

Simulation of the creation of a defect structure of dislocation-free germanium single crystals

V.I. Talanin^{a,*}, I.E. Talanin^a, O. Matsko^b

^a Khortytisia National Academy, Zaporozhye, Ukraine

^b KM Ware US, Austin, TX, USA



ARTICLE INFO

Communicated by Chung wen Lan

Keywords:

A1: Defects

A1: Solid solutions

B1: Diamond

B2: Semiconducting materials

ABSTRACT

The basis for applying the model of high-temperature impurity precipitation is decay of a supersaturated solid solution of point defects near the crystallization front. A necessary condition for high-temperature precipitation is absence of recombination processes of intrinsic point defects (vacancies and intrinsic interstitial atoms, IPDs) at high temperatures. The recombination parameters for dislocation-free germanium single crystals were estimated using the terms and concepts of Voronkov's recombination-diffusion model. It was shown that at high temperatures in germanium there is a barrier against the recombination of IPDs. It is assumed that the formation of structural imperfections, as well as in silicon, proceeds through the interaction "impurity + IPD". The possibility of applying the mathematical apparatus the diffusion model of formation of structural imperfections to the formation of a defective structure in undoped dislocation-free germanium single crystals is considered.

1. Introduction

An extremely actual task of modern materials science and the technology of obtaining perfect crystals are to describe the nucleation, growth and transformation of structural imperfections that arise during cooling of crystal after growth. This is due to the fact that the electrophysical, mechanical, and optical properties of crystals and devices depend on defective structure of crystal and impurities.

Such description should have a mathematical basis with the help of which you can create software products for analysis and calculation of a crystal defective structure. However, until recently, there was no uniform theoretical understanding of processes of defect formation during crystal growth, especially the possibility of impurities precipitation. We were able to solve this problem for silicon single crystals. Over the past ten years we have created a diffusion model of formation and transformation of structural defects during growth of dislocation-free silicon single crystals. The diffusion model is based on elastic interaction of IPDs and impurities with each other near crystallization front. This interaction, depending on thermal growth conditions, leads to creation of a defective crystal structure upon cooling from crystallization temperature. Further technological processing of crystal when creating devices causes the transformation of grown-in defective structure with simultaneous growth of new structural defects. The diffusion model allows the use of software tools for monitoring or controlling the

defective structure of silicon crystals at any stage of growing a crystal or creating devices. The main results of our research are presented in monograph [1]. The diffusion model of nucleation, growth, and transformation of structural imperfections is based on two theoretical positions: the absence of recombination of IPDs near crystallization front [2] and high-temperature impurity precipitation [3].

We believe that the diffusion model can also be used to describe the creation and development of defect structure of other perfect crystals (without dislocations). The similarity of structure of dislocation-free silicon and germanium single crystals allows us to choose a germanium crystal as a test of this assumption.

Dislocation-free high-purity germanium is often used as substrates for epitaxial structures when creating radiation-resistant power MOSFET-transistors for electronic equipment, photoelectric converters, nanoscale transistor structures. Due to more than twice the mobility of charge carriers compared with silicon, germanium is used to create high-speed memory cells. Each of these applications leads to high demands on the quality of crystals and, in particular, to grown-in defects.

Thermal growth conditions (growth rate, temperature gradients, diameter, growing method) determine the type of structural grown-in defects, their distribution in single crystal volume, and their concentration. Unfortunately, in modern scientific literature both experimental and theoretical data on this relationship are absent or incomplete in dislocation-free germanium. Perhaps this is due to the

* Corresponding author.

E-mail address: v.i.talanin@mail.ru (V.I. Talanin).

<https://doi.org/10.1016/j.jcrysgr.2019.125472>

Received 8 September 2019; Received in revised form 26 December 2019; Accepted 30 December 2019

Available online 31 December 2019

0022-0248/ © 2019 Elsevier B.V. All rights reserved.

increased attention of researchers around the world to dislocation-free silicon single crystals.

Currently, there is a semi-quantitative understanding of grown-in defects in germanium [4]. The formation of structural imperfections is described using Voronkov's model which was developed for dislocation-free silicon single crystals [5]. Based on similarity of the structure of silicon and germanium crystals, Voronkov's model began to be used to describe of defective structure of germanium. However, Voronkov's model does not take into account the effect of impurities on the formation of structural imperfections during crystal growth in either silicon or germanium. It is assumed that the formation of precipitates occurs only during thermal processing of crystals during the manufacture of devices. In fact, the problem of the theoretical description of defect formation in germanium is in the same state that a similar problem in silicon was ten years ago.

At the same time, the diffusion model is based on high-temperature precipitation of impurities. Impurity precipitates formed near the crystallization front and depending on the thermal conditions of growth lead to the creation of secondary imperfections (dislocation loops or voids) during cooling of silicon single crystals after growth. Let us try to extend these positions of the diffusion model to the process of formation of a defective structure during the growth of dislocation-free single crystals of germanium.

Therefore, the purpose of this paper is to evaluate the parameters of the process of IPDs recombination (recombination barrier, recombination time, recombination factor) in high-temperature and low-temperature growth regions of germanium single crystals and to consider the process of high-temperature precipitation in dislocation-free germanium single crystals.

2. Estimation of IPDs recombination process parameters in accordance with model of point defects dynamics

When creating a model of high-temperature precipitation in dislocation-free silicon single crystals, the elastic interaction between impurity atoms and IPDs was taken into account. It is possible to take into account the elastic "impurity + impurity" interaction, as well as the Coulomb interaction. However, even without these approximations the high-temperature precipitation model is in good agreement with experimental data [1,3,6].

Creating a high-temperature precipitation model was impossible without calculating the recombination parameters. When calculating the recombination parameters, it was found that process of IPDs recombination is absent near crystallization front [2]. Vacancies and silicon interstitials find sinks on the background impurities of oxygen and carbon respectively. At the same time, it was found that under conditions of low-temperature studies (f.e., during ion implantation), the processes of IPDs recombination occur at a fairly high speed. Our theoretical calculations confirm model of entropy barrier, the essence of which is that decrease in the barrier is caused by a decrease in the configurational entropy with decreasing temperature [7].

The papers [8,9] completely confirm results of our paper [2] about a presence of a barrier against recombination in silicon. In the study of point defects in germanium, the authors [9] found two separate forms of their existence. The first (low-temperature form) is a well-known point defect. The second form has a structure similar to that of an amorphous pocket. This second form was called by authors as "morph" [9]. This high-temperature form has a configurational entropy value ~ 30 k. It exists both for an interstitials and for vacancies. We take into account that in germanium there is a crystalline structure similar to silicon and somewhat different thermal growth conditions. Hence, it is very likely that the recombination of IPDs will also be absent near crystallization front during growth of dislocation-free single crystals of germanium. Therefore, we will evaluate the recombination parameters for the regions of high and low temperatures in germanium.

(a) **High-temperature area.** The temperature dependence of configurational entropy for defect model considered above can be represented in the following form [10]:

$$S_c(T) = S_\infty(1 - T_k/T) \quad (1)$$

where S_∞ is a limit value S_c (at $T \rightarrow T_m$); T_m is a melting temperature; T_k is a characteristic temperature. Suppose that T_k is a minimum temperature for the formation of structural imperfections in dislocation-free single crystals of germanium. Then we estimate $T_k = 300 \text{ }^\circ\text{C} = 573 \text{ K}$ as minimum temperature for the formation of thermal donors in germanium [11]. If we take $S_\infty = -30k$ [9], then we get the $S_c(T) = -30k(1 - 573/T)$.

Since the contribution of enthalpy term ΔH is negligible, the free energy of the recombination barrier is $\Delta G = -T \cdot \Delta S$. The temperature dependence of the recombination barrier height is controlled by entropy of the point defects formation

$$\Delta G(T) = -T \cdot [-S_c(T)] = T \cdot S_c(T) \quad (2)$$

An approximate estimate for $T = T_m$ gives $\Delta G(1211 \text{ K}) \approx 1.65 \text{ eV}$.

The experimental results on self-diffusion in germanium show that vacancies make the main contribution, and the contribution of interstitials is insignificant [12,13]. The diffusion coefficient obeys Arrhenius dependence in a wide temperature range $D(T) = 13.6 \exp(-3.094 \text{ eV}/kT)$ [14]. An approximate estimate for $T = T_m$ gives $D(T) \approx 1.81 \cdot 10^{-12} \text{ cm}^2 \cdot \text{s}^{-1}$.

The recombination time at high temperature (τ_1) is estimated using formula

$$\tau_1 = \Omega/4\pi \cdot D(T) \cdot r_0 \cdot \exp(-\Delta G(T)/kT) \quad (3)$$

where Ω is a lattice volume; $r_0 = 3 \cdot 10^{-8} \text{ cm}$ is a recombination radius. An estimate for $T = T_m$ gives $\tau_1 \approx 243 \text{ s}$.

The recombination factor $k_{IV}(T)$ is described by theory of diffusion-limited reactions together with the kinetic activation barrier [15]. In case of high temperatures

$$k_{IV}(T) = 4\pi \cdot r_0 \cdot D(T) \cdot \exp(-\Delta G(T)/kT) / \Omega \cdot c_s \quad (4)$$

where $c_s = 5 \cdot 10^{22} \text{ cm}^{-3}$ is an atom density. An estimate for $T = T_m$ gives $k_{IV}(1211 \text{ K}) = 8.221 \cdot 10^{-26} \text{ cm}^3/\text{s}$. The criterion of "fast recombination" near the crystallization front was introduced in [16]: $k_{IV}(1211 \text{ K}) \cdot C_{vm} \geq 20 \text{ s}^{-1}$ (where $C_{vm} = 1.3 \cdot 10^{15} \text{ cm}^{-3}$ is a vacancies concentration for $T = T_m$ [11]). The calculation shows that criterion of "fast recombination" in conditions of Voronkov's model is not fulfilled.

The calculation was made in full accordance with Voronkov's model. The obtained calculation results indicate the absence of IPDs recombination near crystallization front in germanium crystal. Vacancies and interstitials find their sinks on impurity atoms.

(b) **Low-temperature area.** The evaluation of recombination time at low temperature (τ_2) is estimated using formula $\tau_2(T) = \tau_\infty \cdot \exp(-\Delta G(T)/TS_c(T))$. The value $\tau_\infty = 661 \text{ s}$ is determined under the condition $T = T_m$. Then

$$\tau_2(T) = 661 \cdot \exp(-\Delta G(T)/TS_c(T)) \quad (5)$$

An estimate for $T = T_m$ gives $\tau_2 = 243 \text{ s}$, and for $T = 583 \text{ K}$ gives $\tau_2 \rightarrow 0$ (when evaluated without vibrational entropy).

Hence, under conditions of low-temperature studies, the processes of IPDs recombination occur at rather high rate. We also note that based on a simple assumption about the similarity of crystalline structures we obtained results similar to the study of the recombination of IPDs in silicon. Our theoretical calculations confirm model of entropy barrier in germanium, the essence of which is that the decrease in barrier is due to a decrease in the configurational entropy with decreasing temperature.

3. High-temperature impurity precipitation during growth of dislocation-free single crystals of germanium

Let us consider a system of a growing undoped dislocation-free single crystal of germanium. The concentrations of all point defects at the crystallization front are equilibrium, while in commensurate concentrations there are both vacancies and interstitials [1]. During crystal cooling after passing through diffusion zone, an excess (non-equilibrium) concentration of IPDs occurs. Since there is no recombination of IPDs, the disappearance of excess IPDs occurs at sinks, the role of which in this process, as well as in silicon, is played by uncontrolled (background) oxygen and carbon impurities. We consider the elastic interaction during the formation of “impurity + IPD” complexes in conditions of absence the IPDs recombination process at high temperatures. First, we find out the processes near crystallization front. We seek a solution in framework of model of dissociative diffusion-migration of impurities [17]. In this case, the difference from the decay phenomenon lies in the fact that in diffusion, as a technological process, the diffusant enters the sample from an external source, and in case of decay from the internal source, i.e. from lattice sites. The theoretical analysis is the same, however, when determining dissociative diffusion, one should take into account the surface concentration, which decreases in the sample volume over time along the coordinate. The time constant is determined by migration mechanism in sample volume, and the dependence on coordinate is determined by shape of the sample and the boundary conditions of diffusion task.

Without stopping on solution of the system of equations of the model of dissociative diffusion-migration of impurities [1], we indicate that three cases are considered in practice. They are defined as sequential, simultaneous and mutual diffusion. Under the conditions of our physical model, we can speak of sequential diffusion, when the condition for the absence of the flow of one component located at the initial time in sample bulk is specified at the interface. This calculation is relevant at initial stages of nucleation, when nuclei's sizes are small and the use of continual Fokker-Planck differential equations is impossible. Let us consider an approach in form of systems of interconnected discrete differential equations of quasi-chemical reactions for describing the initial stages of nucleation of new phases and a similar system of Fokker-Planck differential equations.

We describe the kinetics of simultaneous nucleation and growth (dissolution) of an impurity supersaturated solid solution in germanium of a new type of particles. For this, it is necessary to consider a system consisting of oxygen atoms, carbon, vacancies, and interstitials. To set up and interpret computational experiments, it is necessary to carry out a dimensional analysis of kinetic equations and conservation laws using the characteristic time constants and critical sizes of defects. This will allow a comparative analysis of joint evolution of oxygen and carbon precipitates and to optimize the computational scheme for the numerical solution of equations.

The nucleation and evolution during crystal cooling of a complex system of grown-in microdefects, which consists of oxygen precipitates and carbon precipitates, are described by systems of coupled differential equations for each type of defect. The connection between these systems is carried out through the laws of conservation of point defects, which determine the current values of their concentrations in crystal and affect the growth and dissolution rates of both two types of clusters. In case of a thin plane-parallel crystalline plate of large diameter, when the conditions in plane parallel to crystal surface can be considered uniform and diffusion can only be considered along the normal to the surface (z coordinate axis), the mass balance of point defects in crystal is described by a system of diffusion equations for interstitials, oxygen atoms, carbon and vacancies:

$$\frac{\partial C_o}{\partial t} = D_o \frac{\partial^2 C_o}{\partial z^2} - \frac{\partial C_o^{GeO_2}}{\partial t}$$

$$\frac{\partial C_c}{\partial t} = D_c \frac{\partial^2 C_c}{\partial z^2} - \frac{\partial C_c^{GeC}}{\partial t}$$

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial C_i^{GeO_2}}{\partial t} - \frac{\partial C_i^{GeC}}{\partial t} \quad (6)$$

$$\frac{\partial C_v}{\partial t} = D_v \frac{\partial^2 C_v}{\partial z^2} - \frac{\partial C_v^{GeO_2}}{\partial t} + \frac{\partial C_v^{GeC}}{\partial t}$$

Eq. (6) take into account that oxygen precipitates are both sinks for oxygen atoms and vacancies, and sources of interstitials. Then

$$C_o^{GeO_2} = \sum_{n_o=2}^{n_o^{min}-1} n_o f_{GeO_2}(n_o, z, t) + \int_{n_o^{min}}^{n_o^{max}} n_o f_{GeO_2}(n_o, z, t) dn_o$$

$$C_v^{GeO_2} = \gamma_o C_o^{GeO_2}, C_i^{GeO_2} = \gamma_i C_o^{GeO_2} \quad (7)$$

At the same time, carbon precipitates, in turn, are sinks for carbon atoms and interstitials, as well as sources of vacancies. Then

$$C_c^{GeC} = \sum_{n_c=2}^{n_c^{min}-1} n_c f_{GeC}(n_c, z, t) + \int_{n_c^{min}}^{n_c^{max}} n_c f_{GeC}(n_c, z, t) dn_c$$

$$C_v^{GeC} = \gamma_v^* C_c^{GeC}, C_i^{GeC} = \gamma_i^* C_c^{GeC} \quad (8)$$

In general case, the proportionality factors γ_o , γ_i , γ_v^* , γ_i^* can depend on quantities n_o , n_c and are determined by the conditions of thermodynamic equilibrium. In addition, the recombination of interstitials and vacancies is not taken into account in Eq. (6).

The system of interrelated Fokker-Planck equations can be transformed to a dimensionless form:

$$\frac{\partial f_{GeO_2}^*}{\partial \tau} = - \frac{\partial I_{GeO_2}}{\partial v_o^*}$$

$$\frac{\partial f_{GeC}^*}{\partial \tau} = - \frac{t_o}{t_c} \frac{\partial I_{GeC}}{\partial v_c^*} \quad (9)$$

where $\tau = \frac{t}{t_o}$ is a dimensionless time. The time constants in Eq. (9) are given by the expressions $t_o = (n_o^{cr,o})^2 / g_{GeO_2}^o$; $t_c = (n_c^{cr,o})^2 / g_{GeC}^o$, where are critical growth rates of precipitates $g_{GeO_2}^o = N_o^* v_o \exp(-G_{act}^{GeO_2} / kT)$; $g_{GeC}^o = N_c^* v_c \exp(-G_{act}^{GeC} / kT)$. The normalized sizes of precipitates are defined in Eq. (9) as $v_o^* = \frac{n_o}{n_o^{cr,o}}$; $v_c^* = n_c / n_c^{cr,o}$, where n_o^{cr} , n_c^{cr} is a normalizing critical dimensions of precipitates. The values $N_o^* = 4\pi (r_o^{cr,o})^2 \delta_{GeO_2} C_o^{eq}$; $N_c^* = 4\pi (r_c^{cr,o})^2 \delta_{GeC} C_c^{eq}$ are the number of particles in vicinity of the corresponding critical precipitates. The size distribution functions of precipitates in Eq. (9) are normalized to the initial concentrations of the corresponding nucleation centers:

$$f_{GeO_2}^* = \frac{f_{GeO_2}}{f_{GeO_2}^o}; f_{GeC}^* = \frac{f_{GeC}}{f_{GeC}^o} \quad (10)$$

Particle flows in the right-hand sides of Eq. (9) are described by equations

$$I_{GeO_2} = (g_{GeO_2}^* - d_{GeO_2}^*) n_o^{cr,o} - \frac{\partial B_{GeO_2}}{\partial v_o^*}$$

$$I_{GeC} = (g_{GeC}^* - d_{GeC}^*) n_o^{cr,o} - \frac{\partial B_{GeC}}{\partial v_o^*} \quad (11)$$

in which for normalized kinetic coefficients the following notation is used

$$B_{GeO_2} = \frac{g_{GeO_2}^* + d_{GeO_2}^*}{2}; B_{GeC} = \frac{g_{GeC}^* + d_{GeC}^*}{2} \quad (12)$$

The normalized growth and dissolution rates of precipitates in (11)-(12) have form

$$g_{GeO_2}^* = \frac{g_{GeO_2}}{g_{GeO_2}^0}; g_{GeC}^* = \frac{g_{GeC}}{g_{GeC}^0}; d_{GeO_2}^* = \frac{d_{GeO_2}}{g_{GeO_2}^0}; d_{GeC}^* = \frac{d_{GeC}}{g_{GeC}^0} \quad (13)$$

The critical size of precipitates can be defined as:

$$r_O^{cr} = \frac{2\sigma u V_p}{kT \ln(S_0 S_i^{-\gamma_i} S_v^{-\gamma_v}) - 6\mu\delta\epsilon u V_p} \quad (14)$$

$$r_C^{cr} = \frac{2\sigma u V_p}{kT \ln(S_c S_i^{\gamma_i} S_v^{-\gamma_v}) - 6\mu\delta\epsilon u V_p} \quad (15)$$

where $S_0 = C_0/C_0^{eq}$, $S_c = C_c/C_c^{eq}$, $S_i = C_i/C_i^{eq}$, $S_v = C_v/C_v^{eq}$ are supersaturations of oxygen atoms, carbon, interstitials and vacancies, accordingly; σ is a surface energy density of the interface between precipitate and matrix; μ is a germanium shear modulus; δ and ϵ are relative linear and volumetric deformations of discrepancy between precipitate and matrix; γ_i and γ_v are fractions of interstitials and vacancies per one impurity atom attached to the precipitate; V_p is a precipitate molecule volume; $u = (1 + \gamma_i x + \gamma_v x)^{-1} \cdot (\frac{1+\epsilon}{1+\delta})^3$.

The number of impurity atoms in compressed precipitates with radii r_O and r_C is defined as:

$$n_{O,C} = \frac{4\pi r_{O,C}^3 \cdot (1 + \gamma_i x + \gamma_v x)}{3V_p} \left(\frac{1 + \delta}{1 + \epsilon}\right)^3 \quad (16)$$

where V_p is a precipitate volume, x is a fraction of impurity atoms per one intrinsic defect, $x \leq 2$, $\gamma_i \leq 1/2$, $\gamma_v \leq 1/2$.

At the second stage of precipitation process, clusters grow without changing their number. This significantly reduces the degree of supersaturation of solid solution. We can calculate the average radius of precipitate at some growth stage:

$$R(t) = \sqrt[3]{\frac{3bi(t)}{4\pi}} \quad (17)$$

where $i(t) = \frac{N(0) - N(t)}{N_c}$ is a average number of particles at nucleation centers; $N(0)$ is a particle concentration at the initial time; $N(t)$ is a particle concentration change over time; N_c is a concentration of nucleation centers; b is a free particle capture radius.

At the third stage of the precipitation process, when the particles of formed phase are sufficiently large, the supersaturation is small, new particles are no longer formed, and coalescence plays a decisive role, which is accompanied by the dissolution of small particles and the growth of large particles. The condition for the transition to the stage of coalescence is the ratio $u(t) = \frac{R(t)}{R_{cr}(t)} \approx 1$, where $R_{cr}(t)$ is a critical radius of precipitate. Under this condition, the precipitate is in equilibrium with the solution ($\frac{dR}{dt} = 0$). For $R(t) > R_{cr}(t)$ the precipitate grows, and when $R(t) < R_{cr}(t)$ the precipitate dissolves. Over time $R_{cr}(t)$ increases and the number of particles per unit volume decreases [1]. The solution of the system of equations describing this process is possible only when the supersaturation of dissolved substance tends to zero.

The average size of precipitates at the stage of coalescence is proportional to the cubic root of time [1]:

$$R_{sr}(t) = \sqrt[3]{R_{cr}^3(t_0) + \frac{4D\beta t}{9}} \quad (18)$$

where D is a diffusion coefficient of impurity atoms; $\beta = \left(\frac{\sigma\Omega}{kT}\right)N(0)$; $R_{cr}(t_0)$ is an initial critical radius; σ is a surface tension of "precipitate - solid solution" interface; Ω is an atomic volume.

The interpretation of the aim as determining the feasibility and evaluation of the application of high-temperature precipitation model is due to the fact that, unlike silicon, for germanium many of the calculation parameters are either absent or not precisely determined. This is mainly due to the fact that over the past fifty years, researchers around the world have devoted all their attention to silicon crystals. Therefore, it is very likely that as a result of subsequent studies, the calculations of this our study will be clarified.

The following values were used in the calculations:

$$V_p = 5.47 \cdot 10^{-2} \text{ nm}^3 (\text{GeO}_2); V_p = 0.1094 \text{ nm}^3 (\text{GeC}); \sigma = 250 \text{ erg/cm}^2 (\text{GeO}_2); \sigma = 125 \text{ erg/cm}^2 (\text{GeC}); \mu = 3.1 \cdot 10^{10} \text{ Pa}; \delta = 0.3; \epsilon = 0.15; \gamma_i = 0.4; \gamma_v = 0.1; x = 1.5; \delta_{GeO_2} = 0.5431 \text{ nm}; \delta_{GeC} = 0.4359 \text{ nm}; C_0^{eq} = 8 \cdot 10^{16} \text{ cm}^{-3}; C_c^{eq} = 1 \cdot 10^{16} \text{ cm}^{-3}; k = 8.6153 \cdot 10^{-5} \text{ eV/K}; D_0 = 0.17 \exp(-2.54 \text{ eV/kT}); D_c = 1.9(-3.1 \text{ eV/kT}); G_{act}^{GeO_2} = 2.54 \text{ eV}; G_{act}^{GeC} = 3.17 \text{ eV} [4,9,11-15].$$

The solution of sequential diffusion equations has physical meaning only when $\lambda_0 \approx 0.001$. In the strong complexation approximation λ_0 is interpreted as the boundary of the front of the complex formation reaction [1]. Since x is a crystal length, and the value $x = 0$ position of crystallization front, we can say that the complexation process occurs near crystallization front. Compared with silicon, in germanium this value is an order of magnitude lower [17].

From the physical viewpoint, λ_0 is a diffusion layer on which, due to the absence of IPDs recombination at high temperature, their excess concentration arises. When analyzing the evolution of grown-in microdefects during crystal cooling after its growth, important parameters are characteristic constants in the size space: the critical sizes of corresponding grown-in microdefects, and the associated characteristic time constants that specify the scale of time-dependent changes in the size distribution function of microdefects. The time constants in Eq. (9) allow us to calculate the normalizing sizes $n_O^{cr,0}$ и $n_C^{cr,0}$ by substituting in (14)–(15) the values of supersaturations corresponding to the complete escape of oxygen and carbon atoms into precipitates. Wherein in each equation the supersaturations of the remaining point defects, they are assumed to be equal to unity.

An increase in the values of supersaturation of point defects (oxygen and carbon atoms, interstitials and vacancies) leads to a decrease of the corresponding critical size of precipitates and helps to accelerate their growth. The acceleration of precipitation processes with increasing supersaturation of point defects leads to a decrease in characteristic times. An important property of characteristic times is the inverse proportionality to the products of the characteristics of point defects (diffusion coefficients and equilibrium concentrations):

$$t_0 \sim (D_0 C_0^{eq})^{-1} t_c, \sim (D_c C_c^{eq})^{-1} \quad (19)$$

Since the product for oxygen atoms significantly exceeds the similar product for carbon atoms, the rate of evolution of the size distribution function of carbon precipitates will exceed the corresponding rate for oxygen precipitates. This means that the picture of the microdefect structure development of dislocation-free germanium single crystals is determined mainly by growth rate of oxygen precipitates. Detailed quantitative information about characteristics of primary grown-in microdefects can be obtained by numerical calculations of Eq. (9).

The algorithm for solving the task of simulating the simultaneous growth and dissolution of oxygen and carbon precipitates due to the interaction of point defects during cooling of the crystal from the crystallization temperature is based on the use of a monotonic explicit difference scheme of the first order of accuracy for Fokker-Planck Eq. (9).

On Fig. 1 shows the dependence of critical radius of oxygen and carbon precipitates. Near crystallization front (at $T = 1210$ K), the size of the critical nucleus of oxygen precipitate is 1.1 nm, and the size of the critical carbon nucleus reaches 0.6 nm. The minimum values of $n_O^{cr} = n_O^{cr,0}$ and $n_C^{cr} = n_C^{cr,0}$ are reached in the initial state at $T = 1210$ K and increase with decreasing temperature. An increase of critical radius of precipitates during crystal cooling leads to a sharp decrease in their growth rate and, accordingly, to a sharp decrease in the kinetics of their precipitation.

An accurate estimate of the critical radius of carbon precipitate (GeC) is difficult due to the lack of complete experimental data. It can be assumed that $\sigma = 750 \text{ erg/cm}^2$. The number of impurity atoms in precipitates near crystallization front is $n_O \approx 135$ and $n_C \approx 25$, respectively.

The simulation of the kinetics of defect formation during cooling of a growing crystal according to the exponential law in temperature

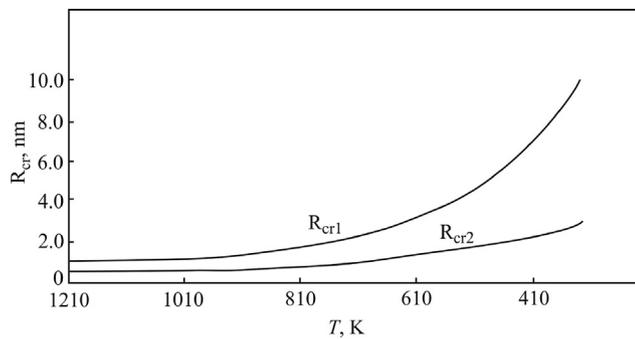


Fig. 1. Dependence the critical radius of oxygen (1) and carbon (2) precipitates on temperature upon crystal cooling after crystal growth.

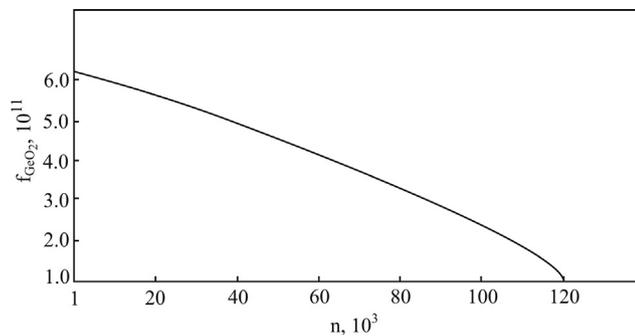


Fig. 2. Oxygen precipitate size distribution function $f_{GeO_2}(n)$ upon crystal cooling after crystal growth.

range from 1210 K to 300 K is shown in Fig. 2. In this computational experiment, by analogy with silicon, it was assumed that the concentration of nucleation centers for oxygen and carbon precipitates is $\sim 10^{12} \text{ cm}^{-3}$. On Fig. 2 shows the size distribution function of spherical oxygen precipitates.

These dependences demonstrate a significant effect of IPDs on the dynamics of mass transfer of point defects between oxygen and carbon precipitates. Absorption of vacancies by growing oxygen precipitates leads to the emission of germanium atoms into the interstices. Germanium interstitials, in turn, interact with growing carbon precipitates, which in process of their growth provide vacancies for growing oxygen precipitates. Such interaction leads to the fact that, firstly, the growth of precipitates is not so strongly suppressed due to a slower increase in the supersaturation of IPDs in the volume of growing crystal and, secondly, the critical radius of formation of carbon precipitates increases more slowly, which contributes to a faster growth of carbon precipitates.

The processes of growth and coalescence of precipitates were considered under the assumption of a fixed number of nucleation centers under the diffusion growth mechanism. Two separate groups of calculations were carried out that simulated precipitation processes when growing crystals of large and small diameters using the Czochralski method. The first Group of calculations (I) was carried out with the following parameters: crystal growth rate $V = 0.6 \text{ mm/min}$, axial temperature gradient $G = 2.5 \text{ K/cm}$, $N(0) = 10^{17} \text{ cm}^{-3}$ for oxygen concentration and $N(0) = 10^{14} \text{ cm}^{-3}$ for carbon concentration. Parameters of the second Group of calculations (II): crystal growth rate $V = 1.2 \text{ mm/min}$, axial temperature gradient $G = 2.5 \text{ K/cm}$, $N(0) = 10^{15} \text{ cm}^{-3}$ for oxygen concentration and $N(0) = 10^{14} \text{ cm}^{-3}$ for carbon concentration. For both Groups of calculations $T = \frac{T_m^2}{T_m + VGt}$, where T_m is a melting temperature; $N(0) = 0, 1N_E, N_c = 10^{12} \text{ cm}^{-3}$; $\alpha = 1/3$.

The calculation results in Groups I and II make it possible to compare the precipitation processes in germanium crystals obtained under

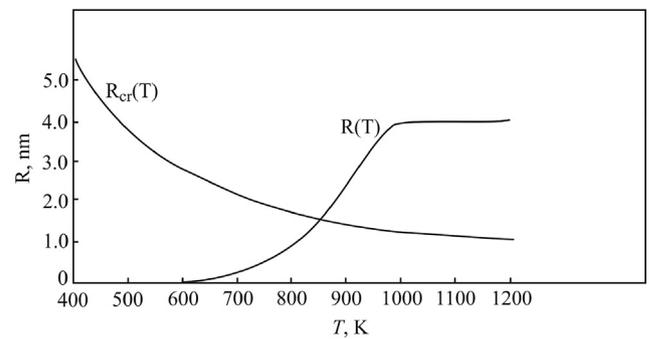


Fig. 3. Transition to the stage of coalescence of oxygen precipitates for crystals of Group I.

various thermal growth conditions. The average size of oxygen precipitates ca. 2 nm (Fig. 3); their initial concentration is determined by analogy from experiments on quenching of silicon crystals ($\sim 10^{12} \dots 10^{13} \text{ cm}^{-3}$). With a decrease in oxygen content, a decrease in the size of precipitates occurs at the stage of their growth. The phase transition occurs according to the mechanism of nucleation and growth of a new phase, and both of these processes are not separated in time and proceed in parallel. A twofold increase in the axial temperature gradient causes a nearly twofold decrease in the average size of oxygen precipitates at the growth stage.

Analyzing the data obtained in Figs. 1–3 we can say the following. Fig. 1 shows that the smallest critical size of precipitate nucleus is reached near the crystallization front. This result mean that impurity precipitation begins at high temperatures. The data on the calculation of the distribution function, presented in Fig. 2, confirm the fact that the probability of precipitate nucleation is greater, the higher of temperature. Fig. 3 illustrates the conditions for transition from stage of growth of the precipitate to its coalescence. The condition for the transition to the coalescence stage is $R(t) \approx R_{cr}(t)$ what is satisfied at $T \approx 850 \text{ K}$ (Fig. 3). With a decrease in the oxygen content in Group II crystals, the condition for the transition to the coalescence stage will correspond to a cooling temperature $T \approx 940 \text{ K}$.

It should be noted that the process of formation and growth of precipitates during crystal cooling is a determining step in the formation of the grown-in defective structure of dislocation-free germanium single crystals. At this stage, the formation and growth of impurity precipitates occurs. The defect structure of dislocation-free germanium single crystals was calculated at the stage of formation and growth of impurity precipitates based on the approximate solution of Fokker-Planck type equations. It was shown that the precipitation process begins near crystallization front and is caused by disappearance of excess IPDs at sinks, the role of which is played by impurity atoms.

4. Conclusion

Thermodynamic calculations show that the process of aggregation of point defects prevails over the process of recombination between IPDs. The contribution of the recombination process at high temperatures to the aggregation process is negligible. Therefore, vacancies and interstitial atoms coexist in thermal equilibrium. Therefore, both types of IPDs participate simultaneously in the aggregation process. The decomposition of a supersaturated solid solution of point defects caused by cooling occurs by two mechanisms: vacancy and interstitial, leading to the formation of “impurity-vacancy” and “impurity-interstitial” agglomerates.

The possibility of applying the mathematical apparatus of a diffusion model of the formation of structural imperfections to the formation of a defective structure in undoped dislocation-free germanium single crystals is considered. Calculations showed that nucleation processes occur very quickly near crystallization front. Therefore, the proposed

kinetic model of defect formation makes it possible to describe the formation and development of a defect structure during the growth of dislocation-free single crystals of germanium.

This conclusion allows us to conclude that the diffusion model of defect formation is of a general nature. It can be used not only for silicon and germanium crystals but also for other dislocation-free materials. It is necessary to take into account the crystal structure, thermal growth conditions, and calculation parameters that would be adequate for experimental studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] V.I. Talanin, I.E. Talanin, *The Formation of Structural Imperfections in Semiconductor Silicon*, Cambridge Scholars Publ, Newcastle, 2018.
- [2] V.I. Talanin, I.E. Talanin, On the recombination of intrinsic point defects in dislocation-free silicon single crystals, *Phys. of the Solid State* 49 (2007) 467–471, <https://doi.org/10.1134/S1063783407030134>.
- [3] V.I. Talanin, I.E. Talanin, Kinetics of high-temperature precipitation in dislocation-free silicon single crystals, *Phys. the Solid State* 52 (2010) 2063–2069, <https://doi.org/10.1134/S1063783410100094>.
- [4] J. Vanhellemont, E. Simoen, I. Romandic, A. Theuwis, Grown-in defects in germanium, in: C. Claeys, E. Simoen (Eds.), *Germanium-based technologies from materials to devices*, Elsevier, Amsterdam, 2007, pp. 41–66.
- [5] V.V. Voronkov, M. Kulkarni, B. Dai, Fundamentals and engineering of the Czochralski growth of semiconductors silicon crystals, in: P. Bhattacharya, R. Fornari, H. Kamimura (Eds.) *Comprehensive semiconductor science and technology*, Elsevier, 2011, pp. 81–169. <https://doi/10.1016/B978-0-44-453153-7.00089-4>.
- [6] V.I. Talanin, I.E. Talanin, Diffusion model of the formation of growth microdefects: a new approach to defect formation in crystals (review), *Phys. Solid State* 58 (2016) 427–437. <https://doi.org/10.1134/S106378341603029X>.
- [7] U. Gosele, W. Frank, A. Seeger, An entropy barrier against vacancy-interstitial recombination in silicon, *Solid State Commun.* 45 (1983) 31–33, [https://doi.org/10.1016/0038-1098\(83\)90878-5](https://doi.org/10.1016/0038-1098(83)90878-5).
- [8] S.S. Kapur, M. Prasad, J.C. Crocker, T. Sinno, Role of configurational entropy in the thermodynamics of clusters of point defects in crystalline solids, *Phys. Rev. B* 72 (2005) 014119–14212, <https://doi.org/10.1103/PhysRevB.72.014119>.
- [9] N.E.B. Cowern, S. Simdyankin, C. Ahn, N.S. Bennett, J.P. Goss, J.-M. Hartmann, A. Pakfar, S. Hamm, J. Valentin, E. Napolitani, D. De Salvador, E. Bruno, S. Mirabella, Extended point defects in crystalline materials: Ge and Si, *Phys. Rev. Lett.* 110 (2013) 155501, <https://doi.org/10.1103/PhysRevLett.110.155501>.
- [10] M. Ian Hodge, Adam-Gibbs formulation of enthalpy relaxation near the glass transition, *J. Res. Natl. Inst. Stand. Technol.* 102 (1997). 195–202. <https://doi.org/10.6028/res.102.015>.
- [11] P. Clauws, Oxygen in germanium, in: C. Claeys, E. Simoen (Eds.), *Germanium-based technologies from materials to devices*, Elsevier, Amsterdam, 2007, pp. 97–130.
- [12] E. Hüger, U. Tietze, D. Lott, H. Bracht, D. Bougeard, E.E. Haller, H. Schmidt, Self-diffusion in germanium isotope multilayers at low temperatures, *Appl. Phys. Letters* 93 (2008) 162104–162113, <https://doi.org/10.1063/1.3002294>.
- [13] P. Śpiewak, K.J. Kurzydłowski, K. Sueoka, I. Romandic, J. Vanhellemont, First principles calculations of the formation energy of the neutral vacancy in germanium, *Solid State Phenomena* 131–133 (2008) 241–246. <https://doi:10.4028/www.scientific.net/SSP.131-133.241>.
- [14] M. Werner, H. Mehrer, H.D. Hochheimer, Effect of hydrostatic pressure, temperature, and doping on self-diffusion in germanium, *Phys. Rev. B* 32 (1985) 3930–3937, <https://doi.org/10.1103/PhysRevB.32.3930>.
- [15] J. Vanhellemont, P. Śpiewak, K. Sueoka, I. Romandic, On intrinsic point defect cluster formation during Czochralski crystal growth, *Phys. Stat. Sol. (c)* 6 (2009) 1906–1911. <https://doi.org/10.1002/pssc.200881456>.
- [16] H. Lemke, W. Sudkamp, Analytical approximations for the distributions of intrinsic point defects in grown silicon crystal, *Phys. Stat. Sol. (a)* 176 (1999) 843–865, [https://doi.org/10.1002/\(SICI\)1521-396X\(199912\)176:2<843::AID-PSSA843>3.0.CO;2-8](https://doi.org/10.1002/(SICI)1521-396X(199912)176:2<843::AID-PSSA843>3.0.CO;2-8).
- [17] V.I. Talanin, I.E. Talanin, A.A. Voronin, About formation of grown-in microdefects in dislocation-free silicon single crystals, *Can. J. Phys.* 85 (2007) 1459–1471, <https://doi.org/10.1139/p07-094>.