

Structure and electronic properties of nitrogen defects in silicon

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Abstract. Nitrogen-vacancy defects in Si are of interest due to their ability to suppress the formation of large vacancy cluster during growth but there are problems in their characterisation. We use local density functional theory to determine the local vibrational modes, electrical levels and stability of a number of nitrogen defects. A prominent nitrogen local vibrational mode at 663 cm^{-1} is attributed to a nitrogen-vacancy centre and tentative assignments of the ABC photoluminescence line and the trigonal SL6 EPR centre are made.

1 Introduction

It has been observed that the density of crystal-orientated-particles or macro-vacancy clusters formed during growth of Czochralski-Si is substantially reduced if nitrogen has been added to the melt [1]. The effect is believed to be caused by the trapping of mobile vacancies by interstitial nitrogen dimers inhibiting the growth of large vacancy clusters [2]. Nitrogen has other effects such as an effect on oxygen precipitation probably through the formation of N-O defects [3] and an ability for locking dislocations [4]. For these reasons, there is increasing interest in nitrogen related defects and their properties.

The equilibrium vacancy concentration at a growth temperature $\sim 1400\text{ }^\circ\text{C}$ depends on the formation energy of the vacancy. Values around 10^{12} cm^{-3} occur assuming a formation enthalpy of $\sim (3.6 - 10k_B T)\text{ eV}$ derived from positron-annihilation studies [5]. However, a considerable uncertainty arises from the large range of formation energies for the vacancy derived both from theory and from experiment ($\sim 2-4\text{ eV}$). In addition, the vacancy concentration at the growth temperature depends in a complicated way on details of the growth, and values of $\sim 10^{15}\text{ cm}^{-3}$ have been suggested at $\sim 1400\text{ }^\circ\text{C}$ [6]. If the nitrogen concentration exceeds that of the vacancy, then it has been suggested that nitrogen-vacancy centres could form [1, 2, 7, 8], suppressing the formation of voids. Such defects have been reported in positron annihilation experiments in Czochralski-Si into which N had been implanted, although no specific defect centre was identified [7].

The nitrogen dimer is a *pair* of interstitial nitrogen atoms, denoted (N_i-N_i) , and is the most common nitrogen defect in either as-grown or implanted material [9]. The binding energy of two nitrogen interstitials has been found to be 3.86 eV [10] and 4.30 eV [11]. Only trace concentrations of substitutional nitrogen (N_s) are found in as-grown or implanted material. The neutral substitutional nitrogen defect has been assigned to the SL5 EPR spectrum [12]. Annealing around $400\text{ }^\circ\text{C}$ removes SL5 and there is then a growth of other nitrogen related EPR centres labelled SL6 and SL7, which contain one N atom. In addition, SL6 possesses trigonal symmetry. Other nitrogen defects have been detected optically. The ABC trigonal photoluminescent centre with emission at 1.1223 eV [13] is known from ^{15}N isotopic effects to

be nitrogen related but as it is an iso-electronic centre must involve another impurity like N, Al or H [14].

Electronic levels at $E_c - 0.19$ eV (E_2), $E_c - 0.28$ eV (E_3) [15], and $E_c - 0.42$ eV (T1) [16] have been observed in deep level transient spectroscopy (DLTS) of n -type material doped during growth with nitrogen. These have been attributed, without direct evidence to nitrogen defects. No nitrogen related levels have been reported in p -type material.

There have been several earlier theoretical studies. Interstitial nitrogen N_i is found to possess a formation energy very similar to the substitutional form N_s but, in contrast, diffuses rapidly [17, 18] 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 [19] and close to the the observed diffusion energy for nitrogen [20]. Formation energies of a number of nitrogen-vacancy complexes have been reported with N_s-N_i and N_s-N_s being particularly stable defects [10, 11, 18, 2, 14].

Here we report the optical, electrical and vibrational properties of nitrogen-vacancy centres with a view that such calculations should be helpful in the characterisation studies [14]. We use a local-density-functional supercell (AIMPRO) which has been fully described previously [21].

2 Results

The table gives the relative formation energies, in increasing value, of various nitrogen defects compared with the nitrogen dimer (N_i-N_i).

Table 1. Relative formation energies (eV), per N atom, for nitrogen-vacancy complexes relative to (N_i-N_i).

Defect	$2(N_i-N_i)$	(N_i-N_i)	(N_s-N_s)
E^f/N atom	-0.06	0.00	0.79
Defect	(N_i-N_s)	N_i	N_s
E^f/N atom	0.99	1.83	1.99

A pair of nitrogen dimers denoted by $2(N_i-N_i)$ has very low binding energy and therefore there is little tendency for nitrogen dimers to cluster. The large formation energies of N_i and N_s ensure that even at high temperatures they are minor defects. On the other hand (N_s-N_s) and (N_i-N_s) have fairly low formation energies.

2.1 Interstitial nitrogen, N_i

The stable configuration for neutral N_i is a slightly distorted $\langle 001 \rangle$ split-interstitial (Fig. 1(b)) and it has a similar formation energy to that of N_s .

The local vibrational modes (LVMs) of N_i (C_{1h}) lie around 550, 773 and 883 cm^{-1} (^{14}N). We find the defect possesses a donor level around $E_v + 0.5$ eV and an acceptor level around $E_c - 0.2$ eV consistent with previous investigations [10]. The Si-N-Si angle in the bond-centred interstitial, Fig. 1(c), is 135° and somewhat smaller than found in interstitial oxygen. Its energy is only ~ 0.5 eV higher than that of the split-interstitial and since the bond-centre structure lies on the diffusion path connecting two split-interstitial structures. This low energy implies that N_i is a mobile defect even around room temperature.

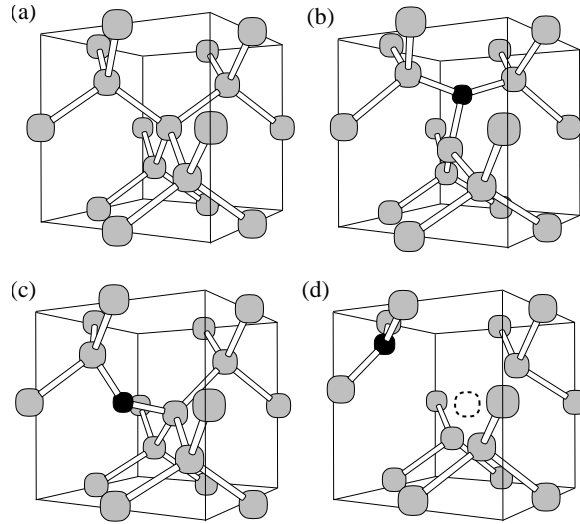


Fig. 1. Schematic representation of defects containing a single N impurity. Black and grey circles represent the N and Si atoms, respectively. (a) Fragment of the Si lattice, (b) the C_{1h} , approximately $\langle 001 \rangle$ split-interstitial structure for N_i , (c) the puckered bond-centered structure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

2.2 The nitrogen di-interstitial pair, (N_i-N_i)

The rapid diffusion of N_i implies subsequent trapping and formation of more stable defects. Suitable traps are oxygen, substitutional and interstitial nitrogen. The latter yields (N_i-N_i) (Fig.2(b)) which is the dominant nitrogen defect found in Si. The binding energy of the two N_i is 3.67 eV [10, 11, 14] and consistent with an anneal temperature of around 800 °C [9]. Its LVMs

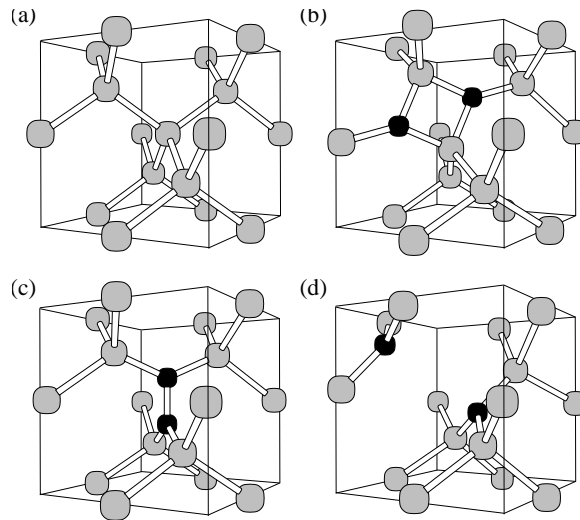


Fig. 2. Schematic representation of defects containing two N impurities. Black and grey circles represent the N and Si atoms, respectively. (a) Fragment of Si lattice, (b) the C_{2h} (N_i-N_i) complex, (c) the D_{2d} , molecule-like split-interstitial (N_i-N_s) , and (d) (N_s-N_s) .

consist of two IR active and two Raman active local modes at 772.9, 967.8 cm^{-1} and 743.1, 1070.0 cm^{-1} (^{14}N) respectively. These are in good agreement with observed IR-active modes

detected at 765.6 and 962.1 cm^{-1} . The defect does not possess any deep donor or acceptor levels.

2.3 Substitutional nitrogen, N_s

EPR experiments have established that the neutral substitutional nitrogen defect has trigonal symmetry [22]. Previous theoretical studies give support to this assignment. Although the energy drop associated with the trigonal distortion from T_d varies considerably with the theory used, the most recent *ab initio* calculations suggest a value of around 0.1 eV [10]. We find that the on-site (T_d symmetry) and distorted (C_{3v} symmetry) defects are within 80 meV of each other. The small energy difference is consistent both with previous theory [10] and with an experimental estimate of around 0.1 eV [23]. 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 favourably with experimental value of 653 with a shift of 11 cm^{-1} [24]. The 2–3% error is within that expected for the method.

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 order 0.2 eV [25]. The donor level is consistent with the deep-nature of the level associated with the SL5 EPR centre [22].

2.4 Substitutional nitrogen–vacancy complex, $(\text{N}_s V)$

Here a substitutional N defect borders a vacancy in analogy with the phosphorus-vacancy complex (E -centre) which is known from EPR to possess C_{1h} symmetry when neutral (Fig. 1(d)). A tentative assignment of the centre is to the SL6 or SL7 EPR centre [22]. Using a vacancy formation energy of 3.3 eV [26], we find V binds to N_s with an energy of 1.6 eV close to a value found previously [18]. This value is the same as the binding energy of oxygen with a vacancy [21]. The defect possesses a single acceptor level calculated to lie around $E_c - 0.7$ eV.

As with the substitutional defect, $(\text{N}_s V)$ possesses a pair of degenerate local vibrational modes above the Raman frequency. These are calculated to lie at 663 and 646 cm^{-1} for ^{14}N and ^{15}N respectively.

2.5 N_i - N_s complexes

The most stable configuration for this defect formed from two N interstitials and a single lattice vacancy is when the pair of nitrogen atoms lie at the centre of the vacancy making equivalent bonds with all four silicon neighbours (see Fig. 2(c)). The structure has D_{2d} point group symmetry and has been suggested previously [9, 10, 11]. 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 $(\text{N}_i\text{-N}_i) + V \rightarrow (\text{N}_i\text{-N}_s)$ is then given by

$$[(\text{N}_i\text{-N}_s)] = \frac{[V][(\text{N}_i\text{-N}_i)]}{[\text{Si}]} \exp(E^b/k_B T),$$

where $[X]$ is the concentration of species X . $[(\text{N}_i\text{-N}_s)]$ is then negligible compared with the concentration of the interstitial nitrogen pair $(\text{N}_i\text{-N}_i)$ at 1400 °C if the vacancy concentration is less than about 10^{15} cm^{-3} . Two IR-active LVMS for the defect lie around 573.4 and 774.1 cm^{-1} (^{14}N). Since all bonds are saturated, the defect is electrically inactive.

2.6 Substitutional nitrogen pair, (N_s-N_s)

This D_{3d} defect (Fig. 2(d)) is the result of a divacancy being trapped by N_i-N_i . Similar pairs are known to form for P [27], and B [28]. The binding energy of (N_i-N_i) with V_2 is 3.4 eV [11, 14] suggesting a thermally stable centre. 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 defect has an IR-active mode at 668.6 cm^{-1} and an acceptor level around $E_c - 0.2\text{ eV}$. This level, the thermal stability and symmetry of the defect suggest a link with the trigonal optical ABC-centre with a zero-phonon line at 1.12 eV.

3 Discussion and Conclusions

Our calculations reveal that (N_i-N_i), dominates 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 cool 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.

When nitrogen is present, during this process (N_i-N_i) could trap a vacancy or di-vacancy forming (N_i-N_s) or (N_s-N_s) with the second structure constituting a particularly stable product. Further investigations [14] show a trend of diminishing binding energy of additional vacancies.

The calculated LVMs 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 LVMs calculated for other systems, and it is hoped that this data might lead to the identification of these other N-related centres. A number of nitrogen related modes are known to occur after implantation [29] but have not yet assigned. A mode at 690 cm^{-1} is close to a mode found for ($N_s V$) at 663 cm^{-1} . The downward shift of the two modes with ^{15}N are exactly the same at 17 cm^{-1} . 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} .

The identity of the N-related EPR centres, SL6 and SL7, remains unclear. The EPR evidence points to a single nitrogen atom together with an intrinsic defect as co-implantation with carbon and oxygen did not enhance its production. One possibility is ($N_s V$) and NV_2 for SL6 and SL7 respectively. The binding energy of ($N_s V$) is high – around 1.6 eV – and consistent with a thermal stability of SL6 of around 400 °C. It also is consistent with a calculated low spin-density on N.

Finally, we comment on the ABC luminescent centre seen in N-doped material. As pointed out above, there are a number of properties that are common to the photoluminescence centre and (N_s-N_s). These include the presence of nitrogen, their thermal stabilities (the ABC defect is stable to 1000 °C [30]), 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 centre.

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