Copious electron emission from triglycine sulfate ferroelectric crystals

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It is shown experimentally that the electron charge emitted from triglycine sulfate pulse ferroelectric cathodes can be as large as 129 μC/cm^2. This charge considerably exceeds the measured value of spontaneous polarization, P_s=2.8 μC/cm^2. A bipolar voltage is found to facilitate the appearance of the electron emission. It is proposed that the source of the emission current is the plasma of uncompleted surface discharges. This plasma is initiated at the metal-vacuum-dielectric triple points both by the field electron emission and the electron emission stimulated by polarization switching. © *1995 American Institute of Physics.*

I. INTRODUCTION

Any changes of spontaneous polarization of a monodomain ferroelectric disturb a charge balance between bound and screening charges that exist in thermodynamic equilibrium state. Relaxation of the appeared excessive electrostatic charges may occur by two quite distinct ways. The first one is the conductivity current flowing both in external short circuit through electrodes deposited on ferroelectric polar surfaces and in a crystal bulk. The second type of this relaxation process is the ferroelectric electron emission (FEE) from a ferroelectric free surface into vacuum.[1] One of the methods to generate the FEE is switching of the spontaneous polarization.[2,3] Visualization of the electron flux makes it possible to image the basic switching stages such as nucleation of new domains and sideways motion of domain walls. The FEE effect is observed in a ferroelectric phase only and it disappears when the crystal temperature exceeds the Curie point.[1] The TV movie of the switching process demonstrates that FEE is caused by the electrostatic field generated on a ferroelectric surface under the polarization reversal. Study of the switching of a low-conductive ferroelectric–ferroelastic crystal $Gd_2(MoO_4)_3$ shows that the FEE charge is large enough to screen the appeared depolarization field.[4] The measured FEE current of triglycine sulfate (TGS) crystals reaches 10^{-7} A/cm^2.[5] Estimations demonstrate that the emitted electron charge for all crystals studied may reach hundreds of nanocoulombs but it never exceeds the value of P_s.

In recent years numerous works have been carried out to create powerful ferroelectric cathodes.[6–11] In works which were done at CERN pulsed PLZT (lead lanthanum zirconate titanate) cathodes have been developed.[6,7] The electron current density was as high as 100 A/cm^2 and the emitted charge attained the value of 1.5 μC/cm^2. These results have been confirmed by other authors.[9,10] It was proposed there that the fast polarization reversal was induced by the application of high voltage to ferroelectric ceramics. The emitted charge recorded in all experiments did not exceed several percentages of the value of the spontaneous polarization for used PLZT ceramics. Thus, irrespective of the studied ferroelectric materials and experimental conditions the emitted charge was always less than P_s. The current of emitted electrons was suggested to be related to ferroelectric properties of the ceramics used.[7] Nevertheless, several results show that this kind of electron emission is observed above the Curie point also.[11] Thus, contemporary experimental and theoretical data cannot unambiguously explain the microscopic mechanism of the emission and of the repetitive regeneration of the electrons to be emitted.

It must be said that dielectric cathodes have been known almost for 30 years.[12–14] A high-density pulsed electron emission current reaching 10^3–10^4 A/cm^2 in a nanosecond time scale was obtained from barium titanate ceramic.[13,14] These cathodes were successively used as electron sources for accelerators. The authors of these works proposed that the source of the electron emission is the plasma generated by uncompleted surface discharges on a dielectric surface. The discharge parameters were studied by electrophysical probes and optical and spectroscopic diagnostics.[15–20] The plasma consisted of ions of desorbed adatoms and the ions of the used dielectric material and cathode surface. It is noteworthy that a strong electron emission was observed for both polarities of applied voltage (0.4–4 kV).[15,16] In a recent work it has been shown that microdischarges are initiated at the triple points: metal-vacuum-barium titanate.[21] It has been suggested that the electron emission from ferroelectric cathodes is caused by an explosive emission at the triple points followed by the surface flashover formation. As is known, $BaTiO_3$ is a ferroelectric material, and the high electric stress that was used in these experiments could lead to a polarization switching; however, the authors of these works did not mention any polarization switching which might take place.

In this work we present new experimental results on simultaneous study of polarization switching and an electron emission.

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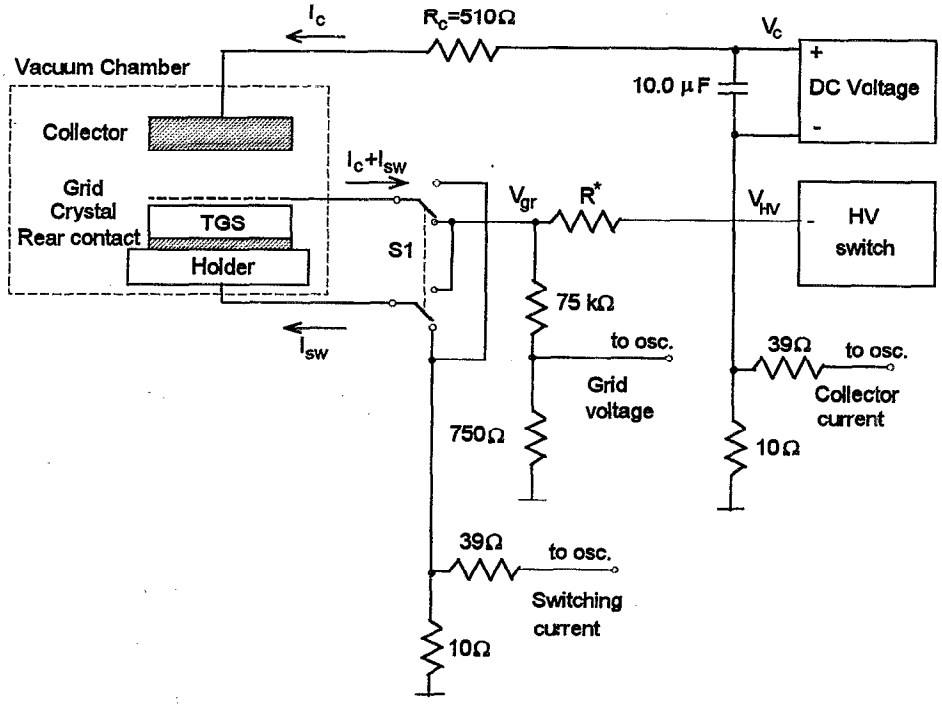


FIG. 1. Schematic circuit of the experimental setup.

II. EXPERIMENTAL TECHNIQUES

TGS polar *Y*-cut plates of a rectangular shape were used. Measured by the Sawyer–Tower circuit values of spontaneous polarization P_s and of coercive field E_c were as follows: P_s=2.8 μC/cm^2, E_c=400 V/cm. The experimental setup is shown in Fig. 1. A TGS sample was mounted on a copper holder. One of the polar surfaces of the samples was coated with a silver paint. A metal grid was pressed against the free-surface face of the crystal. Copper (3 μm thick) nickel (5 μm thick), and stainless-steel (50 μm thick) grids were used. The negative high-voltage pulse V_{HV}, with amplitude up to 1.5 kV, from the transistor switch was applied between the solid silver contact and the metal grid through resistor R^*. By means of the mechanical switch S1 the negative voltage was applied either to the metal grid or to the rear solid electrode, which made it possible to operate in bipolar mode when the stress was successively applied to the metal grid and then, after about 1 s, to the rear contact. The pulse duration of the high-voltage switch was in the range 20 μs–2 ms, and the internal resistance of the switch was 10 Ω. The turn-on time of the switch did not exceed 0.3 μs. The direct voltage applied to the collector was chosen in the range −1000–+1000 V. Resistors R^* and R_c=510 Ω limited the current of the high-voltage switch. A luminescent screen or a copper plate served as the collector. The separation of the metal grids and the anode was selected in the range 0.2–3 mm. The pressure in the vacuum chamber was 10^{-5}–10^{-6} Torr. All measurements were carried out at room temperature.

We controlled the current flowing through a sample (switching current), I_{sw}, the collector (emission) current I_c, and the voltage on a metal grid V_{gr} (Fig. 1). The electron flux was imaged by the luminescent screen. We studied the electron emission effect in two modes: under unipolar and under bipolar voltage pulses.

III. EXPERIMENTAL RESULTS

The experimental results are given in Figs. 2 and 3. Data of Fig. 2 correspond to the bipolar voltage mode for the TGS sample with initial spontaneous polarization directed toward the solid silver contact. The negative voltage V_{HV} = −920 V was applied to the nickel 5-μm-thick grid through resistor R^*. The switching current I_{sw} started simultaneously with high-voltage pulse. One can find that the switched charge density was 2.6 μC/cm^2. The collector current, $I_c \cong 1.1$ A, appeared after a small delay, $t_d \cong 1.2$ μs. These values were reproduced from shot to shot. The emitted charge was 24 μC. The duration of the emission current, 22.4 μs, was less than the duration of the voltage pulse. Sometimes in these experiments the emission charge reached a value of 120 μC. It should be noted that the collector current had a rectangular form. One can see that the emission current was determined by the total resistance in the circuit "HV-switch–grid–collector's power supply:" $I_c \cong V_{HV}/\Sigma R_i$ = 1.16 A (Fig. 1).

The bipolar voltage applied to TGS samples led always to the polarization reversal. The amplitude of the switching current was higher when the voltage pulse was applied to the

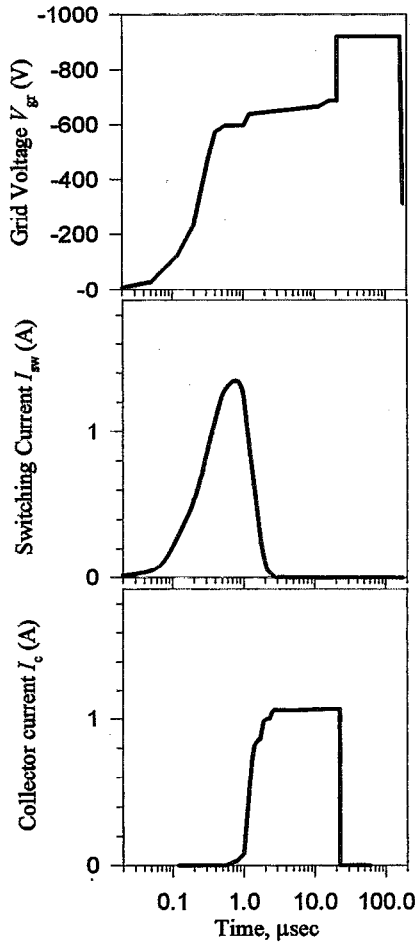
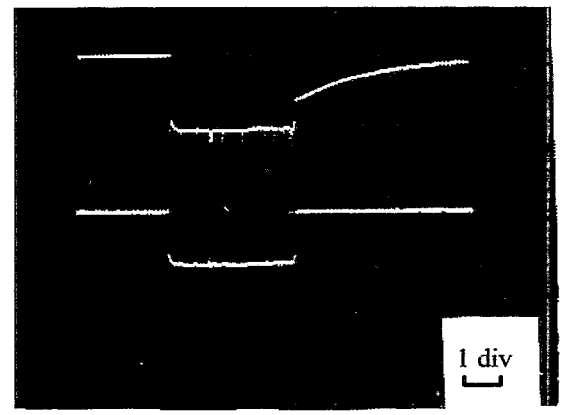
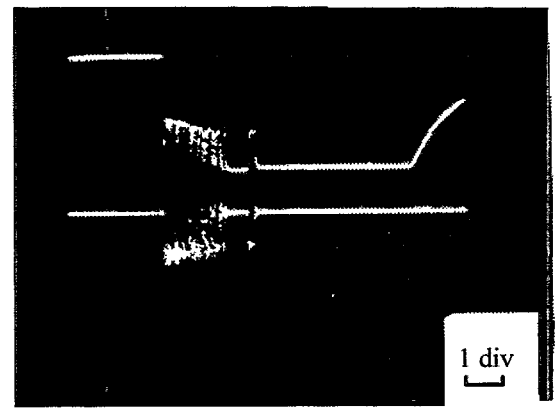


FIG. 2. The grid voltage V_{gr}, the switching current I_{sw}, and the collector current I_c as a function of time. The negative voltage $V_{HV} = -920$ V is applied to the nickel 5-μm-thick grid. The grid/collector separation is 1.3 mm. The resistor R^* is equal to 265 Ω. The TGS sample dimensions are $0.98\times0.95\times0.0465$ cm^3.



(a) $R^* = 275$ Ohm, $I_c = 0.68$ A, $Q = 42.8$ μC



(b) $R^* = 418$ Ohm

FIG. 3. Experimental data showing the voltage across a TGS sample [top of (a) and (b); 200 V/div]; collector current wave forms [bottom traces of (a) and (b); 0.5 A/div]. The time scale is 20 μs/div. The negative voltage $V_{HV} = -560$ V is applied to the copper 3-μm-thick grid. The grid/collector separation is 0.19 mm. The TGS sample dimensions are $0.96\times0.945\times0.049$ cm^3.

metal grid. A copious emission current appeared always when negative voltage was applied to the metal grid and, consequently, the positive end of the spontaneous polarization vector came out to the free surface after switching. Application of the negative retardation voltage to the collector showed that the measured emission current represented itself as an electron current. Luminescent points were observed when a luminescent screen was used as the collector. We would like to note that the anode current dropped to zero if the rear contact was not grounded or the pressure in the chamber raised to 1 atm. When negative pulse was applied to the rear contact any copious emission was not observed irrespective of the spontaneous polarization direction and of the collector voltage, but only isolated short pulses were detected.

In unipolar mode (without switching) the electron emission was also observed when negative voltage was applied to the metal grid. The amplitude and duration of the first collector current pulse was approximately the same as for bipolar mode; however, in this case the collector current appeared without any appreciable delay time. Subsequent negative pulse applied in several seconds to the grid stimulated the collector current as well. Usually duration of this current was shorter than the duration of the first collector current pulse.

Similar results were obtained with 3- and 50-μm-thick grids as well. It was established that the thicker the grid the higher must be the stress causing the collector current. Resistor R^* in the collector circuit (Fig. 1) limited not only the emission current but affected the shape of the emission current as well (Fig. 3). One can see that the increase of R^* leads to a discontinuity of the emission current while the current amplitude decreased rather feebly.

IV. DISCUSSION

Thus, the experimental results presented show that the application of high-voltage pulses to a ferroelectric causes

the appearance of copious electron emission. The effect occurs both under bipolar pulse voltage accompanied by the polarization switching and under unipolar pulse voltage. One can see that the emitted charge density (up to 129 $\mu C/cm^2$) exceeds the spontaneous polarization 2.8 $\mu C/cm^2$ by several dozens of times.

This electron emission cannot be explained by the field electron emission in the gap "collector–grid" because during the emission process the voltage across the gap V_{gap} was rather small, $V_{gap} = V_{HV} - I_c \Sigma R_i$, where ΣR_i is the total resistance in the circuit HV-switch–grid–collector's power supply. For Fig. 2 data V_{gap} is 70 V, for Fig. 3(a) data V_{gap} is 13 V. One can consider the field electron emission from the metal grid in the direction of the dielectric surface resulting in backscattered and secondary electrons. Only the scattered electrons that have enough energy to overcome a voltage barrier near the metal grid can create the collector current. Therefore, a rather low collector current should be accompanied by a rather high current between the metal grid and the dielectric surface. This is not the case in our experiments. We think that the only way to explain the results obtained is to explore the model of the plasma discharge that is formed between a dielectric surface and a collector.This plasma is initiated by the voltage pulse applied to the metal grid. Possible sources of the plasma that is formed above the dielectric surface are: (a) gas of the adsorbed molecules that are released during the dielectric surface discharge;[18] (b) gas of the atoms of a dielectric and a metal cathode that are sputtered off or evaporated during the dielectric surface discharge.[16] It is obvious that in the first stage of the discharge the emission of physisorbed molecules takes place because of a very low binding energy (0.05–0.15 eV).[22] A typical surface binding energy of dielectric atom is in the range 5–10 eV. Therefore, we assume that in our case the desorption process dominates. We would like to note that after the switching for several minutes in sinusoidal voltage (20 kHz), where a solid copper anode was used instead of the metal grid (Fig. 1), we observed a dielectric layer formed on the surface of the anode. This means that long-time periodical switching leads to the emission of TGS crystal atoms.

Contemporary theories assume that the dielectric surface flashover and, consequently, the desorption are stimulated by electron avalanche.[23,24] This avalanche can be caused by the secondary electron emission,[25–29] thermal breakdown,[28,29] electron cascade formation beneath the dielectric surface,[30] impact ionization,[31] and explosive relaxation of depolarization energy.[32,33] All theories recognize that the avalanche start is initiated by the field electron emission in the triple point: cathode (metal grid)–vacuum-gap–dielectric surface.[24] This emission is caused by the electric field in this point.

The experiments presented distinctly show that the application of the bipolar voltage always causes the reproducible stable emission effect from TGS crystals.Two processes can initiate the collector current: The first one is the classic field electron emission in the triple point and the second one is the electron emission stimulated by the polarization reversal.[2]

We propose the following scenario of the plasma discharge developing.When negative voltage is applied to the metal grid the electric field E in the triple point causes the field electron emission from the metal grid. Enhanced by a factor ϵ_r (relative permittivity), the electric field acting in a very thin vacuum gap between a spherical metal wire of the radius r and a dielectric laying on a metal plane[34] can be approximately expressed as

$$E_{gap} = \frac{\epsilon_r V_{HV}}{r \ln(2d_c/r)}, \tag{1}$$

where d_c is a crystal thickness. For the metal grid with diameter 5 μm, d_c=0.465 mm, ϵ_r=40 (static permittivity of TGS crystals), and the high tension 920 V, one can get $E_{gap}=2.49\times10^7$ V/cm. Using the Fowler–Nordheim equation[35] one can find for the nickel grid (work function 4.5 eV)[35] that the field emission current from the grid to the dielectric sample reaches the value 0.37 A/cm^2. This electron flux can stimulate the electron avalanche near the dielectric surface that leads to the desorption of atoms from the dielectric and the metal grid. This gas cloud expands and the cloud edge moves away from the dielectric surface at a velocity about 10^5–10^6 cm/s.[28] This means that the density of a limited gas cloud decreases in time. When the neutral density decreases to a critical value a gas discharge arises.[28] The average neutral number density of $\sim10^{18}$ cm^{-3} in the flashover region has been reported[23] and the time delay of the discharge start does not exceed several dozens of ns.[18,19,26] The time delay of the collector current in our experiments is $\Delta t \sim 1$ μs which approximately equals the polarization switching time (Fig. 2); therefore, we conclude that the plasma starts to form during the polarization switching. As was mentioned above, the TGS polar axis was preliminary oriented toward the rear contact (Fig. 1). Application of the high-voltage pulse to the metal grid leads to the polarization switching and large positive bound charge is generated on the free ferroelectric surface. As a result, the electrons from the plasma move to the surface to compensate this positive charge. It means that the plasma formed contributes to the switching; therefore, this can prevent the electron flux from moving toward the collector during Δt. After the switching is almost finished, the plasma expands and the electron swarm reaches the collector. The desorption continues until depleting of adsorbed layers (desorption of a monolayer takes a few microseconds[26]). When the plasma density decrease to some minimal value, a self-sustained discharge cannot continue[29] and the collector current drops to zero.

When the negative potential is applied to the rear contact of the ferroelectric sample, polarization reversal occurs and the negative end of the spontaneous polarization vector arises at the free polar surface. Large negative charge at the free surface leads to the generation of known ferroelectric electron emission.[1–5] Unlike the metal grid, the sample's free surface is flat; besides, the ferroelectric's ability for the electron emission is lower.[36] Thus, we think that a strong dielectric surface discharge does not start at the relatively low voltage used in our experiments. This also is confirmed by the data of Refs. 15 and 16 where it is shown that the collector

current for negative polarity of the voltage applied to the metal cathode is larger than for positive polarity, especially for low voltage.

It is clear that for TGS crystals it is difficult to separate the contribution of the above-mentioned two different electron emission currents—the field electron emission and the electron emission stimulated by polarization reversal—because every bipolar pulse is accompanied by polarization switching. Therefore, we carried out experiments with a $LiNbO_3$ crystal of 1 mm thickness which cannot be switched by the voltage $V_{HV}=-1.5$ kV ($V_c=1000$ V). The results were on the whole the same as for TGS crystals, however, the applied voltage was larger. The effect of the bipolar pulse in this case can be explained as follows.When negative voltage is applied to the rear solid electrode, field electron emission from the ferroelectric surface occurs. When negative voltage is applied to the metal grid appeared positive, surface potential that did not have time to relax increases the actual voltage in the vacuum gap. This means that the current in the triple point grows which increases the probability of the flashover formation. This assumption is supported by the fact that bipolar stress decreases the flashover voltage of dielectric isolators.[37]

Discontinuity of the collector current upon the increase of resistor R^* is not well understood yet. Possible an explanation could be as follows. The larger R^* is the lower is the voltage across the gap grid–collector; therefore, the rise of the emission current leads to the decrease of the voltage across vacuum gap. If the energy of electrons and ions becomes less than a critical value, the ionization process and desorption cease. Thus, the avalanche discharge in the plasma stops which in turn causes the voltage to increasing, etc.

It is interesting to compare the emission current obtained with the Child–Langmuir law,[38]

$$J_c=2.34\times10^{-6}\frac{V_{gap}^{3/2}}{d_{gap}^2}\ \frac{A}{cm^2}, \tag{2}$$

where d_{gap} is the separation of the metal grids and the collector. For $V_{gap}=70$ V and $d_{gap}=1.3\times10^{-1}$ cm, one can get $J_c=0.081$ A/cm^2. The experimental value is 1.15 A/cm^2. For $V_{gap}=13$ V and $d_{gap}=1.9\times10^{-2}$ cm the calculated current density is $J_c=0.30$ A/cm^2; the experimental value is 0.75 A/cm^2. The reason for the discrepancy obtained may be as follows: The plasma discharge creates a space-charge distribution that differs from the same one in the case of the thermionic vacuum diode.[39]

V. CONCLUSIONS

Thus, the observed copious emission charge from TGS crystals substantially exceeds the value of spontaneous polarization. It makes it possible to propose the formation of the plasma as a result of the surface dielectric discharge. The experiments show that two quite distinct processes can initiate generation of this plasma: The first one is the field electron emission and the second one is the electron emission stimulated by the spontaneous polarization switching. Study of the plasma formation during the surface dielectric flashover is in progress.

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