Silicon-Interstitial–Oxygen-Interstitial Complex as a Model of the 450 °C Oxygen Thermal Donor in Silicon

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The complex of a divalent silicon interstitial and a pair of adjacent oxygen interstitials is proposed as the core of the 450 °C oxygen thermal donor in silicon. The proposal is supported by theoretical calculations which suggest that this complex is stable relative to the self-interstitial and two separated oxygen interstitials, and that it has a doubly occupied level close to the computed conduction-band edge. The calculated spin distribution is in qualitative agreement with the one found experimentally for the NL8 center.

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For more than thirty years[1] it has been known that thermal donors are formed when crystalline silicon containing oxygen is annealed at 450 °C. These thermal donors are destroyed when the crystal is annealed at 590 °C. The thermal donors are believed[2] to consist of a core to which oxygen atoms aggregate to form a series of closely related donor structures. The structure of the thermal donor core has remained unknown despite extensive, careful experimental and theoretical studies.[2]

From electron nuclear double resonance (ENDOR) studies it is known that the core of the donors contains oxygen and silicon. In this paper we propose a novel core structure for the thermal donors which we believe will provide a basis for understanding the vast body of observations in terms of a single-donor core structure. We propose that the core of the 450 °C oxygen thermal donors (TD) is a complex of a divalent silicon interstitial with a pair of adjacent interstitial oxygen atoms as depicted in Fig. 1. Our proposal is based in part on theoretical calculations using the self-consistent, semiempirical MINDO/3 (modified intermediate neglect of differential overlap) and CNDO/S (complete neglect of differential overlap for spectroscopy) approximations applied to a 32-atom unit cell in the cyclic cluster model (CCM). The method has been described in detail elsewhere.[3]

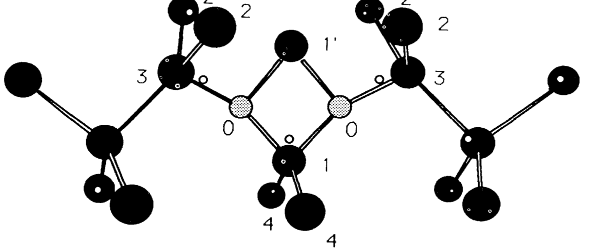

FIG. 1. Computed structure of the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex. Undisturbed lattice positions are shown as small white dots.

The bonding of an interstitial silicon atom to an adjacent pair of interstitial oxygen atoms is computed to form the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex shown in Fig. 1. The coordinates of all atoms shown in Fig. 1 have been optimized. The reaction to form this complex from isolated interstitials is computed to be exothermic with a heat of formation of -0.75 eV. In fact, we expect this complex to be more stable than that, because the given unit-cell size does not allow for a sufficient relief of stress by long-range relaxations. In a calculation on a $\mathrm{Si}_{47}\mathrm{H}_{60}$ molecular cluster (using the hydrogen atoms as terminators) with an elongated shape along [110], we obtain a heat of formation of -1.32 eV. There are also indications that there is a barrier for dissociation.

The $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex has a very low computed ionization energy. The interstitial oxygen atoms may be thought to form dative bonds to the divalent silicon atom. The formation of these dative bonds forces two electrons into a lone pair p-like orbital on the divalent silicon, perpendicular to the plane of the interstitials. This gives the self-interstitial a formal charge of -2. As a consequence, the lone pair orbital has a computed ionization energy of only 4.56 eV, to be compared to the 5.77-eV ionization energy of the 32-atom unit cell without the complex. Thus our calculations suggest that these electrons have an energy placing them in the bottom of the conduction band; these electrons correspond to the TD electrons. Using the CNDO/S method (better suited to describe conduction-band states)[3] to calculate the electronic structure of the previously computed core geometry, we find that the lone pair *p* orbital on the self-interstitial autoionizes into an orbital which is mainly 3*s* on the layer of atoms containing atom 1 (see Fig. 1), mainly $3p_z$ in the next layer along [001], and alternately 3*s* and $3p_z$ in subsequent layers. This would be expected for a linear combination of two conduction-band orbitals from the *X* point of the Brillouin zone. In the CCM calculation for the 32-atom unit cell these correspond to the two conduction-band valleys directed along the twofold *z* axis of the donor.

We have calculated the frequencies of the localized vibration modes[4] related to the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex in comparison with the asymmetric stretching-mode frequency of the isolated oxygen interstitial and of the neutral vacancy-oxygen complex. The results are 1131 and 1036 cm^{-1} for $\mathrm{Si}_I(\mathrm{O}_I)_2$, 1254 cm^{-1} for O_I, and 990 cm^{-1} for *V*-O, respectively. Assuming a systematic error of about 13% giving 1091 cm^{-1} for O_I and 861 cm^{-1} for *V*-O, the frequencies related to $\mathrm{Si}_I(\mathrm{O}_I)_2$ can be estimated to be around 984 and 901 cm^{-1}.

The first reason for us to propose the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex as the core of the 450 °C oxygen thermal donors is the indication by our calculations that it gives rise to a donor level close to the conduction band. The corresponding orbital is composed of the two valleys of the conduction band, along the *z* axis as was found in the infrared studies of Stavola *et al.*[5] The second reason given by our calculations is the fact that this complex is consistent with the results of ENDOR studies.[6,7] It is of C_{2v} symmetry and it does not contain an oxygen atom on the twofold axis. The spin localizations deduced from ENDOR studies of the NL8 center (an EPR active site usually assigned to the TD's) are qualitatively reproduced by the CNDO/S wave function of the donor orbital of the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex. Table I shows the mean hyperfine parameters observed for (TD^+) *B* which has the most intense spectra analyzed in the greatest detail in Ref. 6. The experimental and calculated spin localizations are also shown. Since the unit-cell size is much too small for an effective masslike orbital, all spin populations are computed to be too large by a factor of 10. The assignment of atom types to our computed structure is shown in Fig. 1. It conforms to the assignments made in Ref. 6 based on the symmetry of the observed spectra. Our symbol 2 in Fig. 1 stands for the average of the 2*a* and 2*b* hyperfine parameters. We take this average because our core structure has C_{2v} symmetry. The possibility that the symmetry of the NL8 donors observed by Michel, Niklas, and Spaeth may have been lower has been discussed by Gregorkiewicz, Bekman, and Ammerlaan.[7] The type-1 atom in Fig. 1 has the large isotropic hyperfine interaction on the twofold (*z*) axis. The divalent silicon (1′) is a site of low isotropic spin density and is difficult to observe. Atoms of type 3 and 4 are on layers of bigger spin density in $3p_z$ orbitals. We propose that the TD grows by adding interstitials to one side of this core in the [110] direction. This perturbs the mainly *s*-like effective-mass orbital and causes significant differences in the hyperfine constants in atoms of the *a* and *b* classes in Ref. 6. Our spin localizations at oxygen are also in qualitative agreement with the observed hyperfine interactions.

TABLE I. Comparison between the experimental spin localization deduced from the ENDOR hyperfine constants of the (TD^+) *B* center in Ref. 5 and the calculated values.

	Observed ^{29}Si hyperfine constants (kHz)			Spin localizations (%)			
				Experiment		Theory	
Atom	*a*	*b*	*c*	3*s*	$3p_z$	3*s*	$3p_z$
1	8720	70	20	0.19	0.06	1.4	1.2
2	6985	45	30	0.16	0.05	2.1	0.7
3	5650	370	80	0.13	0.34	1.3	1.5
4	4805	130	70	0.11	0.12	0.4	1.4
1′	3260	30	10	0.07	0.03	0.03	0.02
O^{17}	470	90	80	<0.02		0.05	0.03

The $\mathrm{Si}_I(\mathrm{O}_I)_2$ model of the TD core has some additional features which can explain observed phenomena. As can be seen in Fig. 1, it exerts a compressive force on the lattice in the *z* direction as expected.[8] The presence of the self-interstitial is crucial to the donor behavior. The increasing strain accompanying the growth of the TD's will sooner or later emit the self-interstitial from the complex losing the electrical activity. The relatively low heat of formation for the complex implies a dynamic equilibrium with free self-interstitials, explaining the observed[8] reorientation under uniaxial stress, and the fact that these TD's do not form during annealing at higher temperatures. The need for a self-interstitial in the TD's explains why TD formation is retarded by the presence of carbon which is known to eliminate mobile self-interstitials through the $\mathrm{C}_S + \mathrm{Si}_I \rightarrow \mathrm{C}_I + \mathrm{Si}_S$ reaction.

It is known that the first and second TD's of the series are bistable.[9] Our calculations indicate that there is another stable state of the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex consisting of a [001] split self-interstitial in the triplet state and of two oxygen interstitials on both sides with the oxygen atoms having common silicon neighbors with the self-interstitial. This structure is somewhat lower in energy. The computed ionization energy is 5.61 eV indicating no electrical activity.

We also suggest that the defect NL10 observed in Ref. 7, in particular, NL10-1, has the same structure as the one shown in Fig. 1, but with the divalent Si (1′) replaced by an aluminum atom. This would explain the rapid formation of NL10 centers in Al-doped silicon.

It has been suggested[10,11] that the kinetics of TD formation can be explained by assuming the motion of self-interstitials. A self-interstitial may "pick up" an oxygen atom, and their complex may diffuse faster than an in-

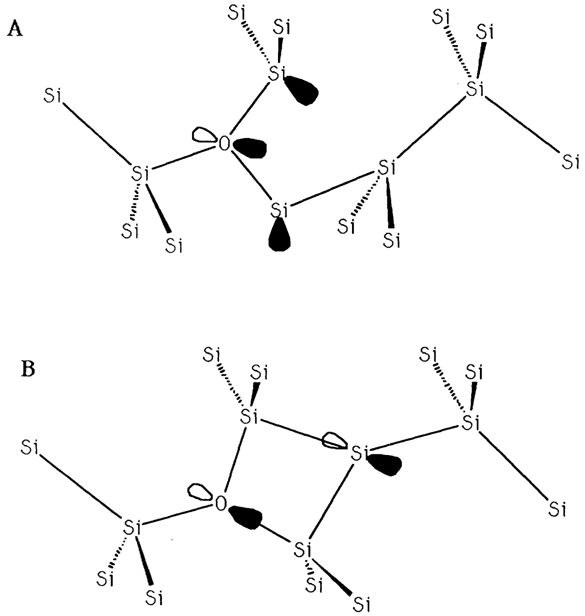

FIG. 2. Stable (*A*) and metastable (*B*) bonding configurations of the $\mathrm{Si}_I\mathrm{O}_I$ complex.

terstitial oxygen. This would explain the 1.8-eV activation energy for TD formation in contrast to the 2.5-eV activation energy for oxygen diffusion. At elevated temperatures the complex would soon dissociate and the process could be repeated. Occasionally, a $\mathrm{Si}_I\mathrm{O}_I$ complex could be trapped at another oxygen interstitial forming the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex, i.e., the core of a TD. Earlier, we reported[12] a stable $\mathrm{Si}_I\mathrm{O}_I$ complex in crystalline silicon. Further calculations in a 32-atom unit cell revealed that the complex has two metastable bonding configurations shown in Fig. 2. The structure *A* is more stable. It has a computed heat of formation (from separated interstitials) of -0.81 eV, and an ionization energy of 5.08 eV. The structure *B* is computed to be less stable by 0.32 eV. We believe that two similar $\mathrm{Al}_I\mathrm{O}_I$ structures may be responsible for the low-symmetry precursor of NL10 centers.[7] The calculated frequencies of the localized vibration modes in structure *A* are 1127 and 974 cm^{-1}. Assuming again a systematic error of about 13%, these values correspond to frequencies around 980 and 847 cm^{-1} in an experimental spectrum. It has been demonstrated that an infrared band at 935 cm^{-1}, stable up to 300 K, is a vibration of the $\mathrm{Si}_I\mathrm{O}_I$ complex.[13,14] Given the uncertainties in calculating vibrational frequencies, we believe that the $\mathrm{Si}_I\mathrm{O}_I$ complex may have one of the structures shown in Fig. 2. We have also reported[12] an activation energy of 1.79 eV for the diffusion of the $\mathrm{Si}_I\mathrm{O}_I$ complex, but further work is necessary to confirm this value. Finally, we note that the heat of formation of the $\mathrm{Si}_I\mathrm{O}_I$ complex increases only to -0.95 eV in the $\mathrm{Si}_{47}\mathrm{H}_{60}$ molecular cluster indicating that $\mathrm{Si}_I(\mathrm{O}_I)_2$ is more stable than isolated $\mathrm{Si}_I\mathrm{O}_I$ and O_I.

Our model, of course, assumes the presence of self-interstitials. There is experimental evidence that these can be formed during thermal annealing of Czochralski-grown silicon.[15] It has been proposed[10,11] that the quadratic dependence of the loss rate of oxygen interstitials on the oxygen concentration can be explained by $\mathrm{O}_I+\mathrm{O}_I \rightarrow \mathrm{Si}_I$ reactions during oxygen precipitation.

Based on theoretical calculations, the $\mathrm{Si}_I(\mathrm{O}_I)_2$ complex has been proposed as the core of the 450 °C oxygen thermal donors. It has been shown that this model offers an explanation for many of the observed properties.

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