ON THE FORMATION OF VACANCY MICRODEFECTS IN DISLOCATION-FREE SILICON SINGLE CRYSTALS

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We have experimentally shown that the vacancy grown-in microdefects of the *D*- and *B*-types are formed in the interstitial mode of the growth of dislocation-free silicon monocrystals. It is determined that the concentration of vacancy *D*- and *B*-microdefects is by two orders less than that of interstitial *D*- and *B*-microdefects.

1. Introduction

The structure imperfections named as grown-in microdefects are formed during the high-temperature growing and the further cooling of dislocation-free single Si crystals. Presently, any local lattice imperfection from a few tens of angstroms to few micrometers is deemed as a grown-in microdefect. According to the generally accepted geometry (size) classification, the grown-in microdefects belong to the transient class of defects between point and linear ones. These grown-in microdefects, such as microprecipitates, dislocation loops, and microvoids are formed in a crystal by the aggregation of intrinsic point defects and impurities. The general strategy to increase a structural perfection of dislocation-free Si monocrystals should be developed by basing on the knowledge and adequate application of the mechanisms of formation and transformation of grown-in microdefects.

The large number of crystals, which were obtained under various thermal growth conditions, enabled us to make a schematic representation of the microdefect distribution in FZ-Si of 30 mm and CZ-Si of 50 mm in diameter under changing the crystal growth rate and by the heterogeneous mechanism of formation and transformation of grown-in microdefects [1—3]. The heterogeneous character of the nucleation of defects determines a further process of their formation in Si.

The basic principles of the heterogeneous mechanism can be outlined as follows:

— recombination of intrinsic point defects at the crystallization temperature is hindered because of the recombination barrier;

— background impurities of oxygen and carbon participate in the defect formation as nucleation centers and participate consequently in the processes of further growth and transformation of grown-in microdefects;

— cooling-induced decomposition of the oversaturated solid solution of point defects in silicon follows two mechanisms: the vacancy-type and interstitial-type ones.

For the vacancy-type mechanism:

1) $\mathrm{O}_i + V_{\mathrm{Si}} \rightarrow n(V\mathrm{O}_2) \rightarrow$ vacancy microdefects.

2) vacancy microdefects $+\ n\mathrm{O}_i\ +\ nI_{\mathrm{Si}} \rightarrow$ *D*-microdefects.

For the interstitial-type mechanism:

1) $\mathrm{C}_s + I_{\mathrm{Si}} \rightarrow n(\mathrm{C}_s I_{\mathrm{Si}}) \rightarrow$ *D*-microdefects.

2) *D*-microdefects $+\ n\mathrm{O}_i \rightarrow$ *B*-microdefects.

3) *B*-microdefects $+\ I_{\mathrm{Si}} \rightarrow$ *A*-microdefects.

We have establish experimentally the following [3, 4]:

— the main and defining factor of the beginning of the defect formation in dislocation-free Si monocrystals is the formation of complexes “impurity— intrinsic point defect”;

— the disintegration of a oversaturated solid solution of point defects results in the formation and the consequent transformation of primary grown-in microdefects (microprecipitates or $(I+V)$-, $D(C)$-, and *B*-microdefects);

— the formation of primary grown-in microdefects is accompanied by the pronounced creation of a structure from secondary violations representing the congestion of intrinsic point defects (secondary grown-in microdefects or *A*-microdefects and vacancy microvoids).

We have shown that these positions are aplicable for dislocation-free Si monocrystals of any diameter [3, 4]. The variations of a microdefective structure of dislocation-free Si monocrystals are connected to modifications of the crystal growth conditions of small and large diameters [3, 4]. Furthermore, we have offered a physical classification of grown-in microdefects which reflects the physics of the defect formation in dislocation-free Si monocrystals [3].

2. Experimental Procedure

We have conducted a series of experiments with FZ-Si and CZ-Si using the preferential etching and transmission electron microscopy. Silicon crystals of 30 mm (FZ-Si) and 50 mm (CZ-Si) in diameter were studied. FZ-Si crystals were not doped, the oxygen and carbon concentrations were less than 5×10^{15} cm^{-3}, the number of passes varied from 2 to 10, and $\rho = (2 \div 4) \times 10^3$ Ω·cm. The concentration of electrically active impurities was less than 10^{12}cm^{-3}. CZ-Si n-type crystals had $\rho = 10 \div 50$ Ω·cm, the oxygen concentration $\sim (4 \div 7)\times10^{17}$ cm^{-3}, and the carbon one $\sim (5 \div 7)\times10^{16}$ cm^{-3}. The crystals were grown at constant growth rates ranging from 1 to 9 mm/min (for FZ-Si) and 0.5 to 3 mm/min (for CZ-Si).

The Sirtl etch was used to identify microdefects of different types and their distribution images. The inside-outside contrast method, black-white contrast method, and defocused dark-field image method (or 2.5D-method) were used to determine the sign of lattice imperfections. An electron microscope with 100 kV acceleration voltage was employed, which excludes the radiation defect introduction. To avoid a contamination of the surface by alkali atoms and hydrogen (which are known to penetrate while etching to a depth of several micrometers), the samples for the TEM study were not subjected to that procedure. Knowing the etch pattern for a certain silicon wafer, one can rather exactly cut the samples for the TEM study from a selected place of a near-by wafer, thus the identity of the distribution of microdefects over the cross-section of both wafers being ensured.

3. Results

The obtained experimental results on the physical nature (the sign of strains in the crystalline lattice) of various types of grown-in microdefects explicitly are shown by us in [1, 2, 5]. The special interest was called by the researches of $D(C)$-microdefects and B-microdefects. Their formation occurs in the interstitial growth mode ($V/G < C_{\rm crit}$), and they produce a strain of compression in the crystalline lattice (that is, they are interstitial-type defects).

We have established the following [1, 2]:

— B-microdefects constitute the clusters of interstitial-type point defects with sizes of 20 to 50 nm, some lie in {100};

— D-microdefects constitute the clusters of interstitial-type point defects with sizes of 4 to 10 nm; they may be considered as a uniform B-microdefect distribution;

We assume that two forms of the existence of D- and B-microdefects are due to the existence of two paths of the heterogeneous mechanism.

In FZ-Si and CZ-Si in the vacancy growth mode ($V/G > C_{\rm crit}$) during the disintegration of the oversaturated solid solution of vacancies, the oxygen-vacancy aggregation occurs. So, the resulting microprecipitates SiO_2 (vacancy-type defects) will be formed. During the disintegration of the oversaturated solid solution of self-interstitials, the carbon-interstitials aggregation and the formation of SiC microprecipitates (interstitial-type defects) take place. Both these microprecipitates are $(I + V)$-microdefects [1, 2].

In the interstitial growth mode ($V/G < C_{\rm crit}$), two interconnected processes are running. At first, the interstitial-type defects grow at a decreasing growth rate and are transformed into interstitial D-microdefects. Secondly, the vacancy-type defects change the strain sign because of the absorption of oxygen atoms and are also transformed into interstitial D-microdefects. Furthermore, it is established that the influence of a high-temperature (more than 923 K) and long-term (more than 60 min) thermal treatment of dislocation-free Si monocrystals results in the inevitable modification of the volumetric distribution and the transformation of interstitial grown-in microdefects. Irrespective of a crystal growth method, this transformation occurs according the following scheme: D-microdefects → B-microdefects → A-microdefects. During the transformation, the size of defects is increased, and their concentration is decreased.

FZ-Si and CZ-Si crystals we investigate in the present paper were grown in the interstitial growth mode ($V/G < C_{\rm crit}$). For the TEM-researches of D- and B-microdefects, we used more than one thousand of samples FZ-Si and about five hundred samples CZ-Si (see the Table). We observed defects which produce a strain of expansion in the crystalline lattice (Fig. 1).

We have established that one or two vacancy defects per one hundred interstitial defects are present in samples with B-microdefects. At the same time, we observed three or four vacancy defects per one hundred interstitial defects in samples with D-microdefects. Vacancy D- and B-microdefects had sizes and contrast as similar appropriate interstitial-type microdefects.

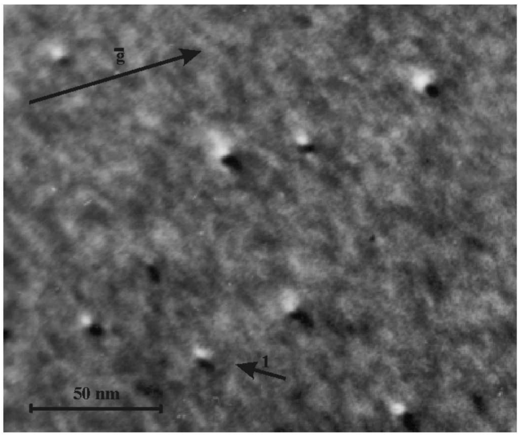

Fig. 1. TEM-image of D-microdefects in the interstitial growth mode ($V = 5$ mm/min, FZ-Si): *1* — vacancy defect; other defects are interstitial

4. Discussion

In [6], the X-ray diffusion scattering by grown-in microdefects in CZ-Si crystals ($V = 0.5 \ldots 1$ mm/min, a diameter of 100 mm, the oxygen concentration $\sim 10^{18}$ cm^{-3}, and the boron concentration $\sim 10^{15}$ cm^{-3}) with various thermal pre-histories, which were determined by conditions of growth, was investigated. A modification of the volume of the crystalline lattice, as well as signs of the "potency" of grown-in microdefects (positive for interstitial-type microdefects and negative for vacancy-type microdefects), depend on the nature of observable defects. The technique of X-ray diffusion scattering by defects allows to evaluate the sign of the "potency" of grown-in microdefects and to reveal the simultaneous presence of grown-in microdefects with different signs of the "potency". It is effective for the study of grown-in microdefects even if their concentration in crystals is small.

In crystals that were grown in the vacancy growth mode, the authors of [6] have observed simultaneously defects with positive and negative "potencies". However, the most interesting results were obtained for the crystals grown in the interstitial growth mode. It was established that, together with a dominant type of defects in the investigated areas of a crystal, there are defects with opposite sign [6]. Unfortunately authors of this work inform nothing on quantitative measurements of the observable defects.

We should like to mention the very interesting experimental results given in [7]. The authors used X-ray topography (the Borman method) for the research of grown-in microdefects in Si monocrystals. It was shown that this method allows one to unequivocally determine the sign of strain in the crystalline lattice of B-microdefects [7].

In experiments, it was established that B-microdefects are coherent inclusions of the second phase (presumably, SiO_2 and SiC) [7]. The authors observed no dislocation loops (A-microdefects). The extremely important result is the presence of defects which have opposite black-white contrast (i.e. vacancy B-microdefects) on topograms together with defects mainly of the interstitial-type. It is established experimentally that, among B-microdefects, interstitial-type defects make up 99%, and vacancy-type defects do 1% [7].

If various experimental methods independent of one another give the same result, it is a regularity. This regularity indicates that, in the interstitial growth mode of crystals FZ-Si and CZ-Si, vacancy-type D- and B-microdefects will be formed. Their concentration is less than that of interstitial-type D- and B-microdefects by at least two orders. Therefore, our suppositions about a symmetry of the heterogeneous mechanism of formation and transformation of grown-in microdefects and the experimental results of the present paper find experimental confirmations in the works of other authors. Our mechanism is schematically presented in Fig. 2.

Determination of the concentrations of interstitial and vacancy defects in the interstitial growth mode

Si monocrystals			TEM-research results			
Growth method	Ingot number	Growth rate, mm/min	Amount of samples	Interstitial defects, %	Vacancy defects, %	Defect type
FZ-Si	1	4.0	198	97.8	2.2	B-defects
(∅ 30 mm)	2	6.0	206	95.8	4.2	D-defects
	3	6.0	186	96.1	3.9	D-defects
	4	5.0	221	97.5	2.5	D-defects
	5	3.0	201	98.0	2.0	D-defects
CZ-Si	1	1.0	242	99.2	0.8	B-defects
(∅ 50 mm)	2	1.5	237	98.5	1.5	B-defects

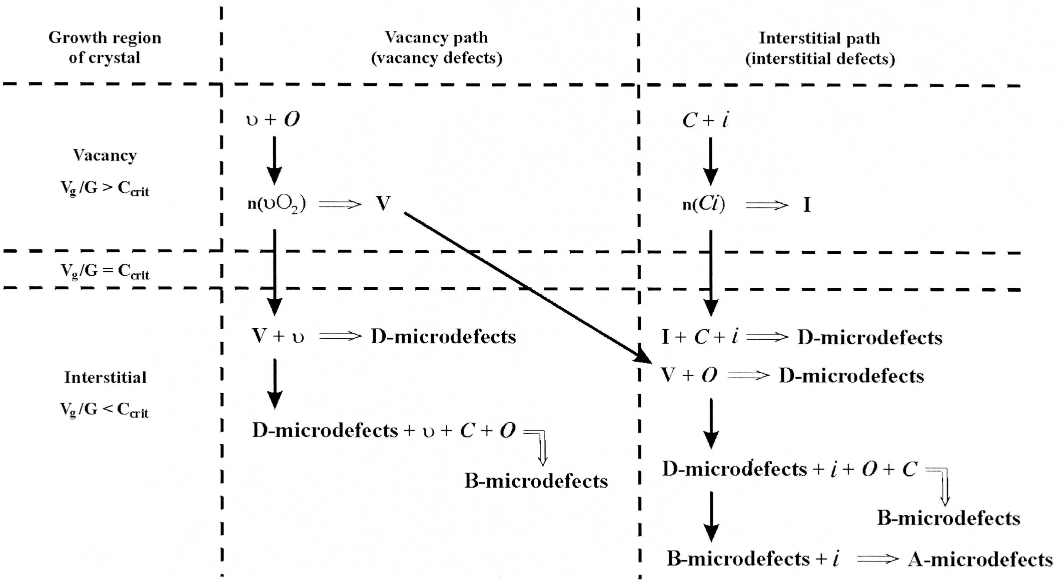

Fig. 2. Scheme of the heterogeneous mechanism of formation and transformation of grown-in microdefects in dislocation-free Si monocrystals: I — interstitial agglomerates, V — vacancy agglomerates, C — carbon, O – oxygen, i — self-interstitials, v — vacancies

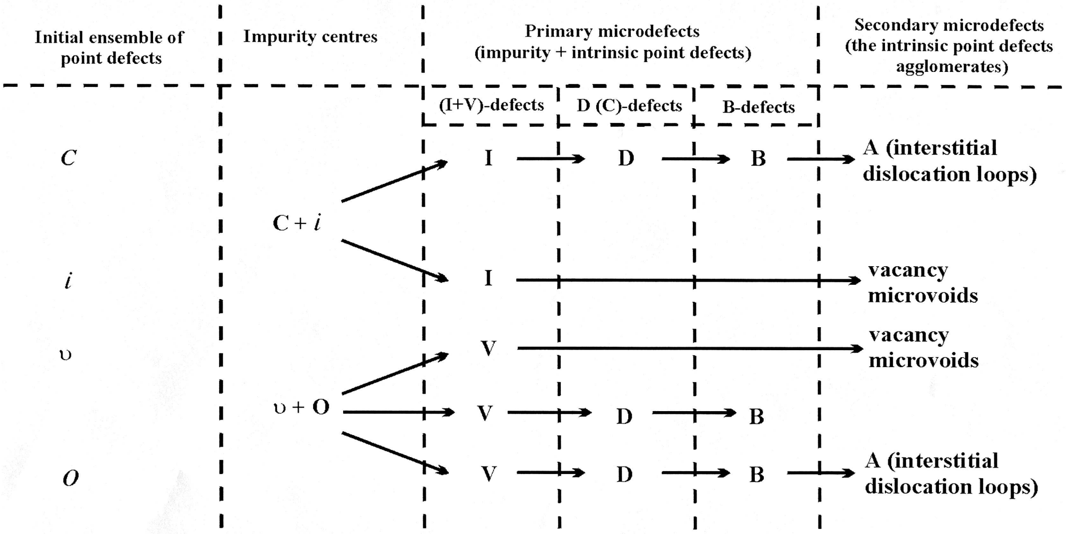

Fig. 3. Scheme of the physical classification of grown-in microdefects in dislocation-free Si monocrystals

Accordingly, the quasichemical equation which illustrates the directedness of the defect formation should be changed in correspondence with the heterogeneous mechanism of formation and transformation of grown-in microdefects.

For the vacancy-type mechanism:

1) $\mathrm{O}_i + V_{\mathrm{Si}} \rightarrow n(V\mathrm{O}_2) \rightarrow$ vacancy microdefects.

2) vacancy microdefects $+\, n\mathrm{O}_i + nI_{\mathrm{Si}} \rightarrow$ interstitial D-microdefects.

3) vacancy microdefects $+\, V_{\mathrm{Si}} \rightarrow$ vacancy D-microdefects.

4) vacancy D-microdefects $+\, V_{\mathrm{Si}} + \mathrm{O} + \mathrm{C} \rightarrow$ vacancy B-microdefects.

For the interstitial-type mechanism:

1) $\mathrm{C}_s + I_{\mathrm{Si}} \rightarrow n(\mathrm{C}_s I_{\mathrm{Si}}) \rightarrow D$-microdefects.

2) D-microdefects $+\, n\mathrm{O}_i \rightarrow B$-microdefects.

3) B-microdefects $+\, I_{\mathrm{Si}} \rightarrow A$-microdefects.

Therefore, it is necessary to change a physical classification of grown-in microdefects earlier offered by us in [3]. The changed classification is shown in Fig. 3.

In conclusion, we make two essential notes. First, it is necessary to take into account that the quasichemical equation and the schemes in Figs. 2 and 3 are idealized systems for four variables (vacancies, self-interstitials, oxygen, carbon). Such conditions are characteristic mainly of non-doped FZ-Si crystals grown in vacuum with the concentrations of oxygen and carbon to be less than 5×10^{15} cm^{-3}. For actual commercial crystals, it is necessary to consider other impurities (e.g., a doping impurity, iron, nitrogen, etc.) which contribute, in correspondence with the heterogeneous mechanism of formation and transformations of grown-in microdefects, to the defect formation in dislocation-free Si monocrystals [3].

Secondly, there exists the problem concerning vacancy dislocation loops (vacancy A-microdefects). Till now, their existence was not observed experimentally. Furthermore, the supposition about the disadvantage of the formation of vacancy A-microdefects was stated from a thermodynamic viewpoint [8]. From our viewpoint, an analog of interstitial A-microdefects in the vacancy path of the heterogeneous mechanism of formation and transformation of grown-in microdefects is presented by vacancy microvoids.

5. Conclusion

The presented experimental results and those of other authors (obtained by transmission electron microscopy, X-ray diffusion scattering, and X-ray topography) show that, in the interstitial growth mode, the vacancy grown-in D- and B-microdefects will be formed. The concentration of vacancy D- and B-microdefects is by two orders of magnitude less than the concentration of interstitial D- and B-microdefects.

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ПРО УТВОРЕННЯ ВАКАНСІЙНИХ МІКРОДЕФЕКТІВ У БЕЗДИСЛОКАЦІЙНИХ МОНОКРИСТАЛАХ КРЕМНІЮ

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Резюме

Експериментально показано, що в міжвузловинному режимі росту бездислокаційних монокристалів кремнію утворюються вакансійні ростові D- та B-мікродефекти. Визначено, що концентрація вакансійних D- та B-мікродефектів на два порядки нижча ніж концентрація міжвузловинних D- і B-мікродефектів.