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Low voltage electrostriction in ultrathin ferroelectric polymer films measured by a Fabry-Perot technique

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Abstract

Electrostriction has been studied in 100-200 nm thick films of a ferroelectric copolymer P(VDF 70%-TrFE 30%) using applied voltages as low as 10-30 V. The films have been prepared by a Langmuir-Blodgett technique that allows one a layer-by-layer variation of their thickness. To detect a small field-induced deformation (down to 0.001 nm), a spectral Fabry-Perot interferometry in combination with a lock-in technique has been used. As a result, a field dependence of the apparent Young modulus attending polarization switching has been found and discussed.

In the last few years we see a reviving interest in ferroelectric materials, especially ultrathin ferroelectric films. The interest is mainly focused on the size effects and near-electrode polarization phenomena. Along with fundamental studies of size effects [1], new prospects for applications are opening up in the area of sensitive electromechanical transducers, infrared detectors, acoustic microsensors, capacitors, non-volatile random-access memory and ferroelectric field-effect transistors. Most of experiments have been fulfilled on crystalline ferroelectrics but in many applications polymer ferroelectrics are much more desirable. Polymer films are usually deposited by a spin coating technique [2,3] but, as a rule, it is difficult to prepare high quality samples of thickness L below 0.1 μm . More recently, ferroelectric properties of ultra-thin P(VDF-TrFE) copolymer films (even below 10 nm) have been demonstrated [4-6]. The so-called a Langmuir-Blodgett (LB) films were prepared by a layer-by-layer transfer of monolayers from the water surface onto a solid substrate. Therefore, we can design nano-structures, in which ferroelectric monolayers alternate with other functionalised monolayers of

dyes, luminophores, magnetic materials, biological preparations etc., which would suffer a very strong mechanical stress and a built-in electric field as high as 10^8 - 10^9 V/m.

Our task here is to study electrostriction of ultrathin, ferroelectric LB films with a focus on the field-dependence of elastic deformation not discussed earlier. With few exceptions [7], traditional studies of electrostriction in thicker films demanded voltages up to few kV [8,9]. Here we operate with 100-200 nm thick films and voltages as low as $U=10$ -30 V. Evidently, the induced deformations are small in ultrathin films and, to detect them, we use a spectral Fabry-Perot interferometry in combination with a lock-in amplifier. This technique allowed us to measure film deformations as small as $\Delta L=0.001$ nm (strain $5\cdot10^{-6}$) and find the field dependence of the Young modulus in the course of polarization switching.

Fig.1(a) shows a scheme of the Fabry-Perot interferometer formed by a top electrode of a polymer film and a semitransparent mirror i.e. a glass plate with a layer of evaporated Al (reflection $\approx 80\%$). The mirror is installed strictly parallel to the sample with a help of two thin Mylar spacers

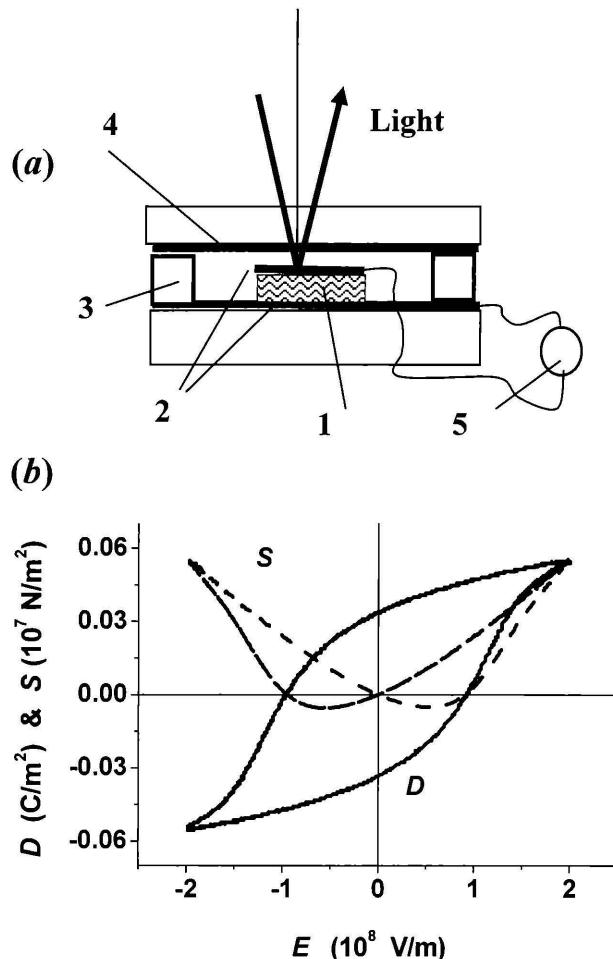


Fig. 1. (a) Scheme of the sample with a semitransparent mirror forming the Fabry-Perot structure. Ferroelectric polymer (1), Al electrodes (2), Mylar spacers (3), semitransparent mirror (4) and voltage source (5). The light of spectrophotometer passes (4), then is reflected from the oscillating top electrode (2), passes again (4) and detected by a photomultiplier. (b) Hysteresis loop $D(E)$ for a 180 nm thick sample (curve D) and butterfly-type curve S for the stress $DE/2$ vs E . For both curves the frequency of sine-form field is 28 Hz.

that provide an air gap of $d=9-10 \mu\text{m}$. The top electrode of each sample consists of two or three elements of area $A=4 \times 6 \text{ mm}^2$ of almost equal thickness. Two LB films of $L=80$ and 180 nm have been prepared from copolymer P(VDF-70%-TrFE-30%) as described in paper [5]. The films have not been poled in order to exclude the linear-in-field piezoelectric terms. The field is applied perpendicular to a film along the z -axis, which is the rotation symmetry axis. Therefore, we always operate with z -components of electric field E_z ,

displacement D_z and polarization P_z vectors, stress X_{zz} , and strain $S_{zz}=\Delta L_{zz}/L$ tensors.

We apply a low frequency (28 Hz) field to a 80 nm thick film and allow the displacement to follow the $D(t)-E(t)$ loop shown in Fig.1(b). Then, polarization $P_z(E,t)$ oscillates with $E(t)$ keeping overall unpolar symmetry of the sample. The stress $X(t)=D(t)E(t)/2$ vs $E(t)$ follows the butterfly-shape loop also presented in the same figure. Note that the strain of the butterfly form is also observed in electrostriction measurements of thick films[8]. The reflectance spectrum on the output of the Fabry-Perot interferometer shows characteristic oscillations, whose spectral positions λ_k follow the Bragg law:

$$k\lambda_k = 2dn \cos \alpha \quad (1)$$

where k is interference order, $n \approx 1$ refraction index of air and $\alpha = 17$ deg is an angle of light incidence on the interferometer. When an a.c. voltage $U = E/L = U_m \sin \omega t$ is applied to an unpoled sample, due to a compression force and spontaneous electrostriction (see below), the sample thickness L reduces by ΔL for each half-period of the field and the air gap $\Delta d = -\Delta L$ increases. Correspondingly, the spectrum of all oscillations is shifted by $\Delta \lambda_k$ to the longer wavelengths, and the shift is registered by a lock-in detector operating at the 2nd harmonic (2ω) of the applied field.

Curve 1 in Fig.2 shows the spectrum of the intensity $R(\lambda)$ of light reflected from the Fabry-Perot structure with a gap of $9.94 \mu\text{m}$ found from Eq.(1). The spectrum of the amplitude of electroreflectance $\Delta R_m(\lambda)$ induced by an a.c. voltage $U_m = 15 \text{ V}$ at frequency $f = \omega/2\pi = 28 \text{ Hz}$ is presented by curve 2 in Fig. 2. The spectrum of derivative $\partial R(\lambda)/\partial \lambda$, as expected, has exactly the same oscillatory shape as $\Delta R_m(\lambda)$ spectrum with a particular minimum of $\partial R(\lambda)/\partial \lambda = -0.0154 \text{ V/nm}$ at $\lambda = 918 \text{ nm}$ located between reflection maxima $\lambda_{k=21}$ and $\lambda_{k=20}$. Taking the value of $\Delta R_m(\lambda) = -7.03 \cdot 10^{-5} \text{ V}$ we find the amplitude of the field-modulated spectral shift of $\Delta R_m(\lambda)$: $\Delta \lambda_m = \Delta R_m / (\partial R / \partial \lambda)$ ($\lambda = 918$

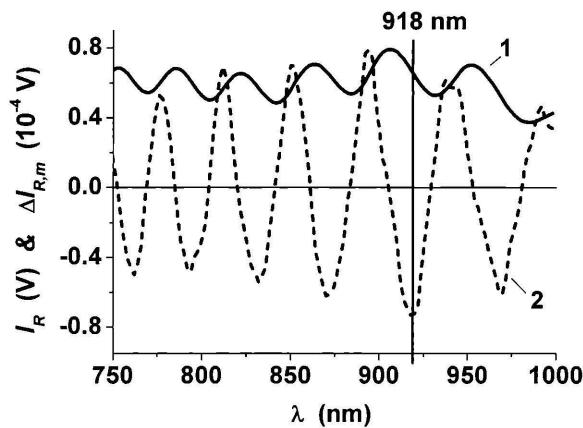


Fig. 2. Spectra of intensity I_R of light reflected from the semitransparent mirror (curve 1) and the increment of reflection $\Delta I_{R,m}$ induced by electric field ($U_m=15$ V, $f=28$ Hz). The ordinate scales for both I_R and $\Delta I_{R,m}$ are given in Volts at the photomultiplier output. The minimum of ΔI_R at $\lambda=918$ nm is selected for measurement of field dependence $\Delta I_{R,m}(E)$.

nm)= $4.56 \cdot 10^{-3}$ nm. This shift corresponds to an increase in the Fabry-Perot gap Δd_m that can be evaluated from the derivative of Eq. (1): $\partial \lambda_m^k / \partial d_m = 2 \cos \alpha / k = 0.093$ at $\lambda=918$ nm. Hence, at $U_m=15$ V, we obtain the amplitude of the field modulation of the Fabry-Perot gap thickness $\Delta d_m = (\partial d / \partial \lambda) \Delta \lambda_m = 0.048$ nm and, consequently, the compression $\Delta L_m = -\Delta d_m = -0.048$ nm and strain $\Delta L_m / L = -2.67 \cdot 10^{-4}$ of the film. The wavelength independent calibration coefficient $\Delta L_m / \Delta R_m = -683$ nm found from the derivatives is valid for any voltage U_m (at $f=28$ Hz) applied to the sample. We use this coefficient to get the voltage dependence of the amplitude values of deformation ($\Delta L_m = 0.21$ nm) and strain ($\Delta L_m / L = 0.12\%$) achieved at the field $E_m = 2.1 \cdot 10^8$ V/m closed to a breakdown. The average value of strain necessary for calculation of field dependence of Young's modulus is presented by curve 1 in Fig. 3.

Our high-symmetric unpoled and non-stretched films resemble polycrystalline ferroelectric films or ceramics. Skipping for clarity all suffices z , we have a system of simple electrostriction equations

$$S = sX + \gamma D^2 \quad \text{and} \quad D = (\epsilon_0 \epsilon E + P) + \kappa X^2 \quad (2)$$

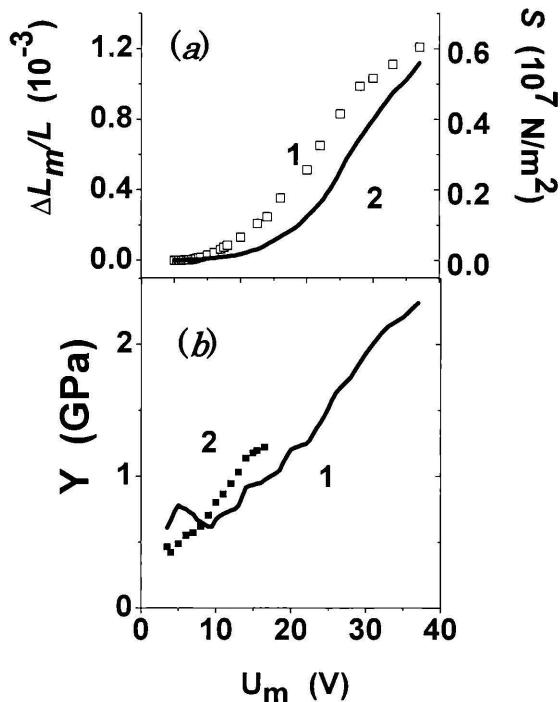


Fig. 3. (a) Voltage dependencies of the strain (curve 1) and stress (curve 2) for a 180 nm thick sample and (b) voltage dependencies of the apparent Young modulus for a samples of thickness 180 nm (curve 1) and 75 nm (curve 2). Field frequency= 30 Hz.

valid in the static case. Here, ϵ and P are dielectric permittivity and polarization, $X = -DE/2$ [10] is the stress caused by the attraction of the capacitor plates connected to the voltage source, s is compliance (inverse of the Young modulus Y), γ and κ are coupling coefficients of spontaneous electrostriction and stress-induced displacement. Note that D is measured in experiment, and we may restrict the discussion by the sole equation $S = DE/2Y + \gamma D^2$.

According to Eq.(2), the ratio of curve 2 to curve 1 would give us a constant value of $2Y$. Evidently it is not our case. In Fig. 3(b), curve 1 represents the voltage dependence of apparent Young's modulus for a 180 nm thick film which is growing with increasing field from 0.6 to 2.2 GPa. For a film of thickness of 75 nm (curve 2) we see the same tendency (note that for bulk PVDF- TrFE copolymers, Young's modulus is varied in the range

of 2-3 GPa and almost independent of applied field [7])

Our result shows that non-poled Langmuir-Blodgett films are rather soft at a low field but become more rigid during and after switching by enormously high field. The rigidity at high voltages is confirmed by the piezoelectric effect observed upon application of a pulse poling voltage of 20 V that leaves a remanent polarization of 0.02 C/m^2 . Then, with an a.c. voltage lower than the coercive one ($U_m=5 \text{ V}$, $f=28 \text{ Hz}$), we obtain $\Delta L_m/L=-3.4 \cdot 10^{-4}$ (at the 1st harmonic), the piezoelectric coefficient $p=5.4 \text{ pN}$ and $Y=1.8 \text{ GPa}$ close to the high field values in Fig. 3(b). As to the softness of our films, especially at low fields, it may be referred to some defects, e.g. local air voids. Such voids (of the size of the order of 1\AA) may appear due to an imperfect wetting of the bottom Al electrode by the polymer upon layer transfer from the water surface [11]. As soon as we apply a stress, the voids are squeezed out and the apparent Young modulus increases.

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