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Ferroelectric Properties of Langmuir-Blodgett Copolymer Films at the Nanoscale

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Abstract

Langmuir-Blodgett (LB) films are well known structures prepared as a result of successive transfer of monolayers (ML) from the gas-liquid interface onto solid substrates. One impressive possibility of LB method is the opportunity to vary the thickness of the film to an accuracy of one transfer, which could coincide with one ML. The ferroelectric properties of a copolymer of vinylidene fluoride and trifluorethylene P[VDF-TrFE] prepared by LB deposition are investigated in the region of a few monolayers.

Keywords: Ferroelectric polymer, critical thickness of ferroelectric film

1. Introduction

The existence of ferroelectricity in the ultrathin films (or small crystals) is limited by the critical size l_{cr} , which is defined as the maximal thickness of film or the maximal size of a crystal at which ferroelectricity is impossible. The Landau-Ginzburg mean field theory [1–3] shows, that l_{cr} is determined by two parameters: surface energy and screening energy. Perhaps the first attempt to determine l_{cr} experimentally was undertaken in [4] where ferroelectric polarization and its switching were observed in Langmuir-Blodgett (LB) films of 2 nominal monolayers (2 ML, approximately 1 nm) of the vinylidene fluoride and trifluorethylene P[VDF-TrFE] copolymer films. In [5] the ferroelectric polarization and its switching was demonstrated in LB films only 1 ML (0.5 nm) thick and therefore ferroelectricity did not appear to be limited by a critical size in this system. Later the experimental value of l_{cr} was evaluated in perovskite films (see e.g., [6, 7]). Theoretically the value of l_{cr} for perovskites has been estimated from first principles (six primitive cells, $l_{cr} = 2.4$ nm) [8]. A detailed review of critical size investigations is given in [9].

It has been suggested [10] that one cannot expect to determine critical size in the framework of the mean field theory [1–3]. It has been shown, however, in [11–13] that

Landau-Ginzburg mean-field theory can be used to describe finite-size effects and calculate the value of the critical thickness l_{cr} (or explain its absence in some cases), if boundary conditions take into account the electrostatic mismatch between the electrode and the ultrathin ferroelectric film.

2. Landau-Ginzburg Theory with Mismatch Boundary Conditions

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

$$G = F_0 + \frac{1}{l} \int_{-\frac{l}{2}}^{+\frac{l}{2}} \left[\frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\gamma}{6} P^6 + \frac{D}{2} \left(\frac{\partial P}{\partial z} \right)^2 - PE \right] dz + \frac{D}{2\delta l} [(P_+ + P_m)^2 + (P_- + P_m)^2] \quad (1)$$

where F_0 is the free energy of the paraelectric phase, $P(z)$ is the polarization 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 Landau-Ginzburg coefficients α , β , and γ and the gradient energy coefficient D are properties of the ferroelectric material, while the interfaces between ferroelectric film and electrodes are accounted for by the decay length d proposed by Tilley [11] and the mismatch polarization P_m introduced by Glinchuk [12, 13]. The material properties are assumed independent of temperature, except for the Curie-Weiss coefficient which has the form $\alpha = \alpha_0(T - T_0)$.

From Equation (1) follows the linearized equation of state in the form of the Euler-Lagrange equation:

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

where \bar{P} is spatial average value of the film polarization P . The boundary conditions for Equation (2) are:

$$P(z) \pm \delta \frac{\partial P}{\partial z} = -P_m, \quad z = \pm \frac{l}{2} \quad (3)$$

The importance of the boundary mismatch effect in the nanoscaled ferroelectric films was first shown in [14], but the boundary conditions in form (3) for the ultrathin ferroelectric films were first introduced by M. Glinchuk in [13] and now are widely used, though with differing interpretations [9, 15–18]. The effect of the interface on film polarization is best represented by the ratio P_m/P_b (where P_b is the spontaneous polarization in the bulk) in order to determine the critical thickness l_{cr} and dielectric properties of the nanoscale films. It was shown in [9], that for $P_m/P_b \approx 0.1$, the critical thickness l_{cr} is of order 1 nm, or even absent.

The solution of (2) and (3) in the linear approximation valid for conditions $l, \delta \gg l_d = (D/4\pi)^{1/2}$ and $\alpha \ll 2\pi$ give the following dependences for the average polarization $\bar{P}(l)$ [12] and average dielectric constant $\epsilon(l)$ [18]

$$\left. \begin{aligned} P &\cong P_b \frac{1 - \frac{P_m}{P_b} \alpha \frac{\Psi(l)}{2}}{\alpha^2 + \alpha \Psi(l)} \\ \Psi(l) &= 4\pi \left(\frac{2l_d}{l} \right) \frac{\text{th}\left(\frac{l}{2l_d}\right)}{1 + \frac{\delta}{l_d} \text{th}\left(\frac{l}{2l_d}\right)} \end{aligned} \right\} \quad (4)$$

$$\varepsilon \cong \frac{2\pi}{\alpha + \frac{2D}{\delta l}} \quad (5)$$

where $\text{th}(x)$ is the hyperbolic tangent function.

Using the experimental data reported in [7], the authors in [13] have shown that the mismatch effect very well explains the observed dependence of the average polarization $\bar{P}(l)$ on film thickness l for ultrathin lead titanate films. In the present paper we use the same mean-field theory analysis summarized in Equations (2) to (3) to interpret the dependence of film polarization on thickness for the nanoscale LB copolymer films.

3. Experimental

The preparation, structure, phase transition, and ferroelectric properties of vinylidene fluoride-trifluoroethylene P[VDF-TrFE] films prepared by LB deposition were reviewed in detail in [19]. They manifest spontaneous polarization $P_b \approx 0.1$ C/m² in the polar orthorhombic phase 2 mm. At a temperature in the range 20°C to 145°C (depending on the proportion of VDF to TrFE [20]) the copolymer pass into nonpolar hexagonal phase 6:m via a first-order phase transition. The structure of the LB films has been studied by means of X-ray [21] and neutron [22] diffraction, as well as scanning tunnel microscopy [4]. The LB copolymer films have (110) orientation [21], meaning that the polarization P , which is along (010) is not exactly perpendicular to the film.

High-quality thin films of ferroelectric P[VDF-TrFE, 70:30] were fabricated by the standard vertical LB method or by the horizontal Schafer variation from a water sub-phase. The copolymer was dispersed on the water from a solution of 0.01 wt % copolymer in dimethyl-sulfoxide and then compressed slowly to the deposition pressure. We have investigated two types of LB films. For the first (type I) the films were transferred at a surface pressure of 5 mN/m. For the second (type II) the surface pressure was 3.5 mN/m. The films for dielectric measurements were deposited on aluminum-coated glass or silicon substrates and overcoated with aluminum evaporated in a vacuum.

The copolymer LB film thickness depends on preparation conditions [23, 24], especially pressure, so we measured the thickness of the films used in this study. Depending on the choice of the working point on the pressure-area isotherm, the average thickness of one nominal monolayer transferred to the substrate ranges from 0.5 nm to 1.8 nm. At a deposition pressure of 5 mN/m, the method of spectroscopic ellipsometry gave for the thickness of one transferred layer the average value 1.78 ± 0.07 nm, which corresponds well to the thickness 3–4 molecules [23]. In the present paper the film thickness was determined both ellipsometrically for the type II samples [24] and by atomic force microscopy (AFM) for the type I samples. For the type II samples, the average thickness of one monolayer transfer was 0.5 nm [24], which corresponds well to the thickness one molecule. The thickness of a type I LB film deposited on polished silicon wafer was measured with a commercial AFM instrument (NT-MDT model Solver P47) operated in noncontact mode with a silicon cantilever. To measure

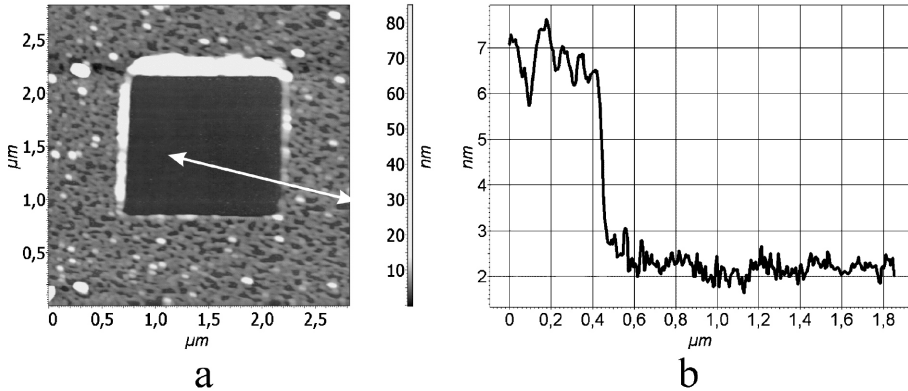


Figure 1. a.) The AFM image of a 2 ML Type I sample on a Si substrate. The black square in center is the Si substrate revealed after the removal of the film. **b.)** The film thickness profile along the white line in (a).

the film thickness, the AFM was operated in contact mode to remove a square patch of the polymer from the substrate (see Figure 1a). Then the area was imaged again in noncontact mode to determine the difference in height between film surface and silicon substrate. The line scan shown in Figure 1b was made along the white line shown in Figure 1a and shows the film edge and height above the substrate. By averaging over all the line scans obtained from profiles similar to the one shown in Figure 1a on samples of different thicknesses, we determined the average thickness of the LB film to be 1.8 nm per nominal monolayer, which agrees well with the value 1.78 ± 0.07 nm obtained earlier by ellipsometry from similar films [23].

The relative film polarization was determined by measuring the pyroelectric response with the Chynoweth method, as described in detail in [25]. The dielectric constant ϵ was measured for the frequency 1 kHz in the temperature interval 5°C to 110°C .

Figure 2 shows the dependence of the relative polarization $P(l)/P_b$ as a function of film thickness for the type I films, where P_b was set equal to the pyroelectric response from the thickest film. For one layer transfer ($l = 1.8$ nm) there is small polarization signal $P/P_b \approx 0.02$. The solid curve $P(l)/P_b$ shown in Figure 2 was calculated from Equation (4) with coefficient values $D = 3 \times 10^{-18} \text{ m}^2$, $\delta = 10^{-9} \text{ m}$ [7, 9, 17], $\alpha = 1$ (at $T = 300 \text{ K}$) [19] and with fitting parameter $P_m/P_b = 0.7$. The nonzero value of the pyroelectric signal in the type I films, even for films of one transfer, indicates a critical thickness of less than 1.8 nm, though the sharp drop in signal at a thickness of 3 transfers implies a critical thickness of as large as 5.4 nm. The films from type II (thickness 0.5 nm per transfer) have shown better correlation with Equation (4) for the same values of D , δ , and α , fitting parameter $P_m/P_b = 0.3$. These results are shown on Figure 3 (the solid curve is theoretical, the experimental points are taken from [24]), indicating a critical thickness of less than 5 nm. The disagreement between experimental and theoretical data is due in part to the linear approximation leading to Equation (2).

The measurements of the dielectric constant ϵ in ferroelectric films of nanometer thickness was first performed in [4]. Figure 4 shows the temperature dependence $\epsilon(T)$, obtained for the type I films with thickness 30 ML (curve 1) and 2 ML (curve 2). The curve (2) reveals the smearing of the phase transition in qualitative agreement with Equation (5). Substituting in Equation (5) the coefficient values $D = 3 \times 10^{-18} \text{ m}^2$, $\delta =$

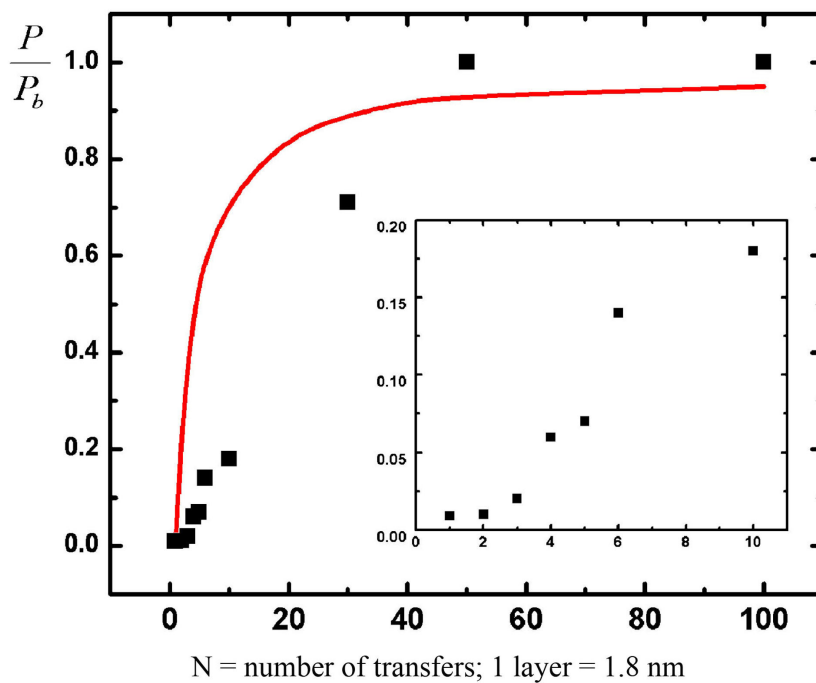


Figure 2. Dependence of the relative polarization $P(l)/P_b$ for type I films from measurements (squares) and from Equation (4). Inset: expanded scale for the thinnest films.

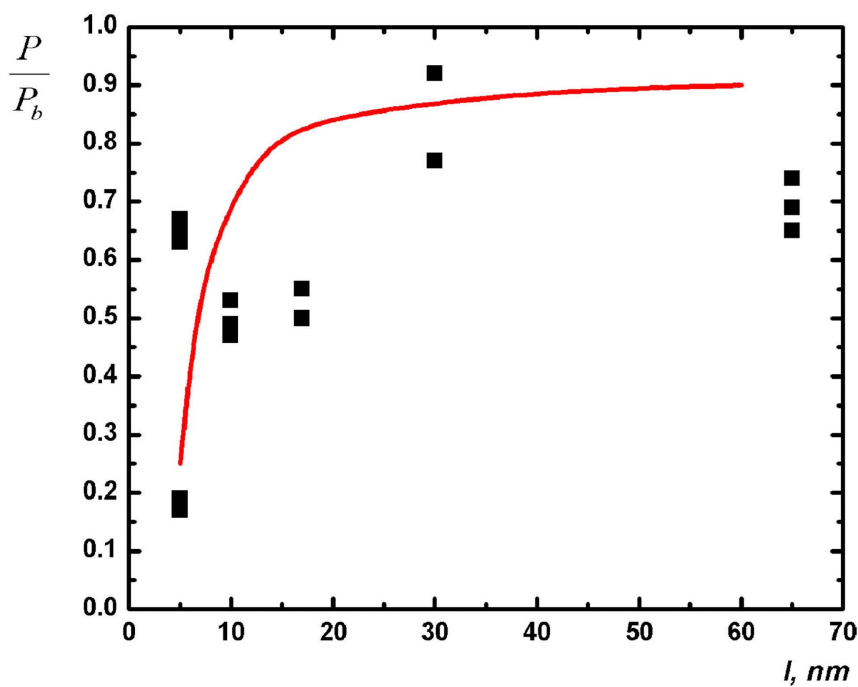


Figure 3. Dependence of the relative polarization $P(l)/P_b$ for type II films from measurements (squares) and from Equation (4) (line). Adapted from Reference [24].

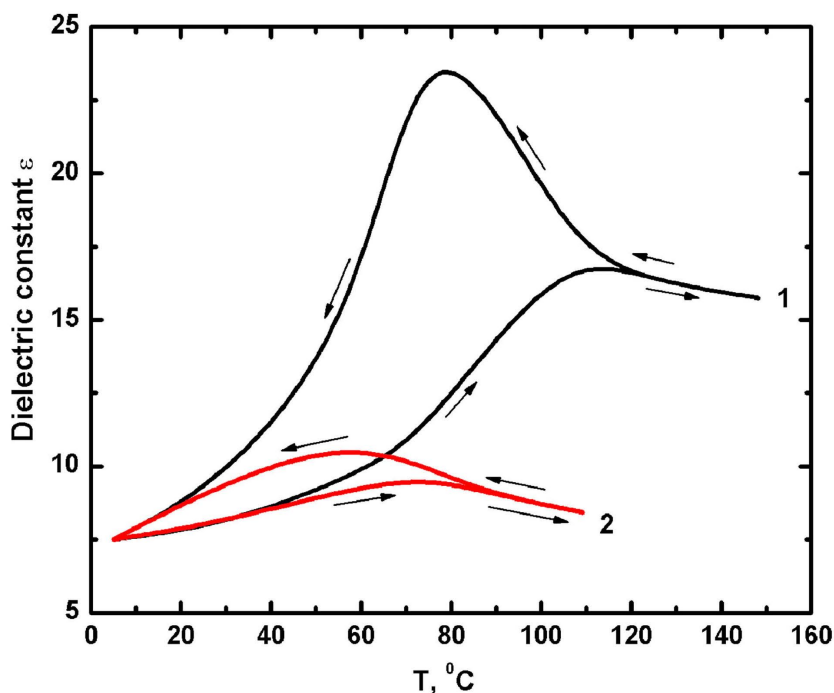


Figure 4. Dependence of the dielectric constant on temperature for two type I samples: (1) 30 ML; (2) 2 ML thick.

10^{-9} m, $\alpha = 1$ [7, 9, 17], we obtain a similar smearing effect for film thicknesses in the range $l \approx 1$ nm to 8 nm. The presence of clear dielectric peaks even in the film of 2 ML indicates that the ferroelectric state is robust even at the thickness of 3.6 nm.

4. Conclusions

The Landau-Ginzburg mean field theory, taking into account the correct boundary conditions, explains the behavior of ferroelectric properties of LB copolymer films at the nanoscale and even 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 have just started. For polymer nanofilms, no calculations have been made so far. Therefore, at present, it is difficult to make for the ferroelectric LB films a reliable comparison of these two approaches.

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