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Polarization switching kinetics of ferroelectric nanostructures of vinylidene fluoride-trifluoroethylene copolymer

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The polarization switching kinetics of ferroelectric polymer Langmuir-Blodgett films and copolymer nanocrystals (nanomesas) was investigated using piezoresponse force microscopy. The nanocrystals were prepared by self-organization from Langmuir-Blodgett films of a 70% vinylidene fluoride and 30% trifluoroethylene copolymer. The polarization switching time exhibits an exponential dependence on reciprocal voltage and decreases with temperature being consistent with the nucleation switching dynamics.

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The speed of polarization reversal, switching, is of critical importance for the performance of the ferroelectric memory technology. It is therefore essential to be able to understand and control switching dynamics in thin films and nanostructures as memories are pushed to ever higher densities. In bulk crystals larger than 50 microns, the switching time generally depends on the electric field [1], but not explicitly on crystal dimensions, and this is understood in terms of the nucleation and domain-growth models [2, 3]. In thinner crystals and films, however, switching becomes progressively slower for a given electric field [1, 4, 5], indicating a qualitative change in the nature of switching. Dimensional effects should be even more evident in isolated ferroelectric nanostructures, however, there have been relatively few studies of polarization hysteresis in ferroelectric nanostructures, such as nanowires [6, 7], nanotubes [8], and nanodots [9, 10].

The importance of nanoscale structure and morphology is underlined by qualitative changes in the behavior of switching in ferroelectric polymer thin films depending on both thickness and sample preparation conditions [4, 11 – 15]. Prior studies of ferroelectric polymer thin films have not been able to distinguish the effects of thickness and morphology because they were made on polycrystalline samples of essentially two types. Most studies have been performed on films made by solution spin coating, resulting in disordered granular films consisting of elongated nanocrystals approximately 200 nm long and 50 nm in diameter [16], where the polymer chains fold back and forth across the short dimensions [17]. On the other hand, samples made by Langmuir–Blodgett (LB) deposition, on the other hand, consist of a polycrystalline mosaic where the polymer chains aligned parallel to the film plane [18, 19], arranged in crystals of irregular shape and typical size of 30 nm to 50 nm [20]. Studies of switching dynamics in the LB films have shown both nucleation-limited [21, 22] and nucleation-free (intrinsic) [23, 24] behavior. To better understand the effects of nanoscale morphology, we have studied switching dynamics at the nanoscale in polycrystalline films [25] and in well-defined nanostructures [26]. The purpose of the present paper is to investigate the kinetics of switching in individual ferroelectric polymer nanocrystals (nanomesas) using Piezoresponse Force Microscopy (PFM).

The nanocrystals were fabricated from a ferroelectric copolymer using Langmuir–Blodgett deposition, followed by the self-assembly by thermal treatment, from a copolymer consisting of 70% vinylidene fluoride and 30% trifluoroethylene (70:30 copolymer) [27]. Deposition was accomplished by dispersing a 1.3% wt. solution of the copolymer in dimethyl sulfoxide on the surface of ultrapure water at room temperature and compressed slowly to a pressure of $3\,\mathrm{mN/m^2}$. One or two copolymer monolayers (ML) were transferred to a silicon substrate coated with a 50-nm thick aluminum film. To make the nanocrystals, the samples was then heated at 125 °C for 3h and cooled to room temperature at a rate of 1 °C per min. The LB deposition and nanocrystal formation methods were described in a more detail elsewhere [27, 28]. The ferroelectric copolymer nanocrystals belong to the monoclinic space group C_2^3 [29].

Measurements were carried out with a scanning probe microscope (model SOLVER P47, NT-MDT, Russia) operating in a contact mode for both topography

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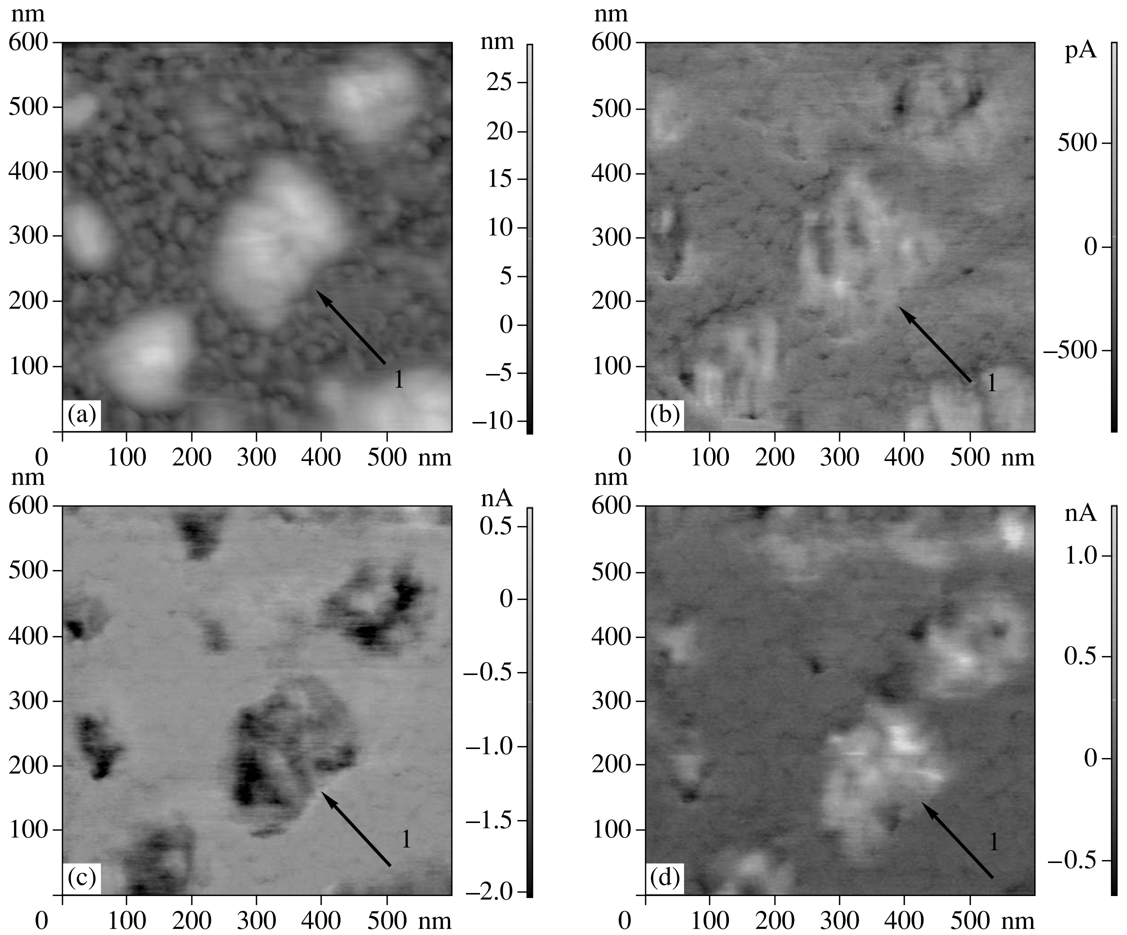

Fig.1. Images of nanocrystal by (a) AFM topography; (b) PFM images of the nanocrystal at the initial phase image; (c) after applying a poling voltage of -10 V; (d) after applying a poling voltage of $V = +10$ V

(contact AFM) and piezoresponse imaging (PFM). Silicon cantilevers coated with Ti/Pt conductive coating (model CSC38 from MicroMash, Estonia) used had a lever force constant of ≈ 0.05 N/m, a resonant frequency of 21 kHz, and tip radius of ≈ 40 nm. Therefore resulting resolution is ~ 60 nm. The polarization switching studies were made by applying an excitation voltage of amplitude 0,5 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 100000 clean room maintained at temperature 26 ± 0.05 °C and relative humidity 40 ± 1%. The sample temperature was held at 27 °C for the majority of reported experiments. The temperature could be varied in the range 27–100 °C.

The self-assembly led to the creation of nanocrystals of ferroelectric copolymer of approximately 20–30 nm thick and 100–200 nm in diameter, with somewhat irregular shapes, as shown in Fig.1a. The PFM contrast of the same region (Fig.1b) demonstrates that the nanocrystals are polarized even before applying a switching voltage. For the switching studies, we chose nanocrystal indicated by the arrow 1 in Fig.1b. Figure 1b, c, d shows the PFM image of nanocrystal 1: (b) before switching; (c) after applying a poling voltage of -10 V; (d) after applying a poling voltage of $+10$ V. The field was applied to the tip continuously during scanning, i.e., to all pixels of the surface area shown in AFM images. The comparison of Figs.1c, d shows, that the negative tip voltage reversed (or switched) the direction of polarization as evinced by the piezocontrast reversal. These images indicate that the nanocrystals could be switched repeatedly between opposite polarization states. Fine structure of PFM contrast inside the nanocrystals may indicate the presence of multiple crystals, or multiple domains, or both.

The switching kinetics is studied by a series of nanocrystal switching measurements. In this method, the crystal was first poled by scanning the tip with a saturating bias of -10 V and imaged under zero bias.

Then the crystal was switched via-applying a voltage pulse of specified amplitude and duration and the resulting piezoresponse was imaged after applying the pulse. To determine the switching time for each poling voltage, we recorded the piezoresponse after pulse application as a function of pulse duration for a given pulse height. The switching time t was defined as the time at which this plot crossed zero piezoelectric response [24, 25]. This procedure was repeated for a range of switching pulse amplitudes.

First, the switching kinetics was obtained for ferroelectric copolymer LB film, consisted of 30 monolayers with the thickness 48 nm (the thickness was determined by AFM). The dependence of switching time logarithm $\ln t$ on V_c/V ($V_c \cong 2.5$ V is the coercive voltage, obtained from hysteresis loop measured in so-called pulse mode) is shown in the inset to Fig.2. Figure 2 presents

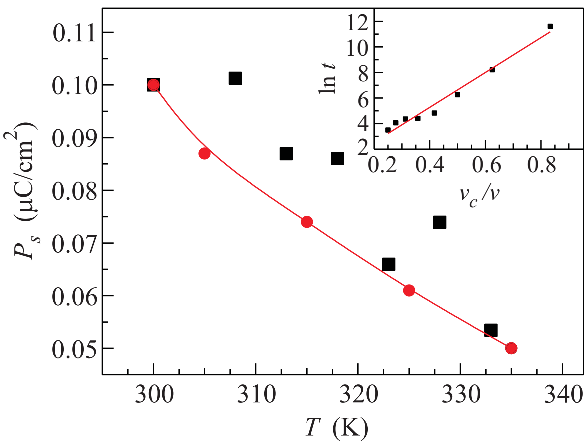

Fig.2. Temperature dependence of spontaneous polarization $P_s = P_s(T)$ for copolymer LB film (30 ML), obtained by Chinoweth method (solid curve) and by AFM in piezoelectric regime (square points). Inset shows voltage dependence of the switching time t (V_c – coercive field)

the temperature dependence of the spontaneous polarization $P_s = P_s(t)$, obtained by pyroelectric Chynoweth method (solid curve) [28], in comparison with that obtained by PFM in piezoelectric regime (square points). In order to compare the results obtained by Chynoweth method and by PFM the value of PFM signal at room temperature was assumed to be 0.1 μC/cm^2 and recalculated for other temperatures. The temperature dependences of switching time $t = t(T)$ are shown in Fig.3. It is seen, that switching time decreases with temperature. It is well known that such dependence is characteristic of the nucleation-limited switching, which is a thermally

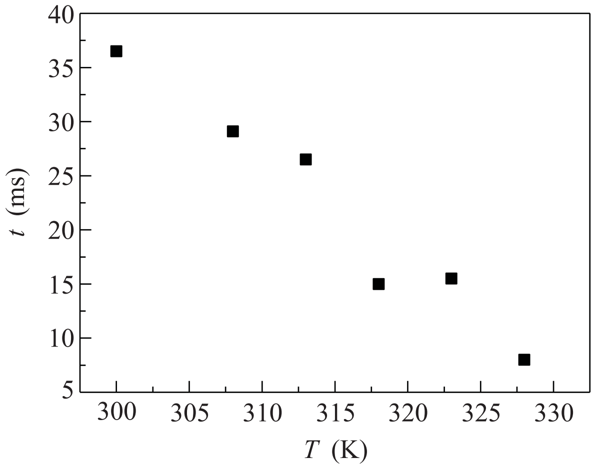

Fig.3. Graph of the temperature dependence of the switching time $t = t(T)$ for ferroelectric LB film (30 ML)

activated process and should following an exponential dependence in the form [1]

$$1/t = \sim \exp\left(-a(V_c/V)\right), \tag{1}$$

where $V_c \cong 2.5$ V and $a = 11.4$. The constant a depends on the energy of nucleus $W = W(P_s, T)$ and decreases with temperature T.

In the same way the switching kinetics was measured for the copolymer nanocrystal 1. The data of Fig.4 also

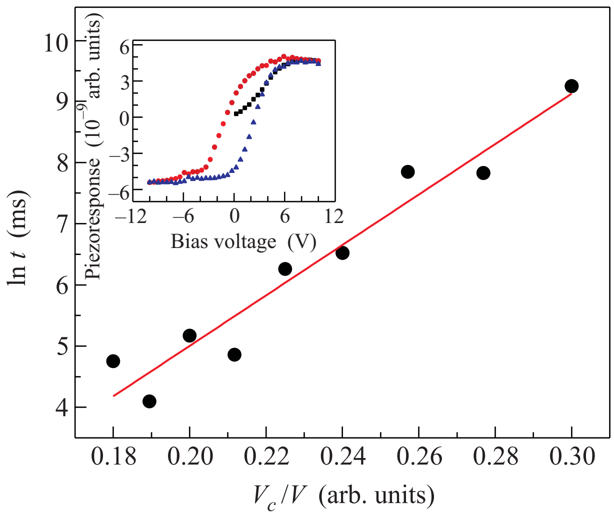

Fig.4. Voltage dependence of the switching time t for the nanocrystal, indicated by the arrow 1 on Fig.1. Inset shows the hysteresis loop for the nanocrystals

follow an exponential dependence (1), where $V_c \cong 1.24$ V is the coercive voltage observed from the hysteresis loop shown in the inset to Fig.4 and $a \cong 33$ is a constant. A hysteresis loop was recorded by applying a sequence of voltage pulses, each followed by a measurement of the piezoresponse at zero bias [30].

In summary, the observed switching kinetics of the individual ferroelectric polymer nanocrystals is consistent with a nucleation-limited switching, as was previously found in arrays of similar nanocrystals [26] and in a 500-nm diameter spot of a continuous LB film. The behavior is commonly observed in ferroelectric polymer films made by solvent spinning [4, 11 – 15] and with LB films made under certain conditions [21, 22, 24]. This behavior is essentially different from the switching kinetics in large area continuous LB films, which typically exhibit intrinsic switching dynamics (i.e., not controlled by the domain nucleation) [23, 24]. Further study of local switching kinetics in thin films and nanostructures will be necessary to fully understand the dominant mechanism and to control it via different preparation routines.

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