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Abstract

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ORIENTED CRYSTALLIZATION ON HIGH-POLYMER BOUNDARY LAYERS THAT COPY, BY AN ELECTRET MECHANISM, THE ELECTRIC RELIEF OF THE SURFACE OF SUBSTRATE CRYSTALS

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Until recently, the problems of oriented crystallization were considered, as a rule, either on the assumption of an ideal defect-free surface, or on the basis of its microgeometry. In studying the processes of nucleation and growth, the properties of the surfaces of real substrate crystals—especially their electrical characteristics—were usually not taken into account. In the authors' works ([1–4]) it was experimentally established that nucleation occurs selectively at active centers, which are point defects and their clusters possessing a definite electrical structure and symmetry and oriented along the corresponding crystallographic directions. In most cases the active centers are charged. The authors also established the long-range action of crystal surfaces, manifested in particular in the oriented crystallization of various substances on the outer side of diffraction-amorphous boundary layers obtained on the surface of these crystals. However, the mechanism by which structural information is transmitted through amorphous layers remained unclear until recently. In works ([5,6]) it was shown that orientational structural information is "frozen" in amorphous boundary layers so stably that it can be detected even after these layers have been separated from the crystal surface. Such a "memory" of the boundary layers was explained by the occurrence in them of a certain induced polarization structure, when the diffraction-amorphous material itself becomes, by an electret mechanism, a kind of information network.

For direct proof of the electret mechanism of the "memorization" of structural information, oriented crystallization was studied on the contact surface of boundary layers whose electrical properties can certainly ensure, or, conversely, cannot ensure, the occurrence of a thermoelectret state in them. Plastic films of polyvinyl chloride (PVC) and nitrocellulose (NC) were used as such layers, since thermoelectrets had previously been prepared from the former ([7]), whereas thermoelectrets could not be obtained from the latter ([8]). In addition, both types of plastic films are diffraction-amorphous, which excludes the possibility of side effects associated with epitaxial growth of these films on substrate crystals. Single crystals of NaCl and mica served as substrate crystals, and anthraquinone was used as the crystallizing substance. The choice of the NaCl (mica)—anthraquinone system was due to the fact that, upon sublimation, anthraquinone crystallizes orientedly on these substrates in the form of needle-shaped crystals of sufficiently large size, making it possible already at the optical level to establish the presence of orientation without resorting to diffraction methods. The study of the oriented crystallization of anthraquinone on the contact side of polymer layers, sepa-

···removed from the surface of the substrates, makes it possible to determine quite simply the presence or absence of structural "memory" in these layers.

Anthraquinone was crystallized both directly on the cleavage surfaces of NaCl and mica (muscovite) crystals and on the contact side of polymer films prepared under various conditions on the surface of the crystals and then separated from it. Sublimation of anthraquinone was carried out at 100° for 3-10 min from a glass flask heated in an electric furnace. All substrates were placed at a distance of 15 cm from the bottom of the flask, where the anthraquinone was located. Onto fresh cleavages of NaCl and mica (area $\sim$ 3 cm^2, thickness 5-6 and 0.1 mm, respectively), obtained in air, 3-4 drops of a 0.5% solution of PVC in butyl acetate or a 0.5% solution of NC in amyl acetate were applied. The films formed in 20-25 min in air at room temperature. Then some of the crystals together with the films were heated above the softening temperature of the films. Samples with PVC were heated to 110° for 1-1.5 min, and samples with NC to 90° for $\sim$ 1 min. After the samples had cooled in air, the plastic films, both preheated and unheated, were separated from the crystals in water. In the case of heating PVC and NC films on mica, the heating procedure was somewhat modified: an NaCl crystal was pressed tightly against a partially dried plastic film on mica, producing a kind of "sandwich," mica—plastic film —NaCl. This "sandwich" was heated, and after slow cooling in air the NaCl crystal was easily peeled off the "sandwich," while the plastic film was separated from the mica in water. The plastic films were then transferred from water onto glass slides or electron-microscope grids with the contact side upward. After the films had dried, anthraquinone was sublimed onto their contact side, and the crystallization patterns were examined in reflection in an MIM-7 metallographic microscope.

When anthraquinone was crystallized directly on the cleavage surfaces of NaCl and mica, it was established, in agreement with previous work ([9,10]), that in the first case needle-shaped anthraquinone crystals form biaxial textures (Fig. 1a), while in the second case they form uniaxial textures (Fig. 1b). In this case [110] NaCl $\parallel$ [001] anthraquinone, and [100], [110] mica $\parallel$ [001] anthraquinone. From Figs. 1a and b it follows that there is a very high degree of orientation of the anthraquinone crystals. The deposition density is $(0.2—1) \cdot 10^6/\text{cm}^2$.

When anthraquinone was crystallized on the contact side of polymer films that had not been preheated above the softening point, it turned out that these films do not "remember" the orienting influence of the substrate surface. Thus, Fig. 1c shows the crystallization pattern of anthraquinone on the contact side of an unheated PVC film, where all anthraquinone crystals are arranged randomly. In this case anthraquinone crystallizes as on an ordinary amorphous nonorienting substrate, for example, as on the surface of glass, on which control depositions of anthraquinone were carried out with similar results. Random crystallization of anthraquinone also occurs on the contact side of an unheated NC film.

Completely different results were obtained when anthraquinone was crystallized on the contact side of preheated PVC films separated from the surface of NaCl (Fig. 1d) and mica (Fig. 1e). The crystallization patterns repeat the corresponding patterns obtained directly on the surface of the crystals (see Figs. 1a and b). Biaxial and uniaxial textures arise, and the degree of orientation is quite high. The deposition density also remains $(0.2—1) \cdot 10^7/\text{cm}^2$. When anthraquinone is crystallized on the contact side of NC films heated above the softening point, oriented crystallization is not observed; all crystals are arranged randomly (Fig. 1f).

Fig. 1. Crystallization patterns of anthraquinone: *a*—on a NaCl cleavage face (200×); *b*—on a mica cleavage face (200×); *c*—on the contact side of an unheated PVC film separated from the NaCl surface (400×); *d*—on the contact side of a PVC film heated to ~110° and separated from the mica surface (100×); *e*—on the contact side of a PVC film heated to ~110° and separated from the mica surface (400×); *f*—on the contact side of an NC film heated to ~90° and separated from the NaCl surface (400×).

The observation of oriented crystallization of anthraquinone on the contact side only of PVC films which, according to the literature data (7), possess thermoelectret properties, on the one hand, and the necessity of heating these films above the softening point, which is required for the appearance of these properties, on the other hand, prove quite unambiguously, in our view, that the mechanism of "memorization" of orientational information is based on the electrical properties of amorphous boundary layers. In the present case the role of an external electric field is played by the local electric fields of charged point defects and their micro- and macro-aggregates, the field strengths of which at distances of atomic order can reach hundreds and thousands of kV/cm, which is certainly sufficient for the occurrence of induced polarization in boundary

layers. In this case, it is likely that in polymers there is a local orientation of the dipole groups of molecular chains, which serve as a kind of "wiring" for the transmission of information. The orientation of dipole groups in polymers is determined primarily by the mobility of segments of chain molecules and is a kinetic process. Therefore, the conditions for obtaining boundary layers (both from polymers and from other substances) on the surface of crystals largely predetermine the nature and degree of "memorization" of the electrical properties of the surface of the substrate crystals by these layers. The absence of "memory" in polymer boundary layers obtained without heating shows that it is precisely the electrical structure of the layers, and not their microgeometry copying the microgeometry of the substrates (which does not coincide with the symmetry of the textures), that determines the orientation effects during the "memorization" of structural information. It should be added that plastic replicas cannot reproduce, at an atomic level or one close to it, the microrelief of the surface of the substrates. The orientation of anthraquinone crystals on the contact side of PVC films, reflecting the corresponding crystallographic directions on the surface of the substrate crystals, shows that the azimuthal orientation of local active centers and their accumulations is also copied. The correspondence of the crystal density in both cases indicates that, evidently, it is precisely those electrically active surface sites that initiate oriented crystallization directly on the substrates which are copied.

The results obtained provide grounds for reconsidering a number of theoretical explanations [11,12] of the epitaxy of organic substances on inorganic substrates, which are based on specific chemical interactions between the substrate and the crystallizing substances, for example, on the formation of two-dimensional molecular compounds [13]. The results obtained once again confirm the limited nature of theories of epitaxy based on geometric correspondence, since the PVC films used as substrates are diffraction-amorphous. In all probability, it is precisely the electrical structure of crystalline and amorphous substrates (at the level of charged point defects and their accumulations) that determines the processes of oriented nucleation and growth. In conclusion, it should be emphasized that the emergence of an induced polarization structure in amorphous boundary layers opens up promising possibilities for their use as active surfaces for various heterogeneous processes, in particular for epitaxy. In addition, it may be possible to apply the electret mechanism to the explanation of processes occurring in biological systems, where there are a large number of solid and liquid boundary layers.

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