First-principles calculations of vacancies in semiconductors

Abstract for Dissertation

First-principles Calculations of Vacancies in Semiconductors

半導体中原子空孔の第一原理計算

Sholihun
1223102009

Graduate School of Natural Science and Technology
Division of Mathematical and Physical Sciences
Kanazawa University

July 2015

I. RESEARCH MOTIVATION

Semiconductor materials have been widely used in electronic devices such as transistor and light emitting diode. Computer, electronic product that is necessary for our daily work, has a main part that is processor containing a large amount of semiconductor-based transistors. Thus, the quality of transistors plays an important role in enhancing the performance of the computer. In 1947, a germanium point-contact transistor was invented [1]. Several years later, a working silicon-based transistor was launched. At that time, silicon transistor replaced germanium transistor because of the ability of silicon to work at high temperature.

Since the time of the invention of the silicon transistor, the development of silicon-based semiconductor devices has been so fast as the Moore's Law predicted [2]. Such devices are widely used in various electronic devices because of their capability to be downsized to several nanometers. One effort to enhance the performance of the semiconductor-based electronic devices is to understand their defect properties.

There are many types of defects (Fig. 1) such as vacancy, interstitial atom, and impurity atom. In this study, we are going to focus on vacancies in silicon and germanium. Vacancies in silicon have been investigated by studying their defects properties such as the formation energy and vacancy concentration.

The formation energy means the energy required to form a certain configuration of defects. In other words, the formation energy may represent the stability of such defect configuration. Some previous studies investigated the defects properties; i.e., the formation energy of the silicon monovacancy. The formation energy of the silicon monovacancy was approximated to be 3.0 – 4.1 eV in the past theoretical [3] and experimental studies [4–6]. A converged value of the formation energy is necessary; i.e., to accurately calculate the concentration of the vacancy. An experimental result of the ultrasonic measurements [7] observed the monovacancy and supposed that the concentration in low-temperature is found to be the same as that near the melting point. However, the defects observed by them might be different from the monovacancy as examined in previous studies [8, 9]. Therefore, the concentration of the silicon monovacancy near the melting point is a need to be clarified.

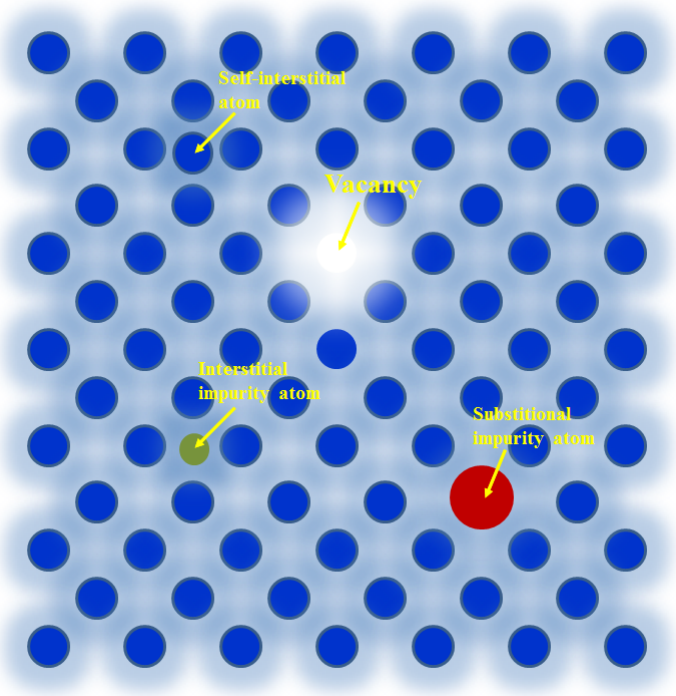

FIG. 1. Some types of defects in semiconductors.

II. SIGNIFICANCE OF THE RESEARCH

As mentioned above that we face a problem, which should be clarified, that is the concentration of the silicon monovacancy near the melting point. To overcome this problem, we carry out a large-scale density-functional-theory calculation 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.

To simulate defects, we use supercell models containing 64, 216, 512, 1000, and 1728 atomic sites. Γ-point sampling is carried out in the Brillouin zone integration. To find the optimized geometry, we fully relax all atoms so that the atomic forces are less than 5 $\times 10^{-2}$ eV/Å. The use of supercell models efficiently reduces computational cost; however, it introduces an error because of defect-defect image interactions [10, 11]. 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 [3]

$$E^f = E^v_{N-1} - (\frac{N-1}{N})E_N, \tag{1}$$

where E_N is the total energy of the perfect supercell consisting of N atoms and E^v_{N-1} is the total energy of the supercell for the monovacancy. By using the formation energy, the concentration of the vacancy is roughly approximated by [4]

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

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 [12]

$$C_S = C_0 n_c \exp(-\frac{F^f_{vib}}{k_B T}), \tag{3}$$

where N_0, k_B, and T are the total number of atoms per unit volume, Boltzmann constant, and temperature, respectively. 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 $S^f_c = 1.1k_B$. F^f_{vib} is the formation vibrational free energy.

III. SOME OF THE IMPORTANT RESULTS

A. Vibrational effect on the vacancy concentration

We carry out calculations of the formation energy and concentration of the neutral monovacancy $V^0_{S_i}$. We first calculate the formation energy, and then the calculated value is used for the calculation of the vacancy concentration.

1. Formation energy

We calculate the neutral monovacancy $V^0_{S_i}$. We find that the most stable geometry of the vacancy has the D_{2d} symmetry for all supercells. In the D_{2d} geometry, four nearest-neighboring atoms form two pairs, as shown in Fig. 2. The two distances between the nearest-neighboring atoms are denoted by L_1 and L_2 ($L_1 > L_2$), which are shown in Table

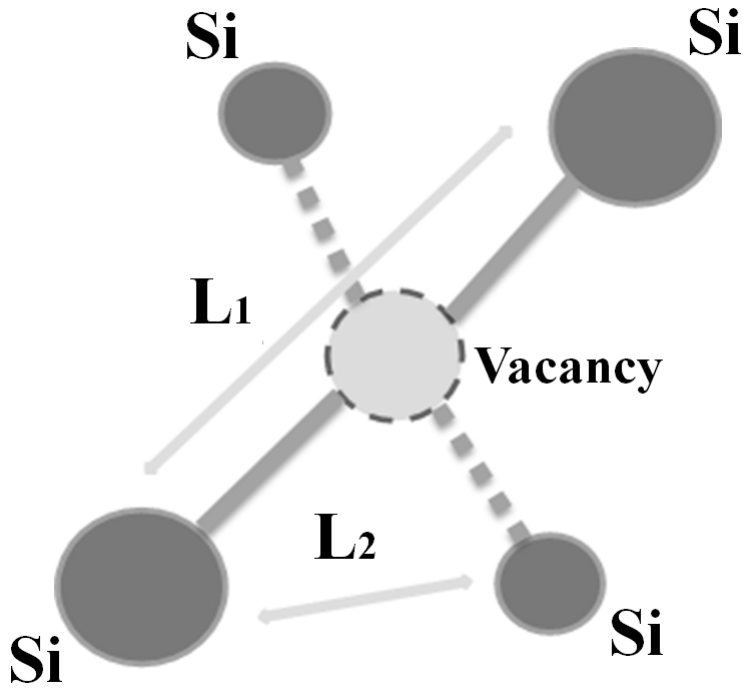

FIG. 2. Geometry of the neutral vacancy: four nearest-neighboring atoms of the vacancy form two pairs. L_1 and L_2 are the distances between two atoms, where $L_1 > L_2$.

I. The calculated volume of the tetrahedron, whose top is placed at a nearest-neighbor site, is smaller than that of the ideal one. 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. 3. 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 [4, 5].

TABLE I. Results of supercell calculations. V_r is the defect volume change defined as $V_r = (V\text{-}V_0)/V_0$, 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 [13]. L_1 and L_2 are distances between the nearest-neighboring atoms in the relaxed geometries (see Fig. 2). The ideal (unrelaxed) bulk distance and defect volume are 3.87 Å and 6.81 Å^3, respectively. E^f is the formation energy and N is the supercell size.

N	k-point	V_r (%)	L_1 (Å)	L_2 (Å)	Symmetry	E^f (eV)
64	Γ	-30.75	3.60	3.16	D_{2d}	3.05
	Γ		3.72	3.72	T_d	3.24
	8		3.57	3.47	D_{2d}	3.48
	64		3.59	3.47	D_{2d}	3.65
216	Γ	-43.00	3.44	2.90	D_{2d}	3.31
	Γ		3.46	3.46	T_d	3.71
	8		3.48	2.96	D_{2d}	3.52
512	Γ	-42.29	3.43	2.94	D_{2d}	3.43
1000	Γ	-42.72	3.42	2.94	D_{2d}	3.48
1728 [a]	Γ	-44.08	3.44	2.87	D_{2d}	3.46(3)
1728 [b]	Γ		3.44	2.89	D_{2d}	3.46(0)

[a] atomic force = 5 $\times 10^{-2}$ eV/Å
[b] atomic force = 2 $\times 10^{-3}$ eV/Å

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

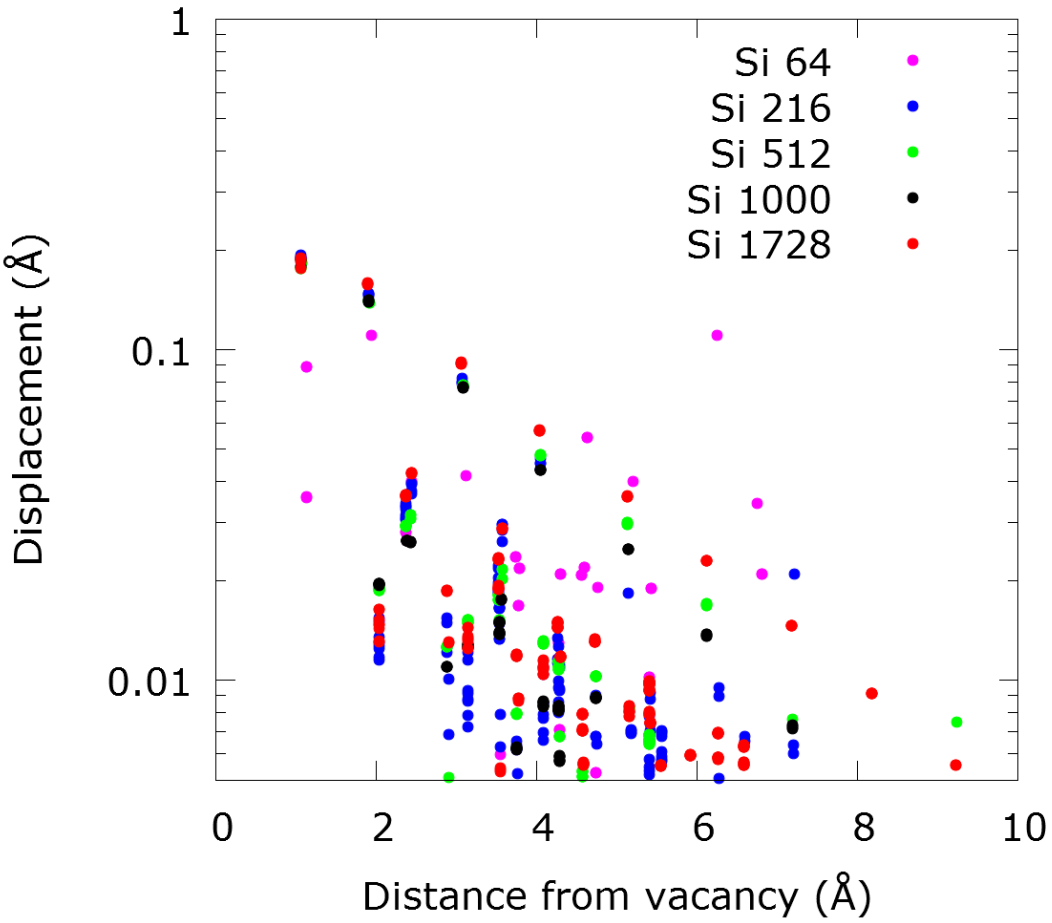

FIG. 3. Displacements of atoms from the ideal position as a function of the distance from the vacancy.

cm^{-1}. 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 (Fig. 4). 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^{-3} 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^{-3}, which is much lower than C_S, by considering the vibrational effect and configurational entropy. The high C_S value is mainly because the vibrational frequencies are softened in the vacancy system.

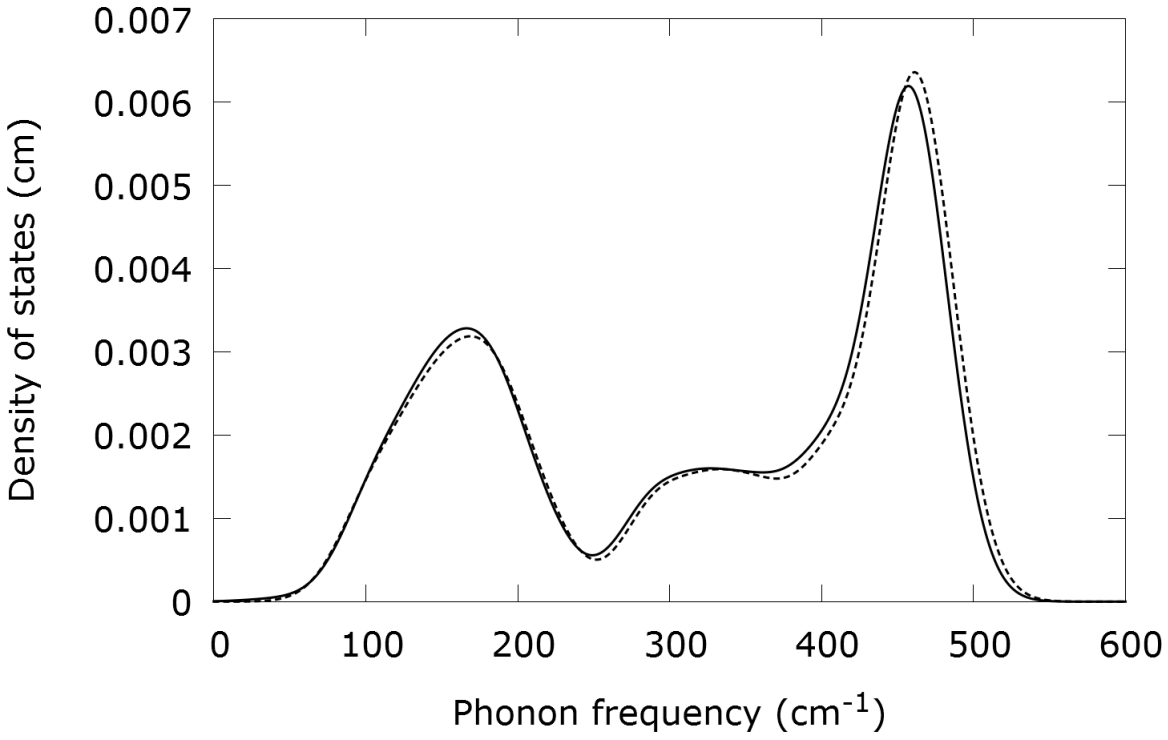

FIG. 4. Vibrational density of states for vacancy system (solid line) and perfect system (dashed line).

The configurational entropy effect increases the concentration only three times, and thus the entropy only slightly affects the concentration. Our calculated value are close to the experimental [4, 14–16] and theoretical results [12, 17–19].

IV. CONCLUSION

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 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. The estimated formation energy is close to the experimental values. 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 4.0×10^{15} and 7.4×10^{16} cm^{-3}, respectively, which are in good agreement with the experimental values. We found that the vibrational effect significantly increases the vacancy concentration about 10^4 times.

---

[1] M. Riordan, L. Hoddeson, and C. Herring, Rev. Mod. Phys **71**, S336 (1999).

[2] I. M. Ross, IEEE Proc., **86**, 7 (1998).

[3] F. Corsetti and A. A. Mostofi, Phys. Rev. B **84**, 035209 (2011).

[4] S. Dannefaer, P. Mascher, and D. Kerr, Phys. Rev. Lett. **56**, 2195 (1986).

[5] G. Watkins and J. Corbett, Phys. Rev. **134**, A1389 (1964).

[6] N. Fukata, A. Kasuya, and M. Suezawa, Physica B **308-310**, 1125?128 (2001).

[7] T. Goto, H. Yamada-Kaneta, Y. Saito, Y. Nemoto, K. Sato, K. Kakimoto, and S. Nakamura, J. Phys. Soc. Jpn. **75**, 044602 (2006).

[8] M. Suezawa and Y. Yonenaga, J. Phys. Soc. Jpn. **76**, 076001 (2007).

[9] K. Uchida and A. Oshiyama, J. Phys. Soc. Jpn. **79**, 093711 (2010).

[10] C. W. M. Castleton, A. Höglund, and S. Mirbt, Phys. Rev. B **73**, 035215 (2006).

[11] G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).

[12] O. K. Al-Mushadani and R. J. Needs, Phys. Rev. B **68**, 235205-3 (2003).

[13] M. J. Puska, S. Pöykkö, M. Pesola, and E. M. Nieminen, Phys. Rev. B **58**, 1318 (1998).

[14] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).

[15] V. V. Voronkov and R. Falster, J. Appl. Phys. **87**, 4126 (2000).

[16] E. Dornberger, D. Graf, M. Suhren, U. Lambert, P. Wagner, F. Dupret, and W. von Ammon, J. Cryst. Growth **180**, 343 (1997).

[17] M. Lannoo and G. Allan, Phys. Rev. B **25**, 4089 (1982).

[18] M. Lannoo and G. Allan, Phys. Rev. B **33**, 8789 (1985).

[19] J. R. Leite, E. C. F. da Silva, and A. Dal Pino, Mater. Sci. Forum **38-41**, 263 (1989).

平成　27年8　月　7　日

学位論文審査報告書（甲）

1．学位論文題目（外国語の場合は和訳を付けること。）

First-principles calculations of vacancies in semiconductors

（半導体中原子空孔の第一原理計算）

2．論文提出者　(1) 所　　属　数物科学　　専攻

(2) 氏（ふり）　名（がな）　SHOLIHUN（しょりふん）

3．審査結果の要旨（600～650字）

7月23日に主査、副査が参加して予備審査を行い、7月30日に学位論文公聴会を行った。公聴会の直後に、主査と副査4名が協議し、合格と判断した。半導体デバイスにおいて、欠陥はデバイスの動作に決定的な影響を与えるため、その制御が必要である。そのため、量子力学に基づくシミュレーションによって欠陥を解析する事が重要である。原子空孔の制御に関して、シリコンの融点付近における単原子空孔の濃度を明確にする事が求められていた。本研究では、これまでで最大規模のスーパーセル計算を行い、信頼性の高い第一原理計算の結果を得る事に成功した。単原子空孔の生成エネルギーの計算では、1728サイトのスーパーセル計算を行い、単原子空孔中心から9.2Å離れると格子緩和の大きさが、0.005Å以下となることを見出し、格子緩和が広い範囲に及ぶ事を明らかにした。また、216サイトのスーパーセル計算により、単原子空孔の濃度に及ぼす格子振動の効果が十分に取り入れられる事を明らかにした。本計算から得られた融点近傍での単原子空孔濃度は、過去の実験結果とよく一致し、これまでに実験研究で推定されてきた単原子空孔濃度が信頼できるものであることを明確にした。本研究では、信頼性の高い計算により、融点付近での単原子空孔の濃度を明らかにしており、さらに、格子振動の効果がどの程度濃度に影響を与えるかを明らかにしている。したがって、博士論文として適切であると結論する。

4．審査結果　(1) 判　　定（いずれかに○印）　（合　格）・　不合格

(2) 授与学位　　博　士（理学）