

## Graphoepitaxy of Langmuir monomolecular layers

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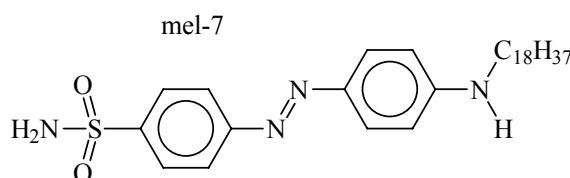
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The artificial epitaxy is an efficient technological method for obtaining oriented crystal films from organic and non-organic materials on crystallite and amorphous substrates [1]. For instance, in the recent thirty years graphoepitaxy was widely used in manufacturing of indicators and displays to obtain orientation of nematic thermotropic liquid crystals (LC). The homogeneous orientation of the long axes of LC molecules is determined by the direction of surface processing using abrasives, special brushes or oblique evaporation of silicon oxide. The orientation of liquid crystals represent a combined effect of at least three mechanisms of oriented crystallization: the action of capillary forces, the influence of topographic relief and the action of deformation forces in the LC itself.

In [2] Langmuir-Blodgett (LB) films from salts of stearic acid were reported to be deposited on the substrates having slit steps. It was found, that the crystallites in the LB films become larger and more homogeneous when exposed to laser radiation. This experimental fact was interpreted as graphoepitaxial effect. The authors of the above work believe that they showed the principal possibility of obtaining monocrystal LB films on large areas. In LB films from stearic acid the long axes of molecules have the orientation close to the normal of the substrate.

In the current work artificial epitaxy was implemented in monomolecular layers of azodye p-(p-octadecylaminophenylazo)benzenesulfamide (mel-7) deposited on hydrophilic silicon substrate with the natural oxide. The compound mel-7 was chromatographically pure; it was synthesized in the Research Institute for Organic Semiproducts and Dyes (Moscow, Russia). Solution of the compound was prepared in the mixture of the solvents: methanol – chloroform – benzene (volume ratio 1:1:6). The concentration was 1 mg/ml.



Distilled water was used as a subphase. The temperature of the water and the air was 18-20 °C with relative air humidity 60-80%.

The formation of the monolayers was made on the NT-MDT LB5 trough. The trough area is 45 x 11 cm<sup>2</sup>. The surface pressure was measured by Wilhelmy plate made of filtering paper. The

rectangular silicon (111) plates with the thickness of 0.35 mm were used as a substrate. Before the deposition of the monolayer the silicon plate was loaded into oxygen plasma. After that, substrate became hydrophilic.

The transfer of the monomolecular layer from the water surface to the substrate was performed at the surface pressure of 33 mN/m. The speed of the withdrawal of the substrate from the water subphase was equal to 20 mm/min. The transfer coefficient approached unity.

The investigation of the changing surface topography as a function of temperature was carried out by means of SPM SOLVER P47 (NT-MDT, Russia). The topography was obtained in tapping mode.

An interesting feature of mel-7 is that in the temperature range from 65 °C to 115 °C it is in smectic liquid crystal phase, while at a higher temperature the substance transfers into isotropic liquid phase. The LB films from the compound under consideration were studied earlier using small-angle X-ray diffraction. At heating to 70 °C, the bimolecular layer period of the structure was found to be 37.9 Å. After cooling the whole volume of the LB film had the layer period 37.3 Å.

It was observed [4], that plain needle-shape crystals were formed. Monolayer of mel-7 was deposited by LB method onto hydrophilic silicon substrate. When stored in room conditions, the crystals spread back on the substrate surface. The typical time of spreading was 12 hours. At further heating-cooling cycles the pattern was repeated. In [4] the following explanation of the observed reversible transformations of the monolayer of mel-7 was proposed. After deposition of the monomolecular layer of mel-7 on the substrate some amount of water (apparently, on the level of 1-3 monolayers) is left between polar groups of the monolayer and the substrate. The water layer stabilises the organised structure of the monomolecular layer of mel-7, due to the ability of the former to increase mean energy of interaction between polar groups and the substrate, at the account of hydrogen bonds formation. At heating to 75 °C the water is removed and some of the hydrogen bonds breaks. Consequently, the mean energy of interaction between the molecules and the substrate decreases, and their free energy grows. In such conditions thermodynamically it is more advantageous for the monolayer substance to transform into crystallite form. In layered crystals of mel-7 (for instance, in LB-films) the hydrogen bonds are formed at the contact of polar groups between adjacent monolayers. As a result, free energy of molecules decreases. Above the point of the phase transition of monolayer of mel-7 into smectic state the energy of intermolecular interaction in planar direction (cohesion energy) is decreased. Therefore, the activation barrier for the transition of molecules from monolayer structure to the free substrate surface also decreases. Molecule diffusion on the substrate surface does not reduce significantly, despite the absence of the water due to the rise of temperature. As a result,

the growth of the crystals on the substrate surface is observed during 50-100 minutes. After cooling in room conditions water from air atmosphere in small amounts is adsorbed at the surface of hydrophilic substrate. This seems enough for the substance from crystallites to start spreading into a monolayer on the substrate surface. A full analogue of this process is the behaviour of small crystals of surface-active substance on the water surface.

In order to initiate the oriented growth of the crystals the geometry of the relief of the substrate surface was formed by two methods: 1) using mechanical processing with an abrasive in the given direction and 2) using photolithography on silicon oxide. By the latter method parallel slit steps were obtained, the height of which was 20-25 nm with the width of 2  $\mu\text{m}$ . For monomolecular films such methods of graphoepitaxy were implemented for the first time.

Figure 1 shows the consequent stages of the crystal growth in the initial time as well as in 16 min and 38 min period, respectively, at 65°C for the substrate processed with the abrasive. As can be seen, the majority of the crystals are aligned along the scrabs. The presence of a small number of crystals having the orientation different from the general direction could be attributed to the possibility of the crystal nucleus with arbitrary orientation to appear on the areas of substrate free from scrabs.

The method used in this paper allows the formation of the films which have anisotropy of the dielectric permittivity in three orthogonal direction.

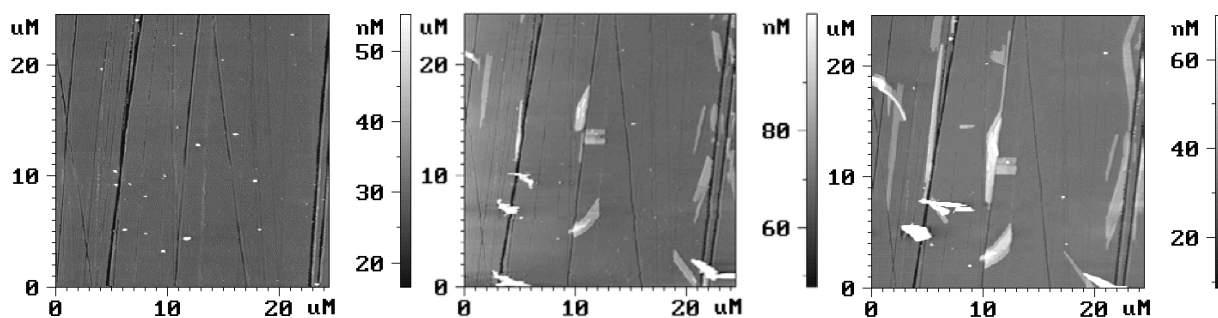


Fig. 1.

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