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PHASE TRANSITIONS

Structure and Electrical Properties of Liquid Crystal Films Grown by the Langmuir Technology

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Abstract—Liquid-crystal-based films of different thicknesses, fabricated by the Langmuir technology, have been studied. Previously, we revealed a structural phase transition in these films at a temperature of ~75°C. To clarify the nature of this transition, the temperature dependences of the capacitance and conductance of these films have been investigated. The results obtained indicate that the samples contain a ferroelectric phase, beginning with one monolayer. The film structure imperfection has been revealed using atomic force microscopy, which explains the size of the temperature range in which the phase transition is observed.

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1. INTRODUCTION

Recently, particular attention has been paid to ultrathin films in the literature. Of special interest are the films fabricated based on liquid crystals by the Langmuir technology [1–3]. Electrical properties of such films can differ appreciably from properties of bulk liquid crystals due to both the manifestation of "size" effects and imperfections in the thin film structure. Therefore, in this work, the structure of films fabricated based on a liquid-crystal material by the Langmuir technology was studied using atomic force microscopy, and the correlation of structural and electrical properties of these films was determined.

2. MEASUREMENT TECHNIQUE

Thin films fabricated based on the Schiff compound para-tetradecyloxybenzyliden-amino-2-methylbutyl-cyanocinnamate (TDOBAMBCC) by the Langmuir technology were studied. A TDOBAMBCC solution in chloroform with a concentration of $(1–3) \times 10^{-2}$ wt % was used. Films of different thicknesses were fabricated by multiple deposition of one by one monolayer from the water surface onto the substrate by the Langmuir–Schaefer method (horizontal lift).

The structure of grown films was studied using a Multimode V (Veeco) atomic force microscope (AFM) in the intermittent contact mode.

To perform electrical measurements, films were deposited on glass substrates with preliminarily deposited aluminum electrodes. The second aluminum electrode was deposited on the film from above. Such an arrangement of contacts made it possible to measure the electrical capacitance and conductance of the structures in the direction perpendicular to the layer surface. The electrode overlap area was 1 mm^2. Current–voltage characteristics were measured using a Keithley 6487 picoammeter/source (direct current (dc) signal) and an NR 4192 impedance analyzer (alternating current (ac) signal) in the frequency range of $10^{-2}–10^{1}$ kHz. The capacitance of the grown structures 1 mm^2 in area was measured using an ac signal at frequencies of 5 Hz–13 MHz.

3. RESULTS AND DISCUSSION

We now dwell on the results of structural studies. The films grown on the quartz substrate (analog of films used in optical measurements) and on an aluminum layer (analog of films studied in electrical measurements of the Al–TDOBAMBCC film–Al) structures) differed significantly from each other. As an example, Fig. 1 shows the AFM images of films grown with the same number of transfers (7 layers) on different substrates. We can see that there is no continuous coating of the substrate surface by a film material in both cases. It was found that rather small particles of deposited material ~20–50 nm in diameter and ~10 nm in height are formed on the quartz substrate (Fig. 1a). Particles are uniformly enough arranged on the surface, almost not forming aggregates. The distance between particles is ~5–40 nm. An even less perfect coating was observed on the aluminum surface

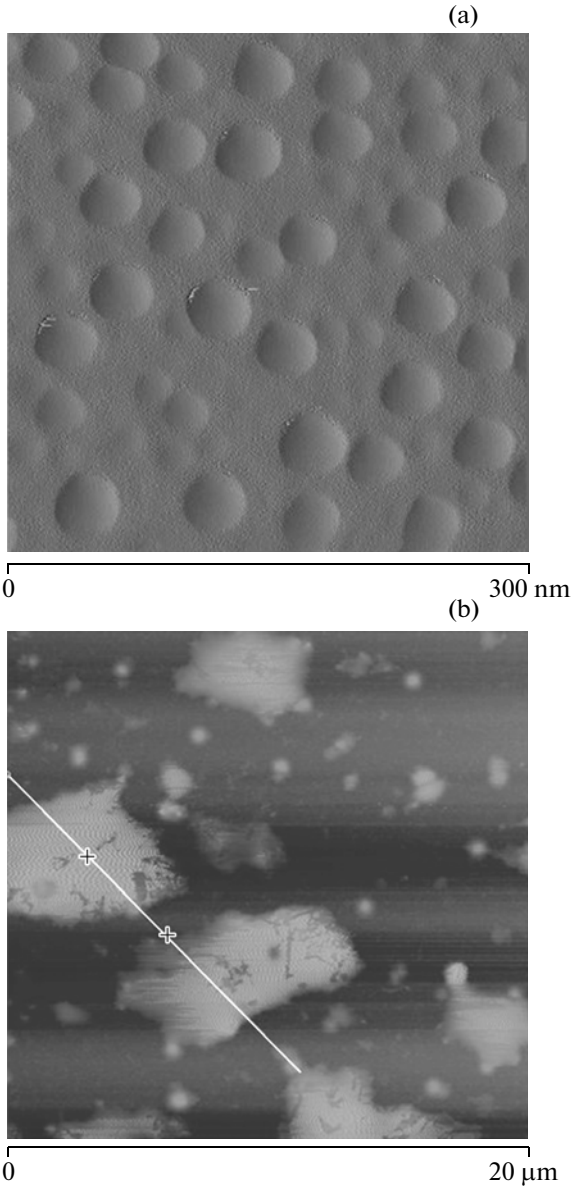

Fig. 1. AFM images of the films fabricated by means of seven transfers according to the Langmuir technology on (a) the quartz substrate and (b) the aluminum surface.

(Fig. 1b). It consisted of larger particle clusters, i.e., islands with an average diameter of ~5–10 μm and a height of ~20–40 nm and individual particles with approximately the same height (10–30 nm), but with significantly smaller sizes (0.2–1 μm). The distances between islands and particles were 5–10 μm and 2–5 μm, respectively. As the number of layers transferred on the substrate by the Langmuir technology decreased to three or even one, the qualitative picture was unchanged. The cluster height on the aluminum surface decreased to 10–20 nm, their diameter decreased to 0.1–1 μm, and the distance between clusters was ~10 μm. As can be seen from these data, the film covers an increasingly larger substrate surface

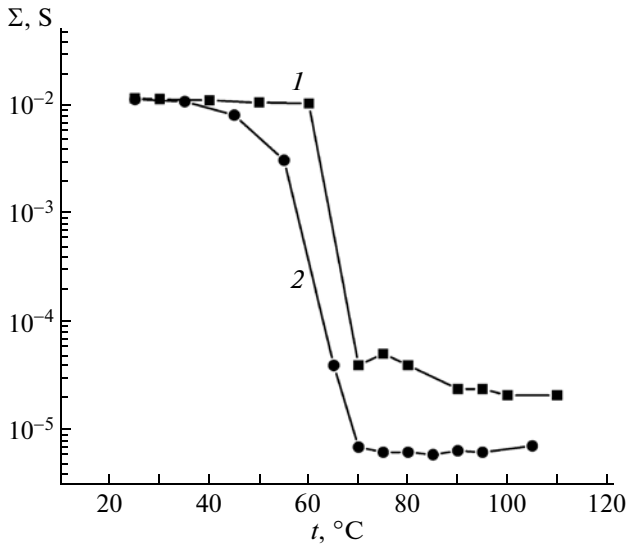

Fig. 2. Temperature dependences of the conductance of the films grown by means of five transfers according to the Langmuir technology, measured with direct (curve *1*) and alternating current at frequency $f = 1$ kHz (curve *2*).

with an increase in the number of deposited layers, and island sizes reach 10 μm.

In the adsorption measurement cycle [4] performed by the technique described in [5, 6], a phase transition on TDOBAMBCC films 5 and 10 monolayers thick was revealed. In both cases, an increase in the sample adsorption capacity, corresponding to the phase transition, was observed in a wide temperature range (70–110°C and 70–90°C). The presence of such broad maxima is in good agreement with the data on the film structural inhomogeneity which can cause a change in the critical in different sample regions toward increasing and decreasing the phase transition temperature.

The optical measurements on TDOBAMBCC samples 30 monolayers thick were performed in the earlier study [7]. During these measurements, rather sharp changes in the diffuse reflectance and the degree of reflected light polarization were revealed, which occurred in the range of 10 degrees near the phase transition temperature. Quartz was used as a substrate. In this case, the film inhomogeneity size did not exceed the tenth fraction of the wavelength (Fig. 1a); hence, this factor could not have an effect on the obtained experimental results.

The results of electrical measurements require the most serious discussion. For all the studied films, a sharp (by several orders of magnitude) decrease in the conductance measured with ac and dc signals was observed as the temperature was increased above a certain value T_0. The value T_0 varied from sample to sample in the range of 55–80°C.

Figure 2 shows the temperature dependences of the conductance of the samples grown by 5 transfers by the

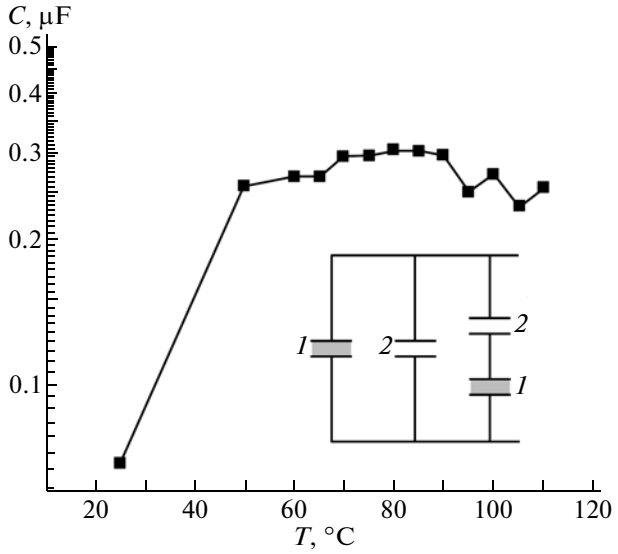

Fig. 3. Temperature dependence of the capacitance (measured at frequency $f = 100$ Hz) of the film grown by means of one transfer according to the Langmuir technology. The inset shows the equivalent circuit for analyzing the results of capacitance measurements for capacitors with (*1*) TDOBAMBCC and (*2*) aluminum oxide Al_2O_3.

Langmuir technology, measured with direct current (curve *1*) and alternating current at frequency $f =$ 1 kHz (curve *2*). The similar dependences were measured for other samples under study. Such changes in the conductance can be associated with the phase transition. It would be assumed that the sample with the structure shown in Fig. 1b should contain regions with closed aluminum electrodes. However, experiments disprove this assumption, i.e., the low conductance of the ultrathin film and its abrupt change during the phase transition are observed.

To explain the conductance measurement results, the features of aluminum surface oxidation should be remembered. Aluminum during the interaction with air transforms to a passive state. When pure metal contacts with air, a protective aluminum oxide film instantly appears on the aluminum surface. Then the film growth is retarded. It is known that the oxide on the aluminum surface consists of two layers [8, 9]. The first compact and amorphous layer is formed in air in a short time within several minutes; its thickness is of the order of one nanometer. On its surface, a less compact (porous) oxide layer begins to form; its thickness increases slowly within months and even years. In this case, a layer of relatively loose crystalline aluminum oxide ~10 nm thick appears in several days. It is most likely that TDOBAMBCC was deposited on a thin (several nanometers) aluminum oxide layer on the bottom electrode. Then, in the intervals between LC material drops, the oxide growth could continue as a result of the interaction of the unprotected electrode surface with a liquid medium of the Langmuir trough until deposition of the top aluminum electrode. As a result of this process, a complex structure including TDOBAMBCC particles surrounded by aluminum oxide with lower conductance is formed between aluminum electrodes.

In the dc measurements, a sharp increase in the sample conductance was observed in going from the films grown by one transfer according to the Langmuir technology to films grown by five transfers. Significantly weaker changes in the conductance were observed as the film material was further built-up. It is possible that the increase in the conductance should be associated with the increase in the coating area on the substrate surface with increasing number of layers.

To determine the nature of the phase transition in TDOBAMBCC films, we studied the temperature dependences of the capacitance of samples of different thicknesses. All curves exhibited the following features. First, the capacitance was increased in all cases in a wide temperature range identical to the temperature range of the phase transition recorded by adsorption, optical, and current–voltage measurements. Such a temperature dependence of the capacitance with hysteresis is characteristic of the ferroelectric transition in the film [10]. Thus, it can be argued that we deal with the ferroelectric-to-paraelectric phase transition. Second, a rather insignificant increase in the capacitance was observed during the phase transition in all cases: it was less than an order of magnitude for the film grown by one transfer, a factor of 2.5 for five transfers, and only 20% for ten transfers. As an example, Fig. 3 shows the temperature dependence of the capacitance for the film grown by one transfer.

In contrast to the curves for thicker films (e.g., ten transfers), a broad maximum was observed in the temperature dependence of the capacitance.

Let us consider in more detail the possible causes of the rather weak change in the capacitance of the studied structures during the phase transition. It follows from the above structural data that the sample contains areas in which liquid-crystal material is absent at all. Thus, the sample can be presented as a set of capacitances (inset in Fig. 3), some of which are filled (capacitors *1*) and not filled (capacitors *2*) with a material exhibiting the phase transition. It is quite probable that aluminum oxide is dielectric in capacitors *2*. The leakage resistance and the capacitances of the layers of compact tunnel-transparent aluminum oxide are not shown in the equivalent circuit.

The sharp change in the capacitance of the capacitor with TDOBAMBCC during the phase transition will be damped by parallel and series capacitors with aluminum oxide as dielectric, whose capacitance is unchanged.

4. CONCLUSIONS

Thus, it was shown that the structural phase transition in TDOBAMBCC films grown by the Langmuir technology is a ferroelectric-to-paraelectric transition. The ferroelectric phase in the films exists beginning with one monolayer. The existence of the wide temperature range of maxima of the adsorption capacity and electrical capacitance of the sample is explained by the structural heterogeneity of the film.

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