ISSN 1063-7834, Physics of the Solid State, 2016, Vol. 58, No. 3, pp. 427–437. © Pleiades Publishing, Ltd., 2016.
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REVIEWS

Diffusion Model of the Formation of Growth Microdefects: A New Approach to Defect Formation in Crystals (Review)

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Received July 8, 2015

Abstract—Theoretical studies of defect formation in semiconductor silicon play an important role in the creation of breakthrough ideas for next-generation technologies. A brief comparative analysis of modern theoretical approaches to the description of interaction of point defects and formation of the initial defect structure of dislocation-free silicon single crystals has been carried out. Foundations of the diffusion model of the formation of structural imperfections during the silicon growth have been presented. It has been shown that the diffusion model is based on high-temperature precipitation of impurities. The model of high-temperature precipitation of impurities describes processes of nucleation, growth, and coalescence of impurities during cooling of a crystal from 1683 to 300 K. It has been demonstrated that the diffusion model of defect formation provides a unified approach to the formation of a defect structure beginning with the crystal growth to the production of devices. The possibilities of using the diffusion model of defect formation for other semiconductor crystals and metals have been discussed. It has been shown that the diffusion model of defect formation is a platform for multifunctional solution of many key problems in modern solid state physics. Fundamentals of practical application of the diffusion model for engineering of defects in crystals with modern information technologies have been considered. An algorithm has been proposed for the calculation and analysis of a defect structure of crystals.

DOI: 10.1134/S106378341603029X

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1. INTRODUCTION

Despite the significant progress made in the theoretical description of properties of solids (metals and semiconductors) and advances in the simulation of characteristics of real systems, there are still problems that have been solved primarily using phenomenological approaches, while consistent theoretical methods have not been sufficiently developed. First of all, it is the problem of an adequate description of the formation and development of a defect (real) structure of crystals both at the stage of their growth and at the stage of the design of devices based on the grown crystals. This line of research is extremely important for the development of the theory of solids and, moreover, is of great practical significance for industrial production.

The practical significance of the development of the theory of defect formation in crystals is associated with the fact that the formation of structural defects and their transformations accompany industrial processes of production of crystals and devices. The microstructure formed during these processes strongly affects electrical, optical, mechanical, and other prop-

erties of crystals and devices. Knowledge of the regularities of the formation of defects in solids can be used to improve technologies for the production of materials and devices with desired properties and to solve problems of controlling the type, density, and spatial distribution of structural imperfections.

From the fundamental viewpoint, in the theory of defect formation in solids, there still remain a number of problems that, until recently, did not receive a satisfactory solution, for example, the problem of an adequate description of the formation of structural defects during crystal growth, the development of a consistent microscopic theory of defect formation in solids, etc. The lack of a common algorithm for solving problems of defect formation in solids leads researchers to the necessity of their phenomenological analysis for each type of crystals separately. At the same time, many phenomena occurring in different crystals have a general character, for example, the interaction of point defects with each other, their interaction with dislocations, the formation and transformation of dislocations, etc.

Over the past five to seven years, based on theoretical studies of defect formation in semiconductor silicon, attempts have been made to solve the aforementioned problems and to develop foundations of the theory of defect formation in silicon. In particular, it has become possible to solve problems of the recombination of intrinsic point defects at high temperatures, the formation of "impurity–intrinsic point defect" complexes near the crystallization front, the development of the model of high-temperature precipitation, etc. This cycle of works has made it possible to develop the diffusion model of the formation and transformation of structural defects during the growth of silicon single crystals and to extend this model to the processes of production of silicon structures and devices.

The purpose of this review is to develop a unified algorithm for solving the problem of defect formation in crystals based on an overview of the theoretical description of the formation of structural imperfections in high-purity dislocation-free silicon single crystals.

2. MAIN RESULTS OF EXPERIMENTAL STUDIES OF GROWTH MICRODEFECTS

Semiconductor silicon is the base material used for the design and fabrication of functional electronic devices with a high degree of integration. At the same time, silicon is the purest material among all currently known substances. In this regard, silicon is a unique laboratory for the study of fundamental interactions between particles, which lead to the formation of a defect structure in solids. In ultrapure undoped silicon, such particles during the crystal growth are interstitial silicon atoms, vacancies, oxygen, and carbon.

The growth of dislocation-free silicon single crystals by the Czochralski method and floating zone melting is accompanied by the formation of structural imperfections, known as microdefects. Growth microdefects are considered to mean any local disturbances of the periodicity of the crystal structure with sizes ranging from several tens of angstroms to several tens of micrometers that can be revealed by direct (optical or diffraction) methods.

Systematic investigations of the character of the distribution, the nature, and regularities of the formation of growth microdefects in silicon were started in the mid-1960s of the last century. Based on the results of investigations of growth microdefects using the methods of selective etching, X-ray topography, and transmission electron microscopy, historically it was accepted to use the letter classification for designations of microdefects (for example, A-microdefects, B-microdefects, etc.) [1, 2]. However, the letter classification based mainly on defect distribution patterns after selective etching introduced unnecessary details and concealed the essence of the physical processes occurring during the formation of growth microdefects. Experimental studies of growth microdefects made it possible to establish the existence of three types of structural imperfections: precipitates of impurities [3–7], dislocation loops [2, 8, 9], and micropores [10, 11].

It was established that, depending on thermal conditions of growth of silicon single crystals, they have the following features:

(i) the sizes of precipitates lie in the range of 3–50 nm, and their concentration varies from 10^{14} to 10^{10} cm^{-3} [12];

(ii) the sizes of dislocation loops lie in the range of 1–5 μm, and their concentration varies from 10^5 to 10^6 cm^{-3} [8, 9];

(iii) the sizes of micropores lie in the range of 100–500 nm, and their concentrations vary from 10^4 to 10^5 cm^{-3} [10].

It was found that micropores and dislocation loops are formed in different regions of the crystal, depending on the growth parameter $V_g/G_g = \xi$ (where V_g is the crystal growth rate, G_g is the axial temperature gradient, and ξ is a constant) [13–15]. Extremely important are the studies of undoped silicon single crystals grown by floating zone melting with the oxygen and carbon concentrations of less than 4×10^{15} cm^{-3}, as well as single crystals subjected to quenching directly in the furnace [7, 16]. In both cases, precipitates of oxygen (SiO_2) and carbon (SiC) were revealed using transmission electron microscopy.

The experimental investigations revealed the following important features of the defect formation.

(1) Types, sizes, and concentrations of growth microdefects are determined by thermal conditions of

crystal growth (growth method, crystal diameter, growth rate, and temperature gradients in the crystal).

(2) In grown single crystals, there are precipitates of uncontrollable (background) impurities.

The construction of a theoretical model of the formation of growth microdefects gives the key to the solution of problems of controlled defect formation during the crystal growth. A quantitative model of defect formation provides an answer to the fundamental question of the solid state physics, which consists in describing the kinetics of a defect structure of the crystal during its cooling after the growth. However, the advantages and disadvantages of the theoretical model are due to the conditions and limitations of the underlying physical model.

3. MODELS OF THE DYNAMICS OF POINT DEFECTS

The first physical model of the formation of growth microdefects were very imperfect and, consequently, were used for a qualitative description of the formation of anyone type of growth microdefects [1]. In solid state physics, it is usual practice to consider simplified models of one or another phenomenon and then to calculate their parameters and properties. These models should be simple enough for their theoretical description, but, at the same time, quite complex in order that they would exhibit the properties under investigation. The first model of the formation of growth microdefects became the physical model proposed by Voronkov [13], who was the first to give a simple theoretical justification of the dependence of the type of growth microdefects formed in the crystal on the growth conditions. In that work, Voronkov obtained basic relationships that make it possible, knowing the parameters of intrinsic point defects and growth conditions, to determine the type and concentration of intrinsic point defects (and, hence, the type and some parameters of microdefects remaining in the crystal).

Based on some experimental results [17], it was assumed that (1) the rate of recombination between silicon self-interstitials and vacancies is very high; (2) the diffusion coefficient of self-interstitials near the melting temperature is higher than the diffusion coefficient of vacancies; and (3) the equilibrium concentration of vacancies near the melting temperature is higher than the equilibrium concentration of self-interstitials [13]. The author noted that the formation of growth microdefects is controlled by the growth parameters $V_g/G_g = \xi$. This mechanism leads to a significant difference between the vacancy ($V_g/G_g > \xi_{crit}$) and interstitial ($V_g/G_g < \xi_{crit}$) regions of the crystal growth [13, 18].

The defect formation in dislocation-free silicon single crystals according to the recombination–diffusion model occurs in four stages: (1) the fast recombination of intrinsic point defects near the crystallization front; (2) the formation of micropores or dislocation loops in the narrow temperature range of 1423–1223 K depending on the growth parameter V_g/G_a; (3) the formation of oxygen complexes in the temperature range of 1223–1023 K [19]; and (4) the formation and growth of precipitates as a result of subsequent heat treatments.

In recent years, the recombination–diffusion model has been revised in part. This has led to a certain convergence of some of its supporters with provisions of the alternative diffusion model of defect formation, which will be considered below. For example, in [20–22], the authors critically discussed the problem of the influence of the growth parameter $V_g/G_g = \xi$ on the formation of micropores and dislocation loops. It was assumed that, for the specified melt zone, diameter, and length of the crystal, the temperature gradient at the crystallization front is a function of the growth rate of the crystal. Furthermore, the bold assumption was made regarding the coexistence of interstitial and vacancy clusters in growing crystals [22]. This drift of supporters of the postulate of recombination of intrinsic point defects near the crystallization front to the main provisions of the diffusion model demonstrates a desire to explain the available experimental results on the defect formation during the growth of silicon single crystals, which do not fit into the framework of the recombination–diffusion model [20–22]. Primary among these experimental results is the precipitation of impurities during the crystal growth [23]. It should be noted that these “revisionist” views were immediately criticized [18].

The recombination–diffusion model underlay the mathematical model of the dynamics of point defects in silicon, which quantitatively explains the homogeneous character of the formation of micropores and dislocation loops and provides the basis for understanding of the relationship between the defect structure of the crystal and the processes occurring in the melt [24]. The concentrations of defects were calculated by assuming a fast recombination of vacancies and silicon self-interstitials in a relatively narrow region near the crystallization front, which leads to equilibrium concentrations of primary defects [13]. The concentration of remaining primary defect after passing a narrow recombination region can be found from the flux of defects deep into the crystal. Upon further cooling of the crystal during pulling, primary defects form clusters: micropores in the region dominated by vacancies and dislocation loops in the region dominated by silicon self-interstitials [24].

The model of the dynamics of intrinsic point defects, in the general case, includes three approximations: rigorous, simplified, and discrete-continuum approaches [25]. The most rigorous model requires the solution of integro-differential equations for the concentration fields of point defects, and the distribu-

tion of growth microdefects in this model is a function of the coordinates, the time, and the time of evolution of the size distribution of microdefects [24, 26–29]. In the simplified (lumped) model, the average radius of the defects is approximated by the square root of their average surface area [25]. This approximation is taken into account in the additional variable, which is proportional to the total surface area of the defects. The lumped model is effective in calculating the two-dimensional distribution of growth microdefects [19, 25]. Both models use the classical nucleation theory and suggest the calculation of the formation of stable nuclei and the kinetics of diffusion-limited growth of defects. The discrete-continuum approximation (discrete-continuous model) involves a comprehensive approach: the solution of discrete equations for the smallest defects and the solution of the Fokker–Planck equations for large-sized defects [30–32]. All these models quantitatively explain the homogeneous character of the formation of micropores and dislocation loops [24]. The formation of micropores or dislocation loops begins at temperatures $T \leqslant T_m - 300$ [13, 14]. It is assumed that the precipitation of impurities occurs only during the heat treatment of the crystal [19, 24, 25, 33].

The denial of the experimental results on the precipitation of impurities during the growth of silicon crystals is a significant disadvantage of the model of the dynamics of point defects. In this case, the concentrations of oxygen and carbon impurities in ultrapure undoped silicon single crystals are two to three orders of magnitude higher than the concentrations of intrinsic point defects. It should be noted that, until recently, a theoretical description of the impurity precipitation during cooling of a crystal after the growth was impossible. This is associated with the fact that, according to the thermodynamic theory of fluctuations, the distribution function of nuclei of different sizes has the form

$$f_0(R) \sim \exp\left\{-\frac{\Delta G(R)}{kT}\right\},$$

where ΔG is the minimum energy required to form a nucleus of a given size and k is the Boltzmann constant [34]. In this case, the formation of critical nuclei at high temperatures is very problematic.

4. DIFFUSION MODEL OF THE FORMATION OF GROWTH MICRODEFECTS

In the last twenty years, the experimental studies of growth microdefects made it possible to develop a new physical model of the formation of growth microdefects. The fundamental difference between this model and other versions of the model of the dynamics of point defects lies in the relation to the problem of recombination of intrinsic point defects at high temperatures. While the models of the dynamics of point defects suggest the fast recombination of intrinsic point defects near the crystallization front [13], the new model of rejects it. This physical model is based on a large number of experimental results [2–4, 6–11, 16, 35] and allows a theoretical description of the formation of all types of growth microdefects. This model is called the diffusion model of the formation of growth microdefects.

The defect formation in accordance with the diffusion model occurs in three stages [12, 23]: (1) the formation of impurity complexes near the crystallization front; (2) the formation, growth, and coalescence of precipitates during cooling of the crystal from the crystallization (melting) temperature to room temperature; and (3) the formation of micropores or dislocation loops at temperatures $T \leqslant 1423$ K depending on the growth parameter V_g/G_a.

This mechanism gave a good qualitative description of the experimental results on the defect structure of silicon. However, the application of this mechanism raised two questions.

(1) Why does the "impurity–intrinsic point defect" interaction at high temperatures have the advantage over the processes of recombination of intrinsic point defects?

(2) On what basis can the high-temperature precipitation be consistent with the provisions of the classical theory of nucleation of second-phase particles?

4.1. Recombination of Intrinsic Point Defects in Silicon and the Classical Nucleation Theory

The answer to the first question was given by the thermodynamic calculation of recombination parameters (height of the recombination barrier, recombination time, and recombination factor) underlying the model of the dynamics of intrinsic point defects. This calculation was performed with the main provisions of the physical model of the formation of growth microdefects [12] and the microscopic model of a recombination barrier [36, 37]. The essence of this model is that the temperature dependence of the recombination barrier is determined by the configuration of intrinsic point defects in the high-temperature range. At high temperatures, silicon self-interstitials and vacancies occupy several atomic volumes; i.e., around the point defect, there is a disordered (amorphous) region that is isotropically extended up to atoms of the second coordination sphere. According to [37], the recombination can occur only in the case of the simultaneous compression of both defects in the vicinity of one atomic volume.

For the proposed model of a defect, the temperature dependence of the configurational entropy at high temperatures (near the crystallization front) can be represented in the form [38]

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

where S_∞ is the limiting value of S_c (at $T \to T_m$), T_m is the melting temperature, and T_k is the characteristic temperature. The temperature T_k is the minimum temperature of the formation of structural imperfections in dislocation-free silicon single crystals, which can be estimated as the average temperature of the formation of thermal donors in silicon: $T_k = 450°C = 723$ K [39].

It was shown that the recombination of intrinsic point defects in dislocation-free silicon single crystals near the crystallization front is almost impossible due to the presence of a recombination barrier [39]. At $T \to T_m$, the height of the recombination barrier is ~2 eV [39]. The theory of extended configurations and a recombination barrier was confirmed in a number of contemporary works [40–44]. We note the work of Kukushkin and Osipov [44], who calculated the energy of the formation of SiC critical nuclei and also showed that, at high temperatures, along a specific direction in silicon, this energy barrier is significantly lower than the barrier to the recombination of intrinsic point defects [44, 45]. In this case, the free energy of the formation of a new phase includes not only the energy of the possible formation of precipitate nuclei but also the energy of the formation of subsequent defects, in particular, dislocation loops and micropores [46]. After the nucleation of precipitates and their consolidation, they can elastically interact in other crystallographic directions [47].

The answer to the second question has recently been obtained in [48]. According to the classical theory of nucleation of second-phase particles, critical nuclei of small sizes with a higher probability should be formed at low temperatures [49]. The critical size of a nucleus increases with an increase in the temperature [50]. On this basis, a theoretical treatment of the critical nucleus size gives the following formula [51]:

$$R_C = \frac{2\sigma u V_p}{kT\ln(S_X S_i^{-\gamma_i} S_v^{\gamma_v}) - 6\mu\delta\varepsilon u V_p}, \quad (2)$$

where $S_X = C_X/C_X^{eg}$, $S_i = C_i/C_i^{eg}$, and $S_v = C_v/C_v^{eg}$ are the characteristics of supersaturation of impurity atoms, silicon self-interstitials, and vacancies, respectively; σ is the surface energy density of the interface between the precipitate and the matrix; μ is the shear modulus of silicon; δ and ε are the relative linear and volumetric misfit strains of the precipitate and the matrix, respectively; γ_i and γ_v are the fractions of silicon self-interstitials and vacancies per impurity atom attached to the precipitate, respectively; V_p is the molecular volume of the precipitate; and $u = (1 + \gamma_i x + \gamma_v x)^{-1}\left(\frac{1+\varepsilon}{1+\delta}\right)^3$. Formula (2) holds true for the case of coherent phase matching and can be used for the description of the precipitation of oxygen in silicon upon heat treatments.

However, the experimental investigations demonstrated that the defect formation in ultrapure silicon single crystals is based on the "impurity–intrinsic point defect" interaction [12]. At the same time, it is well known that the formation and development of a growth microdefect structure of silicon crystals are determined by thermal conditions of growth and cooling of the crystal [1, 12–15, 23]. The temperature distribution along the length of the ingot during the cooling, depending on the thermal parameters of the growth, varies according to the law

$$1/T = 1/T_m + GZ/T_m^2, \quad (3)$$

where Z is the distance from the crystallization front [13, 24]. The radial inhomogeneity of the temperature field can be taken into account in the formula $G(r) = G_a + (G_e - G_a)(r/R_s)^2$, where R_s is the radius of the crystal, G_e is the axial temperature gradient at the edge of the crystal, and r is the current coordinate in the range from 0 to R_s [52]. By introducing the growth rate of the crystal into formula (3), we obtain [48]

$$T(t) = \frac{T_m^2}{T_m + VGt}. \quad (4)$$

Then, taking into account that the concentrations C_v^{eq} and C_i^{eq} depend on the temperature T, expression (2) can be rewritten as

$$R_C = \frac{2\sigma u V_p}{kT(t)\ln(S_X S_i^{-\gamma_i} S_v^{\gamma_v}) - 6\mu\delta\varepsilon u V_p}. \quad (5)$$

The influence of thermal conditions of the growth of silicon single crystals is taken into account in the dependence $T(t)$. This allows us to theoretically describe the conditions of nucleation, growth, and coalescence of precipitates in the range from the crystallization temperature to room temperature (Fig. 1) [48].

The minimum size of a critical nucleus is observed in the initial state at $T = 1682$ K and increases with a decrease in the temperature [48]. At $T \approx 1455$ K, the critical radii of oxygen and carbon precipitates have an identical value; then, the critical radius of oxygen precipitates increases more rapidly. An increase in the critical radius of precipitates during cooling of the crystal leads to a sharp decrease in the growth rate and, consequently, to a sharp decrease in the precipitation rate (Fig. 1) [48]. The minimum values of R_C (at $T = 1682$ K) increase with an increase in the growth rate of the crystal or the axial temperature gradient at the crystallization front [48].

In this case, the Vanhellemont–Claeys model [51] is applicable not only to the description of the nucleation of precipitates in silicon upon heat treatments, but also it is extended to the process of cooling the crystal during the growth. Therefore, the "impurity–intrinsic point defect" interaction has a fundamental character and determines the defect structure of the

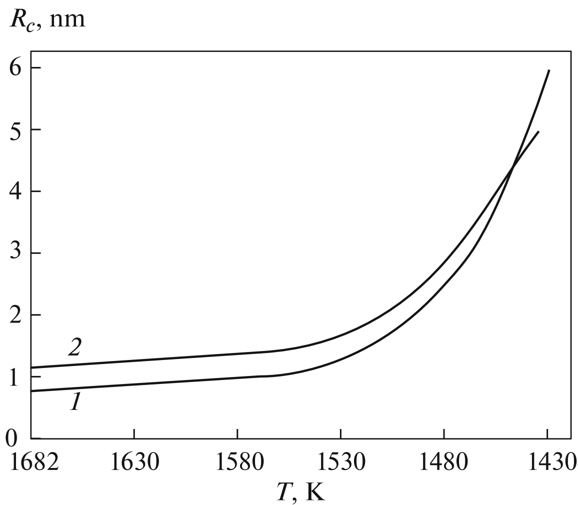

Fig. 1. Temperature dependences of the critical radius of (*1*) oxygen precipitates and (*2*) carbon precipitates (V = 0.6 mm/min, G = 2.5 K/mm, $C_{0,\,C} = 10^{18}$ cm^{-3}) [48].

crystal from the beginning of the crystallization to the fabrication of the finished device.

The answers given to the two fundamental questions made it possible, in a number of studies, to develop theoretical foundations of the diffusion model of defect formation in semiconductor silicon [53–56]. A central place in these developments is occupied by the high-temperature precipitation model [53]. This model allows us to take a fresh look at the processes of decomposition of solid solutions of defects in crystals.

4.2. High-Temperature Precipitation of Impurities during the Crystal Growth

The decomposition of a solid solution begins with the nucleation, i.e., with the formation of physically distinguishable centers, which then grow. This increase leads to the precipitation of a new phase within the initial solid solution. In general, the precipitation of the second phase occurs in three stages: (i) local fluctuation of the chemical potential (nucleation), (ii) formation of a stable nucleus, and (iii) growth and coalescence of precipitates [34].

The absence of recombination of intrinsic point defects in the high-temperature range leads to the fact that, during the cooling of the crystal after passing through the diffusion zone, an excessive concentration of intrinsic point defects appears. Excess intrinsic point defects disappear at sinks whose role in this process is played by uncontrollable (background) impurities of oxygen and carbon [12, 56]. In [57, 58], we calculated the formation of "impurity–intrinsic point defect" complexes during the growth of silicon crystals with the inclusion of the elastic interaction between the components of the complex. This calculation is relevant in the early stages of nucleation, when the sizes of nuclei are small and the use of the Fokker–Planck continuity differential equations is impossible. The analysis of "intrinsic point defect–impurity" interactions showed that the edge of the reaction front of the formation of a complex (oxygen–vacancy and carbon–silicon self-interstitial) is located at a distance of ~3×10^{-4} mm from the crystallization front; i.e., the complex formation occurs near the crystallization front [57]. This distance is the thickness of a diffusion layer on which an excessive concentration of intrinsic point defects appears due to the absence of their recombination at high temperatures.

In order to describe the kinetics of simultaneous nucleation of new-phase particles of several types in a supersaturated solid solution of an impurity in silicon, we considered a system consisting of oxygen atoms, carbon atoms, vacancies, and silicon self-interstitials [53]. The analysis of the mass balance of point defects in the crystal in terms of the system of diffusion equations for silicon self-interstitials, oxygen atoms, carbon atoms, and vacancies led to the corresponding system of coupled Fokker–Planck equations. The interaction of this system during cooling of the crystal from 1683 K leads to the formation of oxygen and carbon precipitates [12, 53, 56]. The results of calculations of the Fokker–Planck partial differential equations confirm that the processes of nucleation occur very rapidly in the vicinity of the crystallization front [53].

In the second stage of the precipitation process, the growth of clusters occurs without a change in their number. This is accompanied by a significant decrease in the degree of supersaturation of the solid solution. The analysis of the change in the average radius of precipitates $R(t)$ at this stage indicates that the phase transition occurs through the mechanism of nucleation and growth of a new phase, and both these processes are not separated in time and occur in parallel [54].

In the third stage of the process, when new-phase particles are large enough, the supersaturation is relatively low, 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 [54]. According to the data of the computer simulation of crystals, the final size of precipitates lies in the range of 2.0–6.5 mm, which agrees well with the experimental data [59, 60].

The process of precipitation (nucleation, growth, and coalescence of second-phase particles) occurs over the entire temperature range of cooling the crystal (T ~ 1682–300 K) after the growth [56]. This process can be slowed down or suspended in a narrow temperature range (at $T \leqslant T_m - 300$ K, where T_m is the crystallization temperature), when, depending on thermal properties of the crystal growth, conditions arise for the homogeneous formation of micropores or dislocation loops [24, 55]. Moreover, the presence of

the already formed precipitates in the crystal at $T \leqslant T_m - 300$ K leads to the fact that the formation of dislocation loops is caused primarily by the deformation mechanism [55].

The data of the computational experiment on the study of micropores was confirmed by the coagulation character of the defect formation [24, 55]. However, the corresponding calculation for dislocation loops revealed that the calculated and experimentally observed concentrations of these defects differ by three orders of magnitude. This is associated with the fact that, unlike micropores which are formed only due to the coagulation mechanism, the formation of dislocation loops occurs through both the coagulation and deformation mechanisms [55]. The kinetic model of the formation and growth of interstitial dislocation loops suggests that the formation and development of dislocation loops are caused by the high-temperature precipitation of background impurities, when there is a mismatch between the lattice parameters of the matrix and the precipitate [61]. The accumulation of the elastic energy during the growth of precipitates results in a loss of coherence with the matrix, when it is already impossible to establish a one-to-one correspondence between the atoms on both sides of the interface. This leads to a structural relaxation of precipitates, which occurs through the formation and motion of dislocation loops. The growth and coalescence of dislocation loops predominantly occur due to the generation of silicon interstitials by growing precipitates and due to the dissolution of small dislocation loops [61].

5. DIFFUSION MODEL OF THE FORMATION OF GROWTH MICRODEFECTS—A NECESSARY CONDITION FOR THEORETICAL DESCRIPTION OF A DEFECT STRUCTURE OF CRYSTALS

In any theoretical model, the formation and development of a defect structure during the growth of a crystal and its technological treatments should be considered in a unified context. In [62], we considered the mathematical apparatus of the diffusion model of the formation of growth microdefects as applied to the formation of a defect structure in undoped dislocation-free silicon single crystals as a result of heat treatments. In this case, formula (4) has the form $T(t) =$ const. Figure 2 shows the dependences of the critical radius of the oxygen and carbon precipitates on the heat treatment temperature.

During the heat treatment at $T = 730$ K, the size of critical nuclei of oxygen precipitates is equal to 2.7 nm, whereas the critical nuclei of carbon precipitates have a size of approximately 8.7 nm. The minimum critical radii of the precipitates are achieved in the initial state at $T = 730$ K and increase with increasing temperature. An increase in the annealing temperature leads to

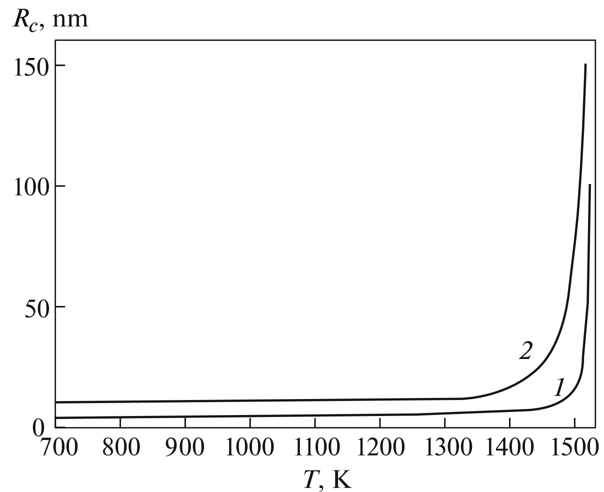

Fig. 2. Dependences of the critical radius of (*1*) oxygen precipitates and (*2*) carbon precipitates on the heat treatment temperature [62].

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 [62].

The kinetics of precipitation during heating of the crystal is similar to the kinetics of precipitation during cooling of the crystal in the course of the growth. However, the results of calculations, together with the large size of critical nuclei of carbon precipitates as compared to the size of critical nuclei of oxygen precipitates, can indicate that heat treatments are accompanied predominantly by the precipitation of oxygen [62].

In real silicon single crystals, there are growth microdefects that, during heat treatments, serve as sinks for intrinsic point defects and impurity atoms. Therefore, the growth of precipitates formed during the growth of single crystals can occur simultaneously with the formation of new precipitates. The transformation and formation of precipitates during heat treatment lead to a supersaturation of the crystal with self-interstitials. This process, depending on the conditions of the initial defect structure and parameters of the heat treatment, causes the formation and growth of dislocation loops and stacking faults, as well as a decrease in the size or dissolution of micropores [12, 56, 62].

The diffusion model of the formation of growth microdefects as applied to the formation of growth and post-growth structures makes it possible, in a unified context, to describe the formation of a defect structure in single-crystal silicon, beginning with the crystal growth to the production of devices. Figures 1 and 2 prove the universality of the diffusion model of defect formation in silicon. The construction of a universal model of defect formation provides the prediction of

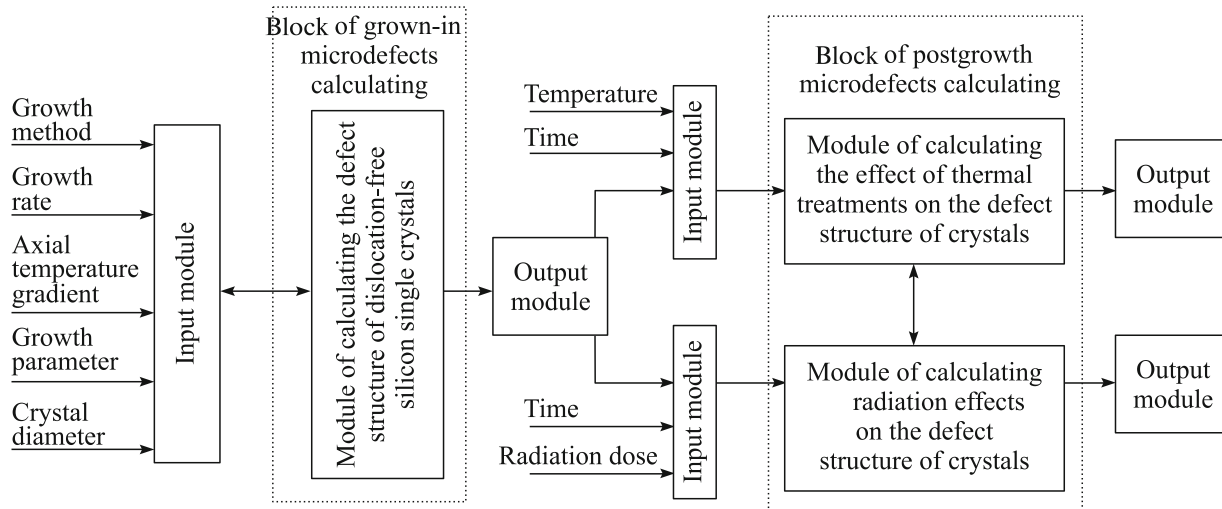

Fig. 3. Informative–logical diagram of the information system [63].

specific features of microdefects at different stages of the technological process.

6. ENGINEERING OF DEFECTS IN SILICON AND ALGORITHM FOR CALCULATING THE DEFECT STRUCTURE OF CRYSTALS

The universality of the diffusion model of defect formation in ultrapure silicon single crystals can have two aspects of application.

The first aspect is associated with the engineering of defects in silicon crystals. It is extremely important not only to grow crystals with a precisely known defect structure (with desired properties) but also to control this structure during the technological process of production of devices [63]. From this viewpoint, the diffusion model is the first theoretical description of formation and development of a defect structure of semiconductor silicon, in which the processes of interaction of point defects are considered in a unified context beginning with the crystal growth to the production of the finished product.

The mathematical apparatus of the diffusion model using modern information technologies can provide the basis for the development of a software complex for analysis and calculation of the formation of growth and postgrowth microdefects in dislocation-free silicon single crystals [56]. This software product makes it possible to determine necessary conditions for the growth of a crystal and modes of its treatments in order to obtain a well-defined defect structure [64]. For the development of the software complex, we elaborated a technique for analysis and calculation of a growth defect structure of dislocation-free silicon single crystals [52].

The software complex provides the simulation of the real experiment, which with the maximum accuracy reproduces the actual characteristics of the growth of silicon single crystals. This software product makes it possible to determine thermal conditions of the crystal growth, to predict and control the defect structure of the crystal, and to save considerable resources and time, which would be expended on performing the experimental studies of the defect structure using optical and transmission electron microscopy, as well as the X-ray diffraction methods for the observation of defects. The replacement of experimental studies of the structure by adequate theoretical investigations using the software complex indicates that the complex is a new virtual experimental device [64].

Possible applications of the diffusion model for the description of the defect formation during crystal growth and technological treatments process were taken into account in the development of a specialized information system for analysis and control of the defect structure of dislocation-free silicon single crystals (Fig. 3) [63].

The values of the growth parameters of dislocation-free silicon single crystals (growth method, growth rate V_g, axial temperature gradient G_a, Voronkov growth parameter $V_g/G_a = \xi_{crit}$, crystal diameter) are input to the system. The output module of the block for calculating growth microdefects displays information on the type of a defect, its size and concentration.

During the production of semiconductor devices, the transformation of a defect structure occurs due to heat treatments and the effect of radiation. The block for calculating postgrowth microdefects contains modules for calculating the effect of heat treatments and radiations on the defect structure of the devices. The modules are interconnected, because the heat treatment is used for annealing of radiation damages. Information on the initial defect structure of crystals,

together with technological parameters (temperature, time, dose), is input to the modules. The output modules of the block for calculating postgrowth microdefects display information on the type, size, and concentration of defects [63].

The block for calculating growth microdefects occupies a central place in the information system. This is associated with the fact that the initial defect structure of the crystal determines the defect structure of the device. This block makes it possible to investigate the defect structure of the crystal grown under specified temperature conditions. And vice versa, for the specified defect structure of the crystal, it is possible to determine the necessary temperature conditions for its growth. Therefore, the information system is not only a virtual experimental device, but also a tool for engineering crystal defects. A similar approach can be applied to the block for calculating postgrowth microdefects. The information system can be used for the following purposes:

(i) engineering simulation of defects in silicon crystals during their growth,

(ii) engineering simulation of defects in silicon crystals during the fabrication of devices,

(iii) use as a tool for investigating the defect formation in silicon.

The first aspect of the universality of the diffusion model is of practical importance for the production of semiconductor silicon and related devices. The second aspect of the use of this model has a fundamental character. The correction of traditional concepts about the dominant role of intrinsic point defects showed that semiconductor silicon, being an extremely pure and structurally perfect material, itself can be considered as the initial model for the construction of theoretical models of defect formation in other semiconductor materials and metals. In this review, we gave only evaluative judgments about the character and use of the second aspect. For a detailed verification of our propositions (hypotheses), it is necessary to consider theoretical works of specialists engaged in studies of other solid materials.

The diffusion model demonstrates that the main role in the process of defect formation is played by the precipitation of impurities [56]. The obtained mathematical models and proposed methods for their solutions in silicon make it possible to formulate and solve many problems on the kinetics of diffusion processes in solids. The diffusion model can be applied to mathematical description of many processes, such as precipitation of impurities, pore formation, formation of dislocation loops in crystals, and others. The two stages of the decomposition of a supersaturated solution of point defects (according to the vacancy and interstitial mechanisms) allow the description of the reactions of interaction between intrinsic point defects and impurities, as well as the modification of a defect–impurity system during cooling of the crystal after the growth. The primacy of high-temperature precipitation processes is a fundamental feature that determines the overall kinetics of defect formation in highly perfect crystals of semiconductors and metals [48, 56].

The generality of the approach does not exclude specific features of the application of the diffusion model for different materials. These features are associated with different thermal conditions used for growing crystals and different types of their structures. The specificity of the defect formation at high temperatures in metals, especially those with a closely packed structure, is determined by the fact that the concentration of equilibrium interstitial atoms is many orders of magnitude less than the concentration of equilibrium vacancies [65]. During cooling of the crystal, the condensation of nonequilibrium vacancies occurs through the formation of vacancy disks [66]. The collapse of vacancy disks results in the formation of prismatic dislocation loops [67]. This mechanism is similar to the mechanism of formation of micropores in a loose lattice of semiconductors, which, however, does not lead to the formation of dislocation loops in semiconductors. At the same time, the high-temperature precipitation of impurities in metals is favorable for the deformation mechanism of the formation of dislocation loops. Possibly, the combined effect of the vacancy and deformation mechanisms of the formation of dislocation loops is the main reason that the growth of dislocation-free single crystals of metals is complicated as compared to semiconductors. At the same time, in the case of growing crystals of semiconductor compounds containing a volatile component, an additional important source of dislocation loops can be a deviation from the stoichiometric composition [68].

The specificity of growth and the difference in the crystal structures of different dislocation-free single crystals must necessarily be taken into account in the physical model and mathematical constructions of the diffusion model. However, in any case, the algorithm of the application of this model is based on the high-temperature precipitation process, which determines the subsequent course of the formation of a defect structure of crystals (Fig. 4).

Experimental database *1* (EDB) should contain all available experimental data on the crystal, for example, (i) data on the crystal structure, growth method, and thermal parameters of the crystal growth; (ii) data on the types of defects, their size and concentration, and temperatures of formation of defects; (iii) data on the physical model of defect formation; (iv) data on the modes and time of heat treatments, etc. The necessary data from EDB are supplied to input module *2* of the diffusion model for the calculation of the defect structure in high-temperature precipitation model *3*. This model should be transformed taking into account the specific features of a particular type of crystals. For example, for semiconductor crystals with a loose structure, it is necessary to use the two-stage mecha-

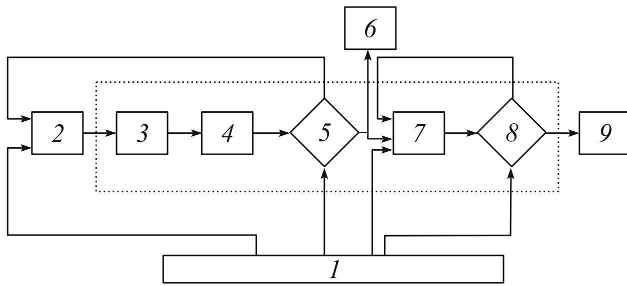

Fig. 4. Schematic diagram of the algorithm for calculating the defect structure of crystals.

nism of the formation of growth defects, whereas its one-stage modification can be used in the case of close-packed crystals of metals.

Next are the calculation and analysis of the formation of the secondary defect structure of crystals *4* (for example, dislocation loops, micropores, stacking faults, dislocations, etc.). The results of calculations are compared with the EDB data (comparator *5*). In the case of good agreement with the EDB data, the results of calculations can serve as the characteristics of the initial defect structure of crystal *6* and used for the calculation and analysis of the defect structure of the crystal after different heat treatments *7*. If a satisfactory agreement is not achieved, the calculations are repeated again until the results are obtained with a desired accuracy. In the process, the mathematical models and (or) experimental data from EDB can be refined.

After calculating heat treatments, the above-described process of calculation is repeated until, until a good agreement between the theoretical results and the EDB data (comparator *8*) is achieved. In this case, the results of calculations can serve as the characteristics of the defect structure of device *9*. The proposed algorithm can provide the basis for the development of a software for analysis and calculation of the defect structure of a crystal and devices based on it.

7. CONCLUSIONS

The experimental and theoretical investigations of ultrapure dislocation-free silicon crystals demonstrated that the formation of a defect structure during the crystal growth occurs in the direction from the high-temperature precipitation of impurities to the formation of secondary growth defects (micropores or dislocation loops). A complete description of the defect formation is provided by the diffusion model of the formation of growth microdefects. The mathematical apparatus of the diffusion model makes it possible to develop software for the analysis and calculation of the defect structure of silicon. The diffusion model can be used to calculate the defect formation in silicon after different heat treatments.

It is suggested that the diffusion model can also be used to calculate and analyze the defect structure of other crystalline materials. As applied to other crystals, the diffusion model should inevitably be transformed taking into account the parameters of the physical model of the formation of defects in a given crystal. The specific features and differences between the crystal structures of different single crystals must necessarily be taken into account in the physical model and mathematical calculations of the diffusion model. But, in any case, the algorithm of its application is based on the high-temperature precipitation process, which determines the subsequent course of the formation of a defect structure of crystals. The diffusion model of defect formation can be an ideal platform for multifunctional solution of many key problems in modern solid state physics, such as defect formation in solids, engineering of defects in solids, control of physical properties of solid-state structures, etc.

In this paper, we proposed an algorithm for the calculation and analysis of a defect structure of crystals and presented the schematic diagram of this algorithm. Based on the schematic diagram, it is possible to develop a software product for analysis and calculation of a defect crystal structure.

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Translated by O. Borovik-Romanova