ISSN 1063-7745, Crystallography Reports, 2012, Vol. 57, No. 7, pp. 26–30. © Pleiades Publishing, Inc., 2012.

REAL STRUCTURE OF CRYSTALS

Analysis and Calculation of the Formation of Grown-in Microdefects in Dislocation-Free Silicon Single Crystals

V. I. Talanin, I. E. Talanin, and N. Ph. Ustimenko

Classic Private University, Zhukovskii str. 70B, Zaporozhye, 69002 Ukraine
e-mail: v.i.talanin@mail.ru

Received December 20, 2010

Abstract—The physical model of the formation of grown-in microdefects in dislocation-free Si single crystals has been analyzed. The mathematical models used to describe the processes of defect formation in crystals during their growth are proven to be adequate to the physical model. A technique is proposed to determine and calculate the defect structure in dependence of the crystal growth conditions (growth technique, growth rate, temperature gradients, cooling rate). It is shown that the theoretical study of the real crystal structure in the dependence of the thermal growth conditions using an original virtual technique for analyzing and calculating the formation of grown-in microdefects is a new experimental technique.

DOI: 10.1134/S1063774512070218

INTRODUCTION

It is well known that the structural quality of silicon crystals determines to a great extent their properties (electric, optical, mechanical, etc.). During crystal growth, grown-in microdefects are formed due to the interactions between point defects; these microdefects, depending on the growth rate and temperature gradients in the crystal, are precipitates of impurities, vacancy microvoids, or interstitial dislocation loops [1].

When semiconductor devices and integrated circuits are fabricated, grown-in microdefects undergo significant transformations, which lead to the formation of dislocations, stacking faults, rodlike defects, dipoles, and platelike precipitates. By analogy with the defect structure formed during crystal growth, all types of defects arising after technological processes can be considered as post-growth microdefects.

The initial (grown-in) microdefects play a key role in the formation of the final defect structure. At the same time, the experimental study of grown-in microdefects meets serious technical and material difficulties, which are mainly related to the detection and determination of the individual characteristics of very small lattice defects (depending on the type of grown-in microdefects, their sizes range from 2 nm to 50 μm) [1]. The corresponding theoretical studies should be adequate to the experimental data; i.e., they should not be reduced to individual (particular) calculations, but must be reproducible in wide ranges of variations in the thermal growth conditions. In this case, instead of rather expensive experiments, one would analyze and calculate grown-in microdefects on a personal computer using inexpensive software.

In this context, our purpose was to develop a method for analyzing (determining) and calculating the formation of grown-in microdefects depending on the crystal growth conditions (growth technique, growth rate, temperature gradients, cooling rate) for its subsequent implementation as software.

PHYSICAL AND MATHEMATICAL MODELS OF GROWN-IN MICRODEFECT FORMATION

Experimental studies of the formation and transformation of grown-in microdefects in dislocation-free Si single crystals by different methods (selective etching, transmission electron microscopy, X-ray topography, etc.) have been performed beginning with the second half of the 1960s. The most complete and exhaustive data on the distribution of defects in crystals, characteristics of individual defects of different types (size, shape, type of crystal structure deformation, concentration), and the processes of their transformation during growth and after different technological processes were reported in [1].

Based on the results of experimental studies, we formulated the main concepts of the physical model of formation and transformation of grown-in microdefects [2]. These concepts are as follows: (1) the recombination of intrinsic point defects can be neglected at high temperatures [3]; (2) background carbon and oxygen impurities are involved in defect formation as nucleation centers [4]; (3) defect formation is determined by the thermal growth conditions (rate of crystal growth, temperature gradients in crystals, cooling rate) [5]; (4) the decay of supersaturated solid solution of point defects in silicon crystals upon cooling from the crystallization temperature occurs according to two independent mechanisms (branches): vacancy and interstitial [4]; (5) the main element in defect formation is primary agglomerates (impurity precipi-

tates), which are formed in silicon crystals upon cooling from the crystallization temperature as a result of interaction of point defects of the impurity–intrinsic point defect type [2]; (6) upon crystal cooling at temperatures below 1150°C, depending on the thermal growth conditions, secondary grown-in microdefects arise (vacancy microvoids or interstitial dislocation loops) [2, 5]; (7) secondary grown-in microdefects are formed due to the mechanisms of coagulation (vacancy microvoids) and deformation (interstitial dislocation loops); and (8) the formation of secondary grown-in microdefects is controlled by the growth parameter $V_g/G_a = C_{crit}$, where V_g is the rate of crystal growth and G_a is the axial temperature gradient (vacancy microvoids are formed at $V_g/G_a > C_{crit}$ and interstitial dislocation loops arise at $V_g/G_a < C_{crit}$) [5].

Historically, literal notation has been used to describe the distribution of grown-in microdefects in crystals: *A* microdefects (interstitial dislocation loop), *B* microdefects, *C* microdefects, *D* microdefects, $(I + V)$ microdefects, and vacancy microvoids [1, 7].

An analysis of the experimental results obtained suggests that the *B*, *C*, *D*, and $(I + V)$ microdefects are different forms of developed precipitates; thus, the literal notation for grown-in microdefects, which was proposed in the beginning of the 1970s, can be rejected because the nomenclature of the found grown-in microdefects includes only three forms: impurity precipitates, vacancy microvoids, and interstitial dislocation loops [1]

Generally, the physical model considers the defect formation in a crystal upon cooling as a process including three stages: (1) the formation of impurity aggregates (primary grown-in microdefects) near the crystallization front; (2) the growth and coalescence of impurity precipitates upon cooling from the crystallization temperature; and (3) the formation of secondary grown-in microdefects: vacancy microvoids or interstitial dislocation loops (depending on the growth parameter V_g/G_a) in a narrow temperature range of 1150–850°C.

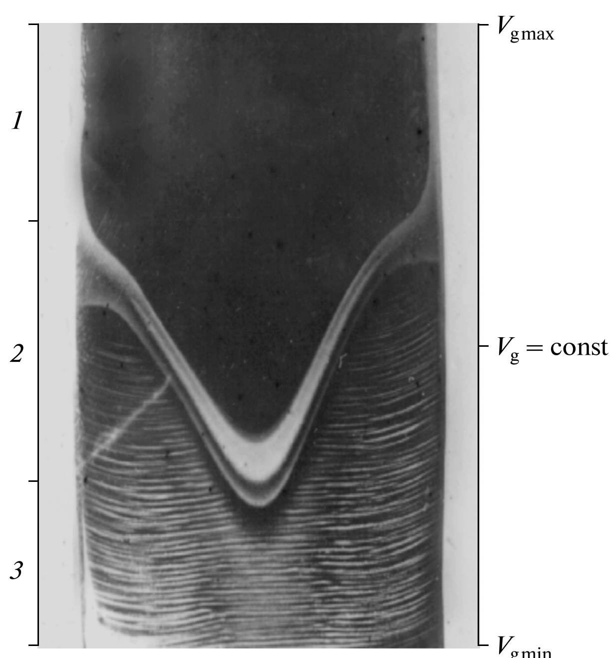
The mathematical models that are currently used to describe the formation of three types of grown-in microdefects are based on two approaches: the model of point-defect dynamics [8] and the diffusion model [9, 10]. The former suggests a homogeneous mechanism of the formation of vacancy microvoids and interstitial dislocation loops as a result of the fast recombination of intrinsic point defects near the crystallization front and generally includes three approximations: rigorous, simplified (lumped), and discrete-continuous [11]. The *rigorous model* implies the solution of integro-differential equations for the concentration fields of point defects; the distribution of grown-in microdefects within this model is a function of coordinates, time, and the time of the evolution of the size distribution of microdefects [12–14]. The large expenditure of time and high cost of calculations in this model called for development of a *lumped model*, in which the average defect radius is approximated by the square root of the average defect area [11]. This approximation is taken into account by introducing an additional variable, which is proportional to the total defect surface area. The lumped model is efficient in calculations of the two-dimensional distribution of grown-in microdefects [11, 15]. Both models use the classical theory of nucleation and allow one to calculate the formation of stable nuclei and the kinetics of diffusion-limited defect growth. The *discrete-continuous model* implies the following complex approach: the solution of discrete equations for very small defects and the Fokker–Planck equations for larger defects [16–18].

Our calculations within the model of point-defect dynamics, with allowance for the absence of recombination of intrinsic point defects near the crystallization front, showed that this model adequately describes the formation of vacancy microvoids and interstitial dislocation loop. Based on the results obtained, we can state that the formation of interstitial dislocation loops has a deformation character, whereas vacancy microvoids are formed homogeneously [6].

The diffusion model allowed us to consider for the first time the impurity precipitation upon crystal cooling from the crystallization temperature to room temperature in terms of the classical theory of nucleation and growth of new-phase particles. In crystals, precipitation is considered to be a first-order phase transition, and the kinetics of this process is divided into three stages: (i) the formation of new-phase nuclei, (ii) the growth of clusters, and (iii) the coalescence stage.

The diffusion model uses a combined simulation method, which is based on solving differential equations for small clusters and Fokker–Planck equations for larger clusters in the cooling range of 1683–300 K. It was theoretically shown for the first time in [9, 19, 20] that precipitation begins near the crystallization front and is caused by the annihilation of excess intrinsic point defects at sinks (oxygen and carbon impurities). According to the data of [10], a change in the thermal growth conditions of crystals strongly affects the stage of precipitate growth.

Currently, there is complete adequacy of the physical and mathematical models of formation and transformation of grown-in microdefects. Therefore, the purpose of our study was to substantiate and develop a unified technique for analyzing and calculating the grown-in defect structure of dislocation-free silicon single crystals of different diameters grown using the Czochralski and floating zone melting methods, as well as to elaborate a virtual experimental tool based on this technique.



Standard distribution pattern of grown-in microdefects in dislocation-free silicon single crystals grown by the Czochralski method with a variable growth rate.

TECHNIQUE FOR ANALYZING AND CALCULATING THE FORMATION OF GROWN-IN MICRODEFECTS

Since the formation of grown-in microdefects in dislocation-free Si single crystals is controlled by thermal growth conditions, the technique for determining and calculating the grown-in defect structure must be based on a parameter interrelating the main thermal growth conditions. An appropriate candidate is the growth parameter $V_g/G_a = C_{crit}$.

The condition $Vg/G_a = C_{crit}$ in real crystals corresponds to a V-shaped distribution of D microdefects in a plane parallel to the growth axis or an annular distribution of D microdefects in a plane perpendicular to the growth direction [1, 4]. It is accepted to relate the condition $V_g/G_a = C_{crit}$ to the so-called *oxidation-induced stacking fault* (OSF) ring, which is observed in crystals after thermal treatments [21, 22]. The use of this term is not quite correct because stacking faults are not grown-in, but rather post-growth microdefects. Stacking faults arise as a result of the transformation of grown-in microdefects (precipitates) during post-growth effects. It was found experimentally that D microdefects are oxygen and carbon precipitates, and their concentration within the ring region is almost an order of magnitude higher than beyond it [1].

Figure 1 shows a standard distribution of grown-in microdefects in the dislocation-free Si single crystals grown by the Czochralski method with a variable growth rate. The crystal diameter is 50 mm and the growth rate changed from V_{gmin} = 0.5 mm/min to V_{gmax} = 3.0 mm/min.

Three regions of defect formation can be selected: region 1, located above the V-shaped distribution of precipitates; region 2, which is the region of V-shaped distribution, and region 3, located below the V-shaped distribution. In small Si crystals, grown-in microdefects (precipitates) of interstitial and vacancy types are formed in comparable concentrations in region 1; in region 2, the same defects are formed within the V-shaped distribution, while interstitial dislocation loops and mainly interstitial-type precipitates arise beyond this distribution [1, 2]. In crystals more than 70 mm in diameter, vacancy microvoids begin to form in regions 1 and 2 (within the V-shaped distribution) [2]. Interstitial dislocation loops and precipitates of mainly interstitial type are formed in region 3 [1].

An increase in the crystal diameter leads to a change in the thermal growth conditions. As a result, the defect-formation pattern in the longitudinal cross section also changes: regions 1 and 3 rapidly disappear [23]. For example, the defect-formation pattern in modern large (150–300 mm in diameter) Czochralski-grown Si single crystals correlates with only region 2 in Fig. 1 [23].

In small crystals, at $V_g/G_a > C_{crit}$, the vacancy concentration in region 1 is comparable to the concentration of intrinsic silicon interstitials (high rates of crystal growth), whereas in region 3, the vacancy concentration is low compared to the concentration of silicon interstitials (low rates of crystal growth). For large crystals, at $V_g/G_a > C_{crit}$, the supersaturation in vacancies is due to the presence of V-shaped distribution of precipitates, which leads to the depletion in impurity atoms in the region of V-shaped distribution and provides the conditions for the homogeneous formation of vacancy microvoids. Therefore, the growth parameter $V_g/G_a = C_{crit}$ controls the system of interacting point defects upon post-growth cooling.

At the first stage of this technique, a certain crystal diameter is set. Since the parameter $V_g/G = C_{crit}$ is determined theoretically and experimentally in some range of values ($0.06 \le C_{crit} \le 0.3$ mm^2/K min) [8, 16, 23], we choose some value of C_{crit} for the calculations.

At the second stage, the values of the axial temperature gradient at the crystal center (G_a) and the minimum (V_{gmin}) and maximum (V_{gmax}) rates of crystal growth are chosen. For each crystal diameter, these values can be determined from an analysis of the corresponding experimental and theoretical data.

The third stage is the choice of axial temperature gradient at the crystal edge (G_e) in the range of G_e/G_a = 1.0–2.5. The parabolic radial distribution of the axial temperature gradient has the form

$$G(r) = G_a + (G_e - G_a)(r/R_s)^2,$$

where R_s is the crystal radius and r is the current coordinate in the range of $0-R_s$.

At the final stage, the dependence of the critical growth rate on the crystal radius is plotted proceeding from the relation $V_{crit}(r)/G(r) = C_{crit}$. Then, the data on the real rate of crystal growth are imposed on the calculated dependence of the critical growth rate to determine the type of defect structure in the real crystal. Obviously, for a crystal of a given diameter, depending on the position of the straight line $V =$ const with respect to the curve $V_{crit}(r)$, three regions can be selected in the defect structure (Fig. 1).

Figure 1 shows some value $V =$ const as an example. In this particular case, we arrive at region 2. Based on an analysis of the defect structure of this region, the formation of precipitates is calculated within the V-shaped distribution of precipitates, whereas beyond this distribution, the formation of both the precipitates and dislocation loops is calculated. The formation of precipitates is calculated in terms of the classical theory of the nucleation, growth, and coalescence of precipitates using both analytical and approximate approaches [9, 10]. Calculating the loop formation makes it possible to determine parameters, such as the loop critical radius, the dependence of the loop diameter on the rate of crystal growth, and the loop concentration [6].

One should note two main advantages of the technique for analyzing and calculating the growth-in defect structure of dislocation-free Si single crystals. The first advantage is that this technique is fairly simple and can easily be implemented as a program product, which can serve as a convenient virtual experimental tool for studying various properties of dislocation-free Si single crystals. The second advantage is that the analysis and calculation of defect formation is determined by only the thermal growth conditions. Two out of three control growth parameters are strictly specified (the crystal diameter and the growth rate), while the axial temperature gradient is set in some range. This uncertainty of the axial temperature gradient introduces an error in the analysis and calculation of the formation of grown-in microdefects using this technique. However, this error can be reduced if the G_a and G_e values are experimentally found during crystal growth.

The reliability of the proposed technique can be experimentally checked using the selective etching of longitudinal or transverse cross sections of the crystal. If there are deviations from the experimental pattern, one can obtain complete correspondence between the calculated and experimental data by fitting the parameters G_a, G_e, and C_{crit}. This experimental verification will exclude the difficulties related to experimental determination of the G_a and G_e values, especially in the case of crystals with large diameters.

CONCLUSIONS

The technique proposed for analyzing and calculating the formation of grown-in microdefects in dislocation-free Si single crystals is fairly simple and, as was noted above, can easily be implemented as a program product on a personal computer. This simplicity only became possible after the development of mathematical models for calculating the formation of precipitates, vacancy microvoids, and interstitial dislocation loops [6, 9, 10].

This technique makes it possible to analyze and calculate the formation of grown-in microdefects based on the thermal growth conditions for dislocation-free silicon single crystals (rate of crystal growth, axial and radial temperature gradients). As a result, one can program the processes of crystal growth with a specified and controlled structure. In addition, necessary furnace accessories can be developed to obtain growth parameters providing a specified defect structure.

We expect this technique to be widely applied in the research practice of not only technologists but also physicists, material engineers, and designers. For example, physicists can use it to relate fluctuations in determining a particular parameter (property) for different crystals with the dependence of this parameter (property) on a certain initial defect structure.

The theoretical study of the real structure of crystals in the dependence of their thermal growth conditions using the original virtual technique for analyzing and calculating the formation of grown-in microdefects is a new experimental technique that makes it possible to replace experimental structural studies with adequate theoretical studies. Therefore, the program product developed based on this technique can be considered a new virtual experimental tool.

REFERENCES

1. V. I. Talanin and I. E. Talanin, *New Research on Semiconductors* (Nova Sci., New York, 2006), p. 31.
2. V. I. Talanin and I. E. Talanin, Crystallogr. Rep. **55** (4), 632 (2010).
3. V. I. Talanin and I. E. Talanin, Phys. Solid State **49** (3), 467 (2007).
4. V. I. Talanin and I. E. Talanin, Defect Diffusion Forum. **230–232** (1), 177 (2004).
5. V. V. Voronkov, J. Cryst. Growth **59** (3), 625 (1982).
6. V. I. Talanin and I. E. Talanin, Phys. Solid State **52** (9), 1880 (2010).
7. A. J. R. de Kock and W. M. van de Wijgert, J. Crystal Growth **49** (4), 718 (1980).
8. M. S. Kulkarni, V. Voronkov, and R. Falster, J. Electrochem. Soc. **151** (5), G663 (2004).
9. V. I. Talanin and I. E. Talanin, Phys. Solid State **52** (10), 2063 (2010).

10. V. I. Talanin and I. E. Talanin, Phys. Solid State **53** (1), 119 (2011).
11. M. S. Kulkarni, Ind. Eng. Chem. Res. **44** (10), 6246 (2005).
12. V. V. Voronkov and R. J. Falster, J. Appl. Phys. **91** (9), 5802 (2002).
13. T. Sinno, R. A. Brown, W. Ammon, and E. Dornberger, J. Electrochem. Soc. **145** (1), 302 (1998).
14. K. Nakamura, T. Saishoji, T. Kubota, and T. Iida, J. Cryst. Growth **180** (1), 61 (1997).
15. M. S. Kulkarni, J. Cryst. Growth **303** (2), 438 (2007).
16. T. Sinno and R. A. Brown, J. Electrochem. Soc. **146** (6), 2300 (1999).
17. Z. Wang and R. A. Brown, J. Cryst. Growth **231** (2), 442 (2001).
18. R. A. Brown, Z. Wang, and T. Mori, J. Cryst. Growth **225** (1), 97 (2001).
19. V. I. Talanin, I. E. Talanin, and A. A. Voronin, Can. J. Phys. **85** (12), 1459 (2007).
20. V. I. Talanin, I. E. Talanin, and A. A. Voronin, Crystallogr. Rep. **53** (5), 1124 (2008).
21. S. Sadamitsu, S. Umeno, and Y. Koike, Jpn. J. Appl. Phys. **32** (9), 3675 (1993).
22. M. Okui and M. Nishimoto, J. Cryst. Growth **237–239** (3), 1651 (2002).
23. W. von Ammon, E. Dornberger, and P. O. Hansson, J. Cryst. Growth **198–199** (1–4), 390 (1999).

Translated by Yu. Sin'kov