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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Preparation of Solid Solutions of the Ge–Si System from the Gas Phase

(Presented by Academician N. V. Belov, 30 XI 1961)

Germanium and silicon form a continuous series of substitutional solid solutions, whose lattice parameters decrease linearly with composition in the direction from germanium to silicon ([1,2]).

Until now, solid solutions of the Ge–Si system have been prepared by the melting method. By this method, single-crystal alloys of germanium with silicon have so far been obtained with a content up to 24% Ge, and alloys of silicon with germanium—up to 6% Si ([3]).

We have developed a new method for preparing solid solutions of germanium and silicon, based on crystallization from the gas phase with the aid of selenium, which plays the role of a solvent component. The proposed method makes it possible to grow single crystals of solid solutions over the entire possible concentration range, both on a germanium base and on a silicon base.

Fig. 1

The technology described below for obtaining solid solutions of germanium and silicon of a specified composition was established by us on the basis of taking into account certain ideas about the mechanism of crystallization. During condensation from vapor, atoms act upon one another while still in the vapor phase ([4]). In the case of isomorphous atoms, interaction of this kind leads to the appearance in the gas phase, as also in the liquid phase ([5]), of structural associations of the short-range-order type, consisting of different atoms and capable of causing the nucleation of a mixed crystal in supersaturated vapor and of participating in its growth. The composition of the structural associations from which the crystal of the solid solution is formed depends on the partial concentrations of each kind of atom in the gas phase and can be specified if the rates of transition of the constituent atoms from the crystals into the vapor are known.

Fig. 2

Figure 2: Fig. 2

Using the method ([6]), we determined the rates of dissolution of single crystals of germanium and silicon by selenium vapors at different temperatures and in a certain most favorable interval of pressures of the vapor of the solvent component. It was found that at temperatures of 1000–1200° and selenium vapor pressures of 13–15 atm, the dissolution rates of germanium and silicon, respectively equal to $6.5 \cdot 10^{-6}$ and $5.2 \cdot 10^{-6}$ g/cm^2 • sec, are closest, which was taken into account in setting up experiments on growing single crystals of solid solutions.

The technology we adopted reduces to the following operations. Into a small quartz ampoule were placed amounts determined for each experiment of···

weights of germanium and silicon corresponding to the specified composition of the solid solution, and a definite weighed portion of selenium. The starting substances were first ground, polished, and etched according to the generally accepted procedure. The ampoules containing the charges were evacuated to a pressure of 10^{-5} mm Hg and sealed under vacuum, after which they were heated in a tubular electric furnace, the temperature of which was regulated with an accuracy of $\pm 3°$. The heating time of the ampoules in individual experiments varied from 2 to 5 days.

The experiments were carried out in the temperature range from 1000 to 1250° at a selenium vapor pressure of 10–15 atm. The weighed amounts of germanium and silicon were selected so that the compositions of the solid solutions changed successively by 5 at. %. Each experiment was considered complete when the initial weighed portions of germanium and silicon had completely dissolved.

In the cooled ampoules, upon opening them, both individual crystals and crystals intergrown in twins were found, mostly of a well-defined octahedral form (Fig. 1).

Fig. 2

The single-crystallinity, homogeneity, and composition of the crystals of the Ge—Si system obtained by us were studied by X-ray diffraction.

Fig. 2 shows a Laue photograph of a crystal of a solid solution containing 50 at. % Ge and 50 at. % Si, taken in tungsten radiation. The primary beam of rays is directed perpendicular to the (100) face. In the Laue photograph one can clearly see the symmetrical arrangement of the interference spots and the sufficiently distinct expression of ellipses, which indicates the single-crystallinity of the specimen.

Fig. 3

Fig. 3 shows the dependence of the lattice parameter of solid solutions on

Fig. 3

Figure 3: Fig. 3

the specified composition. From the figure it is seen that the experimental composition points lie well on the straight line connecting the values of the lattice parameters of pure germanium and silicon. The values of the lattice parameter of single crystals of a solid solution of a given composition grown in repeated experiments, as a rule, agreed well.

The mixed crystals obtained by us were homogeneous to the accuracy attainable in determining this composition by means of our X-ray structural analysis.

Our unsystematic data on measuring the specific resistance of solid solutions showed, for a number of compositions on the germanium side, an increase in resistance with increasing silicon content. For individual-

for the obtained samples of solid solutions the specific resistivity reached values of 200–300 ohm · cm.

Along with selenium, in our experiments sulfur, tellurium, and iodine were used as the solvent component; these also gave positive results.

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