Theoretical and Isotopic infrared absorption investigations of nitrogen – oxygen defects in silicon

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The vibrational spectroscopy of NNO defects in Si introduced by ^{16}O, ^{14}N and ^{15}N ion implantation is studied, and especially the N-isotopic shifts of the localized vibrational modes. These investigations show that the local modes of the three impurity atoms comprising the defect are only weakly coupled dynamically. *Ab initio* cluster calculations of the local mode frequencies of the defect are performed. Several models are investigated, and the model consisting of a bridging O atom adjacent to the N pair defect account for its dynamic properties.

Nitrogen is commonly used as an inert atmosphere for processing Si but it has important effects on the material. For example, N impurities can pin dislocations [1,2] and form electrically active defects such as the substitutional deep donor [3,4]. There have been suggestions that nitrogen-oxygen complexes can form shallow donors [4–6], although whether N does form an essential component of these defects is controversial [7,8].

The dominant N defect in O-free Si consists of a pair of N_i atoms (Fig. 1) and has C_{2h} symmetry [4,9]. The N-pair is stable until about 800°C [4]. In N and O implanted FZ-Si [10], or in CZ-Si grown in a N_2 atmosphere [11,12], NNO complexes are formed by annealing between 400 and 700°C. Under these conditions, the intensity of the localized vibrational modes (LVMs) due to the pair are progressively reduced and three other IR-absorption lines at 1026, 996 and 801 cm^{-1} (room temperature) become increasingly prominent. The intensities of these lines are correlated with each other [12] and they are believed to be due to NNO complexes. This is because O_i atoms become mobile around 400°C and become trapped by N-pair defects which are stable at this temperature. Beyond $\approx$ 700°C , these complexes break up with the emission of O_i leaving the N-pair. Cooling allows the NNO complexes to reform. This dissociation and reformation is reversible.

There are no reports of isotopic effects on the LVMs of the NNO defect even though this information is of the greatest importance in deducing its structure. To remedy this, we have carried out infra-red absorption studies on NNO defects created by ion implantation.

Float-zone n-type Si samples cut from a wafer were implanted at room temperature with ^{16}O and with either ^{14}N, ^{15}N or both N- isotopes. The samples had a typical size of 10×10 × 0.3 mm^3 and were polished and implanted on both sides. The energies (Table I) and doses were chosen to obtain a nearly uniform O and N profile from 0.21 to 0.82 μm below the surface with a concentration of 6.5×10^{19} cm^{-3} for both O and N. All samples were annealed under flowing N_2 ambient for an hour in the temperature range from 500 to 650°C and were subsequently etched by HF to remove surface oxides. Infrared absorption measurements (Fig. 2) were carried out at 77 K using a Nicolet System 800 Fourier Transform Infra-Red spectrometer. The number of scans were typically 1000 and a resolution of 6 cm^{-1} was chosen to avoid fringes in the spectra due to multiple reflection of the beam in the sample. The LVMs due to the NNO defect are given in Table II.

The ^{14}N frequencies agree with the earlier studies [11–13], allowing for their shift ($\approx$ 4 cm^{-1}) between low and room temperature. All the modes shift with ^{15}N showing that at least one N atom is involved in the defect. Unexpectedly, the peak in the 1030 cm^{-1} LVM is shifted by around 3 cm^{-1} with ^{15}N and this suggests that this mode is almost entirely due to Si-O stretch. This lies between the LVMs for O_i (1136 cm^{-1} [14]) and O_s (836 cm^{-1} [15]), suggesting that O_i bridges a dilated Si bond near the N-pair. The modes at 999 and 805 cm^{-1} are slightly above those of an isolated N-pair (967 and 770 cm^{-1}) and show a similar shift with ^{15}N (25 and 19 cm^{-1} compared to 26 and 17 cm^{-1} for the N-pair), suggesting that the pair remains intact but with compressed bonds due to the nearby O_i. No additional LVMs are observed in the mixed implantation, implying that the N atoms are no longer dynamically coupled but vibrate independently of each other. They must also be inequivalent atoms as they possess distinct LVMs. This implies that O lies closer to one N atom than the other.

Calculations on the N pair defect [9] showed that N_i dilated the Si(1)-Si(5) bond (Fig. 1) by 4%, making it a prime site for O_i. The other Si bonds bordering the pair along [100] are compressed making these unlikely sites for the O_i. Previous investigations on the trapping of O_i at dislocation cores showed a marked preference for O to bridge dilated Si bonds [16].

Two models of the NNO defect are shown in Figure 3. They differ in the position off the O atom. In the first, the O atom bridges the nearest Si-Si bond to the pair, and in the second, O bridges the second nearest Si-Si bond along [011].

LDF cluster calculations [17] were carried out on a 134 atom cluster $N_2OSi_{71}H_{60}$ containing the defect as shown in Fig. 1. The method has been described before [17] and gives Si-Si bonds to within 1.5% and successfully describes both the vibrational modes of O_i [18] as well as its activation energy for diffusion [19].

The self-consistent energy and forces on all the atoms were found, and the whole cluster relaxed by a conjugate gradient algorithm. The entries in the dynamical matrix of the cluster between the impurities and their neighbours were determined directly, and the other entries were found from a Musgrave-Pople potential derived earlier [17].

The vibrational modes of the structure are given in table II. The mode at 861 cm^{-1} is due to Si-O stretch as its frequency is almost unaffected by ^{15}N substitution. The two modes at 1070 and 808 cm^{-1} are N(1) and N(2) related and the mixed isotopic results show very little coupling between them. This explains why no new modes are introduced in this case, since the nearby O_i makes the two N atoms inequivalent.

Thus although the modes are in the correct region and display the correct isotopic behavior, their ordering is incorrect: the O mode should lie above the two highest N modes. This ordering and their positions are, however, very sensitive to the position of the common Si atom, Si(1) (Fig. 1). If this is displaced by 0.07 Å along $[0\bar{1}\bar{1}]$, decreasing the Si(1)-O and increasing the N(1)-Si(1) lengths by 0.05 and 0.07 Å respectively, then the O and N modes are within 70 cm^{-1} of the observed frequencies (Table II). Once again the atoms are decoupled. The highest O-mode is simply an asymmetric stretch in the Si-O bonds. There is a symmetric stretch mode at lower frequency. The mode at 949 cm^{-1} is due to N(1)-Si(1) stretch whereas the 813 cm^{-1} mode represents N(2)-Si(3) stretch. The other modes involve motion of both N atoms. The two N-related modes shift by 28 and 19 cm^{-1} with ^{15}N in excellent agreement with the observed shifts of 25 and 19 cm^{-1}. The changes in bond lengths caused by the shift of Si(1) and the discrepancies between the calculated and observed modes lie within the errors of the calculation.

We also investigated three other models of the defect. Moving the O_i away from the N-pair to lie between Si(5) and Si(6) raised the cluster energy by 1.2eV. Neither moving the O_i to lie between N(1) and Si(1) in Fig. 1 or by using O to bridge the dilated bond in the Humble N-pair model [9], gave modes in the right region or caused them to shift correctly when ^{14}N is replaced by ^{15}N.

Our conclusion is that the structure in Fig. 1 represents the NNO defect. The three atoms of the defect are only weakly dynamically coupled because of their inequivalence. The O atom is bound to the defect because the N-pair strains the lattice. The dissociation energy of the NNO complex is then approximately the energy necessary for O to migrate to the barrier top starting from O lying between Si(6) and Si(5) and ending between Si(5) and Si(1). Taking the first figure to be that for O_i diffusion, 2.5 eV [20] and the second one as calculated here, 1.2 eV, we find this dissociation energy to be 3.7 eV. The equilibrium concentration of NNO defects would equal,

$$\frac{[N_2][O_i]}{N_s}e^{(1.2eV/kT)},$$

where N_s is the density of bond-center sites for O_i. The formation energy of NNO from N_2 and O defects is estimated to be around 1.2 eV which gives a concentration of NNO equal to that of N_2 below 800°C if $[N_2] = [O_i] = 10^{-6}N_s = 10^{17}$ cm^{-3}.

Wagner et al [11] report two weak extra LVMs at 810 and 1018 cm^{-1}. We suggest that these lines are not due to NNO but possibly NNO_2 defects.

We remark that as the trapping of O by N pairs has been attributed to the strain field surrounding the pair, then this mechanism would be also be expected to operate for other impurities. H and F would behave like O. However, C would be expected to substitute for Si atoms compressed by the pairs whereas Ge and substitutional transition metals would replace Si atoms subject to tensile stress. This would lead to $\langle 011 \rangle$ oriented aggregates.

Finally, we note that the NNO defect has no deep or shallow donor levels. This suggests that, if shallow thermal donors [5,6] are N-related, they must involve larger numbers of O or N atoms, or possibly include Si interstitials [21].

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TABLE I. Energies, in KeV, of Implanted Ions.

^{16}O	103	171	257	371	457
^{14}N	90	150	225	325	400
^{15}N	96	161	241	348	429

TABLE II. Calculated and Observed LVMs, cm^{-1}, due to N-N-O Complexes in Si.

^{14}N ^{14}N ^{16}O	^{15}N ^{15}N ^{16}O	^{14}N ^{15}N ^{16}O	^{15}N ^{14}N ^{16}O	^{14}N ^{14}N ^{18}O
Calculated				
1070.4	1039.6	1069.8	1040.3	1070.3
861.1	860.1	860.7	860.4	823.9
808.2	788.1	788.2	808.1	804.5
723.9	705.5	708.3	722.2	723.9
671.5	655.8	669.5	656.7	670.6
Displaced Si atom				
962.9	962.7	962.8	962.8	949.2
948.9	920.1	948.0	921.3	918.9
813.3	792.6	792.7	813.0	813.2
727.0	708.2	714.0	723.9	727.0
688.1	672.3	683.5	674.2	687.4
Obs.				
1030	1027	1028		
999	974	999, 974		
805	786	805, 786		

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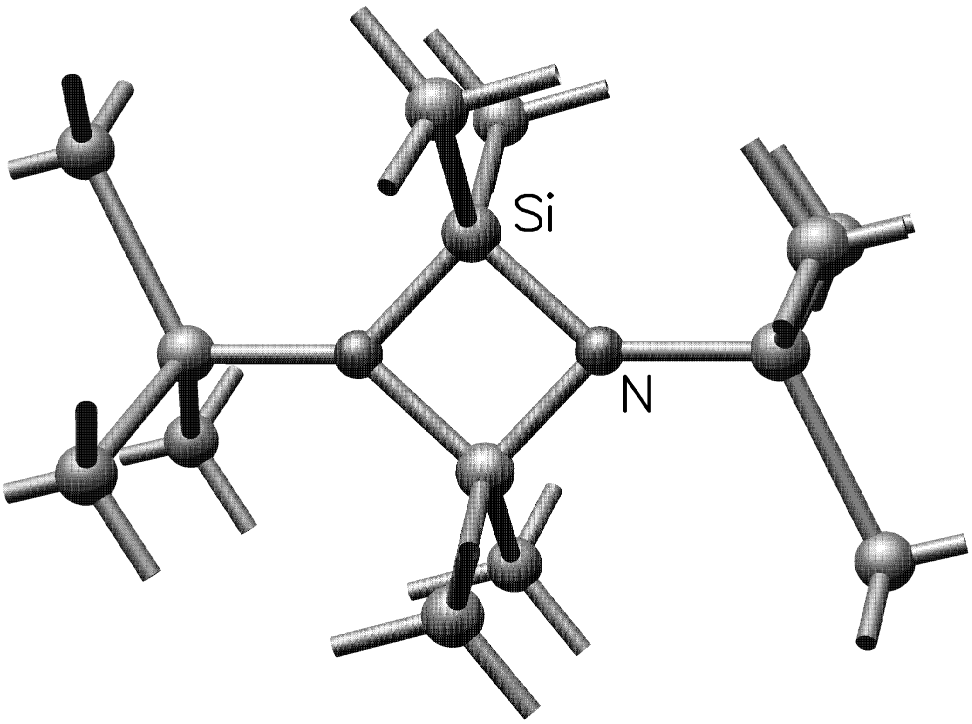

FIG. 1. The N-pair defect.

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FIG. 2. Infra-red absorption intensity (547°C, 1h), a) ^{14}N, b) ^{15}N, c) ^{14}N-^{15}N. The shaded bands are those of NNO defects. The other main peaks are due to N_2 pairs

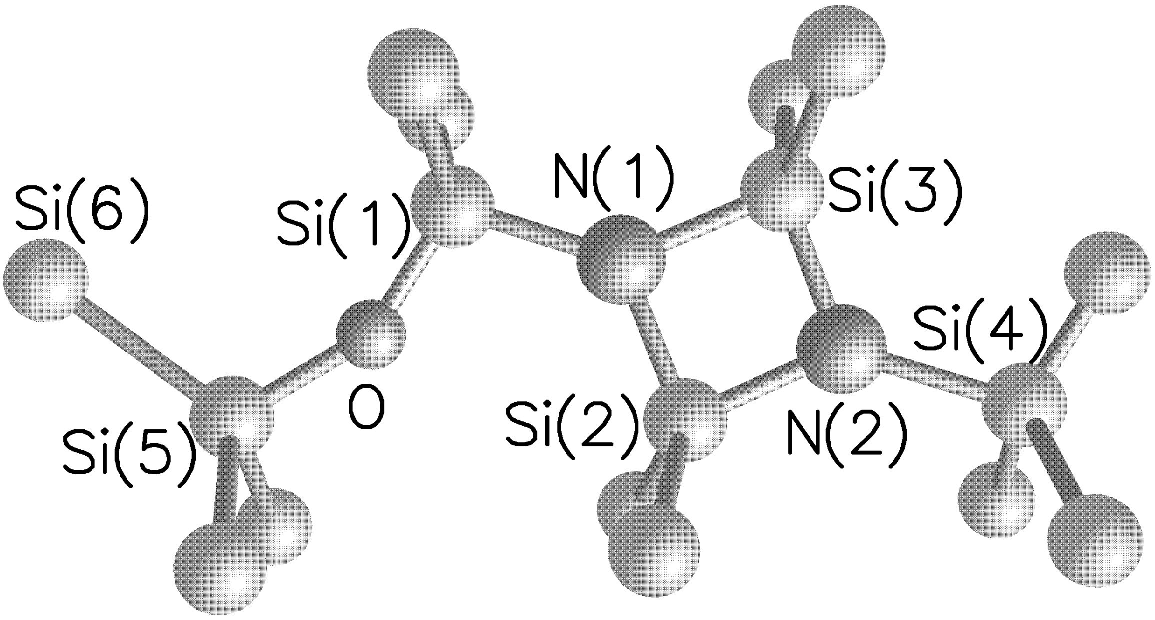

FIG. 3. Structure of the N-N-O defect.