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LONG-RANGE ACTION OF ACTIVE CENTERS OF CRYSTALLINE SURFACES

(Presented by Academician N. V. Belov on 11 IV 1966)

The existence and forms of manifestation of long-range forces have been the subject of numerous investigations. Of particular interest is the study of long-range surface forces of solids at the elementary, or near-elementary, level and the comparison of these forces with the real structure of the surface.

New electron-microscopic methods of chemical and electrical decoration (^1-3), consisting in selective chemical crystallization at active sites on the surface of solids or in the selective interaction of these sites with charged colloidal particles, make it possible to study the character and distribution of surface forces, including their long-range action.

Decoration reactions in the study of long-range effects were carried out through intermediate amorphous plastic layers (parlodion) deposited on the surface of crystals. Decoration through intermediate layers of various thicknesses (from 100 Å to several microns) makes it possible to determine the spheres of action of surface forces. Crystallization of lead sulfide was used as the chemical-decoration reaction, while electrical decoration was effected by selective adsorption of colloidal particles of lead selenide. The long-range action of active surfaces of cleavage faces of mica single crystals (muscovite), polished specimens of silicon, quartz, sodalite, and a number of other crystals was studied. After completion of the reaction the decorating particles were reinforced with a carbon film, stripped from the surface of the crystals with the aid of gelatin, and in some cases were shadowed; after the gelatin had been dissolved in water and the parlodion partially dissolved in amyl acetate, they were examined in a Hitachi-II electron microscope. In addition, the replica method was used, and the presence of orientation of the decorating particles was checked by diffraction studies.

From the decoration patterns it was established that on the surface of crystals there exist qualitatively different types of long-range local active centers, possessing different activation energies for nucleation and adsorption. Centers of the first type possess an orienting action; under their influence epitaxial growth takes place. The second type of center also initiates crystallization, but does not possess an orienting action.

On the surface of mica single crystals the existence of active centers of both types was established. The orienting influence of "epitaxial" centers for the chemical crystallization of lead sulfide extends over distances of the order of 1500 Å, which agrees well with the data of work (⌒4) (1300 Å). The morphological pattern of epitaxial growth of lead sulfide through an intermediate layer (Fig. 1) repeats the corresponding pattern of PbS crystallization directly on the mica surface (⌒5). Flat PbS crystals are oriented with the (111) face parallel to the basal face (0001) of the mica and directed-

of the $\langle 110\rangle$ direction parallel to $\langle 11\bar{2}0\rangle$ in mica, which indicates a definite crystallographic orientation of these epitaxial centers. The observed oriented overgrowth through fairly thick amorphous plastic layers deposited on crystalline surfaces leads to the important conclusion that the geometric factor is not decisive in epitaxy. (This is also confirmed by the results of work (6), in which oriented overgrowth of polyethylene was observed through intermediate amorphous plastic layers about 1000–1500 Å thick, deposited on the cleavage surface of a rock-salt crystal.) When the thickness of the intermediate layer is increased to several thousand angstroms, the morphological picture of PbS crystallization on mica is essentially preserved; however, epitaxy disappears. Apparently, epitaxial centers, even at very large distances from the surface, can remain initiators of crystallization, but without an orienting action.

Active centers of the second type do not possess an orienting action and are characterized by much larger spheres of influence. On the surface of mica these centers are revealed when the supersaturation is increased during decoration reactions (the isometric particles in Fig. 1, arranged randomly with respect to the surface), which indicates their lower activity in comparison with epitaxial centers under the conditions of the decoration reaction being carried out. Analogous centers, arranged in microlayers, were detected in the decoration of a silicon surface cut parallel to the growth axis $\langle 111\rangle$ (Fig. 3). These centers have a long-range action over distances on the order of a micron and cause microlayered crystallization of PbS without any preferred orientation of the crystals in the layers themselves. Epitaxial centers of the first type are revealed on the silicon surface only after its chemical etching.

In most cases, active centers are electrically active, which is directly proved by their interaction with charged colloidal particles of lead selenide (as well as with other colloidal particles, for example, particles of gold or polystyrene latex) during electrical decoration. Figure 2 presents a pattern of selective adsorption of lead selenide particles by a silicon surface through an intermediate plastic layer 700–900 Å thick, characterizing the distribution of long-range active centers of the second type. Adsorption of PbSe particles through intermediate amorphous plastic layers by different faces of quartz and sodalite crystals likewise reveals the microtopography of the distribution of electrically active surface centers, which apparently are charged impurities. As a rule, as the distance from the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

crystal surface increases, the decoration patterns change because the action of less active centers ceases; this makes it possible to reveal the spectrum of surface active centers differing in the radius of their spheres of long-range action.

The very large magnitudes of the spheres of long-range action of surface active centers and the effect of their orienting influence indicate that these centers are not point defects, but aggregates of defects. Such accumulations of defects—mainly vacancies, impurity atoms, and their complexes, investigated in a number of works ($^{7-9}$)—are very stable. Epitaxial centers are built rather regularly and have a symmetry corresponding to the symmetry of the face of the crystal on which they have arisen. The long-range influence of active centers is determined by a complex superposition of electrostatic and molecular forces and, evidently, can be considered on the basis of theories of the interaction of colloidal particles and solids ($^{10-14}$). The character and magnitude of the long-range action are determined by the electrical structure and size-

Fig. 1. Pattern of oriented crystallization of lead sulfide on a mica cleavage through an intermediate palladium film of thickness ~ 1500 Å

Fig. 2. Pattern of selective adsorption of charged particles of lead selenide by the surface of a silicon single crystal through an intermediate palladium film of thickness ~ 700–900 Å

Fig. 3. Decoration patterns of the surfaces of two different silicon single crystals with lead sulfide particles through intermediate palladium films of thickness 500 Å (**a**) and 1 μ (**b**)

···of active centers. It is very important that the area occupied by active centers is substantially smaller than the spheres of action of these centers. Therefore, highly inhomogeneous surfaces may manifest themselves as quasi-homogeneous with respect to certain surface processes. However, investigations at the electron-microscopic level always reveal local active centers that exist quite independently of one another and possess different ranges of long-range action.

Long-range processes are caused by a certain near-surface layer containing both surface and bulk active centers. The magnitude of this active near-surface layer,

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

depending on the macroscopic parameters of the solid body (dielectric constant) and on the nature of the defects, may extend into the depth of solids by tens, hundreds, and perhaps thousands of angstroms. Fig. 4 presents a diagram of the long-range action of the surface forces of a real solid surface, reflecting the existence both of diverse local active centers, including epitaxial ones, with different radii of action, and of a near-surface active layer. From the proposed model it follows that the complex effective active surface of a solid is, as it were, raised by some distance above its geometric surface. This makes possible the occurrence of heterogeneous processes not only directly on the surface, but also at certain distances from it.

Fig. 4. Diagram of the long-range action of the surface forces of a real crystal: **A**—active centers possessing an orienting influence; **B**—active centers without orienting influence

The discovery of such effective surface reactive long-range forces, caused by local active centers and in many cases possessing an orienting influence, provides grounds for reconsidering from new points of view many surface phenomena, for example adsorption, nucleation and crystal growth, catalysis, which apparently in most cases are not purely heterogeneous but heterogeneously homogeneous processes.

N. M. Borisova took part in this work; she carried out the electrical decoration of the crystals.

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