Core Structure of Thermal Donors in Silicon

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Aggregation of oxygen impurities as a result of thermal annealing gives rise to "thermal" double donor defects in Si and Ge. A microscopic structure for the core of these defects is proposed on the basis of first-principles calculations. In Si, the core contains three oxygen atoms, exhibits bistability, and has a total energy appreciably lower than three isolated oxygen interstitials. Impurities such as B, Al, N, and H are found to bind strongly to the defect and to transform it into a shallow single donor. [S0031-9007(96)00773-9]

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Oxygen impurities in Si present one of the most puzzling and challenging phenomena of any impurity in a semiconductor. Crystalline Si typically contains nearly $10^{18}/\text{cm}^3$ of oxygen impurities in electrically inactive twofold coordinated interstitial sites [1]. Annealing of Si at temperatures about 400–500 °C, where oxygen atoms become mobile, leads to the formation of a family of distinct "thermal" double donor defects usually labeled as TD1, TD2, etc. Since their discovery [2] in 1954, extensive experimental and theoretical work has been done to identify the microscopic structure of these defects. Important structural information has been obtained from kinetic [3–7], infrared absorption [8–10], electron paramagnetic resonance (EPR) [11,12], uniaxial pressure [13,14], electron-nuclear double resonance (ENDOR) [15–17], vibrational [18], and photoluminescence [19] studies, but as yet no entirely satisfactory model has emerged.

Many types of atomic structures for thermal donors have been proposed [20–25]. A principal challenge on the theoretical side is to find a structure with a larger binding energy per oxygen than in the simple interstitial bonding configuration while being consistent with experimental data. This has turned out to be difficult since the normal interstitial state in which oxygen breaks a Si-Si bond and replaces it by two Si-O bonds is very stable with a large binding energy of nearly 4.6 eV [26]. The average binding energy in a thermal donor needs to be larger than this value since Needels *et al.* have shown that two oxygen interstitials having a common Si ligand form a neutral state of even lower energy [27].

In this work extensive calculations on many different models consisting of interstitial oxygen atoms, with and without Si defects such as interstitials or vacancies, were carried out and the total energies determined. In the absence of other impurities, only one structure involving a cluster of three oxygen atoms is found to pass the energy criterion and to be an effective-mass type of double donor in Si. The structural and electronic properties of this O_3 complex are found to be in excellent agreement with experimental data. Interactions of the complex with H, B, Al, C, and N impurities were examined. In Ge, a related O_2 complex is found to be a stable double donor.

The total-energy calculations were performed using a first-principles pseudopotential approach [28] for a periodic 32 atom unit cell. The Brillouin zone sampling was done using Γ and one special k point [29]. A converged basis set with cutoff energy of 33 Ry for plane waves and 132 Ry for charge densities was used. The atomic potentials were generated by the method of Troullier and Martins [30] and were of the separable Kleinman-Bylander form [31].

Because of its small ionic bonding radius, oxygen, unlike S or Se, is unstable in a fourfold coordinated substitutional state. Oxygen moves strongly off center to form two Si-O bonds leaving behind two Si dangling orbitals which move towards each other to form a weak bond. The resulting A center [32] in Si is calculated to be 0.8 eV more stable than tetrahedrally coordinated oxygen, and it is not a donor. A trigonally symmetric state was also examined and found to be metastable with an energy 0.5 eV higher than the A center. Under equilibrium conditions, the A center is calculated to be 1.3 eV higher in energy than twofold coordinated interstitial oxygen. As for interstitial oxygen, a Si-O bond length of 1.65 Å and a Si-O-Si angle of 144° were obtained. Bond-centered oxygen ($\theta = 180°$) was found to be only 0.1 eV higher in energy.

Silicon vacancies containing two or more oxygen atoms have been considered as possible candidates for thermal donors [22,23,29]. The double donor property is contingent on threefold coordination of the oxygen atoms and a strong O-O bond. The results of our calculations show, however, a repulsive interaction between the oxygen atoms and a large O-O separation of 2.5 Å. In agreement with previous results [22–24,33], no donor activity is found for an optimized V-O_2 structure.

A large number of models involving Si interstitials in combination with one or more interstitial oxygen atoms were tested. Oxygen was found to lower the formation energy of some Si interstitial geometries to nearly 1–2 eV. A few configurations with double donor activity could be constructed, but the structural symmetry of these states is at variance with experimental data. The results of our study on many different models leave little doubt that, if the electronics properties, symmetry, and stability

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of oxygen aggregates in a thermal donor is to be properly accounted for, then Si vacancies or interstitials cannot be involved [34]. The search was focused, therefore, on structures involving only interstitial oxygen atoms.

The ideal Si lattice is shown in Fig. 1(a). A highly stable oxygen interstitial structure consisting of three oxygen atoms is shown schematically in Fig. 1(b). The complex is an effective-mass type double donor, and its electrical activity arises from the threefold coordinated oxygen and Si atoms at its center. The interaction of the trivalent Si atom with the two divalent oxygen atoms at a distance of 2.2 Å is critical to the stabilization of the complex. Without the two divalent oxygen atoms, the structure is that of a (001)-split-interstitial complex for oxygen, commonly referred to as the "*y*-lid" configuration. Snyder *et al.* [21,22] had proposed the *y*-lid geometry as a prime candidate for the core of thermal donors and suggested that it could be stabilized by two additional oxygen atoms as in Fig. 1(b). A calculation of the O_3 complex using a small atomic cluster was found, however, to give oxygen binding energies significantly below that for isolated interstitials [35]. The presence of an oxygen atom along the (001) axis of the O_3 complex was later considered to be at variance with a strict interpretation of ENDOR data [24,36]. It should be noted that the ENDOR proscription on a (001)-axis oxygen was found for TD3 and higher members of the thermal donor family. It is not yet known whether the first two members in the series, i.e., TD1 and TD2, are also prohibited from having such an oxygen atom [37].

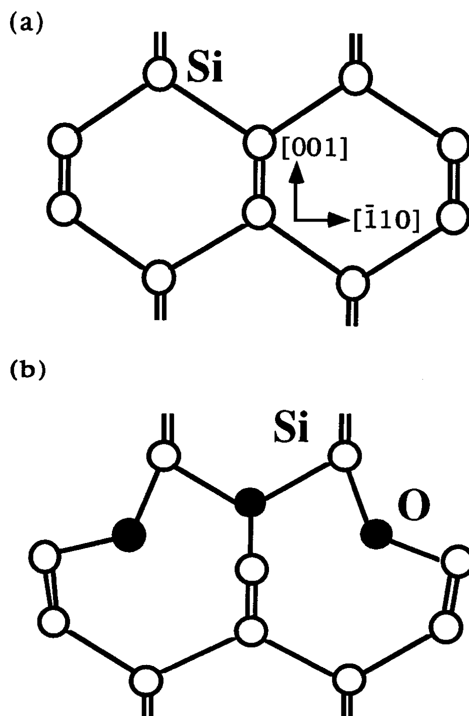

FIG. 1. Projection of a Si lattice onto a (110) plane is shown in (a). The O_3 complex core of a thermal double donor is shown in (b).

The results of our calculations show that the O_3 complex is 0.7 eV more stable than three isolated O interstitials. The total energy is also 0.3 eV lower than that of the combination of the stable O_2 complex (proposed by Needels *et al.* [27]) plus that of an isolated interstitial oxygen. The structural properties of the singly ionized O_3 complex are in good agreement with experimental data. For the proposed O_3 complex, all three oxygen atoms lie on a (110) plane; the structure has C_{2v} symmetry with a symmetry axis along the (001) axis and with (110) and ($\bar{1}$10) mirror planes, consistent with EPR, ENDOR, and stress data [11–13,15–17]. Small 0.05 Å deviations of the atoms from their perfect C_{2v} symmetric positions are found to lower the energy by 0.07 eV. The bonding of the central oxygen atom with the threefold Si atom [Fig. 1(b)] creates a large compressive strain along the (001) axis [13,14], resulting in a displacement of this Si atom by 0.47 Å along the (00$\bar{1}$) direction. Analysis of kinetic data suggests that TD1, the first member of the thermal donor family, contains three oxygen atoms [38]. It is natural, therefore, to assign the O_3 complex in Fig. 1(b) to TD1.

Experimentally, it is known that the TD1 center exhibits bistability. The O_3 complex in Fig. 1(b) is found to exhibit several types of bistability. The lowest energy of these structures is shown in Fig. 2. In this structure all three oxygen atoms become twofold coordinated, and the complex is stable in a neutral charge state. In *n*-type Si, this configuration is 0.1 ± 0.1 eV *more* stable than the double donor state in Fig. 1(b). The structure is characterized by two Si atoms, each with two Si-O bonds. This type of bonding was previously found to give a stable diatomic oxygen complex [27], and the low energy for the structure in Fig. 2 suggests that this result can be generalized to larger chains of oxygen atoms. The barrier for the transformation between the double donor and the neutral states is estimated to be about 0.7 eV.

The O_3 complex has two other higher energy metastable structures. Displacement of the trivalent oxygen by 0.77 Å along the [001] axis breaks the bond to

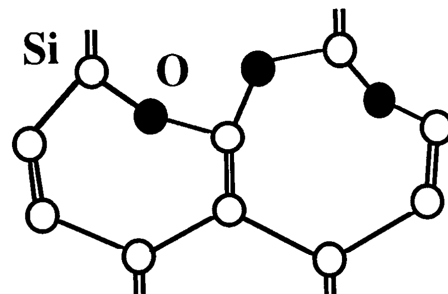

FIG. 2. The stable electrically inactive state of an O_3 complex obtained from atomic rearrangement of the structure in Fig. 1(b) is shown.

the trivalent Si atom and gives one of the two structures. The other corresponds to 0.6 Å in-plane displacements of the two side oxygen atoms away from the trivalent Si atom. The energies of these structures are, respectively, 1 and 2.5 eV above the ground state. The latter energy provides an estimate of the large contribution of the O-Si dative bonds to the stabilization of the O_3 complex in Fig. 1(b).

Interactions between H, B, Al, N, and C impurities with the central and side atoms of the O_3 complex were examined. Exchange reactions in which distant substitutional B or Al acceptor impurities switch positions with the threefold coordinated Si atom of the complex were considered. The total energy decreases by 0.7 eV for Al and 0.35 eV for B, and the double donor is converted into a shallow single donor in each case. In the case of N, the optimal bonding configuration of an isolated impurity in Si is not known. The replacement reaction (starting from either interstitial or trigonally relaxed substitutional N positions) in which N replaces the trivalent oxygen is exothermic by at least 0.8 eV, and the center is transformed into a shallow single donor [39,40]. Replacement of the threefold coordinated atom by N is found to be endothermic. Substitutional C is found to be highly stable against incorporation into the O_3 complex on either the trivalent oxygen or Si sites. Interstitial C does lower its energy, however, by becoming part of the complex. Substitution of C for the trivalent oxygen atom leads to a neutral complex. The exchange reaction is more exothermic, however, for substitution on the central Si atom. For H, bonding with the trivalent oxygen or Si atoms is weak; instead, H behaves as a negatively charged interstitial acceptor with a large Coulombic binding energy to the center. The interstitial H lies in a $(\bar{1}10)$ plane, normal to the plane of the defect. The excess binding energy, as compared to a negatively charged H atom at an interstitial site in the bulk, is 1.3 eV. Experimentally, there is evidence for the participation of H in some Si-NL10 centers [17]. The O_3 complex is found to become completely deactivated when two H atoms bind to the trivalent Si atoms within the (110) plane of the defect. The excess binding energies of each of the H atoms is close to 1.3 eV.

Structures derived from the O_3 complex with fewer and more oxygen atoms were also examined. The extraction of one of the two side oxygens of the O_3 complex in Fig. 1(b) (and rebonding of the Si atoms) leads to a metastable structure that is a deep double donor. The energy of this O_2 complex is 0.65 eV higher than the stable diatomic interstitial complex in which two oxygen atoms share a common Si neighbor [27].

The elimination of the (001)-axis oxygen atom and dimerization of two of its Si neighbors (as shown in Fig. 3 for Ge) gives an O_2 defect that is not as stable as the O_3 complex in Si. Electronically, the defect is on the verge of becoming a double donor, i.e., it has a doubly occupied state close to the conduction band minimum. In contrast to Si, the O_2 complex in Fig. 3 is a very stable entity in Ge, 0.7 eV more stable than two isolated oxygen interstitials, and is a *bona fide* shallow double donor.

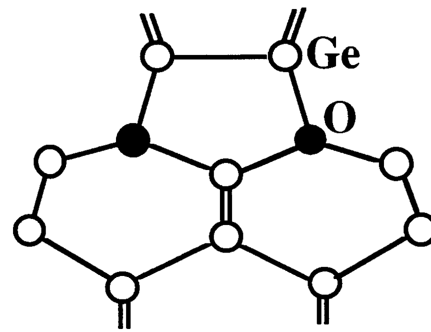

FIG. 3. Thermal double donor defect in Ge.

We propose that, in Si, as more oxygen atoms are added along the $[\bar{1}10]$ axis [i.e., in the plane of the three oxygen atoms in Fig. 1(b)], the central oxygen atom lying along the (001) axis can be dispensed with, and a dimerized structure similar to that in Fig. 3 takes shape. The evolution of the structure with additional oxygen atoms avoids a conflict with ENDOR data on the structure of TDn's for $n \geq 3$. The average binding energy of the oxygen atoms is found to increase slightly (by a few hundredths of an eV) when two additional oxygen atoms are added symmetrically to the O_3 complex in Fig. 1(b).

In summary, we have examined the binding energy of oxygen atoms in Si for a variety of bonding configurations. The state consisting of the smallest number of oxygen atoms with shallow double donor properties and having a greater stability than isolated interstitial oxygen atoms corresponds to the O_3 complex in Fig. 1(b) which we identify with the TD1 thermal donor. The center exhibits bistability, and its stable ground state is a neutral complex shown in Fig. 2. The O_3 center attracts N [40], H, B, and Al impurities and becomes a shallow single donor. In Ge, an O_2 complex (Fig. 3) is found to be very stable and a shallow double donor. The central core of thermal donors in Si is proposed to evolve to that of this O_2 complex as more oxygen atoms are added in the plane of the defect.

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