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Identification of the Dominant Nitrogen Defect in Silicon

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The structure of the dominant N pair defect in Si is determined from channeling, infrared local vibrational mode spectroscopy, and *ab initio* local density functional theory. Channeling experiments show that the N atoms are displaced by 1.1±0.1 Å from lattice sites along ⟨100⟩. Annealing experiments reveal that this N site is associated with two N-related local vibrational modes originating from the N pair. The *ab initio* calculations demonstrate that the pair consists of two neighboring ⟨100⟩ oriented N-Si split interstitials, arranged in an antiparallel configuration, and with four N-Si bonds forming a square lying on {011}.

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Nitrogen in silicon was detected over 30 years ago [1] but the structure and properties of N-related defects have remained enigmatic. There is no consensus on whether the simplest and most prominant N defects are electrically active. Nitrogen complexes can display electrical activity, e.g., an N-related photoluminescence (PL) band has been found at 1.122 eV (a component of the *ABC* system) [2, 3], and N-related electron traps have been detected by deep level transient spectroscopy (DLTS) [4]. However, the identities of these centers are not known. N is also known to complex with C [5], O [6–8], and Al [9] as well as being able to pin dislocations [10, 11]—an effect which may be useful in hardening Si wafers.

The simplest defect, substitutional nitrogen, N_s, gives an electron paramagnetic signal (SL5) [12] whose trigonal symmetry is consistent with N lying off site along ⟨111⟩. N_s also gives a localized vibrational mode (LVM) at 653 cm^{-1} (^{14}N) [6]. However, this form of N is almost unimportant, as the dominant species either in as-grown or in N-implanted material is in the form of a nitrogen pair whose structure was, until now, unknown. This pair gives rise to two LVM's at 766 and 962 cm^{-1} in the case of ^{14}N, which shift to 748 and 936 cm^{-1} with ^{15}N. Using a mixture of ^{14}N and ^{15}N implants, Stein [13] first showed that two further N-related LVM's occurred which were intermediate between those of pure ^{14}N and ^{15}N. Furthermore, the intensities of the six lines were proportional to the expected concentration of pairs of the various isotopes. If the N atoms were inequivalent, four additional modes would be expected in the mixed isotopic case, but only two were observed. This shows that the complex consists of a pair of *equivalent* N atoms. There are two possibilities: either the pair contains an N-N bond or the N atoms are bonded to Si atoms, which must be close together to account for the isotope shifts. We have determined [14] the structure of this pair using channeling, local vibrational mode spectroscopy, and *ab initio* theory and our findings imply the latter.

Float-zone *p*-type single crystals of Si were implanted with N at room temperature with energies of 50, 90, 150, 225, 325, and 400 keV. The doses at each energy were chosen to achieve a nearly uniform N profile from 0.12 to 0.82 μm below the surface with an N concentration of 6.5×10^{19} cm^{-3}. First, we performed an isochronal annealing study which showed that a 5 s rapid thermal anneal (RTA) at 725 °C results in the maximum intensity of the pair LVM's and the disappearance of all other N-related absorption lines. Consequently, all samples were given this annealing treatment unless otherwise stated. After this annealing, infrared (IR) absorption spectra were measured at room temperature with an apodized resolution of 3.8 cm^{-1} using a Nicolet System 800 Fourier transform IR spectrometer. The channeling analysis was carried out at 135 K with a 1015 keV proton beam probing ^{15}N by means of the nuclear reaction $^{15}N(p,\alpha)^{12}C$. The experimental setup and the computer simulations applied in the analysis of the data were described previously [15, 16] and only a brief outline will be given here. The channeling scans, i.e., the angular distributions of the normalized yields of α particles from the nuclear reaction and of backscattered protons, were measured around all major axes and planes. In the case of axial scans, the yield for each tilt angle (the angle between the beam and axis) was averaged over all azimuthal angles, from 0 to 2π, to reduce planar effects and to give a reliable yield at large tilt angles which was then used to normalize the data. The N site was determined as the site giving the best agreement between the theoretical and experimental angular distributions for all axes and planes. Finally, we performed a series of annealing experiments to correlate

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the channeling and IR data. All the samples investigated in this series were preannealed at 600 °C to obtain recrystallization. After this, the samples showed identical IR absorption. Subsequently each sample was RTA annealed for 5 s at a temperature in the range of 600 to 950 °C and the IR absorption together with the channeling scans for the ⟨110⟩ axis were then measured.

Figure 1 shows the channeling scans for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ axes. For the ⟨100⟩ scan, the α yield displays a sharp central peak superimposed on a broader dip. This indicates that the N site is displaced from a substitutional one in a ⟨100⟩ direction and is close to the C site (Fig. 1). This location is also in agreement with ⟨110⟩ and ⟨111⟩ scans. A detailed analysis shows that a fraction $f = (70\pm6)\%$ of N atoms are displaced 1.1±0.1 Å from lattice sites along ⟨100⟩ with a maximum displacement of 0.2 Å perpendicular to this axis. The remaining N atoms are randomly distributed. Figure 2 shows that this fraction f is in quantitative agreement with the amount of paired N found spectroscopically, using a previously determined calibration [17]. The figure also shows that the LVM's assigned to the pair disappear together with the ⟨100⟩-displaced N after annealing at about 950 °C. Thus we conclude that the LVM's attributed to the pair arise from N atoms displaced 1.1 Å from lattice sites along ⟨100⟩.

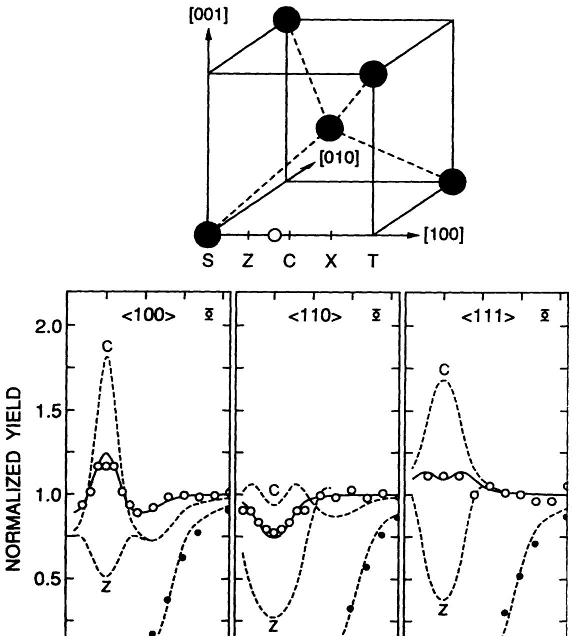

FIG. 1. Top: Si lattice with interstitial sites marked. Bottom: Measured angular distribution of the proton yield (solid circles) and α yield (empty circles). The curves show the simulated yields corresponding to various impurity interstitial sites shown in the top figure.

We then carried out *ab initio* local density functional (LDF) calculations on up to 88 atom H-terminated clusters, $N_2Si_{44}H_{42}$ centered on various models of N defects. In each case the forces on all the atoms were found and the whole cluster relaxed. The energy second derivatives of the N atoms and their neighbors were then evaluated and their vibrational modes found as discussed previously [18]. The method has been used to show that H-terminated Si clusters yield Si-Si bonds within 1.5% of their observed length, and that the force constants calculated from these clusters yield a Raman frequency to within 13 cm^{-1}. The use of clusters to determine the structure and LVM's of defects is vindicated by the experimental observation that LVM's are insensitive to the environment [18] more than a few shells of atoms away from the defect.

We first looked at N_s and, in common with previous calculations [19, 20], found it to be displaced 0.68 Å along ⟨111⟩ with three N-Si bonds equal to 1.81 Å while the fourth is 3.1 Å. The highest LVM, which is a two-dimensional E mode, occurs at 677 cm^{-1} and is close to the observed one at 653 cm^{-1} (Table I). A ⟨100⟩ oriented N-Si split interstitial, N_i, gave a shorter N-Si bond (parallel to ⟨100⟩) of length 1.74 Å and two others at 1.85 Å. The highest local mode now occurred at 700 cm^{-1}. The N atom is displaced by 1.0 Å from the lattice site—close to that found from the channeling study suggesting that the pair contains two N_i. An alternative model, due to Stein [6], consists of a pair of equivalent nitrogen atoms oriented along ⟨100⟩ in a vacancy (also described as N_s-N_i). This defect has D_{2d} symmetry with each N displaced from the lattice site by only 0.7 Å—considerably less than the measured displacement. It possesses a low lying IR active mode at 580 cm^{-1} and

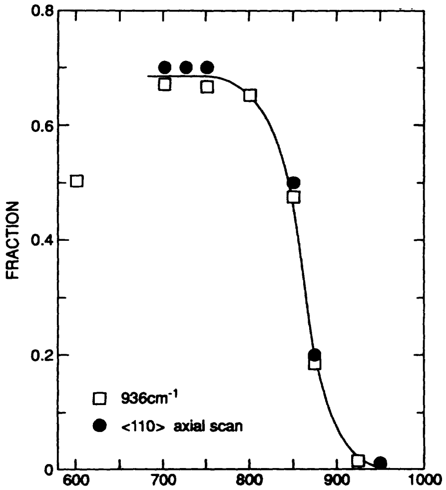

FIG. 2. Isochronal annealing of the 937 cm^{-1} mode and the ⟨110⟩ channeling dip. The solid line is drawn to guide the eye.

TABLE I. Calculated and observed frequencies, cm^{-1}, of local modes of N in Si.

N_s	IR active	^{14}N	^{15}N	
	Yes	677	659	
Observed [6]		653	642	
N_i		^{14}N	^{15}N	
	Yes	700	683	
	Yes	582	567	
N_i-N_s		^{14}N-^{14}N	^{15}N-^{15}N	
A	No	975	942	
E	Yes	580	566	
Pair defect		^{14}N-^{14}N	^{15}N-^{14}N	^{15}N- ^{15}N
A_g	No	932.7	926.9	903.8
B_u	Yes	918.7	898.1	894.8
A_g	No	768.7	759.6	748.3
B_u	Yes	688.6	679.4	672.3
Observed, this work		962.1	946.9	936.3
		765.6	758.5	748.3

a higher inactive one, due to N-N stretch, at 975 cm^{-1}. These results exclude this defect as being responsible for the pair. Indeed they indicate that the pair only involves N_i. The N atoms must be equivalent and bonded either together or with at least one common Si atom to account for the shifts in the LVM's in the mixed isotopic case. Since we expect low-energy structures to involve only threefold coordinated N atoms, there are only two possibilities and these are shown in Fig. 3. The first, the Humble model, involves a parallel pair of N_i sited at next-to-nearest distance and has been suggested previously as a building block of the N platelet in diamond [21]. We found that although the N atoms were displaced 1.0 Å from lattice sites along ⟨100⟩, they were displaced 0.47 Å along ⟨011⟩, which is inconsistent with the channeling data. The second structure has two antiparallel N_i at neighboring sites. In principle, this could have led to an N-N bond being formed, but we found that the repulsion between the N lone pairs pushed the N atoms apart and into the square configuration shown in Fig. 3. The energy of this structure was 0.9 eV lower than that found for the Humble model showing that it is more stable. In this square configuration, the displacements of the N atoms from lattice sites are 1.1 Å along ⟨100⟩, and 0.2 Å along ⟨011⟩ which are consistent with the channeling data. The calculated vibrational modes are given

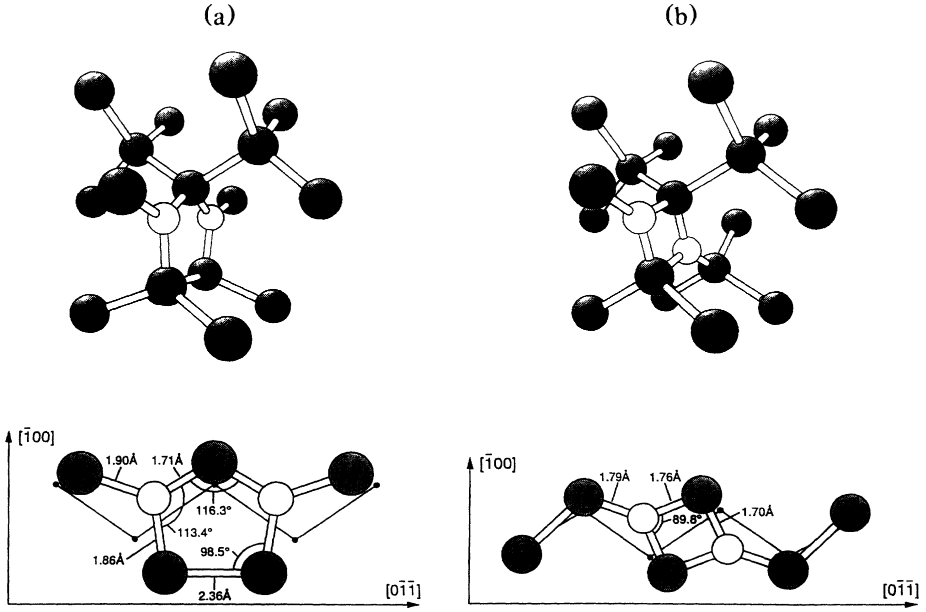

FIG. 3. The Humble (a) and antiparallel (b) models of the nitrogen pair defect. The lower diagrams show a projection onto the $(01\bar{1})$ mirror plane. The points mark the atomic sites in perfect Si. Note the large N displacement along the $[0\bar{1}\bar{1}]$ direction for the Humble model only.

in Table I. There are four modes lying above the Raman frequency but the C_{2h} symmetry only allows the two B_u modes to be IR active. These agree to within 80 cm^{-1} with the observed LVM's. The ^{15}N isotopic shifts are within 2 cm^{-1} of the observed results. These discrepancies, and those between the calculated and observed shifts for the mixed isotopic case, lie within the uncertainties of the calculations. The LVM's are very sensitive to the N-Si bond length. If this were decreased by 0.1 Å, then the modes would increase by 10% and be brought into closer agreement with the experimental ones. This contraction would occur if the surrounding Si lattice was slightly more flexible than given by our theory. These results show that the structure of the N pair is likely to be the square configuration of Fig. 3. Moreover, the two one-dimensional B_u modes might be expected to give IR bands of almost equal intensity as indeed observed.

There are no deep gap states associated with the defect. The C_{3v} symmetry of the *ABC* center observed by photoluminescence [2] excludes the assignment of this defect to the pair whose symmetry is C_{2h}. The intensities of the DLTS lines reported at $E_c - 0.17$ and $E_c - 0.28$ eV [4] imply defect concentrations very much less than that of the total N concentration, ruling out an assignment to the pair. We therefore suggest that the electrical activity of N in Si is either due to N_s, N_i, or to an N-point defect complex but not due to the pair.

The square structure found here is similar to that obtained for the C_i-O_i defect [22] when C and O replace N. The same square structure with O replacing N has been suggested [23] as a low energy saddle point for the migration of the O dimer.

In conclusion, the structure and properties of the principal N defect in Si have been deduced using results from a fruitful combination of three techniques: channeling, IR spectroscopy, and *ab initio* theory. The structure obtained is possibly a common one for various pairs of impurities in Si with valencies two, three, or four.

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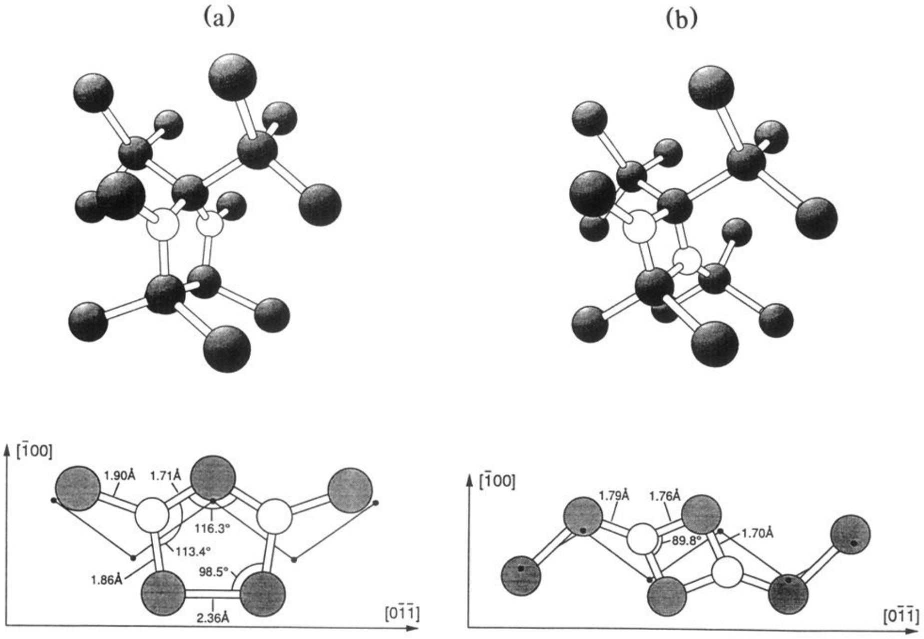

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