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Ferroelectric Behavior of Nano-Layered Heterostructures Composed of Ferroelectric - Linear Dielectric Organic Layers

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Thin-film heterostructures comprising ferroelectric (FE) copolymer layers of vinylidene fluoride with trifluoroethylene (PVDF/TrFE) and linear dielectric (LD) layers of azodye prepared by Langmuir-Blodgett technique are obtained and studied. A simple physical model of a local electric field amplification in layers of FE and LD are presented. Experimental studies of the ferroelectric switching confirm that, for hetero-structures, the external effective coercitive voltage decreases and the switched polarization increases.

Keywords: Nanostructured Langmuir-Blodgett films, Ferroelectric switching.

1. INTRODUCTION

In the last years we see a reviving interest in studying ferroelectric materials, especially ultrathin ferroelectric films. There is also an evident trend to hybridization of ferroelectric and semiconductor materials in new electronic devices [1, 2]. Most of such devices are based on traditional crystalline ferroelectrics but sometimes one has serious difficulties with crystalline materials in preparing ultrathin films compatible with modern electronics. In many applications polymer ferroelectrics are more desirable [3, 4]. Recently, a possibility for studying ferroelectricity in ultra-thin (even below 10 nm) P(VDF-TrFE) copolymer films prepared by Langmuir-Blodgett (LB) technique has been demonstrated [5, 6]. Langmuir-Blodgett technique allows one to design nano-structured films of different materials. In such complex sandwiches (heterostructures), the ferroelectric layers can alternate with other functionalized layers of magnetic materials, dyes, luminophores, biological molecules, etc., which would suffer a very strong built-in electric field of the ferroelectric layers as high as 10^8-10^9 V/m. In addition, the polymer structure allows incorporation of almost any solid nanoparticles. Hence, one may look forward to new discoveries and technical applications in such areas as organic transistors [2], conductivity switchers [7], multiferroic heterostructures [8], and high all-organic capacity data storage devices prepared by modern nanoimprinting techniques [9].

Here we report on preparing and studying all-organic heterostructures prepared by Langmuir-Blodgett (LB) technique and consisting of two subsystems of molecular layers. The first subsystem is presented by molecules of ferroelectic copolymer polyvinylidene fluoride - trifluoroethylene (PVDF/TrFE). For the second subsystem molecules of an azodye MEL-26 were chosen, the films of which were well investigated early [10]. Two problems were considered and studied in this work. Firstly, the problem of retaining ferroelectricity in such a heterostructure is arising, since for the nanometer-thick films the presence of nonferroelectric azodye molecular layers might, in principle, influence the ferroelectric phase state of the copolymer. Secondly, from the simple physical model presented here, it follows that, if the ferroelectric phase of the copolymer is retained, the switching of spontaneous polarization should have an effect on the instantaneous electric field in both the subsystem of azodye molecules and the subsystem of ferroelectric copolymer. Thus, the question of dynamics of ferroelectric switching of such a heterostructure is arising. So, these two questions are addressed to this work.

2. HETEROSTRUCTURE FERROELECTRIC - LINEAR DIELECTRIC

2.1 Samples preparing

We used copolymer vinylidene fluoride with trifluoroethylene P(VDF/TrFE) in composition 70:30. Such a composition guarantees the existence of the ferroelectric phase under heating up to the temperature of about ~120°C. Langmuir-Blodgett films were obtained by the following way. Weak-concentration (0.01% by weight) solution of copolymer in cyclohexanone and azodye (p-octadecyloxi-p'-sulphopiperidid azobenzene, MEL-26) in chloroform were prepared. Then, using home-done set-up [11] two subsystems of molecular layers were deposited onto a glass substrate by a horizontal lift technique [12] (at first copolymer, then azodye layers). Al electrodes (both the bottom and the top at the final step) were deposited by vacuum evaporation technique. Monolayers were transferred from the air-water interface onto the solid substrates at room temperature and a surface pressure of 3 mN/m (for copolymer) and 15 mN/m (for azodye layers). A special design of the device was used as schematically shown in Fig. 2.1. The design consists of three capacitor elements on a common substrate prepared in one technological procedure with a common copolymer layer for all three capacitors. One of these three capacitors comprises only common ferroelectric layer consisting of sixty transferred copolymer monolayers (60 TL). The

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two other capacitors comprise additional azodye transferred layers (3 TL and 7 TL respectively for the 2^d and 3^d capacitor elements).
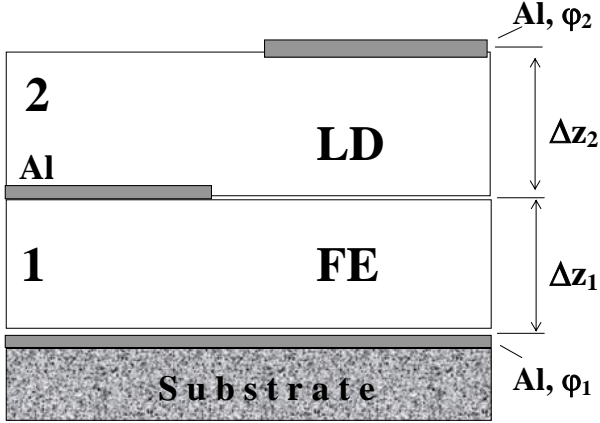

Fig. 1 – The scheme of a design with three capacitors fabricated on a common glass substrate. The right part is a heterostructure capacitor comprising the region **1** (molecular layers of copolymer, PVDF/TrFE - ferroelectric, **FE**) and the region **2** (3 or 7 molecular layers of MEL-26 azodye - linear dielectric, **LD**) confined between common bottom and top Al-electrodes. The left part is a capacitor comprising only individual layers of the copolymer confined between common bottom and intermediate top Al-electrodes.

2.2 Model of a local electric field amplification in a ferroelectric heterostructure

Considering the heterostructure (Fig. 1) to be homogeneous in the substrate plane (*x, y*-directions) and supposing electric conductance of materials to be equal to 0, one can write the following relationships between the electric field strength $E = 0, 0, E_z$) in different parts of the heterostructure and the potential difference $U \equiv U_{12} = \varphi_1 - \varphi_2$ between the electrodes:

$$E_{z,1}\Delta z_1 + E_{z,2}\Delta z_2 = U , \qquad (2.1)$$

$$\varepsilon_{z,1}E_{z,1} + \varepsilon_0^{-1}P_s = \varepsilon_{z,2}E_{z,2} , \qquad (2.2)$$

where indices "1" and "2" refer to the space regions occupied by the ferroelectric copolymer (the thickness Δz_1) and the dye (the thickness Δz_2), respectively; P_s is the spontaneous polarization normal to the substrate surface, $\varepsilon_0 = 8.85\times10^{-12}$ F/m, $\varepsilon_{z,1,2}$ are dimensionless (relative) components of dielectric permittivity tensor along normal direction (*z*-direction). Equation (2.2) concerns one of the Maxwell's Equations (div **D** = 0), requiring a continuity of the normal component of the electric displacement vector **D**, and in the absence of free space charge results in $D_{n,1} = D_{n,2}$. Real LB films have nonzero conductance and Eqns (2.1) and (2.2) would satisfactorily hold just in alternating electric fields of frequency much larger than reverse Maxwell relaxation time ($2\pi f >> (\rho_{z,1,2}\cdot \varepsilon_0 \cdot \varepsilon_{z,1,2})^{-1}$, where $\rho_{z,1,2}$ is the specific resistance of the materials along the normal) under the condition of spontaneous polarization switching. Thus, we proceed from an assumption that the external voltage U is always higher than some minimal coercive voltage U_c that ensures switching the ferroelectric subsystem. It is the fast polarization

switching that excludes polarization screening by free charges.

From Eqs. (2.1) and (2.2) one can easily find the electric field in ferroelectric and dye regions:

$$E_{2,z}(t) = \left(U(t)\varepsilon_{z,1} + \Delta z_1 \varepsilon_0^{-1}P_s(t)\right)\cdot\left(\Delta z_2\varepsilon_{z,1} + \Delta z_1\varepsilon_{z,2}\right)^{-1} (2.3)$$

$$E_{1,z}(t) = \left(U(t)\varepsilon_{z,2} - \Delta z_2 \varepsilon_0^{-1}P_s(t)\right)\cdot\left(\Delta z_2\varepsilon_{z,1} + \Delta z_1\varepsilon_{z,2}\right)^{-1} \qquad (2.4)$$

In Eqs. (2.3) and (2.4) the alternating character of the electric field is expressed by introducing the time-dependent values (*E, U, P_s*). As seen from (2.3) the switched polarization can increase the instantaneous field strength in the region of the dye subsystem and such an increase takes place in the dye region after switching the polarization, when polarization is directed along the external electric field applied. The same field strengthening in the dye part of the heterostructure was earlier demonstrated by electrooptical measurements in [13, 14].

Of importance, from our point of view, is the relationship (2.4). It determines electric field acting in ferroelectric subsystem. Let us consider the situation when the negative external voltage is switched up to the positive one. In this case, up to the next-in-turn switching, the spontaneous polarization is directed opposite to the external electric field (if U is a positive value, then P_s is the negative one). However, since the term with P_s in the numerator of Eq. (2.4) is negative, the both terms in the numerator turn out to be of the same sign, and the effect of field amplification is possible up to the very instant of switching. The latter should promote an acceleration of the switching process and reducing the external coercive voltage across the heterostructure as a whole.

Therefore, the effect of field strengthening in the dye subsystem is possible after switching of the spontaneous polarization, whereas the field in the ferroelectric subsystem can be amplified before the instant of polarization switching.

The effect of field strengthening in the ferroelectric layer can be expressed by the ratio of the field (Eq.2.4) to the corresponding electric field in the absence of the dye layer ($\Delta z_2 = 0$). From Eq.2.4 follows:

$$F_1 = \frac{E_{1,z}\Delta z_1}{U} = \left(\varepsilon_{z,2} - \Delta z_2\frac{\varepsilon_0^{-1}P_s}{U}\right)\cdot\left(\varepsilon_{z,2} + \frac{\Delta z_2}{\Delta z_1}\varepsilon_{z,1}\right)^{-1} \quad (2.5)$$

The strengthening effect is realized if the factor F_1 >1, i.e., when

$$\Delta z_1 > \varepsilon_0\varepsilon_{z,1}\left|\frac{U}{P_s}\right| = \Delta z_{1,c} \qquad (2.6)$$

In Fig. 2 there are given dependencies of the electric field amplification factor, F_1, versus the thickness of azodye layer, Δz_2, for some fixed thicknesses of ferroelectric layer, Δz_1 (from 2 nm to 120 nm), at an external voltage $U = 20$ V and for the material parameters close to the experimental ones: $P_s = 0.04$ C/m²; $\varepsilon_1 = 7$; $\varepsilon_2 = 2.5$.
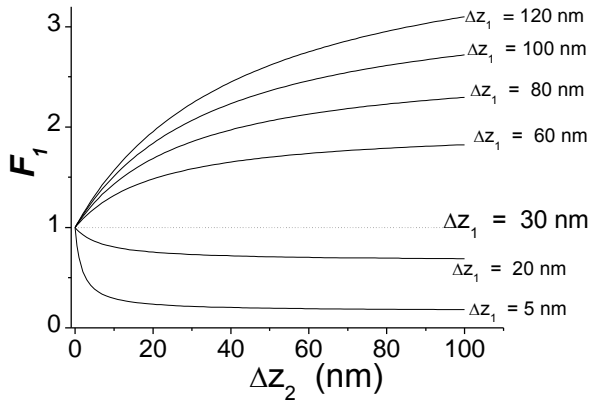
Fig. 2 – Dependence of the electric field amplification factor, F_1, versus the thickness of azodye layer, Δz_2, at different fixed thicknesses of ferroelectric layer, Δz_1, ($U = 20$ V; $P_s = 0.04$ C/m²; $\varepsilon_1 = 7$; $\varepsilon_2 = 2.5$).

Thus, the presence of the additional dielectric layers (dye subsystem) can strengthen the local electric field in the region of ferroelectric if thickness of the ferroelectric layers is sufficiently large. The latter can positively affect the dynamics of ferroelectric switching and the value of switched part of polarization.

3. EXPERIMENTAL RESULTS

Figure 3 shows the temperature behavior of the capacitance of the heterostructure and the individual copolymer film during the thermal cycling. The both structures reveal pronounced temperature hysteresis characteristic of first-order ferroelectric phase transition.
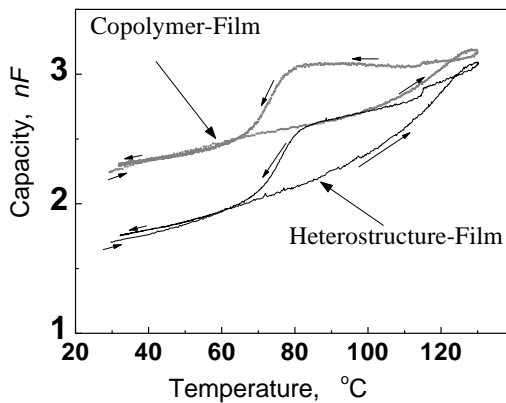

Fig. 3 – Temperature dependencies of the capacity of heterostructure (18 layers of copolymer and 3 layers of azodye) and the capacity of individual copolymer film (18 layers of copolymer) taken at and sine-form voltage of 0.35 V frequency of 68 Hz (overlapped active area S = ~1x1 mm2 for both capacitors). Arrows along the curves indicate the direction of the temperature run.

Merz switching technique [15] was used for characterizing repolarization properties of capacitors. Amplified triangle waveform signal from functional generator was applied to the capacitor tested and in series connected load resistor. Oscillograms taken from the load resistor were registered and saved by a memory oscilloscope joint with a personal computer. The totally

switched polarization was obtained after integrating the area under current curves $i(t)$ in Fig. 4 and subtracting the linear contributions of the resistive and capacitive components of the corresponding current response.

Figure 4 shows some switching curves of ferroelectric repolarization for 3 capacitor elements obtained for different amplitudes (from 10 V to 30 V) of the triangle waveform voltage applied. Beginning with amplitudes of about ~12 V there is a distinctive repolarization bump that, with increasing voltage amplitude, is always larger in value for the heterostructure capacitor compared to the copolymer homo-film capacitor. Here we once more give emphasis to the fact that each of the three capacitors (heterostructures comprised and individual copolymer layer comprised) are placed on the same common substrate and comprised common ferroelectric layer. That minimizes inaccuracy in repolarization measurements associated with a possible nonuniformity in thickness of the ferroelectric layer, the compared capacitors might have if prepared as separate units on three different substrates.
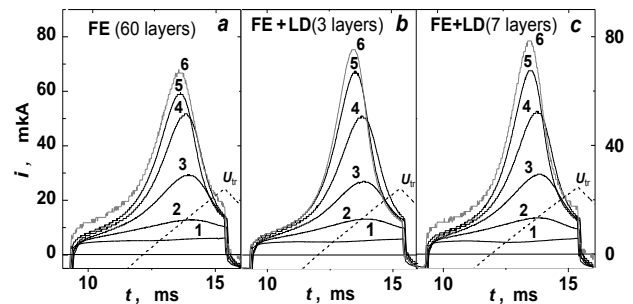

Fig. 4 – Oscillograms $i(t)$ of repolarization current response for individual copolymer PVDF/TrFE film (60 layers) (a), and two heterostructures (60 layers of copolymer + 3 layers of azodye) (b) and (60 layers of copolymer + 7 layers of azodye) (c). Oscillograms are obtained by Merz technique under applying cycling voltage of the triangle form ($f = 80$ Hz) of different amplitudes:10 V (1), 12.5 V (2), 15 V (3), 20 V (4), 25 V (5), 30 V (6)- the same for (a, b, c) curve series. Only parts of the curves for the positive half-period of applied triangle form voltage U_{tr} are given.

The measurements given in Fig. 4 were carried out at the same amplitudes of triangle voltage for all three series. As seen from the figures the switched polarization is occurred larger for the heterostructure ($P_{sw} \approx 5.7$ mkC/cm² for $U_{tr} = 30$ V,curve 6, Fig. 4c) than that for the copolymer capacitor($P_{sw} \approx 5.0$ mkC/cm² for the same $U_{tr} = 30$ V, curve 6, Fig. 4a). This is a clear indication of the presence of the local field amplifying effect in the case of the heterostructure. Moreover, the maximum of the current response in the heterostructure corresponds to a lower instant external voltage (~11.7 V) as compared to the instant voltage (~13.7 V) for the current maximum of the individual copolymer layer (compare curves 6 in Figs. 4*a* and 4*c*). The latter means that the effective external coercive voltage U_c is lower for the heterostructure.

4. CONCLUSIONS

We have demonstrated that polarization switching in a heterostructure can be more effective than

in an individual ferroelectric film. This circumstance is due to the effect of amplification of local electric field acting in the ferroelectric part of the hetero-structure.

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