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Study of the growth and switching kinetics on ferroelectric nanocrystals of copolymer vinylidene fluoride and trifluoroethylene on an atomic force microscope

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Abstract

The growth of nanocrystals obtained from Langmuir-Blodgett films of ferroelectric copolymer consisting of 70% vinylidene fluoride and 30% trifluoroethylene has been investigated by atomic force microscopy (AFM). The radius and concentration of nanocrystals are found to depend on the annealing time of the film. A model for nanocrystal growth is proposed which yields adequate time dependences for nanocrystal size parameters. The switching kinetics of individual ferroelectric nanocrystals with an average diameter of 100–200 nm and a height of 15–20 nm has been investigated in the piezoelectric response mode. It is shown that the switching of nanocrystals has an activation character.

Introduction

In view of the development of nanotechnologies, interest in the fabrication and study of ferroelectric nanostructures constantly increases. The implementation of energy-independent memory with ultrahigh density imposes stringent requirements on such ferroelectric parameters as switching time and coercive voltage. Switching time depends generally on the applied field magnitude, and, in the case of bulk crystals, switching times on the order of few microseconds can be attained only at very high field strengths. To implement fast switching at fairly low field strengths, one needs ferroelectric nanocrystals.

Many studies were devoted to ultrathin films of the ferroelectric copolymer composed of 70% vinylidene fluoride and 30% trifluoroethylene (P[VDF-TrFE]) [1–3]. These films are considered a promising material for ferroelectric digital memory cells [4]. Crystals of this copolymer from 100 nm to 4 μ m in size were obtained for the first time in Langmuir-Blodgett (LB) films in [1]. According to the transmission electron microscopy data, they are rounded isolated copolymer islands, the sizes of which depend on the annealing time and temperature.

In this paper we report the results of studying the growth and switching kinetics of ferroelectric nanocrystals based on (P[VDF-TrFE]) copolymer by atomic force microscopy (AFM). The analysis was performed using an electric modification of AFM, piezoelectric force microscopy (PFM), which makes it possible to re-

cord ferroelectric domains, investigate their dynamics, and measure local electrical characteristics [5, 6].

Experimental

Polyvinylidene fluoride belongs to the class of crystallizing polymers [7]. Its structural unit $-(\text{CH}_2-\text{CF}_2)-$ has a dipole moment $\mu = 7 \times 10^{-30}$ C m (2 debyes). The crystal structure is such that macromolecules form a slightly twisted helix, CH_2CF_2 dipoles are oriented so that their vectors are oppositely directed, and the total polarization in the monoclinic cell is close to zero. Introducing trifluoroethylene into the polymer chain of polyvinylidene fluoride leads to the crystallization of the copolymer from the solution directly into the polar β phase. The P[VDF-TrFE] 70 : 30 copolymer exhibits ranges of coexistence of two phases: ferroelectric and paraelectric.

First we obtained LB P[VDF-TrFE] 70 : 30 films with a thickness of 2 monolayers from a solution of copolymer in water with dimethyl sulfoxide having a concentration of 1.3 wt % at room temperature. We investigated the pressure–area isotherm (which was measured to determine the conditions for the closest packing of molecules in a monolayer on the solution surface) for a solution in triple distilled water. At room temperature these conditions were fulfilled at a surface pressure of 3 mN/m². Substrates were prepared from pure silicon and silicon covered by a 50-nm-thick aluminum film. Then LB films were heated to a temperature of +125°C in an air medium and kept at this temperature for differ-

ent times. This procedure led to the formation of nanocrystals in the superthin film; their size was determined by the annealing time. Kim [3] performed an electron diffraction analysis of the nanocrystals that formed after annealing identical P[VDF-TrFE] films and showed that these nanocrystals consist of the copolymer.

The study was performed on a SOLVER P47 atomic force microscope (NT-MDT, Moscow) at room temperature in air under clean-room conditions with humidity and temperature maintained at a constant level. All the experiments involving long-term measurements of ferroelectric samples were metrologically guaranteed. We used Si probes having a conducting CSC38 Pt/Ti coating (B beam) (MikroMasch, Estonia), with a tip rounding radius $R \leq 40$ nm and beam hardness $k \sim 0.8$ N/m. The experimental images were processed based on the NT-MDT AFM software, which makes it possible to perform data filtering (in different ways) and other operations used in image processing. The lateral sizes of fine-structure elements of the sample surface were statistically processed using the GRAIN ANALYSIS subroutine entering the NT-MDT AFM software package.

Nanocrystals were switched in the following way. Before switching, a transition to the single-domain state of a chosen nanocrystal was performed in the point AFM lithography mode at 20 points by applying a voltage of -10 V to the probe. Then the voltage was turned off and a piezoelectric response image was recorded. In the next stage, the portion in the single-domain state was switched at one point in the AFM lithography mode by applying a voltage of $+10$ V to the probe. Finally, this voltage was turned off again and a piezoelectric response image was recorded.

Results

Figure 1 shows topographic AFM images of unannealed and annealed P[VDF-TrFE] 70 : 30 films 2 monolayers thick. The unannealed initial LB copolymer films have a network structure (Figure 1a) composed of entangled filaments which are sometimes separated by voids. The filament length ranges from several tens of nanometers to several tens of micrometers, the filament thickness reaches several tens of nanometers, and the voids range from several nanometers to several hundreds of nanometers in size. After annealing at 125°C , the film structure becomes more uniform, and the voids disappear (Figure 1b).

An important parameter is the film thickness. We investigated this characteristic by the AFM technique. Figure 2 shows an image of P[VDF-TrFE] 70 : 30 copolymer film 2 monolayers thick formed on silicon. To measure the film thickness, a square portion of the film was removed from the substrate in the AFM contact mode. Then a topographic image of the film surface was obtained again in the AFM tapping mode. The film thickness was estimated from the difference in the heights of the film surface and the silicon base.

Figure 1. Topographic AFM images of P [VDF-TrFE] 70 : 30 films 2 monolayers thick (a) before and (b) after annealing. The scan area is $3 \times 3 \mu\text{m}$ in size.

The cross-section profile in Figure 2b was recorded along the line shown in Figure 2a. This profile was traced through a film portion and a substrate portion to make it possible to estimate the film thickness. Having averaged over all cross-section profiles (obtained in the same way as the profile in Figure 2b) for films of different thicknesses, we determined the average thickness of the LB-film monolayer to be 1.8 nm; this value is in good agreement with the thickness of similar films (1.78 ± 0.07 nm) measured by ellipsometry [8]. The measurement error (determined by the instrumental error in the xy plane) was 5%.

Copolymer nanocrystals were obtained for the first time by annealing LB films [1]. X-ray study revealed a relatively low structural quality of copolymer films before annealing and a significant improvement of the film structure after annealing at 135°C for 2 h. The

Figure 2. (a) Topographic image of P[VDF-TrFE] 70 : 30 film 2 monolayers thick and (b) cross-section profile along the arrow indicated in panel a.

transformation of the polymer film and the nanocrystal formation kinetics were analyzed in detail in [9]. We investigated the nanocrystal growth kinetics as a function of the annealing time at a fixed temperature. A PFM study of nanocrystals showed the presence of spontaneous polarization in the direction of axis 2 and its switching in an external field.

Figure 3 shows topographic images of a film with nanocrystals, which correspond to the initial stage (immediately after the film transformation) and after annealing at three different times (from 1 to 6 min). It can be seen that nanocrystals increase in sizes, while their concentration decreases. We plotted the dependences of the radius of nanocrystals and their concentration on the annealing time of copolymer films. Figure 4 shows the time dependences of the average radius R (curve 1) and the nanocrystal concentration N (curve 2). The R and N values exhibit saturation at approximately equal relaxation times τ . The experiment shows that the average values of the nanocrystal radius R and height h increase from $R_0 \approx 50$ nm and $h_0 \approx 15$ nm to the saturation values $R_s \approx 100$ nm and $h_s \approx 25$ nm.

The nanocrystal growth kinetics is based on the well-known growth kinetics from melt [10] and can be explained within the simplest model of drop coalescence. At $T = 125^\circ\text{C}$ the film material can be considered a set of round drops with radius R_0 , height h_0 , and concentration N_0 (on the substrate surface). Upon cooling, drops are crystallized into the ferroelectric phase. Let us consider a single drop. The flux of other drops toward a drop chosen is given by the expression

$$j_+ = v \exp(-u_1/kT)N \quad (1)$$

and the flux of drops in the opposite direction is given by

$$j_- = v \exp(-u_2/kT)N \quad (2)$$

where v is the drop velocity; u_1 and u_2 are, respectively, the drop coalescence and breakup energies; and N and n are, respectively, the drop concentrations beyond drop 1 and on its surface. The condition for drop growth leads to the inequality $u_1 < u_2$. Then the time dependence of the concentration N can be written as

$$dN/dT = -j_+ + j_- = -a_1N + a_2n, \quad N + n = N_0 \quad (3)$$

where $a_1 = v \exp(-u_1/kT)$, $a_2 = v \exp(-u_2/kT)$, and $a_1 < a_2$.

The solution of (3) for $N(t=0) = N_0$ yields

$$N = N_0 \left\{ \frac{a_2}{a_1 + a_2} + \frac{a_1}{a_1 + a_2} \exp\left(-\frac{t}{\tau}\right) \right\} \quad \tau = \frac{1}{a_1 + a_2} \quad (4)$$

The drop growth rate has the form

$$\begin{aligned} dR/dT = (j_+ - j_-)aS &= \{a_1N - a_2(N_0 - n)\}aS \\ &\cong a_1NaR^2(a_2 \ll a_1) \end{aligned} \quad (5)$$

Here, a is the lattice constant and S is the circumference length of drop. The solution of (5) for $R(t=0) = R_0$ yields

$$R = \frac{1}{\frac{1}{R_0} - a_1a_2N_0\tau \left\{ 1 - \exp\left(-\frac{t}{\tau}\right) \right\}} \quad (6)$$

where τ is taken from expression (4).

This kinetic model for the average size of drops, which neglects their size distribution, explains the concentration and size saturation at equal relaxation times τ . The relationship between the saturation values R_s and T_s was obtained from the condition of copolymer mass conservation:

$$N_s/N_0(R_s/R_0)^2h_s/h_0 \cong 1 \quad (7)$$

The substitution of $N_s \approx 5 \times 10^8 \text{ cm}^{-2}$, $N_0 \approx 4 \times 10^9 \text{ cm}^{-2}$, $R_s \approx 100$ nm, $R_0 \approx 50$ nm, $h_s \approx 25$ nm, and $h_0 \approx 15$ nm into (7) satisfies this condition.

Figure 3. PFM images of P[VDF-TrFE] film, which illustrate the dependence of nanocrystal growth on the annealing time: (a) initial annealing stage and (b–d) after annealing for (b) 1, (c) 4, and (d) 6 min.

In this study we investigated the switching kinetics of nanocrystals. Figures 5a and 5b present the initial nanocrystal topography and piezoelectric response images. Images of a nanocrystal after its switching by voltages of +10 and -10 V are shown in Figures 5c and 5d. One can easily see that the nanocrystal is polarized even in the initial state (i.e., prior to switching voltage to the probe).

The above experiment allowed us to study the switching kinetics of the nanocrystals formed in 2-monolayer-thick films. Figure 6 shows the dependence of the nanocrystal switching time on voltage. The experimental dependences are approximated fairly well by the exponential function determining the activation mechanism of switching:

$$1/t \sim \exp(-aV_c/V) \quad (8)$$

where V_c is the coercive voltage and a is a constant which depends on the inverse temperature. The

Figure 4. Dependences of the (1) average radius R of nanocrystals and (2) their concentration N on the annealing time.

Figure 5. Nanocrystal switching: (a) topographic AFM image and (b–d) PFM images of the nanocrystal (b) in the initial state and after applying voltages of (c) +10 and (d) –10 V.

Figure 6. Dependence of the switching time (on the logarithmic scale) on V_c/V for a nanocrystal formed in a 2-monolayer film on the voltage applied (V_c is the coercive voltage and V is the ac voltage).

switching time was taken to be the time for which the electromechanical response signal reduced to zero.

Note that nanocrystals are switched completely in some cases, but regions with retained contrast are also observed. This may be related to the coalescence of nanocrystals or to different directions of the polarization vector in different regions.

Conclusions

We investigated the dependence of the growth of P[VDF-TrFE] copolymer nanocrystals on the annealing time. It was shown that the average values of the radius R and height h of nanocrystals increase from the initial values $R_0 \approx 50$ nm and $h_0 \approx 15$ nm to the saturation values $R_s \approx 100$ nm and $h_s \approx 25$ nm. In addition, we analyzed for the first time the switching kinetics of ferroelectric nanocrystals and showed that switching is described by an exponential law, which characterizes the activation mechanism.

A study of the growth conditions for ferroelectric P[VDF-TrFE] nanocrystals and their switching is very important for the application of nanocrystals in ferroelectric memory technology. High-density regions with crystalline nanostructures of ferroelectric P[VDF-TrFE] copolymer were recently fabricated by relief nanoimpression [4]. The results of [4, 11] show that ferroelectric copolymer crystals are promising candidates for high-density and stable data storage devices.

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