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Effect of thermal annealing on ferroelectric domain structures in poly(vinylidene-fluoride-trifluorethylene) Langmuir-Blodgett thin films

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We report a piezo-response force microscopy study of the effect of thermal annealing on ferroelectric domain structures in 6 to 20 monolayer (11 to 36 nm) polycrystalline poly(vinylidene-fluoride-trifluorethylene) thin films prepared using the Langmuir-Blodgett approach. Stripe-shape domains have been created at room temperature and subjected to thermal annealing at progressively higher temperatures up to the ferroelectric Curie temperature T_C of approximately 110 °C. The static configuration of the domain walls exhibits no appreciable temperature dependence after thermal annealing, with the domain-wall roughness exponent ζ ranging from 0.4 to 0.5. Above 80 °C, we observed spontaneous polarization reversal at randomly scattered local sites in both polarization states. The number of domain nucleation centers increases rapidly as a function of temperature. We compared the thermally driven domain formation in ferroelectric polymers with those observed in ferroelectric oxides and attributed the difference to the distinct mechanisms for domain formation in these two systems. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4891396>]

I. INTRODUCTION

Ferroelectric poly(vinylidene-fluoride-trifluorethylene) (PVDF-TrFE) are random copolymers composed of long chains of $-(\text{CF}_2\text{--CH}_2)_x-(\text{CF}_2\text{--CFH})_{1-x})_n-$, where the polarization direction depends on the orientation of the constituent $\text{CF}_2\text{--CH}_2$ dipoles.^{1,2} Compared with the widely studied ferroelectric oxides such as $\text{Pb}(\text{Zr,Ti})_3$ (PZT) and BaTiO_3 , where effects such as the depolarization field significantly compromise ferroelectric instability in ultrathin films,³ layered films of PVDF-TrFE prepared by Langmuir-Blodgett (LB) deposition exhibits stable, two-dimensional (2D) ferroelectricity independent of the film thickness.^{4–7} The ferroelectric polymers also have the distinct advantages of light weight, easy fabrication, mechanical flexibility, and low cost,^{1,2} making them a viable material candidate for applications in nonvolatile memories, sensors, and photovoltaic devices.^{8–14} Understanding the nanoscale properties of the ferroelectric domains in polymer thin films, especially in the presence of disorder pinning potential and thermal perturbation, is thus of significant fundamental interests, and is critical for size scaling of the polymer-based ferroelectric device applications. Piezo-response force microscopy (PFM) has proven to be a powerful tool to probe the ferroelectric domain structures and polarization switching dynamics at the nanoscale in ferroelectric polymers.^{7,15–21}

In this work, we report the PFM study of the effect of thermal annealing on ferroelectric domain structures in 6 to 20 monolayer (ML) polycrystalline ferroelectric PVDF-TrFE thin films. Stripe-shape domain structures were written at room temperature and subjected to thermal annealing at

progressively higher temperatures up to the ferroelectric Curie temperature T_C of approximately 110 °C. The static configuration of the domain walls (DWs) does not exhibit appreciable changes in characteristics after thermal annealing, showing an temperature-independent roughness exponent ζ of 0.4–0.5, which is qualitatively different from what has been observed in ferroelectric oxides.²² As the samples were annealed at temperatures close to T_C , we observed spontaneous polarization reversal in randomly scattered sites for both polarization states, with the number of domain nucleation sites increasing with increasing temperature. We extracted the fraction of the switched area as a function of annealing temperature and discussed the difference in the relevant energy scales for domain formation between ferroelectric polymers and oxides, which can lead to their different responses to thermal annealing.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

We deposited the copolymer films one nominal ML at a time by LB deposition⁵ on SiO_2 -Si substrates, where 5 nm Cr and 50 nm Au were evaporated as the bottom electrode. The thickness of one ML is approximately 1.8 nm.²³ The molar ratio of PVDF:TrFE is 0.75/0.25. Variable-temperature capacitance measurements reveal a peak signal for the dielectric constant under heating at approximately 110 °C, corresponding to the ferroelectric to paraelectric phase transition.² After being annealed at 135 °C in a forced-air oven for 90 min, the films become polycrystalline with average lateral grain sizes of 50 nm.^{5,15} Figure 1(a) shows a typical AFM image of the film topography, with RMS surface roughness of ~ 1 nm. X-ray diffraction reveals a [110] crystalline orientation, which corresponds to the polarization

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FIG. 1. (a) The topography, (b) PFM phase and (c) amplitude response images of stripe-domains written on a 15 ML PVDF-TrFE film at room temperature. The lower panels in (b) and (c) are the cross-sectional data along the dashed lines in the corresponding PFM images. The scale bar for all images is shown at the bottom of (a).

direction at 30° with respect to the surface normal.¹⁸ We worked with films ranging in thickness from 6 to 20 ML (11–36 nm) for the PFM studies. The measurements have been carried out using a Bruker Multimode 8 atomic force microscope (AFM) with low spring constant AFM probes (Bruker SCM-PIC 0.2 N/m).

We created stripe-shape domain structures at room temperature by applying alternating positive and negative bias voltages (10 V–15 V) to the scanning AFM tip. Only the out-of-plane polarization is controlled by the bias voltage, while the orientation of the in-plane polarization is disordered among different grains. To image the domain structures, we scanned close to one of the resonant frequencies of the cantilever (170 ± 20 kHz) with 1 V excitation voltage. We used sampling intervals of 5–10 nm, which are close to the AFM tip-sample contact area.⁷ The samples were heated up to a series of progressively higher temperatures in a muffle oven. At each temperature, the samples were annealed for 45 min. We then thermally quenched the sample to room temperature, by placing it on a large metal plate, to “freeze” the high temperature domain structures.

III. RESULTS AND DISCUSSIONS

Figures 1(b) and 1(c) show the phase and amplitude response images, respectively, of the stripe domain structures on a 15 ML film. To quantitatively analyze the domain configurations, we used the middle-level of the phase response signal (Fig. 1(b)) to define the position of the DW. The

results obtained from the minimum signal of amplitude response (Figs. 1(c)) are quantitatively similar.

Figures 2(a)–2(d) show the phase response images of the PFM measurements of a domain structure containing one DW taken on the 15 ML PVDF-TrFE film at various thermal annealing temperatures. The domain structure remains stable for annealing temperatures up to 80°C . As the annealing temperature was further increased, we observed an increasing fraction of the sample exhibiting spontaneous polarization reversal in randomly scattered sites, resulting in a mosaic domain distribution in both the left and right regions that were previously uniformly polarized in the up and down directions. Despite the emerging of a large number of domain nucleation centers, it is interesting to note that the static configuration of the DW between these two regions remain qualitative similar even after the sample was annealed at temperatures close to T_C . Similar temperature evolution of domain structures has been observed in films of all thicknesses (Figs. 2(e)–2(g)).

Theoretically, a ferroic DW can be considered as elastic at a length scale larger than the Larkin length, which is determined by the DW width and the length scale of disorder potential. The static configuration of the DW is determined by the competition between the elastic energy and the disorder pinning potential in the system.^{24–26} The geometric fluctuation of the DWs, also called DW roughness, can be described by the correlation function $B(L) = \langle [u(L) - u(0)]^2 \rangle$, where $u(L)$ is the perpendicular

FIG. 2. PFM phase response images of (a) a DW written on a 15 ML PVDF-TrFE film at room temperature (RT), and the same DW after thermal annealing at (b) 80°C , (c) 100°C , and (d) 110°C . (e)–(g) The phase response images of domain structures thermal annealed close to T_C on 8 ML, 10 ML, and 20 ML PVDF-TrFE films, respectively. (h) The topography image of the same area shown in (g) for the 20 ML PVDF-TrFE film. All scale bars are 500 nm.

displacement of the DW at position $x=L$ relative to a flat configuration (Fig. 3(a) inset), and $\langle \dots \rangle$ and $\overline{\dots}$ represent the thermal and disorder average, respectively. For disorder- or thermal-driven roughening of a DW, one expects the correlation function to exhibit a L -dependence of $B(L) \propto L^{2\zeta}$, where ζ is the DW roughness exponent that can be deduced from the scaling theory. The value of ζ depends on the dimensionality and disorder type of the system.^{24–26}

Figure 3(a) shows the L -dependence of $B(L)$ for 4 DWs on the 15 ML film. For all DWs, $B(L)$ follows well the power law growth at small length scale and then tends to saturate at around 50 nm. This behavior has been observed in all PVDF-TrFE films investigated. The lack of L -dependence in $B(L)$ at $L > 50$ nm implies DW roughening at large length scale becomes uncorrelated. The length scale of saturation is comparable with the polycrystalline grain size. This is consistent with the notion that the polarizations among different crystalline grains are not expected to be correlated.¹⁵

We extracted the DW roughness exponent ζ based on data taken between $L = 10$ nm and 50 nm to avoid the artifact due to the AFM tip-sample contact area. Figure 3(b) shows ζ as a function of the thermal annealing temperature for 8 ML, 15 ML, and 20 ML films up to 100 °C. For higher annealing temperatures, it becomes difficult to unambiguously identify the interface between the two regions with different pre-written polarizations. At room temperature, the extracted values of the DW roughness exponents range from 0.4 to 0.5, consistent with previously reported results.⁷ For films of all thickness, the values of ζ show very weak dependence on the thermal annealing temperature, even at temperatures close to T_C . Such temperature-independent DW roughness is in sharp contrast with what has been previously reported for ferroelectric PZT thin films, where ζ increases from 0.26 at room temperature to 0.5 after the samples have been heated close to T_C .^{22,27} The change of the roughness exponent in PZT has been attributed to a DW dimensionality crossover from 2D to 1D as the dynamical length scale of the DW grows at elevated temperatures and becomes comparable with the film thickness.²² Unlike PZT thin films, the LB copolymer films exhibit thickness-independent 2D ferroelectricity, and the DW is intrinsically one-dimensional.⁷ Without the complicating effect of dimensionality crossover,

FIG. 3. (a) The correlation function $B(L)$ of 4 as-written DWs on a 15 ML film. The dotted line marks $L = 50$ nm. Inset: A schematic roughened DW. (b) DW roughness exponent ζ vs. thermal annealing temperature for 8 ML, 15 ML, and 20 ML films. Inset: Log-log plot of $B(L)$ for DW1 shown in (a) with a fit of $B(L) \sim L^{0.83}$ (dashed line).

the temperature dependence of ζ in PVDF-TrFE should be solely determined by the competition between the disorder pinning and thermal roughening, which is tuned by temperature.

It has been theoretically predicted that for a 1D DW a roughness exponent of $2/3$ is expected in the presence of disorder potential, while thermal fluctuation gives rise to an exponent ζ_T of $1/2$.²⁸ The high temperature roughness exponents extracted from the PVDF-TrFE LB films are close to the theoretical value for thermal roughening. However, at room temperature, DWs in PVDF-TrFE show a roughness exponent of 0.4–0.5, much lower than the value of $2/3$ predicted for roughening due to disorder pinning potential for 1D DW. The deroughening of DW has been previously attributed to the presence of correlated disorder due to the randomly oriented in-plane component of the polarization.⁷ We believe the weak temperature dependence of ζ is a consequence of such DW deroughening, since the ζ value for the deroughened DW is very close to the thermal roughness exponent ζ_T .

We then considered the spontaneous polarization reversal observed following annealing at temperatures above 80 °C. We quantified the density of the switched area based on the histograms of the phase response signal of the PFM image. The amplitude signal was not used to extract the areas of the two polarization states, since both polarization states give similar amplitude responses (Figs. 1(c)). Figures 4(a) and 4(b) show the histograms extracted from the domain structure shown in Fig. 2(f) at room temperature and after

FIG. 4. The histograms of the phase angle extracted from (a) the room temperature as-written domain structure for a 10 ML PVDF-TrFE film, and (b) the same domain structure after thermal annealing at 110 °C. The arrows mark the cutoff angle to define the P_{up} and P_{down} states. The 110 °C image is shown in Fig. 2(f). (c) The fractions of the switched areas as a function of the thermal annealing temperature on the 10 ML PVDF films. (d) The areal switching fraction at temperatures close to T_C as a function of PVDF-TrFE film thickness for both pre-written polarization states. The data for 6 and 8 ML are obtained at 100 °C. The data for 10, 15, and 20 ML are obtained at 110 °C. At higher temperatures, the interfaces between the pre-written P_{up} and P_{down} regions become difficult to resolve.

thermal annealing at 110 °C, respectively, on a 10 ML film. In Figure 4(a), the distribution of the phase angles for the as-written domain structure peaks at -73° and 107° , corresponding to the up and down polarizations, respectively. We defined the angle midway between these two peaks (17°) as the cutoff point to distinguish the polarization up (P_{up}) and down (P_{down}) states, and converted the image to a binary matrix. The fraction of the switched area is then calculated from the binary matrix. We repeated the same procedure for data from all thermal annealing temperatures. As the temperature is close to T_C , there is a larger distribution of phase angles for both polarization states, and the histogram peaks become broader (Fig. 4(b)). To account for the effect of phase angle distribution on the extracted domain areas, we also processed images at cutoff angles that are shifted by $\pm 10^\circ$ and used the resulting values to determine the error bar for the areal switching fraction. Figure 4(c) shows the calculated areal switching fraction in a $(2\ \mu\text{m})^2$ area in the 10 ML film for both pre-written polarization states as a function of the thermal annealing temperature T . The polarization reversal starts at approximately 80 °C (90 °C) for the pre-written P_{up} (P_{down}) states, and the fraction of switched area quickly reaches 30% (10%) of the whole area. As the temperature further increases, the films are approaching the melting temperature similar to in the annealing process.⁵ All the polymer chains are re-organized and the films present a mixed P_{up} and P_{down} domains as in the as-grown state.

It is interesting to note that for both polarization states, the polarization reversal following thermal annealing appears to initiate at randomly distributed sites rather than occurring at the existing domain walls. In addition, while the switched area grows larger with increasing temperature, the number of domain nucleation sites also increases significantly (Fig. 2). Similar domain switching characteristics have also been observed in spin-coated PVDF-TrFE films, where domain structures are likely to conform to the grains of the nano-crystals.^{29,30} This is very different from the results obtained with PZT thin films, where the domain nucleation occurs predominantly at the DW.^{22,31}

This difference in nucleation location may originate from the different mechanisms of ferroelectricity and domain formation processes in these two classes of materials. Polarization in PZT is due to the relative displacement of the cations and oxygen octahedra, and domain formation is a consequence of competition between the short-range lattice elastic energy and the Coulomb energy.³² The epitaxial strain further enhances the energy barrier for ferroelectric instability, as evident from the strong polarization asymmetry and enhanced Curie temperature observed in epitaxial thin films.³³ Due to the high domain wall energy, the system is trying to minimize the surface-to-volume ratio of domain structures. It is thus preferable to have domain switching initiated at the domain wall to minimize the fraction of domain walls. In contrast, PVDF-TrFE LB films consist of long polymer chains crystallized in an orthorhombic structure, and the inter-chain interaction is van de Waal type.⁵ The DW energy is thus highly anisotropic between inter-chain DWs and intra-chain DWs, and the energy involved in forming a DW between different polymer chains is expected to be

dominated by the electrostatic energy due to dipole-dipole interaction. In ferroelectric oxide, on the other hand, DW formation requires considerably higher energy cost from lattice elastic energy.^{34,35} Due to the relatively low DW energy in PVDF-TrFE, thermal fluctuation induced polarization switching can be promoted around disorder sites such as grain boundaries, local defects, and compositional disorders.^{2,5,35} The surface height gradient in morphology can also produce enhanced local electric field, which may promote domain switching (Fig. 2(h)). Similar domain nucleation among individual centers has been observed in PZT small capacitor structures at low bias voltage, where the switching energy is lowered compared to the bulk PZT,³⁶ or in ultrathin ferroelectric films grown on insulating substrates, as the electrostatic energy dominates due to improper screening.³⁷

We also observed that there is a slight polarization asymmetry in PVDF-TrFE film for all film thicknesses. Figure 4(d) plots the areal fraction of polarization reversal as a function of film thickness at temperatures close to T_C . The degree of the asymmetry varies, but for the same annealing temperature, the switched area in the pre-written P_{down} region is always lower than that in the pre-written P_{up} region. This implies the P_{down} state is energetically more stable. Similar asymmetry has previously been observed in DW velocity for different polarization orientations in PVDF-TrFE films.¹⁶ This asymmetry is likely due to the difference in the polymer-substrate interactions for the C-H and C-F bonds, which form the molecular dipole.⁵ However, the polarization asymmetry is not as strong as in epitaxial PZT, where the polarization is always uniformly polarized in the as-grown state.^{22,33}

IV. CONCLUSIONS

In conclusion, we studied the evolution of ferroelectric domain structures in PVDF-TrFE thin films under thermal annealing at different temperatures. The DW roughness exponent shows weak temperature dependence, while spontaneous polarization reversal in randomly scattered nucleation sites has been observed at temperatures close to T_C . Our study provides new insight into the thermal response of polarization in ferroelectric polymers at the nanoscale, which is critical for the technological development of these materials.

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¹A. J. Lovinger, *Science* **220**, 1115 (1983).

²T. Furukawa, *Phase Trans.* **18**, 143 (1989).

- ³M. Dawber, N. Stucki, C. Lichtensteiger, S. Gariglio, and J. M. Triscone, *J. Phys.-Condens. Matter* **20**, 264015 (2008).
- ⁴A. V. Bune, V. M. Fridkin, S. Ducharme, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin, and A. Zlatkin, *Nature* **391**, 874 (1998).
- ⁵S. Ducharme, S. P. Palto, V. M. Fridkin, and L. M. Blinov, in *Handbook of Thin Film Materials*, edited by H. S. Nalwa (Academic, San Diego, 2002), Vol. 3, Chap. 11.
- ⁶S. Ducharme, V. M. Fridkin, A. V. Bune, S. P. Palto, L. M. Blinov, N. N. Petukhova, and S. G. Yudin, *Phys. Rev. Lett.* **84**, 175 (2000).
- ⁷Z. Xiao, S. Poddar, S. Ducharme, and X. Hong, *Appl. Phys. Lett.* **103**, 112903 (2013).
- ⁸N. Setter *et al.*, *J. Appl. Phys.* **100**, 051606 (2006).
- ⁹S. Hong and N. Park, in *Scanning Probe Microscopy: Electrical and Electromechanical Phenomena at the Nanoscale*, edited by S. Kalinin and A. Gruverman (Springer, New York, 2006), Chap. 4.6.
- ¹⁰J. F. Scott, *Science* **315**, 954 (2007).
- ¹¹S. Fujisaki, H. Ishiwara, and Y. Fujisaki, *Appl. Phys. Lett.* **90**, 162902 (2007).
- ¹²Z. Hu, M. Tian, B. Nysten, and A. M. Jonas, *Nat. Mater.* **8**, 62 (2009).
- ¹³T. Furukawa, Y. Takahashi, and T. Nakajima, *Curr. Appl. Phys.* **10**, E62 (2010).
- ¹⁴Q. Liu, I. Khatri, R. Ishikawa, A. Fujimori, K. Ueno, K. Manabe, H. Nishino, and H. Shirai, *Appl. Phys. Lett.* **103**, 163503 (2013).
- ¹⁵B. J. Rodriguez, S. Jesse, S. V. Kalinin, J. Kim, S. Ducharme, and V. M. Fridkin, *Appl. Phys. Lett.* **90**, 122904 (2007).
- ¹⁶Y. Kim, W. Kim, H. Choi, S. Hong, H. Ko, H. Lee, and K. No, *Appl. Phys. Lett.* **96**, 012908 (2010).
- ¹⁷Y. Y. Choi, J. Hong, S. Hong, H. Song, D. S. Cheong, and K. No, *Phys. Status Solidi (RRL)* **4**, 94 (2010).
- ¹⁸P. Sharma, D. Wu, S. Poddar, T. J. Reece, S. Ducharme, and A. Gruverman, *J. Appl. Phys.* **110**, 052010 (2011).
- ¹⁹P. Sharma, T. J. Reece, S. Ducharme, and A. Gruverman, *Nano Lett.* **11**, 1970 (2011).
- ²⁰H. Choi, S. Hong, T. H. Sung, and K. No, *Appl. Phys. Lett.* **99**, 092905 (2011).
- ²¹I. Stolichnov, P. Maksymovych, E. Mikheev, S. V. Kalinin, A. K. Tagantsev, and N. Setter, *Phys. Rev. Lett.* **108**, 027603 (2012).
- ²²P. Paruch, A. B. Kolton, X. Hong, C. H. Ahn, and T. Giamarchi, *Phys. Rev. B* **85**, 214115 (2012).
- ²³M. J. Bai *et al.*, *J. Appl. Phys.* **95**, 3372 (2004).
- ²⁴T. Nattermann, *J. Phys. C-Solid State Phys.* **16**, 4125 (1983).
- ²⁵T. Emig and T. Nattermann, *Eur. Phys. J. B* **8**, 525 (1999).
- ²⁶T. Giamarchi, A. B. Kolton, and A. Rosso, in *Jamming, Yielding, and Irreversible Deformation in Condensed Matter*, edited by M. Miguel and M. Rubi (Springer, Berlin, Heidelberg, 2006), Vol. 688, p. 91.
- ²⁷P. Paruch, T. Giamarchi, and J. M. Triscone, *Phys. Rev. Lett.* **94**, 197601 (2005).
- ²⁸A. B. Kolton, A. Rosso, and T. Giamarchi, *Phys. Rev. Lett.* **94**, 047002 (2005).
- ²⁹D. Guo, X. S. Chen, X. C. Chu, F. Zeng, Y. Bai, J. L. Cao, and B. Dkhil, *J. Appl. Phys.* **113**, 187210 (2013).
- ³⁰Y. M. Liu, S. H. Xie, X. Y. Liu, K. Kitamura, and J. Y. Li, *J. Appl. Phys.* **110**, 052008 (2011).
- ³¹J. Woo, S. B. Hong, D. K. Min, H. J. Shin, and K. No, *Appl. Phys. Lett.* **80**, 4000 (2002).
- ³²R. E. Cohen, *Nature* **358**, 136 (1992).
- ³³P. Paruch and J.-M. Triscone, *Appl. Phys. Lett.* **88**, 162907 (2006).
- ³⁴Y. Takahashi, Y. Nakagawa, H. Miyaji, and K. Asai, *J. Polym. Sci. Part C-Polym. Lett.* **25**, 153 (1987).
- ³⁵G. R. Li, N. Kagami, and H. Ohigashi, *J. Appl. Phys.* **72**, 1056 (1992).
- ³⁶A. Gruverman, D. Wu, and J. F. Scott, *Phys. Rev. Lett.* **100**, 097601 (2008).
- ³⁷S. K. Streiffer, J. A. Eastman, D. D. Fong, C. Thompson, A. Munkholm, M. V. Ramana Murty, O. Auciello, G. R. Bai, and G. B. Stephenson, *Phys. Rev. Lett.* **89**, 067601 (2002).