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Homogeneous switching in ultrathin ferroelectric films

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Abstract

It is well known that there are two possible switching mechanisms in ferroelectric crystals and films (see, e.g., Tagantsev *et al* 2010 *Domains in Ferroic Crystals and Thin Films* (Berlin: Springer)). The first mechanism, which follows from the mean-field theory of Landau–Ginzburg, is a homogeneous one and does not connect domains. This mechanism was never observed before 1998. The second mechanism, connected with nucleation and domain movement, is common for the ferroelectrics and is well known from the time of domain discovery (1956). In the present paper the existence of a homogeneous mechanism of switching in ultrathin copolymer films is confirmed by piezoresponse force microscopy. The results of the present paper permit us to suppose that homogeneous switching exists in other ultrathin ferroelectric films.

1. Introduction

The mean-field theory of Landau–Ginzburg (LG) (1949) explained all the ferroelectric phenomena: the phase transitions of the second and first order (near to the critical point) from the para- to ferroelectric phase, the temperature dependence of the spontaneous polarization and the dielectric properties in the vicinity of the Curie point (or phase transition point) and other ferroelectric properties. It could only not explain the experimentally observed value of coercive field E_C (coercive voltage V_C). Considering the switching of a crystal (or film) as homogeneous, the LG theory predicted very high values of coercive field E_C , which are 2–3 orders of magnitude greater than the experimental ones. For BaTiO₃, LG theory gives $E_C \approx 5 \times 10^8$ – 10^9 V m⁻¹.

This situation remained unclear for almost seven years. In 1956 Chernysheva [1] discovered crystal domains in the Rochelle salt and a little bit later Indenbom showed that these domains move in the external electric field. Thus the ferroelectric switching has been interpreted by a domain mechanism, which explained in turn the low experimental values of E_C . The book of Tagantsev *et al* gives a comprehensive theory of domain switching in the ferroelectric crystals and films [2].

In 1994 the first ultrathin ferroelectric Langmuir–Blodgett films of copolymer vinylidene fluoride trifluoroethylene P(VDF–TrFE) were grown [3]. The films consisting of

only two monolayers ($L \approx 1$ nm) have shown spontaneous polarization $P_s \approx 0.1$ C m⁻² and a hysteresis loop of switching [4]. It gave a start to the investigation of the size effect in the nanoscale, where earlier ferroelectricity has been not observed at all.

The work [4] simultaneously raised the question about the mechanism and kinetics of ultrathin copolymer switching. In accordance with [2] the size of the critical domain nucleus in BaTiO₃ $l = 5$ – 10 nm (even bigger in the copolymer) is greater than the thickness of the films investigated in [4]. Therefore it is possible to suppose that homogeneous switching exists in the ferroelectric copolymer and possibly in other ultrathin ferroelectric films.

2. The theory of homogeneous switching

The theory of homogeneous switching for ferroelectrics with the first-order phase transition has been developed in [5]. The kinetics of homogeneous switching could be described by Lagrange dynamics or the Landau–Khalatnikov equation [6]:

$$\xi \frac{dP}{dt} = -\frac{dF}{dP} = -\alpha P - \beta P^3 - \gamma P^5 + E \quad (1)$$

where P is spontaneous polarization, F is free energy, E is external field, α , β and γ are well-known LG coefficients and ξ is a phenomenological parameter (damping constant).

The solution of (1) leads to the critical character of ferroelectric switching at $V = V_C$, where V_C is coercive

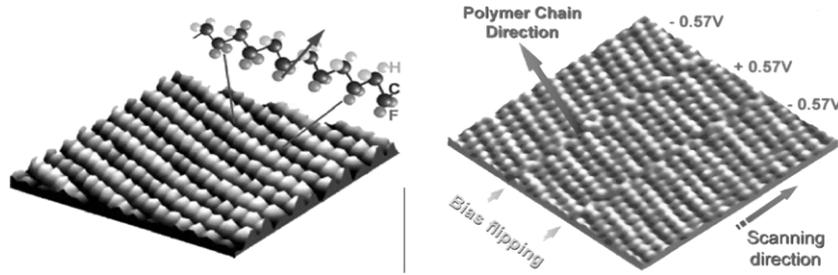


Figure 1. The STM image of the monolayers (2 ML), ferroelectric copolymer films and its switching. Reproduced with permission from [8]. Copyright 2003 American Institute of Physics.

voltage, obtained from the hysteresis loop. The dependence of switching time τ on V is given by (2):

$$\tau^{-1} = \frac{\beta^2}{6.3\gamma\xi} \left(\frac{V}{V_C} - 1 \right)^{1/2}. \quad (2)$$

Equation (2) shows that at $V < V_C$ the switching is absent and at $V = V_C$ the switching time τ is infinitely large. The switching takes place only at $V > V_C$.

3. Ultrathin copolymer P(VDF-TrFE) ferroelectric films

The preparation and ferroelectric properties of copolymer films P(VDF-TrFE), prepared by the Langmuir–Blodgett method, have been described in detail [7]. They reveal spontaneous polarization $P_s \approx 0.1 \text{ C m}^{-2}$ in the 2 nm polar orthorhombic phase and a ferroelectric phase transition of first order to the hexagonal paraelectric phase at $80^\circ\text{--}100^\circ$ (depending on the ratio VDF:TrFE). Figure 1 shows the scanning tunneling microscope image of two monolayers P(VDF-TrFE) (70:30) on the graphite substrate, the structure of the polymer chain and switching of the two monolayers [8].

It was supposed that the switching of such ultrathin films must be homogeneous and its kinetics has to be described by equations (1) and (2).

The first investigation of the switching kinetics was undertaken in [5] by the Chinoweth method. The thick film (like well-known bulk spin copolymer films [9]) reveals a domain switching mechanism with exponential dependence: $\tau^{-1} = \tau_o^{-1} \exp(-V_0/V)$. The thin films show critical behavior and absence of switching at $V < V_C$. Very large scattering of the experimental points did not permit us to check the expression (2). The next attempt to prove (2) was undertaken in [10] by the Merz method. It has shown relatively good coincidence with (2).

In the present paper the switching of the copolymer Langmuir–Blodgett ferroelectric films has been performed by piezoresponse force microscopy (PFM).

4. The PFM switching

The PFM measurements were carried out with a scanning probe microscope, Ntegra Prima (NT-MDT, Moscow). The CSC21 cantilevers (MicroMash, Estonia) coated with a Ti–Pt conductive layer (radius of 40 nm) were used. The

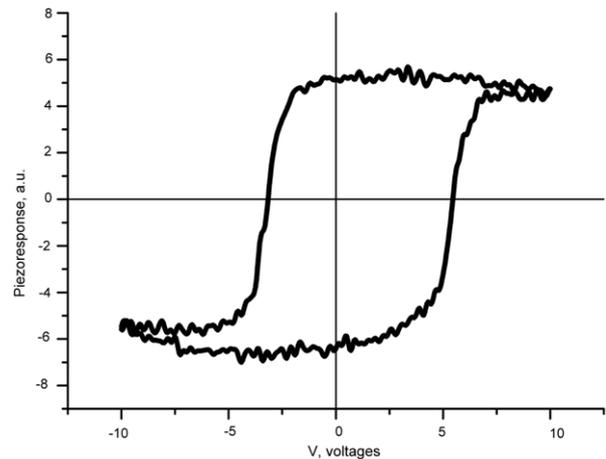


Figure 2. PFM hysteresis loop for ferroelectric copolymer film (10 ML).

piezoresponse was measured by applying an excitation voltage of amplitude 1.0 V and frequency 150 kHz. The measurements were carried out in air in a class 10000 clean room maintained at stable temperature and humidity. The sample temperature was held at 24°C for all reported measurements.

In the present paper the PFM switching of the copolymer Langmuir–Blodgett films with thicknesses $L \approx 10$ and 40 nm, transferred to a silicon substrate, is performed. The method of film preparation is described in [7]. The thickness was controlled by AFM.

The hysteresis loop is recorded by the pulse-measure method which consists of applying a sequence of 1000 ms voltage pulses at the fixed location, starting at -10 V , increasing in steps to $+10 \text{ V}$, and then to -10 V (figure 2). Each bias pulse was followed by a measurement of the piezoresponse at zero bias.

The switching kinetics was also measured by the pulse-measure method, which consists of applying voltage pulses of -10 V ($+10 \text{ V}$) for 100 s with the subsequent application of positive (negative) group pulses of given voltage with increasing pulse duration. Each positive (negative) voltage pulse was followed by a measurement of the piezoresponse at zero bias. The measurements of the switching kinetics were carried out for a series of voltages. The switching time τ for a given pulse amplitude was defined as the value of the pulse duration for which the resulting piezoresponse crossed zero (figure 3).

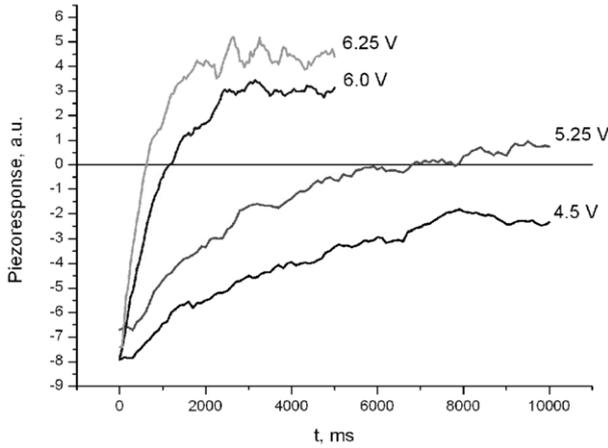
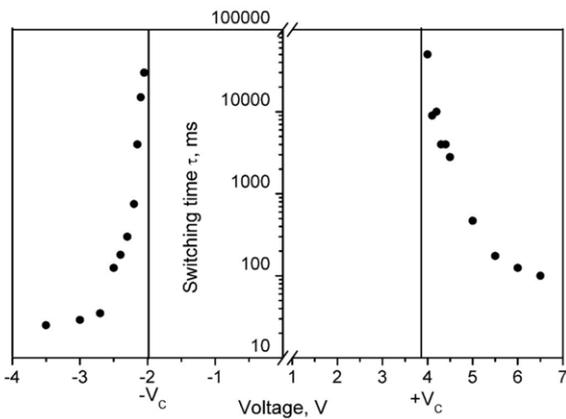


Figure 3. The PFM switching kinetics for ferroelectric copolymer film.



a

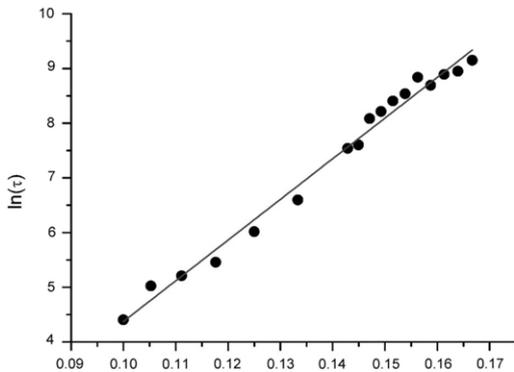


Figure 4. (a) The voltage dependence of switching time $\tau = \tau(V)$, obtained from figure 3 for 10 ML. (b) The same voltage dependence for 30 ML.

In figure 3 for $L = 10$ ML the switching curves, as a dependence of piezoresponse on time, corresponding to four voltages are shown (switching kinetics). It is seen that in the region $V \approx 5$ V (in the vicinity of coercive voltage V_c), see figure 3, the switching curve does not cross the zero line ($\tau \rightarrow \infty$).

The dependence $\tau = \tau(V)$ near the critical point $V_c \sim E_c$ is presented in figure 4(a). Figure 4(b) shows the domain mechanism of switching for 30 ML. Figure 4(a) also indicates

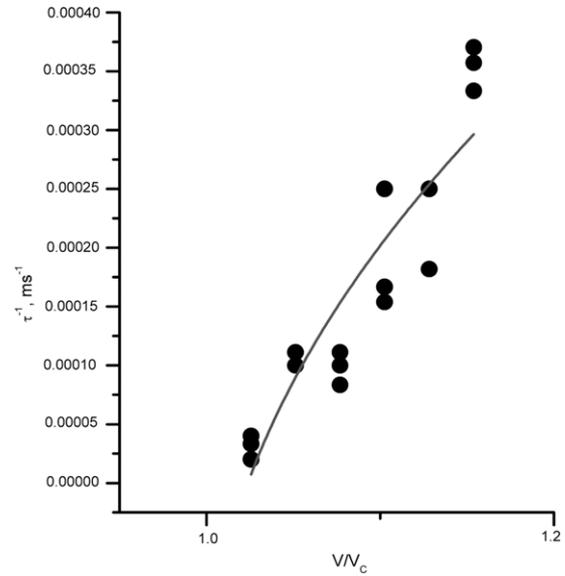


Figure 5. The dependence $\tau^{-1} = \tau^{-1}(V/V_c)$, V_c is the coercive voltage. (10 ML). The solid line is given by (2).

for $L = 10$ ML the nondomain critical mechanism and absence of switching at $V < V_c$.

For $L = 10$ ML the dependence of

$$\tau^{-1} = \tau^{-1} \left(\frac{V}{V_c} \right)$$

is shown in figure 5 and coincides with (2).

5. Conclusion

The investigation of the switching kinetics of the ultrathin copolymer ferroelectric films performed in the present paper by means of PFM confirms the results [5, 10] and shows homogeneous nondomain switching. This kind of kinetics has never been observed experimentally in ferroelectric crystals and films. It was possible to suppose that homogeneous switching could also be observed in the ultrathin perovskite films. In fact, the switching hysteresis loops have been observed in BaTiO_3 films with thickness $L \approx 7\text{--}9$ nm (see, e.g., [11]). Because the middle size of the critical domain nucleus is $L \approx 5\text{--}10$ nm [2], it is difficult to imagine the domain formation in these ultrathin perovskite films. This supposition was recently confirmed in [12] for ultrathin (2–10 nm) PbTiO_3 epitaxial films by the synchrotron x-ray scattering method, where a homogeneous nondomain switching mechanism was found. But up to now the switching kinetics of such ultrathin perovskite films has not been observed.

Acknowledgments

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