Stephen Ducharme Publications   Research Papers in Physics and Astronomy

Two-dimensional ferroelectric films

Alexander V. Bune
University of Nebraska at Lincoln

Vladimir M. Fridkin
Institute of Crystallography, Russian Academy of Sciences, Moscow, fridkin@ns.crys.ras.ru

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

Lev M. Blinov
Institute of Crystallography, Russian Academy of Sciences, Moscow

Serguei P. Palto
Institute of Crystallography, Russian Academy of Sciences, Moscow

See next page for additional authors

Authors

Alexander V. Bune, Vladimir M. Fridkin, Stephen Ducharme, Lev M. Blinov, Serguei P. Palto, Alexander V. Sorokin, S. G. Yudin, and A. Zlatkin

Two-dimensional ferroelectric films

A. V. Bune,[1,2] V. M. Fridkin,[1,2] Stephen Ducharme,[1] L. M. Blinov,[2]

S. P. Palto,[2] A. V. Sorokin,[2] S. G. Yudin,[2] and A. Zlatkin[2]

[1] Department of Physics and Astronomy and Center for Materials Research and Analysis, University of Nebraska–Lincoln, Lincoln, Nebraska 68588-0111, USA
[2] Institute of Crystallography, Russian Academy of Sciences, 117 333 Moscow, Russia
Corresponding author — Stephen Ducharme, email sducharme1@unl.edu

Abstract
Ultrathin crystalline films offer the possibility of exploring phase transitions in the crossover region between two and three dimensions. Second-order ferromagnetic phase transitions have been observed in monolayer magnetic films [1,2], where surface anisotropy energy stabilizes the two-dimensional ferromagnetic state at finite temperature [3]. Similarly, a number of magnetic materials have magnetic surface layers that show a second-order ferromagnetic–paramagnetic phase transition with an increased Curie temperature [4]. Ferroelectricity is in many ways analogous to ferromagnetism, and bulk-like ferroelectricity and finite-size modifications of it have been seen in nanocrystals as small as 250 Å in diameter [5], in perovskite films 100 Å thick [6] and in crystalline ferroelectric polymers as thin as 25 Å [7–10]. But these results can be interpreted as bulk ferroelectricity suppressed by surface depolarization energies, and imply that the bulk transition has a minimum critical size [11–13]. Here we report measurements of the ferroelectric transition in crystalline films of a random copolymer of vinylidene fluoride and trifluoroethylene just 10 Å (two monolayers) thick. We see a first-order ferroelectric phase transition with a transition temperature nearly equal to the bulk value, even in these almost two-dimensional films. In addition, we see a second first-order transition at a lower temperature, which seems to be associated with the surface layers only. The near-absence of finite-size effects on the bulk transition implies that these films must be considered as two-dimensional ferroelectrics.

■ ■ ■ ■ ■

Ferroelectric polymers have been studied in great detail for nearly 30 years and are in wide use in a variety of piezoelectric devices [14,15]. One of the most interesting systems is the random copolymer of vinylidene fluoride with trifluoroethylene, P(VDF-TrFE) [16], consisting of $-((-CF_2-CH_2)_x-(-CF_2-CHF-)_{1-x})n-$ chains with a regular intra-chain period of 2.6 Å, controlled by the C–C bonds between fluorine pairs, as shown in Figure 1a. In the ferroelectric phase, the all-*trans* chains are arranged in parallel rows in a quasi-hexagonal close packing with orthorhombic *mm2* structure [17]. P(VDF-TrFE 70:30) has a first-order ferroelectric–paraelectric phase transition (connected with the conversion of all-*trans* chains to mixtures of *trans* and *gauche* bonds with little or no net dipole moment [16] with Curie temperature $T_c \approx 100$ °C (the Curie temperature increases with the proportion of the VDF component), thermal hysteresis of $\Delta T_c \approx 20$ °C, and a spontaneous polarization $P_s \approx 0.1$ C m^{-2} at room temperature [16]. Thin films have usually been formed by solvent spinning and are polymorphous, containing amorphous material and incompletely orientated crystallites. Finite-size effects were evident from an increase in the coercive field in films as thin as 600 Å [18].

The first crystalline Langmuir–Blodgett-deposited polymer films, of P(VDF-TrFE 70:30), achieved a great improvement in quality [7,8,10]. They have excellent crystalline order and show the first-order ferroelectric–paraelectric transition at $T_c \approx 80$ °C on cooling. These ferroelectric polymer films, 30 monolayers (ML) thick (~150 Å), also showed double hys-

teresis and the critical point [19], and a new conductance switching controlled by the polarization state [8]. Finite-size effects have been demonstrated in these films; the coercive field scaled as the –0.7 power of the thickness in films with 35–135 ML [9].

For the present work we first recorded an atomic-resolution image of a single-monolayer P(VDF-TrFE 70:30) film on graphite by scanning tunnelling microscopy (STM, Figure 1b) showing the excellent short-range order and uniform orientation of all the all-trans polymer chains. Figure 2a–c shows that multilayer ferroelectric Langmuir–Blodgett-deposited polymer (FLP) films with aluminium electrodes have the dielectric anomalies and thermal hysteresis that mark the usual bulk first-order ferroelectric phase transition found at 77 °C on cooling (108 °C on heating) in the 30-ML film and decreasing to 68 °C (98 °C) in the 2-ML film. The pyroelectric response shown in Figure 3 also records the bulk transition near 73 °C, though the precise transition temperature is not as clear as in the dielectric measurements. Therefore, the "bulk" first-order phase transition at ~80 °C remains even in the 2-ML films (Figure 2c)—a result that challenges theoretical predictions that the transition temperature should decrease, and ferroelectricity vanish, in films below a minimum critical thickness [11–13]. FLP films of 30 ML or less all have approximately the same room-temperature relative dielectric constant $\varepsilon = 8 \pm 2$, as shown in Figure 2d, approximately one-half the value found in thick spun films.

The hysteresis loops shown in Figure 4 show good saturation for the 5-ML and 30-ML films and incomplete saturation for the 2-ML film. The 5-ML and 2-ML films show considerable bias, probably due to interactions with the substrate or the top electrode, consistent with our earlier observations on the dynamics of switching FLP films [8,9]. The coercive fields of 0.9 ± 0.2 GV m^{-1} (30 ML), 0.6 ± 0.1 GV m^{-1} (5 ML), and >0.5 GV m^{-1} (2 ML) are far larger than in other ferroelectric materials and are closely approaching the intrinsic coercive field $P_s/\varepsilon\varepsilon_0 \approx 1$ GV m^{-1} expected in the absence of nucleation, consistent with the very high crystallinity (here ε_0 is the permittivity of free space). The films achieved at least 50% of the maximum polarization expected if all dipoles are aligned perpendicular to the film, but our data could not rule out a tendency towards in-plane polarization as is observed in ultrathin magnetic films [20].

Figures 2 and 3 also show a new and unexpected phase transition at a lower temperature of ~20 °C in films of 30 ML or less. The dielectric constant (Figure 2) shows peaks at ~20 °C on cooling (28 °C on heating) in the pyroelectric response (Figure 3) in the 5-ML and 2-ML films. The polarization hysteresis loops from films of 30, 5, and 2 ML (Figure 4) show that ferroelectric switching is obtained at 25 °C in all the FLP films, even those as thin as 2 ML. We attribute the behavior at ~20 °C to a new first-order ferroelectric transition in the surface lay-

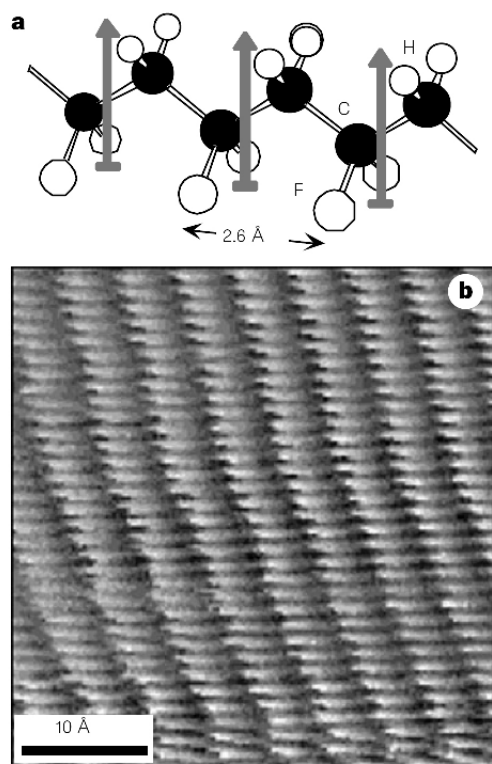ers on the basis of several observations: the new transition is strongest in the thinnest films; there is clear thermal hysteresis in the dielectric constant; and there are peaks in both the dielectric constant and the pyroelectric response. There is other evidence that the surface layers behave differently to the interior layers, because most films of 30 ML or less are found to be partially or fully polarized immediately after fabrication, even before the application of an external electric field. Also, the polarization of the 2–7 ML films reverts in zero field to an orientation determined by the substrate, independent of the history of electric-field application [8,9], consistent with the failure of the pyroelectric response to completely vanish above the Curie temperature in the thinnest films. These observations indicate that the surface layers have a preferred direction controlled by the interaction with the substrate or top electrode.
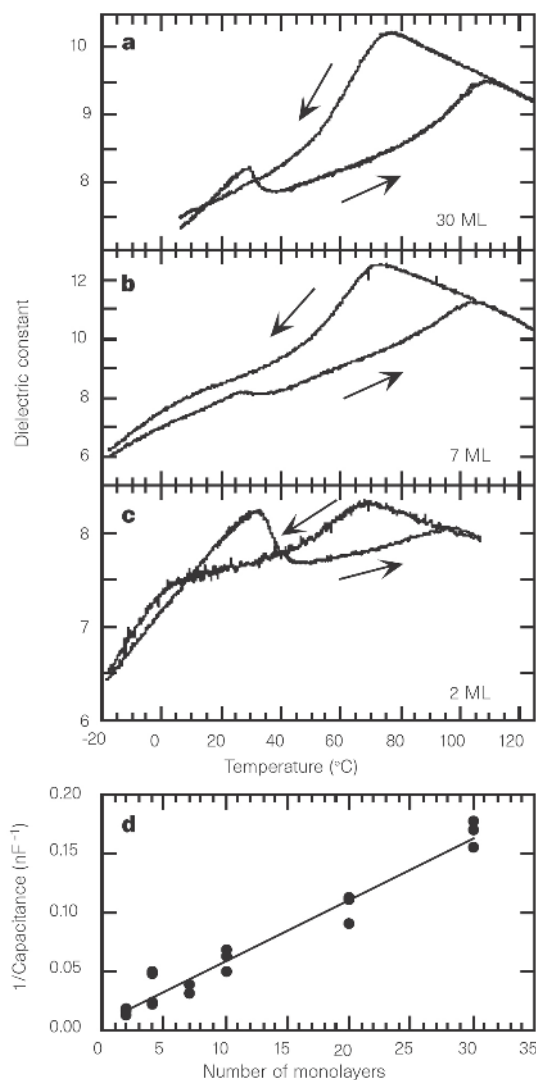

Figure 1. Structure of the polymer chains and films. **a)** Fragment of a P(VDF-TrFE 70:30) copolymer chain. 30% of the VDF (–CH$_2$–CF$_2$–) units have been replaced at random by TrFE (–CHF–CF$_2$–) units. The arrows show the direction of the net dipole moments pointing from the fluorine side to the hydrogen side of the chain. **b)** Atomic-resolution STM image of a single-monolayer film of P(VDF-TrFE 70:30) deposited on graphite.

Figure 2. Dielectric properties of the FLP films. a–c, Dielectric constant ε of the P(VDF-TrFE 70:30) films with different thicknesses, showing peaks at the phase transitions on heating and, due to thermal hysteresis, at different temperatures on cooling: **a)** 30 ML; **b)** 7 ML; **c)** 2 ML. The arrows show the direction of temperature change. **d)** The inverse capacitance at 25 °C for FLP films with different thicknesses.

The present results lead to the following conclusions. First, there is no apparent critical (minimum) thickness in FLP films as thin as 10 Å, much thinner than any previous ferroelectric films, with only a small suppression of the bulk Curie temperature. Second, there is a surface-layer ferroelectric phase transition at ~20 °C observable only in the thinnest FLP films. Therefore, the FLP films must be considered essentially two-dimensional ferroelectrics because of the absence of strong finite-size effects; neither the coercive field nor the bulk phase transition temperature change significantly as the film thickness decreases from 150 to 10 Å, implying that the interlayer coupling is weak. Finite-size calculations based on a three-dimensional mean-field theory are not appropriate for modeling the thinnest FLP films with thickness comparable to size of the individual dipoles. The mean-field theory also predicts the existence of a critical thickness equal to the ferroelectric correlation length (a phenomenological parameter that is unknown in ferroelectric polymers [21]); the surface energy, connected with the truncation of the crystal and the dielectric properties of the external material, introduces another length scale. Similar considerations have been used to calculate [22] a critical size ~25 Å for small spherical particles of lead zirconate-titanate (PZT).

The two-dimensional nature of the FLP films means that the ferroelectric state may be generated by coupling only within the plane of the film. Any coupling between planes is weak and possibly responsible for the lower surface-layer Curie temperature. The 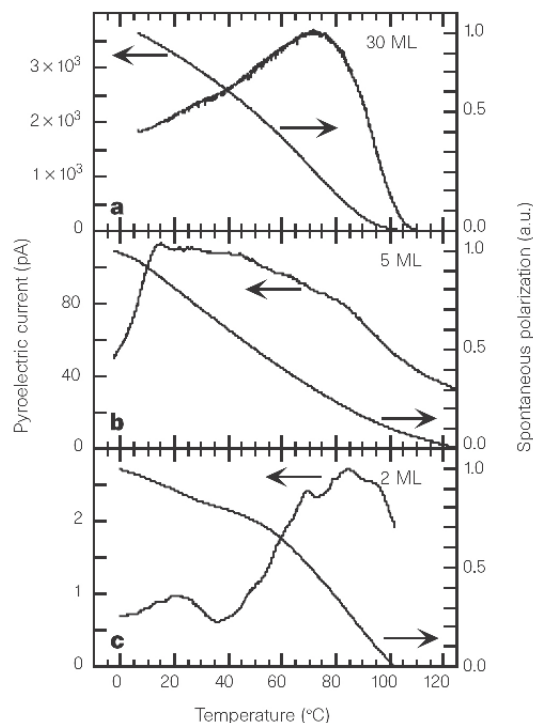Ising model for ultrathin films [23,26] is a more appealing approach to modeling ferroelectricity in two-dimensional polymer films because the dipole moments have restricted freedom—they can rotate only about the chain axis and are further inhibited from rotations about the axis by both interchain steric interactions and intrachain dihedral stiffness. We expect that an appropriate Ising model could be constructed in either of two ways. First, use of anisotropic coupling constants (like the exchange integrals in ferromagnetism) with strong ferroelectric coupling in the plane and a weak coupling perpendicular to the plane. Second, use of a purely two-dimensional model and making a weak inter-plane coupling through a mean-field shared by all layers. Both approaches can achieve ferroelectricity at finite temperature in a single layer and either enhancement or suppression by neighboring layers or electrodes, depending on the sign of the interlayer coupling. Both approaches also suggest that the surface layers, boundaries between the ferroelectric film and the electrodes or other outside material, have a Curie point different from the interior "bulk" layers because they couple with only one other ferroelectric layer. Fluctuations in two dimensions are not expected to destroy ordering as in the case of the isotropic Heisenberg ferromagnet [3] because the coupling is intrinsically anisotropic, and the polymer dipoles have close to one rotational degree of freedom, compared to the two rotational degrees of freedom of the magnetic dipoles.
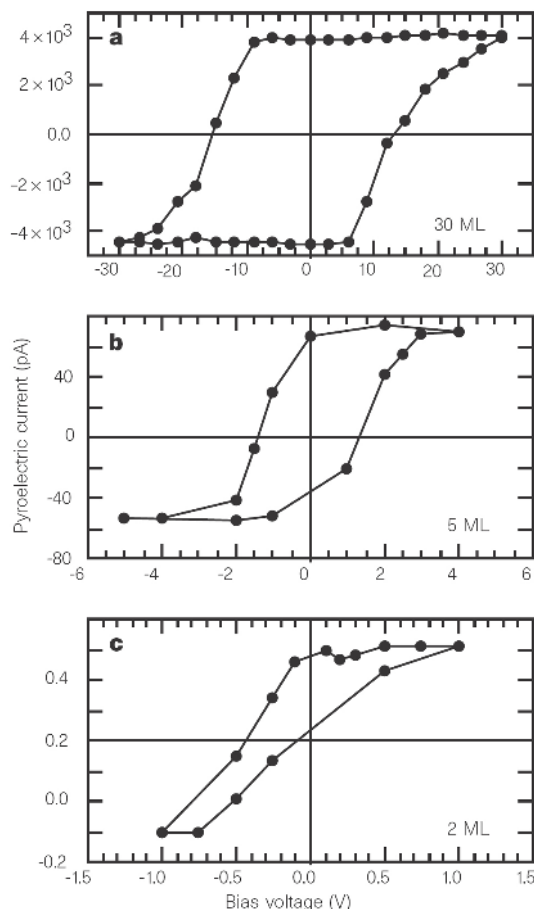

Figure 3. Pyroelectric response and spontaneous polarization P_s, obtained by integration over temperature, of P(VDF-TrFE 70:30) films. **a)** 30 ML; **b)** 5 ML; **c)** 2 ML.

Figure 4. Polarization hysteresis loops at 25 °C, measured by the pyroelectric technique, of the P(VDF-TrFE 70:30) films with different thicknesses. **a)** 30 ML; **b)** 5 ML; **c)** 2 ML.

Methods

The crystalline FLP films were formed by horizontal Langmuir–Blodgett deposition from a water subphase, as reported in greater detail previously [7,24]. The STM image (Figure 1b) was obtained using an MTD (Moscow, Russia) instrument with a 1-ML FLP film deposited on a graphite substrate [25]. The films for electric measurements were deposited on aluminium-coated glass substrates and overcoated with aluminium evaporated in vacuum. The dielectric response (Figure 3) was measured with a commercial RLC meter (Hewlett-Packard 4192A) at 1 kHz frequency and 0.1 V amplitude. The pyroelectric response at zero bias (Figure 2) and the hysteresis loops were measured by periodically heating the sample, with an 80-mW laser beam operating at 514.5-nm wavelength and modulated at 2 kHz, and measuring the short-circuit current with a lock-in amplifier. The relative spontaneous polarization was obtained by integrating the pyroelectric current over temperature.

References

1. Dürr, W., et al. Magnetic phase transition in two-dimensional ultrathin Fe films on Au(100). Phys. Rev. Lett. **62**, 206–209 (1989).

2. Farle, M., and Baberschke, K. Ferromagnetic order and the critical exponent gamma for a Gd monolayer: an electron-spin-resonance study. Phys. Rev. Lett. **58**, 511–514 (1987).

3. Mermin, N. D., and Wagner, H. Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models. Phys. Rev. Lett. **17**, 1133–1136 (1966).

4. Dowben, P. A., McIlroy, D. N., and Li, D. in Handbook on the Physics and Chemistry of Rare Earths (eds., Gschneidner, K. A., Jr., and Eyring, L.) Ch. 159 (Elsevier, Amsterdam, 1997).

5. Ishikawa, K., Yoshikawa, K., and Okada, N. Size effect on the ferroelectric phase transition in $PbTiO_3$ ultrafine particles. Phys. Rev. B **37**, 5852–5855 (1988).

6. Karasawa, J., Sugiura, M., Wada, M., Hafid, M., and Fukami, T. Ultra-thin lead titanate films prepared by tripole magnetron sputtering. Integrat. Ferroelectr. Lett. **12**, 105–114 (1996).

7. Palto, S., et al. Ferroelectric Langmuir-Blodgett films. Ferroelectr. Lett. **19**, 65–68 (1995).

8. Bune, A., et al. Novel switching phenomena in ferroelectric Langmuir-Blodgett films. Appl. Phys. Lett. **67**, 3975–3977 (1995).

9. Blinov, L. M., Fridkin, V. M., Palto, S. P., Sorokin, A. V., and Yudin, S. G. Thickness dependence of switching for ferroelectric Langmuir films. Thin Solid Films **284–285**, 474–476 (1996).

10. Sorokin, A., Palto, S., Blinov, L., Fridkin, V., and Yudin, S. Ultrathin ferroelectric Langmuir-Blodgett films. Mol. Mater. **6**, 61–67 (1996).

11. Scott, J. F. Phase transitions in ferroelectric thin films. Phase Trans. **30**, 107–110 (1991).

12. Tilley, D. R. in Ferroelectric Thin Films: Synthesis and Basic Properties (eds., Paz de Araujo, C., Scott, J. F., and Taylor, G. F.) 11–45 (Gordon & Breach, New York, 1996).

13. Scott, J. F. Properties of ceramic KNO_3 thin film memories. Physica B **150**, 160–167 (1988).

14. Lovinger, A. J. Ferroelectric polymers. Science **220**, 1115–1121 (1983).

15. Wang, T. T., Herbert, J. M., and Glass, A. M. (eds.) The Applications of Ferroelectric Polymers (Chapman & Hall, New York, 1988).

16. Furukawa, T. Ferroelectric properties of vinylidene fluoride copolymers. Phase Transit. **18**, 143–211 (1989).

17. Legrand, J. F. Structure and ferroelectric properties of P(VDF-TrFE) copolymers. Ferroelectrics **91**, 303–317 (1989).

18. Kimura, K., and Ohigashi, H. Polarization behavior in vinylidene fluoride-trifluroethylene copolymer thin films. Jpn J. Appl. Phys. **25**, 383–387 (1986).

19. Ducharme, S. et al. Critical point in ferroelectric Langmuir-Blodgett polymer films. Phys. Rev. B **57**, 25–28 (1998).

20. Allenspach, R., and Bishof, A. Magnetization direction switching in Fe/Cu(110) epitaxial films: temperature and thickness dependence. Phys. Rev. Lett. **69**, 3385–3388 (1992).

21. Qu, B. D., Zhang, P. L., Wang, Y. G., Wang, C. L., and Zhong, W. L. Dielectric susceptibility of ferroelectric thin films. Ferroelectrics **152**, 219–224 (1994).

22. Yamamoto, T. Calculated size dependence of ferroelectric properties in $PbZrO_3$-$PbTiO_3$ system. Integr. Ferroelectr. **12**, 161–166 (1996).

23. Wang, C. L., Zhong, W. L., and Zhang, P. L. The Curie temperature of ultra-thin ferroelectric films. J. Phys.: Cond. Matter **3**, 4743–4749 (1992).

24. Blinov, L. M. Langmuir films. Sov. Phys. Usp. **31**, 623–644 (1988).

25. Palto, S. et al. Ferroelectric Langmuir-Blodgett films showing bistable switching. Europhys. Lett. **34**, 465–469 (1996).

26. Zhang, R., and Taylor, P. L. Theory of ferroelectric-paraelectric transitions in VF_2/F_4E random copolymers. J. Appl. Phys. **73**, 1395–1402 (1993).