On the nature of thermal equilibrium point defects in Si: Are the thermal equilibrium point defects in Si crystals Frenkel pairs or Schottky defects?

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Received February 3, 2017; accepted March 1, 2017; published online March 27, 2017

Thermal equilibrium point defects (TEPD) are generated as Frenkel pairs or Schottky defects. It is still controversial whether the TEPD in Si are Frenkel or Schottky, which is recalled with the recent experimental finding of their formation energies. After reviews of the Frenkel pair and Schottky defects models, the latter was concluded to be the case since their formation energies determined experimentally are different from each other. This result was applied to calculate the critical ratio of the growth velocity/temperature gradient of the Voronkov model on the grown-in point defects in Si and obtained a different result. © 2017 The Japan Society of Applied Physics

Thermal equilibrium point defects (TEPD) play a crucial role in high-temperature phenomena such as self-diffusion, diffusions of various impurities, formation of grown-in defects and so on. They are mainly vacancies in metals such as Cu (fcc crystal) and Mo (bcc) and they are called Schottky defects. Contrarily, both vacancies and interstitials with comparable concentrations exist in Si at thermal equilibrium. To the best of our knowledge, only Si crystals have this property and, therefore, they are unique crystals. A question arises about the nature of those point defects.

Knowledge of the nature of vacancies and interstitials is indispensable for understanding high-temperature phenomena related to TEPD in Si. However, it is still controversial whether they are Frenkel pairs or Schottky defects. Those two kinds of defect models have long been discussed because there have been no data on point defects determined by direct methods. After obtaining experimental results of the formation energy of vacancies and interstitials, we checked various papers related to TEPD. We are noticed that authors of recent papers do not pay attention to the nature of TEPD: Many use the Frenkel pair model and some use both models in the same papers, an inconsistent treatment. Almost all authors assume as if their treatments have been verified already.

Here, we briefly review two representative papers and discuss them to clarify the nature of point defects. Before detailed discussion, we should recall some properties of Schottky defects and Frenkel pairs: Vacancies and interstitials are independently generated in a finite crystal in the Schottky defect model, but are generated simultaneously as pairs and then dissociated in the Frenkel pair model. Hence, the formation energy of a vacancy and an interstitial are generally different in the former model but the same in the latter model since concentrations of vacancies and interstitials are the same: the formation energy of point defects is given by the following equation $E = -k(\ln c_1 - \ln c_2)/(1/T_1 - 1/T_2)$, since the thermal equilibrium concentration is given by $c = c_0 \exp(-E/kT)$. Here, $E$, $k$, and $c_0$ are the formation energy, the Boltzmann constant, and the pre-exponential factor, respectively. $c_i$ ($i = 1, 2$) is the concentration of point defects at temperature $T_i$ ($i = 1, 2$).

Sirtl payed attention to the temperature dependence of thermal expansion coefficients of Si crystals to discriminate Schottky defects and Frenkel pairs. Roughly, the temperature dependence of thermal expansion coefficient is composed of two terms, namely, the lattice term and the defect term. The former is originated from thermal vibration of atoms: mean distances between atoms become larger because of larger amplitudes of atomic vibration in anharmonic potentials at higher temperatures. The latter is proportional to the concentration of defect, i.e., $c_0 \exp(-E/kT)$. The latter has a great dependence on temperature.

Based on an interpretation of the dependence of linear thermal expansion coefficients of Si on temperature in comparison with those of Mo, Sirtl proposed that the thermal equilibrium point defects in Si crystals are Frenkel pairs. For the readers’ convenience, Fig. 1 of Sirtl’s paper is cited as Fig. 1 in an abbreviated form since that paper is not easy to
access. In the case of Mo, the linear thermal expansion coefficient increases rapidly with temperature near the melting point due to the generation of vacancies in thermal equilibrium. This behavior is common in the case of metals. In the case of Si, however, such a rapid increase is not observed but only the lattice term is observed. He interpreted that this behavior was well explained by assuming the generation of similar concentrations of vacancies and interstitials or the generation of Frenkel pairs, in contrast with the case of vacancy formation in Mo. These situations are schematically depicted in Fig. 2. Figures 2(a) and 2(b) are drawn according to Hu’s paper. Atoms which exit the crystal to the surface (slashed squares) and atoms which enter the crystal from the surface (open squares), which are associated with the generation of vacancies and interstitials, respectively, are assumed to exist at kinks of the surface step so as to keep the surface energy constant. Hence, the Schottky defect model is defined under the assumption of a finite crystal.

According to the above model, vacancy generation results in an increase of crystal size. Incidentally, interstitial formation results in a decrease of crystal size. The generation of vacancies and interstitials in similar concentrations results in fairly good cancellation of volume changes due to those defects, resulting in a very slight change of crystal volume. In case of Frenkel pair generation [Fig. 2(c)], whether they are paired or dissociated after the generation, the crystal size changes slightly. In the above discussion, a vacancy and an interstitial in the crystal are tentatively assumed to induce contraction and expansion of a half of an atomic volume, respectively. More rigorous volume changes are probably obtained by, for example, the first principles calculation but probably not so much different from above values. Based on the above considerations, the Frenkel pair model seems to be believed.

According to recent studies of grown-in defects in Si, thermal equilibrium concentrations of vacancies and interstitials at the melting point in Si are estimated to be around $1 \times 10^{15} \text{ cm}^{-3}$. Incidentally, the thermal equilibrium vacancy concentration at the melting point is around $1 \times 10^{18} \text{ cm}^{-3}$ in metals. Hence, the thermal equilibrium concentration of vacancies in Si is smaller than those in metals by a factor of about $1 \times 10^{-3}$, which means that the extra thermal expansion due to the generation of point defects in Si cannot be detected by observation of the ordinary magnitude, even if it is induced. In fact, according to Fig. 1, the extra increase of the linear thermal expansion coefficient due to the vacancy generation in Mo is about $8 \times 10^{-6} \text{ K}^{-1}$, which is estimated using the vertical line in Fig. 1 at about 2600 K. Thus, the extra thermal expansion due to vacancy generation in Si is expected to be about $10^{-8} \text{ K}^{-1}$, too small to be detected in Fig. 1. Hence, Sirtl’s consideration cannot be applied to determine the nature of point defects in Si.

Regarding the difference of the vacancy concentrations in Si and Mo, the thermal equilibrium vacancy concentrations at the melting points ($T_m$) in semiconductors are orders of magnitude lower than those in metals. This is due to the fact that vacancy formation energies ($E_V$) in semiconductors are higher than those in metals with comparable melting temperatures. For example, $E_V/T_m$ of Si is about $2.82 \times 10^{-3}$ since $E_V$ and $T_m$ are $3.85 \text{ eV}^1$ and $1687 \text{ K}$, respectively, and larger than that ($1.12 \times 10^{-3}$, $E_V$ and $T_m$ are $3.24 \text{ eV}^6$ and 2883 K, respectively) of Mo. The vacancy concentration at the melting point is proportional to exp($-E_V/kT_m$) in addition to the pre-exponential factor.

Later, Hu proposed that the thermal equilibrium point defects are Schottky defects when the crystal size is finite, but Frenkel pairs when the crystal size is infinite, based on the free energy calculation in statistical dynamics. [Contrary to Hu, we consider that the Frenkel pair model can be defined even in a finite crystal as depicted in Fig. 2(c). By replacing one atom at lattice site to an interstitial site, one Frenkel pair is generated.] An important point in the former model is that vacancies and interstitials are independent of each other: The thermal equilibrium concentrations of vacancies and interstitials are given as follows: $c_V^c = c_V^0 \exp(-E_V/kT)$, $c_I^c = \frac{c^0}{2} \exp(-E_I/kT)$ where $c_V^0$, $c_I^0$, and $E_V$ are the thermal equilibrium concentration, the pre-exponential factor, and the formation energy, respectively, of a vacancy, and $c_V^c$, $c_I^c$, and $E_I$ have the same meanings for an interstitial. In the Frenkel pair model, the thermal equilibrium concentrations of the vacancy and the interstitial are the same, $c_V^c = c_I^c$, to that of Frenkel pairs since they are generated at the same time. The thermal equilibrium concentration of the Frenkel pair is proportional to exp($-(E_V + E_I)/2kT$) at temperature $T$. Hence, the formation energies of the vacancy and the interstitial are the same, $(E_V + E_I)/2$. It should be noted that vacancies and interstitials of equal numbers are assumed to independently distribute in the crystal, not forming pairs, in the calculation of mixing entropy.

Experimentally, the formation energy of a vacancy and that of an interstitial were determined to be about $3.85 \pm 0.15$ and $4.8 \pm 0.4 \text{ eV}$, respectively, by a direct method, i.e., quenching experiments. They were 2 and $3.18 \pm 0.15 \text{ eV}$, respectively, determined by an indirect method, i.e., Zn diffusion. The difference of formation energies of a vacancy and an interstitial, about 1 eV, are similar between two experimental methods, even though formation energies of both defects are different. Hence, we conclude that the thermal equilibrium point defects in Si are Schottky defects.

According to Fig. 2, the generation and annihilation of vacancies and interstitials are written as follows in chemical reaction equations:

$$V \leftrightarrow \{\text{Si(S)}\}, \ I \leftrightarrow \{\text{Si(S)}\}$$

for the case of Schottky defects, where V, I, and [Si(S)] denote vacancies, interstitials, and a Si crystal of finite size (the existence of surface is emphasized), respectively.
for the case of Frenkel pairs, where $\{\text{Si}\}$ denotes a Si crystal. Equation (1) seems peculiar at first glance because the number of Si atoms is not conserved. This apparent inconvenience is due to the finite size of the crystal, namely, there is a surface in the Schottky defect model, as shown in Fig. 2. Equation (2) clearly shows the simultaneous generation of a vacancy and an interstitial, which is the characteristic nature of the Frenkel pairs.

Equation (3) is deduced straightforwardly from Eq. (2) when the local equilibrium is reached with the use of the mass action law.8)

$$c_v c_I = c_v^* c_I^*.$$  \tag{3}

Equation (3) is very useful since it is enough to use one variable, $c_v$ or $c_I$, instead of two variables ($c_v$ and $c_I$) in discussion of various problems. However, it is useful only for the Frenkel pair model.

In conclusion of this section, thermal equilibrium point defects in the Si crystal are identified as being Schottky defects, not Frenkel pairs, from a comparison of the formation energies of a vacancy and an interstitial, which were determined by quenching experiments1) and diffusion experiments.7)

As an application of above results, we show the critical ratio, $(v/G)_{\text{crit}}$, of the Voronkov model9) using the properties of Schottky defects and compare it with that of Voronkov. Here $v$ and $G$ are the crystal growth velocity and temperature gradient in the grown crystal, respectively.

High-quality Si single crystals are indispensable to fabricate electronic devices, which support modern society. Voronkov9) developed a theory on the grown-in point defects in Si crystals. His theory gives a criterion for grown-in point defects. According to the theory, vacancy-rich crystals or interstitial-rich crystals are grown when $v/G$ is larger or smaller, respectively, than the critical ratio. Hence, we expect to grow high-quality crystals by choosing $v$ and $G$, which give $(v/G)_{\text{crit}}$.

The theory is constructed assuming basic properties of two kinds of TEPD. Concentrations of vacancies and interstitials at the melting temperature are different, and the formation energies of the vacancy and the interstitial are different. These are the properties of the Schottky defects, as discussed already. Incidentally, Voronkov used Eqs. (2) and (3) in discussions. These are the properties of the Frenkel pair. He derived following equation for $(v/G)_{\text{crit}}$:

$$\frac{(v/G)_{\text{crit}}}{G} = \left( \frac{E_v + E_l}{2} \right) \frac{D_v^m c_v^m - D_v^0 c_v^0}{kT^2_m (c_v^m - c_v^0)}.$$  \tag{4}

In the Schottky defects model, $(v/G)_{\text{crit}}$ is derived as follows:

$$\frac{(v/G)_{\text{crit}}}{G} = \frac{E_l D_v^I c_I^m - E_v D_v^I c_I^0}{kT^2_m (c_v^m - c_v^0)}.$$  \tag{5}

Here, the superscript and subscript $m$ mean that those quantities are those at the melting point ($T_m$). $D_v^I$ and $D_v^0$ are the diffusion constant of interstitials and vacancies, respectively, at the melting point. $c_v^0$ and $c_v^m$ are the thermal equilibrium concentrations of vacancies and interstitials at the melting point, respectively, given by $c_v^0 = c_v^0 \exp(-E_v/kT_m)$ and $c_v^m = c_v^m \exp(-E_l/kT_m)$.

Equation (5) is deduced from the assumption that the fluxes of vacancies and interstitials at the interface of liquid and solid were the same. According to Voronkov, the vacancy flux ($J_v$) is given by

$$J_v = -D_v^0 \frac{dc_v}{dx} + v c_v.$$  \tag{6}

The first and the second term of the right hand side are the diffusion term and drift term, respectively. Similar equation is given for the interstitial flux. We also used Voronkov’s assumption that the temperature ($T$) distribution in the grown crystal was given by

$$\frac{1}{T} = \frac{1}{T_m} + \frac{G}{T_m} x.$$  \tag{7}

Here, $x$ is the coordinate in the grown crystal from the interface. Thus, $c_v(x)$ and $c_I(x)$ are assumed to be as a function of $T$. Some details will be given in a separate paper shortly.

Both equations are in similar functional forms except terms including formation energies. The difference of Eqs. (4) and (5) is the place of the formation energy. The formation energy in Eq. (4), $(E_v + E_l)/2$, is the formation energy of the vacancy and the interstitial in the Frenkel pair model, as discussed above, and therefore, it is factorized. As discussed in the preceding section, the formation energies of a vacancy and an interstitial are different in the Schottky defects model. The critical ratio is deduced from comparison of vacancy-related term and interstitial-related term as shown above. Therefore, vacancy-related properties and interstitial-related properties are grouped separately in Eq. (5) and mixing of properties of the vacancy and the interstitial, $(E_v + E_l)/2$, is not reasonable.

The latter expression is found to be useful when we discuss the dependence of the critical ratio on the doped impurities. All of detailed discussion will be shown in separate papers.

We conclude that the Schottky defects, not the Frenkel pair, are thermal equilibrium point defects in Si crystals according to the basic consideration and experimental results. As an example of application of this conclusion, we calculated the critical ratio, $(v/G)_{\text{crit}}$ of Voronkov model under the assumption of the Schottky defects model and obtained a reasonable result.

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