dentification 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, infra-red local 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-interstitials arranged in an anti-parallel configuration, and with four N-Si bonds forming square lying on {011}.

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Nitrogen in silicon was detected over 30 years ago [1] but the structure and properties of the defect have remained enigmatic. It readily interacts with other impurities such as C [2], O [3–5] and Al [6] and gives rise to a photoluminescence (PL) band at 1.122 eV, called the ABC system [7,8], as well as electron traps around 0.2-0.3 eV below the conduction band [9]. N also interacts strongly with dislocation cores [10,11] and immobilizes them and hence is useful in hardening Si wafers.

Substitutional nitrogen, N_s, gives an electron paramagnetic signal (SL5) [12] consistent with it lying off-site along [111], in addition to a localized vibrational mode (LVM) at 653 cm^{-1} (^{14}N) [3]. However, this form of N is almost unimportant, as the dominant species either in as-grown or N-implanted material is in the form of a diamagnetic complex. This complex gives rise to two LVM at 766 and 963 cm^{-1} (^{14}N) shifting to 749 and 937 cm^{-1} with ^{15}N. Using a mixture of ^{14}N and ^{15}N implants, Stein [3] first showed that two further N related LVM occurred which were intermediate between those of pure ^{14}N and ^{15}N. Furthermore, the intensities of the six lines was proportional to the concentrations of pairs of the various isotopes. This proves that the complex consists of a pair of *equivalent* N atoms. There are two possibilities: either N is bonded to a second N atom within the Si lattice, or to Si atoms. We have determined [13] the structure of this pair using channeling, local mode spectroscopy and *ab initio* theory and our findings imply the latter. Since large concentrations of the complexes can be created in N-implanted Si, a proton channeling study using the reaction: $^{15}N(p,\alpha)^{12}C$ is ideal for probing the location of N [14].

Float-zone p-Si samples ([B] $\approx 6\times10^{13}$ to 3×10^{16} cm^{-3}) were implanted with ^{15}N at room-temperature with energies of 50 to 400 KeV. The energy and dose were selected to achieve a uniform N-profile from 0.12 to 0.82 μm below the surface with a concentration of 6.5×10^{19} cm^{-3}. A 5 s rapid thermal anneal (RTA) at 725°C resulted in the maximum intensity of the 749 and 937 cm^{-1} modes and the disappearance of all other N modes.

The channeling measurements were carried out at 135 K with a 1015 KeV proton beam. Full details of the channeling experiment, its interpretation and analysis have been given previously [15–17]. Fig. 1 shows the channeling yields along <100>, <110> and <111> axes. The α-yield shows a sharp peak superimposed on a broad dip for a <100> scan. This shows that N lies along <100> close to the C site. This is supported by an analysis of the <110> and <111> scans. A detailed analysis shows that a fraction f = 70±6 % of N atoms are displaced 1.1±0.1 Å from substitutional sites along <100> with a maximum displacement of 0.2 Å perpendicular to this axis. The remaining N atoms are randomly distributed. Fig. 2 shows that this fraction f is in quantitative agreement with the amount of paired N found spectroscopically using a previously determined calibration [18]. The figure also shows that the LVM assigned to the pair anneal out together with the channeling yield around 950°C. We conclude that the LVM arise from N atoms displaced along <100>.

We then carried out *ab initio* local density functional (LDF) calculations on up to 73 atom H-terminated clusters, $N_2Si_{35}H_{36}$ 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 described previously [19].

We first looked at N_s and in common with previous calculations [20,21] found it to be displaced 0.68 Å along <$\bar{1}\bar{1}\bar{1}$> with three N-Si bonds equal to 1.81 Å and the fourth 3.1 Å. The highest LVM (E symmetry) occurs at 677 cm^{-1} close to the observed one at 653 cm^{-1} (table 1). This mode is well below that due to the pair suggesting that substitutional N atoms are not involved. A <100> oriented N 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 1.0 Å from the substitutional site — rather close to that found from the channeling study. These results support the idea that at least one N_i is involved in the pair. A <100> orientated N_i-N_s defect with D_{2d} symmetry, possessed equivalent N atoms but each was displaced from a substitutional site by only 0.7 Å and the defect possesses a low lying infra-red active mode at 580 cm^{-1}. A higher inactive one due to N-N stretch lies at 975 cm^{-1}. These results exclude this defect as being responsible for the pair. Indeed they suggest that the pair only involves N_i. We therefore looked at two close-by interstitial pairs with equivalent N atoms. The N atoms must be coupled together or with a common Si atom to account for the mixed N isotope shifts. There are only two possibilities illustrated in Fig. 3. The first 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 [22]. The relaxed defect showed that the N atoms were displaced 1.0 Å along <100> from substitutional sites but by 0.47 Å along <011> which is inconsistent with the channeling data. The second structure has two anti-parallel N_i at neighboring sites. In principle, this could have led to an N-N bond being formed but the N atoms repelled each other, due to the overlap of the N lone-pairs, when the defect was relaxed. The resulting configuration of Fig. 3 was obtained with the N-Si lengths of the square being 1.70 and 1.79 Å and the internal Si-N-Si angles are 89.8°. The other two N-Si lengths were 1.76 Å. Its energy was 0.9 eV lower than that found for the Humble model.

In addition, the displacement of the N atoms from substitutional sites are 1.1 Å along <100> and 0.2 Å along <011> which is consistent with the channeling analysis. The calculated vibrational modes are given in Table 1. There are four modes lying above the Raman 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. The ^{15}N isotopic shifts are within 2 cm^{-1} of the observed results. Moreover, the shifts in the mixed case are 21 and 3 cm^{-1} for the upper and 9 and 7 cm^{-1} for the lower. These are to be compared with observed shifts of 15 and 11 for the upper and 7 and 10 for the lower. These errors lie within the uncertainties of the calculations. We note that a decrease in the N-Si bonds by about 0.09 Å would lead to an increase in the LVM by about 10%. The two B modes are expected to give roughly equal intense IR lines as observed. These results show that the square configuration of Fig. 3 is likely to be the pair defect. The defect gives rise to a shallow filled level due to the N lone pairs in the lower part of the gap, although the cluster method and the use of LDF theory preclude an accurate estimate of its position.

The C_{3v} symmetry of the PL center [7] excludes its assignment to the pair whose symmetry is C_{2h}. The intensity of the DLTS lines at E_c-0.17 and E_c-0.28 eV is also much less than that of the total N concentration [9]. This suggests that the electrical activity of N is either due to N_s or to a N-point defect complex and not due to the pair. The square structure found here is similar to that obtained for the C_i-O_i structure [23] when C and O replace N. The same square structure with O replacing N has been suggested [24] as a low energy saddle point for the migration of the O dimer. We suggest that other low energy structures arise when one of the N or Si atoms of the square are replaced by impurities of nearby-valencies such as O, C, Al or B and these, together with N_s, are responsible for the electrical activity.

In conclusion, channeling, IR-spectroscopic and *ab initio* theory have been used to deduce the structure and properties of the principal N defect in Si. The structure obtained is likely to be the basic one for various impurity pairs where either N or one of the bonded Si atoms is replaced by elements with valencies differing by unity.

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TABLE I. Frequencies , cm^{-1} , of Local Modes of N in Si

N_s	^{14}N	^{15}N	
Calculated	677	659	
Observed	653	?	
N_i	^{14}N	^{15}N	
Calculated	700	683	
	582	567	
N_i-N_s	^{14}N-^{14}N	^{15}N-^{15}N	
A	975	942	
E	580	566	
Pair Defect	^{14}N-^{14}N	^{15}N-^{14}N	^{15}N- ^{15}N
Calculated A_g	932.7	926.9	903.8
B_u	918.7	898.1	894.8
A_g	768.7	759.6	748.3
B_u	688.6	679.4	672.3
Observed	963	948	937
	766	759	749