

Diffusion Model of the Formation of Growth Microdefects as Applied to the Description of Defect Formation in Heat-Treated Silicon Single Crystals

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Abstract—The diffusion model of the formation of growth microdefects has been considered as applied to the description of defect formation in heat-treated silicon single crystals. It has been shown that, in the framework of the proposed kinetic model of defect formation, the formation and development of the defect structure during the growth of a crystal and its heat treatment can be considered within a unified context. The mathematical apparatus of the diffusion model can provide a basis for the development of a program package for the analysis and calculation of the formation of growth and postgrowth microdefects in dislocation-free silicon single crystals. It has been demonstrated that the diffusion model of the formation of growth and postgrowth microdefects allows one to determine necessary conditions for the growth of a crystal and the regimes of its heat treatment for the preparation of a precisely defined defect structure.

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1. INTRODUCTION

The presence of structural defects in dislocation-free silicon single crystals determines the physical properties of these crystals and the quality of silicon-based device structures. Structural defects are formed both during the crystal growth (growth microdefects) and in the process of the manufacture of semiconductor devices (postgrowth microdefects).

We have developed a diffusion model of the formation of growth microdefects during cooling of the crystals after their growth [1]. The proposed diffusion model includes a physical model and mathematical models of the formation of precipitates, dislocation loops, and microvoids [2]. The physical model is based on the established fact that there is no recombination of intrinsic point defects in the vicinity of the crystallization front [3]. Using the physical model as the basis, we developed for the first time a model of high-temperature precipitation of impurities [4]. This model describes the processes of nucleation, growth, and coalescence of precipitates in the temperature range of cooling the crystal from 1683 to 300 K. It has been shown that, at temperatures $T < 1423$ K, depending on the growth parameter V_g/G (where V_g is the growth rate and G is the axial temperature gradient), either the homogeneous formation of microvoids or the formation of interstitial dislocation loops occurs under the influence of the deformation mechanism [5]. Recently, we proposed a kinetic model for the formation of dislocation loops during the crystal growth based on the deformation mechanism [6].

The model of high-temperature precipitation in combination with the kinetic models of the formation and growth of dislocation loops and microvoids form a mathematical apparatus that makes it possible to describe theoretically the formation and transformation of growth microdefects in dislocation-free silicon single crystals with any diameter grown by the Czochralski and floating zone melting methods. The main advantage of the mathematical apparatus of the diffusion model is the dependence of the characteristics of growth microdefects on the thermal conditions used for the growth of crystals (such as the growth rate, temperature gradient, cooling rate, and diameter of the crystals). This fact allowed us to develop the first program package for the analysis and calculation of growth microdefects in dislocation-free silicon single crystals [7].

The developed program package makes it possible to solve the following problems: (i) simulation of a real experiment, which with a maximum accuracy reproduces real characteristics of the process of growth of silicon single crystals; (ii) determination of thermal conditions of crystal growth, prediction of the defect structure of the crystal, and control of the defect formation in the crystal; and (iii) reduction of time and material costs for performing experimental investigations of the defect structure using the methods of optical microscopy, transmission electron microscopy, and X-ray diffraction for the observation of surface and structural defects. The replacement of experimental structural investigations by adequate theoretical studies using the developed program package has

demonstrated that this program package is a new virtual experimental tool [7].

Since the diffusion model allows one to adequately describe the formation of a defect structure during the crystal growth, the question arises as to whether the mathematical apparatus of the diffusion model of the formation of growth microdefects can be used for the description of the formation of a defect structure of silicon-based devices. Indeed, it is the postgrowth microdefects that determine the quality of silicon semiconductor devices. In the process of the manufacture of semiconductor devices, the main technological effect exerted on the crystal is provided by heat treatments which critically affect the defect structure of the crystal. It seems reasonable to argue that the formation of growth and postgrowth microdefects should be described within a unified context.

In this respect, the objective of the present work was to formulate and solve the problem of using the diffusion model of the formation of growth microdefects for the description of the formation of a defect structure during the heat treatment of the crystal.

2. MATHEMATICAL MODEL OF THE FORMATION OF POSTGROWTH MICRODEFECTS

In order to evaluate the applicability of the diffusion model of the formation of growth microdefects for the description of the formation of a defect structure in heat-treated single crystals, we use a hypothetical model of a perfect crystal. It is assumed that, in this case, we are dealing with a defect-free undoped silicon single crystal at a temperature $T = 300$ K, which was grown by the Czochralski method. As follows from numerous experimental investigations, the heating of the crystal in the temperature range from 623 to 823 K results in the formation of structural imperfections in the form of SiO_2 precipitates [8]. It is assumed that $T = 723$ K is the minimum temperature of the formation of structural imperfections in dislocation-free silicon single crystals. We will consider the chosen model of the crystal in terms of the diffusion model of the formation of growth microdefects.

According to the diffusion model of the formation of growth microdefects, the determining factor of the beginning of the defect formation process is the formation of "impurity–intrinsic point defects" complexes. It should be noted that, in real silicon crystals, the concentration of uncontrolled (background) impurities of oxygen and carbon is higher than the concentration of intrinsic point defects. The formation of complexes between the intrinsic point defects and impurities is determined, on the one hand, by the fact that both the intrinsic point defects and impurities are sources of internal stresses in the lattice (elastic interaction) and, on the other hand, by the Coulomb interaction between them (if the defects and impuri-

ties are in charged states). At present, the diffusion model takes into account only the elastic interaction. Elastic strains and related mechanical stresses cause the transfer of excess (or deficient) substance from a precipitate (or to it). The accumulation of the elastic energy during the growth of the precipitate results in a loss of coherence with the matrix, when it is impossible to establish a one-to-one correspondence between the atoms on different sides of the interface. This leads to a structural relaxation of precipitates, which occurs through the formation and motion of dislocation loops.

Since the mathematical formalism of the diffusion model of the formation of growth microdefects is thoroughly described in our recent publications [4, 9] and in the review [2], in this paper, we present only the final formulas needed for the calculations.

The critical sizes of oxygen precipitates (SiO_2) and carbon precipitates (SiC) are determined according to the expressions [4, 10]

$$r_{\text{O}}^{\text{cr}} = \frac{2\sigma u V_p}{kT \ln(S_o S_i^{-\gamma_i} S_v^{\gamma_v}) - 6\mu\delta\epsilon u V_p}, \quad (1)$$

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

where $S_o = C_o/C_o^{\text{eg}}$, $S_c = C_c/C_c^{\text{eg}}$, $S_i = C_i/C_i^{\text{eg}}$, and $S_v = C_v/C_v^{\text{eg}}$ are the supersaturations of oxygen atoms, carbon atoms, self-interstitial silicon atoms, and vacancies, respectively; σ is the density of the surface energy of the interface between the precipitate and the matrix; μ is the shear modulus of silicon; δ and ϵ are the linear and volumetric misfit strains of the precipitate and the matrix, respectively; γ_i and γ_v are the fractions of self-interstitial silicon atoms and vacancies per impurity atom attached to the precipitate, respectively; V_p is the molecular volume of the precipitate;

$$\text{and } u = (1 + \gamma_i x + \gamma_v x)^{-1} \left(\frac{1 + \epsilon}{1 + \delta} \right)^3.$$

The number of impurity atoms in compressed precipitates with the radii r_o and r_c is determined as follows [11, 12]:

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

where V_p is the volume of the precipitate, $x \leq 2$, $\gamma_i \leq 1/2$, and $\gamma_v \leq 1/2$.

The average number of particles on nucleation centers is given by the expression [9]

$$i(t) = \frac{\sum_{i=0} iN_i}{\sum_{i=0} N_i} = \frac{N(0) - N(t)}{N_c}, \quad (4)$$

where N_i is the volume-averaged concentration of nucleation centers with i attached particles; $N(0)$ is the concentration of monomers at the initial instant of time; $N_c \sum_{i=1} N_i(t)$ is the concentration of nucleation centers; and t is the time.

The change in the concentration of monomers during the decomposition of a solid solution is determined from the following formula [13]:

$$\frac{dN(t)}{dt} = -k_0 N_c^{1-\alpha} (N(t) - N_E) \times (N(0) + m N_c N(t))^\alpha, \quad (5)$$

where $k_0 = 4\pi R_i D$, m is the initial size of the precipitate; α is the parameter depending on the geometry of the clusters; and N_E is the equilibrium concentration of monomers.

By numerically solving equation (4) together with equation (5), we can calculate the average radius of the precipitate in the growth stage:

$$R(t) = \sqrt[3]{\frac{3ai(t)}{4\pi}}, \quad (6)$$

where a is a quantity of the order of the distance between particles in the precipitate.

The third stage of the process begins to occur after some time, when particles of the new phase are sufficiently large, the supersaturation is small, new particles are not formed, and the decisive role is played by the coalescence, which is accompanied by the dissolution of small particles and the growth of large particles. The condition for transition to the coalescence stage is

the ratio $u(t) = \frac{R(t)}{R_{cr}(t)} \approx 1$, where $R_{cr}(t)$ is the critical

radius of the precipitate. Under this condition, the precipitate is in equilibrium with the solution:

$\left(\frac{dR}{dt} = 0\right)$. When $R(t) > R_{cr}(t)$, the precipitate is growing; and when $R(t) < R_{cr}(t)$, the precipitate is dissolved.

The average size of precipitates during the coalescence is proportional to the cube root of time [14]:

$$R_{sr}(t) = \sqrt[3]{R_{cr}^3(t_0) + \frac{4D(T)\beta t}{9}}, \quad (7)$$

where D is the diffusion coefficient of impurity atoms;

$\beta = \left(\frac{\sigma\Omega}{kT}\right)N(0)$; $R_{cr}(t_0)$ is the initial critical radius; σ is

the surface tension of the "precipitate–solid solution" interface; and Ω is the atomic volume.

During the growth of a precipitate, the elastic field induced by it causes the formation of a circular interstitial misfit dislocation loop, which favors a decrease in the total elastic energy of the system. In the crystal volume, the matrix material displaced by the growing precipitate forms an interstitial dislocation loop near the precipitate simultaneously with the formation of a misfit dislocation loop on the precipitate itself [15].

In this case, the critical sizes of precipitates, for which the formation of dislocations becomes energetically favorable, are of the same order of magnitude as the critical size of dislocation loops [15]. The critical radius of the dislocation loop is given by the expression [6]

$$R_{crit} = \sqrt[3]{\frac{45(1-\nu)b^2 d \ln\left(\frac{4d}{f} - 2\right)}{128\pi(1-\nu)\varepsilon^2}}, \quad (8)$$

where d is the diameter of the dislocation loop, f is the core radius of the dislocation loop, b is the magnitude of the Burgers vector, and ν is the Poisson's ratio.

An increase in the radius of an interstitial dislocation loop as a function of the heat treatment time of the crystal can be determined according to the formula [6]

$$R(t) = \sqrt{R_{crit}^2 + jD_i(T)t}, \quad (9)$$

where $D_i(t)$ is the diffusion coefficient of self-interstitial silicon atoms, t is the annealing time of the crystal, and j is the coefficient of proportionality.

The dependence of the concentration of dislocation loops on the heat treatment time of the crystal is described by the expression [16]

$$n(t) = \frac{M}{10^3 t^{0.8}}, \quad (10)$$

where M is the concentration of precipitates.

3. EXPERIMENTAL RESULTS

In the calculations, we used the following data: $V_p = 4.302 \times 10^{-2} \text{ nm}^3$ (SiO₂); $V_p = 2.04 \times 10^{-2} \text{ nm}^3$ (SiC); $\sigma = 310 \text{ erg/cm}^2$ (SiO₂); $\sigma = 1000 \text{ erg/cm}^2$ (SiC); $\mu = 6.41 \times 10^{10} \text{ Pa}$; $\delta = 0.3$; $\varepsilon = 0.15$; $\gamma_i = 0.4$; $\gamma_v = 0.1$; $k = 8.6153 \times 10^{-5} \text{ eV/K}$; $a = 0.25 \text{ nm}$; $D_O = 0.17 \exp(-2.54/kT)$; $D_C = 1.9 \exp(-3.1/kT)$; $D_i =$

$0.19497 \exp\left[-\frac{0.9(eV)}{kT}\right] \text{ cm}^2/\text{s}$; $\nu = 0.333$, $f = 0.96 \text{ nm}$; $x = 1.5$; and $b = 0.384 \text{ nm}$.

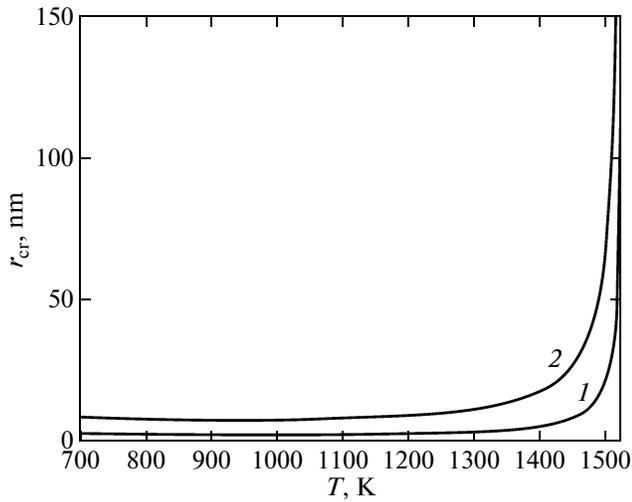


Fig. 1. Dependences of the critical radii of (1) oxygen precipitates and (2) carbon precipitates on the heat treatment temperature.

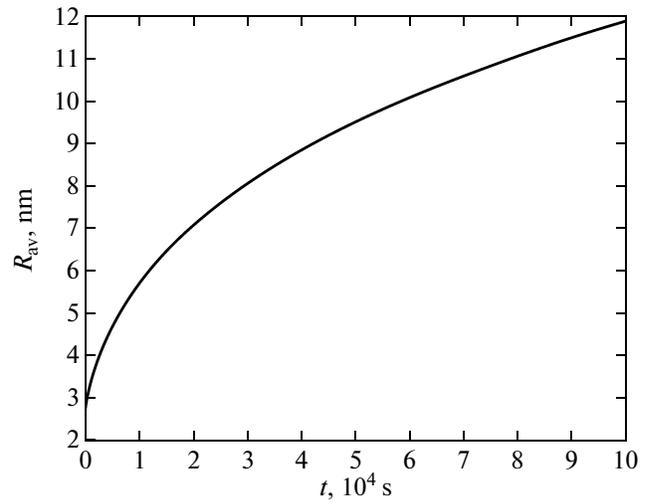


Fig. 2. Dependence of the average radius of oxygen precipitates in the coalescence stage at a constant annealing temperature $T = 1100$ K.

The analysis was performed in the approximation that the growth of precipitates occurs on a fixed number of nucleation centers with the diffusion mechanism of their growth. The model was designed for the uniform precipitation throughout the volume.

Four separate groups of calculations (I–IV), which simulated the processes of precipitation upon heat treatment of defect-free undoped silicon single crystals grown by the Czochralski method, were carried out for the following annealing temperatures: (I) 730, (II) 1000, (III) 1100, and (IV) 1510 K. For all four groups of calculations, we used $N(0) = 10^{18} \text{ cm}^{-3}$ for the concentrations of oxygen and carbon, $N(0) = 0.1N_E$ [13], $N_c = 10^{13} \text{ cm}^{-3}$ [9], and $a = 1/3$ [13].

Figure 1 shows the dependences of the critical radii of oxygen precipitates (curve 1) and carbon precipitates (curve 2) on the heat treatment temperature.

During the heat treatment at a temperature $T = 730$ K, the size of the critical nucleus of an oxygen precipitate (SiO_2) is equal to 2.7 nm, whereas the size of the critical nucleus of a carbon precipitate (SiC) is approximately 8.7 nm. The minimum values of the critical radii of the precipitates are reached in the initial state at a temperature $T = 730$ K and increase with increasing temperature. An increase in the annealing temperature of the crystals leads to an increase in the size of critical nuclei of the precipitates. Furthermore, with an increase in the oxygen concentration at a constant annealing temperature, the size of critical nuclei decreases.

An increase in the critical radius of precipitates during heating of the crystal leads to a sharp decrease in the rate of their growth and, consequently, to a sharp decrease of the kinetics of their precipitation. The kinetics of precipitation during the heating of the crys-

tal is similar to the kinetics of precipitation during the cooling of the crystal in the process of its growth. However, an increase in the critical radius of precipitates during cooling of the crystal occurs with a decrease in the temperature from 1682 to 300 K [4]. This difference is associated with the influence of the growth parameters V_g and G , which determine the processes of defect formation during the crystal growth and are taken into account in the dependence $T(t) =$

$$\frac{T_m^2}{T_m + V_g G t},$$

where T_m is the melting temperature.

The condition for transition to the coalescence stage is the approximate relationship $R(t) \approx R_{cr}(t)$, which is satisfied for the first three groups of crystals (Fig. 2).

In this case, the higher is the annealing temperature of the crystal, the shorter is the time after which the precipitate site begins to satisfy the condition for transition to the coalescence stage. The calculations of the fourth group of crystals have demonstrated that, during annealing of the crystals at a temperature $T > 1500$ K, the coalescence stage at real annealing times does not occur.

The condition for transition to the coalescence stage $R(t) \approx R_{cr}(t)$ in the case of the carbon precipitation does not hold for all four groups of crystals. The results of the performed calculations, together with the larger sizes of critical nuclei of the carbon precipitates as compared to the sizes of critical nuclei of the oxygen precipitates, can indicate that the heat treatment of the crystal occurs predominantly with the oxygen precipitation. In this process, vacancies disappear during the formation and growth of oxygen precipitates, and carbon can participate in the formation of oxygen–carbon complexes. Moreover, the growth

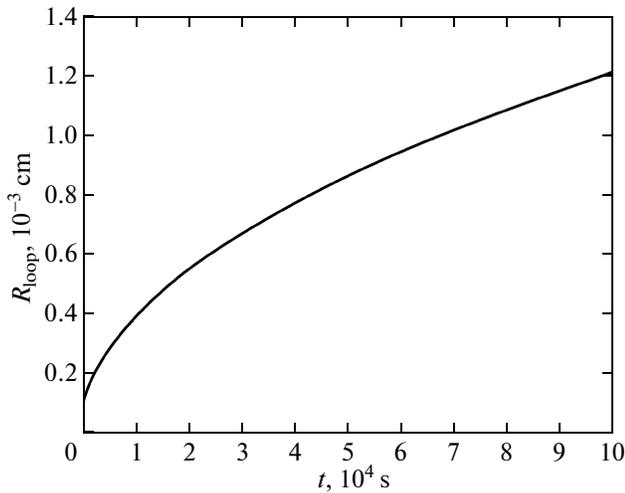


Fig. 3. Dependence of the radius of the interstitial dislocation loops on the heat treatment time at the annealing temperature $T = 1100$ K.

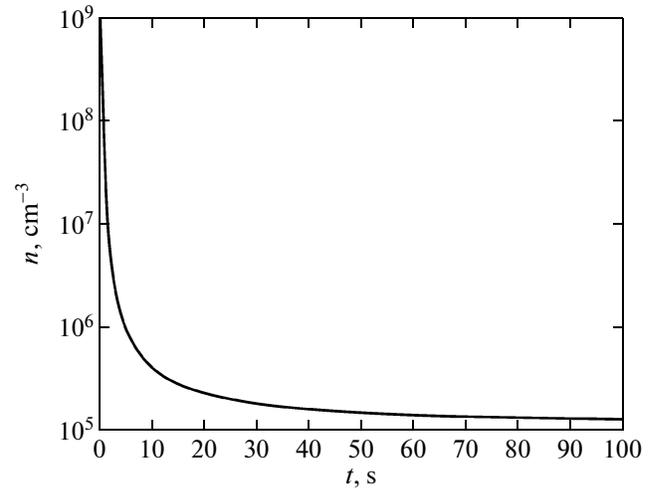


Fig. 4. Dependence of the concentration of dislocation loops on the annealing time.

of oxygen precipitates is accompanied by the precipitation of interstitial silicon atoms in the solid solution of point defects. This leads to the supersaturation in the crystal with interstitial silicon atoms, and microvoids are not formed during the heat treatment. These calculated data are in good agreement with the experimental results obtained from electron microscopy investigations of crystals with microvoids [17]. Short-term heat treatments of these crystals at $T = 1373$ K led to a drastic decrease in the size of microvoids or their complete disappearance [17–19]. At the same time, the growth of precipitates and the supersaturation with interstitial silicon atoms favor the formation and growth of interstitial dislocation loops in the crystal.

Figure 3 shows the change in the radius of an interstitial dislocation loop as a function of the time of heat treatment of the crystal at $T = 1100$ K.

The growth of a dislocation loop during the heat treatment of a silicon single crystal occurs both due to the supersaturation with self-interstitial silicon atoms and by means of the dissolution of small loops with sizes smaller than the critical ones. The results of the computer simulation have demonstrated that the maximum radius of the dislocation loop, whose growth is determined by the diffusion mechanism, is achieved for four groups of crystals, at a heat treatment temperature $T = 1510$ K. An increase in the heat treatment time causes an increase in the size of the dislocation loops and a decrease in their concentration (Fig. 4). For example, the concentration of dislocation loops for $M = 10^{12} \text{ cm}^{-3}$ reaches the value of $6.31 \times 10^5 \text{ cm}^{-3}$.

4. CONCLUSIONS

In this paper, we have considered the possibility of using the mathematical apparatus of the diffusion model of the formation of growth microdefects for the description of the formation of a defect structure in a hypothetically ideal undoped dislocation-free silicon single crystal as a result of its heat treatment. The calculations have demonstrated that the precipitation occurring during the heat treatment of the crystal is primarily associated with the oxygen precipitation. The growth of precipitates causes supersaturation of the crystal with self-interstitial silicon atoms. This process leads to the formation and growth of interstitial dislocation loops. The proposed mechanism of defect formation during the heat treatment of crystals does not contradict numerous experimental and theoretical studies. Consequently, the proposed kinetic model of defect formation allows one to adequately describe the formation and development of a defect structure during the heat treatment of silicon single crystals.

Real silicon single crystals contain growth microdefects that actively participate in the processes of defect formation. Growth microdefects predominantly serve as sinks for intrinsic point defects and impurity atoms. As a result, the growth of defects and the transformation of the initial defect structure proceed in the crystal. Since the distribution of growth microdefects in the crystal is inhomogeneous, the formation and growth of defects can occur according to the proposed mechanism. The transformation of the initial defect structure and the formation of new defects lead to a supersaturation of the crystal with self-interstitial atoms. Therefore, new microvoids are not formed, but the microvoids already formed during the crystal growth either decrease in size or are dissolved [17].

The diffusion model of the formation of growth microdefects, as applied to the formation of growth and postgrowth defect structures, allows one to describe, within a unified context, the formation of a defect structure in silicon single crystals, beginning with the growth of a crystal and ending with the design and fabrication of a device. The construction of a unified (complete) model of defect formation provides a means for predicting specific features of the formation of microdefects at different stages of the process. The mathematical apparatus of the diffusion model can form a basis for the development of a program package for the analysis and calculation of the formation of growth and postgrowth microdefects in dislocation-free silicon single crystals [20]. Using the developed program package, one can determine necessary conditions for the growth of a crystal and the regimes of its heat treatment for the preparation of a precisely defined defect structure.

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