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# Density-functional-theory-based calculations of formation energy and concentration of the silicon monovacancy

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By using first-principles calculations, we study the formation energy and concentration of the silicon monovacancy. We use large-scale supercells containing up to 1728 atomic sites and confirm the convergence of calculational results with respect to the cell size. The formation energy is calculated to be 3.46 eV, and the vacancy concentration at the silicon melting point is estimated to be  $7.4 \times 10^{16} \text{ cm}^{-3}$ . These values are consistent with experimental results. We find that the vibrational effect significantly increases the vacancy concentration about  $10^4$  times.

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## 1. Introduction

The study of point defects in semiconductors has attracted much attention because of the crucial effects of such defects on various properties of materials. Some defects capture carriers and affect the electrical conductivity of semiconductors. Therefore, control of defects is necessary for device fabrication.<sup>1)</sup>

The silicon vacancy is a fundamental defect and has been extensively investigated theoretically<sup>1-8)</sup> and experimentally.<sup>9-13)</sup> Electron paramagnetic resonance (EPR) measurement has clarified the Jahn-Teller effect that lowers the symmetry from  $T_d$ .<sup>9)</sup> Theoretical studies based on the density functional theory (DFT) show the symmetry of  $D_{2d}$  for the neutral charge state.<sup>1,3-7)</sup> Negative-U behavior was examined by experimental<sup>14)</sup> and theoretical studies.<sup>15)</sup>

The formation of defects depends on crystal growth rate.<sup>16)</sup> Vacancies are created at high crystal growth rates, whereas interstitials are created at low crystal growth rates. At high temperatures up to the melting point, a finite vacancy concentration is observed in thermal equilibrium.<sup>17)</sup> The formation energy of the monovacancy is estimated to be 3.1 – 4.1 eV in some experimental studies.<sup>10-13)</sup>

Recently, Goto *et al.*<sup>18)</sup> have observed elastic softening at a very low temperature by

ultrasonic measurements. They found the elastic softening below 20 K. Their analysis leads to the conclusion that the softening is induced by high-symmetry ( $T_d$ ) defects and they considered that the softening originates from the monovacancy. However, the defects observed by them might be different from the monovacancy examined in previous studies.<sup>19,20)</sup> Goto *et al.* supposed that the concentration deduced from the results of a low-temperature experiment is the same as that of the thermal equilibrium monovacancy near the melting point; therefore, the concentration near the melting point should be clarified.

In this study, we carry out large-scale first-principles calculation in order to accurately estimate the concentration of the monovacancy. We use large supercells containing 1728 and 216 sites for calculating formation energy and the vibrational effect on the concentration of the monovacancy, respectively. The calculations are much larger than those in previous studies; i.e., up to 1000-site supercell calculation for the formation energy and up to 64-site supercell calculation for the vibrational effect have been carried out thus far.<sup>1,3,5,6,8,21,22)</sup> By using large supercells, we confirm good convergence. The calculated formation energy and concentration of the monovacancy at 1685 K are found to be 3.46 eV and  $7.4 \times 10^{16} \text{ cm}^{-3}$ , respectively, which are close to experimental values.<sup>10–13,17,23)</sup> We find that the vibrational effect significantly contributes to the increase in the concentration of the monovacancy; thus, the calculation without the vibrational effect is not reliable.

## 2. Computational methods

We carry out the DFT calculations based on the generalized gradient approximation (GGA). We use the norm-conserving pseudopotential and 9 Ryd cutoff energy for the plane wave basis set. First, we calculate total energy as a function of primitive cell volume, then we fit the calculated data to the Birch-Murnaghan equation of state<sup>24,25)</sup> and obtain an optimized lattice constant. The calculated lattice constant is 5.466 Å, which is close to the experimental value of 5.431 Å<sup>26)</sup> and consistent with those obtained in previous DFT studies.<sup>1,3,25)</sup>

To simulate defects, we use supercell models containing 64, 216, 512, 1000, and 1728 atomic sites.  $\Gamma$ -point sampling is carried out in the Brillouin zone integration. The use of supercell models efficiently reduces computational cost; however, it introduces an error because of defect-defect image interactions.<sup>3,27–29)</sup> The error decreases as the supercell size increases. Thus, a larger supercell gives more accurate results of electronic

properties such as formation energy.

The formation energy ( $E^f$ ) of a neutral vacancy is calculated as<sup>1,5)</sup>

$$E^f = E_{N-1}^v - \left(\frac{N-1}{N}\right)E_N, \quad (1)$$

where  $E_N$  is the total energy of the perfect supercell consisting of  $N$  atoms and  $E_{N-1}^v$  is the total energy of the supercell for the monovacancy. By using the formation energy, the concentration of the vacancy is roughly approximated by<sup>10)</sup>

$$C_0 = N_0 \exp\left(-\frac{E^f}{k_B T}\right), \quad (2)$$

where  $N_0$ ,  $k_B$ , and  $T$  are the total number of atoms per unit volume, Boltzmann constant, and temperature, respectively. However, when the vibrational effect and configurational entropy are considered, the concentration is given by<sup>6)</sup>

$$C_S = C_0 n_c \exp\left(-\frac{F_{vib}^f}{k_B T}\right), \quad (3)$$

where  $n_c$  is the number of geometries with the lowest energy. A neutral vacancy has the  $D_{2d}$  symmetry,  $n_c = 3$ , which gives the formation configurational entropy  $S_c^f = 1.1k_B$ .  $F_{vib}^f$  is the formation vibrational free energy given by<sup>6)</sup>

$$F_{vib}^f = F_{vib}^v - \left(\frac{N-1}{N}\right)F_{vib}^p, \quad (4)$$

where  $F_{vib}^v$  and  $F_{vib}^p$  are the vibrational free energies of the vacancy and perfect crystal, respectively. These vibrational free energies are given by<sup>6,30)</sup>

$$F_{vib} = k_B T \sum_i \ln\left[\sinh\left(\frac{h\nu_i}{2k_B T}\right)\right], \quad (5)$$

where  $h$  is Planck's constant and  $\nu$  is the vibrational frequency.  $i$  runs over the vibrational modes.

The formation vibrational entropy  $S_{vib}^f$  is given by<sup>31)</sup>

$$S_{vib}^f = S_{vib}^v - \left(\frac{N-1}{N}\right)S_{vib}^p, \quad (6)$$

where  $S_{vib}^v$  and  $S_{vib}^p$  are the vibrational entropies of the vacancy and perfect crystal, respectively, which can be calculated from the first derivative of  $F_{vib}$  over temperature:<sup>30)</sup>

$$S_{vib} = - \left( \frac{\partial F_{vib}}{\partial T} \right)_V. \quad (7)$$

In the above calculation of the vacancy concentration in Eq. (3), we need to evaluate the vibrational frequencies. Thus, the second derivatives of the energy over atomic coordinates are computed numerically within the harmonic approximation, i.e., the second derivatives are estimated from the atomic force for the geometry where the

atom is in a displaced position. We consider an atomic displacement of 0.05 Å in this calculation. The vibrational frequencies are obtained by diagonalizing the dynamical matrix whose elements are calculated from the second derivatives.

### 3. Results and discussion

#### 3.1 Formation energy

We calculate the neutral monovacancy  $V_{S_i}^0$ . We find that the most stable geometry of the vacancy has the  $D_{2d}$  symmetry for all supercells. The results are in agreement with those of previous theoretical calculations.<sup>1-3,5,8)</sup> In the  $D_{2d}$  geometry, four nearest-neighbor atoms form two pairs, as shown in Fig. 1. The two distances between the nearest-neighbor atoms are denoted by  $L_1$  and  $L_2$  ( $L_1 > L_2$ ), which are shown in Table I. The calculated volume of the tetrahedron, whose top is placed at a nearest-neighbor site, is smaller than that of the ideal one (Table I). This volume reduction originates from the inward relaxation of the nearest-neighbor atom.

We plot the displacement of atoms from the ideal position in Fig. 2. As the distance from the vacancy center increases, the displacement tends to decrease. In the 1728-site cell, the displacement of the atoms, which are more than 9.2 Å from the vacancy center, is very small (less than 0.005 Å).

We calculate the formation energy using supercells whose sizes are up to 1728 atomic sites. As shown in Table I, the formation energy well converges when a 1728-atomic-site supercell is used. The difference between the formation energies calculated from 1000- and 1728-site supercells is very small (0.02 eV). Our calculated value (3.46 eV) is close to the experimental values.

Dannefaer *et al.*<sup>10)</sup> carried out the positron annihilation experiment and estimated the formation energy to be  $3.6 \pm 0.5$  eV. Watkins and Corbett<sup>11)</sup> estimated the formation energy to be  $3.6 \pm 0.5$  eV from the EPR experiment. Shimizu *et al.*<sup>12)</sup> estimated the formation energy to be  $3.6_{-0.1}^{+0.3}$  eV from the Raman shift measurement. Fukata *et al.*<sup>13)</sup> used a quenching method and estimated the formation energy to be about 4.0 eV. These results are consistent with the present value.

The previous theoretical calculations that used 64 – 1000-atomic-site supercells show that the formation energies are 3.0 – 4.1 eV,<sup>1,3,5,8,21,22)</sup> which are close to our value. The 1000-site calculation based on the GGA<sup>3)</sup> gives a value of 3.62 eV, which is close to the present value from the 1728-site calculation (3.46 eV). A recent 512-site calculation based on the Heyd-Scuseria-Ernzerhof screened hybrid functional<sup>22)</sup> gives a formation

**Table I.** Results of supercell calculations.  $V_r$  is the defect volume change defined as  $V_r = (V - V_0)/V_0$ , where  $V$  and  $V_0$  are the volumes of the tetrahedra formed by the four nearest-neighboring atoms of the relaxed and ideal vacancies, respectively.<sup>21)</sup>  $L_1$  and  $L_2$  are distances between the nearest-neighboring atoms in the relaxed geometries (see Fig. 1). The ideal (unrelaxed) bulk distance and defect volume are 3.87 Å and 6.81 Å<sup>3</sup>, respectively.  $N$  is the supercell size and  $E^f$  is the formation energy.

$N$	$V_r$ (%)	$L_1$ (Å)	$L_2$ (Å)	Symmetry	$E^f$ (eV)
64	-30.75	3.60	3.16	$D_{2d}$	3.05
216	-43.00	3.44	2.90	$D_{2d}$	3.31
512	-42.29	3.43	2.94	$D_{2d}$	3.43
1000	-42.72	3.42	2.94	$D_{2d}$	3.48
1728	-44.08	3.44	2.87	$D_{2d}$	3.46

energy of 4.08 eV.

### 3.2 Vacancy concentration

We next calculate the vibrational frequencies by using a 216-site supercell. The density of states (DOS) is computed by introducing Gaussian broadening whose half width is 50 cm<sup>-1</sup> (Fig. 3). Comparing the DOS of the vacancy system with that of the perfect system, we find that the vibrational frequencies are lower in the vacancy case. This softening of the vacancy system is expected to increase the vacancy concentration.

Next, the monovacancy concentration is calculated. We use the formation energy estimated from the 1728-site cell calculation and calculate vibrational frequencies by using the 64- and 216-site supercells. At the melting point (1685 K),  $C_S$  in Eq. (3) is estimated to be  $8.2 \times 10^{16}$  and  $7.4 \times 10^{16}$  cm<sup>-3</sup> by using the 64- and 216-site supercell calculations, respectively. Thus, the result is insensitive to the supercell size used in the calculation of vibrational frequencies.  $C_0$  in Eq. (2) is estimated to be  $2.2 \times 10^{12}$  cm<sup>-3</sup>, which is much lower than  $C_S$ , by considering the vibrational effect and configurational entropy. The high  $C_S$  value is mainly due to the fact that the vibrational frequencies are softened in the vacancy system. The configurational entropy effect increases the concentration only 3 times, and thus the entropy only slightly affects the concentration.

The formation vibrational entropy as a function of temperature is given in Fig. 5. The entropy converges at 1100 K, giving a value of  $9.1k_B$ . At the melting point, the  $S_{vib}^f$  values calculated from the 64- and 216-site supercells are  $9.3k_B$  and  $9.1k_B$ , respectively. Thus, the sum of the vibrational and configurational entropies is  $\sim 10k_B$ .

From a positron annihilation study, Dannefaer *et al.*<sup>10)</sup> estimated the vacancy concentrations to be  $10^{14} - 10^{16} \text{ cm}^{-3}$  at 1500 K.<sup>17)</sup> At this temperature, we estimate the concentration to be  $4.0 \times 10^{15} \text{ cm}^{-3}$ , which shows very good agreement with their estimations. At the melting point (1685 K), Voronkov and Falster<sup>23)</sup> obtained a vacancy concentration of  $10^{15} \text{ cm}^{-3}$  by analyzing experimental results of boron doping.<sup>32)</sup> Our calculated value ( $7.4 \times 10^{16} \text{ cm}^{-3}$ ) is somewhat higher. The small deviation may come from the use of a different formation energy (Voronkov and Falster used the value of 4.5 eV).

Goto *et al.*<sup>18)</sup> detected a defect by low-temperature ultrasonic measurement and considered that the detected defect is a monovacancy. By analyzing the results of the low-temperature experiment, they estimated the concentration to be  $10^{15} \text{ cm}^{-3}$  and expected that the concentration would be the same as that at the melting point. Their estimated concentration is only slightly lower than our present value at the melting point ( $7.4 \times 10^{16} \text{ cm}^{-3}$ ). Thus, this seems to support their expectation. However, it should be noted that monovacancies likely agglomerate in cooling specimens as argued in Ref. 19. If so, the detected defect is not a monovacancy.

Lannoo and Allan calculated the vibrational entropy using Green's-function technique and obtained a vibrational entropy value of  $6k_B$  or more.<sup>33,34)</sup> Using the same technique, Leite *et al.* calculated a 17-atom cluster and showed that the vibrational entropy can reach  $10k_B$ .<sup>35)</sup> Al-Mushadani and Needs conducted a DFT calculation based on the local density approximation (LDA) using 64 atomic sites and obtained a vibrational entropy of about  $1 \times 10^{-3} \text{ eVK}^{-1}$  ( $12k_B$ ) and a vacancy concentration of  $10^{16} \text{ cm}^{-3}$  at 1500 K.<sup>6)</sup> Our calculated vibrational entropy value is  $9.1k_B$  and the vacancy concentration is  $4.0 \times 10^{15} \text{ cm}^{-3}$ . These values are close to the theoretical results.

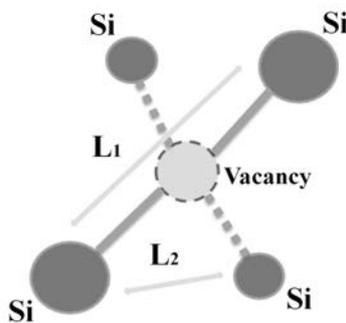
#### 4. Conclusions

We have carried out DFT calculations of  $V_{S_i}^0$  by using large-scale supercells. The supercells were larger than those in the previous studies<sup>1,3,5,6,8,21,22)</sup> and we confirmed the convergence of calculational results. Therefore, we believe that the present DFT calculations give reliable results. In the 1728-site supercell calculation, we found that the displacement of the atoms, which are more than 9.2 Å from the vacancy site, is very small (less than 0.005 Å), suggesting that the calculational formation energy converges. In fact, we found that the formation energy estimated from the 1728-site supercell calculation is 3.46 eV, and we confirmed the convergence (Table I). The estimated formation

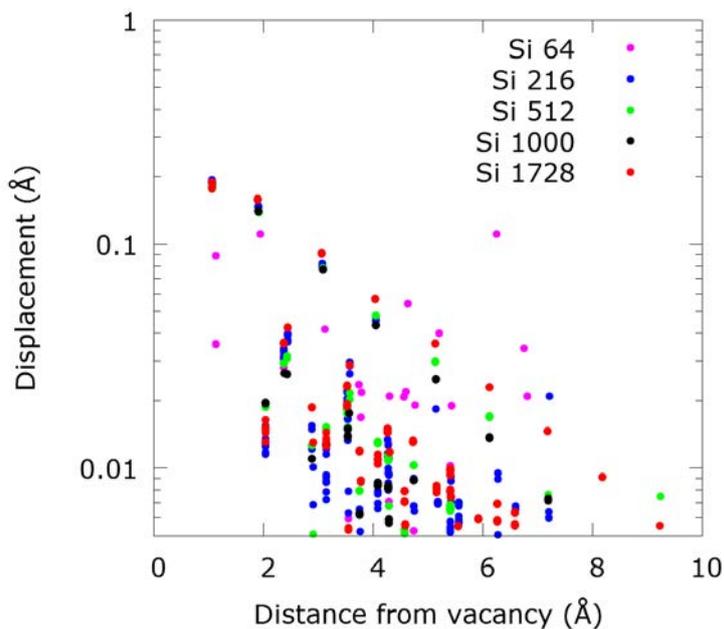
energy is close to the experimental values.<sup>10-13)</sup> As for the vibrational effect, we found that the 64- and 216-site supercell calculations give similar results, indicating that the results well converge. The vacancy concentrations at 1500 and 1685 K (silicon melting point) were estimated to be  $4.0 \times 10^{15}$  and  $7.4 \times 10^{16} \text{ cm}^{-3}$ , respectively, which are in good agreement with the experimental values.<sup>10,17,23)</sup> We found that the vibrational effect significantly increases the vacancy concentration about  $10^4$  times.

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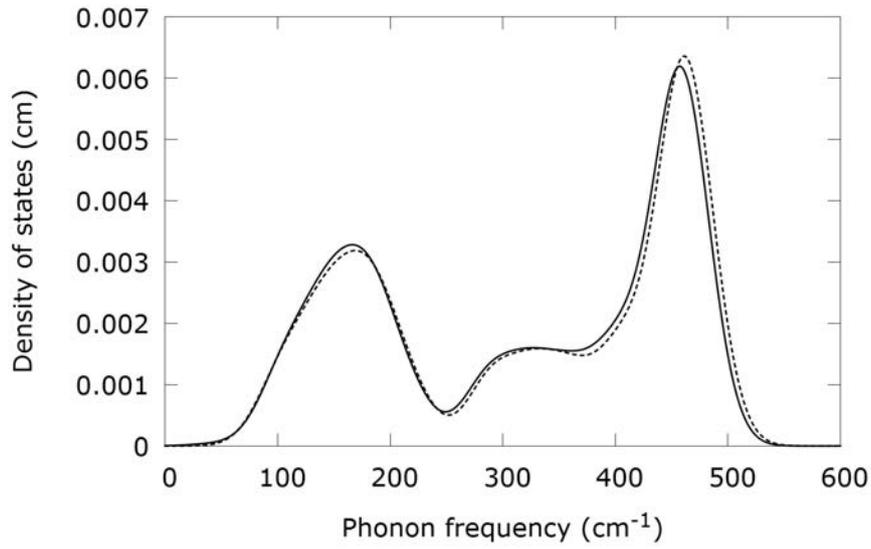
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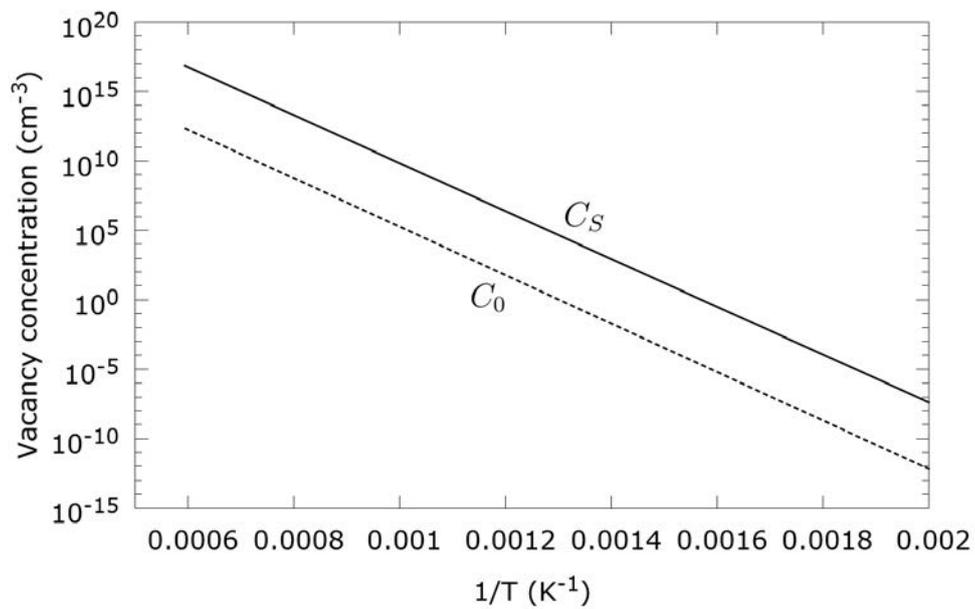
**Fig. 1.** Geometry of the neutral vacancy: four nearest-neighboring atoms of the vacancy form two pairs.  $L_1$  and  $L_2$  are the distances between two atoms, where  $L_1 > L_2$ .



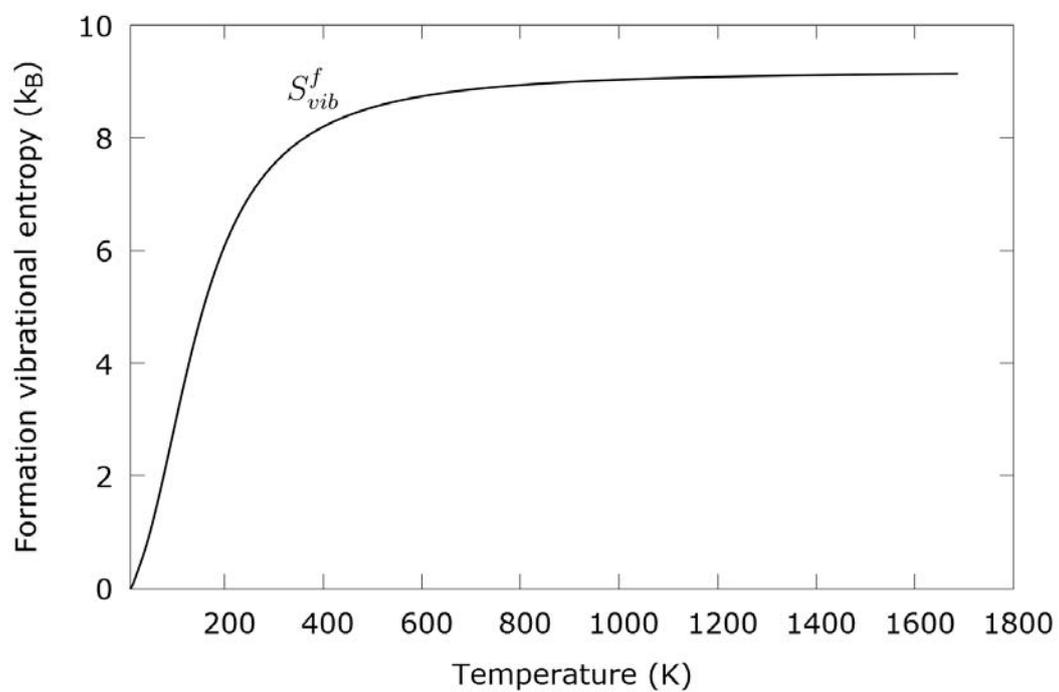
**Fig. 2.** Displacements of atoms from the ideal position as a function of the distance from the vacancy.



**Fig. 3.** Vibrational density of states for vacancy system (solid line) and perfect system (dashed line).



**Fig. 4.** Vacancy concentration as a function of inverse temperature. Calculations of  $C_S$  (solid line) and  $C_0$  (dashed line) are carried out by using Eqs. (3) and (2), respectively.



**Fig. 5.** Formation vibrational entropy ( $S_{vib}^f$ ) in Eq. (6) as a function of temperature.

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