First-principles calculation of the interaction between nitrogen atoms and vacancies in silicon

H. Sawada and K. Kawakami
Advanced Technology Research Laboratories, Nippon Steel Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan
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Stability of several states of nitrogen in silicon were investigated by the first-principles calculation. A single nitrogen at a split interstitial site and bond center site is more stable than that at a tetrahedral and hexagonal site. A nitrogen pair is more stable than the single nitrogen at the split interstitial site by 4.3 eV, which indicates that the nitrogen pair exists even near the melting temperature of silicon. Binding energy between the nitrogen pair and two vacancies indicates that a complex consisting of the nitrogen pair and two vacancies can exist at the temperature of the void aggregation as far as considering thermal equilibrium. Formation of the complex can affect the concentration or the diffusibility of the vacancy.

I. INTRODUCTION

In Czochralski-grown (CZ) silicon single-crystal grown-in defect was found to exist by observation of the void with a shape of an octahedron.[1] The grown-in defect is known to affect the gate oxide reliability.[2] Therefore, it is important to control the number and the size of the grown-in defect in the process of silicon wafer making. Recently nitrogen was found to be an effective dopant for reducing the size of the void.[3,4] Thus, much attention has been paid to the effects of nitrogen doping on the CZ silicon single crystal and the mechanism of the effects. It is possible to consider some mechanisms for simultaneous occurrence of the reduction of the size of the void and the increase of the number of voids. Two possible mechanisms are that the nitrogen promotes reduction of content or mobility of the vacancy at high temperatures above the temperature of the void aggregation. Another possible mechanism is that nitrogen becomes a nucleation center for the void. One more mechanism is that nitrogen suppresses growth of the void. The void aggregation was found to occur at a lower temperature by the nitrogen doping.[5,6] This experimental result indicates that nitrogen cannot be the nucleation center for the void, because the mechanism should make the temperature of the void aggregation higher. It has not been clear, however, which is the dominant mechanism in the remaining above three possibilities.

Up to now the electronic structures of a substitutional nitrogen[7–9] and a nitrogen pair[10] have been studied. However, the stability of variety of nitrogen configurations in silicon has not been investigated, except for the calculations of small clusters.[11] Thus, the first-principles electronic structure calculations were performed to give some information for clarification of the mechanism of the effect of nitrogen. First, a local structure and an electronic structure of a single nitrogen at some interstitial sites and the substitutional site were studied. Second, electronic and structural properties of the nitrogen pair proposed by Jones and Öberg were calculated. Existence of the nitrogen pair was proved by the isotope effect of the infrared spectrum.[12] The purpose of these calculations was to compare the stability of the single nitrogen with that of the nitrogen pair. After that, we will show the interaction between the nitrogen pair and the vacancies, which can be a key to understanding the relation between the nitrogen doping and the void aggregation.

II. CALCULATIONAL DETAILS

The calculations were based on the local-density approximation.[13,14] We adopted the pseudopotential (PP) method and used the plane waves as a basis set for efficient structure optimization. We found that the cutoff energies of 25 Ry and 400 Ry are sufficient for the wave functions and for the augmented electron densities, respectively. The p state of N was treated by the Vanderbilt's ultrasoft PP (Refs. 15 and 16) and the other states by the normconserving PP optimized by Troullier and Martins' prescription.[17] For the exchange-correlation energy in the generalized gradient approximation, the expression proposed by Perdew *et al.*[18] was used. Structural optimization was performed for a unit cell of 64 silicon atoms with nitrogen atoms and/or vacancies by using the Γ point for the Brillouin-zone sampling. The convergence criterion for forces acting on each atom is 0.05 eV/Å . Since the accuracy of the calculation is not enough to allow discussion of the stability of the charge states, a unit cell of 216 silicon atoms was used for the electronic structure optimization by using the Γ point for the Brillouin-zone sampling. For this calculation the optimized structure using the unit cell of 64 silicon atoms is employed as the atomic configuration around the nitrogen atoms and/or vacancies.

Energies for charge states defined as

$$E(Q)=E_{tot}+Q(\mu_e+E_v^Q), \quad (1)$$

where μ_e is the electron chemical potential and E_v^Q is the top of the valence-band energy, were calculated for a variety of charge states $Q(=0,\pm 1,\pm 2)$. The zero of μ_e is defined as E_v^Q . Since the calculation of the charge states consumes computational time, the charge states $Q=\pm 1,\pm 2$ are calculated only for the systems with unoccupied shallow single-electron levels or occupied deep single-electron levels in the energy gap. This is because the negative and positive charge states are expected to be stabilized for the systems with un-

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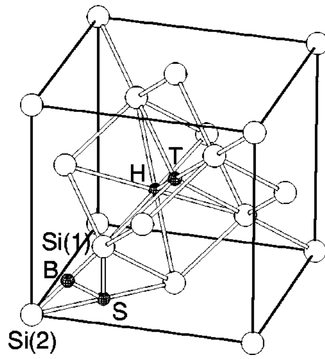

FIG. 1. The ideal interstitial sites in the diamond structure, i.e., the *B*, *S*, *H*, and *T* sites, are shown. Open and closed circles denote silicon and nitrogen atoms, respectively.

occupied single-electron levels near the top of the valence band and with deep occupied single-electron levels in the energy gap, respectively.

III. RESULTS AND DISCUSSION

A. Interstitial nitrogen

The electronic structure, the atomic structure and the stability of nitrogen located at a bond center (*B*) site, split interstitial (*S*) site, hexagonal (*H*) site, and tetrahedral (*T*) site in silicon were investigated. These interstitial sites in the diamond structure are shown in Fig. 1. The ideal *B* site is too tight to allow introduction of the nitrogen atom, therefore a bond length between first neighbor silicon atoms [Si(1) and Si(2) in Fig. 1] and the nitrogen atom is elongated by 0.5 Å. For the *S* site the structural optimization elongates the bond length of Si(1)-N by about 0.4 Å, while Si(2)-N bond undergoes shrinkage by 0.1 Å. In contrast to the *S* and *B* sites, bond lengths between the nitrogen atom and first neighbor silicon atoms shrink by 0.4 Å for the *T* site. However, these bond lengths are still longer than the bond lengths between the nitrogen atom and the first neighbor silicon atoms for the *B* and *S* sites. For the *H* site, bond lengths between the nitrogen atom and first neighbor silicon atoms shrink by only 0.03 Å.

The calculated total energies for the neutral charge state are summarized in Table I. The interstitial nitrogen at the *B* and *S* sites are much more stable than those at the *H* and *T* sites. The energy difference between the *B* and *S* sites is comparable to an error in the computation. To compare the interstitial nitrogen with the interstitial oxygen, the total-energies and the atomic structures for the interstitial oxygen at the *B* and *S* sites were also calculated. The calculated total-energy difference between the *B* and *S* sites of about 1.8 eV is consistent with previous work.[19–21] Though the *S* site is not the exact transition state of the oxygen diffusion,[22] the energy difference between the *B* and *S* sites is accurate enough to allow a rough estimation of the activation energy of the oxygen diffusion. In contrast to the oxygen, the total-energy difference between the *B* and *S* sites is quite small for nitrogen as mentioned above. It seems reasonable to suppose that the interstitial nitrogen diffuses much faster than the interstitial oxygen, if the diffusion path of nitrogen is the same as that of oxygen. This difference between the activation energy of oxygen and that of nitrogen is related to the local atomic configuration as shown in Table II. For the *B* site the angle of Si(1)-X-Si(2) of nitrogen is smaller than that of oxygen by 26° and for the *S* site the angle of Si(1)-X-Si(2) of nitrogen is larger than that of oxygen. These differences between the local atomic configuration around the impurity of nitrogen and that of oxygen imply that the distance between the *B* and *S* sites is shorter for nitrogen than that for oxygen. The activation energy of the diffusion of the nitrogen is experimentally obtained as 2.8 eV.[23] Since this activation energy is not smaller than the activation energy of the oxygen diffusion, we can speculate that the single interstitial nitrogen is not the dominant form of the nitrogen in silicon. We will discuss the dominant form of nitrogen later.

The stability of the charge states of the interstitial nitrogen was examined. The charge states of the *H* and *T* sites are still more unstable than those of the *B* and *S* sites, so the results are presented only for the *B* and *S* sites. Figure 2 shows the calculated relative energy of the charge states for the *B* and *S* sites measured based on the energy of the neutral charge state of the *S* site. As for the *S* site, the charge state $Q=+1$ is more stable than the other charge states when the chemical potential is below the center of the energy gap, while for the *B* site there is no chemical potential region where the charge state $Q=+1$ is stable, and the charge state $Q=-1$ is stabilized instead. The stability of the charge states is closely related to the position of the single-electron level in the energy gap. Both for the *B* and *S* sites, single-electron levels appear in the energy gap. For the *S* site, the single-electron level is located in the middle of the energy

TABLE I. Calculated total energies of $E[\mathrm{Si}_x\mathrm{N}_y]-xE[\mathrm{Si}]-yE[\mathrm{N}]$ for the neutral charge state, where $E[\mathrm{Si}]=E[\mathrm{Si}_{216}]/216$ and $E[\mathrm{N}]=\{E[\mathrm{Si}_{216}\mathrm{N}_2]-E[\mathrm{Si}_{216}]\}/2$. Unit is eV.

Si_{216}	0.00
Si_{215}	3.47
Si_{217}	3.60
$Si_{216}N$ (*S* site)	2.15
$Si_{216}N$ (*B* site)	2.26
$Si_{216}N$ (*H* site)	3.73
$Si_{216}N$ (*T* site)	4.80
$Si_{215}N$	1.74
$Si_{216}N_2$	0.00
$Si_{215}N_2$	2.33
$Si_{214}N_2$	1.26

TABLE II. Local atomic configuration around impurity X, i.e., nitrogen and oxygen. Si(1) and Si(2) denote the neighboring two silicon atoms of the impurity as shown in Fig. 1

	Impurity	Nitrogen	Oxygen
B site	Si(1)-Si(2)	3.05 Å	3.21 Å
	Si(1)-X	1.69 Å	1.64 Å
	∠Si(1)-X-Si(2)	129°	155°
S site	Si(1)-Si(2)	2.76 Å	2.74 Å
	Si(1)-X	1.73 Å	1.71 Å
	Si(2)-X	1.81 Å	1.97 Å
	∠Si(1)-X-Si(2)	102°	96°

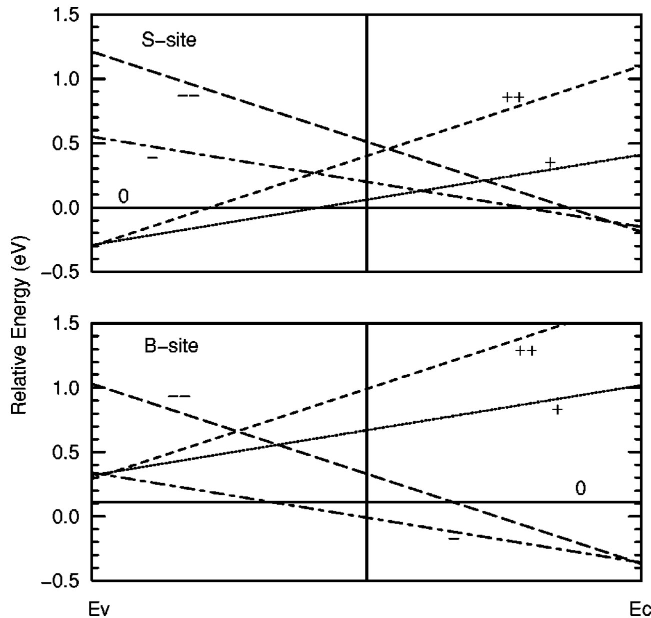

FIG. 2. Energy of the various charge states of the interstitial nitrogen ($Si_{216}N$) at the S and B sites measured based on the energy of the neutral charge state of the S site as a function of the electron chemical potential. E_v and E_c denote the top of the valence band and bottom of the conduction band, respectively. The vertical-solid line indicates the center of the energy gap.

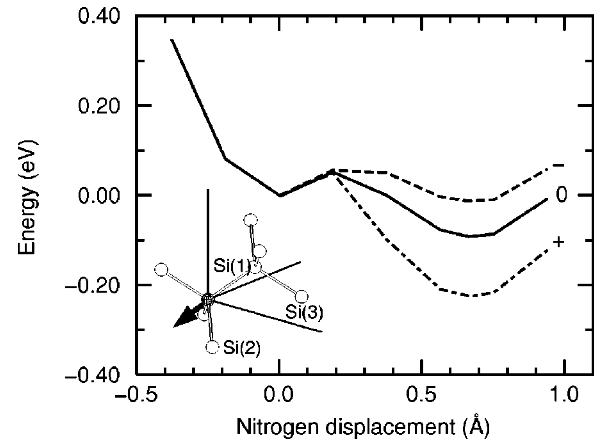

FIG. 3. Total energy of $Si_{63}N$ as a function of nitrogen displacement to $\langle \bar{1}\bar{1}\bar{1} \rangle$ direction, which is measured based on the total energy of the on-center nitrogen for each charge state. The inset shows the local configuration of the substitutional nitrogen. The open and closed circles denote silicon and nitrogen atoms, respectively. The arrow indicates the direction of the nitrogen displacement, i.e., $\langle \bar{1}\bar{1}\bar{1} \rangle$.

gap and has a nonbonding character, which means that a silicon dangling bond is elongated opposite to nitrogen, therefore it is preferable that the level not be occupied. On the other hand, for the B site, the single-electron level is located just above the top of the valence band, so the level prefers to be occupied. As temperature increases, the Fermi level approaches the intrinsic Fermi level, i.e., center of the energy gap. In Fig. 2 a vertical-solid line indicates the intrinsic Fermi level. The stable states of the interstitial nitrogen are the neutral charge state of the S site and the negative charge state of the B site at high temperatures.

B. Substitutional nitrogen

The off-center substitutional nitrogen was found to be more stable than the on-center substitutional nitrogen by the electron-spin resonance study.[24,25] The energy difference between the on-center and off-center substitutional nitrogen and the local atomic configuration were obtained theoretically by varying the displacement of nitrogen from the on-center position. Figure 3 shows the total energy of $Si_{63}N$ as a function of nitrogen displacement to $\langle \bar{1}\bar{1}\bar{1} \rangle$ direction, which is measured from the total energy of the on-center nitrogen for each charge state. The on-center nitrogen is metastable and the energy minimum of the off-center nitrogen is located at about 0.67 Å in a $\langle \bar{1}\bar{1}\bar{1} \rangle$ direction for the charge states of $Q=0$ and ± 1. The energy difference between the on-center and off-center nitrogen is calculated to be 0.09 eV for the neutral charge state. This agrees well with the experimentally obtained value of 0.07 eV.[25] The energy barrier for the reorientation among four equivalent off-center sites of 0.14 eV is also in good agreement with the experimental value of 0.11 eV.[24]

The occupation of the single-electron level in the energy gap changes from 0 to 2 for the change of the charge state from $Q=+1$ to $Q=-1$. The bond lengths of Si(1)-N for the energy minimum of the off-center nitrogen are 3.31, 3.19, and 3.10 Å for the charge states of $Q=+1$, 0, and -1, respectively. The bond angles of N-Si(1)-Si(3) and Si(3)-Si(1)-Si(3) become larger by 5.7° and smaller by 4.6°, respectively, as the charge state changes from $Q=+1$ to $Q=-1$. On the other hand, the bond length of Si(2)-N and the angles of Si(1)-N-Si(2) and Si(2)-N-Si(2) do not change so much for all the charge states. The bond length of Si(2)-N is 1.86 Å, which is much shorter than that of Si(1)-N. The angles of Si(1)-N-Si(2) and Si(2)-N-Si(2) are 93.9° and 119.5°, respectively, which means that the nitrogen atom and the Si(2) are almost on the same plane.

The charge state dependence on the local structure can be understood as follows. The off-center nitrogen has an sp^2-like electronic configuration for all the charge states, while the on-center nitrogen has an sp^3 character. These are surmised by the local atomic structure around nitrogen, especially the flat atomic configuration of the off-center nitrogen and three Si(2) atoms. Furthermore, a rapid shift up of the single-electron level by the elongation of the Si(1)-N bond can be explained by the transformation from the sp^3 configuration to a higher lying p state. It indicates that the interaction between the nitrogen and Si(1) is rather small. Assuming that the interaction between nitrogen and Si(1) is negligibly small, structural optimization of a cluster of Si_4H_9 was performed by the molecular-orbital method [GAUSSIAN94 with basis set of 6-31+G (d,p) and hybrid functional of B3LYP]. The four silicon atoms correspond to one Si(1) atom and three Si(3) atoms. The hydrogen atoms are bonded to Si(3) atoms and fixed at the position of the ideal diamond structure. The result of the cluster calculation shows that the bond angles, which correspond to Si(3)-Si(1)-Si(3) and N-Si(1)-Si(3) in Fig. 3, become smaller and larger, respectively, as the charge state changes from $Q=+1$ to $Q=-1$. These are the same tendency, with the charge state depen-

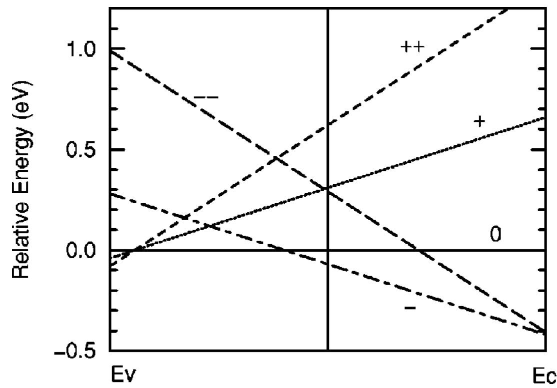

FIG. 4. Energy of the various charge states of the substitutional nitrogen ($Si_{215}N$) measured based on the energy of the neutral charge state as a function of the electron chemical potential. E_v and E_c denote the top of the valence band and bottom of the conduction band, respectively. The vertical-solid line indicates the center of the energy gap.

dence on the angles of Si(3)-Si(1)-Si(3) and N-Si(1)-Si(3) as calculated for $Si_{63}N$. Moreover, the relation between the charge state and the local atomic configuration of the silicon (111) surface presented by Harrison[26] is the same as our results qualitatively. Thus, the elongation of the Si(1)-N bond for a more negatively charged state can be explained as follows. The single-electron level in the energy gap has a character of a dangling bond of Si(1). A repulsive interaction between the dangling bond and the bonding charge of Si(1)-Si(3) makes the bond angle of N-Si(1)-Si(3) larger as the occupation of the dangling-bond state increases, which shortens the bond length of Si(1)–N.

The energies of the charge states of $Q=0,\pm 1,\pm 2$ are shown as a function of the electron chemical potential in Fig. 4. This figure indicates that the charge states of $Q=0$ and -1 are more stable than the other states at high temperatures. Stability of the substitutional nitrogen is estimated by the following expression:

$$E_F=\{E[\mathrm{Si}_{215}\mathrm{N}]+E[\mathrm{Si}_{216}]\}-\{E[\mathrm{Si}_{216}\mathrm{N}]+E[\mathrm{Si}_{215}]\}$$
$$=-3.88\ \mathrm{eV}. \tag{2}$$

This binding energy of the interstitial nitrogen with the vacancy indicates that the substitutional nitrogen can exist near the melting temperature. However, the observed substitutional nitrogen is less than 10% of the total amount of implanted nitrogen.[24] Moreover, only less than 1% of doped nitrogen atoms contribute to the electronic properties for the sample grown by the float-zone method,[27] although the substitutional nitrogen is expected to affect the electronic properties. Thus the experimental observation and the theoretical estimation appear to contradict each other. In order to overcome this contradiction we considered the reaction that nitrogen is ejected from the substitutional site by the interstitial silicon. The kickout energy of the substitutional nitrogen by the interstitial silicon is obtained as,

$$E_F=\{E[\mathrm{Si}_{216}\mathrm{N}]+E[\mathrm{Si}_{216}]\}-\{E[\mathrm{Si}_{215}\mathrm{N}]+E[\mathrm{Si}_{217}]\}$$
$$=-3.19\ \mathrm{eV}. \tag{3}$$

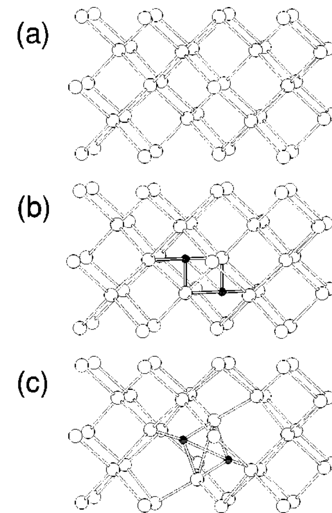

FIG. 5. Structure of the nitrogen pair. (a) is the ideal diamond structure. Two nitrogen atoms are placed at the ideal *S* site in the ideal diamond structure. The structures with two nitrogen atoms before and after the structure optimization are shown in (b) and (c), respectively. Open and closed circles denote silicon and nitrogen atoms, respectively.

This energy indicates the possibility of occurrence of this reaction near the melting temperature. These calculated results imply that the creation and annihilation of the substitutional nitrogen occur through the annihilation of the vacancy and interstitial silicon. If the content of the vacancy and the interstitial silicon is comparable to that of the nitrogen near the melting temperature, the vacancy and the interstitial silicon will be significantly reduced. However, it is impossible to judge whether this mechanism has a major effect on the concentration of the vacancy and the interstitial silicon, because the content of the vacancy and the interstitial silicon is not known exactly at high temperatures.

C. Nitrogen pair

Nitrogen is expected to exist in a pair because of the isotope effect of the infrared spectrum.[12] The structure of the nitrogen pair was proposed by using *ab initio* local-density functional calculations on up to 88 atom H-terminated clusters, $N_2Si_{44}H_{42}$.[10] We optimized the local atomic structure around two nitrogen atoms located at the neighboring *S* sites, and the calculated structure, shown in Fig. 5, is almost the same as that proposed by Jones and Öberg. There is a shallow single-electron level in the energy gap. Since the level is fully occupied, it can be expected that the neutral charge state is the most stable among various charge states of the nitrogen pair. Stability of the nitrogen pair compared with the neutral charge state of the interstitial nitrogen at the *S* site, which is expected to be the most stable state at high temperatures, is evaluated by the binding energy of the nitrogen pair,

$$E_F=\{E[\mathrm{Si}_{216}\mathrm{N}_2]+E[\mathrm{Si}_{216}]\}-\{E[\mathrm{Si}_{216}\mathrm{N}]+E[\mathrm{Si}_{216}\mathrm{N}]\}$$
$$=-4.3\ \mathrm{eV}. \tag{4}$$

The ratio of the nitrogen pair to the total number of nitrogen is estimated as a function of temperature by considering only

TABLE III. Changes of enthalpies(ΔE), entropies (ΔS), and free energies (ΔF) for each reaction at the melting temperature of silicon. 1.0×10^{15} and 2.0×10^{15}atoms/cm^3 are employed for the concentration of vacancy and nitrogen, respectively.

	ΔE (eV)	$T\Delta S$ (eV)	ΔF (eV)
$2N_i \rightarrow N_2$	-4.30	2.84	-7.14
$N_2 + V \rightarrow N_2V$	-1.14	9.99×10^4	-9.99×10^4
$N_2 + 2V \rightarrow N_2V_2$	-5.69	7.30	-12.99

atomic configurational entropy. Blöchl *et al.* found that the contribution of the configurational entropy to each of the total formation entropies for the vacancy and interstitial silicon is about one-third and the rest is attributed to the vibrational entropy.[28] In contrast to the formation of the vacancy or interstitial silicon, however, it is expected that the vibrational entropy is not changed very much by the formation of the nitrogen pair from the interstitial nitrogen. Thus we assume that the dominant contribution to the entropy is the configurational entropy. A change of free energy for the transformation from the interstitial nitrogen (N_i) to the nitrogen pair (N_2) is evaluated as follows,

$$\Delta F = aN_N E_F - T\Delta S, \tag{5}$$

$$\Delta S \cong k_B \ln\left\{\frac{N_I!}{(N_N - aN_N)!(N_I - N_N + aN_N)!} \times \frac{(N_N - aN_N)!}{(aN_N)!(N_N - 2aN_N)!}\right\}, \tag{6}$$

where N_I is the number of interstitial sites in silicon, and N_N, $(1-2a)N_N$, and aN_N are the numbers of the nitrogen, isolated nitrogen and nitrogen pair, respectively. The changes of enthalpy, entropy, and free energy for the transformation of $2N_i \rightarrow N_2$ at the melting temperature of silicon are shown in Table III. It indicates that the ratio of the nitrogen pair to the total number of nitrogen changes around the melting temperature of silicon, because the ΔE and $T\Delta S$ are the same order. The ratio of the nitrogen pair to the total number of nitrogen is obtained by minimizing the change of free energy of Eq. (5) with respect to a. It is shown as a function of temperature in Fig. 6. This figure indicates that most of the nitrogen atoms form the nitrogen pair even near the melting temperature of silicon. We mentioned above that the dominant form of the nitrogen is not the interstitial nitrogen because of the discrepancy between the diffusion constant obtained by theory and that obtained by experiment. The result, finding that the nitrogen pair is the dominant form of the nitrogen, is consistent with the above discussion.

D. Interaction between nitrogen pair and vacancies

We considered two cases regarding the interaction between the nitrogen pair and a monovacancy. In one case a monovacancy approaches the nitrogen pair and is substituted for the silicon atom that bridges between two nitrogen atoms. In this case one nitrogen atom moves to the vacancy site [N(1)] and the other nitrogen atom moves to the bond center site [N(2)] as shown in Fig. 7(a). The angle of Si-N(2)-Si is 143° and the bond length of Si-N(2) is 1.07 Å. Both the

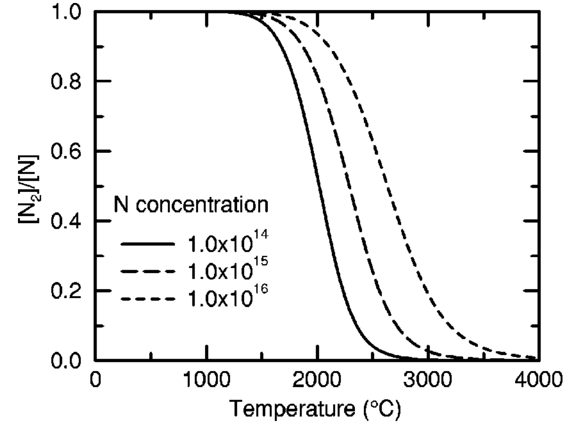

FIG. 6. Ratio of nitrogen pair to total number of nitrogen as a function of temperature for various nitrogen concentrations. The unit of the concentration of nitrogen is in atoms/cm^3.

angle and the bond length are larger than those of the single nitrogen at the *B* site. This is because the bond lengths of Si-N(1) shrink 0.2 Å more than neighboring Si-Si for the single nitrogen at the *B* site. In the other case nitrogen atoms form a N_2 moleculelike structure at a vacancy site [Fig. 7(b)], although we do not know a process for forming this structure. In this case the bond length of Si-N is almost the same as the shorter Si-N bond length for the substitutional nitrogen, and the distance between two nitrogen atoms becomes 1.44 Å, which is much longer than that of the N_2 molecule, i.e., 1.1 Å. As for the former case, an occupied deep single-electron level exists in the energy gap. Thus the stability of the several charge states was examined. The calculated results show that the neutral charge state is the most stable at high temperatures (Fig. 8). The neutral charge state is expected to be the most stable state also for the latter case, since deep single-electron levels are not occupied. The stability of the complex of the nitrogen pair and the monovacancy (N_2V) is estimated as,

$$E_F = \{E[Si_{215}N_2] + E[Si_{216}]\} - \{E[Si_{216}N_2] + E[Si_{215}]\}. \tag{7}$$

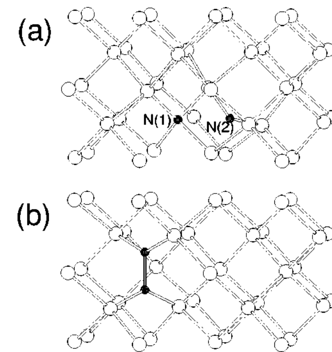

FIG. 7. Complexes consisting of two nitrogen atoms and a monovacancy. (a) One nitrogen is located at the substitutional site [N(1)], while the other nitrogen atom is at the *B* site [N(2)]. (b) Nitrogen atoms form an N_2 moleculelike structure at a vacancy site. Open and closed circles denote silicon and nitrogen atoms, respectively.

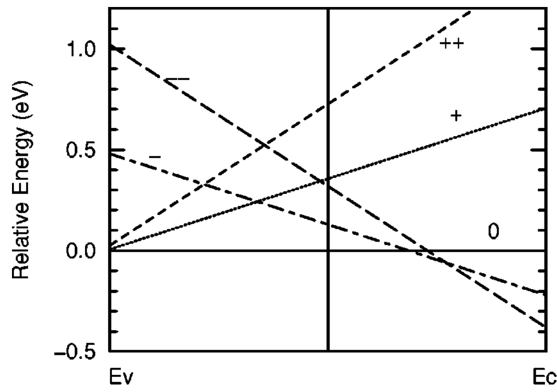

FIG. 8. Energy of the various charge states of the complex consisting of the substitutional nitrogen and the interstitial nitrogen at the *B* site measured based on the energy of the neutral charge state as a function of the electron chemical potential. E_v and E_c denote the top of the valence band and bottom of the conduction band, respectively. The vertical-solid line indicates the center of the energy gap.

The binding energies of the nitrogen pair with the vacancy E_F are -1.14 eV and -1.29 eV for the above two types of complexes. The complex with the substitutional nitrogen atom and the interstitial nitrogen atom at the *B* site is less stable than that with the N_2 molecule-like structure at the vacancy site. A concentration of N_2V is obtained as a function of temperature for various vacancy and nitrogen contents as shown in Fig. 9. The concentration is obtained by minimizing the following change of free energy with respect to the number of N_2V,

$$\Delta F = aVE_F - T\Delta S, \tag{8}$$

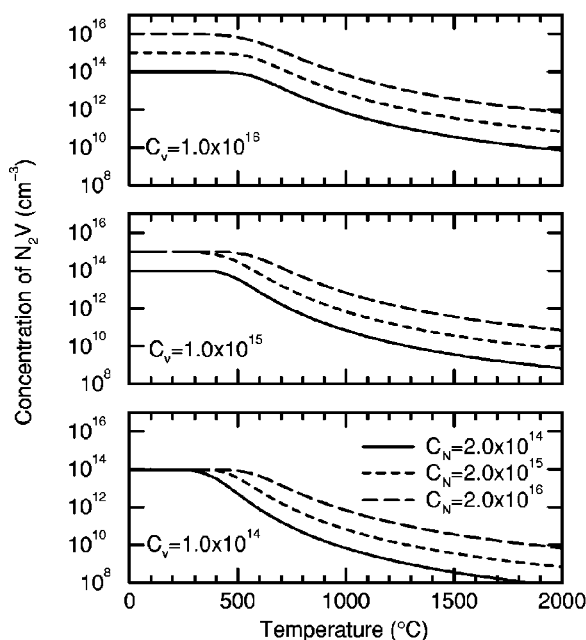

FIG. 9. Concentration of N_2V as a function of temperature for various vacancy and nitrogen concentrations. The unit of the concentrations of vacancies and nitrogen is in atoms/cm^3.

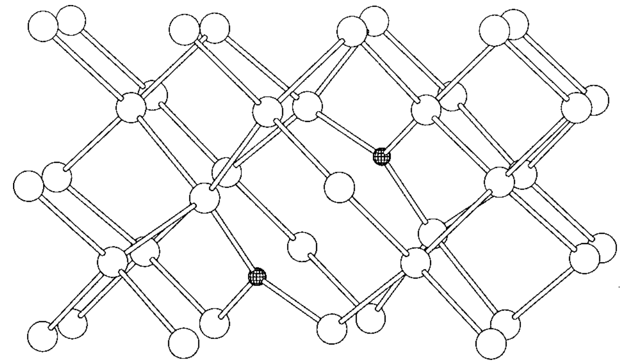

FIG. 10. Structure of the N_2V_2. Nitrogen atoms are substituted for the two neighboring sites of silicon. Open and closed circles denote silicon and nitrogen atoms, respectively.

$$\Delta S \cong k_B ln \left\{ \frac{N_S!}{N_N!(N_S-N_N)!} \times \frac{(N_S-N_N)!}{\{N_S-N_N-(1-a)V\}!\{(1-a)V\}!} \times \frac{N_N!}{(N_N-aV)!(aV)!} \right\}, \tag{9}$$

where N_S is the number of silicon sites, N_N is the number of nitrogen pair sites, $(1-a)V$ is the number of vacancies without a nitrogen pair, and aV is the number of N_2V. In this calculation, the binding energy of the complex with the substitutional nitrogen atom and the interstitial nitrogen atom at the *B* site is employed, since the formation process of the N_2 moleculelike structure is unknown. The changes of enthalpy, entropy, and free energy for the reaction of $N_2+V \rightarrow N_2V$ at the melting temperature of silicon are shown in Table III. It indicates that the N_2V is not a dominant form of the vacancy around the melting temperature of silicon, because the $T\Delta S$ is much larger than ΔE. Figure 9 shows that the temperature where 1% of vacancies are trapped at the nitrogen pair is lower than 1000 °C even though the concentration of nitrogen is higher than the maximum solid solubility of 5×10^{15} atoms/cm^3. In the entropy contribution (Eq. 9) to the free energy only the configurational entropy is considered. Since the vacancy disappears in the reaction of Eq. 7, however, the contribution of the vibrational entropy should not be neglected. In Ref. 28 the vibrational entropy of the vacancy obtained is $4k_B$. When the vibrational entropy of $4k_B$ for the vacancy annihilation is added in Eq. (9), the temperature where the vacancies are trapped at the nitrogen pair decreases by about 100 °C. It is suggested that either the reduction of the concentration of the vacancy or the decrease of the diffusion constant of the vacancy is the mechanism that explains the reduction of the void size and the increase in the number of voids as mentioned above. For both of the above suggested mechanisms a large part of the vacancies are needed to interact with the nitrogen pair, if the N_2V play a role in the mechanisms. The binding energy of the N_2V complex indicates, however, that the N_2V is not stable at the temperature of the void aggregation.

We considered a complex where one more vacancy is added to the above mentioned N_2V. In this case a vacancy is substituted for the silicon atom next to the nitrogen atom at

the B site, and the nitrogen atom moves from the B site to the substitutional site. As a result, two neighboring sites of silicon are occupied by the nitrogen atoms (N_2V_2), as shown in Fig. 10. The bond lengths of three Si-N bonds are almost the same as the shorter bond length of the substitutional nitrogen. The neutral charge state is expected to be the most stable state, since deep single-electron levels are not occupied. The binding energy of adding the monovacancy to the N_2V is obtained as,

$$E_F=\{E[\mathrm{Si}_{214}\mathrm{N}_2]+E[\mathrm{Si}_{216}]\}-\{E[\mathrm{Si}_{215}\mathrm{N}_2]+E[\mathrm{Si}_{215}]\} \\ =-4.55\ \ \mathrm{eV}. \tag{10}$$

Considering the formation of the N_2V_2, the change of free energy of Eqs. (8) and (9) are modified as follows,

$$\Delta F=aVE_a+bVE_b-T\Delta S, \tag{11}$$

$$\Delta S\cong k_B ln\left\{\frac{N_S!}{N_N!(N_S-N_N)!}\times\frac{(N_S-N_N)!}{\{N_S-N_N-(1-a-b)V\}!\{(1-a-b)V\}!}\,\frac{N_N!}{(N_N-aV)!(bV)!\{(a-b)V\}}\right\}, \tag{12}$$

where bV is the number of vacancies that are trapped at the N_2V. E_a and E_b are the binding energies of Eqs. (7) and (10), respectively. The changes of enthalpy, entropy, and free energy for the reaction of $N_2+2V\rightarrow N_2V_2$ at the melting temperature of silicon are shown in Table III. It indicates that the number of N_2V_2 changes around the melting temperature of silicon, because the ΔE and $T\Delta S$ are the same order. The concentrations of vacancies that form the N_2V and N_2V_2 are obtained by minimizing the change of free energy with respect to a and b for various concentrations of vacancy and nitrogen. In Fig. 11 the thin and thick lines denote the concentrations of vacancies contained in the N_2V and N_2V_2, respectively. The vacancies in the N_2V are very little and are reduced as the temperature decreases. The concentration of vacancies contained in the N_2V_2 becomes the concentration of nitrogen pair at least 1300 °C. Since two vacancies disappear for the formation of N_2V_2 in Eqs. (7) and (10), the vibrational entropy is not negligible. Therefore, the contribution of the vibrational entropy is estimated in the same manner as that of the N_2V formation. The vibrational entropy decreases the temperature of the formation of the N_2V_2 by about 200 °C. This indicates that most of the nitrogen pairs interact with the vacancies and change into the N_2V_2 at temperatures higher than 1100 °C in the silicon containing more vacancies than nitrogen atoms. This can be the mechanism for reducing the number or the diffusibility of the vacancies. On the contrary, the N_2V_2 can change to the nitrogen pair by introducing the interstitial silicon, as the binding energy of the N_2V_2 with the two interstitial silicon is,

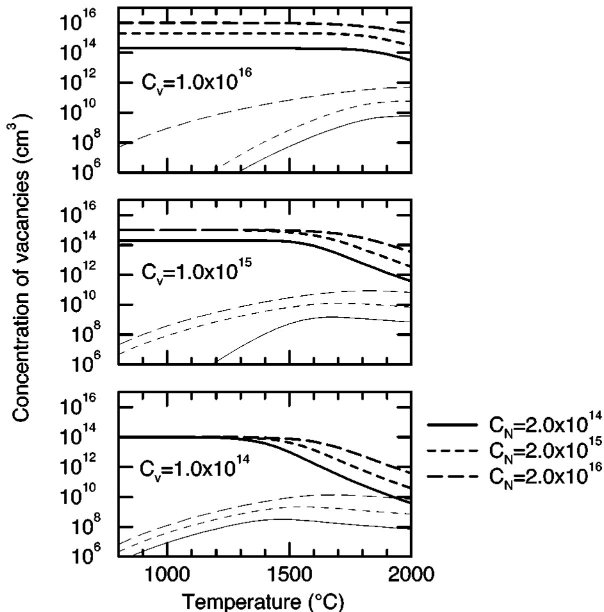

FIG. 11. Concentration of vacancies that form the N_2V and N_2V_2 for various vacancy and nitrogen concentrations. The thin and thick lines denote the concentrations of vacancies contained in the N_2V and N_2V_2, respectively. The unit of the concentrations of vacancies and nitrogen is in atoms/cm^3.

$$E_F=\{E[\mathrm{Si}_{216}\mathrm{N}_2]+2\times E[\mathrm{Si}_{216}]\}-\{E[\mathrm{Si}_{214}\mathrm{N}_2]+2E[\mathrm{Si}_{217}]\} \\ =-8.45\ \ \mathrm{eV}. \tag{13}$$

If this reaction occurs frequently near the melting temperature, the concentration of the vacancies and the interstitial silicon should be much reduced. However, it is unknown whether the reaction determines the concentration of the vacancies and the interstitial silicon as discussed for the substitutional nitrogen, since the exact content of the vacancies and the interstitial silicon is not known near the melting temperature. Furthermore, this reaction needs to pass through the intermediate state, i.e., N_2V. The binding energy of the intermediate state is expressed by the following equation:

$$E_F=\{E[\mathrm{Si}_{215}\mathrm{N}_2]+E[\mathrm{Si}_{216}]\}-\{E[\mathrm{Si}_{214}\mathrm{N}_2]+E[\mathrm{Si}_{217}]\} \\ =-2.52\ \ \mathrm{eV}. \tag{14}$$

This binding energy is not negatively large enough to go through the intermediate state near the melting temperature. It is necessary to consider not only the thermal equilibrium but also the dynamical effect on the stability among the nitrogen pair, N_2V and N_2V_2, in the process of silicon crystal growth.

IV. SUMMARY

The stability of several states of nitrogen were investigated by the first-principles electronic structure calculation. As for the interstitial nitrogen, the S and B sites are much more stable than the H and T sites. The total energies of nitrogen at the S and B sites are almost the same. This con-

trasts with the interstitial oxygen that has a total energy difference of 1.8 eV between the *S* and *B* sites. If the interstitial nitrogen exists dominantly, it can diffuse faster than oxygen, since the energy difference is considered to be the activation energy of diffusion. The substitutional nitrogen is found to be stable, which is contrary to the finding of the experimental observation. This discrepancy may be explained by the fact that the substitutional nitrogen moves to the interstitial site, if the interstitial silicon exists. The nitrogen pair is more stable than the single nitrogen at an interstitial site by 4.3 eV, which indicates that the nitrogen pair exists even near the melting temperature of silicon.

In order to study the interaction between the nitrogen and the monovacancy, two N_2V complexes consisting of two nitrogen atoms and a vacancy, are considered. In one of the complexes, one nitrogen atom moves to the substitutional site and the other nitrogen atom moves to the *B* site. In the other complex, nitrogen atoms form a N_2 moleculelike structure at the vacancy site. The binding energies for both of the N_2V complexes indicate that the N_2V is not stable at the temperature of the void aggregation. When one more vacancy is added to the N_2V complex, two nitrogen atoms are located at the substitutional sites. Since the binding energy of the N_2V_2 is -5.69 eV, the N_2V_2 can exist at the temperature of the void aggregation as far as considering static equilibrium. The formation of the N_2V_2 can affect the concentration or the diffusibility of the vacancies.

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[1] M. Itsumi, M. Tomita, and M. Yamawaki, J. Appl. Phys. **78**, 1940 (1995).

[2] H. Ishii, S. Shiratake, K. Oka, K. Motonami, T. Koyama, and J. Izumitani, Jpn. J. Appl. Phys. **35**, L1385 (1996).

[3] W. Ohashi, A. Ikari, Y. Ohta, A. Tachikawa, H. Deai, H. Yokota, and T. Hoshino, in *Extended Abstracts No.1, The 46th Spring Meeting* (The Japan Society of Applied Physics, Science University of Tokyo, 1999), p. 468.

[4] M. Kato, M. Tamatsuka, M. Iida, H. Takeno, T. Otogawa, and T. Matsui, in *Extended Abstracts No.1, The 46th Spring Meeting* (The Japan Society of Applied Physics, Science University of Tokyo, 1999), p. 470.

[5] M. Iida, M. Kato, H. Takeno, M. Tamatsuka, Y. Hayamizu, M. Kimura, and T. Masui, in *Extended Abstracts No. 1, The 60th Autumn Meeting* (The Japan Society of Applied Physics, Konan University, 1999), p. 356.

[6] T. Saishoji, H. Nakajima, F. Ishikawa, M. Usukubo, K. Nakamura, and J. Tomioka, in *Extended Abstracts No. 1, The 60th Autumn Meeting* (The Japan Society of Applied Physics, Konan University, 1999), p. 356.

[7] G. G. DeLeo, W. B. Fowler, and G. D. Watkins, Phys. Rev. B **29**, 3193 (1984).

[8] H. P. Hjalmarson and D. R. Jennison, Phys. Rev. B **31**, 1208 (1985).

[9] P. A. Schultz and R. P. Messmer, Phys. Rev. B **34**, 2532 (1986).

[10] R. Jones, S. Öberg, B. Rasmussen, and B. Nielsen, Phys. Rev. Lett. **72**, 1882 (1994).

[11] A. Gali, J. Miro, P. Deak, C. P. Ewels, and R. Jones, J. Phys.: Condens. Matter **8**, 7711 (1996).

[12] H. J. Stein, in *Proceedings of the 13th International Conference on Defects in Semiconductors, Coronado, California, 1984*, edited by L. C. Kimerling and J. J. M. Parsey (The Metallurgical Society of AIME, Warrendale, PA, 1985), p. 839.

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[14] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[15] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[16] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10 142 (1993).

[17] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[19] M. Saito and A. Oshiyama, Phys. Rev. B **38**, 10 711 (1988).

[20] M. Needels, J. D. Joannopoulos, Y. Bar-yam, S. T. Pantelides, and R. H. Wolfe, Mater. Res. Soc. Symp. Proc. **209**, 103 (1991).

[21] P. J. Kelly and R. Car, Phys. Rev. B **45**, 6543 (1992).

[22] M. Ramamoorthy and S. T. Pantelides, Phys. Rev. Lett. **76**, 267 (1996).

[23] T. Itoh and T. Abe, Appl. Phys. Lett. **53**, 39 (1988).

[24] K. L. Brower, Phys. Rev. B **26**, 6040 (1982).

[25] K. Murakami, H. Kuribayashi, and K. Masuda, Phys. Rev. B **38**, 1589 (1988).

[26] W. A. Harrison, in *Electonic Structure and the Properties of Solids* (Dover, New York, 1989), p. 237.

[27] M. Tajima, M. Masui, T. Abe, and T. Nozaki, Jpn. J. Appl. Phys. **20**, L423 (1981).

[28] P. Blöchl, E. Smargiassi, R. Car, D. B. Laks, W. Andreoni, and S. T. Pantelides, Phys. Rev. Lett. **70**, 2435 (1993).