CONCENTRATION PROFILES OF COMPONENTS AND IMPURITIES IN Ge_{1-x}-Si_x<Ga> AND Ge_{1-x}-Si_x<Sb> CRYSTALS GROWN BY ZONE MELTING METHOD

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In the Pfann approximation, mathematical calculations were carried out on the distribution of the main components and impurities in germanium-like Ge(1-x)-Si(x)<Ga> and Ge(1-x)-Si(x)<Sb> crystals, grown by the zone melting method. Using this method, $Ge_{0.9}$-$Si_{0.2}$<Ga> and $Ge_{0.9}$-$Si_{0.2}$<Sb> crystals were obtained at different lengths of the molten zone and their concentration profile was studied. Comparison of calculated and experimental data indicates their good agreement. This makes it possible to conclude that with the help of mathematical modeling it is possible within wide limits regulate the concentration profile of the main components and impurities in Ge-Si crystals grown by the zone melting method using different length of the molten zone and choosing the composition of the initial polycrystalline rod.

Keywords: semiconductor, Ge-Si, zone melting, Ga, Sb
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INTRODUCTION

The wide possibilities of modern semiconductor electronics and especially microelectronics are associated with the development and mastering of semiconductor materials with various physical properties. The most used in technology and suitable in their electro-physical parameters to various tasks put forward by modern technical progress are such semiconductor materials as germanium and silicon. The fact that Ge and Si completely dissolve in each other in any ratio makes it possible, by growing Ge-Si solid solutions, to obtain a semiconductor material with the technical characteristics necessary for a specific task by changing the composition of the matrix. In the last two decades, certain successes have been achieving in growing bulk crystals of solid solutions of the classical Ge-Si system (Abrosimov et al., 1997; Azhdarov et al., 2001, 2014; Marin and Ostrogorsky, 2000; Yildiz et al., 2005; Yonenaga, 2005). Of considerable interest are studies related to the growth of crystals of this system with a given composition and concentration profile of impurities in the matrix (Adachi et al., 2005; Azhdarov et al., 2009; Bok-Cheol, Sim. et al., 2006; Kyazimova et al., 2006; Yonenaga and Ayuzava, 2006).

In this work, doped crystals of $Ge_{0.9}$-$Si_{0.1}$<Ga> and $Ge_{0.9}$-$Si_{0.1}$<Sb> solid solutions were obtaining by zone melting (Adachi et al., 2005) and their concentration profiles were studying. In parallel with this, in the Pfann approximation (Глазов и Земсков, 1967) mathematical modeling of the concentration profiles of the main components was carrying out for a wide range of germanium-like Ge-Si crystals, with a silicon content of up to 15 at. % grown by the zone melting method at different lengths of the molten zone. Directly for $Ge_{0.9}$-$Si_{0.1}$<Ga> and $Ge_{0.9}$-$Si_{0.1}$<Sb> crystals grown by the same method, theoretical distribution curves of gallium and antimony impurities along the crystal growth axis were obtaining. Note that Ga and Sb, both in germanium, silicon, and in their solid solutions, belong to the category of typical small impurities, and are widely used for doping these materials. Possessing a fairly high solubility in these materials, these impurities can change their electrical properties within several orders of magnitude.

THEORETICAL ANALYSIS

The procedure for growing crystals of Ge-Si solid solutions by zone recrystallization is well described in (Azhdarov et al. 2009). A prefabricated macrohomogeneous polycrystalline rod of a given composition made of Ge-Si is placing in the crucible above a single-crystalline seed from a more refractory component (Si). In the case of growing doped crystals, an impurity of the required amount is placing between the seed and the rod. In a heater with an axial temperature field, part of the Ge-Si ingot is melting above the seed (depending on the choice of the length of the molten zone). At the pre-starting moment, the temperature at the boundaries of the melt with the seed and the ingot is equal to the liquidus temperature of the given composition of the polycrystalline Ge-Si ingot. Crystal growth occurs on the seed from the moment the mechanism for moving the crucible down (or the furnace up) is turned on and continues until the ingot is completely recrystallized.

The mathematical problem of the distribution of the main components and impurities in crystals, grown by zone melting was solved in the Pfann approximation and within the framework of a virtual environment model for binary solid solutions, under which the following standard conditions are met: there is no evaporation and decomposition of the constituent components in the melt; the diffusion rates of Ge, Si atoms and introduced impurities in the melt are quite high and ensure uniform composition throughout the entire volume; during the growth process, the diffusion of components in the solid phase is negligible; at the crystallization front there is an equilibrium between the liquid and solid phases, determined by the phase diagram of the system; the Si segregation coefficient changes with the composition of the melt in accordance

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with the phase diagram of the Ge-Si system; the equilibrium segregation coefficient *K*(x) of the introduced impurity in the $Ge_{1-x}Si_x$ system changes linearly with changes in the matrix composition (x); the crystallization front is flat; the composition of the initial polycrystalline ingot is macrohomogeneous.

Let's introduce the following notation: V_m^0 and V_m - volumes of the molten zone at the initial and current moments; *Cc*, *Ci*, *Cm* - concentrations (fractions) of atoms of the second component (Si) in the crystal, initial ingot and the melt, respectively; C_m^0 - concentration of the second component in the molten zone at the initial moment; *C* and *Cim* – total amount of Si and introduced impurity in the melt; *Vc* is the volume of the melt crystallizing per unit time; *Vi* is the volume of the Ge-Si ingot melted per unit time; $K = Cc/Cm$, $K^{im} = {C_c^{im}}/{C_m^{im}}$ – equilibrium segregation coefficients of Si and impurities; C_c^{im} , C_m^{im} , $C_m^{im,0}$ – impurity concentration in the crystal, melt at the current and starting moments, respectively; *L*, *l*, and *Z* are the lengths of the initial ingot, the recrystallized part of the ingot and the molten zone, respectively.

According to the conditions of the problem, we assume that the crystallization rate of the melt *Vc* does not depend on time, and then in the notation adopted above we have:

$$C_m = {C}/{V_m}\ , \quad \frac{dC_m}{dt} = \frac{\dot{C}V_m - C\dot{V}_m}{V_m^2} \tag{1}$$

$$V_m = V_m^0 - (V_c - V_m)t \tag{2}$$

We assume that up to the final molten zone, *Z* and *Vi*, as well as *Vc*, do not depend on time. Then, on a section of the ingot with length *L-Z*, the following relations are valid.

$$V_m = V_m^0, \quad C_m^0 = C_i, \quad \dot{C} = -V_c C_m K + V_i C_m^0 \tag{3}$$

Substituting (3) into (1), after separation of variables and integration, we have:

$$\int_{C_i}^{C_m} \frac{dC_m}{C_i - C_m K} = \frac{V_c}{V_m^0} = \frac{l}{Z} \tag{4}$$

Equation (4) determines the composition of the crystal according to its length l in the L-Z section.

From the moment of formation of the final molten zone, we have:

$$V_m = V_m^0 - V_c t, \ \ \dot{V}_m = -V_c\ , \dot{C} = -V_c C_m K \tag{5}$$

Substituting (5) into (1) after integration we obtain:

$$\int_{C_{mf}^0}^{C_m} \frac{dC_m}{C_m(1-K)} = ln\frac{V_m^0}{V_m^0 - V_c t}. \tag{6}$$

Here C_{mf}^0 - is the starting concentration of the second component in the last molten zone. Denoting the fraction of melt crystallized in the final section ${V_c t}/{L}$ by the symbol γ, we write equation (6) in the following form

$$\gamma = a(1 - \exp[-\int_{C_m}^{C_{mf}^0} \frac{dC_m}{C_m(K-1)}]) \tag{7},$$

where $a=Z/L$.

Equations (4) and (7) contain a segregation coefficient *K*, the analytical form of which, depending on the melt composition *Cm*, is not available for the Ge-Si system. In this case, the values of the integrals in (4) and (7) can be determined numerically by determining the values of *K* for the conjugate values of *Cm* from the phase diagram of the Ge(1-x)-Si(x) system (Глазов и Земсков, 1967).

Figure 1 shows the characteristic curves of the concentration profile of the main components in germanium-like crystals Ge(1-x)-Si(x), calculated for the initial stage of crystallization, before the establishment of uniform growth, from equations (4) using the numerical method for *Ci* values from 1 to 15 at. % with an interval of 1 at.%. In calculations it is assumed that $Z=L/10$. As can be seen from Fig. 1 in all cases, the concentration of Si is maximum at the beginning of the ingot and then, decreasing, reaches a uniform value *Cc=Ci*, until the formation of the final molten zone *Z*. The length of the initial section with a variable composition depends on the composition of the initial ingot, which is associated with a change in *K* from composition of the molten zone.

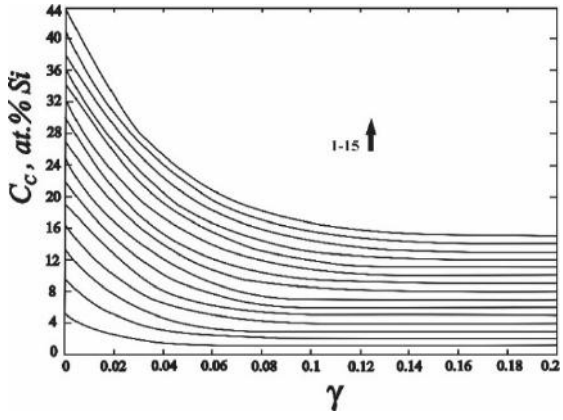

Fig.1. Calculated curves of Si concentration along the Ge(1-x)-Si(x) crystals until a homogeneous area. Curves 1-15 correspond to x of inisial rods -1,2,..15 at.%. *Z*=0.1*L*.

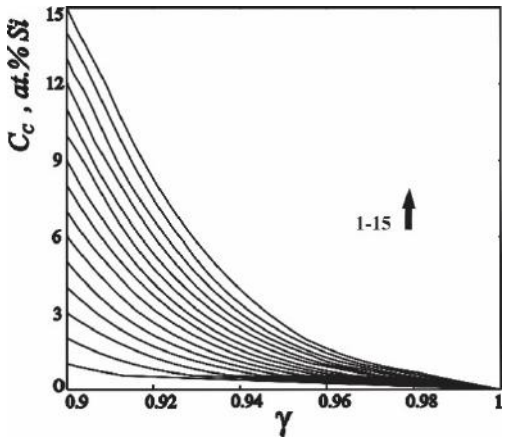

Fig. 2. Calculated curves of Si concentration at the final growth section of Ge(1-x)-Si(x) crystals of length *Z*. Curves 1- 15 correspond to x of inisial rods -1,2,...15 at.%. Z=0.1*L*.

For a final section of a growing crystal with length *Z*, silicon concentration profiles are presented in Fig. 2, calculated from equation (7).

At the end of the ingot, the concentration of the second component begins to fall again and reaches almost zero at *l* = *L*. The length of the final section with a variable composition for all ingot compositions under consideration is equal to the width of the molten zone *Z*. The rate of composition change along the crystallization direction in the final section of the molten zone decreases with decreasing *Ci*, since the length of this zone is fixed according to the conditions of the problem.

For the impurity concentration, equation (1) takes the following form:

$$C_m^{im} = C^{im}/V_m\ , \quad \frac{dC_m^{im}}{dt} = \frac{\dot{C}^{im}V_m - C^{im}\dot{V}_m}{V_m^2} \qquad (8)$$

The change in the total amount of impurity in the solution at any moment of crystal growth is equal to

$$\dot{C}^{im} = -C_m^{im}K^{im}V_c \qquad (9)$$

Substituting (9) into (8) after separation of variables and integration, and taking into account the constancy of the volume of the melt up to the final molten zone, we obtain an expression for the concentration distribution of the impurity along the crystal axis in the *L*-*Z* section:

$$C_m^{im} = C_m^{im,0}\exp(-\tfrac{1}{a}\textstyle\int_0^{\gamma} K^{im}d\gamma)$$

$$C_c^{im} = K^{im}\cdot C_m^{im,0}\exp(-\tfrac{1}{a}\textstyle\int_0^{\gamma} K^{im}d\gamma) \qquad (10)$$

For the final section *Z*, using the expressions for V_m and $\dot{V}_m$ from (5), we have:

$$C_m^{im} = C_{mf}^{im,0}\exp(-\int_0^{\gamma}\frac{K^{im}-1}{a-\gamma}d\gamma)$$

$$C_c^{im} = K^{im}\cdot C_{mf}^{im,0}\exp(-\textstyle\int_0^{\gamma}\frac{K^{im}-1}{a-\gamma}d\gamma) \qquad (11),$$

where $C_{mf}^{im,0}$ – the value of the impurity concentration in the melt at the beginning of the final molten zone *Z*.

The value of the impurity segregation coefficient K^{im} varies linearly between its values in Ge and Si, according to the virtual environment model for binary solid solutions.

$$K^{im} = K_{Ge}^{im} + \left(K_{Si}^{im} - K_{Ge}^{im}\right)x \qquad (12)$$

Since the impurity segregation coefficient depends on the composition of the matrix, the integrals in equations (10) and (11) can be solving numerically by calculating K^{im} from (12) for conjugate values of γ, using the concentration profiles of the main components calculated using formulas (4) and (7).

EXPERIMENTAL RESULTS AND DISCUSSION

To check the mathematical calculations, $Ge_{0.9}$-$Si_{0.1}$<Ga> and $Ge_{0.9}$-$Si_{0.1}$<Sb> crystals were grown by zone recrystallization using the molten zone lengths *Z*=0.1*L* and 03*L*. The length of the obtained crystals was 10 cm; the cross-sectional area was 1.5 cm. The amount of impurity loading at the beginning of recrystallization was 1 gram for Ga and 2 grams for Sb. In this case, the initial concentration of gallium and antimony impurities in the molten zone at the starting moment was equal to $1.223\cdot10^{18}$ cm^{-3} and $1.4\cdot10^{18}$ cm^{-3}, respectively.

Figure 3 shows silicon concentration profiles along $Ge_{0.9}$-$Si_{0.1}$ crystals at different values of the length of the molten zone (*Z*=0.1*L*, 0.2*L*, 0.3*L*, 0.4*L*), calculated using formulas (4) and (7). For zone lengths of 0.1L and 0.3L, experimental results are presented based on the specific gravities of samples from different regions of the grown crystal. As we can see, the experiment agrees well with the calculations. As the length of the molten zone increases, the area with a uniform distribution of components decreases and the extent of the variable composition at the beginning of crystal growth increases. The length of the final section with variable composition is in all cases equal to the length of the molten zone.

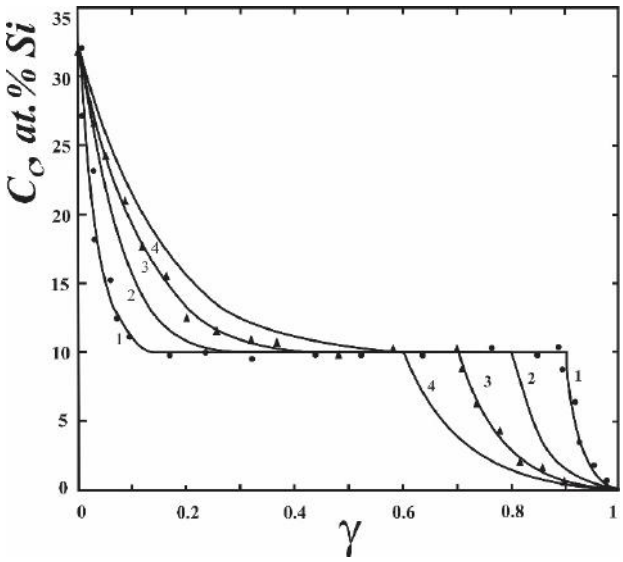

Fig. 3. Concentration profiles of $Ge_{0.9}$-$Si_{0.1}$ crystals at different lengths of the molten zone. Solid lines—calculated; ● and ▲ —experimental data. Curves 1-4 correspond to *Z*=0.1- 0.4.

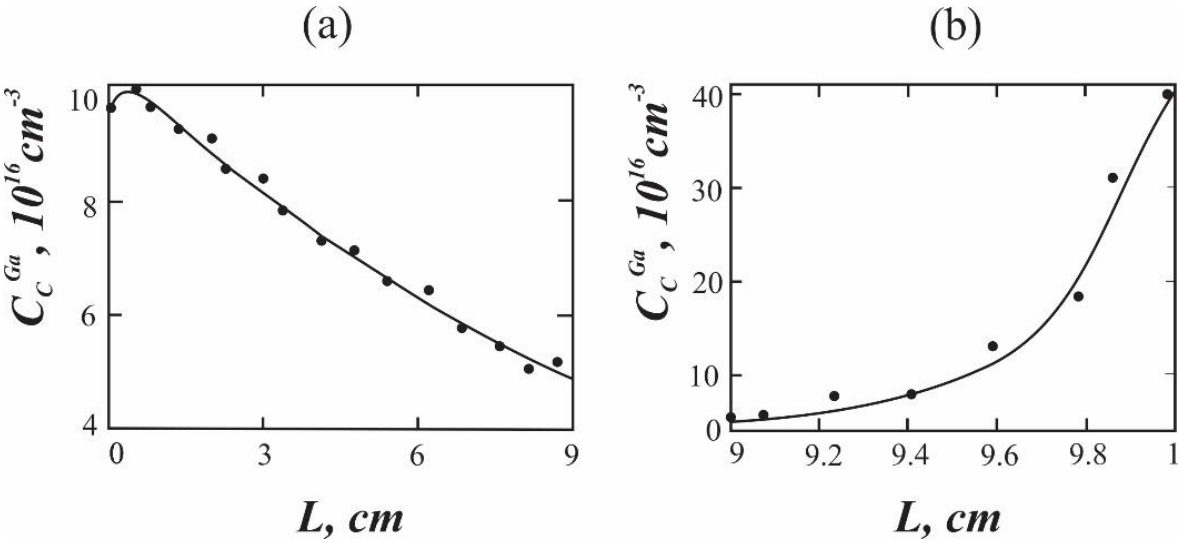

Fig. 4. Gallium concentration profile along $Ge_{0.9}$-$Si_{0.1}$<Ga> crystals. *Z*=0.1. Solid line – calculated, ● – experimental data. (a) – distribution of Ga in the section *l*=*L*-*Z*, (b) - in the final section *Z*.

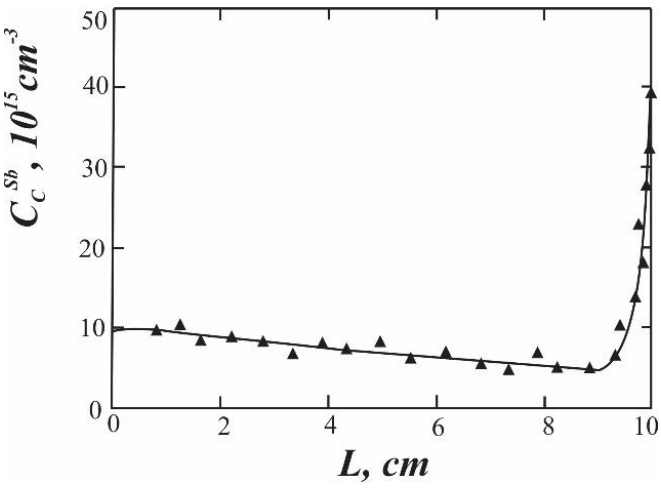

Fig. 5. Antimony concentration profile along $Ge_{0.9}$-$Si_{0.1}$<Sb> crystals. *Z*=0.1. Solid line – calculated, ▲ – experimental data.

Figures 4 and 5 show the concentration profiles of gallium and antimony in the $Ge_{0.9}$-$Si_{0.1}$<Ga> and $Ge_{0.9}$-$Si_{0.1}$<Sb> grown crystals with a molten zone length of 0.1*L*, calculated using the formulas (10) and (11). The figures also show experimental results obtained from Hall measurements (Ashcroft Neil and Mermin, 1976) carried out on samples from grown crystals. The curves in Figs. 4 and 5 also demonstrate good agreement between theory and experiment. At the beginning of growth, an increase in the gallium concentration in the growing crystal is observed in Fig. 3, which is replaced by an almost linear decrease until the final molten zone. A similar increase is not observed in Fig. 4 for the antimony impurity. This is probably due to the strong segregation of gallium from the melt compared to antimony, and therefore the increase in the Ga concentration in the crystal due to an increase in the segregation coefficient at the beginning of growth prevails over its decrease due to a decrease for impurity in the melt. After the beginning of the final molten zone, in both cases an increase in the impurity concentration is observed, which can be explained by a decrease in the volume of the molten zone and, as a consequence, an increase in the impurity concentration in the melt.

CONCLUSION

The results obtained demonstrate the capabilities of mathematical modeling in determining optimal regimes for growing crystals of Ge-Si solid solutions with given concentration profiles of the main components and impurities. Based on the above data and results, the following conclusion can be drawn. Mathematical modeling of the distribution of components in Ge-Si crystals grown by zone recrystallization, carried out taking into account the complex dependence of the segregation coefficient of components and impurities on the composition of the melt, makes it possible to assess the optimal technological parameters for obtaining crystals with a given composition and distribution of components.

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