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ORIENTED CRYSTALLIZATION ON PHOTOELECTRET SELENIUM LAYERS REPLICATING THE ELECTRICAL STRUCTURE OF CRYSTAL SURFACES

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The long-range influence of the surface of solids is manifested in various heterogeneous processes, which therefore acquire a volume character (^{1}). One of the authors (^{2}, ^{3}) has studied in detail oriented crystallization on the outer side of amorphous boundary layers deposited on crystal surfaces. These layers consisted of various materials (carbon, plastics, silicon monoxide and dioxide, etc.) and had thicknesses of tens and hundreds of angstroms. However, until recently the mechanism of transfer and "memorization" of the corresponding structural information by amorphous boundary layers had not been established, since Coulomb forces cannot explain the transfer of information over such large distances (^{4}).

In our laboratory a number of experiments have been carried out which showed that long-range effects are caused by the appearance, in amorphous boundary layers, of a certain electrical state. The appearance of an electrical state requires, above all, the presence of sufficiently strong electric fields. On the surfaces of ionic and semiconductor crystals, electron-microscopic decoration methods have established the existence of a spectrum of charged point defects and their accumulations (^{5}, ^{6}). The strengths of the electric fields of charged point defects at distances of atomic order may reach hundreds and thousands of kilovolts per 1 cm, which is quite sufficient for inducing internal polarization in boundary layers. Indeed, amorphous carbon boundary layers "memorize" the electrophysical properties of the surfaces of crystals on which they were formed, in particular the properties of the surface of a silicon single crystal with an exposed p—n junction (^{7}, ^{8}). When plastic films (for example, polyvinyl chloride) possessing thermoelectret properties are used as boundary layers, a thermoelectret mechanism of "memorization" of structural information is realized (^{9}, ^{10}). In the present work we investigated the possibility of a photoelectret mechanism of "memorization" and transfer of structural information by boundary layers. A photoelectret state can arise in dielectrics and high-resistivity semiconductors possessing photoconductivity. The boundary layers were prepared from amorphous selenium, which possesses photoelectret properties ([11]). As in works ([9], [10]), NaCl crystals were used as substrates, and the electrical structure of the surface of the substrate crystals and of their selenium copies was "developed" by means of the crystallization reaction of anthraquinone.

Chemically pure selenium was evaporated in a vacuum chamber at $\sim 5 \cdot 10^{-6}$ mm Hg from a molybdenum boat at 300°. The distance between the crystal and the evaporator was 7-10 cm. To keep the specimens in darkness during evaporation of selenium, a special cassette-type device was mounted in the vacuum chamber. The amorphous character of the selenium layers was monitored on an EG electron-diffraction apparatus by diffraction studies. Part

selenium layers, both those on substrates and those separated from them (in the latter case the thickness of the layers was 400-500 Å), were illuminated with a 170 W incandescent lamp (sample-illuminator distance 30 cm) through a blue light filter with a transmission band of 400-500 mµ, which corresponds to the region of photosensitivity of selenium layers. Anthraquinone was sublimed at 130°. The substrate-evaporator distance was 18 cm, and the sublimation time was 5-8 min. The NaCl crystals and selenium layers were kept at room temperature during sublimation of anthraquinone. When the contact side of the selenium films was examined, they were separated from the substrate with the aid of polyvinyl chloride tape, on which they remained during subsequent experiments. The crystallization patterns of anthraquinone were observed in reflection in a MIM-7 metallographic microscope.

When anthraquinone is sublimed directly onto the surface of a fresh cleavage of NaCl, needle-shaped crystals, whose length reaches 10-40 µ, form a biaxial texture (Fig. 1a), with $\langle 110 \rangle$NaCl $\parallel$ $\langle 001 \rangle$ of anthraquinone. The deposition density is $5 \cdot 10^5$—$1 \cdot 10^7/\text{cm}^2$.

When anthraquinone is sublimed onto the surface of NaCl crystals coated with a layer of amorphous selenium of thickness $\sim$ 200 Å, a biaxial texture with a sufficiently high degree of orientation of the anthraquinone crystals still arises. The anthraquinone crystals acquire the form of rhombi, whose dimensions are 3-8 µ (Fig. 1b). The density of the anthraquinone particles also decreases to $3 \cdot 10^5$—$5 \cdot 10^6/\text{cm}^2$, while the nonuniformity of the deposition increases. With a further increase in the thickness of the selenium layers (230-250 Å), bent, often coalesced, rod-shaped anthraquinone crystals appear, forming a fairly distinct biaxial texture (Fig. 1c). Oriented crystallization of anthraquinone on the outer side of boundary selenium layers occurs regardless of whether sublimation took place in light or in complete darkness.

The influence of light is sharply manifested in the crystallization of anthraquinone on the contact side of selenium films separated from the surface of NaCl crystals. When selenium films are prepared in the dark and sublimation is likewise carried out in the absence of light, the anthraquinone crystals are arranged disorderly (Fig. 1g). In this case anthraquinone crystals with

Fig. 1. Crystallization patterns of anthraquinone.

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varying degrees of anisometricity are formed. The absence of orientation in the anthraquinone crystals indicates that the contact side of selenium films obtained in the dark does not "remember" any orientational information. This is evidently associated with the fact that amorphous selenium films possess very low dark conductivity, and the polarization structure induced in these films under the influence of charged defects on the NaCl surface is stable only during the action of the electric fields of these defects and is destroyed immediately after the films are detached from the crystals. Therefore, in selenium films obtained in the dark, there is substantial long-range transmission of structural information and no "memory" effect. In order for the films to acquire a "memory," it is necessary, while they have not yet been removed from the surface of the crystals, to irradiate them with scattered light. In this case, on the contact side of the separated selenium films, a biaxial texture of needle-shaped anthraquinone crystals arises (Fig. 1d). At the same time, skeletal growth is observed, in which rhomboid crystals form coalesced groupings oriented with respect to one another and arranged parallel to the ⟨100⟩ direction of the NaCl crystals (Fig. 1e). The observed "memory" can be explained by the fact that, as a result of preliminary illumination of the selenium layers, photoelectrons arise in them which, under the action of the electric fields of charged point defects, ensure the occurrence in the films of a stable photoelectret state that copies the electrical structure of the NaCl surface.

Fig. 1. Crystallization patterns of anthraquinone.

a –on the cleavage surface of a NaCl crystal; biaxial texture; 750×.
b and **c** –on the outer side of an amorphous selenium film deposited on the cleavage surface of NaCl; biaxial texture; **b** –selenium-film thickness ~ 200 Å, 750×; **c** –selenium-film thickness 230-250 Å, 750×.
d –on the contact side of a selenium film separated from a NaCl crystal; deposition of selenium and anthraquinone was carried out in the dark; the anthraquinone crystals are arranged randomly; 500×.
e, **f** –on the contact side of pre-illuminated selenium films separated from NaCl crystals: **e** –biaxial texture, 250×; **f** –oriented dendritic growth, 1000×.
g, **h**, **i** –on the contact side of pre-illuminated selenium films separated from NaCl crystals and then exposed to light: **g** –for 10 sec, 125×; **h** –for 45 sec, 125×; **i** –for 10 min, 125×.

The existence of a photoelectret state in selenium films is convincingly confirmed by the fact that the "memory" that has arisen can be destroyed by additional illumination. The "memory" was destroyed by irradiating the specimens with scattered light from a 60 W incandescent lamp. The lamp-specimen distance was 300 cm. Irradiation of selenium boundary layers separated from NaCl crystals leads to a regular change in the crystallization patterns of anthraquinone on the contact side of these layers. After irradiation for 15 sec. (Fig. 1), needle-like and rhomboid anthraquinone crystals are formed. The needle-like crystals form a biaxial texture with a fairly high degree of orientation, while in local regions of the film orientation of rhomboid crystals occurs. Thus, irradiation for 15 sec. still does not lead to a substantial change in the "memory" of the films. Irradiation for 45 sec. causes an increase in length and a noticeable curvature of the needle-like crystals, and promotes their marked disorientation (Fig. 1). It should be noted that the "memory" is destroyed not uniformly over the surface of the films, but in local regions. This indicates the different character of the photoelectret state in local regions of the films, reflecting the complex electrical relief of the surface (and, correspondingly, the volume) of NaCl crystals, which is a set of charged regions consisting of accumulations of charged point defects ([6], [12]). Irradiation of selenium films with light for 10 min. leads to a disordered arrangement of both needle-like and rhomboid anthraquinone crystals (Fig. 1), i.e., the "memory" practically disappears. We note that in this photograph the discrete structure of the needle-like crystals is clearly revealed.

The experiments carried out, in our opinion, quite unambiguously prove the existence of a photoelectret mechanism for the preservation and transfer of structural information by amorphous boundary layers. From the photoelectret mechanism, in turn, there follows the very important conclusion that active centers and their accumulations on the surface of substrate crystals, which determine oriented crystallization and, evidently, other heterogeneous processes as well, are charged centers. Thus, the active surface of crystals is, as a rule, a charged surface. The prospect is opened of obtaining a large number of amorphous boundary layers that copy, by an electret (in the present case, photoelectret) mechanism, the electrical properties of the surface of one and the same crystal. On these copies, with preservation of the matrix, it is possible to carry out various heterogeneous reactions, in particular processes of oriented crystallization.

The results obtained apparently have general significance. They explain, from new points of view, a number of long-range effects discovered in biological systems, and also indicate yet another possible mechanism of energy migration in boundary layers.

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