Shallow Thermal Donor Defects in Silicon

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An *ab initio* local density functional cluster program, AIMPRO, is used to examine nitrogen related shallow thermal donor defects in silicon. We find the bonding of oxygen with interstitial nitrogen in N_i-O_{2i} to be almost "normal," but the O atoms move slightly out of their bond centered sites causing the deep donor level of N_i to become shallow. The defect has properties consistent with those experimentally observed for shallow thermal donors. We also find that a C_iH-O_{2i} defect has very similar electronic properties, and suggest that shallow thermal donors do not have a unique composition. [S0031-9007(96)00771-5]

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Annealing N rich Cz-Si around 650 °C leads to the formation of a family of shallow thermal donor defects (STDs) [1–5]. As single donors they have ionization energies about 35 meV which are much shallower than the thermal double donors. Hara *et al.* [6,7] found that STD defects possess a spin $1/2$ and a g tensor which is extremely close to that of the NL10 defect [8]. They suggested that they were the same defect. The g tensor shows that the STD possesses an apparent C_{2v} symmetry. However, these magnetic resonance studies have failed to resolve any hyperfine splitting in the defect core [6], and so the existence of N in the defect is only inferred from its presence in the material and remains controversial [5,6,9,10]. Some workers [10] find STDs in nominally N free Cz-Si. If this is correct, it suggests that STDs can arise from impurities other than N. Another argument that has been used against N being part of the STD is that large N concentrations appear to *suppress* STD formation [11]. However, we show here that at least two families of STDs could exist: One is based on nitrogen-oxygen defects and the other on carbon-oxygen ones. We also give reasons for the unexpected dependence of nitrogen related STDs on the N concentration.

Channeling and infrared (IR) absorption studies [12] show that the principal N defect in silicon is a nitrogen pair composed of two adjacent [100] oriented nitrogen interstitials (N_i). Substitutional N is a rare defect although it has been detected by electron paramagnetic resonance (EPR) [13] and IR spectroscopy [14]. Isolated N_i defects also exist in implanted material annealed to 600 °C, but lie below the detection limit in doped as-grown material [15]. In this defect, N and Si share a lattice site and are oriented along [100]. It is similar to the carbon interstitial, C_i, whose structure has been determined by EPR [16]. The C_i defect has two gap levels due to the p orbitals on the C and Si radicals. The greater electronegativity of C implies that the lower filled level is C related while the upper empty level is diffusively localized on the Si radical. The small size of C introduces a tensile strain along [011] leading to dilated Si-Si bonds. These are preferential bonds for attack by interstitial oxygen, O_i. The resulting structure, corroborated by EPR [17], is modified by an important consideration: The Si radical, now positively charged, pulls O_i out of its bond center and leads to an *overcoordinated* oxygen atom [18]. This explains why the O-related vibrational mode is lowered from 1136 cm^{-1} for O_i to 738 cm^{-1} for C_i-O_i [19].

A further oxygen attack leads to a C_i-O_{2i} defect, tentatively identified with the P photoluminescent (PL) center [19]. The effect of increasing the number of negatively polarized oxygen neighbors in the series C_i, C_i-O_i, C_i-O_{2i} is to displace the donor levels upwards as $E_v + 0.28$, $E_v + 0.34$, and $E_v + 0.39$ eV, respectively. This can be understood from the effect of an increasing repulsive electrostatic potential arising from the oxygen atoms.

We anticipate a similar chemistry for N_i-$(O_i)_n$ defects because N is more electronegative than either Si or indeed C, and is expected to pull the charge away from the Si radical even though the upper p-related orbital on Si is now occupied by an electron. We investigate these defects with AIMPRO, an *ab initio* local density functional program, applied to large 150 atom H-terminated clusters of composition $Si_{79}H_{68}NO_2$. Details of the method have been given before [20]. We use a basis similar to recent investigations into vacancy-oxygen defects [21]. The method has previously been used to show that N_i has a similar structure to C_i and possesses a midgap occupied level and a vibrational mode at 700 cm^{-1} [12,15] in close agreement with an experimentally assigned one at 691 cm^{-1}.

We consider first the N_i-O_i defect. Like C_i-O_i, it has C_{1h} symmetry but with a deep donor level close to that of isolated N_i (see Fig. 1). The O atom sits near a bond centered location with Si-O lengths of 1.64 and 1.68 Å, and a Si-O-Si bond angle of only 137°. This is far lower than the ≈170° of isolated O_i, and arises because the O atom has moved closer to the Si radical, becoming to some extent overcoordinated. The asymmetry of the defect allows the wave function to concentrate on the lobe of the p orbital furthest from the oxygen, thus minimizing the Coulombic repulsion with O. This explains why the donor level remains deep in the gap.

There are two likely structures for the N_i-O_{2i} defect which have C_{2v} and C_{1h} symmetries, respectively, depending on whether the second oxygen abuts N or the first O atom. We examined both of these structures, and found the C_{2v} structure (Fig. 2) to have the lower energy by 1.52 eV. Hence N_i-O_{2i} has the same symmetry as that observed experimentally for nitrogen related STDs [6]. This contrasts with a similar calculation for C_i-O_{2i}, where the stable structure has C_{1h} symmetry which is again consistent with PL studies on the P line [19].

The oxygen atoms make Si-O-Si bond angles of 140° which are similar to N_i-O_i. The Si-O bond lengths are 1.69 and 1.64 Å for the outer and inner bonds, respectively, again lying between those of O_i and O_s (1.61 and 1.75 Å, respectively [21]). The distance between the O atoms and the central Si atom is 2.54 Å: considerably longer than would be expected if there was a normal Si-O bond formed. This displacement of the O atoms could be rationalized through a consideration of atomic polarizabilities. Crucially, the defect has a very shallow donor level (Fig. 1) which is more properly described by effective mass theory.

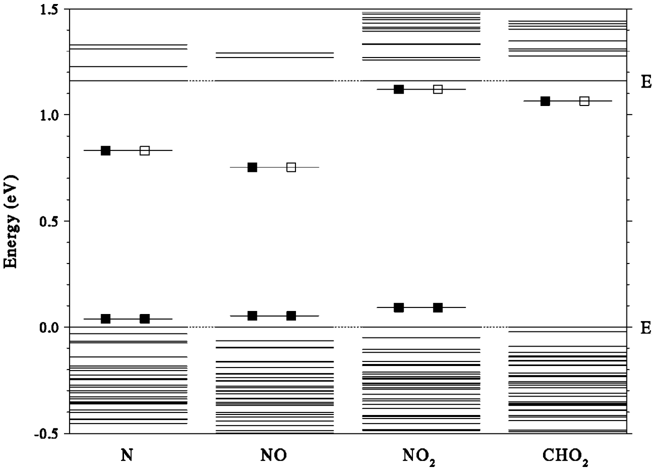

FIG. 1. The Kohn-Sham cluster eigenvalues in the vicinity of the band gap, scaled to the observed gap. The filled (empty) boxes on states near the band edges denote 1 (0) occupancy.

We also optimized the defect structure in the positive charge state, since, at the annealing temperatures described, the shallow level will depopulate. This revealed a very similar structure, where the O atoms move only 0.15 Å towards the central Si. Thus there is a slightly stronger third Si-O bond, although not three equivalent bonds as are shown in related "y-lid" models [22,23]. This small change suggests that cluster size is not playing a significant role. Further information on the bonding is seen from Fig. 3 which plots the pseudo-wave-function of the partially filled shallow level of the neutral defect. The wave function is diffusively localized on the p-type dangling bond of the central Si radical. There is negligible localization on the interstitial nitrogen, consistent with the lack of any hyperfine interaction with N observed by EPR and ENDOR experiments. The nodal surface between O and the Si radical demonstrates an antibonding character to the state. There must then be a bonding orbital lying below this state, and this shows that the O atoms are to some extent overcoordinated. A larger cluster would probably lead to a greater delocalization of the donor state, which would then be properly described by effective mass theory. The occupation of the antibonding orbital implies a lone-pair repulsion which would also contribute to an elevation of the energy of the Si dangling bond state, making it a shallow level. Thus the transformation of a deep to shallow level is a combination of electrostatic interactions together with dative bonding of the Si radical with the oxygen atoms.

The local vibrational modes for the neutral defect are given in Table I. As would be expected, the longer Si-O bonds lead to oxygen-related local vibrational modes at 894 and 858 cm^{-1} which are lower than those of the standard interstitial.

Further calculations show that the C_{2v} defect with two more interstitial oxygen atoms along [011] is stable. These atoms sit in standard interstitial sites but are able to relieve some of their strain through a compression of the weaker central Si-O bonds. These O atoms move closer to the Si radical. This should result in pushing the shallow donor level upwards, but the limitations of

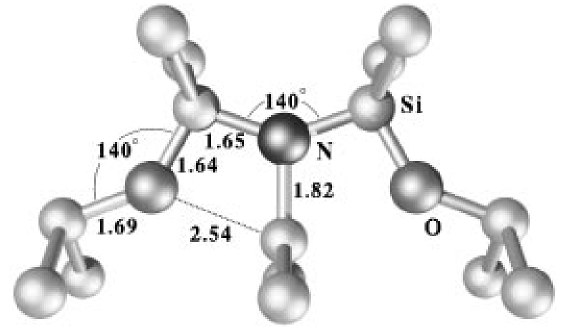

FIG. 2. The core structure of the neutral N_i-O_{2i} defect. The symmetry axis lies along [100] and the O atoms are aligned along [011].

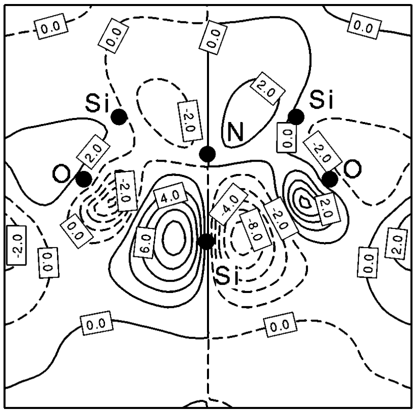

FIG. 3. The pseudo-wave-function (×100 a.u.) of the highest occupied orbital of N_i-O_{2i}. Note that it has little amplitude on N and is localized on the Si radical. There are nodal surfaces lying between this atom and the O atoms demonstrating antibonding behavior.

the cluster method prevent a quantitative estimate of the change. This mechanism whereby larger oxygen aggregates push the nearest oxygen atoms towards the Si radical, increasing the repulsive central cell potential, demonstrates how the family of shallow donor states based on nitrogen develops. This is similar to the model of the thermal donor where levels become increasingly shallow with oxygen addition [24].

It is important to note that this defect is not the only nitrogen-oxygen one to develop in heat treated N-doped Si. IR absorption studies show that the nitrogen-pair complexes with O_i form N_{2i}-O_i defects which are electrically inactive [25]. The existence of at least two kinds of defects may explain the observation of Ref. [11] that increased N doping does not necessarily lead to a greater number of STDs.

The observation of STDs in material that is nominally N free suggests that other families of STDs may exist. Annealing Cz-Si between 450 and 600 °C produces a number of PL bands [26], some of which, e.g., the T line, are due to defects containing interstitial C-H complexes [27,28]. The hydrogen is present as an unintentional impurity, and the concentrations of these centers are comparable with those of thermal donors. These interstitial defects are to be contrasted with the marginally stable substitutional carbon-hydrogen centers [29,30]. The C-H bond length is exceptionally small, 1.1 Å, and, as this unit is isovalent with N, it suggests that a STD might arise if N in Fig. 2 was replaced by C-H. We found that the defect with the C-H bond parallel to $[0\bar{1}1]$, i.e., perpendicular to the plane containing the three C-Si bonds, is stable. The defect has C_{1h} symmetry rather than C_{2v}, and this would appear to rule it out as a strict candidate for a STD. However, if the spin-polarized density is negligible on the H atom, then the symmetry might be misinterpreted in an EPR experiment. This had indeed been the case for the H-related NL10 EPR center [31]. In this defect, the H atom also appears to lie along $[0\bar{1}1]$. The Kohn-Sham eigenvalues of the C_iH-O_{2i} defect are shown in Fig. 1 and demonstrate that it possesses a single shallow donor level. The C-H unit moves slightly out of the $(01\bar{1})$ plane until the Si-C-H bond angles are all 100°, with Si-C bond lengths of 1.89, 1.76, and 1.76 Å. A plot of the wave function of the donor level reveals that it has very little overlap with H or C.

TABLE I. Local vibrational modes, cm^{-1}, of N_i-O_{2i}.

$^{14}N^{16}O^{16}O$	$^{14}N^{18}O^{16}O$	$^{14}N^{18}O^{18}O$	$^{15}N^{16}O^{16}O$
1051	1051	1051	1023
894	883	857	892
858	830	817	857
720	719	718	708
673	671	669	661

In summary, two families of STDs can arise when oxygen atoms surround N_i and C_i-H cores. The assumption that interstitial N is involved, rather than substitutional N [32], is strengthened by the observation that it is essential to preanneal N-doped Si at 1100 °C to create STDs [33]. The anneal is required to dissociate N_{2i} pairs into individual N_i defects. Hara *et al.* [6] examined the effect of cooling rate on Cz-Si annealed at high temperatures and found that subsequent quenching led to high concentrations of STDs, whereas slow cooling led to much lower concentrations. This is consistent with the idea that STDs can be formed from N_i complexed with oxygen dimers, but electrically inactive defects arise if N_i pair up first and subsequently complex with O_i.

In conclusion, the theoretical investigations have shown that interstitial defects like C_i and N_i are expected to form several types of complexes with oxygen. The X-O_{2i} complexes with $X = N$ or C-H possess shallow donor levels. That the former defect possesses a shallow level has also been independently found by Chadi [34]. The mechanism by which a deep level is transformed into a shallow one may be relevant to other materials.

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