

Strong amplification of an electric field and electrooptical response in ultrathin heterostructures ferroelectric–linear dielectric

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An electroded heterostructure consisting of a dye layer sandwiched between two polymer ferroelectric layers is discussed. The dye layer plays a role of the probe of the electric field measured by an electroabsorption technique. Using this new method the electric field in ferroelectric and dielectric layers can be measured separately. When an a.c. voltage is applied to the heterostructure, the electric field in the dye layer increases 2.2 times (up to 0.55 GV/m) whereas the field in the ferroelectric decreases 2 times with respect to the average field in the entire structure. Moreover, the dye layer sandwiched between the ferroelectric layers may stand without breakdown the fields 5–7 times higher than a neat reference dye layer confined between metal electrodes. Therefore, the performance of electrooptical, electromechanical and other field controlled devices may be improved considerably when their functional materials are placed between ferroelectrics layers.

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, fatigue and “dead layer” phenomena [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. There is also an evident trend to hybridization of ferroelectric and semiconductor materials in new electronic devices [2, 3]. 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 [4] but, as a rule, it is difficult to prepare high quality samples of thickness below $0.1\ \mu\text{m}$. More recently, ferroelectric properties of ultra-thin P (VDF–TrFE) copolymer films (even below 10 nm) have been demonstrated [5]. The so-called Langmuir–Blodgett (LB) films are prepared by a layer-by-layer transfer of monolayers from the water surface onto solid substrates [6]. Therefore, we can design heterostructures, in which ferroelectric monolayers alternate with other functionalized monolayers of dyes, elastomers, luminophores, magnetic materials, biological preparations etc. Hence, one may look forward to novel technical applications in the areas of all-organic sensors, transistors [2], conductivity switches [7], and data storage devices based on modern nano-imprinting techniques [8].

As a simple example of such heterostructures is a ferroelectric with a gap filled with a linear dielectric material. Such a heterostructure is placed between two electrodes, which may be short circuit ($U = 0$) or connected to a voltage source. In the absence of free charges and conductivity, even at $U = 0$, there are built-in fields of opposite direction in both elements of the structure. Such fields may influence the properties of the constituent materials [9] and even stimulate an appearance of new phase transitions [10]. With applying electric voltage we may expect some other interesting effects in heterostructures.

Consider a short-circuit layer of unpoled, non-conductive, multidomain polymer ferroelectric with a single rotation symmetry axis z normal to the layer. In the zero field, both macroscopic polarization and surface charge layers near electrodes are absent. The same is true for a heterostructure consisting of a ferroelectric and a nonconductive dielectric. However, a strongly nonlinear polarization $P_z(E)$ is induced by the field applied in the z -direction due to rotation of the spontaneous polarization vector \mathbf{P}_{sp} from the xy -plane to the z -direction [6]. The applied field could be permanent or alternating field of proper frequency, see below.

In the absence of the real component of the current, the Poisson equation $\text{div}\mathbf{D} = \rho = 0$ results in constant electric displacement D_z along the normal z of the heterostructure. The electric field in the ferroelectric (E_F) and dielectric (E_d) layers will follow the law

$$D_z = \varepsilon_0\varepsilon_F E_F + P_z(E) = \varepsilon_0\varepsilon_d E_d, \quad (1)$$

where ε_0 , ε_F , and ε_d are, respectively, dielectric constants of vacuum, ferroelectric and linear dielectric and

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$P_z(E) \leq P_{sp}$ is the field dependent z -component of P_{sp} of the ferroelectric. Adding the equation $U_t = E_F d_F + E_d d_d$, where U_t is a total voltage across the entire heterostructure and $d_F = d_{F1} + d_{F2}$ and d_d are thicknesses of the corresponding layers, we write the expressions for the internal field strength in both elements of the heterostructure:

$$E_F = \frac{U_t \varepsilon_d - d_d (P_z / \varepsilon_0)}{\varepsilon_d d_F + \varepsilon_F d_d} \quad \text{and} \quad E_d = \frac{U_t \varepsilon_F + d_F (P_z / \varepsilon_0)}{\varepsilon_d d_F + \varepsilon_F d_d}. \quad (2)$$

Note that equations (1), (2) are particular case of the classical equations [11, 12]. Evidently, the material parameters ε_F , ε_d , d_F , and d_d are considered to be constant.

Our aim is to make measurements of the local field in both elements of the ferroelectric-dielectric heterostructure. To this effect, we use two thin layers of a ferroelectric copolymer PVDF (70%) – TrFE (30%) and an even thinner dye (linear dielectric) layer in between. The dye serves as a probe of the electric field because the field causes a shift of the dye absorption spectrum, easily measured by an electroabsorption technique. The choice of a dye is not very important and we selected an azo-dye of chemical formula $C_9H_{19}NH-\varnothing-N=N-\varnothing-COOH$ (\varnothing is phenyl ring) because it is easily transferred on the substrates already covered by polymer layers. In addition, the dye manifests a low-noise spectrum of electroabsorption in a convenient wavelength range. The transfer of molecular mono- or multilayers was implemented by the horizontal lift technique. The layers on the water surface were prepared from solutions in cyclohexanone (for copolymer) or chloroform (for dye). As shown in the Inset to Fig. 1, the heterostructure is formed on a fused quartz substrate, and consists of a transparent ITO (indium-tin oxide) electrode, a layered structure “copolymer + dye + copolymer” and a semitransparent Al electrode. To improve crystallization, the first sublayer of the copolymer ($d_{F1} \approx 80$ nm, $\varepsilon_F = 9$) was annealed for 1 hour at 110 °C; the dye layer ($d_d \approx 25$ nm) and the second sublayer of the copolymer ($d_{F2} \approx 25$ nm) were not annealed to save dye electrooptical properties. The thickness of the thin dye layer d_d was found from the calibrated absorption spectra and capacitance measurements and the thickness of thicker layers d_{F1} and $d_t = 130$ nm (the total thickness of the heterostructure) were measured interferometrically. In addition to the heterostructure, a reference sample was prepared with a neat azo-dye layer of thickness $d_{ref} = 35$ nm. Its dielectric permittivity has also been found from the absorption spectra and capacitance measurements ($\varepsilon_d = 3.8$). The absorption spectra of the neat dye layer (1) and the dye layer between the copolymer sublayers (2) with maxima

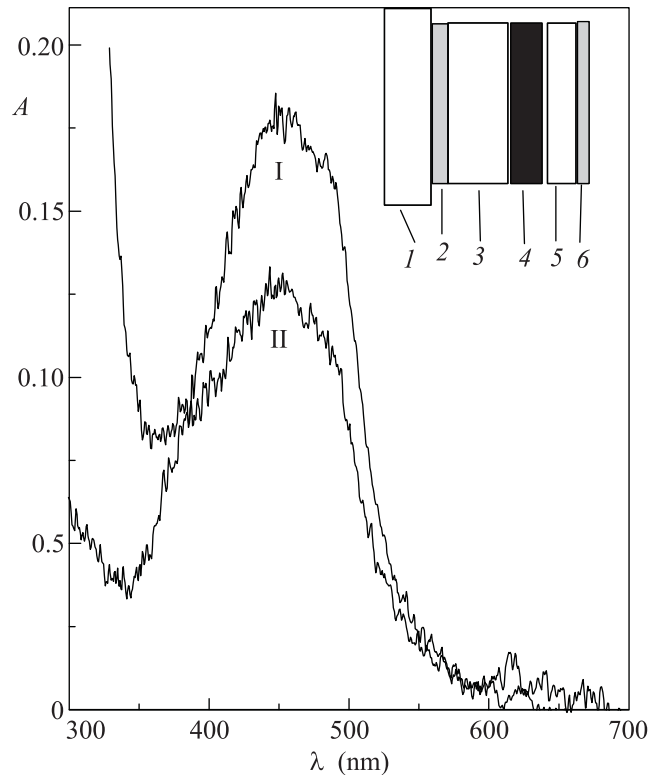


Fig. 1. Absorbance spectra of the neat dye layer on the fused quartz substrate (I) and the dye layer within the heterostructure on the ITO covered fused quartz substrate (II). Correspondent thicknesses of the dye layers (I) and (II) are $d_{ref} = 35$ nm and $d_d = 25$ nm. Inset: geometry of the heterostructure on the fused quartz substrate (1): ITO electrode (2), first sublayer of PVDF–TrFE (3), azo-dye layer (4), second sublayer of PVDF–TrFE (5), Al electrode (6)

$A_{m1} = 0.18$ and $A_{m2} = 0.13$ at $\lambda = 444$ nm are shown in Fig. 1.

The absorption spectrum of the dye is not simple. In fact it may well be represented by four Gaussians. Each of them is related to a certain optical transition between the same ground state and four excited states. In the electric field each band (a Gaussian) is broaden and shifted, and the total absorption spectrum of the dye is changed. The difference spectrum of electroabsorption $\Delta A(\lambda, E) = A(\lambda, E) - A(\lambda, E = 0)$ is a measure of the field applied to the dye layer. In principle, with our software we can calculate all parameters responsible for the spectral shift of each of the four Gaussians [13]. However, if the difference spectrum has the same spectral shape for both the reference neat dye layer and the same dye surrounded by a ferroelectric polymer, the fitting procedure is not necessary. We can only measure and compare the two electroabsorbance spectra $\Delta A_{1,2}(\lambda, E)$

for the two samples and, since the electric field applied to the reference sample is known, we can easily find the electric field in the dye layer within the heterostructure. It is convenient to work with an a.c. voltage $U(\omega)$ and a lock-in amplifier that simultaneously measures the linear-in-field and quadratic-in-field components of $\Delta A = -\Delta T/(T \ln 10)$ on the first and second harmonics of the applied voltage, respectively (here T and ΔT are the sample transmission and its field increment). In our experiment the second harmonic is strongly dominating over the first one. It means that the dye layers of both samples practically isotropic [13].

Fig. 2 shows the electroabsorption spectra for the two samples. One of them (curve 1) corresponds to the ref-

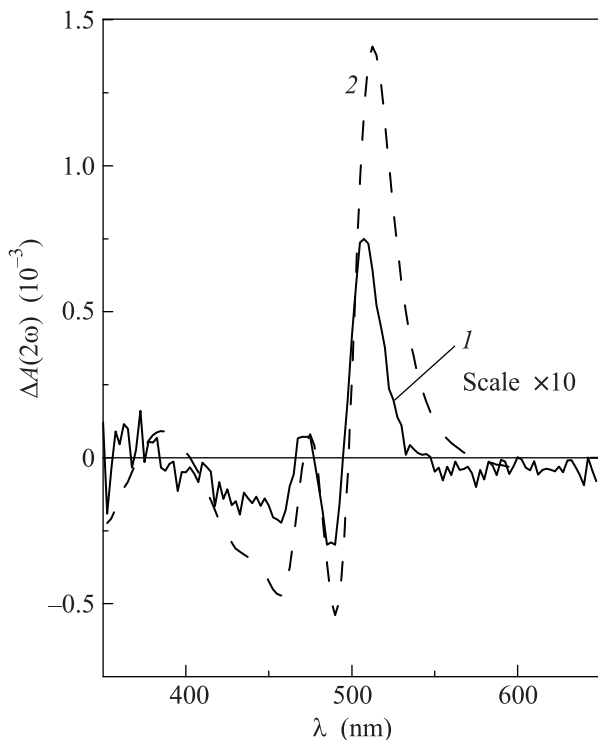


Fig. 2. Electroabsorption spectra of the reference sample (curve 1 with the data multiplied by 10) and the dye layer in the heterostructure (curve 2). Note that the ratio of ΔA (amplitude values) for the two curves at their maxima is 18.7

erence sample (dye layer thickness $d_{\text{ref}} = 35$ nm and $\varepsilon_d = 3.8$) subjected to an a.c. voltage of amplitude $U_{\text{ref}} = 3$ V (i.e. $E_{\text{ref}} = 8.5 \cdot 10^7$ V/m) and frequency $f = \omega/2\pi = 30$ Hz. Curve 2 represents the electroabsorption spectrum of the heterostructure consisting of a somewhat thinner layer (25 nm) of the same dye between two ferroelectric sublayers of the total thickness $d_F = 105$ nm and $\varepsilon_F = 9$. As the ratio of the amplitudes of curve 2 to curve 1 at any wavelength is

roughly constant, we take it at the spectral maximum ($\lambda = 515$ nm): $\Delta A_2/\Delta A_1 \approx 18.7$. Both ΔA spectra in Fig. 2 are recorded at the second harmonic ($f = 60$ Hz) and inevitably proportional to the square of the fields E_d and E_{ref} within dye layers. From the theory of electroabsorption [14] modified for thin anisotropic films [13] the increment of the absorbance at the second harmonic may be written in a very simple and general form:

$$\Delta A(2\omega, \lambda, E) = kE_d^2 \text{Der}(\lambda), \quad (3)$$

where coefficient k takes into account all molecular parameters for the spectral bands of the dye used. Note that k is the same for both dye layers, the reference one and the layer within the heterostructure.

As to function $\text{Der}(\lambda)$, it includes a field independent combination of derivatives $\partial A/\partial \lambda$ and $\partial^2 A/\partial \lambda^2$, both proportional to absorbance A . The ratio of the absorbance maxima seen in Fig. 1 is $A_{m1}/A_{m2} = 0.18/0.13 = 1.4$. With this correction and ratio $\Delta A_2/\Delta A_1 \approx 18.7$, using Eq. (3) the electric field in the dye layer within the heterostructure can be found: $E_d = E_{\text{ref}}(18.7 \cdot 1.4)^{1/2} = 4.3 \cdot 10^8$ V/m (for voltage $U_t = 25$ V applied to the total heterostructure at $f = 30$ Hz). Correspondingly, the field in the ferroelectric layer $E_F = (U_t - E_d d_d)/d_F = 1.36 \cdot 10^8$ V/m and the average field in the heterostructure $E_{av} = U_t/d_t = 1.9 \cdot 10^8$ V/m.

The evolution of the E_d and E_F fields in the dye and ferroelectric elements is shown in Fig. 3a in comparison with the average field E_{av} over the heterostructure. We see that the ratio E_d/E_F grows with the voltage across the structure, stabilizes at a maximum value of (at $U_t = 27$ V) and then decreases. Evidently, the switching of spontaneous polarization is involved in the game. Eqs. (2) allow us to calculate the voltage dependence of polarization $P_z(E)$ shown in Fig. 3b. Function $P_z(E)$ has a zero point at $E_F \approx 0.17$ GV/m that is very close to the coercive field of our ferroelectric copolymer. However, the maximum value of the switched polarization $P_z(\text{max}) = 4.3$ mC/m² in our heterostructure is over one order of magnitude lower than the spontaneous polarization.

The maximum field in the dye layer is very high, $E_d = 0.54$ GV/m. Such a field cannot be reached without the ferroelectric layer. Usually single electroded layers of dyes are broken in the field 5–7 times lower. In our case, e.g., the field in the reference sample (0.085 GV/m) is very close to the breakdown while the maximum field in the dye layer within the heterostructure is 6.3 times higher and still far from the breakdown. Correspondingly, the amplitude of the quadratic electroabsorption effect is enhanced 40 times and could even be increased

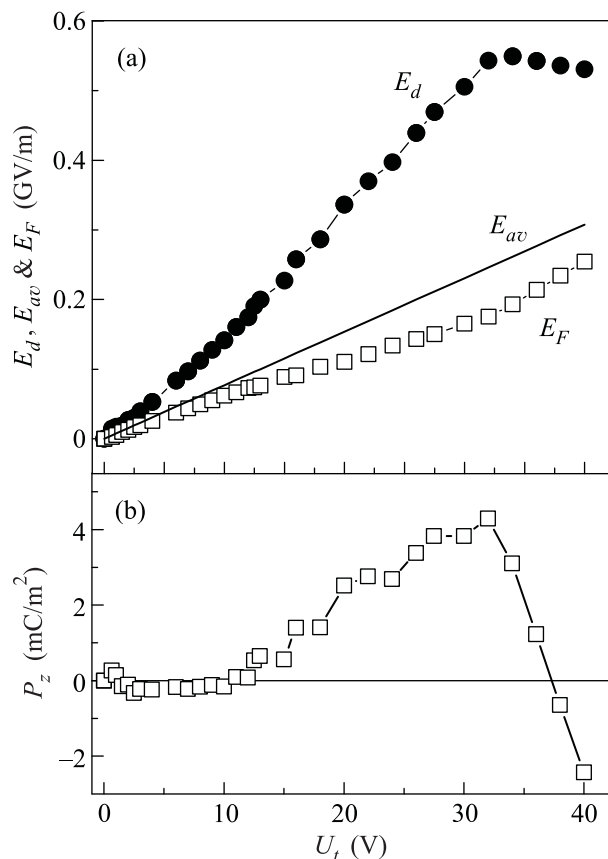


Fig. 3. (a) – Electric fields in the dye layer E_d , in both sub-layers of ferroelectric polymer E_F , and the average field $E_{av} = U_t/d_t$ in the total heterostructure as functions of the a.c. voltage of amplitude U_t ($f = 30$ Hz) applied to the structure. (b) – The amplitude values of the field induced polarization $P_z(E)$ vs U_t

further on. This conclusion is valid for any quadratic-in-field effect (electrooptical or electromechanical). As to the enhanced field stability of materials embedded between ferroelectric layers, in our opinion, it is related not only to intrinsic properties of the used polymer material (rather stable to the breakdown) but also to the

absence of any contact of dielectric layers with metals. Such situation resembles very efficient poling dielectrics by corona discharge when the charge injection from the metal electrodes is excluded. Therefore, we can predict a considerable improvement of performance characteristics of electrooptical, electromechanical, sensorial and other field-controlled materials incorporated in heterostructures with ferroelectric layers.

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