ISSN 1063-7745, Crystallography Reports, 2019, Vol. 64, No. 4, pp. 581–585. © Pleiades Publishing, Inc., 2019.
Russian Text © The Author(s), 2019, published in Kristallografiya, 2019, Vol. 64, No. 4, pp. 550–554.

REAL STRUCTURE OF CRYSTALS

High-Temperature Precipitation of Impurities within the Vlasov Model for Solids

V. I. Talanin[a],* and I. E. Talanin[a]

[a] *Zaporizhzhya Institute of Economics and Information Technologies, Zaporizhzhya, 69015 Ukraine*

**e-mail: v.i.talanin@mail.ru*

Received September 12, 2017; revised April 12, 2018; accepted August 13, 2018

Abstract—It is shown that the Vlasov model for a solid describes the complexing processes when growing real crystals with allowance for the thermal growth conditions. It makes it possible (along with the classical theory of nucleation and growth of second-phase particles in solids) to calculate the defect crystal structure that was formed during the growth. It is established that the high-temperature impurity precipitation is directly related to the subsequent transformation of the defect structure when manufacturing of silicon devices. A qualitative model of the formation of electric centers is proposed, which directly relates their origin to the initial defect structure of silicon. It is shown that the concepts and principles of the Vlasov physics are absolutely applicable in solid-state physics.

DOI: 10.1134/S1063774519040230

INTRODUCTION

Theoretical description of the formation and transformation of the defect solid-state structure is an urgent problem of modern crystallography. The term "defect structure" implies a dynamic system of interacting structural defects, which, depending on various external conditions (temperature, irradiation, etc.), determines the electrical, mechanical, optical, and some other properties of crystals and related devices. Recently, a great advance has been made in the theoretical description of the defect structure of the most popular and high-quality semiconductor material of electronic engineering: silicon. This description is based on two gnoseologically alternative approaches: classical and probabilistic.

Until recently, the theoretical description of the atomic crystal structure was based on the classical (Born) approach [1]. The classical approach postulates the concept of lattice, stipulates the localization of each atom in the vicinity of a fixed lattice site, makes consistent the introduction of the concept of probability and mechanical description of particle behavior, and suggests that the set of atoms in the crystal is an integer. An important result of the Born approach is the development of the classical theory of nucleation and growth of second-phase particles in solids for real crystals [2]. However, this theory has a serious drawback, because it cannot explain the impurity precipitation during crystal growth. Therefore, it is assumed that the precipitation occurs only during heat treatment of a crystal, and the defect formation during the crystal growth is due to the decomposition of the supersaturated solution of intrinsic point defects [3].

The inconsistency between the experimental results and theoretical considerations was eliminated only in the diffusion model of formation and transformation of grown-in microdefects, which was based on the main principles of the classical theory of nucleation and growth of second-phase particles in solids [4]. The theoretical description of defect formation during the growth of semiconductor silicon within the classical approach shows that the impurity–intrinsic point defect interaction has a fundamental character and determines the defect structure of crystal from the crystallization onset to the production of a commercial device. This result was achieved by within two approaches: refusal from the model of fast recombination of intrinsic point defects near the crystal–melt interface [5] and development of the high-temperature precipitation model [6]. The high-temperature precipitation model was constructed by introducing the crystal growth rate V_g and axial temperature gradient G_a into the initial calculation equations: $T(t) = \frac{T_m^2}{T_m + V_g G_a t}$, where T_m is the crystal melting (crystallization) temperature; t is time, and T is temperature. The basic principles and concepts of the diffusion model of formation and transformation of the initial defect structure of semiconductor silicon were considered in [4] within the classical approach.

In the middle of the last century, Russian scientist A.A. Vlasov proposed a probabilistic approach to

describe properties of solids (Vlasov model for solids). Within this approach, the periodic crystal structure is due to the peculiarity of the statistical particle-motion laws, which match the periodic structure and freedom of atomic motion, rather than the limitations on atomic motion freedom throughout the crystal; as a result, the probability of finding an atom at interstitial sites is always nonzero [7].

The probabilistic approach 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 [8, 9]. Vlasov suggested that this method (applied by him to plasma) is universal and can be used to describe gases, liquids, and solids.

The purpose of this study was to analyze the solution to the Vlasov equation for solids by the example of forming impurity–intrinsic point defect complexes during crystal growth and temperature treatment of semiconductor silicon.

COMPLEX FORMATION DURING CRYSTAL GROWTH

The Vlasov theory for solids in the complete form was presented for the first time in [10]. In the general case, the Vlasov equation describes the evolution of the distribution function $f(x, v, t)$ of a continuum of interacting particles in the Euclidean space over velocity v and coordinate x at an instant t. It has the form

$$\frac{\partial f}{\partial t} + \left(\frac{\partial f}{\partial x}, v\right) + \left(\frac{\partial f}{\partial v}, F\right) = 0, \quad F = -\frac{\partial}{\partial x}\int K(x,y) f(y,v,t)\,dv\,dy, \tag{1}$$

where K is the pair interaction potential, which (in real problems) depends on the distance $|x - y|$, and F is the total force exerted on one particle at a point x from all other particles at an instant t [7]. Vlasov proceeded in his considerations from the following concepts: the spatial periodic distribution is one of the particular states of particle motion and certain state of motion for each particle of the set depends weakly on the total number of particles. In other words, one can consider a crystal consisting of two atoms.

The stationary properties of a crystal are described using the concept of particle distribution density $\rho(r) = \int f(r,v)dv$. Vlasov showed that the nonlocal crystal model is based on the following nonlinear equations, which make it possible to calculate the molecular potential and the density of particle location under thermal equilibrium conditions [10]:

$$U(r) = \lambda kT \int_{-\infty}^{\infty} K_{1,2}(r) \exp\left(-\frac{K_{1,2}(r)}{kT}\right) dr, \quad \rho(r) = \lambda kT \exp\left(-\frac{K_{1,2}(r)}{kT}\right), \tag{2}$$

where k is the Boltzmann constant, $K_{1,2}$ is the pair interaction potential, and λ is some characteristic number. The initial equations are equations for two particles under the steady-state conditions $\left(\frac{\partial}{\partial t} = 0\right)$ [10].

Equation (2) is atypical of the theory operating with point particles. The fact of existence of a problem of determining eigenvalues of nonlinear integral equations for two particles is related to the transition to another domain, in comparison with the theories of localized particles. Mathematically, equations in the form (2) are close to Hammerstein equations but differ from themby infinite integration limits and a different kernel type [10]. The mathematical theory of nonlinear equations, as applied to physical problems, involves the main mathematical problem, which consists in searching for the characteristic numbers. Here, the characteristic numbers are considered to be the values of some parameter λ, at which equations in the form (2) have nontrivial solutions. Trivial solutions are the solutions to Eqs. (2) corresponding to the case of uniform density [10].

Characteristic number λ is determined [10] from the main criterion of existence of crystalline state; the crystallization condition can be written as

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

where N is the number of particles and $K_{1,2}^{*} = -K_{1,2}$ [9, 10].

Vlasov showed for the case of crystal that the space of states is determined via temperature changes [10]. The complex distribution density can be presented as a function of the crystal cooling temperature:

$$\rho(T) = \lambda kT \exp\left(-\frac{U_{1\min,2\min}}{kT}\right), \tag{4}$$

where $U_{1\min}$ and $U_{2\min}$ are the minima of the interatomic potentials in, respectively, silicon–oxygen and silicon–carbon complexes.

Vlasov showed that the spatial periodic distribution is one of the particular states of particle motion [10]. This solution was obtained for an ideal (defect-free) crystal. Further studies in this field were hindered, mainly, for the following two reasons. An objective reason was the poor knowledge of structural defects in solids and their origin. A subjective factor was outright rejection of Vlasov's concepts by leading Soviet and Russian theoreticians [11, 12].

Seven decades after, the problem of complexing in semiconductor silicon was considered in accordance with the Vlasov solid model proceeding from the conclusions of the diffusion model of formation and transformation of grown-in microdefects [13]. It was shown that this model can be used not only to study hypothetical ideal crystals but also to describe the

defect-structure formation in real crystals. In particular, the formation of silicon–carbon and silicon–oxygen complexes during post-growth cooling was calculated using the Vlasov crystallization model.

Interatomic interactions in materials and, accordingly, their properties are determined based on the information about the interatomic interaction potential. The exact form of this potential for two atoms is determined from quantum-mechanical calculations. Generally, the potentials obtained are functions with many parameters, which are difficult to be considered analytically. Therefore, one uses model potentials with a smaller number of parameters [13]. To estimate the formation parameters of silicon–carbon and silicon–oxygen complexes, the interatomic interaction can be presented as the Mie–Lennard-Jones potential:

$$U(r) = K_{1,2}(r) = \frac{D}{(b-a)}\left[a\left(\frac{r_0}{r}\right)^b - b\left(\frac{r_0}{r}\right)^a\right], \quad (5)$$

where D and r_0 are, respectively, the depth and coordinate of the potential minimum and b and a are parameters ($b > a$). When a stable interatomic bond is formed, $r = \sqrt[6]{2}r_0$ and $U(r) = U_{\min}$. The parameters of the potential are as follows: $a = 2.48$, $b = 4.0$, and $D = 2.32$ eV for silicon; $a = 2.21$, $b = 3.79$, and $D = 3.68$ eV for carbon; and $a = 2.6$, $b = 4.2$, $D = 3.38$ eV for oxygen [13].

Since the system under study consists of atoms of different types, the potential cross parameters were determined according to the Lorentz–Berthelot combining rule [14]. The calculations yielded the following parameter values: $a = 2.345$, $b = 3.895$, and $D = 2.922$ eV for the silicon–carbon complex and $a = 2.541$, $b = 4.101$, and $D = 2.812$ eV for the silicon–oxygen complex. 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.

To determine the characteristic numbers of the silicon–oxygen (λ_1) and silicon–carbon (λ_2) complexes, we will use Eq. (3) at the number of complex particles $N = 2$ and $K(\rho) = kT\left(1 - \exp\left(-\frac{K_{1,2}}{kT}\right)\right)$ [10]. The calculation yielded the following values: $\lambda_1 = 4.482 \times 10^8$ eV^{-1} and $\lambda_2 = 1.099 \times 10^9$ eV^{-1} [13].

It was revealed that the complexing process begins near the crystal–melt interface. Therefore, the Vlasov model for a solid describes the complexing processes occurring during the growth of real crystals similar to the classical theory of nucleation and growth of second-phase particles in solids. Furthermore, a method for calculating the initial defect crystal structure was proposed, which includes the Vlasov model for solids and the classical theory of nucleation and growth of second-phase particles in solids [15].

COMPLEXING DURING CRYSTAL HEAT TREATMENT

After being subjected to heat-treatment processes with different durations in the temperature range of 300–1200°C, silicon crystals exhibit significant changes in the electrical and structural properties. As was shown in numerous studies, the main reason for the change in the silicon properties upon heat treatment is the transformation of the initial defect structure [16, 17]. The change in the electrical properties is due to the formation of donor (thermal donors I and II) and acceptor (thermal acceptors) centers. Thermal donors I are formed during treatment in the temperature range of 350–550°C and disappear after short annealing at temperatures above 550°C. The treatment at a higher temperature (600–800°C) also induces donor activity (thermal donors II or new thermal donors), which decompose at a temperature of ~900°C or higher [16]. In some cases, a heat treatment leads to the formation of thermal acceptors, which accompany thermal donors II [16].

Over the last six decades, several models of the formation of these centers were proposed based on experimental data obtained when studying the kinetics of their formation and the electrical, optical, and paramagnetic properties. These models were theoretically justified based on the classical approach using the theory of nucleation and growth of second-phase particles in solids. For the sake of brevity, we do not present a detailed analysis of these models; it can be found, e.g., in [16, 18]. However, having summarized the results, one can state that thermal donors I are oxygen and silicon complexes, which arise in the initial (formation) stage of precipitates. At the same time, thermal donors II are oxygen precipitates in their growth and coalescence stages [16]. Some researchers suggested that thermal donors I and thermal donors II have identical nature [19].

The Vlasov model of solids was applied to the complexing processes during heat treatment of silicon crystals. As an example, a calculation was performed using the same crystal parameters as in [20]. In this case, the calculation results obtained within the classical and probabilistic approaches can be compared. The joint use of both approaches makes it possible to consider the known facts from a new point of view and discover new phenomena and regularities when studying real solids. It was shown in [20] that the precipitation kinetics during heating of a crystal is similar to that upon its cooling during growth. The minimum critical radii of precipitates can be achieved in the initial state at $T = 730$ K (the minimum temperature of formation of structural defects in accordance with the classical theory of nucleation and growth of second-phase particles in solids); they increase with an increase in temperature. It was concluded that the formation and growth of precipitates may simultaneously occur during heat treatment.

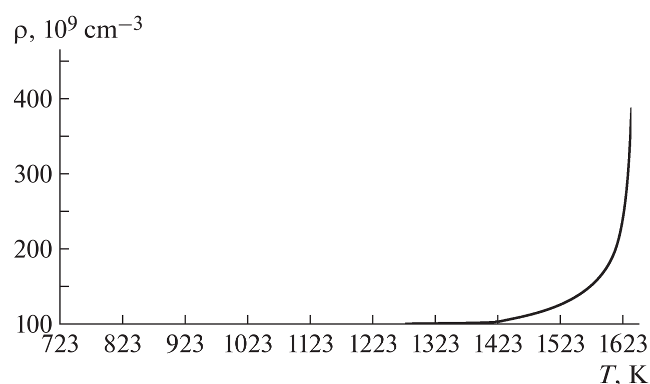

Fig. 1. Dependence of the distribution density of silicon–oxygen complexes on the annealing temperature.

However, the application of the Vlasov model of solids to the complexing processes during heat treatment of silicon crystals yields a somewhat different result. The solution to Eq. (4) has a simple and clear form (Fig. 1). According to the Vlasov model for solids, the complexing process at temperature $T = 730$ K, corresponding to the mean temperature of thermal-donor formation, is unlikely. Complexing in silicon during heat treatment may occur only at high temperatures [15]. Figure 1 shows that precipitates are not formed at temperatures that are generally used in technological treatments. Hence, from the physical point of view, the existing defects are dissolved and no new defects are formed. Let us consider the result shown in Fig. 1 in more detail.

At first glance, there is an insurmountable contradiction between the results obtained with two approaches. However, a precipitate is developed through three stages: complexing (nucleation), growth, and coalescence. During crystal growth the nucleation occurs near the crystal–melt interface. It is based on the complexing processes between the intrinsic and impurity point defects. When the crystal reaches some critical size, defects begin to grow. The stage of precipitate coalescence begins at certain crystal-cooling temperatures T_m (~20 K and ~300 K for small and large crystals, respectively) [21]. In this stage, some of precipitates continue to grow. At the same time, some smaller precipitates undergo a reverse process: they are dissolved [21]. The defect crystal structure is formed depending on the ingot thermal growth conditions; it includes precipitates, dislocation loops, or micropores [17]. As a minimum, oxygen and carbon precipitates are formed in undoped small (diameter 30 mm) silicon single crystals grown by floating zone melting at the growth rate V_g = 5–6 mm/min [17]. After the end of crystal growth, the development of precipitates in the silicon defect structure continues and is fixed at a temperature $T = 300$ K in the coalescence stage [21, 22].

The Vlasov model of solids indicates that there is no complexing in crystals during heat treatment. Therefore, the nucleation stage is also absent. However, the heat treatment activates the precipitate coalescence processes that are very weak at $T = 300$ K. The precipitate growth and dissolution rates increase with an increase in the annealing temperature. The Vlasov model indicates that one should consider the processes of dissolution of precipitates that are already formed during crystal growth rather than the processes of formation and growth of complexes. An analysis of the experimental and theoretical studies shows that, in this case, Si–O, Si–C, and C–O complexes can serve as electric centers in undoped silicon single crystals. In the case of doped crystals, the formation of electric centers may be based on precipitates of different nature (e.g., nitrogen). The heat treatment of silicon crystals occurs in the stage of precipitate coalescence. In this stage, some precipitates continue to grow, while the others (of smaller size) are dissolved. It is the dissolving precipitates that are responsible for the formation and annealing of electric centers in silicon. A characteristic feature of this consideration is not rejection but consideration of various model concepts about the nature of electric centers (beginning with the Kaiser model) [23].

Therefore, the Vlasov model of solids makes it possible to relate the processes of defect structure formation during crystal growth and its subsequent transformation due to the heat treatment. In this case, one can choose the optimal model of the nature of electric centers in silicon that are induced by heat treatment.

CONCLUSIONS

The Vlasov model of solids, which is based on the solution of the Vlasov equation with allowance for the crystal specificity, describes the processes of complexing during the growth of real crystals, depending on the thermal growth conditions. In addition, it makes it possible (along with the classical theory of nucleation and growth of second-phase particles in solids) to calculate the defect crystal structure formed during the growth. The concepts and principles of the Vlasov physics are completely applicable to solid-state physics.

The Vlasov model of solids allows one to consider the known facts from a new point of view and discover new phenomena and regularities when studying real solids. This thesis is confirmed by the consideration of the occurrence of donor and acceptor centers in silicon during heat treatment. The proposed qualitative model of formation of electric centers directly relates their origin with the initial defect structure of silicon. The formation of electric centers is due to the processes of dissolution of impurity precipitates (formed during crystal growth) during heat treatment. Therefore, the high-temperature impurity precipitation is directly related to the subsequent transformation of

grown-in microdefects when silicon devices are fabricated and is a basis for the formation and development of the silicon defect structure.

REFERENCES

1. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
2. J. W. Cristian, *The Theory of Transformations in Metals and Alloys* (Pergamon, London, 1965).
3. V. V. Voronkov, J. Cryst. Growth **59** (3), 625 (1982).
4. V. I. Talanin and I. E. Talanin, Phys. Solid State **58** (3), 427 (2016).
5. V. I. Talanin and I. E. Talanin, Phys. Solid State **49** (3), 467 (2007).
6. V. I. Talanin and I. E. Talanin, Phys. Solid State **52** (10), 2063 (2010).
7. A. A. Vlasov, J. Phys. **9**, 130 (1945).
8. A. A. Vlasov, *Many-Particle Theory and Its Application to Plasma* (Gordon and Breach, New York, 1961).
9. A. A. Vlasov, *Nonlocal Statistical Mechanics* (Nauka, Moscow, 1978).
10. A. A. Vlasov, *Theory of Many Particles* (Izd-vo Tekh. Teor. Lit., Moscow, 1950) [in Russian].
11. V. L. Ginzburg, L. D. Landau, M. A. Leontovich, and V. A. Fok, J. Exp. Theor. Phys. **16**, 246 (1946).
12. V. L. Ginzburg, Quest. Hist. Sci. Technol. **4**, 5 (2000).
13. V. I. Talanin and I. E. Talanin, Phys. Solid State **58** (10), 2050 (2016).
14. D. Boda and D. Henderson, Mol. Phys. **106**, 2367 (2008).
15. V. I. Talanin, I. E. Talanin, and V. I. Lashko, *New Research on Silicon: Structure, Properties, Technology* (INTECH, Rijeka, 2017), p. 5.
16. V. M. Babich, N. I. Bletskan, and E. F. Venger, *Oxygen in Silicon Single Crystals* (Interpress LTD, Kiev, 1997) [in Russian].
17. V. I. Talanin and I. E. Talanin, *New Research on Semiconductors* (Nova Sci., New York, 2006), p. 31.
18. R. C. Newman, J. Phys.: Condens. Matter **12**, R335 (2000).
19. Yu. M. Babitskii and P. M. Grinshtein, Fiz. Tekh. Poluprovodn. **18** (4), 604 (1984).
20. V. I. Talanin and I. E. Talanin, Phys. Solid State **55** (2), 282 (2013).
21. V. I. Talanin and I. E. Talanin, Phys. Solid State **53** (1), 119 (2011).
22. S. V. Bytkin and T. V. Kritskaya, Mater. Elektron. Tekh., No. 3, 9 (2010).
23. W. Kaiser, H. Frisch, and H. Reiss, Phys. Rev. **112** (5), 1546 (1958).

Translated by A. Sin'kov

SPELL: OK