DEFECTS AND IMPURITY CENTERS,
DISLOCATIONS, AND PHYSICS OF STRENGTH

On the Recombination of Intrinsic Point Defects in Dislocation-Free Silicon Single Crystals

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Received June 20, 2006; in final form, July 18, 2006

Abstract—The recombination of intrinsic point defects in dislocation-free silicon single crystals is investigated. It is established experimentally and confirmed by thermodynamic calculations that this process in the vicinity of the crystallization front is hindered by the recombination barrier. The recombination parameters (such as the recombination barrier height, the recombination time, and the recombination factor) for the model describing the dynamics of point defects at low and high temperatures are evaluated in terms of the heterogeneous mechanism of nucleation and transformation of grown-in microdefects. It is confirmed that the decomposition of a supersaturated solid solution of point defects can occur according to two mechanisms, namely, the vacancy and interstitial mechanisms. Vacancies and intrinsic interstitial silicon atoms find sinks in the form of oxygen and carbon background impurities. It is demonstrated that the formation of "intrinsic-point-defect–impurity" pairs is a dominant process in the vicinity of the melting temperature.

1. INTRODUCTION

High-temperature growth and subsequent cooling of dislocation-free silicon single crystals is accompanied by the formation of structural imperfections referred to as grown-in microdefects. At present, the term "grown-in microdefects" has been used in reference to any local disturbance of the periodicity of a crystal lattice with a size from several tens of angstroms to several micrometers. Grown-in microdefects form a transient class of defects intermediate between point and linear defects.

The formation of grown-in microdefects (such as microprecipitates, dislocation loops, and micropores) is associated with the processes of aggregation of intrinsic point defects and impurities. In this respect, knowledge of the mechanism of formation of grown-in microdefects can be the key to understanding the main characteristics of point defects (activation volumes, diffusion coefficients, equilibrium concentrations, etc.). In turn, investigation into the processes of recombination of intrinsic point defects and/or their aggregation with impurities in the bulk of silicon makes it possible to elucidate the mechanism of formation of grown-in microdefects. However, the large amount of contradictory theoretical and experimental data makes it difficult to understand the mechanisms of the processes of defect formation occurring in dislocation-free silicon single crystals.

Currently, the problem associated with the defect formation in dislocation-free silicon single crystals, as a rule, has been solved in two ways. Researchers adhering to the first way believe that an appropriate combination of the conditions responsible for equilibrium, transfer, and solid-state kinetics of intrinsic point defects and impurities can be determined within the theoretical model of the dynamics of point defects, which provides a plausible explanation for the formation of grown-in microdefects [1–3]. In this case, the crystal is considered a dynamic system or a solid-state chemical reactor that ensures transfer and interaction of point defects, complexes, and aggregates. It is agreed that the formation of grown-in microdefects and their sizes, concentration, and spatial distribution are governed by the crystal dynamics and temperature gradients in the crystal. An analogy with chemical reactions suggests that simulating the dynamics of point defects in silicon can offer a clue to understanding and quantitatively evaluating the process of formation of grown-in microdefects and their optimum spatial distribution over the crystal [2].

The model of point defect dynamics includes convection, diffusion, thermal diffusion, and recombination of point defects [4]. It is assumed that all the above mechanisms are essential to understanding the dynamics of point defects; however, rapid recombination of intrinsic point defects in the vicinity of the melting temperature is of the utmost importance [2, 5]. It should be

noted that similar models have also been offered by other authors [6–10]. All these models are based on the theoretical model of formation of grown-in microdefects, which was proposed by Voronkov [11]. An analysis of the experimental results obtained by de Kock et al. [12] and Roksnoer and von der Boom [13] led Voronkov to the following assumptions: (i) the rate of recombination between intrinsic interstitial silicon atoms and vacancies is very high, (ii) the diffusion coefficient of intrinsic interstitial atoms at temperatures in the vicinity of the melting point is larger than the diffusion coefficient of vacancies, and (iii) the equilibrium concentration of vacancies at temperatures in the vicinity of the melting point is higher than the equilibrium concentration of intrinsic interstitial atoms [11]. According to Voronkov, the formation of grown-in microdefects is governed by the growth parameter $V/G = C_{crit}$, where V is the growth rate of the crystal and G is the axial temperature gradient. As follows from this mechanism, the growth of a crystal in the vacancy regime ($V/G > C_{crit}$) differs substantially from that in the interstitial regime ($V/G < C_{crit}$).

The second direction of investigations into the processes of defect formation in dislocation-free silicon single crystals is associated with the experimental observation and determination of the parameters of grown-in microdefects of different types [12, 14–19]. Since experimental observation of very small aggregates consisting of point defects and very weak distortions produced by these defects in the crystal lattice is extremely complicated, it is necessary to employ direct experimental methods to determine the sign of the strain of the crystal lattice. The sign of the strain (frequently defined as the physical nature of grown-in microdefects) produced by a defect in the crystal lattice provides indirect information on the chemical composition of the defect and permits one to uniquely determine the mechanism of nucleation and transformation of grown-in microdefects [20]. This mechanism, which is determined from direct experimental investigations of grown-in microdefects, is of considerable importance for gaining a qualitative understanding of the process of formation of these microdefects [21]. In our opinion, only a combination of the aforementioned two approaches makes it possible to adequately investigate and describe the physical processes associated with the formation of defects in dislocation-free silicon single crystals.

In this paper, the recombination parameters (such as the recombination barrier height, the recombination time, and the recombination factor) for the model describing the dynamics of point defects at low and high temperatures are evaluated in terms of the heterogeneous mechanism of nucleation and transformation of grown-in microdefects.

2. BASIC PRINCIPLES OF THE HETEROGENEOUS MECHANISM OF NUCLEATION AND TRANSFORMATION OF GROWN-IN MICRODEFECTS

In our previous works [18, 19], microdefects of different types in silicon single crystals grown by the floating-zone (*Fz*-Si) and Czochralski (*Cz*-Si) methods were experimentally investigated using transmission electron microscopy with the aim of elucidating their physical nature. As follows from the experimental results obtained in those studies, the formation of primary defects in the form of both oxygen-vacancy and carbon-interstitial aggregates is the deciding factor responsible for the decomposition of a solid solution of point defects in superhigh-purity dislocation-free silicon single crystals.

The analysis of the experimental results enabled us to validate the heterogeneous mechanism of formation of grown-in microdefects [20, 21]. This mechanism is based on the following radically new principles:

(i) the recombination of intrinsic point defects at temperatures in the vicinity of the crystallization point is hindered by the recombination barrier;

(ii) oxygen and carbon background impurities are involved as nucleation centers in the process of defect formation and, moreover, participate in the processes of further growth and transformation of microdefects; and

(iii) the decomposition of a supersaturated solid solution of point defects in dislocation-free silicon single crystals occurs through two mechanisms, namely, the vacancy and interstitial mechanisms.

According to the heterogeneous mechanism, the formation of "impurity-intrinsic-point-defect" complexes is the deciding factor responsible for the onset of the process of defect formation in dislocation-free silicon single crystals. However, within the theoretical model of the dynamics of point defects, the calculations, as a rule, are performed using the "intrinsic-point-defect-intrinsic-point-defect" interaction formalism; in this case, the type of dominant point defects is determined by the rapid recombination of intrinsic point defects in the vicinity of the melting temperature. Therefore, the estimates obtained for the parameters of recombination of intrinsic point defects within the theoretical model of the dynamics of point defects can be useful in eliminating the aforementioned contradictions.

3. EVALUATION OF THE PARAMETERS OF THE PROCESS OF RECOMBINATION OF INTRINSIC POINT DEFECTS WITHIN THE MODEL OF POINT DEFECT DYNAMICS

The inclusion of the entropy barrier and the coefficient of joint self-diffusion of vacancies and interstitial silicon atoms in thermodynamic calculations leads us to the conclusion that there exists a recombination bar-

rier [21]. However, this conclusion is inconsistent with the Voronkov theory. It should be noted that the experimental results obtained from transmission electron microscopy and the heterogeneous mechanism of formation of grown-in microdefects confirm the theoretical assumptions made earlier by Hu [22] and Sirtl [23].

The microscopic model of a recombination barrier was thoroughly developed by Gösele et al. [24, 25]. In essence, this model is as follows: the dependence of the barrier height on the temperature is determined by the configuration of intrinsic point defects at high temperatures. In the framework of the model under consideration, it is assumed that, at high temperatures, intrinsic interstitial silicon atoms and vacancies are extended over several atomic volumes (eleven atoms occupy ten unit cells). This means that, around a point defect, there is a disordered isotropic region extending up to the atoms involved in the second coordination sphere. According to the results reported in the aforementioned papers, recombination can occur only when defects of two types are simultaneously contracted in the vicinity of one atomic volume. Since the extended defect configurations are characterized by a larger number of microstates as compared to those of a point defect, this contraction leads to a decrease in the entropy and, consequently, an entropy barrier $\Delta S < 0$ exists. As the temperature decreases, the entropy barrier is considerably reduced and disappears completely at low temperatures and defects readily recombine. This process is associated with the variations observed in the configurations of intrinsic point defects, which are extended at high temperatures and have a point dumbbell-like configuration at low temperatures, as was shown in [25]. It should be emphasized that the theory of extended defect configurations, as well as of a recombination barrier, was confirmed in a number of recent studies [26–28].

Let us now evaluate the recombination parameters (such as the recombination barrier height, the recombination time, and the recombination factor) for the model describing the dynamics of point defects in terms of the heterogeneous mechanism of nucleation and transformation of grown-in microdefects and the model of a recombination barrier.

3.1. High-Temperature Range

The temperature dependence of the configurational entropy for the aforementioned model of a defect can be described by the relationship [29]

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

where S_∞ is the limiting value of the configurational entropy S_c (at $T \longrightarrow T_m$), T_m is the melting temperature, and T_k is the characteristic temperature. It is assumed that the characteristic temperature T_k is the minimum temperature at which structural imperfections arise in dislocation-free silicon single crystals. This tempera-

ture can be estimated to be $T_k = 723$ K as the mean temperature of formation of thermal donors in silicon. Hence, it follows that $S_c(T) = S_\infty(1 - 723/T)$. According to [25], we can write $S_c(1373$ K$) = -11.5k$ (where k is the Boltzmann constant). Then, we find $S_\infty = -24.3k$. As a result, we obtain

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

According to the model proposed in [25], the free energy of the recombination barrier can be represented by the formula $\Delta G = -T\Delta S$, because the contribution of the enthalpy term ΔH is negligible. The temperature dependence of the recombination barrier height is governed by the entropy of formation of point defects. Hence, we can write

$$\Delta G(T) = -T[-S_c(T)] = TS_c(T). \qquad (3)$$

Approximate estimation at a temperature $T = T_m$ leads to the free energy of the recombination barrier $\Delta G(1685$ K$) = 2.014$ eV.

The experimental data on the self-diffusion in silicon indicate that the diffusion coefficient obeys the Arrhenius dependence over a wide range of temperatures $D(T) = D_0\exp(-E_a/kT)$ with an activation energy $E_a \sim 4$–5 eV and a preexponential factor D_0 that is considerably larger than the preexponential factors for metals [30]. However, the question as to which of the two (vacancy or interstitial) mechanisms makes a dominant contribution remains open. In this study, we use the classical data obtained by Mayer et al. [31], according to which the diffusion coefficient in the temperature range $T = 1320$–1658 K is given by the formula

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

Approximate estimation at a temperature $T = T_m$ leads to the diffusion coefficient $D(1685$ K$) = 1.42 \times 10^{-12}$ cm^2 s^{-1}. Intrinsic interstitial atoms are predominant at high temperatures. Therefore, the recombination time τ_1 at high temperatures can be evaluated from the expression

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

where Ω is the volume of the crystal lattice in the model proposed by Gösele et al. [25] and $r_0 = 3 \times 10^{-8}$ cm is the recombination radius. Approximate estimation at a temperature $T = T_m$ leads to the recombination time $\tau_1 = 316$ s. It should be noted that, according to the estimates made with the use of the recent data reported by Tang et al. [30] and Bracht et al. [32], we obtain $\tau_1 = 110$ and 132 s, respectively.

The recombination factor $k_{IV}(T)$ is described by the theory of diffusion-limited reactions together with the kinetic activation barrier [2]. At high temperatures, the recombination factor can be written in the following form:

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

where $c_s = 5 \times 10^{22}$ cm^{-3} is the atomic density. The estimation at a temperature $T = T_m$ leads to the recombination factor $k_{IV}(1685$ K$) = 6.3 \times 10^{-26}$ cm^3/s. Lemke and Sudkamp [10] introduced the following criterion for "rapid recombination": $k_{IV}(1685$ K$)C_{Vm} \geq 20$ s^{-1}, where $C_{Vm} = 11.7 \times 10^{14}$ cm^{-3} is the vacancy concentration at $T = T_m$. For our model of point defect dynamics, the criterion for rapid recombination does not hold.

Thus, in this paper, we theoretically demonstrated for the first time that the process of recombination of intrinsic point defects in *Fz*-Si and *Cz*-Si single crystals in the vicinity of the crystallization front is hindered by the recombination barrier. These theoretical calculations confirm our experimental results obtained in [21], according to which the recombination of intrinsic point defects in silicon single crystals is not observed in the vicinity of the crystallization front. Consequently, we can make the inference that vacancies and intrinsic interstitial silicon atoms find their sinks in the form of oxygen and carbon background impurities, respectively.

3.2. Low-Temperature Range

The experimental results obtained by a number of researchers suggest that the Arrhenius dependence exhibits a discontinuity at temperatures close to 1323 K. In this case, it is assumed that, at temperatures below and above this temperature, the diffusion can occur through different mechanisms [30]. In particular, Tang et al. [30] showed that, at a temperature of 1353 K, there occurs a crossover from the self-diffusion of intrinsic interstitial atoms (dominating at high temperatures) to the self-diffusion of vacancies (dominating at low temperatures). These results confirm our experimental data, according to which the decomposition of a supersaturated solid solutions of point defects can occur through two (vacancy and interstitial) mechanisms [20].

Therefore, the recombination time τ_2 at low temperatures can be estimated from the relationship [33]

$$\tau_2(T) = \tau_\infty \exp(C/TS_c). \tag{7}$$

Under these conditions, Antoniadis and Moskowitz [34] evaluated the energy barrier at the temperature $T = 1373$ K ($\Delta G = \Delta H = 1.4$ eV) by means of comparing the experimentally measured lifetime of vacancies and the growth rate for a diffusion-limited reaction. The limiting value of the recombination time $\tau_\infty = 634.13$ s can be determined from relationship (7) at a temperature $T = T_m$. As a result, we obtain

$$\tau_2(T) = 634.13 \exp(-\Delta G/TS_c(T)). \tag{8}$$

Approximate estimation leads to $\tau_2 = 316.4$ s at $T = T_m$ and $\tau_2 \longrightarrow 0$ at $T = 723$ K (estimates without regard for the vibrational entropy). At low temperatures, the

recombination factor $k_{IV}(T)$ can be determined from the expression

$$\begin{aligned} k_{IV}(T) = {} & 4\pi r_0 [D_I(T) + D_V(T)] \\ & \times \exp(-\Delta G/kT)/\Omega c_s, \end{aligned} \tag{9}$$

where $D_I(T) = 1.76 \times 10^{-2}\exp(-0.937/kT)$ cm^2 s^{-1} and $D_V(T) = 1.70 \times 10^{-3}\exp(-0.457/kT)$ cm^2 s^{-1} [2]. Approximate estimation at a temperature $T = 723$ K leads to the recombination factor $k_{IV} \approx 10^{-9}$ cm^3 s^{-1}. Therefore, the criterion for rapid recombination is satisfied fairly well.

Consequently, the processes of recombination of intrinsic point defects at low temperatures (for example, under conditions of ion implantation) proceed at a rather high rate. Our theoretical calculations confirm the validity of the entropy barrier model, according to which the decrease in the barrier height is caused by the decrease in the configurational entropy with decreasing temperature.

The theoretical results obtained in this study suggest that, in the high-temperature range, i.e., at temperatures close to the melting point, vacancies and intrinsic interstitial atoms at equilibrium concentrations coexist in dislocation-free silicon single crystals and the decomposition of a supersaturated solid solution of intrinsic point defects occurs through two mechanisms simultaneously, namely, the vacancy and interstitial mechanisms.

4. CONCLUSIONS

Thus, the experimental data and the results obtained from thermodynamic calculations have demonstrated that the process of aggregation of point defects dominates over the process of recombination of intrinsic point defects. At high temperatures, the process of recombination makes an insignificant contribution to the process of aggregation. Consequently, vacancies and intrinsic interstitial atoms coexist in thermal equilibrium. As a result, intrinsic point defects of both types are simultaneously involved in the process of aggregation. The decomposition of a supersaturated solid solution of point defects occurs upon cooling through two mechanisms, namely, the vacancy and interstitial mechanisms, with the formation of oxygen-vacancy and carbon-interstitial agglomerates.

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Translated by O. Borovik-Romanova