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The aggregation of point defects in dislocation-free silicon single crystals

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The formation kinetics for grown-in microdefects nucleation centers in dislocation-free silicon single crystals has been considered. It has been demonstrated that the diffusion-controlled aggregation of point defects defines the process of grown-in microdefects formation. Decomposition of oversaturated solid-state solution follows two mechanisms, namely vacancy-type and interstitial-type. Decomposition of oversaturated solid impurity solutions occurs at temperatures near the crystallization front, while decomposition of oversaturated solid solutions of intrinsic point defects is induced by crystal cooling (at $T < 1200°C$). The good consistency between theoretical and experimental results proves the validity of the proposed model for point defects aggregation.

Рассмотрена кинетика процесса формирования центров зародышеобразования ростовых микродефектов в бездислокационных монокристаллах кремния. Показано, что процесс агрегации точечных дефектов, управляемый их диффузией, обусловливает образование ростовых микродефектов. Распад пересыщенного твердого раствора точечных дефектов происходит по двум направлениям: вакансионному и межузельному. При температурах вблизи фронта кристаллизации идет распад пересыщенных твердых растворов примеси, а во время охлаждения кристалла (при $T < 1200°C$) происходит распад пересыщенных твердых растворов собственных точечных дефектов. Хорошее согласование теоретических и экспериментальных результатов свидетельствует о справедливости предложенной модели агрегации точечных дефектов.

During production of dislocation-free silicon single crystals, a problem of grown-in microdefects arises. The grown-in microdefects as clusters of point defects refer to the transient class between point and linear defects. The grown-in microdefects (clusters of point defects) influence significantly electrophysical and mechanical properties of dislocation-free silicon single crystals and, hence, characteristics of discrete devices and integrated circuits. The solving a problem of grown-in microdefects is of importance not only from the practical point of view, for example, as a possibility to control the silicon defect structure, but contributes to fundamental science as understanding potential of physics of defect structure formation and transformation in high-perfect crystals.

Today, there are two model approaches to explain the grown-in microdefects formation. The first approach is based on the theoretical model of V.V.Voronkov [1] where intrinsic point defects are the crucial factor for aggregation processes. Therefore, a key question in this case is what type of intrinsic point defects dominates in a crystal (vacancy or self-interstitial). A solution is sought within the recombination-diffusion sampling, which takes place in the narrow area near to the crystallization front, and postulates that the type of intrinsic point defects dominating in a silicon crystal depends on the ratio of growth rate V to the temperature gradient G: $V/G = \xi$. While the mathematical background of the model may be reckoned among the advantages of this approach, the neglected interaction between

intrinsic point defects and impurities may be referred to its shortcomings.

We propose another approach developed on the basis of experimental results obtained during direct transmission electron microscopic examinations of dislocation-free silicon single crystals grown by float zone (FZ-Si) and Czochralski (CZ-Si) methods under the growth thermal conditions varying over a wide range. The investigations formed a base for development a qualitative heterogeneous mechanism of grown-in microdefects formation [2] which, however, suffers from a lack of theoretical background. In particular, this concerns kinetics of grown-in microdefects formation, which are kept untouched so far. In view of the latter, the purpose of this study is to consider kinetics of point defects aggregation during growth of dislocation-free silicon single crystals.

Decomposition of solid solution, like most of phase transformations begins from the crystal nucleation, i.e. formation of physically detectable crystallizing nuclei. For one thing, intrinsic point defects (vacancies and self-interstitials) are quite mobile and for the other thing, they are actively interact with drains. In low-doped or undoped dislocation-free silicon single crystals, the background oxygen and carbon impurities serve as drains for intrinsic point defects. We have demonstrated that in high-perfect dislocation-free silicon single crystals, the main (fundamental) interaction near the crystallization front is the "impurity – intrinsic point defect" one that result in formation of impurity precipitates [3]. The recombination of intrinsic point defects does not occur because of high entropy recombination barrier value [4].

The origination of a new phase during the impurity release out of oversaturated solid solution may be considered according to the classic nucleation theory, when the resulting free energy change of the crystal ΔF during the nucleus formation is as follows:

$$\Delta F = \Delta F_V + \Delta F_s + \Delta F_e, \quad (1)$$

where ΔF_V is the free energy change when chemical composition is altered in volume; ΔF_s, the free energy change due to occurrence of interphase boundary; Δ_e, a difference of elastic strain energies induced in the nucleus and matrix. In the case of combined aggregation of oxygen and vacancies, a SiO_2 particle formation by joining n oxygen atoms and absorbing n_V vacancies is accompanied by free energy increment

$$\Delta F = -fn - f_v n_v + \Delta F_s + \Delta F_e, \quad (2)$$

where the surface energy is defined as

$$\Delta F_s = \lambda n^{2/3} = 4\pi R^2 \sigma \quad (3)$$

and elastic strain energy as

$$\Delta F_e = \omega n \left(1 - \frac{n_v}{\gamma n}\right)^2. \quad (4)$$

Here the quantity $\gamma = (\eta - 1)/2 \approx 0.68$ has the sense of such an emission ratio n_v/n, at which SiO_2 particle remains strain-free; the constant ω is defined as $\omega = \gamma^2/S\rho\eta$ and has the sense of elastic strain energy per oxygen atom for a precipitate which has occurred without emitting silicon self-interstitials [5]; S is effective compressibility equal to $K_p^{-1} + 0.75\mu^{-1}$ (μ is the shear modulus for silicon, K_p is the uniform compression modulus for SiO_2). If we assume that K_p modulus is the same as for silicon, then $S = 9(1 - \nu)/4\mu(1 + \nu)$, where ν is Poisson coefficient and in that case, $\omega \approx 1$ eV; R is the particle radius. In (3), $\lambda = \sigma\pi^{1/3}(3\eta/\rho)^{2/3}$, where $\eta \approx 2.36$ is volume ratio of SiO_2 phase and silicon atom; ρ, the density of sites in the silicon lattice; σ, the specific free energy at the $Si–SiO_2$ interface.

When transition of one oxygen atom from SiO_2 strain-free phase into solution takes place, the system free energy changes by f value

$$f = kT\ln\frac{C}{C_e}. \quad (5)$$

Correspondingly, when one vacancy is eliminated from the solution, free energy changes by f_V:

$$f_v = kT\ln\frac{C}{C_{ve}}. \quad (6)$$

According to (2)–(4), minimum ΔF at fixed n is reached at a certain emission ratio:

$$\frac{n_v}{n} = \gamma\left(1 - \frac{\gamma f_v}{2\omega}\right). \quad (7)$$

By inserting (7) into (2), the minimum energy increment which occurs when a precipitate is formed from n oxygen atoms may be found as:

$$\Delta F_{\min} = -f^* n + \lambda n^{2/3} \quad (8)$$

where

$$f^* = f + \gamma f_v \left(1 + \frac{\gamma f_v}{4\omega}\right). \quad (9)$$

The quantity f^* has the sense of a driving force for phase transformations; precipitation is only possible at $f^* > 0$, and condition $f^* = 0$ defines the effective oxygen solubility in case of vacancy oversaturation:

$$C_e^* = C_e (C_{ve} / C_v)^{\gamma}. \quad (10)$$

The formula (10) follows from (9), if the combination $\gamma f_v/4\omega$ is neglected at high temperatures, and then $f^* = f + \gamma f_v$. In formulas (5)–(10) C is the actual oxygen concentration; C_e, oxygen solubility, maximum solubility being $C_e(T_m) \approx 1.8 \cdot 10^{18}$ cm^{-3} [6]; T_m, the crystallization temperature; $C_{ve} = 1.11639 \cdot 10^{27} \exp(-3.9/kT)$ [7] is the equilibrium vacancy concentration C_v, the vacancy solubility.

Transmission electron microscopy studies of high-purity undoped quenched dislocation-free FZ-Si single crystals (oxygen concentration ~$4 \cdot 10^{15}$ cm^{-3}, carbon concentration ~$4 \cdot 10^{15}$ cm^{-3}), have shown that the formation of SiO_2 and SiC precipitates begins at the crystallization front [3]. Therefore, if oxygen and vacancy interact, the oxygen solution becomes oversaturated (i.e. inequality $C > C^*$ is satisfied) at temperatures just below the crystallization temperature, and nucleation of SiO_2 particles begins; in this case, $C_{\text{v}} \sim 6 \cdot 10^{19}$ cm^{-3}.

By differentiating the nucleation rate $I \sim \exp(\Delta F_{crit}/kT)$ with respect to time taking into account the changes in vacancy concentration C_v, a concentration N of oxygen precipitates originated can be estimated. At ΔF_{crit}, the formula (8) may be used for a critical-size nucleus $n_{crit} = (2\lambda/3f^*)^3 = (3\varphi kT/\lambda)^{3/2}$, where $\varphi \approx 60$ [8]. Estimate of critical size gives a value of about 150 atoms. At high temperatures (near to the crystallization front), the size n of SiO_2 precipitates is limited by the vacancy concentration $\gamma n N = C_{ve}$ [9]. Therefrom, a estimate $N \approx 3 \cdot 10^{13}$ cm^{-3} follows, that coincides with experimentally observed concentration of (I + V) microdefects [10]. At lower temperatures, the precipitates can absorb oxygen without vacancies involvement, that results in increase of their size and possible change in sign of deformation around the precipitate from vacancy to interstitial type.

Furthermore, the nucleation rate $d(\ln I)/dT = -E^*/kT^2$ increases very fast because of a high value of nucleus binding energy (estimated value is about 50 eV [5]). The effective nucleation interval is $\Delta T = kT^2/E^* \sim 5$ K. The maximum possible oxygen adjoining frequency to an aggregate of radius r is limited by diffusion and is $\alpha = 4\pi r DC$, where the diffusion coefficient $D = 0.17\exp(-2.54/kT)$. The effective diffusion time, as determined from the condition of diffusion coefficient decay by a factor of e, is $\tau_D = kT^2/E_a V_{cool}$, where $E_a = 2.54$ eV, and $V_{cool} = |dT/dt|$ is the cooling rate. For example, for FZ-Si crystals of 30 mm in diameter grown at the growth rate $V = 6$ mm/min, $|dT/dt| \approx \Delta G \approx 1.3$ K/c, where G is an axial temperature gradient. Then, at $r = 3$ Å (for a nucleus aggregate), we obtain that at the aggregation temperature ($T_m - \Delta T$), the frequency $\alpha \approx 7.6$ s^{-1} and diffusion time $\tau_D \approx 76$ s. It follows therefrom that maximum number of oxygen atoms adjoined to one aggregate $\alpha\tau_D \approx 600$. Since growth of SiO_2 particles is limited by oxygen diffusion, which is slow comparing with vacancy diffusion, then $dn/dt = 4\pi^2 DC$ and from here $r(t) = (\eta DCt/\rho)^{1/2}$. For the above-mentioned FZ-Si crystals, $r \approx 125$ Å that agrees with experimental results [2].

During the crystal cooling at $T < 1200$°C, pure vacancy condensation becomes prevailing. Its occurrence and temperature interval of nucleation depend on thermal conditions of crystal growth (growth and cooling rates, temperature gradients in the crystal, crystal diameter). While at high temperatures $C_v > C_{ve}$ and most of vacancies are spent for joint condensation with oxygen, then when the temperature decreases (for instance, at $T < 1200$°C, $C_{ve} > C_v$) the vacancy oversaturation goes down due to formation of micropores [8] and the precipitates originated before facilitate their aggregation [3].

When a pore is formed, the system free energy changes as follows:

$$\Delta F_v = -f_v' n_v + \lambda_v n_v^{2/3}, \quad (11)$$

where $f_v' = kT\ln(C_v/C_{ve})$ is the free energy change in the vacancy solution when one vacancy is added. The quantity ΔF_v is a function of pore size and passes through the

maximum ΔF_{crit} (nucleation work). The homogeneous nucleation rate is in proportion to $\exp(-\Delta F_{crit}/kT)$ [1, 8]. The authors [5] have derived a fundamental equation for the temperature of vacancy-type micropore nucleation T_v:

$$f' = kT\ln\left(\frac{C_{vo}}{C_{vm}}\right) + E(1 - T_v/T_m), \quad (12)$$

where the left-hand part of the formula is the most sensitive to the exponent $-\Delta F_{crit}/kT_v$ in the expression for the pore formation rate:

$$I = \sigma D_v C_v \left(\frac{16\pi}{3\Delta F_{crit} kT}\right)^{1/2} \exp\left(-\frac{\Delta F_{crit}}{kT}\right). \quad (13)$$

In formula (12), the vacancy concentration is determined from the formula:

$$C_{vo} = (C_{vm} - C_{im})(1 - \xi_1/\xi), \quad (14)$$

where $\xi_t/\xi \approx 0.15$ [2], $C_{vm}/C_{im} \approx 1.2$ [7]. In formulas (12)–(14), $E = 4.4$ eV, $f' = 0.67$ eV, and $\Delta F_{crit} = 5.4$ eV [5]; C_{vm} is the equilibrium vacancy concentration at melting temperature; C_{im}, the equilibrium self-interstitial concentration at melting temperature; T_m, the melting temperature; ξ_t = const, $\xi = V/G$. The estimated value for the pore formation temperature is about 1070°C that is in good agreement both with theoretical calculations [5] and experimental results of vacancy micropores study [11]. Dependence T_v on ξ_t/ξ parameter shows that vacancy micropores are formed within a certain temperature interval, which is defined by actual thermal conditions of crystal growth. The estimated value for vacancy micropore concentration of about $6\cdot10^4$ cm^{-3} has been obtained according to $N_v = 5.5\cdot10^{12}(V_{cool})^{3/2}/(C_e)^{1/2}$ [12] and also agrees with experimental results [11]. During joint condensation of oxygen and silicon self-interstitials, the process of SiC formation due to adjoining of n carbon atoms and absorbing of n_i silicon self-interstitials is accompanied by free energy increment:

$$\Delta F_i = -fn + f_i n_i + \Delta F_s + \Delta F_e, \quad (15)$$

where F_s is defined by (3) and elastic strain energy is defined by (14) with substitution n_i for n_v and $-f_i$ for f_v. A consideration similar to the above-mentioned results in the expression

$$f^* = f - \gamma f_i \quad (16)$$

and for effective carbon solubility, we get

$$C^* = C_1(C_i/C_{ie})^\gamma, \quad (17)$$

where c_1 is maximum carbon solubility; $C_{ie} = 2.52095\cdot10^{26}\exp(-3.7/kT)$ [7] is the equilibrium Si self-interstitials concentration; C_i, the solubility of silicon self-interstitials. The calculation proves that formation of SiC precipitates (when actual carbon concentration $C_e > C^*$) begins near to the crystallization front if $C_v/C_i \approx 1.67$. The estimated value of defect concentration $N \approx 10^{14}$ cm^{-3} and their size $r = 110$ Å (for 30 mm diameter FZ-Si crystals grown at $V = 6$ mm/min) attest to their good consistence with results of direct transmission electron microscopy investigations [2].

During the crystal cooling, the conditions arise when the free energy induced by carbon impurity elimination from oversaturated impurity solution appears to be less than the free energy increase caused by Si self-interstitials emission (I_{Si}) into oversaturated solution of such self-interstitials. The SiO_2 precipitates emitting I_{Si} at their growth contribute to this process. In this case, the main aggregation process is the formation of I_{Si} clusters (A-microdefects). In the oversaturated solution of I_{Si}, A-microdefects are nucleated homogeneously and their nucleation rate increases sharply near to the temperature of condensation, which is determined in numerous experiments in termination of crystal growth as ~1100°C [2, 13]. The quantitative model of aggregation was constructed in [1]. Assuming that A-microdefect looks like a spherical cluster occurring near 1150°C, the following formula was proposed to determine their concentration:

$$N_A = 0.13\left(\frac{\rho}{C_{ie}}\right)^{1/2}\left(\frac{E_{crit}V_{cool}}{D_i kT^2}\right)^{3/2}, \quad (18)$$

where $E_{crit} \approx 1.5$ eV is the critical nucleus binding energy per one I_{Si} atom [1]; $D_i = 0.242\exp(-0.937/kT)$ [14] is the diffusion coefficient for I_{Si}. Calculations for FZ-Si crystal of 30 mm in diameter (at $V = 3$ mm/min) give the value of about $2\cdot10^6$ cm^{-3} that is in agreement with ex-

perimental investigations for A-microdefects. For 50 mm diameter CZ-Si crystals (grown at $V = 1$ mm/min), $N_A \sim 5 \cdot 10^4$ cm^{-3}. The growth of A-microdefects (interstitial dislocation loops) is limited by I_{Si} atoms diffusion, therefore, we can define the size of a single defect m_i (number of I_{Si} atoms therein): $m_i N_A = C_i$, then $m_i \sim 10^7$ to 10^9 I_{Si} atoms.

Thus, the above analysis of grown-in microdefects formation reveals that the process of defect formation during growth of dislocation-free silicon single crystals is controlled by point defect diffusion within the temperature gradient field. This is caused by existence of entropy recombination barrier which prevents the recombination of intrinsic point defects at high temperatures during the crystal growth. As a result, decomposition of oversaturated solid solution of point defects follows concurrently two mechanisms: vacancy and interstitial type. At temperatures near to the crystallization front, the oversaturated solid impurity solutions begin to decompose, while during the crystal cooling (at $T < 1200°C$), the oversaturated solid solutions of intrinsic point defects begin to decompose.

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Агрегація точкових дефектів у бездислокаційних монокристалах кремнію

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Розглянуто кінетику процесу формування центрів зародкоутворення ростових мікродефектів у бездислокаційних монокристалах кремнію. Показано, що процес агрегації точкових дефектів, що керований їх дифузією, обумовлює утворення ростових мікродефектів. Розпад пересиченого твердого розчину точкових дефектів відбувається за двома напрямками: вакансійному і міжвузловому. При температурах поблизу фронту кристалізації відбувається розпад пересичених твердих розчинів домішки, а протягом охолодження кристала (при $T < 1200°C$) має місце розпад пересичених твердих розчинів власних точкових дефектів. Хороша кореляція теоретичних та експериментальних результатів свідчить про справедливість моделі агрегації точкових дефектів, що пропонується.