METHODOLOGICAL NOTES

Contents

PACS numbers: 77.55.-g, 77.80.-e, 77.84.Cg

Ferroelectric nanocrystals and their switching

V M Fridkin, R V Gaynutdinov, S Ducharme

DOI: 10.3367/UFNe.0180.201002f.0209

1.	Introduction	199
2.	from first principles	199
3.	The growth and switching of perovskite nanocrystals	202
4.	The growth and switching of ferroelectric polymer nanocrystals	203
5.	Conclusions	206
	References	206

<u>Abstract.</u> The behavior of ferroelectricity at the nanoscale is the focus of increasing research activity because of intense interest in the fundamental nature of spontaneous order in condensedmatter systems and because of the many practical applications of ferroelectric thin films and nanocrystals to, for example, electromechanical transducers, infrared imaging sensors, and nonvolatile memories. In recent years there has been increasing interest in the growth and characterization of ferroelectric nanocrystals. In spite of the limited number of reported results, we hope that this will be a useful review of important recent developments.

1. Introduction

The existence of ferroelectricity in ultrathin films and nanocrystals is limited by the critical size L_{cr} defined as the minimum thickness of a film or the minimum size of a crystal that is compatible with ferroelectricity. The Ginzburg–Landau mean field theory [1, 2] shows that L_{cr} is determined by two parameters: the surface energy and the screening energy. Perhaps the first attempt to determine L_{cr} experimentally was undertaken in [3], where ferroelectric polarization and its switching were observed in Langmuir–Blodgett (LB) films of two nominal monolayers

V M Fridkin, R V Gaynutdinov Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii prosp. 59, 199333 Moscow, Russian Federation Tel. (7-499) 135 15 00 Fax (7-499) 135 10 11 E-mail: fridkin@ns.crys.ras.ru S Ducharme Department of Physics and Astronomy, Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588-0111, USA E-mail: sducharme1@un1.edu

Received 14 September 2009 Uspekhi Fizicheskikh Nauk **180** (2) 209–217 (2010) DOI: 10.3367/UFNr.0180.201002f.0209 Translated by V M Fridkin; edited by A M Semikhatov

(2 ML, approximately 1 nm) of vinylidene fluoride and trifluoroethylene P(VDF-TrFE) copolymer films. In Ref. [4], ferroelectric polarization and its switching was reported for LB films only 1 ML (0.5 nm) thick, although measurements show that in LB films as thin as 2.7 nm, the remanent polarization of films is reduced by nearly 80% from the bulk value [5]. Therefore, although polarization is reduced, ferroelectricity does not appear to be limited by a critical amount in ferroelectric polymer thin films. Studies of unit cell tetragonality also supported the existence of ferroelectricity in ultrathin lead titanate perovskite films with thicknesses 1.2 nm [6] and 2.4 nm [7]. As with ferroelectric polymer LB films, the lead titanate films show a reduction in tetragonality (and presumably also in remanent polarization) as the film thickness tends to zero. The experimental results therefore imply that the critical thickness $L_{cr} \leq 1$ nm is very small or vanishing for both polymer and perovskite thin films. Theoretically, the value of L_{cr} for perovskites has been calculated from the first principles (six primitive cells, $L_{\rm cr} = 2.4$ nm) [8]. A detailed review of critical size investigations is given in [9].

It was suggested in [10] that one cannot expect to determine the critical size in the mean field theory framework [1, 2]. It has been shown in [11–14], however, that the Ginzburg–Landau mean field theory can be used to describe finite-size effects and to calculate the value of the critical thickness $L_{\rm cr}$ (or to explain its absence in some cases) if boundary conditions take the electrostatic mismatch between the electrode and the ultrathin ferroelectric film into account.

2. Critical size of ferroelectricity in accordance with the Ginzburg–Landau mean field theory and from first principles

For a ferroelectric with a first-order phase transition where the polarization P and the electric field E are perpendicular to the film plane, the polarization state can be described by mean field theory for the free energy per unit area [11-13]:

$$G = F_{0} + \frac{1}{L} \int_{-L/2}^{+L/2} \left[\frac{\alpha}{2} P^{2} + \frac{\beta}{4} P^{4} + \frac{\gamma}{6} P^{6} + \frac{D}{2} \left(\frac{\partial P}{\partial z} \right)^{2} - PE \right] dz + \frac{D}{2\delta L} \left[(P_{+} + P_{m})^{2} + (P_{-} + P_{m})^{2} \right],$$
(1)

where F_0 is the free energy of the paraelectric phase, P(z) is the polarization at a distance z from the center of the film, L is the film thickness, and P_{\pm} are the values of the polarization P at the film boundaries at $z = \pm L/2$. The Ginzburg–Landau coefficients α , β , and γ and the gradient energy coefficient D are properties of the ferroelectric material, while the interfaces between the ferroelectric film and electrodes are accounted for by the decay length δ proposed in [11] and the mismatch polarization Pm introduced in [12, 13]. (In general, P_m should be different at $z = \pm L/2$, but we presently assume that the ferroelectric film is bounded by the same material on both sides, eliminating this asymmetry. When the boundaries are dissimilar [15], the remanent polarization is asymmetric [16], which is also evident in the asymmetry of the conductance [17-22], for example.) The material properties are assumed to be independent of temperature, except for the Curie-Weiss coefficient, which has the form $\alpha = \alpha_0 (T - T_0)$.

Equation (1) implies the linearized equation of state in the form of the Euler–Lagrange equation:

$$\alpha P - D \, \frac{d^2 P}{dz^2} = E + 4\pi (\bar{P} - P) \,, \tag{2}$$

where \overline{P} is the spatial average value of the film polarization *P*. The boundary conditions for Eqn (2) are

$$P \pm \delta \left. \frac{\mathrm{d}P}{\mathrm{d}z} \right|_{z=\pm L/2} = -P_{\mathrm{m}} \,. \tag{3}$$

The importance of the boundary mismatch effect in nanoscale ferroelectric films was first shown in [14], but the boundary conditions in form (3) for ultrathin ferroelectric films were first introduced in [13] and are now widely used, although with different interpretations [9, 21, 23–25]. The effect of the interface on film polarization turns out to depend on the ratio P_m/P_b , where P_b is the spontaneous polarization in the bulk. The parameter P_m/P_b determines the critical thickness L_{cr} and the dielectric properties of nanoscale films and crystals. It was shown in [9] that for $P_m/P_b \simeq 10^{-1}$, the critical thickness L_{cr} is of the order of 1 nm, or effectively zero.

The solution of Eqns (2) and (3) in the linear approximation valid under the conditions $L, \delta \ge L_d = (D/4\pi)^{1/2}$ and $\alpha \le 2\pi$ give the following dependences for the average polarization $\bar{P}(L)$ [12] and average dielectric constant $\varepsilon(L)$ [25]:

$$P = P_{\rm b} \frac{1 - (P_{\rm m}/P_{\rm b}) \, \alpha \psi(L)/2}{\alpha^2 + \alpha \psi(L)} , \qquad (4)$$

$$\psi(L) = 4\pi \, \frac{2L_{\rm d}}{L} \frac{\tanh(L/2L_{\rm d})}{1 + (\delta/L_{\rm d}) \tanh(L/2L_{\rm d})} , \qquad (5)$$

$$c = \frac{2\pi}{\alpha + 2D/\delta L} \,. \tag{5}$$

Based on the experimental data reported in [7], it was shown in [13] that the mismatch effect very well explains the observed dependence of the average polarization $\bar{P}(L)$ on the film thickness L for ultrathin lead titanate films.

A comparison of P = P(L) and $\varepsilon = \varepsilon(L)$ with the mean field theory was performed for nanoscale LB copolymer films in [26, 27]. These films manifest spontaneous polarization $P_{\rm b} \simeq 0.1 \,{\rm C}\,{\rm m}^{-2}$ in the polar orthorhombic phase 2mm. In the temperature range from 20 °C to 145 °C (depending on the proportion of VDF to TrFE), the copolymer passes into the nonpolar hexagonal phase 6:m via a first-order phase transition [28]. The structure of LB films has been studied by means of X-ray and neutron diffraction, as well as scanning tunnel microscopy [29]. The LB copolymer films have a (110) orientation, meaning that the polarization P, which is along (010), is not exactly perpendicular to the film. The copolymer LB film thickness depends on preparation conditions, especially on the surface pressure of the Langmuir film before the transition [30]. At the deposition pressure 5 mN m⁻¹, the thickness of one nominal monolayer transferred to the substrate ranges from 0.5 to 1.8 nm [26]. At the deposition pressure 3.5 mN m^{-1} , the average thickness of one monolayer transfer is 0.6 nm [27], which corresponds to the thickness of one molecule. The thickness of LB films was measured by spectroscopic ellipsometry and atomic force microscopy (AFM) [26, 27].

The measured dependence of the polarization P on the film thickness L for nanoscale ferroelectric films P(VDF-TrFE, 70:30), obtained by the Langmuir-Blodgett method in [26, 27], is shown in Figs 1–3. Figure 1 shows the dependence of the relative polarization $P(L)/P_b$ as a function of *L*, where $P_b = 0.1 \text{ Cm}^{-2}$. The solid curve $P(L)/P_b$ in Fig. 1 was calculated from Eqn (4) with the coefficient values (at T = 300 K) $D \simeq 3 \times 10^{-18}$ m², $\delta \simeq 10^{-9}$ m, $\alpha = 1$ [7, 9, 24], and $\gamma = 1$ [27] and with the fitting parameter $P_{\rm m}/P_{\rm b} = 0.7$. Figure 2 shows a better correlation with Eqn (4) for the same values of D, δ , and α and the fitting parameter $P/P_b = 0.3$ [31]. As can be seen from the inset to Fig. 1, polarization reversal is measured even in a single monolayer, although with a much reduced remanent polarization; ferroelectricity exists in the thinnest possible ferroelectric polymer film. Polarization in a nanoscale film shows the time relaxation that depends on the thickness and substrate material [32].



Figure 1. Dependence of the relative polarization $P(L)/P_b$ for type-I films, from measurements in [27].



Figure 2. Dependence of the relative polarization $P(L)/P_b$ for type-II films from measurements (squares) and from Eqn (4) (line) [27, 31].



Figure 3. Dependence of the dielectric constant on temperature for two type-I samples: (1) 30 ML; (2) 2 ML thick [27].

The measurements of the dielectric constant ε in ferroelectric P(VDF-TrFE) films of nanometer thickness was first reported in [3]. Figure 3 shows the temperature dependence of $\varepsilon(L)$ obtained for films with the thickness 30 ML (curve 1) and 2 ML (curve 2). Curve 2 reveals the smearing of the phase transition, in qualitative agreement with Eqn (5). Substituting the coefficient values D = 3×10^{-18} m², $\delta \simeq 10^{-9}$ m, and $\alpha = 1$ [7, 9, 24] in Eqn (5), we obtain a similar smearing effect for film thicknesses in the range L = 1 nm to 8 nm. The presence of clear dielectric peaks even in a film 2 ML thick indicates that the ferroelectric state is robust even at the thickness 3.6 nm.

In Refs [33, 34], an effective Hamiltonian was constructed that was used to obtain the ferroelectric phase transition in a perovskite crystal (in BaTiO₃ in particular) by means of the Kohn density functional. Later, an *ab initio* method was developed in [8, 35, 36] for determining the critical thickness in perovskites. However, these calculations did not correctly take the boundary conditions into account and assumed that the screening field did not exist in the bulk of the ferroelectric. As a result, these calculations led to the incorrect conclusion that perovskites have no critical thickness. In Ref. [8], the density functional method was used for calculating the critical thickness for ultrathin BaTiO₃ (BTO) crystals placed between short-circuited SrRuO₃ (SRO) metal electrodes grown epitaxially on an SrTiO₃ substrate (Fig. 4). In addition, the finite



Figure 4. (a) Structure of the short-circuited capacitance SRO-BTO-SRO. (b) Atomic structure of the superlattice for m = 2 [8].



Figure 5. The energy of a BaTiO₃ film in the SRO–BTO–SRO heterostructure as a function of the polarization P_s , proportional to the shift ξ . The parameter of the curves is the number of BaTiO₃ primitive cells. The inset shows the critical thickness [8].

screening field in BaTiO₃, which depends on the Thomas– Fermi screening length in SRO and the polarization in the ferroelectric, was taken into account. The results of the calculations are shown in Fig. 5 as the energy of the system versus the shift ξ of a Ba atom, which is proportional to the polarization. The parameters at the curves are the numbers of BaTiO₃ primitive cells. We see that the critical thickness indeed exists and is equal to six primitive cells ($L_{cr} = 2.4$ nm) according to this calculation [8]. It follows that L_{cr} depends on the electrode material through both screening and strain [21, 37, 38]. In the case of complete screening and the absence of surface dopants and strains, it is likely that $L_{cr} = 0$, as was assumed in [8, 35, 36].

Certainly, BaTiO₃ is regarded in this theory as an ideal dielectric with no defects and hence no internal screening or leakages. All these additional reasons (and, in the case of LB films, also the influence of the substrate orienting the dipoles) lead, as we have already mentioned, to polarization relaxation in ultrathin films. For instance, it was shown in [39, 40] that for 6 nm BaTiO₃ films in the SRO–BTO–SRO sandwich, the tunnel current can have a considerable influence on hysteresis loops already at the voltage ~ 1 V.

This, in particular, can explain the discrepancy between the estimate of the critical thickness in Ref. [8] and the experimental results in Ref. [7].

A check of the first-principle conclusions for perovskites was performed in a few studies [6, 7, 41]. In Ref. [7], the tetragonality parameter c/a was measured for epitaxial nanoscale films of PbTiO₃, by $\Theta - 2\Theta$ X-ray diffraction as a function of the thickness. The tetragonality parameter c/awas shown to drastically decrease below the film thickness 200 Å. A detailed review of nanoscale ferroelectric perovskite films is given in [41].

We do not consider the switching of nanoscale ferroelectric films here in spite of the importance of these investigations, which were performed recently in several papers. For example, the investigation by AFM of nanoscale epitaxial lead zirconate titanate film switching in [42] permitted visualization of the nucleation centers controlling polarization switching processes with a nanometer resolution. It permitted, in turn, explaining the origins of the well-known Landauer paradox, that is, the experimentally low values of coercive fields corresponding to implausibly large nucleation activation energies.

Therefore, the Ginzburg–Landau mean field theory, taking the correct boundary conditions into account, explains the behavior of the ferroelectric properties of LB copolymer films at the nanoscale and even the absence of the critical thickness for ferroelectricity in these films, which is observed to be in the range from less than 2 nm to at most 5 nm. The *ab initio* calculation of the critical thickness and nanoscale ferroelectric properties has just started. Although several *ab initio* calculations have been made for the bulk crystal of polyvinylidene fluoride (PVDF) [43–46] and its copolymers P(VDF-TrFE) [47], only one calculation reports the influence of the boundaries. Therefore, at present, it is difficult to reliably compare these two approaches for ferroelectric LB films.

3. The growth and switching of perovskite nanocrystals

The growth and investigation of ferroelectric nanocrystals is the next important step in the development of ferroelectric nanotechnology. One of the first papers devoted to ferroelectric nanocrystals [48] concerned lead titanate particles ranging from 20 nm to 2000 nm in diameter that were produced by a sol-gel process followed by calcining at different temperatures. High-resolution transmission electron microscopy was used to image the nanostructure of these ultrafine ferroelectric lead titanate particles. It was shown that the tetragonality parameter c/a and the domain size decreased with decreasing the crystal size, and the crystals became cubic, and therefore certainly paraelectric, when their diameter was less than 20 nm. In that paper, however, the switching and other ferroelectric properties of nanocrystals were not investigated. Nanocrystalline barium titanate made by sol-gel synthesis and studied by X-ray diffraction and second-harmonic generation exhibited a critical size for the ferroelectric phase at the diameter approximately equal to 50 nm [49]. Barium titanate nanorods with diameters ranging from 3 to 50 nm were shown to exhibit finite-size scaling of both the remanent polarization and the ferroelectric-paraelectric phase transition in rods as small as 3 nm in diameter, at which both the polarization switching and the ferroelectric-paraelectric phase transition

occur [50]. In this case, the ferroelectric properties were shown to be strongly influenced by the surface chemistry; for example, absorption of OH appears to stabilize the ferroelectric state.

Direct observation of polarization switching with nanocrystals was first reported in [51] for $Bi_4Ti_3O_{12}$ (BiT). Selfassembled ferroelectric nanocrystals with the average lateral size 180 nm were obtained by epitaxial growth of BiT by pulsed laser deposition on a metallic film. The switching was observed by a functional form of AFM called piezoresponse force microscopy (PFM), in which the strain occurring as a response to a small ac voltage is imaged as the AFM tip is scanned across a sample. Figure 6 shows AFM topographic images of the nanocrystals. The hysteresis loops obtained for two different crystals show a coercive voltage about 3V, corresponding to the field 55 kV cm⁻¹.

Single ferroelectric lead titanate (PTO) nanocrystals were obtained and investigated by AFM and PFM in [52]. The PTO nanograins were deposited onto Si/SiO₂/TiO₂/Pt substrates. An anhydrous lead acetate-based precursor solution was spin-coated onto the substrate and dried for 2 min on a hot plate at 350 °C. Crystallization was initiated by a rapid thermal annealing process at 700 °C for 10 min, resulting in separate single PTO nanocrystals (Fig. 7). The separate PTO crystals have no predominant crystallographic orientation, as proven by X-ray diffraction. The sizes of the crystals were in the range 15-200 nm. The images obtained by PFM revealed 90° and 180° domain walls. The domain structure of PTO nanocrystals depended on the crystal size. The domain structure and piezoresponse disappear for very small nanocrystals. The authors concluded that the critical size of PTO nanocrystals is in the range 4-14 nm. Subsequent PFM experiments revealed hysteresis loops and ferroelectric switching in PTO nanocrystals (with the lateral size less than 100 nm) [52]. Another group studying PTO nanocrystals came to the conclusion that the critical size of ferroelectric nanocrystals could be less because the nanocrystals are integrated into a circuit and therefore exposed to new electromechanical boundary conditions [42].

Lead zirconate titanate (PZT) nanoislands were obtained by a self-assembly method using the instability of ultrathin films during high-temperature treatments [53]. After hightemperature annealing, the deposited film breaks into islands with a narrow size distribution (10-40 nm). The single-crystal nanoislands were studied by scanning and high-resolution transmission electron microscopy, AFM, and X-ray diffraction. They have shown an epitaxial growth on the Nb-doped (001) SrTiO₃ substrate. Hysteresis loops and switching were revealed by PFM. The ferroelectric-paraelectric phase transition was also investigated in nanocrystals of PZT prepared by the sol-gel method. Nanocrystals with the average size 13 nm exhibited the transition temperature about 470 °C. Unfortunately, there is no data about switching kinetics, which makes it difficult to evaluate the possibility of their application in nonvolatile memories.

An important step for critical size investigation in ferroelectric nanocrystals was reported in [54]. The authors have performed synchrotron radiation X-ray diffraction measurements to investigate the size effect in ferroelectric nanoscale ($Pb_{0.7}Sr_{0.3}$)TiO₃ crystals with sizes ranging from 10 to 200 nm. They have shown that the tetragonality parameter c/a and the atomic distance between anions and cations decrease gradually in the vicinity of the nanocrystal



500 nm

Figure 6. Images of $Bi_4Ti_3O_{12}$ nanocrystals showing (a) topography (AFM) and (b), (c) piezoresponse (PFM). The polarization of the righthand nanocrystal was switched from (b) to (c) by application of a single voltage pulse of 110 V for 100 ms [51].

surface. These results open a new way to obtain the ferroelectric nanocrystal critical size and show the possibility of forming a new gradational system. The formation of regular arrays of ferroelectric nanocrystals is an essential step for the fabrication of nonvolatile random-access memories. Such arrays can, for example, be made by physical deposition through self-assembled nanosphere masks [55] or by nanoimprinting [56–58].



Figure 7. Scanning electron microscope image of PTO nanocrystals deposited onto an $Si/SiO_2/TiO_2/Pt$ substrate using a modified CSD route. Grains of different shape and size can be found. The grain size ranges from about 100 nm down to several dozen nm [52].

4. The growth and switching of ferroelectric polymer nanocrystals

Nanocrystals of copolymers of vinylidene fluoride with trifluoroethylene P(VDF-TrFE) exhibit a structure and physical properties similar to those of the ferroelectric phase of the prototype PVDF polymer. This phase consists of alltrans molecular conformation where the polymer chains are arranged in a close-packed structure with the polarization normal to the mirror plane containing the chain axis [59, 60]. The copolymers crystallize either in lamellar crystals with the chains folding back and forth across the crystal width or in an extended-chain form with little folding [61, 62]. The crystal structure and ferroelectric properties of the two forms appear to be the same [63, 64]. Furthermore, nanocrystalline films of copolymers consisting of nanocrystals as small as 30 nm across or 1 nm thick exhibit robust ferroelectric properties [3, 65, 66]. Isolated lamellar nanocrystals approximately 10 nm thick along the chain axis and 500 nm across were grown from LB films [67]. Electron microscopy of individual crystals (Fig. 8) showed clear lattice images, and tilt-angle electron diffraction studies found that they have the monoclinic space group C_2^3 (axis 2 is the special polar direction) [67], which differs from the widely reported orthorhombic structure [28, 68] by a slight (3) distortion corresponding to a slight longitudinal shift of the chains. No studies were made of the polarization or dielectric properties of these crystals.

Arrays of isolated nanocrystals of the copolymer of vinylidene fluoride and trifluoroethylene P(VDF-TrFE) were made from ultrathin (1–5 monolayers) LB films followed by annealing in the paraelectric phase at 125 °C [69–71]. Self-assembly leads to the growth of nanocrystals (Fig. 9) of ferroelectric copolymer approximately 4–12 nm thick and 50–180 nanometers in diameter, where the dimensions depend on the substrate material, the copolymer composition, the number of monolayers, and the annealing temperature [70, 71]. Remarkably, this nanocrystal self-



Figure 8. (a) TEM image from a nanocrystal found on an 8-monolayer LB film deposited on a TEM copper grid at the pressure 5 mN m⁻¹. (b) The electron diffraction pattern and (c) the lattice image from a single crystal of image (a). The scale bar in (c) shows the direction of the *b*-axis for the standard β -phase lattice [67].

assembly occurs in the paraelectric phase [70] but not in the ferroelectric phase, supporting suggestions that the polymer

conformation is both disordered and fluctuating in the paraelectric phase [28, 63, 72, 73].

Ferroelectricity in copolymer nanocrystals was confirmed by polarization reversal, which was evident collectively in the $\sim 1 \text{ mm}^2$ arrays of nanocrystals by the hysteresis of capacitance and pyroelectric response [69]. The switched polarization and switching time of nanocrystal arrays were measured by the double-pulsed current method (to separate contributions from polarization reversal and capacitor charging) [74]. Switching times ranging from 2 to 50 µs exhibited an exponential dependence on the reciprocal voltage [74], which is consistent with the nucleation and domain-wall growth mechanism [75, 76].

The first investigation of the ferroelectric properties of individual copolymer nanocrystals was reported in [77] and [78] (see also Fig. 10), where switching of the nanocrystals was observed in the AFM piezoelectric regime. As a result, we proposed the domain mechanism of switching and the existence of nanodomains in copolymer nanocrystals. Kinetic studies of polymer nanocrystal switching were also consistent with nucleation-limited switching dynamics [74, 78]. At first sight, the results in [77] contradict the homogeneous (intrinsic) switching of ultrathin copolymer LB films obtained independently in [32, 79], and therefore resolving this puzzle requires measuring the kinetics of polarization domains directly and determining their dependence on the temperature and the electric field [32]. On the other hand, the AFM investigation of switching kinetics at the nanoscale in ferroelectric copolymer LB films reveals a domain (extrinsic) mechanism, which is consistent with nucleation-limited switching dynamics [80]. Polarization switching kinetics were reported recently [78] for individual nanocrystals of a ferroelectric copolymer approximately 20-30 nm thick and 100-200 nm in diameter, with somewhat irregular shapes, as shown in Fig. 10 [78]. The nanocrystal polarization could be repeatedly switched between two stable states (Fig. 11) and exhibits a well-saturated hysteresis loop (Fig. 12). The dependence of switching time on switching voltage (Fig. 13) for an individual nanocrystal with the thickness L = 30 nm



Figure 9. AFM images of 1 ML LB films of a 75:25 copolymer deposited on Si wafers show a gradual development of the morphology as the annealing temperature increases. All the images represent film areas 2 μ m by 2 μ m [70].

nm

500

400

300

200

100

0

100

200

300

400

500 nm

Figure 10. Images of nanocrystals by (a) AFM topography and (b) PFM amplitude times cos(PFM phase) [78].



Figure 11. Piezoresponse (amplitude times cosine phase) images of the nanocrystal indicated by the arrow in Fig. 10a at the following stages: (a) initial phase image; (b) after applying the bias voltage -10 V; (c) after applying the bias voltage +10 V; (d) after again applying the bias voltage -10 V [78].

follows the exponential form $\exp(E_aL/V)$ [75], where the activation field is $E_a = 1.4$ GV m⁻¹, a little larger than the value 1 GV m⁻¹ obtained with thin-film capacitors of a similar 73:27 composition copolymer [81].

We expect that ferroelectric polymer single crystals will support multiple stable domains [82, 83], but the experimental evidence to date is not entirely clear. The main difficulty lies in identifying and delimiting individual crystals, since they tend to be lamellar [60]. Although several papers reported stable polarization patterns in polycrystalline ferroelectric polymer films [65, 66, 84, 85] and polarization reversal with whole grains [66, 77], none of these reports have confirmed whether multiple stable domains exist within a single crystal. Two reports of STM imaging with molecular resolution have provided tantalizing evidence of domain wall motion, but the domain stability was not established in either report of this phenomenon [86, 87]. It is currently unclear whether single crystals of ferroelectric polymers support multiple stable domains. A nanocrystal may support stable domain patterns [77, 88], but it has yet to be verified that they are single crystals. Clearly, we are just beginning to scratch the surface, so to speak, of ferroelectric polymer nanocrystals.

0.5

0

Ч

-0.5

-1.0

-15

-2.0



500

0

-500

₽d

nm

500

400

300

200

100

0

100

200

300

400

500 nm



Figure 12. Piezoresponse hysteresis loop of the nanocrystal indicated by the arrow in Fig. 10a [78].



Figure 13. The switching rate (reciprocal switching time) vs V_c/V for the nanocrystal indicated by the arrow in Fig. 10a [78].

5. Conclusions

The investigation of ferroelectricity and related properties in nanocrystals is an important issue of rapidly growing interest because of its implications for the fundamental understanding of the nature of ferroelectricity and for the success of the many applications of ferroelectric materials, as has been underlined by Ginzburg [89]. The main results of early investigations of ferroelectric nanocrystals show that some, perhaps many, kinds of ferroelectrics do not exhibit a critical or minimum size for stabilizing spontaneous polarization. This is consistent with the Ginzburg-Landau mean field theory, where, with the proper boundary conditions, the critical size in ferroelectricity is very small (or does not even exist). A very small critical size was also obtained for perovskites in the ab initio computational approach, which allows examining the properties with atomic-scale detail.

The application of ferroelectric nanocrystals, e.g., for random access memory (and in other technologies) also strongly depends on the kinetics of the switching. Besides facilitating much higher device densities, ferroelectric nanocrystals should switch more quickly, due to the short distances that domain walls have to travel, under the condition that domain nucleation and domain-wall pinning can be properly controlled. The first investigations of the switching kinetics in ferroelectric nanocrystals of many materials have so far shown promise for device operation speeds ranging from microseconds for polymers [74] to nanoseconds for perovskites [90, 91]. These early results show that ferroelectric nanocrystals are candidates for highdensity nonvolatile storage media devices.

Acknowledgments

The work at the Institute of Crystallography was supported by the European INTAS program (grant No. 1000008-8091) and by the Russian Foundation for Basic Research (grant Nos 05-0216871 and 09-02-00096). The work at the University of Nebraska was supported by the USA National Science Foundation (grant No. ECS-0600130) and by the Nebraska Research Initiative.

References

- 1. Ginzburg V L Zh. Eksp. Teor. Fiz. 15 739 (1945); J. Phys. USSR 10 107 (1946)
- 2 Ginzburg V L Zh. Eksp. Teor. Fiz. 19 36 (1949)
- 3. Bune A V et al. Nature 391 874 (1998)
- Ievlev A, Verkhovskaya K, Fridkin V Ferroelectrics Lett. 33 147 4. (2006)
- 5. Tadros-Morgane R, Kliem H J. Phys. D 39 4872 (2006)
- 6. Fong D D et al. Science 304 1650 (2004)
- 7. Lichtensteiger C et al. Phys. Rev. Lett. 94 047603 (2005)
- 8. Junquera J, Ghosez P Nature 422 506 (2003)
- 9. Fridkin V M Usp. Fiz. Nauk 176 203 (2006) [Phys. Usp. 49 193 (2006)]
- 10 Spaldin N A Science 304 1606 (2004)
- 11. Tilley D R, Žekš B Solid State Commun. 49 823 (1984)
- Glinchuk M D, Morozovska A N J. Phys. Condens. Matter 16 3517 12 (2004)
- 13. Glinchuk M D, Morozovska A N, Eliseev E A J. Appl. Phys. 99 114102 (2006)
- 14. Zembilgotov A G et al. J. Appl. Phys. 91 2247 (2002)
- Miller S L et al. J. Appl. Phys. 70 2849 (1991) 15.
- 16. Wurfel P, Batra I P Phys. Rev. B 8 5126 (1973)
- Bune A et al. Appl. Phys. Lett. 67 3975 (1995) 17
- Abe K et al. Jpn. J. Appl. Phys. 36 5846 (1997) 18.
- Zhuravlev M Ye et al. Appl. Phys. Lett. 87 222114 (2005) 19.
- 20. Zhuravlev M Ye et al. Phys. Rev. Lett. 94 246802 (2005)
- 21. Duan C-G et al. Nano Lett. 6 483 (2006)
- 22. Tsymbal E Y, Kohlstedt H Science 313 181 (2006)
- 23.
- Bratkovsky A M, Levanyuk A P Phys. Rev. Lett. 94 107601 (2005) Duan C-G, Jaswal S S, Tsymbal E Y Phys. Rev. Lett. 97 047201 24 (2006)
- 25. Fridkin V M J. Phys. Condens. Matter 16 7599 (2004)
- 26. Blinov L M et al. Usp. Fiz. Nauk 170 247 (2000) [Phys. Usp. 43 243 (2000)]
- 27. Tolstousov A et al. Ferroelectrics 354 99 (2007)
- 28. Bellet-Amalric E, Legrand J F Eur. Phys. J. B 3 225 (1998)
- 29 Ducharme S, Palto S P, Fridkin V M, in Handbook of Thin Film Materials Vol. 3 Ferroelectric and Dielectric Thin Films (Ed. H S Nalwa) (San Diego: Academic Press, 2002) p. 545
- 30. Sorokin A V et al. J. Appl. Phys. 92 5977 (2002)
- 31. Kliem H, Tadros-Morgane R J. Phys. D 38 1860 (2005)
- Vizdrik G et al. Phys. Rev. B 68 094113 (2003) 32.
- 33. Ivanov O V, Shport D A, Maksimov E G Zh. Eksp. Teor. Fiz. 114 333 (1998) [Sov. Phys. JETP 87 186 (1998)]
- 34. Maksimov E G, Zinenko V I, Zamkova N G Usp. Fiz. Nauk 174 1145 (2004) [Phys. Usp. 47 1075 (2004)]
- 35. Ghosez Ph, Rabe K M Appl. Phys. Lett. 76 2767 (2000)
- Meyer B, Vanderbilt D Phys. Rev. B 63 205426 (2001) 36.
- Stengel M, Spaldin N A Nature 443 679 (2006) 37.
- 38 Stengel M, Vanderbilt D, Spaldin N A Nature Mater. 8 392 (2009)
- 39 Kohlstedt H, Pertsev N A, Waser R, in Ferroelectric Thin Films X: Symp., November 25-29, 2001, Boston, Mass., USA (MRS Symp. Proc., Vol. 688, Eds S R Gilbert et al.) (Warrendale, Penn.: Mat. Res. Soc., 2002) p. 161

- 40. Jesse S et al. Nature Mater. 7 209 (2008)
- 41. Rabe K M, Ahn C H, Triscone J-M *Physics of Ferroelectrics: a* Modern Perspective (Berlin: Springer, 2007)
- 42. Rüdiger A et al. Appl. Phys. A 80 1247 (2005)
- 43. Duan C et al. Europhys. Lett. 61 81 (2003)
- 44. Nakhmanson S M, Nardelli M B, Bernholc J Phys. Rev. Lett. 92 115504 (2004)
- 45. Ramer N J, Stiso K A Polymer 46 10431 (2005)
- 46. Ramer N J, Raynor C M, Stiso K A Polymer 47 424 (2006)
- Nakhmanson S M, Nardelli M B, Bernholc J Phys. Rev. B 72 115210 (2005)
- 48. Zhong W L et al. J. Phys. Condens. Matter 5 2619 (1993)
- 49. Schlag S, Eicke H-F Solid State Commun. 91 883 (1994)
- 50. Spanier J E et al. *Nano Lett.* **6** 735 (2006)
- 51. Alexe M et al. Appl. Phys. Lett. 75 1158 (1999)
- 52. Roelofs A et al. Appl. Phys. Lett. 81 5231 (2002)
- 53. Szafraniak I et al. *Appl. Phys. Lett.* **83** 2211 (2003)
- 54. Shikanai F et al. J. Phys. Condens. Matter 21 025903 (2009)
- 55. Ma W et al. Appl. Phys. Lett. 83 3770 (2003)
- 56. Harnagea C et al. Appl. Phys. Lett. 83 1827 (2003)
- 57. Hu Z et al. *Nature Mater*. **8** 62 (2009)
- 58. Ducharme S, Gruverman A Nature Mater. 8 9 (2009)
- 59. Davis G T et al. Macromolecules 15 329 (1982)
- 60. Lovinger A J Science 220 1115 (1983)
- 61. Hikosaka M et al. Jpn. J. Appl. Phys. 32 2029 (1993)
- 62. Ohigashi H, Omote K, Gomyo T Appl. Phys. Lett. 66 3281 (1995)
- 63. Furukawa T et al. Ferroelectrics 32 61 (1981)
- 64. Omote K, Ohigashi H, Koga K J. Appl. Phys. 81 2760 (1997)
- 65. Fukuma T et al. Jpn. J. Appl. Phys. **39** 3830 (2000)
- 66. Rodriguez B J et al. Appl. Phys. Lett. 90 122904 (2007)
- 67. Bai M, Li X Z, Ducharme S J. Phys. Condens. Matter 19 196211 (2007)
- Tashiro K, in Ferroelectric Polymers: Chemistry, Physics, and Applications (Ed. H S Nalwa) (New York: M. Dekker, 1995) p. 63
- 69. Bai M, Ducharme S Appl. Phys. Lett. 85 3528 (2004)
- 70. Bai M, Poulsen M, Ducharme S J. Phys. Condens. Matter 18 7383 (2006)
- 71. Li J, Luo Y, Bai M, Ducharme S J. Mech. Phys. Solids 54 2162 (2006)
- Kodama H, Takahashi Y, Furukawa T Jpn. J. Appl. Phys. 38 3589 (1999)
- 73. Ahluwalia R et al. Phys. Rev. B 78 054110 (2008)
- 74. Othon C M, Kim J, Ducharme S, Fridkin V M J. Appl. Phys. 104 054109 (2008)
- 75. Merz W J J. Appl. Phys. 27 938 (1956)
- 76. Fatuzzo E, Merz W J Phys. Rev. 116 61 (1959)
- 77. Kim J, PhD Dissertation (Lincoln, NE: Univ. of Nebraska, 2008)
- 78. Gaynutdinov R V et al. Appl. Phys. Lett. 95 023303 (2009)
- 79. Geivandov A R et al. Zh. Eksp. Teor. Fiz. **126** 99 (2004) [JETP **99** 83 (2004)]
- 80. Gaynutdinov R V et al. Appl. Phys. Lett. 92 172902 (2008)
- 81. Nakajima T et al. Jpn. J. Appl. Phys. 44 L1385 (2005)
- 82. Li G-R, Kagami N, Ohigashi H J. Appl. Phys. 72 1056 (1992)
- 83. Ohigashi H, Kagami N, Li G R J. Appl. Phys. 71 506 (1992)
- 84. Chen X et al. Jpn. J. Appl. Phys. **37** 3834 (1998)
- 85. Blinov L M et al. J. Appl. Phys. **89** 3960 (2001)
- 86. Ludwig Ch et al. *Ann. Physik* **505** 323 (1993)
- 87. Qu H et al. *Appl. Phys. Lett.* **82** 4322 (2003)
- Sharma P et al. J. Phys. Condens. Matter 21 485902 (2009)
- 89. Ginzburg V L Usp. Fiz. Nauk 169 419 (1999) [Phys. Usp. 42 353
- (1999)] 90. Fujimoto K, Cho Y Jpn. J. Appl. Phys. **43** 2818 (2004)
- 91. Gruverman A, Wu D, Scott J F Phys. Rev. Lett. 100 097601 (2008)