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ON THE FORM IN WHICH IMPURITIES OCCUR IN HEAVILY DOPED SINGLE CRYSTALS OF GERMANIUM AND SILICON OF *n*-TYPE

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In single crystals of germanium and silicon doped to low concentrations with elements of Group V of the periodic system, practically all of the doping impurity enters into a substitutional solid solution. The study of heavily doped semiconductors gives grounds for assuming that impurities may exist in the crystal simultaneously in several states.

The concentration of the doping impurity in the grown single crystal C is related to its concentration in the melt C by the simple relation

$$C = KC, \tag{1}$$

where K is the effective distribution coefficient of the impurity under the experimental conditions.

In the silicon single crystals grown by us and doped to high concentrations with phosphorus and arsenic, at $C > 2 \cdot 10^{20}$ cm^{-3} the value of C, determined from measurement of the Hall effect, proved to be lower than the values that follow from (1). This discrepancy increased with increasing concentration of the doping impurity in the melt. To explain the results obtained, two assumptions were put forward: 1) with increasing concentration of the doping impurity in the melt, the value of its effective distribution coefficient in silicon decreases; and 2) at a high content of the doping impurity in the crystal, its concentration as measured by the Hall effect is less than the true impurity concentration in the specimen.

Fig. 1. Concentration of the doping impurity in heavily doped single crystals according to radioactivation analysis and Hall-effect measurements: *a*—Sb—Ge, —As—Ge, —As—Si.

A specially undertaken experimental determination of the effective distribution coefficients of P and As in silicon showed that at $C = 10^{19}$—10^{20} cm^{-3} their

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Fig. 2

Figure 2: Fig. 2

values differ little from the values obtained in growing single crystals with a low content of the doping addition, and do not explain the observed discrepancies. To check the second assumption, in a number of heavily doped silicon specimens a parallel determination of the concentration of the doping impurity by the radioactivation method was carried out. Analogous determinations were also performed for heavily doped germanium single crystals, the results of studies of whose electrical conductivity (1) made it possible to expect the manifestation of similar effects. Radioactivation analysis in its gamma-spectrometric variant ensured determination of the impurity concentration with an error on the order of 10–15%. The error in measuring the concentration from the Hall effect did not exceed 5%.

The results of the analysis by these methods are compared in Fig. 1. Both in silicon and in germanium, for all the investigated impurities, at high concentrations of them in the crystal there is a considerable discrepancy between the data of the two determinations. In all cases the total concentration of the doping impurity in the specimen exceeds the concentration found from Hall measurements. The threshold value of the concentration at which this discrepancy begins to appear, and the magnitude of the divergence of the data, depend on the specific conditions of crystal growth. In the general case, however, these effects intensify with decreasing distribution coefficient of the doping impurity and are observed long before its solubility limit in the semiconductor is reached. The results obtained convincingly show that at a high impurity concentration in the crystal not all of it enters into the substitutional solid solution. Part of the impurity is in states in which it does not exhibit donor properties. We shall call this phenomenon the polytropy (“multiformity”) of impurities in semiconductors. An analogous property in germanium single crystals with an arsenic impurity was noted in Ref. (2). In silicon specimens and in the Ge—Sb system, such phenomena are observed for the first time.

Fig. 2. Cellular substructure in a heavily doped silicon single crystal

Polytropy of impurities may be due to at least five factors: 1) the presence of impurity atoms in interstices; 2) the formation of inclusions of a second phase of the arsenide or phosphide type; 3) the formation of an impurity substructure of

Fig. 3

Figure 3: Fig. 3

the cellular-structure type; 4) precipitation of the impurity on various structural defects, for example the formation of "impurity atmospheres" on dislocations; 5) formation of structural complexes in a disordered solid solution of the type $Si_{xAs}y$, $Ge_{xP}y$, etc.

Fig. 3. Change in the concentration of charge carriers and in the specific resistance in a germanium single crystal during heat treatment

Second-phase inclusions of the germanium-arsenide type were discovered in Ref. (3). In our specimens metallographic analysis did not reveal such inclusions. In a number of silicon specimens we found a cellular substructure, one variety of which is shown in Fig. 2. Additional evidence for the existence of impurity polytropy was obtained in mass-spectrometric analysis of silicon doped with arsenic, carried out on an MS-7 mass spectrograph (4) by the method described in (5).* In the mass spectrograms, along with lines corresponding to As^+ ions, distinct lines were observed corresponding to $(SiAs)^+$, $(Si_2As)^+$, $(\mathrm{Si_3As})^+$. The intensity of the lines for the individual ions decreased in the order in which they are listed. Special experiments established that these compounds were indeed present in the samples studied, and were not formed in the spark of the ion source of the mass spectrograph. In particular, analysis of samples that had first been dissolved in a mixture of hydrofluoric and nitric acids, followed by deposition of the precipitate on graphite electrodes, did not reveal silicon-arsenic complexes.

Unfortunately, it was not possible to identify analogous complexes on the mass spectrograms of germanium samples with arsenic, since the GeAs line (mass 146) is superposed on the line of the isotopes $\mathrm{Ge}^{72}\mathrm{Ge}^{74}$ with the same mass.

If part of the impurity does not enter the substitutional solid solution, although the solid solution itself is still far from saturation, then from the thermodynamic point of view such a system is not stable. It could be assumed that, with time, in such crystals there would be an increase in the concentration of charge carriers due to an additional transition of impurity atoms into the solid solution. Indeed, after repeated measurement of a number of germanium samples doped to high concentrations with arsenic and stored for a year in a desiccator at a temperature of about 25°, an increase in the electron concentration by an average of 20–80% was found. The greatest changes were observed in samples with an initial carrier concentration $n_0 > 2 \cdot 10^{19}$ cm^{-3}, which gave the greatest deviation from the straight line in Fig. 1. A similar, although somewhat smaller, increase in

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* The analysis was carried out by M. S. Chupakhin and G. G. Glavin, to whom the authors express their deep gratitude.

Fig. 4

Figure 4: Fig. 4

carrier concentration also occurred in heavily doped germanium samples with phosphorus.

Fig. 4. Dislocation etch pits in a heavily doped germanium single crystal. *a*—after heat treatment, *b*—before heat treatment

Obviously, heat treatment of heavily doped single crystals can accelerate the process of transition of the doping impurity into the solid solution. In connection with this, the influence of heat treatment on the electrical properties of heavily doped germanium and silicon samples was investigated. A specially selected germanium single crystal with As, in which a considerable discrepancy was observed between the Hall-measurement data and the radioactivation-analysis data, was annealed in a hydrogen atmosphere at a temperature of 870° for 3 h, followed by quenching in water. The distribution of the resistivity and electron concentration along the length of the single crystal before and after heat treatment is shown in Fig. 3. As a result of heat treatment, the concentration of charge carriers in the crystal increased almost twofold, and the data of the Hall measurements and activation analysis practically coincided. Metallographic study of the crystal before heat treatment did not reveal signs of a cellular substructure in it. The dislocation density in the sample was approximately 10^4 cm^{-2}. The dislocation etch pits had characteristic "tails," which usually form a network in the field of view and connect individual pits with one another (Fig. 4*a*). After heat treatment

this network completely disappeared (Fig. 4b). It is possible that the formation of "tails" is due to the precipitation of the alloying impurity on dislocations and on other structural defects. Precipitates of this kind in heavily doped germanium single crystals have recently been detected by X-ray methods ([6]). During heat treatment, apparently, the impurity precipitated on defects goes into solid solution, leading to a significant increase in the concentration of charge carriers in the specimen.

Silicon single crystals doped with P and As, with a carrier concentration of $(8—9) \cdot 10^{19}$ cm^{-3}, were annealed in a hydrogen atmosphere at a temperature of 1200° for up to 24 hours, followed by quenching in water. In contrast to germanium, before heat treatment all specimens had a cellular substructure of the type shown in Fig. 2 and exhibited no dislocation etch pits. The increase in the charge-carrier concentration as a result of heat treatment in this case did not exceed 10–12%. In a number of specimens the carrier concentration did not change at all. In all specimens the cellular substructure was preserved, and the data of Hall measurements and activation analysis still did not coincide. Apparently, the polytropy of impurities in the heavily doped silicon specimens investigated is due mainly to the presence of a cellular substructure, which is not eliminated by heat treatment.

Further study of the phenomenon of impurity polytropy in semiconductors seems to us highly necessary, since, apart from its scientific interest, the specific form in which the alloying impurity is present in a single crystal probably also determines the stability of heavily doped semiconductors over time.

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