University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Stephen Ducharme Publications | Research Papers in Physics and Astronomy

10-1-2011

Polarization switching at the nanoscale in ferroelectric copolymer thin films

R. V. Gaynutdinov
Institute of Crystallography, Russian Academy of Sciences, Moscow

S. Mitko
NT-MDT Co., Moscow

S. G. Yudin
Institute of Crystallography, Russian Academy of Sciences, Moscow

V. M. Fridkin
Institute of Crystallography, Russian Academy of Sciences, Moscow

Stephen Ducharme
University of Nebraska-Lincoln, sducharme1@unl.edu

Follow this and additional works at: http://digitalcommons.unl.edu/physicsducharme

Part of the Physics Commons

Gaynutdinov, R. V.; Mitko, S.; Yudin, S. G.; Fridkin, V. M.; and Ducharme, Stephen, "Polarization switching at the nanoscale in ferroelectric copolymer thin films" (2011). *Stephen Ducharme Publications.* Paper 72.
http://digitalcommons.unl.edu/physicsducharme/72

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Stephen Ducharme Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Polarization switching at the nanoscale in ferroelectric copolymer thin films

R. V. Gaynutdinov,[1] S. Mitko,[2] S. G. Yudin,[1] V. M. Fridkin,[1] and Stephen Ducharme[3,a)]
[1]*Institute of Crystallography, Russian Academy of Sciences, Moscow 119333, Russia*
[2]*NT-MDT Co., Moscow 124482, Russia*
[3]*Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, USA*

(Received 25 August 2011; accepted 15 September 2011; published online 5 October 2011)

The polarization switching kinetics were measured at the nanoscale in continuous thin films of a ferroelectric copolymer of vinylidene fluoride and trifluoroethylene. The dependence of the switching rate on voltage for a 54-nm thick film exhibits extrinsic nucleation and domain-growth type kinetics with no true threshold coercive field, and is qualitatively different from the behavior of an 18-nm thick film, which exhibits intrinsic switching kinetics, and a true threshold field. The results are consistent with studies of thin film capacitors of much larger area and with a recent refinement of the theory of the critical size for intrinsic switching. © *2011 American Institute of Physics*. [doi:10.1063/1.3646906]

Since the early studies of ferroelectric crystals, it has been understood that polarization switching, reversal in an opposing electric field, is generally a complex inhomogeneous process involving domain nucleation and growth.[1,2] This process can be understood in terms of the Kolmogorov-Avrami picture of inhomogeneous phase transformation, where local fluctuations initiate the conversion to a lower energy phase.[3,4] In the case of ferroelectric polarization switching, the lower and higher energy "phases" are the polarization states parallel and antiparallel, respectively, to the external electric field.[5] According to mean field theory,[6] the polarization state of a ferroelectric crystal *can* switch homogeneously, without forming domains, but it must be subject to an electric field large enough to overcome the very large energy barrier associated with the long-range correlation of the polarization.[7] The intrinsic coercive field is enormous, of order 10^8 V/m (Ref. 8) to 10^9 V/m,[9] so much larger than the observed coercive fields as to render the intrinsic switching process practically inaccessible; intrinsic switching will be dominant. Because of this, the opportunity to observe intrinsic switching processes comes only in the case of crystals that are thinner than the size of a critical nucleus, the minimum size necessary for domain growth. Landaur estimated this thickness to be of order 1 μm in the case of barium titanate,[7] but experimental studies found that inhomogeneous switching processes continue to dominate in much thinner films.[10] Gerra *et al.*[11] have revised the calculation of critical size for barium titanate and find it to be approximately 10 nm, indicating that homogeneous nucleation should be observable only in ultrathin ferroelectric films.

Pertsev *et al.*[12] measured coercive fields exceeding 10^9 V/m in lead zirconate titanate (PZT) films as thin as 8 nm. Although the measured coercive field was comparable to the theoretical intrinsic value, the authors attributed the large value to substantial enhancments from epitaxial strain and from a conductive nonferroelectric layer[10,13] and, therefore, did not conclude that their results confirmed the observation of intrinsic switching. We found that the coercive field of a vinylidene fluoride-trifluoroethylene copolymer reached the value of the intrinsic coercive field for films with thickess of 15 nm or less, along with the suporting evidence that the temperature dependence agreed very well with mean field theory.[14] Highland *et al.*[15] have demonstrated in a clever experiment that the critical thickness for domain switching may be as small as 5 nm for epitaxial lead titanate thin films. Instead of two metal electrodes, they used one metal electrode and an electrochemical double-layer virtual electrode. Although they could not precisely determine the value of electric field in the ferroelectric, they found that the films had no domains at the coercive voltage point, where the net film polarization was zero, and, therefore, concluded that the switching must be homogeneous.

Another distinctive feature of the switching mechanism is the kinetics, the evolution of the polarization with time after applying the switching field. Consider the switching rate Γ, which is the reciprocal of the characteristic switching time. For nucleation-limited switching, being an activated process, the switching rate Γ has an exponential dependence on temperature T and reciprocal electric field E, as follows:[1]

$$\Gamma = \Gamma_{\mathrm{n}} \exp(a(T)/E), \tag{1}$$

where Γ_{n} is a constant and $a(T)$ typically has a reciprocal dependence on T. Notice that there is no threshold field, no true coercive field in this case, because as the switching field is reduced, switching just becomes slower. The effective coercive field obtained from polarization-electric field hysteresis loops, therefore, is really a function of the measurement frequency. Homogeneous switching, on the other hand, has a true threshold field, below which switching is impossible. The rate of homogeneous intrinsic switching, which is also obtained from mean field theory,[9,16] has a true threshold coercive field E_{C} and a critical dependence on electric field E, as follows:[17]

$$\Gamma = \Gamma_{\mathrm{h}}(T)\mathrm{sqrt}(E/E_{\mathrm{C}} - 1), \tag{2}$$

where $\Gamma_{\mathrm{h}}(T)$ decreases smoothly toward zero as the temperature increases toward the transition temperature. Notice that switching is only possible at fields above the coercive field; the switching rate is imaginary when $E < E_C$. We found that

[a)]Author to whom correspondence should be addressed. Electronic mail: sducharme1@unl.edu.

 © 2011 American Institute of Physics

the switching dynamics of the ferroelectric copolymer agree well with Eq. (2) for films thinner than 18 nm and with Eq. (1) for thicker films.[17] Most remarkably, we found that, in agreement with the factor $\Gamma_h(T)$, the switching rate *decreases* with increasing temperature in the thinner films, which is the opposite of the nucleation-limited case, where the switching rate *increases* as temperature increases. The previous results were obtained with thin film capacitors having macroscopic sized electrodes of approximately 1 mm^2, much larger than the crystal size of approximately 30 nm to 50 nm.[18] Here, we report a similar study of switching kinetics at the nanoscale in films 18 nm and 54 nm thick, by using an atomic force microscope (AFM) to probe the local polarization state by means of the piezoelectric response.

The samples for the present study consisted of a crystalline silicon substrate, 50-nm thick aluminum electrodes, and a ferroelectric copolymer thin film. The electrodes were deposited onto the substrate by vacuum evaporation. Then, the random copolymer of 70% vinylidene fluoride and 30% trifluoroethylene was deposited to the desired thickness by horizontal Langmuir-Blodgett (LB) deposition, as described in detail elsewhere.[19] Briefly, in this method, a dilute solution of the copolymer in dimethyl-sulfoxide (DMSO) was dispersed onto the surface of a trough of ultrapure water at room temperature. Barriers contacting the water surface slowly compressed the copolymer Langmuir layer to a surface pressure of 4 mN/m^2. The films were then deposited on the substrate layer-by-layer to the desired thickness, 30 layers for sample 1 and 10 layers for sample 2. The samples were annealed in the paraelectric phase to improve their crystallinity[20] and had a nominal thicknesses of 54 ± 5 nm for sample 1 and 18 ± 2 nm for sample 2.[21]

Measurements were carried out with a scanning probe microscope (model SOLVER P47 from NT-MDT, Moscow) operating in contact mode for imaging both topography by AFM and relative polarization and by piezoresponse force microscopy (PFM). The sharp tips of soft silicon cantilevers (model CSC21 from MicroMash, Estonia), which were coated with a Ti-Pt conductive layer, had an estimated radius of 40 nm and an estimated imaging resolution of 60 nm. The film topography (Fig. 1(a)) was imaged in tapping mode with a resonance frequency of 150 kHz and the piezoresponse in contact mode by applying an excitation voltage of amplitude 1.0 V and frequency 150 kHz to the tip, and recording the amplitude and phase of the resulting tip deflection signal from the cantilever position detector with a lock-in amplifier. The piezoresponse image (Fig. 1(b)) 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 10 000 clean room maintained at temperature 26 ± 0.05 °C and relative humidity $40\% \pm 1\%$. The sample temperature was held at 27 °C for all reported measurements.

The hysteresis loops (Fig. 2) were recorded at a fixed location on the film by a pulse-measure method, which consisted of applying a sequence of 1 s voltage pulses of varying amplitude and measuring the piezoresponse at zero voltage. The sequence of pulse amplitudes started at −10 V, increasing by 0.05 V steps to +10 V, then back to −10 V. The coercive voltage, which was obtained by measuring the half width of the hysteresis loop, was 6.1 ± 0.1 V for sample 1 and 4.2 ± 0.1 V for sample 2. Assuming that the threshold switching field is the field directly underneath the tip, the corresponding coercive fields were 110 ± 13 MV/m for sample 1 and 230 ± 26 MV/m for sample 2. These values are smaller that the value of 500 MV/m obtained for continuous LB films, and larger than the value of 50 MV/m typically reported for films made by solvent spinning[22] and also obtained from mean field theory by Iwata and Ishibashi.[8]

The switching kinetics were measured at a fixed point on the film by a prepare-pulse-measure method as follows. Each measurement was prepared by applying −10 V to the tip for 100 s to saturate the film in the negative polarization state (lower left of Fig. 2). Then, a positive pulse of given voltage and duration to set a polarization state. Finally, the piezoresponse for the polarization state was measured at zero bias. The switching time t for a given pulse amplitude was defined as the value of the pulse duration for which the resulting piezoresponse crossed zero, and the switching rate was calculated from $\Gamma = 1/t$.

The distinction between the intrinsic and extrinsic behaviors is well illustrated Fig. 3, which shows the dependence of the switching rate on the bias voltage for the two samples. For sample 1 (30 ML), the dependence of the switching rate on voltage agrees best with the extrinsic switching kinetics (Eq. (1)), as indicated by the dashed line. For sample 2 (10 ML), the switching rate data agree with the intrinsic switching kinetics. Notice that the switching rate for Sample 2 drops abruptly toward zero at the coercive voltage,

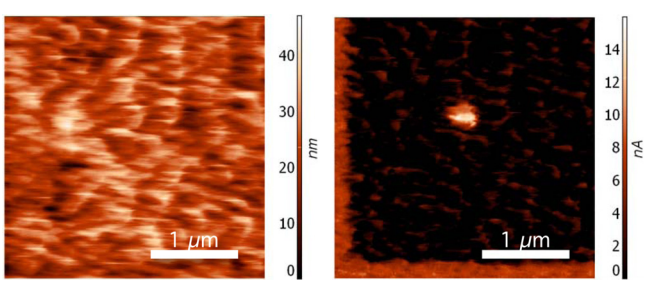

FIG. 1. (Color online) Images of Sample 1 (30 ML film) by (a) AFM topography; and (b) PFM amplitude times sine (PFM phase). The black area was polarized with a −10 V tip bias while scanning 3 μm by 3 μm square, taking 15 min to complete the scan. The bright central spot was then polarized with the tip stationary at a bias of +10 V for 10 min.

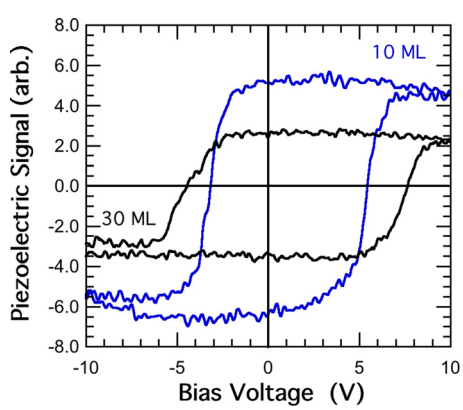

FIG. 2. (Color online) Hysteresis loops from P(VDF-TrFE) LB films measured with the pulse-probe technique, The data are from Sample 1 (30 ML, tall loop) and Sample 2 (10 ML, wide loop).

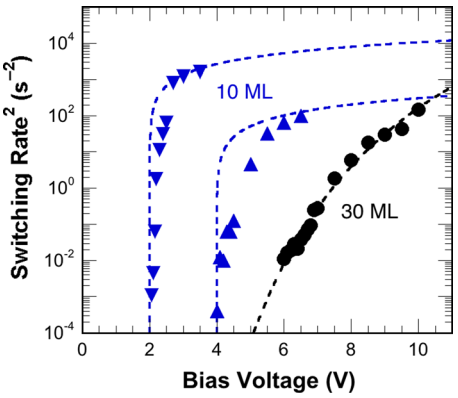

FIG. 3. (Color online) The voltage dependence of the switching rate $\Gamma(V) = 1/t(V)$ for P(VDF-TrFE) LB films as measured by the prepare-pulse-probe technique. For sample 1 (30 ML, black circles), the direction of switching was toward positive tip voltage. The black dashed line shows the fit of Eq. (1) to the data from Sample 1. For Sample 2 (10 ML, blue triangles), the direction of switching was toward positive tip voltage for up triangles and to negative voltage for down triangles. The black dashed line shows the fit of Eq. (2) to the data from Sample 2.

in excellent qualitative confirmation of the critical behavior inherent in intrinsic switching, as described by Eq. (2). For Sample 1, on the other hand, the switching rate shows only the gradual decline as the voltage decreases, showing no true coercive voltage and consistent with extrinsic switching, as describe by Eq. (1).

The results reported here, which were obtained with a continuous LB film by local voltage application using an AFM tip, are consistent with our previous results, which were obtained with flat aluminum electrodes on continuous LB films.[14,17] In all three studies, the qualitative nature of switching changed from extrinsic to intrinsic at a critical thickness in the range 15 nm to 18 nm, which is in reasonable agreement with the predictions of Gerra *et al.*[11] Other studies of the coercive field or of kinetics of ferroelectric copolymers mostly involved films much thicker than the critical thickness and were consistent with extrinsic switching mechanisms.[23–25] For example, the latter two studies[24,25] argue that the electrode material determines the nature of switching, but the present results, as well as our prior studies[14,17] show that both intrinsic and extrinsic nature can be found with the same electrode configuration and film fabrication technique, by changing only the film thickness. One study of switching kinetics in ferroelectric copolymer films made by Langmuir-Blodgett deposition found the high coercive fields, up to 10^9 V/m, expected for intrinsic switching, but with kinetics better matching extrinsic switching (Eq. (1)).[26]

Other studies have shown that thickness is not the only criterion—nanoscale morphology also plays a role in determining the nature of switching in ferroelectric copolymer thin films. For example, nanomesas, which are formed by self-assembly from the LB films of ferroelectric copolymer, are approximately 10 nm thick and 100 nm in diameter.[27] Capacitors made from large arrays of nanomesas exhibit extrinsic switching, with low coercive field and no exponential field dependence (Eq. (1)).[28] Nanoscale studies of individual nanomesas, using the same AFM-based techniques as in the present work, also reveal extrinsic switching behavior.[29] It is possible that the shape and size of the nanomesa, or perhaps chain folding during the annealing process used to induce self-assembly,[30] promotes surface nucleation even below the critical thickness. Imaging of domain patterns within the nanomesas by PFM support this hypothesis.[31]

In conclusion, nanoscale studies of ultrathin ferroelectric copolymer films reveal a critical thickness of approximately 18 nm at which the nature of polarization switching changes from extrinsic, for thicker films, to intrinsic, for thinner films. These results are consistent with prior studies that find a critical thickness of 15 nm to 18 nm and with theoretical predictions of the size of the critical nucleus.

The work in Moscow was supported by the Russian Foundation for Basic Research, Grant No. 09-02-00096. Work at the University of Nebraska was supported by the U.S. Department of Energy (DE-FG02-08ER46498).

[1]W. J. Merz, Phys. Rev. **95**, 690 (1954).
[2]W. J. Merz, J. Appl. Phys. **27**, 938 (1956).
[3]A. N. Kolmogorov, Izv., Akad. Nauk SSSR Ser. Mat. **1**, 355 (1937).
[4]M. Avrami, J. Chem. Phys. **7**, 1103 (1939).
[5]Y. Ishibashi and Y. Takagi, J. Phys. Soc. Jpn. **31**(2), 506 (1971).
[6]V. Ginsburg, J. Phys. USSR **10**, 107 (1946).
[7]R. Landauer, J. Appl. Phys. **28**(2), 227 (1957).
[8]M. Iwata and Y. Ishibashi, Jpn. J. Appl. Phys. **44**(9A), 6667 (2005).
[9]Y. Ishibashi, Jpn. J. Appl. Phys. **31**(9A), 2822 (1992).
[10]J. F. M. Cillessen, M. W. J. Prins, and R. M. Wolf, J. Appl. Phys. **81**(6), 2777 (1997).
[11]G. Gerra, A. K. Tagantsev, and N. Setter, Phys. Rev. Lett. **94**, 107602 (2005).
[12]N. A. Pertsev, J. R. R. Contreras, V. G. Kukhar, B. Hermanns, H. Kohlstedt, and R. Waser, Appl. Phys. Lett. **83**(16), 3356 (2003).
[13]A. K. Tagantsev and I. A. Stolichnov, Appl. Phys. Lett. **74**(9), 1326 (1999).
[14]S. Ducharme, V. M. Fridkin, A. V. Bune, S. P. Palto, L. M. Blinov, N. N. Petukhova, and S. G. Yudin, Phys. Rev. Lett. **84**(1), 175 (2000).
[15]M. J. Highland, T. T. Fister, M.-I. Richard, D. D. Fong, P. H. Fuoss, C. Thompson, J. A. Eastman, S. K. Streiffer, and G. B. Stephenson, Phys. Rev. Lett. **105**(16), 167601 (2010).
[16]L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954).
[17]G. Vizdrik, S. Ducharme, V. M. Fridkin, and S. G. Yudin, Phys. Rev. B **68**(9), 094113 (2003).
[18]B. J. Rodriguez, S. Jesse, S. V. Kalinin, J. Kim, and S. Ducharme, Appl. Phys. Lett. **90**, 122904 (2007).
[19]S. Ducharme, S. P. Palto, and V. M. Fridkin, in *Ferroelectric and Dielectric Thin Films*, edited by H. S. Nalwa (Academic Press, San Diego, 2002), Vol. 3, pp. 545–591.
[20]J. Choi, C. N. Borca, P. A. Dowben, A. Bune, M. Poulsen, S. Pebley, S. Adenwalla, S. Ducharme, L. Robertson, V. M. Fridkin, S. P. Palto, N. N. Petukhova, and S. G. Yudin, Phys. Rev. B **61**(8), 5760 (2000).
[21]M. Bai, A. V. Sorokin, D. W. Thompson, M. Poulsen, S. Ducharme, C. M. Herzinger, S. Palto, V. M. Fridkin, S. G. Yudin, V. E. Savchenko, and L. K. Gribova, J. Appl. Phys. **95**(7), 3372 (2004).
[22]T. Furukawa, Phase Trans. **18**, 143 (1989).
[23]K. Kimura and H. Ohigashi, Jpn. J. Appl. Phys. **25**, 383 (1986).
[24]R. C. G. Naber, P. W. M. Blom, and D. M. d. Leeuw, J. Phys. D: Appl. Phys. **39**, 1984 (2006).
[25]T. Nakajima, Y. Takahashi, S. Okamura, and T. Furukawa, Jpn. J. Appl. Phys. **48**, 09KE04 (2009).
[26]H. Kliem and R. Tadros-Morgane, J. Phys. D: Appl. Phys. **38**, 1860 (2005).
[27]M. Bai and S. Ducharme, Appl. Phys. Lett. **85**(16), 3528 (2004).
[28]C. M. Othon, J. Kim, S. Ducharme, and V. M. Fridkin, J. Appl. Phys. **104**, 054109 (2008).
[29]R. V. Gaynutdinov, O. A. Lysova, S. G. Yudin, A. L. Tolstikhina, A. L. Kholkin, V. M. Fridkin, and S. Ducharme, Appl. Phys. Lett. **95**, 023303 (2009).
[30]M. Bai, M. Poulsen, and S. Ducharme, J. Phys.: Condens. Matter **18**, 7383 (2006).
[31]P. Sharma, T. J. Reece, S. Ducharme, and A. Gruverman, Nano Lett. **11**(5), 1970 (2011).