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Abstract

Full Text

CRYSTALLOGRAPHY

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EARLY STAGES OF CRYSTALLIZATION AS A METHOD FOR ESTABLISHING THE HETEROGENEITY OF CRYSTALLINE SURFACES

(Presented by Academician N. V. Belov on 6 XII 1963)

The heterogeneity of single-crystal surfaces, the presence of active sites, determines to a considerable extent the mechanism of many processes occurring on these surfaces. Such processes include adsorption, nucleation and crystal growth, heterogeneous catalysis, and also various electrophysical surface processes. It is very important to develop direct methods of investigation that would make it possible to identify the corresponding active sites with specific defects, such as steps and kinks, impurity centers, dislocation outcrop sites, vacancies, etc. An effective structural method for investigating surface heterogeneity is electron microscopy. However, in order for active surface sites to be observed directly in an electron microscope, they must be "developed," decorated with particles of sufficiently large size. Electron-microscopic studies of the very earliest stages of crystallization during vacuum evaporation of gold onto the surface of alkali-halide crystals^(1-3) have shown that discrete gold crystallites decorate elementary cleavage and glide steps (with steps of monoatomic height being revealed), dislocation outcrop sites, and point defects.

Of particular interest is the decoration method we have developed by means of crystallization occurring as the result of a chemical reaction^(4). Crystallization of this kind, depending on the type of chemical reaction and the conditions under which it is carried out, should reveal defects of various kinds, in particular impurity centers that were not detected by gold decoration. The main requirement for the crystallization reaction used for decoration is its very low rate, ensuring observation of the early stages of crystallization, at which decoration takes place.

Over a long period we studied the process of crystallization of lead sulfide on various single-crystal surfaces—mica, carborundum, silicon, germanium. Lead sulfide crystallized from an aqueous solution as a result of the decomposition of a complex compound of lead acetate with thiourea. It turned out that at the early stages of crystallization diverse decoration patterns are observed, and the forming lead sulfide crystallites are located predominantly not along individual straight and curved lines, as in the evaporation of gold, but arise on comparatively large areas of regular and irregular shape. It seemed very interesting

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Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

and important to establish the nature of those active sites of the single-crystal substrates, the specific defects, that are decorated by lead sulfide crystallites, i.e., are crystallization centers.

On the basis of an analysis of numerous decoration patterns, we suggested that the active sites of the surface during crystallization are impurity centers. To test this assumption, it was advisable to carry out deposition of lead sulfide on the surfaces of single crystals with a sufficiently well known character of impurity distribution.

To the article by G. I. Distler, S. L. Darosina, and Yu. M. Gerasimov

Fig. 1. Pattern of the layered distribution of decorating crystals of lead sulfide on the surface of a silicon plate cut parallel to the growth axis. The arrow indicates the direction of the growth axis of the silicon crystals

Fig. 2. Pattern of decoration by lead sulfide crystals of the surface of a silicon plate cut perpendicular to the growth axis

A number of authors ([5–7]), using various methods, have established a layered distribution of impurities in semiconductor crystals grown from the melt by the Czochralski method. The layered distribution of impurities depends on the growth rate and on the orientation of the crystals. It is quite obvious that, if the impurities are active centers during the crystallization of lead sulfide, then the decoration patterns of the surface of a plate cut from such a crystal parallel to the growth axis should, in their general appearance, correspond to the layered pattern of impurity distribution and, moreover,

Fig. 3. Lead sulfide crystals detached from the surface of a silicon plate cut parallel to the growth axis

should differ from the decoration pattern of a plate cut from the same crystal perpendicular to the growth axis.

A silicon crystal grown by the Czochralski method and doped with boron and

Fig. 3. Lead sulfide crystals detached from the surface of a silicon plate cut parallel to the growth axis

Figure 3: Fig. 3. Lead sulfide crystals detached from the surface of a silicon plate cut parallel to the growth axis

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Fig. 4

Figure 4: Fig. 4

antimony* was cut parallel and perpendicular to the growth axis. Thoroughly washed crystals were treated in a reaction mixture consisting of a 4% solution of lead acetate, 2% thiourea, and 2.8% potassium hydroxide, taken in a ratio of 1 : 3 : 3. Deposition of lead sulfide was carried out at 3°, and the deposition time ranged from 15 to 160 min. After deposition, the silicon crystals were examined by the replica method; from some samples the lead sulfide crystallites were stripped off with gelatin, and electron micrographs were obtained from such preparations. The samples were viewed with a Hitachi-11 electron microscope.

The decoration patterns of plates cut parallel to the growth axis (Fig. 1) consist of parallel bands of different widths, made up of rather small lead sulfide crystallites. The width of the bands varies from fractions of a micron to several microns. In the intervals between the bands, lead sulfide crystallites are almost completely absent, which indicates the high selectivity of the surface crystallization reaction. The direction of these bands relative to the growth axis (111) was established by comparing the direction of shading with the orientation of the replica. It was confirmed that the decoration bands are arranged perpendicular to the growth axis, i.e., the distribution of decorating crystals over the silicon surface corresponds to the layered distribution of impurities. On plates cut perpendicular to the growth axis, entirely different decoration patterns arise. In this case (Fig. 2), crystallization does not proceed in parallel bands. On

* The crystal was kindly provided by I. N. Voronov, to whom we express our gratitude.

on the surface, regions are formed that are characterized by different densities and different sizes of lead sulfide crystallites; there are also areas of irregular shape on which crystallization has not occurred. In general, it is difficult to establish any regularity, although it is quite obvious that the surface of such a silicon plate is very inhomogeneous.

The experiments carried out on a number of silicon crystals have shown quite convincingly that there is good agreement between the layered distribution of impurities and the observed patterns of crystallization of lead sulfide. In other words, the crystallization of lead sulfide in the early stages occurs predominantly at impurity centers. The electron-microscopic photographs obtained apparently demonstrate for the first time, with high resolution, the character of the distribution of these centers.

Fig. 4. Electron diffraction pattern from lead sulfide crystals stripped from the surface of a silicon plate cut parallel to the growth axis

It was of great interest to establish whether epitaxial growth of lead sulfide crystallites takes place on the surface of silicon single crystals. Figure 3 presents

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an electron-microscopic photograph of lead sulfide crystals stripped from the silicon surface (the photograph shows that the arrangement of the crystallites repeats the decoration pattern), and Fig. 4 gives the electron diffraction pattern from these crystallites. The electron diffraction pattern corresponds to polycrystalline lead sulfide. Thus, it was shown that lead sulfide crystallizes at impurity centers without any preferred orientation. This very interesting fact attracts attention, since in the decoration of cleavage steps of rock salt by gold, epitaxial growth takes place ([2]). Apparently, nucleation at impurity centers proceeds by a different mechanism, possibly as the result of an exchange chemical reaction.

Crystallization on heterogeneous surfaces begins at various defects possessing an increased chemical potential. Depending on the type of reaction and the crystallization conditions—first of all on the degree of supersaturation—certain particular types of defects will be decorated preferentially. When the crystallization conditions are changed, decoration of other defects should be expected, and in this way one may hope to obtain patterns of the distribution on single-crystal surfaces of active sites differing in their nature.

This work is one of the first electron-microscopic studies aimed at establishing the specific nature of active centers on a crystalline surface.

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