Low-voltage electron emission from thin \([\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]_{0.72} \text{[PbTiO}_3]_{0.28}\) single crystals induced by ferroelectric polarization switching

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Abstract. Electron emission from \([\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]_{0.72} \text{[PbTiO}_3]_{0.28}\) (PMN–PT) thin ferroelectric single crystals is reported at ultralow voltages down to 20 V per 400 \(\mu\)m thickness, and for up to \(10^9\) switching cycles. The PMN–PT samples were prepared with split gold top electrodes exhibiting a 25 \(\mu\)m wide gap region. Applying a sinusoidal voltage between the two top electrodes and the bottom electrode initiated electron emission from the gap region. The emitted electrons were collected under UHV conditions using two single electron counters arranged under an angle of 90°. Two emission regimes have been identified. Both are attributable to weak electron emission, however, clearly separated by the onset of complete ferroelectric polarization switching. This is also confirmed by recording nanoscale ferroelectric hysteresis loops by means of piezoresponse force microscopy. The emitted electrons are found to have a broad energy distribution with the maximum kinetic energies reaching 110 and 50 eV for applied switching voltages of 140 and 110 V, respectively. Our results confirm that polarization reversal is the governing mechanism behind the electron-emission process in the thin PMN–PT samples.

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Also, the applied electric field strengths needed to trigger electron emission from the PMN–PT crystals are about 10 times lower compared to most other (ferroelectric) materials reported in the literature.

Ferroelectric electron emitters are known to be a promising alternative to other cathode-type electron emitters (e.g. thermionic and tunnelling electron emitters), and have already found their way into applications, e.g. in microwave generators [1, 2]. In several years of research, many kinds of ferroelectric samples and electrode structures have been investigated in order to identify possible trigger mechanisms for ferroelectric electron emission (FEE) [3, 4]. One common feature in the FEE is the change in spontaneous ferroelectric polarization that may be induced, for instance, by pyroelectric or piezoelectric effects, through phase transitions of the material, or alternatively by applying an external electric field [4, 5]. Also, the emitted charges depend on the experimental details originating, for instance, either from a surface layer of the ferroelectric or from an electrode on top of the ferroelectric surface. Strongest emission currents were reported for complete switching of the ferroelectric polarization when the sample is biased by a large enough external voltage.

Two regimes of FEE can be discerned: the so-called ‘weak electron emission’ (WEE) is characterized by low-emission currents in the range of $10^{-14}$–$10^{-9}$ A cm$^{-2}$ [4]. Changes in the depolarization field give rise to strong electric fields near the ferroelectric surface, which repel the screening charges of the former polarization state. Usually, the top electrode is not in direct contact with the ferroelectric surface, but in close proximity leaving a small gap of some tens of micrometres. Emitted electrons have to cross this gap in order to reach the anode. Additionally, an extraction voltage may be applied to the anode to help electrons overcome the work function difference [6].

In contrast, ‘strong electron emission’ (SEE) shows current densities of up to 100 A cm$^{-2}$ [7]. A conductive but structured electrode is prepared directly on top of the ferroelectric leaving open some emission windows (apertures) on the ferroelectric surface. Various electrode structures have been tested with the most common one being a stripe-like electrode pattern of interdigitating fingers having a period of several hundreds of micrometres. High-tangential field components within the apertures parallel to the ferroelectric surface accelerate free-charge carriers and lead to the formation of a surface plasma that acts as a reservoir for mobile electrons and ions. Hence, the emitted charge density is drastically increased.

A wide range of different materials have been tested as ferroelectric electron emitters both for WEE and SEE. Most research though focused on thick crystals, ranging from organic single crystals such as TGS [8] to polycrystalline PLZT systems of different compositions [9]. Nevertheless, in order to extract electrons from a crystal of several hundred micrometres in thickness by complete polarization reversal needs a rather high voltage, mostly in the kilovolt regime, which is not compatible with the low operation voltage request for modern applications. Nevertheless, this request may be accomplished with thin ferroelectric emitters, at least as far as the low switching voltage issue is concerned. However, only very few reports exist on this topic [6, 10], and all of them seem to suffer from the low current densities achievable, as well as from the problem of how to fabricate reliable top electrodes that have a low short-circuit probability. Moreover, in order to achieve an electric field distribution within the aperture region favouring FEE from thin ferroelectric emitters needs a down scaling of aperture sizes, which clearly demands nanotechnological approaches to be implemented.
Here, we present to our knowledge the first results on ferroelectric electron emission from PMN–PT single crystals. These samples combine advantages of single crystallinity having low leakage currents with the thin film feature of low switching voltages on the order of approximately 3 kV cm\(^{-1}\). Furthermore, PMN–PT is of great general interest due to its high piezoelectric coefficients and is widely used in piezoelectric-related applications \([11]\). It is also used as a substrate for adsorbing different oxide thin films, in particular, for substrate–strain dependence measurements \([12]\).

The PMN–PT samples used here contain 28% lead titanate and therefore are in the rhombohedral relaxor-ferroelectric phase at room temperature. Both electrodes are made of \(\sim 60\,\text{nm}\) thick gold, and the top electrode is structured into two parts, left and right, leaving a 25 \(\mu\text{m}\) wide gap for electron emission. This method of electrode preparation avoids both unnecessary heating of the crystal and the formation of oxygen vacancies.

Investigations on the ferroelectric domain structure within the 25 \(\mu\text{m}\) gap by means of piezoresponse force microscopy (PFM) showed domain patterns with polarization components pointing both parallel and perpendicular to the sample surface plane \([13]\). The smallest detected domain size lies on the order of several hundred nanometres \([13]\).

After PFM inspection, PMN–PT samples were mounted on a goniometer holder (Panmure Instruments Ltd) that enables sample manipulation with six degrees of freedom, i.e. three for translation and three for rotation. This allows the allocation of any desired surface spot on the sample. For all experiments a sinusoidal ac voltage of 5 kHz was applied to the bottom electrode in order to periodically switch the sample polarization (see upper inset in figure 1). The amplitude was varied from 0 to 200 V. Emitted electrons were measured by two single electron detectors (MD 502, Amptek Inc.) mounted under a 90° angle at a distance of \(\sim 5\,\text{cm}\) to the sample. This corresponds to a numerical aperture of 0.03. Both detectors operate with a built-in +500 V extraction voltage to collect the emitted electrons.

To access also the energy distribution of emitted electrons, detector 2 was modified by positioning an electrically biased metallic TEM grid in front of the collector aperture (see inset in figure 2). The grid, on the one hand, screens the built-in detector voltage, whereas, on the other hand, acts as an energy filter when biased with a negative dc voltage. Then, only electrons that have a sufficient kinetic energy are able to overcome the repelling force from the grid and pass through to the detector. Note that all measurements were performed under ultrahigh vacuum (UHV) conditions at a base pressure of \(< 10^{-7}\,\text{mbar}\).

Figure 1 illustrates the dependence of the number of counted electrons on the voltage amplitude \(U_0\) applied to the bottom electrode. As mentioned above, an ac voltage \(U_\text{ac} = U_0 \sin(\omega t)\) was used and a continuous emission current was measured with an integration time of 1 s by detector 1. All data points shown in figure 1 were averaged over hundreds of measurements, and the plotted error bars represent the standard error of the mean values for all measurements. As can be seen, electron emission sets in already at voltages \(U_0\) of \(\sim 20\,\text{V}\) and increases quasi-linearly with rising voltage amplitude. Two distinct regimes for electron emission can be identified, characterized by different slopes of the measured count rate: the first one ranges from the onset of the emission up to \(U_0 \approx 80\,\text{V}\), where the second regime takes over. The dashed lines in figure 1 are linear fits to the two regimes, having corresponding slopes of 100 and 12 000 counts (V s\(^{-1}\)) for the low- and high-voltage regimes, respectively. For our 400 \(\mu\text{m}\) thick PMN–PT crystals used in this experiment, a drive voltage \(U_0\) of 80 V corresponds to an applied field of 2 kV cm\(^{-1}\) and therefore closely hits the coercive field values reported in the literature \([14, 15]\).
Figure 1. Dependence of electron emission count rate on voltage amplitude $U_0$ applied to the bottom electrode. The signal increases for higher voltages. Two regimes with different slopes can be identified: a low-voltage regime from 20 to 80 V with a slope of 100 electrons (V s)$^{-1}$, and a high voltage regime for larger voltage amplitudes having an increase of 12 000 electrons (V s)$^{-1}$. The respective slopes are indicated by the dashed lines. The error bars of the count rates represent the standard error of the mean values for all measurements. The upper inset depicts the electrical connections to the sample, whereas the lower inset shows the electron-emission count rate for applied voltage amplitudes $<80$ V.

In order to extract the kinetic energy of emitted electrons, the metal grid placed in front of detector 2 was biased with a negative dc voltage (see inset in figure 2). Hence, only electrons with a large enough kinetic energy overcome the repulsive field and are counted by detector 2. The measured count rates were normalized to the total emission signal as measured simultaneously by detector 1, which was used as an in-situ reference. Figure 2 illustrates the results for emission voltages of $U_0 = 140$ and 110 V applied to the bottom electrode. All count rates were normalized to the signal ratio for zero grid voltage measured by detector 1. As clearly seen, the signal decreases continuously for a rising negative grid voltage. This indicates a broad energy distribution of emitted electrons. Furthermore, we deduce from figure 2 the maximum kinetic electron energies of about 110 and 50 eV for the emission voltages of 140 and 110 V, respectively. This is much lower compared to the values of several kilovolts reported so far in literature for other samples and experimental setups [4]. In fact, the measured extraction fields manifest, to the best of our knowledge, one of the lowest ever reported values for electron emission from ferroelectrics.
Figure 2. Emission signal for different voltages $U_{\text{grid}}$ applied to the metal grid placed in front of detector 2 (see inset). The count rates were normalized to the signal with zero grid voltage. The measured signal continuously decreases in both curves that are collected for emission voltages of 140 and 110 V. This is interpreted as a broad energy distribution of the emitted electrons. The maximum energy corresponds to the first grid voltage with no counted electrons, and is determined to be 110 and 50 eV for emission voltages of 140 and 110 V, respectively.

Electron emission originates from the groove area between the two parts of the top electrode. To prove this, the experiment was repeated with the voltage applied to only one part of the top electrode. Then, only a very small emission signal in the range of 100 counts s$^{-1}$ could be detected for voltage amplitudes up to 200 V compared to the count rates shown in figure 1. If the emitted electrons stemmed from the electrode material or electrode edges, the measured count rates would be similar to the one shown in figure 1. Hence, for the onset of FEE a voltage must be applied from both the sides to a bare surface area.

In order to clarify the influence of ferroelectric polarization reversal, the switching behaviour of the PMN–PT samples was investigated by means of PFM. This technique is a well-established method [16] not only to map the ferroelectric domain distribution [13], but also equally to investigate the local switching behaviour on the nanometre length scale. In PFM [16], an atomic force microscope (AFM) is operated in contact mode, while an ac voltage is applied between cantilever and bottom electrode of the ferroelectric (or polar) sample. Due to the piezoelectric properties, the sample mechanically oscillates at the ac-drive frequency, and the cantilever transfers this oscillation into an oscillating electrical signal via a laser beam deflection. A lock-in amplifier records both amplitude and phase of the piezomechanical sample oscillation which are direct fingerprints of magnitude and orientation of the ferroelectric polarization, respectively. The domain distribution can be imaged by scanning the AFM tip across the surface. Moreover, by additionally applying a dc voltage to the system, a local hysteresis loop may be recorded (as shown in figure 3). The resolution in PFM is solely limited by the tip radius that usually falls in the range of several tens of nanometres; nevertheless, a 5 nm resolution has been reported in thin ferroelectric films [17].

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Figure 3. Hysteresis loops of PFM phase-signal measured directly on the crystal surface (a) and on the gold top electrode (b). The switching between two stable states is clearly seen in both curves. The coercive voltages are lower for free surface measurements (−15 and 20 V) than for electrode measurements (−60 and 75 V).

Local hysteresis measurements were performed on our PMN–PT samples with the AFM tip positioned either directly on the crystal surface or on the gold top electrode. The ac voltage frequency and amplitude were 20 kHz and 2 V, respectively. The dc voltage \( U_{\text{tip}} \) ranged from −120 to +120 V and was varied by 4.8 V s\(^{-1}\). A Topometrix Explorer AFM was used for the experiments and the PFM signals were measured by means of a Stanford Research Systems SR 830 lock-in amplifier. The phase of the PFM-signal was recorded for different voltages \( U_{\text{tip}} \) applied to the AFM tip. Figure 3(a) depicts the results for measurements performed directly on the ferroelectric surface, whereas figure 3(b) shows the case for the tip located on the top electrode. In both the images two stable states can be observed that correspond to the ferroelectric polarization pointing up and down in the out-of-plane direction (normal to the sample surface). Furthermore, the coercive voltages can be read as the voltage values where the phase changes drastically. The measured values are −15 and +20 V for the free surface measurements, and −60 and +75 V for measurements on the top electrodes. Note that a much larger voltage is needed to switch the larger area of \( \sim 2 \text{ mm}^2 \) below the gold top electrode as compared with the smaller area under the AFM tip. A reason for this might be that in a relaxor-ferroelectric material the long-range ferroelectric ordering is suppressed and therefore the switching process is different from usual ferroelectrics. There, the switching process starts with the appearance of nucleation centres that grow in the direction of the applied electric field with a reversed polarization state. This is followed by a sidewise motion of the domain walls until the whole material is switched. Disturbing this mechanism requires more nucleation centres in order to create complete polarization reversal. Additionally, the PMN–PT crystals used here are closer to the morphotropic phase boundary and several phase transitions take place when an external electric field is applied \([18]\). Thus, more energy is needed to activate the small randomly oriented polar nanoclusters existing in a relaxor-ferroelectric material below the electrode than in the smaller area below the AFM tip.

A comparison between the electron-emission measurements (figure 1) and the local hysteresis loops (figure 3) reveals that the coercive voltages of the electrode measurements very
much coincide with the threshold voltage of 80 V where the regime of strong electron emission starts (see figure 1). This confirms that polarization reversal is the governing mechanism behind FEE and that onset of complete switching increases the electron emission significantly. It should be noted that because of the electric field distribution, the ferroelectric polarization in the gap region is not reversed for the measured coercive voltages. A uniform field distribution can be assumed for the sample volume covered by the top electrode, whereas the free-surface area is only affected by fringing fields coming in from the electrode edges. This results in a lower electric field strength in the gap region. However, for increasing voltage amplitudes the electric field values are sufficient to switch the free-surface area as well which has been proven by the PFM measurements. This might also explain the continuous increase of the recorded emission rate for voltage values well above the coercive voltages measured on the top electrode. The switching voltages obtained from the hysteresis measurements on the free-crystal surface show that a smaller area can be switched with lower voltage values and the onset of the first emission regime for voltages between 20 and 80 V might be explained by local polarization reversal probably close to the electrode edges. Of course, the electric field distribution under an AFM probe is different to the one beneath the electrode edges but this could explain the small difference between the measured coercive voltage values and the threshold voltage for electron emission.

To date, the following picture describing FEE from our thin single-crystal ferroelectrics can be sketched. The voltage applied between the top and bottom electrodes induces a change of the dielectric polarization state that most likely starts at electrode edges due to the high electric field strength and gradient. Mobile charges close to the surface are repelled from the regions where polarization reversal has taken place. They are either pushed to non-switched regions of the surface area, collected by the top electrode, or repelled from the surface into vacuum. The larger the voltage, the larger the switched surface area, with the reversed region propagating away from the electrode edges to the centre of the groove. Hence, more charges are crowded together in the centre of the aperture and finally emitted through Coulomb repulsion. Whether polarization switching affects the whole surface area is a question that is still under debate; nevertheless, the electrons emitted from our samples possess a rather low kinetic energy, and therefore are accelerated by the biased top electrode only, and not by any additional electric fields such as that stemming from charges accumulating in the gap region or any plasma.

After several hours of operation, i.e. for \(\sim 10^9\) switching cycles in the strong emission regime at voltages larger than 80 V, the gold top electrode shows degradation and partially disappears. The emission current densities measured here are in the range of \(10^{-10} - 10^{-9}\) A cm\(^{-2}\) and thus fall into the WEE regime. Hence, a surface discharge effect involving a surface flashover plasma is unlikely to occur. Accordingly, no emission of positively charged particles could be detected which should be present if the surface is covered by a plasma. Electrode damage is the limiting factor for the lifetime of our PMN–PT singe-crystal emitter samples. A partial disappearance of the electrode material changes the capacitance of the emission structure and equally the effective area responsible for FEE. Hence, the FEE process becomes unreliable being reflected in large emission signal fluctuations. Accordingly, different electrode materials are needed in order to improve the long-time performance and stability of these samples. Note that applying a voltage \(>200\) V should be avoided since the piezoelectric effect generates large mechanical stress that leads to mechanical breakdown of the crystals for high voltages. However, the PMN–PT material itself is very well suited for operating for much longer times and switching cycles, provided that moderate voltage amplitudes are applied.

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In conclusion, we have shown electron emission from PMN–PT single crystals at very low applied electric fields. Two different regimes of electron emission could be identified, which are separated by the onset of complete polarization reversal under the top electrode at about 80 V. This was confirmed by measuring nanoscale ferroelectric hysteresis loops by means of PFM. Moreover, the energy distribution of emitted electrons could be determined. Since electrons are found to be accelerated by the external voltage only, the maximum energy is lower than the energy induced to the system by the external switching voltage. All energies between 0 eV and the maximum energy were found corresponding to a broad energy distribution, which did not change even when operating our devices for more than $10^9$ switching cycles. It should be noted that the whole sample/electrode system is far from being optimized thus leaving a lot of room for further improvements, such as the choice of electrode material, electrode design and driving voltage cycles. Nevertheless, the successful demonstration of electron emission from PMN–PT should be taken as the starting point for developing more sophisticated device structures.

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