

## Structures of Thermal Double Donors in Silicon

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Accurate total-energy calculations are used to study the structures and formation energies of oxygen chains as models for thermal double donors (TDD's) in Si. We find that the first three TDD's (TDD0–TDD2) consist of one four-member ring, with one or two adjacent interstitial O atoms. These metastable TDD's form bistable negative- $U$  systems with the corresponding stable, electrically inactive staggered structures. The TDD3–TDD7 structures are found to consist of four-member rings with adjacent interstitial O atoms at both ends. The TDD's with a central “di-Y-lid” core are found to become energetically competitive with the four-member ring TDD's only for clusters larger than ten O atoms.

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A scientifically challenging and technologically important phenomenon is the appearance of thermal donor (TD) families in Czochralski-grown Si during annealing [1–3]. TD's are believed to have a common core into which oxygen is aggregated. The most studied TD family consists of up to 17 thermal double donors (TDD's, TDD0–TDD16) appearing in the temperature range 350–550 °C [4–6]. Despite years of intensive studies, the structures of TDD's are still not known, nor is the source giving rise to their donor property based on the (0/+) and (+/++) levels at around  $E_c - 0.07$  eV and  $E_c - 0.15$  eV, respectively [1]. The early TDD's (TDD0–TDD2) exhibit still unexplained bistability [2,5,7]. Also unexplained remains the anomalously high formation rate of TDD's as well as the relation between adjacent TDD's [1]. Electron nuclear double resonance (ENDOR) experiments have revealed that TDD's have  $C_{2v}$  symmetry from TDD3 onwards: the O atoms lie on the same (110) mirror plane and the  $C_2$  symmetry axis lies in the [001] direction [1–3,8,9]. According to the interpretation of the ENDOR results the  $C_2$  symmetry axis should not contain O atoms [8]. If the  $C_{2v}$  symmetry is to be maintained during the growth process, the O atoms must be added in pairs [2,8,9]. However, if the O atoms are added one by one then an alternating  $C_{2v}$ - $C_{1h}$  symmetry should occur [2,8,9].

The aim of this Letter is to report systematic studies on the structures and formation energies of oxygen chains as atomistic models for TDD's using density-functional-theory (DFT) methods in the local-density approximation (LDA) [10]. We find that the first three TDD's (TDD0–TDD2) consist of one four-member ring (R) containing two threefold coordinated O atoms ( $O_r$ ) responsible for the donor property [11], and one or two adjacent interstitial O atoms ( $O_i$ ). These metastable R-TDD structures and the corresponding stable electrically inactive staggered  $O_i$  structures form bistable negative- $U$  systems. TDD2 is found to form from TDD1 via a restructuring process. TDD3 is found to consist of two adjacent R's and TDD4–TDD7 are found to consist of more adjacent R's with  $O_i$ 's at the ends. The TDD's

with a central “di-Y-lid” core (two O atoms denoted by  $O_{2Y}$  each bonded to three near Si atoms in a Y-shape fashion and two adjacent side  $O_i$ 's) [12] are found to become energetically competitive with the R-TDD's only at ten O atoms. The DFT LDA total energy calculations are performed using the self-consistent plane-wave pseudopotential (PP) method [10]. For Si we use the norm-conserving Hamann PP [13] with the nonlinear core valence exchange-correlation scheme [14]. The PP is of the fully separable Kleinman-Bylander form [15] and the  $s$  component is used as the local one. For oxygen we use the ultrasoft Vanderbilt PP [16]. A kinetic-energy cutoff of 28 Ry, the  $\Gamma$ -point sampling and cubic 128 or elongated 108 or 162 atom-site supercells are used. The elongated supercells allow us to study long oxygen chains, because the intersupercell [110] distance is in this case about 22 and 35 Å for the 108 and 162 atom-site supercell, respectively. All ionic coordinates are allowed to relax without any constraints until the largest remaining Hellmann-Feynman force component is typically less than 5 meV/Å. The calculations for shallow donors are done for the case where the donor level is empty, i.e., for the doubly positive charge state. This seems to be justified because the shallow donor state is delocalized and can have only a marginal effect on the defect relaxations.

In agreement with Chadi [17], we find that the energetically most favorable TDD structures contain only O atoms (no Si interstitials or vacancies). The optimized lowest energy structures are shown in Fig. 1 and the corresponding formation energies [18] as functions of the electron chemical potential  $\mu_e$  in Fig. 2. The TDD structures consist of R's and adjacent  $O_i$ 's. The simplest calculated TDD structure, shown in Fig. 1(a), contains one  $O_i$  and one R [11] consisting of two  $O_r$ 's responsible for the donor property. The calculated staggered  $O_{3i}$  [19], shown in Fig. 1(b), is electrically inactive. As seen from Fig. 2,  $O_{3i}$  and  $O_i$ - $O_{2r}$  form a bistable negative- $U$  system [the  $O_i$ - $O_{2r}^+$  line (not shown) lies above the intersection of the  $O_i$ - $O_{2r}^{++}$  and  $O_{3i}$  lines]. It is thus natural to identify  $O_i$ - $O_{2r}$  as TDD0 because it obeys the experimentally observed bistability [2].

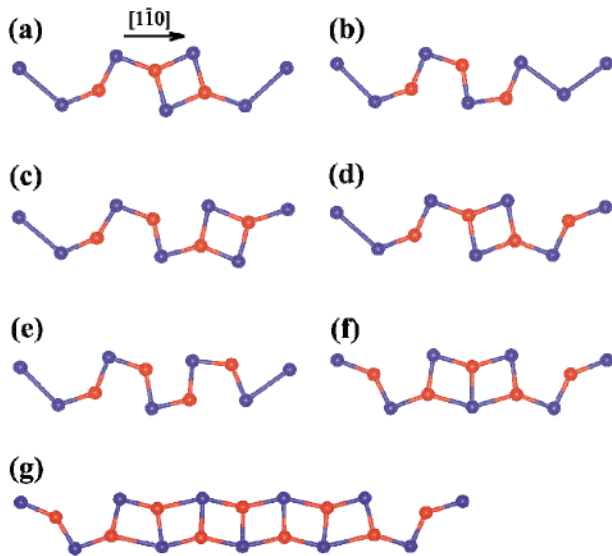


FIG. 1 (color). Calculated first thermal double donor structures containing four member rings and electrically inactive ( $X$ ) structures. (a)  $O_i-O_{2r}^{++}$ . (b) Staggered  $O_{3i}$ . (c)  $O_{2i}-O_{2r}^{++}$ . (d)  $O_i-O_{2r}-O_i^{++}$ . (e) Staggered  $O_{4i}$ . (f)  $O_i-O_{3r}-O_i^{++}$ . (g)  $O_i-O_{7r}-O_i^{++}$ . Red and blue balls denote oxygen and silicon atoms, respectively. Si-O bonds  $\leq 2.3$  Å have been drawn.

Chadi [17], using similar methods to ours and a 32-atom site supercell, found a stable  $C_{2v}$  symmetric  $O_3$  complex and suggested it as a candidate for TDD1. Ramamoorthy and Pantelides [20], with a 64-atom site supercell, speculated this  $O_3$  complex to be unstable by 0.1 eV with respect to  $O_i-O_{2r}$ . Using a 128-atom supercell, we confirm this instability. Our calculation results in an energy 0.28 eV higher than for the ring structure.

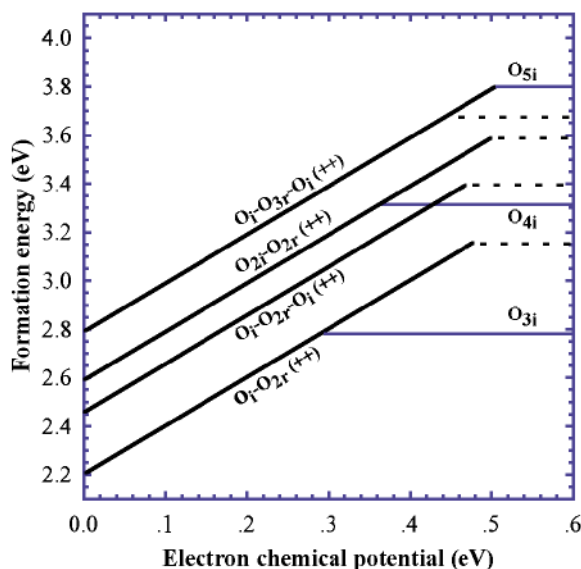


FIG. 2 (color). Calculated formation energy plots for the oxygen complexes containing 3–5 oxygen atoms. Formation energies for the neutral configurations of the centers are shown as dotted lines. The electron chemical potential is measured from the valence band maximum.

Adding one  $O_i$  to  $O_i-O_{2r}$  results in two calculated TDD structures,  $O_{2i}-O_{2r}^{++}$  and  $O_i-O_{2r}-O_i^{++}$ , shown in Figs. 1(c) and 1(d), respectively. The calculated staggered  $O_{4i}$  [19], shown in Fig. 1(e), is electrically inactive and will be called the  $X$  state in the following. As seen from Fig. 2 both  $O_{2i}-O_{2r}$  and  $O_i-O_{2r}-O_i$  form with  $O_{4i}$  a bistable negative- $U$  system [the  $O_i-O_{2r}-O_i$  ( $O_{2i}-O_{2r}$ ) line lies above the intersection of the  $O_i-O_{2r}-O_i^{++}$  and  $O_{4i}$  ( $O_{2i}-O_{2r}^{++}$  and  $O_{4i}$ ) lines] in fair agreement with the infrared (IR) absorption experiments [21,22].  $O_i-O_{2r}-O_i^{++}$  can be relatively easily formed from  $O_{2i}-O_{2r}^{++}$  (the calculated barrier equals 0.36 eV) in agreement with the experimental kinetic study implying that TDD2 may form via reconfiguration from TDD1 [23]. The calculated barriers from  $O_{2i}-O_{2r}^{++}$  and  $O_i-O_{2r}-O_i^{++}$  to the staggered  $O_{4i}$  equal 0.36 and 0.50 eV, respectively, which after adding the experimental difference from TDD $^{++}$  to TDD $^+$  of 0.15 eV agree quite closely with the experimental values of 0.54 eV for TDD1  $\rightarrow$   $X$  and 0.71 eV for TDD2  $\rightarrow$   $X$  [5,7]. It is thus natural to identify  $O_{2i}-O_{2r}$  as TDD1 and  $O_i-O_{2r}-O_i$  as TDD2.

Adding one  $O_i$  to  $O_i-O_{2r}-O_i$  results in the calculated R-TDD structure  $O_i-O_{3r}-O_i^{++}$ , shown in Fig. 1(f). The formation energy of the staggered  $O_{5i}$  is so high that no bistability occurs any more (Fig. 2).  $O_i-O_{3r}-O_i^{++}$  contains two adjacent R's (the  $R_2$  core) and has the required  $C_{2v}$  symmetry. However,  $O_i-O_{3r}-O_i^{++}$  contains one  $O_r$  on the  $C_2$  symmetry axis which seems to conflict with the interpretation of the experimental ENDOR results [8]. Nevertheless, this is not necessarily a disagreement because ENDOR does not detect an increase of the number of O atoms in the TDD structures [24] contradicting the usual belief of an increasing number of O atoms in the TDD family. Moreover, ENDOR and electron paramagnetic resonance experiments do not always detect light elements on the  $C_2$  axis of a defect [25]. Since we also find that the di-Y-lid structure is unstable for  $O_5$ , it is natural to identify  $O_i-O_{3r}-O_i$  as TDD3.

The next four calculated TDD structures contain more adjacent R's and are  $O_i-O_{4r}-O_i^{++}$  (three R's),  $O_i-O_{5r}-O_i^{++}$  (four R's),  $O_i-O_{6r}-O_i^{++}$  (five R's), and  $O_i-O_{7r}-O_i^{++}$  (six R's) shown in Fig. 1(g). All these R-TDD $^{++}$  structures have the same  $C_{2v}$  symmetric  $R_2$  core as  $O_i-O_{3r}-O_i^{++}$  and also contain one  $O_r$  on the  $C_2$  symmetry axis.  $O_i-O_{5r}-O_i^{++}$  and  $O_i-O_{7r}-O_i^{++}$  with an odd number of O atoms have  $C_{2v}$  symmetry.  $O_i-O_{4r}-O_i^{++}$  and  $O_i-O_{6r}-O_i^{++}$  with an even number of O atoms have approximately  $C_{2v}$  symmetry in their centers but their overall symmetry is  $C_{1h}$ . We identify  $O_i-O_{4r}-O_i$ ,  $O_i-O_{5r}-O_i$ ,  $O_i-O_{6r}-O_i$ , and  $O_i-O_{7r}-O_i$  as TDD4, TDD5, TDD6, and TDD7, respectively. We have not calculated larger R-TDD's but it is very likely that they can be formed by adding more  $O_i$ 's to the chains attached to the  $R_2$  core.

The formation energies per O atom for  $\mu_e = 0$  and the unoccupied Kohn-Sham donor levels of the calculated TDD $^{++}$ 's are shown in Fig. 3. The calculated donor levels

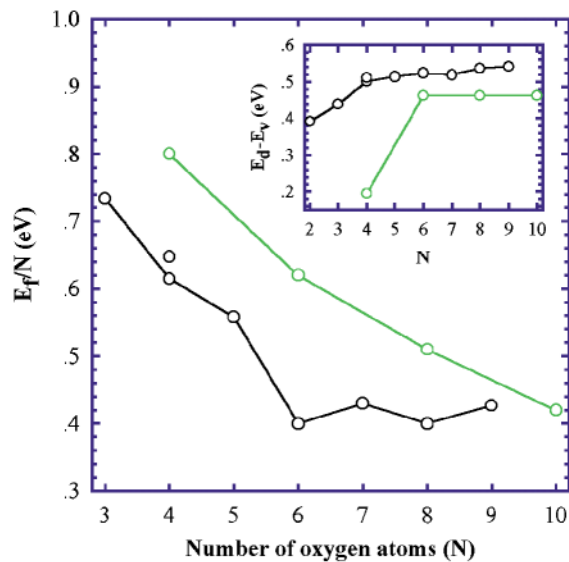


FIG. 3 (color). Formation energy per oxygen atom of calculated oxygen-only TDD<sup>++</sup>'s for the electron chemical potential  $\mu_e = 0$ . Inset: Unoccupied Kohn-Sham donor levels measured from the valence band maximum at  $\Gamma$ . The calculated band gap equals 0.56 eV. Black dots denote the energies of R-TDD<sup>++</sup>'s and green dots those of di-Y-lid  $O_{xi}-O_{2Y}-O_{xi}^{++}$ ,  $x = 1, 2, 3, 4$ .

of the R-TDD's (upper data points in the inset of Fig. 3) approach the conduction band minimum with an increasing number of O atoms consistently with the IR absorption experiments [2,4–6].

Consider then  $C_{2v}$ -symmetric TDD's having the di-Y-lid core [12]. The calculated di-Y-lid structure [12] is shown in Fig. 4(a). This  $O_i-O_{2Y}-O_i$  has the required  $C_{2v}$  symmetry without any O atoms on the  $C_2$  symmetry axis. However, we find that the formation energy of  $O_i-O_{2Y}-O_i^{++}$  is by 0.84 eV higher than that of  $O_i-O_{2Y}-O_i^{++}$  (Fig. 3). Moreover, the (neutral)  $O_i-O_{2Y}-O_i$  is not a thermal, but a deep donor: the calculated distance of the occupied Kohn-Sham donor level from the valence band maximum equals 0.2 eV and the corresponding orbital is very localized [Fig. 4(a)]. Increasing the number of adjacent  $O_i$ 's shifts the unoccupied Kohn-Sham donor level higher towards the conduction band minimum (lower data points in the inset of Fig. 3) consistently with the IR absorption experiments [2,4–6]. Because of the steady decrease of the formation energy per O atom of the di-Y-lid-TDD's (upper data points in Fig. 3) the formation energy per O atom of  $O_{4i}-O_{2Y}-O_{4i}^{++}$  shown in Fig. 4(b) falls to the region of the lowest formation energies per O atom of the R-TDD<sup>++</sup>'s (Fig. 3). Thus,  $O_{xi}-O_{2Y}-O_{xi}$  ( $x \geq 4$ ) seem to become the last members of the TDD series which, however, also causes the change of the core. However, it is difficult to assess the exact transition from R-TDD's to di-Y-lid-TDD's because also other factors besides the formation energy (such as kinetics) play a role.

The difference between the R and di-Y-lid cores is as follows. At first, the R core can gain energy fast by form-

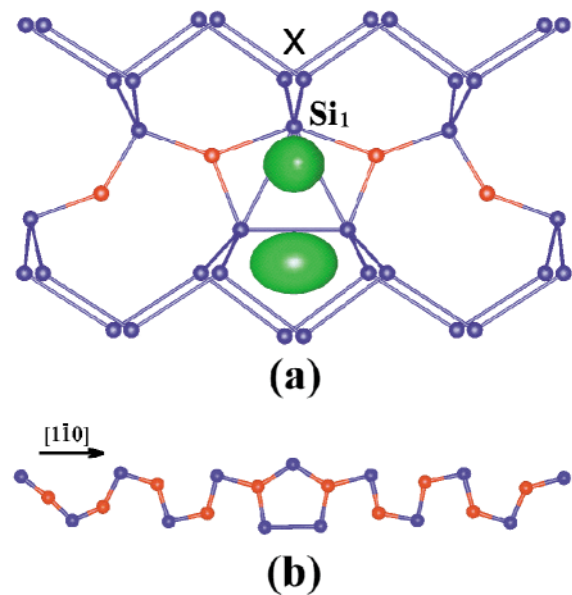


FIG. 4 (color). (a) Calculated constant-value surface of the electron density of the uppermost occupied electronic state of the neutral charge state of  $O_i-O_{2Y}-O_i$  (di-Y-lid). The electron density isosurface is at half of the maximum value of  $0.03 \text{ e}/\text{\AA}^3$ . (b)  $O_{4i}-O_{2Y}-O_{4i}^{++}$ . Si-O bonds  $\leq 2.3 \text{ \AA}$  have been drawn. Red and blue balls denote oxygen and silicon atoms, respectively.

ing new adjacent R's. This mechanism seems to get exhausted at  $N = 6$  (Fig. 3). On the other hand, although the formation of the di-Y-lid core requires originally more energy, it has a better ability to deform and release the strain caused by aggregating  $O_i$ 's, making the di-Y-lid-TDD's eventually competitive with the R-TDD's (Fig. 3).

In the di-Y-lid-related oxygen-semivacancy complexes the Si atom on the  $C_2$  axis ( $Si_1$  in Fig. 4) is displaced to the interstitial position (the cross in Fig. 4). The calculated formation energy for a neutral semivacancy consisting of  $O_{2Y}$  and two (four) side  $O_i$ 's (see Fig. 4) equals 3.9 (4.4) eV. The calculated oxygen-semivacancy structures show no electrical activity. The observation that displacing the Si atom on the  $C_2$  axis of the di-Y-lid core to the interstitial position relieves strain may explain the finite number of the members of the di-Y-lid-TDD family: increasing the number of  $O_i$ 's causes increasing strain that at some point is relieved by ejecting the center Si atom to the interstitial position which simultaneously destroys the electrical activity.

As to the structures containing Si interstitials ( $Si_i$ ) and vacancies we find in agreement with Chadi [17] that the formation energies for these structures are high. All models containing  $Si_i$ , including the  $O_i-Si_i-O_i$  model proposed by Deák *et al.* [26], have a formation energy of more than 4 eV in their doubly positive charge states at  $\mu_e = 0$ . We further find that the O atoms of  $O_i-Si_i-O_i^{++}$  relax out of the (110) plane. We also studied several other structures composed of one  $Si_i$  and two or four  $O_i$ 's. Placing one  $Si_i$  to the nearest  $T_d$  position resulted

in a staggered structure remaining in the (110) plane: The binding energy between  $O_{2i}$  and  $Si_i$  equals 1.7 eV and between  $O_{4i}$  and  $Si_i$  0.9 eV [27]. Thus,  $Si_i$ 's—if available—may bind to  $O_i$ 's and form shallow double donor complexes.

To summarize our results: (i) The first three R-TDD's ( $O_i-O_{2r}$ ,  $O_{2i}-O_{2r}$ , and  $O_i-O_{2r}-O_i$ ) [Figs. 1(a), 1(c), and 1(d)] with the lowest formation energies of the double donor structures are identified as TDD0, TDD1, and TDD2, respectively. (ii) They also form with the electrically inactive staggered  $O_{3i}$  and  $O_{4i}$  [Figs. 1(b) and 1(e)] bistable negative- $U$  systems. (iii)  $O_i-O_{xr}-O_i$ ,  $x = 3, 4, 5, 6, 7$  [see Figs. 1(f) and 1(g)] with the same  $C_{2v}$  symmetric  $R_2$  core are identified as TDD3-TDD7 despite the fact that their cores contain one O atom on the  $C_2$  symmetry axis. (iv) At ten O atoms the di-Y-lid-TDD's are found to become energetically competitive with the R-TDD's.

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