Recombination parameters of point defects in dislocation-free silicon single crystals

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The recombination parameters of the point defects dynamics (recombination barrier, recombination time, recombination factor) at high and low temperatures are discussed proceeding from the heterogeneous mechanism of grown-in microdefects formation and transformation. The cooling-induced decomposition of the oversaturated solid solution of point defects in silicon follows two mechanisms: vacancy-type and interstitial-type ones. Therefore, vacancies and intrinsic silicon interstitials find drains in the form of background impurity atoms like oxygen and carbon. The formation of intrinsic point defect-impurity pairs is the dominant process at temperatures near the silicon melting point.

Рассмотрены рекомбинационные параметры модели динамики точечных дефектов (рекомбинационный барьер, рекомбинационное время, рекомбинационный фактор) для высоких и низких температур, исходя из гетерогенного механизма образования и трансформации ростовых микродефектов. Вызванный охлаждением распад пересыщенного твердого раствора точечных дефектов в кремнии протекает по двум механизмам: вакансионному и межузельному. Поэтому вакансии и собственные межузельные атомы кремния находят стоки в виде атомов фоновых примесей, таких как кислород и углерод. Образование пар "собственный точечный дефект — примесь" является доминирующим процессом при температурах, близких к точке плавления кремния.

The structure imperfections referred to as grown-in microdefects are formed during high-temperature growing and further cooling of dislocation-free single Si crystals. These grown-in microdefects, such as microprecipitates, dislocation loops and microscale voids, are formed in the crystal due to aggregation of intrinsic point defects and impurities. Therefore, the key to understanding fundamental parameters of intrinsic point defects (formation volumes, diffusivities and thermal equilibrium concentrations of vacancies and intrinsic interstitials and others) is to understand the formation mechanism of grown-in microdefects. At the same time, investigating the recombination process of intrinsic point defects or/and their interaction with impurities is a way to understand the formation mechanism of grown-in microdefects. At present, the qualitative and quantitative understanding of defect formation physics in silicon is far from satisfactory.

To date, there are two approaches to solve this problem for dislocation-free silicon single crystals. In the first one, the combination of equilibrium, transport and solid state kinetics of intrinsic point defects and impurities that leads to microdefect formation is referred to as defect dynamics [1–3]. The model of point defect dynamics includes point defects convection by crystal motion, diffusion by both Fick and thermal diffusion driving forces and point defect recombination [4]. It is supposed that all mechanisms are of importance for the point defect dynamics in specific regions of the crystal; however, point defect recombination plays the most crucial role [2, 5]. These models are based on theoretical model of grown-in microdefects formation by Voronkov [6]. Voronkov assumed that the

recombination rate between isolated vacancies and intrinsic interstitials is very high and further that the diffusivity of intrinsic interstitials exceeds that of vacancies near the melting point; and, finally, that the concentration of vacancies is higher that of intrinsic interstitials at the melting point, where both concentrations are in thermal equilibrium [6]. The author pointed out that the microdefect formation is governed by the growth parameter $V/G = C_{crit}$ (where V is the crystal growth rate; G, axial temperature gradient). This mechanism results in a distinction between the crystal regions enriched in vacancies ($V/G > C_{crit}$) and in intrinsic interstitials ($V/G < C_{crit}$).

The authors of second method proceed from experimental data on properties of the grown-in microdefects [7, 8–10]. High difficulties in observing the aggregations of point defects having such a small size and causing a slight lattice imperfection requires the direct research methods, which allow analyzing the sign of lattice imperfection. The sign of lattice imperfection caused by a defect informs us indirectly on the defect chemical composition and enables to define unambiguously the mechanism of growт-in microdefects formation and transformation [11]. Being based on direct experimental results, such a mechanism provides a qualitative understanding of the grown-in microdefect formation process [12]. Basing on experimental results, we suggested the heterogeneous formation mechanism of the grown-in microdefects [11, 12], developed a new physical classification and introduced concepts of primary and secondary grown-in microdefects [12]. In our opinion, it is only a combination of the two approaches (theoretic and experimental) that would enable an actual understanding of physics of the defect formation in dislocation-free silicon single crystals.

The purpose of this paper is to estimate parameters of the recombination process (recombination factor, recombination time, recombination barrier) occurring in the model of the point defect dynamics for high and low temperatures in accordance with heterogeneous formation and transformation mechanism of the grown-in microdefects in dislocation-free silicon single crystals.

Considering the concept of entropy barrier and the factor of simultaneous self-diffusion of vacancies and silicon interstitial atoms, we may reason in this way, in contrast to the V.V.Voronkov theory that there is a recombination barrier [12]. Experimental results of TEM studies [9, 10] and heterogeneous formation mechanism of the grown-in microdefects [11] prove the theoretical considerations of Hu and Sirtl [13, 14] to be true. In the context of physical nature of defect formation in real crystals, the Voronkov theoretical model is inconsistent.

The microscopic model of recombination barrier was developed in detail in [15, 16]. The model is based on the fact that the configuration of intrinsic point defects at high temperatures defines the temperature dependence of the barrier. As is assumed within the model frame, at high temperatures, the intrinsic interstitials and vacancies are extended through several atomic volumes (11 atoms occupies 10 cells), i.e., there is a disordered area around the point defect, which is isotropically extended up to the atoms of the second coordination sphere. Recombination occurs only if both defects are simultaneously contracted all-around the same atomic volume. As the extended defect configurations have more microstates than the point defect, such a contraction reduces entropy and, consequently, an entropy barrier $\Delta S < 0$ exists. As temperature drops, the barrier decreases and disappears at low temperatures at all, so the defects recombine easily. This is connected with changing in configuration of intrinsic point defects, which are extended at high temperatures and have a point-like dumbbell shaped configuration at low temperatures, as shown in [16]. It should be emphasized that the theory of extended defect configurations as well as the theory of recombination barrier have been acknowledged in a number of up-to-date papers [17, 18].

Basing on the heterogeneous mechanism of grown-in microdefects formation, we proceed to estimation of recombination parameters (recombination barrier, recombination time and recombination factor) of the point defects dynamics model. Temperature dependence of configuration entropy can be described as follows [19]:

$$S_c(T) = S_\infty(1 - T_k/T), \qquad (1)$$

where S_∞ is the limiting S_c value (at $T \to T_m$); T_m, the melting point; T_k, a characteristic temperature. Let us suppose that T_k is the minimum temperature when the lattice imperfections are formed in the dislocation-free silicon single crystals. Then estimate $T_k = 450°C = 723$ K as a temperature when thermodonors are formed in silicon crystal. It follows that $S_c(T) = S_\infty$ $(1 - 723/T)$. Accord-

ing to [16], $S_c(1373\ \text{K}) = -11.5k$ (where $k = 0.86181\cdot10^{-4}$ eV/K is the Boltzmann constant). Then we can get $S_\infty = -24.3k$. Therefore,

$$S_c(T) = -24.3k \cdot (1 - 723/T). \quad (2)$$

According to the Gosele model [16], the free energy barrier to recombination $\Delta G = -T\cdot\Delta S$, since the contribution of enthalpy member ΔH is negligible. The temperature dependence of the barrier is thus controlled by the entropies of the point defects formation. Then

$$\Delta G(T) = -T \cdot [-S_c(T)] = T \cdot S_c(T). \quad (3)$$

Approximate evaluation at $T = T_m$ gives $\Delta G(1685\ \text{K}) = 2.014$ eV.

Experimental data on Si self-diffusion show that the diffusion coefficient exhibits the Arrhenius' behavior over a wide temperature range, $D(T) = D_0\cdot\exp(-E_a/kT)$, with an activation energy E_a of 4...5 eV and the pre-exponential factor D_0 much larger than that for typical metals [20]. However, the relative contribution from different mechanisms, namely, from vacancies and interstitials, is still a matter of discussion. For the purpose of this work, we used Mayer classical data as reference [21], according to those, within the T interval 1320 to 1658 K,

$$D(T)=1460 \cdot \exp(-5.02/kT). \quad (4)$$

Approximate evaluation at $T = T_m$ gives $D(1685\ \text{K}) = 1.42\cdot10^{-12}\ \text{cm}^2\cdot\text{s}^{-1}$. It is just the intrinsic interstitials that dominate the self-diffusion at high temperature. Hence, to estimate the recombination time at high temperature (τ_1), we use the formula

$$\tau_1 = \Omega/4\pi \cdot D(T) \cdot r_0 \cdot \exp(-\Delta G(T)/kT), \quad (5)$$

where Ω is the lattice volume; $r_0 = 3\cdot10^{-8}$ cm, the capture radius for recombination. Estimation at $T = T_m$ gives $\tau_1 = 316$ s. It should be noted that estimation based on modern data of Bracht [22] and Tang [20] gives values $\tau_1 = 132$ s and $\tau_1 = 110$ s, respectively.

The recombination factor $k_{IV}(T)$ is described by diffusion-limited reaction theory, coupled with a kinetic activation barrier [2]. If high temperatures are concerned,

$$k_{IV}(T) = 4\pi \cdot r_0 \cdot D(T) \cdot \exp(-\Delta G(T)/kT)/\Omega \cdot c_s, \quad (6)$$

where $c_s = 5\cdot10^{22}\ \text{cm}^{-3}$ is the atomic density. Estimation at $T = T_m$ gives k_{IV} (1685 K) = $6.3\cdot10^{-26}\ \text{cm}^3/\text{s}$. In [23], a "fast recombination" criterion $k_{IV}(1685\ \text{K})\cdot C_{Vm} \geq 20\ \text{s}^{-1}$ (where $C_{Vm} = 11.7\cdot10^{14}\ \text{cm}^{-3}$ is the concentration of vacancies at $T = T_m$) is introduced. The "fast recombination" criterion does not comply with our conditions in the model of point defect criterion.

So, the recombination process of intrinsic point defects in FZ-Si and CZ-Si single crystals near the crystallization front is hindered due to the recombination barrier. The vacancies and intrinsic interstitials find out drains in the form of background oxygen and carbon impurities. Experiments in crystal quenching demonstrate that the vacancies and interstitial microdefects are first to appear near the crystallization front, and then during the cooling, the $D(C)$-microdefects, B-microdefects and A-microdefects are formed [12]. In addition, several experiments suggest a break of the Arrhenius' behavior at about 1323 K, suggesting that different mechanisms act above and below this temperature [20]. In [20], it has been shown that at 1353 K, a crossover occurs between intrinsic interstitials dominating self-diffusion at high temperature and vacancies dominating that at low temperature. These results prove our experimental results that evidence two types of decomposition of oversaturated point defects solid solution (vacancy and interstitial).

Therefore, we estimate the recombination time at low temperature (τ_2) according to formula [24]:

$$\tau_2(T) = \tau_\infty \cdot \exp(C/TS_c). \quad (7)$$

In this case, Antoniadis and Moskowitz [25] provide a single estimation for activation energy barrier at $T = 1373$ K ($\Delta G = \Delta H = 1.4$ eV), by comparison of experimentally measured vacancy lifetimes to diffusion-limited reaction rate theory predictions. The value $\tau_\infty = 634.13$ s we define from (7) if $T = T_m$. Then,

$$\tau_2(T) = 634.13 \cdot \exp\left(-\Delta G/TS_c(T)\right). \quad (8)$$

The estimation at $T = T_m$ gives $\tau_2 = 316.4$ s, and at $T = 723$ K, we have $\tau_2 \to 0$ (if estimated not allowing for an oscillating entropy). Under low temperatures the recombination factor $k_{IV}(T)$ is defined by

$$k_{IV}(T) = \quad (9)$$
$$= 4\pi \cdot r_0[D_I(T) + D_V(T)] \cdot \exp(-\Delta G/kT)/\Omega \cdot c_s,$$

where $D_I(T) = 1.76 \cdot 10^{-2} \cdot \exp(-0.937/kT)$ cm$^2 \cdot$s^{-1} and $D_V(T) = 1.70 \cdot 10^{-3} \cdot \exp(-0.457/kT)$ cm$^2 \cdot$s^{-1} [2]. The estimate at $T = 723$ K gives $k_{IV} \approx 10^{-9}$ cm$^3 \cdot$s^{-1} and the "fast recombination" criterion is well satisfied.

Thus, the reduction of the recombination barrier is caused by a reduction of configuration entropy with lowering temperature. Since at temperatures close to the melting point, the equilibrium concentrations of vacancies and intrinsic interstitial atoms co-exist simultaneously in dislocation-free silicon single-crystals, the oversaturated solid-state solution of intrinsic point defects decomposes concurrently according to two mechanisms: vacancy-type and interstitial-type.

The heterogeneous formation mechanism of the grown-in microdefects in dislocation-free silicon single crystals uses completely new approaches [12]: (i) concentrations of vacancies and intrinsic interstitial silicon atoms at the crystallization front near the melting point are comparable, recombination of intrinsic defects are hindered at high temperatures; (ii) the decomposition of the oversaturated solid-state solution of point defects during the silicon cooling below the crystallization temperature follows two independent mechanisms: vacancy-type and interstitial-type; (iii) it is just the initial oxygen-vacancy agglomerates and carbon-vacancy agglomerates formed on impurities centers that form the driving force of the defect formation; (iv) the dominating feature in decomposition of the oversaturated solid-state solution of point defects is the generation of secondary defects (clusters of intrinsic point defects), which accompanies the growth of a new phase.

Within the frame of the heterogeneous mechanism, the vacancies and intrinsic interstitials do react with impurities. Such the interaction might be direct, with formation of chemical bonds between the point defects or the impurity in solid solution, or indirect, when the interaction occurs through the strain fields or the static electrical fields associated with the defects and solutions. The background oxygen and carbon impurities are involved in the defect formation process as nucleation centers, and consequently participate in the processes of further growth and transformation of the grown-in microdefects [12]. As nucleation centers for oxygen-vacancy aggregates are the contraction areas close to oxygen interstitial atoms, the redundant vacancies and other oxygen interstitial atoms are directed towards them. The areas of strain around carbon substitutions act as nucleation centers for carbon-interstitial aggregates, the redundant intrinsic interstitial atoms and oxygen interstitial atoms are directed towards them. Such agglomerate growth results in the formation of the vacancy and interstitial microdefects. The latter are primary microdefects, which are formed near the crystallization front.

Thus, recombination parameters of the model representing point defect dynamics (recombination barrier, recombination time, recombination factor) for high and low temperatures have been estimated basing on heterogeneous mechanism of grown-in microdefect formation and transformation. The presented theoretical results indicate that at high temperatures, the point defect aggregation process is predominated by the recombination process between intrinsic interstitials and vacancies. In this case, the contribution of the recombination process to the aggregation process is negligible.

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Рекомбінаційні параметри точкових дефектів у бездислокаційних монокристалах кремнію

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Розглянуто рекомбінаційні параметри моделі динаміки точкових дефектів (рекомбінаційний бар'єр, рекомбінаційний час, рекомбінаційний фактор) для високих та низьких температур, виходячи з гетерогенного механізму утворення і трансформації ростових мікродефектів. За рахунок охолодження розпад пересиченого твердого розчину точкових дефектів у кремнії відбувається за двома маханізмами: вакансійним та міжвузловинним. Тому вакансії і власні міжвузловинні атоми кремнію знаходять стоки у вигляді атомів фонових домішок, таких як кисень та вуглець. Утворення пар "власний точковий дефект — домішка" є домінуючим процесом при температурах, близьких до точки плавлення кремнію.