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Polarization switching kinetics at the nanoscale in ferroelectric copolymer Langmuir–Blodgett films

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The polarization switching kinetics of ferroelectric Langmuir–Blodgett films of vinylidene fluoride-trifluoroethylene copolymer were investigated by piezoresponse force microscopy with a resolution of 100 nm. The switching time in response to a localized voltage pulse exhibits an exponential dependence on reciprocal voltage, which is consistent with nucleation-limited switching dynamics. © 2008 American Institute of Physics. [DOI: 10.1063/1.2916707]

There is increasing interest in the dynamics of polarization at the nanoscale in ferroelectric thin films motivated by the application of ferroelectric thin films to, e.g., nonvolatile random-access memories,¹ and enabled by the advances in the technology of ferroelectric thin film fabrication and nanoscale patterning and the application of scanning probe microscopy to probe ferroelectric properties at the nanoscale.² Piezoelectric force microscopy (PFM) has become the preferred method for imaging polarization domain structure³ and dynamics⁴ in ferroelectric films. Studies of ferroelectricity in films of nanometer thickness were made with Langmuir–Blodgett (LB) films of copolymers of vinylidene fluoride and trifluoroethylene copolymers P(VDF-TrFE).^{5,6} Although the equilibrium ferroelectric properties of the LB films are weakly dependent on the thickness,⁷ the polarization switching properties are sensitive to both film thickness^{8,9} and LB fabrication conditions,^{10,11} indicating that crystal morphology plays an essential role. These switching studies, however, were all made with large-area (of order 1 mm²) polycrystalline LB film capacitors and, therefore, could not reveal detailed domain structures nor discern the role of crystal morphology. Nanoscale piezoelectric imaging studies of P(VDF-TrFE) films made by solvent spinning¹² and LB deposition¹³ indicated a connection between domain structure and crystal morphology. Recent PFM studies¹⁴ with an imaging resolution of 5 nm have made this clear by demonstrating that the polarization of LB copolymer films could be patterned with feature sizes as small as the crystallites, which is 30–50 nm. Here, we report a PFM study of polarization switching kinetics, probing a region approximately 500 nm in diameter in ferroelectric copolymer LB films.

The ferroelectric random copolymer consisting of 70% vinylidene fluoride and 30% trifluoroethylene (70:30 copolymer) was deposited to the desired thickness by horizontal LB deposition, as described in detail elsewhere.¹⁵ Briefly, in this method, a solution of 1.3% by weight copolymer in dimethyl-sulfoxide was dispersed onto the surface of a sub-phase of ultrapure water at room temperature. Barriers on the water's surface slowly compressed the Langmuir film to a surface pressure of 3 mN/m², which is well below the

collapse pressure. The copolymer LB films were transferred layer by layer to a silicon substrate coated with 50 nm thick aluminum film. The samples consisting of 10, 30 and 120 ML were then annealed at 120 °C for 3 h and cooled to room temperature to optimize the crystallinity and stabilize the ferroelectric properties. The LB film fabrication methods are described in detail elsewhere.^{5,15} The film thickness is estimated to be 1.8 nm per 1 ML transfer, based on spectroscopic ellipsometry studies made on similarly prepared LB films of this copolymer.¹⁶ Measurements were carried out with scanning probe microscope (model Solver P47 from NT-MDT, Moscow) operating in contact mode for imaging both topography [atomic force microscopy (AFM)] and piezoresponse (PFM). The measurements were made with silicon cantilevers (model CSC38 from MicroMasch, Estonia), which had a lever force constant of approximately 0.05 N/m, a resonant frequency of 21 kHz, and a tip radius of 10 nm or less. The PFM measurements were made by applying an excitation voltage of amplitude 1.5 V and frequency 200 kHz to the tip and recording the resulting tip deflection signal from the position detector with a lock-in amplifier. The measurements were carried out in air in a class 10 0000 clean room maintained at temperature of 26 ± 0.05 °C and relative humidity of 40 ± 1%. For the PFM measurements, a CSC38 tip was coated with Ti/Pt conductive coating and had an estimated radius of 40 nm and an estimated imaging resolution of 60 nm, which is insufficient to resolve individual crystal grains, which are typically 30 nm in size in the copolymer LB films.¹⁴

The local polarization switching studies were conducted in two operating regimes, which are switching spectroscopy for measurement of the local hysteresis loop and voltage pulse switching followed by PFM for imaging of the switched spot. In switching spectroscopy, the piezoresponse was recorded after each of a series of voltage pulses cycling between positive and negative limits.⁴ The local piezoresponse hysteresis loops of representative spots on the three films are shown in Fig. 1. The hysteresis loop from the 10 ML film [Fig. 1(a)] exhibits a coercive voltage of $V_c = 2.3$ V, defined as the average voltage amplitude at which the piezoresponse crosses zero. The loop does not appear to be saturated, meaning that this is a lower limit of the coercive field. The hysteresis loop from the 30 ML film [Fig. 1(b)] appears well saturated with a coercive voltage

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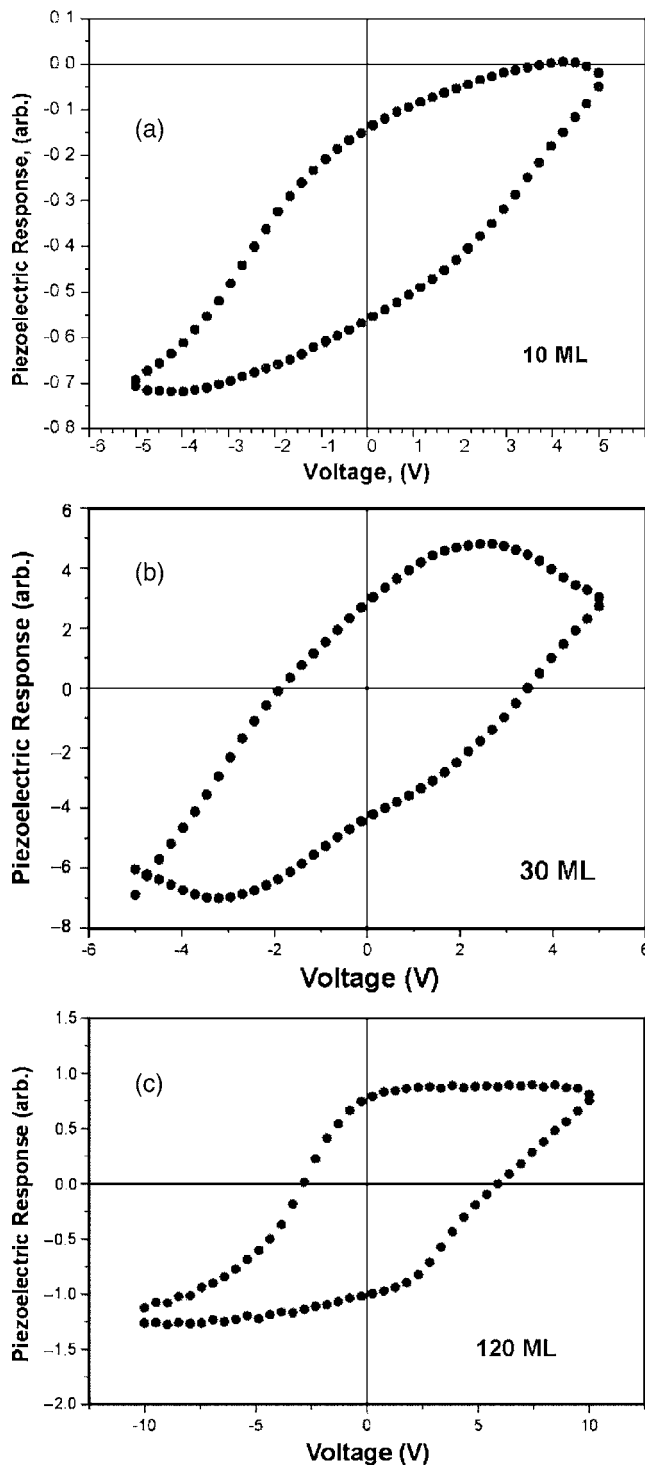


FIG. 1. Hysteresis loops for films (a) 10 ML, (b) 30 ML, (c) and 120 ML.

$V_c=2.7$ V. The hysteresis loop from the 120 ML film [Fig. 1(c)] appears well saturated with a coercive voltage $V_c=4.4$ V.

The imaging of local switching was carried out by the method of point voltage pulse switching. In this method, the imaging area was first saturated by scanning the tip with a saturating bias of -10 V and imaged under zero bias. Then, a small spot was switched by applying $+10$ V to the tip at a specific location on the film. Figure 2 shows two views of the 30 ML film, which had the topography in Fig. 2(a). The PFM signal [amplitude \times sin (phase)] shown in Fig. 2(b) was recorded after application of a local voltage pulse of $+10$ V

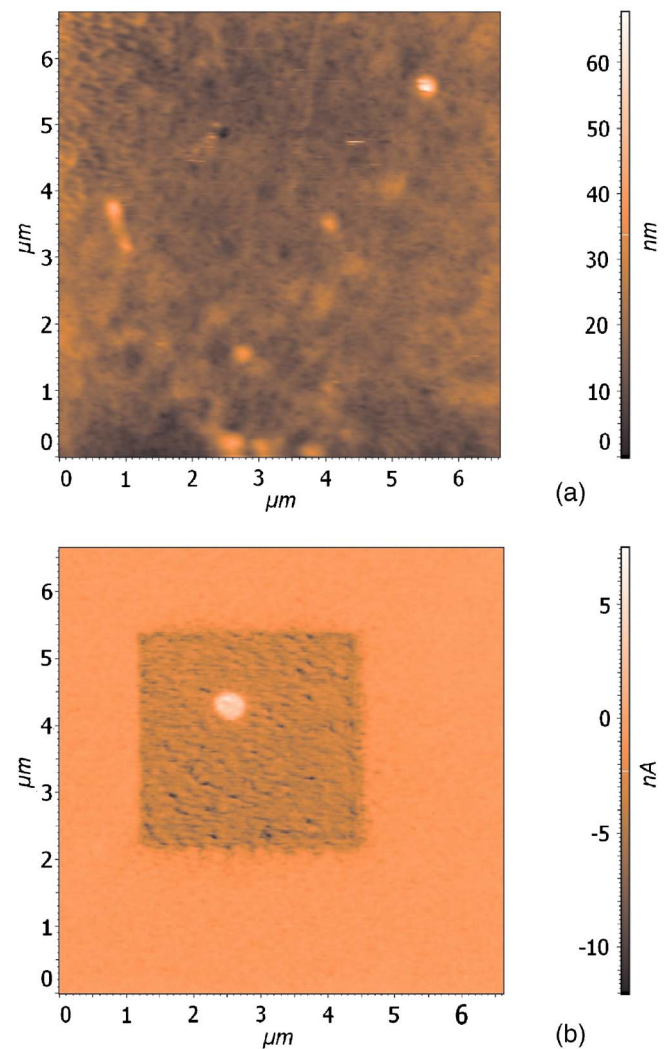


FIG. 2. (Color online) PFM images from the 30 ML film AFM topography image and (a) PFM topography and phase (b) image shows the square with $P=-P_s$ and spot with $P=+P_s$.

amplitude and 30 s duration shows a switched spot of approximately 500 nm in diameter.

The switching kinetics were studied by a series of local switching measurements. In this method, the imaging area was first saturated by scanning the tip with a saturating bias of $+10$ V and imaged under zero bias. Then the local spot was switched, applying a voltage pulse of specified amplitude and duration at a fixed point and the resulting piezoreponse was imaged after applying the pulse. To determine the switching time for each voltage pulse amplitude, we recorded the piezoreponse after pulse application as a function of pulse duration and plotted this as function of pulse, as shown in inset to Fig. 3 for the 120 ML sample. The switching time was taken as the time at which this plot crosses zero piezoelectric response. In this way, the value of the switched piezoreponse was recorded as a function of voltage pulse amplitude and duration. A graph of switched piezoreponse versus pulse duration, for a given pulse amplitude, was then analyzed to determine the switching time τ , defined at the time at which the piezoreponse crossed zero.⁹ Figure 3 shows the dependence of the switching time τ on pulse amplitude V for the 10, 30 and 120 ML films.

The dependence of the switching time τ on switching voltage V is a useful indicator of the dominant switching

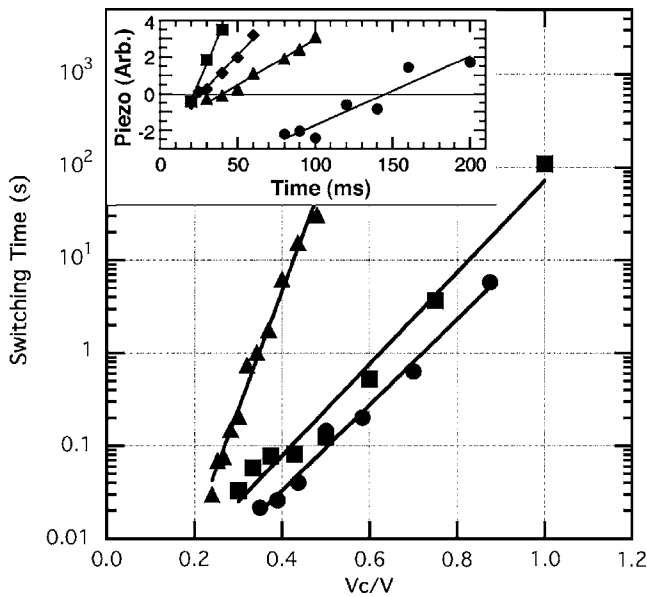


FIG. 3. Graph of $\log(t)$ vs (V_c/V) for the 10 ML film (purple triangles), the 30 ML film (green squares) and the 120 ML film (blue circles). The solid lines are linear least squares fits to the data. Inset: peak PFM signal after switching from the 120 ML sample as a function of switching pulse duration for pulse amplitudes of (left to right) 10, 9, 8, and 7 V.

mechanism. The data in Fig. 3 are most consistent with nucleation-limited switching, which is an activation process with an exponential dependence on reciprocal voltage, expressed as follows:¹⁷

$$(1/\tau) = (1/\tau_0)\exp(-aV_c/V), \quad (1)$$

where τ_0 is a constant and a depends on reciprocal temperature. The fits in Fig. 3 return the following values for these parameters: $\tau_0 = 27 \times 10^3$ s and $a = 29.3$ for the 10 ML film, $\tau_0 = 1.2 \times 10^3$ s and $a = 11.4$ for the 30 ML film, and $\tau_0 = 2.1 \times 10^3$ s and $a = 10.6$ for the 120 ML film. Extrinsic switching shows no true threshold voltage, which appears to be the case here. If switching were domain-wall limited, the dependence would be a power law of the form^{17,18} $(1/\tau) = (1/\tau_0) \times (V/V_c)^p$, also with no true threshold. Intrinsic switching exhibits a true threshold with a square-root dependence of the form⁹ $(1/\tau) = (1/\tau_0)(V/V_c - 1)^{1/2}$, which form is clearly not consistent with the data in Fig. 3. The interpretation of the present experiments, however, is complicated by the fact that the applied electric field is far from uniform, decreasing as a function of distance from the tip. The switching voltage V is not a single value, as required for the use of Eq. (1).

Previous studies have found that copolymer thin films made by solvent spinning¹⁹ and LB copolymer films of 30 ML or more⁹ exhibit extrinsic switching kinetics [Eq. (1)], while thinner films often^{6,9} (but not always¹⁰) exhibit intrinsic

switching kinetics. None of these studies, however, probed the effects of lateral dimensions on the switching mechanism. The present study of local switching kinetics measured using PFM supports the extrinsic nucleation-initiated switching mechanism in LB films of 10, 30 and 120 ML for a region approximately 500 nm in diameter. Further study of local switching kinetics in thin films and nanostructures is necessary if we are to understand the dominant mechanisms, and possibly control them.

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