1. Introduction
Dielectric-barrier discharges (DBDs), also referred to as barrier discharges or silent discharges have found a number of interesting industrial applications in addition to the historical ozone generation. The generation of powerful coherent infrared radiation in CO\textsubscript{2} lasers and of incoherent ultraviolet (UV) or vacuum ultraviolet (VUV) excimer radiation in excimer lamps are examples of more recent developments. VUV excimer radiation generated in DBDs can excite phosphors to emit visible light. This is the basis of mercury-free fluorescent lamps and of flat plasma display panels that will be used as wall hanging TV sets. Processes like pollution control and surface treatment with DBDs show great promise for the future.

The most important characteristic of DBDs is that non-equilibrium plasma conditions can be provided at elevated pressure, for example atmospheric pressure. In DBDs this can be achieved in a much simpler way than with other alternative techniques like low pressure discharges, fast pulsed high pressure discharges or electron beam injection. The flexibility of DBD configurations with respect to geometrical shape, operating medium and operating parameters is remarkable. In many cases discharge conditions optimized in small laboratory experiments can be scaled up to large industrials installations. Efficient low cost power supplies are available up to very high power levels.

2. Discharge physics
Typical electrode configurations of planar and cylindrical dielectric-barrier discharges are given in Fig. 1. DBDs are characterized by the presence of one or more insulating layers in the current path between metal electrodes in addition to the discharge gap(s).

A discharge having one or two dielectric boundaries has many similarities with discharges operated between metal electrodes. For the first ignition breakdown in a homogeneous electrical field is governed by the same Paschen law that is known from breakdown between metal electrodes. One fundamental difference is, of course, that DBDs cannot be operated with dc voltages because the capacitive coupling of the dielectric(s) necessitates an alternating electric field to drive a displacement current. Prudent utilization of the current limiting properties of the dielectric barriers is one of the major features in designing DBD configurations and their matching to the power supplies. As soon as charges are deposited on the dielectric they have an influence on local fields. After the first ignition these memory charges soon dominate DBD behavior. DBDs can be operated with sinusoidal or square-wave currents between line frequency and microwave frequencies or with special pulsed wave forms. For large-scale industrial applications power supplies operating between 500 Hz and 500 kHz are preferred.
2.1 Filamentary dielectric-barrier discharges

In atmospheric pressure gases breakdown in a plane parallel gap with insulated electrodes normally occurs in a large number of individual tiny breakdown channels, referred to as microdischarges. When an overvoltage is applied to the discharge gap electron avalanches soon reach a critical stage where the local “eigenfield” caused by space charge accumulation at the avalanche heads leads to a situation where extremely fast streamer propagation becomes possible. As a result thin conductive channels are formed. The properties of these microdischarges have been investigated experimentally as well as theoretically [1-10]. Typical parameters for air discharges in a 1 mm gap are summarized in Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration</td>
<td>$10^{-8}$ s</td>
</tr>
<tr>
<td>Filament Radius</td>
<td>about $10^{-4}$ m</td>
</tr>
<tr>
<td>Peak Current</td>
<td>0.1 A</td>
</tr>
<tr>
<td>Current Density</td>
<td>$10^6 - 10^7$ A m$^{-2}$</td>
</tr>
<tr>
<td>Total Charge</td>
<td>$10^{10} - 10^9$ C</td>
</tr>
<tr>
<td>Electron Density</td>
<td>$10^{20} - 10^{21}$ m$^{-3}$</td>
</tr>
<tr>
<td>Mean Electron Energy</td>
<td>1-10 eV</td>
</tr>
<tr>
<td>Filament Temperature</td>
<td>close to average gas temperature in the gap</td>
</tr>
</tbody>
</table>

At a dielectric surface the microdischarge channels spread into surface discharges covering a much larger region than the original channel diameter. The microdischarge filaments can be characterized as weakly ionized plasmas with properties resembling those of transient high pressure glow discharges. They start when the breakdown field is reached locally and extinguish when the field is reduced to such an extent that electron attachment and recombination dominate over ionization. Due to charge build-up on the dielectric surfaces the field at the location of a microdischarge collapses within a few ns after breakdown, thus terminating the current flow at this location. The short duration results in little transient gas heating of the current channel. Humidity tends to increase the strength of a microdischarge while irradiating the cathode with UV photons tends to decrease it. The dielectric barrier limits the amount of charge and energy deposited in an individual microdischarge and distributes the microdischarges evenly over the entire electrode surface. As long as the external voltage is rising additional microdischarges are initiated at new locations because the presence of residual charges on the dielectric has reduced the electric fields at positions where microdischarges have already occurred. When the voltage is reversed, however, the next microdischarges will form at old microdischarge locations. Consequently, high voltage low frequency operation tends to spread the microdischarges, while low voltage high frequency operation tends to reignite the old microdischarge channels every half period. This memory effect due to charge accumulation on the dielectrics is a dominant feature in all DBDs.

2.2 Diffuse dielectric-barrier discharges

It has been demonstrated that homogeneous diffuse discharges can also be obtained in DBD configurations even at atmospheric pressure. In 1976 K. Donohoe obtained a uniform glow discharge with pulsed excitation in a helium/ethylen mixture [11]. S. Okazaki and her group at Sophia University in Tokyo did pioneering work in this field using sinusoidal feeding voltages in different gases with and without additives [12-14]. They proposed the term APG, standing for atmospheric pressure glow. To generate uniform glow discharges at atmospheric pressure in helium, air, argon, oxygen and nitrogen even when using a 50 Hz power source they used an electrode configuration consisting of two metal foils covered with a special metal mesh and ceramic plates. More detailed investigations followed by F. Massines and her group at Toulouse [15, 16]. Apparently independently of these investigations, a group around J.R. Roth at the University of Tennessee at Knoxville re-invented what they called an OAUGDP (one atmosphere uniform glow discharge plasma) and even obtained a US patent for a “Method and apparatus for glow discharge plasma treatment of polymer materials at atmospheric pressure” [17].

Glow discharges in atmospheric pressure gases were already mentioned by von Engel, Seeliger and Steenbeck in 1933 [18] and by Gambling and Edels in 1956 [19]. The subject became an important issue when transversely excited atmospheric pressure (TEA) lasers were investigated in N$_2$, in CO$_2$/N$_2$/He, and in excimer forming gas mixtures. It was found that
sufficient preionization by x-rays, electron beams or by double-discharge techniques helped to establish such a uniform glow phase. Necessary requirements of a minimum initial electron density were formulated by Palmer [20] and by Levatter and Lin [21]. One requirement for establishing a volume-stabilized glow discharge is that the preionization electron density is large enough to cause appreciable overlap and coalescence of primary avalanche heads and smoothing of space-charge field gradients at the stage when streamer formation would otherwise occur. More recently Brenning et al. [22] formulated more detailed conditions for obtaining homogenous high-pressure pulsed avalanche discharges. They point out the importance of an additional minimum preionization rate just prior to and during breakdown. The most important quantity is the effective primary ionization coefficient $\alpha_{eff}$ (including all attachment and detachment processes) at the moment of breakdown or, more precisely, its derivative with respect to the reduced field: $d(\alpha_{eff}/n)/d(E/n)$. This quantity is strongly effected by impurities, gas additives and the presence of metastables and residual ions. In dielectric-barrier discharges we can make use of residual species from the previous half period. Thus, in addition to the already mentioned memory charges on the dielectric surface(s), we also have a memory effect in the volume if the repetition frequency is properly chosen. Also special dielectric properties can help to establish a homogeneous volume discharge. As Tepper et al. [23] demonstrated, electret dielectrics are capable of accumulating appreciable amounts of charges on the surface. Supported by the applied voltage the charges are trapped uniformly on the surface. When the electric field changes its polarity and exceeds a certain threshold value, the charge carriers are expelled spontaneously from the surface and initiate a homogeneous discharge.

Up to now it is difficult and tricky to reliably control homogeneous glow discharges at atmospheric pressure. For instance, changes of the electrode configuration or small variations of the amplitude or repetition frequency of the applied voltage can cause a transition into a more stable filamentary discharge mode. For industrial applications this could be a severe drawback compared to filamentary discharges. If however reliable control can be provided and if an average energy transfer into the discharge can be obtained comparable to that of filamentary discharges, this type of discharge may become of particular interest for certain industrial applications.

3. Applications of dielectric-barrier discharges

Most industrial DBD applications utilize filamentary discharges [3, 9, 24]. The technology for large-scale applications was initially developed with ozone generation in mind. In the meantime novel DBD applications have established new markets that reach annual sales amounting to at least ten times the original ozone market.

3.1 Industrial ozone generation

Technical ozone generators use cylindrical discharge tubes of about 20-50 mm diameter and 1-3 m length [25, 26]. Borosilicate glass tubes have for a long time been the favorite dielectric material. They are mounted inside stainless steel tubes to form annular discharge gaps of about 1 mm radial width. Metal coatings, e.g. thin aluminum films, inside the glass tubes serve as high voltage electrodes, which are contacted by metal brushes. Modern high-performance ozone generators use special layered dielectrics with characteristics optimized for ozone formation. Large ozone generators use several hundred discharge tubes in big steel tanks to provide the required electrode area for mass ozone production. The outer steel tubes are welded between two end flanges and form a sealed cooling compartment. A transverse water flow cools the steel tubes in a classical heat exchanger configuration. Efficient cooling is essential for good ozonizer performance.

Modern high-power ozone generators take advantage of semiconductor power conditioning. They utilize thyristor or transistor controlled frequency converters to impress square-wave currents or special pulse trains in the medium frequency range. Typical operating frequencies are between 500 Hz and 5 kHz. Using this technology, applied voltages can be reduced to the range of about 5 kV. With large ozone generators power factor compensation...
has become an important issue. Typical power densities now reach 1-10 kW/m² of electrode area.

Large ozone generating facilities produce several hundred kg ozone per hour at a power consumption of several MW. The ozone production capacity of a big ozone generator is of the order 100 kg/h. Progress with respect to attainable ozone concentrations and energy consumption has continued to be achieved in recent years [27]. It has been suggested that ozone generation might be further improved by homogeneous discharge conditions [28-31].

3.2 Excimer lamps and plasma displays
Excimer lamps, spontaneous emission sources based on excimer formation, can be pumped by pulsed or dc longitudinal discharges, by preionized pulsed transverse discharges, by microwave discharges or by dielectric-barrier discharges. More recently, discharges in supersonic jets, constricted glow discharges and microhollow cathode discharges have also been proposed to generate excimer emission. When DBDs are operated in high-pressure rare gases or rare gas/halogen mixtures each microdischarge can act as an intense source of ultraviolet (UV) or vacuum ultraviolet (VUV) radiation. During the last decade powerful and efficient excimer lamps have been developed [3, 32-36] and have found several applications in industrial UV induced processes [9, 24, 33, 37-39]. For large-scale industrial applications dielectric-barrier discharges using fairly simple discharge configurations currently represent the most mature excimer lamp technology. Their main advantage is simplicity, lack of internal electrodes, high efficiency and low cost. Sealed lamps of different planar and cylindrical geometries are common (Fig. 2). Recent applications of excimer lamps include UV curing of photoreactive polymers, photo-deposition of large area or patterned thin metal or semiconductor films, of high- and low-dielectric-constant insulating layers, photo-assisted low-temperature oxidation of Si, SiGe and Ge, polymer etching and microstructuring of polymer surfaces. Applications investigated so far clearly demonstrate that high power excimer lamp systems can provide an interesting alternative to excimer lasers for industrial large-scale low-temperature materials processing.

![Fig. 2: Sealed cylindrical and planar dielectric-barrier discharge excimer lamp configurations](image)

The width of the discharge gap ranges from 0.1 mm to several mm. Filling pressures range from 10³ to 5·10⁵ Pa. In many cases a third buffer gas (He, Ne) is added to the binary excimer forming mixture. This facilitates ignition and provides additional control over the electron energy distribution. Operating frequencies range from 50 Hz to some GHz, applied voltages from a few hundred V to several kV. Commercial excimer lamps are offered for the wavelengths 126 nm (Ar₂*), 146 nm (Kr₂*), 172 nm (Xe₂*), 222 nm (KrCl*) and 308 nm (XeCl*). For UV curing applications cylindrical XeCl* lamps up to 2 m length are available. Typical efficiencies range from 5–40%. In recent years also powerful and efficient XeF* and XeBr* lamps radiating at 253 nm [40] and 282 nm [41], respectively, have been investigated. Most excimer lamps concentrate their emission in a narrow wavelength region. Even at high electrical input powers cooled versions can operate close to room temperature.

By far the most important representative is the xenon excimer lamp. It reaches an efficiency of 40%. Phosphors can be used to transform its VUV radiation to visible light. This
wavelength conversion is utilized in mercury-free fluorescent lamps, in flat panels illuminating liquid crystal displays and in flat plasma display panels with up to 1.5 m picture diagonal. In tiny addressable DBD cells of 0.1 mm electrode spacing and 0.2 mm width xenon VUV radiation is converted to red, green or blue image points by activating internally applied phosphor layers. Gas mixtures containing 5-10% Xe in Ne or He are used at pressures of 50-70 kPa. The operating voltage is only 200-300 V. Multi-billion dollar investments in production facilities for these flat television screens in Japan, Taiwan and South Korea have recently led to a new dimension of large-scale industrial DBD applications. In 1998 already about 50’000 flat plasma displays with 1 m picture diagonal were sold. The market volume is expected to increase to 5 million sets by the year 2005 [42].

3.3 Silent-discharge CO\textsubscript{2} lasers
DBDs have also found applications in high power CO\textsubscript{2} lasers. Based on their experience with ozone generators N. Tabata and S. Yagi at Mitsubishi Electrical Corporation developed an industrial high power laser. This SD CO\textsubscript{2} laser (SD stands for silent discharge) soon became the most successful commercial laser for material processing on the Japanese market. The water-cooled plane metal electrodes, separated by 50 mm, are covered with glass or alumina dielectrics. A high-velocity transverse gas flow passes the discharge gap at a speed of 50-80 m/s for heat removal and discharge stabilisation. Due to the large fraction of helium in the laser gas mixture (about 30%) and the low operating pressure (6.4 kPa) the discharge appears uniformly diffused. Operating at 160 kHz there is not enough time for the ions to decay or to be swept out between succeeding half periods. As a consequence, the discharge behaves very much like a resistive load (ion trapping discharge). Nearly diffraction limited infrared radiation at the wavelength $\lambda =10.6 \mu$m is obtained with output powers up to 5 kW. The efficiency exceeds 10%. The main application of this SD CO\textsubscript{2} laser is high speed welding and cutting of thick metal plates and other materials [43].

3.4 Pollution control
Applications of DBDs for pollution control and for the destruction of poisonous compounds have received growing attention. After initial work on military toxic wastes an increasing number of investigations have been devoted to the treatment of nitrogen oxides and sulphur oxides in flue gases, and to the decomposition of volatile organic compounds (VOCs). Typical examples are hydrocarbons, chlorocarbons and chlorofluorocarbons (CFCs). Contamination of exhaust air streams with gaseous hydrocarbons or organic solvent vapors occurs in many industrial processes, e.g., in chemical processing, in print and paint shops, in semiconductor processing as well as in soil remediation and water treatment. Recent reviews of the subject were published by B.M. Penetrante et al. [44, 45] and by L.A. Rosocha [46, 47].

Many hazardous organic molecules are readily attacked by free radicals, electrons or UV photons. DBDs are utilized to provide reactive species such as N\textsubscript{2}(A'\textsubscript{3}\\Omega_{g})$, N\textsubscript{2}(B'\textsubscript{3}\\Pi_{g})$, O\textsubscript{2}(a'\textsubscript{1}\\Delta_{g})$, O(\textsubscript{1}D), O(\textsubscript{3}P), H, OH, and N. These species are initially generated by electron collisions in the microdischarge filaments and subsequently initiate a number of reaction paths generating additional O, OH or HO\textsubscript{2} radicals for decomposing pollutants.

3.5 Surface modification and surface coating
Plasma treatment of polymer surfaces to promote wettability, printability and adhesion has a long tradition [48, 49]. In many publications this process is referred to as “corona treatment”. In reality, in most applications a dielectric barrier is used to guarantee stable operation without arc formation. Large-area plastic foils are treated on one or both sides by passing them at high speed through a DBD maintained by an alternating high voltage applied between knife edge electrodes and a rotating drum covered by a dielectric. Electrode assemblies of several parallel knife edges or tube electrodes covered with dielectric layers are also used. Foils up to 10 m width are treated at speeds up to 10 m/s. This application requires discharge powers of about 100 kW. Useful operating frequencies are in the range 10-50 kHz.

As an additional process the deposition of thin films in DBDs has been investigated. A number of authors used homogeneous glow discharges for this purpose [50-52]. An
alternative approach has been taken by J. Salge and co-workers [53-56]. They showed that by using pulsed dielectric-barrier discharges microdischarge properties can be influenced in such a manner that superior surface modification and coatings of excellent quality can be obtained. Special power supplies were developed to generate repetitive pulse trains resulting in improved statistical distribution of the microdischarges across the surface, a prerequisite for uniform treatment. Working in acetylene pin-hole free polymeric films with properties resembling those of polycarbonate were obtained. Also thin deposits of silicon oxide were obtained at atmospheric pressure in an atmosphere of propargyl alcohol vapor and silane. In both cases the surface tension of polypropylene foils could be doubled.

The treatment of surfaces at low temperature and close to atmospheric pressure is an important advantage for large-scale industrial applications. It is to be expected that coating techniques using vapor or gas phase deposition in DBDs and also the annealing and oxidation of sol-gel films subjected to DBDs will be further developed.

4. Outlook: Catalytic dielectric-barrier discharges

In recent years research activities investigating the combination of DBDs and special catalytic substances have evolved. The idea is to enhance the selectivity of the plasma chemical reactions. In catalytic chemistry this selectivity towards certain desired reaction paths can often only be attained at high temperature and pressure. The immersion of a catalyst in a DBD plasma can substantially lower its apparent activation energy and achieve activity already at much lower temperature. Typical examples are different types of packed bed reactors in which pellets or granular materials are introduced into a DBD. We have investigated the inverse geometry, where DBDs are operated in miniature pores of reticulated ceramic foams [57]. The internal surface of the foam structure can be covered with catalytic coatings. This way close contact between the DBD plasma and a very large specific surface area with catalytic activity is established. Conceivable applications are utilization of greenhouse gases and gas to liquid conversion.

5. References
