent}}}{Q_{\text{crystal}}} = \frac{k_{\text{m}} * (dT/dx)_{\text{m}} + L_{\text{H}} * R}{k_{\text{s}} * (dT/dx)_{\text{s}}}$$
(5.6)

with the thermal conductivity of melt and crystal $\lambda_{m,s}$, axial temperature gradient in the melt and in the crystal $(dT/dx)_{m,s}$, latent heat $L_{\rm H}$, growth rate R.

From Eq. (5.6) the crystal grower can estimate, for a given growth rate *R*, which temperature gradients in the melt and in the crystal have to be adjusted in order to grow a crystal with a flat interface, that means $\Delta Q = 0$. But, Eq. (5.6) gives no information on which heater temperatures have to be chosen in order to achieve these temperature gradients and thus a flat solid/liquid interface.

For this purpose, the inverse modeling approach described in Section 5.2 allows the crystal grower in a very comfortable way to obtain the required information. By inverse modeling the heater temperature–time profiles can be optimized in order to achieve an almost flat solid/liquid interface. Therefore, for a certain growth stage the position of the solid/liquid interface is fixed in the center of the crucible at a certain height h_1 by setting the temperature $\vartheta_1(0, h_1) = T_m$ (see Fig. 5.13). The condition of a planar crystal-melt interface for low thermal stress is simulated by setting a second temperature $\vartheta_2(r, h_1) = \vartheta_1 = T_m$ at the same height h_1 , but on the periphery of the crystal at radial position r. Furthermore, additional constraints can be defined such as a certain axial temperature gradient in the crystal or the melt, etc. (see also [5]). The results of such an inverse simulation are the heater powers, respectively, the heater temperatures, which fulfill best the conditions on the required thermal field for a certain growth stage. By shifting the control points through the crucible and repeating the simulations for other growth stages, the optimized heater–time profile is obtained for the whole growth run. The strategy of using the inverse simulation approach and other advanced mathematical techniques to achieve a flat solid/liquid interface is described in more detail in [5, 31, 46–48].

The optimization of the thermal conditions in Bridgman-type crystal growth of GaAs and InP with respect to low thermal stress conditions by using numerical simulation results mainly in a reduction of the dominant type of dislocations, the so-called 60° -dislocations with curved line vectors [49]. In Table 5.4 typical dislocation densities reported for different crystals grown by Bridgman-type growth techniques are summarized.



Fig. 5.13 Controlling conditions (fixed temperatures $\vartheta_1 - \vartheta_3$) for an optimization of a VGF growth process (see text).

Material	Diameter in mm	Dopant	EPD in cm ⁻²
CaF ₂	150	undoped	$10^4 - 10^5$
InP	100	Fe	<1000
InP	50	S	<500
GaAs	75	Si	<100
GaAs	75	Те	\sim 2000
GaAs	100	Si	<500
GaAs	150	С	<5000

Table 5.4 Typical Dislocation Densities for DifferentMaterials with Different Dopants and Diameters Grown byBridgman-Type Methods (see [8, 10, 32, 49]).

In crystals with very low dislocation densities of less than 1000 cm^{-2} the 60° -dislocations are no longer the dominant type. Further types of dislocations like 45° -, 60° -, 30° -, screw and edge dislocations are detected [49]. In GaAs, the dislocations are forming a cellular structure with a typical cell diameter of a few mm. Such cellular structure cannot be observed in InP with low dislocation density [50]. The formation of the cellular structure in GaAs and other materials is a field of recent research activity [50]. A review of the present knowledge about the residual dislocations in low defect GaAs and InP for various dopants can be found in [49].

5.4.2

Defect Control in the Seed Channel and Conical Part of the Crucible

In Bridgman-type crystal growth one of the most important parts is the crucible, as it is in direct contact with the growing crystal. It is well known that the material and the shape of the crucible influence the quality of the growing crystal. The selection of the crucible material is determined mainly by the requirements on chemical stability against the melt, on reusability and on low costs. Most frequently crucibles made of pyrolitic boron nitride are in use for III-V compound semiconductors. Graphite-coated silica crucibles are applied for CdZnTe, Si₃N₄-coated silica crucibles for photovoltaic silicon, graphite crucibles for fluorides, and iridium or molybdenum crucibles for high melting oxides (especially for sapphire).

Except for solidification of photovoltaic silicon, a cylindrical crucible is normally applied with a seed channel at the bottom with a diameter of typically 5–10 mm. The seed channel is followed by a conical part with a certain cone angle. Within the conical part the diameter increases continuously from the value of the seed diameter up to the final crystal diameter in the upper cylindrical part of the crucible. The main reason for this conical shape of the crucible is to use a seed with small diameter and eventually to reduce the dislocation density after seeding during the growth of the crystal in the seed channel [46]. The latter has been demonstrated



Fig. 5.14 Representation of the three-phase boundary (TPB) having a facetted solid/liquid interface during VGF growth of <100>-oriented GaAs and InP crystals in a conical crucible with cone angle φ . The angle ν between the facet and the crucible wall is obtained by simple geometrical considerations as: $\nu=35.3^\circ\,+\,\varphi$ /2 [54].

experimentally, e.g. for the VGF growth of GaAs [46]. In this case a reduction of the dislocation density is observed because the distance between the annihilation process becomes more efficient due to a concave interface during growth in the seed channel [46].

In the seed channel, the occurrence of pronounced long-edge facets is also observed when low temperature gradients are applied [51]. The length of the edge facets can be reduced when applying higher axial temperature gradients. Therefore, twin formation can be controlled in principle by reducing the length of the facets [46]. But, the usage of higher temperature gradients means also to grow the crystal under higher thermal stress conditions. Therefore, a compromise for the optimum process window must be found between the probability of the avoidance of twin formation and low dislocation density.

The application of a conical-shaped crucible has a major drawback. From Hurle's theory [52] and from experimental observations [53] it is known that the occurrence of edge facets on the growth interface at the crystal periphery that reach the three-phase boundary is a necessary condition for twin formation. If the angle between the facet and the crucible wall exceeds a critical value v_{crit} (see Fig. 5.14) then the edge facet should theoretically detach from the three-phase boundary and break down into steps, i.e. twin formation should be avoided under such conditions. In principle the angle v can be controlled by the cone angle ϕ of the crucible. A simple geometrical consideration gives: $v = 35.3^{\circ} + \phi/2$ [53].

For Bridgman-type growth of InP the so-called flat-bottom crucible with a cone angle of 180° as well as a crucible with a cone angle of 160° fulfill the theoretical requirement on $\nu > \nu_{crit} = 109.47^{\circ}$ [10].

For the flat-bottom crucible it has been shown that the twin formation can be strongly reduced [45, 47]. However, from an industrial point of view the usage of

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Fig. 5.15 Numerically calculated thermal stress (maximum von Mises stress) during the VGF growth of 2" InP crystals using crucibles with different cone angles [10].

the flat bottom crucible has severe drawbacks: It requires the application of a very expensive seed with high structural perfection (not only low dislocation density, but also free of local dislocation clusters, etc.), the advantage of reducing the dislocation density during outgrowth in the seed channel is lost, and the seeding must be more precisely controlled in terms of low thermal stress conditions [47].

On the other hand, the results of the numerical analysis presented in Fig. 5.15 show that for optimized growth setup and heater temperatures–time profiles the InP crystal would grow under much lower stress conditions when a crucible with a cone angle of 160° is used instead of the flat-bottom crucible [10]. It is confirmed by experimental growth runs that semi-insulating twin-free 4" InP crystals with very low dislocation densities can be grown when using such conical crucibles [10]. However, the transition from the seed channel to the cone as well as from the conical region to the cylindrical part are still critical because here the angle ν changes its value continuously and *a priori* it cannot be avoided that ν is always greater than the critical angle $\nu_{\rm crit}$. Therefore, it is not possible, so far, to avoid completely the formation of twins in the case of a conical crucible [10].

The use of the conical crucible cannot only affect the probability for twin formation, but can also be crucial with respect to the formation of dislocations. The strong change of the geometry of the crystal when the crystal is growing out from the seed channel into the conical region can cause the occurrence of high



Fig. 5.16 Numerically calculated temperature distribution (left) and von Mises stress (right) during growth of CaF₂ crystals for the same boundary conditions but different values of the thermal conductivity $k_{support}$ [32]: a) $k_{support} = 1 \text{ W/m K}$; b) $k_{support} = 10 \text{ W/m K}$; c) $k_{support} = 100 \text{ W/m K}$.

thermal stress of the crystal [10]. Furthermore, due to the continuous variation of the crystal diameter the control of the shape of the solid/liquid interface becomes difficult because the thermal conditions change, too. In addition, it was shown experimentally that during growth in the crucible cone strong fluctuations of the lengths of the edge facets may result in the formation of dislocation bundles or twins [46].

In order to control the formation of the defects described above in the conical region, the crucible support on which the actual crucible is positioned, plays an important role. It has to be constructed in such way that in the conical region stable thermal conditions are present with a heat flux mainly in the axial direction.

Figure 5.16 shows a numerical analysis of the influence of the thermal conductivity of the crucible support $k_{support}$ on the temperature distribution and thermal stress during growth of CaF₂ crystal with 6" diameter [32]. For $k_{support} < k_{melt} < k_{solid}$ a pronounced w-shaped interface shape occurs. As a result, the maximum von Mises stress is larger than 8 MPa. With increasing thermal conductivity of the crucible support the bending of the solid/liquid interface is reduced. If the thermal conductivity of the crystal, more or less optimum conditions are achieved. The shape of the solid/liquid interface is stress is only 0.5 MPa.

Mainly from an industrial point of view the requirements on the construction of the crucible support are not only to achieve an almost flat solid/liquid interface during growth of the crystal in the conical region, but also to have a construction that is not sensitive from growth run to growth run or from one furnace to another furnace identical in construction [54]. Thermal modeling can help to solve this task, too. For example, the influence of small gaps that might exist between the crucible and the crucible support on the thermal field can be analyzed in a simple way [54].

Table 5.5 Thermal Conductivity of Typical Crucible Materials as Well as the Thermal Conductivity of Melt (M) and Crystal (S) at Melting Temperature T_M for various Semiconductor and Optical Crystals. For pBN, \parallel Means the Thermal Conductivity Parallel to the Crucible Wall and \perp that Perpendicular to the Crucible Wall.

Material	Thermal conductivity in W/m K
SiO ₂	3 (1600 K)
graphite	20 (1700 K)
pBN	60 (1300 K); ⊥ 3 (1300 K)
Мо	90 (1700 K)
Si	S: 22; M: 64 at T _M
GaAs	S: 7.1; M: 17.8 at T _M
InP	S: 9.1; M: 22.8 at T _M
CdZnTe	S: 0.9; M: 1.1 at $T_{\rm M}$
CaF ₂	S: 100; M: 10 at $T_{\rm M}$
Al_2O_3	S: 5.8; M: 10 at <i>T</i> _M

5.4.3

Defect Control in the Cylindrical Part

In the ideal case, the thermal conductivity of the crucible should be smaller than the thermal conductivity of the crystal and of the melt. Then, all the heat coming from the melt and generated at the solid/liquid interface due to the release of latent heat would flow through the crystal, resulting in a flat or even convex interface depending on the growth parameters (compare also Eq. (5.6)).

However, for III-V compound semiconductors the application of pBN crucibles is most frequent because of its chemical stability against different melts. But, one disadvantage of the pBN is the high thermal conductivity of \sim 60 W/m K parallel to the crucible wall and only 2 W/m K perpendicular to the crucible wall, in comparison to the lower thermal conductivities of, e.g. GaAs and InP (see Table 5.5). As a result a concave bending of the solid/liquid interface close to the crucible wall always occurs because the pBN crucible acts as a thermal short cut. Therefore, this region close to the crucible wall is a potential region for the origin of crystal defects. On the one hand, the strong curvature of the solid/liquid interface results in high thermal stress conditions. This can lead to the formation of locally high dislocation densities acting as a source for polycrystalline growth.

But, when the curvature of the interface becomes very strong the Gibbs–Thomson effect close to the crucible wall has to be taken into account [55]. The consequence is that the phase boundary must not follow completely the melting isotherm and an extended undercooled region exists in front of the solid/liquid interface that also increases the probability for defect formation as shown in Fig. 5.17. The extension of the undercooled region can be expressed by, for example, increasing the temperature gradient in front of the solid/liquid interface.

Under-cooled melt





Fig. 5.17 Schematic view of the interface shape close to the crucible wall. For a strong curvature of the melting isotherm, the Gibbs–Thompson effect may be of importance. Therefore, the phase boundary is not identical to the melting isotherm and an undercooled region close to the crucible wall may develop.

5.4.4 Temperature Fluctuations

It is well known that temperature fluctuations are harmful because they are one major cause for, e.g., fluctuations of the length of the edge facets that are considered as the main source for the formation of dislocation bundles or twins, especially during growth of InP under high-pressure conditions. Therefore, their minimization or even avoidance is of central importance for the crystal grower. The strategy for solving this task consists of a variety of individual actions such as reduction of gas-filled cavities in the furnace, the usage of coated insulation parts and nonporous foils that act as convection barriers, positioning of the control thermocouples inside massive, almost isothermal solid parts with large heat capacity.

Thermal modeling can also support this optimization task. Thermal modeling provides an easy way to change material parameters, the geometry of the equipment, or the parameters for processing. Therefore, the results of thermal modeling help to identify proper furnace concepts even before realizing any hardware or to redesign a given crystal-growth equipment, e.g. with respect to minimize temperature fluctuations caused by turbulent gas convection.



Fig. 5.18 Simulated temperature fluctuations in the crystal close to the crucible wall for the VGF growth of 2" InP crystals in a R&D facility for typical fluctuations of the heater temperatures: nonoptimized setup (top) optimized setup (bottom).

In Fig. 5.18 the numerically calculated temperature fluctuations in the crystal close to the crucible wall for growth of 2" InP crystals in a nonoptimized VGF furnace are shown [47]. The convective heat transfer in the gas due to the high-pressure conditions is taken into account by using the model of an effective thermal conductivity for the inert gas. The input parameters for this time-dependent simulation are the temporal evolution of the measured heater temperatures. The temperature fluctuations of the heaters have amplitudes of 0.5–0.9 K, which results in temperature oscillations close to the solid/liquid interface of 0.2 K [47]. As a consequence the formation of twins occurs frequently during growth of InP crystals in this furnace setup.

After optimization of the whole setup by redesigning the furnace, thermal simulations are again carried out for the modified setup, but for the same measured heater temperatures as before. As shown in Fig. 5.18, the temperature fluctuations close to the solid/liquid interface can be reduced by almost one order of magnitude for the modified growth setup [47]. This is an important prerequisite to stabilize the lengths of the edge facets and thus to minimize the probability of twin formation during growth of InP.

5.4.5 Magnetic Fields

In Bridgman-type crystal-growth configurations one possibility to control convection and therefore the shape of the solid/liquid interface, as well as the dopant distribution, is the so-called accelerated crucible rotation technique (ACRT). This technique was developed by Scheel [56] and has been applied especially to the Bridgman growth of CdHgTe and CdZnTe crystals, e.g. [57, 58].

The use of magnetic fields is an interesting option to control the solid/liquid interface shape in the growth of semiconductor crystals [59].

There is already quite a lot of experience in the use of static magnetic fields for damping time-dependent flows in Czochralski configurations [59] as well as for controlling the oxygen transport in silicon Czochralski growth [60, 61]. For Bridgman-type crystal-growth configurations several articles were published about the application of axial steady magnetic fields for damping the buoyant convection [62–67]. The damping action N_{SMF} can be estimated according to the following formula [64]:

$$N_{\rm SMF} = \frac{\sqrt{\rm Gr}}{\rm Ha}$$
(5.7)

with Gr the Grashof-number for the melt and Ha the Hartmann number, which are defined as follows:

$$Gr = \frac{\beta * g * G_{ax} * \Delta x * r^3}{\nu^2}; Ha = B * r * \sqrt{\frac{\sigma}{\rho * \nu}}$$
(5.8)

However, there is only a minor influence of a steady magnetic field on the heat transport in Bridgman-type crystal growth of semiconductors due to the fact that the heat transport in the melt is mainly governed by heat conduction. Therefore, for not highly doped semiconductors there is only a minor influence of a steady magnetic field on the shape and position of the solid/liquid interface. But, the damping effect of a steady magnetic field reduces temperature fluctuations. Therefore, a reduction of the fluctuations of the edge facts in the conical region at the periphery of the crystal and thus of the probability of the formation of twins seems to be possible as reported for GaAs in [68].

The influence of a steady magnetic field on convection mainly changes the species transport. Therefore, the distribution of the species is rearranged under the influence of the magnetic field. Thus, for highly doped semiconductors the characteristics of the liquidus temperature in the vicinity of the moving phase boundary is changed, resulting in a variation of the position and shape of the solid/liquid interface [51, 65]. Furthermore, on a laboratory scale diffusion-controlled heat and mass transport conditions can be achieved under the action of very high field strengths for values of B > 500 mT [62, 67].

In contrast to steady magnetic fields time-dependent magnetic fields generate a controlled forced flow in the melt [69]. Two kinds of field configurations are of interest to be used in Bridgman-type growth configurations [70]: traveling magnetic
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Fig. 5.19 Calculated (below) and experimentally (above) observed interface shapes for VGF growth of Ga-doped Ge crystals with 20 mm diameter under the influence of a rotating magnetic field (induction is given in mT) [71].

fields (TMF) with a Lorentz force pointing upward (TMF+) or downward (TMF–) and rotating magnetic fields (RMF) with a Lorentz pointing in the azimuthal direction. Although the forced flows generated by a RMF and TMF are different [70] their application can influence the temperature distribution within the melt and the shape of the solid/liquid interface in a positive way. For both, RMF and TMF it is observed experimentally [71, 72] and in numerical simulation [35, 70, 72] that for small and medium values of the generated Lorentz force the magnetic field reduces the bending of the interface during growth of Ge, GaAs and InP crystals, which is concave without magnetic field. For higher values of the Lorentz force, the interface becomes w-shaped. This is illustrated in Fig. 5.19. Figure 5.19 shows results of simulations and experiments of the influence of a RMF on the shape of the solid/liquid interface for the growth of Ge crystals (1" diameter) by the vertical gradient freeze (VGF) method [71].

However, in order to achieve a considerable reduction of the thermal stress by a reduced bending of the solid/liquid interface, the use of a TMF seems to be more efficient than a RMF. This has been recently demonstrated by a simulation study of the VGF growth of InP (2" diameter) [67].

5.4.6 Cooling Phase

The thermal treatment of a crystal after growth during the cooling phase is also very important for the control of the formation of structural defects. In order to achieve a high productivity of the crystal-growth process, the cooling rate should be as high as possible. But, in general, the periphery of the crystal cools more



Fig. 5.20 Calculated maximum von Mises stress versus cooling rate of an as-grown CaF_2 crystal (150 mm diameter, VFG-type configuration) [32].

quickly then the center of the crystal. The resulting nonuniform temperature field can lead to thermal stress and plastic deformation. The optimization of the cooling phase means therefore to find the optimum between minimum cooling time and maximum tolerable thermal stress in the crystal.

For a numerical study of the cooling down phase, the QSS approach is not well suited because the time-dependent effects are causing the non uniform temperature field. Therefore, full time-dependent thermal simulations are more appropriate. In Fig. 5.20 the result of such a numerical study for the cooling down process of a CaF_2 crystal is shown [32]. In this analysis, the desired temperature–time profiles at the positions of the control thermocouples at the heaters are used as input parameters. In this way, the thermal field and the von Mises stress in the crystal are obtained for different cooling rates. There is obviously a linear correlation between the cooling rate and the maximum von Mises stress. Now, an optimum cooling rate can be selected for which a given maximum von Mises stress in the crystal is not exceeded.

A similar numerical-based optimization of the cooling phase was performed for the Bridgman-type growth of GaAs in [46]. The reduction of the von Mises stress in the crystal by an improved cooling process was confirmed experimentally [46]. The occurrence of slip lines could be strongly reduced.

5.5 Conclusions

Numerical modeling has proven to be an indispensable and widely acknowledged tool for yield improvement and defect control in industrial crystal production. Today, it is widely used in almost any field of development and optimization of

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bulk crystal-growth equipment and processes for both industrial and academic purpose. The importance of modeling in crystal growth will be significantly increasing when the continuous development makes available new numerical techniques, improved software tools, and more powerful hardware. Then, many more new application fields will open up besides the classical use of crystal-growth modeling in Bridgman-type or Czochralski melt growth facilities.

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6.1 Introduction

6

The Czochralski (Cz) growth of silicon single crystals began over five decades ago and has evolved from 50 g crystals to 400- and 450-mm diameter crystals with charge weights up to 450 kg [1]. An outstanding level of quality and size of silicon crystals is achieved today. Still, the design of new growth furnaces and the development of new growth processes to meet the ever-increasing quality and cost requirements remains expensive in terms of both time and money. A simple scaling of the growth furnace according to the crystal dimension does not work due to the nonlinearity of the underlying physical phenomena: for example, the Reynolds number scales linearly with the length, the Grashof number as a third power, while the Marangoni number does not depend directly on the length scale. Numerical simulation could be of great help provided it is fast (a low turn-around time), robust, and its predictions could be trusted.

A simulation of the crystal growth requires solution of the conjugated multidisciplinary problem [2–4]. The key subproblem is the computation of the melt flow coupled to the heat transfer in the growth furnace. Since the characteristic time of the crystal-shape changes is large compared to the hydrodynamic/thermal time, a quasistationary approximation of the growth process is usually used, that is, a set of stationary problems corresponding to the different stages of the growth process is considered.

Computations of the global heat transfer in an axisymmetric approximation are routine now (see, e.g. [3–10] and references therein). The character of the melt flow strongly depends on the crystal size. One can judge whether the melt flow in the growth system should be laminar or turbulent by the Rayleigh number and the rotational Reynolds number. In the case of melt mixed convection in crystal growth a winner is surely the silicon Cz growth due to the large size of the crystal and the crucible and the low melt viscosity. Silicon melt flow in industrial Cz systems is turbulent. Turbulent melt convection is recognized today as a phenomenon of high complexity, affecting the growth stability, impurity transfer, and the formation of the crystallization front.

"Modeling" and "simulation" are frequently used as synonymes. However, the former usually refers to the development or the modification of a model, while the latter is reserved for the application of the model [11]. A model should relate the furnace geometry and process parameters such as the pulling rate, the heating power and the heater(s) position, the crystal and the crucible rotation rates, external electromagnetic fields, etc. to growth outputs: crystal yield, the crystal quality (the uniformity of the oxygen distribution, density of dislocations, point defects), the process duration and production costs. Numerical simulation should be capable of explaining and predicting effects to be useful. It is not a substitute for experiment, but rather a complement to it. Numerical models can provide detailed information on the flow, temperature field, strain in the crystals, etc. that can be measured experimentally only partly or not at all. To give reliable predictions, however, models should be validated in the widest possible range of macroscopic parameters. Once validated, numerical models may assist the development of both growth facilities and growth processes as well as serve as a basis of the active growth control [4].

Sometimes it is stated that the nature of the simulation software (research, pilot, production) is determined by its maturity with respect to the validation level [12]. This is an oversimplification. If one needs a single (ideally, quantifiable) criteria to estimate the practical usefulness of simulation, the best choice is probably the reliability of a computer prediction [13]. It should be stressed, however, that this parameter, depending on the adequacy of the model and the accuracy of the computations as well as on the particular aim one pursues, characterizes not the code itself, but the simulation. Evidently, the same results could be considered successful if one is interested in unveiling some trend - and unsatisfactory if the goal of the simulation is to find, for example, the optimal size of some specific element of the growth furnace.

The aims of the chapter are

- to describe a numerical model of the large-scale silicon single-crystal growth with the emphasis on the two crucial features:
 - 1. A combined 2D/3D approach with a judicious choice of a local 3D domain to make the problem tractable;
 - An advanced turbulence modeling based on hybridization of large eddy simulation (LES) and Reynolds-averaged Navier–Stokes equations (RANS) allowing one to use the best of both worlds;
- to assess its accuracy by comparison with available experimental data on the industrial silicon growth processes.

6.2

Numerical Model

Modeling of Czochralski growth process has a rich history [14–20]. First computations were done assuming the melt flow to be laminar, steady and axisymmetric;

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however, conclusions drawn could be applied with any assurance to small-sized Cz systems used mainly for laboratory purposes only. Three-dimensional computations started in [21, 22] and continued by other contributors (e.g., [23, 24]) have shown that nonaxisymmetric unsteady flow patterns develop in the silicon melt as the Rayleigh number approaches 10^4 , which corresponds to crucible diameters of 50-80 mm. In the case of crucible rotation, the resulting wave patterns are attributed to the baroclinic instability [23, 24]. Experiments (see [25] for more references) demonstrated that for moderately sized Cz systems, with 40-100 mm diameter crystals, the flow in the silicon melt is unsteady and nonaxisymmetric, and even turbulence is likely to occur. The authors of Ref. [26] have discussed the evidence for turbulent behavior of the silicon melt in larger, industrial-scale Cz systems and have concluded that the Reynolds-averaged equations should be used. The standard high Reynolds number $k-\varepsilon$ turbulence model in combination with the wall-function method to satisfy the no-slip wall boundary condition [27] was first used in [28, 29]. The application of this model and known wall functions for the silicon melt convection seems to be unjustified for two reasons. First, the conventional wall functions are established for shear layers with local equilibrium turbulence, where the turbulence generation is nearly balanced by the dissipation, and the convection/diffusion transport plays a secondary role. The near-wall layers, both for the crystal and crucible surfaces, are laminarized, so that turbulence is not generated inside them but is supplied from the flow core. Secondly, the stabilizing action of the crucible rotation and, possibly, buoyancy forces in the outer region of the melt may strongly suppress the turbulence, so that the eddy viscosity will become of the same order as the molecular one. Note that stable temperature stratification in the flow core is typical for convection in domains with side-heated walls. The authors of Ref. [30] employed a low-Reynolds number $k-\varepsilon$ model that required much finer grids than the above standard one. Both the high- and low-Reynolds number $k-\varepsilon$ models used are based on the isotropic eddy-viscosity concept.

Ristorcelli and Lumley [31] have noted that nonisotropic features of turbulence developing in the silicon melt can be of importance. They have suggested to use a second-order turbulence modeling for prediction of the melt flow and have performed preliminary computations. In general, involving the balance equations for the Reynolds stresses/fluxes is a straightforward way to take into account the direct effects of buoyancy/curvature/rotation on turbulent mixing. Nevertheless, the complete formulation of the second-moment model suggested by Ristorcelli and Lumley is extremely difficult to use for accurate computations because of the large number of additional partial differential equations and algebraic closure relations, especially when the conjugate problem of heat–mass transfer has to be solved. Besides, each of the second-order models presented in the literature, including that suggested by Ristorcelli and Lumley, has not been validated for a wide enough range of test cases that may be associated to all the phenomena playing a significant role in silicon melt convection.

To summarize, the turbulent melt flow in the industrial-scale crucible is nonsteady and essentially three-dimensional [32]. An approach based on the

Reynolds-averaged Navier–Stokes equations (RANS) could not predict with a sufficient (for the engineering purposes) accuracy such growth characteristics as the melt/crystal phase boundary shape or the oxygen concentration in the silicon crystal that are critical for the crystal quality.

On the other hand, at the present time, direct numerical simulation (DNS) of the melt flow is feasible for highly viscous melts such as oxides or in the simple model geometrical configurations [33]. DNS in the large-scale industrial furnace is hardly possible in the near future. For example, for Cz growth of 300-mm Si crystals the typical Reynolds numbers based on the crystal and crucible rotation rates are about $Re_{crys} \approx 10^5$ and $Re_{cruc} \approx 3 \times 10^5$, respectively. These values correspond to the Taylor-scale Reynolds numbers $Re_{\lambda} \approx 400-600$ [34]. The highest value of $Re_{\lambda} = 1200$ reported so far has been achieved for homogeneous turbulence in a periodic box using a spectral method with 4096³ (69 × 10⁹) grid points; for the Re_{λ} interval of interest for the large-scale Cz silicon growth the size of the grid for this simple problem should contain about 1024^3 (1 × 10⁹) – 2048³ (8.6 × 10⁹) cells [35, 36]. Direct simulation of the oxygen transport in Cz silicon growth will require the use of even finer computational grids due to the high value of the Schmidt number. Evidently, one should consider with caution the results of the so-called "coarse grid DNS" or "quasi-DNS" computations.¹

Thus, at present, the most adequate methods for the modeling of the turbulent flow in industrial growth systems are large eddy simulation (LES) and a hybrid method mixing the best features of LES and RANS approaches [7, 37].

6.2.1 Problem Decomposition

Since frequently the growth furnace has an axisymmetric configuration, it is desirable to restrict 3D computations to the melt domain. Almost everybody fails to resist this temptation. This leads, however, to the additional artificial constraints on the flow – axisymmetric thermal boundary conditions, be they taken from the experiment or from the 2D global heat-transfer computations. Moreover, these conditions usually are the stationary ones. Extension of the 3D domain by adding at least the crystal, quartz and massive graphite crucibles results in attenuation of the azimuthal nonuniformities caused by the turbulent flow and reduces the errors of assuming the axisymmetric conditions at the boundary dividing 2D and 3D domains.

¹These approaches do not provide the necessary spatial resolution, but, as their advocates claim, reproduce the flow structures observed experimentally. Indeed, the coherent structures in the developed turbulent flow are known to weakly depend on the Reynolds number. However, in the crystal-growth problems one is interested first of all in the flow behavior near the crystal, the crucible and the free surface since it determines the heat and mass transfer through boundaries. This situation resembles the numerous attempts made about two decades ago to simulate the separated viscous flows using Euler equations: such computations could reproduce the overall flow structure if a separation point/line is defined by the geometrical singularity, but could not give the skin friction and the heat flux.

Thus, the problem has been divided into two subproblems (Fig. 6.1):

- Global heat-transfer problem: Heat transfer in the whole crystal growth furnace in the domain *D*_{global}^{2D};
- Hot-zone heat-transfer problem: Convection and heat transfer in the melt and the surrounding solid parts of the growth furnace $D_{local}{}^{3D}$.

Self-consistent solution of the problem is obtained via the iteration of the solution of the heat-transfer problems in the domains $D_{\text{global}}^{2\text{D}} \setminus D_{\text{global}}^{3\text{D}}$ and $D_{\text{global}}^{3\text{D}}$, coupled by the thermal conditions on the common boundary ∂D .

Computations based on the extended 3D model of the hot zone have shown, in particular, that the distribution of the temperature and of the heat at the melt/crucible and the crystal/melt boundaries are essentially nonstationary and greatly deviate from the axisymmetric ones [37, 38]. Note that strong spatial and temporal nonuniformity of the heat flux at the crystal/melt interface (and, hence, of the growth rate) is probably a cause of striations in the resistivity and the oxygen level in the grown crystals.

Global Heat Transfer This subproblem includes heat conduction in the solid parts of the furnace, the gas flow and the radiative heat transfer. This is a relatively easy task in 2D formulation, provided material thermal and optical properties are known.

The temperature distribution inside the solid block without heat sources satisfies the usual scalar equation of thermal conductivity; if needed, the thermalconductivity tensor should be used for anisotropic materials.



Fig. 6.1 Left: a general view of the 100-mm crystal-growth furnace and the computational grid in the D_{global}^{2D} domain; right: the computational grid in the D_{local}^{3D} domain.

Gas flow in crystal growth is laminar in most cases, except in the high-pressure LEC of A₃B₅ semiconductors and is governed by the low-Mach number (hyposonic) Navier–Stokes equations [39]. These equations follow from the full compressible Navier–Stokes equations under the following assumptions [40]:

- 1. the Mach number is small, $M^2 \ll 1$;
- 2. the hydrostatic compressibility parameter $\varepsilon = gL/R_gT_0$ is small (where g is gravity, L is the height scale, R_g is the gas constant and T_0 is the reference temperature);
- 3. the characteristic time τ is large compared to an acoustic time scale $\tau \gg L/a$.

Low Mach number equations similar to incompressible flow equations do not describe acoustic phenomena: the only compressibility effect retained is the local thermal gas expansion. To obtain a well-known Boussinesq approximation, one should additionally require a low relative temperature (density) variation.

Radiative heat exchange between opaque solid surfaces through a nonparticipating fluid can be accounted for under the assumption of gray-diffusive surface radiation. Computation of the configuration factors (view factors) with account for the shadowing effect is described in detail in [41]. The total radiative flux incoming to the elementary surface element $i(i = \overline{1, N_e}$, where N_e is the total number of elementary surfaces on the boundary) is

$$q_i^{in} = \sum_{j=1}^{N_{\rm e}} q_j^{\rm out} F_{ij}$$

where q^{in} and q^{out} are the radiation fluxes to and from the wall, and F_{ij} are the view factors. The radiative flux out from the wall inside the region can be calculated by the Stefan–Boltzmann law and definitions of emissivity (*E*) and reflectivity (*R*) are as follows: $q_i^{\text{out}} = \sigma E_i T_i^4 + R_i q_i^{\text{in}}$, where σ is the Stefan–Boltzmann constant.

Melt Flow The melt flow in the general case where a magnetic field is present is governed by the following equations

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = 0 \tag{6.1}$$

$$\frac{\partial(\rho\vec{V})}{\partial t} + (\vec{V}\cdot\nabla)\rho\vec{V} = -\nabla p + \nabla\cdot\hat{\tau} + (\rho - \rho_0)\vec{g} + \vec{j}\times\vec{B} + \vec{S}_{\nu}$$
(6.2)

$$\frac{\partial(\rho C_{\rm p} T)}{\partial t} + \nabla \cdot (\rho C_{\rm p} \vec{V} T) = \nabla \cdot (\lambda_{\rm eff} \nabla T) - \nabla \cdot \vec{q}^{\rm rad} + S_T$$
(6.3)

$$\Delta \Phi = \vec{B} \cdot (\nabla \times \vec{V}) \tag{6.4}$$

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$$\frac{\partial (\rho \phi_i)}{\partial t} + \nabla \cdot (\rho \vec{V} \phi_i) = \nabla \cdot (D_{\phi_i, \text{eff}} \nabla T) - \nabla \cdot \vec{q}^{\text{rad}} + S_{\phi_i}$$
(6.5)

where ρ is the density, ρ_0 is the reference density, \vec{g} is the gravity vector, p is the pressure, $\hat{\tau}$ is the stress tensor, $\mu_{\text{eff}} = \mu_{\text{mol}} + \mu_{\text{t}}$ is the effective dynamic viscosity, C_{p} is the specific heat, T is the temperature, ϕ_i is the *i*th passive species (e.g., oxygen), $\lambda_{\text{eff}} = \lambda_{\text{mol}} + \mu_{\text{t}}/\text{Pr}_{\text{t}}$ is the effective thermal conductivity, \vec{q}^{rad} is the radiative heat flux, $D_{\phi_i,\text{eff}}$ is the effective diffusivity, \vec{j} is the current, \vec{B} is the magnetic induction.

Boundary conditions are mainly the usual ones such as the no-slip condition for the velocity at the melt/crucible boundary or the continuity of the temperature and the heat flux. At the free melt surface the normal melt velocity is set equal to zero, while the tangential velocities of the melt and gas are subjected to the following conditions:

$$\begin{pmatrix} \mu_{\text{eff}} \frac{\partial V_{\tau}}{\partial n} \end{pmatrix}_{1} = \left(\mu_{\text{eff}} \frac{\partial V_{\tau}}{\partial n} \right)_{2} + \frac{\partial \sigma}{\partial T} \nabla_{\tau} T$$
$$(V_{\tau})_{1} = (V_{\tau})_{2}$$

The Reynolds-averaged Navier–Stokes (RANS) equations describe transport of the mean flow quantities; in the large eddy simulation (LES) large-scale eddies are described directly, while the effect of small (unresolved) ones is accounted for by the subgrid-scale (SGS) model. The hybrid LES/RANS approach [7, 37] consists in choosing a minimum effective viscosity given by the SGS model and the "complete" turbulence viscosity produced by the low-Re $k-\varepsilon$ model. In practice, the SGS model is activated in the melt flow core, while the low-Re $k-\varepsilon$ model generates a reasonable effective viscosity near the solid wall with a proper lowering to the molecular one at the wall.

Parallel Computations Numerical simulation of industrial-scale Cz silicon growth is a computer-intensive application, 3D turbulent melt flow computation being the most time-consuming part. Parallel computations could be used to greatly reduce the turn-around time of simulation.

The efficiency of a parallel algorithm can be characterized by speed up S_n and total efficiency E_n^{tot} defined as [42] $S_n = T_s/T_p$, $E_n^{\text{tot}} = T_s/nT_p$, where *n* is the number of processors, while T_s and T_p are the execution times for serial and parallel algorithms, respectively. The total efficiency is less than 1 and can be written as a product of three factors [43]: parallel efficiency, numerical efficiency and load-balancing efficiency. The parallel efficiency is defined as $E_n^{\text{par}} = T_{\text{comp}}/(T_{\text{comp}} + T_{\text{comm}})$, where T_{comp} is the pure computation time and T_{comm} is the communication time.

Load-Balancing Problem A finite-volume representation of a partial differential equation can be solved most efficiently by a single-instruction multiple-data (SIMD) computer system if the grid is partioned approximately proportionally for each

processor productivity and the amount of communication between processors is minimized.

This optimization problem for grid distribution is known as the load-balancing problem. Its solution requires the minimization of the cost function $H = T_{\text{comp}} + T_{\text{comm}}$, where T_{comp} is the time needed for an iteration and T_{comm} is the time for the following interprocessor communications. The first addend in this equation is obviously $T_{\text{comp}} = \max_q(N_q T_q)$, where N_q is the number of the nodes assigned to the processor q, and T_q is the time in which it performs one iteration on one node (we allow the processors to differ in productivity). The communication time T_{comm} is determined by communication matrix C_{pq} , which is the number of vertices of the grid that belong to the processor p but are necessary to the processor q to perform an iteration. The dependency of T_{comm} on C_{pq} is not obvious and may be strongly affected by the architecture of a multiprocessor complex. We assume that for a cluster of workstations it has the following form [44]:

$$T_{\text{comm}} = \sum_{pq} (C_{pq}/b + \delta(C_{pq})L)$$

where *L* is the *latency* of the network (time necessary to start communication between two processors) and *b* is the *effective bandwidth* $b = 1/t_{vertex}$, where t_{vertex} is the time necessary to transmit through the network all the information about one vertex.

The present implementation of a parallel version of the solver using the message-passing interface (MPI) communication library is described in [45]; a key feature enabling an efficient multiblock-structured grid paritioning is an auxillary internal representation of the computational grid by a unique unstructured index for each cell, so that this numeration is continuous. The parallel version of the solver assembles those linear equations that correspond to the current subdomain, so that only part of the matrix is assembled on each processor. After the distributed set of equations is built, the iterative solver is called (the SSOR preconditioned BiCGSTAB algorithm has been used (see, e.g. [46])) that implies two communication calls to refresh vector elements and four calls providing distributed summation of scalars. So, each sweep of the linear solver contains six calls to the MPI communication procedures. Since every variable requires several iterations of the preconditioned BiCGSTAB to achieve convergence (about 3 for velocities and about 40 for the temperature and pressure), the iterative solver is the most critical program unit to the overall parallel-code effectiveness.

Speedup Results The parallel-solver efficiency in 3D simulation of the industrial growth of 100-mm and 300-mm silicon crystals has been assessed using two workstation clusters with Fast Ethernet and Myrinet as the communication hardware that differ in the latency and the effective bandwidth of communication. Typical speedups are presented in Table 6.1 (the efficiencies are indicated in the parentheses).

Table 6.1 Parallel Code Speedup and Efficiency.

Number of processors	Fast Ethernet		Myrinet	
1	1	(100%)	1	(100%)
2	1.67	(84%)	1.7	(85%)
6	3.35	(56%)	4.0	(67%)
10		. ,	5.92	(59%)
20			9.15	(46%)

6.3

Model Validation

Numerical models should be tested to prove their predictive power. The next two sections contain a discussion of general validation issues and an assessment of the model described above using available data on Czochralski silicon growth in industrial furnaces.

6.3.1 Verification and Validation

The necessary stages of the code development are verification (an assessment of the correctness of the model implementation) and validation (an assessment of the adequacy of the model to the real world) [47].

Verification Verification is primarily a mathematical issue [47]. The major sources of errors in the numerical solution have been listed in ref. [48]: insufficient spatial and temporal discretization convergence; insufficient convergence of an iterative procedure; computer round-off; computer programming errors. Errors of the latter type are the most difficult to detect and fix when the code executes without an obvious crash, yielding "moderately incorrect results" [48]. The study reported in ref. [49] revealed a surprisingly large number of such faults in the tested scientific codes (in total, over a hundred both commercial and research codes regularly used by their intended users).

Verification is performed by comparison of the numerical results with "highly accurate" (benchmark) solutions such as 1) exact analytical solutions; 2) benchmark solutions of ordinary differential equations (ODE); or 3) benchmark solutions of partial differential equations. The usual use of ODE solution is based on exploiting the symmetry properties: one can solve an essentially one-dimensional problem (for example, having spherical symmetry) using a general three-dimensional grid. There are a few well-known multidimensional benchmark solutions such as laminar convection in a square cavity [50, 51] and the flow over a backward-facing step with heat transfer [52].

Validation Validation is the second step in the assessment of the software quality. It should be stressed that verification should not be skipped: successful validation

alone does not prove the reliability of the code due to the limited set of validation cases, a "graphical" comparison with experimental data in most cases and a possible cancellation of multiple numerical and experimental errors that can give an impression of a success.

The validation of the heat-transfer and crystal-growth computations in the complete furnace can be extremely difficult due to uncertainty in the properties of different materials, and the necessity to quantify a complete set of test conditions and provide a comprehensive set of measurements of major parameters with the error estimates. Thus, a decomposition of the system into a hierarchy of subproblems can be useful [48]. A few model problems inspired by crystal growth are listed in ref. [53] including an "annular configuration" (a cylindrical container with a small coaxial cylindrical heater) that can be used to study thermocapillary convection and a "half-zone" [54] that emulates the liquid bridge of the melt in the floating-zone method.

There are, however, serious technical difficulties in the systematic *in-situ* measurements of the temperature field and flow visualization during industrial crystal growth. Semiconductor melts are opaque, however, flow visualization is possible using at least two approaches. The first is the introduction of radioactive tracers [55], the second, called real-time X-ray radioscopy (radiography) [56, 57] is based on the dependency of the X-ray absorption on the material density. Thus, for a melt of pure substance this method gives the temperature distribution. The case of alloy melts is more complex since both the temperature and the concentration variations contribute to the variation of the density, and, hence, absorption. When the absorption coefficient of one component of the binary solution is much greater than that of the other, one gets an approximate visualization of the concentration distribution [58]. X-ray radioscopy could be used for *in-situ* monitoring of the melt/crystal phase boundary [59]. Recently, a confocal scanning laser microscope with an infrared-imaging furnace has been used to observe the evolution of the morphology of silicon crystal with increasing growth rate [60].

Probably the most advanced in-situ high-temperature measurements have been reported in refs. [32, 61]. The authors were able to measure the temperature and temperature fluctuations within the silicon melt during industrial crystal growth using thermocouples and optical sensors. The superiority of the latter has been established, since signals from thermocouples do not adequately reproduce the high-frequency part of the turbulence spectrum.

The difficulties of the study of real growth processes in situ force one to exploit physical simulation of crystal growth. Thus, in ref. [62] silicone oil has been used to study the flow in the Cz crucible. An outstanding study has been reported recently in ref. [63]. To simulate the processes in the large-scale silicon growth, the authors exploited a eutectic mixture of InGaSn with a melting point about 285 K. Tuning the crucible size, the magnetic induction and the "crystal" and crucible rotation rates, the authors were able to achieve the simultaneous equality of four criteria (the Grashof number, the Hartmann number and two Reynolds numbers, determined by the "crystal" and the crucible rotation) in the physical experiment to those in the industrial 200-mm silicon growth. However, there

Property	Unit	Crystal	Melt
Melting temperature, $T_{\rm m}$	K	1685	
Density, p	$kg m^{-3}$	2530	2570
Specific heat, $C_{\rm p}$	J (kg K) ⁻¹	1000	915
Thermal conductivity, λ	$W (m K)^{-1}$	$\lambda(T)^{a}$	66.5
Thermal expansion coefficient, β	K ⁻¹	_	1.44×10^{-4}
Dynamic viscosity, µ	Pa s	_	$8 imes 10^{-4}$
Emissivity, ε		0.7	0.3

Table 6.2 Physical Properties.

a $\lambda(T) = 75(T/300)^{-0.32} \exp(5.3 \times 10^{-4}(T-300))$

are a few differences in simulation from the real process related to the radiative heat transfer; it is barely possible to emulate the Marangoni effect and the shear stress caused by the gas flow over the melt free surface; the "crystal" part of the InGaSn melt upper boundary was flat, while in silicon growth it is highly curved.

Fortunately, the shape of the fluid/crystal phase boundary is quite sensitive to the local heat and mass transfer and this information, being available in the majority of growth experiments (either via visualization of the growth striations or using intentional "pulsed" doping for interface evolution monitoring), is certainly one of the major "measures" for code validation.

6.3.2

Examples: Industrial Growth of Silicon Crystals

The numerical model described in Section 6.2 has been implemented as the software package Crystal Growth Simulator (CGSim) [64] and applied to Cz silicon growth in a number of industrial systems. Some of the early results have been obtained using the in-house software [65] and a customized version of the CFD-ACE code (CFD Research Corporation, Huntsville, AL, USA, http://www.cfdrc.com).

Only the melt-flow structure and its effect on the crystal/melt interface are considered below as the validation examples.² The material properties of the silicon in the solid and liquid phases are listed in Table 6.2.

Growth of 100-mm and 300-mm diameter silicon crystals in the industrial Cz pullers Ekz-1300 and Ekz-2405, respectively, has been considered. The scheme of the first growth system along with the computational grids for 2D and 3D domains D_{global}^{2D} and D_{local}^{3D} are presented in Fig. 6.1.

²Discussion of other issues related to large-scale Cz growth of single silicon crystals can be found in the following papers: oxygen transport and incorporation into the crystal [38, 65–68]; effect of magnetic field on the melt flow 69–71; formation and evolution of point defects [67, 68, 72, 73].

The computed temperature and flow fields for a crystal height of 50 mm using an engineering model of the global heat transfer, including the self-consistent RANS (based on the modified low Reynolds number turbulence model of Chien) computations of the melt convection, inert gas flow, and the melt/crystal interface geometry [8] are shown in Fig. 6.2 (2D computation of the global heat transfer) and Fig. 6.3 (the melt flow). It should be noted that the crystal and crucible are rotated in opposite directions. There exist the temperature boundary layers along the crystal/gas interface as seen in Fig. 6.2; however, the heat flux due to the crystal cooling by the argon flow is insignificant and does not exceed 1% of the radiative heat loss. The velocity distribution for this regime is shown in the right part of Fig. 6.2. Forcing the argon flow near the melt free surface is mainly due to decreasing gas density in the high-temperature region. In addition, the heat-shield geometry also significantly contributes to the gas velocity. The melt velocity is two orders lower than the characteristic



Fig. 6.2 Temperature distribution and argon velocity vectors in the Ekz-1300 system. The crystal pulling rate is 2 mm min⁻¹, argon pressure and flow rate are 15 mbar and 1500 SLH, respectively, the crystal/crucible rotation rates are 20 and -5 rpm, respectively.

gas velocity and can not be graphically distinguished in the general velocity distribution.

The multiblock grid of about 12 000 cells with mismatched boundaries at liquid/solid interfaces has been used. To test grid convergence a refined grid of about 43 000 cells has been used to produce discrepancies of about 1.1% for the temperature differences in the melt and 0.5% for the heater powers.

The computed heater power 67.05 kW is in fair agreement with the experimental value of 62 kW [74] for this puller. The difference in the heater powers can be related to the fact that the external wall temperature is really higher than the adopted value of 300 K. Thus, the accuracy of the model of global heat transfer in the entire system seems to be acceptable.

The distributions of the temperature, the turbulent effective viscosity referred to the molecular viscosity, and stream function are shown in Fig. 6.3 to illustrate the basic heat-transfer mechanisms. The smooth patterns of the temperature distribution indicate that heat transport through the melt is provided largely by the turbulent mixing represented in the computations by the effective viscosity. A



Fig. 6.3 Distributions of the melt temperature (a), effective viscosity μ_t/μ (b), and stream function (c) in the Ekz-1300 system.

considerable contribution to the convective heat exchange is observed just under the crystal. The stream function distribution displays a two-vortex flow structure with a stagnant region under the heat shield. In this region, the melt motion to the crystal is changed to the opposite direction due to the contribution of the shear stress from the argon flow.

This engineering model has been used to qualitatively study the effect of the argon flow rate on the melt/crystal interface geometry. Changes in the interface deflection for the different argon flow rates were found to be comparable with the deflection variation provided by strong changes in the crucible rotation. The argon flow influences the interface geometry just through the gas shear stress on the melt free surface, which is responsible for melt-flow reconstruction. It has also been shown that the gas-flow effect in a "gas-controlled" hot zone is much more pronounced than the Marangoni tension and largely governs the melt flow near the free surface [8].

Still, such an engineering model providing an adequate description of the global heat transfer is not able to correctly describe turbulent melt flow in the large-scale growth furnace. Results of computations using the hybrid LES/RANS model with an algebraic Smagorinsky-type SGS model [75] are presented in Fig. 6.4. The grid contained about 250 000 finite volumes in the melt blocks; time-average characteristics were obtained by treating hydrodynamic fields over the time interval of about 1000 s after an initial transient period of 700 s. Comparison with experimental data [32] (Fig. 6.5) shows that the "pure" RANS



Fig. 6.4 Instant (dashed) and time-averaged (solid) isotherms (a); instant (b) and time-averaged (c) velocity vectors in the central vertical cross section.



Fig. 6.5 Temperature distribution along the melt/crucible interface.

approach provides a fair prediction of the mean temperature difference in the melt, however, only 3D computations reproduce details of the temperature distribution. Note that the difference between the computed and experimental values of the temperature is comparable with the amplitude of the temperature fluctuations.

A detailed comparison of computed and experimental [75] temperature variation in time in a few reference points and corresponding power spectral density is presented in Fig. 6.6. The maximal melt depth under the crystal is about 10 cm, $r_{\rm ref} = 3$ cm for all points. The underestimation of the temperature of about 10 K is seen, in contrast to the distribution along the melt/crucible boundaries; probably, this systematic discrepancy is related to the difficulties of the high-temperature measurement. The reproduction of the spectral characteristics is good at the free melt surface and becomes poorer with the lowering of the reference point position deeper into the melt, probably, due to a weakening of the regularizing action of the crystal rotation on the flow.

So far, results of computations for the relatively short crystals, that is for the initial growth stage, have been presented. Systematic study of the heat transfer and melt flow for rather long crystals has been done recently in [10] for 100-mm and 300-mm silicon crystal growth. The choice of the crystal height was forced by the availability of the reliable experimental data obtained in Wacker Siltronic. The instant distribution of the temperature and instant velocity vectors





Fig. 6.6 Left: the temperature distribution in time; right: the spectral power density. Reference points (from top down): the free melt surface; 2 cm lower; 4 cm lower.

for the two crystal heights for both crystal diameters are shown in Figs. 6.7 and 6.8.

The melt depth is not changed significantly for the smaller crystal (Fig. 6.7). However, the temperature difference in the melt noticeably reduces by about 6 K since a higher crystal position results in decreasing conductive heat flux from the



Fig. 6.7 Temperature (a, c) and velocity (b, d) instant distributions for two crystal positions during 100-mm crystal growth. The crystal heights are 240 mm (a, b) and 300 mm (c, d).

crystallization front through the crystal, at least for this hot-zone configuration. So, the averaged heat flux from the melt should also be decreased to keep a nearly constant crystallization rate. This decrease in temperature difference leads to weakening natural convection in the melt, as can be seen from an analysis of the velocity vector distributions. There are a number of energetic turbulent vortices of 2-4 cm diameter for the lower crystal position (Figs. 6.7(a) and (b)), which are not seen or depressed for the higher crystal position (Figs. 6.7(c) and (d)).

For growth in the Ekz-2405 puller the crystal heights equal to 300 and 700 mm have been considered with more than a two-fold reduction of the melt depth for the latter (Figs. 6.8(c) and (d)). The resolved turbulent energetic vortices (Fig. 6.8(b)) are of the same scale of about 3 cm as in 100-mm diameter crystal



Fig. 6.8 Temperature (a, c) and velocity (b, d) instant distributions for two crystal positions during 300-mm crystal growth. The crystal heights are 300 mm (a, b) and 700 mm (c, d).

growth. This seems to be due to the transition in turbulence characteristics. For weak turbulence, energetic structures are of about the spatial scale of the flow domain. For fully developed turbulence, there is a slow large-scale motion and energetic flow structures of intermediate scale. The Rayleigh and Reynolds numbers for the melt flow, computed for the crystal and crucible for the 300-mm diameter growth, can be estimated as Ra = 2.9×10^8 ; Re_{crys} = 9.1×10^4 ; and Re_{cruc} = 2.8×10^5 . The respective parameters for the 100-mm diameter growth are Ra = 2×10^7 ; Re_{crys} = 1.7×10^4 , and Re_{cruc} = 3.8×10^4 .

The effect of the crucible rotation rate on the temperature distribution along the melt/crucible interface is illustrated by Fig. 6.9, where results of measurements are also plotted. Comparison of the computed shape of the crystal/melt interface with experimental data for the crystal heights of 300 mm and 700 mm is shown in Fig. 6.10.



Fig. 6.9 The temperature distribution along the melt/crucible interface for 100-mm diameter crystal growth.

6.4 Conclusions

A numerical model for simulation of the global heat transfer and the melt flow in the Czochralski growth of large silicon crystals is presented. The key model features are an extended 3D domain for the 2D/3D computations and a hybrid LES/RANS approach to turbulence modeling. It is shown that use of parallel computations on affordable multiprocessor systems assembled from the COTS hardware could reduce the turn-around time of simulation by an order of magnitude. The model validation using the experimental data on the growth of 100-mm and 300-mm silicon crystals in the industrial pullers Ekz-1300 and Ekz-2405 has proved its predictive power.

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Fig. 6.10 The computed and experimental interface shapes for the 300-mm diameter crystal. The crystallization rate is about 0.6 mm min⁻¹.

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7 Global Analysis of Effects of Magnetic Field Configuration on Melt/Crystal Interface Shape and Melt Flow in a Cz-Si Crystal Growth

Koichi Kakimoto and Lijun Liu

7.1 Introduction

Since crystal quality, especially the distribution of point defects and voids, depends on the temperature distribution in a crystal during crystal growth, the shape of the melt/crystal interface, which affects the temperature distribution near the interface, should be controlled quantitatively. Application of magnetic fields to silicon Czochralski (CZ) crystal growth is an effective method for controlling melt convection in a crucible. Therefore we can control the shape of the melt/crystal interface by selecting an appropriate set of magnetic fields. Such a method is more effective for crystals with large diameter, since flow in a crucible becomes unstable due to large Grashof and Reynolds numbers of the melt in a quartz crucible. Two types of magnetic fields, cusp-shaped and transverse magnetic fields, have been utilized in the commercial production of crystals with a large diameter, so far. Here, this chapter introduces how the transverse magnetic field affects the shape of the solid/liquid interface.

A transverse magnetic field applied to silicon CZ growth processes (TMCZ) has a great potential for controlling melt flow. The melt flow in a crucible and, hence, the global thermal field within the growth furnace, are principally three-dimensional (3D) under the influence of the transverse magnetic field. Although there are many published studies on numerical modeling of TMCZ growth [1–9], these models of 3D analysis are limited to the melt or to the melt and the crystal domains due to the requirement of large computer memory and a long time of computation for a full 3D global modeling. Therefore, a new algorithm to solve such a problem by using a reasonable time and memory size for computation is proposed.

Kakimoto and Liu [10] developed a partly 3D global model that takes into account feasible 3D global modeling with moderate requirements of computer memory and computation time. All convective and conductive heat transfers, radiative heat exchanges between diffuse surfaces and the Navier–Stokes equations for the melt are all coupled and solved simultaneously by a finite-volume method in a 3D configuration.

7.2

Model Description and Governing Equations Under a Transverse Magnetic Field

The configuration of a small CZ furnace for silicon crystal growth that was used in the calculation is illustrated in Fig. 7.1. The growth process is assumed to be quasisteady since velocity of crystal growth is small in the order of 1 mm/min. All of the components in the furnace are divided into a set of blocks, in which structured grids were distributed. In order to perform 3D global modeling with moderate requirements of computer memory and computation time, a mixed 2D/3D finite volume scheme was developed [11]. The components in the core part of the furnace, which corresponds to the 3D domain, are discretized in a three-dimensional configuration. The domains away from the central part, which has a 2D domain, are discretized in a two-dimensional configuration. The crystal, melt, crucible and heater are imposed to have the 3D domain in the study. The other regions in the furnace are imposed to have the 2D domain. The calculation of view factors in the radiation modeling is an important part of the model. Let ∂V^2 and ∂V^3 , respectively, denote the radiative surfaces that fall in the 2D domain and 3D domain of a furnace. For any two radiative surface elements \vec{x}_c and \vec{x}_{ic} , the view factor $K_e(X, X_i)$ between them is deduced and calculated as follows: when $X_i \in \partial V^2$ and $X \in \partial V^2$

$$K_e(X, X_i) = K_C(\vec{x}_c, \vec{x}_{ic})$$
(7.1)

when $X_i \in \partial V^3$ and $X \in \partial V^2$,

$$K_{e}(X, X_{i}) = \frac{(\theta_{i2} - \theta_{i1})}{2\pi} K_{C}(\vec{x}_{c}, \vec{x}_{ic})$$
(7.2)

when $X_i \in \partial V^3$ and $X \in \partial V^3$,

$$K_{e}(X, X_{i}) = \int_{\theta_{i1}}^{\theta_{i2}} K(\vec{x}_{c}, \vec{x}_{i}^{*}) \mathrm{d}\theta^{*}$$
(7.3)

where \vec{x}_c and \vec{x}_{ic} are the respective azimuthal projections in a meridional plane of the geometrical centers of X and X_i . The azimuthal angle range (θ_{i1} , θ_{i2}) is covered by the radiative surface element $X_i \in \partial V^3$ and $\vec{x}_c^* = (r'_{ic}\cos\theta^*, r'_{ic}\sin\theta^*, z'_{ic})$. The axisymmetric view factor $K_C(\vec{x}_c, \vec{x}_{ic})$ is defined by the integral

$$K_C(\vec{x}_c, \vec{x}_{ic}) = \int_0^{2\pi} K(\vec{x}_c, \vec{x}_i^*) \mathrm{d}\theta^*$$
(7.4)

The view factor was precisely calculated by taking into account all objects in view and all hidden objects in the furnace with a view and hidden algorithm [11].

The governing equations for melt convection under the influence of a magnetic field with the assumption of incompressible laminar flow are as follows:

$$\nabla \cdot \vec{V} = 0 \tag{7.5}$$

$$\rho \vec{V} \cdot \nabla \vec{V} = -\nabla p + \nabla \cdot [\mu (\nabla \vec{V} + \nabla \vec{V}^T)] - \rho \vec{g} \beta_T (T - T_m) + \vec{J} \times \vec{B}$$
(7.6)



Fig. 7.1 Configuration and domain partition of a typical Czochralski growth furnace: 3D domain (gray) and 2D domain (open).

$$\rho c \dot{V} \cdot \nabla T = \nabla \cdot (k \nabla T) \tag{7.7}$$

where \vec{V} , ρ , p, μ , \vec{g} , β_T , \vec{J} , \vec{B} , c and k are melt velocity, melt density, melt pressure, melt viscosity, gravitational acceleration, thermal expansion coefficient, electrical current density, magnetic flux density, heat capacity and thermal conductivity, respectively. The melt flow is solved by a finite-volume method.

The global solution is obtained by an iterative procedure that consists of a set of local iterations for all block regions, the calculation of radiative heat transfer among the blocks in the furnace, and a global conjugated iteration among them. The input heater power and melt/crystal interface are unknowns *a priori*. They are solved during the iterative procedure. Details of the model, including treatments of boundary conditions, were published elsewhere [12].

7.3 Computation Results for Model Validation

A growth process was numerically calculated to demonstrate the validity of the proposed method [12]. The furnace was set in a condition of a transverse magnetic field with nonrotating crystal and crucible. The homogeneous magnetic field is

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Fig. 7.2 Temperature distribution in a furnace in a transverse magnetic field. (a) Temperature distribution in the furnace and in the locations under consideration. Isotherms are plotted every 30 K in solids and every 10 K in the melt. (b) Temperature distribution at the melt top surface. Isotherms are plotted every 3.5 K. (c) Temperature differences over circumference at different locations.

applied in the *x*-direction with an intensity of 0.3 T. The crystal, melt, crucible, heater and heat insulators were included in the 3D domain. Figure 7.2(a) shows the temperature distributions in the melt as well as in solid components in the furnace. The 3D distribution of temperature can be obviously observed in the central region of the furnace, especially in the melt. The temperature distribution at the melt top surface is presented in Fig. 7.2(b). In order to check the noticed temperature



Fig. 7.3 Top view of the melt/crystal interface.

nonuniformity in the azimuthal direction in the furnace, some representative locations (point A through point J) were selected for consideration, as shown in Fig. 7.2(a). The temperature differences in azimuthal direction at these locations are shown in Fig. 7.2(c). It is found that the temperature difference decreases rapidly as a function of distance from the central part of the furnace, which corresponds to the melt region. Such inhomogeneity remains even at the outside wall of crucible when the crucible was not rotated. However, in the heat insulators that are away from the melt region, the temperature distribution is rather uniform in the azimuthal direction. This means that the central part of the furnace must be treated in 3D, however the heat insulators away from the central part can be treated in 2D in order to save computation time.

The melt/crystal interface shape was found to be 3D in this growth process, which can be observed in Fig. 7.2(a). A top view of the interface with identification to the isothermal surface of the melting temperature of silicon is shown in Fig. 7.3. These results are in agreement with the experimental result carried out by Kajigaya *et al.* [13]. In their experiment, ellipsoid crystals with 3D interface shapes were grown in a transverse magnetic field with the same intensity under a condition without crystal rotation.

7.4 Numerical Analysis of a TMCZ Growth

Some results of convection of the melt, temperature distributions and the shape of melt/crystal interface are shown in Figs. 7.4 and 7.5(a) for a TMCZ configuration with crucible and crystal rotation. The transverse magnetic field is 0.1 T oriented in the *x*-direction. The rotation rates of crystal and crucible are set to -30 rpm and 5 rpm, respectively.

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Fig. 7.4 Melt convection, thermal field and melt/crystal interface profiles in symmetric planes x = 0 (right) and y = 0 (left). Isotherms are plotted every 5 K in the melt and every 15 K in the crystal.



Fig. 7.5 3D view of the melt/crystal interface and the temperature distribution on the melt top surface as well as on the interface. Isotherms are plotted every 3 K. (a) rotating crucible and crystal; (b) nonrotating crucible and crystal.

Figure 7.4 shows the melt convection, temperature distribution and melt/crystal interface in symmetric planes x = 0 (perpendicular to the magnetic field) and y = 0 (parallel to the magnetic field). A pair of vortex occupies plane x = 0, while, in plane y = 0, the melt flows downward to the crucible bottom with a complex pattern just beneath the melt/crystal interface. The temperature distributions in plane x = 0 and plane y = 0, which are dominated by the flow pattern of the melt, are distinctly different. However, even though the flow and thermal field of melt have three-dimensional structure, the melt/crystal interface shapes in the two orthogonal planes are almost symmetric, as shown in Fig. 7.4. Figure 7.5(a) shows a 3D view of the melt/crystal interface shape and the temperature distribution on the top of the melt as well as on the melt/crystal interface. For the sake of



Fig. 7.6 Axial temperature gradients in the crystal (upper part) and melt (lower part) near the interface as a function of pulling rate of a crystal at different intensities of the applied magnetic field.

comparison, the corresponding results are also shown in Fig. 7.5(b) for the case in which both the crystal and crucible are stopped. Although the three-dimensional interface shape can be recognized in Fig. 7.5(b), the deflection of the melt/crystal interface is almost uniform in the azimuthal direction shown in Fig. 7.5(a). This indicates that crystal and crucible rotation homogenize the melt/crystal interface deflection in the azimuthal direction.

In Voronkov's theory [14], the ratio between the crystal growth rate (V_g) and the temperature gradient in the crystal near the interface (*G*), as well as the melt/crystal interface shape, is a key parameter of the formation of voids and interstitial clusters based on the agglomeration of point defects such as vacancy and interstitial atoms. In Figs. 7.6 and 7.7, we summarize the results of a series of computations with various intensities of magnetic field and various crystal-pulling rates to investigate their influences on the axial temperature gradients at the interface and the interface deflection [15]. Figure 7.6 shows the averaged axial temperature gradients in both the crystal and the melt at a melt/crystal interface as a function of crystal-pulling rate. The values of axial temperature gradients in the melt and crystal at the interface are not identical even when the crystal-pulling rate is zero since the thermal conductivity of the crystal is not equal to that of the melt. These results show that the axial temperature gradients in the melt and crystal near the interface increase with increased intensity of the magnetic field. With increase



Fig. 7.7 Interface deflection as a function of pulling rate of a crystal at different intensities of the applied magnetic field.

in the crystal-pulling rate, the temperature gradient near the interface in the crystal increases, while that in the melt decreases. Meanwhile, the difference becomes smaller between the case with magnetic field intensity of finite values including zero and the case without melt convection with increase in the crystal-pulling rate. Since this difference is due to the melt convection, this result indicates that the contribution of melt flow becomes smaller with increase in crystal-pulling rate.

Figure 7.7 shows the interface deflection toward the melt as a function of the ratio between the crystal-pulling rate (V_p) and the temperature gradient in the crystal near the interface (*G*). The interface moves upward to the crystal side with increase in either the magnetic field intensity or the value of the parameter V_p/G . This trend is consistent with that of the axial temperature gradient in the crystal near an interface, as shown in Fig. 7.6. This is because the interface shape is mainly determined by the temperature distribution in the crystal close to the interface and the melt convection in a crucible.

7.5 Conclusions

A partly 3D global model was developed for analyzing heat and mass transfer in a silicon CZ configuration with transverse magnetic fields by using moderate computer memory and computation time. The model was demonstrated to be valid and reasonable for the TMCZ case. The model can analyze temperature distribution in both a crystal and a melt by using a partly three-dimensional analysis.

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8.1 Introduction

8

Radiative heat transfer (RTH) in crystal growth is, as a rule, an important heat-transfer mechanism and in the case of semitransparent crystals grown at high temperatures it is a dominant one. In the case of opaque semiconductors [1], when all surfaces reflect diffusively and all solids and fluids present in the growth facility are either opaque or transparent, computation of grey radiation using configuration (view) factors (a "surface-to-surface" model) [2] is usually all one needs.¹A more complex problem arises when some surfaces can exhibit specular reflection and/or the crystal or the melt should be treated as a semitransparent medium. Growth of such crystals is the oldest industrial process: it was started over a century ago with oxide crystals (ruby and sapphire) [4]. Numerous technologically important oxide, halide and fluoride crystals (laser and nonlinear crystals, optical crystals, jewelry, scintillation crystals) are semitransparent. Modeling of RHT is more involved in this case: one should account for all the relevant optical phenomena in the system (absorption, scattering, refraction, diffuse and specular reflection).

8.1.1 Semitransparency

Internal radiation through the crystal depends largely on the absorption coefficient and the refraction index. The first parameter determines the radiative heat absorption and emission inside the crystal, while the second determines reflection and refraction of radiation at the crystal side surface. The absorption coefficient of a melt is generally much greater than that of a crystal. Therefore, radiation is crucial in heat removal from the melt through the crystal/melt interface; RTH within the crystal can even lead to instability of the crystallization front [5]. The refraction

¹However, specular reflection from the melt surface in silicon growth has been considered in Ref. [3] and was found to result in a marked temperature decrease of the melt surface in the meniscus region that depends on the surface curvature.

index significantly exceeds unity, thus multiple reflections and refractions at the crystal side surface occur. The side surface of these crystals is specular rather than diffusely reflective.

8.1.2 Thermal Conductivity

Oxides and other semitransparent crystals are distinguished by a small thermal conductivity in both the solid and liquid phases. Thus, heat transfer is determined by convection in the melt and by radiation in the crystal. The radiative heat transfer through the crystal renders the interface deeply convex toward the melt, while the effect of convection is two-fold. If the rotationally driven convection dominates, the maximum of the thermal flux distribution along the interface on the side of the melt is at the center of the interface, and convection tends to deflect the interface to the crystal. Otherwise, if the buoyant convection is dominant, then the maximum of the thermal flux is shifted to a trijunction line and the crystallization front is deflected to the melt. Increase of the absorption coefficient of a crystal and decrease of the absorption coefficient of a melt diminish the convexity of the crystal/melt interface toward the melt. In traditional Czochralski growth, thermal gradients in the melt turn out to be rather significant. Increase of the crystal radius or the crystal rotation rate lead to a change in the flow pattern in the melt, which is accompanied by interface inversion, that is, the abrupt change of the crystal/melt interface from convex to concave toward the melt when forced convection becomes dominant. The influence of the crystal length is manifested mainly through the variation of the melt depth that can result in a change in the flow pattern in the crucible. It is just this aspect of the problem that was given most attention in simulating oxide growth (see, for example [6-13]). However, although the inversion phenomenon is barely possible in the absence of volume radiation transport, internal radiation here plays more likely an auxiliary role, and the shape of the crystal/melt interface is controlled mainly by convection. Another situation takes place in the low thermal gradient Czochralski (LTG Cz) growth. In this case, the temperature differences in the melt are small and, therefore, natural convection is weak and can hardly be responsible for the observed variations of the crystallization front. The flow pattern in the melt is not changed significantly with the crystal length; thus, variations of the crystallization front during the growth are determined mainly by internal radiation [14], which in turn depends on the absorption coefficients of the crystal and melt, the refraction index of crystal and the reflective properties of the crystal side surface.

8.1.3 Faceting

Finally, semitransparent crystals frequently demonstrate the pronounced tendency toward faceting of the solidification front, and, thus, the shape of the crystals can strongly deviate from a circular cylinder and present an irregular polyhedron. The simulation of crystal growth from the melt includes a self-consistent determination of the unknown crystal/melt boundary. For solidification of a "pure" substance (that is when mass diffusion effects can be neglected), the process is driven by the temperature gradient alone and is described as a classical Stefan problem [15]. In the quasistationary formulation the interface should be fitted in such a way that pulling velocity projection on the normal to the front is equal to the growth rate. The interface description is more difficult when faceting of the crystal surface occurs: the phase boundary does not follow the melting point isotherm, but coincides locally with a crystallographic plane. Interface undercooling can be large: for example, up to 20 K in bismuth germanate growth [16]. It is often claimed that the faceting is harmful for crystal quality [17] and thus should be avoided by keeping the thermal gradient above a critical value. However, recently, large nearly perfect crystals of bismuth germanate have been grown with the fully faceted solidification front [18]. A numerical treatment of the partially faceted interface has been discussed recently in Ref. [19].

Thus, semitransparency of the crystal significantly influences both the global heat transfer in the growth facility and the shape of the crystal/melt interface [7, 20]. The intensity and the distribution of the radiative heat flux from the interface can markedly change with the crystal length during the growth of crystals with a high refraction index, the effect of the total inner reflection being responsible for this variation [14]. Other effects are also observed. For example, incorporation of microbubbles at the phase boundary results in the occurrence of a diffusively transmitting and scattering boundary that could lead to the nonmonotonic temperature variation in optical crystals [21]. The internal radiation in the melt usually is less important due to the higher absoption. However, it has been shown that neglecting the internal RHT in the oxide melt LiNbO₃ results in the formation of a spoke pattern [22]. The spoke and wave patterns on the free surface are seen in some oxide melts during Czochralski growth. These phenomena, attributed to the thermocapillary instability and the baroclinic instability, respectively, have been considered in detail in the recent review [23].

8.1.4 Numerical Simulation

Simulation of multidimensional RHT in a participating medium remains so far difficult. Detailed comparison with experimental data [24] shows that the diffusion approximation of RHT via an additional "radiative" thermal conductivity (for example in Ref. [25] to study CaF_2 melt growth), does not describe the correct temperature distribution in the growth system. Thus, advanced models, such as the discret exchange factor method [26] or the characteristics method [27, 28] are needed.

Different assumptions and approximations are commonly used in considering RHT problems in crystal growth. In an effort to study the effects of internal radiation within yttrium aluminum garnet (YAG) and gadolinium gallium garnet (GGG), Xiao and Derby [7, 8] assumed that the crystal is totally transparent and

its side surface is covered by a vanishingly thin opaque film. This simplification frequently is claimed to be valid for real systems due to the parasitic deposition of impurities. Note that sometimes such statements do not prevent the authors from indicating the incorporation of the refraction description into the model as future work. Indeed, wall deposits are usual in chemical vapor deposition reactors (and often are semitransparent, increasing considerably the complexity of computations of RHT if the film thickness is comparable with the radiation wavelength), but this phenomenon is not a universal one in melt crystal-growth processes. An opaque crystal surface means that the refraction index of the crystal has no effect on the heat transfer and the latter becomes similar to that in the Bridgman process. These restrictions were removed in Ref. [29], yet the crystal absorption coefficient was taken as constant and quite large since for solving of the radiant transport equation the P1-approximation was used. A similar approach was used also in [9-11] to study the effect of the absorption coefficient on the crystal/melt interface for lithium niobate and garnets. The spectral dependence of the absorption coefficient is often approximated by a simple two-band model when the medium is assumed either totally transparent or opaque [30, 31]. An accurate treatment of the radiation problem has been done in Ref. [10] to study the effect of the top surface boundary condition on the temperature profile, the crystal/melt interface and the process stability for YAG crystal growth. A unified exchange factor model was used; yet, the crystal surface was considered opaque. Heat transfer in growing sillenite compounds was studied in [11, 30, 31], the crystal was assumed to be transparent and the main attention was concentrated on the study of conditions providing growth with a flat crystallization front.

The effects of specular reflection in crystal-growth modeling have drawn less attention (compared to semitransparency issues) so far. The first computations accounting for this phenomenon have been done for bismuth germanate (BGO) crystal growth in a LTG Cz system using the characteristics method [27]. The shape of the crystal/melt boundary was fixed; self-consistent computations have been reported in Ref. [14]. It has been shown that incorporation of the specular reflection from the crystal inner surface, first from its conical part (and thus taking into account the large value of the refraction index for BGO crystal), allows one to reproduce the marked change of the interface shape with crystal length observed in the experiments.

8.2

Numerical Model

A numerical study of bulk crystal growth requires the use of either moving computational grids or a regeneration of the grid. The latter approach is attractive since usually the characteristic time of crystal-shape changes is large compared to the hydrodynamic/thermal time and one can consider a set of stationary problems corresponding to the different stages of the growth process.

The problem statement is decribed below for the axisymmetric geometry. The numerical method for RHT has been extended to the 3D case in Refs. [34, 35].

8.2.1 Problem Decomposition

The problem has been divided into two subproblems:

- Hot-zone heat-transfer problem Convection and heat transfer in the melt and the surrounding solid parts of the growth facility;
- Radiation problem Heat transfer in the crystal and the gap between crystal and the crucible.

For the solution of the first subproblem the usual model of heat transfer in the melt based on the incompressible Navier–Stokes equations with the Boussinesq approximation is exploited. The high viscosity of the melt allows one to consider its flow laminar.

Thermal boundary conditions on the external boundary ∂D of the hot zone domain D_{inner} could be known, for example, from experiments. Otherwise, one is forced to solve the global heat-transfer problem for the domain D_{tot} that includes the entire growth facility, exploiting some approximation of the crystal properties (e.g., totally transparent or opaque). If needed, the self-consistent solution of the problem could be obtained via the iteration of the solution of the heat-transfer problems in the domains $D_{\text{tot}}/D_{\text{inner}}$ and D_{inner} , coupled by the thermal conditions on the common boundary ∂D .

The radiation problem has been solved using a new approach already mentioned above. The following assumptions have been made: the melt is opaque, the absorption coefficient of the crystal is wavelength dependent, the crystallization front is black, the crucible wall is diffusely reflective, while the crystal side surface and the free melt surface can be either diffusely or specularly reflective. Scattering, as a rule, was neglected.

Coupling of Subproblems Both subproblems were matched along the free melt surface and the crystal/melt interface where the following boundary conditions were set:

free melt surface z = 0:

$$-k_{\rm L}\nabla T_{\rm L} \cdot \vec{n} = \varepsilon_{\rm L} \, \left(\sigma T_{\rm L}^4 - q^{\rm inc}\right) \tag{8.1}$$

crystal/melt interface (z = h(r,t)):

$$T_{\rm L} = T_{\rm S} = T_{\rm m} \tag{8.2a}$$

$$-k_{\rm S}\vec{n}\cdot\nabla T_{\rm S} + k_{\rm L}\vec{n}\cdot\nabla T_{\rm L} + q_{\rm rad} = L(\vec{n}\cdot\vec{e}_z)\left(V - \frac{{\rm d}h}{{\rm d}t}\right)$$
(8.2b)

Here, \vec{n} is the unit vector normal toward the crystal region, \vec{e}_z is the *z*-directional unit vector, *L* is the latent heat of solidification per unit volume, *V* is the pulling rate, T_m is the melting temperature, *k* is the thermal conductivity, indices "L" and

"S" correspond to liquid and solid phases, respectively, ε_L is the melt emissivity, q^{inc} is the density of radiative flux incident on the free melt surface, q_{rad} is the density of radiative flux at the crystal/melt interface in the range of semitransparency of the crystal and *h* is the current coordinate of the crystallization front along the pulling direction. Since a triple point is stationary, the pulling rate can be determined from Eq. (8.2b) as follows

$$L(\vec{n} \cdot \vec{e}_z)V = -k_{\rm S}\vec{n} \cdot \nabla T_{\rm S} + k_{\rm L}\vec{n} \cdot \nabla T_{\rm L} + q_{\rm rad|r=R}$$

$$(8.2c)$$

where *R* is the crystal radius. Substituting Eq. (8.2c) in Eq. (8.2b) we obtain the equation for determining the crystal/melt interface

$$\frac{-k_{\rm s}\vec{n}\cdot\nabla T_{\rm s}-k_{\rm L}\vec{n}\cdot\nabla T_{\rm L}-q_{\rm rad}}{(\vec{n}\cdot\vec{e}_{z})} - \frac{-k_{\rm s}\vec{n}\cdot\nabla T_{\rm s}-k_{\rm L}\vec{n}\cdot\nabla T_{\rm L}-q_{\rm rad}}{(\vec{n}\cdot\vec{e}_{z})}\Big|_{r=R_{0}}$$

$$= L\left(\frac{\mathrm{d}h}{\mathrm{d}h}\right) \tag{8.2d}$$

Because the steady-state problem is considered, the time t plays the role of iteration parameter. The energy equation in the crystal is given as follows:

$$\nabla \cdot (k_{\rm S} \cdot \nabla T_{\rm S}) = \nabla \cdot \int Q^{\rm rad}(\vec{r},\lambda) d\lambda = \int_{\lambda} \int_{\Omega = 4\pi} k_{\lambda} (B_{\lambda}(T_{\rm S}) - I_{\lambda}(\vec{r},\Omega) d\lambda d\Omega)$$
(8.3)

where Q^{rad} is the density of the radiation heat flux, λ is the wavelength of the radiation, I_{λ} is the radiation intensity, k_{λ} is the absorption coefficient and $B_{\lambda}(T)$ is the monochromatic blackbody radiation intensity. A convective term in Eq. (8.3) related to the crystal motion was neglected due to the small value of the pulling rate. Boundary condition for Eq. (8.3) were taken in the form: *the crystal side surface*:

$$-k_{\rm S}\frac{\partial T_{\rm S}}{\partial N} = \varepsilon_{\rm S} W_1(T) (n^2 \sigma T_{\rm L}^4 - q_1^{\rm inc})$$
(8.4a)

where *N* is the outward normal to the crystal side surface, *n* and ε_S are the refraction index and the emissivity of crystal, q_1^{inc} is the incident radiation flux and $W_1(T)$ is the fraction of blackbody radiation in the wavelength range wherein the crystal is opaque

$$W_1(T) = \frac{\int_{\Delta_{1\lambda}} B_{\lambda}(T) d\lambda}{n^2 \sigma T_4 / \pi}$$

the centerline:

$$\frac{\partial T_{\rm S}}{\partial r} = 0 \tag{8.4b}$$

The radiation intensity I_{λ} is described by the radiant transport equation (RTE), which in cylindrical geometry with the axis of symmetry Oz and neglecting scattering has the form

$$\frac{\sin\theta}{r} \left[\cos\phi \frac{\partial (rI_{\lambda})}{\partial r} - \frac{\partial (\sin\phi I_{\lambda})}{\partial \phi} \right] + \cos\theta \frac{\partial I_{\lambda}}{\partial z} + k_{\lambda}I_{\lambda} = k_{\lambda}B_{\lambda}$$
(8.5)

where $\phi = \phi_{\Omega} - \phi_r$, ϕ_r is the azimuth angle in cylindrical coordinates locating (with *r* and *z*) a point in space and ϕ_{Ω} is the azimuth angle in spherical coordinates determining (with polar angle θ) the direction (sin $\theta \cos \phi_{\Omega}$, sin ϕ_{Ω} , cos θ) of the ray at this point.

Solution of Eq. (8.5) allows for two representations according to which angle ϕ_{Ω} or ϕ_r is equal to zero. We have used the first case. A detailed description of this approach and its numerical realization is given in [27, 28, 36]. Here, we only state in brief the key ideas of the method.

8.2.2 Radiation Model

At $\phi_{\Omega} = 0$ solution of Eq. (8.5) is sought at points (r, z, ϕ_r) of the usual three-dimensional physical space, but for the rays parallel to the plane rz and dependent only on polar angle θ , that is for directions $\Omega = (\sin \theta, 0, \cos \theta)$. Then, transforming Eq. (8.5) to Cartesian coordinates *x*, *y*, *z*, where $x = r\cos \phi_r$, $y = r\sin \phi_r$ ϕ_r , we obtain:

$$\sin\theta \frac{\partial I_{\lambda}}{\partial x} + \cos\theta \frac{\partial I_{\lambda}}{\partial z} + k_{\lambda} I_{\lambda} = k_{\lambda} B_{\lambda}(T)$$
(8.6)

Boundary conditions to Eq. (8.6) depend on the kind of the boundary.

Diffuse opaque (crucible wall):

$$I_{\lambda}^{\text{out}}(\vec{r},\theta) = \rho_{d} \frac{q_{\lambda}^{\text{inc}}(\vec{r},z)}{\pi} + (1-\rho_{d})B_{\lambda}(T_{\text{cr}}), \qquad \vec{\Omega} \cdot \vec{\nu} > 0$$

$$q_{\lambda}^{\text{inc}}(r,z) = 2 \int_{\vec{\Omega}',\vec{\nu}'<0} |\vec{\Omega}' \cdot \nu'| I_{\lambda}(r',\theta') \sin \theta' d\theta' d\phi'$$
(8.7a)

where v is the inner unit normal to the boundary, ρ_d is the diffusive reflection coefficient, q_{λ}^{inc} is the incident radiant flux, $\nu' = (\sin \theta_{\nu} \cos \phi', \sin \theta_{\nu} \sin \phi', \cos \phi')$ θ_{ν}), $\phi' \in (0,\pi)$ and index "out" denotes radiation outgoing from the boundary. Besides, here and later, $\vec{r} = (r \cos \phi_r, r \sin \phi_r, z)$ and $\vec{r}' = (r \cos \phi'_r, r \sin \phi'_r, z)$. Note that angles ϕ_r and ϕ'_r in Eq. (8.7a) determine the position of the boundary points.

Specular opaque (free melt surface):

$$I_{\lambda}^{\text{out}}(\vec{r},\theta) = \rho_{\text{s}} I_{\lambda}(\vec{r}',\theta') + (1-\rho_{\text{s}}) B_{\lambda}(T_{\text{L}}), \qquad \vec{\Omega} \cdot \vec{\nu} > 0$$
(8.7b)

where ρ_s is the specular reflection coefficient and θ' is the polar angle of the direction $\vec{\Omega}'$ of a beam incident onto the boundary and reflected into the direction $\vec{\Omega}$ with polar angle θ . The relation between \vec{r} , θ and \vec{r}' , θ' is determined by the reflection law $\vec{\Omega}' = \vec{\Omega} - 2(\vec{\Omega} \cdot \vec{\nu})\vec{\nu}$.

Diffuse transparent (crystal side surface):

$$I_{\lambda_{1}}^{\text{out}}(\vec{r},\theta) = \rho_{d_{1}} \frac{q_{\lambda_{1}}^{\text{inc}}(\vec{r},z)}{\pi} + (1 - \rho_{d_{2}}) \frac{q_{\lambda_{2}}^{\text{inc}}(\vec{r},z)}{\pi}, \qquad \vec{\Omega} \cdot \vec{\nu} > 0$$

$$I_{\lambda_{2}}^{\text{out}}(\vec{r},\theta) = \rho_{d_{2}} \frac{q_{\lambda_{2}}^{\text{inc}}(\vec{r},z)}{\pi} + (1 - \rho_{d_{1}}) \frac{q_{\lambda_{1}}^{\text{inc}}(\vec{r},z)}{\pi}, \qquad \vec{\Omega} \cdot \vec{\nu} < 0$$
(8.7c)

where indices 1 and 2 denote the gas and crystal, respectively, and ρ_{d_1} and ρ_{d_2} are related as

$$1 - \rho_{d_1} = (1 - \rho_{d_2})n^2 \tag{8.8}$$

Specular transparent (crystal side surface):

$$I_{\lambda_{1}}^{\text{out}}(\vec{r},\theta) = \rho_{s_{1}}I_{\lambda_{1}}^{\text{inc}}(\vec{r},\theta') + (1-\rho_{s_{1}})\frac{I_{\lambda_{2}}^{\text{inc}}(\vec{r}'',\theta'')}{n^{2}}, \qquad \vec{\Omega} \cdot \vec{\nu} > 0$$

$$\frac{I_{\lambda_{2}}^{\text{out}}(\vec{r},\theta)}{n^{2}} = \rho_{s_{2}}\frac{I_{\lambda_{2}}^{\text{inc}}(\vec{r}',\theta')}{n^{2}}(1-\rho_{s_{2}})I_{\lambda_{1}}^{\text{inc}}(\vec{r}'',\theta''), \qquad \vec{\Omega} \cdot \vec{\nu} < 0$$
(8.7d)

where θ'' is the polar angle of direction $\vec{\Omega}''$ of a beam incident onto the boundary and refracted into the direction $\vec{\Omega}$ with polar angle θ . The directions $\vec{\Omega}''$ and $\vec{\Omega}$ are related by Snell's law, and \vec{r}'' and θ can be easily derived from \vec{r} and θ . The specular reflection coefficients in Eq. (8.7d) depend on angles and are determined by the Fresnel formulae. Note that $\rho_{s_2} = 0$, if $|\vec{\Omega} \cdot \vec{\nu}| > \cos \phi_B$, where ϕ_B is the critical angle of the total inner reflection.

For the solution of RTE a variant of the discrete transfer method adjusted to consideration of axisymmetric problems in complex domains is used. The method is based on the numerical integration of the RTE along the specified directions $\hat{\Omega} = (\sin \theta_i, 0, \cos \theta_i), \theta_i \in (0, \pi), j = 1, \dots, N_{\theta}$. The solution is sought in the domain $D_{r\phi z} = D_{rz} \otimes [0,\pi]$ of the variables r, ϕ, z where D_{rz} is the longitudinal section of an original (axisymmetric) domain in the coordinates r, z. The domain $D_{r\phi z}$ is subdivided into 3-dimensional cells (for different directions the subdivisions are generally different) using a subdivision of the plane domain. The 3D cells have the form $V_n = \{\vec{r} : (r, z) \in t_m, \phi \in (\phi_{i-1,j}, \phi_{i,j})\}$, where t_m is a planar cell, $\phi_{i,j} = \pi i / N_{\phi,j}$, $i = 1, ..., N_{\phi i}(N_{\phi,i})$ depends, generally, on a direction). The radiation intensity is given by its mean values at those faces of the cells that lie on the block boundaries. To relate intensities on the block boundaries a radiation beam is fired from a point at the center of a cell face on the boundary for each direction selected above. The path of the radiation beam is followed until it hits another boundary. Although, in general, the impingement point is not the central point of the boundary cell, it is assumed that the radiation intensities at these points are equal. These radiation intensities are either known from the boundary conditions or from results of calculation of previous iteration. Then, the path of the beam is followed back to the origin point, and (RTE) is integrated analytically along this path yielding the intensity at the origin point. In doing so, the medium temperature and radiative properties are assumed to be constant in each cell. This procedure repeats until the converged solution has been achieved. The incident heat flux at the boundary was approximated as follows:

$$q_{\rm inc} = \sum_{i=1}^{N_{\rm fb}} \sum_{m \in \Gamma_{k'}} w_i \sum_{\vec{\Omega}_i \cdot \vec{n}_m > 0} S_{mi} I_{mi}^{\rm inc}$$

where Γ_k is a set of faces, which can be superposed with the face k by the rotation about the symmetry axis, \vec{n}_m is an "averaged" outward normal to the face m, $S_{mi} = |\vec{\Omega}_i \cdot \vec{n}| S_m$, and S_m is an area of the face m. For calculating a divergence of the vector of radiative heat flux inside grid cells a special algorithm was developed. A more detailed description is given in Ref. [36].

Global Solution Procedure Global analysis was carried out as follows:

- (A) The radiation problem (Eqs. (8.6) and (8.7)) along with the heat-transfer problem in a crystal (Eqs. (8.3) and (8.4)) and convection and heat transfer in a melt are computed using the shape of the crystallization front from the previous step.
- (B) After convergence of both processes the new shape of the crystal/melt interface is calculated from Eq. (8.2d) and boundary conditions (Eqs. (8.1) and (8.7b)) are corrected.
- (C) Steps (A) and (B) are repeated until the steady state in Eq. (8.2d) is attained and boundary conditions (Eqs. (8.1) and (8.7b)) are satisfied.
- (D) Growth rate is calculated from Eq. (8.2c). If it does not coincide with the prescribed value, the new value of temperature or radiation intensity correction is found and steps (A)–(D) are repeated.

The described model was implemented in the CGSim software package [37].

8.3 An Example: Growth of Bismuth Germanate Crystals

The method described is efficient if the optical thickness is not too large. Examples of growth simulations of bismuth germanate crystals with eulithine and sillenite structure are presented below. ²Properties of the materials considered are listed in Table 8.1.

8.3.1 Czochralski Growth of Bi₄Ge₃O₁₂ Crystals

BGO crystals with eulithine structure (Bi₄Ge₁₂O₃) are widely used in many fields ranging from high-energy and nuclear physics to medical equipment (positron emission tomography). BGO crystals demonstrate the pronounced tendency toward faceting of the solidification front due to kinetic effects associated with growth in the different lattice directions. As a result, the crystal/melt interface can be composed of both rounded and faceted parts that significantly deteriorate the properties of crystals. Two strategies are commonly used. In the first, high temperature gradients

 $^{^2} Results of simulation of some other semitransparent crystal growth can be found in Refs. [38] (Bi₁₂SiO₂₀), [39] (Al₂O₃), and [40] (CsI(Na)).$

Property	Unit	Bi ₄ Ge ₁₂ O ₃	Bi ₁₂ GeO ₂₀
CRYSTAL			
Refraction index		2.15	2.36
Melting temperature	К	1323	1203
Thermal conductivity	W (m K) ₁	1.2	0.18
Heat of fusion	kJ (kg)_1	150	56
MELT			
Density	$\rm kg \ m^{-3}$	6650	8130
Specific heat	$J(kg K)^{-1}$	300	390
Thermal conductivity	$W (m K)^{-1}$	0.14	0.345
Thermal expansion coefficient	K ⁻¹	$7.6 imes 10^{-5}$	$1.2 imes 10^{-4}$
Kinematic viscosity	$\mathrm{m^2~s^{-1}}$	$6.2 imes 10^{-6}$	$2.09 imes 10^{-6}$

Table 8.1 Properties of Crystals and Their Melts.

are applied to suppress facet formation and to achieve the rounded or even flat crystal/melt interface, while in the second, in contrast, very low temperature gradients are maintained so that the solidification front would be fully faceted. The last technique was developed in the Institute of Inorganic Chemistry (Novosibirsk, Russia) and at present allows nearly perfect BGO crystals up to 140 mm in diameter and up to 400 mm in length to be obtained [18].

Nevertheless, at the initial stage of pulling these crystals, the crystal/melt interface turns out to be strongly deflected toward the melt and only partially faceted. As a result, the upper part of the boules contains many gas inclusions, and the quality of the crystal near the cone of shouldering turns out to be noticeably lower than that in its central and lower parts. Then, as the crystal is pulled, the deflection of the interface is diminished, the size of facets <112> increases and the interface becomes fully faceted. Correspondingly, the capture of gas inclusions ceases and the crystal grows completely transparent.

Simulation of heat transfer was performed for an experimental setup [14] that allows growing crystals up to 80 mm in diameter. A schematic diagram of the setup is presented in Fig. 8.1. The temperature distribution along the crucible wall was given and the meniscus shape near the triple point was neglected, the crystal cone angle was equal to 45°. The crystal side surface and free melt surface could be either diffusely or specularly reflective.

The diffuse reflection coefficient of the crystal side surface was taken equal to $\rho_{d_1}^{cr} = 0.18$ for radiation coming from the gas and $\rho_{d_2}^{cr} = 0.823$ for radiation coming from the crystal. The first value was obtained by averaging of the Fresnel reflection coefficient over an incident angle, while the second follows from relation between $\rho_{d_1}^{cr}$ and $\rho_{d_2}^{cr}$, Eq. (8.8). The specular reflection coefficient was calculated by the Fresnel formulae. The reflection coefficient of a free surface of a melt is unknown at present and was taken equal to $\rho_{d_1}^{cr}$ both for diffuse and specular reflection that can be justified by a small difference between refraction index of solid and liquid phases. The latter, along with opacity of the melt, permits consideration of the



Fig. 8.1 Scheme of the growth setup: 1 - crystal, 2 - melt, 3 - crucible.

crystal/melt interface as black. Note also that the value of $\rho_{d_1}^{cr}$ correlates with the emissivity of a melt used in Ref. [32]. The spectral absorptivity of the crystal taken from [41] was approximated by a three-band model. For wavelengths beyond 6 µm the crystal was assumed opaque ($k = \infty$), for the range 4 < λ < 6 µm: k = 95.5 m⁻¹ and for λ < 4 µm: k = 3 m⁻¹. The emissivity of the diffusely reflecting crucible wall was taken as 0.1.

For the simulations, the diameters of crystal and crucible were equal to 77 and 100 mm, and the height of crucible and the initial height of a melt were equal to 250 and 160 mm, respectively. The dynamic viscosity and thermal conductivity of a melt (Table 8.1) lead to a rather high Prandtl number of 87. Since a simulation performed earlier [42] showed that experimental and computed values of the pulling rate agreed at significantly lower values of the Prandtl number, it was assumed the Pr = 20. The actual operational parameters were applied. The crucible was stationary; the rotational velocity of the crystal was equal to 15 rpm and the pulling rate was 0.5 mm h^{-1} . Due to the decrease of the melt level, the growth rate is 1.5 mm h^{-1} . The crucible temperature T_{ex} was obtained by interpolation of thermocouple measurements at 15 points. Five crystal lengths (to seed) 33, 50, 84, 119 and 197 mm, covering the whole growth process from shouldering to the stage when the crystal practically fills the crucible were considered. The corresponding heights of the melt were equal to 152, 141, 118, 96 and 51 mm, respectively.

Flat Crystal/Melt Interface The basic peculiarities of heat transfer in LTG Cz growth of semitransparent crystals were first studied for the case of the flat crystallization front. It is obvious that in this case the condition (Eq. (8.2d)) can be satisfied only in the average. The computed isotherms and streamlines in the melt are presented in Fig. 8.2.

It is seen that due to crystal rotation the so-called biaxial flow type arises in the melt. A rotationally driven vortex dominates under the crystal/melt interface, while a flow driven by the buoyancy force is confined to the lower part of a crucible. Even





Fig. 8.2 Temperature distributions (left) and flow patterns (right) in the melt for the different growth stages in the case of a flat crystallization front. Contour spacings for temperature are equal to (from the left to right) 0.67, 0.92, 0.67, 0.67 and 0.31 K, respectively.

just after completing shouldering the thermal convective flow is not able to reach the crystallization front since the thermal gradients in the melt are too small. As the melt depth decreases the vortex induced by the buoyancy force becomes smaller and at the end of the process only the upward flow at the center caused by crystal rotation occurs. Thus, no qualitative rebuilding of the flow structure leading to interface inversion takes place. These results are valid both for diffuse and specular reflection of the crystal side surface: the distribution of heat fluxes along the interface on the side of the melt does not depend significantly on the kind of reflection.



Fig. 8.3 Radiative heat density fluxes at the crystallization front for different growth stages. Solid lines – specular reflection and dashed ones – diffuse reflection. Numbers 1–3, 5 correspond to the crystal lengths 33, 50, 89 and 197 mm.

A different situation is observed in the solid phase. Figure 8.3 shows that owing to specular reflection the distribution of radiation heat flux at the crystal/melt interface can be extremely nonuniform, depending on the crystal length.

For the short crystal, the radiation flux at the center of the crystal/melt interface exceeds that at the periphery by a factor of six. At the same time, the distribution of radiation heat flux for the crystal of length 197 mm is nearly uniform and similar to the flux obtained when the crystal surface is diffuse. This effect is mainly related to the specular reflection at the conical part of the crystal (its shoulder) while the contributions of the cylindrical part and the free surface of the melt are less significant. Therefore, it is clear why the effect of the specular reflection depends on the crystal length. The shorter the crystal, the closer is the conical part of the crystal to the crystal to the crystal/melt interface and the more nonuniform is the radiation heat-flux distribution.

The cause of such behavior can be explained as follows. First, the specular reflection coefficient is strongly dependent on the incidence angle and for BGO crystals is varied more than a factor of six from 0.15 to 1 in the narrow range from 26 to 28 degrees. Furthermore, from general geometric considerations it follows that in the case of specular reflection the incident radiation flux at the center of the crystal/melt interface consists of the rays that are reflected from the crystal side surface mainly under small incidence angle. By contrast, the incident radiation flux at the periphery of the interface contains a considerable fraction of the rays undergoing total inner reflection. Therefore, the incident radiation flux will be a minimum at the center of the interface and maximum at its periphery, and conversely, the net radiation flux will have the peak at the center and the minimum at the periphery of the interface. In the case of diffuse reflection neither of these factors works. If we assume that the specular reflection coefficient is constant, then not only is the nonuniformity

in the radiation heat-flux distribution diminished, but the maximum of the net radiation flux is moved to the periphery of the crystallization front.

Evolution of the Crystal/Melt Interface Figure 8.4 shows the evolution of the crystal/melt interface and the temperature field in the crystal as it is pulled for diffuse and specular crystal side surfaces.

In the case of diffuse reflection the deflection of the crystallization front toward the melt during the whole process is small and does not exceed 7 mm. These results are similar to those obtained earlier in the case of dominating rotationally driven convection [7–9]. However, they fail to reproduce the observed shapes of the crystal/melt interface in actual LTG Cz growth. Thus, in the case of a diffusely reflective crystal side surface the role of internal radiation is reduced mainly to the increase of the heat removal from the interface, while the formation of the strongly deflected interface toward the melt at the initial stage of the growth and its variations with crystal length is related directly to the specular reflection at the conical part of the crystal side surface.

Temperature Fields The temperature fields in the crystal shown in Fig. 8.4 are characterized by a rather strong deformation of isotherms. Even for diffuse reflection the curvature of isotherm is higher than reported in Refs. [7-9, 33]. This difference is explained by two factors. First, in contrast to Refs. [7, 8, 33] where the crystal side surface was assumed to be opaque, in this study it was considered transparent. Secondly, the authors of Ref. [9] restricted themselves to the consideration of radiation transfer in a grey approximation with sufficiently large absorption coefficient in the solid phase (optical thickness of the order of unity). We have used the three-band model taking into account the radiation transfer in the spectral ranges where the crystal is transparent, semitransparent and opaque. Figure 8.4 shows that the effect of specular reflection on the temperature field is two-fold. On the one hand, the temperature gradients decrease. On the other hand, the distortion of isotherms becomes more significant. Moreover, in the upper part of the crystal near the shoulder the isotherms take the distinct "convex-concave" shape. In the range of wavelengths where the crystal is opaque the crystal is cooled from the side surface. Therefore, according to the boundary condition (4d), isotherms near the crystal side surface have to be deflected down because the upper part of the crystal is hotter than the crucible. This is true both for specular and diffuse surfaces. On the other hand, in the range of semitransparency the crystal is cooled from the volume. Moreover, as was shown in [43], in the case of specular reflection the radiative heat exchange between crystal and environment is mainly concentrated near the centerline. Isotherms in this region have to be deflected down. The combined action of these factors results in an unusual temperature distribution in the crystal. Note that this phenomenon arises in spite of the very small absorption of radiation in Bi₄Ge₃O₁₂ crystals.

Effect of Perturbations of the Side Surface of the Crystal Thus far it was assumed that the side surface of crystal consists of conical and circular cylindrical parts. In this



Fig. 8.4 Evolution of the crystallization front and temperature field in a crystal for the cases of diifuse (left) and specular (right) reflection. Contour spacing for temperature is equal to 1 K.

model specular reflection at the conical surface results in significant nonuniformity in the radiation heat-flux distribution near the crystal/melt interface, while the role of specular reflection at the cylindrical side surface is reduced mainly due to the light-guided axial radiation flux [5], which conserves this nonuniformity at some moderate level. Yet, in practice, the shape of real oxide crystals pulled from the melt is appreciably different from a circular cylinder or a cone that has to lead to the scattering of radiation at the crystal surface and, consequently, to the smoothing of the radiation heat-flux distribution at the crystal/melt interface. This phenomenon could be related basically to the scattering at the cylindrical part of the crystal side surface because even small deflections from a circular cylinder can result in significant weakening of the light-guided radiation heat flux, if the crystal is long enough, while the effect of small perturbations of a conical surface does not depend on the crystal length and consequently, has to be insignificant. Simulations performed in Ref. [44] confirmed this suggestion.

In practice, the deflections of the crystal side surface from a circular cylinder or a cone generally lead to three-dimensional distortions of the crystal shape. However, to keep the problem tractable, we have considered the radial perturbations of the crystal side surface $R = R_0 + \varepsilon_1 \sin(2\pi n/L)z$ and $z = (R_0 - R)\cot \alpha + L - (\varepsilon_2/\sin d \sin 2\pi n/R/R_0)$ for the cylindrical and conical parts of the crystal side surface, respectively. Here, R_0 and L are the radius and length of the cylindrical part of an ideal crystal, α is half of a cone angle, and $\varepsilon_{1,2}$ are perturbation amplitudes. We also assume a flat crystallization front.

Results of computations of the radiation heat-flux distribution at the crystal/melt interface for crystal length of 200 mm are shown in Fig. 8.5.

As expected, the perturbations of a specular cylindrical surface lead to significant smoothing of the radiation heat-flux distribution at the interface, while the effect of perturbations of a specular conical surface turns out to be insignificant. For



Fig. 8.5 Effect of perturbation of only cylindrical (left) or only conical (right) parts of the crystal side surface on the radiation heat-flux distribution at the crystal/melt interface. The unperturbed part of the side

surface is specularly reflecting, while the perturbed one is either specular with perturbation parameters indicated in figures or diffusely reflecting with $\epsilon_{1,2} = 0$.

shorter crystals, the impact of the deviations from the ideal cylindrical side surface is diminished, while the nonuniformity in the radiation heat-flux distribution increases since the distance between the shoulder and crystal/melt interface is shortened. To elucidate this issue we have performed computations wherein the perturbed specular side surface was replaced by the diffusely reflecting "ideal" one (with zero amplitude) (Fig. 8.5).

It is seen that the perturbed specular and the diffusely reflecting ideal cylindrical surfaces exert a similar influence on the radiation heat-flux distribution at the interface, while at the shoulder surface the diffuse reflection in contrast to the specular one (in both the perturbed and unperturbed cases) leads to strong smoothing of the radiation heat-flux distribution. Thus, in simulating real oxide growth we can consider the cylindrical part of the crystal side surface as diffusely reflecting. This is valid both for long and short crystals because in the latter case the nonuniformity in the radiation heat-flux distribution at the interface is determined principally by reflection at the shoulder surface, while the influence of the cylindrical surface is not essential. At the same time, the shoulder surface of oxide crystals has to be treated as a specular one, at least for the short crystals. Although we have considered only long-wave perturbations of the side surface, there are serious grounds to believe that these conclusions remain valid for the short-wave perturbations as well.

8.3.2 Czochralski Growth of Bi₁₂GeO₂₀ Crystals

BGO crystals with eulithine structure have a very small absorption coefficient in the wavelength band where the main part of the blackbody radiation is concentrated. In contrast to this, the absorption coefficient of sillenite crystals reaches 0.3-0.4 cm⁻¹ in the wavelength range from 2 to $6\,\mu$ m. One can expect that absorption and emission of radiation by a crystal appreciably influence the heat-transfer process. Two growth processes were simulated. The first was performed in the setup used for the growth of BGO eulithine crystals, while the second was carried out in the Laboratory of Crystal Growth of the Autonomic University of Madrid. Results of simulation are described in Refs. [38, 45], respectively. Here, we focus on the second process.

In contrast to simulation of $Bi_4Ge_3O_{12}$ crystals, wherein the temperature distribution along a crucible wall was known from experiment, in the present case the global modeling of heat exchange inside the whole growth setup was undertaken. A specific feature of the growth setup is that there is a gap between the crucible and the afterheater through which the direct exchange of heat radiation between the crystal and the heater takes place.

To simulate this feature we used two approaches. In the first we replaced the gap between the crucible and the afterheater by a black (nonreflective) boundary with an appropriate temperature distribution, taken from the computation at the first stage of simulation, which practically coincides with the temperature of the gas. So, in this case the computational domain did not include the heater at all



Fig. 8.6 Domains used in calculation of radiative heat transfer in a crystal and the gap between the crystal, the crucible, the afterheater and the heater. Left – the gap between the crucible and the afterheater is replaced by a black (radiant, nonreflective) surface. Right – the gap is transparent for radiation exchange between the crystal and the heater.

(Fig. 8.6(a)). In the second approach the computational domain included additionally a part of the heater (Fig. 8.6(b)) and radiation passing through the gap was calculated directly in the course of solution of the radiant transport problem. The temperature of the black boundary involved in the domain B was also equal to that of the gas. These domains were denoted as A and B, respectively. The radiative properties of materials and boundaries appearing in the radiation problem are given in Ref. [38]. The melt was opaque, the crystallization front was black. Spectral absorption of the crystal, calculated from the infrared transmission spectra given in Ref. [46], was approximated by the three-band model: the absorption coefficient was taken equal to 0.482 cm^{-1} for wavelengths $\lambda < 6.89 \,\mu\text{m}$, 5.9834 cm⁻¹ for the range $6.89 < \lambda < 9.16 \,\mu\text{m}$ and infinity beyond 9.16 μm .

The temperature distribution over the crucible wall and the afterheater obtained at the first stage coincided satisfactorily with the measured values at the reference points, which demonstrated a validity of the developed model of global heat transfer. Simulation at the second stage showed that, as in the case of LTG growth of Bi₄Ge₃O₁₂ crystals, convection in the melt is forced and a rotationally driven vortex occupies the whole crucible due to the high rotation rate of the crystal, the rather modest temperature gradients along the crucible wall and the relatively small height of the melt. For a diffusely reflecting crystal surface the temperature fields inside the crystal turned out to be practically identical for both domains A and B. As would be expected, in this case the crystal/melt interface was slightly curved and convex toward the melt (per 0.5 mm), while the temperature decreased monotonically from the crystallization front to the shoulder without appreciable variations in the radial direction. Thus, the picture was similar to that obtained for BGO eulithine crystal and, probably, is typical for all cases when the crystal side surface is diffusely reflecting and convection is controlled by crystal rotation.

However, the results changed drastically when the crystal surface (namely, its conical part) was assumed to be specularly reflecting (Fig. 8.7(a)). It is seen that, firstly, specular reflection causes the crystallization front to deflect deeper toward the melt (up to 7 mm). Secondly, in both cases the distortion of isotherms becomes much more significant not only as compared with the previous case of diffuse reflection, but in relation to a Bi₄Ge₃O₁₂ crystal with a specular surface. The maximum of the distortion of the temperature field takes place near the axis in the upper part of the crystal where a thin cool region appears. As a result, the temperature distribution in the radial direction becomes nonmonotonic (Fig. 8.7(b)). This effect is especially distinct in strict consideration of the radiation exchange between the crystal and the heater (computational domain B). In this case, the temperature field turns out to be nonmonotonic also along the crystal axis and isotherms near the axis take the fusiform (cigar) shape. This phenomenon is explained probably by a greater absorption and smaller conductivity of sillenite crystals as compared with the eulithine one. A small thermal conductivity cannot smooth the irregularities of the temperature fields caused by radiative heat loss. To verify this explanation we have performed computations with thermal conductivity as high as 0.018 W (cm K)⁻¹ and with absorption coefficient in the first wavelength band as low as 0.03 cm^{-1} . The shape of the crystal/melt interface was fixed.



Fig. 8.7 Temperature fields in the sillenite crystal in the case of specular reflection at the shoulder surface. (Left half) Temperature isolines for calculation domains A (left) and B (right). (Right half) Radial temperature distributions for several values of the *z*-coordinate. Solid symbols correspond to calculations performed for domain A and open symbols for domain B.



Fig. 8.8 Effect of absorption coefficient α in the first wavelength band and thermal conductivity λ on the temperature field in crystal. (left) $\alpha=0.482\,cm^{-1},\ \lambda=0.0018\,W$ (cm K)⁻¹; (b) $\alpha=0.03\,cm^{-1},\ \lambda=0.0018\,W$ (cm K)⁻¹; (c) $\alpha=0.03\,cm^{-1},\ \lambda=0.018\,W$ (cm K)⁻¹.

Results (Fig. 8.8) confirm the explanation given above and show that in transparent and sufficiently thermally conductive crystals a cool region along the axis is not formed. Naturally, this is also valid for opaque crystals. It is necessary to note that an increase of the crystal length does not lead to essential changes in the temperature distribution. Thus, this phenomenon is inherent to the present growth process and is directly related to the specular reflection at the shoulder surface because in the case of diffuse reflection the temperature field inside the crystal is monotone and the cool region is not formed.

The temperature fields in the case of specular reflection correlate surprisingly well with the dark core observed in the center of the grown sillenite crystals. The peculiarities of the temperature field near the axis in Fig. 8.7 can be responsible for the appearance of corresponding elevated thermal stresses revealed in Ref. [47]. In sillenite crystals grown by LTG technology [45] the dark core was absent and distortion of isotherms was appreciably less.

8.3.3

Effect of Internal Radiation on Facet Formation

In considering the effect of internal radiation in Czochralski growth of oxides the crystal/melt interface is commonly assumed rounded. Yet, many oxide crystals

demonstrate a pronounced tendency toward faceting of the solidification front. Simulation of the faceted interface is a rather difficult task, [48-50]. In these papers, however, only the Bridgman process was considered. Besides, internal radiation transport was treated using either the Rosseland diffusion approximation [49] or the P1-approximation [50] that is valid for the case of rather large absorption coefficients. Accurate treatment of volume radiation transfer in the case of a faceting interface was undertaken in Ref. [44], results of which are described in this section. For computation of faceting a different approach from that used in Refs. [48-50] has been developed that is a numerical expansion of the analytical approach suggested in [51]. As in [49-51], a small deflection of the facet from a close-packed plane is ignored. In this case the position of the facet is determined by a single parameter, which is the maximum supercooling ΔT_{max} at the point of origin of a new layer, while the temperature in the other points of the face has to be calculated. On the rounded part of the interface the boundary conditions (Eqs. (8.2a) and (8.2b)) were used. In axisymmetric geometry, only interfaces with a horizontal facet can be considered. Consideration of oblique facets requires a three-dimensional simulation. On the other hand, there are situations when several inclined facets of the same type can be formed at the interface. In this case some elements of rotational symmetry are retained and can be used in simulation. Therefore, in order to treat cases similar to those in Ref. [44] a set of oblique facets was replaced by a sole "conical" facet, which is a conical surface with a cone angle depending on the inclination of the facets and a lateral size depending on the maximum supercooling. Other aspects of the model were the same as described in the previous sections.

Two cases corresponding to small and large convexity of the rounded crystal/melt interface toward the melt were studied in detail. The first can be achieved when the cylindrical side surface is diffuse, and the second, when it is specularly reflecting. Computations showed that the relation between the facet radius and supercooling is very close to a well-known square root law in the first case and it is strongly different in the second. Thus, in the case of large convexity of the rounded interface the effect of internal radiation on the facet formation turns out to be very significant. This is clearly seen in Fig. 8.9 where the rather unusual temperature fields in the crystal, which were not observed in earlier simulations of similar problems, are demonstrated.

The appearance of the local maximum temperature inside the crystal is explained by heating the volume of the crystal above the facet (whose temperature is $T_m - \Delta T$) by the radiation with higher temperature T_m emitted by the rough part of the interface.

Figure 8.10 demonstrates the crystal/melt interface with a "conical" facet imitating a system consisting of three oblique facets <112>. In this case the point where the condition of maximal supercooling should be applied is not known a priori and has to be found during the iterations. It is interesting to note that the point of maximum supercooling is located at a distance of order 5-6 mm from the axis and is not shifted with supercooling.

Other details of the statement of the problem and numerical approach along with properties of material and boundaries can be found in Ref. [38].



Fig. 8.9 Temperature field in a crystal near the crystal/melt interface for $\Delta T_{max} = 1.2$ K (left) and temperature distributions in the crystal along the axis (right) for the different supercoolings: $1 - \Delta T_{max} = 0$; 2 - 0.45; 3 - 0.8; 4 - 1.2; 5 - 1.6; 6 - 1.8 K.



Fig. 8.10 Temperature field in a crystal for $\Delta T_{max} = 1.2$ K (left) and the shapes of the crystal/melt interface (right) in the case of a "conical" facet at the crystal/melt interface. Curves: $1 - \Delta T_{max} = 0$; 2 - 0.45; 3 - 0.8; 4 - 1.2; 5 - 1.6 K.

8.4 Conclusions

Numerical simulation of the melt growth of oxides and other semitransparent crystals is considered. Specific features of these crystals (internal radiative heat transfer, specular reflection from the crystal side, low thermal conductivity of both the crystal and the melt, the tendency to faceting of the crystallization front) and their effect on the growth process are discussed. An efficient numerical method is described and applied to the study of bismuth germanate crystal growth from the melt.

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Part III Compound Semiconductors

Recent Progress in GaAs Growth Technologies at FREIBERGER

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9.1 Introduction

9

During the last decade GaAs-based micro- and optoelectronics has developed from a military niche to a global commercial player that does not replace but supplement silicon-based devices. This development has been due to some unique physical properties of compound semiconductors allowing for superior functionality of devices and the progress made in the production of single crystals and wafers/substrates, which has now reached maturity.

Typically, GaAs device manufacturers look for the lowest cost wafers that will meet their requirements. The device must work reproducibly and reliably not deteriorating with age. Therefore, high-quality substrates with device-specific properties are required without any substrate-related problems that could adversely affect the performance of the device. To fulfill these demands the structural quality and electrical homogeneity must be controlled including control and stability of (exand intrinsic) defect structure and defect density, mechanical strength, flatness, surface finish, etc. Thus, the wafer producer is permanently confronted with the challenge to introduce new and optimize running technologies and to continuously develop the scientific background of the technologies.

The driving force for this development is illustrated by Fig. 9.1 showing the sales volume of FREIBERGER by area and revenue. High annual growth rates, which initiated extensive investments to increase crystal and wafer production capacities at the end of the last century, were followed by a sharp decline of wafer demand (Fig. 9.1) in 2001/2002. The subsequent recovery of the market was accompanied by the shift from LEC (liquid-encapsulated Czochralski)-grown GaAs for MESFETs (metal-semiconductor field effect transistor) to low-epd (etch pit density) wafers grown by low-temperature gradient methods as LEVGF (liquid-encapsulated vertical gradient freeze, in the following VGF) for epitaxy-based devices like HEMTs (high electron mobility transistor) and HBTs (heterojunction bipolar transistor). The comparison of Figs. 9.1 (above) and (below) shows clearly the continuous decline of wafer prices. As a result, in the last few years, research and development activities have been mainly focused on cost reduction in crystal growth and wafering.





Fig. 9.1 Sales volume of FREIBERGER by area (above) and revenue (below).

FREIBERGER follows two main strategies to reduce production costs: yield increase of technological steps and reduction of process costs. In the following, recent developments at FREIBERGER in the field of crystal growth with special emphasis on device-related properties of the crystal will be outlined.

9.2 Properties of GaAs

Welker [1–3] was the first who recognized that the already known III-V compounds could compete with and/or supplement silicon and germanium. The first I–V characteristic of a diode rectifier on a GaAs crystal with point contacts was published in his paper [3]. Therefore, this paper can be regarded as the "birth" of GaAs-based electronics (see [4, 5] as historical reviews). These pioneering publications were followed by efforts to synthesize these compounds and grow single crystals. The obtained materials were used for detailed investigations of electronic and structural properties. Some of the properties reviewed in [6] are briefly summarized in the following.

With the exception of the III-nitrides, the remaining III-V compounds crystallize in the cubic zincblende structure with the lattice constant of undoped GaAs being a = 0.5653 nm at T = 300 K. In this structure each atom is tetragonally coordinated. The [111] direction of the zincblende structure is a polar axis, i.e. this direction and the counter direction are not equivalent. These structures are piezoelectric, resulting in electric fields if the crystal is strained. This is of great importance also for device design of transistors and diodes.



Fig. 9.2 Band structure of GaAs.

In contrast to silicon, GaAs and the other III-Vs, except for GaP, are direct semiconductors, i.e. the conduction-band minimum and the valence-band maximum are at the same *k*-vector, the Γ -point (Fig. 9.2). This is essential for an effective conversion of electrical energy to optical energy and vice versa. The bandgap of GaAs is 1.424 eV at 300 K, which is significantly larger than that of silicon ($E_G = 1.12 \text{ eV}$ at 300 K) and allows high-temperature and radiation-tolerant electronics, optical and mechanical sensors, and high-voltage rectifiers. Due to a larger curvature at the minimum of the conduction band GaAs has a lower effective electron mass ($m_{e\Gamma} = 0.063 m_0, m_0 - \text{rest}$ mass of electrons) resulting in a higher electron mobility – $\mu = 8500 \text{ cm}^2/\text{V}$ s versus 1450 cm²/V s, respectively – and drift velocity of carriers compared to silicon (see Fig. 9.3). This allows devices working at higher frequencies.

GaAs and other III-V compounds can rather easily be doped to get p- and n-type conductivity in the range of 10^{-3} to 10^{-1} Ω cm at room temperature (semi-conducting SC GaAs), which is necessary for optoelectronic devices. Elements of the second group of the periodic table of elements act as acceptors (Zn, C), group VI elements (Te, S) as donors. Group IV elements (Si) show an amphoteric behavior. Furthermore, GaAs with medium resistivity and semi-insulating (SI) behavior characterized by an electrical resistivity around $10^3 \Omega$ cm and above $10^6 \Omega$ cm can be obtained by pinning the Fermi level at the effective oxygen level and the native midgap double donor EL2, respectively. Details will be discussed in Section 9.5.1. This allows devices to be manufactured directly on or in the substrate without isolation of the devices from each other. Therefore, the number of technological steps in device manufacturing has been reduced. This is one of the reasons why the more expensive GaAs can compete with silicon at least for rf (radio frequency) electronics. Metallic and Schottky contacts can also be easily produced.



Fig. 9.3 Drift velocity of compound semiconductors vs. silicon.

The mutual solid solubility of the III-Vs is a further property of fundamental importance of this class of compounds. Alloying results in ternary or quaternary (and higher) compounds with electronic and other physical properties that roughly obey Vegard's rule. This makes heterojunctions possible with tailored band structure for bipolar opto- and microelectronic devices. In layer structures the lattice mismatch can be controlled by appropriate alloying to reduce defect generation or to determine the strain in the layers, if required.

The thermal conductivity of GaAs ($\lambda_{GaAs} = 0.46$ W/cm K at 300 K) is lower than that of silicon ($\lambda_{Si} = 1.41$ W/cm K at 300 K). Therefore, heat dissipation and extraction from operating devices is less effective and limits the growth rate in crystal growth from the melt.

The critical shear stress of GaAs near the melting temperature is significantly lower than that of silicon. Therefore, thermoplastic relaxation of thermally induced stress by generation and multiplication of dislocations during crystal growth and subsequent thermal treatment is more important. So, it is impossible to grow large-diameter GaAs single crystals free of dislocations, in contrast to silicon where growth of dislocation-free material is common practice. Doping with appropriate elements can reduce thermoplastic relaxation [7] and, if compatible with the required electrical characteristics, this property can be used to grow low-dislocation GaAs crystals. An example is silicon doping of GaAs. Details of n-doping of GaAs will be discussed in Section 9.5.3.

GaAs is a brittle material with distinct {110} cleavage planes being an important property for laser fabrication. Fracture toughness of GaAs as a measure of resistance to crack propagation is lower than that of silicon: $K_{\rm Ic} = 0.458$ MPa m^{1/2} versus 0.90 MPa m^{1/2}. Therefore, breakage is also a critical yield influencing factor in mechanical wafering and device manufacturing.

Semi-insulating GaAs is mainly used for broadband amplifiers and switches at high frequencies with low power consumption (MESFET, HBT, HEMT) in mobile

9.3 Growth of Large-Diameter GaAs Single Crystals 235

telecommunication, satellite TV and radar systems. The main application fields of semiconducting GaAs are optoelectronic devices like lasers (edge-emitting and vertical-cavity surface-emitting lasers) and high-brightness light-emitting diodes in the visible and near-IR spectral range, IR detectors and solar cells. The FREIBERGER Si-doped VGF and Te-doped LEC material is used for these optoelectronic applications.

9.3 Growth of Large-Diameter GaAs Single Crystals

9.3.1 A Short Historical Survey

For the growth of large-diameter GaAs single crystals two methods are of commercial interest: the pulling of crystals from a melt in a crucible by the Czochralski technique using liquid boron oxide encapsulation (LEC) and the directional solidification of the melt in a vertically mounted crucible according to the Bridgman method. The latter method is usually subdivided into the vertical Bridgman (VB) and the vertical gradient freezing method (VGF). In the VB method, the charge in the crucible is solidified upward by moving either the crucible in a fixed heater system or vice versa. For VGF, the temperature field is moved along the fixed charge by controlling the power of several furnace heaters. Usually, in both methods a liquid boron oxide encapsulation is used.

The directional solidification in a horizontal boat used for many years to grow doped GaAs single crystals lost its importance because of the D-shaped cross section, which is inappropriate for device manufacturing.

Looking back, the Czochralski method was first applied successfully to grow GaAs single crystals by Gremmelmeier [8] in a hot-wall equipment. This consisted of a sealed quartz ampoule with a charged crucible and a seed crystal mounted on a pulling rod that could be moved from outside by a magnetic levitation system. To avoid condensation of arsenic evaporated from the uncovered melt and the grown crystal and to establish an arsenic atmosphere, the ampoule was sealed and arranged in a resistance furnace and heated to an appropriate temperature. A separate rf heater was used for melting the charge in the crucible. Later, this method was improved by Steinemann and Zimmerli [9] who obtained the first dislocation-free GaAs single crystals up to 15 mm in diameter.

The application of a liquid boron oxide coverage for the GaAs charge to suppress evaporation of As was introduced by Mullin *et al.* [10] in 1964. This liquid-encapsulation Czochralski (LEC) process has since been developed to a reproducible and reliable production technology for single crystals with a circular cross section well suited for wafer production. Due to the relatively high thermal stress level in the grown crystals and the thermoplastic relaxation, the dislocation density of LEC crystals is rather high. This resulted in the development of the vapor-pressure-controlled (VCz) [11] and the fully encapsulated Czochralski



Fig. 9.4 Evolution of the GaAs wafer diameter.

method (FEC) [12]. In VCz growth, in addition to a liquid boron oxide encapsulant, an As partial pressure is established in the growth atmosphere that suppresses decomposition of solid GaAs emerging from the encapsulant. As a result, temperature gradients in the crystal could be reduced leading to a lower dislocation density compared to LEC. The same philosophy was applied in FEC growth.

The Bridgman method first applied by Beljackaja and Grishina for III-V compounds [13] was rediscovered by Gault *et al.* [14] in 1986 and Hoshikawa *et al.* [15] in 1989. As the nonlinearities of the temperature field in the grown crystals are significantly lower than in the LEC method, low-dislocation-density crystals can be grown by this method.

The development of the diameter of GaAs single crystals over time is represented in Fig. 9.4.

9.3.2

Phase Diagram

Synthesis, crystal growth and heat treatment of GaAs take place near the thermodynamical equilibrium. Therefore, some comments will be made regarding the constitutional diagram of Ga-As and its relation to these processes. The overview of the phase diagram is represented in Fig. 9.5(a) [16] with an enlarged part around the compound GaAs in Fig. 9.5(b) [17]. Accordingly, GaAs is a congruently melting compound dividing the phase diagram into two eutectic partial systems with eutectics close to pure arsenic and gallium and eutectic temperatures at about 810 °C and 30 °C, respectively [16]. On the basis of crystal growth experiments using Asand Ga-rich melts and an analysis of the grown crystals it was concluded that the congruent melting point (cmp) is situated on the slightly arsenic-rich side. GaAs crystal growth should be alternatively possible from a Ga- or As-rich melt, but growth from an As-rich melt is preferred. This is due to a better control of the EL2 defect [18], a reduced probability of twin formation [19], and a better homogeneity of electrical properties [20].



Fig. 9.5 (a) Phase diagram of Ga-As. (b) Homogeneity range of GaAs.

The equilibrium partial pressures of As₄- and As₂-species along the solidus lines of GaAs are represented in Fig. 9.6. The upper branches belong to the As-rich compound. Obviously, GaAs and some other III-V compounds decompose into elements with the vapor pressure of the group V element being several orders of magnitude higher than that of group III elements. The As-equilibrium pressure at the congruent melting point of GaAs amounts to about 2 bar [21]. With increasing deviation from stoichiometric GaAs the As partial pressure increases. So, special measures have to be taken to avoid As losses and As bubble formation in the melt during synthesis and crystal growth.

Solid GaAs possesses a narrow homogeneity range. This was concluded from experiments and thermochemical approaches. The extension and the temperature dependence of the homogeneity range are not well known and are therefore controversially discussed in the literature (see [16] for an assessment). This is mainly due to the lack of sensitivity of the chemical and physical methods to determine the deviation from stoichiometry. Therefore, a thermodynamical approach was used [17] to calculate the homogeneity range of GaAs depicted in



Fig. 9.6 Equilibrium partial pressures of As and Ga over GaAs.

Fig. 9.5(b). A simplified model containing the species Ga_{Ga}, As_{As}, As_{Ga}, V_{Ga}, As_V, As_I and V_I (V means a vacant site, I an interstitial) has been assumed. The main features that are at least qualitatively in agreement with experimental results are: The homogeneity range is asymmetric with regard to the stoichiometric GaAs with a larger extension on the As-rich part of the phase diagram. Starting from the congruently melting compound the homogeneity range first broadens up to a maximum solid solubility of about $[\Delta As] \approx 1 \times 10^{19} \text{ cm}^{-3}$ at 1150 °C and then decreases with decreasing temperature. As a consequence, As precipitates will be formed as soon as the (retrograde) solidus line is reached during cooling of off-stoichiometric GaAs.

According to Fig. 9.5(b) the preparation of off-stoichiometric GaAs with a defined deviation from stochiometry would require control of the As content of the melt and the As partial pressure in the working atmosphere. This was done in experimental hot-wall setups, but it is rather complicated and has been replaced by a liquid boron oxide encapsulation of the melt and an inert overpressure. Precise adjustment of the As/Ga ratio in the melt is difficult under these conditions. This is due to the fact that Ga and As can be oxidized and incorporated into liquid boron oxide encapsulant – depending on the O potential in the system [22] and the method used to synthesize GaAs and to grow crystals. Because of the higher affinity of Ga for O and the greater vapor pressure of Ga oxides over liquid boron oxide compared to As and As oxides, respectively, there is a higher loss of Ga from the GaAs melt. This leads to a continuously increasing As excess in the melt and a corresponding increase of the boron content in the melt. Therefore, instead of an active stoichiometry control of solid GaAs by melt composition, synthesis and/or growth have been empirically optimized. The parameters are now held constant to ensure a high reproducibility and reliability of the products.

Finally, as shown in Fig. 9.5(b), the deviation from stoichiometry can be influenced to a limited extent by boule annealing after crystal growth under



Fig. 9.7 GaAs single-crystal growth methods (VCz, LEC, VB, VGF).

mass-conserving conditions. For this, the as-grown material is at first heated into the single phase region for dissolving the As precipitates and then cooled to control the amount and distribution of reprecipitated As. In this way, the concentration and distribution of native defects is influenced.

9.3.3 State-of-the-Art

Figure 9.7 shows a scheme of methods used for commercial GaAs single-crystal growth. They all have in common a water-cooled pressure vessel for pressures up to about 100 bar if compounding of GaAs from the constituents is done prior to growth in the same equipment. It houses a pretreated reusable charged pBN crucible that is surrounded by the furnace including heat insulation. For the Bridgman method, a furnace outside the (hot wall) pressure vessel has also been described in [23]. The pullers are equipped with a fully computerized process control system that includes a gas-management system allowing control of total and partial gas pressures. This is necessary, e.g., for carbon control (see Section 9.5.2). It is apparent that the complexity of design reduces from VCz to VGF. Whereas the LEC/VCz method requires two pulling rods with feedthroughs and control systems for translation and rotation of crucible and seed/crystal, only one or even no feedthrough is necessary for VB or VGF. In addition, the crystal diameter in LEC/VCz growth is controlled by meniscus stability. This implies a closed-loop control system based on continuous observation of the apparent crystal weight to follow the reference trajectory of the diameter e.g. [24-28]. Usually, the furnace is composed of several heaters the temperatures of which are separately controlled. The progress made with respect to GaAs single-crystal growth during the last decade was closely linked to the development and application of a near-to-reality computer modeling for furnace design and the development/optimization of the growth technology.

During the last years, FREIBERGER has developed both the LEC and the VGF technology to maturity. Photographs of LEC and VGF pullers are given in Fig. 9.8. Crucibles up to 14-inch diameter allowing charges up to 50 kg are used to grow semi-insulating GaAs single crystals up to 200 mm diameter under



Fig. 9.8 LEC and VGF equipment at FREIBERGER.

carbon-controlled conditions [29] by the LEC method. The temperature gradient at the solid/liquid interface is estimated to be about 120 K/cm, the growth rate is (7-10) mm/h, the total gas pressure below 10 bar. On- and off-axis (up to 15 degrees) <100> seeds are used.

The VGF process is performed in a Tamann–Stoeber furnace with an advanced heater system similar to that first described by Ramsperger and Melvin [30]. It is based on a design given in detail in [31]. Similar to LEC growth, carbon control is realized by controlling the C and O chemical potentials in the gas phase. The temperature gradient at the phase boundary is adjusted to 3-5 K/cm, the growth rate is between 2 and 3 mm/h. Crystals up to 150 mm are commercially grown in this equipment. The capability of the equipment to grow crystals with 200 mm diameter has been proven recently [32]. <100> oriented seeds cut from LEC or VGF material are usually used and growth of off-oriented crystals is possible.

Crystals grown at FREIBERGER by LEC and VGF methods are represented in Fig. 9.9.

9.3.4 Copy Exactly

Mass production requires simultaneous operation of several pullers. These pullers have to produce single crystals with properties fulfilling the customer specification. In addition, the processes have to be very efficient to meet the demanding yield target of the company. For this, unified but versatile pullers and highly flexible growth technologies are necessary for a "copy exactly" strategy. This implies detailed knowledge about the influence of hardware tolerances and growth parameters on the global and local temperature field in the growth region and the measures to compensate these effects by modification of the growth program.


Fig. 9.9 150-mm LEC- and VGF-grown SI GaAs single crystals.

Computer simulation is an efficient means to acquire the respective knowledge. FREIBERGER uses the codes CRYSVUN, STHAMAS and STHAMAS3D [33] for these calculations.

As a first example, the influence of crucible and crucible support tolerances is analyzed for VGF using the CRYSVUN-3.0.07 code that includes heat conduction, radiation, latent heat but not convection in the melt and the gas phase. For the calculation, it is assumed that:

- the cone angles of crucible and crucible support are different; this results in a wedge-shaped slit that will enhance thermal resistivity in this region,
- the wall thickness of the crucible reduces with the number of runs, this results in changing thermal conductivity,
- the thermal conductivity of the crucible support is higher than the average.

Growth of a 3-inch GaAs single crystal is calculated at an average temperature gradient at the solid/liquid interface of 5 K/cm, a growth rate of 2 mm/h and a fixed heater power. The temperature field in the crystal and the melt, the von Mises stress, the position and bending of the solid/liquid phase boundary are calculated.

The results of the calculations are represented in Fig. 9.10. At the left, the reference setup is given. Due to the slit between the crucible and the support the bending of the solid/liquid interface is higher and its position is lower compared to the reference state. A reduction of the heat conductivity of the crucible due to a larger wall thickness leads to a reduction of the bending and a small downward shift of the interface. An increase of the thermal conductivity of the support is only of minor influence on bending and the position of the interface. Finally, the influence of all above-mentioned deviations from the reference state is considered





Fig. 9.10 Influence of manufacturing tolerances of crucible and support on VGF growth.

at the right. There is not only a shift of the phase boundary, but also a significant increase of the von Mises stress in the grown crystal.

In the second example, the influence of the growth rate, the temperature gradient at the solid/liquid interface and the thermal conductivity of the crucible on the bending of the interface and the crystal quality has been studied for VGF growth using the 2D CRYSTVUN code. To assess the quality of the crystal, the distribution of the von Mises invariant has been calculated.

As can be seen from Fig. 9.11(a), the von Mises stress in the crystal increases with growth rate. In agreement with experimental results the stress is larger at the periphery of the crystal than at the center. An interface concave with regard to the crystal is observed, the bending of which increases with increasing growth rate. The concave shape of the interface is caused by the higher heat conductivity of the pBN crucible wall compared to liquid and solid GaAs. Correspondingly, the thermal stress in the crystal increases with the temperature gradient at the interface at constant growth rate (Fig. 9.11(b)). The bending of the interface decreases with increasing temperature gradient.

The thermal conductivity of pBN crucibles is highly anisotropic with a higher conductivity along the wall compared to the thermal conductivity perpendicular to it (about 20:1). The texture and thus the degree of anisotropy of the polycrystalline BN can be influenced by the conditions during crucible fabrication. Thus, fluctuations and their influences, e.g. on the interface, have to be considered. The results of a respective simulation are shown in Fig. 9.11(c). At a constant thermal conductivity across the pBN of 2 W/m K the bending of the solid/liquid interface was calculated in dependence of the conductivity in the plane direction. A relatively strong upwards bending is observed at the crucible wall with increasing thermal conductivity.

9.3.5

Limits for LEC and VB/VGF Growth

Are there any limits for the scalability of the LEC and VGF technology with regard to crystal diameter and crystal length? This question will be briefly discussed in the following.



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Fig. 9.11 (a) Influence of growth rate on stress distribution in a VGF crystal. (b) Influence of temperature gradient at the solid/liquid interface on thermal stress distribution in a VGF crystal. (c) Bending of solid/liquid interface in dependence of inplane thermal conductivity of pBN.

At first, a limitation due to melt convection is considered. It is well known that the axial temperature gradient and the gravity vector are antiparallel in the VB/VGF, but parallel in the LEC geometry. As a consequence, in LEC colder melt near the crystal is situated above hotter melt with a lower density near the bottom of the crucible. This is an unstable layering causing buoyancy (natural) convection. Due to the existence of radial gradients in the melt this convection starts without critical conditions. The natural convection is characterized by the Rayleigh number: Ra = $\frac{g\beta h^3 \Delta T}{\nu\kappa}$ (g – gravitational acceleration, β – thermal expansion coefficient, h – height of the melt, ΔT – characteristic temperature difference, ν – kinematic viscosity, κ – heat diffusivity of the melt). Typically, the Ra number is in the range of 10⁶ to 10⁸ for GaAs LEC growth, therefore, the convection in the melt can be reduced by a forced



Fig. 9.12 Stability diagram for LEC and Cz growth of GaAs and Si single crystals.

convection due to crystal or crucible rotation. The latter is characterized by the Taylor number $Ta = \frac{4\omega^2 h^4}{\nu^2}$ with ω the rotation rate of the crucible.

As shown by Rossby [34] and represented in Fig. 9.12, a critical Ta number in dependence of the Ra number exists for the transition from oscillating to turbulent convection. It is well known that the single-crystalline yield and the structural quality of the crystals are lower if growth is performed with a working point in the turbulent region. In the diagram, typical (Ta, Ra) pairs of variates for the present-day GaAs LEC and Si-Cz growth are plotted that have been calculated for crucible rotation rates of 2 s⁻¹ (GaAs) and 1 s⁻¹ (Si), respectively, $\Delta T = 15$ K, and a melt height of h = 50, 100, 200 mm. It can be seen that the LEC growth of large-diameter GaAs crystals already takes place beyond this border line in the nonstationary turbulent regime. As a conclusion, the height of the melt cannot be further enhanced. Therefore, the diameter of the crucible and the related dimensions of the hot zone of the LEC puller have to be enlarged to grow longer crystals. Another way would be the application of time-dependent magnetic fields in order to suppress turbulent melt convection. In any case, financial aspects will determine the further development.

In VB/VGF the above-mentioned limitation does not exist. Due to the stabilizing temperature distribution in the melt and the significantly smaller temperature differences there is a rather weak stationary convection in the melt that consists of one or more vortices (depending on the melt height).

The strength of the seed is another issue the crystal grower is confronted with in GaAs LEC growth. This is illustrated in Fig. 9.13. Etched cross sections at different positions of two seeds are shown. In the first case (on the left-hand side of Fig. 9.13) the seed with an initial diameter of 6 mm was used to grow a crystal with a mass of 15 kg. The etch pit density as a measure of the dislocation density increases from about 5×10^4 cm⁻² at the mounting position to $\gg 5 \times 10^5$ cm⁻² at the regrown part. Obviously, the seed was plastically deformed under the load of the crystal, implying the possibility of a fracture during the growth. On the right side, only a neck has been grown. The epd did not change in the part remaining solid and was significantly



Fig. 9.13 Etched cross sections of seed crystals (left: loaded, right: unloaded).



Fig. 9.14 Minimal seed diameter as a function of GaAs crystal mass.

lower in the regrown part due to the well-known annihilation process of dislocations. These findings lead to the conclusion that the diameter of the seed crystal has to be chosen appropriately. Figure 9.14 shows the estimated minimal diameter of the seed crystal in dependence of the mass of the crystal to be grown [35]. A fracture strength of 10 MPa has been used for this estimation. Therefore, without a special supporting device as used in Cz growth of large-diameter Si single crystals, the mass of GaAs crystals is limited to about 50 kg when using seeds of about 10 mm diameter.

In VGF growth the latent heat and the heat flux from the melt is mainly conducted through the already solidified crystal to a heat sink in the crucible support (see Fig. 9.15). This determines the maximum growth rate, as can be seen from the following balance equation:



Fig. 9.15 Heat balance in VB/VGF growth.

$$v = \frac{q_{\text{melt}} - q_{\text{crystal}}}{\Delta h \rho_{\text{crystal}}} = \frac{\lambda_{\text{crystal}} \nabla T_{\text{crystal}} - \lambda_{\text{melt}} \nabla T_{\text{melt}}}{\Delta h \rho_{\text{crystal}}}$$

 $(q_{\text{melt}}, q_{\text{crystal}} - \text{heat flux in the melt and the crystal, respectively, } \Delta h - \text{latent heat,} \rho - \text{density}, \lambda - \text{thermal conductivity in the melt and crystal, respectively}). Setting <math>\nabla T_{\text{melt}} = 0$, the maximum possible growth rate is obtained:

$$v_{\max} = \frac{\lambda_{crystal}}{\Delta h \rho_{crystal}} \nabla T_{crystal} \text{ or } \frac{\nu}{\nabla T} \leq \text{ const.}$$

The constant amounts to $5.4 \times 10^{-5} \text{ cm}^2/\text{K} \text{ s}$, $4.5 \times 10^{-5} \text{ cm}^2/\text{K} \text{ s}$ and $2.0 \times 10^{-5} \text{ cm}^2/\text{K} \text{ s}$ for Si, InP and SI GaAs, respectively. Thus, the maximum growth rate is about $\nu_{\text{max}} \approx 2 \text{ mm/h}$ assuming $\nabla T_{\text{crystal}} = 3 \text{ K/cm}$ in agreement with the above-mentioned growth rates and cannot be further increased if the temperature gradient in the crystal is as low as possible in view of a low dislocation density.

9.4

LEC versus VB/VGF GaAs Wafers

The question whether LEC or VB/VGF GaAs wafers are better suited for device manufacturing is often controversially discussed. In the following, a comparison of the most relevant crystal properties will help to support this decision. For this comparison, the authors use FREIBERGER data base since FREIBERGER is the only wafer manufacturer applying both technologies on a high production level. The comparison comprises only semi-insulating wafers with a diameter of 150 mm.

After appropriate annealing, each LEC and VGF crystal is subjected to an intensive seed- and tail-end wafer inspection program that includes structural control, measurement of electrical parameters and other physical and chemical properties relevant for device manufacturing. Spot checks of wafers between seed and tail are carried out additionally. All data are stored in a data base for continuous and detailed evaluation in relation to technological synthesis, crystal growth and wafering parameters.



Fig. 9.16 Etched LEC and VGF SI GaAs wafers <110> horizontal.

9.4.1 Structural Properties

For assessment of the dislocation density the etch pit density (epd) is measured according to DIN 50454-1 for LEC crystals and by a full-wafer mapping for VGF material using automated equipment. To reveal the emerging points of dislocations, the as-cut wafers are chemically polished in a H_2SO_4 -based solution to remove the damage and etched in a KOH melt at 400 °C. Typical examples of etched wafers are represented in Fig. 9.16.

As well known, the dislocations are arranged in a cellular structure the size of which amounts to $(100-200) \mu m$ for LEC and up to several mm for VGF material. The size depends on the position [36]. The density of dislocations is higher in the cell boundaries of LEC wafers. Usually, a weak W-shaped local etch pit density is observed that can be easily explained by the distribution of global thermal stress during growth [37]. As can be seen from Fig. 9.16, the epd is higher in the <100> radial direction than in the <110> direction. This indicates that gliding of dislocations on $\{111\}/<110>$ glide systems is an important relaxation process of thermally induced strain. The average epd slightly increases from the seed to the tail end of the crystals.

The crystals are also free from subgrain boundaries, lineage structure and slip lines.

As a further parameter to characterize structural quality {004}-Cu-K_{α 1} doublecrystal rocking curve mappings are measured with 1 × 1 mm step size, 1 × 2 mm² foot print and <110> rocking axis [38]. These measurements do not, however, include all wafers (regular spot checks). Figure 9.17 shows mappings of full width





Fig. 9.17 Double-crystal rocking-curve mappings of LEC (left) and VGF (right) wafers <110> horizontal.

at half maximum (FWHM). The average FWHM amounts to (15 \pm 2) arcsec for LEC and (10.5 \pm 0.3) arcsec for VGF wafers, with a larger scatter for LEC material. Furthermore, small areas with rather high FWHM can be observed indicating locally higher dislocation density. The results are in qualitative agreement with epd data.

In addition, regular spot checks are made to characterize global and local residual strain in the wafers. These measurements are performed by the SIRD^M analyzer, details of which are given in [39]. Examples are represented in Fig. 9.18. The difference between the principal stresses in the wafer plane taken as a measure of residual stress ranges between 0.3 and 0.7 MPa for LEC and 0.1 and 0.4 MPa for VGF wafers. Annealing of VGF wafers to homogenize electrical properties does not change the stress level.

As already mentioned in Section 9.3.2, precipitation of arsenic takes place during cooling of the crystals after growth. These precipitates can be revealed by laser scattering tomography (LST) which is described in detail in [40]. Due to heterogeneous nucleation the precipitates are preferentially formed at dislocations (dislocation precipitates) leaving behind an up to $100\,\mu$ m wide area around the dislocations that does not contain As precipitates (Fig. 9.19). The size distribution of As precipitates is shifted to greater characteristic dimensions in VGF material due to the lower dislocation density. In addition, As precipitates are found in the center of the cellular structure (matrix precipitates), which are smaller in size than dislocation precipitates. The decoration of dislocations by As precipitates indicates



Fig. 9.18 Depolarization mappings of LEC (left) and VGF (right) wafers.



Fig. 9.19 Dislocation precipitates revealed by LST (left: LEC, right: VGF).

that the rearrangement of dislocations has already been concluded when precipitation starts. In agreement with this, slip lines in the crystals are not decorated. The size distribution and the distribution of As precipitates can be influenced by ingotor wafer-annealing procedures [41]. If annealing is applied, the time-temperature procedures have to be optimized in order to avoid multiplication of dislocations by thermal stresses during heating and cooling.

Arsenic precipitates are the cause of so-called COPs, i.e. crystal originated particles on the surface of polished wafers. They are formed during polishing when the precipitates reach the surface. This is due to the different mechanical and chemical properties of As precipitates and GaAs matrix. Accordingly, the average COP size is greater for VGF than for LEC material. The COPs exhibit an anisotropic scattering behavior and can thus be distinguished from real particles, which scatter the laser light isotropically.

9.4.2 Electrical Properties of GaAs Wafers

The global electrical resistivity of SI GaAs is determined by the concentration of the midgap donor EL2 that is partly compensated by the net shallow acceptor, mainly carbon. Therefore, the macroscopic and mesoscopic distributions of EL2 and carbon will influence the resistivity homogeneity. The compensation mechanism will be discussed in detail in Section 9.5.1.

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Fig. 9.20 Typical EL2 topographs of LEC (left) und VGF (right) material.

The mesoscopic distribution of EL2 and resistivity is assessed by IR absorption measurements [42] and the contactless TDCM method [43], the lateral resolution of which amounts to $30\,\mu\text{m}$ and $1\,\text{mm}$, respectively. Typical EL2-topographs are shown in Fig. 9.20.

As well known from literature the EL2 concentration is enhanced around dislocations and causes by this way an inhomogeneity scaled by the cell size. This is described by the mesoscopic homogeneity, and is due to an interaction of defects with dislocations [44]. The larger cell size of VGF GaAs is clearly visible. The average EL2 concentration is higher in semi-insulating LEC GaAs compared to VGF GaAs. At the same time the mesoscopic homogeneity amounts to 5% for LEC and 7% for VGF GaAs.

As can be concluded from the mesoscopic EL2 distribution, the mesoscopic homogeneity of the resistivity is higher for LEC compared to VGF material.

9.4.3

Mechanical Properties of GaAs Wafers

FREIBERGER applies a breakage test for regular spot checks to define the breakage behavior of SI GaAs wafers as an additional measure to control the reliability of production processes. Furthermore, these data are used to establish a probability distribution that allows probability statements to be made concerning the breakage strength of wafers in device manufacturing.

A scheme of the test equipment is given in Fig. 9.21. The finally polished surface (front side) of the wafer is turned downwards and put on a supporting ring made of PTFE (Teflon). It is loaded from above by a steel sphere of 1/8-inch diameter on its center, i.e. the front side experiences a tensile stress that is maximum in the wafer center. The test equipment is installed in a conventional material testing machine. The bending tests are performed with a constant displacement rate (cross-head speed) of 1 mm/min at a stabilized temperature of (22 ± 2) °C. The load-displacement curves are measured to fracture, corrected for stiffness of the machine and stored. The fracture strength is derived from the load at fracture using the results of a numerical solution of the corresponding von Karman equation with Hertzian stress in the center [45].



Fig. 9.21 Experimental setup for breakage tests.

The average fracture strength is typically higher for LEC wafers ((1860 \pm 260) MPa) compared to VGF wafers ((1400 \pm 260) MPa). It is assumed that this behavior is caused by the larger average size of As precipitates acting as nuclei for cracking in VGF GaAs. In view of the residual stress it follows that the fracture of well-annealed wafers is obviously not influenced by the residual stress level.

Finally, the fracture toughness has been measured by the indentation method described in [46]. It amounts to $K_c = (0.46 \pm 0.05)$ MPa m^{1/2} independently of growth method, doping type and doping level.

9.4.4 Conclusions

Table 9.1 shows the qualitative classification of the above-mentioned data. The advantage of LEC over VGF SI GaAs is the higher mesoscopic homogeneity of the electrical properties. This is particularly suitable for microelectronic devices produced in a wafer by ion implantation (MESFETs). On the other hand, VGF GaAs wafers with a lower epd are preferred for epitaxy-based devices like HEMTs and HBTs.

9.5 Doping

9.5.1 Compensation

GaAs is called semi-insulating (SI) if the electrical resistivity is above 10⁶ Ω cm. Although this behavior is basically connected with the existence of a wide bandgap it is not an intrinsic property, but the result of a complex compensation including the native midgap double donor EL2 and extrinsic dopants and impurities. The localized EL2 level belongs most probably to a single arsenic atom on a Ga lattice site (As_{Ga}) [47]. Referring to the 3-level model of Martin *et al.* [48] (see Fig. 9.22), the Fermi level will be pinned at the EL2, if the following condition is fulfilled: $N_{EL2^0} > N_{\Sigma A} > N_{\Sigma SD}$, where N_{EL2^0} , $N_{\Sigma A}$, $N_{\Sigma SD}$ are the concentrations of the neutral EL2, of the acceptors and the donors shallower than EL2, respectively. The charge carrier concentration in the conduction band is than given by:

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Darameter	IEC	VCE
r alametei	LEC	VGI
epd	Δ	\bigcirc
residual strain	higher	low
EL2	higher	lower
C control	\checkmark	\checkmark
homogeneity/macro	\bigcirc	\bigcirc
homogeneity/meso	\bigcirc	Δ

Table 9.1 Comparison of LEC and VGF/VB GaAs.

(\bigcirc - good, \triangle - fair, \checkmark - possible)



Fig. 9.22 Compensation in case of SI GaAs.

$$n[\text{cm}^{-3}] = 4.7 \times 10^{17} [\text{cm}^{-3}] N_{\text{EL}2^{\circ}} / (N_{\Sigma \text{A}} - N_{\Sigma \text{SD}}) \cdot \exp(-E_{\text{EL}2}/kT)$$

with $E_{\text{EL2}}(T) = 0.75 \text{ eV} + 2.4 \times 10^{-4} T$. Semi-insulating GaAs is n-conducting. In state-of-the-art SI GaAs, residual impurities are reduced to lower than 10^{14} cm^{-3} using high-purity constituents and the purifying properties of liquid boron oxide. Carbon is intentionally added as a shallow acceptor. Then the above condition reads $N_{\text{EL2}^{0}} > [C] - (N_{\Sigma A} - N_{\Sigma \text{SD}}) > 0$ with $(N_{\Sigma A} - N_{\Sigma \text{SD}}) < 10^{14} \text{ cm}^{-3}$. It follows that carrier concentration, and therefore the electrical resistivity of SI GaAs can be controlled by two parameters, EL2 and carbon concentration (see Fig. 9.22). It should be mentioned that there is a relationship between carbon concentration and EL2 concentration, i.e. the EL2⁰ concentration increases with the C content [49].

As already discussed in Section 9.3.2, the EL2⁰ concentration can principally be controlled by adjusting the composition of the melt from which the solid is grown and by post-growth annealing. But in practice, the variations of EL2 concentration accessible by these processes are within a factor of 2 at a maximum and $[EL2^0]$ is typically around 1.4×10^{16} cm⁻³. Therefore, the electrical resistivity is controlled by carbon doping keeping the EL2 concentration constant. The latter is done by keeping constant the initial composition of the charge and the annealing procedure of the crystals.



Fig. 9.23 Electrical resistivity vs. C content for LEC and VGF GaAs (solid lines calculated by an advanced compensation model [51]).

In addition to semi-insulating, so-called medium-resistivity GaAs characterized by $10^3 \Omega \text{ cm} < \rho < 10^4 \Omega \text{ cm}$ is of some importance for certain device manufacturing processes. In this case the Fermi level is pinned at the EL3 level, which is related to oxygen on an off-center arsenic sublattice site [50], and oc-O_{As} exhibits negative U-properties and the charge state O^{-/0/+} with an effective level at 360 meV below the conduction band. Pinning at the EL3 requires [EL2] < [EL3] > N_{\substarboxlowleft} Site of N_{\substarboxlowleft} and N_{\substarboxlowleft} below the concentration is then $n \propto N_{
m O}/(N_{
m C} - N_{
m SSD})$ with $N_{
m O}$ and $N_{
m C}$ being the oxygen and carbon concentration, respectively.

In Fig. 9.23 the electrical resistivity as a function of the carbon content is given for LEC and VGF GaAs demonstrating the range that is accessible by C and O doping.

Semi-conducting GaAs of n- and p-type is produced by adding shallow acceptors (mainly Zn, Be, C) and shallow donors (mainly Si, Te) with concentrations of $O(10^{18} \text{ cm}^{-3})$ directly into the melt. Then, the Fermi level is pinned near the valence and conduction band, respectively. Silicon, which is most frequently used as a n-type dopant, shows amphoteric behavior in GaAs, i.e. it can be substituted for an As, as well as a Ga atom with roughly [Si_{Ga}] ≈ 0.9 [Si].

Furthermore, interactions between native (nonstoichiometry) defects like vacancies and impurities/dopants are observed in GaAs, resulting in electrically active complexes that influence compensation in SC GaAs and, therefore, have to be taken into account. Post-growth heat treatment of the crystals can by applied to influence the defect equilibria.

Besides with each other, native point defects and dopants interact with structural defects ("gettering") like single dislocations and precipitates resulting in

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segregation zones and related local changes of, e.g., electrical properties around the defects. This is the reason for a mesoscopic inhomogeneity scaled by the characteristic dimension of the dislocation structure (see Section 9.4.2). As an example, the Petroff–Kimmerling mechanism [52] should be mentioned in which interstitial arsenic As_i as a main native point defect in nonstoichiometric GaAs can be absorbed by a dislocation resulting in a single climb step producing a Ga vacancy that is then occupied by another As_i generating an EL2 at the dislocation: As_i + Ga_{Ga} = GaAs_{unit climb} + V_{Ga}. Therefore, an enhanced EL2 concentration is found around dislocations.

9.5.2

Doping of Semi-Insulating Material

Carbon possesses an equilibrium distribution coefficient around 2 in GaAs [54]. Therefore, an axial and radial macrosegregation will occur in a mass-conserving system with a certain starting carbon concentration. It follows that, to avoid macrosegregation, an open system must be run with an active carbon control at a defined and controlled oxygen potential.

As a first approach, a thermochemical analysis of the complex reaction system was carried out. This means that transport of reactants in the fluid phase was neglected, but a fast reaction kinetics was assumed. The system under study comprised the gas atmosphere, the boron oxide melt, solid and liquid GaAs, the crucible and the graphite heaters. Figure 9.24 shows a scheme of the system.

Instead of attempting to describe the system by a complete set of chemical reaction equations and solving the corresponding mass action laws, the total Gibbs free energy of the system is minimized to calculate the equilibrium concentration of the species at the melting temperature:



Fig. 9.24 Scheme of the complex LEC reaction system.



Fig. 9.25 Predominance area diagram for liquid-encapsulated VGF growth system.

 $G = \sum_{\varphi,k} Z_{\varphi k} \mu_{\varphi k} (p,T,z_{\varphi k'}) \rightarrow \text{Min}$ $\mu_{\varphi k} = \mu_k^0 (p,T) + RT \ln a_{\varphi k}$ $\mu_{\varphi k} - \text{chemical potential, } a_{\varphi k} - \text{activity}$

The commercially available ChemSage code [55] has been used. Further details are given in [22].

As mainly redox equilibria are of importance, the results of the calculations are best visualized as so-called *predominance area diagrams* [56]. These represent the stability region of the GaAs melt in the presence of the boron oxide encapsulant at the GaAs melting temperature on a plot of log a_C over log p_{O_2} with a_C and p_{O_2} the activity of carbon and the oxygen partial pressure (see Fig. 9.25). As can be seen from Fig. 9.25, the stability region of GaAs-melt/liquid boron oxide essential for crystal growth is bounded by the dissociation of boron oxide at lower and oxidation of Ga in the GaAs melt at higher oxygen chemical potentials. The upper boundary of the stability region is given by $a_C = 1$, i.e. by the solubility limit of carbon in liquid GaAs. On fixing the chemical potential of the control species carbon and oxygen in this stability region there are no degrees of freedom left in the system.

But not the entire stability region of GaAs/boron oxide is accessible for carbon/oxygen control during LEC and liquid encapsulation VGF growth. Instead, the working area marked in Fig. 9.25 was calculated under the assumption that

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the chemical potential of carbon and oxygen will be determined by the CO and N_2 partial pressures, respectively, keeping in mind that nitrogen reacts with boron oxide [58].

The dotted line in Fig. 9.25 indicates a constant CO partial pressure. Therefore, keeping the CO partial pressure constant is not sufficient to unambiguously control the carbon content in the GaAs melt, the oxygen potential must also be fixed.

Attempts to control the oxygen potential by controlling the water content of boron oxide suffer from a continuous decrease of the water content in boron oxide due to the evaporation/reaction of water with the other constituents (graphite, gallium, etc.).

Using the activity coefficient of carbon in GaAs [58], the carbon content in the melt is obtained. In addition, semiquantitative scales for oxygen, nitrogen and boron are calculated in Fig. 9.25. It was assumed that there is no interaction between these solutes. It is obvious that their concentration is only determined by the oxygen potential. Finally, the concentration of carbon and the other solutes in solid GaAs can be estimated using the equilibrium distribution coefficients.

Inversely, measured concentrations of carbon, oxygen, boron and nitrogen in solid GaAs can be used to estimate the corresponding concentrations in the melt in order to verify the calculations. The open squares in Fig. 9.25 represent the carbon concentration at constant N_2 partial pressure and varying CO partial pressure and demonstrate the applicability of the thermochemical approach.

In the framework of the equilibrium approach there are no differences in the *predominance area diagrams* of LEC and VGF growth of GaAs, i. e. similar procedures can be used for carbon control. To prove the applicability of this procedure crystals were grown under different CO partial pressure at fixed oxygen chemical potential and fixed EL2⁰ concentration. Results are represented in Fig. 9.23 indicating the expected relationship between electrical resistivity (inversely proportional to the electron concentration) and carbon concentration in the semi-insulating region.

Having demonstrated now that carbon concentration and thus electrical resistivity can be defined according to the requirements of device manufacturers by controlling the chemical potentials of carbon and oxygen in the gas phase, the transport phenomena in the system must be clarified [59, 60]. This is obvious from the radial and axial macrosegregation of carbon found in LEC and VGF crystals grown without active carbon control. It clearly indicates that transport of reaction products in the fluid phases and/or reaction kinetics at phase boundaries cannot be neglected. To demonstrate this, the axial carbon content at a constant carbon potential, and the response to a step-like increase of carbon potential at constant oxygen chemical potential is shown in Fig. 9.26. Macrosegregation with decreasing C concentration ($k_C \approx 2$) for constant C chemical potential is followed by a transient region where carbon content increases without reaching a new equilibrium state.

Therefore, a transport model has been developed to establish a control procedure for compensation of axial macrosegregation. According to the thermochemical model it must include carbon and oxygen as control species and system-related



Fig. 9.26 Axial C concentration at constant and stepwise increased chemical potentials of carbon.



Fig. 9.27 Advanced transport model for GaAs LEC growth.

parameters like area and thickness of the boron oxide layer and its transport properties. The processes included in the model are illustrated in Fig. 9.27. An equivalent model was used for VGF.

According to this model, carbon is supplied to or extracted from the melt by decomposition or formation of CO at the boron oxide/GaAs melt interface with the assumption of a preset CO partial pressure in the gas phase and diffusional transport in boron oxide. Carbon in the GaAs melt is incorporated into the growing crystal according to the equilibrium distribution coefficient but can react with dissolved oxygen in the melt. The dissolved oxygen content in the melt is determined by an incorporation of oxygen from the B_2O_3 melt and an extraction due to oxidation of As and Ga at the GaAs/B₂O₃ interface and evaporation of Ga₂O at the surface of the encapsulant.

Due to convective flow in the melt, transport in the GaAs melt should be quick enough so that concentration differences in the melt can be neglected. Assuming a planar solid/liquid interface the balance of carbon and oxygen in liquid GaAs can be expressed by the respectively extended well known SCHEIL equation:

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$$\begin{aligned} \frac{\mathrm{d}N_{\mathrm{m}}^{\mathrm{C}}}{\mathrm{d}t} &= -\frac{\mathrm{d}N_{\mathrm{s}}^{\mathrm{C}}}{\mathrm{d}t} + \frac{\mathrm{d}N_{\mathrm{B}_{2}\mathrm{O}_{3}}^{\mathrm{C}}}{\mathrm{d}t} - \frac{\mathrm{d}N_{\mathrm{R}}^{\mathrm{C}}}{\mathrm{d}t};\\ \frac{\mathrm{d}N_{\mathrm{m}}^{\mathrm{O}}}{\mathrm{d}t} &= -\frac{\mathrm{d}N_{\mathrm{s}}^{\mathrm{O}}}{\mathrm{d}t} - \frac{\mathrm{d}N_{\mathrm{B}_{2}\mathrm{O}}^{\mathrm{O}}}{\mathrm{d}t} - \frac{\mathrm{d}N_{\mathrm{R}}^{\mathrm{O}}}{\mathrm{d}t} + \frac{\mathrm{d}N_{\mathrm{res}}^{\mathrm{O}}}{\mathrm{d}t} \end{aligned}$$

The first term on the right-hand side describes the incorporation of carbon and oxygen into the growing crystal (usual Scheil equation), the second an effective transport of carbon (CO) and oxygen (Ga₂O) containing species through boron oxide including reaction kinetics at the phase boundaries, and the third a decrease of carbon and oxygen in the melt due to a chemical reaction between both constituents. The last term in the balance equation of oxygen takes into consideration that boron oxide can serve as a reservoir for oxygen due to the heterogeneous reaction of nitrogen with boron oxide. Further details can be found in [59].

The system of nonlinear differential equation given above, has been numerically solved and applied to analyze the axial C distributions in 150-mm crystals grown by LEC and VGF. As an example, the axial carbon concentration as a function of the solidified fraction for several VGF crystals grown at constant or step-wise changes of CO partial pressure is represented in Fig. 9.28. All these results can be described (solid lines in Fig. 9.28) by one and the same set of parameters (see Table 9.2) only adjusting the initial concentrations of carbon in the GaAs melt and oxygen in the boron oxide encapsulant.

When applying the model for LEC growth, an enhanced transport of carbon oxides in the boron oxide melt has to be regarded due to stronger (natural and forced) convection as compared to VGF, again adjusting the initial concentrations of carbon and oxygen. Based on this model, a control procedure has been developed using a predetermined function $p_{CO} = f$ (g) at a preset oxygen chemical potential to ensure a nearly constant axial carbon concentration. It works equally for LEC and VGF growth. Examples are shown in Fig. 9.29.



Fig. 9.28 Comparison of measured (dots) and calculated (solid lines) axial carbon distribution in VGF crystals grown under different conditions.

Table 9.2 Set of Parameters Used in the Extended Scheil Equation.

Eff. segregation coefficient of carbon	2.0
Eff. segregation coefficient of oxygen	0.25
Growth rate	3 mm/h
Height of boron oxide	2.5 cm
Transport coefficient of carbon	$0.75 imes 10^{-9} { m cm^2/s}$
Transport coefficient of oxygen	$3.0 imes10^{-6}\mathrm{cm^2/s}$
Oxygen reservoir	$2.0 imes 10^{16} \mathrm{cm^{-3}}$
Exponent of oxygen release	0.15
Carbon-oxygen reaction rate	$3.0 \times 10^{-13} \text{ s}^{-1}$



Fig. 9.29 Axial homogeneity of 150-mm SI GaAs single crystals grown by LEC and VGF under active carbon control.

Furthermore, the model has been used to analyze data found in the literature [62] for C distribution in LEC-grown GaAs single crystals due to a step-wise increase of the CO partial pressure in the gas atmosphere (Fig. 9.30). The same set of parameters was used with the exception of crucible, crystal diameter and growth rate. Estimates of initial carbon and oxygen concentrations were made additionally. There is a satisfactory correspondence between the calculated and the experimentally determined C distribution.

9.5.3 Doping of Semiconducting Material

Referring to n-type semiconducting GaAs for optoelectronic applications, FREIBERGER produces LEC-grown Te-doped GaAs for LEDs and VGF-grown low-epd Si-doped GaAs for LEDs and laser diodes. The offered portfolio comprises wafers from 50 to 100 mm diameter, while 150 mm substrates are under development.

Te is completely substituted for an As-sublattice site, whereas about 90% of the dissolved Si is substituted for a Ga site forming a donor, the remaining 10% for an As site. Since Si_{As} is an acceptor, self-compensation takes place, reducing the doping efficiency of silicon. In addition, the substituted constituents interact with native





Fig. 9.30 Application of the model to data from literature [61].

defects to give electrically active complexes with the double acceptors V_{Ga} -Te_{As}and V_{Ga} -Si_{Ga}-being the most important ones. They also influence compensation.

In liquid-encapsulation growth tellurium and silicon react with the watercontaining boron oxide melt forming oxides that are dissolved in the encapsulant. As a result, boron is introduced into the GaAs melt and then into the growing crystal. So, the boron content in the Te- and Si-doped crystals amounts to around 10^{16} cm⁻³ and 10^{18} cm⁻³, respectively. The higher value in Si-doped GaAs is due to the higher reactivity of silicon. As this reaction takes place during the entire growth process, the boron content increases slightly from the seed to the tail of the crystals. Boron is mainly substituted isoelectrically on a Ga site, but at higher concentrations it also occupies As sites. Since B_{As} is a double acceptor, this further reduces the doping efficiency of silicon. Furthermore, the B_{As} -Si_{Ga} complex is formed [62], which is an acceptor and thus also influences compensation.

The compensating defects limit the achievable charge carrier concentration of Si-doped GaAs to about 3×10^{18} cm⁻³ at a doping level of 8×10^{18} cm⁻³. This is shown in Fig. 9.31.



Fig. 9.31 Doping efficiency of Te- and Si-doped GaAs.



Fig. 9.32 Charge-carrier mobility as a function of charge-carrier concentration for Te- and Si-doped GaAs (solid lines calculated by the Brooks-Herring equation [64]).

Te is added to the stoichiometric GaAs charge as GaTe, Si as the element, taking into account the loss of dopants to the boron oxide melt. This loss is empirically compensated by a surplus of the dopants. The equilibrium distribution coefficients of Te and Si in GaAs are $k_0 \approx 0.016$ and 0.028 [63]. The effective distribution coefficients depend on the convection in the GaAs melt and the above-mentioned reaction of the dopants with the boron oxide melt and are thus not well defined. If the axial macrosegregation is tentatively described by a Scheil equation, an approximate effective distribution coefficient of $k_{\text{eff}}^* \approx 0.03$ for Te doping will be obtained. Constitutional supercooling and interface breakdown is neither a problem for LEC nor for VGF growth of doped crystals.

Due to the time-dependent forced (LEC) and natural (VGF) flow in the melt, microsegregation occurs resulting in striations with a distance of about $5\,\mu$ m in Te-doped crystals and up to several mm for Si-doped crystals. As Te-doped crystals have to be annealed after growth for stress relaxation, the striations are partly homogenized. All in all, striations do not influence the application of semiconducting GaAs wafers.

The carrier mobility in doped GaAs is mainly determined by the scattering of the charge carrier at ionized defects. Therefore, it decreases up to about 2000 cm²/Vs with increasing doping level at the highest achievable dopant concentrations (see Fig. 9.32). The solid lines in Fig. 9.32 are calculated by the Brooks–Herring equation [64]. As can be seen from Fig. 9.32, Te-doped GaAs has a higher carrier mobility than Si-doped material for the same carrier concentration. Furthermore, higher charge-carrier concentrations can be obtained by Te doping resulting in a higher electrical conductivity of Te-doped wafers.

In addition to the electrical conductivity of doped GaAs, the structural quality, i.e. the dislocation density, is an important parameter especially for laser applications. This is due to the fact that dislocations act as sites for nonradiative recombination of carriers leading to a local release of heat and possibly to an avalanche-like



Fig. 9.33 epd mapping of a Si-doped GaAs wafer.



Fig. 9.34 Mapping of charge-carrier concentration of a Si-doped GaAs wafer.

destruction of the device. For laser applications the dislocation density should be below 500 cm⁻². This can be reached easily by the VGF method with an optimized temperature field in the crystal. Furthermore, Si [65] and probably to the same degree also B are of lattice-hardening influence and thus facilitate the growth of low-epd GaAs crystals. As an example, the full-wafer epd mapping of Si-doped GaAs is represented in Fig. 9.33. The epd is enhanced in the center and at $r \approx R/2$ in <100> directions [66]. Native and extrinsic defects interact with dislocations. This is obvious from Fig. 9.34 showing the local distribution of the charge-carrier concentration, which is measured by NIR absorption. The carrier concentration is enhanced in the regions with a higher dislocation density.

9.6 Summary

In the last few years research and development activities at FREIBERGER have been mainly focused on cost reduction in crystal growth and wafering. Costs could be significantly reduced by increasing crystal growth yields and improving the reproducibility of wafer properties to meet the customer-specific requirements. This could be reached by the following:

- computer-aided optimization of the growth hardware and the growth technologies for 75 to 150 mm SI and 75–100 mm SC GaAs;
- realization of a "copy exactly" strategy;
- carbon and oxygen control for both LEC and VGF methods on the basis of an advanced transport model using the results of a thermochemical modeling of the complex reaction system;
- comprehensive characterization of structural, electrical and other properties relevant for device manufacturing for each crystal and data assessment in relation to technological parameters of synthesis and crystal growth.

The basic technologies for the carbon-controlled LEC and VGF growth of SI crystals with 200 mm diameter have been developed.

FREIBERGER is the sole producer applying both methods in parallel to provide substrates according to customer requirements.

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Interface Stability and Its Impact on Control Dynamics

Frank J. Bruni

10

10.1 Introduction

During the growth of crystals by the Czochralski method the solid/liquid interface typically assumes a curved shaped convex into the liquid defined by the intersection of the freezing point isotherm and the melt. Facets will form on the interface where the local curvature lies parallel to a low energy plane [1]. A faceted growth interface is generally undesirable because the growth dynamics on a facet plane are considerably slower than on an atomically rough surface and because the center of the facet is supercooled relative to the equilibrium freezing point [2]. Dopant and impurity concentrations exhibit a gradient across the facet generally resulting in a stressed volume of crystal.

To avoid the problems resulting from growth with a faceted interface, it is common to grow many crystals with a relatively flat solid/liquid interface. The interface depth or curvature of the crystal is impacted by a number of factors, the most significant being the vertical temperature gradient. A high temperature gradient promotes a deep crystal interface in the melt because of the shape of the freezing point isotherm. Controlling the vertical gradient, while important, is not usually sufficient to promote a flat solid/liquid interface. The most common method used to flatten the growth interface is to modulate the crystal rotation rate. Rapid rotation of the crystal stirs the melt causing hot liquid in the crucible to well up and distort the shape of the freezing-point isotherm [3]. This phenomenon is shown schematically in Fig. 10.1. Figure 10.1(a) shows the conventional view of stable Czochralski crystal growth. Melt flow patterns are dominated by natural convection. Hot liquid rises up along the walls of the crucible and flows across the surface of the melt losing heat by radiation and conduction into the crystal. As it cools and its density increases, it falls to the bottom of the crucible where it is reheated and resumes the cycle.

Figure 10.1(b) shows the convection patterns when the crystal is rotated rapidly. Stirring by the crystal causes hot liquid to rise up from the depths of the crucible and flow outward counteracting natural convection. This hot liquid "melts back" the deep interface and allows the crystal to grow with a nominally flat interface. The



Fig. 10.1 (a) Left, natural convection. (b) Right, forced convection. Rapid rotation of the crystal stirs up hot liquid that melts back the solid/liquid interface to a flatter configuration.

crystals that are routinely grown with a flat interface include gadolinium gallium garnet (GGG), lithium niobate, lithium tantalate and alexandrite, among others [4–7]. The interface-shape change and the stability of the interface shape have a significant impact on the diameter control process in a system that weighs the crystal. When the interface transitions from convex to flat, material is melted off, resulting in a substantial weight change. The controller interprets this as a change in diameter and makes corresponding power changes. This will be discussed in greater detail below.

While not discussed in any detail below, growth with a concave interface is generally to be avoided. Linear defects such as dislocations and grain boundaries tend to propagate perpendicular to the local interface in order to minimize their energy. When growing with a convex interface they would tend to propagate outward to the free surface of the crystal. A concave interface would cause them to propagate into the body of the crystal.

10.2 Diameter Control

Controlling the diameter of a crystal during Czochralski growth serves two purposes. It maximizes productivity of material of the desired size, and it ensures stable and reproducible thermal conditions in order to maintain optimum crystal quality. Over the years many techniques have been developed to control the diameter of Czochralski crystals. Two general control schemes have come to predominate – optical control and weight control. Optical control is the standard method employed for silicon crystal growth while the weighing method is the preferred technique for oxides. There are fundamental reasons for this dichotomy of control methodology. Semiconductors such as silicon, germanium and gallium arsenide expand on freezing. This complicates the mathematics of control for a weighing system because a small weight *loss* can result from an *increase* in diameter. This is a transient effect, however, which is subsequently overshadowed by a net weight gain. In 1977, Bardsley *et al.* [8] developed an algorithm to overcome this effect and demonstrated excellent diameter control of semiconductors using the weighing method. But optical control remains the method of choice for silicon crystal growth.

Conversely, oxides such as GGG, sapphire, the niobates and tantalates are routinely controlled by the weighing method. Even neodymium-doped yttrium



Fig. 10.2 The more open configuration of a silicon crystal growth system provides a clear view of the meniscus for an optical pyrometer.

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aluminum garnet (Nd:YAG), which historically was controlled using optical pyrometry, is now grown primarily with weight controllers. Basic materials issues also dictate this dichotomy of control techniques. With their lower melting points, semiconductors are grown in relatively open hot zone designs (Fig. 10.2) making optical control easier. Also, as a consequence of their higher thermal conductivity, they can be pulled fairly quickly. This requires a control system with a fast response time. Optical control gives a true real-time determination of the crystal's actual diameter. The weighing method, by contrast, requires the collection of weight data over some finite period of time and, thus, has an inherent time lag between an actual diameter variation and its appearance in the control algorithm.

Oxides, with their usually higher melting points, tend to be grown in more closed (that is, more insulated) hot zone designs (Fig. 10.3). This complicates control by optical pyrometry because of the difficulty of achieving a clear line of sight to the meniscus throughout the growth process and also because light radiated from the crucible wall can overwhelm the light coming from the meniscus. Nd:YAG,



Fig. 10.3 Oxide hot zones tend to be more heavily insulated providing a less clear viewing path to the meniscus. Light radiated from the crucible walls can overwhelm the light emitted from the meniscus.

the former exception to this rule, is generally grown in a more open thermal environment to achieve the high temperature gradients required to stabilize the growth interface against constitutional supercooling. Also, as a consequence of neodymium accumulation in the melt, it is atypical to crystallize more than about 35% of the starting material making the problem of the exposed crucible wall less important.

10.3 Interface Transitions

It has long been recognized that the interface melt-back associated with the transition to a flat interface will be interpreted by a weight controller as a change in diameter resulting in a corresponding power change as the controller attempts to correct for this fictitious diameter change. For small crystals, this was not a major problem. A rotation rate could be selected such that, when the crystal reached the desired maximum diameter, the interface transition would occur spontaneously. The body of the crystal would be grown with a flat interface at a constant rotation rate. Figure 10.4 shows a view in polarized light of the cross sections of a GGG



Fig. 10.4 View in polarized light of the cross section of a GGG crystal showing the transition from a convex to a flat interface. Photo reproduced from reference [5].

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crystal (nominally grown to a target diameter of about 55 mm) where the transition from a convex to a flat interface can be seen. This photo also shows the highly stressed "cores" formed by faceting on the {112} and {110} planes. It is the elimination of these stressed regions that is the reason for growing the crystal with a flat interface. As crystal diameters increase, a more complex situation arises. The transition from a convex to a flat interface for a large crystal (on the order of 100 mm diameter and larger) results in a significant decrease in the contact area between the crystal and the liquid. Assuming a conical interface shape with an aspect ratio of unity (diameter of the crystal, D_c , divided by the depth of the interface, D_i), the surface area in contact with the melt decreases by nearly 100 cm² for a 100-mm diameter crystal when it transitions from convex to flat. The loss of that surface area in contact with the melt means that there is a corresponding loss of the stirring effect that is the driving force for achieving the flat interface in the first place. This can result in an unstable situation where the stirring effect causes the interface to flatten that reduces the stirring effect which then leads the interface to return to its convex shape resulting in the resumption of the stirring effect and the cycle begins again.

Figure 10.5 shows data from the growth of a 100-mm diameter sapphire crystal. Although there was no intention to grow this crystal with a flat interface, the combination of rotation rate, crystal diameter and crucible diameter resulted in a melt-stirring effect that caused an interface shape change. Starting at an elapsed time of about 90 h, the "diameter" begins to oscillate. These oscillations are the result of an unstable interface shape. One can conclude that the oscillations are not induced by the controller from the fact that, during the period from 96 h to 106 h of elapsed time, the power to the crucible is virtually constant yet the oscillations persist. In time, the severity of the oscillations diminishes appreciably as the thermal conditions in the crucible shift to favor one of the opposing



Fig. 10.5 Data from a sapphire crystal growth run showing the desired diameter (smooth curve), the measured diameter and the process power (arbitrary units).



Fig. 10.6 Data from a sapphire crystal growth run showing the growth rate and rotation rate. Oscillations in the growth rate begin when the crystal reaches a diameter of 90 mm and end when the rotation rate drops below 6 rpm.

forces – natural or forced convection. However, starting at an elapsed time of 146 h, the oscillations resume (albeit on a very fine scale) and continue for the remainder of the crystal growth run. The melt level in the crucible has now decreased to the point that natural convection is weak compared to the stirring force of rotation.

Figure 10.6 shows data from another sapphire crystal grown in the same thermal configuration. This figure shows growth rate data (dW/dt, the rate of change of crystal weight) versus time. As this figure illustrates, starting at a growth rate of about 60 g/h (corresponding to a diameter of about 90 mm), the growth rate becomes unstable eventually oscillating by as much as ±25%. As the rotation rate is ramped downward, the oscillations virtually stop below 6 rpm. (They decrease to a level of ±0.5%, which is essentially instrument noise in the weighing system.) The lower rotation rate no longer induces melt stirring, and natural convection becomes the dominant factor in determining the interface shape.

Figure 10.7 shows data from another material – lithium tantalate. The melt-back indicating the transition to a flat interface can clearly be seen at point A. The diameter fluctuations at points B and C might appear to be typical noise in the control algorithm. However, this run was stopped at an elapsed time of about 45 h, the crystal was remelted and the run was started over with higher feedback gains, which explains the higher power variations in response to diameter changes. The interface transition of point A can be seen to repeat at point D. Similarly, the two perturbations at points B and C recur at points E and F. Figure 10.8 shows the same data with the rotation rate superimposed. It can be seen that the interface transition and the two spurious perturbations reproducibly occur at the same diameters and rotation rates.



Fig. 10.7 Data from a lithium tantalate crystal growth run showing the desired diameter (smooth curve), the measured diameter and the process power (arbitrary units). The run was restarted after 45 h. In addition to the interface transition at point A, which repeats at point D, the minor interface fluctuations at points B and C repeat at points E and F.



Fig. 10.8 Diameter data from the run shown in Fig. 10.7 along with rotation-rate data. The interface transitions and fluctuations occur at precisely the same diameters and rotation rates.



Fig. 10.9 Regimes of interface shapes as a function of rotation rate and diameter.

We can map out a generalized regime of diameter and rotation rate that describes the expected interface shape for any set of coordinates as shown in Fig. 10.9. Since many factors influence the shape of the solid/liquid interface, as will be discussed below, it is not possible to put specific values to the coordinate axes in Fig. 10.9 even for a particular material. Also, the boundaries between the various stability fields themselves shift during the growth of the crystal as thermal conditions change. Figure 10.5 shows evidence of this where the interface fluctuations largely disappeared after the crystal reached a certain size and the melt level dropped below a particular value (only to return when conditions changed again at the end of the run). In understanding the behavior of the examples discussed above, it is clear that the sapphire crystal described in Fig. 10.5 follows a path approximately as defined by the line a-a', that is, it is grown at a constant rotation rate, the interface begins in the convex regime and transitions to unstable as the diameter increases. The sapphire crystal whose data is shown in Fig. 10.6 follows a path roughly defined by the lines a-a'-a''. It also begins in the stable convex regime, transitions to an unstable regime at a fixed rotation rate, and then transitions back to a stable convex interface as the rotation rate is decreased while the diameter is fixed. The GGG crystal shown in Fig. 10.4 follows a path as defined by the line b-b'. The rotation rate is fixed throughout the process and the interface transitions smoothly from convex to flat at a diameter that can be reproducibly obtained based on the thermal gradients in the hot zone.

The lithium tantalate crystal whose data is shown in Figs. 10.7 and 10.8 is more complex. The rotation rate is ramped down throughout the growth of the shoulder. While the rotation rate change is linear with respect to time, the diameter change is not. Nevertheless, one can imagine the path this system takes through the interface stability field as roughly defined by the line c-c' in Fig. 10.9. The crystal goes through a transition from a convex to a flat interface abruptly as indicated by point A in Fig. 10.7. Then, it remains primarily in the field defining a flat interface but moves close to the area of interface instability resulting in the interface shape changes indicated by points B and C in Fig. 10.7.

10.4

Factors Influencing the Shape of the Solid/Liquid Interface

There are a number of causes that play a role in determining the shape of the solid/liquid interface. The main parameter is the vertical temperature gradient. Many important factors influence the interface depth of the crystal through their role in affecting the temperature gradient, for example, the thermal conductivity of the crystal. Table 10.1 lists several key factors influencing the interface depth and shows the direction of the effect. One factor often overlooked in oxide crystal growth is the role of the oxygen partial pressure in the ambient atmosphere in influencing the shape of the interface. Figure 10.10 shows data for sapphire. The shape of the solid/liquid interface in sapphire also appears to be unusually sensitive to rotation rate. This can be deduced from the data in Figs. 10.5 and 10.6. Figure 10.11 shows data for 100-mm diameter crystals grown in the same hot zone configuration. Significant changes in interface depth result from incrementally small changes in rotation rate.

Convective flow, which is driven by temperature gradients and buoyancy, is a strong driving force in shaping the growth interface. A myriad of factors come into play in determining the strength of the convective flow. Such parameters as the Prandtl number, Reynolds number, Grashof number, thermal conductivity of the crystal, emissivity of the crystal surface and refractive index of the crystal, among others, combine to determine the convective flow [9–11]. Since these parameters are all material specific and since they combine with parameters of the hot-zone design that determine temperature gradients, it is obvious that each system represents a unique set of parameters that will determine the interface shape.

As mentioned previously, the transition from a convex to a flat interface involves significant weight loss by the crystal which is interpreted by a weight control system as a rapid change in diameter. This is shown clearly in Fig. 10.7 where the apparent diameter undergoes a sharp break at point A even though the actual diameter is, in fact, unchanged. The response of the controller using a typical

An increase in this parameter	causes the interface depth to
Ratio of crystal diameter to crucible diameter	Decrease
Seed rotation rate	Decrease
Ratio of crucible diameter to crucible depth	Decrease
Oxygen partial pressure	Decrease
Opacity of the crystal	Decrease
Vertical temperature gradient	Increase
Heat flow out of the bottom of the crucible	Increase
Melt depth in the crucible	Increase

 Table 10.1
 Some of the Process Parameters that Impact the Interface Shape.


Fig. 10.10 Aspect ratio (crystal diameter/interface depth) as a function of oxygen partial pressure for sapphire. Data are from reference [4].



Fig. 10.11 Aspect ratio of the interface for 100-mm diameter sapphire crystals pulled from a 180-mm diameter crucible versus rotation rate.

power feedback algorithm is to drop the power in proportion to the perceived change in diameter. A sudden drop in power will cause a corresponding increase in the growth rate of the crystal. This occurs at a delicate point in the growth process when the crystal is coming to equilibrium with the melt in a new thermal regime. For a very large crystal, the weight change is proportionately larger as is the power correction. In order to ensure a smooth transition from a convex to a flat interface without a significant, and spurious, controller input the author developed a hybrid control system that utilized both optical and weight control. This is shown schematically in Fig. 10.12. An optical pyrometer views the edge of the crystal through a prism mounted on a motor-driven spindle. Simultaneously, a load cell

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Fig. 10.12 Schematic of a hybrid diameter control system combining elements of both optical and weight control.

is used to monitor the weight of the crystal. A computer collects data from both instruments and modulates the power output of the induction heater to maintain the crystal diameter. When the crystal goes through the transition from a convex to a flat interface, the pyrometer sees no significant change in the temperature signal. Consequently, the control algorithm introduces no spurious power change. Once the crystal is fully in the regime of a flat interface, diameter control reverts to the data coming from the load cell.

This hybrid controller has another advantageous feature. For the growth of a very large crystal, a large load cell is required. This, in turn, results in a loss of resolution in the measurement of weight at the start of the growth process when the initial neck is being grown. The analog-to-digital converters used in these applications have a fixed resolution independent of the size of the load cell. So a larger load cell results in a corresponding loss in resolution at the start of the growth process where the growth rate can be two orders of magnitude or more lower than the growth rate at full diameter. For an optical controller, on the other hand, the



Fig. 10.13 A GGG crystal grown using the hybrid control scheme shown in Fig. [10.12]. An interface transition was forced before the crystal reached the final diameter and control was switched over to weight control.

resolution is largely independent of the crystal diameter. So precise control can be achieved independent of the size of the crystal. Figure 10.13 shows a GGG crystal grown with this hybrid control system. This crystal had a nominal final diameter of 110 mm and weighed about 25 kg. As the photograph shows, the diameter control at seed diameter (where the growth rate was less than 2 g/h) is excellent and comparable to the diameter control at full diameter (where the growth rate was approximately 250 g/h). There are no indications of controller-induced diameter fluctuations where the interface transition from convex to flat took place.

Figure 10.14 shows the path used for the rotation rate during the growth of this crystal. The process begins at seed diameter with a constant rotation rate. At a diameter of about half the final target, the rotation rate is ramped up fairly quickly to induce a flat interface. Then, as the diameter continues to increase, the





Fig. 10.14 The rotation-diameter path used during the growth of the crystal shown in Fig. 10.13 (see text).

rotation rate is reduced to stay within the regime of a stable, flat interface. Further rotation-rate changes were typically employed at two other stages during the growth of the full-diameter section. A reduction in rotation rate would take place when the melt level had dropped to about half its starting value. At this stage in the process, natural convection weakens because of the reduced melt level and because the temperature gradient in the melt itself is lower. Then, during the growth of the final 20–35 mm, the rotation rate would be increased again to prevent the formation of large facets on the growth interface.

10.5

Conclusions and Discussion

All advanced Czochralski systems employ some form of diameter sensing and feedback control mechanism to maintain a uniform diameter. The nature of the material (oxide, metal, semiconductor, etc.) and its physical characteristics (thermal conductivity, density change on freezing, etc.) largely dictate which form of control is used. In weight control systems, interface shape changes are interpreted as diameter changes by the controller. This can have a negative impact on the control operation. The interface shape can be unstable in certain regimes of temperature gradient, crystal diameter, crucible diameter and rotation rate. A hybrid control system utilizing both optical and weight control can overcome the signal-to-noise limitations of a weight control system and also eliminate the diameter ambiguity associated with an intentionally induced interface-shape change.

Although weight controllers would appear to be at a disadvantage in a growth regime where the interface is unstable, they offer the benefit of seeing the instability as it is occurring. An optical controller, in many of these cases, would not sense the fluctuating shape of the interface and pass this information on to the growth engineer.

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11 Use of Forced Mixing via the Accelerated Crucible Rotation Technique (ACRT) in Bridgman Growth of Cadmium Mercury Telluride (CMT)

Peter Capper

11.1 Introduction

SELEX Sensors and Airborne Systems Infrared Ltd. has been producing infrared (IR) detector materials, mainly $Cd_xHg_{1-x}Te$, CMT, since about 1965. This was shortly after the discovery of CMT by Lawson *et al.* [1]. CMT has since become the pre-eminent IR detecting material and is the third most researched semiconductor after Si and GaAs, although much of the work has been done in industrial/military labs and hence has not been published in the open literature. A variety of growth techniques has been employed in the field, from several bulk methods through liquid phase epitaxy (LPE) and, more recently, metal-organic vapor phase (MOVPE) and molecular beam (MBE) epitaxy techniques [2]. Bulk growth is still used for 1st-generation photoconductive products, of which tens of thousands of systems are still in service. Second-generation photovoltaic detectors are made in LPE/MOVPE/MBE material, including high operating temperature devices and multicolor detectors [3].

There is an estimated 1.5\$B pa. IR systems business worldwide, of which IR arrays account for perhaps \$600 M pa. CMT is used in \sim half of these arrays, i.e. \sim \$300 M pa, and it can be estimated that the materials element of this amounts to \sim \$30 M pa. This figure includes both bulk and epitaxial material, with \sim \$5 M and \sim \$25 M pa. values attaching, respectively, to the 2 areas. Currently, SELEX probably accounts for over half of the bulk total.

The main compositional requirements (*x* in $Cd_xHg_{1-x}Te$) are for $x \sim 0.21$ and $x \sim 0.3$ for the atmospheric IR transmission windows of 8–14 and 3–5 µm, respectively, although a much wider range of *x* has been produced by both bulk and epitaxial growth methods for various applications, e.g. we are currently extending our bulk growth process to higher *x* values to cover the 1–3 µm region. Very low carrier concentration n-type material (<3 × 10¹⁴ cm⁻³, or ~10 ppb atomic) is required for photoconductive detectors (particularly SPRITES – signal processing in the element) still in production. Annealing schedules have been developed to modify and control electrical properties to desired levels at any required *x* value. Central to the successful use of these materials are the dual issues of elemental

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purity and cleanliness in all stages of preparation and handling, particularly prior to high-temperature heat treatments. A wide variety of assessment techniques has also been developed to characterize the compositional, electrical and structural properties as well as chemical purity. For details of the various device types made from the range of materials produced the reader is referred to Chapters 11 and 12 of [3].

This chapter is split into 4 sections. The first deals briefly with purification of elemental mercury and tellurium, the second covers bulk growth of CMT by the Bridgman process and the third describes the addition of the accelerated crucible rotation technique (ACRT) to the basic Bridgman process. Finally, a few comments on the devices that have been and continue to be made from this material are given.

11.2

Elemental Purification (Mercury and Tellurium)

All bulk growth processes for CMT use pure elements as the starting materials and high-purity silica ampoules. Despite this, our experience has shown that problems can occur when using bought-in elements directly, even when such material is the purest grade available, i.e. 99.99999% (7N). These problems manifest themselves as charges sticking to silica ampoules, believed to be due to oxygen on Te and/or Cd surfaces, or as high background donor levels in the resulting CMT. For these reasons, and to maintain a consistent and controlled product, facilities to purify both Hg and Te prior to use were established some years ago. As cadmium is the smallest fraction of most CMT material, and it is available in very high purity in rod form, it is used as-received from the manufacturer with no prior treatment on site.

Bought-in Hg, in triply distilled form, is passed through a subboiling point vacuum distillation process in a high-purity, all-silica apparatus. From an initial batch of \sim 9 kg the first fraction (\sim 3 kg) is used for low-temperature Hg annealing processes, while the second fraction (the purest) is used in both bulk and epitaxial growth processes. The remaining fraction is re-cycled to the supplier for re-distilling. We have shown by atomic absorption spectroscopy (AAS) that the amounts of Cu and/or Ag (both acceptors in CMT) are significantly reduced by this process and possibly other elements also, although the differences were small with other elements.

Tellurium purification is by zone-refining in flowing hydrogen at ~500 °C. Bought-in material is loaded into a cleaned silica boat in 5 kg batches. This is then placed into a silica tube in a 5-zone furnace arrangement. After flushing with argon, hydrogen is introduced and the furnaces ramped to temperature. These temperatures and furnace spacings have been adjusted to ensure that there is still solid Te between each molten zone. Zones are traversed down the boat at ~25 mm/h and 5 passes of 5 zones each are carried out. This has the effect of moving impurity elements with segregation coefficients, *k*, of <1 to the tail of the bar, while those with *k* > 1 segregate to the tip of the bar. The furnaces are then slowly moved off the bar to give the material the correct "longitudinal" structure for subsequent cleaving prior to use. On removal, the tip and tail sections are removed, for re-cycling, while the central section (~4 kg) is ready for use with no further chemical cleaning necessary.



Fig. 11.1 Bridgman/ACRT process flow. (Reprinted from Capper *et al. J. Cryst. Growth* 275 (2005) 259, copyright (2005) reproduced with permission from Elsevier Science.)

11.3 Bridgman Growth of CMT

11.3.1 Introduction

Historically, the first technique used at SELEX Sensors and Airborne Systems Infrared Ltd. was the Bridgman process. Later, the emphasis switched to the accelerated crucible rotation technique (ACRT), a modification of the Bridgman process. Reviews of bulk growth can be found in [2, 4].

11.3.2 Processing

Elemental Cd (unetched) plus in-house purified Hg and Te are loaded, within a nitrogen-purged glove box, into an etched, washed, heavy-wall (3 mm) silica ampoule (diameter 12–13 mm). A start composition of x = 0.12 is used and homogenization is by melting/rocking (see Fig. 11.1). Charges are then placed in a vertical grower (see Fig. 11.2), remelted and then frozen slowly (0.5 mm h⁻¹) from one end in a vertical system to produce a large-grained ingot. Slow rotation about the vertical axis is used to reduce radial temperature variations. Slices are cut from the resulting crystals using an abrasive slurry on a multiblade cutting machine. Slices are then assessed for wavelength, i.e. *x*, uniformity with infrared transmission (IRT) measurements and for the electrical parameters by Hall effect measurements at 77 K.

Figure 11.3 shows the arrangement used for crystal slicing. A carborundum powder in glycol slurry is fed over the spring steel blades and the crystal is moved reciprocally over the blades to abrade the crystal to produce slices of 0.35–0.5 mm thickness. Diamond slicing, on a similar machine, on a peripheral-wheel machine and on single- and multiwire machines has also been tried but problems with



Fig. 11.2 Bridgman/ACRT growth apparatus. (Reprinted from Capper *et al. J. Cryst. Growth* 46 (1979) 575, copyright (1979) reproduced with permission from Elsevier Science.)

cracking and breaking at <0.5 mm thickness brought us back to the current technique. Diamond slicing on a peripheral-wheel machine is used, however, for producing thicker (>1 mm) slices of material. The kerf loss is ~260 μ m (the blade is ~160 μ m thick with ~50 μ m of lapping on both sides of the blades). The cutting rate is typically ~7 h for a 20-mm crystal and the uniformity of cut is ~4% across the blade pack.

11.3.3 Results

There is marked segregation of HgTe down the length of the crystals that represents an advantage of the Bridgman process over other bulk-growth techniques, i.e. material in several ranges of interest $(1-3, 3-5 \text{ and } 8-12 \mu \text{m})$ is produced



Fig. 11.3 Slicing arrangement using multiblade machine (courtesy of SELEX Sensors and Airborne Systems Infrared Ltd.).

in a single run, but has the disadvantage of only producing low yields in each of these regions. In [5] it was shown how radial *x* variations decreased as the distance from the first-to-freeze end increased and as the growth rate decreased. The extent of the radial *x* variation was due to the combination of a concave growth surface (with respect to the solid) and density-driven convective flow within a boundary layer close to the interface. This, added to the normal segregation of the low melting-point HgTe to the center of the concave interface, leads to the observed variation. Figure 11.4(a) shows data from a typical long wavelength (LW) slice with a variation of $\sim 0.5 \,\mu\text{m}$ from center to edge.

Photoconductive devices require low carrier concentration n-type material and this was produced by improving the purity of the starting materials. Low n-type levels ($<3 \times 10^{14}$ cm⁻³) were achieved in the as-grown state for x = 0.2-0.3, an obvious advantage in terms of reduced handling for Bridgman growth as no annealing stage was required – unlike other bulk methods. Bridgman material was used [6] to establish the pressure–temperature diagram, by a combination of isothermal and two-temperature annealing. On the Hg-rich side at temperatures below 320° the n-type carrier concentration is controlled by residual impurities. The p \rightarrow n conversion is due to Hg filling metal vacancies. Conversion from n \rightarrow p was achieved by two-temperature annealing with the Hg at a lower temperature than the CMT slice, in order to introduce metal vacancies. Bridgman material is n-type as the long-wavelength material is cooled in the presence of free mercury, causing the metal vacancies to be reduced in number and n-type material to be formed.

By growing specifically doped crystals we were able to show that most impurity elements are electrically active in accordance with their position in the periodic table [7]. This behavior is linked to stoichiometry at growth, i.e. those elements that substitute on Te lattice sites have to be somehow forced into the correct sites in

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Fig. 11.4 Radial variations in wavelength (in μ m at room temperature) in 13-mm diameter Bridgman (a) and 20-mm diameter ACRT (b) material. Upper – full area coverage, lower – vertical and horizontal line scans. (Reprinted from Capper *et al. J. Cryst. Growth* **275** (2005) 259, copyright (2005) reproduced with permission from Elsevier Science.)

Te-rich material. Group I and III elements are acceptors and donors, respectively, on the metal sites. There is evidence, however, that some Group I elements can migrate at low temperatures to grain boundaries or to the surface of samples. Bridgman also benefits from marked segregation of impurities due to its slow growth rate, leading to very low levels of impurities [7].

In the early phase of work 13-mm diameter samples were assessed for purity using laser scan mass spectrometry (LSMS) and Table 11.1 gives results for Bridgman and ACRT crystals [5]. Segregation effects lead to highly pure regions near to the first-to-freeze end. Very low levels of all impurities (including C and O) can be seen in the Bridgman material. This low impurity level in as-grown material makes Bridgman material the ideal vehicle for testing new tellurium or mercury batches. If a new batch of Te or Hg is used and the normal low carrier concentration n-type material is obtained in the as-grown state then the batch is deemed to be qualified for use in ACRT production material.

Bridgman crystals contain several major grains and numerous subgrains within each major grain. A Berg–Barrett X-ray topography study of Bridgman material

Table 11.1 LSMS impurity survey in Bridgman and ACRT bulk CMT samples ($\times 10^{15}$ atoms cm⁻³, precise to factor of 3, accurate to factor of 2, * Intentional Dopant). (Reprinted from Capper, *Prog. Cryst. Growth Charact.* **28** (1994) 1, copyright (1994) reproduced with permission from Elsevier Science.)

Element	Bridgman	ACRT
Li	<0.005	0.6
С	3	30
0	< 0.05	0.1
F	0.06	< 0.2
Na	0.03	0.6
Al	0.2	< 0.09
Si	1	< 0.3
S	1	< 0.06
К	0.03	0.6
Cr	0.2	< 0.06
Cu*	<0.5	30

showed it to contain grains of size 0.2-0.6 mm, near to the crystal center, and 0.05-0.2 mm near to the crystal periphery.

11.4 Accelerated Crucible Rotation Technique (ACRT)

11.4.1 Introduction and Theory

Limits on controlling melt mixing in the Bridgman process necessitated a means of stirring melts contained in sealed, pressurized ampoules. The ACRT of Scheel [8] was utilized as it increased the size of crystals, eliminated unwanted phases, and increased stable growth rates. The first reported use of ACRT in CMT Bridgman growth was given in [9]. These effects were developed and discussed in more detail in later papers (see [5, 10] for reviews) and are outlined here.

Three processes that are fast by comparison with bouyancy-driven convection and occur on acceleration/deceleration are:-

a. Transient Couette flow that occurs on rapid deceleration (spin-down) particularly in tall containers. Liquid adjacent to the container walls decelerates faster than liquid in the bulk and centrifugal forces drive the inner portions of liquid towards the wall. Horizontal vortices form in counter-rotating pairs. This only occurs beyond a critical rotation rate, given by a value of 270 for the dimensionless Reynolds number:

$$Re = R^2 \Delta \Omega_c \sigma / \eta \tag{11.1}$$

where

$$\Delta\Omega_{\rm c} = {\rm step} {\rm change in rotation rate (rpm)} = \Delta\Omega_{\rm c} \times 2\pi/60 {\rm ~rads^{-1}}$$

 $R = {\rm container radius (cm)}$
 $\sigma = {\rm fluid density (g {\rm cm^{-3}})}$
 $\eta = {\rm dynamic viscosity of fluid (g {\rm cm^{-1} s^{-1}})}$

b. Spiral shearing flow, which occurs on both spin-down and spin-up, and is again caused by fluid at the walls changing its velocity faster than liquid in the bulk. It is characterized by the thickness, *d*, of a layer close to the wall where the rotation rate is half its initial value and by τ_1 , the time taken by the central part of the fluid to reduce to this level.

$$d = R(E\Omega_0 t)^{0.5} \approx (\eta t/\sigma)^{0.5}$$
(11.2)

$$\tau_1 = 0.1 (E\Omega_0)^{-1} \approx 0.1 \sigma R^2 / \eta \tag{11.3}$$

where

t = time after container stops rotating (s) $\Omega_{o} =$ maximum rotation rate (rpm) E = Ekman number ($\eta / \Omega_{o} R^{2} \sigma$)

Spin-up/spin-down times should be $<\tau_1$ to maximize stirring.

The number of spiral arms is given by:

$$N = \Omega_0 \sigma R^2 / 16\pi \eta \tag{11.4}$$

with separation,

$$\Delta r = 4\pi\eta/\sigma\Omega_{\rm o}r\tag{11.5}$$

where *r* is the radius of the point in question. (Δr should be kept at 0.01–0.1 cm to ensure diffusion can act as the mixing process.)

c. Ekman flow that occurs above a solid boundary placed perpendicular to the axis of rotation. During spin-up, fluid adjacent to the boundary is forced to the side walls and returns diffusely and more slowly through the bulk, with the reverse occurring on spin-down.

The Ekman layer thickness is given by:

$$d_{\rm E} = (\eta / \Omega_0 \sigma)^{0.5} \tag{11.6}$$

with maximum radial fluid velocity of:

$$V = \Omega_0 R \tag{11.7}$$



Fig. 11.5 ACRT rotation sequence. (Reprinted from Capper *et al. J. Electron. Mater.* 15 (1988) 363, copyright (1988) reproduced with permission from The Minerals, Metals and Materials Society.)

and maximum vertical fluid velocity of:

$$W = (\eta \Omega_0 / \sigma)^{0.5} \tag{11.8}$$

The flow decreases within a time:

$$\tau_{\rm E} = R(\sigma/\eta\Omega_{\rm o})^{0.5} \tag{11.9}$$

Figure 11.5 shows the ACRT rotation sequence used and Fig. 11.6 depicts the various flows as seen in water simulation trials. All three predicted flow patterns were seen and showed qualitative agreement with the parameters given in Eqs. (11.2)–(11.9). The most vigorous stirring arose due to Ekman flow for distances of $\sim R$ to 2R from the container base (Ekman volume), particularly when a flat-based container was used.

Brice et al. [10] reviewed the models developed for flows induced by ACRT and summarized by identifying three distinct flow regimes as the acceleration/deceleration rate increases. For small accelerations, axially symmetric fluid flows increase the symmetry of heat and mass flows. Moderate accelerations produce axial and radial fluid flows at the base of the column (R to 2R) that stir the fluid in this region only. Large accelerations give rise to unstable asymmetric flows. The system is characterized by the Reynolds number, and Table 11.2 lists the critical Reynolds numbers and the corresponding rotation rates for the values of *R* (0.65 cm) and η/σ (0.006 cm² s⁻¹) typical of CMT melts. These values of Re_c are superimposed onto the interface depth (from crystal quenching studies - see below) versus rotation plot of Fig. 11.7. For points (a) and (b) Ekman flow is delayed as the ampoule base is not perpendicular to the rotation axis in the conical-based ampoules used for growth. Once Ekman flow is fully established, the interface depth decreases to a minimum. Couette instabilities are predicted to occur at point (c) and were seen in the simulations, although they do not affect the interface depth as they only occur in the upper regions of the liquid not near to the solid/liquid interface. As the Reynolds number increases further, Ekman flow will become unstable, at point (d), and the interface depth consequently increases. Too much melt mixing can be introduced by certain ACRT conditions and this leads to a deterioration in crystal properties.



Fig. 11.6 Flows in a flat-based container during a) spin-up and b) spin-down. (Reprinted from Capper *et al. J. Electron. Mater.* 15 (1988) 361, copyright (1988) reproduced with permission from The Minerals, Metals and Materials Society.)

Bidirectional rotation is employed and rapid acceleration/deceleration (in 1–2 s) is easily achieved at any rotation rate. The Ekman layer thickness, $d_{\rm E}$, from earlier flux growth, should be <0.05 cm, which necessitates rotation rates >20 rpm. Horizontal and vertical flow velocities, *V* and *W*, are $\gg R/\tau_{\rm E}$ for all rotation rates, ensuring that the Ekman volume passes through the Ekman layer each ACRT cycle. Rotation rates >20 rpm will ensure that Δr is within the preferred range of 0.1–0.01 cm to homogenize the fluid body by diffusion. Both run (at maximum rate)

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Fig. 11.7 Interface depths measured in quenched crystals of 13 mm diameter with critical rotation rates noted according to Table (11.2) (the numbers along the top of the figure are for the 20-mm diameter case). (Modified from Capper *et al. J. Cryst. Growth* **89** (1988) 171, copyright (1988) reproduced with permission from Elsevier Science.)

Table 11.2 Critical Reynolds number (Re_c) and corresponding critical rotation rates (in rpm) for ACRT in 13 and 20 mm diameter ampoules. ($\nu = \eta / \sigma = 0.006$, kinematic viscosity in cm² s⁻¹). (Modified from Capper, *Prog. Cryst. Growth Charact.* **28** (1994) 1, copyright (1988) reproduced with permission from Elsevier Science.)

Event	Rec	rpm	
		13 mm	20 mm
Ekman flow starts a)	15	~2	~ 1
Ekman flow fully developed b)	70	10	4
Couette flow unstable c)	270	38	16
Ekman flow unstable d)	500	69	30

and stop times, τ_r and τ_s , can be set to values close to the Ekman time, τ_E , to ensure mixing occurs for as long as possible and that decaying Ekman flow is minimized.

11.4.2 Results

Application of ACRT opened up a large number of possible parameter combinations. Quenching studies of crystals grown under a wide variety of conditions showed interface depths of \approx 1 mm for *x* = 0.12 and 0.19 start crystals, unlike the values of 1 and 4 mm, respectively, seen in equivalent standard Bridgman crystals.

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Increasing the maximum rotation rate produced the interface depths shown in Fig. 11.7. The preferred region in which to operate is clearly $25 < \Omega_o < 60$ rpm. As growth rate increased, interface depth changed much less than in Bridgman growth, suggesting that faster stable growth rates are possible with ACRT. From the simulation studies, it was apparent that a small stagnant region occurred in the tip of a conical-based ampoule. Quenching studies in flat-based ampoules revealed not only a flat interface but also that the slow-grown material, produced prior to quenching, was single crystal. This demonstrated the power of Ekman stirring and the importance of initiating the growth of a single crystal grain.

In the early days of ACRT development various rotation sequences and start compositions were investigated using 13-mm diameter crystals and *x* uniformity and crystal structure determined. After comparing results, x = 0.19 was chosen as the preferred start composition. For these crystals grown with short run and stop times (8 and 1 s) there was a region (several cm long) of x = 0.21 material with axial and radial *x* uniformity of ± 0.002 . A similar Bridgman crystal would produce <0.8 cm of similar *x* material with considerably larger radial *x* variations, i.e. ACRT gives a five- to ten-fold increase in potentially usable material. Figure 11.4(b) shows the improvement in the radial wavelength variations (now within $\pm 0.01 \,\mu$ m over a 20-mm area). This suggests that relatively flat interfaces are present throughout the growth process, a marked improvement over normal Bridgman growth.

A secondary benefit obtained from ACRT was a decrease in the number of major grains, typically from 10 to 1 in the x = 0.2 region. A Berg–Barrett X-ray topography study of ACRT samples showed that the misorientations of subgrains was reduced, compared to Bridgman, but the density was essentially unchanged.

The electrical properties of 13-mm diameter ACRT material differ markedly from those of equivalent Bridgman crystals [7]. Material with x > 0.3 is n-type as-grown, at a level above that found for Bridgman crystals but, at x < 0.3, the material is p-type. Such material converts to low $(<1 \times 10^{15} \text{ cm}^{-3})$ n-type on the standard anneal treatment [6] indicating that metal vacancies are the cause of the p-type behavior. We conclude from this that the long-wavelength material in an ACRT crystal is in such a position within the crystal that it cools down on the mercury-deficient, or tellurium-rich, solidus line, although the details of this process are unknown. Impurity segregation behavior in ACRT material was also found to be different from Bridgman growth [5]. In general, impurity segregation coefficients decrease in ACRT crystals, when compared to standard Bridgman. Table 11.1 summarizes the impurity levels found in an early 13-mm diameter ACRT slice. Very low levels of impurities can be seen, apart from Cu that was deliberately added to dope this crystal p-type.

11.4.3 High-x Material

This section focuses on the work undertaken to produce near-IR material, where higher starting x values are used. The assessment of the near-IR material has included wavelength mapping of both radially cut slices and axially cut planks.



Fig. 11.8 Pseudobinary phase diagram for HgTe-CdTe system (L = liquid, S = solid). (Reprinted from Brebrick in *Properties of Narrow Gap Cadmium-based Compounds* (1994) 56, copyright (1994) reproduced with permission from IEE.)

The latter gives useful information on the shape and change in the solid/liquid interface as growth proceeds. Quenching experiments reveal actual solid/liquid interfaces that confirm the findings of the wavelength mapping. Images taken with an IR camera reveal features in slices, e.g. cracks, inclusions of second phase and swirl patterns, the origin of the latter is unknown. This work is being undertaken to improve our basic understanding of the properties of CMT in the near-IR region and to investigate the suitability of the material for use in various IR optical applications.

Figure 11.8 shows the pseudobinary phase diagram of the HgTe-CdTe system [11]. This demonstrates the fundamental problem in the near-equilibrium growth of CMT by melt growth methods, i.e. the wide separation between the liquidus and the solidus. However, this is actually a benefit when we are trying to produce higher *x* material. As the starting *x* is increased the first-to-freeze material also increases in *x*, although not at quite the same rate due to the relative curvatures of the liquidus and solidus. The initial goal was to produce material of $x \sim 0.7$, corresponding to $\sim 1.3-1.4\,\mu\text{m}$ cut-off wavelength. Figure 11.8 shows that this necessitates using starting *x* values of 0.33-0.35. Figure 11.9 shows the pressure–temperature phase diagram for various *x* values [11]. The region above the P^o_{Hg} line is essentially Hg vapor, with solid of the indicated *x* values existing in the loops on the lower right and liquid to the left of the loops. This amply demonstrates how the maximum growth temperature and hence the Hg vapor pressure increases as *x* increases.

As for the earlier crystals, elemental Cd (unetched), plus in-house Hg and Te are loaded within a nitrogen-purged glove box, into an etched and washed, heavy-wall (7 mm) silica ampoule (diameter 20 mm). After pumping, the thick-walled ampoule is sealed off at the upper constriction, using stainless steel torches to avoid





Fig. 11.9 Pressure-temperature diagram for CMT. (Reprinted from Brebrick in *Properties of Narrow Gap Cadmium-based Compounds* (1994) 59, copyright (1994) reproduced with permission from IEE.)

contamination with fast-diffusing impurities. We have had to develop this seal-off procedure to reduce the possibility of explosions due to the high pressures. This entailed ensuring that the wall thickness remained at the 7-mm value of the ampoule body and ensuring that there were no re-entrant angles in the seal-off area. By making the internal surface of the seal-off smooth we have greatly reduced the occurrence of explosions and have successfully grown at temperatures >900 °C, i.e. some 80 °C above "standard" temperatures.

Start compositions of x = 0.25-0.35 have been used and the melts were homogenized by melting/rocking as for standard charges. The growth process remained essentially unchanged for these high-*x* crystals. Slices were cut (at >1 mm thickness) from the resulting crystals using a diamond peripheral-wheel cutting machine and then polished and assessed for *x* uniformity with infrared transmission (IRT) measurements and also using the mid-IR camera system.

Figure 11.5 shows the ACRT sequence that was also used for these high-*x* crystals. Standard bi-directional rotation is still employed with rapid acceleration/deceleration (in 1–2 s). From considerations of the simple model [5] it was seen that maximum rotation rates for these 20-mm diameter crystals should be between 4 and 30 rpm. Also for these crystals short run and stop times (8 and 1 s, respectively) were used as for standard crystals. To maximize the Ekman stirring, i.e. increase the vertical and horizontal flow velocities (to values of $> R/\tau_E$), we



Fig. 11.10 Axial composition profiles of high-x ACRT crystals. (Reprinted from Capper *et al. J. Mater. Sci. Mater. Electron.* 15 (2004) 721, copyright (1988) reproduced with kind permission of Springer Science and Business Media.)

chose to use 25 rpm as the maximum rate. This rotation rate also ensures that the spiral separation is \sim 0.03 cm at its maximum value, which ensures full mixing by diffusion between the spiral arms, see Eq. (11.5).

Figure 11.10 shows the axial composition profiles of some of the crystals grown. As expected, as the start *x* value increases so does the "plateau" region of near-constant composition, although not necessarily linearly with start *x* due to variations in ampoule shape and diameter, note we are only plotting against slice number and not normalized distance. The plots in Fig. 11.10 also show some evidence of growth transients in the first-to-freeze sections of some of the crystals. This could be caused by constitutional supercooling in the tip regions, possibly linked to a lack of adequate stirring in these conically shaped regions. In fact, a slower-grown crystal (0.25 mm h⁻¹) produced a much reduced initial transient, suggesting that constitutional supercooling could well be the cause.

Figure 11.11 shows the FTIR map of a 20-mm diameter (from the conical tip region) short-wavelength slice ($\lambda \sim 1.3 \,\mu$ m) demonstrating excellent radial uniformity in this extremely short wavelength region. To try to simultaneously assess the radial and axial uniformity we sliced an axial plank, $\sim 20 \times 40 \,\text{mm}$ in size, and mapped the wavelength variations in the normal way. Figure 11.12 shows the results of this measurement and it can be seen that at the lower (first-to-freeze) end the "interface depth" is small and the shape is slightly convex (not ideal). As growth proceeds the interface shape takes on a "seagull wing" shape, although the uniformity is still good. In the upper half of the plot the sample is again uniform in both the axial and radial directions ($\pm 0.1 \,\mu$ m over a 20 \times 20 mm area). This is the plateau region for this particular start x crystal.



Fig. 11.11 Radial distribution of wavelength (in μ m at room temperature) in high-x slice.

To further investigate the interface region in these high *x* crystals we carried out quenching studies in several crystals. Figure 11.13 shows the interfaces delineated by quenching followed by axial sectioning and etching to reveal the differences in structure for the slow-grown and the cast material. Three different crystals were quenched at positions 5, 90 and 190 mm from the first-to-freeze position. It can be seen that flat (~1 mm) convex interfaces are present near to the first-to-freeze end and in the *x* ~ 0.2–0.3 regions, i.e. at 5 and 90 mm, respectively, mirroring the excellent compositional uniformity in these regions. At the 190-mm position the interface depth is large (>10 mm) but it should be noted that this is approaching the HgTe-rich section of the crystal, i.e. where the Cd content is very low. Under these conditions there is no segregation of HgTe and hence its homogenization is not relevant.

Another assessment tool that is used for these high-*x* crystals is that of IR imaging. By placing a blackbody on one side of the slice (polished on both sides to \sim 1 mm thickness) and a MW camera system (CEDIP) on the other, images can be taken that reveal IR-absorbing defects. (This camera system uses an OSPREY detector manufactured at SELEX Sensors and Airborne Systems Infrared Ltd. from LPE material.) This is a rapid, noncontact assessment method that can be used for all slices with cut-off wavelengths less than that of the camera system's detector. Figure 11.14 shows several such images from slices taken from one crystal, although the features seen are also observed in other crystals. The low-numbered slices are from the first-to-freeze end of the crystal and it can be seen that they are essentially



Fig. 11.12 Variations in wavelength (in μ m at room temperature) in high-*x* ACRT axially sliced plank. (Reprinted from Capper *et al. J. Mater. Sci. Mater. Electron.* **15** (2004) 721, copyright (1988) reproduced with kind permission of Springer Science and Business Media.)

free of absorbing defects. As the slice number increases, first edge cracks (slices 21 and 22) and finally second-phase inclusions (slices 34 and 37) probably of Te, and "swirl-like" patterns of light/darker contrast, rather than black/white, appear. The origin of the latter patterns is unknown at present. Possible causes include ACRT stirring flow patterns frozen in, p-type regions in an otherwise n-type slice or areas of different strain. Work is continuing in this area of assessment to understand the origin and extent of these IR-absorbing defects.

Several different methods have been applied to reduce cracking in these high-x start crystals. The first was carbon coating of the inside of the growth ampoules to eliminate sticking of the charges to the ampoule wall. Figure 11.15 shows IR camera images of slices from such a crystal, where it can be seen that there is

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Fig. 11.13 Solid/liquid interfaces in quenched high-x ACRT crystals. (Reprinted from Capper *et al. J. Mater. Sci.:Mater. Electron.* 15 (2004) 721, copyright (1988) reproduced with kind permission of Springer Science and Business Media.)

no cracking but some "structure" is still evident. Seeding, using both 10-mm and 20-mm seeds of (111)-oriented Cd(Zn)Te has also been attempted. Preliminary results show that seed-on to produce (111) CMT takes place, but cracking and extra grain growth still occurs. Halving the normal growth rate, to \sim 0.2 mm/h, also reduces crystal cracking, as shown in the IR images of the short-wavelength slices in Fig. 11.16. To improve the degree of stirring by ACRT, flat-based ampoules have also been used. The IR camera images of Fig. 11.17 show that this approach has also been successful in reducing crystal cracking.

To compare results from the various approaches, we plot in Fig. 11.18 the maximum transmission values versus wavelength for these \sim 1-mm thick slices. It can be seen that as the wavelength reduces to \sim 1.3 µm the theoretical maximum transmission value of \sim 64% is approached. The decrease in the maximum transmission values at longer wavelength is due to free-carrier absorption. These high maximum transmission values and uniformity of transmission (as evidenced by the IR camera images and FTIR maps) make this material highly suitable for use in IR window applications.

As the LSMS chemical analysis technique is no longer available to us, current chemical analysis is by secondary ion mass spectrometry (SIMS) which has been used to assess the impurity levels in this recent ACRT material. The distributions of known donors and acceptors in CMT were measured. The Cr, Al, K, Br, I, H, C and Si were at, or below, the detection limits of the technique, while Na, Ga, In and Cl were at or above the detection limits. The Na and Ga were only present at the mid-10¹³ atoms cm⁻³ level, while the Cl was present in the low-10¹⁴ atoms cm⁻³ region. The silica used for the growth ampoules was a "chlorine-free" synthetic type that perhaps still has a small residue present. This chemical analysis attests to the high purity and reproducibility of this ACRT material.



Slice 37 (3.1 µm)



Slice 34 (2.6 µm)



Slice 22 (1.6 $\mu\text{m})$



Slice 21 (1.6 µm)





Slice 20 (1.6 µm)

Slice 17 (1.5 µm)

Fig. 11.14 IR camera images in high-*x* ACRT slices (number in brackets = cut-off wavelength of slice). (Reprinted from Capper *et al. J. Mater. Sci.:Mater. Electron.* **15** (2004) 721, copyright (1988) reproduced with kind permission of Springer Science and Business Media.)

11.5 Uses in IR Devices

For first-generation IR detectors the low n-type carrier levels and high lifetime of Bridgman/ACRT material produced high-performance SPRITE (signal processing in the element) detectors [12]. Figure 11.19 shows the operating principle of the

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Fig. 11.15 IR camera images in high-*x* ACRT slices from 33% start crystal grown in carbon-coated ampoule (number in brackets = cut-off wavelength of slice) (courtesy of SELEX Sensors and Airborne Systems Infrared Ltd.)



Fig. 11.16 IR camera images in high-x ACRT slices from crystal grown at half the standard rate (number in brackets = cut-off wavelength of slice) (courtesy of SELEX Sensors and Airborne Systems Infrared Ltd.)



Fig. 11.17 IR camera images in high-x ACRT slices from crystal grown in flat-based ampoule (number in brackets = cut-off wavelength of slice) (courtesy of SELEX Sensors and Airborne Systems Infrared Ltd.)



Fig. 11.18 Maximum transmission values versus slice wavelength (courtesy of SELEX Sensors and Airborne Systems Infrared Ltd.)

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device where the image is scanned along the CMT strip at a rate similar to the rate at which carriers diffuse under bias. In the lower part of this figure the processing of a slice is depicted. On thinning to $\sim 10 \,\mu$ m, the slice is cut into strips (monoliths) and these are mounted on sapphire carriers prior to metallization and dicing to delineate the elements. In a study of far-IR detection at 350-1200 µm, Kimmitt et al. [13] found that ACRT CMT (0.39 < x < 0.53 and $3 \times 10^{13} - 2 \times$ 10^{14} cm^{-3} n-type) acted as an impurity photoconductor. Charlton *et al.* [14] listed the various space applications that have used bulk material to make discrete IR detectors, both photoconductive and photovoltaic. Ashley et al. [15] demonstrated room-temperature operation in photoconductors made in ACRT-grown material using excluding contacts to suppress Auger-generated noise. ACRT was also critical in producing sufficient material of the required composition and carrier concentration for several large photoconductive detector programmes. There are some 5000-6000 UK Common Module imagers in service worldwide that are based on this bulk material. This material is still used at BAE SYSTEMS for a wide range of single and multielement photoconductive arrays of IR detectors, including several types of SPRITEs. Currently, the 20-mm diameter ACRT material is in production for several large photoconductive detector programmes.

For second-generation IR detectors the first staring array imagery in the 8–14 μ m band (77 K) was demonstrated [16] using ACRT CMT. Ballingall *et al.* [17] discussed the detrimental effects of major grain boundaries on 2-dimensional array performance. Baker *et al.* [18] also reported that such structure leads to anomalous crosstalk between adjacent diodes. Uniformity of diode properties could be high, however, in 32-element linear arrays. Despite this subgrain structure, a 32 \times 32 array (4.5 μ m cut-off) with only a single defective element was made in ACRT material. Both 3–5 and 8–14 μ m band arrays of 64 \times 64 elements have been made in ACRT material [18]. Yields of these larger arrays, however, are low due to the subgrain structure, hence the movement to using epitaxial material. These device aspects are fully discussed in [3].

11.6 Summary

In the Bridgman growth of CMT, a controlled increase in melt mixing produced by ACRT leads to an improvement in radial compositional variations and good axial uniformity resulting in a factor of ten increase in overall material yield over normal Bridgman growth. Large-diameter crystals (up to 20 mm) have been grown with a high degree of radial *x* uniformity by ACRT. Crystals of 20 mm diameter with a length of 200 mm weighing \sim 0.5 kg are now routinely produced. Electrical and chemical characterization shows that high-purity material is obtained (when pure elements are used) and this allows the manufacture of a wide variety of high-performance photoconductive infra-red detectors. Bulk-growth techniques for CMT are still in production in a few places across the world and continue to satisfy the needs of first-generation long-wavelength infrared detectors, based on



Fig. 11.19 Principle of SPRITE operation (upper) and processing steps (lower). (Reprinted from Wotherspoon *et al. Proc. SPIE* **501** (1984) 102, copyright (1994) reproduced with permission from SPIE.)

photoconductors, for both military and commercial use. We have shown that higher x crystals can be grown using the Bridgman/ACRT technique, providing that the ampoule seal-off is improved to minimize the risk of ampoule explosions. Crystals with starting x values of up to ~0.35 have been grown at temperatures up to ~900 °C. Slices with x values up to ~0.7 ($\lambda \sim 1.3-1.4 \mu$ m) have been obtained from the tip regions of such crystals. These slices are highly uniform in x, indicating flat solid/liquid interfaces. The latter have been confirmed via quenching experiments. Imaging of material with an IR camera has revealed no IR-absorbing defects in the first-to-freeze short-wavelength slices but cracks, second-phase inclusions and "swirl-like" patterns of varying contrast are revealed as growth proceeds, i.e. as the wavelength increases. The origin of some of these defects is unknown at this time and work is progressing to determine their cause and hopefully eliminate them. SIMS analysis shows low levels of common impurities in this material, which is due to purification of the starting materials and the use of chlorine-free synthetic silica ampoules.

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The use of ACRT at SELEX Sensors and Airborne Systems Infrared Ltd also made possible the fabrication of early 2-dimensional arrays of photodiodes with a high degree of uniformity of response. This type of material was also used to demonstrate nonequilibrium detector operation. The quality and costs of epitaxial material are improving continuously but it will be some years yet before bulk-grown material ceases entirely to be produced, at least for long-wavelength photoconductive applications.

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12 Crystal-Growth Technology for Ternary III-V Semiconductor Production by Vertical Bridgman and Vertical Gradient Freezing Methods with Accelerated Crucible Rotation Technique

Partha S. Dutta

12.1 Introduction

In semiconductor device technology, multilayered thin-film structures comprising various ternary and quaternary compounds are grown on binary substrates using liquid phase epitaxy (LPE), metal-organic vapor phase epitaxy (MOCVD or OMVPE) or molecular beam epitaxy (MBE) techniques [1-5]. Due to the lattice mismatch between the epilayer and the substrate, misfit dislocations originate at the growth interface and propagate into the device layers [6]. Typical misfit dislocation densities are in the range of $10^6 - 10^9$ cm⁻² [6]. Such high density of dislocations leads to degradation of electrical and optical characteristics of the devices. To reduce the misfit dislocation density, a variety of buffer layers are grown between the substrate and the device layers. The buffer-layer technology necessary to relieve misfit-related stresses is not optimized for all systems and often devices exhibit poor characteristics due to interfacial defects. By using lattice-matched ternary substrates, enhancement in performances of electronic and optoelectronic devices has already been demonstrated [7-16]. However, bulk single-crystal substrates of ternary semiconductors are still not available for commercial applications due to inherent problems in growing them from the melt [17-31]. The high cost of ternary wafers due to poor yield of the substrates grown from melt with the same alloy composition has restricted their usage in commercial semiconductor devices. This chapter lays out the challenges and potential solutions that could be adopted for future commercial development of ternary substrates. We will first discuss the fundamental issues encountered during ternary crystal growth and then present a process developed in our group to meet the requirements for large-diameter homogeneous ternary crystal growth. The crystal-growth method is a combination of vertical Bridgman or vertical gradient freezing technique with accelerated crucible rotation technique and a periodic solute-feeding process [32-34]. The optimization of the growth parameters to obtain compositionally homogeneous wafers of 50-mm diameter GaInSb with high yield will be discussed.



Fig. 12.1 Typical microcracks seen in ternary III-V crystals. The composition of the wafer shown here is $Ga_{0.4}In_{0.6}Sb$.

12.2 Fundamental Crystal Growth Challenges for Ternary Compounds

The two primary challenges faced during ternary crystal growth are (a) continuously changing composition along the growth direction and (b) cracking of the crystals. Figure 12.1 shows a $Ga_{0.4}In_{0.6}Sb$ wafer with cracks typically seen in any melt-grown bulk III-V ternary crystal. The cracks inevitably appear in the crystals irrespective of the growth technique used. Special growth conditions are necessary for avoiding these cracks as will be discussed in this article. The origin of cracks is related to the changing alloy composition in the crystal, which is a consequence of the phase diagram used for growing ternary crystals [17, 28, 29].

12.2.1

Crystal Composition Along Growth Direction

Considering the $Ga_{1-x}In_xSb$ pseudobinary phase diagram shown in Fig. 12.2, the separation between the solidus and liquidus curves leads to alloy segregation. Starting from a melt of alloy composition (C_o), when the liquid is cooled below the liquidus temperature T_o , the composition of the solid precipitating out of the liquid will have a composition corresponding to the point on the solidus (C_{so}) at the temperature T_o . Since the composition of the precipitating solid is different from the liquid composition, the melt composition will continuously change during the solidification process. It is clear from the phase diagram that the crystal is richer in the higher-melting binary component (such as GaSb content in $Ga_{1-x}In_xSb$) compared to the melt. Due to the preferential incorporation of the higher-melting binary constituent (such as



Fig. 12.2 Pseudobinary phase diagram of (GaSb)_{1-x} (InSb)_x.

InSb in $Ga_{1-x}In_xSb$ will accumulate at the crystal/melt interface. The accumulated constituents will slowly spread into the melt by diffusion and fluid mixing induced by convection. This will lead to a change in the melt composition to a point indicated as (C_1) in Fig. 12.2 as well as a lowering of the growth temperature. The next precipitation event occurs at a lower temperature shown by T_1 with the precipitating solid of composition (C_{s1}). This process continues and hence during a normal directional solidification process from a melt as in Bridgman or Czochralski growth, the melt composition continuously changes with time and in turn so does the composition of the solidifying crystal. If the melt is mixed continuously during the experiment, the alloy composition in the solid (C_s) changes according to the well-known Scheil equation [35, 36]:

$$C_{\rm s} = k_{\rm eff} \ C_0 \left(1 - g\right)^{k_{\rm eff} - 1} \tag{12.1}$$

where *g* is the fraction of melt solidified and C_0 is the initial alloy composition of the melt (at the beginning of the growth). The parameter k_{eff} , known as the effective segregation coefficient, varies with alloy composition, growth rate and hydrodynamic conditions in the melt. In a typical crystal-growth experiment, the accumulated species at the solid/liquid interface takes a finite amount of time to diffuse back into the melt. This gives rise to a diffusion boundary layer of thickness δ . Within this layer, the concentration of the accumulated species decreases continuously from the melt/solid interface to the end of the boundary layer [37]. Beyond the edge of the boundary layer, a homogeneous melt exists. Burton, Prim and Slichter (BPS) derived the following equation to correlate the boundary layer thickness with the effective segregation coefficient [37]:

$$k_{\rm eff} = \frac{k_0}{k_0 + (1 - k_0) \exp(-\Delta)}$$
(12.2)
$$\Delta = R\delta/D$$

$$k_0 = C_{\rm s}/C_{\rm l}$$
(12.3)

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where k_0 is the equilibrium segregation coefficient as estimated from the ratio of solidus concentration (C_s) and liquidus concentration (C_l) of any constituent at a given temperature in the phase diagram (see Fig. 12.2). *D* is the diffusion coefficient of the accumulated species at the melt/solid interface and *R* is the crystal growth rate. The diffusion coefficient *D* is a fundamental material property and is dependent on the alloy composition as well as the temperature. For example, the diffusion coefficient of InSb in Ga_{1-x}In_xSb melt at 600 °C is lower than that at 650 °C. Similarly, the diffusion coefficient of InSb in a Ga melt at 600 °C is different from that in a Ga_{1-x}In_xSb melt at the same temperature.

In the presence of forced convection in the melt, the boundary layer thickness, δ , can be approximately estimated by:

$$\delta = 1.6D^{1/3}v^{1/6}\Omega^{-1/2} \tag{12.4}$$

where v is the kinematic viscosity of the melt, Ω is the rotational rate of the crystal with respect to the melt. As can be seen from Eq. (12.2), when Δ approaches zero, the $k_{\rm eff}$ equals k_0 . This can be achieved by decreasing the growth rate, thinning the diffusion boundary layer or by choosing alloy systems with higher melt diffusion coefficients D. The diffusion boundary layer thickness can be decreased by enhancing the homogenization rate of the accumulated species with the rest of the melt. This can be achieved by increasing the temperature gradient at the melt/solid interface, decreasing the crystal growth rate and by using forced convection. These parameters need to be optimized as there are trade-offs between each of these processes as discussed in Section 12.3. Assuming a perfectly homogeneous melt ($k_{\text{eff}} = k_0$), one can theoretically calculate the alloy composition along the crystal growth direction from the equilibrium phase diagram (Fig. 12.2). It must be noted that for each corresponding liquidus and solidus points in Fig. 12.2, the equilibrium segregation coefficient k_0 is different. Figure 12.3 shows the theoretically calculated gallium mole fraction along the length of $Ga_{1-x}In_xSb$ crystals for different starting melt compositions [33]. In these plots, the varying equilibrium segregation coefficient (k_0) with change in melt composition was taken into account. It is clear from these plots that for growing a crystal with uniform ternary composition, one would need to replenish the melt continuously during the experiment, as discussed in Section 12.5.

12.2.2 Origin of Crack Formation in Ternary Crystals

There are two origins of crack formation in ternary crystals. One is due to constitutional supercooling and the other is due to misfit strain associated with compositional grading. Due to alloy segregation, if the growth rates are not low enough, constitutional supercooling occurs close to the liquid/solid interface resulting in composition fluctuations. The local compositional inhomogeneity in the solid along with the wide difference in the lattice constants and the thermal expansion coefficients of the constituent binary compounds introduces considerable strain, and invariably



Fig. 12.3 Theoretical gallium concentration along the growth axis for $Ga_x ln_{1-x}Sb$ crystals grown from different starting melt compositions (under normal freezing conditions). The fractions next to each curve represent the gallium mole fraction in the starting melt.

leads to cracking of the crystals. Cracking in the crystal can also occur without constitutional supercooling. These cracks are due to misfit strain in the crystal and are related to the rate at which the alloy composition and more importantly the lattice parameter and other physical properties like thermal expansion coefficient changes along the length of the crystal. For the GaInSb system, the lattice parameter varies from 6.096 Å (for GaSb) to 6.479 Å (for InSb) and the thermal expansion coefficient from 7.75 \times 10⁻⁶ °C⁻¹ to 5.37 \times 10⁻⁶ °C⁻¹ [1]. Figure 12.4 shows the theoretical misfit strain-gradient curves calculated using the theoretical alloy composition profiles shown in Fig. 12.3 and the lattice parameter a_0 for each composition using the Vegard's law [1]. It has been empirically observed that crystals inevitably crack if the misfit strain gradient exceeds 1-2% [17]. It is obvious that an alloy system with larger separation between the solidus and liquidus curves will have higher strain gradient than those with smaller separation. Moreover, cracking may occur even below 1% of misfit strain gradient if there is a thermal strain due to a large temperature gradient in the solid during growth and during postgrowth cooling. Figure 12.5 shows typical misfit strain-gradient related cracks in a Ga0.95 In0.05 Sb polycrystal wafer grown using the vertical Bridgman method. Referring to Fig. 12.5, the strain-related cracks originate in the crystal where the strain gradient exceeds 1-2%, as shown by the horizontal dashed line. For a crystal grown with a starting gallium mole fraction of 0.7 in the melt, the cracks should appear when the fraction solidified (G) reaches 25%. The highest probability for cracking has been experimentally observed around the peak of the strain gradient [32], which is close to 60% for the melt with 0.7 starting gallium mole fraction. The visual appearance of the supercooling-related cracks (shown in Fig. 12.1) and that of misfit strain-gradient-related cracks (Fig. 12.5) are quite different and can be easily distinguished. Nevertheless, the fundamental



Fig. 12.4 Theoretical misfit strain gradient versus fraction of melt solidified calculated from theoretical concentration curves shown in Fig. 12.3 for $Ga_xIn_{1-x}Sb$ crystals.



Fig. 12.5 A $Ga_{0.95}In_{0.05}Sb$ wafer showing strain-gradient-related cracks.

origin for both types of cracks is due to alloy segregation. Crystal-growth parameters necessary for crack elimination will be discussed in Section 12.4.

12.3

Key Requirements for Ternary Substrates and Crystal-Growth Process

For ternary substrates to be commercially viable in semiconductor device technology, many important criteria must be met. These criteria pose numerous

constraints during crystal growth, many of them are counteractive and appropriate trade-offs in the growth conditions are necessary. For ternary crystals to be of any commercial significance, single-crystal wafers of 50 mm or larger diameter that could be used in commercial epitaxial growth and device-fabrication equipments are necessary. The wafers must have the following additional attributes:

- 1. The spatial compositional variations must be less than 0.5 mol% from center to edge of the wafers.
- 2. The wafers should be completely free from cracks, metallic inclusions or multiphase regions and have a dislocation density similar to that in existing high-quality commercial binary substrates (less than 1000 cm^{-2}).
- 3. A wide range of doping should be possible in the substrate material so as to achieve desirable optical and electrical properties [38–44]. For electronic devices, semi-insulating substrates are necessary. For infrared photodetector applications with backillumination (radiation incident from the back of the substrate) or for light-emitting diodes, the substrate must be optically transparent for wavelengths that are being detected or emitted in the epilayers.
- 4. Ternary crystals are prone to damage during wafer slicing and polishing due to high built-in strain. Ensuring appropriate thermal conditions during crystal growth and postgrowth annealing treatments is crucial.
- 5. The wafer should have a high-quality epitaxial-growth-worthy polished and chemically treated surface. Some substrate materials such as aluminum-based compounds have highly reactive (oxidizable) surfaces and are generally not suitable for epitaxial growth.
- 6. Though bulk substrates contribute to a smaller fraction of the cost for the entire device, high cost of the substrates poses a barrier for adaptation. Unless it is clearly established that by using lattice-matched substrates, significant improvement in device characteristics has been achieved, the cost of final wafers should not be significantly higher than commercially available binary substrates.

The crystal-growth conditions that are necessary to achieve all the attributes listed above are quite stringent and are discussed below:

1. A low temperature gradient in the melt and solid is necessary for (a) achieving low dislocation density or strain in the crystal, (b) maintaining a planar melt/solid interface shape during growth and (c) reducing temperature fluctuations at the growth interface induced by forced or natural convection in the melt. The planar interface shape and eliminating temperature fluctuations are crucial for homogeneous spatial alloy composition in the substrate and avoiding microscopic compositional fluctuation along the growth direction, respectively.
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- 2. A low temperature gradient, however, enhances the probability for constitutional supercooling. To avoid supercooling, the crystal growth rate must be reduced. But lower growth rate translates to higher final wafer cost. Hence, for maintaining reasonable growth rate (without supercooling) under a low temperature gradient, forced convection in the melt such as using ACRT is necessary.
- 3. To lower substrate costs, it is also essential to have high yield of wafers of the same composition from a single ingot. This requires maintaining a homogeneous melt composition during the entire growth by replenishing the depleted constituents (solute feeding) in the melt. The solute dissolution and feeding process must be augmented by appropriate melt stirring to ensure a homogeneous melt at all times. Under a low temperature gradient, the natural convection is not strong enough to transport species effectively to and from the growth interface, thus leading to macroscopic composition fluctuations along the growth direction.
- 4. Rapid or uncontrolled melt replenishment leads to high level of supersaturation in the melt. This triggers polycrystalline growth due to random nucleation in the melt especially under a low temperature gradient. To maintain single crystallinity during growth, the rate at which the solute is fed to the melt must be precisely controlled at all times to match the crystal growth rate. This requires special solute-feeding processes and forced convective mixing in the melt.

In summary, the three main parameters that are desirable for crystal growth of ternary alloys are: (a) low temperature gradient, (b) melt stirring by forced convection and (c) a precise solute dissolution process. Since large-diameter wafers are necessary for commercial applications, scaling up the production would require a crystal-growth process where optimization of the heat and mass transport is relatively easy to implement. The Bridgman and gradient freezing type methods are becoming more popular for large-diameter binary crystal growth with very low defect content. Fortunately, these growth systems could be easily upgraded to incorporate ACRT and solute-feeding mechanisms and adopted for future ternary crystal-growth technology.

12.4

Optimization of Growth Parameters for Radially Homogeneous Crystals

From the above discussions, it is apparent that optimization of melt homogenization and solute-feeding processes in conjunction with the temperature gradient in the melt and solid is necessary for the successful growth of high-quality compositionally homogeneous ternary crystals. In this section, we will discuss the combined effects of axial temperature gradient and melt stirring using ACRT on the radial compositional profile in ternary crystals.

12.4.1 Melt Homogenization Using ACRT

The role of melt stirring during ternary crystal growth is crucial. There are many ways for achieving melt stirring such as by using magnetic fields [45], stirrers and baffles in the melt [25, 28, 32–34] and ACRT [28, 32–34, 46–51]. In this chapter, we will focus the discussion on ACRT due to its ease in adaptability for large-size melts as well as for sealed crucible configurations.

Due to the fact that ternary crystals need to be grown under low temperature gradient, melt stirring during growth becomes very important and necessary for many purposes:

- 1. It helps transporting accumulated constituents from the melt/solid interface to the bulk melt by thinning the diffusion boundary layer. This helps in maintaining a reasonable growth rate that is necessary for large-scale production.
- 2. It helps the solute dissolution during the solute-feeding process (as discussed later). In the absence of forced convection and with a low temperature gradient in the melt, it takes a long time for the accumulated species (at the melt/solid interface) to thoroughly mix with the bulk melt. Hence the supersaturation level in the melt does not change, which results in no dissolution of the solute. Forced convection helps in rapid homogenization of the melt and thus an efficient solute dissolution process could be achieved.
- 3. It helps in avoiding random nucleation in the growth melt as well as constitutional supercooling at the growth interface. The latter helps in eliminating cracks in the crystal that originate from interface breakdown.

One of the primary goals during ternary crystal growth is to identify growth conditions that could eliminate cracks in the crystal. ACRT has been found to be very efficient in eliminating the constitutional-supercooling-related cracks in large-diameter crystals [28, 32–34, 51]. To stress the importance of ACRT for crack elimination, let us review the theoretical analysis of Tiller *et al.* [52] for preventing constitutional supercooling. According to this analysis, the ratio of temperature gradient in the melt near the growth interface (*G*) to the growth rate (*R*) should exceed a critical value given by:

$$\frac{G}{R} \ge \frac{mC_0(1-k_0)}{k_0 D}$$
(12.5)

where m is the slope of the liquidus in the phase diagram. While increasing the axial temperature gradient helps in avoiding constitutional supercooling, it increases the melt/solid interface curvature due to which the radial composition profile in the wafers varies (as discussed later). High axial temperature gradient also lowers the threshold for strain-related cracks in the crystal, as discussed earlier and hence is not desirable. Hence, ternary crystals need to be grown under a low temperature gradient. To avoid constitutional supercooling under a lower

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temperature gradient, the crystal growth rates necessary for crack-free crystals are very low [28]. Such growth rates are not viable for commercial production. The constitutional supercooling can be avoided and the growth rate can be enhanced by appropriate melt stirring processes such as by ACRT. It must be noted that ACRT has no effect on the misfit-related cracks. These can be avoided only by ensuring a gradual change in alloy composition in the crystals during growth such as to maintain the strain gradient below the threshold level (Fig. 12.4).

Fluid-mixing patterns used for forced convection could be very complicated and significantly impacts the crystalline quality. Melt-mixing schemes reported in the literature [25, 28, 32-34, 51] during ternary crystal growth include: unidirectional rotation of crucible, using baffles and stirrers and by accelerated crucible rotation technique (ACRT). Unidirectional rotation even at higher rotation rates 100-200 rpm does not result in effective mixing for large-diameter crystals (50 mm and higher). In the baffle-mixing scheme [25], the melt is homogenized very efficiently either by rotating the baffle in the melt or by translating the baffle back and forth perpendicular to the growth interface. In the case where the baffle is translated perpendicular to the growth interface, obtaining single crystals is quite difficult due to thermal fluctuations at the melt/solid interface. Typically, very small sized grains have been observed by using this process (Fig. 12.6). Nevertheless, it is worth mentioning that these wafers are compositionally homogeneous and no cracks are seen. Melt mixing using a stationary stirrer held inside the melt while the crucible is uniformly rotated in one direction has been found to be very effective in eliminating cracks as well as providing efficient solute transport during solute-feeding processes [32-34]. One of the limitations with any mixing process that incorporates foreign object in the melt such as stirrer or baffle is that the height of the melt needs to be deeper. For shallow melts, it is very difficult to use stirrers or baffles and avoid undesirable disturbances in the melt. ACRT is perfectly suitable for melts of any size or depths and has been successfully used for ternary crystal growth [28, 32-34, 51].

In ACRT, the crucible is periodically accelerated and de-accelerated (around the growth axis) to promote efficient mixing of the melt as shown in Fig. 12.7. However, there can be dead-zones (unmixed) even in a thoroughly mixed melt especially at the center of the crystal [51]. This is specially seen in smaller-diameter crystals. These types of unmixed zones lead to compositional fluctuations in the grown crystals. Hence, it is essential to optimize the rotation schemes for each crucible diameter, melt size and fluid viscosity in the ACRT scheme [46-50]. We have observed that by using ACRT, the growth rates of ternary III-V compounds can be enhanced by a factor of 3-4. In vertical Bridgman grown crystals without any melt stirring, typical growth rate necessary for obtaining crack-free GaInSb of any composition is less than 0.5 mm/h with axial temperature gradient of 10-15 °C/cm (near the melt/solid interface). By using optimized ACRT scheme as shown in Fig. 12.7, the growth rate for crack-free crystals can be increased to 1.5-2 mm/hunder the same thermal gradient. Figure 12.8 shows a crack-free 50-mm diameter polycrystalline wafer of Ga_{0.25}In_{0.75}Sb grown using the ACRT scheme. The growth rate was ~1 mm/h similar to that used for the cracked wafer shown in Fig. 12.1. In



Fig. 12.6 Small-grain crack-free $Ga_{0.8}In_{0.2}Sb$ wafer extracted from a polycrystal grown using vertical Bridgman technique with an oscillating baffle near the melt/solid interface.



Fig. 12.7 Accelerated crucible rotation rates used for melt mixing and solute transport during vertical Bridgman and VGF growth of GaInSb crystals.

general for III-V ternary crystals, with an axial temperature gradient of ~ 10 °C/cm and no melt stirring, the maximum growth rate for crack-free single crystals is in the range of 0.02–0.5 mm/h depending on the specific alloy system and its composition [28]. These rates are significantly lower than the binary growth rates (1–3 mm/h) under similar thermal gradient. A delicate balance between heatand mass-transport strategy is necessary for ternary single-crystal growth without cracks. By using efficient melt stirring, the crystal growth rates for ternary materials can approach the binary compounds grown under same temperature gradient.



Fig. 12.8 Large-grain crack-free $Ga_{0.25}In_{0.75}Sb$ wafer extracted from a polycrystal grown using VGF with ACRT.

12.4.2 Role of Temperature Gradient

The shape of the melt/solid interface determines the radial compositional profile in ternary crystals [32, 34]. A planar interface is absolutely necessary for obtaining wafers with uniform alloy composition. Hence, it is very important to understand the heat-transfer processes during ternary crystal growth and identify suitable conditions that could lead to a planar interface during growth. During Bridgman growth of ternary crystals, the temperature gradient in the melt, at the melt/solid interface and in the crystal plays a significant role in deciding the curvature of the interface. Interestingly, the effect of forced convection on interface curvature seems to be weaker than the temperature-gradient effect. Figures 12.9-12.11 show the radial InSb composition profiles for VGF grown GaInSb crystals with furnace temperature gradients of 25-30°C/cm, 15-20°C/cm and 5-10°C/cm, respectively. Under an axial temperature gradient around 30 °C/cm, the growth interface is highly concave with respect to the solid (leading to a convex InSb radial profile). Without forced convection, at low temperature gradient below 10 °C/cm, constitutional supercooling is a major problem. Composition fluctuation due to interface breakdown (constitutional supercooling) is observed. The gradient between 10-15 °C/cm seems to be optimum for stable growth of 50 mm diameter GaInSb [32, 34]. The radial profiles for crystals grown using ACRT have also been shown. ACRT certainly helps avoid constitutional supercooling in the case of a low temperature gradient. However, the curved compositional profile at high axial gradients is very difficult to flatten even with ACRT. This clearly demonstrates the strong influence of temperature gradient on the interface curvature. Higher temperature gradients are known to produce concave melt/solid interface shapes. Lowering



Fig. 12.9 Radial InSb profiles in 50-mm diameter GaInSb wafer measured from the center (0 mm) to the edge (25 mm): (a) without melt stirring and (b) with melt stirring using ACRT. The temperature gradient near the melt/solid interface was 25-30 °C/cm.

the gradient would only flatten the interface. By using a temperature gradient of 10-15 °C/cm in conjunction with ACRT, compositionally homogeneous wafers have been obtained for a wide range of GaInSb alloy compositions [32, 34].

12.5 Controlled Solute-Feeding Process for Axially Homogeneous Crystals

While the optimized temperature gradient and ACRT will provide compositional homogeneity in the radial direction (perpendicular to growth axis), melt replenishment is necessary for an axially homogeneous crystal. Hence, development of an appropriate solute-feeding system that could deliver homogeneous melt compositions during ternary crystal growth is very important. The first step in ternary crystal growth is to generate a single-crystalline seed of a specific ternary



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Fig. 12.10 Radial InSb profiles in 50-mm diameter GaInSb wafer measured from the center (0 mm) to the edge (25 mm): (a) without melt stirring and (b) with melt stirring using ACRT. The temperature gradient near the melt/solid interface was 15-20 °C/cm.

composition starting from a binary seed. During this process, the melt composition needs to be continuously changed for grading the alloy composition of the crystal. The second step in ternary crystal growth is to grow a homogeneous crystal of a specific composition. For this step, the melt needs to be maintained at a constant composition throughout the growth. For both these steps, precise control over the solute-feeding process and melt composition is necessary. Figures 12.13 and 12.15 show two solute-feeding configurations that have been developed and successfully used by us during the growth of ternary GaInSb and AlGaSb crystals. In the schematic diagrams shown here, we have used the GaInSb system as an example.

A lot of experimental efforts have been dedicated by various groups to develop the ternary crystal-growth technology. Below we briefly summarize the methods used and their limitations for large-scale ternary-crystal production.





12.5.1 Single-Crystalline Ternary Seed-Generation Process

Unlike binary compounds, growth of spontaneously nucleated single crystal ternary seeds such as from the tip of a crucible in Bridgman method [53] has not been possible. The preferred method for generating a seed of any ternary composition is by starting from a binary seed. However, there are several challenges encountered during this process, as discussed below:

 It has been empirically observed that for alloy systems with a large lattice mismatch between the end binaries (GaAs-InAs, GaSb-InSb, InAs-InSb, etc.), the first-to-freeze section of the crystal must have a composition less than or equal to 5 mol% with respect to the seed in order to maintain single crystallinity [19–24]. For example, during the growth of single-crystal





Fig. 12.12 Ideal composition profile (schematic) necessary to generate a GaInSb single-crystal seed from a binary InSb or GaSb seed.

Ga_{1-x}In_xAs on GaAs seed, the first to freeze Ga_{1-x}In_xAs should have x < 0.05 [54–56]. With (x > 0.05), polycrystalline growth occurs on a single-crystal seed [54]. This makes the conventional *bootstrapping* process unattractive. In this process, a ternary seed of any target composition is grown starting from a binary seed by step-grading the composition by x = 0.05 in a series of experiments. The ternary seed obtained from the first experiment (with x = 0.05) is used to grow a seed with x = 0.1 in the second experiment, a seed with x = 0.15 in the third experiment and so on. Since the step change between subsequent growth run is restricted to x = 0.05, a seed of any concentrated ternary-alloy composition (e.g. x = 0.5) could be time consuming. Furthermore, it is difficult to use the bootstrapping process in the vertical Bridgman configuration. The ternary melt composition for successive growth needs to be carefully monitored to avoid excessive dissolution of the ternary seed crystal from the previous step.

2. If a graded composition seed is grown, such as by directional solidification process [54, 57–59], the transition from single to polycrystallinity and cracking remain major issues during the steep rise in composition. ACRT, low growth rates and slow compositional grading could be used to avoid both problems. However, even if one manages to grow a complete single crystal, the graded composition seed is not easy to use for a subsequent crystal-growth experiment. The seed needs to be dissolved very carefully by contacting with the ternary melt. Since any dissolution in the steep compositionally graded region will change the composition of the seed at the growth interface, the subsequent crystal could be polycrystalline (due to a step change in composition beyond x = 0.05).



Fig. 12.13 Periodic solute-feeding process for the growth of a graded region followed by a homogeneous composition GaInSb seed crystal in a single experiment by VGF and ACRT starting from a InSb seed.

3. Controlling solute-transport rates to maintain single crystallinity has been a challenge in graded-composition seed-generation processes that are based on solute diffusion in the melt due to concentration gradient [14, 28, 33, 60, 61]. Typically binary charges (such as GaAs and InAs) are stacked with baffles having narrow channels separating them to avoid over-supply of dissolved constituents. The precise control of melt composition for balancing the crystal growth rate with dissolution rate is extremely difficult. Optimizing the temperature gradient necessary to achieve dissolution and solute transport in the melt could be time consuming and complex. These problems could be solved by special solute-feeder designs and processes that could control the supply of desired amount of material into the growth melt during the experiment. Proper homogenization of the melt such as by using ACRT is necessary at all times to ensure stable growth.

From the above discussions it is clear that for ternary single-crystal growth, one would require a homogeneous ternary seed of the same composition as the crystal. Hence, starting from a binary seed, one needs to grow a compositionally graded seed followed by a uniform region as depicted in Fig. 12.12. If InSb seed is used, then the GaSb concentration will increase along the seed crystal. On the other hand, if a GaSb seed is used, the InSb concentration will increase along the length of the seed. These ternary seeds could be grown by using the experimental configurations and processes shown in Figs. 12.13 and 12.15. A combination of



Fig. 12.14 GaSb composition profile along the growth direction of a GaInSb seed crystal grown using periodic solute-feeding process shown in Fig. 12.13.

ACRT and controlled solute feeding is necessary to avoid rapid growth that leads to polycrystallinity.

Typically, smaller-diameter seeds (5 mm) are being used for binary III-V crystal growth. However, for ternary growth, a seed of the same diameter as the crystal is preferable to maintain single crystallinity throughout the ingot. Furthermore,



Fig. 12.15 Periodic solute-feeding process for the growth of a graded region followed by a homogeneous composition GaInSb seed crystal in a single experiment by VGF and ACRT starting from a GaSb seed.

since the crystal growth rates for ternary crystals are significantly lower than the binaries, it does not justify the time spent in growing conical regions (between the smaller seed and the final crystal diameter) such as in Bridgman growth.

12.5.1.1 Ternary Seed Generation from a Lower Melting Binary Seed

A schematic diagram of the approach using VGF with ACRT is shown in Fig. 12.13 for growing GaInSb seeds. To start with, a InSb single-crystalline seed is placed at the bottom of the crucible along with InSb polycrystalline charge. A GaSb polycrystal feed is suspended from the top of the growth chamber. After heating and stabilizing the furnace to obtain a specific temperature gradient, the InSb feed melts along with a part of the InSb seed to obtain a melt/solid interface (Fig. 12.13(a)). At this point, the GaSb feed is lowered and allowed to touch the top of the InSb melt for a few seconds. The crucible is set to perform accelerated crucible rotation (ACRT) as shown in Fig. 12.7 and a homogeneous GaInSb melt is prepared. The GaSb feed is lowered periodically to touch the GaInSb melt. The dissolved species are transported rapidly to the InSb seed interface as a result of ACRT melt mixing. Crystal growth is initiated in the crucible as a result of the increasing level of the solute concentration at the solid/liquid interface with time. When the solute concentration in the melt near the seed interface reaches the liquidus composition, precipitation takes place and GaInSb starts growing on InSb. As the GaSb feed is periodically lowered to touch the melt for a few seconds, more solute is dissolved and transported to the growth interface and the crystal growth continues. The seed crystal grown by this method is compositionally graded along the growth axis with increasing gallium concentration in Ga1-xInxSb (decreasing indium concentration). The rate of compositional grading is decided by the solidus temperature in the pseudobinary phase diagram and the axial furnace temperature gradient. The axial composition in the seed crystal is graded until a desirable alloy composition is achieved and then a homogeneous composition crystal length is grown. For the next step (axially uniform composition seed) of crystal growth, the temperature gradient is translated by changing the power supplied to individual zones (Fig. 12.13(b)) while the GaSb feed dissolution is continued by the periodic dipping method. While the GaSb at the melt/solid interface is depleted by preferential incorporation in the crystal, it is being replenished by the feed dissolution. Hence, the melt/solid interface remains at the same position in the furnace until the entire melt is solidified (Fig. 12.13(b)). During the compositionally graded seed growth, the melt/solid interface automatically rises from the cooler to the hotter zone in the furnace. Thus, the melt/solid interface shape could change continuously during the growth. To maintain a planar melt/solid interface shape throughout the growth, the axial temperature profile in the furnace should be optimized to have a long linear region.

The periodic solute-feeding process described above in conjunction with efficient melt mixing provides a complete control over the composition profile in the graded seed and the homogeneous crystal [33]. The entire experimental process could be automated using programmable stepper motors for periodic solute feeding, ACRT and crucible-translation processes (if vertical Bridgman is used instead of VGF). The main advantage of this process is the single experiment in which a ternary

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homogeneous seed crystal of any alloy composition can be obtained starting from a binary single-crystal seed and polycrystalline binary feed materials. For ensuring the success of this process, the periodic solute-feeding process parameters need to be fine tuned. This is necessary to precisely control the rate at which solute depletes and replenishes in the melt. The major process parameters that affect the crystalline quality of the seed include solute dipping time and dipping frequency. Dipping time denotes the actual time the melt is in contact with the feed. This determines the amount of feed introduced in the melt over one period of the dipping cycle. Due to the temperature gradient in the melt, the top of the melt (higher temperature zone) is usually under-saturated. Hence, the danger of uncontrolled dissolution exists if the solute feeding rod is dipped for more than the required time. Thus, a precise control of the dipping time is required. Excess dissolution of the solute can promote random nucleation in the entire melt volume. Additionally, this can lead to an oversupply of the solute to the growth interface leading to small grains or causing a change in grain structure. The dipping frequency defines the period of the dipping cycle and should depend on the growth rate. It takes a finite time for the solute to thoroughly mix with the growth melt. Further, the growth kinetics determines the actual growth rate. Based on experimental crystal-growth results [33], a set of optimized periodic solute-feeding parameters for GaInSb growth include: solute contact area of 20 mm, solute dipping time of 2-3 s, solute dipping frequency of 3-4 times per hour, temperature gradient near the melt/solid interface of 15 °C/cm and ACRT melt mixing process. Figure 12.14 shows the GaSb mole% along the length of the seed crystal starting from InSb using the process described above. The superior control of the composition profile shown in this diagram clearly demonstrates the effectiveness of the periodic solute-feeding process.

12.5.1.2 Ternary Seed Generation from a Higher-Melting Binary Seed

Another method for single-crystal seed generation using VGF and ACRT is shown in Fig. 12.15. In this process, the higher melting binary is used as the starting seed material for the ternary seed crystal growth. The process for GaInSb seed generation starting from a GaSb seed has been demonstrated. The experiment starts with a GaSb single-crystalline seed and a GaSb melt in the crucible. The lower melting point binary (InSb in this case) is present in a quartz melt displacer. After the furnace has been heated, the GaSb feed melts to form a melt/solid interface. The crucible is set to accelerated crucible rotation (ACRT) as in the previous case. By pressing the piston, the InSb can be periodically fed to the GaSb melt. By controlling the lowering rate of the piston, the concentration of InSb in the growth melt can be increased in a controlled fashion. After the initial InSb melt dispenses into the growth melt to form GaInSb liquid, the temperature of the furnace is slowly lowered to translate the gradient along the melt like in a VGF process. The graded-composition GaInSb ternary starts from the GaSb seed with increasing InSb content in the crystal. The InSb concentration in the melt increases with time as it is fed into the melt periodically. After the graded GaInSb seed growth, a GaSb feed is introduced into the melt periodically like in the previous case. The gradient freezing is continued while the



Fig. 12.16 Cross section of a GaInSb polycrystal seed grown using the method shown in Fig. 12.15. The GaInSb composition was graded from a tip-nucleated GaSb seed to a homogeneous region.

GaSb feed is periodically fed into the melt (Fig. 12.15(b)). This step results in compositionally uniform GaInSb region. The processes described in Fig. 12.15 can also be implemented by the vertical Bridgman method as long as care is taken to ensure that the GaSb feed shown in Fig. 12.15(b) is introduced into the lower-temperature zone of the furnace without melting. Figure 12.16 shows the cross section of a large-grain GaInSb polycrystal seed grown by the method described above starting from a tip-nucleated GaSb seed. No cracks could be seen in the entire crystal, demonstrating the success of the solute-feeding process. Figure 12.17 shows the axial InSb mole% in a GaInSb seed grown by the above method starting from a GaSb seed.

12.6 Steps in Ternary Crystal Production

Having grown a ternary single-crystal seed of the desired composition, the next step is to grow a ternary crystal of homogeneous composition from which a large number of wafers (of the same composition) could be sliced. There are several experimental configurations that could be used to grow homogeneous ternary crystals [62–76]. For ternary crystal growth in bottom-seeded crucibles (as discussed here), the preparation of the growth melt needs to be carried out in a particular fashion. Ensuring the melt composition to be in equilibrium with the seed composition is crucial for avoiding excessive seed dissolution. Hence, ternary crystal production is a three-step process. Once a seed of a specific alloy composition exists, only steps 2 and 3 are necessary for regular production.





Fig. 12.17 InSb composition profile along the growth direction of a GaInSb seed crystal grown using periodic solute-feeding process shown in Fig. 12.15.

- 1. The first step is to grow a single-crystal seed of the same alloy composition as the homogeneous ternary crystal that needs to be produced for generating large number of wafers. For example, if a homogeneous $Ga_{0.8}In_{0.2}Sb$ crystal needs to be grown, one needs a single-crystal seed of the same alloy composition. The single-crystal seed must have the same diameter as the diameter of the crystal to be grown. The seed-generation processes were discussed in Sections 12.5.1.1 and 12.5.1.2. The homogeneous section of the seed should be sufficiently long (at least 2-3 cm) such that typical seed remelting (to expose a clean interface) could be carried out before growth.
- 2. The second step is to grow a homogeneous polycrystalline ternary feed material that could be remelted in the third step discussed below. According to the GaSb-InSb pseudobinary phase diagram, to grow a Ga_{0.8}In_{0.2}Sb crystal, one would require a melt composition of Ga_{0.3}In_{0.7}Sb with a growth temperature of 600 °C. Hence one needs to prepare a homogeneous polycrystalline ingot of Ga_{0.3}In_{0.7}Sb. For synthesizing the homogeneous polycrystalline ingot of Ga_{0.3}In_{0.7}Sb, one could simply use the process shown in Fig. 12.18. Initially, a flat-bottom crucible containing appropriate quantities of GaSb and InSb polycrystals is heated to 550 °C to obtain a melt of Ga_{0.1}In_{0.9}Sb (liquidus composition corresponding to Ga_{0.3}In_{0.7}Sb solid). The melt is then directionally solidified while periodically dissolving GaSb.
- 3. In the third and final step, the ternary seed crystal is stacked with the ternary polycrystalline feed crystal as shown in Fig. 12.19. The polycrystalline feed is carefully melted and a seeding interface is obtained. The melt is then directionally solidified while periodically replenishing by dissolving the GaSb feed rod. This results in a homogeneous ternary single crystal.

In both steps 2 and 3, ACRT is used along with the growth conditions discussed earlier for stable growth. The need for a three-step process discussed above is to save the overall crystal production time. The most time-consuming process during



Fig. 12.18 Vertical Bridgman process with ACRT and periodic solute feeding used for synthesis of homogeneous polycrystalline GaInSb feed.

ternary crystal growth is the seed-generation process in the graded region. This is due to the fact that the solidus temperature for ternary compositions changes over a large temperature range and the limitations on how rapidly the composition grading can be implemented in the crystal without creating cracks. In principle, one could grow a ternary homogeneous crystal of any composition in one single experiment as in step 1. However for large-scale production, the three-step process is more reliable and economical. Figure 12.20(a) shows a cross section of a 50-mm diameter single crystal $Ga_{0.25}In_{0.75}Sb$ (~1 cm long) produced using the three step process. Figure 12.20(b) shows a cross-sectional view of a 35-mm diameter $Ga_{0.3}In_{0.7}Sb$ single crystal (~1.7 cm long). Twins can be clearly seen in this crystal.

While the steps and growth conditions discussed so far are absolutely essential for ternary crystal-growth technology, there are other important parameters that must also be used to ensure single-crystal growth with high optical and electrical properties. These growth parameters include: usage of melt encapsulation, vapor-pressure control for group V volatile species, crucible material and post-growth crystal annealing. Depending on the ternary alloy system to be grown, the equipment and growth configurations should be adopted from an existing higher-melting binary crystal-growth process [77–81]. For example, if one needs to grow GaInAs, a system that is being currently used for growing GaAs should be adopted. The VGF process has achieved widespread commercial usage in both III-V and II-VI binary crystal growth [78–82]. Due to the fact that VGF can be carried out under a low temperature gradient, it is perfectly suited for ternary



Fig. 12.19 Growth process for homogeneous GaInSb single crystals by vertical Bridgman method with ACRT and periodic solute-feeding schemes.

crystal growth. The VGF method with temperature gradients in the range of 1-10 °C/cm has resulted in dislocation densities less than 1000 cm⁻² for binary III-V crystals [80, 81]. The same is expected as the ternary crystal-growth process is optimized.

Postgrowth cooling rates for ternary crystals can be similar to that used for binary crystals $(20-30^{\circ}C/h)$. Cooling rates faster than these could lead to thermal strain-related cracking in the wafers during processing. Melt encapsulation is necessary for two reasons: (a) to avoid volatile species to escape from the melt and (b) to avoid contact between the semiconductor melt and the crucible walls during growth so that secondary nuclei do not originate that lead to polycrystalline grains. For the growth of GaInSb, the B2O3 encapsulation is not suitable since it is very viscous at low temperatures. Instead of B₂O₃, low viscosity alkali-halide eutectic salts such as LiCl-KCl (58:42 mol%) with low melting temperatures (350 °C) are being used [83, 84]. These alkali-halide salts do not react with the antimonide-based compounds and have no effect on the electrical and optical properties of the grown crystals [83]. Silica (quartz) crucibles are commonly used for GaInSb growth. The growth setup for GaInSb is much simpler since there is no need for a high-pressure vessel. For GaInAs or InAsP growth (in the open-crucible configuration), the entire melt needs to be pressured with an inert gas up to a level of 10-20 atm for GaInAs and 45-50 atm for InAsP. pBN crucibles along with ultralow water content boric oxide (B₂O₃) encapsulation is used. The boric oxide melts at 450 °C and has a low viscosity at the growth temperatures of GaInAs and InAsP. A typical furnace temperature gradient for stable growth is in the range of 10-15°C/cm and crystal growth rate is in the range



(a)





Fig. 12.20 Cross sections of homogeneous single crystals: (a) 50-mm diameter $Ga_{0.25}In_{0.75}Sb$ and (b) 35 mm-diameter $Ga_{0.3}In_{0.7}Sb$.

of 0.5–1 mm/h. For aluminum-based compounds such as AlGaSb, due to high oxidation rates and reactivity with crucible materials, special encapsulation and charge-stacking processes, such as that developed for AlSb growth, are necessary [85].

12.7

Current Status of Ternary Substrates

Most of the ternary III-V crystal production efforts are focused towards large-grain polycrystalline growth for applications such as thermophotovoltaics, infrared optical components, homojunction optoelectronic devices such as photodetectors and terahertz emitters, etc. [11, 12, 33, 38-44, 86]. The optical and electrical properties of these crystals are close to their highest theoretical limits and are perfectly suited for the above applications. Evaluation of single-crystalline material for heteroepitaxial device fabrication has not yet been initiated. This is due to lack of a steady supply of epiready ternary wafers from any high-profile commercial vendors. Data on crystalline quality such as spatial dislocation density profile, microscopic alloy fluctuation, thermal properties, etc., is still lacking. Limited measurements on GaInSb single crystals grown using vertical Bridgman and VGF methods have revealed dislocation densities of 1000-2000 cm⁻², which is very encouraging. Proving high crystalline quality using X-ray rocking curves, availability of misoriented substrates and demonstration of high surface quality are absolutely necessary for widespread usage in electronic and optoelectronic applications where lattice-matched substrates are needed.

12.8 Conclusion

Substrates of III-V ternary compounds with variable properties have potential for many large-scale emerging photonic, electronic and photovoltaic applications. The materials-science issues and crystal-growth challenges have already been understood and established. This chapter presented a comprehensive treatment of various problems encountered during bulk ternary crystal growth from the melt and methods to solve them. The only barrier to large-scale ternary crystal production is the development of an appropriate engineering infrastructure. This could be accomplished by starting from existing binary crystal-growth systems. From extensive work, it has been concluded that the vertical Bridgman or vertical gradient freezing process is the most suitable method for growing large-diameter III-V ternary bulk crystals. In this chapter, a crystal-growth process designed for large-diameter ternary crystals has been described. The established process has been successfully demonstrated in laboratory-scale experiments for growing GaInSb crystals (up to 50 mm diameter) with a wide range of alloy compositions. Limited experiments on AlGaSb, GaInAs and InAsP have also been carried out to evaluate the growth parameters necessary to grow crystals with high optical and electrical properties. Crucial growth parameters include: low temperature gradient, low growth rate compared to binary compounds and melt stirring using forced convection to avoid constitutional supercooling. For generating ternary single-crystal seeds, a two-step process is necessary. Growth of homogeneous single crystals requires precise melt composition control using periodic solute replenishment and continuous melt stirring such as with ACRT.

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X-Ray Diffraction Imaging of Industrial Crystals

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13.1 Introduction

Large single crystals are used in vast quantities to fabricate electronic, and many other, devices. Single crystals are chosen for their unique electronic, mechanical, optical or other properties. Defects in crystals, whether induced by growth or by processing, can seriously degrade and even destroy such properties. Consequently, defects in single crystals adversely affect device performance, severely reduce the production yield and can even lead to destruction of silicon wafers in rapid thermal treatments used in advanced technology nodes. It is, therefore, important to have means of inspecting single crystals in order to detect, measure and visualize the location and density of crystalline defects in both R&D and production environments. Such assessment is an integral part of process development and, if available in a non-destructive matter, in-line process control.

Large crystals of any sort are expensive. It is, therefore, desirable to have non-destructive defect imaging methods so that good material can be reintroduced into the production line after inspection. Using recent figures on wafer costs, losses and yields from International Sematech [1] we calculate that the annual value of wafers lost to defects in a single 300-mm silicon fab processing 20 000 wafer starts/month is approximately \$240 k. However, the related value of overall processing and end-product yield loss in these wafers, for custom products at 180–90 nm nodes, is about \$2.4 M. Since the area of a die of a given circuit is approximately inversely proportional to the node dimension, the value of the lost product has similar proportionality. The return on investment for new, automated wafer-inspection tools is compelling, for advanced technology nodes.

Optical inspection methods are used routinely but have serious limitations for certain types of defects. Methods that measure a reflected optical signal often cannot detect defects that do not break the surface and may require that the crystal be chemically etched. Etching will reveal many defects but is usually destructive and thus coupled to the need for expensive monitor wafers. Infrared

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(IR) microscopy techniques are used for silicon, which is IR-transparent, but not suitable for many other single-crystal materials. Even in silicon it has limited resolution or sensitivity to the kinds of defects that must be detected, and severe restrictions apply to backside treatment and doping levels. The defect density in high-quality industrial crystals is generally too low to use electron microscopy, which is also destructive. Finding a single defect on a wafer with a TEM would be far worse than finding a needle in a haystack. Yet this single defect could destroy a number of devices or even result in breakage of the wafer during processing.

X-ray diffraction imaging (also known as X-ray topography [2, 3]) has for almost 50 years been the mainstay of crystal-defect visualization. Significant advances in speed and resolution have been made possible using synchrotron radiation sources [4], though these are inappropriate for use in fabrication lines. But it has to be said that destructive methods have often been preferred in industry because of the large size of the X-ray tools for large wafers, the very low throughput of traditional tools, the need to process film and the lack of a simple quantitative output. Furthermore, a skilled scientist has normally been required to operate such tools.

13.2

Digital X-Ray Diffraction Imaging

The problems with X-ray diffraction imaging have recently been overcome with the use of high-brightness X-ray sources and digital methods of data collection and image processing [5–7]. The underlying principle of the so-called BedeScan[™] system is that of X-ray diffraction imaging (XRDI) [8]. XRDI is recognized as a powerful tool for directly imaging defects in single crystals, such as semiconductor substrates and epitaxial thin films. To obtain an X-ray diffraction image, the wafer is oriented with respect to the incident X-ray beam such that a single set of planes, designated by the Miller indices (hkl), satisfy the Bragg condition for diffraction, namely

 $2d\sin\theta_{\rm B} = \lambda$

where *d* is the spacing of the diffracting planes, θ_B is the Bragg angle and λ is the X-ray wavelength. The diffracted intensity is mapped across the surface of the crystal. For wafers that contain no defects, the crystalline lattice is essentially perfect, leading to a constant X-ray intensity diffracted from the wafer. However, defects that disturb the perfection of the lattice alter the *d* spacing and/or Bragg angle (i.e. those defects that introduce strain and/or tilt), give rise to variations in the diffracted intensity in the vicinity of the defects [8, 9]. It is important to note that the strain field that can be detected by X-rays is often much larger than the physical size of the defect. For example, dislocations are normally thought of as faults on an atomic scale; however, their detectable strain field extends to tens of



Fig. 13.1 Principles of Bedescan $^{\rm \tiny M}$ digital X-ray imaging. (a) in transmission, (b) in reflection.

 μ m. Likewise, voids and precipitates can be detected that are below the resolution of optical imaging methods.

The BedeScan[™] imaging method is outlined in Fig. 13.1.

A high-brightness microfocus X-ray source is positioned close to the sample at an appropriate angle for the X-ray beam to diffract, in either reflection or transmission. In the case of reflection Cu radiation is used, but this is not sufficiently penetrating for transmission and so Mo radiation is used, which has a shorter wavelength and is more penetrating. The wafer is scanned, and limited-area diffraction images are acquired by the camera and these are stitched and tiled together by software in the computer to create an image of the whole wafer. Image integration and preprocessing is thus performed in the computer by a "virtual scan" of the detector. This scanning method allows a limited-area camera to image single crystals of any size without compromising the resolution and has only become possible quite recently because of the very large amounts of data transferred and processed. The high-resolution X-ray sensitive CCD must capture and transfer data at up to 40 Mpixels/s, and many gigabytes of data will be processed in the reconstruction

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Fig. 13.2 Whole-wafer scan of a 200-mm silicon wafer, showing slip bands and thermal slip dislocations nucleated from BMDs. (220) reflection in transmission mode. (a) whole wafer image, (b) Detail of indicated area showing individual dislocations.

of the image of a 300-mm wafer. Nevertheless, a complete 300-mm wafer can be scanned and imaged in less than 30 min and selected areas viewed at high resolution in a few min. Figure 13.2 shows a defect image¹ of slip bands and thermal slip dislocations nucleated predominantly from precipitated bulk microdefects (BMDs) in a 200-mm wafer. The high oxygen content in this sample introduced large lattice strain and dislocations. Single dislocation lines and curved threading ends can easily be distinguished in the high-resolution inset.

The scanning method also allows the rapid production of selected-area images, for example to examine the wafer edge for polishing-induced defects. Figure 13.3 shows an example, again on Si. The edge defects, probably microcracks introduced

¹Mo radiation is used for all transmission images, and Cu radiation for all reflection images in this chapter. The convention adopted in all images is that extra X-ray intensity results in a darker image.



Fig. 13.3 Edge scan of a 200-mm silicon wafer (courtesy of Dr. D.K. Lee, LG Siltron) showing edge damage that has nucleated slip bands on thermal treatment. Dopant striations are also visible. 220 reflection, transmission mode.

by wafer handling, have nucleated slip bands on thermal treatment. In some cases these can result in catastrophic shattering of the wafer in rapid thermal annealing (RTA) processes.

Finally, the scanning method with a compact source allows a reduction in tool footprint by a factor of more than two, compared to a traditional film-based instrument with similar resolution. Such tools are now operating in semiconductor research laboratories. We expect them to move to the manufacturing environment in order to reduce yield losses and make the substantial savings mentioned above [10].

13.3 Applications Examples

The following sections give examples of a number of applications of X-ray diffraction imaging and wafer inspection (XRDI).

13.3.1 Dislocation Imaging

Dislocations can be imaged in all cases where the line length is more than a few μ m. Individual dislocations can be observed, as already seen in Fig. 13.2(b). Threading, growth and interface misfit dislocations in relaxed epilayers can all be observed



Fig. 13.4 The image of Fig. 13.2(a) is shown here, divided into regions the size of typical semiconductor chip dies. The total integrated intensity in each die is calculated, and those above a

certain threshold are automatically marked with a black dot. Calibration against the manufacturing process allows this to be used for automatic yield prediction on the basis of defect density.

providing that the dot product of the Burgers vector **b** and the diffraction vector (normal to the diffracting planes) **g**, satisfies the criterion $\mathbf{g}.\mathbf{b} \neq 0$. Systematic use of different reflections and observation of dislocation contrast allows determination of the Burgers vector, as in transmission electron microscopy. Bundles of dislocations as in slip lines or bands are easily seen, as in Fig. 13.2(a). The overall blackening of the image (integrated scattered intensity) is proportional to the dislocation density, up to the point at which images overlap and hence saturate. Thus, a quantitative measure (or at least indication) of dislocation density can be obtained. This may be performed automatically and marked on an image, as shown in Fig. 13.4, providing a method for predicting yield loss based on defect density.

Process-induced dislocations are a secondary cause of yield loss. These may also be detected by XRDI, since the image may be taken on a patterned and processed wafer; the X-rays easily penetrate the layers comprising the circuitry. Strains due to the manufacturing process, such as those at the edge of oxide windows, are visible, and dislocations (above a few μ m length) generated from faults in the manufacturing process are visible. Figure 13.5 shows XRDI defect images of 300- μ m-square-sized pads after SiGe epilayer deposition. Images of individual misfit dislocations in the slightly relaxed epilayer/substrate interfaces, and of the surrounding die pattern can be seen.



(a)



(c)

Fig. 13.5 XRDI defect images of 300-µm-square-sized pads after SiGe epilayer deposition. (115) reflection in reflection mode. (a) to (c), decreasing layer thickness. Scale bars 100 $\mu m.$ Images of the misfit dislocations and of the surrounding die pattern can be seen. Samples courtesy of Dr. Wiebe de Boer, Philips Semiconductors, Fishkill, USA.

A common problem in the growth of large single crystals from the melt is the extensive slip that is generated if there is catastrophic termination of the crystal growth, for example by a power fault. For many applications it is important to ensure that the wafers or crystal slices used further do not contain any slip. X-ray diffraction imaging can show the slip bands unambiguously and clearly, even on thick slices that are simply sawn and/or lapped. Figure 13.6 shows a 1.8-mm slice taken from the end of one such boule. Slip bands are clearly shown, and simple geometry based on the orientation of slip planes can be used to predict the termination of these events, since the (111) slip bands are at 54.7° to (001).





Fig. 13.6 (a) Images of slip bands (white, horizontal bands) in a 1.8-mm sawn slice of silicon near the collapsed end of a boule. Diagonal dark lines are saw marks. The origin of the bands is shown in (b).

Such slices can be obtained and imaged within 1 h of the boule removal and provide reliable indication of the beginning of "good" material. The white-on-black contrast seen is typical of imaging in thick crystals, and it is remarkable that slip bands can be detected even in the presence of surface damage caused by diamond sawing.

13.3.2 Stress Concentration Points

This is a very important feature of XRDI. While some optical techniques can reveal surface stresses, the sensitivity of X-rays is much higher, X-rays can reveal subsurface stresses, and the technique can be made quantitative.

Dislocations are induced by stress at supporting points during RTA. Figure 13.7 is an image of defects around a supporting pin mark. The intense damage at the pin mark itself is seen. Around the pin, dislocations ending at the wafer surface (termination of slip bands) are visible. In this reflection mode, only the top 10 or so μ m of the material are imaged. Dislocations buried in the wafer bulk are not detected, giving high visibility to near-surface defects.

Microcracks at wafer handling or supporting zones are becoming a topic of great importance to overall process yield. The high speeds of wafer handling robots require a firm grip on the wafer by vacuum or mechanical clamps, and



Fig. 13.7 XRDI image around the region of a supporting pin for thermal treatment. 115 reflection in reflection mode. Data courtesy of Dr. Frans Voogt, Philips Semiconductor, Netherlands.



Fig. 13.8 (a) reflection, top surface, (b) reflection, bottom surface, (c) transmission, (d) cartoon of proposed defect configuration in the region shown by a rectangular inset box.

if these are not in proper adjustment, microcrack damage can occur. The higher RTA gradients necessitated by smaller technology nodes (which imply steeper but shallower diffusion profiles) make it more likely that some such defects will propagate, either as cracks or as slip bands. Figure 13.8 shows reflection and transmission images of the edge of a wafer that has experienced normal robotic handling plus thermal annealing. There are gross defective regions (slip bands) at the left and right of the image, and it is interesting to note from the image intensities in reflection and transmission that the dislocations generated lie mostly in the bulk rather than at the surface. A more subtle feature is shown in the rectangular inset. The reflection images show virtually no defects, but these are clear in the transmission image. The schematic in Fig. 13.8(d) shows the type of subsurface damage that could give rise to this contrast. Similar edge damage has also been observed to occur in shipping wafers in normal transport boxes.

Regular wafer manufacturing processes are also observed to give rise to defects on thermal processing. The strip at the top right of Fig. 13.3 corresponds to the wafer identification number (blanked out for IP protection) written with the normal laser scribe. Orientation notches are seen at the top of Fig. 13.2 and the bottom right of Fig. 13.8(c). All of these have resulted in dislocation creation and propagation on thermal processing.

13.3.3 Precipitate and Void Imaging

Oxygen-rich regions in silicon can sometimes coalesce to form voids. The partial lattice collapse around voids causes strain fields that extend over distances much larger than the physical size of the void and hence can be imaged by X-ray diffraction. Figure 13.9 shows voids (as well as slip bands and edge damage) in a silicon wafer. The zero-contrast line perpendicular to the diffraction vector is an indicator of the dilatational strain field of voids and precipitates.

It may be necessary to determine the depth distribution of such features, as well as that of dislocation damage. This is easily done at ${\sim}10\,\mu{\rm m}$ resolution by the technique of section topography in transmission. Referring to Fig. 13.1(a), it is seen that the image on the detector when both it and the sample are static is the projection of the section through the sample traced by the incident beam. If the latter is made very narrow, ${<}10\,\mu{\rm m}$, a depth distribution is immediately seen. Figure 13.10 shows backside damage, dislocations and precipitates and their distribution through the wafer thickness. This type of image can also reveal, for example, the depth of oxygen-denuded zones near the wafer surface.



Fig. 13.9 A region near a wafer edge, showing edge damage at A, slip bands at B and voids at C. The (220 transmission) diffraction vector is vertical, resulting in a horizontal line of zero contrast on the void images. This is typical of a pure dilatation strain field caused by voids and precipitates.

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Fig. 13.10 Section topograph through a silicon wafer approx. 0.7 mm thick. The backside damage depth caused by grinding is seen. Contrast in the interior of the wafer is caused by both dislocations and precipitates.

13.3.4 Subgrains, Superdislocations and Micropipes

Whilst silicon comprises by far the largest bulk and value in single crystal technology, other materials are of critical importance in key areas of semiconductor and laser technology, as discussed throughout this volume. Defects are often of critical importance in such materials – which are often compounds – and may be much harder to eliminate than in the elemental silicon. Two examples will be given.

A subgrain in a sample of the piezoelectric material lithium niobate is shown in Figure 13.11. The image is seen as a simple displacement of the subgrain, due to its slightly different orientation. The misorientation may be measured from the displacement and the projection properties of the image. Such subgrains are common in crystal growth. For example, in piezoelectric materials they scatter the acoustic waves and the transducer performance falls, while in calcium fluoride lenses for UV lithography they scatter the UV light and decrease contrast and resolution in the lithographic process.

Silicon carbide crystals are important substrates for gallium nitride epilayer for blue-light optoemission. Defect images of both substrate and epilayer are shown Fig. 13.12. Such images can be used to optimize the growth process and significantly reduce defect densities.



Fig. 13.11 Reflection image of lithium niobate showing subgrains.



Fig. 13.12 Epitaxial growth on SiC. Reflection images. (a) SiC substrate, showing superdislocations and micropipe defects, (b) GaN epilayer, showing the strains that have been transmitted through to the layer.

Naturally, all the defects noted above for silicon may also be imaged in other crystalline materials. However, they are often of lower importance, whereas the larger-scale defects that have been eliminated from the silicon growth process can assume prime importance.

13.4 Summary

X-ray diffraction imaging and inspection methods are now suitable for use in fab manufacturing environments as well as in research and development laboratories. They can be applied to all classes of good-quality single crystals. They are capable of revealing defects (especially subsurface defects) that are not imaged by other techniques, and the strains that the defects cause are measurable and quantifiable. Their application is likely to result in considerably accelerated development and reduced manufacturing costs for processes based upon single crystals.

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Part IV Scintillator Crystals

Continuous Growth of Large Halide Scintillation Crystals

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14.1 Introduction

The history of growth techniques of alkali halide crystals (AHC) dates back nearly one hundred years. Each stage of this progress was associated with new applications areas and novel engineering solutions. It can be said that the advancement of science and technology was the driving force behind the maturation of the present-day techniques of AHC growth. These trends are very discernible when analyzing the AHC market over the past two decades.

One of the most dynamic areas of AHC applications is found for scintillators used in single-photon emission computer tomography (SPECT) medical systems. In the mid-1980s, these were average-sized (300-350 mm in diameter) NaI(Tl) crystal detectors. In the 1990s, the size of the detectors increased to 600×500 mm to enable instantaneous whole-body scanning. Nowadays, we deal with both plane and cylindrical scintillation detectors of varying thickness and diverse configurations. Another segment of the high-tech market for large-size AHC single crystals is high-energy physics. Electromagnetic calorimeters in such flagship projects as BELLE [1] and BaBar [2] warranted the use of tens of thousands of homogeneous CsI(Tl) single crystals up to 300-330 mm long, with the KTeV project relying on the use of pure CsI crystals 500 mm long [3]. The state-of-the-art lithography applications involve the use of crystals up to 400 mm in diameter also. That is to say, the necessity gradually emerged for carrying out R&D on mass production technologies for large-size single crystals. What is the most suitable crystal-growth technique?

The choice of alkali halide single-crystal growth was not originally very widespread. Actually, all of the known industrial-scale technologies were based on the Bridgman and Stockbarger techniques [4, 5]. These techniques have, fundamentally, inherent limits in the production of large-size single crystals with a high structural perfection and homogeneous activator distribution. Moreover, there are other drawbacks that are impossible to circumvent when using them for the production of large-size and homogeneous single crystals of high quality. The main problems encountered here have to do, above all, with the following:

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- Weak convective mixing of the melt prior to the crystallization front that brings about the appearance of inhomogeneities, capture of dopants, nonuniform distribution of the activator along the ingot;
- Impossibility to control the crystallization front shape and bring to perfection the structure of the growing crystal;
- -Adhesion of growing crystal to the crucible.

The methods of seed-crystal pulling from the melt (the Kyropoulos and Czochralski techniques) have a number of inherent merits as compared to the normal crystallization in a crucible. First, there is the possibility of rotation of the crystal pulled that provides for intensive mixing of the melt before the crystallization front. Secondly, there are no problems associated with crystal adhesion. But, at the same time, these methods are very sophisticated from the technical standpoint.

In all cases, the development of a stable crystal-growth technique was dependent on the ways of empirical selection of the crystallization conditions. The yield of perfect crystals was not high, since the optimum activator concentration was achieved in the middle zone of the ingot only.

It is not surprising then that the 1980s and 1990s proved the period of intense search for novel physical approaches and technological breakthroughs in the production of large-size AHCs.

Efforts aimed at the implementation of automatic growth control were typical of this period. They were used to correct the parameters of crystal growth with the purpose of preserving a constant crystallization mass rate. It was in that period that the ideas of process stabilization owing to feeding the melt with starting materials were germinated. That is to say, one can suggest here the birth of the idea of continuous crystal pulling occurred during that period.

In this respect, the evolution in the growth techniques of halogenide dielectric crystals was linked to the progress in methods and hardware achieved in growing semiconductors (silicon, in the first place). The first attempts at growing semiconductors via a continuous growth method were made in the mid-1970s. Yet, it was only in [6] that the modern approach was offered for continuous single-crystal seed-pulling simultaneously with the feeding of starting raw material.

The research case history relative to halogenide single crystals went through similar steps. There were attempts to implement the "metallurgical" approach [7] in which during horizontal crystallization the melt feeding was to provide for large crystal dimensions. With that, the polycrystallization of the blank due to multinucleation processes and volatile activator evaporation prevented the idea from moving to industrial-scale production. Continuous feeding in the Bridgman–Stockbarger method [8] leading to the presence of activators in crystals was much too sophisticated to be applicable to industrial-scale production.

However, there was some noticeable success in growing large-size single crystals. This accomplishment (as in the case of semiconductor single crystals) was based on a successful development of the methods of continuous single-crystal seed-pulling with the simultaneous feeding of starting material (powder, granules or melt) [9, 17]. During the last decade a technological platform has been developed, and on its base

the relevant methods and hardware for continuous single-crystal growth have been established. Not only do these modifications allow for the pulling of single crystals of large sizes, but they also satisfy the delicate requirements for the performances of the process (for example, to perform additional purification of starting material, to employ reactive atmospheres, to utilize single-crystal fragments, to vary both feeding material and its condition, etc.).

Within the framework of this chapter, both the description of the principles and merits of the continuous crystal pulling techniques are given and the notions are provided about the hardware for industrial-scale technologies. Separately, we shall dwell on the state-of-the-art technologies, i.e. we shall try both to demonstrate the possibilities of the universal approach to the continuous crystal-growth process and prove that these techniques enable us to vary and modify the level of perfection of the grown single crystal.

14.2 Physical Principles Underlying Continuous Single-Crystal Growth

This chapter is devoted to the development of continuous pulling methods for AHC.

The basic motivation for this search lay in the desire to stabilize the crystallization process and to minimize various kinds of fluctuations on the melt/crystal interface. Physically, it means that the crystallization mass rate must remain constant during the course of the entire process. However, this kind of problem is far from being trivial. The basic methods of single-crystal-seed growth from the melt presupposed variation of the temperature conditions on the crystallization front, as the crystal grew, with subsequent displacement of the melt level relative to the thermal field. This shortcoming can be compensated by uninterrupted correction of the temperature field, yet the total stabilization of the thermal conditions is successfully achieved only upon single-crystal growth via the Czochralski method, with the crystal diameters being small compared to the diameter of the crucible.

In the case of crystal growth, when the crystal's diameter is comparable to that of the crucible, the only way to overcome this problem is to feed the melt continuously, while preserving its level and the position of the crystallization shape.

In this way, the physical problem called for an engineering and technological solution. As a result, an idea was proposed of continuous growth of alkali halide single crystals with the simultaneous melt feeding with starting material.

The realization of continuous pulling from the melt requires the matching, in the first place, of the mass balance between the crystal pulled and the starting material fed into the system.

In its ultimate form, the problem of controlled continuous pulling boils down to the production of a single crystal that has a transverse cross section that is unchanging with height, and grows with a constant axial rate. (In the first approximation, we shall consider that the melt should crystallize only on the growing crystal; evaporation of substances from the free surface of the melt can be

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neglected, while the crystallization front does not change its shape when the melt volume remains unchanged.)

So, it might be very desirable that one of the parameters (transverse cross section or axial speed) should be kept constant independently of each other, which is feasible only in the event that the adjustment is done by way of variation of a third parameter, which exercises an influence on these parameters, to be more precise, on the crystallization rate in general. Since the latter is determinable by the difference between heat removal from the crystallization front through the growing crystal and the heat influx from the melt to the crystallization front, this parameter would be either temperature in the crystal or that in the melt.

Thus, the general principle of continuous pulling can be formulated in the following way. To pull a single crystal with a constant axial growth rate and a constant transverse cross section, it is necessary and self-sufficient that constant values be maintained of any of the two following parameters: (i) axial crystal growth rate, (ii) crystal transverse cross section at the level of the melt surface; (iii) melt crystallization mass rate on the growing single crystal under such conditions that the melt volume remains unchanged in the crystallization zone.

In continuous pulling the automatic adjustment is achieved by controlling just one parameter, the temperature regulation (either of crystal or of melt), using the measurements of either: (*) crystal diameter; (**) crystal weight; (***) melt weight; (****) growing crystal length; (*****) level of melt.

There are references of the implementation of all of the above adjustment principles [9–12]. However, when we deal with crystals whose mass is in the range of several hundred kilograms and growth duration is several days, such factors like ruggedness, stability and dependability are crucial. From this standpoint, the advantages of melt-level detectors used for growing large-size crystals turned out to be decisive.

The only potential shortcoming of growth control using the melt-level gauge is a circumstance when melt-volume variation occurring due to melt evaporation would be accepted by this detector as evidence of crystal growth. Consequently, if the evaporation rate changes in the course of the growth, the crystal diameter would change as well. This limitation is hardly substantial, since in most cases the evaporation rate is either low, or it can be stabilized or decreased, while growing crystals in an excessive gas pressure. In all other respects, the melt-level detection technique is deemed as the preferred one. The adjustment of crystal diameter depends neither on the growing crystal cross section, nor on the mass of crystal or melt. The electrocontact melt-level measurement method allows changes in the melt level to be detected with an accuracy down to $10 \,\mu m$ [13].

The first successful endeavor to control the continuous process of AHC crystallization was described in references [9, 14]. The starting material was fed continuously into the crucible, with the crystal being pulled at a constant rate and the melt level remaining unchanged, i.e. the equality was secured of the mass rate of the feeding and melt crystallization. The automatic process control was based on melt-temperature adjustment as triggered by the signal from the melt-level detector. The gauge constantly monitored the level position, and, if the crystal growth mass rate was different from the assigned mass velocity of the feeding, then the melt-level displacement in the crucible occurred at which the control signal was formed and used for correction of the melt temperature.

The major features of this, essentially continuous, method of crystal growth with simultaneous feeding consist in the following. The growth is made via crystal pulling at a certain rate v_p while simultaneously feeding the melt with some starting raw material that has a certain mass rate W_f for preserving the level of the melt h_L in the crucible. Not only does this technique provide continuous crystal growth, but it also leads to a constant value of the axial temperature gradient in the region of crystallization and the form of the crystallization shape in the course of the entire process. That is to say, the physical requirements for the approximation to the ideal case and the technological stability of the crystal-growth process for large-diameter crystals are both satisfied.

It is understood that the proposed process is quasicontinuous in nature due to the discontinuity of the principle of melt-level control in the crucible. *A priori*, it is implied that the most stationary conditions must be realizable at a completely continuous feeding or at a maximum frequency of the feeding cycles.

The equation of material balance during continuous crystal pulling acquires the following form:

$$\dot{\boldsymbol{m}} = \dot{\boldsymbol{m}}_{\rm S} + \dot{\boldsymbol{m}}_{\rm L} \tag{14.1}$$

where \dot{m} is a feeding mass rate, \dot{m}_s is a crystal growth mass rate, \dot{m}_L are increments of the melt mass in the crucible.

For conservative systems (with no mass transfer through the gaseous phase), the mass balance in the approximation of the melt/crystal plane interface can be written as follows:

$$\frac{\pi}{4}d_{\rm S}^2\rho_{\rm S}\upsilon_{\rm k} = \frac{\pi}{4}\dot{h}_{\rm L}({\rm D}^2\rho_{\rm L} - d_{\rm S}^2\rho_{\rm S}) + W_{\rm f}$$
(14.2)

where the velocity v_k stands for a resulting crystal pulling rate.

In the case of $\dot{h}_L = 0$:

$$\frac{\pi}{4}d_{\rm S}^2\rho_{\rm S}\upsilon_{\rm p} = W_{\rm f}(h_{\rm L}) \tag{14.3}$$

and

$$d_{\rm S} = 2\sqrt{W_{\rm f}(h_{\rm L})/\upsilon_{\rm p}\rho_{\rm S}\pi} \tag{14.4}$$

The value of $W_f(h_L)$ indicates that the feeding mass rate is a function of the crystallization mass rate, although it is rigidly connected with the melt level in the crucible. From the expression (14.4) it follows that, at an assigned crystal pulling rate, temperature-field configurations and value of the radial temperature gradient, the feeding mass rate control provides for stabilization of the diameter of the crystal grown.

In this way, the growth process control comes down to the control exercised over three parameters: temperatures of the bottom (T_{bot}) or lateral (T_{lat}) heaters, crystal pulling, and melt feeding rates. Since d_S is determinable mostly by the value of W_f/v_p , programming of this ratio leads to automatic radial outgrowth of the single crystal from the seed to the final diameter.

14.2.1

Continuous Crystal Pulling and Uninterrupted Control over Growing Crystal Diameter

The stabilization of the melt level is achieved owing to periodic feeding of the melt with starting material. Because the crystal pulling is performed at a constant rate, then the rupture of the meniscus in the vicinity of contact of the melt-level detector feeler gauge with the melt surface occurs in certain time intervals $\Delta \tau$, when the meniscus height reaches its limit and surface tension forces cannot maintain it any longer. When the meniscus breaks, a subsequent dose of the melt Δm_0 comes into the crucible and the contact is re-established.

The feeding mass rate can be represented as follows:

$$\dot{m} = \Delta m_{\rm o} / \Delta \tau = \pi \{ [d_{\rm L}(t)]^2 - [d_{\rm S}(t)]^2 \} \cdot \Delta h \cdot \rho_{\rm L} / 4 \Delta \tau$$
(14.5)

where $\Delta \tau$ is the time interval between dosed feedings.

It can be deduced from Eq. (14.5) that the constancy of $\Delta \tau$ attests to the constancy of the melt-free area $[d_{\rm L}(t)]^2 - [d_{\rm S}(t)]^2 = const$, or to the constancy of the crystal diameter $d_{\rm S}(t)$.

In this way, the value of $\Delta \tau$ is a very accurate and convenient parameter for construction of the automatic control system. It characterizes the value of the growing crystal diameter rigorously at the level of the melt surface.

It must be said that to measure the parameter $\Delta \tau$ does not require any additional gauge. This information comes from the electrocontact feeler gauge that governs the feeding, for the purpose of which the control system measures time intervals from the discontinuation of the feeding (the moment when the melt surface touches the feeler gauge tip and recovery of the feeler–melt contact) until the beginning of subsequent feeding (the moment of rupture of the meniscus).

The relationships of the grown crystal diameter, while taking into account the volume of the crystal submerged part V_S^L , variations of the melt column height in crucible h_L , average melt temperature T_L and evaporation rate from the open surface of the melt, are described by the following expression [9, 14]:

$$d = \left\{ \frac{W_{\rm f} + \left(\frac{\pi D^2}{4}h_{\rm L} - V_{\rm S}^{\rm L}\right)\rho_{\rm L}\alpha\dot{T} - (\rho_{\rm S} - \rho_{\rm L})\dot{V}_{\rm S}^{\rm L} - \frac{\pi D^2}{4}(\rho_{\rm L}\dot{h}_{\rm L} - \gamma)}{\pi\rho_{\rm S}\nu_{\rm p}\left[1 - \left(\frac{\dot{h}_{\rm L}}{\nu_{\rm p}} + \frac{\gamma}{\rho_{\rm S}\nu_{\rm p}}\right)\right]}\right\}^{\frac{1}{2}}$$
(14.6)

Since $\dot{h}_{\rm L} << \nu_{\rm P}$ and the melt evaporation rate is usually lower than the growth rate (i.e. $\gamma << \rho_{\rm S} v_{\rm P}$), from Eqs. (14.4) and (14.6) one can derive the approximate value *d*:

$$d \approx d_{\rm S} \left\{ 1 + \frac{1}{2W_{\rm f}} \left[\begin{array}{c} \left(\frac{\pi D^2}{4} h_{\rm L} - V_{\rm S}^{\rm L}\right) \rho_{\rm L} \alpha \dot{T} - (\rho_{\rm S} - \rho_{\rm L}) \dot{V}_{\rm S}^{\rm L} \\ -\frac{\pi}{4} (D^2 \rho_{\rm L} - d_{\rm S}^2 \rho_{\rm S}) \dot{h}_{\rm L} - \frac{\pi}{4} (D^2 - d_{\rm S}^2) \gamma \end{array} \right] \right\}$$
(14.7)

As can be deduced from Eq. (14.7), from the standpoint of variation of the values $h_{\rm L}$ and *T*, the growth process can be conditionally divided into three stages [9]. In

the first stage $\dot{h}_{\rm L} > 0$ and $\dot{T} < 0$, in the second one $\dot{h} < 0$ and $\dot{T} < 0$, while in the third stage h and T remain, actually, unchanged. The first stage, and sometimes a part of the second one, coincides with the radial crystal growth until the assigned final diameter is reached, accompanied as it is, quite naturally, by an increase of $V_{\rm S}^{\rm L}$. In the second stage, the growing crystal diameter can exceed the value of $d_{\rm S}$, if the contribution from the variations of T and $h_{\rm L}$ is not compensated by melt evaporation. In the third stage, the value d must gradually decrease until it reaches the value of $d_{\rm S}$, or a somewhat lower one owing to the melt evaporation.

In this way, in the course of the entire process of crystal growth, some deviations must take place of the growing crystal diameter from the value determined from Eq. (14.4): toward decreasing at the stage of radial growth (if it is done by way of programming of W_f/v_p); toward increasing with a subsequent gradual fall-off at the stage of crystal stretching over its length.

As one can see from Eq. (14.7), the minimization of deviation of the growing crystal diameter from the calculated value of $d_{\rm S}$ can be achieved, all other conditions being equal, by decreasing of $\dot{h}_{\rm L}$, while choosing the appropriate set of parameters via automatic adjustment and with a low height of the melt column in the crucible. In addition, the stability of the diameter of crystal growing in length can be enhanced by selecting the minimum possible value of the difference $D^2 \rho_{\rm L} > d^2_{\rm S} \rho_{\rm S}$.

14.2.2

Momentum Extraction of Growing Crystal and Discrete Control Over Growth Process

From the practice of the single-crystal production via continuous pulling and uninterrupted process adjustment, it can be gathered that the cause of the instability of the transverse crystal cross section can be attributed to the melt/crystal interface and increasing of V_S^{L} . Another cause of this may be the nonuniformity of the feeding of starting material into the melt. The above factors can be excluded by employing the following method of momentum crystal extraction with a discrete variation of the melt level [15].

The crystal pulling is performed by momentum over certain time intervals t_{\ni} . The rate of discontinuous lifting of the crystal holder υ_{∂} is many times the rate ν_{p} assigned during continuous pulling. The relationship of the value Δh_{s} vs. time t_{1} (rate υ_{∂}) of the momentum extraction, as well as the system workout time as triggered from the signal of the melt-level gauge t_{2} , feeding time t_{3} and subsequent exposure t_{4} until the next lifting of the crystal holder, is derived from the following expression:

$$\upsilon_{\rm p} \ge \frac{\Delta h_{\rm S}}{t_1 + t_2 + t_3 + t_4} \tag{14.8}$$

or

$$\upsilon_{\rm p} \ge \frac{\Delta h_{\rm S} \upsilon_{\partial}}{\Delta h_{\rm S} + (t_2 + t_3 + t_4) \upsilon_{\partial}} \tag{14.9}$$

The value of discontinuous lifting of the crystal holder (Δh_S) is selected in such a way as to make the growing crystal contact area with the melt vary as little

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as possible, with the value of the variation of the melt level (Δh_L), at the same time, being rather tangible. Respectively, the increasing of Δh_L relative to Δh_S is determinable from the ratio of the areas of the crystallization front (S_S) and the melt-free mirror (F_L) in the gap:

$$\Delta h_{\rm L} = \beta (h_{\rm S}^{\rm L}) \Delta h_{\rm S} \frac{S_{\rm S}}{F_{\rm L}} \tag{14.10}$$

where $\beta(h_s^{L})$ is a correction to the change of the melt–crystal gap value, with the melt/crystal interface being different from the plane.

Fixed by the melt-level detector, the value of melt-level variation $\Delta h_{\rm L}$ may rather easily be associated with the growing crystal diameter $d_{\rm S}$, if the profile of the melt/crystal interface is known.

For instance, in the approximation of the plane melt/crystal interface, the growing crystal diameter is determinable from the following relation:

$$d_{\rm S} = {\rm D}\sqrt{\frac{\Delta h_{\rm L}}{\Delta h_{\rm L} + \Delta h_{\rm S}}} \tag{14.11}$$

When the melt/crystal interface has the appearance of a hemisphere, the following can be written:

$$d_{\rm S} \approx {\rm D}\sqrt{\frac{\Delta h_{\rm L}}{4\Delta h_{\rm S} + \Delta h_{\rm L}}} \tag{14.12}$$

Accordingly, judging by the discontinuous variation of the melt level Δh_L , as determinable by the melt-level gauge, the current value of the growing crystal diameter can be gathered at the melt surface level, which is the underlying basic idea of the momentum-extraction method.

The control-circuit operation principle is as follows. The value of Δh_L , as measured by the melt-level detector, is employed to determine the current value of crystal diameter. Upon comparing the current value with the assigned one, the appropriate correction of the temperature is made and the command is issued to feed the melt in order to restore the original level (including the feeding mechanism). The melt-level gauge monitors the increasing melt level and turns off the feeding at the appropriate moment. Then, another momentum extraction of the crystal takes place and the cycle repeats itself.

14.3

Technological Platform for Family of Continuous Crystal Growth Hardware

The above physical principles of continuous single-crystal growth and technological fundamentals of the crystal growth adjustment represent rather the research base than the essence of the appropriate techniques of the growth of alkali halide single crystals. To a higher degree, these are more likely to be the necessary preconditions than sufficient actions that are needed to realize the single-crystal growth via the continuous-growth method. For this reason, the real breakthrough in the techniques of continuous single-crystal growth came with the advent of the crystal-growth facilities of the "ROST" type [9, 14] producing single crystals 300 mm in diameter.

The techniques of continuous AHC growth became more mature and new modifications of the hardware occurred elsewhere [16–18]. Nowadays, the growth facilities of the types "ROST", "CRYSTAL" and "CROSS" form a technological family employed for continuous growth of crystals with diameters up to 600 mm. Common to them all is the process-control principle based on adjustment of crystal diameter from the data of the melt-level detection. The balance of materials is provided by the feeding that is made with starting material in the form of either powder or melt. Each type of facilities and techniques have peculiarities of their own that are used to take into account specific features of the materials and to realize most fully the conditions for production of the perfect single crystals.

14.3.1 "ROST" Facility for Continuous Growth of Large-Size Single Crystals

For reproducible control over the temperature field in the crystal while it is being pulled out of the melt, it is necessary that the interface boundary between solid and liquid phases does not change its position relative to the furnace heaters. Another two conditions must be met in order to provide for stability and reproducibility of the temperature field in the growing crystal. First, the crucible should not move in the vertical direction, because its walls, rising above the melt surface, and that act as heat shield, make a transient contribution to the heat exchange of crystal with the growth furnace working area. Secondly, it is indispensable that the constancy be provided of the volume or, more strictly speaking, of the geometry of the melt contained in the crucible, since the crystallization front shape depends on the temperature field and the nature of convection in the melt.

If one uses the melt-level detector in the course of continuous feeding of the melt with starting material in order to control the growth, then at a stable melt-mirror position in the crucible all three above conditions are fulfilled. Simultaneously, there is no necessity any longer to determine the accurate value of the feeding rate; the melt evaporation rate will exert an influence only on the absolute value of the growing crystal diameter.

A schematic of the growth furnace is given in Fig. 14.1. One can see that its heating unit is disposed in the lower part of the furnace. Flat on the furnace bottom, in its coldest part, there is a bearing on which the rotating crucible of a proprietary design is found. To compensate for the melt-level fall-off, in the crucible during crystal growth there is a circular peripheral crucible vessel, to which the starting material is supplied from the feeder through the transport pipe. Upon being molten by the lateral heater, the starting material flows through openings into the space between the walls of the crucible and its shield to become mixed with the melt, the level of which is measured by the melt-level detector feeler gauge. The deliberate

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Fig. 14.1 Setup of "ROST" vacuum-compression facility employed for growth of AHCs. 1 – crucible with circular peripheral shelf, 2 – crystal, 3 – replaceable bunker with starting materials, 4 – vibration batcher, 5 – transport pipe, 6 – bottom heater, 7 – melt drainage holes, 8 – internal crucible shield, 9 – melt, 10 – melt-level detector, 11 – crucible-rotation unit.

rotation of the crucible promotes a uniform melting of the starting material fed into the circular cavity, while bringing symmetry to the thermal field in the crucible.

All labor-intensive operations of the facility are mechanized. The loading of the crystal is carried out as follows. The uppermost part of the furnace is fixed rigidly, while its lowermost part is movable in the vertical and in the horizontal directions. Once the growth process is over, the single crystal is lifted up above the plane

between them. The lowermost part is brought down some distance and to one side. A transport dolly with a thermos is brought simultaneously underneath the crystal that is held on the seed. Then the crystal is brought down until it rests on the thermos bottom, and afterwards the direction of the crystal holder stem rotation is reversed, the coupling nut of the seed being screwed off the crystal holder thereby separating the grown crystal.

The unit of starting material melt feeding contains two replaceable bunkers that secure continuity of feeding. The replaceable bunkers are placed on brackets being movable vertically and capable to turn the furnace over in the horizontal direction. The main dosing element of the vibration batcher is an intricate gated shelf used to preclude the possibility of uncontrollable seepage of powder-like starting material into the crucible. With the batcher off, the flow of dehydrated starting material is stopped on the shelf, while, with the batcher on, the starting material movement speed is determined by the vibration frequency of the gated shelf.

Facilities of the "ROST" type (Fig. 14.2) are also adapted for the modified Kyropoulos technique (with a changeable level of the melt in the crucible) and the automated continuous growth method (with constant melt level) in its two versions for crystal pulling: continuous and discrete.

Facilities of the "ROST" type produce large-size optical KCl crystals 600 mm in diameter and conventional scintillation CsI(Tl), NaI(Tl), CsI(Na) crystals up to 520 mm in diameter and weighing up to 500 kg.

14.3.2 "CRYSTAL"-Type Facilities

The peculiarity of crystal growth in "ROST"-type facilities is also associated with the presence of a large original surface of the melt available for the growth of large-diameter single crystals. In this case, an intensive evaporation of some components of the melt may occur from its large surface. The evaporation of volatile activator brings about its nonuniform distribution in the initial part of the single-crystal ingot.

These difficulties can be avoided by employing a technique of crystal pulling from the melt that has a variable geometry of the free surface [4, 5]. As a matter of fact, this implies the use of crucibles with a variable transverse cross section.

The essence of this technique is to provide the minimum free surface of the melt both at the early stage of radial growth and in the course of the entire process irrespective of the diameter of the growing single crystal.

The underlying idea of this method is to make the diameter of the original melt surface at the early stage commensurate with the seed-crystal diameter. Henceforth, as the crystal grows in the radial direction, the melt surface diameter must increase as well. The condition of variable melt-surface geometry is easy to produce, if one pulls the crystal from the melt at the stage of radial growth with a concomitant continuous increasing level of the melt in the variable cross section crucible.

The principle of this method and growth stages are illustrated in Fig. 14.3 in the case of a conical crucible. The radial growth is begun in the very lowermost part of



Fig. 14.2 General layout of "ROST"-type facility for large-size single-crystal growth.

the conical crucible (Fig. 14.3(a)), when the original diameter of the melt surface $d_{\rm L}$ is commensurate with the seed crystal diameter. By performing the feeding with the mass velocity \dot{m} , one increases the level of the melt in the crucible at the rate $V_{\rm L}$, wherein $V_{\rm p} \ge V_{\rm L}$. As the level of the melt gets higher or its free surface diameter increases, the single-crystal radial growth is made (Figs. 14.3(b)-(d)), the melt temperature being corrected so that the linear radial growth rate should be



Fig. 14.3 Stages of crystal pulling from the melt with variable free surface geometry. a) - Seeding, b), c), d) - Radial growth, e), f), g) - Axial growth.

equal to the linear rate of radius increasing of the melt free surface. In this way, the radial single-crystal growth, from the seed diameter up to the assigned final value, can be made at the minimum value of the melt free surface. When the desired crystal diameter is reached, the position of the melt level is stabilized ($V_L = 0$) and the crystal grows in height (Figs. 14.3(e)–(g)). If the feeding is triggered by the melt-level detector signal, then the feeding mass rate \dot{m} at the stage of in-height growth will be the exact copy of the single-crystal growth mass velocity, if melt evaporation is neglected.

The principle of crystal pulling from a variable cross section crucible was realized in the "CRYSTAL"-type facilities (see Fig. 14.4). These facilities employ the melt feeding triggered by an electrocontact gauge signal. The melt level in the crucible during the radial growth increases by doing the feeding upon command from the upward-moving gauge. During the axial growth the gauge motion stops altogether, and, from this moment on, the position of the melt level remains unchanged.

A layout of the "CRYSTAL"-type facility is given in Fig. 14.4. The platinum feeder with the melt is situated in a pressurized growth furnace underneath the crucible, which is also made of platinum. The feeder is shaped as a torus with a rectangular cross section [19] that permits the bottom heater to be placed in the immediate proximity to the conical crucible apex. The feeding of the melt into the crucible from the feeder is performed at a slight excess pressure of the inert gas (argon or nitrogen). The necessary gas pressure in the feeder is maintained with the aid of an electromagnetic valve. The platinum gauge belongs simultaneously to two control loops: a feeding control loop and a crystallization mass rate control circuit. The control system, upon each act of feeding, computes $\Delta \tau$ for a given growth object at the assigned pulling parameters and determines the deviation of the actual values of $\Delta \tau$ from those set by the program. The signal, which is proportional to this deviation, is employed for the automatic temperature correction of the bottom heater. The control system based on the principle of measurement of $\Delta \tau$ provides



Fig. 14.4 "CRYSTAL"-type facility layout: 1 - feeder; 2 - crucible; 3 - bottom heater; 4 - gas valve; 5 - feeding control unit; 6 - feeler gauge; 7 - control computer; 8 - temperature correction unit; 9 - lateral heater; 10 - feeder heater; 11 - crystal.

for automated radial outgrowth, actually, from the seed diameter to the assigned final diameter, as well as for stability of the single-crystal diameter during the axial growth with an accuracy better than 1% (with diameters of 400-450 mm and pulling rates 3.0 to 6.5 mm/h).

One of the most important features of such a facility is the presence of a toroidal feeder. It allows for diverse chemical procedures of the treatment and an additional purification of the melt both prior to the growth procedure and in the process of crystal growth.

14.3.3 "CROSS"-Type Facility

The operational analysis of major units and engineering solutions of the "ROST" and "CRYSTAL" facilities enabled the most dependable and experience-supported options to be selected for their inclusion in the "CROSS"-type facility [18]. These proprietary solutions were a powder-like material feeding from external feeders ("ROST"), a conical crucible and an automatic control system that uses the informative parameter $\Delta \tau$ ("CRYSTAL").

The informative parameter $\Delta \tau$ makes for a smooth crystal pulling at a constant rate that also simplifies the structure of the facility and the growth process itself. Employment of an intermediate heater with the melt enabled the crucible rotation unit to be omitted and the structure of the facility to be made more rugged.



Fig. 14.5 Layout of "CROSS" facility: 1 – crucible; 2 – bottom heater; 3 – lateral heater; 4 – bunker; 5 – intermediate feeder crucible; 6 – feeler gauge; 7 – feeding control unit; 8 – computer; 9 – feeder heater; 10 – vibration batcher; 11 – feeder filter; 12 – overflow pipe; 13 – crystal; 14 – crystal holder; 15 – feeding control unit.

A setup of the "CROSS" facility is shown in Fig. 14.5. The conic platinum crucible that is 620 mm in diameter at the base is placed in a pressurized growth chamber. The furnace, as in the facilities of the "ROST" and "CRYSTAL" types, consists of upper and lower half-frames connected with the aid of a horizontal joint. The lower half-frame houses the heating unit (heaters, heat insulation components, heat-reflecting shields and crucible). The upper half-frame contains the intermediate feeder, complete with a heater, and a filter element that is made of a fine platinum wire mesh. Two bunkers with starting materials provide for uninterrupted work of the feeding system, as triggered into action by a signal from the feeler gauge.

The merits of the "CROSS"-type facility are found in the feasibility of automated radial growth, additional heat and chemical treatments of the melt in the intermediate feeder, and a reduced weight of the platinum crucible.

14.4 State-of-the-Art Crystal Performance for Continuous-Growth Techniques

The progress in the techniques of continuous single-crystal growth allowed, in the final form, not only to develop industrial-scale technologies for production of alkali halide crystals of large sizes, but also to assume an entirely new level of structural perfection control for such crystals. On the one hand, the realization

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of continuous crystal growth undoubtedly complicates the relevant hardware and the growth procedure. On the other hand, these techniques present a multitude of additional capabilities of stabilization of the crystallization mass rate and position of the melt/crystal interface, controlling the activator distribution along the axis of the growing crystal, additional treatment (purification) of starting materials, etc. We shall just bring up specific instances within the limits of the present chapter. The purpose is to demonstrate the capabilities of controlling the quality of single crystals. We would also like to show that even the use of sufficiently full implementation algorithms for the process leaves some outstanding issues concerning many aspects of crystal growth. And in this respect, the automated crystal-growth techniques give much to the technologist in order to apply their "artistry" for elaboration on the optimum crystal-growth conditions.

14.4.1

Activator Distribution Along Growing Crystal-Growth Axis

Since all of the alkali halide scintillators are doped crystals, the homogeneity of activator distribution along the crystal determines the scintillation quality of the material. The classical methods of the growth of these crystals (the Bridgman–Stockbarger method and the Kyropoulos method) presuppose originally the crystal growth with inhomogeneous distribution of the dopants, i.e. just a part of the ingot is efficiently used for the scintillation applications. The idea of continuous crystal pulling with simultaneous feeding of starting material supplies an additional possibility to adjust the activator distribution, because, in principle, the feasibility is there to feed both initial material and activator.

The plethora of research on activator distribution and capabilities of production of homogeneous crystals is covered in references [17, 20].

Now, we shall consider the principal features of this process.

The mass transfer of dopant through evaporation can be reduced to one stage: the mass transfer of dopant across the melt/gas interface boundary which, in the ultimate case, is described by the Nernst equation:

$$w = \frac{dn}{dt} = K_{\rm LG} \cdot F(t)[C_{\rm L}^0 - C_{\rm L}(t)]$$
(14.13)

where *w* is a dopant evaporation rate; *dn* is a mass of such dopant component that has traversed the time-variable surface *F*(*t*) of the interface boundary in the time *dt*; K_{LG} is a coefficient that characterizes the rate of substance transport across the interface boundary; $C_L(t)$ is a true concentration of volatile dopant in liquid; C_L^0 is a constant for this scale of reference representing the hypothetical concentration of dopant in the melt that is in equilibrium with gaseous phase at the temperature T_w (at the dopant component pressure $P(T_w, C_L^0)$).

In view of the peculiarity of the above system and assuming complete melt mixing, the dopant mass transfer can be written as:

$$j = \frac{dn}{dt \cdot dF(t)} = K_{\rm LG}[A - C_{\rm L}(t)]$$
(14.14)

where *j* is a specific rate of dopant evaporation from unit area of the interface boundary per unit time; *A* is a constant that pertains to the ratio of vapor pressure of the dopant over the solution $P(T_w, C_L^0)$ vs. partial pressure of its vapor $P(T_w)$ at the same temperature.

For the case of crystal growth from the constant liquid-phase volume with simultaneous feeding of the melt with starting material, it can be demonstrated that the expression (14.14) turns into j = const, resulting in the feasibility to calculate separately the mass-transfer parameters due to evaporation and due to crystallization.

In this case, the crystallization is made from a liquid of constant volume, with a constant dopant concentration in it being C_0/k . This is exactly what predetermines the uniform dopant distribution over the length of the grown crystal and, in the option of seed pulling, the equality and constancy of the mass rate of crystallization and feeding, the constancy of the diameters of pulled crystal and melt surface.

On the whole, the mass transfer of dopant at the set-in stage of the zoning crystallization process can be viewed as two autonomous processes that, conditionally, are independent of each other: the mass transfer over the chain "feeding-melt-crystal" and the transit process of dopant component over the route "feeding-melt-gaseous phase-furnace cold walls". In the meantime, each process has only its own part of participating dopant component C_s and C_g , the sum of which constitutes the dopant concentration in the feeding material $C_f = C_s + C_g$.

Since the dopant concentration in the melt at the set-in stage of the process is constant ($C_L = C_S/k_0 = \text{const.}$), from the balance of dopant component mass flows it follows that the dopant evaporation mass rate would be:

$$w_{\rm g} = (C_{\rm f} - C_{\rm S}) \cdot S_{\rm S} \cdot \rho_{\rm S} \cdot \upsilon_{\rm p} \tag{14.15}$$

Accordingly, the specific evaporation rate *j* can be determined as:

$$j = \frac{(C_{\rm f} - C_{\rm S}) \cdot d_{\rm S}^2 \cdot \rho_{\rm S} \cdot \upsilon_{\rm p}}{D^2 - d_{\rm S}^2}$$
(14.16)

The expression (14.16) establishes the interrelationships between crystallization rate, feeding rate and composition, growing crystal diameter and composition. Appropriately, all of those values acquire the status of controlling parameters and they can be used to control the composition of crystals grown.

As regards the NaI(Tl) or CsI(Tl) scintillators, it must be borne in mind that, in order to achieve the assigned activator distribution in crystal, the activator concentration in the feeding melt must be increased considering the high volatility of thallium iodide. The activator evaporation intensity depends not only on the free melt surface, but also on the peculiar features of the feeding system of each facility. The equation of material balance between base material and activator can yield the dependence of the activator concentration in the crystal $C_{(S)}$ on the concentration in the feeding melt $C_{(L)}$ and on other pulling parameters, as well as on the intensity

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of evaporation that is characterized by the specific evaporation rate χ .

$$C_{(L)} = C_{(S)} \cdot [1 - (1 - \kappa) \cdot d_{S}^{2} \cdot (V_{L} - V_{P}) \cdot \rho_{S} \cdot \Delta \tau / (d_{L}^{2} - d_{S}^{2}) \cdot \Delta h \cdot \rho_{L}] / \kappa$$

+ $\chi \cdot \Delta \tau / \Delta h \cdot \rho_{L}$ (14.17)

As one can gather from Eq. (14.17), during crystal pulling from the variable cross section crucible, several possibilities emerge to control the volatile activator in crystal. The direct path is variation of $C_{(L)}$. Besides, $C_{(S)}$ depends on the crystal pulling rate and the relation of the values of crystal transverse cross section vs. free melt surface $d_S^2/(d_L^2 - d_S^2)$. In the variable cross section crucible, the value of this relation can be easily varied, the volatile activator concentration for ingots of various diameters being kept constant and made the same.

If one chooses to use as a controlling parameter the mass of initial in-load that provides the required crystal composition (controlled parameter C_S), it can be determined from:

$$n_{\rm f} = \rho_{\rm L} \cdot V_{\rm L} \cdot \left[\frac{j}{\rho_{\rm S} \cdot \upsilon_p} \cdot \left(\frac{{\rm D}^2}{d_{\rm S}^2} - 1 \right) + C_{\rm S}/k_0 \right]$$
(14.18)

where $n_{\rm f}$ is a mass of dopant initial in-load, $V_{\rm L}$ is a volume of the melt in the crucible at the set-in stage of the process that is determinable at the constant crystal diameter. However, as the dopant distribution coefficient in the systems CsI(Tl) and NaI(Tl) is 0.18 and 0.2, respectively, in order to obtain compositionally homogeneous crystals, the composition of the subsequent feeding can be determined using the above relations.

By way of a concluding remark, it must be noted that the above regularities allow the activator distribution to be adjusted across the family of single-crystal continuous-growth techniques. The uniform activator distribution in the crystal volume is made constant with an accuracy $\pm 5\%$ and determined by the principle of crystal pulling from a constant liquid-phase volume ($V_{\rm L} = \text{const}$), the constant free melt surface value and the feasibility of preserving the melt/crystal interface constant over the entire length of the ingot.

14.4.2

Inspection of Melt/Crystal Interface Position

The feasibility of fixation of the melt/crystal interface position is a marked advantage of continuous single-crystal growth. Here, it must be said that, in practice, this can be done only with a certain accuracy. The nonuniformity of temperature gradients and melt convection can substantially influence the shape of the interface. For this reason, the experimental methods of registration or even inspection of the interface position are of crucial importance. In this respect, the optical and scintillation materials represent very convenient objects of study.

The scintillation crystals are known to emit light not only under the impact of high-energy ionizing radiation, but also during UV light excitation. Considering



Fig. 14.6 Light-scattering nonuniformity decorated the melt/crystal interface as a result of the local growth-rate change.

this, the efficiency of luminosity depends, to a considerable degree, on the activator concentration in the crystal lattice of the (for example, Tl ions in the NaI or CsI crystals). Any oscillations of the crystallization mass rate result in variation of the activator ions in the vicinity of the melt/crystal interface. Thus, a decoration of the interface by activator is achieved by the crystal radiance. As a result (as shown in Fig. 14.7 when the temperature variation decreased by more than $0.5^{\circ} \cdot min^{-1}$), the interface position can be inspected easily using the UV lamp.

Another option for inspection of the interface is associated with observation of the distribution of optical inhomogeneities in the crystal. Oscillations of the crystallization mass rate vary not only the concentration of activator ions, but also that of foreign insoluble impurities and gaseous inclusions that scatter the light in the crystal. The light diffusion effect determines the so-called microstriation structure. Figure 14.6 shows the nature of this kind of striation in a KCl crystal. Each region of the capture was provoked by crystal jitter, i.e. a spontaneous jump of the crystal pulling rate or a sharp variation of the heater temperature. One can see that the crystal perfection responds immediately to these kinds of deviations from the optimum crystallization conditions. Quite naturally a question arises about the optimum crystallization conditions.

This question is of acute significance relative to continuous crystal growth, because this process is quasicontinuous. It is understood *a priori* that the shorter the time interval between individual feedings of the melt or separate cycles of crystal jitter, the higher is the degree of crystal homogeneity. This is why the cycling periodicity is determined not only by technical parameters of the crystal-growth



Fig. 14.7 Variations of crystallization front form in CsI(TI) crystals, 520 mm in diameter, during temperature changeovers: increasing of the bottom temperature and decreasing of the lateral one (a) and *vice versa* (b). The upper arrow indicates the outset of the changeover, the lower one is reflective of the situation in 4 (a) and 6 (b) h.

hardware, but also by the feasibility of production of the homogeneous crystals. And this problem is thus referred to a dedicated study and the art of balancing and optimization of the multiparametric task.

As an example of this kind of study, let us consider the variation of the melt/crystal interface shape in the case of temperature fluctuations. Temperature oscillations on heaters and, quite naturally, in the melt are inherent to any adjusting and control systems. This phenomenon was discovered during growth of the single crystals of silicon, KCl, NaI(Tl) and CsI(Tl) [21].

Figure 14.7 presents two variants of interface oscillations during intended temperature variations of heaters with the opposite sign. One can see that the temperature redistribution (with increasing T_{bot} and decreasing T_{lat}) leads to the preferential growth on the crystal periphery and, practically, a total growth stop in the center of the crystal.

The experiments indicate that to achieve the optical quality of crystals, the control and random temperature perturbations of the heaters should not exceed 0.2 °C min⁻¹. In this connection, a practical implementation is important of a staged circuit of temperature regulation to permit the stabilization, with great accuracy, of the temperature of the heaters, when the maximum deviation does not go beyond 0.3 °C, and the control over crystal diameter.

Thus, from the standpoint of operation of the automated growing crystal diameter control system, the interface shape should not be too flat, otherwise during the

momentum extraction of the crystal a partial or full breakaway may occur of the crystal from the melt surface.

14.4.3 Crystal Deformation During Growth

The optical and scintillation applications do not set such rigorous requirements for crystal perfection as semiconductor applications. However, the presence of low- and large-angle grain boundaries and of individual dislocations is potentially dangerous. The segregation of activator and impurities near such defects contributes to the optical and scintillation nonhomogeneity of the material.

The process of AHC growth is always accompanied by a nonuniform temperature distribution throughout the ingot and, consequently, the presence of elastic stresses at a certain level. The relaxation of these stresses is exactly what leads to formation of structural imperfections (dislocations, dislocation and grain substructures), with these phenomena being more prevalent in crystals that have a low strength yield (and AHCs are such materials).

The most typical instance of this kind of phenomena is a curvature of transverse crystallographic planes [21, 22].

The bend is localized on boundaries between subgrains, i.e. in a majority of cases each subsequent grain is turned in the same direction as the preceding one; this is what makes the lattice curvature macroscopical. One can also find subgrains with the opposite misorientation, and, in this way, the unitization of single crystals can be conditionally separated between "flexural" and "random". The "random" unitization is known to be drastically smaller than the "flexural" one.

Only the elastic stresses can relax without affecting the crystal structure. If the axial temperature gradient is constant, the flexure of the cleavage planes will disappear as the temperature smoothes out. However, the temperature fields in the crystal are always of a more complex nature and the emergence of a free temperature bend, i.e. a constant axial temperature gradient, becomes possible only upon suppression of the radial heat curvature in the growing crystal. The models of formation of the cleavage-plane flexures are described in reference [22].

The positive-sign cleavage plane curvature, as proposed by the model, with the growing crystal diameters being 450–550 mm and at low temperature gradients, is much easier to realize than at large temperature gradients. As noted above, this proved possible (Fig. 14.8) at the topmost allowable values of the melt level in the crucible (H_{yp}). The reproduction of the conditions for the positive sign-curvature of the transverse cleavage plane was a rather simple task, as shown in Fig. 14.8, where two crystals are presented that were grown under identical conditions.

The region of temperature conditions with "zero" curvature of the transverse cleavage planes, in this specific case, is found at a lower value of H_{yp} . As a result, such large-size ingots were obtained that had, actually, no flexure of the transverse cleavage planes (Fig. 14.9): at a diameter of 520 mm the sag did not exceed 0.5 mm [22].

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Fig. 14.8 Transverse cleavage (shown with arrows) with a curvature of the transverse positive-sign cleavage planes, as detected in Na1(Tl) single crystals 520 mm (a) and 450 mm (b) in diameter.



Fig. 14.9 Transverse cleavage without cleavage plane curvature, as detected in the upper (a) and lower (b) parts of NaI(TI) single crystal 520 mm in diameter.

All considered, there is one more substantial cause for crystal deformation, its weight. During growth of large-size single crystals with weights of 350–500 kg, the factor of crystal weight becomes comparable to or even more significant than the stress relaxation.

For example, an extremely low yield strength is characteristic of CsI crystals. As a result, during the seed-pulling of such crystals from the melt, with their diameters ranging from 300 to 500 mm, the growing ingot is subject to plastic strain that skirts its periphery. Afterwards, under the action of increasing weight of the single crystal the seed itself becomes deformed. A result of the strain in a large-size ingot is presented in Fig. 14.10.

One can see that maturation of gliding striations in the systems of the type {110} <100> causes not only the formation of low- and large-angle boundaries, but also the emergence of fault-release striations (Fig. 14.10) for crystals oriented along the directions [001] and [111]. Such a crystal just loses its continuity and breaks down into separate fragments.



Fig. 14.10 Formation of fault-release striations of conic shape (shown with arrows) in CsI(Tl) crystal underneath seed, which is 80 mm in diameter and oriented along the direction [001]. The image is made in polarized light and subsequently inverted.





(a)

Fig. 14.11 (a) left-hand side. Traces of plastic strain on end-face surface of CsI(Tl) single crystal, 520 mm in diameter, grown along the direction [001]. The arrows indicate the direction of "forbidden" easy gliding plane. (b) right-hand side. Image of fissures in the transverse plane (001) of a fragment of CsI(Tl) crystal 400 mm in

diameter. The arrow indicates the direction of a slope boundary formed between two quarters of the crystal (the imaginary fissure line AA belongs to the left part of the crystal, while the imaginary fissure line BB belongs to the right part of the crystal). The image is made in polarized light.

Physically, the crystal has an outward appearance as shown in Fig. 14.11.

The dislocations of the type <100>{110} glide in the directions [100] and [010] and [100] and pile up there, thereby changing the original crystallographic orientation of the crystal (Fig. 14.12).

As a result of the deformation of the crystal, as brought about by its weight, the shape of outward appearance of the growing crystal also changes, reflecting the processes occurring throughout the crystal bulk.

The solution of the deformation problem of the CsI crystal was based on the analysis and choice of the seed crystal orientation to minimize dislocation glide over the easy gliding planes. The solution of this problem is not straightforward, yet, as shown experimentally, it is quite feasible. It was established that the most admissible crystal orientation under specific temperature conditions corresponded 376 14 Continuous Growth of Large Halide Scintillation Crystals



Fig. 14.12 Schematic of formation of the macroscopic misorientation boundaries as a result of plastic curvature of growing single crystal: CsI with seed axis orientation along [001]; (a) initial stage of the production of

dislocations of the type <100>{110} (the arrows indicate the directions of dislocation motion); (b) emergence of pile-ups of sister dislocations of the type <100>{110}.

not to the zero value of the Schmid orientation factor (as can be deduced from theory), but to the value 0.35 with a slight spread, roughly $\pm 2.5^{\circ}$.

In this way, the problem of both elastic and plastic strains of the single-crystal composition can be resolved to a considerable degree. At least, the minimization of the deformation level allows growth on a seed of 500 mm in diameter, a cesium iodide single-crystal ingot weighing up to 550 kg.

14.5

Crystal Press Forging for Large Scintillator Development

The above development of techniques of continuous alkali halide single-crystal growth is a step forward in the production of large-size perfect crystals. Clearly, the length of the ingot in these techniques is limited only by the height of the growth chamber and its diameter by the dimensions of the crucible. However, even in these cases, the transition to even greater crystal sizes calls for engineering advances in new growth facilities, and, secondly, maturation of the technique of perfect crystal growth. Both points need sufficient investment and time for R&D. This determines the present challenge of alternative routes for increasing dimensions of crystal blanks.

One such route is press forging of single crystals to transform them into large-size polycrystals. For the first time, such an approach was applied for KCl crystals for high-power IR lasers [23]. The purpose of this transformation was enhancement of mechanical strength and decreasing of cracking of the optical windows over the cleavage planes. An important result thereof was not only the demonstration of the feasibility of increasing the crystal transverse dimensions, but also presenting the proof-of-principle result that the polycrystal medium can be as transparent as that of single crystal. In the case of scintillation crystals, the scintillation homogeneity becomes as important as optical homogeneity. In



Fig. 14.13 Press-forged NaI(TI) crystal.

this case, the transformation must result in preservation of the uniform activator ion distribution and in minimization of the activator ion segregation to grain boundaries. In other words, the press-forging technique must take into account a large number of factors.

Conventionally, press forging implies the deformation of single crystals at elevated temperatures. On the whole, the constitution diagrams for deformation of alkali halide single crystals are described in [24]. Sodium iodide is - as regards crystal lattice, dislocation processes and mechanisms of plasticity - the closest analog of NaCl and KCl crystals. For that matter, the optimum range of deformation conditions (temperature, deformation rate and degree) is predictable from the beginning. In the region of low temperatures (below $0.5T_{melt}$), the crystal is still brittle and fractures over the cleavage plane. In the region of high temperatures (above $0.75T_{melt}$), an active recrystallization process is underway, i.e. there is growth of large-angle boundaries and segregation of activator ions on them. In this way, intermediate elevated temperatures are acceptable, when, replacing the unitized structure, different kinds of dislocation and subgrain structures are rapidly maturing in the crystal [24]. Under those deformation conditions, a plastic flow of material is realizable in a crystal without any changes in the activator distribution. As a result, the uniformity of scintillation characteristics of polycrystalline samples is not different from those of the initial single crystals.

The typical view of pressed scintillation crystal is shown in Fig. 14.13. From initial single crystals, 400–500 mm in diameter, sizes of polycrystalline slab of 800–1000 mm, and more, are easily obtainable.

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The above example points out the importance of complementary production technologies for large-size crystals. This kind of technology does not require development of dedicated sophisticated equipment, and it is not capital intensive, which is different from the hardware used in continuous single-crystal growth. However, when combined, they allow, for example, for rapid R&D and fabrication of detectors for SPECT systems.

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Part V Oxides

Phase Equilibria and Growth of Langasite-Type Crystals

Satoshi Uda, Shou-Qi Wang, Hiromitsu Kimura and Xinming Huang

15.1 Introduction – What is Langasite?

15

Langasite has been used for the past several years as a piezoelectric substrate mainly for the surface acoustic wave (SAW) filters employed in the base stations of 3rd-generation mobile communication systems (for instance, NTT DoCoMo in Japan). SAW filters fabricated on langasite have a large passband so that a tremendous amount of data can be handled and their SAW velocity is stable over a wide temperature range around room temperature. Most strikingly, the langasite substrate allows the SAW to propagate in a certain orientation without any dispersion, which enables the rectangular-shaped passband (the shape factor is close to unity) [1] so that interference with different mobile communication systems can be avoided. This specific orientation is represented by the Euler angle (0, -41.5, 26.6), and thus, the crystal grown along $[01\overline{1}1]$ (54°-rotated Y-axis), which is 5.7° oblique to (0, -41.5, 26.6), is the most appropriate for slicing wafers for SAW device applications [1]. Other potential applications of langasite would draw on the fact that langasite does not show any phase transformation until it melts at around 1500 °C, while other piezoelectric crystals such as quartz (SiO₂), lithium niobate (LiNbO₃), lithium tantalate (LiTaO₃) and lithium tetraborate (Li₂ B_4O_7), undergo phase transition or decomposition at 300-700 °C [2]. Thus, langasite-type crystals are good candidates as temperature or pressure sensors used at high temperature, and some langasite-based sensor applications are already being manufactured [3]. In practice, langatate modified by adding a specific element and/or thermal treatment is considered to be the most promising candidate for high-temperature sensors. The recent development of the combustion sensor for automobiles employing a langatate diaphragm contributes to energy conservation by selecting the most suitable mixing ratio of air and fuel. For this application, the crystal is grown along the $[2\overline{1} \ \overline{1} \ 0]$ (X-axis) direction since the sensor makes use of a piezoelectric mechanism in terms of the piezoelectricity d_{11} .

Langasite crystals are normally grown via the Czochralski technique [4–7] or Bridgman technique [8] even though langasite melts incongruently [9].

15.2

Structure of Langasite-Type Crystals

Langasite-type crystals have the structural form $A_3BC_3D_2O_{14}$, where A is a dodecahedral site, B is an octahedral site, while both C and D are tetrahedral sites where D is smaller. The structure is illustrated in Fig. 15.1. There are several elements with appropriate ionic radius for each site, and thus, various langasite-type crystals can be synthesized. More than 200 langasite-type crystals have been widely synthesized in Russia [10], some of which can be grown with a diameter of more than one inch. Langasite-type crystals that have been used in practice or can potentially be used are listed in Table 15.1 [11]. Looking at the structure of langasite, La₃Ga₅SiO₁₄, site A is occupied by La, sites B and C are occupied by Ga, about half of the D sites are occupied by Ga, while the other half are occupied by Si. The ratio of Ga to Si at the D sites varies around unity, which leads to a solid solution of langasite about Si and Ga. A crystal with such an unfixed occupancy is called disordered here, while a crystal with a fixed occupancy state is called ordered. In Table 15.1, the ordered-disordered state is described for each crystal. Whether a langasite-type crystal is ordered or disordered has nothing to do with the number of constituent elements. Looking at the structure of the langasite-type crystal in Fig. 15.1, the largest site, namely site A, seems to dominate the characteristics of the crystal. Site B, the second largest site, may also influence crystal characteristics.

The equality of chemical potential of an element or vacancy between sites should hold. Thus,

$$\mu_A^j = \mu_B^j = \mu_C^j = \mu_D^j \tag{15.1}$$

where "*j*" is an element or vacancy in the site. For instance, the relationship between the chemical potentials of Ga for the *B*, *C* and *D* sites of langasite is given by

$$\mu_B^{Ga} = \mu_C^{Ga} = \mu_D^{Ga} \tag{15.2a}$$

or, more exactly,

$$\mu_B^{Ga} = \mu_{C1}^{Ga} = \mu_{C2}^{Ga} = \mu_{C3}^{Ga} = \mu_{D1}^{Ga} = \mu_{D2}^{Ga}$$
(15.2b)

Langasite type: A3BC3D2O14



Fig. 15.1 Crystal structure of langasite-type crystals, A₃BC₃D₂O₁₄.

Langasite-type Crystals	a (Å)	k ₁₂ (N/m²)	d ₁₁ , d ₁₄ (pC/N)	Site occupancy
La3Ga5SiO14	8.170	0.161	-6.16, 4.96	Disordered
Sr ₃ NbGa ₃ Si ₂ O ₁₄	8.282	0.190	-5.99, 6.65	Ordered
Ca ₃ NbGa ₃ Si ₂ O ₁₄	8.092	0.182	-6.78, 4.02	Ordered
Sr ₃ TaGa ₃ Si ₂ O ₁₄	8.293	0.174	-6.78, 6.70	Ordered
Ca3TaGa3Si2O14	8.109	0.163	-6.80, 4.48	Ordered
La ₃ Ta _{0.5} Ga _{5.5} O ₁₄	8.228	0.169	-7.02, 4.49	Semiordered
La3Ta0.25Nb0.25Ga5.5O14	8.219	0.165	-6.92, 4.12	Disordered
La _{2.95} Ba _{0.05} Ta _{0.525} Ga _{5.475} O ₁₄	8.253	0.172	-7.01, 6.42	Disordered
La ₃ Ta _{0.5} Ga _{5.4} Al _{0.1} O ₁₄	8.201	0.163	-6.58, 5.14	Disordered
La ₃ Ta _{0.5} Ga _{5.2} Al _{0.3} O ₁₄	8.199	0.165	-6.43, 5.23	Disordered

Table 15.1 Langasite-Type Crystals [11].

where each of the three sites in *C* and the two sites in *D* are noted separately. The ratio of Ga to Si is variable for site *D*2, and thus, the molar free energies of sites *B* and *C* vary with the chemical potential of Ga in site *D* although the Ga content in sites *B* and *C* is almost constant (Fig. 15.2(a)). This variation in molar free energy at sites *B* and *C* may occur through deformation of the shape and size of the site. It should be noted that the chemical potentials of Ga in sites *B* and *C* should change accordingly. However, the *B* site in langatate (La₃Ta_{0.5}Ga_{5.5}O₁₄), which is occupied by both Ga and Ta, is much more rigid. The limited complex of Ga and Ta in the *B* site results in a steep molar free energy curve, and thus the change of Ga to Ta ratio is quite restricted even though the molar free energy of the *C* or *D* site varies in the similar magnitude (Fig. 15.2(b)). Thus, langatate is referred to as a *semiordered* crystal. Furthermore, the variation of the chemical potential of the ordered restricted is more constrained. Let us compare the chemical potentials





Fig. 15.2 The molar free energy and chemical potential of Ga at each site as a function of Ga occupancy (a) in the *D* site of LGS (langasite) and (b) *B* site of LTG (langate).

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Fig. 15.3 The molar free energy and chemical potential of a vacancy at each site as a function of the vacancy occupancy in the D sites of (a) LGS and (b) CNGS.

of a vacancy in the sites of langasite with those of CNGS (Ca₃NbGa₃Si₂O₁₄), which is an ordered crystal. Vacancies are normally generated in order to keep charge neutrality when an atom is replaced by another atom with a different valence. When the dodecahedral *A* site is occupied by La, the molar free energy curve of the *A* site is round so that compositional change may be accompanied by a change in the vacancy concentration (Fig. 15.3(a)). By contrast, when the *A* site is occupied by Ca, the molar free energy curve becomes so sharp that the vacancy population in the *A* site is quite restricted and results in little change in the molar free energy and chemical potential of vacancies in other sites (Fig. 15.3(b)). This means the cation occupancy in each site is totally constrained. This is why CNGS is referred to as an *ordered* crystal. The same is true for the other ordered crystals, namely SNGS (Sr₃NbGa₃Si₂O₁₄), CTGS (Ca₃TaGa₃Si₂O₁₄) and STGS (Sr₃TaGa₃Si₂O₁₄).

Figure 15.4 plots the relationship between the lattice constant of the *a*-axis of langasite-type crystals and their piezoelectric constant, d_{11} [10, 12]. The piezoelectric constant increases with the lattice constant of the *a*-axis. This is an empirical diagram, but is useful for designing new crystals with higher piezoelectric constant.

15.3 Study of Equilibrium Phase Diagram Around Langasite [9]

15.3.1

Preparation of Samples

Samples of over 50 compositions widely distributed in the system La₂O₃-Ga₂O₃-SiO₂ were prepared. Compositions selected in the experiment are shown in Fig. 15.5. Raw materials of 99.99% pure La₂O₃, Ga₂O₃ and SiO₂ were weighed to an accuracy of 0.0005 g and were mixed to make samples with a weight of 5 g each. Mixtures of the selected compositions were pressed at 10 kgf/cm² to pellets and calcined at a temperature of 1300–1600 °C for 5–48 h. Samples of Ga₂O₃-rich



compositions were calcined at 1300 °C while samples of Ga₂O₃-poor compositions were calcined at 1400 °C. Binary compounds La₂Si₂O₇, La₁₄Si₉O₃₉, La₂SiO₅ and LaGaO₃ were calcined at 1600 °C. Phases of the calcined samples were identified by X-ray diffraction (XRD) analysis and intermittent grinding was carried out until the calcinations were completed.

15.3.2 Melting and Freezing of Samples

Powder of the calcined samples after 2–3 cycles of crushing, grinding and calcining was charged into Pt crucibles with a diameter of 10 mm and a height of 10 mm. Its weight of about 0.5 g, which was much less than the volume of the crucible, was measured in order to prevent overflow from the crucibles when the powder was molten. Since the amount of materials charged in the crucibles was limited, it was very important to provide as accurate a composition as possible. This was guaranteed by the intermittent grinding in the preparation of the calcined samples, which increases their homogeneity.

The basic process was to melt the powder completely and then cool it to observe the crystallized phases in order to establish the liquidus phase relations. The crucibles were suspended in the thermal center of a resistance furnace from which the crucibles could be dropped into water of room temperature. Samples were heated to 1580 °C and held for 3 h for complete melting and then were cooled down by different methods. The first method was continuous cooling from 1580 °C to room temperature. In this way, the whole process of crystallization was completed, thus the phases representing the crystallization path could be obtained. In order to confirm the crystallization sequence of the obtained phases in the continuously



Fig. 15.5 Compositions of calcined samples (denoted by \bigcirc and \triangle) and phase relations determined by the phases present in the calcined samples. (Reproduced by the permission of Elsevier Ltd.)

cooled samples, we quenched some samples on cooling at several temperatures. The second method was to cool the samples to a certain temperature, hold them at the temperature for 3 h and then water quench them to room temperature. In this way, equilibrium between melt and solid phase at the temperature could be attained assuming that the equilibrium phase relation was retained after quenching. Langasite is abbreviated as LGS hereafter.

In addition, the melting and freezing process of LGS crystal was observed by differential thermogravimetric analysis (DTA) at a heating rate of 5 °C/min using Pt pans. In order to calibrate the thermal couple of the DTA equipment, Au (with a melting point of 1063 °C) and Si (with a melting point of 1414 °C) were used as standard samples. Two cycles of heating and cooling were performed on each LGS crystal sample. In the first cycle, crystallization of multiphases could be detected during the cooling process. In the second cycle, the temperature of the eutectic could be measured during the heating process. This indicates the incongruency of LGS.

15.3.3

In-Situ Observation of Crystallization

In-situ observations were performed by preparing a self-made apparatus to confirm the crystallization sequence of the phases obtained from the melt. Pt boats with a length of 15 mm and a width of 2 mm were heated by DC current passed through them. Powder of the calcined samples was charged in the center region of the Pt boats and the whole process of melting and crystallization was observed through a microscope set above the Pt boats. Since the temperature distribution on the Pt

boat exhibited a peak in the center and a gradient down to the two ends, molten samples began to crystallize from one or two ends gradually to the other end or the center until the whole sample was frozen when the current was gradually turned down. Since the process was slow, the composition of the residual melt changed along the liquidus surface according to the crystallized phases and the residual melt was considered to be uniform due to natural convection. The crystallization sequence was determined by analyzing the phases crystallized in different portions in the Pt boats with an electron probe micro analysis (EPMA).

15.3.4 Characterization

The phases presented in the calcined samples were identified by XRD using Cu as a target. The proportion of each phase was estimated by the ratio of the intensities of its diffraction peaks to that of its standard sample. Phases were also determined by scanning electron microscope (SEM) observation and simultaneous EPMA. The crystallization sequence of the phases in the continuously cooled samples was estimated by the appearance of different phases based on the fact that the first crystallized phases are usually relatively large euhedral crystals while phases crystallized thereafter are usually either eutectics or peritectics among them. The crystallization sequence was also confirmed by EPMA measurement on *in-situ* observed samples.

The weight losses of the samples in the calcining, melting and cooling processes were measured to an accuracy of 10^{-5} g. In the calcining process, weight loss was less than 0.01%, thus the influence on the composition was negligible. In the quenching and continuous cooling process, a weight loss less than 1% was observed. This happened in the stage where the samples were in a molten state. Supposing that the weight loss was caused by the evaporation of Ga₂O₃ from the melt, as usually observed in the Czochralski growth of LGS single crystal, the weight loss less than 1% of the total weight could cause an error of Ga₂O₃ concentration less than -0.5 mol% around the stoichiometric LGS composition.

15.3.5 Subsolidus Phase Relations

The phase relations obtained from the XRD patterns of the calcined samples around stoichiometric LGS composition are shown in Fig. 15.5. One or two phases out of LaGaO₃, Ga₂O₃, La₂Si₂O₇ and a ternary compound having apatite structure (including La₁₄Si₉O₃₉) were observed coexisting with LGS depending upon the composition of the samples. La₂SiO₅ was not found at compositions close to that of LGS, thus it will not be discussed hereafter.

The Ga₂O₃-poor portion of the system, where the ternary compound was observed, was of great interest because a Ga₂O₃-poor phase was frequently crystallized in the continuously cooled samples as will be described in Section 15.3.6. Different from the previous report where the solid solubility of La₁₄Si₉O₃₉ was not mentioned

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[13], the apatite structure phase was found to possess a large solid-solution range extending from La₁₄Si₉O₃₉ to the Ga₂O₃ component, suggesting that some of its Si⁴⁺ sites were substituted by Ga³⁺. Thus, the chemical formula of the ternary compound may be expressed as La₁₄Ga_xSi_{9-x}O_{39-x/2} ($0 \le x < 3.5$) and the ternary compound will be referred to as "LS(G)" hereafter. The solubility limit of Ga₂O₃ in LS(G) can be estimated to be a little more than 11 mol% corresponding to $x \approx 3.5$. The compositional limits of LS(G) are indicated by a hatched line in Fig. 15.5. On the other hand, LGS possesses a limited solid-solution range as well due to the random occupation of a tetrahedral site by Si⁴⁺ and Ga³⁺ [14]. Therefore, swarms of Alkemade lines were determined by the identified phases in the calcined samples and were placed for both LS(G) and LGS as shown in Fig. 15.5.

15.3.6

Liquidus Phase Relations

Congruency of LGS was investigated by cooling the molten specimen by various methods. The sample was molten at 1580 °C and held at this temperature for 3 h, then brought to 1450 °C at a cooling rate of 1 °C/min and finally water quenched to room temperature without holding at 1450 °C. Quenching experiments using single crystal of LGS as well as calcined samples of compositions around stoichiometric LGS as starting materials proved that LS(G) crystallizes from the melt before LGS, as shown by \blacktriangle in Fig. 15.6(a). This fact suggests that LGS is an incongruent-melting compound rather than a congruent-melting one, and LS(G) is the primary phase in this case.

By cooling samples with the same starting composition further to $1400 \,^{\circ}C$ and finally water quenching to room temperature without holding at $1400 \,^{\circ}C$, LGS was obtained among the LS(G) grains. Considering that the composition of the melt moves away from LS(G) with the crystallization of LS(G), deposition of LGS



Fig. 15.6 (a) Primary phases crystallized in the cooling process of the melt corresponding to the starting compositions (liquidus phase). (b) Phases coexisting with the melt at equilibrium corresponding to the starting compositions (subliquidus phase). (Reproduced by the permission of Elsevier Ltd.)
suggests that the composition of the melt has moved to the liquidus surface of LGS. Therefore, the liquidus surface of LGS lies in the Ga₂O₃-rich portion towards the composition of stoichiometric LGS. By changing the starting composition of samples, crystallization of phases other than LGS was also observed after the crystallization of LS(G) in the samples denoted in Fig. 15.6(a). LaGaO₃ crystallized after LS(G) for La₂O₃-rich compositions, while La₂Si₂O₇ crystallized after LS(G) for SiO₂-rich compositions.

Another type of quenching experiments was carried out for the above compositions, where samples were quenched from thermal equilibrium state. In detail, samples were first molten at 1580 °C, held for 3 h, cooled down to a temperature between 1350 °C and 1470 °C at the same cooling rate as described above, and held at this temperature for 3 h and finally quenched to room temperature. Crystallized phases were observed coexisting with quenched melt and they are shown in Fig. 15.6(b). For most of the compositions where LS(G) crystallized as primary phase shown in Fig. 15.6(a), LGS crystals were found coexisting with melt while LS(G) grains were not found. This indicates that LGS was equilibrated with melt at these temperatures, while LS(G) was no longer the stable phase.

For other compositions where primary phases were other than LS(G), the obtained phases coexisting with melt were consistent between samples quenched with and without holding, i.e. LaGaO₃ crystallized first in the SiO₂-poor portion, Ga₂O₃ crystallized first in the Ga₂O₃-rich portion, and La₂Si₂O₇ crystallized first in the SiO₂-rich portion.

Two cycles of DTA were performed continuously on a sample taken from an LGS single crystal and the DTA traces are shown in Fig. 15.7. In the heating process of the first cycle, only one endothermic peak was observed at 1500 °C. In the cooling process, a small exothermic peak was observed at 1410 °C before a



Fig. 15.7 DTA traces of two continuous cycles taken on a LGS single crystal. (Reproduced by the permission of Elsevier Ltd.)

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large exothermic peak appeared at 1270 °C, indicating that more than one phase crystallized. Large amounts of LS(G) aciculate were identified by EPMA in the matrix of eutectic texture of LGS, LaGaO₃ and Ga₂O₃. In the heating process of the second cycle performed on the identical sample, two endothermic peaks were observed at 1370 °C and 1450 °C, before a main endothermic peak appeared at 1500 °C. The endothermic peak at 1370 °C indicates the melting of eutectic texture, and the main endothermic at 1500 °C probably represents the peritectic melting of LGS into LS(G) + liquid.

15.3.7 Phase Diagram

All experimental works are combined to give a picture of a primary phase diagram around LGS in air in the ternary system La_2O_3 - Ga_2O_3 - SiO_2 as shown in Fig. 15.8. The liquidus surface of LS(G) was determined to be the field on the Ga_2O_3 -poor side of the boundary curve *ABCD*. The liquidus surface of LS(G) covers the stoichiometric composition of LGS. In this field, crystallization of LS(G) grains was observed in all of the samples that were heated to the temperatures above 1500 °C. The liquidus volume of LGS is denoted by the field *BCEF*. It seems to be a narrow field in composition between the liquidus surfaces of LS(G)



Fig. 15.8 A primary phase diagram of the ternary system La_2O_3 - Ga_2O_3 - SiO_2 around LGS. (Reproduced by the permission of Elsevier Ltd.)

and Ga₂O₃. The temperature range of this field was roughly estimated to be a little more than 100 °C by the holding temperatures at which LGS coexisted with melt. The boundary curve *BC* between the liquidus surfaces of LS(G) and LGS is a reaction curve. The liquidus surface of Ga₂O₃ is denoted by the field on the Ga₂O₃-rich side of the boundary curve *GFEH*, where rectangular Ga₂O₃ crystals were observed to crystallize first in both quenched and continuously cooled samples. The liquidus surface of LaGaO₃ is denoted by the field on the SiO₂-poor side of the boundary curve *ABFG*. The liquidus surface of La₂Si₂O₇ is denoted by the field of the SiO₂-rich side of boundary curve *DCEH*. The system consists of two eutectics *F* and *E*, where the phase assemblages LGS + LaGaO₃ + Ga₂O₃ + liquid and LGS + Ga₂O₃ + La₂Si₂O₇ + liquid were found, respectively.

The crystallization sequence in the ternary system was investigated by continuously cooling the samples to room temperature at a cooling rate of 1° C/min after melting and keeping them at 1580 °C for 3 h. The primary phases were determined by the large euhedral crystals, and the phases crystallized after them could be determined by analyzing the eutectics texture among them. The crystallization sequence provided information about the slopes of boundary curves shown by arrows in Fig. 15.8.

15.4 Study of Equilibrium Phase Diagram Around Langatate [15]

Using a similar procedure, the equilibrium phase around langatate (LTG: $La_3Ta_{0.5}$ Ga_{5.5}O₁₄) and its incongruency has been established.

15.4.1 Solid-Solution Range of Langatate

Samples of over 100 compositions were prepared covering the major portions of the system La₂O₃-Ga₂O₃-Ta₂O₅. They were sintered at 1300–1350 °C. The compositions investigated in the experiment are shown in Fig. 15.9. Tie lines connecting each phase were drawn. We found that three phases, LaGaO₃, LaTaO₄ and Ga₂O₃ could coexist with LTG. Tie lines studied previously are shown by dashed lines in Fig. 15.9 [13]. These lines were presumed on the basis of analogy to the system La₂O₃-Ga₂O₃-Nb₂O₅. A new phase, δ-phase, about the composition 53 mol% La₂O₃, 25.5 mol% Ga₂O₃ and 21.5 mol% Ta₂O₅ (atomic ratio of La:Ga:Ta was about 8:4:3), was found. It has a hexagonal crystal structure with its unit cell parameters a = 3.975 Å and c = 11.082 Å, and it is stable above 1485 °C. About 20 different compositions were selected around the stoichiometric composition of LTG for the investigation of the solid-solution range of LTG. The solid-solution range at 1300–1350 °C was determined with XRD analysis by plotting the compositions of the samples that yielded only single-phase LTG which is demonstrated in Fig. 15.10.



Fig. 15.9 Subsolidus phase relationship in the system La_2O_3 - Ga_2O_3 - Ta_2O_5 in the temperature range from 1300 °C to 1350 °C. Compositions of sintered samples are denoted by \bigcirc . Solid tie lines: Kimura *et al.* [15]; dashed lines: Khodzhabagyan *et al.* [13]. DSC measurement line denoted by line *A*-*B*. (Reproduced by the permission of Elsevier Ltd.)

15.4.2 Distribution of Primary Phase

In-situ observations were performed to study the crystallization sequence from melts with various compositions. These observations were particularly effective in identifying the primary phase precipitating from the melt. After the optical microscopic observation, the sample was quenched and the primary phases were identified by EPMA. The question of whether or not LTG was congruent was investigated by examining the primary phase precipitating from the melt through *in-situ* observation. LaGaO₃ blocks were first precipitated from the melt of a stoichiometric composition of LTG. Then, LTG crystallized as a secondary phase during or after the crystallization of LaGaO₃. This showed that LTG was an incongruent-melting compound, and it had a peritectic relation to LaGaO₃. The possible location of the primary phase volume of LTG should be in contact with that of LaGaO₃, LaTaO₄ and Ga₂O₃ since LTG has a triangular relationship with each of those phases.

Differential scanning calorimetry (DSC) measurements were also performed using Pt pans on sintered samples with compositions ranging from 61 to



Fig. 15.10 Solid-solution range of LTG. (Reproduced by the permission of Elsevier Ltd.)

80 mol% Ga₂O₃ at a constant Ta₂O₅ content along the line A-B in Fig. 15.9 in order to investigate the relationship between melting points, eutectic and peritectic points, and the melt composition. This also helped to determine the location of the primary phase volume of LTG with more precision. Fourteen samples marked along line A-B in Fig. 15.9 were analyzed. The results are shown in Fig. 15.11(a). Most samples had peaks at nearly the same temperature, namely, around 1430 °C and 1440 °C. These peaks represented the transition from $(LTG + Ga_2O_3 + LaTaO_4)$ to $(LTG + Ga_2O_3 + Liq)$ and from $(LTG + Ga_2O_3 + Ca_2O_3 + Ca_2O_3)$ Liq) to (LTG + Liq) or $(Ga_2O_3 + Liq)$, respectively. A strong endothermic peak was observed at about 1500 °C for each of the samples of 61 (= stoichiometric LTG), 63, 64.5 and 65 mol% Ga₂O₃, which possibly corresponded to the transition either from (LTG + Liq) to (LaGaO₃ + LTG + Liq) or from (LaGaO₃ + LTG + Liq) to (LaGaO₃ + Liq) or from (LaGaO₃ + Liq) to Liq. Because these transitions took place so close together, probably within 10 °C, they were difficult to differentiate and only a single peak apparently appeared. The peak temperature decreased toward more Ga2O3-rich compositions until the peak disappeared at 70 mol% Ga₂O₃. The trace of the peaks, shown by the dotted line in Fig. 15.11(a), represented the liquidus surface of LTG, while the peaks in the region $Ga_2O_3 > 71 \text{ mol}\%$ corresponded to Ga_2O_3 melting and their trace reflected the liquidus surface of Ga₂O₃. Because the quantity of Ga₂O₃ in the melt was so small, its endothermic peak was subtle, showing up as a mere deflection in the signal curve. Such small reactions are shown in magnified view in Fig. 15.11(b).







(b) Magnified view of the transition peaks in the boxed region in (a). (c) Phase diagram of the pseudobinary system Ga_2O_3 - La_2O_3 at 5.5 mol% Ta_2O_5 . (Reproduced by the permission of Elsevier Ltd.)

On the basis of the phase transition data obtained by DSC analysis, the pseudobinary phase diagram is drawn (see Fig. 15.11(c)) along the composition A-B in Fig. 15.9 with constant Ta₂O₅ content. On the basis of all these data, the phase relationship between LTG and associated phases has been established; the result is illustrated in Fig. 15.12 as a phase diagram around LTG in the system La₂O₃-Ga₂O₃-Ta₂O₅.



Fig. 15.12 Phase diagram of the system La_2O_3 - Ga_2O_3 - Ta_2O_5 around LTG. (Reproduced by the permission of Elsevier Ltd.)

Although LTG is an incongruent-melting material, it can grow directly from the melt using a LTG seed crystal when the appropriate supercooling is provided. This is probably because the given supercooling is small for the nucleation and growth of the primary phase, LaGaO₃, on the LTG seed while it is large enough for the growth of LTG. This is very similar to the mechanism of direct growth of LGS from the melt, which is also incongruent-melting material. This direct growth will be discussed in Section 15.6. However, the primary phase, LaGaO₃, exists in the melt, which could be a source of defect in LTG. For the fundamental solution to the incongruency problem, we may apply an external electric field to convert the melting state of LGS or LTG from incongruent to congruent. We will see this effect in the next section.

15.5 Conversion of Melting State of Langasite from Incongruent to Congruent [16]

Langasite (LGS) that melts incongruently became congruent melting under an external electric field of 600 V/cm. This conversion was attributed to the inversion of the stability relationship in terms of the molar free energy between the primary phase in equilibrium with liquid and the liquid phase at the composition of LGS. Such a transformation is generally possible when the electrical permittivities of liquid, primary phase and incongruent-melting material increase toward the end component of the primary phase.

15.5.1

Analytical Solution of the Electric Field Required for the Transformation from Incongruent-Melting State of Langasite to Congruent

The chemical potential of the *j*th species in a liquid, η_L^j , and that of a solid, η_S^j , modified by an external electric field can be expressed as:

$$\eta_{\rm L}^{j} = \mu_{0_{\rm L}}^{j} + RT \ln(\gamma_{\rm L}^{j} X_{\rm L}^{j}) + N_{\rm A} z_{\rm L}^{j} e \phi_{\rm L} + \frac{1}{2} \Omega_{\rm L}^{j} \overline{E}_{\rm L}^{2} \frac{\partial \varepsilon_{\rm L}}{\partial X_{\rm L}^{j}}$$
(15.3)

and

$$\eta_{\rm S}^j = \mu_{0_{\rm S}}^j + RT \ln(\gamma_{\rm S}^j X_{\rm S}^j) + N_{\rm A} z_{\rm S}^j e \phi_{\rm S} + \frac{1}{2} \Omega_{\rm S}^j \overline{E}_{\rm S}^2 \frac{\partial \varepsilon_{\rm S}}{\partial X_{\rm S}^j}$$
(15.4)

where, for the *j*th species, μ_{0s}^{j} ($\delta = L \text{ or S}$) is the standard state chemical potential, R is the gas constant, γ^j_δ is the activity coefficient, X^j_δ is the mole fraction of the concentration, N_A is Avogadro's number, z^j_δ is the valence of the ion, φ_δ is a local potential, \overline{E}_{δ} is the strength of the external electric field on the δ -phase, Ω_{λ}^{j} is the molar volume and ε_{δ} is the electrical permittivity of the δ -phase. The second term on the right-hand side (RHS) of Eqs. (15.3) and (15.4) is a mixing energy term, the third is the charge potential and the fourth is the derivative of the electric-field-induced energy with respective to the concentration of the *i*th species. In the derivative of the field-induced energy, the electric field is assumed to be constant, while the electrical permittivity varies with composition. Thus, the chemical potential of each phase is modified by the electric field. Consequently, the equilibrium relationship between the associated phases can change. Whether the chemical potential increases or decreases due to the electric field depends on the sign of the derivative of the electrical permittivity. The sign of the derivative also plays an important role in determining the feasibility of the transformation from incongruency to congruency. This will be discussed later.

The congruent melting state requires that the chemical potential of the *j*th species in liquid and in solid be equal at a certain temperature, *T*. Thus, combining Eqs. (15.3) and (15.4), we obtain Eq. (15.5), which must hold at the interface:

$$\mu_{0_{L}}^{j} + RT\ln(\gamma_{L}^{j}X_{L}^{j}) + N_{A}z_{L}^{j}e\phi_{L} + \frac{1}{2}\Omega_{L}^{j}\overline{E}_{L}^{2}\frac{\partial\varepsilon_{L}}{\partial X_{L}^{j}} = \mu_{0_{S}}^{j} + RT\ln(\gamma_{S}^{j}X_{S}^{j}) + N_{A}z_{S}^{j}e\phi_{S}$$
$$+ \frac{1}{2}\Omega_{S}^{j}\overline{E}_{S}^{2}\frac{\partial\varepsilon_{S}}{\partial X_{S}^{j}}$$
(15.5)

where the equivalence of the concentration of the *j*th species in the solid and liquid is also ensured so that X_S^j/X_L^j be equal to unity. Assuming a planar interface, $z_L^j = z_S^j$, and neglecting the charge density at the interface, the conservation of electron flux holds at the interface:

$$E_{\rm S}/E_{\rm L} = \varepsilon_{\rm L}/\varepsilon_{\rm S} \tag{15.6}$$



Fig. 15.13 *In-situ* observation system with an electric-field generator attached to the microelectric furnace. (Reproduced by the permission of Elsevier Ltd.)

Then, \overline{E}_{S} and \overline{E}_{L} are calculated to meet the above condition:

$$\overline{E}_{L}^{2} = 2 \frac{\left(1 - \frac{T}{T_{0}}\right) \Delta \mu_{0}^{j} - RT \ln \frac{x_{S(0)}^{j}}{x_{L(0)}^{j}}}{\Omega_{L}^{j} p_{L}^{j} - \Omega_{S}^{j} p_{S}^{j} \left(\frac{\varepsilon_{L}}{\varepsilon_{S}}\right)^{2}}$$
(15.7a)

and

$$\overline{E}_{S}^{2} = 2 \frac{\left(1 - \frac{T}{T_{0}}\right) \Delta \mu_{0}^{j} - RT \ln \frac{X_{S(0)}^{j}}{X_{L(0)}^{j}}}{-\Omega_{S}^{j} p_{S}^{j} + \Omega_{L}^{j} p_{L}^{j} \left(\frac{\varepsilon_{S}}{\varepsilon_{L}}\right)^{2}}$$
(15.7b)

where $\Delta \mu_0^j = \mu_{0_s}^j - \mu_{0_L}^j + N_A z_S^j e(\phi_S - \phi_L), p_S^j = \frac{\delta \varepsilon_S}{\delta X_S^j}, p_L^j = \frac{\delta \varepsilon_L}{\delta X_L^j}, X_{S(0)}^j$ and $X_{L(0)}^j$ are the equilibrium concentration of the *j*th species in the solid and liquid at the peritectic temperature, T_0 , respectively.

15.5.2 Experimental Analysis of the Required Field for the Conversion

An *in-situ* observation furnace was assembled (Fig. 15.13), in which sintered source material of varying composition was placed into a sample container and heated above its melting point. The container was made of Pt-Rh (10%), which served as a heater as well. Power was supplied to the container at 500 Hz in order to avoid the migration of the ionic solute by the unidirectional current. This is important for keeping the melt composition homogeneous. Once the source material had melted

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completely and was held at temperature for 10 min, the melt temperature was gradually lowered until the primary phase appeared. The melt was then reheated for complete melting and subsequently cooled until the primary phase precipitated again. This process was repeated three times to confirm the appearance of the primary phase. Once the primary phase appeared and grew to show a euhedral shape, the power was adjusted to maintain its shape and size. Then, the power was varied only slightly, just enough to decrease or increase the equilibrium size. Accordingly, remelting and regrowth occurred in a manner that ensured that the primary phase was completely in equilibrium with the melt. Finally, the sample was quenched and the primary phases were identified by EPMA and XRD.

The distribution of the primary phase was studied in the same manner under an external electric field. The external field was imposed vertically by placing electrodes onto the Al₂O₃ insulating plate parallel to the sample's free surface. Application of the external field horizontally was ineffective since the wall and bottom of the Pt-Rh container diminished the potential difference and led to an equipotential state. The field was generated by the power supply set at a frequency of 500 Hz since the effect of the electric field on the chemical potential is given by \overline{E}^2 as defined in Eq. (15.7) and the directionality of the electric field could be neglected on the macroscopic scale.

The primary phases distributed around the stoichiometric composition in the absence of the electric field are illustrated in Fig. 15.14(a). The primary phase volume for each of the five phases was distributed around the stoichiometric composition of LGS. The five phases are LGS, LS(G), lanthanum silicate (La₂Si₂O₇) abbreviated as LS, lanthanum gallate (LaGaO₃) abbreviated as LG and gallium oxide G. We should note that the stoichiometric composition of LGS lies in the field of LS(G) and is displaced from the field of LGS, which clearly indicates that LGS is an incongruent-melting material. When the electric field exceeded 600 V/cm, the LGS primary phase volume moved considerably, enough to cover the stoichiometric composition of LGS completely (Fig. 15.14(b)), which demonstrated that the incongruent-melting LGS was successfully transformed into a congruent-melting state.

15.6 Direct Growth of Langasite from the Melt [17]

Even though LGS is an incongruent-melting material, it can grow directly from a "pseudocongruent melt" via the Czochralski method using a LGS seed crystal when the appropriate supercooling is provided.

15.6.1

Growth Mechanism of Langasite from an Incongruent Melt

LGS is grown directly from the melt with nearly stoichiometric composition even though it is an incongruent-melting material. Figure 15.15 shows a pseudobinary





Fig. 15.14 Primary-phase volume diagram around the stoichiometric composition of langasite under an external electric field of (a) 0V/cm and (b) 600V/cm. LGS: langasite, LS(G): Ga-bearing lanthanum silicate,



phase diagram in the ternary system La₂O₃-Ga₂O₃-SiO₂ [9] that represents the phase relationship along Ga-bearing lanthanum silicate (LS(G): La₁₄Ga_xSi_{9-x}O_{39-x/2}) – gallium oxide (G) with LGS as an intermediate peritectic compound. When composition 1 is taken as the initial melt composition, the primary phase to precipitate is not LGS, but rather LS(G). When the melt reaches the reaction point, P, with decreasing temperature, LGS starts to crystallize via the peritectic reaction of LS(G) with the melt. However, the Czochralski technique, which uses a LGS seed, enables direct growth from the melt. This type of growth from the incongruent melt is observed in several functional materials, including superconducting, magnetic and thermoelectric conversion materials. In these cases, the large supercooling was attributed to the direct growth from the incongruent-melting phase field, and a semiquantitative analysis was conducted on several superconducting materials [18, 19].

The supercooling, ΔT_{total} , for growth from the melt is the undercooling from the equilibrium thermodynamic melting point. Figure 15.16 is an estimated illustration of the expanded portion of the circled region adjacent to the peritectic reaction point in Fig. 15.15, where the univariant line of LGS coexisting with the melt metastably extends into the primary phase field of LS(G). This is accompanied by the rise of the solid-solution region of LGS. When the temperature of the melt drops to a certain temperature, T_{u} , we define the actual supercooling for LS(G), $\Delta T_{supercool}^{LS(G)}$, as the difference between the corresponding melting temperature, $T^{LS(G)}$, and the temperature of the system, T_{u} , while the actual supercooling for LGS is $\Delta T_{supercool}^{LGS}$, the difference between the melting temperature T^{LGS} and T_{u} . The supercooling, ΔT_{total} , corresponds to the free energy difference, ΔG_{total} , between a liquid and solid at that temperature, which is the driving force for the crystallization process. Here, we introduce the coupling equation that defines the partitioning of the total bulk supercooling into its component parts [20]:

$$\Delta T_{\text{total}} = \Delta T_{\text{T}} + \Delta T_{\text{K}} + \Delta T_{\text{S}} + \Delta T_{\text{D}}$$
(15.8)

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and

$$\Delta G_{\text{total}} = \Delta G_{\text{T}} + \Delta G_{\text{K}} + \Delta G_{\text{S}} + \Delta G_{\text{D}}$$
(15.9)

Equation (15.8) is the coupling equation in terms of the supercooling, while Eq. (15.9) is in terms of free energy. Equations (15.8) and (15.9) are equivalent; $\Delta T_{\rm T}$ and $\Delta G_{\rm T}$ are for the solute transport, $\Delta T_{\rm K}$ and $\Delta G_{\rm K}$ are for the kinetic attachment of the solute to the growth interface, $\Delta T_{\rm S}$ and $\Delta G_{\rm S}$ are for surface creation, and $\Delta T_{\rm D}$ and $\Delta G_{\rm D}$ correspond to defect generation. The magnitude of each component depends on the growth method and changes as crystallization proceeds. Here, we compare each component of the coupling equation between LS(G) and LGS, and discuss the total supercooling degree required for crystallization of these phases.

The crystallization of LS(G) requires a certain ΔG_T for extracting the necessary constituents from the bulk LGS melt to form its own chemical formula, while LGS requires almost no energy for solute transport since there is little difference in composition between the LGS crystal and the LGS melt. As for $\Delta G_{\rm K}$, we assume that there is little difference in the free energy associated with growth kinetics between these two phases. On the other hand, the formation of LS(G) on the LGS seed generates a new surface and results in a lattice mismatch, which leads to defect formation. Thus, $\Delta G_{\rm S}$ and $\Delta G_{\rm D}$ are significant, whereas the corresponding energies for LGS crystallization are expected to be much smaller since the growth of LGS on the LGS seed occurs naturally. The overall comparison is presented in Fig. 15.17. The total free energy needed for the crystallization of LS(G), $\Delta T_{total}^{LS(G)}$, is larger than the actual supercooling in the system for LS(G), $\Delta T_{\text{supercool}}^{\text{LS(G)}}$ (see Fig. 15.16), and thus, it is difficult for LS(G) to crystallize on the LGS seed. On the other hand, the supercooling necessary for the growth of LGS, $\Delta T_{\text{total}}^{\text{LGS}}$, is smaller than the actual supercooling in the system for LGS, $\Delta T_{supercool}^{LGS}$, and thus, it is possible for LGS to crystallize on the LGS seed from the incongruent melt.



Fig. 15.15 Schematic phase diagram of Ga-bearing lanthanum silicate – gallium oxide pseudobinary system. LS(G): Ga-bearing lanthanum silicate, LGS: langasite and G: gallium oxide. (Reproduced by the permission of Elsevier Ltd.)



Fig. 15.16 Schematic illustration of the expanded portion of the region adjacent to the peritectic reaction point in the pseudobinary phase diagram (Fig. 15.15). Dotted line: extension of univariant line of langasite coexisting with melt (metastable). $\Delta T_{supercool}^{LS(G)}$: actual

supercooling for Ga-bearing lanthanum silicate (LS(G)), $\Delta T^{LS(G)}_{supercool}$: actual supercooling for langasite (LGS). (Reproduced by the permission of Elsevier Ltd.)



Fig. 15.17 Comparison of supercooling degree required for growth of Ga-bearing lanthanum silicate (LS(G)) and langasite (LGS). (Reproduced by the permission of Elsevier Ltd.)

15.7

Optimal Composition for the Growth of Langasite via the Czochralski Method [21]

The optimal melt composition for direct growth of LGS from the melt was studied by investigating the solid-solution region of LGS and the compositional shift of crystals as well as residual melt during growth. The optimal composition could be addressed as a pseudocongruent-melting composition.



Fig. 15.18 (a) Solid-solution range of langasite with investigated compositions and the resultant phases. The area indicated by the solid ellipsoidal line represents the solid-solution range of langasite at 1450°C.

(b) Compositional variation during growth. Compositions of initial material (solid symbols), crystals (① upper, ② middle, ③ bottom) and residual melt (open symbols) are on the variation curves.

Around the stoichiometric composition of LGS, about 50 different compositions were selected for the investigation of the solid-solution range. Mixtures of those compositions were sintered at a temperature of 1450 °C. The compositions selected for the investigation of solid-solution range and the resulted phases are shown in Fig. 15.18(a). The solid-solution range of LGS at the temperature of 1450 °C was found to be a narrow area around the stoichiometric composition. The variable span of La₂O₃ component of the solid-solution range is much narrower than that of Ga₂O₃ and SiO₂. Coexisting phases were detected outside this area. In detail, LaGaO₃ was detected in the La₂O₃-rich area, Ga₂O₃ in the Ga₂O₃-rich area and La₂Si₂O₇ in the SiO₂-rich area. One should note that the optimal composition must lie within the boundary of single LGS phase, i.e. the solid-solution region of LGS.

Several compositions in the region of high melting points were selected from which single crystals were grown with an index of melt solidified of about 80%. The compositions of the initial materials, various parts of the crystals along the growth direction and the residual melt were analyzed using X-ray fluorescence spectroscopy (XFS) and the results are shown in Fig. 15.18(b). As can be seen, the compositions of the upper parts (①) of the crystals were located within a circled area surrounded by the initial compositions defined by solid symbols. The compositions of the middles (②) and bottoms (③) of the crystals were located slightly outside the circled area while the compositions of the residual melts were located considerably away from the circled area. This is consistent with the crystallization process from the off-congruent melting composition. Thus, it is believed that the optimal composition (pseudocongruent-melting composition) is located inside the circled area.

The compositional shift of the crystal bottom, especially the residual melt, was large enough to draw the line connecting compositions of the initial material, crystal bottom and residual melt. The compositions of the crystal top, initial material, bottom part and residual melt should lie on these extrapolated lines in this order. These lines generally show the so-called "S-type" curve [22] since each of the three major melt constituents, La₂O₃, Ga₂O₃ and SiO₂, changes their concentration independently. However, the initial melt that is close enough to the optimal composition should vary its melt constituents in the same manner during growth and the ratio among them becomes nearly constant leading to the straight connecting line. We see in Fig. 15.18(b) that the shorter line is straighter than the longer one, which experimentally supported the above discussion. The optimal composition should be found on the extrapolated line from the composition of the crystal top. Thus, the optimal melt should lie in the region existing inside the circled area where four lines would intersect. As a result, a composition of $La_2O_3 = 30.10 \pm 0.05 \text{ mol}\%$, $Ga_2O_3 = 50.60 \pm 0.05 \text{ mol}\%$ and $SiO_2 = 19.3 \pm 0.05$ mol% showed an insignificant shift in compositions of both the crystal and the residual melt, thus it is concluded to be the optimal composition (pseudocongruent-melting composition) for the growth of LGS via the Czochralski method.

15.8 Growth Technology of Four-Inch Langasite Along [0111] [17]

The growth technology of four-inch crystal along $[01\overline{1}1]$, which is the optimal orientation for the wafer fabrication for SAW device use, is optimized by elucidating (i) the importance of preannealing of the melt for acquiring a suitable supercooling for growth, (ii) the transformation of the unstable growth interface, $(01\overline{1}1)$, into a complex of more stable principal planes, and (iii) the necessity of an accurate evaluation method for examining the homogeneity of grown crystals. Steps (i) and (ii) are interrelated.

15.8.1 Fundamental Issues Concerning Growth Along [0111]

Four-inch LGS was grown along $[01\overline{1}1]$ by the conventional Czochralski technique using 8 kHz radio frequency heating [6, 9]. An iridium crucible with 160–170 mm diameter was used. Ga₂O₃, La₂O₃ and SiO₂ powders of 99.99% purity were mixed in the desired proportion, pressed into tablets, and then calcined at 1400 °C for 5 h. The growth atmosphere was Ar with 2 to 3 vol% oxygen. The pulling rate was 0.5 to 3 mm/h, while the crystal rotation rate was 5 to 20 rpm. Both rates were maintained during growth.

15.8.2

Preannealing of the Langasite Melt

The melt was held 20 °C below the melting temperature for 15 h and then quenched up to the seeding temperature since the seeding process should only start after the physical properties of the melt, such as viscosity, surface tension, density and electrical conductivity, become stable [23]. Holding the melt a little below the melting temperature has another advantage for the growth. Oxide melts are generally assumed to consist of clusters with various sizes. The free energy of the melt is predominated by the size and population of the unit cluster, i.e. the smallest cluster with the highest population in the melt. This is based on the cluster-size dependent entropy theory developed by one of the present authors [24]. This theory states that the size of the unit cluster is dominated by the melt temperature: a higher melt temperature leads to a smaller unit cluster size. This, in turn, increases the number of unit clusters per unit volume, which results in higher configurational entropy, i.e. lower free energy of the melt. It should be noted that at high temperatures (e.g., around the melting temperature), the increase in entropy combined with temperature has a much larger effect than the increase in enthalpy. Thus, the free-energy relationship between the melt and solid can be adjusted so as to maintain a supercooling appropriate for growth. For instance, when the melt is held below the melting temperature, the seeding temperature tends to increase and a smaller temperature drop is required for the progress of facet formation [25]. This enables stable facet growth, which minimizes volume-defect formation due to polycrystallization.

15.8.3 Instability of the (0111) Interface

The crystallographic interface plane is $(01\overline{1}1)$, which is unstable and readily splits into more stable planes, such as the $(01\overline{1}0) - Y$ plane and (0001) - Z plane during



Fig. 15.19 (a) Dissolution mode of unstable interface $(01\overline{1}1)$ into the more stable (0001)-Z plane and $(01\overline{1}0)$ -Y plane. (b) The dominant temperature gradient for determining the advance rates of these planes. (Reproduced by the permission of Elsevier Ltd.)



Fig. 15.20 Four-inch langasite grown along [0111]. (Reproduced by the permission of Elsevier Ltd.)

growth (Fig. 15.19(a)). The principle planes ($01\overline{1}0$) and (0001) have specific growth rates, the rate of the latter being much larger. To obtain the optimal interface morphology, one needs to adjust the facet growth rates and local supercooling degrees by the respective temperature gradients in the melt near the interface. The vertical temperature gradient dominates the advance speed of ($01\overline{1}1$), while the horizontal temperature gradient dominates that of (0001) (Fig. 15.19(b)). An improper temperature distribution in the melt and poorly maintained rate balance tend to result in a strongly convex interface toward the melt and bring a strong Z-plane facet on one side and Y-plane facet on the other, which often leads to volume-defect formation. It should be re-emphasized that the correct supercooling degree conducive to the advancement of the planes is obtained by preannealing the melt at the appropriate temperature, as discussed in the previous section. In the light of these discussions, we grew a four-inch LGS crystal along [$01\overline{11}$] (Fig. 15.20).

15.8.4 Evaluation of Crystal Homogeneity

The compositional variation in terms of the Ga/Si ratio in D site greatly affects the uniformity of the grown crystal, which reflects the distribution of SAW velocities [26]. About 600 transversal SAW filters of the 190 MHz central frequency were

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Fig. 15.21 Distribution of SAW velocity on wafers made from (a) the top and (b) bottom portion of the four-inch crystal. The velocity is represented by a gray scale. The average velocity and standard deviation of

wafer (a) were 2375.72 m/s and 108 ppm, respectively, while those for wafer (b) were 2735.94 m/s and 118 ppm, respectively. (Reproduced by the permission of Elsevier Ltd.)

fabricated on a wafer with 200 pairs of aluminum interdigital electrodes. Then the distribution of SAW velocities was measured and the standard deviation was calculated. Figure 15.21 illustrates the SAW velocity distribution on a wafer sliced from the top (Fig. 15.21(a)) and from the bottom (Fig. 15.21(b)) of the grown crystal [17]. The average SAW velocity was 2375.7 and 2375.9 m/s and the standard deviation was 108 and 118 ppm for the top wafer and bottom wafer, respectively, which is good enough for the best SAW filter designed today.

(b)

15.9 Growth of Langasite by the Bridgman Technique [8]

Two-inch LGS single crystals were grown via the vertical Bridgman method assisted by the accelerated crucible rotation technique (ACRT) along [0001] (Z-axis), [211 0] (X-axis) and $[01\overline{1}1]$ (54°-rotated Y-axis) for piezoelectric applications.

15.9.1 **Furnace Setup**

(a)

A vertical Bridgman furnace with three sets of Kanthal Super heating elements was employed. Each heating element operates independently so that the temperature gradient near the melt/crystal interface was varied from 4 to 15 °C/cm by changing the ratio of the power applied to the upper, middle and lower heating element. Figure 15.22(a) schematizes the furnace used, and Fig. 15.22(b) shows the temperature distribution profile. A platinum container having a 2-inch diameter, 0.1–0.2 mm thickness and 200 mm height bore sintered tablets with a specific compositions placed on a 2-inch-diameter cylindrical seed crystal. An ultrahigh-purity



Fig. 15.22 (a) Schematic illustration of the Bridgman furnace. T1 and T2 denote the temperatures at the crucible bottom and crucible wall, respectively. (b) Temperature distribution profile near the melt/solid interface.

The origin corresponds to the seeding point. T1 and T2 denote the temperature at the crucible bottom and crucible wall, respectively. (Reproduced by the permission of Elsevier Ltd.)

alumina or silicon carbide pillar was placed beneath the seed holder to aid the dissipation of the latent heat during solidification. Attached to the furnace was the accelerated crucible rotation technique (ACRT) equipment, which rotates the crucible at 0 to 25 rpm at various acceleration rates. The typical acceleration cycle was: from 0 to +15 rpm in 5 s, stay at 15 rpm for 140 s, accelerate to -15 rpm in 10 s, stay at -15 rpm for 140 s, and finally accelerate to 0 rpm in 5 s. This cycle was repeated during growth.

15.9.2 Crystal Growth

A two-inch-diameter cylindrical seed crystal with a 15–20 mm height was placed at the bottom of a cylindrical platinum tube having a thickness of 0.1 to 0.2 mm, and several source tablets (total weight 600–700 g) were put on the seed. The top end of the platinum tube was sealed. The furnace was heated in air up to about 1500 $^{\circ}$ C at the seeding position so that all the tablets melted entirely, while only the upper portion of the seed crystal was fused. The furnace was kept under this temperature condition for 10 h to obtain a homogeneous melt with stable physical properties.

Crystals were grown by lowering the platinum tube container at a rate of 0.5 to 1 mm/h and the solid/liquid interface was kept at a certain level during growth to maintain a constant thermal environment. The grown crystal was about 50–60 mm long. A comparison of the growth runs with and without ACRT revealed that ACRT was effective in reducing the occurrence of secondary phases.

Growth Along [0001] The temperature gradient at the solid/liquid interface was set to 10° C/cm. The shape of the interface was concave toward the melt. The



Fig. 15.23 Langasite crystal grown via the Bridgman method along [0001]. (a) Langasite boule and (b) a cross section showing the inclusions consisting of lanthanum gallate and gallium oxide. Note that the seed crystal occupied a 20-mm long portion at the bottom. (Reproduced by the permission of Elsevier Ltd.)

shape of the interface was dominated by the lateral temperature distribution, in contrast to growth by the Czochralski method, where the interface plane, (0001), equivalent to the Z-plane, is stable and completely flat. This is presumably because heat was released more easily from the peripheral region than from the core, and thus, the temperature was lower at the periphery. The curved interface was stable and constitutional supercooling was not observed. However, the secondary phases lanthanum gallate (LaGaO₃) and gallium oxide (Ga2O3) formed inclusions aligned parallel to the interface from the beginning of the growth. It should be noted that these secondary phases are different from volume defects. According to the phase diagram of the La₂O₃-Ga₂O₃-SiO₂ system (Fig. 15.8), the initial melt composition close to the LGS stoichiometric composition did not lie in the primary phase field of lanthanum gallate or gallium oxide, but rather, in that of LS(G). However, these inclusions were observed at a very early stage in LGS crystallization, which cannot be explained in terms of the crystallization process on the basis of the phase diagram. These inclusions can be explained by assuming a liquid immiscibility that separated the initial melt into one rich in SiO₂ and one rich in Ga₂O₃, from which lanthanum gallate and gallium oxide precipitated, respectively. The use of ACRT reduced the amount of the inclusions. The immiscibility state was presumably unstable and easily suppressed by stirring the melt. A crystal boule is shown in Fig. 15.23(a), and a cross section showing the inclusions consisting of lanthanum gallate and gallium oxide can be seen in Fig. 15.23(b).

Growth Along [2110] The crystal grown along [2110] yields X-cut wafers that can be used as high-temperature sensors utilizing the piezoelectricity d_{11} . The growth conditions were the same as those for [0001] growth except that, in



Fig. 15.24 Langasite crystal grown via the Bridgman method along [2110]. The external crystal surface has been polished. Note that the seed crystal occupied the bottom 20-mm long section. White materials deposited on the langasite surface edge are terminal transient products. (Reproduced by the permission of Elsevier Ltd.)

the present case, the temperature gradient at the solid/liquid interface was determined to be 15 $^{\circ}$ C/cm. The growth proceeded in the lateral growth mode along [0110]. Growth striations parallel to the (0110)-Y plane were sometimes observed on the (2110) wafer. The growth rate of (0110) is much lower than that of other principal planes, and thus, constitutional supercooling was often observed for (0110) and lanthanum gallate (LaGaO₃) formed featherlike inclusions aligned parallel to (0110). Since the lower growth rate and larger temperature gradient yielded fewer inclusions and the adoption of ACRT also reduced the number of inclusions, defect formation was linked to the constitutional supercooling. For instance, changing the growth rate from 1.0 mm/h to 0.5 mm/h proved effective in reducing the amount of inclusions. A crystal containing few lanthanum gallate inclusions is shown in Fig. 15.24.

Growth Along [0111] The crystal grown along $[01\overline{1}1]$ is used to make substrates for SAW filters since filters fabricated on wafers that are 5.7° oblique to $(01\overline{1}1)$ have a moderately large electrical-mechanical coupling coefficient and a temperature coefficient of nearly zero at frequencies around ambient temperature [1]. The crystal growing along $[01\overline{1}1]$ via the Czochralski method has an unstable interface,

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Fig. 15.25 Langasite crystal grown via the Bridgman method along $[01\overline{1}1]$. (a) Langasite boule and (b) a cross section showing the inclusions consisting of lanthanum gallate (LaGaO₃) aligned parallel to (01\overline{10}). (Reproduced by the permission of Elsevier Ltd.)

(0111), which easily dissolves into the more stable (0001)-Z plane and (0110)-Y plane. It should be noted that the dissolution mode is heavily dependent on the interface shape. A strong convexity toward the melt yields a strong Z-plane facet on the one side and Y-plane facet on the other, which often leads to the formation of polycrystalline volume defects. In contrast to growth by the Czochralski method, the crystal growing via the Bridgman method showed no faceting, but rather, a rounded outer shape (Fig. 15.25(a)). This hindered the formation of polycrystalline volume defects. However, (0111) dissolved into (0001) and (0110), and lanthanum gallate inclusions aligned parallel to (0110) (Fig. 15.25(b)) were observed more often than in the case of growth along [2110].

15.9.3 Crystal Defects

The occurrence of secondary phases can be linked, on the one hand, to precipitation from the Ga-rich melt, which may be attributable to the immiscibility of the initial melt, and on the other, to deposition during the terminal transient. The former involves the appearance of lanthanum gallate and gallium oxide as inclusions even in the early stages of LGS crystallization during [0001] growth, while lanthanum gallate inclusions aligned parallel to $(01\overline{10})$ were observed in $[2\overline{110}]$ and $[01\overline{11}]$ growth. None of these led to cracking. The latter case was the formation of gallium oxide (Ga₂O₃) and lanthanum silicate (La₂Si₂O₇) or lanthanum gallate (LaGaO₃), which often did lead to cracking. An electrical twin was sometimes observed at the boundary parallel to the X-axis. Subgrains and other macrodefects were not observed.

Our X-ray topographic study showed a large distortion in the peripheral region in contact with the platinum crucible. This occurred during the cooling process as a result of the stress due to the difference in thermal expansion coefficient between LGS and platinum. The distortion was large in regions where secondary phases were observed in the case of growth along $[2\overline{11}0]$ and $[01\overline{1}1]$, while it was small in the transparent region where no macro defects were observed.

15.9.4

Optimal Composition Determined by the Differentiation Process during Growth via the Bridgman Method

The Bridgman technique provides an efficient way of determining the appropriate composition for growth since growth consumes almost the entire melt, often yielding terminal transient products other than LGS, which reflects the deviation from the optimal source composition. Here, we chose five initial melt compositions, viz., A (30.0L, 50.0G, 20.0S), B (30.0L, 50.1G, 19.9S), C (30.0L, 50.2G, 19.8S), D (30.0L, 50.3G, 19.7S) and E (30.0L, 50.6G, 19.4S), where L, G and S denote La₂O₃, Ga₂O₃ and SiO₂, respectively. The composition A is stoichiometric. Terminal transient phases other than LGS were obtained when the composition diverged from the optimal. The secondary products formed during the terminal transient were a mixture of gallium oxide (Ga_2O_3) and lanthanum gallium oxide $(LaGaO_3)$ or a mixture of gallium oxide and lanthanum silicate (La₂Si₂O₇). A sample was taken from the white polycrystalline materials that precipitated as residual phases on the LGS crystal edge surface (see Fig. 15.24). A combination of optical microscopy and semiquantitative analysis using X-ray diffraction was employed. The relationship between the composition of the source material and the terminal transient phase is summarized in Table 15.2. Growth from melts with compositions A and B yielded lanthanum silicate and gallium oxide, while composition D yielded gallium oxide and E yielded gallium oxide and lanthanum gallate. Composition C did not yield any terminal secondary phases and is thought to be optimal. This result reflected the position of the initial melt relative to the tie line connecting the LGS solid solution with gallium oxide in the La2O3-Ga2O3-SiO2 system assuming equilibrium and some fractional crystallization, and excluding deposited phases from the system. The terminal transient process is illustrated in Fig. 15.26. It should be noted that for all melts, lanthanum silicate bearing a certain amount of Ga ($La_{14}Ga_xSi_{9-x}O_{39-x/2}$) (denoted as LS(G) in Fig. 15.26), which was the primary phase precipitating from

	Α	В	с	D	E
Lanthanum silicate (La ₂ Si ₂ O ₇)	38	25	0	0	0
Gallium oxide (Ga ₂ O ₃)	12	35	0	35	25
Langasite (La3Ga5SiO14)	60	40	100	65	63
Lanthanum gallate (LaGaO3)	0	0	0	0	12

Table 15.2 Volume Ratio (%) of the Terminal Transient Products Dependent on the Initial Melt Composition.

A(30.0L, 50.0G, 20.0S), B(30.0L, 50.1G, 19.9S), C(30.0L, 50.2G, 19.8S), D(30.0L, 50.3G, 19.7S), E(30.0L, 50.6G, 19.4S)

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Fig. 15.26 (a) Portion of the ternary phase diagram of La_2O_3 -SiO₂-Ga₂O₃ around langasite (Fig. 15.8). Single arrows show the subtraction curve, while double arrows show the reaction curve. (b) Crystallization path of melts with different compositions: A (30.0L, 50.0G, 20.0S), B (30.0L, 50.1G, 19.9S), C (30.0L, 50.2G, 19.8S), D (30.0L, 50.3G, 19.7S) and E (30.0L, 50.6G, 19.4S). LGS represents langasite, while LS(G) represents lanthanum silicate containing a certain amount of Ga. The chemical formulae and

abbreviations denote the primary phase fields. The shaded band represents the equilibrium tie lines between langasite and gallium oxide. For all melts, LS(G) was completely reacted with the melt to form langasite, and the melts did not stay on the reaction curve anymore but moved on the liquidus surface of langasite down to the cotectic line with gallium oxide. Solid circles represent the final positions where the melts were completely consumed. (Reproduced by the permission of Elsevier Ltd.)

the melt, was partially isolated from the melt or completely reacted with the melt to form LGS and extinguished. Thus, the melts no longer stayed on the reaction curve but moved on the liquidus surface of LGS down to the cotectic line with gallium oxide. Then, A and B traced the entire univariant line to the invariant point, where lanthanum silicate joined. E moved to the opposite invariant point, at which lanthanum gallate joined, whereas D used up its melt somewhere on the univariant line before the invariant point. When the optimal melt composition (i.e. C) was selected, it crossed on the surface of the LGS primary phase field tracing the tie line of the LGS solid solution with gallium oxide and stopped before reaching the univariant line.

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Flame-Fusion (Verneuil) Growth of Oxides

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16.1 Introduction

The oldest method of industrial crystal production named after Verneuil [28] is still nowadays applied in about 18 factories with more than 10 000 growth stations [44]. About 600 tons of sapphire, ruby, rutile, spinel and other oxides of total value of approximately \$65 M are produced annually mainly in Switzerland, China, Czech Republic, France, Germany, Japan, Korea, Ukraine, USA, and Russia. The total value of machined parts of Verneuil-grown crystals may reach \$1B. The largest fraction of Verneuil crystals is used in jewelry, and other significant applications are as watch windows and as watch stones, the latter from earliest times. Figure 16.1 shows the application of flame-fusion-grown crystals estimated for 2005. Recently, the application as substrates for GaN-based light-emitting diodes has increased, although one would expect that eventually SiC and GaN substrates will become dominant for high-quality devices based on nitrides.

In the Verneuil process the finely dispersed powder of the starting material is introduced through the vertical torch into a hydrogen–oxygen flame that is directed towards the molten cap layer of the growing crystal. The particles partially melt in the flame and partially in the liquid surface layer. The flame temperature, the powder feed supply and the downward pulling of the growing crystal are adjusted so that the crystallization front and the melt surface remain at the height of the observation window. The scheme of the Verneuil apparatus is shown in Fig. 16.2.

The rate of powder supply is adjusted by the frequency of the hammer, and the flame temperature by the flow rates of hydrogen and oxygen. Figure 16.3 shows the stages of Verneuil growth without applying a seed crystal. First, a sinter cone is formed on a ceramic rod, then a small melt droplet is formed on top of the sinter cone (Fig. 16.3(a)) followed by growth of a narrow neck for nucleation control (Fig. 16.3(b)), then the diameter is increased and the boule grown (Fig. 16.3(c)).

Thus, the flame-fusion process is a crucible-free crystal growth process for high-melting compounds, an economic process that allows control of nucleation and crystal diameter within a relatively simple apparatus, and was a significant breakthrough achieved by Auguste Verneuil around 1900.

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Fig. 16.1 The applications of flame-fusion-grown crystals estimated for 2005.

Nowadays, the practically unchanged technology is so matured that publications on flame-fusion growth have become scarce, and a summary of literature until 1977 has been given by Falckenberg [9]. Nevertheless, one could still expect significant improvements of structural perfection of the crystals and with respect to energy (gas) consumption and thus economics by a thorough process analysis, process simulation, and apparatus optimization. In the following, specific aspects of powder preparation and of apparatus and process control as well as the characteristics of Verneuil-grown crystals will be discussed.

16.2 Historical Background

The early study of the origin of rocks by melting and solidification of lavas and of stones [15, 43] was followed by attempts to synthesize individual minerals, especially of gemstones, in the early 19th century. The first syntheses of ruby rhombohedra of nearly one carat size by melting potassium alum and potassium chromate [13] was widely recognized and soon confirmed by Böttger [4] and by Elsner [7]. However, despite several attempts by mainly French mineralogists, the size of crystals could not be significantly increased, even by using very large melts and crucibles. For example, Frémy and coworkers [11, 12] obtained from a 12-liter batch 24 000 ruby crystals weighing 1200 g, instead of the desired few crystals of larger size [29]. We can now appreciate the experimental difficulties at that time that were responsible for the lack of success: high-purity chemicals were not available, temperature control and programming of the gas-fired glass kilns was poor, phase diagrams and solubility curves were not



Fig. 16.2 Scheme of the Verneuil apparatus: 1) oxygen, 2) hammer mechanism with 3) cam drive, 4) powder container with sieve bottom, 5) funnel, 6) hydrogen supply, 7) torch, 8) muffle kiln with a viewing port, 9) crystal, 10) crystal support with rotation and withdrawal mechanism.

known, and basic principles of nucleation control and of maximum stable growth rate were not sufficiently known. Auguste Verneuil, first as an assistant of Prof. E. Frémy, later as professor of applied chemistry in Paris, had participated in the syntheses of small ruby crystals from flux, and from high-temperature solutions, see Frémy and Verneuil [12] and Frémy [11].

Around 1886 a new type of ruby appeared on the gem market that was first claimed to be natural ruby from a mine near Geneva. However, after a short time it was recognized that this "Geneva ruby" represented "reconstructed ruby", i.e. that natural or synthetic rubies too small to be used as gemstones where united to a multigrain piece by means of a hydrogen–oxygen flame, or that Cr-doped alumina powder was used to be fused together [28, 26]. According to Verneuil [38] the problem of cracking could be reduced if the contact area between the growing crystal and the polycrystalline support was minimized, which led him to develop the flame-fusion growth technology named after him. Some details of this process were described in two sealed documents that Verneuil deposited in December 1891 and December 1892 with the Paris Academy of Sciences and that were opened in 1910, see Verneuil [38]. Great interest started with his publications 1902 and 1904, which included the illustration of the Verneuil apparatus shown in Fig. 16.4.





Fig. 16.3 Stages of Verneuil growth of ruby without seed crystal, schematic: (a) formation of sinter cone and central melt droplet onto alumina rod, (b) growth of the neck for nucleation

control, (c) increase of the diameter without overflow of the molten cap followed by growth of the crystal boule. (Reprinted from H.J. Scheel, **2000**, *J. Cryst. Growth* 211, 1–12.)



Fig. 16.4 The relatively simple apparatus of Verneuil (Reprinted from H.J. Scheel, 1993, *Handbook of Crystal Growth Part A*, (ed.) D.T.J. Hurle, Elsevier, Amsterdam, Chapter 1).

Soon, industrial ruby production started in the Paris laboratory of the L. Heller and Son Company of New York and the company H. Djevahirdjian in Paris. Verneuil also solved the problem of the blue color of sapphire that he found to be due to the combined presence of iron and titanium [38, 42].

The annual ruby production reached 5 million carat in 1907 and 10 million carat ruby and 6 million carat sapphire in 1913. The Heller Company did not transfer the ruby production to the USA because of the high labor costs there. Thus, the Verneuil–Heller laboratory was moved to Annecy in Savoie and continued as Baikowsky S.A. Independently, Hrand Djevahirdjian had been involved in the production of Geneva ruby and from 1903 started ruby production by the Verneuil process. In World War I there was an increasing demand from the French government of hydrogen for balloons so that Djevahirdjian moved to Monthey/Valais in Switzerland where the Swiss company CIBA had excessive hydrogen production. Now, the Djeva company uses independent hydrogen and oxygen production by modern electrolysis and has about 2200 Verneuil furnaces for an annual output of about 120 tons of colorless sapphire and of ruby. Other industries started worldwide, mainly in Germany, Russia, Japan, China, and Korea, whereas in the US the company National Lead in New Jersey started production of rutile and strontium titanate with the help of Art Linz (later MIT) and Leon Merker. Rutile and SrTiO₃ have also been fabricated by the Nakazumi Company [25].

Further historical details can be found in Nassau and Nassau [29] and Nassau and Crowningshield [28].

16.3 Impact of Verneuil's Principles

Auguste Verneuil can be regarded as the father of crystal-growth technology [33] because his process is still applied today, and because his principles of nucleation control by a narrow neck and diameter control in growth from melts are the basis for most other crystal production processes, like Tammann/Stöber, respectively, Bridgman/vertical gradient freeze (VGF), Stockbarger, Kyropoulos, see Fig. 16.5.

Crystal pulling, named after Czochralski, can be regarded as an inverse Verneuil process and ought to be named after Teal and Little who in 1950 developed pulling of germanium crystals [33, 34] whereas Czochralski measured the crystallization velocity by pulling metal fibers and had the crystals for his studies grown by the Bridgman method, not by crystal pulling.

The diameter control in flame-fusion growth requires optimization and continuous adaptation of several growth parameters: Temperature of the hydrogen-oxygen flame and the distance between torch and crystal, reducing or oxidizing flame conditions, powder supply rate, and pulling speed. For optimization of the structural perfection of Verneuil-grown crystals the growth interface should be nearly flat, which requires, as a function of crystal diameter, the proper symmetrical design of the growth chamber, the use of the optimum type of torch to achieve a low (yet economic growth rates) vertical temperature gradient, and the proper ratio of crystal diameter and chamber diameter. The measured temperature profiles under growth conditions assist with this task. By adjustment of these parameters in this multiparameter process the crystals can be grown very economically with minimum use of energy. Verneuil growth experience is valuable for beginners of crystal growth to understand basic crystal growth and to learn to optimize multiparameter processes with the advantage that the process can be optically observed. Especially valuable is the recognition of the time constants when growth parameters are changed.

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Fig. 16.5 Application of Verneuil's principles of nucleation control and increasing crystal diameter in other crystal growth methods. (Reprinted from H.J. Scheel, 2000, J. Cryst. Growth 211, 1-12.)

16.4 Apparatus

From Figs. 16.2 and 16.4 it can be realized that the apparatus for flame-fusion growth can be simple, consisting of powder feed supply, the water-cooled torch with hydrogen and oxygen supplies, the growth chamber consisting of two muffles with a hole for observation, and a pedestal with rotation and pulling mechanism for holding the ceramic rod or the seed crystal. Groups of such simple furnaces with mutual cam drives for the powder supply are used in Verneuil factories. A description of Verneuil equipment has been given by Popov [30].

For crystal-growth laboratories commercial flame-fusion growth equipment had been available from Division 500 of Arthur D. Little (ADL, Cambridge Massachusetts), VEECO (Versailles), and Nakazumi Crystal Corporation (Osaka).



Fig. 16.6 Versatile laboratory apparatus using drill machine stand and 3 tables for powder feed and gas supply, for growth chamber with optical observation system and with afterheater, and crystal withdrawal and rotation mechanisms, partially assembled (H.J. Scheel, unpublished).

A simple and versatile apparatus has been designed by applying a 2-m long drill machine stand with 3 tables that can be coaxially and vertically translated (Scheel, unpublished, see Fig. 16.6).

The upper table holds the powder-feed mechanism and the torch, the center table holds the muffle furnace with optical observation system and SiC afterheater, and the lower table holds the ceramic rod (with seed crystal) and the pulling/rotation mechanism. The powder-feed mechanism is driven by a vibrator, the frequency and amplitude of which can be adjusted. Two torches have given excellent results in growth of sapphire, ruby, rutile (up to 2 cm diameter, 10 cm length), and SrTiO₃ (see below): the tricone burner of Moore [23] and the multitube burner of Lefever and Clarke [21]. Figure 16.7 shows these burners and the modification of the Moore burner used at MIT by Smakula [36] and Linz.

The flame was adjusted by parallel coarse and fine flow meters and by the ratio of central and peripheral oxygen. The growth chamber consisted of concentric alumina-rich tubes into which holes were cut in the side for the optical observation



Fig. 16.7 (a) Tricone burner of Moore (1949), (b) front of modified tricone burner applied at MIT, (c) multitube burner of Lefever and Clarke (1962).

system. The opening was closed by a silica glass window that was provided with an infrared-reflecting coating of sufficient transparency for enlarged self-projection of the growing crystal, by means of a mirror system, onto the transparent projection screen at the front side of the apparatus. The screen had a mm grid so that the diameter and the growth rate could be monitored during the growth process, the growth rate was derived from a vertically moving scale attached to the pulling mechanism. The SiC afterheater allowed reduction of the temperature gradient during growth and programming of the annealing and cooling rate after growth.

16.5 Powder Preparation and Feeding Control

Powders for flame-fusion growth are mostly prepared by purification of the precursors by recrystallization or by distillation, dissolving in water or acid followed by controlled precipitation from the well-stirred solution. For sapphire, alum is used as precursor, and for SrTiO₃ strontium titanyl oxalate is used. The precipitate is then decomposed by an annealing treatment, the temperature and duration of which are optimized to achieve small particle size, typically 1000 to 1150 °C and 2 h. Agglomerates of particles are removed by milling followed by sieving or by improved powder separation as discussed in the following.

The regular supply of powder is the most critical factor in flame-fusion growth. Grain boundaries and gas bubbles (pores) are formed when the particle size or the particle clusters are larger than the thickness of the molten surface layer, or when the powder flow is irregular. This problem has been studied at the Institute of Single Crystals in Kharkov/Ukraine [6]. In the flame, the particles experience an increasing degree of melting that depends on their travel distance, the diameter of the torch nozzle d_n , and on the hydrogen/oxygen ratio. The depth of the dip *a* into the melt of the particles with radius *r* depends on their size and velocity *v* as is shown in Fig. 16.8(a), whereas Fig. 16.8(b) shows the corresponding role of the melt (dynamic) viscosity μ .

The maximum allowed size of the particles r_{max} is given by the thickness of the molten layer δ , and the density ρ and velocity ν of the particles by

 $r_{\max} < B(1 + \delta/B)^{1/2} - 1$ with $B = 9 \,\mu/2\rho\nu$

Therefore, one should firstly apply the lowest economic feeding rate and secondly remove the coarse fractions of the powder that should not reach the crystallization front. Special equipments in laboratory scale and industry scale have been designed for fabrication of Verneuil powder and are shown in Fig. 16.9.

Air separation in the pseudoliquefied layer as shown in Fig. 16.9(a) allows separation of particles with respect to their geometric form and their weight. The particles move in the turbulent gas flow for several hours so that the powder looseness is increased and the specific surface of the particles is reduced. The separation efficiency by air separation is greater than by sieving, as is indicated in Fig. 16.9(b).

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Fig. 16.8 (a), (b) The depth of dip of particles with radius *r* in the melt of different viscosity for different degrees of particle melting in the flame. d_n is the diameter of the nozzle. The particle velocity is $1 - \nu = 5$ m/s, $2 - \nu = 10$ m/s, $3 - \nu = 20$ m/s.

Table 16.1 Purification of powder by air separation.

Impurities (wt.%)	Si	Mg	Ca	Ti	Fe	Cu	SO4
In selected fractions In remainder	2.2×10^{-3} 1.2×10^{-2}	$\begin{array}{c} 2\times10^{-4}\\ 9\times10^{-4} \end{array}$	$\begin{array}{c} 1\times10^{-3}\\ 4\times10^{-3} \end{array}$	$\begin{array}{c} 3\times10^{-4}\\ 4\times10^{-4} \end{array}$	$\begin{array}{c} 1\times10^{-3}\\ 1\times10^{-2} \end{array}$	$\begin{array}{c} 2\times10^{-4}\\ 5\times10^{-4}\end{array}$	0.6 0.85

Simultaneously, a certain purification of the powder from specific impurities by factors between 2 and 10 is observed as indicated in Table 16.1.

The looseness of the powder is an important factor to achieve a steady feeding rate in the growth process. The looseness is determined by the forces between powder particles, namely cohesion, capillary and electromagnetic forces, and by chemical interaction of adsorbed surface films. The looseness is increased by reducing the total forces. For the neutralization of static electricity and of cohesion forces the powder is moistened up to the formation of a monomolecular surface layer. For γ -Al₂O₃ the maximum looseness corresponds to 3–4% humidity, see Fig. 16.10.

The normal feed containers have a horizontal sieve as shown in Figs. 16.11(a) and (b) that, however, have large fluctuations of the powder feeding rate, whereas the vertical sieve arrangement shown in Fig. 16.11(c) reduces the feeding fluctuations. Also, the powder level in the powder container influences the feeding rate and its fluctuations.


Fig. 16.9 (a) Air powder separator: (1) separation chamber, (2) feeder, (3, 4) sensors of density and level of pseudoliquified layer, (5) receiver, (6) compressor, (7) humidification of air, (8) filter, (9) sensor feedback control; (b) Powder-size distribution (1) after passing through a sieve, (b) after air separation (2).

For optimization of the feeding process the weight control of the total powder consumption in relation to the weight of the grown crystal boule is helpful and allows the internal diameter of the growth chamber to be adjusted in relation to the crystal diameter for highest feeding efficiency.



Fig. 16.10 Powder looseness as a function of humidity (1) powder annealed in electric furnace, (2) powder annealed in gas furnace.

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Fig. 16.11 Sieve feeders with hammer drive (a) with horizontal sieve grid, (b) with horizontal unloaded grid, (c) with a vertical grid.



Fig. 16.12 Feeders with automatic optical control of powder feeding rate.

A significant improvement of feeding control has been achieved based on a photodetector on top of the feeding tube, as is shown in Fig. 16.12 [22, 45]. The growing crystal is the intensive light source, and the signal, being inversely proportional to the powder density, is used to control the strokes of the hammer, respectively, the intensity of the vibration system.

The flame-fusion process allows the dopant concentration of the growing crystals to be changed during growth by means of a double-feeder system shown in Fig. 16.13. This allows growth of, for example, ruby laser crystals with sapphire ends for high-power laser crystals with reduced surface damage.



Fig. 16.13 Growth of crystal fractions of different composition by feeder exchange.

16.6 Thermal Conditions

The temperature distribution in the growth chamber has an impact on the possible growth rate and on the structural perfection and shape of the crystal. Several factors determine the thermal conditions in the growth chamber, namely the type of burner, the ratio and the flow rates of hydrogen and oxygen, the diameter and the thermal properties of the chamber walls, and the growing crystal. Also, the viewport will influence the local temperature and even introduce an undesirable asymmetry. The temperature distributions for the simple two-nozzle burner of Verneuil and of the tricone burner are shown in Fig. 16.14, along with the reaction/burning zones and with the temperature homogeneity increasing with the distance from the burner.

A still more efficient mixing is achieved with the multitube burner by which the diffusion – burning zones can be broadened and the temperature gradients in the flame reduced. This is demonstrated in Fig. 16.15. Thus, the distance between the exit of the burner and the crystal surface can be reduced, an advantage with respect to growth-temperature stability and thus crystal uniformity, and with reduced powder consumption.

The effective temperature distribution for a multitube burner under growth conditions for $SrTiO_3$ (see below) has been measured by means of a two-color pyrometer using a porous zirconia ceramic body as shown in Fig. 16.16 [2] and is shown in Fig. 16.17.

Other temperature measurements in the Verneuil process have been reported by Ikornikova and Popova [18] and by Khambatta *et al.* [20].

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Fig. 16.14 Structure of flames with one and with two surfaces of diffusion burning and the temperature distribution (simple burner and tricone burner).



Fig. 16.15 Comparison of multitube burner and tricone burner with respect to crystal position and temperature distribution.

The redox potential for the growing crystal can be adjusted by the gas ratio and by the position of the crystal within the flame, thus the crystals can be grown in oxidizing and in reducing conditions.

The vertical temperature gradient dT/dz in simple muffle chambers is typically 250 to 300 °C/cm. Both the vertical and the radial temperature gradients are reduced by additional heating of the walls of the growth chamber, either electrically or by using the exhaust gas. dT/dz can be reduced to 40 to 50 °C/cm so that the structural perfection and the optical homogeneity can approach the quality of Czochralski-grown crystals. A flat temperature gradient will slightly decrease



Fig. 16.16 Zirconia ceramics, replacing the crystal under growth conditions using a multitube burner, for measurement of the temperature distribution in the flame.

the thickness of the molten surface layer, modify the convex growth interface to become flat or even concave, and will enhance the tendency to facet formation. Popov [30] reported a large thickness of the molten surface of a convex ruby crystal of 1 mm that he determined by removing the liquid, whereas for a flat surface the liquid layer thickness was about 3 to 5 times smaller. Also, Pastor *et al.* (1966) found a thick molten layer on 1 cm diameter ruby of $500 \,\mu\text{m}$, whereas Grabmaier [14] and Adamski et al. [1] measured molten layer thicknesses of about 20 µm only. The thickness of the molten layer depends also on the material as is demonstrated with SrTiO₃ that in the center is 0.4 mm and near the rim 1.4 mm [2]. An initial thermal model has been developed by Khambatta et al. [20] but a real theoretical approach is hampered by the very high growth temperature and the lack of reliable thermophysical data and the difficulty to perform measurements at growth conditions. The flat growth interface yields the highest uniformity of the dopant concentration, as can be seen in Fig. 16.18 in polished crystal sections after annealing. Normally, the Verneuil-grown crystals are annealed to remove excessive strain and to allow machining of the crystals. Thereby, the efficiency of annealing increases nonlinearly when the annealing temperature approaches the melting point. When the annealing temperature is increased from $0.990T_{melt}$ to $0.995T_{melt}$ the residual stresses in ruby and their nonuniformity along the crystal length are reduced by more than a factor of two [19]. Figure 16.18 shows the effects of growth isotherm and of annealing temperature on the optical homogeneity of ruby crystals.

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Fig. 16.17 The measured temperature distribution and the position of two crystals during growth. (Reprinted from J.G. Bednorz and H.J. Scheel, 1977, *J. Cryst. Growth* 41, 5.)



Fig. 16.18 Optical inhomogeneities of ruby crystals as a function of the growth isotherms (concave, flat, convex) and annealing temperature T_a . ξ is the optical resolution power.

16.7 Growth of Compounds with Volatile Constituents

As an example, the Verneuil growth of strontium titanate SrTiO₃ is discussed where at the growth temperature SrO is lost due to evaporation. This compound is of specific interest for crystal growers as it shows the importance of structural defects and of impurities for physical studies. SrTiO₃ has, at room temperature, the ideal cubic perovskite structure that transforms below 105 ± 5 K to the tetragonal structure. The nature of this second-order phase transition, with the rotation angle of TiO₆ octahedra as order parameter, had first been established by Unoki and Sakudo [37] and then by Müller *et al.* [24]. The dynamics of this phase transition depends on the strain fields of impurities [16] and similarly on the strain fields of dislocations and other structural defects. Besides the physics of phase transitions SrTiO₃ has found applications due to its outstanding optical properties (high refractive index of 2.4 and large optical dispersion of 0.1) and as a substrate for epitaxial deposition of the high-temperature superconductor YBa₂Cu₃O_{7-x}.

Most SrTiO₃ crystals have been grown by flame-fusion methods where initially the overflow problem was observed after growth of the initial crystal cone, even when excess SrO was added to the starting powder. This phenomenon is explained by the SrO – TiO_2 phase diagram shown in Fig. 16.19: overflow is expected both for shortage and for excess of SrO.

The exact compensation of the evaporated species (SrO) as a function of the growth rate has to be established in the starting powder, as was shown in the masters thesis of Bednorz [2] who later received together with K.A. Mueller the Nobel Prize for physics for stimulating the discovery of high-temperature superconductivity above liquid-nitrogen temperature. The relation of growth rate



Fig. 16.19 The phase diagram $SrO - TiO_2$ shows low-melting eutectics to both sides of the compound $SrTiO_3$ (from A. Cocco, F. Masazzi, 1963, *Ann. Chim. Rome* 53, 883) explaining the overflow when the SrO evaporation losses are not exactly compensated by the SrO excess in the feeding powder.



Fig. 16.20 X-ray results of the overflowed caps in relation to the SrCO3 excess in the feed powders versus the average growth rate (which is approximately inversely proportional to the SrO evaporation). Large crystals H.J. Scheel, 1977, J. Cryst. Growth, 41, 5). without overflow can only be grown in the

narrow range between SrO excess in the melt(o) and TiO₂ excess (\times). This range without overflow is indicated by the two dashed lines (reprinted from J.G. Bednorz,

and SrO excess, and the narrow range where large crystals can be grown, is shown in Fig. 16.20.

This was confirmed by Nassau [27] who grew SrTiO₃ crystals at 4% excess SrCO₃ and a growth rate of 10 mm h^{-1} .

The Verneuil-grown SrTiO₃ crystals show strong strain birefringence, despite the cubic room-temperature structure, which is explained by the high dislocation density of 10⁶ to 10⁷ cm⁻². Crystals with higher structural perfection have been grown at lower temperature gradients by top-seeded solution growth, TSSG, and from high-temperature solutions but require much longer growth times, as is seen in Table 16.2.

16.8 Conclusions

Flame-fusion growth has the advantages of simple apparatus, a crucible-free process, high growth rates, low cost of ownership of crystal production, higher dopant concentration possible compared to other growth methods, an absence of dopant concentration along the crystal, realization of group growth of crystals at simultaneous control of 45 to 50 apparatus, and the possibility to change dopant concentration during growth by exchange of feed powder. Due to these advantages the practically unchanged Verneuil method is still nowadays applied for industrial crystal production.

	Verneuil	TSSG	Borate flux
Reference	Bednorz and Scheel (1977)	Belruss et al. (1971)	Scheel <i>et al.</i> (1976) Hutton <i>et al.</i> (1981)
T (growth)	1920 °C	1500 °C	1400 - 1100 °C
dT/dz [°C cm ⁻¹]	400 - 800	\sim 50	0.5 – 5
Growth rate [Å s ⁻¹]	5×10^4	8×10^2	80
Duration of growth	1 day	1 week	2 months
Etch pits/cm ²	$10^6 - 10^7$	$10^1 - 10^2$	$0 - 10^2$
Strain birefringence	strong	weak	not detected
Mosaicity [FWHM]	5 - 8'	2 – 3'	${<}1^{\prime}$; 0.16 $-$ 0.38 $^{\prime\prime}$

Table 16.2 Growth conditions and structural perfection of $SrTiO_3$ crystals grown by three different methods [32].

In doped crystals like ruby or blue sapphire the typically observed striations allow natural and synthetic crystals to be distinguished. Disadvantages of flame-fusion growth include high dislocation densities, grain boundaries and strain caused by the large temperature gradients during growth, by fluctuations of the powder feeding rate, by too coarse a powder, and to some extent also by curved solid/liquid interfaces. The structural perfection can be improved by annealing at high temperatures like 0.99 and 0.995 of the melting temperature. However, if quasidislocation-free crystals are required they can be grown at low temperature gradients at the growth interface from high-temperature solutions [8, 31] or by the Kyropoulos method [10]. Many crystals can be grown by different methods. However, for each application and its performance requirements there can be only a *single optimum growth technology* [34] when all aspects like thermodynamics, cost of ownership, timeliness, infrastructure, ecology and energy consumption, etc., are considered.

Education of crystal growth engineers will help in establishing this optimum technology and will reduce the multiyear training required to become a flame-fusion crystal grower.

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Part VI Crystal Growth for Sustaining Energy

17 Saving Energy and Renewable Energy Through Crystal Technology

Hans J. Scheel

17.1 Introduction

After the oil crisis, the Club of Rome [5] predicted in "Dynamics of Growth in a Finite World" a shortage of fossil energy resources and a severe energy crisis including armed conflicts for the end of the last century. It is realized now that this report was too pessimistic, but it contributed to start or enforce the "green" political initiatives and parties mainly in central European countries and in Japan. This green political influence, while being partially understandable, developed as a burden for the industries and therefore enhanced economic slowdown and recession. With respect to energy the green public and political influence caused a widespread concern about nuclear fission energy and nuclear waste so that in several countries the efficient fast-breeder reactors and even the conventional nuclear reactors were stopped or will be stopped in the foreseeable future. This is not understandable, neither from a technical nor from a safety point of view. Studies of the risks (deaths and health) of the energy sources have shown that nuclear fission energy is much safer with respect to mortality and health, by at least an order of magnitude, than oil and coal. There is a propagandistic overemphasis of the terrible accident of Chernobyl, whereas the daily accidents in connection with coal and oil mining, oil transport and utilization, and with gas explosions as well as the negative health effects of polluted air are ignored.

The combined effect of the limited resources of fossil energy and the political demand to reduce nuclear fission energy in certain countries will lead to a serious energy crisis in the next 30 years if there is not a timely and sufficient development of alternative and renewable energy sources in combination with energy saving and a revival of nuclear energy. This should compensate for the increasing worldwide demand of electricity of annually 2.6% as shown in Fig. 17.1, due to the growth of population and due to the increasing standard of living in large parts of the world, notably in the former communist states, in China, India, Africa, South America, and other developing countries.

The energy problem is interconnected with the *climate problem*, with global warming, which has become clear and internationally recognized especially after

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Fig. 17.1 The future world energy consumption, due to population growth and increasing standard of living, will show an annual increase of 2.6% and thus will double by the year 2040.

the report of the UN Intergovernmental Panel on Climate Change (IPCC) which published the first part of their conclusions (of a total of 4 parts) on February 2, 2007 in Paris.

The production of carbon dioxide by burning the fossil energy sources coal, oil and gas has to be reduced (or CO2 has to be absorbed) in order to prevent an increase of catastrophic effects of the climate change such as the rising sea level and extreme weather situations like hurricanes, flooding, and droughts. The International Disasters Database shows a significant increase of hydrometeorological disasters since 1986 (see CRED website [3]). The regional differences of CO2 emission per person are shown in Fig. 17.2. They clearly depend on the development stage of the area, on the transport characteristics of people and material, and whether electricity is produced from fossil primary energy sources. These aspects should be seriously considered in North America and Australia, for example, the USA could contribute by reducing electricity production of presently 70% from fossil resources, by increasing the gasoline price, and by introducing a CO₂ tax. However, one would expect an increased CO2 production with future development of China, India and other less-developed countries along with the increasing standard of living of more than 4 billion people. The proposals of the Kyoto Protocol for reduction of the CO2 generation demand a worldwide faster reduction of the share of fossil energy than the reduction forced by the limited resources lasting 40 to 60 years only. The coal reserves will last longer, but coal for producing electric energy should only be increased if the higher CO₂ output can be absorbed by storage in deep ground or deep sea, or by new technological processes, since the natural absorption of CO₂ by photosynthesis of trees and plants in general does not suffice. In any case, oil reserves should be kept as high-value base material to service the chemical and plastic industries for future generations.



Fig. 17.2 Regional differences of the annual CO_2 production per person are very large. The less-developed countries have to increase CO_2 output parallel with their development, whereas USA and Australia should reduce CO_2 production.

According to the World Energy Outlook [15] of the IEA there are 1.6 billion people, of which more than 80% are in rural areas, without electricity. This problem could be solved by bio-energy or by photovoltaic solar energy (and corresponding investments) as discussed below.

In the following, the developments of the conventional energy sources and possibilities to save electrical energy by high-power, high-temperature electronics and by new illumination sources will be discussed along with the decisive role of crystal technology. High-temperature superconductivity (HTS) could have an enormous effect on energy transport, on energy storage, and on energy saving if the crystal/epilayer/materials problems for development of the required devices, cables and coils could be mastered. Then, the renewable energy sources will be treated where also crystal technology, including epitaxy technology, is the crucial factor for progress. Finally, the need for publicity, education, and funding for the multidisciplinary and complex field of crystal technology will be discussed.

17.2

Storage, Transport and Saving of Energy

The conventional forms of energy like coal, oil, and gas are high-density and condensed forms of energy, so that *storage* of fossil energy is not a major problem. However, the renewable wind energy and solar energy generate electric energy only at specific times for limited periods, and these periods do not, in general, coincide with the peak energy-consumption times. Thus, economic storage of electrical energy becomes a problem since conventional lead-based batteries and also novel batteries require too high an investment, besides their large weight and space requirements. In many countries the geographic structure allows excess electricity to be stored in water pump systems with reservoirs, which has to be further exploited. The energy storage by means of very high energy storage systems (up to 5 GWh) based on supercapacitors, superconducting magnetic energy storage (SMES), and using large flywheels on superconducting friction-free bearings are too expensive for most applications. Energy storage based on superconductors has to await the material development of the necessary HTS-magnet systems, especially the development of thin reliable HTS wires and coils, so that economic cooling by liquid nitrogen can be applied instead of expensive and complex helium cooling. Another possibility of energy storage is hydrogen, using first the hydrogen contained in natural gas and later the electric energy from the renewable energy sources directly for electrolysis, or efficient in-situ electrolytic solar cells or other hydrogen-producing technologies, for instance in high-temperature nuclear reactors of the fourth generation, are developed. However, other forms of energy storage should also be found, investigated and developed.

The *transport* of the high-density energy carriers like oil and gas is not problematic as long as the pipelines are not interrupted due to natural events or due to human interference (sabotage, fire, politics, war). The conventional transport of electricity is done with power lines and high-voltage alternating current (AC). This has relatively large losses that could be significantly reduced by changing to high-voltage direct-current (DC) power transmission. This will become economic when efficient AC–DC and DC–AC converters, fault-current limiters, and transformers are developed, for instance based on improved high-power devices with GaN and SiC and on high-temperature superconductivity discussed in the following.

After the initial rise of the highest superconducting temperature from 23 K to 30 K [2] and the discovery of *high-temperature superconductivity* (HTS) at 92 K, i.e. above the boiling point of liquid nitrogen and above the classical BCS theory, by Wu *et al.* [16], there was hope that HTS could have a large impact on storage, transport and especially on saving of energy. Unfortunately, the complex chemical and structural nature of the HTS compounds and their limited thermodynamic stability were not appropriately considered in the physics-dominated research, even reproducibility of solid-state physical experiments was in general not achieved in the hectic ten years following the promising HTS discovery so that the development of HTS theory was also hampered.

The lack of reproducibility in HTS solid-state physics is explained firstly by the fact that the processes of HTS crystal, epilayer and ceramic fabrication are not reproducible due to the complex HTS compounds and the numerous preparation parameters, and secondly because *sufficient characterization* of the samples was never done. (Sufficient characterization is the analysis of all those chemical and structural features of the sample that have an influence on the specific physical measurement, Scheel [7].) Thus, the contributions of HTS to the energy problem have to wait for a serious materials, crystal growth and epitaxy effort to master these delicate HTS compounds.

There are many forms of saving energy: everybody can contribute by improving the efficiency in using electric appliances, thermal insulation of buildings, in heating and air-conditioning and the application of heat pumps, in personal and material transport, etc. Here, we will show with a few examples how crystal technology can contribute to energy saving. After solving the growth and doping problems of GaN by the Akasaki group [1] and after the development of industrial GaN-based light-emitting diodes (LEDs) in 1993 by Nakamura of Nishia company [6] the incandescent and fluorescent lamps of typical 15 and 50% efficiency will be replaced by high-efficiency colored LEDs for traffic lights and successively by white LEDs for general illumination. Figure 17.3 compares the brightness and the lifetimes of incandescent lamps, fluorescent and the new energy-saving lamps with the very promising values of the LEDs. The latter undoubtedly will become the dominating light source when their efficiencies and lifetimes are further improved and their fabrication costs reduced by crystal technology. Worldwide, these new illumination sources will lead to energy savings corresponding to > \$10¹² per year. Just the replacement of the green, yellow and red traffic lights by LEDs of LPE- and MOCVD-grown compound semiconductors will allow worldwide energy savings of about \$1.3 billion and reduce annual greenhouse gas production by about 400 million tons. High-power, high-temperature electronics based on either GaN or SiC also allows tremendous savings of energy of more than \$10¹². In these latter cases the crystal technology is the main progress-determining factor.

17.3 World Energy Consumption and Conventional Energy Sources

The consumption of energy will increase dramatically during this century as is shown in Fig. 17.1. The main causes for this increase are the growing world population and the increasing standard of living in most of the Asian, African and South-American countries. In Fig. 17.4 are schematically shown the trends of conventional energy sources and the quite optimistic increase of renewable energy until the year 2050, a scenario proposed by Shell in 2001. In this diagram the relative absolute values for the year 2050 have been derived by multiplying the 2050 percentages of the original Shell scenario by a factor 2.5 corresponding to the increased energy consumption from Fig. 17.1. If the excessive use of *fossil*





Fig. 17.3 The energy efficiency of lighting is shown and indicates that an enormous amount of energy can be saved by light-emitting diodes that at the same time have very long lifetimes. Even further improvements and cost reductions of LEDs are expected due to crystal technology, as is indicated by the arrows.

energy (thermal power stations, large cars, etc.) continues, there will be a more rapid reduction of this form of energy as a consequence of the limited oil resources.

Hydraulic energy will increase slightly, but of course has an inherent natural limit except for hydraulic storage of excess energy by means of pumping stations and water reservoirs. Also, sea waves and tide energy may be developed at certain coastal sites.

Nuclear fission energy could, in principle, be increased in all industrialized countries if there were not the green political efforts to even stop the nuclear energy due to misled concerns about safety and about storage of nuclear waste, the latter being not a technical but a purely political problem. Furthermore, there is no technological base for the concerns about nuclear energy, so that the important energy problem should not be left to politicians. Instead, it should be left to technocrats and energy managers. Furthermore, it is necessary to increase the fast-breeder technology and the high-temperature reactors, following the recommendations of the "Generation IV International Forum (GIF)" and the proper safety measures, since these reactors of the fourth generation have a significantly higher overall



Fig. 17.4 From the scenario of SHELL (2001), the relative contributions to the total energy in the years 2004 (1x %) and 2050 (2.5x %) are shown taking into account the 2.5-fold energy consumption in the nuclear fusion is developed.

year 2050, as shown in Fig. 17.1. The steep increase of renewable energy seems unrealistic and probably has to be replaced by steeply increased nuclear fission energy until

efficiency than conventional water-moderated reactors, use less resources, produce much less radioactive waste, and present a reduced proliferation risk of isotopes for nuclear bombs. Furthermore, the ultrahigh temperature reactor allows the production of hydrogen that is needed for the fuel-cell-driven cars allowing personal transport without CO₂ production.

From this discussion it follows that, unless nuclear power is drastically increased, mankind will face a severe energy crisis in this century. An example is demonstrated with Switzerland where around 2020 two nuclear power stations are planned to be switched off as demonstrated in Fig. 17.5. In view of the increasing consumption of electricity there will arise a problem of which the solution is not in sight. Switzerland missed the chance of a timely replacement of the nuclear power stations because of the political pressure of opponents of nuclear fission





Fig. 17.5 The energy scenario for Switzerland that will have a problem when around the year 2020 two nuclear power stations are planned to be switched off.

energy and the malinformed public. Not only in Switzerland but worldwide it seems doubtful, if not impossible, that energy-saving efforts in combination with novel energy sources will be developed fast enough to fill the energy gap and to prevent armed conflicts for the last resources that started in 2003 with the Iraq war.

17.4 Future Energy Sources

The optimistic development of the major new energy sources is shown in Fig. 17.4. Presently, there is great interest in *wind energy*, which could become economic in areas with sufficient frequent wind if the oil price were to be increased, and if efficient electricity storage could be developed. Various forms of energy from

biomass are in development and will contribute to the share of renewable energy, but at present a large impact is not in sight due to the surface-area requirement and the competition with food production for the growing world population. However, in rural areas local biogas production, gas motors and electricity generators will increasingly provide heating, air-conditioning and electric power.

Geothermal energy looks quite straightforward and could be developed in numerous areas where the rock structure and the temperature profile are suitable, especially near volcanic regions. However, a pilot project near Bale, Switzerland caused earthquakes of magnitude 3.4, so that people became afraid, with the consequence that the project was temporarily interrupted. Hopefully, ways to prevent earthquakes can be found or the project shifted to less-populated areas so that this promising quasipermanent source of energy can be exploited. In geologically favorable areas 10 to 30% of electricity demand could be provided by economic geothermal energy.

Solar thermal energy is widely used in countries of sufficient sunshine for heating water, for air-conditioning, and for evaporating water for drying and for salt production.

Photovoltaic solar cells are in development using a large variety of materials and of technologies, but a real breakthrough has not yet been achieved, see Surek [14]. Single-crystalline and polycrystalline silicon have the major share with about 87%, leading to a temporary shortage of economic solar-grade silicon, and the remaining fraction consists of compound semiconductors. According to a 1998 estimate by the German Fraunhofer Institute for Solar Energy Systems, solar PV power will reach the 1% level of total electric energy, at 30% annual growth, only in the year 2040.

The company Spectrolab in California and several research laboratories have reported efficiencies of over 40%, and theoretically over 45% could be achieved at maximum utilization of the full wavelength spectrum of solar radiation by means of multilayer/tandem structures of compound semiconductors and concentration of solar light by mirrors or lenses by factors of 100 to 1000. As a consequence of this concentration approach only very small PV cells are required so that their price is not so critical.

The minimum required efficiency for solar cells, to become economic for energy generation, depends on the oil price and should be at least 20%. In Fig. 17.6 the efficiencies of various research solar cells at the beginning of their life are shown: amorphous silicon has, at the beginning of its life, less than 10% and is decreasing with time, and crystallinity and crystalline perfection of silicon increases the efficiency to single-crystalline silicon, which marginally passes the 20% level. In view of the generally observed degradation there is the question whether Si-based solar cells will be used in large-scale power stations for generation of electricity not only for the low efficiency but also for the area requirement. Low-cost Si PV cells will be widely used for architecture (roofs, etc.) and for economic reasons in remote villages and homes, in combination with batteries, especially in less-developed countries, for instance to provide electricity to the 1.3 billion people in rural areas.

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Fig. 17.6 Efficiencies of silicon-based research solar cells (blue) reach 23%, whereas efficiencies of >36% can be achieved in III-V compound tandem cells with concentrators. Only for solar-cell modules with >20% efficiency can one hope for economic large-scale electricity production.

The urgent development of mass-production technology for highest-efficiency PV cells and the optimized concentration methods are needed in order to increase the share of solar energy in total energy consumption. For a specific photovoltaic cell structure there can be only one optimum or a combination of two optimum epitaxial technologies for economical and ecological mass production, as discussed by Scheel [12]. Thus, the progress in solar-electric energy depends clearly on advances in industrial crystal, epilayer and multilayer fabrication and again in economic energy storage.

Nuclear fusion energy is the great hope for the future, and tremendous efforts were and are being spent to demonstrate and to achieve breakeven for this type of energy, especially for the magnetic inclusion of the high-temperature plasma



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Fig. 17.7 The principle of laser-fusion energy is shown where the laser crystal is pumped by laser-diode arrays and where the frequency of the infrared radiation from the high-power laser crystal is multiplied by

passing through the nonlinear optical crystal. The essential role of crystal technology for the high-power laser crystals, for the radiation-resistant nonlinear-optical crystals, and for the laser-diode arrays is indicated.

(TOKAMAK). However, this has to await the solution of the most severe material problem, to find long-lasting materials for the first and second wall around the plasma. Only this will allow energy generation by the TOKAMAK technology. The alternative is laser fusion that was demonstrated with glass lasers and large nonlinear-optic (NLO) crystals, so far KDP, for frequency multiplication, to achieve high-power UV pulses. The principle of future laser fusion is shown in Fig. 17.7. For continuous laser-fusion energy the development of highest-power laser crystals, with reduced thermal and surface degradation problems, of economic high-power laser diode arrays for pumping the lasers, and of improved large NLO crystals of excellent radiation hardness is required: These are solvable yet difficult problems for crystal-growth technology, for instance with special garnet- or apatite-type laser crystals and with CLBO or other NLO borate crystals.

17.5 Costs and Risks of Conventional and of Future Energy Sources

The utilization of the various forms of energy should be based on technological and economic factors taking into account ecological and environmental considerations. The estimated electricity production costs for the conventional and the new energy sources are shown in Fig. 17.8. Ideally, the role of politics ought to be limited to ensure low risks for workers in the energy field and for the population, to establish





Fig. 17.8 The cost of electricity from renewable energy is still higher than present electricity cost so that significant technological improvements including crystal technology for the new energy sources are required. Also, the CO_2 /climate and the energy-storage problems and the risks for the energy sources are indicated.

rules for the environment and the climate control, and to support the start-up of future energy sources in order to prevent a crisis due to energy shortage. The risk of nuclear power is, in general, overestimated as follows from the discussion of Shepherd and Shepherd [13]. Nuclear power is needed and has to be increased as discussed above, so that it would be quite harmful if it were to be reduced or even stopped. In the period 1976 to 1984 several studies on the risks of energy sources from Canadian and Swiss institutions were published, see Scheel [11]. A more recent study of energy-related accidents was done by Hirschberg *et al.* [4] and their mortality data, normalized to 1000 Megawatt electricity per year, is shown in Fig. 17.9. Coal and oil have by far the largest risk from exploration through transport to utilization, which is only rarely mentioned in the mass media. In contrast, hydraulic, fossil gas and nuclear power are connected with comparably small risks. Therefore, it is necessary to inform politicians and the general population about these statistical analyses of ministries and of insurance companies, and perhaps to initiate new unbiased risk studies.



* Data from "Severe accidents in the energy sector" 1st Ed., S. Hirschberg, G. Spiekermann and R. Dones, PSI Bericht Nr. 98-16, ISSN 1019-0643, Nov. 1998.

Fig. 17.9 The risks of the various energy sources expressed as number of annual casualties per GWh electricity are shown [4].

17.6 Crystal Technology and its Role for Energy

The various contributions of crystal-growth technology, CT, to the energy problem discussed above are summarized in Table 17.1. For energy-saving lighting the development of highest efficiency LEDs based on GaN and its solid solutions with AlN and InN is hampered by the nonavailability of GaN and solid-solution substrates. These would allow the preparation of epilayers and multilayers with reduced structural defects due to the very low misfit and very similar thermal expansion coefficients. Depending on the required layer structures even epitaxial growth near thermodynamic equilibrium by liquid phase epitaxy (LPE) could be considered, which would yield extremely flat surfaces and interfaces and very low dislocation densities (Scheel [10] Chapter 28, Scheel [12] Chapters 1 and 7). Similarly, epitaxial layers of improved structural perfection could increase the performance of power devices based on SiC and GaN where the harmful pipe defects, which lead to electrical breakthrough, can be overgrown by LPE.

Material problems in general and crystal-technology problems in specific areas will have to be solved if economic energy storage and energy transport are to be achieved. The role and problems of high-temperature superconductors have been

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 Table 17.1 Problems of crystal and epitaxy technology and of material technology for sustainable energy (Examples).

Energy saving

- White light-emitting diodes (GaN solid solutions) for general illumination/ interior architecture and for traffic lights.
- High-power devices (GaN, SiC transistors, thyristors, etc.) for energy technology.
- High-temperature superconductors HTS for electric energy transport.
- HTS for motors, generators, current limiters, transformers, MHD ships, etc.

Energy storage

- Material for economic high-power batteries.
- Material for high-density hydrogen storage.
- HTS for flywheel or superconducting magnetic energy storage (SMES) of electrical energy.

Renewable energy sources

- Mass production of highest-efficiency (> 36%) photovoltaic solar cell modules for various concentrator principles (lenses, mirrors, etc.) for power plants and for roofs/architecture.
- High-efficiency silicon and CIGS solar cell modules (~20%) on low-cost substrates for localized energy consumption (roofs, architecture in general).
- Photovoltaic solar cells for direct hydrogen production by electrolysis.
- Efficient thermophotovoltaic devices, thermoelectric devices.
- Corrosion-resistant metal-cooling system for fast-breeder fission reactors.
- Novel high-power laser crystals and radiation-resistant nonlinear-optic crystals for laser-fusion energy (and for future ultraintegrated microelectronic/UV-lithography).
- Economic laser-diode arrays of long lifetime for pumping the laser for laser-fusion energy.
- Materials for the first and second walls in TOKAMAK nuclear fusion technology.

discussed above, and further the material problems for high-power batteries and for hydrogen storage need to be mentioned.

It is not widely recognized that crystal technology is a major factor for progress in renewable photovoltaic energy and especially in the future hope of nuclear fusion energy. A variety of materials and of preparation methods are applied for industrial production of photovoltaic solar cells, whereas in principle there can be only *one optimum material* (or material combination) and only *one optimum fabrication technology* for a specific application of solar cells if all factors like thermodynamics, economics, energy and resources consumption, ecology are considered [10].

A serious contribution of CT is more easily demanded than fulfilled because there is no education for this field, which is multidisciplinary and complex [8, 9, 11], and most crystal growers are specialized with respect to technology and material thus limiting crossfertilization. Education in the technology of crystal and epilayer fabrication is urgently required: most companies would hire engineers and scientists of this area if they were available: The estimate is more than 400 specialists per year. The first difficulty is the multidisciplinary nature of CT: Chemistry and chemical engineering, materials science and engineering, thermodynamics, mechanics including hydrodynamics, applied crystallography, solid-state physics and surface physics, statistical mechanics, and electrical engineering. This requires the study of the basics of most of these disciplines followed by a 2-year specialized course in crystal technology in combination with experimental work and industry visits and practice. The second difficulty is the structure of the universities with their specialized departments and the difficulty to introduce a novel multidisciplinary course.

Education of crystal-growth scientists and engineers would not only allow them to derive the *single optimum technology* for the production of a specific crystal or epilayer, but it would also lead to enormous savings of R&D and production expenses, to accelerated developments in the energy problem, and it would save energy!

17.7 Future Technologies for Mankind

The technological and scientific developments in the past 150 years and especially the electronic/communications revolution in the past 50 years are presenting mankind with a modern world that requires novel approaches to education, to communication, to work, and that also raises sociological, economic and environmental changes and problems. The advances in medicine prolong average life, so that the resulting growth of world population will lead to limited supplies of food and of energy. The main technologies contributing to the future of mankind are biotechnology for food and health, and crystal technology for saving energy and renewable energy and contribution to the CO_2 /climate problem, see Fig. 17.10. Advances in the fashionable nanotechnology including microelectronics and optoelectronics are desirable and are also interesting research areas, but do not have the crucial impact and urgency of the food, health, energy and climate problems. In conclusion one may state that the technology of crystal and epilayer fabrication has been somewhat neglected in all aspects, with education, funding, and recognition. This has to change soon in view of the crucial importance of CT for energy, for the future of mankind.

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Fig. 17.10 The relative importance of the technologies for the future of mankind are schematically shown, the large arrow indicating the increasing importance from bottom to top.

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Part VII Crystal Machining

18

Crystal Sawing Technology

Hans J. Möller

18.1 Introduction

Multiwire sawing is the main slicing technique for large multi- and monocrystalline silicon crystals in the photovoltaic and microelectronic industry [1]. While in recent years the cost of solar-cell processing and module fabrication has been reduced considerably, the sawing costs remain high, about 30% of the wafer production [2]. The incentive to improve the sawing technique for further cost reduction in mass production is thus high. The sawing process depends on several variable parameters, which makes it difficult to optimize the process in view of throughput, material losses, reduction of supply materials and wafer-surface quality. Basic knowledge about the microscopic details of the sawing process is required in order to slice crystals in a controlled way. In the following the principles of the sawing process will be described as far as they are understood today.

18.2 Multiwire Wafering Technique

The principle of the multiwire technology is depicted in Fig. 18.1. A single wire is fed from a supply spool through a pulley and tension control unit to the wire guides that are grooved with a constant pitch. Multiple strands of a wire net are formed by winding the wire on the wire guides through the 500–700 parallel grooves. A take-up spool collects the used wire. The wire is pulled by the torque exerted by the main drive and slave. The tension on the wire is maintained by a feedback control unit. The silicon crystal on the holder is pushed against the moving wire web and sliced into hundreds of wafers at the same time. Solar cell wafers are mainly cut by a wire that is moving in one direction, which allows higher wire speeds between 5 to 15 m s^{-1} but yields less planar surfaces. Smoother and more even surfaces are obtained by oscillating sawing. Depending on the pulling speed the wires have a length between 150-500 km in order to cut a single column in one run. Currently, solar-cell wafers are cut with a thickness between 200 and $300 \,\mu\text{m}$, but a thickness

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Fig. 18.1 Schematic diagram depicting the principle of the multiwire sawing technique. The crystal is pushed against the wire web with a constant feeding rate, which is equal to the material-removal rate. The force on the wire determines the wire bow. The wire speed is maintained constant.

down to about $100\,\mu m$ can be achieved by the technique. The wafer sizes vary between 15×15 to $20\times20\,cm^2$ with a trend towards larger wafers.

Cutting is achieved by an abrasive slurry that is supplied through nozzles over the wire web and carried by the wire into the sawing channel. The slurry consists of a suspension of hard lapping particles. Today SiC is the most commonly used abrasive. This material is very expensive and accounts for 25-35% of the total slicing cost. The volume fraction of solid SiC particles can vary between 30-60% and the mean grain size between $5-30\,\mu$ m. The main purpose of the slurry is to transport the abrasive particles into the sawing channels and to the crystal surface. Most of the commercial slurries are based on ethylene glycol or to a lesser extent on oil. The entry of the slurry is a result of the interaction between the wire and the highly viscous slurry. Normally only a small amount of slurry enters the cutting zone. The factors that are important here are the viscosity and the wire speed, but to understand the fluid dynamic problems that are involved a complex physical modeling is required. The first attempts of a description have been reported recently [3–8].

Material is continuously removed through the interaction of the SiC particles below the moving wire and the silicon surface. The abrasive action of the SiC depends on many factors such as the wire speed, the force between the wire and the crystal, the solid fraction of SiC in the suspension, the viscosity of the suspension, the size distribution and the shape of the SiC particles. The viscosity of the slurry depends on the temperature and the solid fraction of particles and changes because of the continuous abrasion of silicon and iron from the wire. This gradually deteriorates the abrasive action and the slurry finally has to be replaced. The kerfloss is determined by the diameter of the wire, the size distribution of the SiC particles and the transverse vibrations of the wire [9]. Typical diameters of the steel wires are around $140-180 \,\mu$ m. This yields kerf losses around $200-250 \,\mu$ m per wafer.

The objective of efficient sawing is to slice with a high throughput, a minimum loss of slurry and silicon, and a high quality of the resulting wafers. Since many parameters can be changed the optimization of sawing is a difficult task and today is mainly done by the wafer manufacturers. They are mostly guided by experience. In the following the main results of investigations are summarized, which describe the current understanding of the microscopic details of the wire sawing and to some extent of lapping processes in general.

18.3 Basic Sawing Mechanism

Figure 18.2 shows schematically the situation in the sawing channel. The space between wire and crystal surface is filled with slurry and abrasive particles. The crystal is pushed against the wire web and causes a bow of the wire. The bow angle varies typically between $1-5^{\circ}$. The resulting force on the wire varies along the contact area. The forces are maximum directly below the wire and decrease towards the side faces (Fig. 18.3). Because of the observed transverse vibrations of the wire additional forces may be exerted sideward. The cutting process at the side faces is important because it determines the final surface quality of the sliced wafers.

The microscopic material-removal process can be explained by the interaction of loose, rolling SiC particles that are randomly indented into the crystal surface until small silicon pieces are chipped away. Since SiC particles are facetted and contain sharp edges and tips, they can exert very high local pressures on the surface. This "rolling–indenting grain" model forms the physical basis of the wire-sawing process. Similar surface structures also occur after lapping surfaces of brittle materials with loose abrasive particles [10, 11, 17]. A review of material removal mechanisms can be found in Refs. [12, 13].

The individual process of the interaction of a single particle with sharp edges and the surface of a brittle material has been studied by microindentation experiments



Fig. 18.2 Schematic diagram of wire, slurry with abrasive, and crystal in the cutting zone. Under external force the wire bows and exerts forces on the particles and the slurry.





Fig. 18.3 Cross section of wire, slurry with abrasive, and crystal in the cutting zone.

[14]. The main results are summarized schematically in Fig. 18.4 for a "sharp" indenter with a pyramid geometry. Loading by sharp indenters first leads to the generation of a remnant plastic impression in the surface known as the elastic–plastic zone. With increasing pressure the material begins to break and so-called median and/or radial cracks are generated parallel to the load axis emanating from the plastic zone. Upon unloading residual stresses from the elastic–plastic zone can lead to lateral cracks parallel to the surface. When these lateral cracks reach the surface, material is chipped away. This is the main process for material removal during sawing. When material is removed by chipping the median and radial cracks remain. This crack system is part of the saw damage that has to be removed for further processing of the wafers. By combining the rolling–indenting process of free abrasive grains with the fracture mechanics of brittle materials a quantitative description of the material-removal process can be derived.

18.3.1 Material Removal Rate

The material volume V_0 that can be removed by lateral cracks below the indentation of a single grain (Fig. 18.4) depends on the applied normal force F_N according to [6]:

$$V_{\rm o} \approx F_{\rm N}^{(4n+1)/2}$$
 (18.1)



Fig. 18.4 Indentation of a single particle into the surface. Under the action of the shear and normal forces a plastic zone and cracks are formed. The extension of the lateral cracks and the depth of the plastic zone determine approximately the chipped volume.

Experimentally, an exponent n = 0.85 has been determined for silicon, which gives $V_o \approx F_N^{2.2}$. The sawing rate or velocity v_s , which is the thickness of a removed layer per unit time, can be calculated from the number of indentation events *m* per contact area A_{tot} and time Δt multiplied by the volume of material V_o that is removed in a single event

$$\nu_{\rm s} = \frac{mV_{\rm o}}{A_{\rm tot}\Delta t} \tag{18.2}$$

If a rolling grain makes one indentation per cycle one can calculate the time interval for a single indentation event from the angular velocity of the rotation. For a laminar flow of the slurry the mean angular frequency $f = 1/\Delta t$ can be determined from the linear velocity profile between crystal surface and moving wire and is given by $f = \nu/2 h_0$ where ν is the wire velocity and h_0 the distance between wire and surface. Combining the equations yields for the sawing rate the fundamental relationship, which forms the basis for the following theoretical description

$$\nu_{\rm s} = \nu_{\rm so} \nu m F_{\rm N}^{(4n+1)/2} \tag{18.3}$$

where the prefactor v_{so} summarizes material and geometry parameters. The remaining problem that has to be solved is to determine the number *m* of indenting grains in the slurry and the normal force F_N acting upon each grain. Both factors can only be average values that have to be determined from the global stochastic behavior of many particles in the slurry under the external sawing conditions such as wire velocity *v*, wire load F_{tot} , particle-size distribution or slurry viscosity. These conditions will be analyzed in the following.

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18.3.2

Elastohydrodynamic Behavior of Slurry and Wire

The global behavior of the abrasive particles is controlled by the hydrodynamic conditions in the slurry film between the ingot surface and the wire. The slurry transports the abrasive particles into the cutting zone and determines the distance between the wire and the crystal surface. Depending on the film thickness between the wire and the surface, some of the particles are either in direct contact with both the wire and the surface (semicontact case) or all of the particles are floating freely (noncontact case). In the first case the force on the grains in contact is exerted by the wire directly, whereas in the second case the force is supplied by the shear stress or other factors in the moving slurry. It is also evident that if the slurry film thickness is much lower compared to the average size of the abrasive grains, fewer particles would enter the cutting zone, thus leading to very low sawing rates and the risk of wire rupture due to dry friction.

It is therefore necessary to determine the slurry film thickness under the various sawing conditions. The hydrodynamic behavior of slurry films has been studied in lubrication or polishing processes, where many fundamental aspects have been derived from experimental and theoretical results [15, 16]. An important aspect is that the wire, and to some extent the crystal, can deform elastically in response to the slurry pressure. Considering that the wires are thin and long it is very likely that mainly the elastic response of the wire has to be considered when the slurry transport is analyzed. In the following the main aspects of the problem are derived from a one-dimensional treatment of the hydrodynamic slurry transport below a flexible wire.

The space between the wire and the crystal surface is filled with slurry, which is transported into the sawing channel by the moving wire. The starting point to describe the slurry flow is the Reynolds equation. In the one-dimensional case under steady flow conditions one has

$$\frac{\partial}{\partial x} \left(\frac{h^3}{\eta} \frac{\partial p}{\partial x} \right) = 6\nu \frac{\partial h}{\partial x} \tag{18.4}$$

where *x* is the coordinate along the wire, h(x) the distance between wire and crystal surface, *v* the wire velocity, η the slurry viscosity, and p(x) the hydrodynamic slurry pressure (Fig. 18.5). Integration of the equation yields

$$\frac{\partial p}{\partial x} = 6\nu\eta \frac{h - h_{\rm o}}{h^3} \tag{18.5}$$

where h_0 is the integration constant from the condition that the derivative of p is zero for $h = h_0$. The hydrodynamic pressure in the slurry exerts forces on the wire, which will then deform elastically. As for a pulled string the bow of the wire or the local curvature determines the resulting backward force T_n normal to the wire. The (negative) curvature is given by the second derivative of the vertical displacement y(x)

$$y'' = -\frac{1}{T} \frac{\partial T_n}{\partial x}$$
(18.6)



Fig. 18.5 Schematic diagram of the wire bow y(x) and the crystal surface $y_0(x)$ along the cutting zone from x = -a to a. The position of the wire is fixed at the ends at $x = \pm d$ by the spools. It is assumed that the crystal surface has a circular shape, whereas the wire shape is determined by the pressure in the slurry film in the space between.

where T is the tensile force along the wire. The pressure below the wire, which causes the curvature, can be expressed together with Eq. (18.6) by

$$p = \frac{1}{\pi R_{\text{eff}}} \frac{\partial T_{\text{n}}}{\partial x} = -\frac{T}{\pi R_{\text{eff}}} \gamma''$$
(18.7)

Considering the cross section of the sawing channel (Fig. 18.3) the pressure below a wire of radius *R* changes from a maximum value directly below the wire towards the side faces where the pressure must be zero at the free surfaces of the fluid bed. In the one-dimensional treatment here this is taken into account by an effective radius $R_{\text{eff}} = \alpha R$. α has to be determined from a three-dimensional treatment of the problem but is assumed to be <1.

If slurry flows between the wire and the crystal and a hydrodynamic pressure builds up due to the flow conditions, the wire will be pushed up and assumes such a shape that the local forces exerted by the hydrodynamic pressure and the normal force components T_n of the bent wire are balanced locally.

The material-removal process depends on the local forces, therefore the removal rate will vary along the crystal surface correspondingly. In a steady state situation, however, cutting of the wire through the crystal occurs at a constant rate along the wire length. This is only possible if the wire and the crystal surface adopt a shape such that the normal force is constant everywhere and material removal occurs at the same rate. The crystal surface will thus adjust to the wire shape depending on the flow conditions and the applied force on the wire. Investigations of the shape of the surface during cutting have shown that it is slightly curved and deviates only very little from a circular shape along the cutting length. Therefore we assume in the following that under flow conditions the crystal surface assumes a constant curvature γ''_{0} with radius r_{0} . The distance *h* between crystal surface described by $\gamma_{0}(x)$ and wire $\gamma(x)$, which is the width of the slurry transport channel, is given then by

$$h(x) = y(x) - y_0(x)$$
(18.8)
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Combining Eqs. (18.6)–(18.8) one obtains with the cutting length $l_0 = 2a$

$$p = -\frac{T}{\pi R_{\rm eff}} \left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 \gamma_{\rm o}}{\partial x^2} \right) = p_{\rm o} - \frac{T}{\pi R_{\rm eff}} \frac{\partial^2 h}{\partial x^2}$$
(18.9a)

$$p_{\rm o} = -\frac{T}{\pi R_{\rm eff}} \frac{\partial^2 \gamma_{\rm o}}{\partial x^2} = \frac{T_{\rm n}^{\rm o}}{\pi l_{\rm o} R_{\rm eff}}$$
(18.9b)

where the surface curvature γ''_{o} has been expressed by a constant pressure p_{o} and a constant normal force T_{n}^{o} . In equilibrium between wire and slurry the pressures in Eqs. (18.5) and (18.9) have to be equal. Since γ''_{o} is assumed constant here the third derivative is zero and one obtains by inserting

$$\frac{\partial^3 h}{\partial x^3} + \frac{6\pi\nu\eta R_{\rm eff}}{T} \frac{h - h_{\rm o}}{h^3} = 0$$
(18.10)

In order to solve the differential equation one needs appropriate boundary conditions. From Eq. (18.9) together with Eqs. (18.6) and (18.7) one derives

$$\frac{\partial^2 h}{\partial x^2} = -\frac{\pi R_{\text{eff}}}{T} (p - p_{\text{o}})$$
(18.11)

The hydrodynamic pressure at the exit of the sawing channel must be zero, thus p(a) = 0. This yields the first boundary condition

$$\frac{\partial^2 h}{\partial x^2}(a) = \frac{\pi R_{\rm eff}}{T} p_{\rm o} \tag{18.12}$$

The pressure $p(-a) = p_a$ at the entry is determined by the build-up of slurry, which is carried by the wire to the cutting zone. The entry pressure p_a has been estimated approximately by [4]

$$p_a \approx \frac{\rho v^2}{3} \tag{18.13}$$

where ρ is the density of the slurry and ν the wire velocity. The second boundary condition can be written then

$$\frac{\partial^2 h}{\partial x^2}(-a) = -\frac{\pi R_{\text{eff}}}{T}(p_a - p_o)$$
(18.14)

A third condition can be obtained from geometrical considerations. Since the position of the wire is fixed at the spools, located at a distance $x = \pm d$ from the center of the wire, the film thickness *h* at $x = \pm a$ can be related to the slopes of the wire at the same positions by (Fig. 18.5)

$$h(a) = -(d - a)\gamma'(a))$$
(18.15)

Approximating the wire bow by a circular segment y(x) the slope at x = a can be derived from Eq. (18.7). One obtains the film thickness h(a) at the exit

$$h(a) = (d-a)\frac{T_{\rm n}^{\rm o}}{2T} = \frac{\pi l_{\rm o} R_{\rm eff} (d-a)}{2T} p_{\rm o}$$
(18.16)

If the surface curvature y''_{o} is determined by the mean slurry pressure $p_{o} = \overline{p}_{S}$ (Eq. (18.9b)) it can be calculated from the applied external force $F_{tot} = T_{n}^{o}$ on the wire.

The numerical solution of Eq. (18.10) requires a starting value for h_o . The simulation results show that for typical values of the input parameters the distance h varies only little, therefore one can approximately use $h_o \approx h(a)$ as a starting value for the iterative process. From the solution h(x) one can calculate p(x) using Eq. (18.9) and then determine h_o and $p_o = \overline{p}_S$. These values are fed into the equations again until convergence of the results is obtained.

18.3.3 Numerical Results

The differential equation (18.10) together with the boundary conditions (Eqs. (18.12), (18.14) and (18.16)) has been solved numerically with the following parameters: cutting length $l_0 = 10$ cm, spool distance 2d = 30 cm, effective wire radius $R_{\rm eff} = 10 \,\mu\text{m}$, wire speed $\nu = 10 \,\text{m s}^{-1}$, viscosity $\eta = 100 \,\text{cP}$, wire tension $T = 50 \,\text{N}$, vertical wire force $T_n^0 = 1$ N, and an entry pressure $p_a = 0.0127 \,\text{MPa}$. These values correspond to parameters that are used in typical wire-sawing experiments. Figure 18.6 shows the variation of the slurry film thickness along the wire position *x*. Apart from the entry and exit region the thickness remains almost constant.

The actual shape of the wire is calculated from equation $y(x) = y_0(x) + h(x)$ and shown in Fig. 18.7. The comparison with the shape of the crystal surface, given by $y_0(x)$, indicates that the wire bow is almost parallel to the crystal surface. The mean film thickness is almost equal to h_0 and is about 40 µm in this case. The slight deviations from this value given by h(x) determine however the hydrodynamic pressure p(x), which carries the wire. The corresponding pressure distribution is shown in Fig. 18.8. The results show an almost constant pressure over most of the wire length. A maximum occurs in the exit region before the pressure drops to zero at the exit (x = a). The pressure in the entry region increases from $p = p_a$ to the mean value of about 0.31 MPa. One can see from the calculation that only



Fig. 18.6 Numerical calculation of the slurry film thickness h(x) along the wire length. The parameters are given in the text.



Fig. 18.7 Calculated wire shape and crystal surface, which is separated by the slurry film of thickness h(x). On this scale the small variations in the distance h(x) cannot be resolved. The crystal surface in this calculation has the shape of a circular segment with a radius of 500 cm for the parameters given in the text.



Fig. 18.8 Calculated hydrodynamic pressure p(x) in the slurry film along the wire length. The parameters used in the numerical calculation are given in the text.

slight changes of the film thickness and the curvature of the wire are necessary to balance the pressure changes in the slurry.

The calculation also shows that the film thickness of about 40 μ m is in the same range as the largest particles in conventional SiC particle distributions used for industrial wire-sawing processes. Therefore, one can assume that over the entire length of the wire some of the abrasive particles are in direct contact with the wire and the ingot. This result is important in view of the forces that are exerted on the particles and the modeling of the sawing process.

18.3.4 Particle-Surface Interaction

In a slurry that contains free-floating particles the total force F_{tot} of the bent wire is balanced both by the slurry pressure and those particles that are in direct contact

between wire and crystal surface. If we assume a uniform pressure \overline{p} the total wire force is given by $F_{\text{tot}} = \overline{p}A_{\text{tot}}$, where A_{tot} is the total contact area below the wire. A_{tot} $= A_{\text{P}} + A_{\text{S}}$ is the sum of the particle contact area A_{P} and the wire area A_{S} in contact with the slurry, thus $F_{\text{tot}} = \overline{p}(A_{\text{P}} + A_{\text{S}}) = F_{\text{tot}}^{\text{p}} + F_{\text{tot}}^{\text{s}}$. Both terms depend on the film thickness h_{o} , which on average will be assumed in the following to be uniform over the entire wire length. The slight variations due to the pressure variations in the slurry discussed in the previous section are neglected here. Therefore, depending on which term dominates, either the slurry or the particles carry the main load. Furthermore, A_{P} can be expressed by $A_{\text{P}} = m A_{\text{N}}$, where A_{N} is the average contact area between a single particle and the wire, and *m* the number of particles in direct contact. Introducing the average force on a single particle $F_{\text{N}} = \overline{p}A_{\text{N}}$ one obtains for the average total force $F_{\text{tot}}^{\text{p}}$ on all particles

$$F_{\rm tot}^{\rm p} = mF_{\rm N} = F_{\rm tot} - F_{\rm tot}^{\rm s}$$
(18.17)

The basic assumption in the wire-sawing model is that only the force F_{tot}^p determines the material-removal process. Using Eq. (18.17) one can eliminate *m* in Eq. (18.3) and yields the sawing rate v_s for the semicontact case

$$\nu_{\rm s} = \nu_{\rm so} \nu F_{\rm tot}^{\rm p} F_{\rm N}^{(4n-1)/2} \tag{18.18}$$

Both F_N and F_{tot}^p depend on the applied total force F_{tot} . Since F_{tot} can be measured directly this quantity is important from the experimental point of view. In the following their dependences on F_{tot} will be derived.

The average force F_N on each particle and the number of particles *m* in contact can be calculated from the grain-size distribution. For commercial SiC, particle sizes can be described rather well by a Gaussian distribution (Fig. 18.9). Assuming again a uniform distance h_o , all grains with a size $l > h_o$ are in direct contact. If a force is applied on the wire the distance h_o decreases and more grains come into contact with the surface. These grains are indented both into the wire and the crystal, but in the following the indentation in the wire is neglected. The total force F_{tot}^p exerted on the particles, which are actually indented into the crystal surface, and their number *m*, can be derived from the particle-size distribution *g*(*l*) by the relation

$$F_{\rm tot}^{\rm p} = \int_{h_{\rm o}}^{\infty} F(l - h_{\rm o})g(l) \,\mathrm{d}l \tag{18.19}$$

 $F(l - h_o)$ is the individual force on each particle in contact and *m* is equal to the integral over the shaded area in Fig. 18.9. The force *F* increases with the indentation depth $l - h_o$ for a particle with size $l > h_o$. The force law depends on the elastic and plastic behavior of the particle and the crystal surface. For Vickers indentations in brittle materials one obtains $F \approx (l - h_o)^2$ but other force laws can be derived as well depending on the shape of the indented grains.

Calculating Eq. (18.19) with a Gaussian size distribution for g(l) one obtains in agreement with Eq. (18.17) the following approximation

$$F_{\rm tot}^{\rm p} = mF_{\rm N} \tag{18.20}$$



Fig. 18.9 Schematic particle-size distribution g(l). In the semicontact case grains with a diameter $l > h_o$ are in contact both with wire and workpiece surface. The total number of grains *m* in contact is proportional to the shaded area.



Fig. 18.10 Average normal force $F_{\rm N} = F_{\rm tot}^{\rm p}/m$ on a single particle as a function of the wire–crystal distance $h_{\rm o}$ for different edge curvature radii of the indenting particles.

where F_N is the average normal force on each particle in contact. The important result is, however, that when the film thickness decreases, F_N remains almost constant and only the number *m* of indented particles increases (see Fig. 18.10).

According to Eq. (18.17) the total force on the particles $F_{\text{tot}}^{\text{p}} = F_{\text{tot}} - F_{\text{tot}}^{\text{p}}$ is equal to the total external force F_{tot} on the wire reduced by the force, which arises from the slurry pressure p(x). In the case that $F_{\text{tot}}^{\text{s}}$ is small compared to F_{tot} the particles carry the main load and one obtains $F_{\text{tot}}^{\text{s}}$ directly. With the experimentally determined value n = 0.85 the sawing rate is given then by $v_{\text{s}} \approx v F_{\text{tot}} F_{\text{N}}^{1.2}$. The removal rate is mainly proportional to v and F_{tot} in this case since F_{N} is almost constant.

In general, the slurry pressure and thus F_{tot}^s cannot be neglected. In order to calculate $F_{tot}^p(F_{tot})$ we start from the assumption that the wire maintains a uniform distance h_o from the crystal surface. The dependence of $F_{tot}^s(h_o)$ on the distance h_o has been discussed above. The dependence of $F_{tot}^s(h_o)$ can be calculated approximately from the equations in Section 18.3.2. For simplicity, the slurry pressure



Fig. 18.11 Calculated force $F_{tot}^s(h_o)$ on the wire arising from the hydrodynamic pressure as a function of the distance h_o between wire and crystal surface for different slurry viscosities. The parameters are the same as given in Section 18.3.3.



Fig. 18.12 Calculated particle force $F_{tot}^{p}(h_{o})$ and slurry force $F_{tot}^{s}(h_{o})$ as a function of the distance h_{o} between the wire and the crystal surface. The parameters are the same as given in Section 18.3.3. The total applied force F_{tot} is the sum of both terms.

variation has been approximated here by $p(x) \approx a^2 - x^2$ using the parameters given in Section 18.3.3. The results are shown in Fig. 18.11 for different slurry viscosities. The results both for $F_{tot}^{p}(h_{o})$ and $F_{tot}^{s}(h_{o})$ are depicted in Fig. 18.12.

For a given slurry film thickness the total applied force is the sum of both terms $F_{\text{tot}}(h_o) = F_{\text{tot}}^{s}(h_o) + F_{\text{tot}}^{p}(h_o)$ according to Eq. (18.17). Depending on the distance, either the particles or the slurry carries the main load of the wire. It is assumed that the best sawing conditions occur in the region where both curves intersect, since this allows both high material-removal rates due to particle contact and good particle transport in the slurry.

According to $F_{tot}(h_o) = F_{tot}^s(h_o) + F_{tot}^p(h_o)$ an applied force F_{tot} determines the distance h_o . Therefore one can express the particle force $F_{tot}^p(F_{tot})$ as a function of





Fig. 18.13 Calculated total particle force $F_{tot}^{p}(F_{tot})$ as a function of the total force F_{tot} on the wire. The parameters are the same as given in Section 18.3.3.

the total force F_{tot} by eliminating the thickness h_0 . The result is shown in Fig. 18.13 for different slurry viscosities.

The particle force $F_{tot}^{p}(F_{tot})$ increases linearly with the applied wire force F_{tot} above a certain threshold value, which depends on the slurry viscosity. Slurries with higher viscosities require higher forces to apply force on the particles and lead to lower sawing rates. This is due to the larger wire distance, when the slurry has a higher viscosity. In the linear regimes the particle force can be approximated by $F_{tot}^{p} = f(\eta)F_{tot}$, where the proportionality factor $f(\eta)$ summarizes the dependence on the slurry viscosity η . Equation (18.18) can be written then

$$v_{\rm s} = v_{\rm so} v F_{\rm tot} f(\eta) F_{\rm N}^{(4n-1)/2}$$
(18.21)

The sawing rate remains proportional to F_{tot} . Below certain threshold values, which depend on the viscosity, the sawing rates are reduced considerably. In the next section the main dependencies will be compared with experimental results.

18.4 Experimental Results

18.4.1 Wire Sawing

An industrial multiwire saw equipped with force sensors has been used for the measurements. Oil slurry and SiC powders were commercial products. Figure 18.14(a) shows the sawing rate as a function of the applied total force on the wire for different wire velocities. In both cases the sawing rate is proportional to the load. One can also observe that the material removal starts above a certain threshold value of about 0.1 N. This can be explained with the minimum load on the abrasive particle that is required for the chipping mechanism to operate.



Fig. 18.14 Measurement of the sawing rate on an industrial multiwire saw as a function of the wire load (a) for two different wire velocities and on the wire velocity (b). The material removal starts above a certain threshold value of about 0.1 N.

Figure 18.14(b) shows the dependence on the wire velocity. In the typical velocity regime of industrial multiwire saws between $5-15 \text{ m s}^{-1}$ a linear dependence is observed. For velocities below 2 m s^{-1} the dependence becomes nonlinear and the slope decreases. We assume that this is outside the range of parameters where the described model is applicable. The proportionality to the total force and the velocity is in agreement with the predictions of Eq. (18.21) at least for higher speeds. The result also implies that the effective force $F_{\text{tot}}^{\text{P}}$ is equal or at least proportional to the total force F_{tot} in agreement with the model.

18.4.2 Lapping Between Rotating Discs

A similar abrasive process compared to wire sawing is lapping between rotating discs. The principle is shown in Fig. 18.15. The space between the rotating plate and the rotating crystal is filled with slurry and free-floating abrasive particles. The difference between disc lapping and wire sawing lies in the hydrodynamic behavior of the slurry. Because of the different geometries of the machines the flow pattern

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Fig. 18.15 Schematic diagram of the disc lapping process. The space between the rotating plate and the rotating crystal is filled with slurry and free-floating abrasive particles. The crystal is pushed downwards in the experimental setup.

and thus the hydrodynamic pressure distribution is different. In addition, the elastic response of the lapping plate and the crystal also differ from that of the wire. But the hydrodynamic pressure also exerts a counter force on the grinding plate and the crystal. If it is large enough it will reduce F_{tot} and lead to an effective force F_{tot}^{p} .

Particles with a diameter *l* greater than the slurry film thickness h_o are in contact both with the crystal and the workpiece surface. Their number *m* can be calculated in the same way as before from Eq. (18.19). Therefore, one obtains the same equation (Eq. (18.21)) for the material-removal rate. However, the number of particles that are in direct contact, the effective total force F_{tot}^p and thus the material-removal rate will be different from the wire-sawing case.

In the experimental setup for the lapping experiments a small commercial lapping machine has been used for the measurements [17]. The crystal is pushed downwards with constant force. The slurry velocity varies across the contact area below the crystal, but the average velocities were comparable to the wire velocities of industrial saws. Different slurries and commercial SiC powders were used. After a certain time, the removed material was determined both from weight and length measurements. In all cases the removal rates were proportional to the applied load and the averaged slurry velocity. Figure 18.16 shows the removal rate as a function of the applied total force for different slurries. It shows the proportionality to the load but also a dependence on the slurry that is used. It turns out that the removal rate for water is about three times higher than for the oil slurry. The main difference between the slurries is their viscosity, which is $\eta = 0.08$ cP for water and about 150 cP for oil. According to the previous calculations the hydrodynamic pressure in oil is higher then. This leads to a higher counter force and reduces the sawing rate according to Eq. (18.21).

18.5 Summary

The "rolling–indenting" model of free-floating particles in the slurry forms the basis of the wire-sawing process. Combined with the fracture-mechanical processes of individual particles indenting into the crystal surface one can derive a



Fig. 18.16 Lapping measurements of the removal rate of silicon as a function of the total applied force for oil and water slurries. The rotation velocity corresponds to an average slurry velocity of about 5 m s⁻¹.

quantitative description of the material-removal rate. An important result is that only the largest grains of the particle-size distribution contribute to the sawing process, about twice as large as the average size. How many of the grains interact depends on the distance between the wire and the crystal surface. The distance is determined by the hydrodynamic flow properties of the slurry in the sawing channel, which builds up a hydrodynamic pressure that lifts the wire.

If the main load of the wire is carried by the film, only a small force is exerted on the interacting particles, resulting in a low material-removal rate. If the film thickness decreases the large particles begin to carry the main load and abrasive action begins. The slurry is then mainly responsible for the transport of the particles. If the film thickness decreases further transport becomes more difficult and dry friction and wire rupture may occur.

The transition between the two load regimes depends on the flow properties of the slurry such as viscosity and impact pressure at the slurry entry, and the other parameters such as wire speed, wire tension and the force that presses the crystal against the wire. The hydrodynamic simulations have shown that a slurry with higher viscosity builds up a higher slurry pressure, which pushes the wire away from the crystal surface. This reduces the total force on all particles, whereas the average force on each particle remains mainly constant, as was shown in the simulation results. However, fewer particles then come into contact and take part in the sawing or lapping action. This explains qualitatively and quantitatively how the flow properties of the slurry contribute to the sawing process. One can expect that three-dimensional calculations will reveal more quantitative details. In particular the interaction processes between wire, particles and wafer surface at the sides of the sawing channel require a more detailed analysis. These processes determine the surface damage of the wafers, which is essential for the fracture properties and mechanical stability of the wafers after sawing, as was shown in Refs. [18, 19].

The current development towards thinner and larger wafers already shows that the fracture stability is a limiting factor. Sawing conditions that reduce the surface

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damage are essential here and can be derived from a better understanding of the microscopic particle interactions in the slurry.

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Plasma Chemical Vaporization Machining and Elastic Emission Machining

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19.1 Introduction

19

Plasma chemical vaporization machining (PCVM) and elastic emission machining (EEM) are ultraprecision machining methods based on chemical reactions that were developed in our laboratory. Their concepts and the results of basic research were described in a previous edition of "Crystal Growth Technology" [1, 2]. In this chapter, the results on both PCVM and EEM achieved since the first publication are described. In addition, a new abrasive-free planarization method called catalyst-referred etching (CARE) is introduced in the last part of this chapter.

19.2 Plasma Chemical Vaporization Machining (PCVM)

19.2.1 General Description [3-7]

PCVM is a gas-phase chemical etching method in which reactive species generated in an atmospheric-pressure plasma are used. PCVM has a high removal rate equivalent to those of conventional machining methods such as grinding and lapping, because the radical density of the atmospheric-pressure plasma is much higher than that of normal low-pressure plasma. PCVM also has high spatial resolution, since the atmospheric-pressure plasma is localized only in the area of high electric field intensity because of its short mean free path. Furthermore, because of the short mean free path at atmospheric pressure, the ion energy of the plasma is so small that there is little damage to the processed surface. The evaluation of the surface-state density of the processed surface by the surface photovoltage method (SPV) showed that the defect density on the PCVM surface was very low and comparable to that of the chemical wet-etched surface.

Various applications of PCVM have been studied since the early 1990s. Figure 19.1 shows some examples. Electrodes such as those in Figs. 19.1(c)-(e) are



Fig. 19.1 Electrode types for PCVM; (a) wire type for cutting and patterning, (b) pipe type for fine figuring, (c) inner-blade type for slicing, (d) cylindrical type for polishing, and (e) spherical type for numerically controlled figuring.

called rotary electrodes. By rotating the electrode in an atmospheric-pressure environment, a large amount of reactive gases is stably supplied to a narrow machining point because of its viscosity, and effective ejection of reaction products is also realized. Furthermore, the cooling effect enables a large RF power supply to be used. Thus, a rotary electrode enables high-speed machining. In the following results on polishing and numerically controlled machining applications are presented.

19.2.2

Polishing Application

19.2.2.1 Planarization Mechanism

Figures 19.2 and 19.3 show the basic concept of the planarization mechanism. Figure 19.2 shows a schematic of conventional mechanical polishing. In mechanical polishing, a workpiece with roughness *a* is rubbed with abrasive and a polishing pad or plate. The convex parts of roughness on the surface are flattened. Hence, polishing finishes when stock removal *d* exceeds roughness *a*, but there is much damage left on the polished surface. Figure 19.3 shows a schematic of PCVM polishing. PCVM uses no reference plane. A chemically stabilized surface is formed by the etching process. Thus, although much stock removal *d* is needed for planarization, there is no damage on the surface. This example is for a material suitable for PCVM planarization, however, there are materials unsuited to PCVM. Figure 19.4 shows an example of a polycrystalline sample. There are many different crystal orientations and grain boundaries on a polycrystalline surface. Thus, etching selectivity occurs because of the existence of grain boundaries, and the etch rate



Fig. 19.2 Schematic of planarization by conventional mechanical polishing method.



Fig. 19.3 Schematic of planarization by PCVM or general chemical etching.



Fig. 19.4 Schematic of machining polycrystalline by PCVM.

varies because of the crystal orientation resulting in a rough surface. Therefore, polycrystalline materials are not suitable for PCVM planarization. Another example is a damaged surface (see Fig. 19.5). If there is a point defect or a microcrack on the surface, an etch pit or a groove, respectively, should be formed in the etching process. Therefore, a much larger amount of stock removal *d'* is needed for planarization. A single-crystal material or an amorphous material with no damage on the surface is required for making a smooth surface by PCVM.

19.2.2.2 Polishing of Silicon

A polishing characteristic of silicon was observed using a cylindrical-type rotary electrode equipment, like that shown in Fig. 19.1(d). Figure 19.6 shows the relationship between the amount of stock removal and surface roughness of the silicon wafer polished by PCVM. The premachined plane is lapped and chemically etched. It is seen that surface roughness improved with increasing amount of stock removal. A roughness of 1 nm Ra was obtained after 50-micrometer removal. Figure

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Fig. 19.5 Schematic of machining damaged surface by PCVM.



Fig. 19.6 Relationship between surface roughness and stock removal. (Reactive gas $He:SF_6:O_2 = 98.9:1:0.1$, RF power 8 kW, machining gap 0.3 mm.) (PV is the peak-to-valley roughness and Ra is the centerline average roughness.)

19.7(a) shows the surface roughness of the mechanically polished as-received silicon wafer. Figure 19.7(b) shows the surface roughness of the wafer after $6 \,\mu m$ removal by PCVM polishing; the roughness was improved from 0.26 nm Ra to 0.11 nm Ra.

19.2.2.3 Polishing of Silicon Carbide [8]

Silicon carbide has favorable properties such as a wide bandgap, high thermal conductivity, high breakdown electric field strength, and high thermal stability. It



(a) Mechanically polished surface

(b) Plasma CVM polished surface

Fig. 19.7 Surface roughness of Si wafer. (Reactive gas $He:CF_4:O_2 = 98.9:0.1:0.1$, removal depth 6 μ m.) (rms is the root mean square roughness.)

Table 19.1 Removal Rate of SiC Wafer.

CF ₄ , O ₂ concentration(%)	RF power	Removal rate ($\mu m \min^{-1}$)			Ratio of C/Si face
		(Si wafer)	Si face	C face	•
1	50	0.53	0.10	0.16	1.60
5	500	16	1.70	3.50	2.06
5	1000	39	4.00	8.00	2.00

is a suitable substrate for high-temperature and high-power applications. However, because of its hardness and chemically stability, there are few efficient machining methods for it. Thus, we choose silicon carbide as a target of PCVM polishing.

A commercial 4H-SiC (0001) wafer was used as a specimen. A gas mixture of helium, carbon tetrafluoride and oxygen was used as the reactive gas. Table 19.1 shows the removal rates of both Si- and C faces of the SiC wafer under various experimental conditions. We achieved a high removal rate of $4\,\mu$ m/min for the Si face and $8\,\mu$ m/min for the C face. It is shown that the removal rates of the C face are higher than those of the Si face. In most cases, the former are twice the latter. Generally, the oxidative rate of SiC varies with the SiC surface orientation, and the C face is oxidized more rapidly than the Si face. Thus, there is a possibility that oxidation plays a prominent role in the etching of SiC.

Figure 19.8 shows the typical surface morphology of the Si face of the machined SiC wafer using a microscope interferometer. The results in Figs. 19.8(a)–(c) were obtained at almost the same site. Therefore, the changes in surface morphology induced by PCVM can be monitored. Although roughness in a narrow area seems to be improved, pits and scratches appeared with increasing removal depth. The pit density in Fig. 19.8(c) is equivalent to the original defect density of the substrate, 10^5 defects per square centimeter. This indicates that pits and scratches were formed because fluorine radicals selectively etch defects originally present on the substrate. Figure 19.9 shows the morphology of the C face. In Figs. 19.9(a)–(c), it was found that there are no pits on the C face with increasing removal depth and that the C face is flattened. It can be said that PCVM does not have etch selectivity for defects on the C face. For additional details on the C face machined by PCVM,

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Fig. 19.8 Surface morphologies of Si face of SiC (area: $258\,\mu m\,\times\,$ 194 μm): (a) preprocessed, (b) after 155-nm depth removal, and (c) after 1100-nm depth removal.



Fig. 19.9 Surface morphologies of C face of SiC (area: $258\,\mu m\,\times\,194\,\mu m)$: (a) preprocessed, (b) after 80-nm depth removal, and (c) after 1360-nm depth removal.



Fig. 19.10 Surface roughness of C face imaged using atomic force microscope (area: $500 \text{ nm} \times 500 \text{ nm}$). (a) Preprocessed surface and (b) 10- μ m machined surface (CF₄:O₂:He = 5:5:90, 500 W, 1 min).

an atomic force microscope (AFM) image of the surface that was machined up to a $10 \,\mu$ m depth is shown in Fig. 19.10. The measurement area was 500 nm square. The starting surface roughness (7.51 nm peak-to-valley (PV), 1.04 m rms) was successfully improved to 1.89 nm PV, 0.17 nm rms.

19.2.3

Numerically Controlled Machining Application [9-13]

19.2.3.1 Machining Process

The great advantage of numerically controlled (NC) PCVM is that it is a "noncontact" process. In conventional NC machining, the workpiece and the tool come into contact, and machining is carried out with cutting-depth control or



Fig. 19.11 Flowchart of NC-PCVM.

table positioning. Thus, it is sensitive to machine stiffness, vibration, and thermal deformation, and it is very difficult to achieve an accuracy of 10 nm. In contrast, in NC-PCVM, machining is done by controlling the dwelling time of plasma. Obviously, there are fluctuations in PCVM, but, these fluctuations are negligible in comparison with the machining gap between an electrode and a workpiece, which is normally from 0.5 to 1 mm. Hence, very precise NC machining can be expected as long as the plasma is stable.

Figure 19.11 shows the work flow of NC-PCVM. First, the outline of the workpiece is measured. The scanning speed distribution is calculated as shown on the right side of the figure. Then, the workpiece is cleaned and NC machined. After machining, the outline is measured again. If the surface does not have sufficient accuracy, we repeat these processes. As can be observed, the outline measurement process is very important in NC-PCVM. Although, the machining accuracy depends on the machine accuracy in conventional mechanical machining methods, it depends on the measurement accuracy in NC-PCVM.

19.2.3.2 Application to Silicon-on-Insulator Wafer

Metal-oxide semiconductor field-effect transistors (MOSFETs) fabricated on siliconon-insulator (SOI) wafers operate faster and at a lower power than those fabricated on bulk silicon wafers. Scaling down, which improves their performance, requires thinner SOI wafers. Although ultrathin (less than 50 nm) SOI wafers are already available, they do not yet have sufficient thickness uniformity. Thus, we undertook to form ultrathin and uniform-thickness SOI wafers by NC-PCVM.

A commercial 8-inch SOI wafer was used for the demonstration of thinning by NC-PCVM. The initial thickness distribution of the SOI layer measured by spectroscopic ellipsometry (SE) is shown in Fig. 19.12(a). The deviation of thickness



Fig. 19.12 Thickness distributions of top silicon layer of SOI wafer measured by SE: (a) as-received SOI wafer, (b) wafer thinned by NC-PCVM, and (c) A–A cross sections of both (a) and (b).

was 97.5 \pm 4.7 nm in an area of diameter 190 mm and the standard deviation was 2.40 nm. Figure 19.12(b) shows the thickness variation of the SOI wafer thinned by NC-PCVM. The SOI layer was successfully thinned to 7.5 nm and the deviation was improved to \pm 1.5 nm. The standard deviation was also improved to 0.38 nm. The thickness along the cross sections A–A in Figs. 19.12(a) and (b) are shown in Fig. 19.12(c). It is clear that the initial concave thickness distribution was corrected with high accuracy.

We evaluated the electronic properties of SOI processed by PCVM. Figure 19.13 shows the I-V characteristic curves of MOSFETs fabricated on the two kinds of SOI wafers; one thinned by NC-PCVM and the other thinned by a combination of thermal oxidation and hydrofluoric acid etching. The thickness of SOI was reduced from 100 nm to 60 nm for both wafers. From these I-V curves, it is seen that the leakage currents of the MOSFETs on both wafers were equally small, and that the subthreshold slopes were steep and almost equal. It should be mentioned that these results were the same for all other transistors on both kinds of wafers. This means that PCVM prevents both ion-bombardment damage and trace metal contamination, which normally degrade MOSFET performance.

19.3

Elastic Emission Machining

19.3.1 General Description

To realize ultraflat and crystallographically well-ordered surfaces of functional materials on wafer-size scales is highly demanded in many fields of physics. For example, total reflection mirrors for steering synchrotron hard X-rays, optical cavity



Fig. 19.13 (a) SOI wafer with devices and (b) $I_{ds}-V_g$ curves for SOI n-MOSFETs on PCVM wafer and on reference wafer. The gate length was 0.35 mm and the gate width was 10 mm.

elements of the gravitational-wave detector, imaging optics of extreme ultraviolet lithography and semiconductor substrates for future nanoscale devices are strongly required to have atomically flat and/or crystallographically perfect surfaces [14–18]. However, conventional mechanical polishing methods cannot be applied to make such surfaces because of the nature of accompanying crystallographic damage and the limitation in the reduction performance of the surface roughness. These facts led us to develop new surface flattening methods having removal mechanisms based on chemical phenomena in which crystallographic properties are preserved. A novel method called elastic emission machining (EEM) [19–22], which is a precise surface preparation method utilizing chemical reactions between solid surfaces, has been developed to solve these problems.

19.3.2 Flattening of the Si (001) Surface

Si (001) is a worthwhile surface as the first target to be flattened and evaluated in atomic scale. It is well known that Si (001) surface is the most important surface for electronic devices because of its ability to control interfacial electronic states at surface oxide films. This will be the case in future nanotechnology, in which atomically flat and crystallographically perfect Si (001) surfaces will be in high demand so as to realize extremely integrated and functionally enhanced devices. However, it is the most difficult surface to flatten at the atomic level compared to the other oriented surfaces. The difficulty in flattening the surface mainly originates in the large surface energy. Micropits and/or bumps mainly with <111> facets, of

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Fig. 19.14 Schematic view of the EEM mechanism.

which the surface energy is smaller than that of the (001) surface, are formed and grow continuously during wet-chemical processing due to the anisotropic etching effects of OH⁻ ions [23–25] that exist in all aqueous solutions. In current precise polishing methods such as chemical and mechanical polishing (CMP), this problem still exists because wet-chemical etching processes must be simultaneously utilized to avoid the introduction of crystallographic damages [26].

19.3.3 EEM Method

The general view of the EEM processing and its advantages over other chemical processes are as follows. When two solid surfaces come into contact with each other and then separate, there is a notable probability that the atoms on one surface will adhere and move onto the other. Fine powder particles, whose surfaces are reactive to the target material, are employed as working solids in the practical process. As shown in Fig. 19.14, they are uniformly mixed with ultrapure water and transported to the processed surface via a controlled flow. They roll on the processed surface along the streamlines and preferentially remove the topmost atoms on the surface. In conventional chemical etching processes, reactive species are molecules or ions with sizes of angstrom order so that they attack atoms in the micropit on the processed surface whereby the depth of the micropit increases. In contrast, reactive species in EEM are atoms on the powder particles with a large diameter, such as more than 1 µm, so that atoms on the powder particles selectively interact with the topmost atoms on the process surface. The interacting probability between atoms on the powder particle and inside the micropit on the processed surface is effectively reduced, geometrically. A transmission electron microscope photograph of the typical powder particles made of amorphous SiO₂ with a diameter of 2 µm is displayed in Fig. 19.15. They are seen to have spherical shapes with smooth surfaces to reduce the probability of unwanted interatomic reaction more effectively. Figure 19.16 shows the relationship between the dwelling time and removal depth in EEM processing when the processed surface is p-type Si (001) having a resistivity of 10Ω cm and the powder particles are those shown in Fig. 19.15. Good linearity is obtained, which indicates good controllability in precise surface processing. From the slope



Fig. 19.15 Transmission electron microscope photograph of the powder particles typically employed. The material is amorphous SiO₂ and the diameter is $2\,\mu$ m.



Fig. 19.16 Relationship between the dwelling time and the removal depth. Processed surface and employed powder particles were Si (001) and spherical SiO₂ particles with a diameter of $2\,\mu$ m, respectively. The removal rate is found to be 2 nm min⁻¹, which is higher than the rate of micropit growth by OH⁻ ions, 0.5 nm h⁻¹.

of the fitted line, the removal rate is found to be 2 nm min^{-1} . The growth rate of the micropit or bump in ultrapure water is about 0.5 nm h⁻¹ [23–25]. The removal rate of 2 nm min^{-1} in EEM is two orders higher than the growth rate. In addition, the topmost atoms are selectively reacted and removed. Hence, the surface becomes flat without any pit formation. Microbumps are considered first to be removed.

19.3.4 Evaluation of Processed Surface

The atomic force microscope (AFM) images of the EEM processed Si (001) surface and highest commercial quality Si (001) surface for ULSI devices are shown in Fig. 19.17. The removal depth in this EEM processing is 2 nm. The processed surface is cleaned by rinsing in ultrapure water (with dissolved-oxygen concentration 486 19 Plasma Chemical Vaporization Machining and Elastic Emission Machining



Fig. 19.17 AFM images of the EEM processed Si (001) surfaces (a) and the present high-quality Si (001) wafer for ULSI devices (b). The rms roughness values of the EEM-processed surface and the present wafer surface were 0.087 nm and 0.187 nm, respectively.

<1 ppb) for three minutes with 1 MHz ultrasonic waves. The rms roughness values of the EEM-processed surface and the present Si surface were 0.087 nm and 0.187 nm, respectively. Since surface flattening proceeds despite a small EEM removal depth of merely 2 nm, which is almost the same as the peak-to-valley height of the preprocessed surface profile, it is evident that removal of the topmost atoms is extremely efficient.

We show the STM images of the processed surface in Fig. 19.18 from the perspective of the atomic structures. The processed surface is cleaned in the same way as that for AFM observation, and is set on the STM stage in the ultrahigh vacuum without any heat treatment. A probe tip made of Pt (90%)–Ir (10%) is employed and positively biased under the tunnel current of 0.3 nA. Observed areas are 40 nm × 40 nm (Fig. 19.18(a)) and 100 nm × 100 nm (Fig. 19.18(b)). Atomic resolutions are obtained in both images. The top-layer-atom images elliptically expanded along the [110] or [$\overline{1}$ 10] direction [27–29] indicate that the Si atoms on the surfaces are terminated with two hydrogen atoms. All surface atoms are found to be well ordered. No distorted structures are observed. Low-energy electron diffraction patterns are



Fig. 19.18 Atomic-level structure of the EEM-processed surface observed by scanning tunneling microscopy, (a) $40 \text{ nm} \times 40 \text{ nm}$ and (b) $100 \text{ nm} \times 100 \text{ nm}$.

simultaneously observed during STM measurements. The diffraction spots show a 1 \times 1 surface structure, which corresponds to the atomic configurations observed in the STM images. These images indicate that EEM processing proceeds without introducing crystallographic damage. Occupancy proportions of each atomic layer were estimated in the 100 nm \times 100 nm STM image, and 95% of the measured area was found to be composed of only 3 atomic layers. In particular, the center layer L₁ accounted for close to 50%. This is the flattest surface compared to other surfaces are realized by heating in ultrahigh vacuum, they can presently be utilized only in basic research because of the unfeasibility for industrial use, i.e. it requires enormous energy consumption for heating of more than 1000 °C over an extended area.

19.3.5 Removal Mechanism

To clarify the atom-removal process, first-principles molecular-dynamics simulations were carried out. The density-functional theory and the local-density approximation [30-34] are adopted in this simulation. The norm-conserving pseudopotential, the plane-wave expansion method and repeated slab configuration are applied with the cut-off energy 24 Ry. The models of Si (001) surfaces with and without an atomic step were employed, in which surface Si atoms are terminated by hydrogen atoms [23-25]. An Si₄O₁₃H₁₀ cluster was adopted as a model of the SiO₂ powder particle with hydroxide termination [35-37] to consider the aqueous circumstances in EEM processing. Three images in the case of the surface with a step are shown in Figs. 19.19(a)-(c). In the first image, a hydrogen atom on the Si surface and a hydroxide molecule on the observed powder particle physically interact with each other. In the second image, they bond through an oxygen atom with the release of an H₂ molecule as a reaction product. The density of the valence electron at the backbond of the surface Si decreases because of the high electronegativity of the interface oxygen atom. The barrier energy of this reaction is calculated to be 1.7 eV, and is considered to be supplied easily by the kinetic energy of the rolling powder particle. In the final image, the target Si atom on the Si surface is removed as the cluster is lifted. This simulation suggests that the surface-atom removal should be performed atom-by-atom and no additional defects should be introduced. The EEM processing is considered to proceed with increasing such atom-by-atom removal. No notable difference between the above results and the results with other calculation models, such as terrace or adatom, indicated that the dominant effect for surface flattening is not the selective removal at the step edge originating in high chemical activity but the selective removal of the topmost atoms originating in the employment of large-diameter spherical solids.

19.3.6 Conclusion and Additional Result

We proposed a novel chemical process EEM, utilizing solid surface reactivity, to realize atomically flat and well-ordered surfaces on a wafer-size scale. The

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configuration are completed with the release of an H_2 molecule as a reaction product. Decrease of valence electron density at the backbond of the target surface Si atom is observed. (c) Images after the powder particle cluster is lifted to 0.4 nm from the initial position. The target atom is removed due to adhesion to the powder particle cluster.

phenomenon is so efficient that it is a very useful infrastructure technology for flattening various kinds of functional materials. We continue to study to make the method a practical technology for progress in many fields of physics such as surface science, nanotechnology, X-ray optics and astrophysics. Especially in X-ray optics, we have already established hard-X-ray nanofocusing under diffraction-limited conditions [38, 39]. In this achievement, a 100-mm long total-reflection mirror having an elliptical shape was fabricated by EEM with an ultrasmooth surface and an outline accuracy of 3 nm in the peak-to-valley height. The obtained spot size of 25 nm \times 30 nm is the smallest in the hard X-ray region. The wave-optically estimated and experimentally measured beam profiles are shown in Fig. 19.20 in the case of the 25-nm focusing. They are in good agreement, mutually. This means that a diffraction-limited focusing of hard X-ray is realized and is achieved by mirror optics for the first time.

19.4 Catalyst-Referred Etching [40]

19.4.1 Concept of CARE

Looking back at Figs. 19.2 and 19.3, the surface is polished mechanically with a small amount of removal but much damage, whereas it is polished chemically with no damage but a large amount of removal. We consider that the most efficient planarization would involve chemical removal and simultaneous flattening of the



Fig. 19.20 Focused X-ray beam profiles. The solid line shows the theoretically expected beam profile under diffraction-limited conditions, and the dots shows experimentally obtained beam profile measured by a knife-edge method. The employed X-ray energy was 15 keV in which the wavelength is 0.08 nm.



Fig. 19.21 Schematic of planarization by catalyst-referred etching.

surface; this can be achieved using a catalyst as a polishing plate. If the catalyst generates reactive species that are activated on the catalyst surface, the surface of the workpiece will be chemically removed at areas in contact with the reactive flat catalyst (Fig. 19.21). We named this new abrasive-free planarization method catalyst-referred etching (CARE). It is important that the reactive species are activated only next to the catalyst surface and deactivated when they are away from the catalyst surface. If the reactive species are activated away from the catalyst surface, removal will occur independent of the flat catalyst surface, which is the same as conventional chemical etching.

19.4.2

Experimental Setup

To accomplish CARE, a catalyst and reactive species appropriate for the material to be processed are selected. We used SiC as a sample material because there are few efficient machining methods because of its hardness and chemically stability, as previously noted. We selected F and OH radicals as reactive species for the removal of SiC because these species chemically remove SiC in plasma and aqueous solutions. We used platinum as a catalyst in a hydrogen fluoride (HF) solution, because Pt has catalytic properties, such as the ability to dissociate various molecules, and the interaction between Pt surfaces and hydrogen fluoride molecules in an aqueous solution can generate F and OH by self-dissociation.

The CARE setup has a catalytic polishing pad made of Pt placed on a rotational table. SiC wafers are fixed on the sample stage using wax and then placed on the pad with a controlled pressure of 0.02 MPa, which is appreciably lower than that in conventional chemical mechanical polishing (CMP). The polishing pad and sample are immersed in 2 mol 1^{-1} hydrofluoric acid. The rotation speeds of the sample stage and pad are fixed at 20 rpm and 19 rpm, respectively. The SiC wafers (4H n-type) are lapped to expose the (0001) Si plane on-axis, and have resistivities and micropipe densities of $0.02-0.03 \ \Omega \text{ cm}$ and $50-100 \ \text{cm}^{-2}$, respectively. The removal rate of SiC is $0.1-0.2 \ \mu \text{m} \ \text{h}^{-1}$, under such conditions. First, the processed surfaces were observed by Nomarski differential interference contrast (NDIC) microscopy. Then, the surface qualities were evaluated by optical interferometry, atomic force microscopy (AFM), and low-energy electron diffraction (LEED) analysis.

19.4.3 Surface Evaluations

Figures 19.22 and 19.23 show the NDIC images in the areas of 880 μ m × 1140 μ m and 60 μ m × 80 μ m, respectively. They show that scratches and microcracks on the SiC surfaces were reduced progressively by CARE. Many of the microcracks observed on the surfaces shown in Fig. 19.23(a) were introduced during lapping, which generates and accumulates scratches and cracks on the surface as shown in Fig. 19.22(a). After CARE to a removal depth of 1 μ m, some microcracks were still not removed; for example, the microcrack marked by the arrow in Fig. 19.23(a). As removal increased, such microcracks were completely removed (Fig. 19.23(a)). The results show that CARE preferentially removes the topmost wafer surface in contact with the pad surface, and that the frictional force between the pad and SiC surfaces was sufficiently small so as not to introduce mechanical scratches or cracks.

A CARE-processed surface with a removal depth of $3 \mu m$ from the lapped surface and a surface of a commercially available SiC wafer prepared by conventional CMP were observed by optical interferometry (Fig. 19.24). The maximum height of the surface irregularity, peak to valley (PV), and root-mean-square roughness (rms) of the CARE-processed surface were evaluated to be 1.236 nm and 0.142 nm,



Fig. 19.22 NDIC $880\,\mu m \times 1140\,\mu m$ images of 4H-SiC wafer: (a) as-lapped surface, and CARE-processed surface with removal depths of (b) 1 μm and (c) 2 μm .



Fig. 19.23 NDIC $60 \mu m \times 80 \mu m$ images of a 4H-SiC wafer: (a) as-lapped surface, (b) CARE-processed surface with removal depth of $1 \mu m$, and (c) with removal depth of $2 \mu m$.



Fig. 19.24 Optical interferometry images of 4H-SiC wafer: (a) as-received (after CMP) surface, RMS: 0.548 nm [PV: 3.856 nm, Ra: 0.436 nm], and (b) CARE-processed surface with removal depth of 3 mm, RMS: 0.142 nm [PV: 1.236 nm, Ra: 0.114 nm].

respectively. The roughness of the CARE-processed surface is markedly lower than that of the CMP surface, which suggests that CARE has a higher potential as a planarization method than conventional CMP.

The surface morphology of the processed surface was measured by AFM over a $500 \text{ nm} \times 500 \text{ nm}$ area (Fig. 19.25). A step terrace with a step height of approximately 0.3 nm, corresponding to the thickness of a single bilayer of Si and C structures, was observed on the CARE-processed surface. Such a surface structure strongly indicates that the removal mechanism is based on chemical phenomena, and that a type of step-flow removal occurs on the (0001) Si surface of SiC.

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Fig. 19.25 AFM images of 4H-SiC wafer: (a) as-received surface, RMS: 0.174 nm [PV: 1.761 nm, Ra: 0.131 nm], and (b) CARE-processed surface with removal depth of 3 mm, RMS: 0.093 nm [PV: 0.724 nm, Ra: 0.076 nm].



Fig. 19.26 LEED spots obtained with probe-beam energy of 65 eV, which corresponds to estimated thickness of 0.4 nm: (a) as-received (after CMP) surface and (b) CARE-processed surface with removal depth of $3 \mu m$.

To estimate the crystallographic properties of the CARE-processed surface, CARE-processed and CMP-processed surfaces were observed by LEED analysis with a probe beam energy of 65 eV, which corresponds to an estimated thickness of 0.4 nm (Fig. 19.26). LEED analysis is used for the estimation of crystal structures in a surface. When an electron beam penetrates a well-ordered crystalline structure in a surface, a sharp diffraction spot is observed on a detection screen. The estimated thickness is determined from the electron penetration depth. Sharp LEED spots were observed from the CARE-processed surface (Fig. 19.26(b)) compared with the CMP surface, in which only diaphanous and blurry spots were observed under such low-energy probe-beam conditions (Fig. 19.26(a)). The results indicate that the removal mechanism of CARE is not mechanical but chemical, because the crystalline structure of the CARE-processed surface is well ordered.

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