NIPPON STEEL TECHNICAL REPORT No. 83 JANUARY 2001

UDC 669 . 782 : 669 . 786 : 548 . 4

First Principles Calculation of Interaction between Nitrogen Atoms and Vacancies in Silicon

Hideaki SAWADA*1 Kazuto KAWAKAMI*1

Abstract

Stability of several states of nitrogen in silicon was investigated using the first principles calculation. It was made clear that single interstitial nitrogen was more stable at a split interstitial site (S-site) or a bond center site than at a tetrahedral or hexagonal site. A nitrogen pair at two adjacent S-sites is more stable than the single nitrogen at an S-site by 4.3 eV, which fact indicates that nitrogen exists as the nitrogen pair even near the melting temperature of silicon. The interrelation between the nitrogen pair and two vacancies results in a strong negative binding energy and this suggests that there is a complex consisting of the nitrogen pair and two vacancies at the temperature of the void aggregation as far as thermal equilibrium is considered. Formation of this complex is presumed to affect the concentration and diffusion of the vacancies.

1. Introduction

The authors have been involved in development and application of the first principles calculation technique, a method to theoretically examine electronic structure. The calculation, details of which will be described in section 2, is based on the density functional theory[1,2], which says that the ground state of a system is univocally determined by one-electron density, and that the one-electron density in the ground state will result in a minimum energy. The authors have developed and applied the full-potential linearized augmented plane wave method[3] dealing with the entire electrons of an atom and the pseudo-potential method[4] dealing only with valence electrons. These methods have been applied to subjects such as magnetic influence of nitrogen impurities in iron[5], Jahn-Teller distortion and magnetic structures in transition metal oxides[6-9], and electronic structure of materials for high dielectric constant capacitor[10]. In the present paper are discussed energy stability and other aspects of nitrogen impurities in silicon crystals as one of the fields of application of the first principles calculation.

In Czochralski-grown (CZ) silicon single crystal, octahedral voids have been found to exist as grown-in defects[11]. The grown-in defects are known to affect the gate oxide reliability[12], and it is important to control their number and size in the process of silicon wafer manufacturing. Recently, nitrogen was found to be an effective dopant for reducing the size of the void [13,14]. Thus, much attention has been paid to the effects of nitrogen doping on the CZ silicon single crystal and the mechanism of the effects. The following mechanisms have been proposed to explain simultaneous occurrence of reduction of the void size and the increase in their number by the nitrogen addition.

One of the possible mechanisms is that nitrogen reduces the number or mobility of vacancies at temperatures above the void aggregation temperature (roughly 1,100°C). Other possible mechanisms include such as nitrogen becoming a nucleation center for the voids, its suppressing effect on growth of the voids, etc. The void aggregation temperature was found to lower with the nitrogen doping[15,16]. This experimental result indicates that nitrogen cannot be the nucleation center for the voids, because this mechanism should make the void aggregation temperature higher. It has not been made clear, however, which is the dominant mechanism among the outstanding two hypotheses.

Various calculations have been made up to now regarding the electronic structure of substitutional nitrogen[17-19] and nitrogen pairs[20] in silicon. However, stability of variety of nitrogen configurations in

*1 Advanced Technology Research Laboratories

silicon has not been investigated, except for calculations on small clusters[21]. Thus, the first principles electronic structure calculations were performed in the present study to obtain some information to clarify the mechanism of the effects of nitrogen addition. Firstly, local structure and electronic structure of single nitrogen at an interstitial site and a substitutional site were studied. Secondly, the same structures were studied regarding nitrogen pairs proposed by Jones et al. Existence of the nitrogen pair was confirmed through the isotope effect of infrared spectra[22]. The purpose of these calculations was to compare the stability of single nitrogen with that of the nitrogen pair. After that, the interactions between nitrogen pairs and vacancies were studied, which can be a key to the understanding of the relation between the nitrogen doping and void aggregation.

2. Calculation Details

The calculations were based on the density functional theory[1,2]. We adopted the pseudo-potential (PP) method and used plane waves as a basis set for efficient structural optimization. It was verified that the cutoff energies of 25 Ry and 400 Ry were sufficient for the wave functions and for the augmented electron densities, respectively. Only the *p* state of nitrogen was treated by Vanderbilt's ultra soft PP[23,24] and the other states by the norm-conserving PP optimized by Troullier and Martins' prescription[25].

The expression proposed by Perdew[26] was used for the exchange-correlation energy in the generalized gradient approximation. 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. Here, the total energy was recalculated, using optimized local structures, on a unit cell of 216 silicon atoms by using the Γ point for the Brillouin zone sampling. The structural optimization was carried out until the force acting on each atom fell to 0.05 eV/Å or smaller.

3. Results and Discussion

3.1 Interstitial nitrogen

The local structure, electronic structure and stability of single interstitial nitrogen were investigated at a split interstitial (S) site, bond center (B) site, tetrahedral (T) site and hexagonal (H) site. **Fig. 1** shows these interstitial sites. The relative energies of nitrogen at the S, B, T and H sites are 0, 0.11, 1.58 and 2.65 eV, respectively. It is seen here that interstitial nitrogen is much more stable at the S and B sites than at the T and H sites. While the energy difference of interstitial nitrogen between the S and B sites is comparable to an error in computation, it is in contrast to the fact that, in the case of interstitial oxygen, the energy difference between the S and B sites is 1.8 eV. But this does not contradict with the fact that the distance between the S and B sites is shorter for nitrogen than for oxygen since the angle Si(1)-X-Si(2) of nitrogen for the B site is smaller than the same of oxygen by as much as 26°.

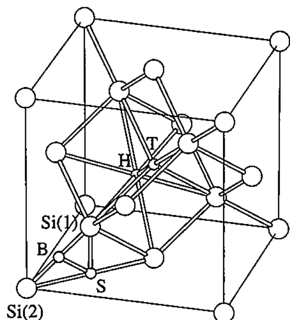


Fig. 1 Ideal interstitial sites (B, S, H and T sites) in silicon crystal Black and white circles are nitrogen and silicon atoms, respectively

It is reasonable to understand that the angle Si(1)-X-Si(2) of nitrogen is smaller than that of oxygen because the ionic radius of nitrogen is larger than that of oxygen by as much as 0.3 Å. The energy difference of oxygen between the S and B sites corresponds to a diffusion barrier for oxygen atoms. If we are to assume that nitrogen diffuses likewise through the S and B sites, the diffusion barrier for it is suspected to be very low. But, the diffusion barrier of nitrogen atom experimentally obtained is 2.8 eV, higher than that of oxygen[27]. It can be speculated [from this that single interstitial nitrogen is not a dominant form of nitrogen in silicon. The dominant form of nitrogen in silicon is discussed later.

3.2 Substitutional nitrogen

Substitutional nitrogen was found to be more stable at an off-center position than at an on-center position through the electron spin resonance study[28,29]. **Fig. 2** shows the energy of substitutional nitrogen expressed as a function of nitrogen displacement from the on-center position in the <-1-1-1> direction. From the figure, it is understood that nitrogen is stable at a position away from the on-center position by about 0.67 Å. The energy difference between the on-center and off-center nitrogen is calculated to be 0.09 eV for a neutral charge site. This agrees well with the experimentally obtained value of 0.07 eV[29]. The calculated energy barrier for the re-orientation among four equivalent off-center sites of 0.14 eV is also in good agreement with the experimental value of 0.11 eV[28].

Stability of substitutional nitrogen is estimated by the following expression:

$$E_F = \{E[Si_{215}N] + E[Si_{216}]\} - \{E[Si_{216}N] + E[Si_{215}]\}$$
$$= -3.88eV \quad \cdots\cdots\cdots (1)$$

The binding energy of interstitial nitrogen with a vacancy indicates that the substitutional nitrogen can exist even at high temperatures near the melting temperature of silicon. However, the substitutional nitrogen detected in the samples obtained through ion injection is 10% or less of the total amount of the implanted nitrogen[28]. Moreover, it has been known that only 1% or less of the doped nitrogen atoms contribute to the electronic properties in the samples grown by the floating zone method, although the substitutional nitrogen is

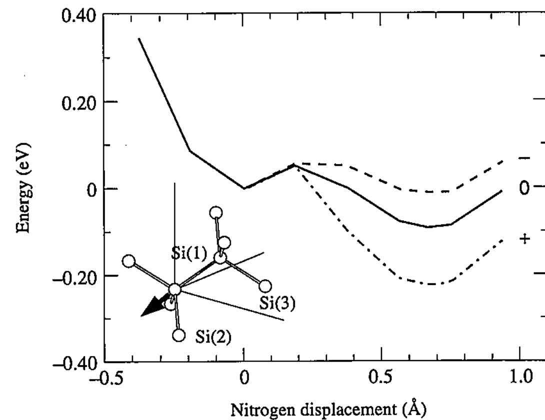


Fig. 2 Total energy of $Si_{63}N$ as a function of nitrogen displacement in the <-1-1-1> direction, measured based on the total energy of on-center nitrogen for each charge site. Black and white circles are nitrogen and silicon atoms, respectively. The arrow indicates the direction of nitrogen displacement, i.e., the <-1-1-1> direction.

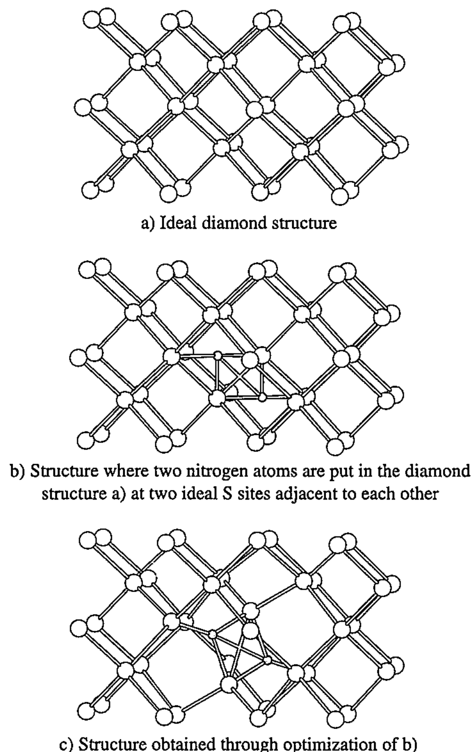
expected to affect the electronic properties[30]. Thus the experimental observation and the theoretical estimation appear to contradict each other. In order to overcome this contradiction we considered a reaction where nitrogen is ejected from a substitutional site to an interstitial site by interstitial silicon. The kick-out energy of the substitutional nitrogen by the interstitial silicon is obtained as:

$$E_F = \{E[Si_{216}N] + E[Si_{216}]\} - \{E[Si_{215}N] + E[Si_{217}]\}$$
$$= -3.19eV \qquad \cdots\cdots\cdots (2)$$

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 vacancies and interstitial silicon. If the concentration of vacancies and interstitial silicon near the melting temperature is comparable to that of nitrogen, the concentration of vacancies and interstitial silicon will be significantly reduced. However, it is impossible to judge whether this mechanism has a major effect on the concentration of vacancies and interstitial silicon, because the concentration of vacancies and interstitial silicon at high temperature is not known exactly.

3.3 Nitrogen pair

Nitrogen pairs have been confirmed to exist through an isotope effect of infrared spectra[22]. Structure of a nitrogen pair was proposed on a basis of a cluster calculation of $N_2Si_{44}H_{42}$ based on the first principles calculation[20]. It was also optimized to local atomic structure around nitrogen atoms at two S sites adjacent to each other and obtained a result very close to what Jones et al. obtained (see **Fig. 3**). With regards to the stability evaluation of the nitrogen pair, it was assumed that the following equation for expressing the binding energy of a nitrogen pair:


a) Ideal diamond structure

b) Structure where two nitrogen atoms are put in the diamond structure a) at two ideal S sites adjacent to each other

c) Structure obtained through optimization of b)

Fig. 3 Structure of nitrogen pair
Black and white circles are nitrogen and silicon atoms, respectively.

$$E_F = \{E[Si_{216}N_2] + E[Si_{216}]\} - \{E[Si_{216}N] + E[Si_{216}N]\}$$
$$= -4.3eV \qquad \cdots\cdots\cdots (3)$$

On this assumption and in consideration of the binding energy and atomic configurational entropy, the ratio of nitrogen pairs to the total of nitrogen atoms as a function of temperature was calculated.

Blöchl et al. reported that the contribution of configurational entropy to each of the total formation entropies for vacancies and interstitial silicon was about one-third and that the rest was attributed to vibrational entropy[31]. Different from the formation of vacancies or interstitial silicon, however, the vibrational entropy is not expected to change very much with the formation of nitrogen pairs from two interstitial nitrogen atoms. For this reason, we assumed that the configurational entropy was dominant.

On the assumption, a change of free energy for a transformation of two interstitial nitrogen atoms into a nitrogen pair was expressed as follows:

$$\Delta F = aN_N E_F - T\Delta S$$

$$\Delta S \equiv k_B \ln\left\{\frac{N_I!}{(N_N - aN_N)!(N_I - N_N + aN_N)!} \times \frac{(N_N - aN_N)!}{(aN_N)!(N_N - 2aN_N)!}\right\} \qquad \cdots\cdots\cdots (4)$$

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 all the nitrogen, isolated nitrogen and nitrogen pairs, respectively. The ratio of nitrogen pairs to the total number of nitrogen is obtained by minimizing ΔF of Eq. (4) with respect to a (see **Fig. 4**). This figure indicates that most nitrogen atoms form nitrogen pairs even near the melting temperature of silicon (1,410°C). It is mentioned in 3.1 above that the dominant form of nitrogen was not interstitial nitrogen because of the discrepancy between the diffusion constant obtained through theoretical calculations and the same obtained through experiments. The conclusion to the effect that the nitrogen pair is the dominant form of nitrogen is consistent with the above discussion in 3.1.

3.4 Interaction between nitrogen pair and vacancy

Firstly, as an interaction between a nitrogen pair and a monovacancy, a case was considered where one of the silicon atoms bridging the two nitrogen atoms forming a nitrogen pair is substituted with a monovacancy (see **Fig. 5** (a)). In this case, one nitrogen atom enters a substitutional site (N(1)) moving to the position of the vacancy, and the other nitrogen atom moves to a B site (N(2)). In the local structure around the nitrogen atom having entered the B site,

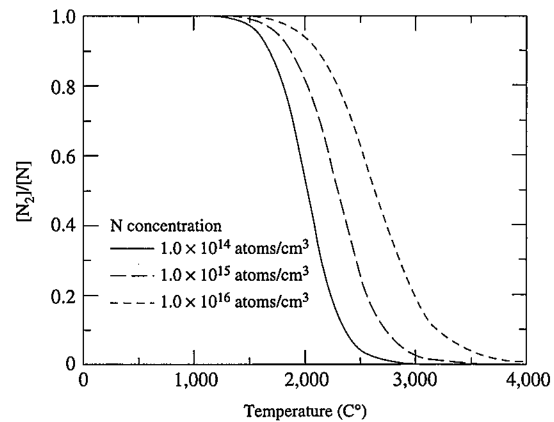
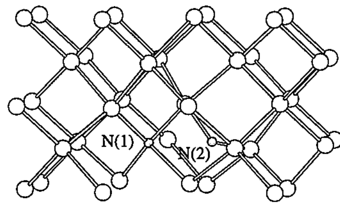
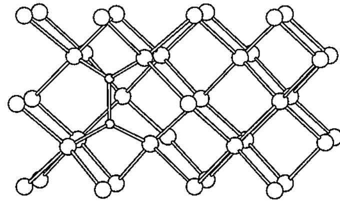


Fig. 4 Ratio of nitrogen pairs to total nitrogen



a) One nitrogen atom is at substitutional site (N(1)) and the other nitrogen atom at B site (N(2))



b) Nitrogen forms molecule-like structure at vacancy site

Fig. 5 Complex consisting of two nitrogen atoms and one vacancy Black and white circles are nitrogen and silicon atoms, respectively.

the angle Si-N(2)-Si is 143° and the bond length of Si-N(2) is 1.07 Å. Both the angle and the bond length are larger than those of the single nitrogen at the B site. This is because, due to N(1)'s having entered the substitutional site, the bond length of Si-N(1) shrinks more than that of neighboring Si-Si by 0.2 Å when a single nitrogen is provided at the B site. As another case of interactions between a nitrogen pair and a monovacancy, we considered a case where nitrogen forms a molecule-like structure at a vacancy site (see Fig. 5 (b)). The bond length of Si-N in this case is almost the same as the shorter Si-N bond length for the substitutional nitrogen, and the distance between the two nitrogen atoms is as long as 1.44 Å, much longer than that of a normal N_2 molecule, which is 1.1 Å.

Stability of the complex of a nitrogen pair and a monovacancy (N_2V) is estimated using the equation below.

$$E_F = \{E[Si_{215}N_2] + E[Si_{216}]\} - \{E[Si_{216}N_2] + E[Si_{215}]\} \quad \cdots\cdots (5)$$

The binding energies of the nitrogen pair with the vacancy were −1.14 eV and −1.29 eV for the above two types of complexes, respectively. The complex consisting of a substitutional nitrogen atom and an interstitial nitrogen atom at the B site is a little less stable than that consisting of an N_2 molecule-like structure at the vacancy site. From the above values of the binding energy, however, it was considered difficult for N_2V to exist stably at temperatures near the void aggregation temperature.

Next, a case was considered where another vacancy is added to the N_2V. Here, it was presumed that the new vacancy came to the site of a silicon atom adjacent to the nitrogen at a B site, but it was found out that in such a case the nitrogen moved from the B site to the substitutional site where the vacancy came to. The result is that two neighboring sites of silicon atoms are occupied by two nitrogen atoms (N_2V_2) as shown in **Fig. 6**. The bond lengths of three Si-N bonds are almost the same as the shorter Si-N bond length of the substitutional nitrogen. The binding energy for adding a monovacancy to the N_2V is obtained as:

$$E_F = \{E[Si_{214}N_2] + E[Si_{216}]\} - \{E[Si_{215}N_2] + E[Si_{215}]\}$$
$$= -4.55eV \quad \cdots\cdots\cdots (6)$$

The free energy when the N_2V_2 is formed from a nitrogen pair was estimated by the following equations:

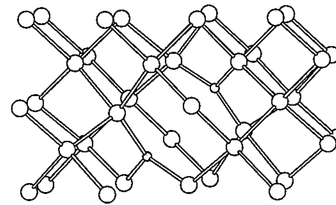


Fig. 6 Complex consisting of two nitrogen atoms and two vacancies Nitrogen atoms take positions at two silicon atoms adjacent to each other. Black and white circles are nitrogen and silicon atoms, respectively.

$$\Delta F = aVE_a + bVE_b - T\Delta S$$

$$\Delta S \cong k_B \ln\left\{\frac{N_I!}{N_N!(N_S - N_N)!} \times \frac{(N_S - N_N)!}{(N_S - N_N!(1-a-b)V)!((1-a-b)V)!} \times \frac{N_N!}{(N_N - aV)!(bV)!((a-b)V)!}\right\} \quad \cdots\cdots\cdots (7)$$

where aV and bV are the numbers of vacancies trapped in the N_2V and N_2V_2, respectively, N_S is the number of silicon sites, and N_N the number of nitrogen pair sites.

The numbers of vacancies trapped in 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. The thin and thick lines in **Fig. 7** denote concentrations of the vacancies trapped in N_2V and N_2V_2, respectively. Concentration of the vacancies trapped in N_2V is very little compared with that of the vacancies trapped in N_2V_2. What is more, most of vacancies are trapped in N_2V_2 as the temperature decreases and, thus, concentration of vacancies trapped in N_2V falls. The concentration of vacancies contained in N_2V_2 becomes equal to the concentration of nitrogen pair at least at 1,300°C.

In Eq. (7) only the configurational entropy is taken into account with regards to the contribution of entropy to the change of free energy. However, since vacancies disappear when N_2V and N_2V_2 are formed from nitrogen pairs and vacancies, the contribution of vibrational entropy becomes significant. Since the vibrational entropy of a vacancy is 4 k_B according to Blochl et al., when the vibrational entropy for a vacancy to disappear is added to Eq. (7), the temperature to form N_2V_2 is decreased by about 200°C, in other words, it is suspected that nitrogen pairs interact with vacancies at a temperature higher than 1,100°C to form N_2V_2. This mechanism may reduce concentration and mobility of vacancies.

On the contrary, an N_2V_2 can change to a nitrogen pair once again by introducing interstitial silicon, as the binding energy of an N_2V_2 with two interstitial silicon atoms is expressed as follows:

$$E_F = \{E[Si_{216}N_2] + 2 \times E[Si_{216}]\} - \{E[Si_{214}N_2] + 2 \times E[Si_{217}]\}$$
$$= -8.45eV \quad \cdots\cdots\cdots (8)$$

If this reaction occurs frequently near the melting temperature, concentrations of vacancies and interstitial silicon should be much reduced. However, it is impossible to judge whether the reaction determines the concentrations of vacancies and interstitial silicon, like in the discussion on the substitutional nitrogen, since the exact concentrations of vacancies and interstitial silicon near the melting temperature are not known.

Further, this reaction needs to go through an intermediate state, i.e., N_2V. The energy for forming an N_2V from an N_2V_2 and an interstitial silicon atom is expressed in the following equation:

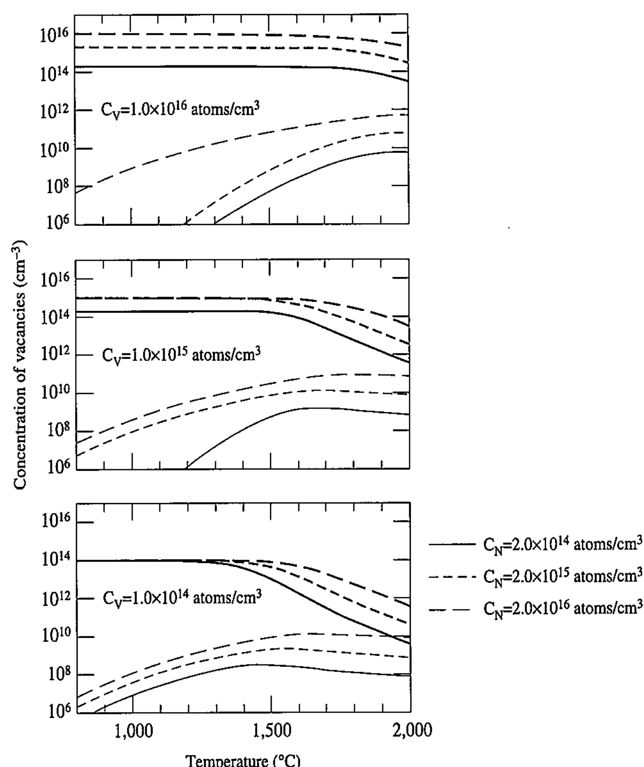


Fig. 7 Concentration of vacancies in N_2V and N_2V_2 for various vacancy and nitrogen concentrations
Thin and thick lines denote concentrations of vacancies trapped in N_2V and N_2V_2, respectively.

$$E_F = \{E[Si_{215}N_2] + E[Si_{216}]\} - \{E[Si_{214}N_2] + E[Si_{217}]\} = -2.52eV \qquad (9)$$

A yet larger negative energy is required for this reaction to take place near the melting temperature. From the above, it is necessary to consider not only the thermal equilibrium but also the dynamic effect on the stability among the nitrogen pair, N_2V and N_2V_2 when studying the process of silicon crystal growth.

4. Summary

Stability of several states of nitrogen in silicon was investigated using the first principles electronic structure calculation. Interstitial nitrogen was found to be significantly more stable in S and B sites than in H and T sites. The total energies of nitrogen at the S and B sites are almost the same. This contrasts with the interstitial oxygen that has a total energy difference of 1.8 eV between the S and B sites. If the single interstitial nitrogen is the dominant form of nitrogen in silicon, then it is suspected that nitrogen can diffuse faster than oxygen, since the energy difference between the S and B sites is considered to be the activation energy of diffusion. Contrary to the finding of experimental observations, substitutional nitrogen was found to be stable. The discrepancy between the experimental observations and the theoretical calculation of substitutional nitrogen may be explained by the fact that the substitutional nitrogen is driven to an interstitial site by interstitial silicon. A nitrogen pair is more stable than a single nitrogen atom at an interstitial site by 4.3 eV, which fact indicates that the nitrogen pair exists even near the melting temperature of silicon.

In order to study the interaction between nitrogen pairs and monovacancies, two types of N_2V complexes are considered. In one of the complexes, one nitrogen atom moves to a substitutional site and the other nitrogen atom moves to a B site. In the other complex, nitrogen atoms form an N_2 molecular-like structure at a vacancy site. The binding energies for both of the N_2V complexes indicate that the N_2V is not stable at the void aggregation temperature. When one more vacancy is added to the N_2V complex, two nitrogen atoms are located at substitutional sites adjacent to each other forming an N_2V_2. Since the binding energy to form an N_2V_2 from a nitrogen pair and two vacancies is –5.69 eV, the N_2V_2 can exist at the void aggregation temperature as far as thermal equilibrium is considered. The formation of N_2V_2 can affect concentration or diffusibility of vacancies.

Reference

1) Hohenberg, P., Kohn, W.: Phys. Rev. 136, B864 (1964)
2) Kohn, W., Sham, L.J.: Phys. Rev. 140, A1133 (1965)
3) Terakura, K., Hamada, N.: Solid Physics. 19, 448 (1984)
4) Kanamori, J., Yonezawa, F., Kawamura, K., Terakura, K.: Solid Matter - Structure and Material Properties. Iwanami Shoten, 1994, p.60
5) Sawada, H., Nogami, A., Matsumiya, T., Oguchi, T.: Phys. Rev. B 50, 10004 (1994)
6) Sawada, H., Hamada, N., Terakura, K., Asada, T.: Phys. Rev. B 53, 12742 (1996)
7) Sawada, H., Morikawa, Y., Terakura, K., Hamada, N.: Phys. Rev. B 56, 12154 (1997)
8) Terakura, K., Sawada, H., Solovyev, I., Hamada, N.: Solid Physics. 32, 273 (1997)
9) Sawada, H., Terakura, K.:Phys. Rev. B 58, 6831 (1998)
10) Sawada, H., Kawakami, K.: J. Appl. Phys. 86, 956 (1999)
11) Itsumi, M., Tomita, M., Yamawaki, M.: J. Appl. Phys. 78, 1940 (1995)
12) Ishii, H., Shiratake, S., Oka, K., Motonami, K., Koyama, T., Izumitani, J.: Jpn. J. Appl. Phys. 35, L1385 (1996)
13) Ohashi, W., Ikari, A., Ohta, Y., Tachikawa, A., Deai, H., Yokota, H., Hoshino, T.: The 46th Spring Meeting Extended Abstracts No.1, The Japan Society of Applied Physics, Science University of Tokyo, 1999, p.468
14) Kato, M., Tamatsuka, M., Iida, M., Takeno, H., Otogawa, T., Masui, T.: The 46th Spring Meeting Extended Abstracts No.1, The Japan Society of Applied Physics, Science University of Tokyo, 1999, p.470
15) Iida, M., Kato, M., Takeno, H., Tamatsuka, M., Hayami, Y., Kimura, M., Masui, T.: The 60th Autumn Meeting Extended Abstracts No.1, The Japan Society of Applied Physics, Konan University, 1999, p.356
16) Saishoji, T., Nakajima, H., Ishikawa, F., Usukubo, M., Nakamura, K., Tomioka, J.: The 60th Autumn Meeting Extended Abstracts No.1, The Japan Society of Applied Physics, Konan University, 1999, p.356
17) DeLeo, G.G., Fowler, W.B., Watkins, G.D.: Phys. Rev. B 29, 3193 (1984)
18) Hjalmarson, H.P., Jennison, D.R.: Phys. Rev. B 31, 1208 (1985)
19) Schultz, P.A., Messmer, R.P.: Phys. Rev. B 34, 2532 (1986)
20) Jones, R., Oberg, S., Rasmussen, F.B., Nielsen, B.B.: Phys, Rev. Lett. 72, 1882 (1994)
21) Gali, A., Miro, J., Deak, P., Ewels, C.P., Jones, R.: J. Phys.: Condens. Matter 8, 7711 (1996)
22) Stein, H.J.: Proceedings of the 13th International Conference on Defects in Semiconductors, Coronado, California, 1984, edited by L. C. Kimerling, J. J. M. Parsey, Warrendale, PA, 1985, The Metallurgical Society of AIME, p.839
23) Vanderbilt, D.: Phys. Rev. B 41, 7892 (1990)
24) Laasonen, K., Pasquarello, A., Car, R., Lee, C., Vanderbilt,D.: Phys. Rev. B 47, 10142 (1993)
25) Troullier, N., Martins, J.L.: Phys. Rev. B 43, 1993 (1991)
26) Perdew, J.P., Burke, K., Ernzerhof, M.: Phys. Rev. Lett. 77, 3865 (1996)
27) Itoh, T. Abe, T.: Appl. Phys. Lett. 53, 39 (1988)
28) Brower, K.L.: Phys. Rev. B 26, 6040 (1982)
29) Murakami, K., Kuribayashi, H., Masuda, K.: Phys. Rev. B 38, 1589 (1988)
30) Tajima, M., Masui, M., Abe, T., Nozaki, T.: Jpn. J. Appl. Phys. 20, L423 (1981)
31) Blochl, P., Smargiassi, E., Car, R., Laks, D.B., Andreoni, W., Pantelides, S.T.: Phys. Rev. Lett. 70, 2435 (1993)