Theoretical studies on the core structure of the 450 °C oxygen thermal donors in silicon

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Results of molecular- and cyclic-cluster calculations using semiempirical Hamiltonians on a wide range of small oxygen complexes in crystalline silicon are reported. It is shown that a core involving (at most) two oxygens and a self-interstitial can explain the observed behavior of the thermal-double-donor complexes arising in silicon after heat treatment around 450 °C, while all other oxygen complexes proposed so far can be excluded as the core of these centers.

I. INTRODUCTION

After almost four decades of intensive research following their discovery,[1] the atomic structures of the double-donor centers arising after heat treatment around 450 °C in oxygen-rich silicon are still not known. The experimental information about the properties of these thermal-donor centers (for the sake of brevity, we will refer to them as TD centers, although this term is also applied sometimes to "new thermal donors"[2] and "shallow thermal donors,"[3] which are not subjects of this study) may be summarized shortly as follows.[4-6]

(1) Kinetic information. There is a series of $(TD)_n$ complexes[7-11] (usually $n = 1, \ldots, 9$ are mentioned but further species up to 17 have recently been identified[5,12,13]) arising in heat treatments between 300 °C and 550 °C and destroyed at temperatures above 550 °C. The individual $(TD)_n$ centers appear and disappear sequentially with increasing annealing time. The initial rate of formation $d[\sum[(TD)_n]]/dt$ is proportional to the fourth power[14] of the original interstitial concentration $[O_i]$. While the maximum concentration, $(\sum[TD]_n)_{max} \sim [O_i]^3$, those of $(TD)_1$ and $(TD)_2$ are proportional only to $[O_i]^{1.2}$ and $[O_i]^{1.7}$, respectively.[5] The activation energy for TD formation, about 1.8 eV,[15,16] is significantly smaller than the 2.5-eV (Ref. 17) barrier for O_i diffusion. Carbon inhibits[18] the formation of TD's while hydrogen plasma treatment enhances[19] it. The growth of TD's is accompanied with a loss in the O_i vibration band intensity[20] without a simultaneous enhancement[21] in VO_n (V indicates vacancy) band intensities. (No local vibration mode characteristic of TD's is known.[6])

(2) Electronic information. TD's are double donors[7,8,22] with the donor wave function constructed mainly from Bloch functions of only one pair of conduction-band minima along the [001] axis.[23] The $(0/+)$ and $(+/++)$ occupancy levels are around

$E_c - 0.07$ and 0.15 eV, respectively,[5] getting gradually shallower for increasing n. The excited states of each $(TD)_n$ are in agreement with predictions of effective-mass theory. The EPR centers[24] NL8 (studied mainly in B-doped Si) correlate with these characteristic electronic transitions[25-27] while the NL10 centers (studied mainly in Al-doped Si) correlate with the change in carrier concentration related to TD's.[28] Details of the donor wave functions have been deduced by electron-nuclear double resonance (ENDOR) for both:[29,30] they appear to be similar for NL8 and NL10, the latter being considerably less localized.[31] TD's can be passivated by hydrogen;[32] the passivation seems to be more effective for smaller TD's.[33]

(3) Structural information. The point-group symmetry of the TD's is $C2v$ (Refs. 25 and 34) with possible small deviations[31] and they exert compressive stress along [001] (the C_2 rotation axis).[27] Subsequent members of the TD series are more and more anisotropic. Therefore, it is generally assumed that all TD's have a common core[5,6] to which an increasing number of oxygen[14] atoms or self-interstitials[20,35] are added in a (110) plane. ENDOR experiments[29,30] have resolved two[30] to four[29] oxygens in the first few TD species, but none on the C_2 axis. Direct evidence exists only for the involvement of two oxygens in the core.[31] There is no on-center lattice silicon atom at the center of the complex. No other impurity has been found to be involved in the core of NL8,[29] while NL10 exhibits hyperfine interactions with Al in aluminum-doped samples.[30] Recently it has been proven that $(TD)_1$ and $(TD)_2$ are bistable.[5,36,37]

Based on the accumulating knowledge about TD centers, a variety of structural models of the core have been put forward throughout the years. They can be compiled in four main groups, according to the constituents of the model.

(a) Oxygen-only complexes. Attempts to explain the fourth power dependence of the initial TD formation rate on oxygen concentration led to the assumption[14] of four interstitial oxygens with one common Si neighbor form-

ing the core of TD's. This $(O_i)_4$ unit (a SiO_4 tetrahedron) is also a natural seed for quartz precipitation. The low activation energy of TD formation has led to the proposal that the TD core is formed at the encounter of two fast-diffusing O_2 molecules[38] which build an O_4 complex weakly bound to the lattice.[39] Another line of oxygen-only complexes have been borne out to the notion that complexes of O_i are unlikely to show electrical activity. The O_i occupies a puckered bond-center position between two neighboring silicon atoms[40,41] and is electrically inactive. On the other hand, on the way of jumping from one bond center to another, it passes through a configuration of C_{2v} symmetry in which the oxygen is bonded to three silicon atoms. The silicon on the C_2 axis is also threefold coordinated and has a doubly occupied p-type dangling bond in the (110) plane of oxygen motion. If this so-called ylid (O_Y) configuration could be stabilized by additional O_i atoms on both sides, it could give rise to a donor state.[42] Later, when it was realized that there is no oxygen atom on the twofold axis of the TD core, an $(O_Y)_2$ complex was suggested as the core instead of (O_Y).[43,44] Recently, a complex of two oxygen atoms intercepting parallel Si-Si bonds in a (111) plane and also bonded to each other has been suggested.[45]

(b) Oxygen + vacancy complexes: VO_n complexes are well known from irradiation studies of Czochralski-silicon[46] and are not related to the TD centers.[21] It has been proposed, however, that under the stress exerted by accumulating O_i's around the core, the oxygen in a VO complex may be forced to become an on-center substitutional (unlike an isolated VO center) and become a donor.[47,48] It has also been suggested that, under similar circumstances, the VO_2 center may undergo a reconstruction with the two oxygen atoms forming a bond and emitting two electrons into the bottom of the conduction band.[49,45]

(c) Oxygen + semivacancy complexes: The Ourmazd-Bourret-Schröter (OBS) model[50]—the most elaborate in the early years and persisting up to the appearance of ENDOR information—was based on the partial dissociation of an $(O_i)_3$ complex into a structure, where three oxygens in a vacancy form a configuration of C_{2v} symmetry. One oxygen is on the C_2 axis and saturates two dangling bonds of the vacancy while the other two oxygens, saturating one vacancy bond each, are still bonded to the silicon atom removed from the vacancy into an interstitial position along the C_2 axis [see Fig. 3(a)]. Basically similar models have been proposed based on the ENDOR investigations of the NL8 and NL10 centers. In the study of the NL8 center,[29] two sets of oxygen atoms with the z axis of their field gradient tensors pointing in $\langle 111 \rangle$ directions have been detected for both $(TD)_3$ and $(TD)_4$. Since both sets have been assumed to belong to the core, a model[29] has been constructed with four oxygens (two in each of the perpendicular $\{110\}$ planes containing [001]) saturating the dangling bonds of a vacancy. Since, at the same time, a silicon atom on the C_2 axis has been resolved, it was assumed that the core also contains a semidissociated self-interstitial on the [001] axis close to the tetrahedral interstitial site [see Fig. 3(c)]. The

ENDOR observations on NL10 in aluminum-doped silicon[30] have led to a similar picture[31] but, since the possibility for oxygens being simultaneously in both perpendicular $\{110\}$ planes could be ruled out, it has been assumed that only two of them belong to the core. The model[30] constructed is based on a semidissociated vacancy-aluminum pair with two O_i's placed symmetrically in adjacent bond-center sites [in a (110) plane]. It is assumed that, in boron-doped silicon, the aluminum is replaced by a silicon self-interstitial [see Fig. 3(b)]. The latter two models will be referred to in this paper as the "NL8" and "NL10" models. By this we do not mean to imply that they are really the structures of the corresponding EPR centers (quite the contrary).

(d) Oxygen + self-interstitial complexes. To explain the fast formation rate of TD's, it has also been proposed[11,35,51,52] that self-interstitials (I) may play a role in the formation and probably in the electrical activity of the thermal donors. The production of self-interstitials under conditions identical with TD formation has been proven in carbon-rich samples.[52,53] Based on the kinetics of O_i loss, an IO_2 composition was suggested recently as the core of the TD's.[6] However, no structural model of the IO_n type has yet been put forward.

The models proposed for the core of TD's have to be tested against experimental findings and also against quantum-mechanical calculations, i.e., it has to be checked whether the models are really in accordance with what is assumed about them. Considering the large number of experiments and the number of models born out of them, the list of calculations is rather short. Most of the calculations ever performed on oxygen in silicon are concerned with the VO center,[54−63] while relatively few of them have been carried out in order to address the problem of oxygen aggregation in general[64−67] or of the core of TD's in particular.[43−45,60,68−74] The reason for that is the enormous computational demand posed by a defect complex which involves a number of nonsubstitutional atoms, induces long-range relaxation, and gives rise to a delocalized defect orbital. The fact that it contains oxygen, an atom with an incompletely screened core, makes it even more difficult: no local pseudopotential can be applied and a very high-energy cutoff is required in a plane-wave basis. Due to these reasons it was only very recently that even the energetic feasibility of oxygen aggregation could be reproduced computationally.[67] The usual way of economizing is to cut back on the size of the defect environment treated explicitly and/or to choose a quicker (and less accurate) approximation to solve the Schrödinger equation.

Earlier such calculations concentrated mainly on one or two current models of the time with the main goal of verifying the donor activity attributed to them. A characteristic feature of these calculations was that, even if the stability of the complex has been at all considered, the energy minimization was restricted to structures of C_{2v} symmetry, assuming that additional interstitial oxygens (not treated explicitly in the calculation) will enforce that. The possibility of donor activity for VO_n models,[60,68] the ylid,[43,69−71,73] and the OBS model[69,73] seemed

to be confirmed by molecular-cluster calculations using tight-binding,[69] Hartree-Fock (both *ab initio* and semiempirical[43,60,68,71]), and local-density-approximation (LDA) methods,[73] while the results of another LDA calculation[74] using the Green-function technique seemed to contradict that for the VO_n and the single-ylid models. Anyway, the finding by ENDOR investigations that no oxygen atoms are located on the twofold axis of the TD core[26,29-31] discarded the VO_n complexes as well as the single-ylid (O_Y) and the OBS model. On the other hand, the "semivacanc + oxygen" type models based directly on the ENDOR results have been shown to be highly unstable with respect to the recombination of the vacancy and the self-interstitial. A large molecular cluster calculation using a semiempirical Hamiltonian has shown[72] that the NL8 model[29] relaxes spontaneously into an electrically inactive $(O_i)_4$ complex, while localized LDA calculations on the same cluster resulted[44] in an $(O_Y)_2$ complex if starting from the NL10 model.[30]

From the computational studies so far, it is clear that, given the difficulty of the task, accurate reproduction of experimental results regarding TD properties is not soon to be expected. Therefore, a more useful contribution from theory could be an attempt for the systematic study on oxygen aggregates, that is, to compare the stability of different complexes without prescribing symmetry and to monitor the defect wave functions and their energies. Such a study is worth doing even if sacrifices have to be made regarding the accuracy of the computational method. Recently, a tight-binding supercell approach has been used to cover "oxygen-only" and "oxygen + vacancy" complexes[45] confirming that the electrical activity in oxygen complexes can only be expected from trivalent oxygens.[42-45] In an earlier, similar effort[65] (using a semiempirical-Hartree-Fock cyclic-cluster approach), we have established the importance of "oxygen + self-interstitial" complexes, and very recently we have shown[75] how a particular IO_2 structure can account for TD properties. The aim of this paper is to summarize the results of our calculations on small oxygen complexes in order to show that, out of the four groups of oxygen complexes mentioned, only the "oxygen + self-interstitial" complexes are likely to explain the known properties of TD's. In Sec. II the computational framework and its limitations will be described, Sec. III contains our results on "oxygen-only," "oxygen + vacancy," and "oxygen + semivacancy" complexes while Sec. IV presents a model of the TD's based on "oxygen + self-interstitial" complexes.

II. COMPUTATIONAL METHOD

In most of our calculations the host silicon crystal is simulated by the cyclic-cluster model[76] (CCM) using a cluster of 32 silicon atoms, i.e., a large unit cell with unit vectors

$$\begin{bmatrix} \mathbf{A}_1 \\ \mathbf{A}_2 \\ \mathbf{A}_3 \end{bmatrix} = \begin{bmatrix} 3 & -1 & -1 \\ -1 & 3 & -1 \\ -1 & -1 & 3 \end{bmatrix} \begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{bmatrix} , \qquad (1)$$

where $\mathbf{a}_i$ are the primitive unit vectors of the silicon lattice. The first Brillouin-zone (BZ) corresponding to such a large unit cell has a volume reduced 16 times relative to the primitive BZ, i.e., each point in the former represents 16 points of the latter. In particular, the center ($\mathbf{K} = 0$) of the reduced BZ represents the Γ [(0,0,0,)] the 3 X [$(2\pi/a)(1,0,0)$], and 12 Σ [$(\pi/a)(1,1,0)$] symmetry-related points of the primitive BZ. These points form a high-quality representative set[77] in the sense defined by Chadi and Cohen.[78]

In the CCM, the cluster is treated as a separate entity, i.e., not as part of a periodic solid. However, to mimic the full point-group symmetry of the silicon crystal and to avoid surface states, the cyclic boundary condition of Born and von Kármán is applied in the sense of "tying one end of the cluster to the other."[79] In other words, the space is filled by periodically repeating the original cluster[80] but, since only the atoms in the latter are physically existent, interactions within the appropriate Wigner-Seitz cell around each atom are considered only. Due to the imposed macroscopic periodicity,[81] the one-particle states of this system belong to the group of the $\mathbf{K} = 0$ vector of the reduced BZ and, therefore, can be unambiguously classified as belonging to one of the $\mathbf{k}$ vectors in the set represented by $\mathbf{K} = 0$ (for the Si_{32} cluster the $\{\Gamma, X, \Sigma\}$ set), even though, the calculation is performed entirely in the direct space. In the case of a perfect cluster—apart from the restriction on the interaction length—such a calculation is equivalent to a band-structure calculation performed at those representative $\mathbf{k}$ points with the BZ integration replaced by a weighted sum over the same representative points. Since the sum over the $\{\Gamma, X, \Sigma\}$ set provides a very good approximation to the BZ integral of the electron density, the restrictive approximation is the limitation in long-range interactions. In a defect calculation, on the other hand, this restriction is helpful in avoiding undesired interactions between repeated defects. The CCM is, therefore, an approximation well balanced between reproducing extended crystalline states and isolated defect states. A limiting factor in the calculation of defects with shallow levels is the fact that only a finite sampling of "crystalline" states are available to form the defect state from. (The limited number of atoms, the relaxation of which can be considered explicitly, is a common feature to all computations.) In principle, cyclic clusters involving a larger (but not necessarily better) set of representative $\mathbf{k}$ vectors can also be chosen.[77] A more general and accurate description, as well as tests of the CCM, is given in Ref. 76.

A "first-principles" solution (either LDA or Hartree-Fock) to the Schrödinger equation of a 32-atom CCM is still too time consuming for performing extensive studies on a wide range of rather complex defects. Earlier, we have found[76] that the semiempirical Hartree-Fock theories devised to account for dynamic correlation effects (for a review see Ref. 82) are capable of a reasonably good reproduction of crystalline properties at a fraction of the cost required by "first-principles" theories. In a comparative study,[76,83] the MINDO/3 (modified intermediate neglect of differential overlap) (Ref. 84) approximation has been shown to be the most successful in

describing silicon. Results of a 32-atom CCM and of a full band-structure calculation[85] using MINDO/3 are compared with experimental data[86–88] in Table I. Since the agreement is fair enough and the computational effort required is low, this method provides an appropriate framework for extensive defect studies.

The only problem with really serious consequences appears in the reproduction of the conduction band. Due to the neglect of overlap integrals in MINDO/3 [as in any approximation based on the zero differential overlap (ZDO) approximation], the stability of mainly s-like states is overestimated.[76] As a consequence, these methods predict a lowest conduction band for Si similar to that of Ge, that is, e.g., the Γ'_2 state precedes Γ_{15} at the center of the BZ. The implications for defect calculations have been discussed in Ref. 76. In case of the CCM, only discrete points of the BZ are considered: in our 32-atom cluster the $\{\Gamma, X, \Sigma\}$ set. Fortunately, in this case the only dominantly s-type orbital in the conduction band is Γ'_2 which is predetermined by symmetry. Therefore, a correction to the MINDO/3 Hamiltonian could have been introduced[89] with the only effect of pushing that orbital above Γ_{15}. Unfortunately, no simple procedure can be applied for other states, therefore, an increase in the cluster size might result in a decrease in the quality of results, if the defect wave function has a significant admixture of conduction-band states. The interpolated band structure around the gap region as obtained from the 32-atom CCM calculation with the modified MINDO/3 Hamiltonian's shown in Fig. 1(a) (the stability of the mainly s-like lower valence-band states is also overestimated). As can be seen, the indirect gap is at $\Gamma \rightarrow \Sigma$, an error caused by the valence $3s$-$3p$ basis set. In Fig. 1(b), the band structure is shown which was obtained by CNDO/S (Ref. 90) (the spectroscopic version of the complete neglect of differential overlap approximation),[91] parametrized[92] on a $3s$-$3p$-$3d$ basis for silicon. Here the lower part of the conduction band is correctly reproduced. Since the correct description of the lower conduction bands is crucial, we will use CNDO/S for investigating the defect wave functions of prospective TD cores at the geometry given by a MINDO/3 calculation (CNDO/S is not suited for geometry calculations).

While producing agreeable results for the extended states of the crystal, the MINDO/3-CCM proves to be
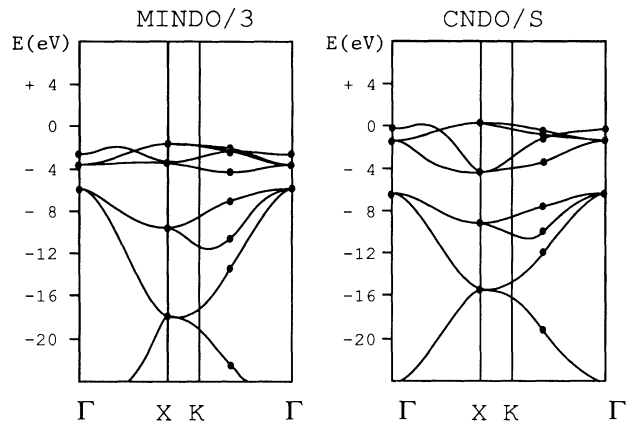

FIG. 1. The band structure of silicon as interpolated from the values obtained at the $\{\Gamma, X, \Sigma\}$ points (solid dots) using (a) MINDO/3 and (b) CNDO/S in a 32-atom CCM calculation.

quite successful in defect calculations. The basic and well-known[93–95] features of the vacancy and the self-interstitial are well reproduced, including their negative-U property. The energy of Frenkel-pair formation in a 32-atom cluster was calculated to be 7.4 eV. The method has been successfully applied for the study of hydrogen in silicon.[89,96,97]

With regard to the limitation on the number of host atoms which are allowed to relax in the presence of a defect, it is generally desirable to perform a convergence test. The systems we are interested in are expected to be anisotropic (in the [110] direction) and so the necessary increase in the (per definitionem) isotropic cyclic cluster would quickly outgrow the available computer capacity (not to mention the aforementioned difficulties with the s-type conduction-band states if using ZDO approximations). Therefore, we used the same 32-atom cluster in every case and allowed the same atoms (all second neighbors and the third neighbors in the [110] direction) to relax using the Davidon-Fletcher-Powell algorithm.[98] Accordingly, we should only compare directly the stabilities of such complexes which extend to the same number of bond-center sites in the [110] direction. In some cases we

TABLE I. Calculated properties of the perfect silicon crystal.

	MINDO/3 32-atom CCM	MINDO/3 Full band structure (Ref. 85)	Expt.
Bond length (Å)	2.44	2.45	2.35 (Ref. 86)
Binding energy (eV/atom)	3.74	3.70	4.65 (Ref. 87)
$\Gamma_{25'}$ phonon freq. (cm^{-1})	525		519 (Ref. 86)
Ionization threshold (eV)	5.76[a]	5.3	5.35 (Ref. 88)
First electronic trans. (eV)	2.10[a] (Γ-Σ)		1.17 (Γ-Δ) (Ref. 86)

[a]The ionization threshold and the first electronic transition in the CCM were calculated as the energy of the cyclic cluster in the singly ionized and in the excited triplet state, respectively, relative to that of the neutral, ground state. As the ionization threshold from the band-structure calculation, the energy of the $\Gamma_{25'}$ state is taken as being read from Fig. 2 of Ref. 85.

made use of an auxiliary molecular-cluster model (MCM), $Si_{47}H_{60}$, having an elongated shape along the [110] direction (the hydrogens saturating the surface bonds).[64]

The MINDO/3-CCM code has been developed from an open-shell version[99] of MINDO/3. We have found the inclusion of the dynamic damping procedure[100] and the level-shifting method[101] crucial in improving convergence properties of the self-consistent field (SCF) calculations.

III. OXYGEN COMPLEXES WITHOUT A SELF-INTERSTITIAL

A. Oxygen-only complexes

First, we have studied the aggregation of O_i in the (110) plane using a large molecular cluster, $Si_{47}H_{60}$ with elongated shape along [110].[64] Our calculation reproduces the O_i bond-center (BC) interstitial position as the equilibrium site of an isolated oxygen in an otherwise unperturbed silicon crystal. Due to strong relaxation of the host atoms, the resulting Si-O distances are 1.61 Å with a Si-O-Si angle of 180°. The latter is at variance with the 162° deduced from experiment[41] and is a basis-set effect of little consequence considering the flexibility of the bond angle.[102] The one-electron states associated with the defect are well inside the bands. The energy barrier for diffusion from one BC site to the next is calculated to be 2.5 eV at the ylid configuration.[64] The lone-pair p orbital on the threefold coordinated silicon has an energy of -5.6 eV, in comparison with the highest filled orbital of the perfect cluster at -7.1 eV. This is the first suggestion about the role of overcoordinated oxygen in donor formation.[42]

In case of two O_i's in the (110) plane, earlier we have found[64] two configurations with about equal bonding energies of -0.1 eV. One of them, $(O_i)_2$, is a complex of two O_i's with a common Si neighbor [Fig. 2(a)]. In a recent very sophisticated calculation, Needels et al.[67] have found a binding energy of -1.0 eV for this complex, thereby establishing its stability beyond doubt. Based on those results we believe that the four-member ring structure, $(O_r)_2$ [Fig. 2(b)] predicted to be of the same energy as $(O_i)_2$ in both $Si_{47}H_{60}$-MCM and in Si_{32}-CCM calculations, is also a stable di-oxygen complex. We have also shown earlier[64] that $(O_r)_2$ lies on the path of the correlated motion of the two oxygens of $(O_i)_2$. The calculated activation energy[64] between the two configurations is 1.4 eV, i.e., significantly lower than that calculated for the diffusion of isolated oxygen. Therefore, fast oxygen diffusion can be expected once $(O_i)_2$ complexes are generated.

In 32-atom CCM calculations it turns out that, while the $(O_i)_2$ complex is still electrically inactive (no defect level in the gap), the $(O_r)_2$ complex is—by virtue of its two trivalent oxygen atoms—a double donor. As can be seen from Fig. 2(b), only five of the six electrons of each oxygen is accommodated by the three Si-O bonds and the one lone-pair orbital (for each oxygen). The one excess electron from both oxygen atoms will go into an orbital

detached from the conduction-band edge due to the electric and strain fields of the complex. However, the symmetry of the $(O_r)_2$ complex as well as the nature of the arising donor wave function (as compared to the one deduced by ENDOR) excludes it as a core for TD's.[43]

The di-ylid, $(O_Y)_2$, is another di-oxygen complex in the (110) plane [see Fig. 2(c)] which has been proposed as the core of TD's, assuming that additional O_i's stabilize it as a C_{2v} structure and increase the delocalization of its donor orbital (thereby making its donor level shallower).[43,44] The present calculations (both MCM and CCM with prescribed C_{2v} symmetry) confirm the donor character of $(O_Y)_2$ but the calculated total energy is more than 2 eV higher than that of $(O_i)_2$. MCM computations with up to five oxygens in the (110) plane[103] suggest that a tri-ylid may be stabilized by adjoining O_i's. The aggregation of O_i's in [110] chains is energetically favorable, but the most stable complexes are the $(O_r)_2$ ring with one or two adjacent O_i's. The energy gains with respect to isolated O_i's are 1.1 and 1.4 eV, respectively. The $O_i + (O_r)_2 + O_i$ complex is still more stable than $O_i + (O_Y)_2 + O_i$ by 1.5 eV. Since $(TD)_1$ does not contain more oxygens than that, we exclude "pure" [110] chains of O_i's as TD's.
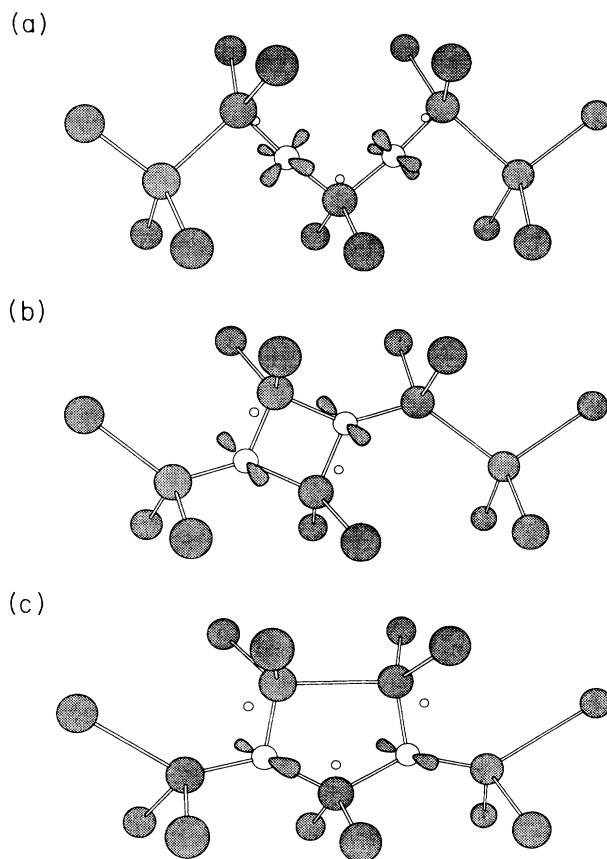
To explore other oxygen-only aggregates, we have per-

(a)

(b)

(c)

FIG. 2. Di-oxygen complexes: $(O_i)_2$, $(O_r)_2$, and $(O_Y)_2$. The unperturbed lattice positions are marked by small, open circles. The lone-pair orbitals are also shown; the occupied ones are shaded.

formed 32-atom CCM calculations. The results for the isolated O_i are essentially identical with those of the MCM calculation, only the diffusion barrier is somewhat lower (2.1 eV). The formation of the $(O_i)_2$ and $(O_r)_2$ complexes are calculated to be endothermic by 0.5 eV. This is clearly a cluster size effect and the consequence of the different errors committed by excluding long-range relaxation for two defect centers of different sizes. As a test, we have performed two separate sets of MCM calculations. First, we allowed the first and all second neighbors of the oxygens to relax. Then, in addition, the third neighbors along [110] were also relaxed. The additional energy gain was 0.42 eV in the case of $(O_i)_2$ while only 0.04 for O_i. This indicates that long-range relaxation would result in significant further energy gain upon the formation of $(O_i)_2$ as it indeed happened in the calculation of Needels et al.[67]

We have investigated the interaction of two oxygen atoms with the lattice and with each other in the most general fashion possible in the 32-atom CCM. It has already been reported that an O_2 molecule placed at the tetrahedral (T_d) interstitial site is less stable then isolated O_i's.[67,74] Our calculation without symmetry restrictions in the geometry optimiziation results in a spontaneous dissociation of the molecule with the oxygens invariably ending up in BC sites. Starting from various positions (with the center of the molecule either at T_d or at the hexagonal interstitial site) and with various orientations, we find that the final state of lowest energy [excluding complexes in the (110) plane] is two O_i's at the center of two parallel and adjacent Si-Si bonds in a (111) plane. There is no bonding between the oxygen atoms and the energy gain with respect to isolated interstitials (calculated as the energy difference $E[Si_{32}2O_i] + E[Si_{32}] - 2E[Si_{32}O_i]$) is close to zero in agreement with the results of Ref. 45. Chadi has also found[45] that, in the doubly positive charge state of this complex, a strong bond is formed between the oxygens, with the bonds to their respective silicon neighbors retained. If, through the formation of such a bond in the neutral charge state, the oxygens became trivalent (i.e., one electron being in each of three sp^2 hybrids forming the bonds and two electrons in a perpendicular lone p orbital) they would be forced to emit a pair of electrons into the conduction band, i.e., to act as a donor. Our calculation does not indicate such trivalency in the neutral charge state, and since the symmetry of this center is C_{2h} instead of C_{2v}, we do not consider it further. The $(O_i)_4$ complex turns out to be electrically inactive as expected.

In conclusion, we can confirm our earlier suggestion[42,43] (now supported by other calculations as well)[44,45] that electrical activity in an oxygen-only cluster may come only from trivalent oxygens. The results of Needels et al.[67] lend greater credibility to our earlier claim that the [110] chainlike aggregation of oxygen is energetically favored and fast diffusion of di-oxygen complexes is possible.[64] In MCM studies we find that extended [110] chainlike complexes involving trivalent oxygens may be stable but their symmetry and the donor wave function associated with them exclude these complexes as core of TD's.

Since, despite a very thorough search, no other stable donor complexes of (close to) C_{2v} symmetry have been found, we conclude that "oxygen-only" complexes cannot explain the observed behavior of TD's.

B. Oxygen-vacancy complexes

Some theoretical studies[60,68,45] indicated that, under hydrostatic stress, VO or VO_2 complexes may exhibit donor behavior. Our own calculations using CCM (Ref. 65) along with the LDA–Green-function calculation of Kelly[74] have shown that the VO complex can by no means be a donor. If the oxygen is forced on center, the doubly occupied a_1 defect level of the A center (VO with oxygen off center in the [001] direction) moves down into the valence band (VB) instead of up. We also find that, in the neutral charge state of VO_2, the configuration with strongly interacting oxygens is not even metastable. As for VO_n complexes with $n \geq 2$, we find that a VO_3 complex of C_{2v} symmetry is less stable than the $VO_2 + O_i$ complex proposed by Corbett, Watkins, and McDonald based on infrared studies,[46] despite the fact that the latter is a more extended defect (its stability may increase further if long-range relaxation is taken into account). Our
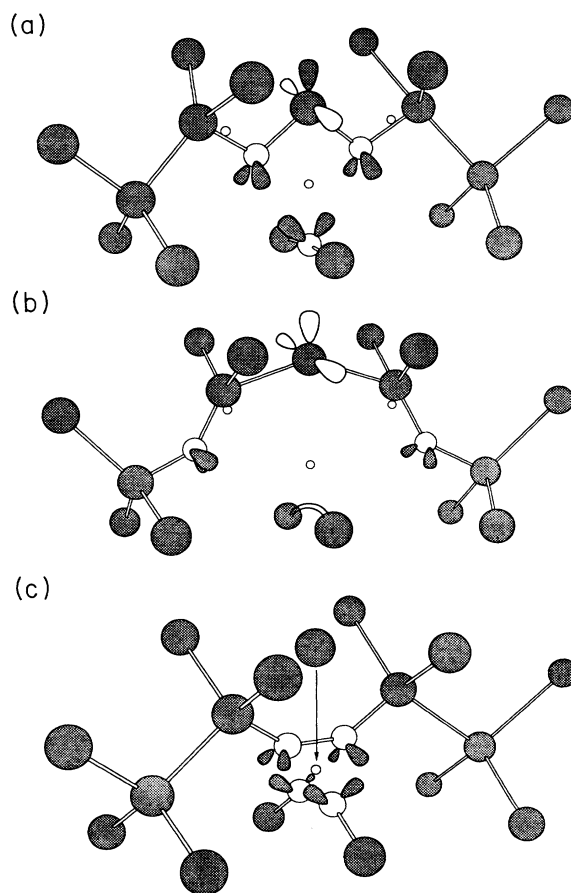
(a)

(b)

(c)

FIG. 3. Oxygen+semivacancy models of TD's: (a) OBS (b) NL10, and (c) NL8.

results for the local vibration mode frequencies (see Table III) also support the latter model. It has also been suggested[29,45] that four oxygen atoms in a vacancy may be at the core of the TD's. In a CCM calculation for the neutral VO_4 complex with no symmetry restraints in the geometry optimization, we find that the oxygen atoms do not stay in the cage of the vacancy [note the lone pairs on the oxygens pointing toward each other in Fig. 3(c)]. The lowest-energy configuration obtained is a VO_2+2O_i complex with C_{2v} symmetry and with two noninteracting oxygens on the C_2 axis.

In summary, our calculations predict that the most stable oxygen+vacancy complexes up to $n=4$ have (close to) C_{2v} symmetry but always have oxygen on the C_2 axis. Because of the experimental evidence[26,29–31] for no oxygen on the twofold axis of TD's, we feel confident[104] about also eliminating these complexes as candidates for the core of TD's.

C. Oxygen+semivacancy complexes

Apart from the ylid model, all other viable candidates proposed so far: the OBS,[50] the NL8,[29] and the NL10 (Ref. 30) models [Figs. 3(a)–3(c)] fall in this category. Also, invariably, all three of them prove to be unstable against V-I recombination if the constraint of C_{2v} symmetry is lifted in the geometry optimization. The NL8 model relaxes into an electrically inactive $(O_i)_4$ complex with an energy gain over 20 eV. The energy gain on V-I recombination is about 7 eV for the OBS and NL10 models. (We note that, if the geometry optimization is restricted to maintain C_{2v} symmetry, V-I recombination does not spontaneously occur. Even so, the OBS and NL10 models do not give rise to a shallow delocalized donor orbital of proper symmetry as indicated in Fig. 3.) The calculated energy gains on V-I recombination are far greater than the expected calculational error. Therefore, the oxygen+semivacancy models for the core of TD's can also be discarded.

IV. OXYGEN+SELF-INTERSTITIAL COMPLEXES

A. The IO_2 donor complex

The only class of oxygen complexes left is the one involving self-interstitials. Even though the calculated energy of Frenkel-pair formation, 7.4 eV, is high, there is experimental evidence that self-interstitials are generated previous to or during TD formation.[52,53] Their incorporation into TD's would readily explain the known formation kinetics.[6] If looking for a TD, the smallest entity of C_{2v} symmetry has to include two oxygens. Kinetic considerations have also led to the assumption of an IO_2 composition of the core.[6] In MINDO/3-CCM calculations we have found[75] that the structure depicted in Fig. 4, involving two trivalent oxygen neighbors and a divalent self-interstitial bonded to them, is stable in C_{2v} symmetry and has an extremely low ionization energy due to a doubly occupied defect orbital. In a subsequent check of the donor wave function by CNDO/S we have found that its characteristics correspond to a linear com-
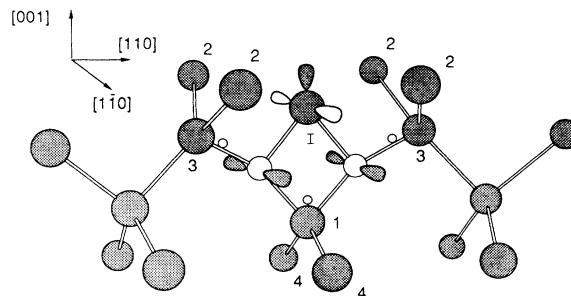

FIG. 4. Structure of the IO_2 complex. Unperturbed lattice positions are marked by small, open circles. Beside the electrons in lone-pair orbitals and in bonds, two electrons are in a delocalized orbital.

bination of two conduction-band states along [001].[75] This orbital with an energy level above the cluster VB edge by 1.83 eV (cf. the CNDO/S cluster gap of 2.14 eV) is rather delocalized: only 0.3% is on the IO_2 unit, 12.0% in all on the three silicon atoms to which the IO_2 unit is bonded, altogether 31.0% on first neighbors of those silicon atoms, and the rest is spread out on the remainder of the cluster. Table II shows a comparison between the squares of the linear combination of atomic orbital (LCAO) coefficients and the spin localizations deduced from the ENDOR studies of NL8 (Ref. 29) [using the average of Si hyperfine constants for the a and b sets in the best resolved "B" center in Ref. 29, thought to correspond to $(TD_4{}^+)$]. The calculated values are generally higher by a factor of 10 due to the confinement in a cluster too small for an effective masslike orbital. Nevertheless, the trends in the s- to p-orbital ratio are well reproduced. It should be emphasized that all hyperfine interactions with atoms of the core are of the same magnitude (i.e., there is no single large hf interaction). The overall qualitative agreement is by far the best we have found for any of the complexes investigated.

Apparently, the IO_2 complex depicted in Fig. 4 conforms with what is explicitly known about the structure of the TD core. (We have not been able to find a stable configuration of C_{2v} symmetry with two additional oxygens in the plane perpendicular to the other two, as assumed by Michel, Niklas, and Spaeth.[26,29] It was shown, however, by Gregorkiewicz, Bekman, and Ammerlaan[31] that this assumption is not really warranted by the ENDOR results themselves.) The complex is of C_{2v} symmetry—the geometry in the singly and doubly positive charge states is, apart from minor changes, basically the same as in Fig. 4. The two oxygens are—within 1°—on ⟨111⟩ axes and there is no oxygen on the [001] axis. The trivalent oxygens have two bond angles of 101°.[105] The relaxation of the neighbors of the IO_2 unit indicate that the complex exerts a compressive stress along [001].

Although the shape of the IO_2 complex bears a slight resemblance to the OBS, NL10, and (apart from the additional two oxygens) to the NL8 models (cf. Figs. 3 and 4),

TABLE II. Comparison of spin localizations (%) for the donor wave function of IO_2 (calculated in the neutral charge state by CNDO/S at the geometry found by MINDO/3 in the + + charge state) with those deduced from ENDOR hyperfine constants for NL8 (Ref. 29).

| | CNDO/S | | | ENDOR $[NL8\text{-}B^+:(TD)_4^+]$ | |
Site[a]	s	p_z	s	p	Site
1	1.42	1.18	0.19	0.06	Single atom on [001]
2	1.94	0.84	0.16	0.05	Equiv. pairs in (100) and (010)
3	0.52	1.34	0.13	0.34	One pair in (110) or (1$\bar{1}$0)
4	1.40	1.42	0.11	0.12	One pair in (110) or (1$\bar{1}$0)
I	0.02	0.02	0.07	0.03	Single atom on [001]
O	0.04	0.02	<0.02		One pair in (110) or (1$\bar{1}$0)

[a]See Fig. 4.

the origin of the donor activity is very different, being the result of the presence of trivalent oxygens. As explained earlier, with three of their electrons in bonds and two in a lone pair, each oxygen has one electron in excess. The self-interstitial is in a divalent configuration, with two of its electrons in bonds and the other two in a sp^2 hybrid orbital pointing toward [001] (the corresponding levels are in the cluster VB). It also has an empty p orbital perpendicular to the plane of the IO_2 unit. If the excess electrons from the oxygens were put on this p orbital, the self-interstitial would have a formal charge of -2. Therefore, the occupancy level is very high, in fact, it is above the conduction-band (CB) edge. Due to the defect, the degeneracy of the six equivalent valleys is locally lifted, and the symmetric combination of the two valleys along [001] is of the lowest energy among the states available for those two electrons. In short, the electrical activity comes from the trivalent oxygens, but the donor electrons are in an effective-mass-like orbital induced by the presence of the defect complex. The role of the self-interstitial is to transform the divalent oxygens into trivalent ones. In the doubly positive charge state, the net charge is -0.4 on each of the oxygens, $+0.8$ on I, $+0.5$ on atom No. 1, and $+0.3$ on each of the atoms No. 3 of Fig. 4.

One way of forming IO_2 is the reaction

$$(O_i)_2 + I \rightarrow IO_2 \ . \tag{2}$$

The corresponding energy balance in the 32-atom CCM is calculated to be

$$\{E[Si_{32}IO_2] + E[Si_{32}]\}$$
$$- \{E[Si_{32}I] + E[Si_{32}(O_i)_2]\} = -0.8 \text{ eV} \ . \tag{3}$$

Although the defects compared here are about the same size and, therefore, the errors committed by neglecting long-range relaxations is roughly the same, an additional source of error could be the overestimation of the gap, and accordingly, the overestimation in the energies of the donor electrons (which are on an orbital formed from CB states). In p-type silicon we may also consider the following reaction:

$$(O_i)_2 + I^{++} \rightarrow IO_2^{++} \tag{4}$$

with

$$\{E[Si_{32}IO_2^{++}] + E[Si_{32}]\}$$
$$- \{E[Si_{32}I^{++}] + E[Si_{32}(O_i)_2]\} = -2.1 \text{ eV} \ . \tag{5}$$

The self-interstitial is calculated to be a negative-U defect. In the neutral charge state it is divalent, binding to two lattice atoms in an asymmetric puckered BC configuration. In the doubly positive charge state it is at the T_d site, not bonded to the lattice. The singly positive charge state is less stable than the other ones for every Fermi-level position. The occupancy level $E(0/++)$ is close to the middle of the gap. These results are in good agreement with those reported in Refs. 93 and 94 which also predict $E(0/++)$ to be around midgap for the self-interstitial. Therefore, Eq. (5) would indicate a binding energy of about -1.1 eV for the neutral charge state. The relatively low binding energy implies a dynamic equilibrium between IO_2 on one hand and free interstitials and $(O_i)_2$ on the other. Such a dynamic behavior may explain the observed quick reorientation under uniaxial stress.[27]

Based on the properties outlined above, it is reasonable to assume that it is the IO_2 complex which is at the common core of TD's. A question is whether IO_2 can be identified with $(TD)_1$. Kinetic studies have already indicated that the first TD species may involve oxygens as few as three, two, or only one.[15] The oxygen concentration dependence of $[(TD)_1]_{max}$ and $[(TD)_2]_{max}$ ($[O]^{1.2}$ and $[O]^{1.7}$, respectively) also indicates[5] that $(TD)_1$ might very well contain one oxygen only. Therefore, it is interesting to explore the behavior of an IO complex.

B. The fast-diffusing IO complex

In an earlier study,[65] we have reported on a stable IO complex and on the possibility of its fast diffusion. We have reinvestigated very carefully the two metastable configurations found[65] for IO. Bearing in mind the difficulties involved in the incorrect description of the conduction band in MINDO/3, we started an optimization from the doubly positive charge state of IO_2 but with one of the oxygens removed. The resulting structure is shown in Fig. 5 on top of the IO_2^{++} complex. Not only are the two structures very similar, so are the charge distributions. A CNDO/S calculation for the neutral
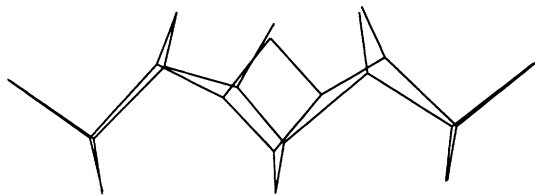
FIG. 5. Comparison of the structures of $(IO)_i^{++}$ and IO_2^{++}. Note the slight deviation from C_{2v} symmetry in the former.
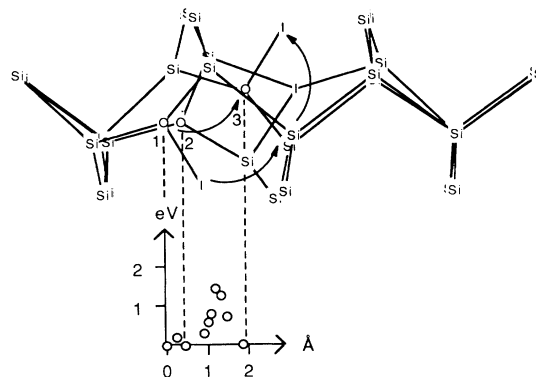

FIG. 6. The transition $(IO)_i \rightarrow (IO)_r \rightarrow (IO)_i$. In the corresponding energy diagram, the configuration coordinate is the [110] displacement of oxygen.

charge state at this geometry puts the two extra electrons in a double-donor level, 1.80 eV above the cluster VB edge (cf. the donor level of IO_2 at 1.83 eV). The orbital is also very similar in nature to the donor state of IO_2. In the case of IO, one donor electron originates from the trivalent oxygen, the other from the self-interstitial which has two electrons on a basically s-type orbital and one in a p-type orbital forming the bond with the oxygen. Alternatively, the complex can be thought of as an O_i trapping an I^{++} and two electrons weakly bound in an orbital formed from CB states along [001]. In contrast to the CNDO/S results, the calculation for the neutral charge state with MINDO/3 ends up with the two electrons in a localized antibonding state between the two silicons around the removed oxygen. Unlike in the case of IO_2, the atoms rearrange considerably relative to the dipositive state, with the main effect of increasing the distance between the silicons which host the occupied antibonding orbital. It is quite likely that this is an artifact due to the incorrect description of the CB by MINDO/3, resulting in the occupation of a localized antibonding orbital. Nevertheless, more accurate calculations are necessary to confirm the TD-like character of IO.

The calculated MINDO/3 formation energies of IO in the two charge states are

$$\{E[Si_{32}(IO)_i] + E[Si_{32}]\}$$
$$- \{E[Si_{32}I] + E[Si_{32}O_i]\} = -0.7 \text{ eV}, \quad (6)$$

$$\{E[Si_{32}(IO)_i^{++}] + E[Si_{32}]\}$$
$$- \{E[Si_{32}I^{++}] + E[Si_{32}O_i]\} = -1.2 \text{ eV}. \quad (7)$$

If the CNDO/S results are "right," i.e., IO has TD-like donor orbitals, Eq. (6) can be discarded. Using the same argument as in case of Eqs. (3) and (5), Eq. (7) would imply a binding energy of about only -0.2 eV in the neutral charge state.

In addition to $(IO)_i^{++}$, a ringlike $(IO)_r^{++}$ structure has also been found [Figs. 6 and 7(a)] with its total energy higher by 1.0 eV. In the dispositive charge state the ring is planar, and the threefold coordinate self-interstitial has an empty p orbital perpendicular to that plane. In the neutral charge state, the self-interstitial buckles out of the (110) plane and the two electrons go into an sp^3-like hybrid with an energy level around midgap. The formation energy of this ring structure is calculated to be

$$\{E[Si_{32}(IO)_r] + E[Si_{32}]\}$$
$$- \{E[Si_{32}I] + E[Si_{32}O_i]\} = -0.8 \text{ eV}, \quad (8)$$

$$\{E[Si_{32}(IO)_r^{++}] + E[Si_{32}]\}$$
$$- \{E[Si_3I^{++}] + E[Si_{32}O_i]\} = -0.2 \text{ eV}, \quad (9)$$

indicating bistability with $(IO)_i$. This finding lends support to the candidacy of IO as $(TD)_1$ (see Sec. IV E). The energy barrier to transform the neutral $(IO)_i$ configuration marked 1 in Fig. 6 into $(IO)_r$ (marked as 2) is calculated to be about 0.3 eV. The transformation proceeds by means of an interstitalcy motion in which the self-interstitial switches roles with a lattice silicon atom.

As can be seen from Fig. 6, the $(IO)_r$ configuration may go over into the next $(IO)_i$ configuration (marked as 3). The calculated barrier is around 1.6 eV (assuming that neutral charge state is preserved), which is significantly lower than the one calculated for $(O)_i$ (2.1 eV). Accordingly, IO is a fast diffuser which can accelerate the formation of IO_2.

To summarize this subsection, we have found a bistable IO complex with possible TD-like character. The calculated binding energy is in agreement with the -0.8 eV deduced for an IO complex identified through its local
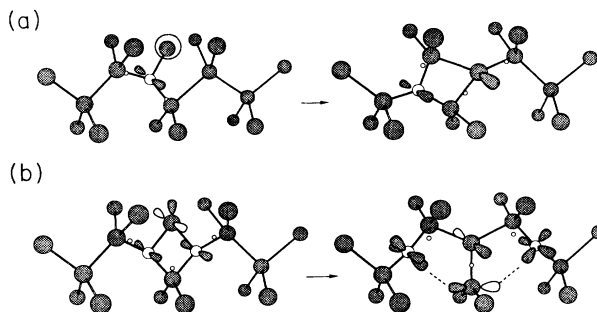

FIG. 7. Metastable configurations $(IO)_i$ and $(IO)_r$ for IO (a) and their analogues, IO_2 and OIO. [The open circle on I in $(IO)_i$ denotes a doubly occupied s orbital.]

model vibrations.[106] The activation energy for its diffusion, ~ 1.6 eV, is significantly lower than the 2.1 eV calculated for the diffusion of isolated oxygen. Therefore, the formation of IO_2 complexes can be greatly increased by the fast diffusion of oxygen assisted by self-interstitials. The low binding energy of the IO complex implies that the diffusion enhancement can be thought of as a repeated process of I atoms picking up an oxygen, carrying it for a short time, and then leaving it behind again.

C. The oxygen+self-interstitial complex model of thermal donors

We have shown that the IO_2 complex depicted in Fig. 4 is a donor and both its structure and wave function compare very well with what we know about the thermal donors. If we assume that this is the core of the TD's (not excluding the possibility that the smallest TD is IO), we may account for a number of other observations as well.

There is experimental evidence, that one I atom is produced while two O_i's are lost from solution.[51-53] If I is produced at the case of two oxygens, the subsequent production of the electrically active IO_2 complex would explain the $[O_i]^4$ dependence of the initial rate of TD formation. We note, however, that our calculations indicate that the reaction

$$2O_i \rightarrow I + VO_2 \qquad (10)$$

is not energetically feasible. On the other hand, both O_i loss at the formation[15] and O_i gain at the destruction[13,107,108] of TD's indicate that larger oxygen complexes other than the TD's are formed as well. It seems more likely that self-interstitials are emitted during the growth of these silica-type precipitates. The volume ratios of silicon and silica explains the 2:1 ratio of O_i loss to I gain.

We assume that TD complexes grow by the addition of oxygen atoms to the core. (Of course, we cannot rule out the possibility of growth by additional BC site self-interstitials.) These additional oxygens may form stable side chains in the (110) plane. Due to the repulsive effect of the oxygen lone-pair electrons, the donor wave function will become gradually more and more delocalized and accordingly shallower in the manner predicted by Borenstein and Corbett.[109] The fast-diffusing IO complex we have found gives support to Newman's suggestion regarding the kinetics of TD growth.[6] We note, however, that $(O_i)_2$ dimers can be expected to have an enhanced diffusion rate as well. In any event, the fast formation rate of TD's (relative to the rate of "normal" oxygen diffusion) can be explained at least qualitatively. Since, in our model, the self-interstitials are crucial for both the formation and for the electrical activity of TD's, it explains why carbon (shown to compete with oxygen in trapping self-interstitials) (Ref. 20) retards TD formation.

The most interesting question is, how many oxygens do the the individual $(TD)_n$ species contain. Our calculations predict the IO_2 complex stable and electrically ac-

tive without any additional oxygens. Therefore, it is reasonable to assume that this is $(TD)_1$ itself. However, based on its bistability and on the CNDO/S results regarding its electronic structure, one may speculate that the IO complex might be $(TD)_1$ while IO_2 is $(TD)_2$. It would then follow that $(TD)_n = IO_n$ (with I not necessarily at the middle of the [110] chain of oxygens). More sophisticated calculations are necessary to confirm this assumption though. Until then the most we can say with certainty is that $(TD)_1$ does not contain more than two oxygens.

The IO_2 model of the core also offers a natural explanation for the NL10 center in Al-doped samples. Since self-interstitials will replace substitutional aluminum, free-moving Al interstitials can be expected. Due to the strong bond of aluminum to oxygen, the formation of AlO_2 complexes analogous to IO_2 will replace the latter. A similar procedure is not likely in boron-doped samples. At first thought the AlO_2 complex is expected to be a shallow single donor and be detectable in infrared. This infrared spectrum is apparently not observed, so further calculations in this direction have still to be done.

In general, with a TD model based on an IO_2 core [with the possibility of $(TD)_1$ being just an IO complex], the behavior of thermal donors can be well accounted for, as suggested earlier by Newman.[6] Our calculations provide a microscopic model for those suggestions. Beside reproducing known facts and confirming assumptions, it would, of course, be desirable to predict properties of these complexes not known in advance. After decades of investigations, however, there is not much room left for such properties. Among the few things unknown is the local mode vibrations connected with TD's. Also the mechanisms of bistability and hydrogen passivation still need explanations.

D. The possibility of bistability for the IO and IO_2 complexes

The first two in the series of TD's have been proven to be bistable.[5,36,37] According to Wagner and Hage,[5] the electrically inactive configurations, X_1 and X_2, are more stable in the neutral charge state than the electrically active configurations, $(TD)_1$ and $(TD)_2$, by 0.10 and 0.03 eV, respectively. At Fermi-level positions $E_c - 0.32$ eV and $E_c - 0.24$ eV, respectively, the neutral X configurations transform directly into the dipositive TD configurations. In this sense these centers exhibit negative-U behavior.

The accurate prediction of energy differences in the order of 0.1 eV between different defect configurations is beyond the capabilities of our method. Nevertheless, it is interesting to point out that the exclusive bistability of the first TD's can be explained with oxygen+self-interstitial complexes. The IO complex has been shown to be bistable—another argument supporting its candidacy for $(TD)_1$. With all precautions for inaccuracies, from our results [Eqs. (6)–(9)], it follows that $(IO)_r$ is definitely more stable than $(IO)_i$ in the neutral charge state. In Fig. 8 we compare the stability of the $(IO)_i^{++}$ complex with that of $(IO)_r$ in different charge states.[110] The ener-
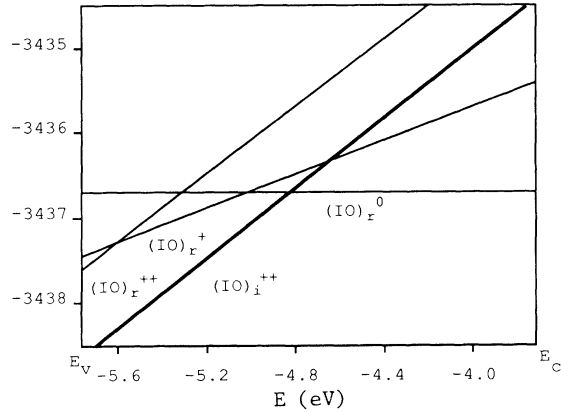
FIG. 8. The stability of the $(IO)_r$ complex in various charge states compared with that of $(IO)_i^{++}$ as the function of the Fermi energy. (It is assumed that the cluster is connected to a reservoir of electrons having the Fermi energy.)

FIG. 9. The stability of the OIO complex in various charge states compared with that of IO_2^{++} as a function of the Fermi energy.

gies of the neutral and singly positive charge states of $(IO)_i$ are uncertain (with occupancy levels close to the CB edge) but it is clear that $(IO)_r^{++}$ and $(IO)_r^+$ are not stable at any Fermi-level position. Therefore, we believe that $(IO)_r^0$ is converted immediately into $(IO)_i^{++}$ below a certain Fermi-level position. That is, the coexistence of two "positive-U" configurations leads to a "negative-U" behavior of the complex in this case as expected[5,36] for $(TD)_1$ [and $(TD)_2$].

A similar pair of bistable configurations can be constructed for IO_2 as well. Figure 7(a) shows the two configurations, $(IO)_i$ and $(IO)_r$, side by side. The primary difference is in the position of the oxygen which has moved toward the next BC site to the left in $(IO)_r$, relative to its position in $(IO)_i$. $(IO)_r$ can be thought of as one silicon from a split self-interstitial pair interacting with an adjacent O_i. A similar configuration can also be constructed from the IO_2 complex—as shown in Fig. 7(b). Due to the O_i's on both sides, an overcoordination[111] of the lower silicon in the split self-interstitial pair is expected with the upper one undercoordinated as shown in Fig. 7(b) (although a conventional bond to just one of the oxygens with the lower silicon flipping toward the oxygen and forming a four-member ring with an adjacent interstitial oxygen $[I(O)_r + O_i]$ is computed to be of equal stability). Unfortunately, the very localized basis set of MINDO/3 is *a priori* not suitable to describe such type of bonding, and our calculation results in a higher energy for this OIO structure than for IO_2 by about 0.6 eV. (Of course, the more compact structure also favors the IO_2: the neglected relaxation is certainly more significant for the OIO structure.) From the comparison of stabilities in Fig. 9, it can be seen that, here again, the dipositive charge state of IO_2 is always more stable than the singly or doubly positive charge states of OIO [and also more stable than the singly or doubly positive charge states of $(IO)_r + O_i$ not shown in Fig. 9]. Since, in the neutral charge state, the expected energy difference in favor OIO is expected to be 0.10 eV [if IO_2 is $(TD)_1$] or
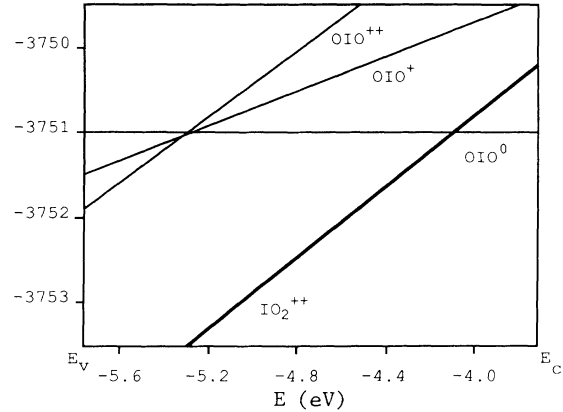
maybe only 0.03 eV [if IO_2 is $(TD)_2$], a more sophisticated calculation and allowance for a longer range of relaxation might easily prove that the metastable configurations OIO [or $(IO)_r + O_i$] and IO_2, are indeed, bistable and behave as a negative-U system the way the IO complex does. Since the transformation $IO_2 \rightarrow OIO$ [or $(IO)_r + O_i$] requires the outward movement of oxygens in the [110] direction it would be definitely blocked after the side chains of additional oxygens are formed in higher TD's. This could explain why bistability can be observed only for the first two species.

E. Vibrational frequencies of IO and IO_2 complexes

The accurate calculation of vibrational frequencies is a very difficult task since it requires the calculation of minute differences between huge total-energy values. Nevertheless, we have shown that trends in the vibrational frequencies of hydrogen complexes can be reproduced reasonably well.[112] We have performed vibration calculations for various oxygen defects in the 32-atom CCM by diagonalizing the mass-weighted force-constant matrix calculated for the oxygen atoms and their immediate neighbors in the rigid cage of the rest of the atoms. The results shown in Table III contain a systematic overestimation of roughly 10%, as noted earlier.[113] Therefore, to facilitate comparison with experimental values, they have been scaled down uniformly. The trend in the asymmetric stretching mode frequency of divalent oxygen is indeed well reproduced. The predicted frequencies associated with the core of the doubly ionized TD's (Ref. 114) are significantly lower. This is a consequence of the change in the bonding configuration of oxygen (from divalent to trivalent). Of course, our scaled values can only be taken as indicators for the range where the frequencies should be looked for. Apart from the inaccuracies apparent from Table III, it has to be noted that the scaling factors in two systems with similar composition but different bonds should not necessarily be equal. As a test, we have calculated the vibrational frequencies of the

TABLE III. Calculated and scaled stretching mode frequencies of oxygen in various defects (cm^{-1}).

Defect	Calculated	Scaled	Expt. (Ref. 21)
O_i	1248	1106	1106
VO	990	877	830
VO_2	995	882	877
$VO_2 + O_i$	1171	1038	1001
	1071	949	969
	1051	931	905
$(IO)_i^{++}$	985	873	
	702	622	
IO_2^{++}	1090	966	
	980	868	

FIG. 10. The structure of the IO_2H complex. (The hydrogen is the small, solid circle.)

molecular entities $O(SiH_3)_2$ and $O(SiH_3)_3^+$ by MINDO/3 and compared them to the results of an *ab initio* Hartree-Fock calculation using 6-31G* basis.[115] The stretching frequencies of oxygen in the two calculations are 1267 and 1234 cm^{-1} for the divalent oxygen in $O(SiH_3)_2$, and 940 and 886 cm^{-1} for the trivalent oxygen in $O(SiH_3)_3^+$. Although the deviations between the results of the two methods are different for the two molecules, they unambiguously show the significant lowering of the oxygen frequency on changing from divalent to trivalent bonding. Accordingly, the vibration frequencies associated with TD's are to be expected somewhere below 966 cm^{-1}. We note that Wagner and Hage observed[5] a number of infrared transitions from 783 to 575 cm^{-1} which could not be identified with effective-mass states.

We note that, in irradiated silicon, an infrared band at 935 cm^{-1} has been identified with an oxygen+self-interstitial complex[106,116] which anneals out at room temperature. A band at the same frequency has been found stable up to 300 °C but its relation to oxygen was doubted.[117] The reason for that was partly the assumption that oxygen in an IO complex has to have a higher vibration frequency than that of isolated O_i. We have shown that this is not true. We also feel that the other argument given in Ref. 117, namely, that no correlation has been found between the intensity of the band and the O_i concentration in randomly selected samples, is not sufficient either. A systematic search for that band after subsequent steps of thermal annealing would be necessary.

F. The interaction of hydrogen with the IO_2 complex

To investigate the possibility of hydrogen passivation, a single proton has been added to the $Si_{32}IO_2$ cluster. The resulting $IO_2 + H^+$ complex is shown in Fig. 10. The excess electrons from the two oxygens are transferred into a lone pair in the dangling sp^3 hybrid of I, with an energy close to the VB edge. At the same time, there is an empty orbital below the CB edge, i.e., the system is an ionized single donor. A CNDO/S calculation for the neutral charge state (at the geometry for IO_2H^+ by MINDO/3) results in a delocalized donor orbital formed from conduction-band states but different from the original IO_2 donor wave function. In a MINDO/3 calculation for the neutral charge state, the donor electron oscil-
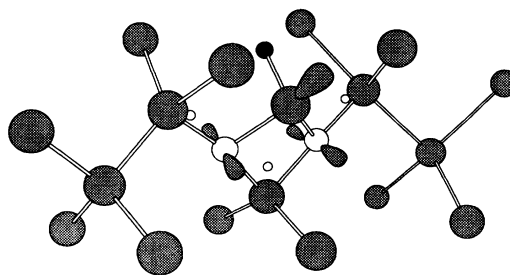
lates between localized antibonding orbitals on various silicon neighbors, and convergence could not be achieved in the geometry optimization. Adding a second proton to the IO_2H^+ complex has proven to be endothermic.

Independent of the nature and exact energy of the donor orbital, it is clear that hydrogen reduces the double-donor IO_2 into the single donor IO_2H, i.e., hydrogenation should result in at least a "50% passivation" of each TD species. Our calculation is not able to tell whether these single donor states will be ionized at a Fermi-level position where the original TD's are. The calculated binding energy of hydrogen to the IO_2 complex is 1.2 eV. If the model given in the previous subsection for the bistability is correct, the higher binding energy of hydrogen to a split self-interstitial [as the one on the right-hand side of Fig. 7(b)], 1.4 eV,[112] would stabilize the inactive X configuration over the active TD configuration in early, bistable TD species. This could explain the higher effectivity of hydrogen passivation if the sample contains mainly early TD species.

V. CONCLUSIONS

In a series of calculations on various oxygen complexes we have investigated systematically every complex proposed so far as the core of the thermal donors. In a careful analysis of the results allowing for the possible errors in the calculation, we have shown that oxygen-only, oxygen+vacancy, and oxygen+semivacancy complexes can all be excluded as possible candidates. We have found, however, that a complex in which a silicon self-interstitial is bonded to two neighboring oxygen interstitials has a stable structure of C_{2v} symmetry and produces a shallow, doubly occupied donor orbital in qualitative agreement with ENDOR results on thermal donors. The properties of this complex and the energies of its formation provide reason to identify it with one of the first TD species, $(TD)_1$ or $(TD)_2$. (A single oxygen interstitial capturing a silicon self-interstitial might exhibit thermal-donor character as well.) Based on this, we have proposed that thermal donors are interstitial oxygen chains of different sizes in a (110) plane with a self-interstitial captured somewhere along the chain. This model is capable of explaining most TD properties. We have predict-

ed mechanisms for fast formation, bistability, and for hydrogen passivation, as well as frequencies of local mode vibrations associated with TD's.

Finally, we note that we were fully aware of the limitations of our computational methods and tried to take them into account in the interpretation of the results. At rather important points that led to considerable uncertainties: the application of a more sophisticated theory would have been clearly advantageous. Nevertheless, the simple theoretical approach used in these computations allowed us to sift through the vast number of possible models until one has been caught in its sieve. A more accurate study of this oxygen + self-interstitial complex can now follow, but it seems to be in order to summarize our results before that.

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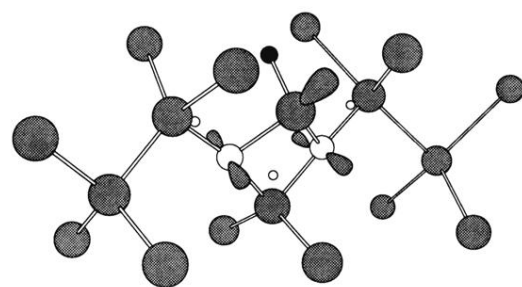
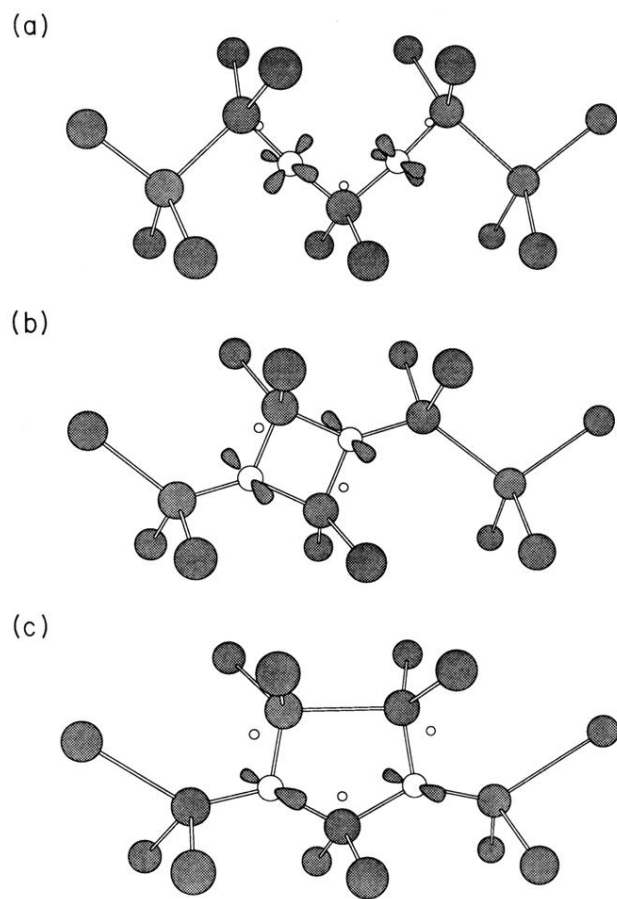FIG. 10. The structure of the IO_2H complex. (The hydrogen is the small, solid circle.)

FIG. 2. Di-oxygen complexes: $(O_i)_2$, $(O_r)_2$, and $(O_\gamma)_2$. The unperturbed lattice positions are marked by small, open circles. The lone-pair orbitals are also shown; the occupied ones are shaded.
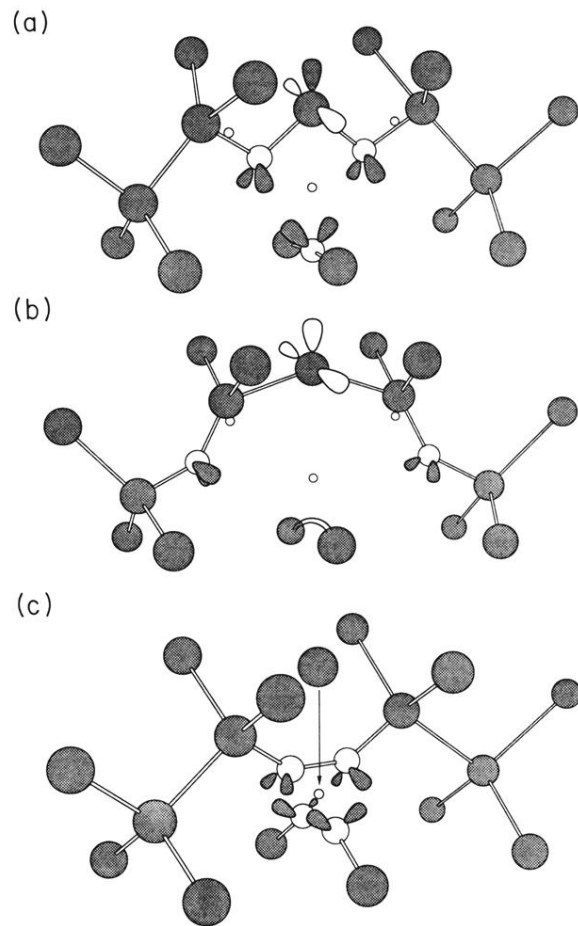
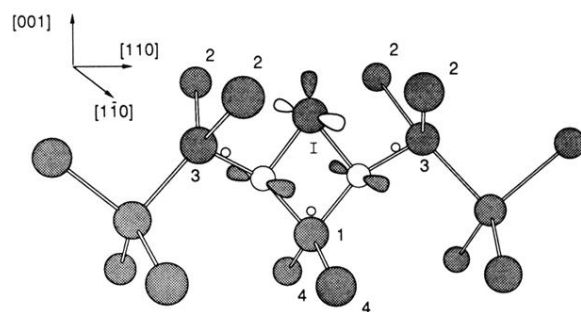FIG. 3. Oxygen + semivacancy models of TD's: (a) OBS (b) NL10, and (c) NL8.

FIG. 4. Structure of the IO_2 complex. Unperturbed lattice positions are marked by small, open circles. Beside the electrons in lone-pair orbitals and in bonds, two electrons are in a delocalized orbital.
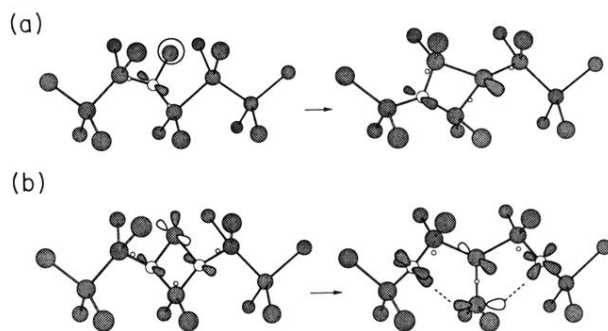
FIG. 7. Metastable configurations $(IO)_i$ and $(IO)_r$ for IO (a) and their analogues, IO_2 and OIO. [The open circle on I in $(IO)_i$ denotes a doubly occupied s orbital.]