

## Stable atomic geometries of oxygen microclusters in silicon

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Atomic and electronic structures of oxygen-impurity microclusters in crystalline silicon have been explored by a first-principles pseudopotential total-energy cluster calculation within the local-density-functional formalism. The stable atomic geometry of each cluster has been obtained by allowing the atoms in the cluster to relax, according to the calculated forces acting on the atoms, to the total-energy-minimized configuration. It is found that a drastic rearrangement of bond configuration between the oxygen and the silicon atoms occurs in the theoretically determined stable atomic geometry for the three-oxygen-atom cluster in silicon, and that the calculated stabilization energy for the geometry, 3.9 eV per oxygen atom, is comparable with that of the most stable isolated bond-centered interstitial configuration, 4.6 eV. The stability of other atomic configurations is also examined, and a mechanism for the oxygen diffusion process along the bond-centered and the split-interstitial sites is proposed. Bistability between the two stable three-oxygen-atom configurations is found, and its manifestation is briefly discussed.

### I. INTRODUCTION

Oxygen plays an important role in various aspects of semiconductor science and technology. In particular, as impurities in crystalline silicon, oxygen atoms have considerable but unresolved effects on the mechanical and electronic properties of the materials.<sup>1</sup> During Czochralski crystal growth oxygen atoms are incorporated into silicon with concentrations up to  $10^{18}$  cm<sup>-3</sup>, and add mechanical strength to the resulting silicon crystal. Further, oxygen impurities in silicon are likely to diffuse and aggregate at high temperature, contribute to gettering of other undesirable contaminants, and induce electronic levels in the energy gap (thermal donors) in certain conditions of annealing.<sup>1,2</sup> Microscopic understanding of these interesting features of oxygen impurities in silicon, however, is rather poor, although several pioneering measurements<sup>3,4</sup> and cluster calculations<sup>5-7</sup> have provided us with suggestive information. The aim of this work is thus to clarify the stable atomic configurations of oxygen-impurity microclusters in silicon from a first-principles calculation and to obtain insights into the microscopic mechanisms of oxygen diffusion, aggregation, and occurrence of thermal donors.

We report here a total-energy electronic-structure calculation within the local-density-functional formalism<sup>8,9</sup> for sufficiently large neutral clusters that mimic the oxygen-impurity microclusters in crystalline silicon. The clusters consist of oxygen-impurity atoms (up to three oxygen atoms are considered here), the surrounding silicon atoms, and the hydrogen atoms that terminate the covalent-bond network of silicon atoms at the boundary of the clusters. The calculation has been performed with first-principles norm-conserving pseudopotentials<sup>10</sup> and a Gaussian-orbitals basis set. For each oxygen microclus-

ter, we calculate the forces acting on atoms in the cluster, move the atoms so that the forces virtually disappear, and finally reach the stable atomic configuration. In the stable configuration obtained we perform accurate total-energy electronic-structure calculations. Among the new results emerging from the present calculation are (i) that, for the isolated oxygen impurity, the bond-centered interstitial configuration in which two puckered bonds between the oxygen atom and the two silicon atoms are formed is stable with a stabilization energy of 4.6 eV, (ii) that the  $y$ -lid configuration (the split interstitial configuration of  $C_{2v}$  symmetry) is unstable against the displacement of oxygen atom along the [110] direction, (iii) that upon adding two more oxygen atoms at the interstitial sites the  $y$ -lid configuration becomes stable, but (iv) that another atomic configuration (similar to but different from the configuration proposed for the thermal donors by Ourmazd *et al.*<sup>11</sup>), in which a drastic rearrangement of bond configuration between three oxygen atoms and the silicon atoms occurs, is stable with a stabilization energy of 3.9 eV per oxygen atom.

In Sec. II, we give a description of the calculational method. The obtained results are presented and the discussion is given in Sec. III. Section IV concludes the paper.

### II. CALCULATION

The first-principles norm-conserving pseudopotential approach based on density functional theory is an effective tool for the study of atomic and electronic structures of atoms, molecules, and solids.<sup>10,12</sup> We employ here the method to reveal stability and level structures of the clusters, which mimic the oxygen-impurity microclusters embedded in a silicon crystal. In this section, we

summarize the present relativistic pseudopotential approach combined with the basis set consisting of Gaussian localized orbitals.

In the pseudopotential scheme, the Kohn-Sham equation<sup>13</sup> containing the Coulomb potential  $V_C$  and the exchange-correlation potential  $V_{xc}$  along with the pseudopotential  $V_{ps}$  becomes (in a.u.)

$$\begin{aligned} \hat{H} |\Psi_i\rangle &= (-\Delta + V_{ps} + V_C + V_{xc}[\rho]) |\Psi_i\rangle \\ &= \varepsilon_i |\Psi_i\rangle, \end{aligned} \quad (1)$$

where valence-electron charge density  $\rho$  is, in turn, written as

$$\rho(\mathbf{r}) = 2 \sum_{i:\text{occ}} |\Psi_i(\mathbf{r})|^2. \quad (2)$$

In (1),  $V_{ps} = \sum v_m$  is a sum over the atomic (ionic) norm-conserving nonlocal pseudopotentials  $v_m$  located at the  $m$ th site. We have constructed  $v_m$  by solving the all-electron atomic (ionic) Dirac equation and following the procedure described in Ref. 10. As for the exchange-correlation potential  $V_{xc}$  which is the functional derivative of the exchange-correlation energy  $E_{xc}$  with respect to the electron charge density  $\rho$ , we use the form by Ceperley and Alder<sup>14</sup> in this calculation

In order to solve (1), we expand the wave function in terms of a Gaussian-orbitals basis set:  $\Psi_i = \sum_j c_{ij} \Phi_j$ . The exponents of  $\Phi_j$  are determined by fitting the numerical atomic orbitals. The exponents of  $\Phi_j$  in (a.u.)<sup>-2</sup> are 1.2220, 0.2595, and 0.093 11 for the silicon  $s$  orbitals;

2.5800, 0.2984, and 0.088 48 for the silicon  $p$  orbitals; 4.4573, 1.0996, and 0.2812 for the oxygen  $s$  orbitals; and 5.5000, 1.0694, and 0.2213 for the oxygen  $p$  orbitals, and 4.5004, 0.6813, and 0.1514 for the hydrogen  $s$  orbitals. Then (1) is converted into the usual secular equation. Matrix elements for  $V_{xc}$  have been calculated numerically and other parts of the matrix elements have been obtained using analytical expressions. Since the Hamiltonian  $\hat{H}$  in (1) depends on the total charge density (2), it is necessary to obtain the solution self-consistently by the iterative procedure.

Using the self-consistent solution of the Kohn-Sham equation, the total energy is expressed as

$$\begin{aligned} E &= 2 \sum_{i:\text{occ}} \varepsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc} \\ &\quad - \int \rho(\mathbf{r}) V_{xc}[\rho] d\mathbf{r} + \frac{1}{2} \sum'_{m,m'} \frac{Z_m Z_{m'}}{|\mathbf{r}_m - \mathbf{r}_{m'}|}, \end{aligned} \quad (3)$$

where  $\mathbf{r}_m$  and  $Z_m$  are the position and core charge of the  $m$ th atom, respectively, and  $\varepsilon_i$  is the energy of the  $i$ th occupied state. We carefully perform the self-consistent calculation so that the total energy converges with a relative error of less than 0.1%.

The force calculation is performed to determine the stable atomic configurations of the clusters. The force acting on the atom at the  $m$ th site,  $\mathbf{F}_m$ , is obtained by differentiating the total energy with respect to the nuclear coordinates:<sup>15</sup>

$$\begin{aligned} \mathbf{F}_m &= - \left[ \sum'_{m'} \frac{Z_m Z_{m'}}{|\mathbf{r}_m - \mathbf{r}_{m'}|^3} (\mathbf{r}_m - \mathbf{r}_{m'}) + 2 \text{Re} \sum_{i:\text{occ}} \sum_{j,j'} c_{ij}^* c_{ij'} \left\langle \frac{\partial \Phi_j}{\partial \mathbf{r}_{m'}} \middle| v_m \middle| \Phi_{j'} \right\rangle \right] \\ &\quad + 2 \text{Re} \left[ \sum_{i:\text{occ}} \sum_{j,j'} c_{ij}^* c_{ij'} \left\langle \frac{\partial \Phi_j}{\partial \mathbf{r}_m} \middle| \hat{H} - \varepsilon_i \middle| \Phi_{j'} \right\rangle \right], \end{aligned} \quad (4)$$

where  $m'$  denotes the atomic site where the  $j$ th localized orbital is placed. It is found from the present calculations with the Gaussian-orbitals basis set that the correction term [last term in (4)] is comparable with the ordinary Hellmann-Feynman force<sup>16</sup> [first and second terms in (4)]. In obtaining the expression (4), the following identity has been used:

$$\left\langle \Phi_j \middle| \frac{\partial v_m}{\partial \mathbf{r}_m} \middle| \Phi_{j'} \right\rangle = - \left\langle \frac{\partial \Phi_j}{\partial \mathbf{r}_{m'}} \middle| v_m \middle| \Phi_{j'} \right\rangle - \left\langle \Phi_j \middle| v_m \middle| \frac{\partial \Phi_{j'}}{\partial \mathbf{r}_{m''}} \right\rangle. \quad (5)$$

The total-energy-minimized geometry of the cluster is determined by seeking the atomic configuration in which the force on each atom in the cluster becomes smaller than a certain value: it is 0.01 Ry/a.u. in the present work (in some unstable configurations the value is 0.1 Ry/a.u.). The quasi-Newton method is used for the op-

timization of the atomic coordinates. All the numerical calculations in this paper are performed by using the NEC SX-2 supercomputer system.

### III. RESULTS AND DISCUSSION

In this section, we present the calculated results on atomic and electronic structures of oxygen-impurity microclusters in silicon. First, we investigate the isolated oxygen impurity, which is important for understanding microscopic mechanisms of oxygen diffusion. Second, the three-oxygen-atom impurity is explored to get an insight into oxygen aggregation and into the thermal donors in silicon.

Throughout the calculation for each cluster that consists of the oxygen impurity atoms, the host silicon atoms and the hydrogen atoms at the boundary, we determine the stable atomic configuration at first by obtaining forces. Errors for the calculated forces are less than

0.001 Ry/a.u. from moderately converged self-consistent solutions. In this geometry optimization of the clusters, positions of oxygen and neighboring silicon atoms are determined, while the other silicon atoms are fixed at the original sites in the silicon lattice. The Si—Si bond length in the crystal and the Si—H bond length are taken to be 2.35 and 1.48 Å, respectively. Second, we perform sufficiently converged self-consistent total-energy electronic-structure calculations at the optimized atomic configurations. In order to study the stability of the optimized geometry, we calculate stabilization energy which is the energy difference between the oxygen-impurity microcluster with optimized geometry and corresponding silicon pristine microcluster plus isolated oxygen atoms.

### A. Isolated oxygen impurity

First, we concentrate on the bond-centered interstitial and the  $\gamma$ -lid (split interstitial) configurations [Figs. 1(a) and 1(b)]. They are of  $C_2$  and  $C_{2v}$  symmetries, respectively.

In the calculation for the bond-centered interstitial configuration, we have used the  $\text{Si}_{10}\text{H}_{20}\text{O}$  cluster which includes the oxygen impurity, the two first-neighboring, and six second-neighboring silicon atoms from the center of the Si—Si bond and further contains two of the third-neighboring silicon atoms. We restrict ourselves to the  $C_2$  symmetry in the process of the geometry optimization. The important features of the stable atomic geometry obtained [Fig. 1(a)] are as follows (see also Table I). By inserting an oxygen atom, the two nearest silicon atoms are dislodged from the lattice sites along the Si—Si bond: the distance between the two Si atoms changes from 2.35 to 3.26 Å. These two silicon atoms are

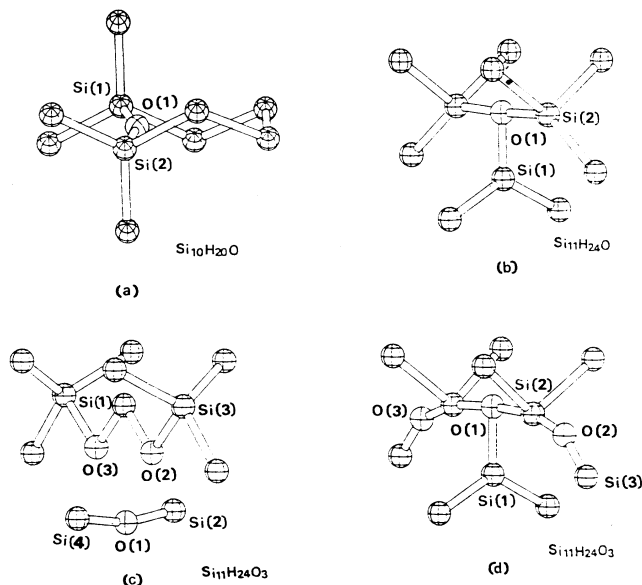


FIG. 1. Calculated stable oxygen microclusters in Si. The boundaries of the clusters are terminated by H atoms (not shown here). (a) The bond-centered interstitial configuration, (b) the  $\gamma$ -lid configuration, and [(c) and (d)] the three-oxygen-impurity configurations.

found to be located almost on the axis of the original Si—Si bond within the present accuracy of the calculation. The calculated O—Si bond length is 1.68 Å and the O—Si—O angle is 152°. This bond length is comparable with that in typical crystalline forms of  $\text{SiO}_2$ : 1.59 Å.<sup>17</sup> As the contour map of the electron charge density in Fig.

TABLE I. Calculated bond lengths and angles for the optimized atomic geometries of the clusters.

Cluster	Symmetry	Bond	Bond length (Å) (bond angle (deg))
(a)	$C_2$	Si(1)—Si(2)	3.26
		Si(1)—O	1.68
		Si(1)—O—Si(2)	(157)
(b)	$C_{2v}$	Si(1)—Si(2)	2.62
		Si(1)—O	1.74
		Si(2)—O	1.90
		Si(1)—O—Si(2)	(92.2)
(c)	$C_{2v}$	Si(1)—O(2)	1.69
		Si(3)—O(2)	1.85
		Si(2)—O(1)	1.71
		O(2)—Si(1)—O(3)	(88.9)
		Si(1)—O(2)—Si(3)	(89.1)
		Si(2)—O(1)—Si(4)	(166)
(d)	$C_{2v}$	Si(1)—Si(2)	2.44
		Si(1)—O(1)	1.82
		Si(2)—O(1)	1.70
		Si(2)—O(2)	1.39
		Si(3)—O(2)	1.39
		Si(1)—O(1)—Si(2)	(87.6)
Si(2)—O(2)—Si(3)	(151)		

2(a) shows, the Si—Si bond is completely broken and the inserted oxygen atom attracts electrons from the neighboring silicon atoms. The Mulliken population analysis indicates that the oxygen attracts 1.20 electrons and the nearest silicon loses 0.41 electrons (Table II). The electron population of the second-neighbor silicon ranges from 3.87 to 3.93 and that of the third-neighbor silicon is 3.97. Thus the influence of oxygen on the third-neighbor silicon atoms is small.

The stabilization energy of the oxygen-impurity cluster is defined as the total energy of the cluster subtracted from the sum of the total energies of the pristine silicon cluster and the isolated oxygen atoms. In the case of the bond-centered interstitial configuration, the corresponding pristine cluster is  $\text{Si}_{10}\text{H}_{20}$ , and the calculated stabilization energy is 4.6 eV. This large stabilization energy results from the fact that one Si—Si bond is broken and then two Si—O bonds are formed. Actually, since the binding energies of the Si—Si bond in crystalline silicon and the Si—O bond in  $\text{SiO}_2$  are estimated to be 2.4 and 4.7 eV, respectively,<sup>18</sup> the stabilization energy of the interstitial oxygen defect is roughly estimated to be a large positive value (7.0 eV). The calculated stabilization energy, 4.6 eV, which is 2.4 eV lower than the above estimated value is due to distortion from the stretching displacement of silicon atoms. The electronic-level structure is shown in Fig. 3. The highest occupied molecular orbital (HOMO) has large amplitude at the oxygen site (see Table III) and has oxygen-nonbonding character.

Accumulation of the experimental data<sup>1,2,4</sup> indicates that the bond-centered interstitial configuration is the most stable site for an isolated oxygen impurity in silicon. The calculated large stabilization energy of 4.6 eV supports this notion. Further, the dominant absorption band at  $1106\text{ cm}^{-1}$  has been observed from the infrared absorption measurement<sup>4</sup> and assigned to the antisymmetric stretching mode of oxygen and silicon atoms.

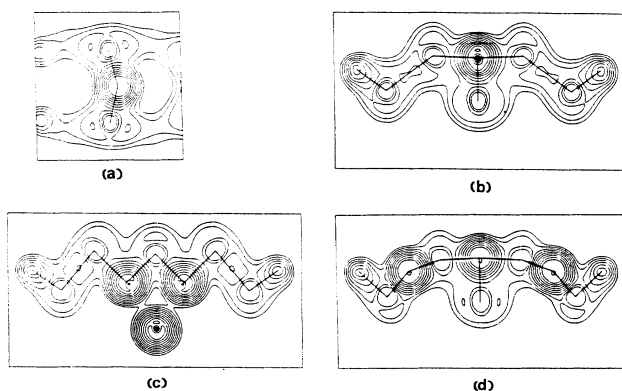


FIG. 2. Contour plot of the valence charge density of (a) the bond-centered interstitial configuration on the  $(11\bar{2})$  plane, (b) the  $y$ -lid configuration of the  $(1\bar{1}0)$  plane, (c) the stable three-oxygen-atom configuration on the  $(1\bar{1}0)$  plane, and (d) the  $y$ -lid plus two-interstitial configuration on the  $(1\bar{1}0)$  plane. The value for each contour is  $1.1/2^{n/2}$  electrons/a.u.<sup>3</sup> ( $n > 0$ ).

TABLE II. Electron population of an atom in the clusters.

Cluster	O(1)	O(2)	Si(1)	Si(2)	Si(3)
(a)	7.20		3.59		
(b)	7.13		3.93	3.97	
(c)	7.07	6.99	3.21	3.23	4.01
(d)	7.01	7.09	4.25	3.27	3.16

Then we calculate the normal vibrational-mode frequency for the antisymmetric stretching mode: we calculate the total-energy change due to the displacement of the oxygen and the nearest-neighbor silicon atoms along the above antisymmetric motion. The second derivative of the total-energy change leads to the normal-mode frequency. The calculated value is  $1187\text{ cm}^{-1}$ , which is in good agreement with the experimental value.

Since the stabilization energy for the bond-centered interstitial configuration is found to be large, the configuration is expected to be abundant in Czochralski-grown silicon crystal, and plays an important role in various properties. The stretching displacement of the nearest-neighbor two-silicon atoms leads to the increase of the volume of the crystal in the case of high concentration. The mechanical strength enhanced by intervening oxygen may be ascribed to the rigid Si—O bond, which prevents the glide of dislocation.

Next, we focus on the  $y$ -lid configuration. We have used the  $\text{Si}_{11}\text{H}_{24}\text{O}$  cluster to simulate this configuration. The optimized atomic geometry under restriction of  $C_{2v}$  symmetry is shown in Fig. 1(b). In this figure, the central silicon [Si(1)] moves along the  $[00\bar{1}]$  direction by  $0.41\text{ \AA}$  from the original lattice site; the distance between Si(1) and the oxygen is  $1.74\text{ \AA}$ , while the distance between the next-neighbor silicon [Si(2)] and the oxygen is  $1.90\text{ \AA}$ . As is clear from the contour map of the charge density [Fig. 2(b)], the original bonds between Si(1) and Si(2) are broken and instead each silicon atom forms a covalent bond with the oxygen atom. The Mulliken population analysis indicates that the trivalent oxygen gains 1.13 electrons, while Si(1) and Si(2) lose only 0.07 and 0.03 electrons, respectively (Table II). Thus oxygen gathers electrons not only from the three Si atoms bonded to the oxygen atom but also from surrounding silicon atoms. The stabilization energy is calculated to be 3.4 eV: 1.2 eV smaller

TABLE III. Electron population of an atom for HOMO and LUMO.

Cluster	Levels	O(1)	O(2)	Si(1)	Si(2)
(a)	$b$ (HOMO)	0.41		0.07	
	$a$ (LUMO)	< 0.01		0.25	
(b)	$b_1$ (HOMO)	0.08		0.46	0.04
	$a_1$ (LUMO)	0.02		0.06	0.25
(c)	$b_1$ (HOMO)	0.67	0.01	0.01	0.01
	$b_2$ (LUMO)	< 0.01	0.04	0.47	0.09
(d)	$b_2$ (HOMO)	0.09	0.04	< 0.01	0.11
	$a_1$ (LUMO)	0.09	0.03	0.27	0.19

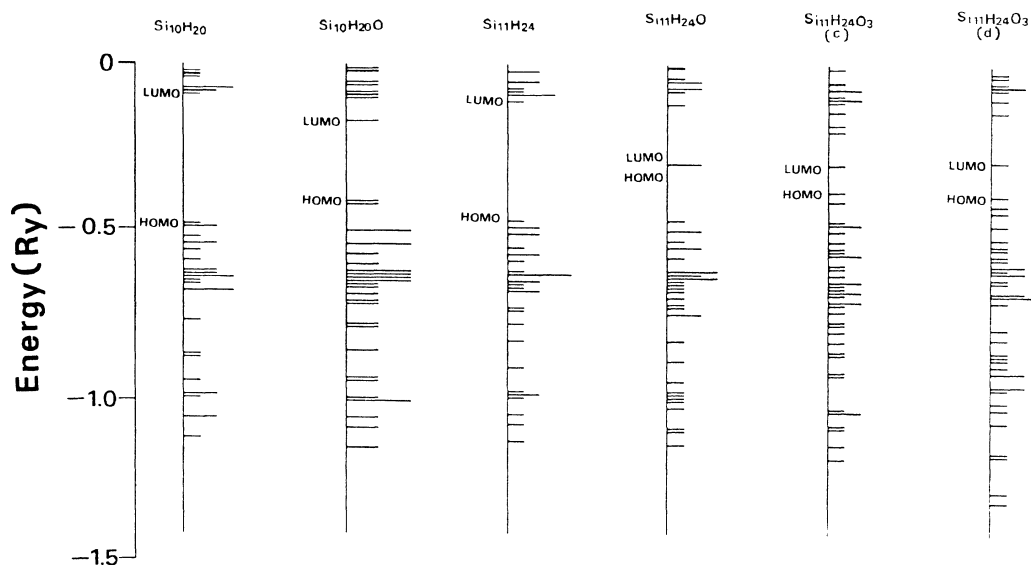


FIG. 3. Level structures of the clusters (see the text for description of each cluster).

than the value for the bond-centered interstitial configuration.

As Fig. 3 shows, both HOMO and the lowest unoccupied molecular orbital (LUMO) are located close to the silicon  $p$  orbital ( $-0.29$  Ry) in the  $y$ -lid configuration. It is indicated from the electron population analysis (see Table III) that HOMO is the  $p$  nonbonding orbital of Si(1) and the LUMO is also the  $p$  nonbonding orbital of Si(2). Since the energy-level difference between HOMO( $b_1$ ) and LUMO( $a_1$ ) is very small, this optimized geometry is unstable to a  $b_1$  mode distortion because of the pseudo-Jahn-Teller effect: displacement of the oxygen atom from the original O(1)-Si(1) axis induces the splitting of the almost degenerate HOMO and LUMO levels, and the associated electronic energy gain triggers the oxygen motion away from the  $y$ -lid configuration. We have confirmed this instability from the force calculation: the calculated force on the oxygen atom in the atomic configuration in which the oxygen is displaced along the  $[110]$  direction ( $b_1$  symmetry) impels further the oxygen away from the original location of the  $y$ -lid.

We are now in a position to discuss microscopic mechanisms of oxygen diffusion in silicon. An oxygen atom is first located at the stable bond-centered interstitial site. Since diffusion experiments<sup>19</sup> are performed at high temperature, the oxygen atom easily moves away from the stable interstitial site, and reaches the saddle-point  $y$ -lid site. The  $y$ -lid site is unstable against the displacement of oxygen in, for example, the  $[110]$  direction, so that the oxygen atom could proceed to the next bond-centered interstitial site, i.e., the possible diffusion path along the bond-centered and the  $y$ -lid sites. The calculated barrier height for this oxygen motion is 1.2 eV. The effects of lattice relaxation around the interstitial impurity are important to determine its stabilization energy.<sup>20,21</sup> For the self-interstitial bond-centered configuration in silicon, the long-range relaxation, which is not considered in the

present cluster approach, results in an energy gain of more than 0.5 eV.<sup>20</sup> Then the plausible value for the barrier height for oxygen motion along the bond-centered and the  $y$ -lid sites would be 1–2 eV. Other mechanisms associated with intrinsic defects in silicon could be pertinent, as in diffusion of dopants.<sup>21</sup> Yet, the oxygen diffusion triggered by the pseudo-Jahn-Teller effect along the bond-centered and the  $y$ -lid sites may still be a dominant process.

### B. Three-oxygen-atom cluster

In this section, the results for three-oxygen-atom clusters in silicon are presented. It is important to reveal atomic and electronic structures of the three-oxygen-atom clusters for microscopic identification of thermal donors, although the formation rate of oxygen aggregates suggests more than three oxygen atoms involved in the thermal donors.<sup>11,22</sup> Further, this size of oxygen microcluster in silicon is expected to play an important role in oxygen aggregation in silicon. The calculated results for stable geometries and their level structures provide us with fruitful information about behaviors of oxygen atoms in silicon.

In this paper, the three-oxygen-atom impurities with  $C_{2v}$  symmetry are investigated. We have found an extremely stable configuration in which a drastic rearrangement of bonding between silicon and oxygen atoms occurs. The  $y$ -lid configuration becomes stable also upon intervention of two more oxygen atoms at the nearby bond-centered sites. The two stable configurations constitute bistability in oxygen microclusters in silicon.

The most stable atomic configuration that we have found for the three-oxygen-atom impurities in silicon is shown in Fig. 1(c). Two oxygen atoms [O(2) and O(3)] intervene at the nearby bond-centered sites. Consequently, the silicon atom [Si(1)] which has participated in the for-

mation of the two bonds is repelled upward by 1.53 Å. The remaining two bonds between the silicon atom [Si(1)] and other silicon atoms [Si(2)] and Si(4)] are no doubt broken. One more oxygen atom [O(1)] comes close to Si(2) and Si(4) [1.63 Å below the original lattice site of Si(1)] and repairs the two broken bonds. In this configuration, the bond length between the central oxygen [O(1)] and its nearest-neighboring silicon [Si(2)] is 1.71 Å and the Si(2)—O(1)—Si(2) angle is 166°. The calculated Si(2)—O(1) bond length is very close to that in the stable interstitial bond-centered configuration. For the divalent silicon [Si(1)], the Si(1)—O(2)—Si(3) bond angle is 89.1° and Si(1)—O(2) bond length is 1.69 Å. These values are close to those of amorphous SiO (1.64 Å for bond length and 96.7° for bond angle)<sup>23</sup> and to those of stable cyclic dimers of silicon monoxide (1.68 Å bond length and 85.7° O—Si—O angle).<sup>24</sup> We have found that the stabilization energy of this atomic configuration is 11.7 eV, i.e. 3.9 eV per oxygen atom. This large stabilization energy is comparable with that of the isolated bond-centered interstitial configuration. This stable configuration is to some extent similar to an atomic model for the thermal donor proposed by Ourmazd, Schröter, and Bourret (OSB model).<sup>11</sup> In many details, however, there are differences between the OSB model and the present stable configuration determined by the total-energy minimization.

The HOMO of the present stable configuration is a *p* nonbonding orbital of O(1) and the LUMO is a nonbonding orbital of the divalent silicon [Si(1)]. On the contrary, the calculation<sup>6</sup> based on a simple version of the OSB model indicates that the divalent nonbonding orbital is occupied. The central silicon [Si(1)] and the two nearest-neighboring oxygen [O(2)] are found to be positively and negatively ionic, respectively, from the present calculation (Table II). This is a consequence of the electron transfer from the silicon nonbonding orbital to the oxygen orbitals, and thus the nonbonding orbital is unoccupied.

Next, we turn to the *y*-lid configuration. In the optimization of the atomic geometry, the interstitial oxygen [O(2)] is restricted to the upper side of the Si(2)—Si(3) axis [Fig. 1(d)]. The instability of the isolated oxygen *y*-lid configuration disappears upon adding two more oxygen atoms at the nearby bond-centered sites. The total-energy-minimized configuration is shown in Fig. 1(d). The stabilization energy for this configuration is 4.1 eV (1.4 eV per oxygen). The configuration is a metastable state. In fact, the almost degenerate HOMO and LUMO of the isolated *y*-lid configurations split by inserting two oxygen atoms at the bond-centered sites (Fig. 3) so that the pseudo-Jahn-Teller instability is not effective. The calculated distance from the central oxygen [O(1)] to the central silicon [Si(1)] increases by 0.08 Å, whereas that from O(1) to the side silicon [Si(2)] decreases by 0.20 Å, compared with the distances in the isolated *y*-lid configuration. As a result, the side silicons [Si(2)] are 0.12 Å nearer to the central oxygen [O(1)] than the central silicon [Si(1)], in contrast with the isolated *y*-lid configuration in which the central silicon is 0.16 Å nearer to the oxygen than the side silicon. The bond length

from the interstitial oxygen [O(2)] to the side [Si(2)] and peripheral [Si(3)] silicon atoms is 1.39 Å. This value is very small compared with the length, 1.68 Å, of the stable bond-centered interstitial configuration.

As is seen from Fig. 2, side silicon [Si(2)] loses electrons because of the electron transfer to the two types of oxygen atoms [O(1) and O(2)]. As a result, the charge of side silicon [Si(2)] is +0.73, which is 0.70 larger than that in the isolated *y*-lid case (Table II): the addition of two more oxygen atoms to the isolated *y*-lid configuration leads to a considerable change in electron distribution.

The two stable configurations shown in Figs. 1(c) and 1(d) constitute bistability in three-oxygen-atom clusters in silicon. The calculated total-energy difference is 2.5 eV per oxygen atom. When there are many carriers at high temperature, their recombination could provide sufficient energy to overcome the barrier from the most stable configuration [Fig. 1(c)] to the metastable configuration [Fig. 1(d)]. Injection of carriers could also induce the manifestation of the bistability.

The total-energy difference between the stable three-oxygen-atom cluster [Fig. 1(d)] and the most stable isolated bond-centered interstitial configuration is 0.7 eV per oxygen atom. Then, at high temperature the configuration shown in Fig. 1(c) is abundant in silicon crystal. It is likely that the configuration is a precursor state for oxygen aggregation and plays some role in the experimental data related to the thermal donors.

#### IV. CONCLUSION

We have explored atomic and electronic structures of oxygen impurities in silicon by performing a first-principles norm-conserving pseudopotential total-energy calculation for a sufficiently large cluster model containing up to three oxygen atoms. For the isolated impurity, it is confirmed that the bond-centered interstitial configuration is stable with a stabilization energy of 4.6 eV. Further, it is found that the *y*-lid (split interstitial) is a saddle-point configuration unstable against the displacement of the oxygen atom along the [110] direction. Thus the oxygen diffusion process along the bond-centered and the *y*-lid configuration is plausible. Upon addition of two more oxygen atoms at the nearby bond-centered sites, the *y*-lid configuration becomes stable with respect to the displacement along the [110] direction. The stabilization energy is 4.1 eV (1.4 eV per oxygen atom). Yet we have found that another configuration, in which a drastic rearrangement of the bonds between the three oxygen atoms and the host silicon atoms occurs, is more stable and its stabilization energy is 7.6 eV (2.5 eV per oxygen atom). The two configurations constitute bistability in oxygen microclusters in silicon. The most stable configuration of three-oxygen-atom clusters theoretically determined here for the first time is expected to be a precursor state of oxygen aggregation.

#### ACKNOWLEDGMENTS

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