CRYSTALLOGRAPHY

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Fig. 1

Figure 1: Fig. 1

Abstract

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DECORATION OF A GROWING CRYSTAL SURFACE

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The study of the microrelief of a crystalline surface is of considerable interest for understanding the mechanism of crystal growth. One of the methods of such study is the decoration of the surface with particles of some substance.

The “dew method” is known (^{1}), by means of which it is possible to reveal the complex relief of a crystalline surface (in particular, the presence on it of growth spirals). Decoration of the cleavage of alkali-halide crystals by depositing small amounts of gold made it possible to observe elementary growth steps, dislocations, and other defects of atomic dimensions (^{2}). A recent work by G. I. Distler and S. A. Darosina (^{3}) has given a new example of the great possibilities of the decoration method.

Fig. 1. Microphotographs of the surface (111) of grown germanium layers: *a* —without decoration; *b* —with subsequent decoration. 875×

All these methods, however, have the limitation that the decorated surface is not “fresh” ; having been subjected to the action of the surrounding medium, it becomes covered with a layer of adsorbed atoms and molecules, which are fixed first of all on the most active (and, consequently, most important for crystallization) areas of the surface, thereby making it difficult to reveal its true structure.*

In the course of studying the mechanism of formation of germanium layers from the gas phase with the participation of the chemical decomposition reaction of $GeCl_4$ in a stream of hydrogen (^{4}), we discovered the possibility of decorating the “fresh” (just grown) surface of a crystal. The essence of the phenomenon is as follows.

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* Although in work (^{2}) cleavage was carried out in vacuum, it was apparently not possible to avoid the action of the surrounding medium, since at the pressures used ($\sim 10^{-5} \div 10^{-6}$ mm Hg) the number of residual-gas particles striking the surface is still quite large ($\sim 10^{15}$ cm^{-2} sec^{-1}).

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

With a sharp decrease in the concentration of the decomposed compound in the initial gas mixture, the growing surface is selectively covered with germanium particles, distinguishable in an optical microscope in the form of strokes and dots. Thus, decoration of the germanium surface with germanium itself occurs as a direct continuation of the crystal-growth process*. This type of decoration could be called "self-decoration."

Fig. 2. Microphotograph of a strongly decorated (111) surface of germanium grown under conditions of strong gas etching. 875×

Fig. 3. Microphotograph of a decorated (111) surface of germanium. 260×

In Fig. 1a is shown the (111) surface of a germanium crystal not yet subjected to decoration. In Fig. 1b a microphotograph of the same surface, but already decorated, is presented. It is evident that the slopes of the growth figures, in contrast to the rest of the surface, are covered with dense fine striation. This indicates that they are, in Stranski' s terminology (^{5}), roughened (or imperfect) faces.

Figure 2 shows a relatively strongly decorated (111) surface of a crystal grown under conditions in which gas etching of the growing surface appears (this occurs at high concentrations of $GeCl_4$ in the initial mixture (^{6})). In the figure one can distinguish three types of faces: densely covered with germanium particles (the lateral faces of the growth figures), relatively weakly covered (regions approximately parallel to the original substrate surface—in Fig. 1b they still look clean), and absolutely clean plateaus. The latter, in our opinion, are precise atomically flat planes (111), characterized by layer-by-layer (reproducible) growth. Electron-microscopic studies at a magnification of 13,000× revealed no disturbances on the plateaus. Thus, by varying the intensity of decoration, it is possible to determine the degree of relative roughening of the faces.

* A special study showed that the decorating particles possess a single-crystal structure of the same orientation as the substrate.

It was of interest to investigate the relative susceptibility to decoration of growth figures differing in size. It turned out that the faces of the larger figures are covered with striations more intensely than the smaller ones (Fig. 3). With the aid of a thermoprobe it was established that the relatively strongly decorated regions of the germanium film have p-type conductivity, whereas the remaining regions of the layer exhibit n-type conductivity. From this a number of conclusions follow.

1. Since autodecoration is a kind of crystal growth (admittedly very slow and therefore selective), one may draw a conclusion about the dependence of the growth rate of germanium layers on the character of doping: regions with a p-type impurity grow faster than those with an n-type impurity. This agrees with analogous data for the growth rate of silicon layers during crystallization from the gas phase by a chemical method (7).

2. The distribution of impurities in epitaxial layers of germanium is nonuniform: in the regions corresponding to growth figures, segregation of impurities of different types occurs. As a result, "channels" are formed that differ in conductivity from the surrounding regions of the crystal (8)*. Since it is known (10) that growth figures of epitaxial germanium layers correspond to accumulations of dislocations, it may be assumed that the indicated "channels" are caused by bundles of dislocations extending into the layer from the surface of the substrate. The high contrast of the decoration, in our opinion, indicates that these bundles differ sharply in the efficiency of impurity segregation.

3. Autodecoration makes it possible to reveal p—n junctions and, possibly, p—p^+ and n—n^+ junctions, i.e., it can serve as a special method for visualizing the electrical properties of epitaxial layers.

The results presented above on decoration are explained by the peculiarities of crystallization from the gas phase with the participation of a chemical reaction. In this case the concentration of $GeCl_4$ in the initial gas mixture is usually such that, if all the germanium were deposited instantaneously in atomic form, the supersaturation with respect to the equilibrium (for example, at 700°) germanium vapor would be $\sim 10^7$. The possibility of obtaining perfect crystals under such conditions is ensured, as was analyzed in detail earlier (6), by the dissolving action of the reaction products, which again detach weakly attached additions arising in violation of the growth sequence. The relative role of dissolution is the greater, the higher the concentration of $GeCl_4$ in the initial mixture. Conversely, as the concentration of $GeCl_4$ decreases, the role of dissolution is reduced to nothing, as a result of which the process of chemical deposition at low concentrations approaches growth from a "pure" vapor of the substance (the latter occurs, for example, in the evaporation of gold (2)). As a result, selective deposition of the crystallizing material takes place predominantly on active regions of the surface (steps, dislocations, etc.). Since the edges of steps are considerably more active than the rest of the surface, the germanium particles arrange themselves on them, revealing the fine relief of the faces.

A feature of this decoration method is the continuous transition from build-up to decoration. Thanks to this, it is possible to reveal the precise state of the growing surface at a given moment, which is important for studying the mechanism of crystal formation**. Such a transition is made possible by the ability to deposit single-crystal layers from reaction mixtures whose composition varies over a very wide range of concentrations of the crystallizing material (by several orders of magnitude).

[*] Apparently, precisely these channels are responsible for the relatively low electrical properties of epitaxial p—n junctions (9).

[**] Let us also note the applicability of the method to the study of such a specific stage of growth as the nucleation of layers on the initial substrate.

The method described can be used in all those cases where, by regulating the crystallization conditions, it is possible to change sufficiently sharply the ratio of the fluxes of the crystallized material to the growing surface and away from it (6). This is precisely the situation in crystallization involving a chemical reaction.

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Note: Figure translations are in progress. See original paper for figures.