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1996 J. Phys.: Condens. Matter 8 7711

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Theoretical studies on nitrogen–oxygen complexes in silicon

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Received 30 May 1996

Abstract. Semi-empirical PM3 cluster calculations are used to show that stable, electrically active NO complexes may exist in silicon. Based on their relative stability with respect to oxygen and nitrogen pairs, the retardation of thermal double donor formation in the presence of nitrogen is explained, but an equilibrium concentration much less than that of NN pairs is predicted. It is also shown that interaction of NO with a single nitrogen atom creates a bistable NNO defect, while encounter with an oxygen or an NN pair preserves the electrical activity of the NO centre. The possible role of the NO complex in shallow thermal donor formation is discussed.

1. Introduction

Heat treatment of silicon in inert ambient is most often treatment in the presence of nitrogen. Indeed, the equilibrium solid solubility of nitrogen is low in silicon and the nitrogen impurity is known to be electrically inactive. Nitrogen is, however, also introduced into silicon by the deposition of silicon nitride as a diffusion barrier or as a dielectric layer in metal insulator insulator semiconductor systems. Once in the crystal, nitrogen may interact with other defects, especially oxygen. It has recently been shown that nitrogen doping of Czochralski silicon can be used to suppress vacancy and interstitial defects and to increase gate oxide integrity [1].

Nitrogen occurs as substitutional impurity in irradiated silicon [2], but the majority of the nitrogen concentration is in interstitial pairs to which infrared (IR) bands at 962 and 766 cm^{-1} have been assigned [3]. In samples implanted with a $^{14}\text{N}/^{15}\text{N}$ mixture, it can be shown that the members of the pair occupy equivalent positions [4]. Channelling studies by the same authors in ^{15}N -implanted Si has shown that the nitrogen atoms are at 1.1 ± 0.1 Å from lattice positions along $\langle 001 \rangle$ directions, with a maximum deviation of 0.2 Å perpendicular to the $\langle 001 \rangle$ axis. Calculations have predicted a structure (figure 1), where the N atoms form a four member ring with two lattice silicon atoms [5]. The displacement of the nitrogen atoms from lattice sites were calculated to be 1.1 Å along $\langle 001 \rangle$ and 0.2 Å along $\langle 110 \rangle$. Taking into account the inaccuracy in calculating frequencies, the computed vibration modes, 919 and 689 cm^{-1} , fit the experimentally observed frequencies well and the isotope shifts are also correctly reproduced. The (NN) ring structure of nitrogen pairs in silicon can therefore be regarded as established.

In oxygen rich samples, the vibration frequencies characteristic of N pairs are reduced, and a new set of bands at 1030, 999, and 805 cm^{-1} appear [6, 7]. Since the Si–Si bonds in the (110) plane next to the (NN) ring are elongated, they can easily accommodate an

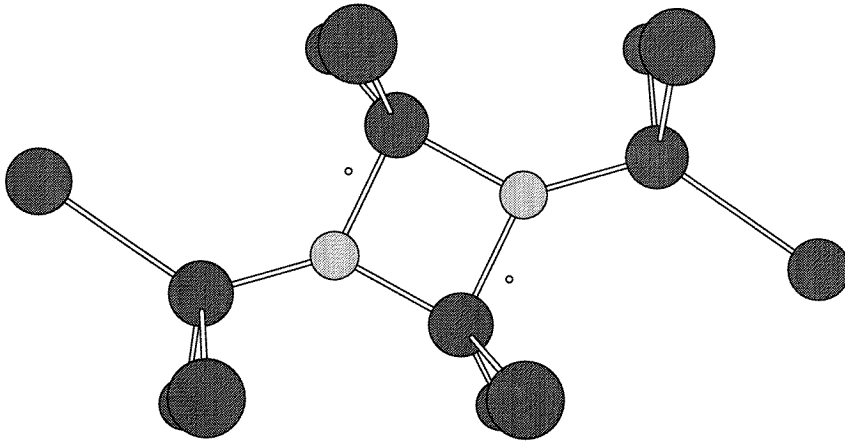


Figure 1. The NN complex (dark shaded circles are silicon atoms, light shaded circles are nitrogen atoms, small circles show the original silicon lattice positions).

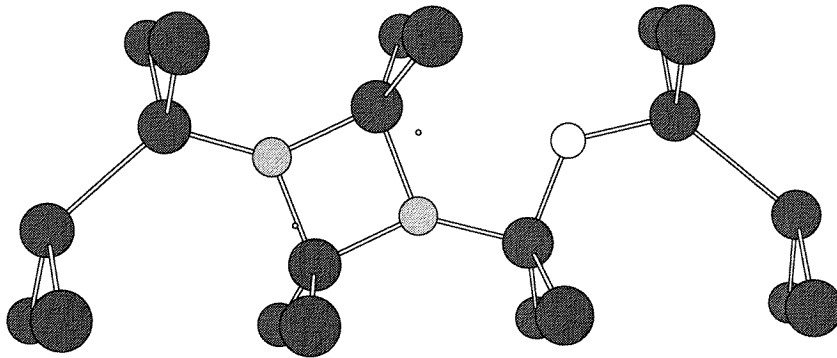


Figure 2. The (NN)O complex.

interstitial oxygen. Calculations carried out for this (NN)O complex [8] prove this structure (figure 2) to be stable and provide vibration frequencies in reasonable agreement with the measured ones and also correct isotope shifts.

In diffusion studies [9] on float zone (FZ) silicon samples co-implanted with oxygen and nitrogen, it has been shown that nitrogen diffuses faster in the presence of oxygen. In an earlier theoretical work [10] it has been postulated that di-oxygen complexes are stable and diffuse faster than a single oxygen interstitial. The di-oxygen complex alternates its configuration between a four member ring, (OO) similar to that of figure 1, and a pair of normal interstitials, O_{2i} sharing one common silicon neighbour [10]. (Fast diffusion of oxygen pairs is corroborated experimentally [11].) It is conceivable that four member ring structures can also be formed by a trivalent O and one N atom (figure 2). Trivalent oxygen atoms (bonded to a silicon self-interstitial) have been predicted [12] to be at the core of the oxygen related thermal double donors (TDD) [13], an assumption that is obtaining more

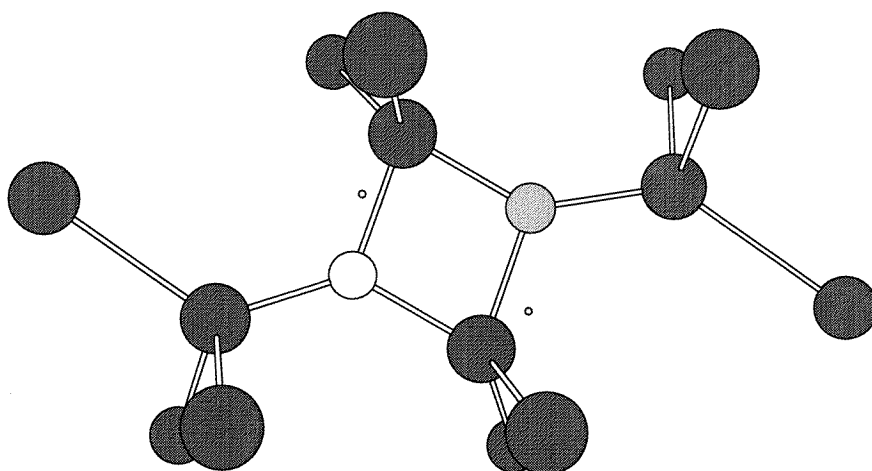


Figure 3. The NO complex (dark shaded circles: Si, light shaded circle: N, empty circle: O, the small circles represent the original lattice positions).

and more experimental support [14, 15]. It is important to realize that the four member ring (NO) is a single donor. The trivalent oxygen can accommodate three electrons in bonds and two more in a lone pair orbital perpendicular to those bonds. The sixth valence electron of oxygen has to be given up. Since the nitrogen, also with three bonds and one lone pair, cannot accommodate it either, this electron will occupy an orbital formed from the conduction band valleys due to the electric and stress field of the defect, according to effective mass theory (EMT).

It is well known that shallow, single donor complexes, called shallow thermal donors (STDs), are formed in oxygen-rich silicon after annealing between 300 and 600°C [16, 17]. Controversy has existed over a long period of time as to whether these donor centres contain nitrogen or not. No direct spectroscopic evidence exists for the involvement of N in these defects, but a number of studies [17–23] have shown that their appearance is related to the presence of nitrogen. On the other hand, the STDs become apparent after longer anneals in oxygen rich samples without intentional nitrogen doping [16, 24–27]. It appears likely that the term STD is used for different families of defects, as has been shown by Hara *et al* [22]. Some of them appear to be related to hydrogen passivated TDDs [25], probably giving rise to the low symmetry NL-10 signal in ESR [28], while others may contain nitrogen [22]. One of the STDs found in Al doped samples has proven to be bistable [27].

Hara *et al* [22] attributed the C_{2v} component of the NL10 signal to a nitrogen containing defect. Based on the analysis of annealing kinetics, Suezawa *et al* [18] postulated that the STDs consist of a core of one oxygen atom and an NN pair, with additional NN pairs contributing to the bigger members of the family. A C_{2v} defect with two nitrogens and one oxygen at the core would imply an oxygen on the C_2 axis, contradicting ENDOR results [30]. Also, the stable configuration of two nitrogens and an oxygen has lower symmetry (figure 2) and was calculated to be electrically inactive [8]. The only model of an N–O complex acting as an STD has been proposed by Jones *et al* [29]. This model is based on a di-ylid configuration [31] of oxygen atoms with a single substitutional (overcoordinated) nitrogen atom at the centre. The defect has a deep doubly occupied and a singly occupied shallow level in the gap. The electron on the latter has a negligible probability density on

the N atom.

Part of the controversy related to NO complexes may stem from the way nitrogen is introduced (during growth or in post treatment), and from the different annealing procedures applied. The relative stability of nitrogen–oxygen complexes is therefore of crucial importance. For the explanation of the ambiguous relation of STDs to nitrogen, Snyder has suggested [32] that (NO) rings could be energetically more favourable than di-oxygen complexes, but less favourable than (NN) rings. So nitrogen could capture oxygen into (NO) rings which would be the core of STDs. However, if N was in abundance then electrically inactive (NN) or (NN)O complexes would be formed instead.

The aim of this paper is to calculate relative stabilities for various nitrogen–oxygen complexes. Based on self-consistent semi-empirical quantum chemical calculations (briefly described in section 2), the stability of (NO) rings relative to the (NN) ring and di-oxygen complexes will be investigated. The possibilities of the NO ring to act as a core of STDs will be studied by adding N and O atoms to an (NO) ring (section 3).

2. Model and computational method

The cyclic cluster model (CCM) [33] has been proven to be an economic and fruitful way of modelling defect complexes in silicon [12, 34]. A 32-atom unit cell with cyclic boundary conditions is used here to compare the stabilities of diatomic complexes. The centre of the reduced Brillouin zone for this unit cell ($\mathbf{K} = 0$) represents a special \mathbf{k} vector set (Γ , three X and twelve $\Sigma(1/3, 1/3, 0)$ points) of the primitive Brillouin zone, allowing for a reasonable simulation of the crystal in a $\{\mathbf{K} = 0\}$ approximation. (In addition, only interactions within the first Wigner–Seitz cell are taken into account in the CCM. This reduces the interaction between repeated defects.)

A special characteristic of the CCM is the requirement of selecting clusters with full point group symmetry of the crystal (to ensure correct weighting factors for the special \mathbf{k} set represented by $\mathbf{K} = 0$) [33]. The size of the cluster is determined by the size of the defect complex. Since the triatomic complexes dealt with here are anisotropic in the [110] direction, a very large symmetric CCM would be needed. Instead, we have performed molecular cluster model (MCM) calculations in these cases (the stability of complexes with the same number of atoms will be compared anyway) using an $\text{Si}_{71}\text{H}_{60}$ molecular cluster (as in reference [10]).

For the investigation of relative stabilities of complicated defect complexes with many possible configurations, semi-empirical quantum chemical methods offer an economic solution. Even though they are semi-quantitative in nature, they are capable of predicting trends reliably. The applicability of these basically ‘chemical’ approximations to solid state studies has been tested in crystalline silicon [33] and α -quartz [35]. They have been successfully applied to predict the behaviour of hydrogen [34] and oxygen complexes [12], to investigate the phenomenon of quantum confinement [36], as well as surface reconstruction and adsorption phenomena [37–39] in Si.

The total energy of both the Si_{32} CCM and the $\text{Si}_{71}\text{H}_{60}$ MCM have been minimized (subject to T_d and C_{2v} symmetry, respectively) within the framework of the self-consistent PM3 semi-empirical approximation [40]. The results of a CCM-PM3 calculation for crystalline silicon are shown in table 1. The PM3 method was also shown to be successful in calculating oxygen defects in silicon [41]. Even though its performance in Si–N systems is less convincing (the relative electronegativity of N is underestimated), it has been favoured over the AM1 method [42], since the latter gives very poor results for Si–O bond distances. (PM3 and AM1 are different parametrizations of the modified neglect of diatomic overlap

Table 1. Properties of crystalline silicon.

Properties of c-Si	PM3-CCM	Experimental
Bond length (Å)	2.36	2.35
Lattice energy (eV/atom)	5.20	4.70
Valence bandwidth (eV)	10.20	12.30
Gap (eV)	0.99	1.17
Ionization threshold (eV)	7.64	5.35
Raman frequency (cm ⁻¹)	484	518

Table 2. Calculated CCM energies for different complexes.

Complex	E_{TOT} (eV)
Si ₃₂	-2337.88
Si ₃₂ N _i	-2501.18
Si ₃₂ N _i ⁺	-2493.77
Si ₃₂ O _i	-2632.28
Si ₃₂ O _{2i}	-2927.26
Si ₃₂ (NO) ⁺	-2790.72
Si ₃₂ (NN)	-2666.21

approximation introduced to the Hartree–Fock molecular orbital theory by the Dewar group; for further details see references [40, 41].) The stability of different defect complexes were compared by calculating their total energy, minimized with respect to all atomic coordinates except the 3rd and 4th neighbour silicon shell in CCM and the H atoms and their Si neighbours in MCM.

In calculating properties of a defect wavefunction with energy in the gap, it is extremely important that the approximation for the Hamiltonian allows a correct description of states at both the valence and conduction band edges [33]. Thus the CNDO/S approximation (as described in references [12, 33]) has been used for that purpose at defect geometries obtained from the PM3 calculation. Parameters for nitrogen have been worked out by fitting to ionization potentials of trisililamine, N(SiH₃)₃.

3. Results

Our PM3-CCM calculation reproduces the puckered bond-centre site for interstitial oxygen (O_i). The Si–O distance is 1.606 Å with a Si–O–Si angle of 155.89°, in good agreement with experiment [43]. Interstitial nitrogen (N_i) is found in the [001] split-interstitial configuration in both the positive and neutral charge states. The distances from the lattice site in both cases are about 0.6 Å for N and 1.2 Å for its Si pair. The ionization energy of the split-interstitial is about the same as that of the ideal cluster, indicating that the level connected with the trivalent silicon is close to the top of the valence band. The stable configuration of a nitrogen pair is the (NN) ring in the (100) plain as depicted in figure 1. The N atoms are 1.02 Å from the lattice site in the ⟨001⟩ direction, and 0.19 Å in the ⟨110⟩ direction, in excellent agreement with the LDA-MCM calculations of Jones *et al* [5]. According to our calculations the (NN) ring is electrically inactive because the levels of the nitrogen lone pairs fall into the valence band.

In order to check the possibility of a stable (NO) ring, we have replaced one of the

Table 3. Calculated MCM energies for the NNO complex.

Complex	Energy (eV)
[(NN)O] ⁰	-6708.47
[(NO)N] ⁰	-6707.20
[(NN)O] ⁺	-6700.78*
[(NO)N] ⁺	-6701.96

*see Appendix B.

nitrogens with oxygen in the equilibrium (NN) complex. Geometry optimization (energy minimization) has failed in the neutral charge state because the small size of the cluster does not allow the extra electron of the trivalent oxygen to delocalize into a real EMT orbital. During the energy minimization the electron keeps switching between various antibonding orbitals which subsequently become localized. (Unlike in case of the thermal double donors, where the C_{2v} symmetry fixed the EMT orbital [12].) The geometry optimization was successful in the positive charge state showing that the (NO) ring is at least metastable. The nitrogen and the oxygen atoms are almost symmetrically placed: 1.03 and 1.04 Å, respectively from the appropriate lattice sites in the $\langle 001 \rangle$ directions, and 0.13 and 0.11 Å, respectively in the $\langle 110 \rangle$ direction. These results are also confirmed by LDA-MCM calculations. A CNDO/S calculation for the neutral system, with the geometry fixed at the equilibrium obtained for the positively charged case in PM3, results in a delocalized, singly occupied state close to the conduction band. The electrons with unpaired spin 0.20% and 0.17% are localized on the N and O atoms, respectively, 13.07% on their immediate silicon neighbours and the rest are spread out in the cluster. A pile-up of spin density on the boundary atoms show that the size of the Si_{32} cluster limits the delocalization. It is therefore clear that (NO) represents a single, rather shallow, EMT donor.

To compare the relative stabilities of (NO), (NN) rings and (O_{2i}), the energetics of the following reactions have to be considered:



The heats of formation can be obtained from the calculated total energies:

$$\Delta H(NO) = \{E[Si_{32}(NO)] + E[Si_{32}]\} - \{E[Si_{32}N_i] + E[Si_{32}O_i]\} \quad (2a)$$

$$\Delta H(NN) = \{E[Si_{32}(NN)] + E[Si_{32}]\} - \{E[Si_{32}N_i] + E[Si_{32}N_i]\} \quad (2b)$$

$$\Delta H(O_{2i}) = \{E[Si_{32}O_{2i}] + E[Si_{32}]\} - \{E[Si_{32}O_i] + E[Si_{32}O_i]\} \quad (2c)$$

No convergent result for the neutral state of (NO) is available, but $\Delta H(NO)$ can be calculated from a Born-Haber cycle (see appendix A). For the equilibrium geometry of a complex of two neighbouring oxygen interstitials, a staggered geometry, similar to the one found by Needels *et al* [44], has been obtained. The calculated total energies needed to evaluate equations (2a-c) are given in table 2. The resulting binding energies are

$$\Delta H(NO) = -1.52 \pm 0.05 \text{ eV} \quad (3a)$$

$$\Delta H(NN) = -1.72 \text{ eV} \quad (3b)$$

$$\Delta H(O_{2i}) = -0.53 \text{ eV} \quad (3c)$$

The binding energy for the di-oxygen complex is more than the one (0.1 eV) obtained previously [12] using the MINDO/3 approximation [45] for the Hamiltonian, but less than

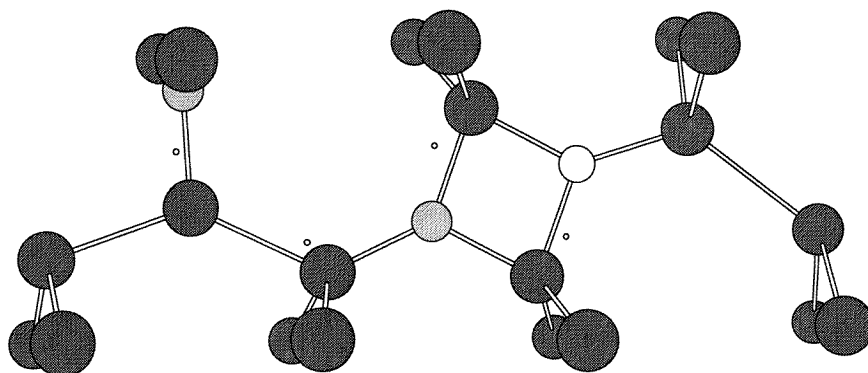


Figure 4. The N(NO) complex.

the value (1 eV) given in reference [44]. The differences show the significance of lattice relaxation. The MINDO/3 approximation gives a 180° Si–O–Si angle, exaggerating the strain around the defect. Even for a proper bond angle, the lattice relaxation necessary to accommodate the complex extends to several lattice constants. This has been taken into account in reference [44] by a Keating model, while the present calculation is restricted to the cluster. This means that the binding energies given in (3) can only be compared among themselves, and they represent a lower bound only. The comparison of equations (3a–c) shows that, even accounting for the error in the estimation of $\Delta H(\text{NO})$, (NO) rings are less favourable energetically than (NN) rings, but definitely more favourable than di-oxygen defects, as predicted [32]. (NB: the small difference between the binding energies of (NO) and (NN) can lead to more than one order of magnitude difference in concentration as shown in the next section.)

The interaction of the (NO) complex with an additional nitrogen atom has been investigated by adding N to the positively charged $(\text{NO})^+$ ring, in a $\text{Si}_{71}\text{H}_{60}$ MCM. The resulting configuration is shown in figure 4. The (NO) ring is preserved, and the N atom is at a neighbouring [001] split interstitial position. On the other hand, addition of an oxygen atom to an (NN) ring results in the structure shown in figure 2, the same as found in LDA-MCM calculations [8]. Comparing the structure (NN)O in figure 2 with N(NO) in figure 4, it is clear that they can be transformed into each other by flipping the nitrogen atom on the left back and forth. Apparently, these are two configurations for the same defect. The calculated total energy for the two configurations in both charge states are given in table 3.

The results clearly show that while (NN)O is more stable in the neutral state, N(NO) is more stable in the positive charge state. Accordingly the NNO defect is bistable. The (NN)O configuration is electrically inactive, with no levels in the gap. The N(NO) configuration is a single donor by virtue of the double occupied dangling bond of the Si atom near the split interstitial N atom.

Since an ONO complex of C_{2v} symmetry might explain the EPR data of Hara *et al* [22], the addition of an oxygen atom to the $(\text{NO})^+$ complex has been studied in a Si_{32} CCM in order to assure the correct simulation of the electronic structure of the crystal. The most stable configuration is an (NO)O complex with monoclinic (C_s) symmetry as shown in figure 5. The binding energy relative to an isolated $(\text{NO})^+$ ring and an oxygen interstitial is -1.43 eV. A CNDO/S calculation for the neutral charge state at this geometry gives

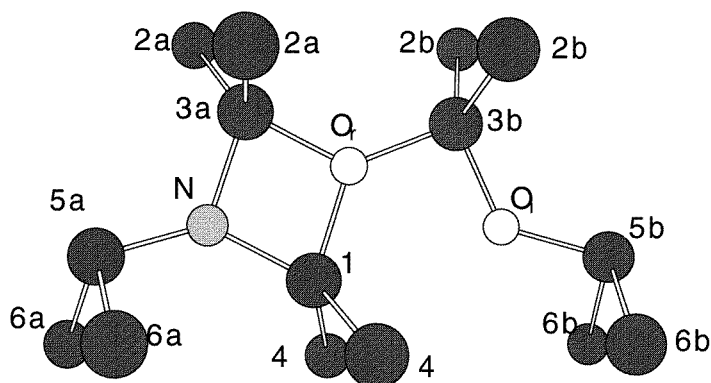


Figure 5. The (NO)O complex with C_s symmetry. Numbers denote atomic positions used in table 4.

Table 4. Spin distribution of the donor orbital in the (NO)O complex.

Position (see figure 5)	s (%)	$p_x + p_y$ (%)	p_z (%)
N	0.03	0.07	0.29
O _r	0.00	0.00	0.08
O _i	0.00	0.01	0.07
Si(1)	2.35	0.00	0.81
Si(2a)	0.87	0.97	2.43
Si(2b)	0.85	0.34	1.92
Si(3a)	1.90	0.11	0.50
Si(3b)	1.15	0.01	0.85
Si(4)	1.44	0.59	1.61
Si(5a)	0.52	0.00	0.57
Si(5b)	0.71	0.02	0.89
Si(6a)	0.49	0.05	1.18
Si(6b)	0.82	0.07	1.18

a shallow EMT donor orbital with spin distribution shown in table 4. It is basically an asymmetric combination of orbitals from the conduction band edge in the [001] direction. The spin density is small on the nitrogen and oxygen atoms, especially taking into account the fact that the finite cluster limits the delocalization possibility for the orbital.

An (ONO) configuration with C_{2v} symmetry (figure 6) has been found to be metastable with respect to a monoclinic O(NO) configuration. The binding energies are -0.73 and -1.05 eV, respectively. The energy difference between the two is only 0.32 eV, so it is conceivable that further oxygens in the (110) plane will stabilize the (ONO) structure, because the latter can relieve the stress caused by an adjacent interstitial oxygen (cf the inward ‘bending’ of atoms 5 in figure 6). In this interesting structure, the central silicon is overcoordinated. The extra bond to the nitrogen accommodates the sixth electron of one of the oxygens (with energy in the valence band), so only the other is given up for an EMT orbital. The spin distribution on the donor orbital from a CNDO/S calculation for the neutral charge state is shown in table 5. The orbital is a symmetric combination of conduction band edge orbitals along the [001] axis. The spin density is very small on the

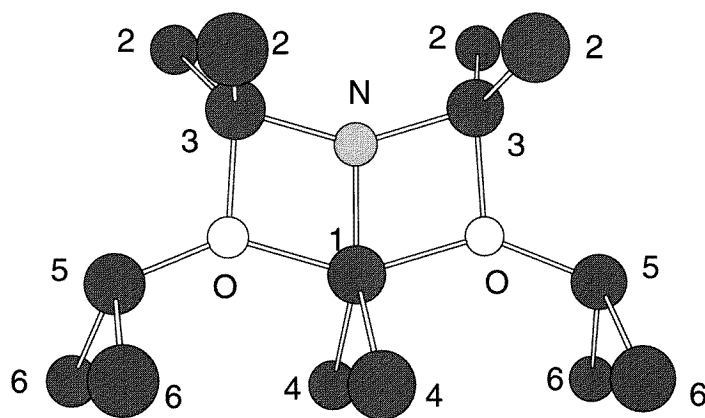


Figure 6. The metastable (ONO) complex with C_{2v} symmetry. Numbers denote atomic positions used in table 5.

Table 5. Spin distribution of the donor orbital in the (ONO) complex.

Position (see figure 6)	s (%)	$p_x + p_y$ (%)	p_z (%)
N	0.01	0	1.25
O	0.00	0.17	0.11
Si(1)	0.27	0	0.05
Si(2)	0.22	0.88	2.10
Si(3)	1.78	0.00	0.74
Si(4)	0.15	0.40	0.04
Si(5)	0.01	0.22	3.47
Si(6)	1.89	0.11	0.08

oxygen, but big enough to be observed on nitrogen. No hyperfine interaction with nitrogen has been observed in NL10. It should be noted, however, that additional interstitial oxygens are needed in the (110) plane to stabilize this structure. The effect of additional oxygens is (due to the repulsion of their lone pair electrons) an increase in the delocalization of the EMT donor orbital. This might lower the spin density on the single nitrogen atom of the defect while hyperfine interaction with oxygens are still detectable.

4. Discussion and conclusions

Summarizing the results outlined in section 3, it has been found that a stable complex of a nitrogen and an oxygen atom exists in the form of an (NO) ring. The binding energy of this complex is about 10% smaller than the one calculated for the (NN) ring, but considerably bigger than that of di-oxygen complexes. Consequently, the presence of nitrogen will retard oxygen pair formation, a major factor in the kinetics of TDDs [11]. It was also found that both (NN) and (NO) rings may capture further interstitial oxygens in the (110) plane. These findings can explain why the presence of nitrogen diminishes the concentration of TDDs [18, 19, 46].

The relative concentration of (NO) and (NN) in thermal equilibrium will roughly be (if

kinetic effects are not considered):

$$[\text{NO}]/[\text{NN}] \approx \exp\{-[\Delta\text{H}(\text{NO}) - \Delta\text{H}(\text{NN})]/kT\} \quad (4)$$

The concentration of (NO) is more than one order of magnitude smaller than that of (NN) after a heat treatment at 450 °C. If created, however, (NO) rings may survive further annealing, as the encounter with an (NN) pair leaves them intact.

The triatomic complex of an oxygen and two nitrogen atoms was found to be bistable. In the neutral charge state it has an (NN)O configuration, and in the positive charge state an N(NO) configuration. This also means that (NO) rings will not be created upon encountering an (NN) ring and an oxygen interstitial, both being electrically inactive and so inherently neutral. On the other hand, (NO) is a shallow single donor and will generally be positively charged. An encounter with a single nitrogen, therefore, may preserve the (NO) ring. The neutral (NN)O complex has no level in the gap. It can only be transformed into N(NO) by temperature induced motion of the atoms, similar to a diffusion step. During the transformation a gap level emerges. Ionization of this orbital helps to complete the transformation into the N(NO) configuration.

In conclusion, it is predicted that (NO) complexes can be formed in nitrogen doped Cz-Si but their concentration will generally be much smaller than the nominal nitrogen concentration as obtained from the IR frequency of the (NN) pairs. Generally, (NO) pairs will be present if created before or simultaneously with (NN) pairs.

There is experimental indication [47] that NN pairs do not form in heavily p-doped silicon. The likely explanation for that is the nature of a single N interstitial, as found in the present paper and in reference [5]. In its [001] split interstitial configuration, the Si atom sharing the lattice site with the nitrogen is triply coordinated and possesses a pure p dangling bond in the [110] direction. Accordingly, the centre can be charged in heavily p-doped Si, preventing NN pair formation. In such a situation the formation of positively charged (NO) pairs is more likely.

While the (NN)O complex, to which the known IR bands at 1030, 999 and 805 cm⁻¹ can be assigned, is electrically inactive, it was shown that the (NO) ring is a shallow single donor. The (NO) ring, attracting further oxygen atoms or (NN) pairs in the (110) plane, can form families of EMT donors. In the case of nitrogen aggregation the core will be bistable (because of the bistability of (NN)O and N(NO)). The donor wave function of (NO) based systems has C_{1s} symmetry, and is generally constructed from a pair of states at the conduction band edge in the [001] direction. The spin distribution is very low on the N and O atoms of the core. One metastable structure with C_{2v} symmetry has been found. This (ONO) double-ring structure might be expected to be stabilized by adjacent oxygens in the (110) plane. If that is the case, the spin density on the nitrogen atom of this centre seems to be too big to escape ENDOR detection, provided a sufficient concentration of this complex is available.

In conclusion it can be stated that aggregates with an (NO) ring as a core could serve as STDs. Observations on some of the STDs can be explained by the properties of the (NO) ring: the shallow, effective-mass-like single donor behaviour, the lower concentration but higher stability with respect to TDDs, and some of the ambiguities with respect to nitrogen concentration. Typical concentration of STDs are between 10¹³–10¹⁴ cm⁻³, even for (NN) concentrations of 10¹⁵. This agrees well with the predicted relative stability of (NO) and (NN) if they are created simultaneously (equation (4)). However, under special circumstances (e.g., heavy doping), (NO) rings can also be created, in excess to (NN) rings.

Long term annealing in air may also lead to nitrogen contamination in samples without intentional N doping. NNO complexes may then form and serve as core of STDs, explaining

the observed bistability [27]. It must be emphasized, however, that some of the centres termed STD [25] are certainly not related to nitrogen but are most probably hydrogen passivated TDDs [22, 25, 48].

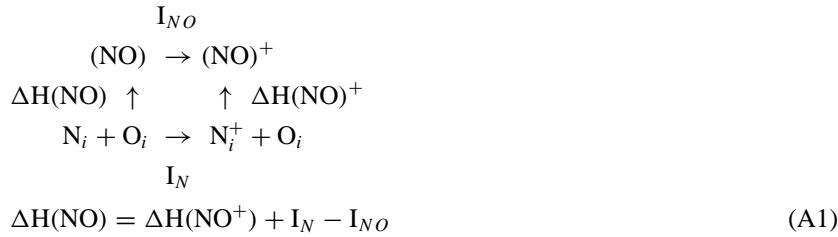
Whether any of the experimentally detected STD centres can be identified with (NO) ring type defects, remains to be seen until detailed ENDOR results are available. For that purpose, characteristic (qualitative) spin distributions for (NO) based EMT donors have been presented.

Acknowledgments

The authors wish to thank the support of the British-Hungarian Intergovernmental S&T Cooperation administered jointly by the British Council and the Hungarian National Committee for Technological Development (Project Nr. 11). This work was also supported by the Hungarian OTKA grant Nr. 2744 and the British SRC grant GR/H1404. Helpful discussions with J Weber and L C Snyder are appreciated.

Appendix A

The Born–Haber cycle used to calculate the heat of formation of the neutral (NO) is:



where the ionization energies of the single N_i and of the (NO) ring, as well as the heat of formation of the positively charged NO ring are defined as

$$I_N = E[\text{Si}_{32}N_i^+] - E[\text{Si}_{32}N_i] \quad (A2)$$

$$I_{NO} = E[\text{Si}_{32}(\text{NO})^+] - E[\text{Si}_{32}(\text{NO})] \quad (A3)$$

$$\Delta H(\text{NO}^+) = \{E[\text{Si}_{32}(\text{NO})^+] + E[\text{Si}_{32}]\} - \{E[\text{Si}_{32}N_i^+] + E[\text{Si}_{32}O_i]\} \quad (A4)$$

Using the data of table 2, $\Delta H(\text{NO}^+) = -2.554$ eV and $I_N = 7.414$ eV. Within the accuracy of the other data I_{NO} can be taken to be equal to the negative of the energy of an electron at the bottom of the conduction band in the perfect Si_{32} cluster, since (NO) is a shallow EMT donor. This can be calculated as the ionization energy of the ideal cluster minus the width of the gap. Using the data of table 1, $I_{NO} \approx 6.43 \pm 0.05$. Substitution into (A1) gives $\Delta H(\text{NO})$.

Appendix B

Since there is no gap level related to the (NN)O configuration, the ionization in this case occurs at the expense of the ‘extended states’ of the cluster. As the single occupation in this case oscillates between the close lying states in the upper part of the ‘valence band’ no convergence could be achieved in the optimization of the $[(\text{NN})\text{O}]^+$ configuration. The result shown in this case has been estimated from the energy of $[(\text{NN})\text{O}]^o$ with

$$E\{[(\text{NN})\text{O}]^+\} \approx E\{[(\text{NN})\text{O}]^o\} + I. \quad (B1)$$

Since $[(\text{NN})\text{O}]^{\circ}$ has no gap levels, the *de facto* ionization energy is that of the perfect cluster.

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