Physical Chemistry

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1963

SovietRxiv

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Abstract

Full Text

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On Crystallization from the Gas Phase by the Chemical Method

(Presented by Academician N. V. Belov, 29 VIII 1962)

Thin semiconductor layers (for example, germanium layers) on substrates identical in composition are usually grown by crystallization from the gas phase (the chemical-reaction method [1,2]) or in vacuum (the molecular-beam method [3,4]). It turned out that the properties of layers grown by different methods differ substantially: whereas the former are identical to bulk single crystals in the most important electrical parameters, in the latter the mobility of charge carriers is lower by an order of magnitude, and the resistivity is lower by several orders of magnitude, than in single crystals. It was natural to relate these differences to features of the mechanism of crystal formation under different conditions. In the present work the process of crystallization by the chemical method was investigated.

Experiments were carried out in a quartz reactor, inside which single-crystal germanium substrates were placed on a graphite support heated by high-frequency induction currents. With such a design, the mixture entering the reactor ($H_2 + GeCl_4$) has room temperature and is heated only on approaching the substrates, which are maintained at 700–800°C.

The most important of the data obtained are reduced to the following.

Fig. 1. Dependence of the crystal growth rate on the concentration of $GeCl_4$ in the initial mixture. Flow rate in the reactor: 0.6 cm/sec.

Figure 1 presents the results of a study of the crystal growth rate as a function of the concentration of $GeCl_4$ in the initial mixture at an unchanged gas-flow rate. Morphological study of growth figures on the surface of the layer (III) showed that, on passing through the maximum of the curve, regular triangular pyramidal formations with an apex become truncated. Comparison of Fig. 1

Fig. 2

Figure 2: Fig. 2

with this change in the morphology of the grown layers suggests that, at sufficiently high concentrations of $GeCl_4$, gaseous etching of the growing crystal manifests itself. This is consistent with the data [5] on the interaction of $GeCl_4$ and Ge with formation of a volatile subchloride:

$$GeCl_4 + Ge \rightleftarrows 2GeCl_2. \tag{1}$$

Figure 2 presents the results of a study of the crystal growth rate as a function of the flow rate at an unchanged concentration of $GeCl_4$ in the initial mixture. The initial portion of the decline of the curve in Fig. 2 corresponds to transformations of the growth figures quite analogous to those indicated above. These results can be explained by intermediate processes of partial reduction of $GeCl_4$ in accordance with the reaction:

$$GeCl_4 + H_2 \rightleftarrows GeCl_2 + 2HCl, \tag{2}$$

Fig. 3. Microphotographs of (III) germanium layers grown at different initial concentrations of $GeCl_4$.
a —concentration corresponds to a vapor pressure of $GeCl_4 \sim 10^{-7}$ mm Hg;
—concentration corresponds to a vapor pressure of $GeCl_4 \sim 1$ mm Hg. 1000×

the degree to which equilibrium is attained, which depends on the thickness of the heated layer, i.e., on the flow rate.

A joint analysis of equations (1) and (2), and also of the equilibrium constant of reaction (1),

$$K_p = \frac{[GeCl_2]^2}{[GeCl_4]} \tag{3}$$

makes it possible to explain the features of the curves in Figs. 1 and 2 (in particular, the presence of a maximum in the first) and to draw conclusions about the nature of the process. The participation of the crystallizing substance (Ge) in the reversible reaction (1) means that the latter simultaneously determines both the growth and the etching of the crystal, while the "growth rate" determined in practice is the algebraic result of these two processes. In this connection, the higher the concentration of $GeCl_4$ in the initial mixture, the more noticeable is the role of etching, and conversely.

Fig. 2. Dependence of the growth rate of crystals on the gas-flow rate. Vapor pressure of the chloride: 0.6 mm Hg.

Comparison of the results of deposition at different initial concentrations of $GeCl_4$ indicates a very favorable role, for perfect crystal formation, of etching accompanying growth. Figure 3 shows microphotographs of layers of equal thickness (about $2\,\mu$), deposited at sharply differing concentrations of $GeCl_4$. It is seen that at very low concentrations (Fig. 3a) the formation of geometrically regular growth figures proceeds much more slowly than at higher concentrations (Fig. 3b), although in both cases the deposition was single-crystalline. Assuming that morphological perfection is evidence of perfection of the internal structure, one may conclude from this that the relatively high etching rate corresponding to high concentrations of $GeCl_4$ promotes the formation of more perfect crystals.

The experimental results obtained make it possible to express some general observations on the nature of the process under investigation.

Crystallization by means of a chemical reaction differs from other methods not simply in the form of material delivery, as is commonly assumed in the literature on crystal growth ([6]). It is a fundamentally special type of crystallization, in which both the initial chemical compound and the intermediate reaction products participate directly in the very process of crystal growth. This feature distinguishes this method of crystallization from the others and gives it substantial advantages with respect to the possibilities of controlling crystal growth.

To ensure perfect crystal formation, evaporation and dissolution of the crystal, as processes reverse to the growth process, are of great importance. It is precisely through them that irregularities in the sequence of attached particles are removed and growth errors thereby corrected. The methods of crystallization of thin layers compared at the beginning of the present article differ above all in the nature of the reverse process.

In the case of crystallization from the vapor of a substance (in vacuum or in an inert gas atmosphere), the reverse process is thermal evaporation; in this case the fluxes of substance to the crystal and away from it are mutually independent, as a result of which the limits of supersaturations allowable for perfect crystal formation are determined by the well-known conclusions of the molecular-kinetic theory of crystal growth and usually do not exceed several tens of percent. At the same time, germanium layers obtained by evaporation in vacuum are usually formed from molecular beams whose density corresponds to a manyfold supersaturation of the vapor of the substance, i.e., the process

crystal growth proceeds under extremely nonequilibrium conditions. As a result, the layers have a very defective structure and low electrical parameters ([3], [4], [7]).

In a chemical process in the gas phase, each act of attachment of a particle to the crystal is accompanied by the appearance, in the immediate vicinity of the growing surface, of a decomposition product capable subsequently of interacting with the crystal. Moreover, the greater the equivalent concentration of the substance and, consequently, the more intense the process of attachment of particles, the more decomposition products are formed and, correspondingly, the more intense is the dissolution of defective attachments. In other words, owing to the participation of the chemical reaction, crystal growth acquires the features of a self-regulating process: when the parameters of the latter change, conditions close to equilibrium are automatically maintained. This circumstance greatly broadens the range of permissible equivalent supersaturations and makes crystallization only to a very small degree sensitive to changes in the process parameters.* It is precisely the participation of the chemical reaction in the process of crystal growth that explains the formation, by the method considered here, of germanium layers of very high structural quality and properties at material feed intensities equivalent to giant supersaturations of $\sim 10^7$.

In conclusion, the author expresses sincere gratitude to N. N. Sheftal' for guidance of the work and discussion of the results obtained, and to A. M. Kevorkov, M. V. Gavrilova, and G. I. Spiridonova for assistance in the experimental work.

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Received
27 VIII 1962

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* The practice of our work (several hundred experiments) has shown that, over a wide range of variation of the experimental conditions (substrate temperatures from 700 to 800°, gas-flow velocities from 0.2 to 3 cm/sec, concentrations of $GeCl_4$ in the initial mixture corresponding to vapor pressures from $\sim 10^{-7}$ to 2 mm Hg, i.e., by several orders of magnitude), single-crystal growth occurred.

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