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

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This papers considers the formation kinetics for grown-in microdefects nucleation centers in dislocation free silicon monocrystals. It demonstrates that diffusion-controlled aggregation of point defects determines 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 to the crystallization front, while decomposition of oversaturated solid solutions of intrinsic point defects is induced by crystal cooling (at $T < 1200\ ^0C$). The nice consistence between theoretical and experimental results proves a validity of the proposed model of point defects aggregation.

Introduction

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

Presently there are two model approaches to explain a 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 posits that a type of intrinsic point defects dominating in silicon crystal depends on the ratio of growth rate V to the temperature gradient G: $V/G = \xi$. If mathematical background of the model may be attributed to the advantage of this approach, then neglected interaction between intrinsic point defects and impurities may be referred to its shortcomings.

We propose the other approach, which is developed on the basis of experimental results obtained during direct transmission electron microscopy investigations for dislocation free silicon monocrystals grown by float zone (FZ-Si) and Czochralski (CZ-Si) methods under thermal growth conditions varying over a wide range. The investigations served as a ground for building a qualitative heterogeneous mechanism of grown-in microdefects [2], which however suffers from a lack of theoretical background. In particular, this concerns kinetics issues for grown-in microdefects formation, which are kept untouched so far.

In view of the latter, the objective of this study is to consider kinetics of point defects aggregation during growth of dislocation free silicon monocrystals.

Kinetics of grown-in microdefects formation

Decomposition of solid solution like most of phase transformations begins from the crystal nucleation, i.e. formation of physically detectable crystallizing nucleus. 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 monocrystals the background oxygen and carbon impurities serve as drains for intrinsic point defects. We demonstrated that in high-perfect dislocation free silicon monocrystals the base (fundamental) interaction near the crystallization front is ‘impurity – intrinsic point defect’ that result in forming impurity precipitates [3]. The process of recombination does not occur because of high entropy recombination barrier value [4].

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

$$\Delta F = \Delta F_v + \Delta F_s + \Delta F_e, \qquad (1)$$

where ΔF_v is a free energy change when chemical composition is altered in volume ; ΔF_s is a free energy change due to occurrence of interphase boundary; ΔF_e is a difference of strain energies induced in the nucleus and matrix.

In the case of combined aggregation of oxygen and vacancies, a SiO_2 particle is formed by joining n oxygen atoms and absorbing n_v vacancies is followed by free energy increment ΔF

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

where a surface energy is determined by the expression:

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

and elastic strain energy:

$$\Delta F_e = \omega n (1 - n_v / \gamma n)^2 \qquad (4)$$

Here a value $\gamma = (\eta - 1)/2 \approx 0.68$ has meaning of such a emission ratio n_v / n, at which SiO_2 particle remains strain-free; constant ω is defined by the expression $\omega = \gamma^2 / S\rho\eta$ and has meaning 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 a shear modulus for silicon, K_p is an uniform compression modulus for SiO_2). If we assume that K_p modulus is the same as for silicon, then $S = \frac{9(1-\nu)}{4\mu(1+\nu)}$, where ν is Poisson coefficient and in that case $\omega \approx 1$ eV; R is a particle radius.

In the formula (3) $\lambda = \sigma\pi^{1/3}\left(3\eta / \rho\right)^{2/3}$, where $\eta \approx 2.36$ is volume ratio of SiO_2 phase and silicon atom, ρ is density of points in a silicon lattice, σ is a specific free energy on the Si-SiO_2 interface.

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

$$f = kT \ln(C/C_e) \qquad (5)$$

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

$$f_v = kT \ln(C/C_{ve}) \qquad (6)$$

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

$$\frac{n_v}{n} = \gamma(1 - \gamma f_v / 2\omega) \qquad (7)$$

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

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

when $f^* = f + \gamma f_v (1 + \gamma f_v / 4\omega)$ (9)

Value f^* has meaning 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:

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

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

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

By differentiating the nucleation rate $I \sim \exp(\Delta F_{crit} / kT)$ with respect to time allowing for changes in vacancy concentration C_v a concentration N of oxygen precipitates originated may be estimated. At ΔF_{crit} a 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 ~ 150. At high temperatures (neat to the crystallization front) a size n of SiO_2 precipitates is limited by the vacancy concentration $\gamma n N = C_{ve}$ [9]. It follows that estimate $N \approx 3 \cdot 10^{13}$ cm^{-3}, that coincides with experimentally observed concentration of (I+V)-microdefects [10]. At lower temperatures precipitates can absorb oxygen without vacancies that results in increasing of their size and possible change in sign of deformation around the precipitate from vacancy to interstitial type.

Furthermore, the rate of nucleation $\frac{d(\ln I)}{dT} = -\frac{E^*}{kT^2}$ increases very fast because of a high value of nucleus binding energy (estimated value is ~ 50 eV [5]). Effective nucleation interval is $\Delta T = kT^2 / E^* \sim 5$K. Maximum possible oxygen adjoining frequency to the aggregate with r radius is limited by diffusion and equals to $\alpha = 4\pi rDC$, where a diffusion coefficient D = 0.17exp(-2.54/kT). The effective diffusion time, which is determined by the condition of diffusion coefficient decay in e times, equals to $\tau_D = kT^2 / E_a V_{cool}$, where E_a = 2.54 эВ, and $V_{cool} = \left|\frac{dT}{dt}\right|$ is a rate of cooling. For example, for FZ-Si crystals 30 mm in diameter grown at the growth rate V = 6 mm/min, $\left|\frac{dT}{dt}\right| \approx \Delta G \approx 1.3 {}^{K}\!/_{c}$, where G is an axial temperature gradient. Then, at $r = 3\overset{0}{A}$ (for a nucleus aggregate) we obtain that at the aggregation temperature (T_m-ΔT) a frequency $\alpha \approx 7.6$ sec^{-1} and diffusion time $\tau_D \approx 76$ sec. From this it follows 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 $\frac{dn}{dt} = 4\pi^2 DC$ and from here $r(t) = (\eta DCt / \rho)^{1/2}$. For above mentioned crystals FZ-Si $r \approx 125\overset{0}{A}$ that tallies with experimental results [2].

During the crystal cooling at T < 1200 ^{0}C purely 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 used for their joint condensation with oxygen, then when the temperature decreases (for instance, at T < 1200 ^{0}C $C_{ve} > C_v$) the vacancy oversaturation goes down owing to formation of microvoids [8] and the earlier originated precipitates facilitate their aggregation [3].

Free energy in the system changes when a void is formed as follows:

$$\Delta F = -f_v n_v + \lambda_v n_v^{2/3} \qquad (11)$$

where $f_v = kT \ln(C_v / C_{ve})$ is a free energy change in the vacancy solution when one vacancy is added. Value ΔF is a function of void size and passes through the maximum ΔF_{crit} (nucleation work). The rate of homogeneous nucleation is in proportion to $\exp(-\Delta F_{crit} / kT)$

[1, 8]. The authors of paper [5] found a fundamental equation for the temperature of vacancy-type microvoid nucleation T_v:

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

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

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

In formula (12) the vacancy concentration is defined from the formula:

$$C_{vo} = \left(C_{vm} - C_{im}\right)\left(1 - \xi_t/\xi\right) \qquad (14)$$

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 ΔF_{crit} = 5.4 eV [5], C_{vm} is an equilibrium vacancy concentration at melting temperature, C_{im} is an equilibrium self-interstitial concentration at melting temperature, T_m is melting temperature, ξ_t = const, $\xi = V/G$, V is a rate of growth, G is an axial temperature gradient. Estimated value for the temperature of void formation is ~ 1070 ^{0}C that is in good agreement both with theoretical calculations [5] and experimental results of vacancy microvoids study [11]. Dependence T_v on parameter ξ_t/ξ shows that vacancy microvoids are formed within a certain temperature interval, which is defined by actual thermal conditions of crystal growth. Estimated value for vacancy microvoids ~ $6\cdot10^4$ cm^{-3} has been obtained according to $N_v = 5.5\cdot10^{12}(V_{cool})^{3/2}/(C_e)^{1/2}$ [12] and also corresponds to experimental results [11].

During joint condensation of oxygen and silicon self-interstitials the process of SiC formation by adjoining n carbon atoms and absorbing n_i silicon self-interstitials is followed by free energy increment:

$$\Delta F = -fn + f_i n_i + \Delta F_s + \Delta F_e \qquad (15)$$

where F_s is defined by formula (3) and elastic strain energy is defined by formula (14) with substitution n_v to n_i and f_v to $-f_i$. Analysing similarly to above mentioned, we obtain the following:

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

and for effective carbon solubility we get

$$C^* = C_1\left(C_i/C_{ie}\right)^{\gamma} \qquad (17)$$

where C_1 is maximum carbon solubility; C_{ie} = $2.52095 \cdot 10^{26} \exp(-3.7/kT)$ [7] is an equilibrium Si self-interstitials concentration; C_i is solubility of silicon self-interstitials. Analysis proves that formation of SiC precipitates (when actual carbon concentration $C_e > C^*$) begins near to the crystallization front if $C_v / C_i \approx 1.67$. Estimated value of defect concentration N ≈ 10^{14} см$^{-3}$ and their size r = 110 $\overset{0}{A}$ (for FZ-Si crystals 30 mm in diameter 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 decrease in free energy induced by carbon impurity elimination from oversaturated impurity solution appears to be less than increase in free energy caused by Si self-interstitials emission (I_{Si}) into oversaturated solution of such self-interstitials. Precipitates SiO_2, which are emitting I_{Si}, at their growth, contribute to this process. In this case the main process of aggregation is the formation of I_{Si} clusters (A-microdefects). In the I_{Si} oversaturated solution A-microdefects are nucleated homogeneously and their rate of nucleation sharply increases near to the temperature of condensation, which is determined in numerous experiments in termination of crystal growth as ~ 1100^0C [2, 13]. The quantitative model of aggregation was built in paper [1]. On the assumption of that A-microdefects look like a spherical cluster occurring at near the temperature ~ 1150 ^{0}C, the following formula to define their concentration was proposed:

$$N_i = 0.13 \left(\frac{\rho}{C_{ie}} \right)^{1/2} \left(\frac{E_{crit} V_{cool}}{D_i k T^2} \right)^{3/2} \qquad (15)$$

where E_{crit} ≈ 1.5 eV is a critical nucleus binding energy per one I_{Si} atom [1]; $D_i = 0.242 \exp(-0.937/kT)$ [14] is a diffusion coefficient for I_{Si}. Calculations for FZ-Si crystal 30 mm in diameter (at V = 3 mm/min) give the value ~ $2 \cdot 10^6$ cm^{-3} that is in agreement with experimental investigations for A-microdefects. For CZ-Si crystals 50 mm in diameter (grown at V = 1 mm/min) N_A ~ $5 \cdot 10^4$ см$^{-3}$. A-microdefects growth (interstitial dislocation loops) is limited by I_{Si} atoms diffusion, therefore we can define a size of one defect m_i (number of I_{Si} atoms in it): $m_i N_i = C_i$, then m_i ~ $10^7 \ldots 10^9$ I_{Si} atoms.

Conclusion

The above analysis of grown-in microdefects formation reveals that the process of defect-formation occurred during growth of dislocation free silicon monocrystals is controlled by point defect diffusion within the range of temperature gradient. This is caused by existence of entropy recombination barrier, which prevents form recombination of intrinsic point defects at high temperatures during the crystal growth. As a result of this, 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 and during the crystal cooling (at $T < 1200\ ^0C$) the oversaturated solid solutions of intrinsic point defects begin to decompose.

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