

Vibrational modes and electronic properties of nitrogen defects in silicon

J. P. Goss, I. Hahn, and R. Jones

School of Physics, The University of Exeter, Exeter EX4 4QL, United Kingdom

P. R. Briddon

Department of Physics, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, United Kingdom

S. Öberg

Department of Mathematics, Luleå University of Technology, Luleå S-97187, Sweden

(Received 5 August 2002; published 30 January 2003)

Nitrogen impurities form complexes with native defects such as vacancies and self-interstitials in silicon which are stable to high temperatures. These complexes can then suppress the formation of large vacancy and self-interstitial clusters. However, there is little known about their properties. We use first-principles density-functional theory to determine the local vibrational modes, electrical levels and stability of a range of nitrogen-interstitial and vacancy complexes. Tentative assignments of the *ABC* photoluminescence line and the trigonal SL6 EPR center are made to substitutional-nitrogen pair and the substitutional-nitrogen–vacancy complex.

DOI: 10.1103/PhysRevB.67.045206

PACS number(s): 61.72.Bb, 61.72.Ji, 61.72.Tt, 71.15.Nc

I. INTRODUCTION

Nitrogen defects in Si have recently come under scrutiny for their effect on the formation of deleterious defects. For instance, nitrogen is known to reduce the concentration of substitutional Au centers introduced into Czochralski-Si at 750 °C probably by trapping vacancies.¹ It is also known that nitrogen interacts with oxygen in a complex way, and some of these products are electrically inactive,^{2,3} while others are possibly shallow thermal donors.^{4–10} Nitrogen also locks dislocations,^{11–13} modifies oxygen precipitation,^{14,15} and may induce transient-enhanced diffusion of dopants.¹⁶ It also suppresses void formation which are known to degrade the properties of semiconductor devices, as they can cause failure of gate oxides.¹⁷ The mechanism may be due to the formation of nitrogen-vacancy centers stable at the growth temperature.¹⁸

The equilibrium vacancy concentration at a growth temperature of ~ 1400 °C depends on the formation energy of the vacancy. Values around 10^{12} cm⁻³ occur assuming a vacancy enthalpy of $\sim (3.6 - 10k_B T)$ eV derived from positron-annihilation studies.¹⁹ However, a considerable uncertainty arises from the large range of formation energies for the vacancy derived both from theory and from experiment ($\sim 2 - 4$ eV, Refs. 19–24). In addition, the vacancy concentration at the growth temperature depends in a complicated way on details of the growth, and values of $\sim 10^{15}$ cm⁻³ have been suggested at ~ 1400 °C.²⁵ If the nitrogen concentration exceeds that of the vacancy, then it has been suggested that nitrogen-vacancy centers could form,^{17,26–28} suppressing the formation of voids. Such defects have been reported in positron-annihilation experiments examining Czochralski-Si into which N had been implanted, although no specific defect center was identified.²⁷ Recent studies²⁹ have, however, indicated that nitrogen-oxygen defects² may also play an important role in complexing with vacancies and suppress void formation.

The most common nitrogen defect in Si is a *pair* of interstitial nitrogen atoms, denoted (N_i-N_i), which was identified from a combination of channeling and infrared absorption experiments coupled with *ab initio* modeling.³⁰ The binding energy of the pair relative to isolated N_i centers has previously been calculated to be 3.86 eV (Ref. 31) and 4.30 eV (Ref. 32). Substitutional nitrogen (N_s) is detected in relatively small concentrations in implanted material and gives rise to a C_{3v} electron-paramagnetic-resonance (EPR) spectrum labeled SL5.^{33,34} The defect disappears around 450 °C and has a structure similar to N_s in diamond,³⁵ and with the spin density mainly localized on one Si atom (73%) with little spin density on N (7%). The defect can be aligned under stress and has a piezospectroscopic stress tensor with an axial component of -3.14 eV, indicating a small compression of the surrounding lattice along the unique $\langle 111 \rangle$ axis. The defect thermally reorients with the low activation barrier of 0.107 eV, and a high preexponential factor which suggests a thermally activated atomic jump. Although described as trigonal, the SL5 EPR center exhibits unusual properties as a function of temperature, which has been interpreted in terms of a close-by, metastable structure in which the nitrogen atom lies at a lattice site.³⁶ Annealing around 400 °C removes SL5 and there is then a growth in other EPR centers associated with nitrogen labeled SL6 and SL7, which contain one N atom and SL6 possesses $\langle 111 \rangle$ symmetry,³⁴ although to date, these centers have not been assigned to specific defects. The spin density on nitrogen in SL6 is lower than in SL5 suggesting a larger defect.

An optical center labeled “*ABC*” has also been correlated with the presence of nitrogen in the material. This series of three lines is characterized by a zero-phonon line labeled “*A*” at 1.1223 eV.^{37,38} Both Zeeman and uniaxial stress experiments indicate a $\langle 111 \rangle$ axial symmetry.³⁹ It appears after annealing above 700 °C, and must therefore represent a rather stable defect, although the concentrations are very low,³⁷ typically $\sim 10^{13}$ cm⁻³. The *ABC* center gives rise to

two zero-phonon lines separated by 3.0 meV, which represents the splitting of two excited states, with a third excited state only visible under a perturbation such as an applied magnetic field.³⁷ The involvement of nitrogen in this optical center can be inferred from the rough correlation between the N concentration and the optical intensity,⁴⁰ but is made unambiguous from the 0.22 meV shift in energy when ¹⁴N is replaced with ¹⁵N.⁴¹ However, since the optical data is consistent with an isoelectronic or spin-zero defect, it is believed that N is paired with a second component, such as an acceptor (e.g., Al), or a second nitrogen atom. The *ABC* center is thought to involve a deep electron trap, to which a hole is Coulombically bound^{37,42} and can be described as a pseudoacceptor.³⁹ The symmetry of the *ABC* lines may be thought to point to nearest-neighbor donor-acceptor pairs, and in particular N-Al, although early reports seemed to rule this out.^{37,40}

Limited data are available regarding the location of N-related electrical levels in the band gap. Early experiments suggested that N_s possesses a shallow level ($E_c - 0.017$ eV).⁴³ However, this was later shown to be in error since the SL5 EPR center is associated with a “deep level.”³⁴ N-related levels at $E_c - 0.19$ eV (E_2) and $E_c - 0.28$ eV (E_3) have been observed in deep-level transient spectroscopy (DLTS) of *n*-type material doped during growth,⁴⁴ although these centers constitute, respectively, only 0.1% and 0.01% of the total nitrogen concentration of the material (10^{15} cm⁻³). No levels were detected in *p*-type material. An acceptor level labeled *T1* at $E_c - 0.42$ eV and concentration $\sim 10^{15}$ cm⁻³ was found when *n*-type silicon, into which nitrogen had been diffused at around 700 °C, was quenched.⁴⁵ This was assigned to a vacancy-dinitrogen complex, although there was no direct evidence for the number of nitrogen atoms in the center. In the material that was quenched (1 s) from the nitrogen in-diffusion temperature (750–850 °C) to room temperature and subsequently annealed at room temperature or 100 °C for a few hours, the depth profile of *T1* followed that of the nitrogen profile and was activated with an energy of 2.65 eV: a value close to the diffusion barrier of (N_i-N_i).⁴⁶ *T1* was not formed when interstitials were also introduced during the process by oxidation. The suggestion was made that *T1* was a complex of (N_i-N_i) with a vacancy introduced by the quench. One might have expected DLTS levels due to *VP* or *V₂* complexes, which are close to the *T1* level, to be also formed but these were not reported.

Previous modeling studies^{31,47} suggest that interstitial nitrogen has a formation energy very similar to the substitutional form but diffuses rapidly⁴⁷ with a barrier of only 0.4 eV. Thus, any conversion of the substitutional species into the interstitial one would be followed by loss of nitrogen to traps such as other impurities (including nitrogen), vacancies or self-interstitials. The activation energy for the motion of the interstitial nitrogen pair is found to be ~ 2.8 eV (Ref. 48) and close to the the observed diffusion energy for nitrogen.⁴⁶

A number of nitrogen-vacancy complexes have recently been the subject of theoretical investigations.^{26,31,32,49} The

complexes where one or two interstitial N atoms form complexes with various numbers of vacancies have been discussed. The binding energy of a single vacancy with N_i , which creates substitutional nitrogen N_s , is roughly the formation energy of the vacancy. This results in approximately equal formation energies for substitutional and interstitial nitrogen. Nelson *et al.*⁴⁹ calculated that a complex of N_s and a lattice vacancy is bound by 1.73 eV and the N_s migration energy barrier, controlled by a vacancy mechanism, is 4.44 eV. An interstitial pair (N_i-N_i) binds to 1–5 lattice vacancies with incremental binding energies of 0.82–1.29 eV, 4.07–4.55 eV, 1.68 eV, 1.50 eV, and 2.16 eV, respectively.^{31,32,26}

In this paper, we determine the vibrational properties of nitrogen-vacancy centers with a view that these might be helpful in the characterization of the defects. Such an approach has proved successful in identifying the dominant nitrogen center—the interstitial pair.³⁰ However, an unambiguous identification is more likely to be made if other properties can be correlated with the defect, such as their electrical levels and likely thermal stability. We describe the details of our computational method in the following section. In Sec. III, we give our results, and conclude in Sec. IV.

II. METHOD

We employ a spin-polarized local-density-functional supercell code (AIMPRO),^{50,51} together with a Perdew-Wang exchange-correlation energy parametrization.⁵² The Bachelet-Hamann-Schlüter pseudopotentials are used for Si and the Martins-Troullier pseudopotentials for N to eliminate core electrons.^{53,54} The calculations were carried out in 64–216 atom cubic supercells and typically eight special \mathbf{k} points generated by a Monkhorst-Pack scheme (MP-2³) were used to sample the Brillouin zone.⁵⁵ The Si wave function basis is composed of independent sets of *s* and *p* Gaussian orbitals with four different widths, and one addition set of *d* orbitals centered at each atomic site. The N atoms were treated using four independent sets of *s*, *p*, and *d* Gaussians. The charge density is expanded in plane waves with an energy cutoff of 150 Ry. The error in the lattice constant and bulk modulus of silicon using this basis is less than 1%, while the direct and indirect band gaps are within 3% and 4% of previously published plane-wave local-density-approximation values (2.67 eV and 0.49 eV, Ref. 56).

Local vibrational mode frequencies were obtained from the second derivatives of the total energy with respect to the positions of the defective atoms and their Si neighbors. The contributions to the dynamical matrix from other Si atoms in the supercell were found from a Musgrave-Pople interatomic potential⁵⁷ fitted from the double derivatives of bulk silicon obtained using AIMPRO. Typically, modes are calculated to within 5–10% of experiment.

We use the formation energy of a defect *X* in charge state *q* defined by

$$E^f(X, q) = E^{SC}(X, q) - \left(\sum_i \mu_i \right) + q(E_v + \mu_e) + \chi(X, q), \quad (1)$$

where $E^{SC}(X, q)$ is the energy of the supercell containing the defect, μ_i are the chemical potentials of atom types i in the cell, and the sum is over all atoms. E_v and μ_e are the valence-band top and electron chemical potential, respectively, and $\chi(X, q)$ is a correction term that includes the electrostatic energy due to the supercell approximation as well as the quadrupole interaction, and higher-order terms.⁵⁸ There is also an influence from the difference in asymptotic potential between a defective and bulk cell, although this is usually small enough to be neglected. Typically for charged cells, the dominant term is the electrostatic term of the order of 0.1 eV for $q = \pm 1$. The chemical potentials for Si and N may be taken to be the energy per atom in the bulk and nitrogen molecule, respectively, although, due to the numerical uncertainty in such calculations, one typically refers to the formation energy per N atom, or binding energies where the terms in μ_N cancel. However, the absolute formation energy controls the equilibrium density of defects and allows us to compare the concentration of, for example, substitutional and interstitial nitrogen defects. These is obtained from the expression

$$[X] \approx N_s(X) e^{-E^f(X)/k_B T}, \quad (2)$$

where $[X]$ is the concentration of defect X , $N_s(X)$ is the site density for X in the material, k_B is Boltzmann's constant, and T is the temperature. Relative solubilities are independent of μ_N where the number of impurity species is the same, such as for the ratio of the concentrations of interstitial and substitutional nitrogen:

$$\frac{[N_i]}{[N_s]} \sim \frac{N_s(N_i)}{N_s(N_s)} \exp\left(\frac{E^f(N_s) - E^f(N_i)}{k_B T}\right), \quad (3)$$

since in the difference in formation energy $E^f(N_s) - E^f(N_i)$, the μ_N cancel.

Binding energies are defined for the reaction $A + B \rightarrow C$ as

$$E^b(C) = E^f(A) + E^f(B) - E^f(C), \quad (4)$$

so that a positive binding energy represents a bound system.

The acceptor and donor activities can be established by comparing the ionization energy or electron affinity of the defect cell with some known marker. It is convenient to use bulk silicon, as suggested previously.⁵⁹ Then, for example, a single donor and acceptor level can be evaluated by replacing E_v in Eq. (1) by $E^{SC}(\text{Bulk}, 0) - E^{SC}(\text{Bulk}, 1)$ and using $E_c = E^{SC}(\text{Bulk}, -1) - E^{SC}(\text{Bulk}, 0)$. Assuming that the terms in χ are similar for different cells, this yields

$$E(0/+) = E_v + \{E^{SC}(X, 0) - E^{SC}(\text{Bulk}, 0)\} - \{E^{SC}(X, 1) - E^{SC}(\text{Bulk}, 1)\} \quad (5)$$

$$E(-/0) = E_c - \{E^{SC}(X, 0) - E^{SC}(\text{Bulk}, 0)\} + \{E^{SC}(X, -1) - E^{SC}(\text{Bulk}, -1)\} \quad (6)$$

Typically, errors of the order of 0.2 eV are anticipated from such calculations, although in some cases, the error can be

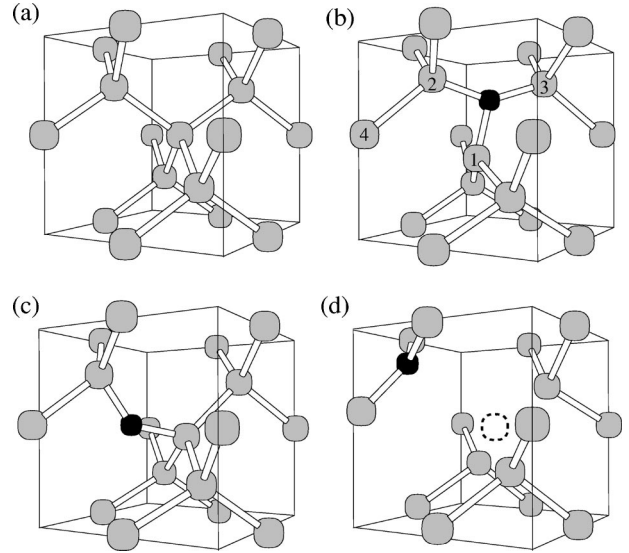


FIG. 1. Schematic representation of defects containing a single N impurity. Black and gray circles represent the N and Si atoms, respectively. (a) Fragment of the Si lattice, (b) the C_{1h} , approximately $\langle 001 \rangle$ split-interstitial structure for N_i , (c) the puckered bond-centered structure for N_i , and (d) the $(N_s V)$ complex. The vacant site in (d) is represented schematically by a dashed circle.

larger still, especially where there are reconstructed dangling bonds such as found in vacancy centers which are not properly treated using supercells.

III. RESULTS

To compare with previous results, we first investigated the single nitrogen interstitial (N_i) and the interstitial-nitrogen pair (N_i-N_i), together with self-interstitials. The interstitial nitrogen pair is known experimentally to be the dominant N-related center in silicon. Then we have examined complexes formed by the addition of lattice vacancies: namely, the isolated substitutional nitrogen (N_s), the substitutional-interstitial pair (N_i-N_s), the complex of substitutional nitrogen with a lattice vacancy ($N_s V$), the close-by substitutional pair (N_s-N_s), and the disubstitutional-nitrogen-vacancy complex, $(N_s-N_s)V$. Other complexes including higher-order vacancy aggregates with nitrogen and complexes of interstitial nitrogen with self-interstitials are also discussed. For all these defects, a structural optimization was performed and their vibrational and electronic properties investigated.

A. Interstitial nitrogen, N_i

Several sites for N_i were investigated: the bond-center, $\langle 001 \rangle$ split-interstitial, hexagonal, and tetrahedral site configurations. The lowest-energy configuration for the neutral defect is the distorted $\langle 001 \rangle$ -oriented split-interstitial, where the ideal C_{2v} symmetry has been lost through a slight displacement of the core Si atom along $\langle 110 \rangle$. The angle between the central N—Si bond and $\langle 001 \rangle$ is 13° . The structure can be understood as a pair of N and Si atoms sharing a lattice site, and is shown schematically in Fig. 1(b). As one might expect, the N atom has threefold coordination. The

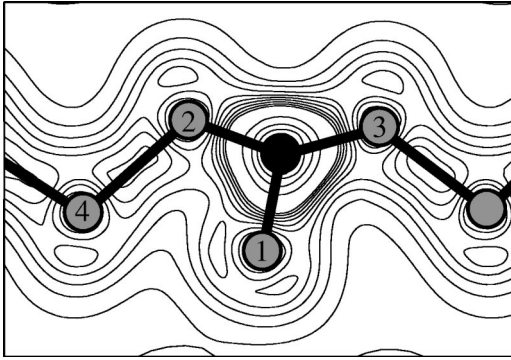


FIG. 2. A contour plot of the charge density in the $(1\bar{1}0)$ mirror plane of the neutral N_i center in silicon. The gray and black circles indicate Si and N sites, respectively. The horizontal and vertical axes are $[110]$ and $[001]$, respectively.

charge density in the mirror plane is shown in Fig. 2. This confirms that there is weak bonding interaction with the nearest Si neighbors, labeled 2 and 3 in Figs. 1(b) and 2, and none between the atoms labeled 1 and 4, as suggested in Ref. 47. The structure is similar to that of the carbon interstitial which possesses C_{2v} symmetry in all the three charge states.^{60,61} The distortion along $\langle 110 \rangle$ does not occur in the positive charged center. The split-interstitial ground-state structure of N_i is in agreement with previous work,^{31,32} but it is not clear whether the small distortion from C_{2v} was always considered. The formation energy of N_i is very close to that of N_s , and hence one would expect similar equilibrium concentrations.

For the stable neutral defect, we find that the three N—Si bond lengths are very similar to each other: 1.72, 1.76, and 1.77 Å, the $\sim\langle 001 \rangle$ bond being the shortest. These are only around 5–7% shorter than the sum of the covalent radii of N and Si (75 and 111 pm, respectively). The Si—Si distances from the central Si atom are 2.27, 2.27, and 2.60 Å, where the long “bond” leads to the over coordination. These values deviate from the bulk silicon by just 2%, 2%, and 11%. The energy of the split interstitial constrained to C_{2v} symmetry is around 0.1 eV higher than the ground-state structure, in broad agreement with a previous study.³²

The local vibrational modes (LVM’s) of the C_{1h} defect are listed in Table I. The two higher-frequency modes are made up from N—Si stretch modes, and are confined to the plane of the defect. The lower lying mode is localized mostly

TABLE I. Local vibrational modes and their symmetries for the C_{1h} N_i defect (cm^{-1}). All modes are IR and Raman active due to the low symmetry. The Si isotopes refer to the core Si atom.

Isotopes	Frequencies (symmetries)		
$^{14}\text{N}^{28}\text{Si}$	550 (A'')	773 (A')	885 (A')
$^{15}\text{N}^{28}\text{Si}$	550 (A'')	754 (A')	862 (A')
$^{14}\text{N}^{29}\text{Si}$	547 (A'')	771 (A')	884 (A')
$^{15}\text{N}^{29}\text{Si}$	547 (A'')	752 (A')	860 (A')
$^{14}\text{N}^{30}\text{Si}$	544 (A'')	769 (A')	882 (A')
$^{15}\text{N}^{30}\text{Si}$	544 (A'')	750 (A')	859 (A')

on the central Si atom and consists of the Si atom interacting with its two close-by Si neighbors. The energy associated with the calculated local modes is comparable to the barrier between the two equivalent C_{1h} structures. This suggests that tunneling effects may be significant and the effective symmetry would then be C_{2v} .

A competing structure places the N interstitial into the bond center [Fig. 1(c)], which is the preferred location for an isolated interstitial-oxygen impurity in silicon.^{62,63,51} In our calculations, the trigonal bond-centered structure possesses compressed N—Si bonds of 1.62 Å. This highly strained system can be relaxed by puckering the Si—N—Si bond, and thus relaxing the symmetry from D_{3d} to C_{1h} , C_2 , or no symmetry. We find the lowest energy bond-centered defect possesses a Si—N—Si bond angle of 135° , and Si—N bond lengths of 1.66 and 1.67 Å. For the C_2 structure, the nitrogen atom is displaced by 0.8 Å along $\langle \bar{1}10 \rangle$ [see Fig. 1(c)], reducing its energy by 0.13 eV. The displacement and energy drop are very similar in the C_{1h} geometry, suggesting that there is no strong preferential direction for the bucking. The low energy suggests that tunneling is possible between equivalent minima and the defect assumes D_{3d} symmetry.

The energy of the bond-centered neutral interstitial is only ~ 0.5 eV higher than that of the split interstitial and since the bond-center structure lies on the diffusion path connecting two split-interstitial structures, it supports previous modeling studies⁴⁷ indicating a relatively fast diffusing species. A crude estimate of the diffusion barrier comes from the energy difference of the bond-centered species and the split interstitial, i.e., around 0.5 eV. This suggests that the interstitial is mobile at room temperature like that of the boron and carbon interstitials, but in strong contrast with oxygen.

The interstitial at the nonbonded hexagonal and tetrahedral sites have energies 2.37 and 2.06 eV, respectively, in comparison with the ground-state structure. These structures can, therefore, be discounted on energy grounds, and previous studies have indicated that these sites are unstable in the absence of a symmetry constraint.⁴⁷

We have also examined various charge states. In all cases, we find that the $\langle 001 \rangle$ split interstitial is the lowest in energy. Using the approach outlined in Sec. II, we find that this structure possesses a donor level around $E_v + 0.5$ eV and an acceptor level around $E_c - 0.2$ eV. These results are in line with previous studies using a slightly different method based on formation energies.³¹

B. The nitrogen di-interstitial pair, (N_i-N_i)

It is known that this is the dominant nitrogen defect in Si, possesses C_{2h} symmetry, and is stable to about 800°C .³⁰ The structure is shown in Fig. 3(b), where the nitrogen atoms and two silicon atoms form a square.³⁰ The binding energy of the two N_i is found here to be 3.67 eV in reasonable agreement with the value obtained previously.^{31,32}

The large binding energy coupled with the high mobility of the isolated nitrogen interstitial is consistent with the observation that the (N_i-N_i) is the dominant nitrogen species at the growth temperatures $\sim 1400^\circ\text{C}$. The calculated LVM’s of the defect are given in Table II, where they are compared

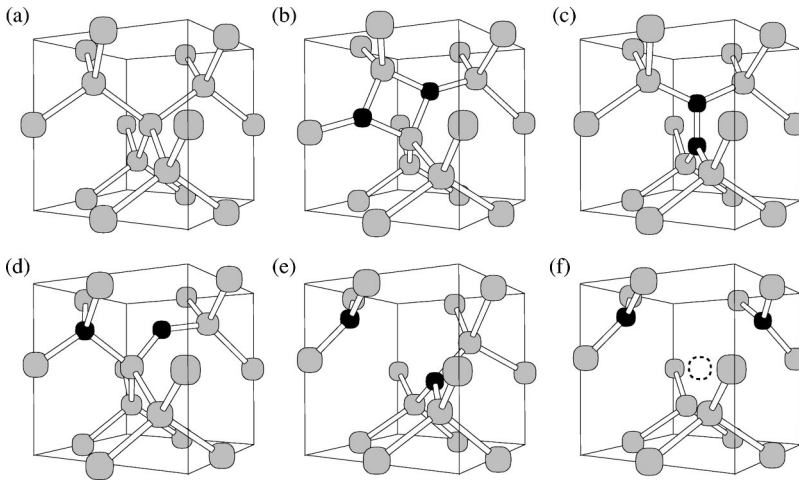


FIG. 3. Schematic representation of defects containing two N impurities. Black and gray circles represent the N and Si atoms, respectively. (a) Fragment of Si lattice, (b) the C_{2h} (N_i-N_i) complex, (c) the D_{2d} , moleculelike split interstitial (N_i-N_s), (d) the N_s -bond-centered N_i complex, (e) (N_s-N_s), and (f) the (N_s-N_s) V complex. The vacant site in (f) is indicated schematically by the dashed circle.

with experimental data. There are two IR-active and two Raman-active local modes. The error in the calculated frequencies is around 1% or less and is a much better agreement than previous studies.³⁰ The effect of Si isotopes is to shift the two lower modes by around 2 and 4 cm^{-1} for ^{29}Si and ^{30}Si , respectively, with a smaller effect ($\leq 1 \text{ cm}^{-1}$) on the higher-frequency modes.

Our calculations show that the defect does not possess any deep donor or acceptor levels.

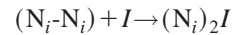
An alternative possible structure is composed of split interstitials at next-nearest-neighbor sites. This is called the Humble ring. This structure is around 2 eV higher in energy than the C_{2h} defect. Another candidate is based on the lowest-energy di-self-interstitial model of Kim *et al.*⁶⁴ In the nitrogen-containing analogous structure, an interstitial pair of nitrogen atoms along $\langle 110 \rangle$ are placed near an interstitial-Si atom. This is 4.5 eV higher in energy than the C_{2h} defect. A third alternative where the N interstitials lie in parallel bond centers and reconstruct to form a π -bonded structure, similar to that of the ground-state di-self-interstitial in diamond⁶⁵ is 3.5 eV higher in energy. We conclude that the C_{2h} structure shown in Fig. 3(b) is the stable form of the di-interstitial.

TABLE II. Local vibrational modes and their symmetries for the most stable interstitial nitrogen pair (cm^{-1}). Modes that are infrared or Raman active by symmetry are denoted by IR and RA, respectively. Also listed are the experimental values from Ref. 30.

Isotopes	Symmetry	Calculated	Activity	Observed	% Error
$^{14}\text{N}^{14}\text{N}$ (C_{2h})	A_g	1070.0	RA		
	B_u	967.8	IR	962.1	0.6
	B_u	772.9	IR	765.6	1.0
	A_g	743.1	RA		
$^{14}\text{N}^{15}\text{N}$ (C_{1h})	A'	1056.0	IR, RA		
	A'	952.5	IR, RA	946.9	0.6
	A'	766.5	IR, RA	758.5	1.1
	A'	731.8	IR, RA		
$^{15}\text{N}^{15}\text{N}$ (C_{2h})	A_g	1037.8	RA		
	B_u	941.4	IR	936.3	0.5
	B_u	755.4	IR	748.3	0.9
	A_g	725.4	RA		

C. (N_i-N_i)-self-interstitial complexes

Since nitrogen appears to reduce swirl defects linked to self-interstitial aggregates,^{28,46,66} we have examined complexes formed when self-interstitials are added to (N_i-N_i). Such aggregates may play a role where there is an excess of self-interstitials in the lattice, such as during oxygen precipitation or irradiation. The lowest energy form found for a $N_i + N_i + I$ complex, where I represents the self-interstitial, is depicted schematically in Fig. 4. This is in agreement with earlier studies.²⁶ The structure can be thought of as the tri-self-interstitial structure assigned to the W-photoluminescence center,⁶⁷ but where two of the self-interstitials have been replaced with N. The resulting structure has C_{1h} symmetry. The reaction



is exothermic by 1 eV assuming a formation energy for the isolated neutral self-interstitial of 3.4 eV.⁶⁸ This binding energy, which is close to that derived by Kageshima *et al.*,²⁶ is relatively small when compared to, for example, the binding energy of (N_i-N_i). Nevertheless, this result shows that N pairs can act as shallow trap for self-interstitials. Alternative structures based on the O3 EPR center in diamond,^{65,69} or the compact structures seen for self-interstitials aggregates^{70,71} have much higher energies.

The structure gives rise to a number of LVM's above the Raman frequency, as indicated in Table III. The effect of Si isotopic substitution is relatively small ($< 2 \text{ cm}^{-1}$), and has

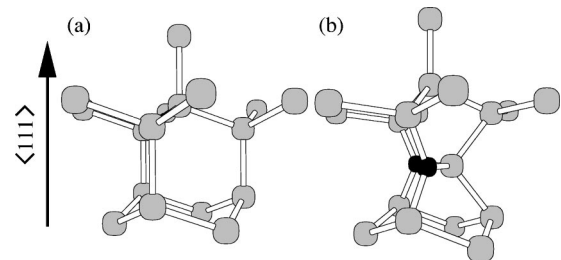


FIG. 4. Schematic representation of (N_i) $_2I$ complex (b). Black and gray circles represent the N and Si atoms, respectively. Also shown in (a) is a section of defect-free material for comparison.

TABLE III. Local vibrational modes and their symmetries for $(N_i)_2I$ (cm^{-1}). Modes are all infrared and Raman active by symmetry. The Si isotopes refer to the atom bonded to both N atoms.

Isotopes	Frequencies						
$^{14}\text{N}^{14}\text{N}^{28}\text{Si}$	566.3	570.4	574.8	810.4	834.8	936.2	947.6
$^{14}\text{N}^{15}\text{N}^{28}\text{Si}$	566.3	570.1	574.8	796.4	827.7	915.3	943.0
$^{15}\text{N}^{15}\text{N}^{28}\text{Si}$	566.3	569.8	574.8	790.5	812.5	910.9	921.9
$^{14}\text{N}^{15}\text{N}^{29}\text{Si}$	563.4	568.5	572.1	807.4	833.3	936.2	947.6
$^{15}\text{N}^{15}\text{N}^{30}\text{Si}$	560.9	566.7	569.7	804.7	832.0	936.2	947.5

been neglected in all cases other than the self-interstitial atom bonded to both N impurities.

We predict that $(N_i)_2I$ does not possess an acceptor level, and a single-donor level lies around $E_v + 0.2$ eV.

We have also examined a candidate structure for $(N_i)_2I_2$ based on the tetra-self-interstitial, which in the positive-charge state is likely to be responsible for the B3 EPR center.⁷² This structure is not bound when compared to the ground-state structure of (N_i-N_i) and an isolated di-self-interstitial. An alternative structure might exist with lower energy.

D. Substitutional nitrogen, N_s

As stated above, it has been established by electron paramagnetic resonance that the neutral substitutional-nitrogen defect has trigonal symmetry,³⁴ and this has been reproduced by various levels of theory.^{30,31,73–75} Although, the energy drop associated with the trigonal distortion varies considerably with the theory used, the most recent *ab initio* calculations suggest a value of around 0.1 eV.³¹ We find that the on-site (T_d symmetry) and distorted (C_{3v} symmetry) defects are within 80 meV of each other, and that this result is independent of basis set, and is also found in a 216-atom unit cell. However, despite the incorrect ordering of the energies of the two symmetries, the small-energy difference is consistent both with previous theory³¹ and with the experimentally obtained energy difference of around 0.1 eV.³⁶ The trigonal form possesses a single dilated bond of 2.89 Å, and three strong Si—N bonds of 1.86 Å, which corresponds very closely to the sum of the Si and N covalent radii, and is in a broad agreement with previous calculations. The formation energy of the neutral substitutional defect is calculated to be around 0.1 eV higher than the isolated interstitial.

The local vibrational modes consist of a doubly degenerate mode around 637 cm^{-1} for ^{14}N with a downward shift of 16 cm^{-1} for ^{15}N . This compares favorably with experimental value of 653 with a shift of 11 cm^{-1} .⁷⁶ The 2–3 % error is within that expected for the method.

The axial component of the piezospectroscopic stress tensor has been evaluated experimentally³⁴ to be -3.14 eV per unit strain. The experimental value is relatively small,⁹² consistent with the ease with which the defect can reorient. We have calculated the theoretical value using an approach described elsewhere,^{51,77} and derive a value of -1.5 eV per unit strain in a reasonable agreement with the measured value. N_s is a tensile defect and would cause a lattice con-

traction which, in principle, could be measured by x rays, assuming a sufficiently high concentration of nitrogen. We find that $\delta a_0/a_0$ would be $\eta[N_s/N_{\text{Si}}]$, where η is -0.05 .

In the neutral charge state, the highest occupied level is orbitally nondegenerate state as in diamond, and *not* a degenerate e level. The spin density is localized on the unique Si neighbor to N (40%) and weakly on N (4%) which agree to within a factor of 2, typical for our method, with experimental values of 73% and 7%, respectively.³⁴ The p components on the Si and N atoms are calculated to be 91% and 79%, respectively, which compares favorably with the experimental values of 88% and 72%.³⁴

We have calculated the donor and acceptor levels for N_s using the method described in Sec. II. In contrast with values previously obtained from theory,³¹ we find a donor level around $E_v + 0.5$ eV and an acceptor level around $E_c - 0.4$ eV. There are likely to be corrections to these levels of the order of 0.2 eV.⁷⁸ The donor level is consistent with the deep nature of the level associated with the SL5 EPR center.³⁴

E. Substitutional-nitrogen–lattice vacancy complex, (N_sV)

We have considered a structure, where a substitutional-N defect borders a single lattice vacancy. This is analogous to the phosphorus-vacancy complex or E center which is known from EPR to have C_{1h} symmetry when neutral.²⁰ In the one-electron picture, the neutral trigonal center can be described as $a_1^2 e^1$ corresponding to a 2E ground state, as is the case in diamond.⁷⁹ This is expected to lead to a Jahn-Teller distortion leading to pairing of two Si dangling bonds. We find no significant-energy reduction found when two of the Si neighbors are paired leading to a defect with C_{1h} symmetry. This possibly represents a failure in the density-functional supercell approach for treating vacancylike reconstructions. However, the unique Si-Si pair in the planar version is around 3.16 Å compared to 3.35 Å in the trigonal case, suggesting the formation of a weak reconstruction.

The spin density in the neutral charge state is localized mainly on the Si-dangling bonds, with around 1% located on the N atom and less than that found for N_s . If any distortion from trigonal symmetry is small or dynamic in nature, this might therefore represent a model for either the SL6 or SL7 EPR center, in which the spin density on the N atom is also less than in SL5.

Assuming a vacancy formation energy as 3.3 eV,²⁴ we find a binding energy of 1.6 eV for V with N_s , close to a value found previously.⁴⁹ This value is the same as the binding energy of oxygen with a vacancy.⁵¹ Moving the nitrogen atom to a second-neighbor site to the vacancy increases the energy by 1.3 eV. Thus, we conclude that nitrogen does indeed border the vacancy, as for phosphorus, but in contrast with boron where the next-nearest-neighbor location is believed to be most stable for the neutral defect.⁸⁰

The defect possesses single and double acceptor levels which are calculated to lie at around $E_c - 0.7$ eV and $E_c - 0.5$ eV, respectively. The small separation between the first and second donor levels is probably unrealistic and a failing of the method.⁷⁸

TABLE IV. Local vibrational modes for (N_i-N_i) in the D_{2d} configuration (cm^{-1}). The notation follows that in Table II.

Isotopes	Symmetry	Frequency	Activity
$^{14}\text{N}^{14}\text{N}$ (D_{2d})	A_1	1003.6	RA
	E	774.1	IR, RA
	B_2	573.4	IR, RA
$^{14}\text{N}^{15}\text{N}$ (C_{2v})	A_1	987.0	IR, RA
	B_2	773.9	IR, RA
	B_1	753.4	IR, RA
$^{15}\text{N}^{15}\text{N}$ (D_{2d})	A_1	569.1	IR, RA
	A_1	969.8	RA
	E	753.3	IR, RA
	B_2	565.3	IR, RA

As with the substitutional defect, (N_sV) possesses a pair of degenerate local vibrational modes above the Raman frequency. These are calculated to lie at 663 cm^{-1} and 646 cm^{-1} for ^{14}N and ^{15}N , respectively. Substituting a single silicon neighbor of the N atom with ^{29}Si or ^{30}Si splits the degeneracy and lowers one mode by around 1.5 cm^{-1} or 2.9 cm^{-1} , respectively.

F. (N_i-N_i) -vacancy complexes

We considered two different structures for the interaction between two N interstitials and a single lattice vacancy. In the first, the pair of nitrogen atoms lay at the center of the vacancy making equivalent bonds with all four silicon neighbors [see Fig. 3(c)]. The structure has D_{2d} point-group symmetry and has been suggested previously.^{30–32} We find the binding energy E^b of the interstitial pair with a vacancy to be 1.3 eV, taking the formation energy of the vacancy to be 3.3 eV, as before. The equilibrium concentration of these defects formed by the reaction $(N_i-N_i) + V \rightarrow (N_i-N_s)$ is then given by⁹³

$$[(N_i-N_s)] = \frac{[V][(N_i-N_i)]}{[Si]} \exp(E^b/k_B T),$$

where $[X]$ is the concentration of species X . $[(N_i-N_s)]$ is then negligible compared to the nitrogen pair at 1400°C if the vacancy concentration is $\leq 10^{15} \text{ cm}^{-3}$. However, during nonequilibrium cool down conditions,⁹⁴ these defects might be formed in measurable quantities, and can be detected via their LVM's (see below).

The N-N bond length is calculated to be 1.43 \AA , which is much longer than that in the N_2 molecule (1.1 \AA), and the surrounding N—Si bonds are 1.80 \AA . The Si—N bonds are around 15% longer than that in a Si-N crystal, but are close to the sum of appropriate covalent radii.

The calculated LVM's for this structure are given in Table IV. In particular, we found that there are two IR active modes above the Raman frequency. Isotopic substitution of the Si neighbors lowers the 753.4 cm^{-1} mode by around 1 and 2 cm^{-1} for ^{29}Si and ^{30}Si , respectively, and splits the E mode by around the same amount. There is no appreciable

TABLE V. Local vibrational modes of the N_s-N_i complex (cm^{-1}). The low symmetry renders all modes infrared and Raman active.

Isotopes ($N_{\text{sub}}N_{\text{bond}}$)	Frequencies		
$^{14}\text{N}^{14}\text{N}$	1163.1	672.8	592.8
$^{14}\text{N}^{15}\text{N}$	1131.9	667.9	592.5
$^{15}\text{N}^{14}\text{N}$	1163.0	669.9	580.2
$^{15}\text{N}^{15}\text{N}$	1131.8	664.8	580.0

affect on the 1003.6 cm^{-1} mode. The defect does not possess a deep donor or acceptor level, but might possess shallow levels.

In a second form of the defect, one nitrogen atom lies at the substitutional site and the other to the bond-center site [see Fig. 3(d)]. This has been claimed to be competitive in energy,³¹ however, we find that the energy of this structure is about 0.6 eV higher than the D_{2d} form. Vibrational modes for this alternative geometry are given in Table V. One can understand these modes as they resemble those of the isolated bond-centered defect (the high-frequency mode), and those of N_s where the E mode is split by $80\text{--}90 \text{ cm}^{-1}$.

G. Substitutional-nitrogen pair, (N_s-N_s)

To investigate more stable vacancy nitrogen complexes, we considered a reaction where a divacancy interacts with N_i-N_i forming a close-by pair of substitutional-nitrogen defects. Similar pairs are known to form for P,⁸¹ and B (Ref. 82) and nitrogen pairs form the highly stable “A center” in diamond.⁸³ The symmetry of the defect is D_{3d} [see Fig. 3(e)]. The relaxed N—Si bond lengths are 1.83 \AA and the two nitrogen atoms are separated by 3.51 \AA . This agrees with previous calculations.^{75,32} The Si—N—Si angle is 118° and the Si—N bonds are 98° from the trigonal axis, indicating that the nitrogen atoms are nearly sp^2 hybridized.

The reactions $(N_i-N_s) + V \rightarrow (N_s-N_s)$ and $(N_i-N_i) + V_2 \rightarrow (N_s-N_s)$ are exothermic by around 3.7 and 3.4 eV, respectively, using $E^f(V) = 3.3 \text{ eV}$ and the binding energy of two vacancies in V_2 to be 1.6 eV.²⁴ These values are close to the previous results,³² especially given the uncertainties in $E^f(V)$ and $E^b(V_2)$. The formation energy of this substitutional-N pair is 1.6 eV higher than the (N_i-N_i) defect, and hence the *equilibrium* concentration of this defect at 1400°C is negligible mainly because the concentration of V_2 is negligible. However, in the presence of a supersaturation of vacancies, this defect is the most stable aggregate of nitrogen so far considered. Such defects might easily form in implantation experiments.

The energy second derivatives of the N atoms and their neighbors were then evaluated and their LVM's calculated. The results are given in Table VI. We found just one IR-active mode and one Raman-active mode above the Raman frequency. The affect of Si isotopes on these modes is less than 2 cm^{-1} .

Cunha *et al.*⁷⁵ found by using hydrogen terminated clusters containing just the defect and six host atoms that the

TABLE VI. Local vibrational modes of (N_s-N_s) (cm^{-1}). The notation follows that in Table II.

Isotopes	Symmetry	Frequency	Activity
$^{14}\text{N}^{14}\text{N}$	E_u	668.6	IR
(D_{3d})	E_g	666.8	RA
$^{15}\text{N}^{14}\text{N}$	E	667.8	IR, RA
(C_{3v})	E	650.5	IR, RA
$^{15}\text{N}^{15}\text{N}$	E_u	651.5	IR
(D_{3d})	E_g	649.6	RA

substitutional pair distorts to a C_{3v} structure in the positive-charge state, such that the hole was localized on only one of the N atoms. We do not find this to be the case in our calculations, with a C_{3v} starting structure relaxing to D_{3d} , and we suspect that the earlier result was due to the size of their system. The defect does not possess a deep-donor level, but the calculations suggest that an acceptor level may lie around $E_c - 0.2$ eV. It is interesting to note that this is consistent with all the available data regarding the ABC center—the “isoelectronic” ($S=0$) nature, the link with nitrogen, the $\langle 111 \rangle$ symmetry, the shallow acceptorlike nature, the anticipated thermal stability, and the likely low concentration. Furthermore, the assignment does not depend on the presence of a specific acceptor impurity, such as Al. We, therefore, tentatively assign (N_s-N_s) to the ABC center. This assignment could be put on a firmer footing if evidence could be found for the presence of a pair of *equivalent* nitrogen atoms in the center. This might be achieved if mixed nitrogen isotopic studies were carried out on the PL line in a similar way to the I2 optical center associated with a pair of boron atoms.⁸⁴

Finally, although the available experimental data appears to make it an unlikely candidate, we have examined the possibility that the ABC center is a nearest-neighbor pair made up from substitutional N and Al. This defect is, as with (N_s-N_s) , found to exhibit a shallow acceptor level and possess trigonal symmetry. The complex is bound by ~ 1.3 eV, which is larger than the binding of substitutional-nitrogen pair, and is broadly consistent with the thermal stability of the ABC defect. We cannot rule out this complex as the source of the ABC lines based on these calculations, but it requires that Al is a residual impurity in nominally Al-free Si.

H. The (N_s-N_s) -vacancy complexes

We have added a further lattice vacancy to the nitrogen pair, and following the structure of the (N_sV) defect, we have assumed that both N atoms border the vacancy. This defect is analogous to one in diamond which as a neutral and negative center gives the $H2$ and $H3$ optical bands respectively.^{85–87} In the case in Si, the spin-zero C_{2v} symmetry defect [Fig. 3(f)] relaxes so that each of the nitrogen atoms is approximately coplanar with their three Si neighbors. The reconstruction of the other pair of Si bonds is weak as their bond length is 3 \AA and probably underestimated by the theory. The binding energy of the vacancy to (N_s-N_s) is around 1.5 eV, consistent with the previous theory.²⁶

TABLE VII. Local vibrational modes of $(N_s-N_s)V$ (cm^{-1}). The notation follows that in Table II.

Isotopes	Symmetry	Frequency	Activity
	A_1	672.0	IR, RA
$^{14}\text{N}^{14}\text{N}$	B_1	664.9	IR, RA
(C_{2v})	B_2	664.8	IR, RA
	A_2	662.9	RA
	A'	669.1	IR, RA
$^{14}\text{N}^{15}\text{N}$	A'	664.0	IR, RA
(C_{1h})	A''	650.4	IR, RA
	A''	646.8	IR, RA
	A_1	654.5	IR, RA
$^{15}\text{N}^{15}\text{N}$	B_1	647.9	IR, RA
(C_{2v})	B_2	647.7	IR, RA
	A_2	645.8	RA

The local vibrational modes are given in Table VII. They closely resemble those of (N_sV) , as one would expect since the two N atoms in this complex exist in very similar environments to that of the nitrogen impurity in (N_sV) . As with (N_sV) , the effect of isotopic substitution for the silicon neighbors of the two N atoms is modest ($\leq 2 \text{ cm}^{-1}$).

This defect possesses a deep single acceptor level, which we estimate to lie around $E_c - 0.5$ eV, but no donor level.

Finally, we investigated the addition of a vacancy to $(N_s-N_s)V$. It is likely that this forms a vacancy chain along $\langle 110 \rangle$ with the N atoms replacing the end Si atoms with dangling bonds. The remaining dangling bonds can be paired as in the divacancy. The defect was investigated in a 128 atom cell and has C_{2h} symmetry. The relaxed structure is stable with a respect to the reaction $(N_s-N_s) + V_2 \rightarrow (N_s-N_s)V_2$ which is exothermic by around 1.5 eV. This energy must be uncertain as the structure of vacancy defect is not well described by the supercell method. An additional vacancy is bound to $(N_s-N_s)V$ by 1.6 eV. The reconstructed Si bonds have lengths of 2.8 \AA and the N atoms relax to form approximately planar structures with their three Si neighbors, in a manner similar to (N_sV) and $(N_s-N_s)V$.

The stability of the defect can be understood since the geometry leaves it effectively with no dangling bonds. Normally, the multivacancy defect reconstructs by pairs to minimize the number of dangling bonds that remain,⁸⁸ forming a trapping site for impurities, particularly hydrogen. In the current defect, the two nitrogen atoms tie off these two dangling bonds with all the Si atoms forming reconstructed bonds. The reconstructed bonds are around 2.8 \AA , and the N atoms relax to form approximately planar structures with their three Si neighbors, in a manner similar to (N_sV) and $(N_s-N_s)V$.

Following this generic mechanism, it seems likely that there are also bound $(N_s-N_s)V_n$ structures with $n > 2$, similar to vacancy chains with hydrogenated ends,⁸⁸ although we have not modeled such complexes. This is in line with the trend found by Kageshima *et al.*,²⁶ although some of the $(N_i-N_i)-V_n$ structures investigated in that study are not known.

TABLE VIII. Relative formation energies per N atom for the various configurations discussed in this report (eV). The zero of energy is defined by that of the (N_i-N_i) defect.

Defect	$2(N_i-N_i)$	(N_i-N_i)	(N_s-N_s)	(N_i-N_s)	$(N_i)_2I$
E^f/N atom	-0.06	0.00	0.79	0.99	1.25
Defect	$(N_s-N_s)V$	N_i	N_s	$(N_s-N_s)V_2$	(N_sV)
E^f/N atom	1.71	1.83	1.99	2.54	3.71

IV. DISCUSSION AND CONCLUSIONS

Table VIII gives the formation energy per N atom relative to that of the dominant center, (N_i-N_i) , of the complexes investigated here. It is clear that the only defect which is more stable than (N_i-N_i) is made up from a pair of (N_i-N_i) , but this possesses a very small binding energy and may then not be significant.

Therefore, it is clear that nitrogen di-interstitial pairs (N_i-N_i) will dominate the *equilibrium* concentration of nitrogen defects at the growth temperature. A concentration of nitrogen $\sim 10^{15} \text{ cm}^{-3}$ is likely to be comparable with or exceed the vacancy concentration. During cooling down, the thermal equilibrium concentrations of vacancies drops to zero, but it seems that the vacancies do not follow their equilibrium values and are frozen in as vacancy clusters which eventually make voids, although the details of this aggregation are far from clear.

Where nitrogen is present, during this process (N_i-N_i) could trap a vacancy, divacancy, or even three vacancies forming (N_i-N_s) , (N_s-N_s) , or $(N_s-N_s)V$, with the second structure constituting a particularly stable product. At least within the range examined in this study, a trend of diminishing binding energy of additional vacancies or self-interstitials to the nitrogen dimer seems to occur, but in the presence of a supersaturation of such native defects, a dynamic equilibrium of these centers would be expected.

The calculated LVM's of (N_i-N_i) are in excellent agreement with experiment, and those of N_s are also within 3%. This gives us confidence in the LVM's calculated for other systems, and it is hoped that this data might lead to the identification of these other N-related centers. A number of nitrogen related modes are known to occur after implantation⁸⁹ but have not yet been assigned. A mode at 690 cm^{-1} has been associated with N_i (Ref. 90), but this seems too low a frequency according to our calculations (see Table I). Instead, it is closer to a mode found for (N_sV) at 663 cm^{-1} . The downward shift of the two modes with ^{15}N are exactly the same at 17 cm^{-1} . Indeed, we find N_i to be a highly mobile defect, whereas the 663 cm^{-1} mode disappears by 600°C . Modes due to unknown defects at 782 and 790 cm^{-1} are in the region of a mode found here for (N_i-N_s) at 774 cm^{-1} (Table IV). Again the calculated isotope shifts with ^{15}N , 21 cm^{-1} , is close to that of the 782 cm^{-1} mode at

20 cm^{-1} . This defect disappears at 400°C . It is clear that much could be learned through a careful infrared study of these modes.

The various defects examined can also be characterized by the electrical levels they possess. The deep-donor level of N_s is in agreement with experiment,³⁴ and in contrast with previous theory.³¹ The $(N_s-N_s)V$ and $(N_s-N_s)V_2$ centers both possess relatively deep acceptor levels that might be correlated with the $T1$ DLTS center at $E_c - 0.42 \text{ eV}$, although further corroboration would be required from experiment, such as EPR. However, we note that N_s is calculated to possess an acceptor level in this area, and the concentration of $T1$ (10^{13} – 10^{14} cm^{-3}) is close to that of $SL5$.³⁴

The E_2 and E_3 defects occur in very low concentrations. This may be due to a high-formation energy, or perhaps due to the formation of aggregated defects such as nitrogen-vacancy or nitrogen-self-interstitial complexes. In the absence of more detailed experimental data, such as might be obtained from EPR spectra, a firm assignment of these two deep levels is problematic. However, the location of the levels in the gap are consistent with both N_i and (N_s-N_s) . Due to the accuracy of the theoretical approach, one cannot rule out the acceptor levels of the (N_sV) or $(N_s-N_s)V$.

We have shown that the spin localization of N_s is consistent with the interpretation of the EPR data, especially that of the p -orbital components on the N and the unique Si atom. Furthermore, we have a reasonable agreement in the piezospectroscopic stress response of N_s .

The identity of the N-related EPR centers, $SL6$ and $SL7$, remains unclear. The EPR evidence points to a single nitrogen atom, together with an intrinsic defect as coimplantation with carbon and oxygen did not enhance its production. One possibility is (N_sV) and NV_2 for $SL6$ and $SL7$, respectively. The binding energy of (N_sV) is high—around 1.6 eV —and consistent with a thermal stability of $SL6$ of around 400°C (The OV center with a similar binding energy anneals around 300°C). It also is consistent with a calculated low spin density on N. The symmetry of (N_sV) would be nearly trigonal if the distortion to C_{1h} was weak. Alternatively, a complex of nitrogen with a hexavacancy⁹¹ could possess trigonal symmetry and a spin density mainly on Si. Clearly, however, further work and especially stress alignment studies is required on the centers to clarify their identity.

Finally, we comment on the ABC luminescent center seen in N-doped material. As pointed out above, there are a number of properties that are common to the photoluminescence center and (N_s-N_s) . These include the presence of nitrogen, their thermal stabilities (the ABC defect is stable to 1000°C),³⁷ their axial symmetry and the acceptor level close to E_c . However, the symmetry of (N_s-N_s) is D_{3d} and not C_{3v} as assumed for the ABC center. We suggest that the presence of a second equivalent nitrogen atom in the defect could be tested by mixed nitrogen isotopic studies on the shift of the zero-phonon lines of the ABC center.

- ¹A.L. Parakhonsky, E.B. Yakimov, and D. Yang, *J. Appl. Phys.* **90**, 3642 (2001).
- ²F. Berg Rasmussen, S. Öberg, R. Jones, C. Ewels, J. Goss, J. Miro, and P. Deák, *Mater. Sci. Forum* **196-201**, 791 (1995).
- ³R. Jones, C. Ewels, J. Goss, J. Miro, P. Deák, S. Öberg, and F. Berg Rasmussen, *Semicond. Sci. Technol.* **9**, 2145 (1994).
- ⁴H. Navarro, J. Griffin, J. Weber, and L. Gentzel, *Solid State Commun.* **58**, 151 (1986).
- ⁵M. Suezawa, K. Sumino, H. Harada, and T. Abe, *Jpn. J. Appl. Phys., Part 2* **25**, L859 (1986).
- ⁶M. Suezawa, K. Sumino, H. Harada, and T. Abe, *Jpn. J. Appl. Phys., Part 1* **27**, 62 (1988).
- ⁷B.J. Heijmink Liesert, T. Gregorkiewicz, and C.A.J. Ammerlaan, *Phys. Rev. B* **47**, 7005 (1993).
- ⁸Yu.V. Martynov, T. Gregorkiewicz, and C.A.J. Ammerlaan, *Phys. Rev. Lett.* **74**, 2030 (1995).
- ⁹C.P. Ewels, R. Jones, S. Öberg, J. Miro, and P. Deák, *Phys. Rev. Lett.* **77**, 865 (1996).
- ¹⁰V.V. Voronkov, M. Porrini, P. Collareta, M.G. Pretto, R. Scala, R. Falster, G.I. Voronkova, A.V. Batunina, V.N. Golovina, L.V. Arapkina, A.S. Guliaeva, and M.G. Milvidski, *J. Appl. Phys.* **89**, 4289 (2001).
- ¹¹K. Sumino, I. Yonenaga, M. Imai, and T. Abe, *J. Appl. Phys.* **54**, 5016 (1983).
- ¹²M.I. Heggie, R. Jones, and A. Umerski, *Phys. Status Solidi A* **138**, 383 (1993).
- ¹³M. Akatsuka and K. Sueka, *Jpn. J. Appl. Phys., Part 1* **40**, 1240 (2001).
- ¹⁴K. Nakai, Y. Inoue, H. Yokota, A. Ikari, J. Takahashi, A. Tachikawa, K. Kitahara, Y. Ohta, and W. Ohashi, *J. Appl. Phys.* **89**, 4301 (2001).
- ¹⁵X. Ma, X. Yu, R. Fan, and D. Yang, *Appl. Phys. Lett.* **81**, 496 (2002).
- ¹⁶C. Murthy, K. Lee, R. Rengarajan, O. Dokumaci, P. Ronsheim, H. Tews, and S. Inaba, *Appl. Phys. Lett.* **80**, 2696 (2002).
- ¹⁷H. Ishii, S. Shiratake, K. Oka, K. Motonami, T. Koyama, and J. Izumitani, *Jpn. J. Appl. Phys., Part 2* **35**, L1385 (1996).
- ¹⁸W. Ohashi, A. Ikari, Y. Ohta, A. Tachikawa, H. Deai, H. Yokota, and T. Hoshino, in *Extended Abstracts No. 1, The 46th Spring Meeting* (Japan Society of Applied Physics, Tokyo, 1999), p. 468.
- ¹⁹S. Dannefaer, P. Mascher, and D. Kerr, *Phys. Rev. Lett.* **56**, 2195 (1986).
- ²⁰G.D. Watkins and J.W. Corbett, *Phys. Rev.* **134**, A1359 (1964).
- ²¹J.A. Van Vechten, *Phys. Rev. B* **33**, 2674 (1986).
- ²²H. Bracht, N.A. Stolwijk, and H. Mehrer, *Phys. Rev. B* **52**, 16 542 (1995).
- ²³J.L. Mercer, J.S. Nelson, A.F. Wright, and E.B. Stechel, *Modell. Simul. Mater. Sci. Eng.* **6**, 1 (1998).
- ²⁴M. Kaukonen, R. Jones, S. Öberg, and P.R. Briddon, *Phys. Rev. B* **64**, 245213 (2001).
- ²⁵V.V. Voronkov and R. Falster, *J. Electrochem. Soc.* **149**, G167 (2002).
- ²⁶H. Kageshima, A. Taguchi, and K. Wada, in *Defect and Impurity Engineered Semiconductors and Devices III*, edited by S. Ashcok, J. Chevallier, N.M. Johnson, B.L. Sopori, and H. Okushi, MRS Symposia Proceedings No. 719 (Materials Research Society, Pittsburgh, 2002), p. 3.3.
- ²⁷L.S. Adam, M.E. Law, S. Szpala, P.J. Simpson, D. Lawther, O. Dokumaci, and S. Hegde, *Appl. Phys. Lett.* **79**, 623 (2001).
- ²⁸W. von Ammon, R. Hölzl, J. Virbulis, E. Dornberger, R. Schmolke, and D. Gräf, *J. Cryst. Growth* **226**, 19 (2001).
- ²⁹X. Yu, D. Yang, X. Ma, J. Yang, L. Li, and D. Que, *J. Appl. Phys.* **92**, 188 (2002).
- ³⁰R. Jones, S. Öberg, F. Berg Rasmussen, and B. Bech Nielsen, *Phys. Rev. Lett.* **72**, 1882 (1994).
- ³¹H. Sawada and K. Kawakami, *Phys. Rev. B* **62**, 1851 (2000).
- ³²H. Kageshima, A. Taguchi, and K. Wada, *Appl. Phys. Lett.* **76**, 3718 (2000).
- ³³K.L. Brower, *Phys. Rev. Lett.* **44**, 1627 (1980).
- ³⁴K.L. Brower, *Phys. Rev. B* **26**, 6040 (1982).
- ³⁵M.E. Newton and J.M. Baker, *J. Phys.: Condens. Matter* **1**, 10 549 (1989).
- ³⁶K. Murakami, H. Kuribayashi, and K. Masuda, *Phys. Rev. B* **38**, 1589 (1988).
- ³⁷J. Weber, W. Schmid, and R. Sauer, *Phys. Rev. B* **21**, 2401 (1980).
- ³⁸H.Ch. Alt and L. Tapfer, *Appl. Phys. Lett.* **45**, 426 (1984).
- ³⁹G. Davies, M. Zafar Iqbal, and E.C. Lightowers, *Phys. Rev. B* **50**, 11 520 (1994).
- ⁴⁰R. Sauer, J. Weber, and W. Zulwhner, *Appl. Phys. Lett.* **44**, 440 (1984).
- ⁴¹H.Ch. Alt and L. Tapfer, in *Proceedings of the 13th International Conference on Defects in Semiconductors, Coronado, California, 1984*, edited by L. C. Kimerling and J. M. Parsey, Jr. [*J. Electron. Mater.* **14a**, 833 (1985)].
- ⁴²J. Wagner and R. Sauer, *Phys. Rev. B* **26**, 3502 (1982).
- ⁴³J.B. Mitchell, J. Shewchun, D.A. Thompson, and J.A. Davies, *J. Appl. Phys.* **46**, 335 (1975).
- ⁴⁴Y. Tokumaru, H. Okushi, T. Masui, and T. Abe, *Jpn. J. Appl. Phys., Part 2* **21**, L443 (1982).
- ⁴⁵N. Fuma, K. Tashiro, K. Kakumoto, and Y. Takano, *Jpn. J. Appl. Phys., Part 1* **35**, 1993 (1996).
- ⁴⁶T. Itoh and T. Abe, *Appl. Phys. Lett.* **53**, 39 (1988).
- ⁴⁷P.A. Schultz and J.S. Nelson, *Appl. Phys. Lett.* **78**, 736 (2001).
- ⁴⁸H. Sawada, K. Kawakami, A. Ikari, and W. Ohashi, *Phys. Rev. B* **65**, 075201 (2002).
- ⁴⁹J.S. Nelson, P.A. Schultz, and A.F. Wright, *Appl. Phys. Lett.* **73**, 247 (1998).
- ⁵⁰R. Jones and P. R. Briddon, in *Identification of Defects in Semiconductors*, edited by M. Stavola, Semiconductors and Semimetals Vol. 51A (Academic, Boston, 1998), Chap. 6.
- ⁵¹J. Coutinho, R. Jones, P.R. Briddon, and S. Öberg, *Phys. Rev. B* **62**, 10 824 (2000).
- ⁵²J.P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13 244 (1992).
- ⁵³G.B. Bachelet, D.R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- ⁵⁴N. Troullier and J.L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ⁵⁵H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ⁵⁶D.A. Liberman, *Phys. Rev. B* **62**, 6851 (2000).
- ⁵⁷M.J.P. Musgrave and J.A. Pople, *Proc. R. Soc. London, Ser. A* **268**, 474 (1962).
- ⁵⁸G. Makov and M.C. Payne, *Phys. Rev. B* **51**, 4014 (1995).
- ⁵⁹J.-W. Jeong and A. Oshiyama, *Phys. Rev. B* **64**, 235204 (2001).
- ⁶⁰G.D. Watkins and K.L. Brower, *Phys. Rev. Lett.* **36**, 1329 (1976).
- ⁶¹P. Leary, R. Jones, and S. Öberg, *Phys. Rev. B* **57**, 3887 (1998).
- ⁶²W.L. Bond and W. Kaiser, *J. Phys. Chem. Solids* **16**, 44 (1960).
- ⁶³J.W. Corbett, R.S. McDonald, and G.D. Watkins, *J. Phys. Chem. Solids* **25**, 873 (1964).

- ⁶⁴J. Kim, F. Kirchoff, W.G. Aulbur, J.W. Wilkins, F.S. Khan, and G. Kresse, *Phys. Rev. Lett.* **83**, 1990 (1999).
- ⁶⁵J.P. Goss, B.J. Coomer, R. Jones, T.D. Shaw, P.R. Briddon, M. Rayson, and S. Öberg, *Phys. Rev. B* **63**, 195208 (2001).
- ⁶⁶T. Abe, H. Harada, and J. Chikawa, in *Oxygen, Carbon, Hydrogen, and Nitrogen in Crystalline Silicon*, edited by J. C. Mikkelsen, Jr., S. J. Pearton, J. W. Corbett, and S. J. Pennycook, Mater. Res. Soc. Symp. Proc. 59 (Materials Research Society, Pittsburgh, 1986), p. 537.
- ⁶⁷B.J. Coomer, J.P. Goss, R. Jones, S. Öberg, and P.R. Briddon, *Physica B* **273–274**, 505 (1999).
- ⁶⁸T.A.G. Eberlein, N. Pinho, R. Jones, B.J. Coomer, J.P. Goss, P.R. Briddon, and S. Öberg, *Physica B* **308–310**, 454 (2001).
- ⁶⁹D.C. Hunt, D.J. Twitchen, M.E. Newton, J.M. Baker, J.K. Kirui, J.A. van Wyk, T.R. Anthony, and W.F. Banholzer, *Phys. Rev. B* **62**, 6587 (2000).
- ⁷⁰M. Gharaibeh, S.K. Estreicher, and P.A. Fedders, *Physica B* **273–274**, 532 (1999).
- ⁷¹A. Bongiorno, L. Colombo, F. Cargnoni, C. Gatti, and M. Rosati, *Europhys. Lett.* **50**, 608 (2000).
- ⁷²B.J. Coomer, J.P. Goss, R. Jones, S. Öberg, and P.R. Briddon, *J. Phys.: Condens. Matter* **13**, L1 (2001).
- ⁷³H.P. Hjalmarson and D.R. Jennison, *Phys. Rev. B* **31**, 1208 (1985).
- ⁷⁴F.G. Anderson, *Phys. Rev. B* **39**, 5392 (1989).
- ⁷⁵C. Cunha, S. Canuto, and A. Fazzio, *Phys. Rev. B* **48**, 17 806 (1993).
- ⁷⁶H.J. Stein, in *Oxygen, Carbon, Hydrogen, and Nitrogen in Crystalline Silicon*, edited by J. C. Mikkelsen, Jr., S. J. Pearton, J. W. Corbett, and S. J. Pennycook, Mater. Res. Soc. Symp. Proc. 59 (Materials Research Society, Pittsburgh, 1986), p. 523.
- ⁷⁷J.P. Goss, R. Jones, and P.R. Briddon, *Phys. Rev. B* **65**, 035203 (2002).
- ⁷⁸J. Coutinho, V. J. B. Torres, R. Jones, and P. R. Briddon, *Phys. Rev. B* (to be published).
- ⁷⁹J.P. Goss, R. Jones, S.J. Breuer, P.R. Briddon, and S. Öberg, *Phys. Rev. Lett.* **77**, 3041 (1996).
- ⁸⁰G.D. Watkins, *Phys. Rev. B* **13**, 2511 (1976).
- ⁸¹E.G. Sieverts, S.H. Muller, and C.A.J. Ammerlaan, *Solid State Commun.* **28**, 221 (1978).
- ⁸²A.K. Tipping and R.C. Newman, *Semicond. Sci. Technol.* **2**, 389 (1987).
- ⁸³B.P. Allen and T. Evans, *Proc. R. Soc. London, Ser. A* **375**, 93 (1981).
- ⁸⁴K. Thonke, N. Bürger, G.D. Watkins, and R. Sauer, in *Proceedings of the 13th International Conference on Defects in Semiconductors, Coronado, California, 1984*, edited by L. C. Kimerling and J. M. Parsey, Jr. [*J. Electron. Mater.* **14a**, 823 (1985)].
- ⁸⁵R. Jones, P.R. Briddon, and S. Öberg, *Philos. Mag. Lett.* **66**, 67 (1992).
- ⁸⁶A. Mainwood, *Phys. Rev. B* **49**, 7934 (1994).
- ⁸⁷G. Davies, M.H. Nazaré, and M.F. Hamer, *Proc. R. Soc. London, Ser. A* **351**, 245 (1976).
- ⁸⁸P. Stallinga, P. Johannesen, S. Herström, K. Bonde Nielsen, B. Bech Nielsen, and J.R. Byberg, *Phys. Rev. B* **58**, 3842 (1998).
- ⁸⁹F. Berg Rasmussen, Ph.D. thesis, Institute of Physics and Astronomy, University of Århus, Denmark, 1994.
- ⁹⁰H.J. Stein, *Appl. Phys. Lett.* **47**, 1339 (1985).
- ⁹¹B. Hourahine, R. Jones, A.N. Safonov, S. Öberg, P.R. Briddon, and S.K. Estreicher, *Phys. Rev. B* **61**, 12 594 (2000).
- ⁹²Substitutional and interstitial oxygen in silicon have principal piezospectroscopic stress tensor elements of 8.8 and -15.2 eV per unit strain, respectively. See Ref. 51, and references therein.
- ⁹³This expression neglects all but configurational entropic terms.
- ⁹⁴Applying equilibrium conditions, the concentration of vacancies at lower temperatures will be reduced and the relative concentration of (N_i-N_s) reduced commensurately.