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Behavior of phosphorus impurities during Czochralski growth of high-purity germanium single crystals

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The effect of evaporation of phosphorus impurities from the melt is investigated as well as the contaminating effect of quartz glass crucibles on residual content and distribution of this impurities by length of high-purity germanium single crystals. The residual content of phosphorus impurities is mainly influenced by the contaminating effect of crucible material and its distribution by length of crystals is described by the model accounting for the impurities income from crucible material.

1 Introduction

Phosphorus is one of the most common electro-active impurities in high-purity germanium single crystals [1]. The content of this impurity and its distribution in crystals affect their electro-physical characteristics. Thus, it is of interest to investigate the factors affecting the residual concentration and the distribution of phosphorus impurity in single crystals during their growth. These factors may be represented by the contaminating effect of apparatus material and transfer of impurity from the melt as a result of evaporation.

The Czochralski method is widely used for growth of high-purity single crystals. The growth process is carried out with the use of quartz glass crucibles. It is known [2] that the quartz glass interacts with Ge melt with formation of volatile monoxides of Ge and Si. During this process the impurities, including phosphorus, enter from glass into Ge melt. The possible evaporation of phosphorus impurity from the melt may be connected with the fact that phosphorus has a high pressure saturated vapor at the melting temperature of germanium.

The goal of work is to investigate the effect of evaporation of phosphorus impurity from germanium melt and of the contaminating effect of quartz glass crucibles on residual content and distribution of this impurity in high-purity germanium single crystals grown by Czochralski method.

2 Experimental

Experiments on investigation of evaporation of phosphorus impurity from the melt are carried out using the initial germanium with the content of phosphorus impurity 10^{12} at./cm^3. The concentration of phosphorus in the initial germanium was determined by the methods of photothermal ionization spectroscopy [3], measurements of Hall effect, and of field intensity of impurity breakdown [4]. To reduce the contaminating effect of crucibles the initial germanium was specially doped with phosphorus impurity up to concentration $4\cdot10^{15}$ at./cm^3. At this doping level the contaminating effect of crucible material did not noticeably affected the content of phosphorus in Ge melt during its prolonged holding in quartz glass crucible. For determination of evaporation rate of phosphorus from the melt the following experimental technique was used: germanium, doped with phosphorus,

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melted in quartz crucible of the set-up for growth of single crystals by Czochralski method. High-purity hydrogen was blown through the chamber. Periodically samples were taken from the melt in the form of small (~2 g) single crystals. The total weight of the single-crystal samples was less than 5 % of the charged weight in crucible. Since the sample weight was substantially less than the melt weight in crucible, the change in phosphorus concentration in the melt as a result of redistribution of impurity between the solid and the liquid phase in the process of sampling did not exceed the error in measurement of phosphorus concentration (10 %). In this experiment we specially used the germanium doped with phosphorus up to concentration more than 10^{15} at./cm^3 and concentration of phosphorus was more then 1000 times higher than that of other acceptor and donor impurities. In this case the net concentration of charge carriers N_d–N_a is determined by the content of phosphorus impurity N_P (N_P=N_d–N_a). Therefore, the concentration of phosphorus impurity in the samples was determined by measuring N_d–N_a using the Hall effect.

The contaminating effect of crucible material was estimated by comparison of the experimentally observed distribution of phosphorus impurity by length of germanium single crystals with the results calculated by material balance equation accounting for impurity income into the melt from crucible material. Single crystals were grown by Czochralski method in the flow of high-purity hydrogen from the crucibles made of technical quartz glass, synthetic quartz glass manufactured by hydrolysis of high-purity silicon tetrachloride in oxygen-hydrogen flame and from the crucible with protective coating from high-purity amorphous silicon dioxide. As the initial charge a high-purity zone-melted germanium was used with the content of phosphorus impurity less than $5 \cdot 10^{10}$ at./cm^3. Since the high-purity germanium could comprise, apart from phosphorus, some comparable amounts of other electro-active impurities, the Hall effect is insufficient for quantitative determination of the content of phosphorus impurity. That is why we used a set of methods including photothermal ionization spectroscopy [3], measurements by Hall effect and measurements of field strength of impurity breakdown [4]. The method of photothermal ionization spectroscopy made it possible to determine the chemical nature of the main electro-active impurities and the ratio of their concentrations. This method allowed us to determine two impurities in high-purity zone-melted germanium, i.e., phosphorus (donor) and aluminum (acceptor). The content of other electro-active impurities was lower than the limits of detection of this method (10^9 at./cm^3). The measurements of the Hall effect made it possible to determine the net concentration of donors and acceptors N_d–N_a=N_P–N_{Al} and the measurements of field intensity of impurity breakdown – the concentration ratio N_d/N_a=N_P/N_{Al}. The use of results, obtained by the above-mentioned methods, allowed us to quantitatively determine the phosphorus impurity in the studied concentration range 10^{10} -10^{13} at./cm^3 both in the initial high-purity zone-melted germanium and in single crystals grown on its basis.

Analysis of experimental data was carried out assuming the constant rate of income of phosphorus impurity from the unit surface of crucible contacting the germanium melt. The constancy in dissolution of quartz glass in germanium melt was found in [5]. In this case the equation of material balance for impurity component during growth of a single crystal accounting for the contaminating effect of crucible can be given in the following form:

$$dx/d(m_0-m_k)=[(1-\alpha)\cdot x+\alpha\cdot S(m_k)\cdot V_{imp}/V_k]/(m_0-m_k), \quad (1)$$

where x is the molar fraction of impurity in crystal, m_k is the mass of the crystallized part of melt, m_0 is the mass of the initial charge, V_{imp} is the rate of impurity income from crucible material, $S(m_k)$ is the contact area of melt with crucible, V_k is the crystallization rate and α is the effective factor of «solid – liquid» distribution.

The value of distribution factor α and its dependence upon crystallization rate was found in individual experiments using germanium doped with phosphorus up to $(1\text{-}3)\cdot 10^{15}$ at./cm^3. The value of equilibrium distribution factor, obtained by extrapolation of the dependence of the efficient distribution factor upon crystallization rate with respect to zero rate was 0.06 which is close to value 0.08 found in [6].

3 Results and discussion

Figure 1 gives the experimental results on investigation of evaporation rate of phosphorus impurity from germanium melt. It is seen from figure 1 that the concentration of phosphorus impurity in samples, and, thus, in the melt does not decrease in time, and evaporation of phosphorus impurity from germanium melt is not experimentally observed. After 10 hours hold time of the melt at melting temperature of germanium the change in phosphorus concentration in crystal samples did not exceed the error of measurement of its concentration (10 %). The obtained results make it possible to make a conclusion on strong interaction between the atoms of phosphorus and the atoms of germanium in the melt and on substantial deviation of germanium-phosphorus impurity system from the ideal state. These results are in agreement with the data [7] where the authors investigated the process of purification of germanium by the method of vacuum distillation and also did not find the effect of purification from phosphorus impurity.

Figure 2 gives the results of experiments on investigation of the contaminating effect of crucible material on the residual concentration of phosphorus impurity and on its distribution by length of single crystals grown by Czochralski method.

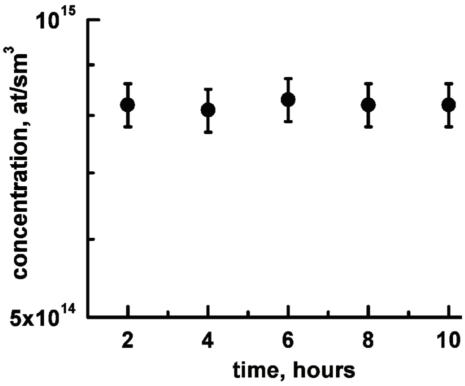

Fig. 1 Dependence of phosphorus concentration in single-crystal samples upon the hold time of the melt at melting temperature of germanium.

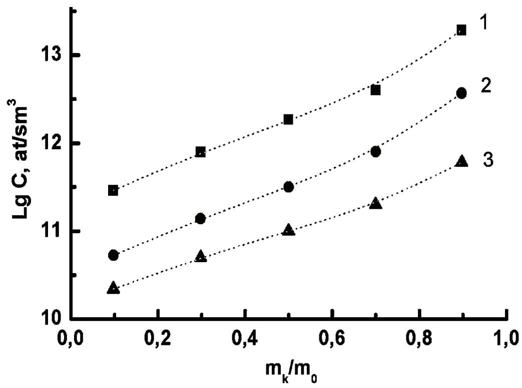

Fig. 2 Distribution of phosphorus impurity by length of single crystals grown from quartz crucibles. ■ – crucible from technical quartz glass. ● – crucible from synthetic quartz glass produced by hydrolysis of silicon tetrachloride. ▲ – crucible with protective coating from high-purity amorphous silicon dioxide. The dotted lines – calculation by equation (1): at income rate of impurity (V_{imp}) equal to: $1 – 2 \cdot 10^{12}$ at./cm^3 h; $2 – 2\cdot 0^{11}$ at./cm^3 h; $3 – 1\cdot 10^{11}$ at./cm^3 h.

The experimental data are well described by equation (1). The values for the income rate of impurity and purity of the produced crystals substantially depend upon crucible material. It proves the determining contaminating effect of crucible material on the residual concentration of phosphorus impurity in high-purity single crystals of germanium grown by Czochralski method.

4 Conclusions

The effect of evaporation of phosphorus impurity from the melt and the contaminating effect of quartz glass crucible material on the residual content and on the distribution of this impurity in single crystals of high-purity germanium grown by Czochralski method was investigated. Evaporation of phosphorus impurity from the germanium melt was not observed experimentally. The change of phosphorus concentration in the melt after 10 hours hold time at melting temperature of germanium did not exceed the error of determination (10%). With the use of the initial charge of high-purity zone-melted germanium with the content of phosphorus at the level of 10^{10} at./cm^3 the residual content of phosphorus impurity in single crystals drown by Czochralski method is determined by the income rate of impurity from crucible material and its distribution by length of crystals is described by the model accounting for the contaminating effect of crucible material.

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