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Complexation in germanium in accordance with Vlasov's model for solids

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ABSTRACT

Using Vlasov's model for solids, the diffusion model of defect formation in germanium was verified. The possibility of applying Vlasov's model for solids to describe complexation in dislocation-free germanium single crystals is shown. Vlasov's model for solids allows one to interpret the processes of defect formation in a crystal from a single viewpoint both at the stage of its growth and at the stage of heat treatment.

1. Introduction

The main task in studying structural imperfections in crystals is both obtaining experimental data and constructing theoretical models that could explain these experimental data. Such a theoretical model should link together both the processes of crystal growth and the processes of creating devices. We have now succeeded in developing such a theoretical model for semiconductor silicon crystals, which was called the diffusion model of defect formation [1]. This model is based on the elastic interaction 'intrinsic point defect (IPD) + impurity'. The diffusion model allows one to create software products with which it is possible to predict and control the defective structure of the crystal and devices during their creation.

There are two methods of verification of theoretical models: a) experimental confirmation of calculations; b) confirmation using alternative solids models. The study of structural imperfections using various experimental research methods confirms the reliability of the diffusion model of defect formation in semiconductor silicon. Based on these results, it was assumed that the basic principles and provisions of the diffusion model can be extended to other crystals.

We used the diffusion model to explain the processes of defect formation during the growth of dislocation-free single crystals of germanium [2]. It was shown that the process of recombination of IPDs near the crystallization front is significantly complicated. The coexistence of vacancies and silicon intrinsic interstitial atoms leads to the decay of a supersaturated solid solution of point defects during crystal cooling according to the 'IPD + impurity' mechanism. Under certain temperature conditions of crystal growth, either microvoids or interstitial dislocation loops form. These defects are secondary to impurity precipitates. The similarity of the processes of defect formation in dislocation-free single crystals of silicon and germanium is immediately evident. It is only necessary to take into account the type of crystal structure, thermal conditions of crystal growth, calculation parameters adequate to experimental studies. It should be noted that at present time the germanium crystals are grown in vacancy growth mode. In this regime, vacancies prevail over intrinsic interstitial germanium atoms and lead to the formation of microvoids [3,4].

The diffusion model of defect formation was built on the basis of the classical model of the structure of a solid state [5,6]. This is the science of the structure and practical use of substances in the solid state, which is based on the concept of an elementary crystalline cell. The assignment of an elementary crystalline cell was critically examined by A.A.Vlasov. He suggested that the crystalline structure of a solids has a probabilistic nature [7]. He extended his approach to the process of interaction between atoms of matter to all aggregate states (plasma, gas, liquid, and solids). In his work, Vlasov described the structure of ideal solid. He considered the interaction of two identical particles and built all the elementary cells. But he could not solve the problem of a defective (real) solid, since the structural defects were not precisely determined at that time.

The application of Vlasov's model for solids to describe the real structure of semiconductor silicon has shown that the classical and probabilistic approaches adequately consider the defective structure. In particular, this concerns the complexation that occurs near the crystallization front and determines the entire course of development of the defective structure of semiconductor silicon [8]. The combination of the classical and probabilistic approaches allows us to explain some issues. This concerns the issue of creating a defective structure as a result of

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heat treatments. Using Vlasov's model for solids, it was shown that the formation of thermal donors and thermal acceptors is associated with coalescence of precipitates [9]. These precipitates were obtained during the growth of a silicon crystal.

The aim of this paper is the possibility of applying Vlasov's model for solids to describe complexation in dislocation-free single crystals of germanium, as well as verification of the diffusion model of defect formation in germanium.

2. Vlasov's model for solids

Based on a system of equations for describing the evolution of a continuum of particles with a pair interaction potential, Vlasov suggested that using this approach one can describe any aggregate state of matter. He developed an approach to describing the structure of a solids based on the following basic principles [10–12]: 1) rejection of the principle of spatial and velocity localization of particles (in terms of classical mechanics), which takes place independently of force interactions; 2) the introduction of force interactions by analogy with classical mechanics, but taking into account the new principle of non-localization of particles; 3) the behavior of each particle in the system is described using a function extended in phase space. With this approach, the ideas of continuity and corpuscularity are combined, since the original way of describing the motion of a particle is associated with an extended function, and the particle's as a point is manifested only in a particular case [12].

In the general case, Vlasov's equation describes the evolution of the distribution function $f(x, v, t)$ of the continuum of interacting particles in Euclidean space with respect to speed v and coordinate x at time t. It has the form

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

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

where K is a pair interaction potential, which in real problems depends on distance $|x - y|$, and F is a the total force with which all particles act on one of them, which is at time t at point x [7].

To describe the stationary properties of a crystal, the concept of particle density distribution is used: $\rho(r) = \int f(r, v)dv$. The molecular field is determined not by exact, but only by probable atomic locations, which is expressed by the potential function containing the particle probability density taking into account the temperature distribution of the particles [7,11].

The choice of the pair interaction potential depends on the problem under consideration. Then the non-local model of the crystal is based on the following nonlinear equations, which make it possible to calculate the molecular potential and density of the particle location under conditions of temperature equilibrium [7,11]:

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

$$\rho(r) = \lambda kT exp\left(-\frac{K_{1,2}(r)}{kT}\right) \tag{2}$$

where k is a Boltzmann constant; $K_{1,2}$ is a pair interaction potential; λ is a some characteristic number; T is a temperature. The initial equations are equations for two particles in a stationary state $\left(\frac{\partial}{\partial t} = 0\right)$ [11]. Wherein by the characteristic number we mean such values of a parameter λ for which Eq. (2) possess solutions other than trivial [11]. If the position of one of the particles is taken as the origin, then we can determine $\rho(0) = \lambda kT$ [11]. Finding the characteristic numbers in Vlasov's model for solids is the most important task.

The characteristic number λ is determined from the main criterion for the existence of a crystalline state, while the crystallization condition can be written as follows:

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

where N is a number of particles; T_m is a melting/crystallization temperature; $K^*_{1,2} = -K_{1,2}$ [11].

Eq. (2) is written for the conditions of temperature equilibrium of the system. Since the minimums of interatomic potentials correspond to a stable equilibrium arrangement of atoms in complexes ('silicon-oxygen' and 'silicon-carbon'), then we can determine the distribution density of the complexes as a function of the cooling temperature of the crystal

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

Using this probabilistic approach, Vlasov calculated all the ideal structures of solids. The lack of accurate knowledge about defects in solids and the dependences of defect formation on real thermal growth conditions did not make it possible to continue these studies.

Vlasov's model for solids is an alternative to the classical approach (Born theory of the crystal). Born (classical) theory of a crystal is based on: 1) the postulate of the concept of a crystal lattice; 2) the localization of each atom in the vicinity of a fixed node of the crystal lattice; 3) the consistency of introducing the concept of probability and a mechanical description of the behavior of particles; 4) the premise that the set of atoms in a crystal is an integer [5]. Using this theory, a diffusion model of defect formation in semiconductor silicon and germanium was developed [1,2].

3. Experimental part

We need to find out the possibility of creating stable complexes 'IPD + impurity' as a result of elastic interaction. As an example, it suffices to consider the interaction 'oxygen-vacancy' and 'carbon-intrinsic interstitial germanium atom'. In addition, to trace the evolution of their distribution density depending on the nucleation temperature in a certain temperature range. Since, in accordance with the diffusion model of defect formation, the precipitation process begins near the crystallization front, the upper limit is $T = T_m = 1210$ K. The choice of the lower temperature limit is determined by the results of [2]. In this work, it was shown that the transition from the precipitate growth stage to the coalescence stage, depending on the thermal growth conditions, occurs in the temperature range $950 - 840$ K. We choose the average value of $T \approx 900$ K.

The interaction between atoms is determined by the potential of interatomic interaction. The exact form of the interaction potential of two atoms is determined from quantum-mechanical calculations. Usually potentials are functions with a large number of parameters. Therefore, need to using model potentials. There are several approaches to the construction of interatomic potentials for materials with covalent bonds. For germanium the most widely used are the Stillinger-Weber potential, Morse potential, Tersoff multiparticle potentials, modified embedded-atom method (MEAM) [13,14]. In our work, we used modified embedded-atom method [13–15]. From these literature sources, to estimate the formation parameters of the complexes 'germanium-carbon' and 'germanium-oxygen' we use the potential values $U_{1min} = 0.4$ eV and $U_{2min} = 2.18$ eV, accordingly [12–14]. For the number of particles of the complex $N = 2$ and $K(\rho) = kT\left(1 - e^{-\frac{K_{1,2}}{kT}}\right)$ using Eq. (3), we determine the characteristic numbers of the 'germanium-carbon' (λ_1) and 'germanium-oxygen' (λ_2) complexes. The calculation made it

possible to obtain the following values $\lambda_1 = 1.028 \cdot 10^3$ eV^{-1} and $\lambda_2 = 5.615 \cdot 10^{10}$ eV^{-1}. Note that, unlike silicon, for germanium many parameters for calculation are either absent or are not precisely determined. Therefore, it is very likely that as a result of new studies, the calculations of this study will be clarified [2].

The minima of the interatomic potentials determine a stable equilibrium arrangement of atoms in the complexes of 'germanium-carbon' and 'germanium-oxygen'. Then the distribution density of the complexes as a function of the cooling temperature of the crystal is described by formula (4).

Assume that the concentration of nucleation centers for carbon and oxygen complexes is 10^{12} cm^{-3}. This assumption is based on the fact that electron microscopic studies of silicon show just such an average concentration of precipitates after growing the ingot [1]. From this, the evolution of the distribution density upon cooling of the growing crystal in the temperature range from 1210 K to 900 K for the 'germanium-carbon' and 'germanium-oxygen' complexes is shown in Figs. 1 and 2.

During growth of dislocation-free single crystals of germanium, 'germanium-impurity' complexes are formed near the crystallization front. These complexes during cooling of the crystal grow, coalesce, and lead to the formation of precipitates. Moreover, the probability of the formation of a complex of 'germanium-carbon' is approximately equal to the probability of the formation of a complex of 'germanium-oxygen' (Figs. 1 and 2). Thus, the situation in germanium is not significantly different from silicon. In silicon, both processes are also approximately the same [1].

A modern understanding of the formation of extended lattice defects by condensation of IPDs during Czochralski pulling of silicon crystals is based on Voronkov's recombination-diffusion model [16]. Based on experimental and theoretical comparison of defective structures of germanium and silicon, it was proposed to use this theoretical model for germanium [17]. This decision was made on the basis of a semi-quantitative understanding of grown-in microdefects in germanium and control of dislocation-free growth in crystals with a diameter up to 300 mm. However, Voronkov's theoretical model is one-sided. During crystal growth, it completely ignores the effect of impurities. The diffusion model, which completely describes the defect formation in silicon, is deprived of this drawback. Use diffusion model for dislocation-free single crystals of germanium made it possible to describe in detail the processes of defect formation during growth of undoped single crystals [1]. Taking into account the 'IPD + impurity' elastic interaction allows us to understand and explain the early stages of defect formation in germanium. This interaction underlies the further development of its defective structure. So, based on a simple assumption about the similarity of the crystal structures of germanium and silicon, we obtained results similar to the study of the recombination of IPDs in silicon. It was shown that the formation of structural imperfections, as well as in silicon, occurs due to the interaction of 'IPD + impurity'. The possibility of applying the mathematical apparatus of a diffusion model of the

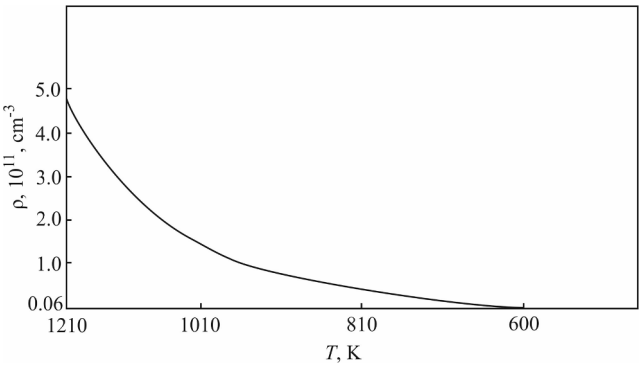

Fig. 1. Temperature dependence of the distribution density of 'germanium-carbon' complexes.

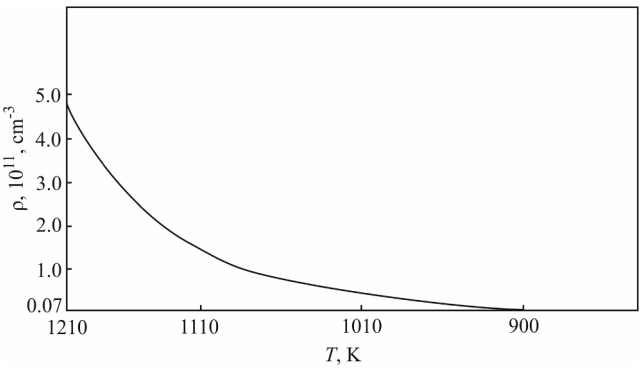

Fig. 2. Temperature dependence of the distribution density of 'germanium-oxygen' complexes.

formation of structural imperfections to the formation of a defective structure of undoped dislocation-free germanium single crystals is considered and proved [2].

The application of Vlasov's probabilistic model for solids (in a particular case for dislocation-free germanium single crystals) shows that the complexation process near the crystallization front is most probable (Figs. 1 and 2). The precipitation process begins near the crystallization front and is caused by the disappearance of excess IPDs at sinks, the role of which is played by impurity atoms. This is not only a confirmation of the classical diffusion model but also a proof of the unity of two theoretical models (classical and probabilistic), which are based on various principles.

As noted above, the similarity of the crystal structures of silicon and germanium leads to the formation similar defective structures during crystals growth [2,17]. The decisive role in creating a defective structure is played by impurities precipitation. During crystal cooling, precipitates grow and transform, which leads to the formation of dislocation loops or microvoids. In this case, dislocation loops and microvoids are secondary defects. Heat treatment of the grown crystals leads to the formation of other structural imperfections.

For example, after heat treatment processes of various durations of silicon crystals in the temperature range 573 K…823 K, significant changes in their electrophysical and structural properties are observed. Thermal donors are formed in this temperature range. Processing at higher temperatures causes their disappearance and the appearance of precipitates [18]. Existing models for the formation of thermal donors agree that they are complexes of oxygen and germanium and are the initial stage of the formation of precipitates. A further increase in temperature leads to an increase in complexes and the formation of precipitates [17].

We examined the processes of defect formation during the heat treatment of silicon from the viewpoint of the diffusion model. It was concluded that during heat treatment, the formation and growth of precipitates are simultaneously possible [19]. However, in accordance with Vlasov's model for solids, complexation in silicon during heat treatment is possible only at high temperatures [9].

Fig. 3 shows the solution of Eq. (4) for a germanium single crystal.

Therefore, only the transformation of the initial germanium growth structure can explain the processes of defect formation during heat treatments. Vlasov's model says that it is necessary to consider not the processes of formation and growth of complexes, but the dissolution processes of precipitates already created during the growth of crystals.

Complexation at an average temperature of thermal donor formation $T = 700$ K is unlikely. This suggests that the reverse process occurs during heat treatment. The development of precipitate passes through three stages: complexation (nucleation), growth, and coalescence [19]. In [2], it was shown that the transition to the coalescence stage is performed at $T \approx 850$ K. With a decrease in the oxygen content in the crystals, the condition for the transition to the coalescence stage will

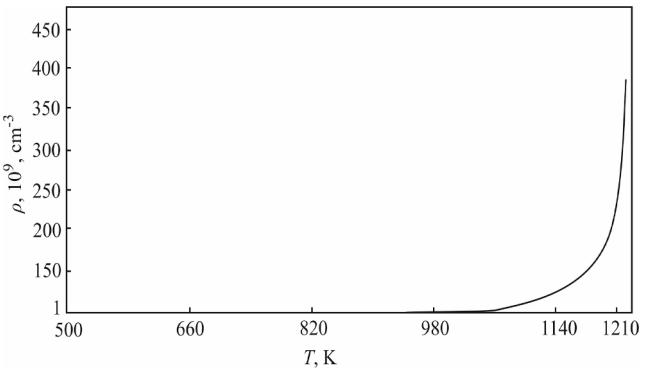

Fig. 3. Dependence of the distribution density of 'germanium-oxygen' complexes on the annealing temperature.

correspond to the cooling temperature $T \approx 940$ K. As is known, at the coalescence stage, one part of the precipitates continues its growth, and the other part of precipitates of smaller sizes dissolves [20]. Therefore, the development of precipitates at $T = 300$ K is fixed at the stage of coalescence. Heat treatment activates the coalescence of precipitates. An increase in temperature leads to an increase in the rate of growth and dissolution of existing precipitates. Precipitates that dissolve lead to the formation and annealing of electrical centers in germanium. In other words, during heat treatment, new precipitation centers have no possibility of formation and development. Growth and coalescence of grown-in precipitates occurs. This conclusion from Vlasov's model for solids contributes to understanding the problem of electrical centers in semiconductors.

Vlasov's model for solids allows one to interpret the processes of defect formation in a crystal from a single position both at the stage of its growth and at the stage of heat treatments. It not only does not contradict, but also complements our classical ideas about the structure of a solids.

4. Conclusion

The application of Vlasov's model for solids for calculating the defect structure of dislocation-free single crystals of germanium made it possible to obtain a number of interesting results. These include: (i) the formation of complexes of 'germanium-carbon' and 'germanium-oxygen' during cooling after growth begins near the crystallization front; (ii) Vlasov's model for solids describes the processes of complex formation during the growth of real crystals in accordance with the classical theory of nucleation and growth of second-phase particles in solids; (iii) it is possible to use Vlasov's model to describe the defect structure during the crystals growth of other solids; (iv) during heat treatment of crystals, which are used to create devices, complex formation is unlikely, but in this case, the processes of growth and transformation of growth precipitates occur.

The authors confirmed the validity of Vlasov's model for solids using an example of real material. It is shown that Vlasov's model for solids is, in fact, an analogue of the concept of classical ideas about the structure of a solid.

CRediT authorship contribution statement

V.I. Talanin: Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Investigation, Formal analysis, Validation. **I.E. Talanin:** . **:** Writing - original draft. **:** Visualization, Investigation, Formal analysis.

Declaration of Competing Interest

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

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