

# Complex Formation in Semiconductor Silicon within the Framework of the Vlasov Model of a Solid State

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**Abstract**—The formation of silicon–carbon and silicon–oxygen complexes during cooling after the growth of dislocation-free silicon single crystals has been calculated using the Vlasov model of crystal formation. It has been confirmed that the complex formation begins in the vicinity of the crystallization front. It has been shown that the Vlasov model of a solid state can be used not only for the investigation of hypothetical ideal crystals, but also for the description of the formation of a defect structure of real crystals.

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## 1. INTRODUCTION

A theoretical description of defect formation in crystals during their growth has attracted considerable interest of researchers around the world. This is associated with the fact that the defect structure of a grown crystal serves as the basis for its transformation and the development of a new defect structure as a result of various technological influences exerted on the crystal.

Until recently, the description of defect formation in ultra-pure dislocation-free silicon single crystals was based on the physical model proposed by Voronkov (the recombination-diffusion model) [1]. This physical model, in turn, was based on the classical theory of nucleation and growth of second-phase particles in solids [2] and explained the homogeneous formation of dislocation loops or micropores depending on thermal conditions of growth [1, 3]. This postulation of the dominant role of intrinsic point defects led to the denial of the possibility to theoretically describe the precipitation of impurities in the processes of defect formation during the crystal growth [4]. The Voronkov physical model provided the basis for the construction of different modifications of the mathematical model of the dynamics of point defects [5].

However, this denial of the role of impurities in the processes of defect formation during cooling of the crystal after the growth was inconsistent with the majority of the experimental results [6]. Consequently, over the last five to seven years, a new diffusion model of defect formation in silicon has been developed [7]. The diffusion model is based on the key role of the high-temperature precipitation of impurities during the crystal growth [8] and provides a complete theoretical description of the nucleation and

development of a defect structure, both at the stage of growth and at the stage of technological treatment of a crystal [7]. This became possible after the diffusion model was brought into line with the classical theory of nucleation and growth of second-phase particles in solids by introducing the temperature  $T$  as a function of time  $t$  into the initial equations [9]. In this case, the mathematical apparatus of the classical nucleation theory is applicable to the formation of impurity precipitates in a solid during its cooling after the growth [7]. It was suggested that the diffusion model can also be extended to other semiconducting and metallic crystals [7].

The processes of defect formation have always been considered on the basis of classical concepts of a periodic structure of a crystal. These concepts are based on physical limitations, such as the localization of each atom in the vicinity of a fixed site of the crystal lattice, the consistency of introducing the concept of probability and the mechanical description of the behavior of particles, and the assumption that the number of atoms in a crystal is an integer. Meanwhile, in [10–13], Vlasov developed a different model of a crystal. In this model, the periodic structure of a crystal not is a consequence of the restrictions on the freedom of movement of atoms in the crystal, but is determined by specific statistical laws of motion of particles, in accordance with which the periodic structure agrees with the freedom of movement of atoms, so that the probability of finding an atom in interstitials is always different from zero [13]. The model is based on the solution of the kinetic Vlasov equation, which is a system of equations describing the evolution of a continuum of particles with a pair interaction potential [14]. The solution of this equation, under certain con-

ditions, leads to the description of an ideal periodic structure of a crystal [13]. However, until recently, the Vlasov model of a solid state was not used to describe the real structure of the crystal [15]. Taking into account the successful construction of the theoretical description of defect formation in semiconductor silicon on the basis of the classical approach, it is of considerable interest to analyze the possibility of describing the process of defect formation in the Vlasov model of a solid state.

In this regard, the purpose of the paper is to demonstrate the possibility of solving the problem of the mathematical description of the complex formation in semiconductor silicon within the framework of the Vlasov model of a solid state.

## 2. THE MATHEMATICAL MODEL

The Vlasov model is based on the following basic physical concepts [13]: (1) the rejection of the principle of the spatial and velocity localization of particles (in terms of the classical mechanics), which takes place regardless of the force interactions; (2) the introduction of force interactions by analogy with the classical mechanics, but with the inclusion of a new principle of nonlocalization of particles; and (3) the behavior of each particle of the system is described by means of an  $f$ -function extended in phase space. This approach combined the ideas of continuity and corpuscular since the original way of describing the motion of a particle associated with an extended function, and point particles occurs only in a particular case [11].

In the general case, the Vlasov equation describes the evolution of the distribution function  $f(x, v, t)$  of the continuum of interacting particles in the Euclidean space over the velocity  $v$  and the coordinate  $x$  at the moment of time  $t$ . This equation has the form

$$\frac{\partial f}{\partial t} + \left( \frac{\partial f}{\partial x}, v \right) + \left( \frac{\partial f}{\partial v}, F \right) = 0, \quad (1)$$

$$F = -\frac{\partial}{\partial x} \int K(x, y) f(y, v, t) dv dy,$$

where  $K$  is the pair interaction potential, which in real problems depends on the distance  $|x - y|$ , and  $F$  is the total force exerted by all the particles on one of them, which is located at the moment of time  $t$  at the point  $x$  [14]. In order to distinguish between the types of interactions, it is usual practice to consider systems of Vlasov equations (Vlasov–Poisson, Vlasov–Maxwell, Einstein–Vlasov, and Vlasov–Yang–Mills equations [16]).

The problem of constructing the theory of the crystalline state, which is based on first principles, is reduced to the choice of the initial system of equations for the distribution function and to the development of methods for their solution. The obtained solution will allow us to calculate the equilibrium properties of a

crystal for a specified interaction potential and at a given temperature and density of the particles [17].

The stationary properties of a crystal are described using the distribution density of particles  $\rho(r) = \int f(r, v) dv$ . The molecular field is determined by only probable, rather than exact, positions of the atoms. This is expressed by the potential function containing the probability density of the particles with the inclusion of the temperature distribution of the particles [13]. The choice of the pair interaction potential depends on the problem under consideration. Then, the nonlocal model of a crystal is based on the following nonlinear equations, which allow us to calculate the molecular potential and the particle position density under thermal equilibrium conditions [13]:

$$V(r) = \lambda k T \int_{-\infty}^{\infty} K_{1,2}(r) \exp\left(-\frac{K_{1,2}(r)}{k T}\right) dr,$$

$$\rho(r) = \lambda k T \exp\left(-\frac{K_{1,2}(r)}{k T}\right), \quad (2)$$

where  $k$  is the Boltzmann constant,  $K_{1,2}$  is the pair interaction potential, and  $\lambda$  is a certain characteristic number. The initial equations are equations for two particles under the steady-state conditions  $\left(\frac{\partial}{\partial t} = 0\right)$  [12]. The characteristic number is considered to mean such a value of the parameter  $\lambda$  for which the equations of system (2) have solutions other than trivial [12]. If the position of one of the particles is taken as the origin of the coordinates, we can determine  $\rho(0) = \lambda k T$  [12]. The determination of characteristic numbers in the Vlasov model of a solid state is an important problem.

The characteristic number  $\lambda$  can be determined from the main criterion for the existence of the crystalline state. In this case, the crystallization condition can be written as follows:

$$\frac{4\pi N}{k T_m} \int_0^{\infty} K_{1,2}^*(\rho) \rho^2 d\rho = 1, \quad (3)$$

where  $N$  is the number of particles,  $T_m$  is the melting (crystallization) temperature of the crystal, and  $K_{1,2}^* = -K_{1,2}$  [12].

## 3. EXPERIMENTAL PART AND DISCUSSION

In order to achieve the desired goal, it is necessary to evaluate the possibility of forming stable complexes and the evolution of their distribution density depending on the nucleation temperature in the temperature range from  $T_m = 1682$  K to  $T = 1382$  K. The choice of the lower temperature limit is caused by the fact that, in the diffusion model of defect formation in this temperature range from the crystallization front, there is

the formation of “impurity–intrinsic point defect” complexes with the further development of impurity precipitates [7]. The choice of the upper temperature limit, in turn, is motivated by the fact that, depending on the thermal conditions of crystal growth, interstitial dislocation loops or micropores are formed at temperatures  $T < T_m - 300$  [18]. It was shown both theoretically and experimentally that, at these temperatures (in the range from the crystallization temperature to  $T \sim T_m - 300$ ), in the undoped dislocation-free silicon single crystals, the formation of silicon–carbon and silicon–oxygen complexes occurs in the vicinity of the crystallization front is formed [8]. The process of precipitation (nucleation, growth, and coalescence of second-phase particles) proceeds over the entire range of cooling temperatures ( $T \sim 1683$ – $300$  K) after the growth [9].

The interactions between the atoms of the substances and, consequently, their properties are determined on the basis of information about the potential of interatomic interaction. The exact form of the interaction potential of two atoms is determined from the quantum-mechanical calculations. The obtained potentials are usually described by the functions with a large number of parameters, which complicates their analytical treatment. Therefore, it is usual practice to operate model potentials that contain a small number of parameters.

Currently, there are many approaches to the construction of interatomic potentials for materials with covalent bonds, including widely used model potentials, such as the Lennard-Jones potential, Mee–Lennard-Jones potential, Stillinger–Weber potential, Morse potential, many-particle Tersoff potential, and many-particle Brenner potential [19]. For the description of real substances on the basis of model interatomic interaction potentials, it is necessary to identify their parameters. The parameters of an interatomic interaction potential can be selected in accordance both with any individual thermodynamic properties and with any set of these properties for different thermodynamic state conditions. An unambiguous determination of the interatomic potential for silicon crystals is complicated [20]. Therefore, theoretical predictions within their formalism have used different fitting parameters whose behavior under various temperature conditions is difficult to predict or justify [21].

For the evaluation of the parameters of the formation of silicon–carbon and silicon–oxygen complexes, the interatomic interaction can be represented in the form of the Mee–Lennard-Jones potential

$$U(r) = K_{1,2}(r) = \frac{D}{(b-a)} \left[ a \left( \frac{r_0}{r} \right)^b - b \left( \frac{r_0}{r} \right)^a \right], \quad (4)$$

where  $D$  and  $r_0$  are the depth and the coordinate of the minimum of the interatomic potential, respectively; and  $b$  and  $a$  are the parameters,  $b > a$ . In the case of the formation of a stable bond between the atoms, we have

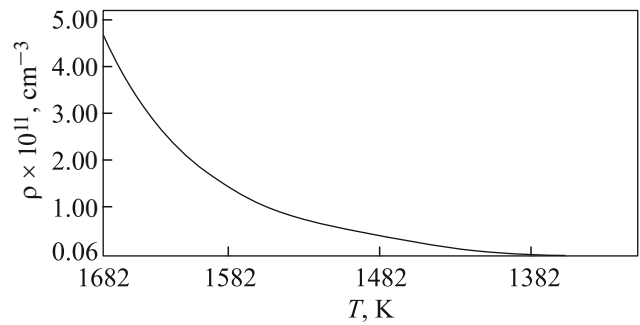


Fig. 1. Temperature dependence of the distribution density of silicon–carbon complexes.

$r = \sqrt[3]{2} r_0$  and  $U(r) = U_{\min}$ . For silicon, the parameters of the interatomic potential are as follows:  $a = 2.48$ ,  $b = 4.0$ , and  $D = 2.32$  eV; for carbon, the parameters of the potential are  $a = 2.21$ ,  $b = 3.79$ , and  $D = 3.68$  eV; and for oxygen, the parameters of the potential are  $a = 2.6$ ,  $b = 4.2$ , and  $D = 3.38$  eV [22–28].

Since the system under investigation consists of unlike atoms, the values of the cross-parameters of the potential were determined according to the Lorentz–Berthelot combination rule [29]. The calculations of the interatomic potentials gave the following results: for the silicon–carbon complex,  $a = 2.345$ ,  $b = 3.895$ , and  $D = 2.922$  eV; and for the silicon–oxygen complex,  $a = 2.541$ ,  $b = 4.101$ , and  $D = 2.812$  eV. Then, we obtain  $U_{1\min} = 2.840$  eV for the silicon–carbon complex and  $U_{2\min} = 2.710$  eV for the silicon–oxygen complex.

The characteristic numbers of the silicon–oxygen ( $\lambda_1$ ) and silicon–carbon ( $\lambda_2$ ) complexes were determined using equation (3) for the number of particles in the complex  $N = 2$  and  $K(\rho) = kT \left( 1 - e^{-\frac{K_{1,2}}{kT}} \right)$  [12]. The calculation gave the following values:  $\lambda_1 = 4.482 \times 10^8$  eV $^{-1}$  and  $\lambda_2 = 1.099 \times 10^9$  eV $^{-1}$ .

Equation (2) is written for the conditions of thermal equilibrium of the system. Since the minima of the interatomic potentials correspond to stable equilibrium positions of the atoms in the silicon–oxygen and silicon–carbon complexes, the distribution density of the complexes can be determined as a function of the cooling temperature of the crystal

$$\rho(T) = \lambda kT \exp\left(-\frac{V_{1\min,2\min}}{kT}\right) \quad (5)$$

The evolution of the distribution density during the cooling of a growing crystal in the temperature range from 1682 K to 1382 K is illustrated in Figs. 1 and 2.

In our computational experiment, the concentrations of nucleation centers for oxygen and carbon complexes were assumed to be equal to  $\sim 10^{12}$  cm $^{-3}$ .

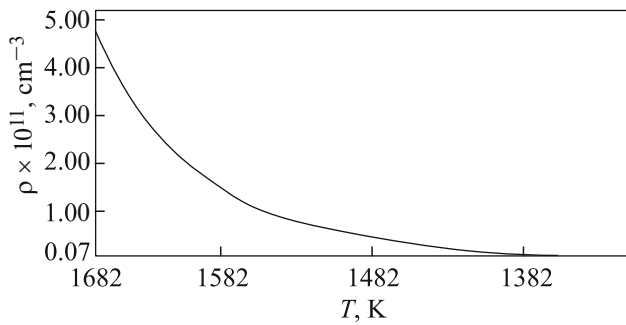


Fig. 2. Temperature dependence of the distribution density of silicon–oxygen complexes.

These values correspond to the experimental data obtained using transmission electron microscopy [6, 8]. The results of the calculations on the determination of the distribution density of silicon–carbon complexes are shown in Fig. 1, while the results of the calculations on the determination of the distribution density of silicon–oxygen are presented in Fig. 2.

During the growth of dislocation-free silicon single crystals, the formation of silicon–impurity complexes occurs in the vicinity of the crystallization front. During cooling of the crystal, these complexes grow and coalesce, which results in the formation of carbon precipitates SiC and oxygen precipitates SiO<sub>2</sub>. The performed calculations of the complex formation within the framework of the Vlasov model of a solid state allow us to draw the following three inferences.

First, the actual equality of the values of the distribution density of silicon–oxygen ( $\rho_1 = 0.493$ ) and silicon–carbon ( $\rho_2 = 0.492$ ) complexes in the vicinity of the crystallization front ( $T = 1682$  K) has found experimental confirmation. Using transmission electron microscopy it was shown that, at high crystal growth rates, interstitial and vacancy defects are formed in approximately equal concentrations [6].

Second, in the calculation of the homogeneous formation of micropores and interstitial dislocation loops in accordance with the model of the dynamics of point defects, the temperatures of their formation were found to be as follows:  $\sim 1333$  K for microvoids and  $\sim 1153$  K for interstitial dislocation loops [18]. The Vlasov model does not operate with the concept of crystal growth or the concept of axial temperature gradient, which are used in the classical theory of nucleation and growth of second-phase particles in solids [30]. However, the condition of the transition to the coalescence stage ( $T \sim 1683$ – $300$  K), where all the impurities are bound and supersaturation of intrinsic point defects occurs depending on thermal conditions of growth [30], corresponds to the completion of the complex formation process. This correspondence is characteristic of large-sized silicon single crystals (with a diameter of more than 100 mm). At the same time, for small-sized silicon single crystals, as shown

by the classical theory of nucleation, the coalescence stage occurs even at  $T \sim 1683$ – $20$  K [30]. Therefore, the classical theory of nucleation and growth of second-phase particles in crystals and the Vlasov model of crystal formation describe the processes of high-temperature precipitation, which provides the basis for the defect formation in crystals.

Third, until recently, the evolution of the distribution density during cooling of a growing crystal in the temperature range from 1682 to 1382 K (Figs. 1, 2) could indicate the impossibility of applying the Vlasov models to real crystals, because it contradicted the classical theory of nucleation and growth of second-phase particles in solids. However, the development of the model of high-temperature precipitation of impurities made it possible to extend the mathematical apparatus of the classical theory of nucleation to the formation of nuclei in a solid during its cooling after the growth [9]. As a result, two theories of nucleation of second-phase particles, which are based on different epistemological approaches (the classical theory of nucleation and the Vlasov model for solids), lead to identical results. It is important to note that the Vlasov model of a solid state does not require introduction of additional parameters, such as the growth rate and the axial temperature gradient of the crystal, into the calculations.

#### 4. CONCLUSIONS

The formation of silicon–impurity complexes during the growth of undoped dislocation-free silicon single crystals followed by the growth and coalescence of precipitates is the decisive stage in the formation of a defect structure. Depending on the thermal conditions of growth, interstitial dislocation loops or microvoids are formed in the crystal during the further cooling.

The calculation of the formation of silicon–carbon and silicon–oxygen complexes during the cooling after the growth was performed within the framework of the Vlasov model of crystal formation. It was found that the complex formation begins in the vicinity of the crystallization front. It was shown that the Vlasov model of a solid state can be used not only for the investigation of hypothetical ideal crystals, but also for the description of the formation of a defect structure of real crystals.

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