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A kinetic model of the formation and growth of interstitial dislocation loops in dislocation free silicon single crystals

V.I. Talanin *, I.E. Talanin

Classic private university, Zaporozhye, Ukraine

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ABSTRACT

A kinetic model of the formation and growth of dislocation loops in course of consequent as-grown crystal's cooling has been proposed It demonstrates that dislocation loops are formed following the processes of high-temperature precipitation of background oxygen and carbon impurities during crystal growth. Elastic deformation caused by growing precipitate is released due to the formation and growth of dislocation loops. Interstitial dislocation loops are formed, when the crystal growth ratio is $V_g/G < \xi_{crit}$. We have compared the kinetic model calculation data with the experimental research findings related to the formation of dislocation loops.

1. Introduction

Recently, we proposed a model of impurity precipitation in course of dislocation free silicon single crystals cooling after being grown within the temperature range of 1683 to 300 K [1]. It includes the kinetic models of oxygen and carbon precipitates formation, and as well as the kinetic model of their growth and coalescence [2,3]. The model of impurity precipitation in course of crystal growing is based on the experimentally and theoretically established fact that there is no recombination of intrinsic point defects at high temperatures, and there is elastic interaction between impurities and intrinsic point defects [4,5].

Either microvoids or interstitial dislocation loops are formed under specific thermal conditions of crystal growth depending on the growth ratio V_g/G (where V_g is a crystal growth rate, G is an axial temperature gradient) within the cooling temperature range of 1403 to 1223 K [6,7]. The authors of these papers made an assumption of a fast recombination of intrinsic point defects near the crystallization front. From this assumption many researchers have developed different variations of the point defect dynamics model [8–11]. The papers implied only that a homogeneous nature of the formation of microvoids and interstitial dislocation loops, and never allowed for impurity precipitation during the crystal cooling [9].

We calculated the formation of microvoids and interstitial dislocation loops according to rigorous approximation for the point defect dynamics model subject to no recombination of intrinsic point defects at high temperatures [12]. It was proved that the process of microvoid formation has a homogeneous nature. However, the formation of interstitial dislocation loops is determined, mainly, by the deformation mechanism. This conclusion was made on the basis of a three order of magnitude discrepancy between the experimentally observed concentration of interstitial dislocation loops and their estimated value. As a result, there is a need in the development of a kinetic model of the formation and growth of interstitial dislocation loops based on the deformation mechanism. Therefore, the objective of this paper is to develop a kinetic model of the formation and growth of interstitial dislocation loops in course of consequent as-grown crystal's cooling based on the deformation mechanism.

2. Nomenclature of grown-in microdefects

The most of the papers related to the observation of a defect structure of dislocation free silicon single crystals are connected with the study of the point defects interaction during the crystal growing, the clarification grown-in microdefects nature, and as well as identification of interaction between thermal conditions of crystal growth and grown-in microdefects formation. The experimental classification of grown-in microdefects employs the terms such as A-microdefects, B-microdefects, D(C)-microdefects, (I+V)-microdefects and microvoids [5]. The classification

* Corresponding author.
E-mail address: v.i.talanin@mail.ru (V.I. Talanin).

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is based on the use of the methods of preferential etching, X-ray topography and transmission electron microscopy. It was found that A-microdefects constitute interstitial-type dislocation loops, and B-microdefects, D(C)-microdefects, (I+V)-microdefects constitute precipitates of background oxygen and carbon impurities at different stages of their evolution [1,5]. The origin and sizes of precipitates in the silicon lattice are defined by oxygen and carbon concentration in it, and as well as by thermal conditions of single crystal growth [1]. For example, in small-scale FZ-Si single crystals of 30 mm in diameter if the crystal growth rate decreases from 9 to 3 mm/min, then the precipitate sizes increase from the range of 3 to 9 nm ((I+V)-microdefects) to the range of 20 to 50 nm (B-microdefects) [5]. At the same time, the concentration of precipitates changes from the range of 10^{13} to 10^{14} cm^{-3} ((I+V)-microdefects) to the range of 10^{10} to 10^{11} cm^{-3} (B-microdefects) [5]. The detailed TEM-observations of A-microdefects have shown that A-microdefects constitute interstitial dislocation loops or their clusters with sizes ranging from 1 to 40 μm [13,14]. A-microdefect size is inversely proportional to the crystal growth rate. The experimental researches demonstrate the concentration of dislocation loops within two orders of magnitude $\sim 10^6$ to 10^7 cm^{-3} [13,14]. Find more details about the experimental researches of grown-in microdefects in the papers [5,15].

At present, it is difficult to apply the experimental classification, since it is necessary to interpret the terms of every type of the grown-in microdefects for each publication. At the same time, from the physical point of view there are only three types of grown-in microdefects, i.e. impurity precipitates, interstitial dislocation loops and microvoids. Besides, when considering the formation of defects in silicon after processing (post-growth microdefects) the terms such as precipitates, dislocation loops and microvoids are also employed. Therefore, in order to harmonize a defect structure, we propose to switch to the physical classification of grown-in microdefects [15].

3. Model

The kinetics of high-temperature precipitation covers three stages: new phase nucleation, precipitate growth and coalescence stage [1,2]. Precipitates originate from elastic interaction between point defects. They are, initially, present in coherent, elastic and deformable state, when lattice distortions close to the precipitate-matrix boundary are not large, and one atom of the precipitate corresponds to one atom of the matrix [16]. Elastic deformations and any mechanical stress connected with them cause a transfer of excessive (deficient) substance from the precipitate or vice versa. Storage of elastic strain energy during the precipitate growth results in a loss of coherence by matrix. In this case it is impossible to establish one-to-one correspondence between atoms at different sides of the boundary. It results in structural relaxation of precipitates which occurs due to formation and movement of dislocation loops.

To simulate a stress state of the precipitate and the matrix surrounding it, it is sufficient to observe the precipitate which is simple spherical in shape. There can be found analytical solutions in respect of spherical precipitates [17]. Let us take the theoretical and experimental researches of stress relaxation at volume quantum dots as initial model [18–21]. According to these representations, as far as the precipitate grows, its elastic field induces the formation of a circular interstitial dislocation loop of mismatch. This process contributes to the decrease in total strain energy of the system. A growing precipitate displaces the matrix material in the crystal volume. Interstitial atoms form an interstitial dislocation loop near to the precipitate. At the same time, a mismatch dislocation loop is formed on the very precipitate [21]. At the same time, the critical sizes of precipitates, at which formation of dislocations is energy favorable, have the same order as the critical size of dislocation loops [21].

In the volume of silicon the precipitate produces a stress field caused by mismatch between the lattice parameters of precipitate (a_1) and surrounding matrix (a_2) [21]. Then, the intrinsic deformation of the precipitate is defined as described below:

$$\varepsilon = \frac{a_1 - a_2}{a_1} \tag{1}$$

In general, the precipitate intrinsic deformation in the matrix volume can be expressed as follows:

$$\varepsilon^* = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix} \delta(\Omega_{pr}) \tag{2}$$

where the diagonal terms constitute a dilatation mismatch between the precipitate and matrix lattices; the other terms are shear components; $\delta(\Omega_{pr})$ is the Kronecker delta. The elastic fields of precipitate (stress σ_{ij} and deformation ε_{ij}) and the field of total displacement are calculated accounting for intrinsic deformation (2) and regions of precipitate localization $\delta(\Omega_{pr})$. The elastic fields of precipitate are calculated according to the known scheme using elastic moduli, elastic Green function or its Fourier transform [20].

Let us consider the easiest model of a spherical precipitate with equiaxial intrinsic deformation, i.e. $\varepsilon^*_{ii} = \varepsilon, \varepsilon^*_{ij} = 0 (i \neq j; i,j, = x,y,z)$. Elastic strain energy of a spheroidal defect rises according to the cube law as the precipitate radius (R_{pr}) increases [21]:

$$E_{pr} = \frac{32 \cdot \pi}{45 \cdot (1 - \upsilon)} \cdot J \cdot \varepsilon^2 \cdot R^3_{pr} \tag{3}$$

where J is the shear modulus; υ is the Poisson's ratio. Starting from a certain critical value of the R_{crit} radius, the elastic strain energy mechanism begins to work. This mechanism results in the formation of a prismatic interstitial dislocation loop [21]. The energy criterion for such mechanism is the $E^{initial} \geq E^{final}$ condition, where $E_{initial}$, E_{final} constitute elastic energy of the system with precipitate before and after relaxation [21].

In respect of a spherical precipitate with equiaxial intrinsic deformation, the calculation of elastic fields of the precipitate is substantially simplified. Let us assume that the intrinsic elastic strain energy of the precipitate before and after the formation of a dislocation loop of mismatch remains constant $E^{initial}_{pr} = E^{final}_{pr}$. Then, a nucleation criterion for mismatch loop can be presented as $0 \geq E_D + E_{prD}$ condition, where E_D is energy of a dislocation loop of mismatch; E_{prD} is energy of precipitate-dislocation loop interaction [21].

For the purpose of assessment let us assume that a dislocation loop of mismatch has equatorial location on the spheroidal precipitate $R_D = R_{pr}$, and intrinsic energy of a prismatic loop is equal [21]

$$E_{loop} = \frac{J \cdot b^2 \cdot R_D}{2 \cdot (1 - \upsilon)} \cdot \left(\ln \frac{2 \cdot R_D}{f} - 2 \right) \tag{4}$$

where f is the radius of the core loop; b is the magnitude of the Burgers vector. A critical value of the precipitate radius corresponds to a value at which the loop is formed on the precipitate [21]

$$R_{crit} = \frac{3b}{8\pi(1+\nu)\varepsilon} \left(\ln \frac{1.08 \alpha R_{crit}}{b} \right) \tag{5}$$

where α is a constant contribution of the dislocation core. Formula (5) is approximate and can be used only to determine the value of R_{crit} critical radius.

This paper [22] theoretically considers the increase kinetics for dislocation loops at the stages of loop growth and coalescence.

It is assumed that, in general, the growth is either controlled by energy barrier when atom is captured by the loop, or by activation energy of interstitial atom diffusion. In conditions of cooling the crystal after being grown, we presume that the diffusion processes play a core role. The model [23] is further used in the calculations for evolution in size-dependant distribution of loops and for evolution in loop density.

The dislocation loops with a radius of $R > R_{crit}$ become bigger in size at the coalescence stage, while small dislocation loops with a radius of $R < R_{crit}$ will dissolve [22,23]. The growth of dislocation loop in course of consequent as grown silicon crystal's cooling occurs both due to the dissolution of small loops with the sizes less than critical, and the oversaturation of silicon self-interstitials. In this case, the crystal growth ratio is $V/G < \xi_{crit}$ (where 0.12 mm^2/K min $\leq \xi_{crit} \leq$ 0.3 mm^2/K min [10]). When oversaturation of vacancies ($V/G > \xi_{crit}$) occurs, the interstitial dislocation loops start to dissolve. Increase in the radius of interstitial dislocation loop can be defined by the formula depending on the crystal cooling time [23]:

$$R(t) = \sqrt{R_{crit}^2 + j \cdot D(t) \cdot t} \tag{6}$$

where $D(t)$ is the diffusion coefficient of intrinsic interstitial silicon atoms; t is the time cooling the crystal; j is the proportionality factor. The crystal cooling time value is defined from the dependence: $T(t) = (T_m^2/T_m + U \cdot t)$[1,9], where T_m is the crystallization temperature (melting) of silicon; $U = V_g \cdot G$ is the cooling rate of the crystal.

Let us assume that the formation of dislocation loops is defined only by deformation mechanism. Then, a concentration of dislocation loops during the crystal cooling shall be considered as the concentration function of precipitates. We have shown earlier that at the stage of growth and coalescence of precipitates their concentration is the function of the crystal cooling time [1]. Then, the loop concentration depends on the crystal cooling time [23]:

$$N(t) = \frac{M(t)}{1 + D(t) \cdot t/2 \cdot R_{crit}^2} \tag{7}$$

where $M(t)$ is the concentration of precipitates.

4. Experiment and discussion

We have carried out two individual groups of calculations which simulated the formation of interstitial dislocation loops during the growth of large-diameter and small-diameter crystals by Czochralski methods (CZ-Si) and float zone (FZ-Si). The first group of calculations (I) was carried out based on the following parameters: the crystal growth rate was $V_g = 0.3$ mm/min, the axial temperature gradient was $G = 2.5$ K/mm. These conditions correspond to the large-scale silicon single crystals growth by using Czochralski method at the growth ratio $V/G < \xi_{crit}$. The relevant parameters of the second calculation group (II) are as follows: the crystal growth rate was $V_g = 3$ mm/min, the axial temperature gradient was $G = 19.0$ K/mm. These conditions correspond to the small-scale silicon single crystals growth by using float zone method. For all groups of calculations $T = (T_m^2/T_m + VGt)$, where T_m is the melting temperature; $a_1 =$ 0.768 nm (SiO_2), $a_1 =$ 0.4359 nm (SiC), $\upsilon =$ 0.333, $k = 8.6153 \cdot 10^{-5}$ eV/K, $b = 0.384$ nm, $a_2 = 0.5431$ nm, $f = 0.96$ nm, $D = 0.19497 \cdot \exp[-0.9(eV)/kT]cm^2/s$.

The formation of precipitates results in occurrence of local fields and stress concentration that affect the generation and kinetics of dislocation loops. The intrinsic deformations of precipitates defined through the mismatch parameters of silicon and precipitates lattices are $\varepsilon_{SiO_2} = 0.293$, $\varepsilon_{SiC} = -0.246$. Elastic strain energy relaxation by precipitate results in occurrence of one or more dislocation loops [21]. The critical radiuses of precipitates which are energy favorable to the nucleation of dislocation loop shall be $R_{crit} =$ 3.028 μm (SiO_2) and $R_{crit} =$ 3.402 μm (SiC), correspondently. It is assumed that the nucleated loop has a radius which is equal to the precipitate radius, and elastic strain energy is decreased due to the diffusion of silicon atoms adjoining the precipitate [21]. A dislocation loop on the precipitate boundary is considered to be a dislocation loop of mismatch, in common, there can be several such loops, and they can surround the precipitate in different directions. Moreover, a satellite dislocation loop may form simultaneously with a dislocation loop of mismatch [19]. A radius of loop-satellite (R_1) is directly proportional to a radius of mismatch loop (R_2), i.e. $R_1 = \beta \cdot R_2, \beta = \sqrt{b_2/b_1}$, where b_1 and b_2 are Burgers vector values of a loop-satellite and a mismatch loop, correspondently [21].

Calculation results related to the evolution of loop radius in time for the crystals of the I group are shown in Fig. 1. Fig. 2 shows the calculation of change in the dislocation loop radius depending on a crystal cooling rate.

Maximum value of a dislocation loop radius for the crystals of both groups can be reached at the cooling temperature of 1423 K. Final diameter of dislocation loops for a crystal of the I group is 35.4 μm, and for a crystal of the II group is 4.1 μm. Rise in the crystal cooling rate results in a sharp reduction in loop size and increase in their concentration (Figs. 3 and 4).

As well known, precipitate sizes and concentration may change depending on the thermal conditions of crystal growth. For example, a maximum change in concentration of precipitates can reach three orders of magnitude [1]. Depending on the initial

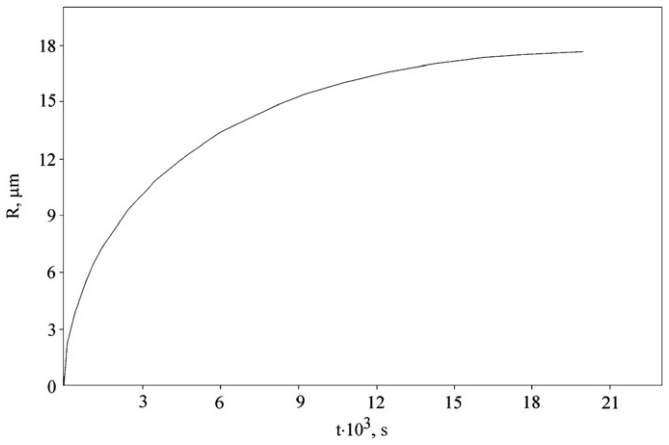

Fig. 1. Evolution of the radius of the dislocation loops in crystals of group I.

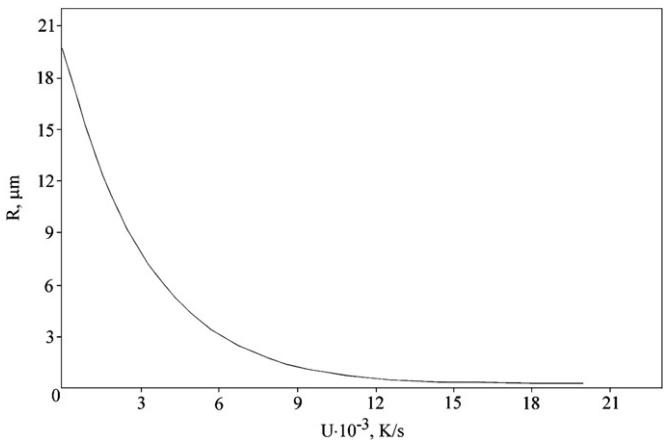

Fig. 2. The radius of the dislocation loop depending on the cooling rate of the crystal group I.

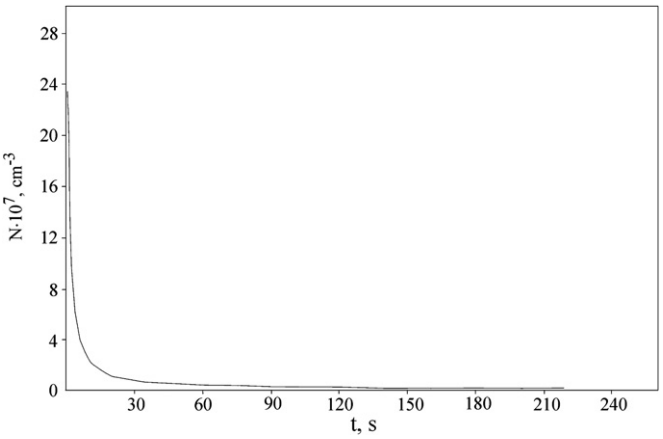

Fig. 3. Dependence concentration of the dislocation loops from time for the crystals of group II.

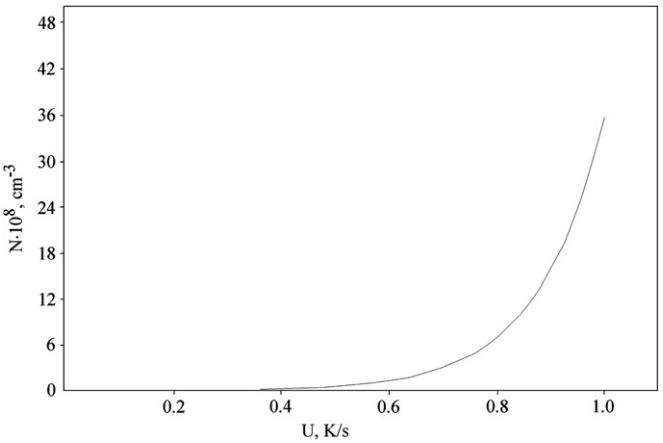

Fig. 4. Dependence concentration of the dislocation loops on the cooling rate of the crystal.

concentration of the precipitates the final concentration of dislocation loops varies from $2.45 \cdot 10^5$ to $2.45 \cdot 10^7$ cm^{-3}. For example, if M$=5 \cdot 10^{13}$ cm^{-3} the final concentration of dislocation loops for a crystal of the II group can reach $2.45 \cdot 10^7$ cm^{-3}.

Analyzing the TEM-data related to the study of precipitates in silicon single crystals which were obtained under various thermal growth conditions enables us to state that: (1) there are coherent precipitates which do not contain dislocation defects nearby; (2) there are precipitates with single dislocation loops; (3) there are precipitates with multiple dislocation loops [5].

Initially, the precipitates act as stoppers for the dislocation loops restraining their distribution and generation. Then, the precipitates facilitate the formation of dislocation loops due to the action of Bardeen-Herring or Frank-Read sources. These processes result in the growth and formation of complex dislocation loops (Fig. 5). Growth and coalescence of dislocation loops are generally maintained due to the generation of growing precipitates instead of silicon self-interstitials, and as well to the dissolution of small dislocation loops.

For release of stresses caused by the precipitate which is growing in the course of cooling it is required that the precipitate is to generate silicon self-interstitials into the interstitial sites or is to absorb vacancies. The first case corresponds to the crystal growth ratio $V/G < \xi_{crit}$, and is considered in this study. The second case corresponds to the crystal growth ratio $V/G > \xi_{crit}$ that results in suppression of the formation of interstitial dislocation

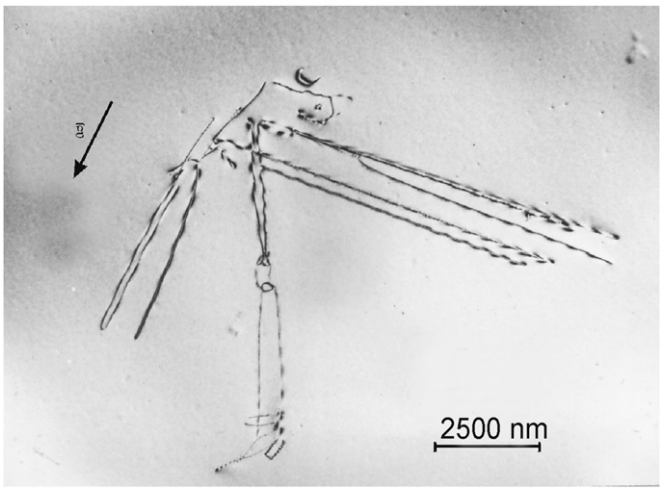

Fig. 5. TEM-image multiple dislocation loops.

loops and in the formation of microvoids under specific thermal conditions [5,24].

5. Conclusion

This paper considers a kinetic model of the formation and growth of interstitial dislocation loops formed in dislocation free silicon single crystals due to structural relaxation of the precipitates of background oxygen and carbon impurities. High-temperature oxygen and carbon precipitation is a fundamental process in the formation of silicon defect structure during the crystal cooling after being grown. Elastic deformation caused by the growing precipitate is released due to the formation and transition of dislocation loops.

We have compared the obtained results with the experimental findings within the framework of the proposed model. The observed compatibility proves the reliability of the proposed model, and enables us to use it for a correct count of precipitate effect on the formation of interstitial dislocation loops.

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