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Oxygen-oxygen complexes and thermal donors in silicon

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The suitability of several vacancy-oxygen and interstitial oxygen complexes as cores of thermal donors in silicon is examined. Tight-binding-based total-energy-minimization calculations were used in the determination of the atomic structure of the complexes. Vacancy-O_2 and interstitial O-O complexes are found to exhibit bistability and are the simplest structures exhibiting double-donor behavior. Atomic relaxations leading to oxygen-oxygen bonding and a threefold coordination of the oxygen atoms are critical in producing the double-donor activity.

I. INTRODUCTION

Oxygen impurities in crystalline Si are well known to give rise to electrically active double-donor defects known as thermal donors (TD's) under certain annealing conditions.[1,2] These defects have been studied extensively during the past 30 years and a large body of information on their properties has been gathered and reviewed in recent articles.[3-5] However, their precise atomic structure, especially the number of oxygen atoms at the core of TD centers, is still not known with certainty.

Infrared studies[5-9] have shown that TD's are a series of up to eleven defects (TD1–TD11) that are formed one after the other with annealing. The TD's differ by approximately 2 meV in their successive electron binding energies and their effective-mass-like wave functions arise from only one pair of states of the silicon conduction-band minima.[10,11] This suggests a preferential $\langle 100 \rangle$-like axis, arising from an internal strain in the structure of the TD's.[12,13] The small variations in the ionization energies of TD's are generally attributed to differences in the numbers of electrically inactive, twofold-coordinated, interstitial oxygen atoms around the active core.[7]

Early kinetic studies suggested an approximately $[O]^4$ dependence for the initial growth rate of TD's as a function of the oxygen concentration [O].[2,14] This led to the suggestion that the core of TD's consisted of approximately four to five oxygen atoms, and several models consistent with this picture were proposed.[2,14,15] A major problem for TD models requiring more than one or two oxygen atoms in the core is that the observed concentration of thermal donors is inconsistent with the measured[16] oxygen diffusion rate. More recent analyses have shown that it is difficult to extract the precise number of oxygen atoms in TD centers from kinetic studies[17-22] and that a growth rate proportional to $[O],^2$ indicative of oxygen "dimer" formation, provides an equally good agreement with the experimental data.[20,21]

Thermal donors have also been examined through electron-spin-resonance (ESR) and electron-nuclear double-resonance (ENDOR) measurements.[15,23] In combination with the infrared studies, the Si-NL8 spectrum in ESR has been definitively associated with thermal donors. The Si-NL10 center which arises from heat treatment may also be associated with thermal donors but could involve an additional impurity such as Al or B. The ESR and ENDOR studies have provided important information on the symmetry and possible atomic arrangements of oxygen atoms in thermal donors.[15,23]

In this paper the electronic structure of two types of oxygen complexes, consisting of vacancy-oxygen and interstitial oxygen complexes, are examined to test their suitability as cores of thermal donors in Si. Vacancy-oxygen complexes denoted here by V-O_n (with n representing the number of oxygen atoms contained in the vacancy) are one of the structural possibilities raised by analyses of various experimental data.[15,23] Wagner *et al.*[24] found from a combination of infrared and uniaxial pressure measurements that the stress coupling tensor components for the thermal donor were very similar to those for the A (or, equivalently, the V-O) center and suggested that this result could be consistent with models involving either a substitutional oxygen in the TD core or with a V-O_2 model proposed earlier by Corbett.[4] A study of electron-irradiation-induced oxygen-vacancy defects has led, however, to the conclusion that the V-O_2 center is not a thermal donor but possibly a nucleus for oxygen precipitation.[17] Theoretical studies on this center by DeLeo *et al.*[25] and more recently by Kelly[26] for several V-O_2 bonding configurations have also led to the conclusion that this center does not have a shallow donor state.

The tight-binding parameters for the calculations in this paper were derived, as shown in the Appendix, from results on bulk Si, α-quartz, and the free O_2 molecule. Section II contains the results of energy-minimization calculations for the Si lattice vacancy and for the V-O defect. The most important results of the calculations, as they relate to TD's concern the V-O_2, V-O_4, and interstitial O-O centers examined in Secs. III–V, respectively. The V-O_2 and the interstitial O-O complexes have C_{2v} point-group symmetries consistent with experimental data[9-13,23] and provide the simplest models for a thermal donor. Their atomic bonding geometries exhibit bistability with the oxygen atoms going from well-separated twofold configurations to strongly interacting threefold ones as the centers change from neutral to doubly ionized charge states. The discrepancy between the present results and previous theoretical findings[25,26] on the electrical activity of the V-O_2 center is most probably caused by the use of different lattice relaxations for the strongly interacting O-O configuration. The energy of the doubly ionized interstitial O-O state is calculated to be $\simeq 1.3 \pm 0.5$ eV higher than that of the V-${O_2}^{2+}$ center. However, since V-O_2 formation involves the creation of an energetically costly[27] (greater than or equal to 4 eV) Si vacancy-interstitial pair, the interstitial O_2 structure that entails only oxygen migration with a barrier[16] of $\simeq 2.54$ eV may correspond to the initial, metastable phase of the thermal-donor formation.

The atomic coordinates for V-O, V-O_2, V-O_4, and interstitial O_2 complexes were determined via empirical tight-binding total-energy-minimization calculations and are partially given in the following sections. The results of the present study do not allow an identification of the atomic structure of any individual TD1–TD11 thermal-donor species but provide information only on the possible core structures for these defects.

II. THE SILICON VACANCY AND *V*-O CENTERS

A. The Si lattice vacancy

The lattice vacancy in silicon has been extensively studied via ESR by Watkins[28] and its charge-state-dependent symmetries have been identified. The Si vacancy was predicted[29] and later shown to be an example of a "negative-U" system.[28,30] For the neutral state of the vacancy, two different structures were found. The first structure corresponds to the usual Jahn-Teller relaxed state of the vacancy in which the nearest neighbors of the vacancy are displaced by about 0.28 Å from their ideal positions. A second metastable geometry in which the atomic displacements are much larger ($\simeq 0.61$ Å) leading to the elimination of the four dangling bonds of the ideal vacancy and to the formation of two weak bonds is also found. The bonds are under strong tension and are elongated by $\simeq 11\%$ as compared to the ideal bond distance in the bulk. The results of the tight-binding calculations indicate that the energy of this rebonded structure is nearly the same as that of the unrelaxed vacancy but is 0.5 eV higher than that of the Jahn-Teller relaxed structure.

B. *V*-O center

The V-O center consists of an oxygen atom bound to a Si vacancy. The substitutional oxygen atom is known to move off center and to bond to two of the Si atoms.[31–33] The remaining two Si atoms move towards each other forming weak bonds as in the case of the strongly rebonded Si lattice vacancy.[34] For the fully optimized structure in the neutral charge state, the calculated off-center displacement of 1.03 Å for O and the Si—O—Si bond angle of 149° are in good agreement with the theoretically derived 1.1 Å and 152° values of Hjalmarson *et al.*[35] and Saito *et al.*,[36] respectively. As in the case of the strongly rebonded Si lattice vacancy, the stretched Si—Si bond of the structure is found to give rise to an unoccupied antibonding level at $E_c - 0.1 \pm 0.2$ eV, where E_c denotes the energy of the conduction-band minimum. The position of this level is nearly the same as the experimentally known acceptor level at $E_c - 0.17$ eV.[37] Without the Si—Si rebonding, an acceptor position closer to midgap would be expected.

For the negatively charged state a slightly different Si—O—Si angle of 150° is found. This value is in relatively good agreement with the ENDOR-derived 155° value of Gregorkiewicz *et al.*[23] The Si—O bond lengths

TABLE I. The atomic coordinates for the neutral and negatively charged states of the V-O center are shown. A Cartesian coordinate system is used. The unit of length is the cubic lattice constant a of Si ($a \simeq 5.43$ Å). The positions of corresponding bulk lattice positions are given to facilitate the determination of atomic displacements. The atoms denoted by Si_i with $1 \le i \le 4$ are the four nearest neighbors of the vacancy. The silicon atoms bonded to these four atoms are denoted by Si_{ij}, where $j \le 3$ represents the jth Si nearest neighbor of atom Si_i. The atoms listed in Table I represent only a portion of the atoms in the unit cell used in the calculations.

Atom	Bulk silicon	V-O^0	V-O^-
O		(−0.189,0.000,0.000)	(−0.189,0.000,0.000)
Si_0	(0.000,0.000,0.000)	Vacancy	Vacancy
Si_1	(0.250,0.250,0.250)	(0.245,0.170,0.170)	(0.232,0.171,0.171)
Si_2	(0.250,−0.250,−0.250)	(0.245,−0.170,−0.170)	(0.232,−0.171,−0.171)
Si_3	(−0.250,0.250,−0.250)	(−0.272,0.213,−0.213)	(−0.270,0.214,−0.214)
Si_4	(−0.250,−0.250,0.250)	(−0.272,−0.213,0.213)	(−0.270,−0.214,0.214)
Si_{11}	(0.000,0.500,0.500)	(0.011,0.453,0.453)	(0.016,0.461,0.461)
Si_{12}	(0.500,0.500,0.000)	(0.505,0.483,0.000)	(0.503,0.482,0.005)
Si_{13}	(0.500,0.000,0.500)	(0.505,0.000,0.483)	(0.503,0.005,0.482)
Si_{21}	(0.500,−0.500,0.000)	(0.505,−0.483,0.000)	(0.503,−0.482,−0.005)
Si_{22}	(0.500,0.000,−0.500)	(0.505,0.000,−0.483)	(0.503,−0.005,−0.482)
Si_{23}	(0.000,−0.500,−0.500)	(0.011,−0.453,−0.453)	(0.016,−0.461,−0.461)
Si_{31}	(−0.500,0.000,−0.500)	(−0.514,−0.009,−0.500)	(−0.511,−0.009,−0.499)
Si_{32}	(0.000,0.500,−0.500)	(0.000,0.467,−0.467)	(0.000,0.469,−0.469)
Si_{33}	(−0.500,0.500,0.000)	(−0.514,0.500,0.009)	(−0.511,0.499,0.009)
Si_{41}	(0.000,−0.500,0.500)	(0.000,−0.467,0.467)	(0.000,−0.469,0.469)
Si_{42}	(−0.500,0.000,0.500)	(−0.514,0.009,0.500)	(−0.511,0.009,0.499)
Si_{43}	(−0.500,−0.500,0.000)	(−0.514,−0.500,−0.009)	(−0.511,−0.499,−0.009)

are calculated to be $\simeq 1.7$ Å and the stretched Si—Si bond is $\simeq 0.26$ Å (11%) longer as compared to the ideal value of 2.35 Å. The symmetry of the defect is C_{2v} and its calculated atomic coordinates are shown in Table I. Comparison with results for the isolated vacancy shows that the two structures share similarities in their structural properties. The structural similarity of the two defects has also been emphasized as a result of recent ENDOR measurements.[38,39]

III. V-O_2 CENTER

A. Neutral and negative charge states

In the neutral charge state the V-O_2 center shown in Fig. 1(a) is very similar to the V-O center in that each oxygen atom makes two bonds with adjacent Si atoms.[40] The atomic coordinates displayed in Table II show that the center has C_{2v} symmetry and the deviations from the higher D_{2d} symmetry (which may be caused by the small unit cell dimensions used in the calculations) are very small. Two inequivalent Si—O—Si angles of $\simeq 151.4°$ and $\simeq 152.4°$ and Si—O bond lengths of 1.62 Å are found. In the neutral state, the two oxygen atoms are displayed by 1.03 Å from the center of the vacancy along the $\langle 100 \rangle$ axis and are 2.07 Å apart. The V-O_2 center in this configuration has an unoccupied level at $E_c - 0.21$ eV. The negatively charged state of the defect is found to have a structure very similar to that of the neutral state. The calculated atomic structure for the neutral state of V-O_2 center is consistent with the previous results of DeLeo *et al.*[25] for an $O_2Si_2H_{12}$ cluster simulation of the V-O_2 defect. They found an energy minimum for an O-O separation of 2.4 Å at which the oxygen atoms completely passivated the Si dangling bonds.

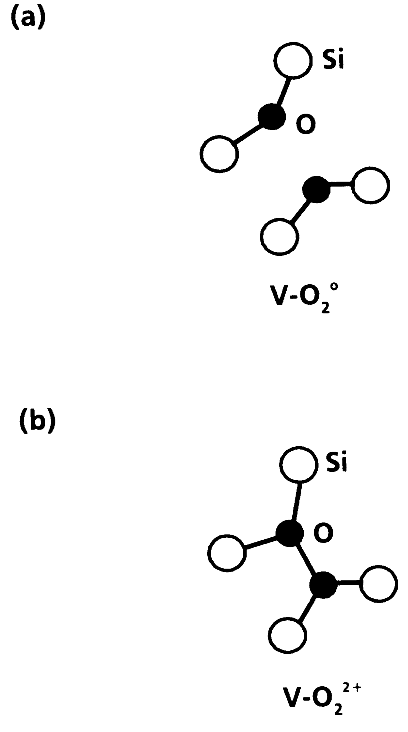

FIG. 1. The atomic structure of a V-O_2 complex in the neutral charge state is shown in (a). The two oxygen atoms are separated by 2.07 Å and are weakly interacting. The atomic structure for the stable V-$O_2{}^+$ state is shown in (b). The oxygen atoms are 1.38 Å apart and are strongly interacting. The oxygen atoms are aligned along the $\langle 100 \rangle$ axis in both cases.

Alignment of the two oxygen atoms of the V-O_2 center along $\langle 110 \rangle$ instead of a $\langle 100 \rangle$ axis was also examined in the present study. Optimization of the atomic coordinates shows that this configuration has a higher energy than the $\langle 100 \rangle$ alignment and it does not seem to lead to a stable configuration.

B. Positively charged state of V-O_2

The neutral V-O_2 center is found to become a double donor as a result of a structural transformation shown schematically in Fig. 1(b) in which the two oxygen atoms within the center move closer to each other by displacements of $\simeq 0.38$ Å along the $\langle 100 \rangle$ axis. In this configuration the oxygen-oxygen separation is reduced to 1.38 Å (close to the O_2 molecular value of 1.28 Å) and O—O—Si bond angles of $\simeq 114°$, Si—O—Si bond angles of $\simeq 132°$, and Si—O bond lengths of 1.70 Å develop. The binding of the substitutional oxygen atoms to the vacancy gives rise to Si—Si bond-length strains of between 2–4% for the Si atoms in the vicinity of the vacancy. The calculated atomic structure for the singly ionized charge state is essentially identical to that of the doubly ionized state. The predicted symmetries of the V-$O_2{}^+$ and V-$O_2{}^{2+}$ centers are C_{2v} but as in the case of the neutral center the deviations from D_{2d} symmetry are small. The structural parameters for the doubly ionized charge state are shown in the last column of Table II. A different structure for the V-O_2 center in which the two oxygen atoms are aligned along a nearly $\langle 110 \rangle$ instead of the $\langle 100 \rangle$ direction was examined and found to have a higher energy than the structure with a $\langle 100 \rangle$ alignment.

A Mulliken-type population analysis of the orbital occupancies of the oxygen and silicon atoms of the V-O_2 center shows that in the doubly ionized state the oxygen atoms are still *negatively* charged and have an excess electronic charge of $\simeq 0.2e$. The four surrounding Si atoms are positively charged with an electron deficiency of $\simeq 0.6e$.

The calculated electronic and structural properties of the V-$O_2{}^{2+}$ center are consistent with a number of experimental results on TD's in Si. The local, spherically nonsymmetric charge density of the V-O_2 center, the $\langle 100 \rangle$ orientation of the O—O bonds, and the lack of inversion symmetry are consistent with experimental data from stress and electric-field-dependent measurements.[41,42] The C_{2v} symmetry of the center that results from a small departure from D_{2d} symmetry (Table II) is consistent with experimental data that indicate the same two types of symmetries.[11,23,41,43]

The identification of V-O_2 centers with TD's in Si is also consistent with kinetic analyses showing a quadratic dependence of the TD growth rate with oxygen concentration and suggestions that O_2 "dimers" were involved in TD formation.[20,21] Recently, Messoloras *et al.*[44] have measured the loss of oxygen as a function of heating time

TABLE II. The atomic coordinates for the neutral and doubly ionized states of the V-O_2 center are shown. The same conventions as in Table I are used.

Atom	Bulk silicon	V-O_2^0	V-O_2^{2+}
O_1		(−0.192,0.000,0.000)	(−0.127,0.000,0.000)
O_2		(0.189,0.000,0.000)	(0.127,0.000,0.000)
Si_0	(0.000,0.000,0.000)	Vacancy	Vacancy
Si_1	(0.250,0.250,0.250)	(0.260,0.204,0.204)	(0.255,0.202,0.202)
Si_2	(0.250,−0.250,−0.250)	(0.260,−0.204,−0.204)	(0.255,−0.202,−0.202)
Si_3	(−0.250,0.250,−0.250)	(−0.266,0.204,−0.204)	(−0.256,0.201,−0.201)
Si_4	(−0.250,−0.250,0.250)	(−0.266,−0.204,0.204)	(−0.256,−0.201,0.201)
Si_{11}	(0.000,0.500,0.500)	(0.009,0.472,0.472)	(0.000,0.464,0.464)
Si_{12}	(0.500,0.500,0.000)	(0.504,0.496,−0.004)	(0.508,0.493,−0.009)
Si_{13}	(0.500,0.000,0.500)	(0.504,−0.004,0.496)	(0.508,−0.009,0.493)
Si_{21}	(0.500,−0.500,0.000)	(0.504,−0.496,0.004)	(0.508,−0.493,0.009)
Si_{22}	(0.500,0.000,−0.500)	(0.504,0.004,−0.496)	(0.508,0.009,−0.493)
Si_{23}	(0.000,−0.500,−0.500)	(0.009,−0.472,−0.472)	(0.000,−0.464,−0.464)
Si_{31}	(−0.500,0.000,−0.500)	(−0.504,−0.011,−0.496)	(−0.509,−0.009,−0.493)
Si_{32}	(0.000,0.500,−0.500)	(−0.007,0.466,−0.466)	(−0.002,0.464,−0.464)
Si_{33}	(−0.500,0.500,0.000)	(−0.504,0.496,0.011)	(−0.509,0.493,0.009)
Si_{41}	(0.000,−0.500,0.500)	(−0.007,−0.466,0.466)	(−0.002,−0.464,0.464)
Si_{42}	(−0.500,0.000,0.500)	(−0.504,0.011,0.496)	(−0.509,0.009,0.493)
Si_{43}	(−0.500,−0.500,0.000)	(−0.504,−0.496,−0.011)	(−0.509,−0.493,−0.009)

and temperature by infrared measurements. Their data indicate the existence of clusters consisting of only two oxygen atoms at $T=450\,^{\circ}\mathrm{C}$. The oxygen loss from the center is found to follow second-order kinetics. The theory of interstitial oxygen migration in Si has been examined by Snyder *et al.*[45] and, more recently, by Kelly[26] and Needels *et al.*[46]

The possibility that the V-O_2 complex could be a shallow double donor has been considered in previous theoretical work by Corbett *et al.*,[4] DeLeo *et al.*,[25] and Kelly.[26] Using an $O_2Si_4H_{12}$ cluster, DeLeo *et al.*[25] found that in a neutral state, the configuration corresponding to the threefold oxygen coordinated system had an energy about 2 eV higher than the twofold-coordinated case but that the total energy showed a shoulder or possibly a local minimum at an O-O separation of about 1.3 Å close to the 1.38-Å value found in the present study. They noted that the filled antibonding level arising from the oxygen lone-pair interactions could move higher in energy with decreasing oxygen separation leading to a double-donor defect. A larger cluster may be helpful for a definitive assessment of this question by allowing greater freedom for atomic relaxation around the O and Si atoms.

Kelly has examined the electronic properties of the V-O_2 center by first-principles calculations using a Gaussian basis set.[26] As the O-O distance is decreased, he finds that an antibonding O-O level does indeed go above the conduction-band minimum of Si. No double-donor behavior is found, however, because an A_1 symmetric level arising from the lattice vacancy dangling bonds comes into the gap as the O-O separation is reduced and the Si—O bonds are stretched. We do not find the corresponding A_1 state in our calculation because atomic relaxations around the core (see Table II) keep the Si-O distances at 1.7 Å, which is only 5.5% larger than the 1.61-Å bond length in α-quartz. As a result, there are no dangling bond states with A_1 symmetry that destroy the double-donor activity of the V-O_2 center. At this point, the possible role and importance of lattice relaxations around the core of the V-O_2 center needs to be examined more carefully in order to resolve the disagreement between the empirical tight-binding and the two previous theoretical results on the electrical activity of the V-O_2 center. The possibility of an overestimation of the strength of oxygen-oxygen interactions in the tight-binding calculations leading to double-donor activity was tested by reducing the magnitudes of the O-O interactions by 10%. The double-donor character was found to persist.

IV. OTHER V-O_n COMPLEXES

A. V-O_3 center

The annealing of the V-O_2 center at about 450 °C leads to a new series of infrared bands that have been identified with the V-O_3 center.[17,40] The electronic properties of the neutral V-O_3 center consisting of one oxygen atom bonded to two Si atoms and the remaining two oxygen atoms bonded to each other and to one Si atom each were examined. Bond angles of 153° between the Si—O—Si ligands and 142° between the Si—O—O ligands are found in the neutral state. An oxygen-oxygen bond length of 1.37 Å and Si—O bond lengths of 1.69 Å are calculated. The calculated structure has C_{2v} symmetry. The structure is predicted to have an unoccupied level at about $E_c - 0.2$ eV.

The possibility that the V-O_3 center could become a shallow double donor via a change in atomic configuration in which the oxygen atoms become threefold coordinated was examined. The results of the calcu-

TABLE III. The atomic coordinates of the neutral and doubly ionized V-O_4 center are shown. The same conventions as in Table I are used.

Atom	Bulk silicon	V-$O_4{}^0$	V-$O_4{}^{2+}$
O_1		(0.129,0.087,0.087)	(0.093,0.097,0.097)
O_2		(−0.129,−0.087,0.087)	(0.093,−0.097,−0.097)
O_3		(−0.111,0.092,−0.092)	(−0.100,0.097,−0.097)
O_4		(−0.0111,−0.092,0.092)	(−0.100,−0.097,0.097)
Si_0	(0.000,0.000,0.000)	Vacancy	Vacancy
Si_1	(0.250,0.250,0.250)	(0.291,0.269,0.269)	(0.268,0.268,0.268)
Si_2	(0.250,−0.250,−0.250)	(0.291,−0.269,−0.269)	(0.268,−0.268,−0.268)
Si_3	(−0.250,0.250,−0.250)	(−0.285,0.267,−0.267)	(−0.271,0.270,−0.270)
Si_4	(−0.250,−0.250,0.250)	(−0.285,−0.267,0.267)	(−0.271,−0.270,0.270)
Si_{11}	(0.000,0.500,0.500)	(−0.003,0.500,0.500)	(−0.006,0.506,0.506)
Si_{12}	(0.500,0.500,0.000)	(0.514,0.510,−0.008)	(0.505,0.505,−0.008)
Si_{13}	(0.500,0.000,0.500)	(0.514,−0.008,0.510)	(0.505,−0.008,0.505)
Si_{21}	(0.500,−0.500,0.000)	(0.514,−0.510,0.008)	(0.505,−0.505,0.009)
Si_{22}	(0.500,0.000,−0.500)	(0.513,0.008,−0.510)	(0.505,0.008,−0.505)
Si_{23}	(0.000,−0.500,−0.500)	(−0.003,−0.500,−0.500)	(−0.006,−0.506,−0.506)
Si_{31}	(−0.500,0.000,−0.500)	(−0.513,−0.008,−0.510)	(−0.505,−0.009,−0.505)
Si_{32}	(0.000,0.500,−0.500)	(0.003,0.500,−0.500)	(0.007,0.505,−0.505)
Si_{33}	(−0.500,0.500,0.000)	(−0.513,0.510,0.008)	(−0.505,0.505,0.009)
Si_{41}	(0.000,−0.500,0.500)	(0.003,−0.500,0.500)	(0.007,−0.505,0.505)
Si_{42}	(−0.500,0.000,0.500)	(−0.514,0.008,0.510)	(−0.505,0.009,0.505)
Si_{43}	(−0.500,−0.500,0.000)	(−0.513,−0.510,−0.008)	(−0.505,−0.505,−0.009)

lations show that, in the new geometry, V-O_3 is unstable and that it transforms back to the neutral-state configuration.

B. V-O_4 center

1. Neutral state

In the neutral charge state a low symmetry structure in which all the oxygen atoms are twofold coordinated is found. The atomic coordinates are given in Table III. Each oxygen is bonded to one Si atom and to one other oxygen atom. Two inequivalent Si—O—O angles of 152° and 141° are calculated. The angular distributions around the Si atoms range from 103° to 107°. The interacting oxygen atoms are separated by 1.38 Å (similar to the result for the V-O_2 center) and the "noninteracting" ones by 1.69 Å.

2. Positively charged state

In the doubly ionized charge state a structure in which each oxygen is bonded to one Si atom and is interacting with all the remaining oxygen atoms is obtained. In the fully relaxed structure the oxygen-oxygen separations are nearly 1.48 Å and all Si—Si bond lengths are within 1% of their ideal values. The structure arises from a simple distortion of the oxygen atoms in the neutral configuration. The atomic coordinates given in Table III show a C_{2v} symmetry for the center which results from small departures from T_d symmetry. The oxygen atoms are aligned almost along the four ⟨111⟩ axes. A very similar structure with slightly larger departures from a T_d symmetry is found for the singly ionized charged state. For both the singly and doubly ionized states, Si—O—O bond angles of 144°–145° are calculated.

A Mulliken population analysis of the orbital occupation for the doubly ionized configuration shows the four oxygen atoms to be *negatively* charged with excess electron charges of 0.2e each. The surrounding four Si atoms are positively charged with electron deficiencies of 0.48e on each atom. Smaller positive charges occur on the more distant Si atoms. The charge density of the V-$O_4{}^{2+}$ complex is much more spherically symmetric than the V-$O_2{}^{2+}$ center.

The number of oxygen atoms in the center, their ⟨111⟩-like alignment, and the absence of a Si atom at the core of the vacancy are all in very good agreement with the most recent ENDOR results of Michel *et al.* on the TD-related Si-NL8 center.[15] The model si also consistent with the first four-oxygen model proposed over 30 years ago by Kaiser *et al.* on the basis of their kinetic analysis of TD growth.[2] The problem of how such oxygen-rich clusters can form in view of the large 2.54-eV oxygen diffusion barrier remains unresolved. Another problem is that the repulsive core-core interactions between the oxygen atoms may lead to a high-energy state for this complex.

The possibility that the Si-NL10 center has the same core structure as the Si-NL8 TD-related center but differs from it in its charge state has been raised by Bekman *et al.* on the basis of ESR and ENDOR studies.[47] In this scenario the Si-NL8 center would correspond to the positively charged state of the V-O_2 center and the Si-NL10 to its negatively charged state. This cannot be ruled out by the present calculations. Since the structures for the V-$O_2{}^-$ and V-$O_2{}^+$ centers are calculated to be very similar to those for the V-$O_2{}^0$ and V-$O_2{}^{2+}$ centers, respectively, the information in Table II on the latter two states will hopefully prove useful in the evaluation of this alternative. In an earlier study, Michel *et al.* had also proposed that the core of the NL10 center contained two oxygen atoms.[48] The present theoretical results on V-O_2 and V-O_4 clusters do not allow a unique assignment of these complexes to either the Si-NL8 or Si-NL10 centers.

V. INTERSTITIAL OXYGEN COMPLEXES

The equilibrium atomic structure of a single interstitial oxygen atom was determined first via total-energy-minimization calculations in a three dimensionally periodic 64-atom cubic unit cell. A Si—O—Si bond angle of 172°±5° and Si—O bond lengths within 1% of those in α-quartz are found. The two Si atoms bonded to the oxygen get displaced by 0.39 Å from their ideal bulk positions and the next-nearest-neighbor shells are moved by $\simeq 0.1$ Å. The lone pair states of the twofold-coordinated oxygen atom are found to be nearly 12 eV below the Si valence-band maximum. No impurity related states lying in the band gap are found and the single oxygen interstitial is electrically inert.

The possible pairing of two interstitial oxygen atoms along two separate Si—Si bonds aligned along the [111] cubic axes are shown in Fig. 2 was examined. In the neutral charge state, the distance between the two oxygen atoms is large ($\simeq 3$ Å) and there is a negligible interaction between the lone pair orbitals of the two oxygen atoms. Oxygen-oxygen bonding leads to distortions of the surrounding lattice that are equal in magnitude to those for the single interstitial case and results in a stable (or at least metastable) configuration when the center is in a doubly ionized charge state. In this state the Si—O bonds are within 1.2% of those in α-quartz and the O—O bond length of 1.39 Å is 8.5% longer than that of the free O_2 molecule and has nearly the same magnitude as the O-O separation in the V-$O_2{}^{2+}$ complex. For the optimized structure, the Si—O—Si and Si—O—O bond angles are calculated to be 122.5° and 123.7°, respectively. For the doubly ionized configuration, each of the two O atoms has an *excess* electric charge of $0.2e$ and the four nearest-neighbor Si atoms each has a deficiency of $0.5e$.

The two oxygen atoms of the center are oriented along a cubic [101] axis in the fully optimized structure and the center has a C_{2v} symmetry consistent with that of TD centers. The displacements from ideal bulk positions of the four Si atoms surrounding the oxygen atoms are significantly larger along either the [100] or the [001] axes than other directions.

Within the present tight-binding scheme, the total energy of the doubly ionized interstitially paired oxygen configuration can be compared with that of the corresponding V-$O_2{}^{2+}$ center since both contain equal numbers of O—O and Si—O bonds. The calculations for a 64-atom cubic cell show that the V-O_2 center is about 1.3 ± 0.5 eV more stable than the interstitial configuration with no vacancies. The calculation assumes that the Si interstitial created during vacancy formation has been transferred to the surface. Despite the higher energy of the interstitial pairing, initial annealing of Si may lead to a larger number of these centers because of the smaller activation barrier for oxygen diffusion as compared to that for Si vacancy-interstitial formation and oxygen migration to the Si vacancy. The paired interstitial oxygen configuration may be an important component of thermal-donor centers for annealing temperatures of 450 °C.

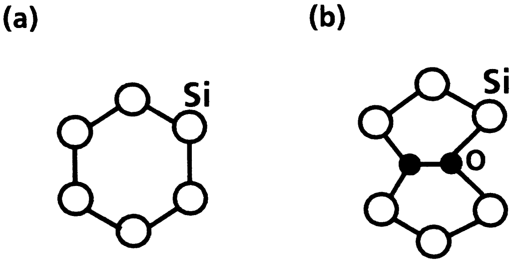

FIG. 2. The atomic structure of ideal Si and an interstitial O_2 complex are shown schematically in (a) and (b), respectively.

A partial listing of the atomic coordinates of the interstitial O-O^{2+} center and its nearest-neighbor Si atoms determined from calculations on a (64+2)-atom unit cell is given below. A Cartesian coordinate system with axes oriented along the three cubic [100] directions is used. The unit of length is taken to be the cubic lattice constant ($\simeq 5.44$ Å) of Si. The two oxygen coordinates are at (0,0,0) and (−0.181,0,0.181). The nearest-neighbor Si atoms are at (−0.026,−0.141,−0.259), (0.259,0.141,0.026), (−0.440,−0.141,0.154), and (−0.154,0.141,0.440). The nearest neighbors of these Si atoms are at (0.281,−0.355,−0.507), (−0.226,0.130,−0.532), (−0.237,−0.437,−0.056), (−0.687,−0.356,0.462), (−0.712,0.130,−0.046), and five other atoms related to these via the coordinate transformations $(x,y,z)\rightarrow(-z,-y,-x)$.

VI. CONCLUSIONS

The atomic structure of the Si lattice vacancy and various vacancy-oxygen and interstitital oxygen complexes denoted were determined using a tight-binding-based energy-minimization approach. The main results of the calculations are the identifications of V-O_2, V-O_4, and interstitial O_2 complexes as possible sources of TD centers in Si. All three centers have electrically inactive atomic configurations in which the two oxygen atoms are well separated and noninteracting. A structural change leading to an overcoordination of the oxygen atoms is found to be necessary for the double-donor activity of these centers. The symmetry of all three centers is C_{2v}, consistent with that for TD centers. The V-$O_2{}^{2+}$ complex is calculated to be about 1.3±0.5 eV more stable than the interstitial $(O$-$O)^{2+}$ one but the interstitial O-O complex may be the dominant TD species at low annealing temperatures. The O-O alignments are calculated to be along a [100] axis for the V-O_2 center and along a [110] axis for the interstitial O-O complex. The bistability of the V-O_2 structure and its suitability as a core for thermal donors in Si has been addressed by DeLeo *et al.*[25] and more recently by Kelly.[26] The results of the present calculations show that the inclusion of lattice relaxation around oxygen atoms leads to Si—O bond lengths very close to those in α-quartz and to double-donor behavior of the system in the strongly interacting limit. The identification of V-O_2, V-O_4, and interstitial O-O complexes as candidates for the core of thermal donor leaves unresolved the problem of the distinction between the atomic structure of individual members of the TD1–TD11 family.

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APPENDIX

The empirical tight-binding method has been used extensively in structural determinations, particularly in the determination of semiconductor surface reconstructions.[49,50] The approach used here is the same as that used in these previous studies. Bloch functions constructed from s, p_x, p_y, and p_z atomic orbitals were used in the calculation of the electronic structure. The Si-Si, Si-O, and O-O Hamiltonian matrix elements were obtained by fitting the electronic structure of bulk crystalline Si,[50] α-quartz,[51] and the O_2 molecule,[52] respectively, and are given below. The U_1 parameters entering in the total-energy expression[49,50] were determined by requiring that the first derivative of the total energy with respect to volume, or bond length, be equal to zero at the equilibrium bulk volume, or bond length. The U_2 parameters were determined from the bulk modulus or vibrational data. A $2\times2\times2$ cubic unit cell normally containing 64 silicon atoms was used in many of the calculations. In nearly all cases a smaller 32-atom cell was found to give equally good results. All atoms in the unit cell were allowed to relax. The equilibrium atomic positions were determined in an iterative process through a minimization of Hellmann-Feynman forces.[50] These forces can be calculated within the tight-binding method through first-order perturbation theory. Typically, 100 iterations were used in reaching the optimal structure from an initial guess structure. No symmetry restrictions were imposed during the energy-minimization process. This approach is useful in that a lowering of symmetry from the original structure would sometimes occur as a result of the energy minimization.

The tight-binding parameters used in the calculations are listed below. For Si-Si interactions, the nearest-neighbor parameters (in eV) for the reference Si-Si separation of 2.35 Å are

$$E_s(\mathrm{Si})=-5.25 \quad E_p(\mathrm{Si})=1.20\ ,$$

$$V_{ss\sigma}=-1.94,\quad V_{sp\sigma}=1.74\ ,$$

$$V_{pp\sigma}=3.05,\quad V_{pp\pi}=-1.08\ ,$$

and

$$U_1=-4.09,\quad U_2=13.9\ .$$

A d^2 dependence of all electronic matrix elements on nearest-neighbor distance is assumed in the calculations.

The Si-O parameters were extracted by fitting the electronic structure of α-quartz. For a reference Si—O bond length of 1.609 Å, they are given by (in eV)

$$E_s(\mathrm{O})=-24.3,\quad E_p(\mathrm{O})=-11.5\ ,$$

$$V_{ss\sigma}=-2.85,\quad V_{sp\sigma}=5.4\ ,$$

$$V_{pp\sigma}=5.4,\quad V_{pp\pi}=-1.4\ ,$$

and

$$U_1=-10.14,\quad U_2\simeq25\ .$$

The parameters (in eV) for O-O interactions extracted from a fitting of the energy levels of the molecule at a nearest-neighbor separation of 1.28 Å are

$$V_{ss\sigma}=-8.5,\quad V_{sp\sigma}=10\ ,$$

$$V_{pp\sigma}=14,\quad V_{pp\pi}=-2.1\ ,$$

$$U_1=-22.6,\quad U_2=47.7\ .$$

These parameters reproduce the correct ordering, and approximately the correct spacing, between the σ_g, σ_u, π_u, and π_g molecular levels.[52] The relatively small value of the $V_{pp\pi}$ interaction parameter as compared to the other O-O parameters is a reflection of the small $\simeq$4-eV splitting between the π_u, and π_g molecular levels. A somewhat better fit to the O_2 molecular levels can be obtained if $E_s(\mathrm{O})$ and $E_p(\mathrm{O})$ were treated as free parameters. However, the values listed above which are obtained from previous work on SiO_2 (α-quartz)[51] were used for consistency.

The above parameters are sufficient for calculating the atomic and electronic properties of Si-O complexes for a specified bonding topology and were used in the calculations described in the previous sections. The estimation of the relative stabilities of differently bonded configurations requires the specification of three extra additive constants for the total-energy comparisons. These correspond to the core-core parameters: U_0(Si-Si), U_0(Si-O), and U_0(O-O).[50] The difficulty with oxygen is that the U_0(O-O) and the U_0(Si-O) parameters are coordination number (and distant) dependent and cannot be assigned structure-independent values. A similar situation was previously encountered with carbon and resolved through a slightly different approach.[53] A comparable approach for treating the core-core repulsive interactions for the Si-O and O-O systems would be very desirable and needs to be devised for studying the relative stabilities of various oxygen clusters in Si.

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