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R. Gaynutdinov
Russian Academy of Sciences

M. Minnekaev
NRNU Moscow Engineering Physics Institute

S. Mitko
NT-MDT Co

A. Tolstikhina
Russian Academy of Sciences

A. Zenkevich
NRNU Moscow Engineering Physics Institute

See next page for additional authors

Authors
R. Gaynutdinov, M. Minnekaev, S. Mitko, A. Tolstikhina, A. Zenkevich, Stephen Ducharme, and V. Fridkin
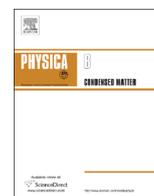
Polarization switching kinetics in ultrathin ferroelectric barium titanate film ☆

R. Gaynutdinov [a,*], M. Minnekaev [b], S. Mitko [c], A. Tolstikhina [a], A. Zenkevich [b,d], S. Ducharme [e], V. Fridkin [a]

[a] Institute of Crystallography, Russian Academy of Sciences, Moscow 119333, Russia
[b] NRNU Moscow Engineering Physics Institute, Moscow 115409, Russia
[c] NT-MDT Co., Moscow 124482, Russia
[d] NRC Kurchatov Institute, Moscow 123182, Russia
[e] Department of Physics and Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, NE 68588-0299 USA

A B S T R A C T

The investigation of polarization switching kinetics in an ultrathin barium titanate film reveals true threshold switching at a large coercive electric field, evidence that switching is of intrinsic thermodynamic nature, rather than of extrinsic nature initiated by thermal nucleation, which has no true threshold field. The switching speed of a 7 nm thick epitaxial film exhibits a critical slowing as the threshold is approached from above, a key characteristic of intrinsic switching. In contrast, a bulk crystal exhibits nucleation-initiated switching, which has no threshold, and proceeds even at fields well below the nominal coercive field, which was determined independently from the polarization-electric field hysteresis loop. Previously, this phenomenon was only reported for ultrathin ferroelectric polymer Langmuir–Blodgett films. Since both the thermodynamic coercive field and the intrinsic switching kinetics are derived from the mean field theory of ferroelectricity, we expect that these phenomena will be found in other ferroelectric films at the nanoscale.

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1. Introduction

From the time the discovery of polarization domains in ferroelectric crystals, the switching kinetics of ferroelectric crystals and thin films has been explained by the process of domain nucleation and domain wall motion [1]. The domain switching theory of Kolmogorov–Avrami–Ishibashi (KAI) successfully, for example, describes the polarization switching kinetics of ferroelectric crystals and even most thin films [2]. A recent review of domain switching in the ferroelectric crystals and films is presented in the book by Tagantsev et al. [3]. In the simplest case, KAI switching is dominated by an activated process, where the switching rate τ^{-1} has an exponential dependence reciprocal electric field E, as

follows [1,2,4,5]:

$$\tau^{-1} = C(T,E) \exp[-\alpha/E], \tag{1}$$

where the activation field α typically has a reciprocal dependence on the temperature T, and the prefactor $C(T,E)$ has a much weaker dependence on E and T [1]. Notice there is no threshold for switching, no true threshold coercive field E_C, because as the switching field is reduced, switching becomes progressively slower. The value of the extrinsic coercive field is typically obtained from the width of polarization-field hysteresis loops recorded at a fixed frequency, the so-called Sawyer–Tower method [6]. The coercive field obtained in this way is not the true coercive field, but the field at which the sample switches in a time of order of the reciprocal of the Sawyer–Tower frequency. If one decreases the frequency of the hysteresis loops, then the apparent coercive field is necessarily smaller, because the sample has more time to switch at a given voltage. Although other processes, such as finite domain wall velocity and pinning, can alter the dependence of the switching rate on electric field, deviating from Eq. 1, it is the initiation by nucleation that gives extrinsic switching its essential threshold-less character.

In contrast to the nucleation and domain growth kinetics, the intrinsic switching process derived from the mean field theory [7], does have a true threshold voltage and exhibits critical

behavior [8,9]. That is, in the infinite crystal switching is energetically impossible below a well defined mean-field coercive field E_C and becomes infinitely slow as the limit is approached from above. This is because such a homogeneous mean-field type process must proceed by collective polarization reversal by the entire domain (at least within the coherence length), or not at all. The dependence of the switching rate τ^{-1} on the applied electric field has the form near E_C as follows [10]:

$$\tau^{-1} = \beta(T)[E/E_C - 1]^{1/2}, \qquad (2)$$

where $\beta(T)$ also has critical dependence on temperature. The intrinsic thermodynamic coercive field E_C decreases steadily with increasing temperature. We note that according to Eq. (2) switching is only possible at the field above intrinsic coercive field, for $E > E_C$; there is a distinct threshold field for switching. Intrinsic switching is generally not observable in bulk crystals or thick films because the intrinsic coercive field is so large, of order 10^8 V/m, to over 10^9 V/m [8,9], much higher than the typical extrinsic coercive field of most samples. It is only possible to observe intrinsic switching in thin films or nanostructures that are smaller than the minimum critical nucleation size l_C, which is estimated to be of order 10 nm [11]. Such thin ferroelectric films have been available only in the last fifteen years. Examples include ferroelectric polymer films made by Langmuir–Blodgett (LB) deposition [12], and epitaxial ABO_3 perovskite films [13–15]. The first reported observation of intrinsic switching was made with the ferroelectric polymer LB films [8]. Other studies of switching at or approaching the intrinsic coercive field involve ultrathin epitaxial films of lead zirconate-titanate [16] and lead titanate [17].

Prior studies of polarization switching in ultrathin ferroelectric polymer film capacitors have revealed the intrinsic coercive field [8] and confirmed the functional form (Eq. (2)) of intrinsic switching kinetics [10], as predicted from the LGD theory, as long as the film thickness was below the critical thickness of approximately 15 nm. Furthermore, we have observed extrinsic switching behavior at the nanoscale in ultrathin ferroelectric polymer films using a conducting-tip atomic force microscope (AFM) to initiate switching on a film without a top electrode, and piezoresponse force microscopy (PFM) to monitor the polarization resolution locally [18]. In this paper, we report the results of a similar study of the switching kinetics of barium titanate (BTO). Using AFM switching and PFM monitoring, we found that a 7 nm thick BTO film also exhibited intrinsic switching kinetics with a critical threshold behavior on switching voltage, consistent with an intrinsic switching process. We highlight the qualitative difference in behavior by measuring the switching kinetics in a bulk single crystal 1 mm thick in comparison to an epitaxial thin film only 7 nm thick.

2. Experimental methods

The BTO single crystal (MaTecK GmbH, Germany) was cut and polished into a $1 \times 10 \times 5$ mm^3 slab. The sample thickness was 1 ± 0.1 mm along the spontaneous polarization [1 0 0] direction, which was normal to the large crystal face. Carbon adhesive tape was used at the ground electrode on one large face. Ultrathin heteroepitaxial BTO/Pt bi-layers were grown by the pulsed laser deposition (PLD) technique on a polished single-crystal MgO (0 0 1) substrate 10×10 mm^2 in size and cut in [0 0 1] direction. A home-made PLD setup with the base pressure P≈10–6 Pa was used to ablate from Pt and sintered stoichiometric BTO targets with a YAG:Nd laser ($\lambda = 1064$ nm) operating in the Q-switched regime (pulse length 15 ns) with the variable output energy ranging from 50 mJ to 200 mJ and a repetition rate 5–50 Hz [19,20]. An epitaxial Pt underlayer 10 nm thick was grown at a substrate temperature of 250 °C in ultra high vacuum on the MgO

substrate that was previously annealed at 600 °C for 30 min prior to deposition. The 2–15 nm thick strained heteroepitaxial BTO films were grown on top of the Pt layer in the same vacuum cycle at a substrate temperature of 550 °C at an oxygen pressure of 0.1 Pa and annealed at 550 °C at an oxygen pressure of 1 Pa for 30 min. The thickness of the BTO film used for this study was 7 ± 1 nm, as measured by Rutherford backscattering spectrometry (RBS) with 2 MeV He^{++} ions [20]. The structural properties of BTO/Pt/MgO samples were investigated by the channeling mode in RBS and the cross-sectional transmission electron microscopy (TEM), as described in detail elsewhere [19,20]. The structural quality of BTO(0 0 1)/Pt(0 0 1) heteroepitaxial growth on MgO(0 0 1) is illustrated by the high resolution cross-sectional TEM image (Fig. 1a) and the fast Fourier transform taken at both MgO/Pt and Pt/BTO interfaces (Fig. 1b, c).

The polarization hysteresis loops and kinetics of switching in these films was investigated by piezoresponse force microscopy (PFM). Measurements were carried out with a scanning probe microscope (NTEGRA PRIMA, NT-MDT, Moscow) operating in contact mode for imaging of topography by atomic force microscopy (AFM) and relative polarization by PFM. Sharp tips of soft silicon cantilevers (CSC21, MicroMash, Estonia), which were coated with a Ti–Pt conductive layer, have an estimated radius of 40 nm and an estimated imaging resolution of 60 nm [21]. The piezoresponse was imaged in contact mode by applying an excitation voltage of amplitude 1.0 V to the tip with respect to the bottom Pt electrode at a frequency 350 kHz, and recording the amplitude and phase of the resulting tip deflection signal from the cantilever position detector using a lock-in amplifier. The piezoresponse image consists of an x–y map of the composite PFM signal, which is equal to the PFM amplitude times the sine of the PFM phase. The measurements were carried out in air in a class 100 clean room maintained at temperature 24 ± 0.05 °C and relative humidity 40 ± 1%. The sample temperature was held at 24 °C for all reported measurements.

3. Results and discussion

The nanoscale ferroelectric properties of the BTO samples were probed by PFM imaging and hysteresis measurements. To test polarization reversal and stability, the initially unpolarized 7 nm thick BTO films were uniformly polarized by scanning the AFM tip in contact mode with a −6 V bias over a 2×2 μm^2 square, taking 15 min to complete the scan. This was followed by a PFM imaging scan recorded at zero bias (Fig. 2a), showing that the polarized region had a uniform piezoelectric response. (The white dots in the image are regions that were switched by +6 V bias applied for 10 s at a fixed location.) These images show that the film polarization could be switched locally and remained stable for a day or more.

The local ferroelectric properties of the bulk and thin film BTO samples were probed by recording piezoelectric hysteresis loops recorded at a fixed location in contact mode. This was done by first saturating the polarization with a −6 V bias applied to the AFM tip for 20 s. followed by series a brief 1 s voltage pulses in 0.05 V steps from –6 V to +6 V and back to –6 V. The hysteresis loops obtained in this way (Fig. 3) show well-saturated hysteresis loops. The hysteresis loop from the 1.0 mm thick BTO crystal (Fig. 3a) yields an average coercive voltage of 1.3 ± 0.2 V (from the half-width of the loop).

It is difficult to estimate the value of the effective coercive field when the crystal thickness is much larger than the AFM tip radius [22], but one estimate is to take the average field over the typical nucleation radius, which is of order 260 nm in BTO [23], to yield an effective coercive field $E_C = 5$ MV/m, which is much smaller than
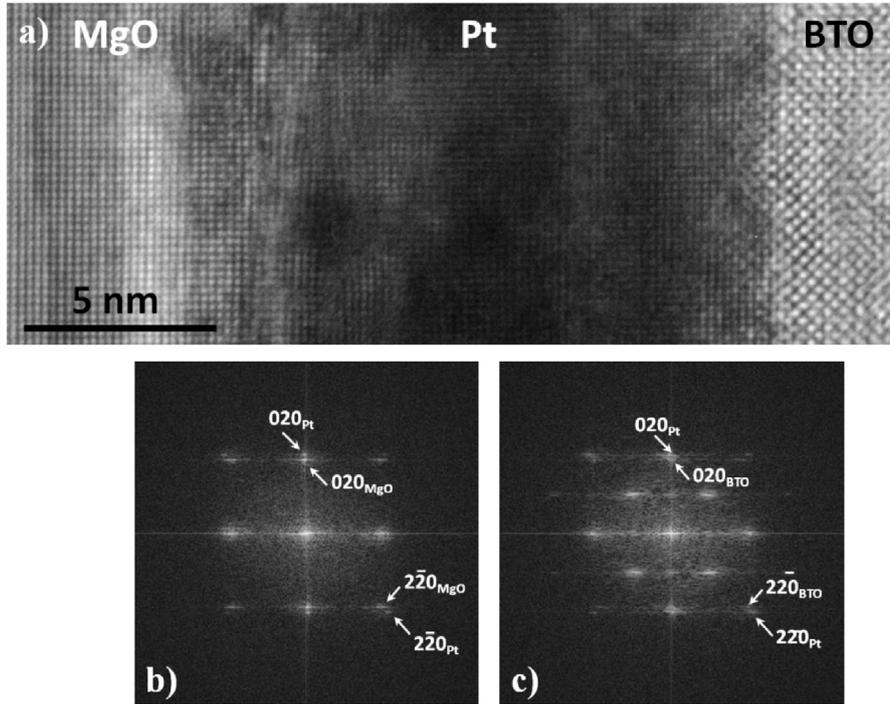
Fig. 1. Cross-sectional electron microscopy employing Zeiss–Libra 200 FE high resolution microscope from the MgO/Pt/BTO epitaxial thin film sample. (a) A cross-sectional lattice image showing the three layers. Fast Fourier transforms from the (b) Pt/MgO interface and (c) the Pt/BTO interface.
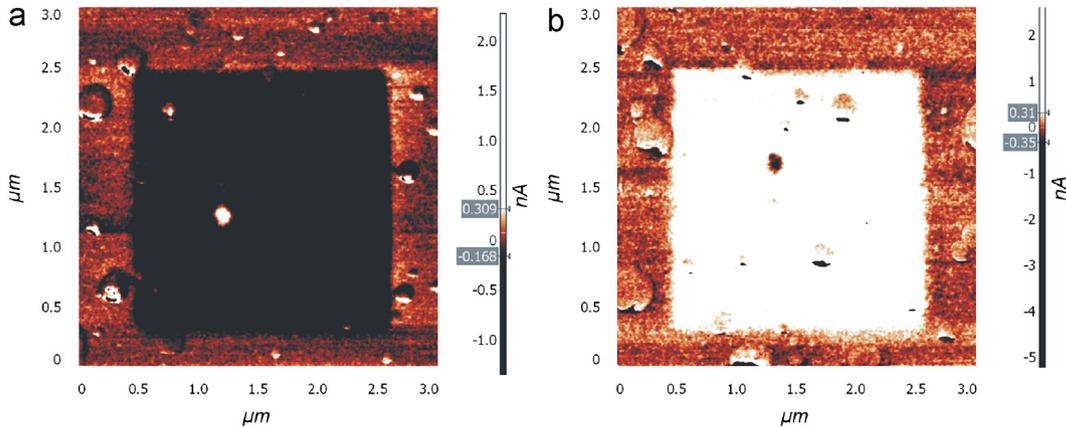
Fig. 2. Images representing the PFM amplitude times cos(PFM phase) over a 3 μm by 3 μm square section of the epitaxial film sample. (a) The PFM image recorded after polarizing a 2 μm by 2 μm square area with –6 V tip bias. The bright spot was obtained by application to the tip a bias voltage of +6 V for 10 s. (b) The PFM image recorded after polarizing a 2 μm by 2 μm square area with +6 V tip bias. The black central spots were obtained by application to the tip a bias voltage of –6 for 10 s.

the value of 70 MV/m for thermodynamic coercive calculated from the mean field theory [9]. The hysteresis loop from the 7 nm thick BTO film (Fig. 3b), on the other hand yields an average coercive voltage of 1.1 ± 0.2 V and a coercive field $E_C = 160 \pm 30$ MV/m, which is somewhat larger than the value of 70 MV/m for thermodynamic coercive calculated from the mean field theory [9]. This is in part due to the fact that even the relatively slow process of recording the hysteresis loop in 1 s steps results in an overestimate of the true threshold field. Such threshold field is better determined from the Eq. (2), in the limit of long switching times. To do this, we turned to a study of switching kinetics.

The switching kinetics were measured at a fixed location as a function of the amplitude and duration of a voltage applied to switch the polarization state. Each measurement was performed by applying –6 V (+6 V) to the tip for 100 s to saturate the film in the negative (positive) polarization state. Then, a positive (negative) pulse of specified voltage and duration was applied to set a

new polarization state. Finally, the piezoresponse for the new polarization state was measured at zero bias. The results of these switching pulse measurements (Fig. 4) show that for each pulse amplitude, the PFM signal crossed zero for a specific pulse duration, which we designate τ, the characteristic switching time for applied voltage V [18,24].

While the zero-crossing time τ is not strictly equal to the switching time [25], we are interested here in how this time interval scales with switching voltage. This allows us to probe the most fundamental question of this investigation, whether or not there is a true switching threshold (Eq. (2)) or an activation process (Eq. (2)).

For the bulk BTO crystal, the dependence of the switching time τ on voltage pulse amplitude V fits very well to the exponential form of Eq. (1), as shown in Fig. 4c, where the solid lines are least-squares fits to Eq. (1), yielding an average activation voltage of 7.0 ± 0.25 V. If we consider that the effective thickness for
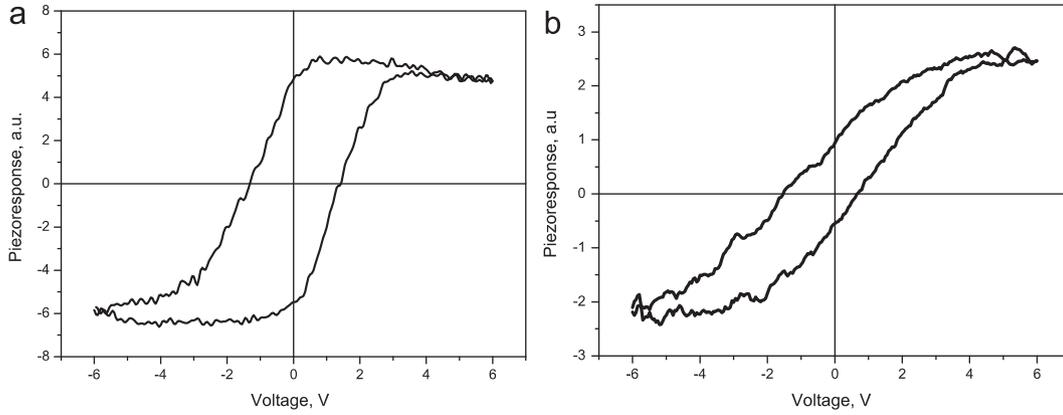
Fig. 3. Hysteresis loops, measured by a pulse-measure method for: (a) the BTO crystal and (b) the BTO film.
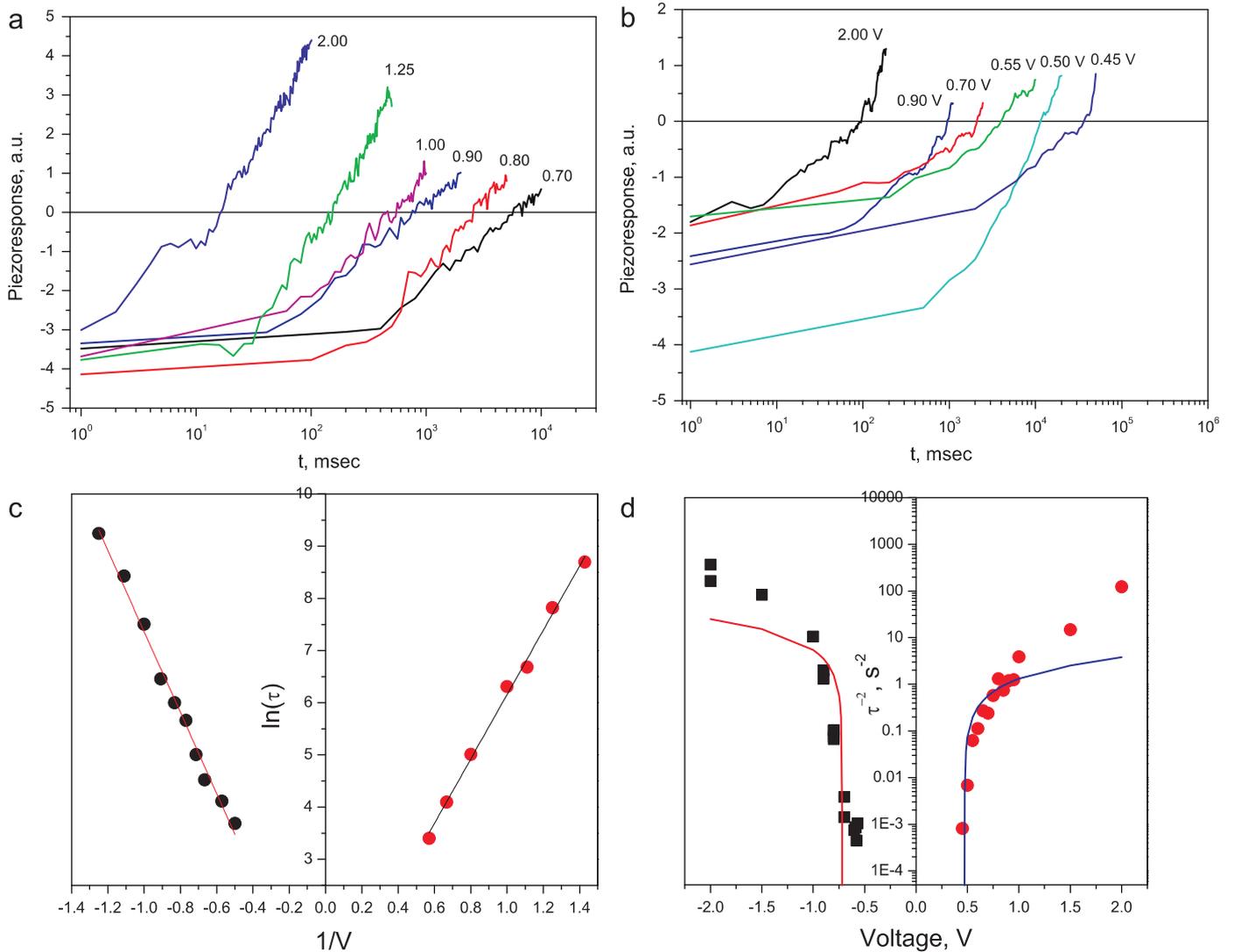
Fig. 4. Peak PFM signal after switching a function of switching pulse duration for: (a) the BTO crystal at pulse amplitudes as indicated and (b) the BTO film at pulse amplitudes as indicated. The voltage dependence of the switching time obtained from the zero-crossing of PFM signal vs. pulse duration graphs for: (c) the BTO single crystal and (d) the BTO film. The solid lines are least-squares fits to Eqs. (1) and (2), in parts (c) and (d), respectively.

switching is of order 10 nm [26], then we obtain from the data in Fig. 4c results a value for the activation field $\alpha \pm$ of order 1.4 MV/m. Fig. 4c also shows that polarization switching in the bulk crystal gave no indication of a threshold, or true coercive field, near the coercive voltage of ± 1.3 V obtained from the hysteresis loop

(Fig. 3a). The switching time varies smoothly as a function of voltage, as expected from Eq. (1), even below the nominal coercive voltage.

The distinction between the intrinsic and extrinsic behavior is well illustrated in Fig. 4d which shows switching rate (reciprocal

switching time) as a function of the bias voltage for the ultrathin epitaxial BTO film. The switching shows a distinct threshold, a true coercive field, with the switching rate decreasing precipitously as this threshold is approached from above. The solid lines are least-squares fits to Eq. (2), where the threshold coercive field averaged for both signs is 84 MV/m, which is much closer to the thermo-dynamic coercive field of 70 MV/m. Eq. (2) reproduces well the critical behavior near the coercive field E_C, but not as well the behavior at much higher fields, where extrinsic nucleation and domain growth will dominate switching dynamics [11]. This is because rate of extrinsic switching depends exponentially on the applied field (Eq. (1)), while the rate of intrinsic switching process only increases as the square root of the field (Eq. (2)). The extrinsic nature of the high-field regime was well illustrated by the recent work of Chanthbouala et al. [27], who imaged domain processes occurring at switching fields more than an order of magnitude higher, well into the extrinsic regime.

4. Conclusions

These results highlight the qualitative difference in switching kinetics between bulk crystals and ultrathin films of barium titanate, the very material that led Mertz to formulate the nuclea-tion initiation model of polarization switching in bulk ferroelectric crystals [28]. The bulk crystal of BTO exhibits the familiar expo-nential dependence of switching time on field of nucleation limited switching behavior, which is described by Eq. (1), has no true threshold, and switching that proceeds at fields well below the thermodynamic coercive field. The 7 nm thick epitaxial film of BTO exhibits a distinct threshold for switching, a true threshold close to the expected thermodynamic coercive field, and exhibits switching kinetics corresponding to intrinsic polarization switch-ing [10], as described by Eq. (2).

The results are consistent with the expected transition from extrinsic to intrinsic behavior [8], which should occur at a thick-ness comparable to the crucial nucleation size, which is of order 10 nm for oxide ferroelectrics [11]. The observation of intrinsic switching polarization behavior in ultrathin BTO films demon-strates that this behavior is not unique to ferroelectric polymers, and therefore may be a general property of ferroelectric materials. As with the polymers, it will be useful to further explore the nature of polarization switching on temperature [10] and thick-ness [8], as well as on nanostructure and epitaxial strain, and in other kinds of ferroelectric materials. The results will be particu-larly pertinent to applications of ferroelectric thin films and nanostructures.

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