

# The structure and properties of (aluminum, oxygen) defect complexes in silicon

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(Received 22 May 2013; accepted 31 July 2013; published online 14 August 2013)

The atomic structure and electronic properties of aluminum (Al)-related defect complexes in silicon (Si) are investigated using first-principles calculations. Individual substitutional Al (Al<sub>Si</sub>), interstitial Al (Al<sub>i</sub>) and their possible complex configurations with oxygen (O) atoms are studied. We find a unique stable complex configuration consisting of an Al<sub>i</sub> and an oxygen dimer, Al<sub>i</sub>-2O<sub>i</sub>, which introduces deep levels in the band gap of Si. The formation energies of the Al<sub>i</sub>-2O<sub>i</sub> complexes could be lower than that of individual Al<sub>i</sub> atoms under oxygen-rich conditions. The formation of Al<sub>i</sub>-2O<sub>i</sub> complexes may explain the experimental observation that the coexistence of Al and O results in reduced carrier lifetime in Si wafers. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818515>]

## I. INTRODUCTION

Silicon (Si) is one of the most abundant elements in the earth's crust. It is a semiconductor material suitable for photovoltaic applications. Multicrystalline and monocrystalline Si solar cells dominate the current photovoltaic market. More than 80% of the global solar-cell production is from Si-based cells.<sup>1,2</sup> The photovoltaic industry has been growing at a steady annual rate of 25%–30% over the past several years, and this progress is driven mainly by Si-based solar cells.

Aluminum (Al) is a common dopant for producing *p*-type Si. A substitutional Al (Al<sub>Si</sub>) atom is a shallow acceptor. Thus, Al is often used as back contact to create back surface fields for Si-based solar cells. However, experimental results have shown that when Al and oxygen (O) coexist, the lifetime of the minority carriers in Si decreases dramatically.<sup>3–7</sup> It is speculated that Al and O may form complexes, causing the observed reduction of lifetime of minority carriers. However, the atomistic origin of the reduction mechanism is still unclear. Therefore, it is important to understand the structure and electronic properties of Al-O complexes.

Both Al and boron (B) belong to the group IIIA family. It is expected that Al and B may exhibit similar electronic properties in Si. B is also a commonly used dopant for producing *p*-type Si. B-O complexes have been found to be responsible for the experimentally observed reduction of carrier lifetime.<sup>8,9</sup> Several theoretical models have been proposed to explain the effects of B-O complexes. It was predicted that interstitial B (B<sub>i</sub>) trap an O dimer to form a bistable complex that produces a donor level in the upper half of the band gap of Si.<sup>10–12</sup> Two distinctive configurations of B<sub>i</sub>-2O<sub>i</sub> complexes were reported in the literature: one is the {B<sub>i</sub>, 2O<sub>i</sub>}-complex with a monoclinic-I symmetry and three-fold coordinated O atoms;<sup>10</sup> the other is that the O<sub>i</sub> is bound to the Si atom at a second nearest site to B.<sup>11</sup> The calculated electronic properties of the above two

configurations of defect complexes using density-functional theory (DFT) are in good agreement with experimental observation: B<sub>i</sub>-O complexes do not present detrimental effects to the minority carrier lifetime in Si. However, our DFT calculations reveal a very different scenario for Al-O complexes in Si, even though B and Al belong to the same group: an Al<sub>i</sub>-2O<sub>i</sub> complex is identified to create deep gap states and therefore are detrimental to the minority carrier lifetime in Si. In this paper, we study the energies, configurations, and electronic properties of Al-O defect complexes and compare the results with that of B-O defect complexes.

## II. METHODOLOGY

Our first-principles calculations are based on DFT using the standard frozen-core projector augmented-wave method and the generalized gradient approximation (GGA-PBE),<sup>13</sup> as implemented in the Vienna *ab-initio* simulation package (VASP).<sup>14</sup> A well-converged plane-wave basis set with a cutoff energy of 400 eV was used. We used a (10.95 Å × 10.95 Å × 10.95 Å) cubic supercell with 64 atoms to model the studied defects. A 3 × 3 × 3 grid was used for Monkhorst-Pack *k*-point sampling. All atoms were fully relaxed until the forces become smaller than 0.01 eV/Å.

The ionization and formation energies of Al-O complexes were calculated by<sup>15,16</sup>

$$\varepsilon_g^\Gamma(\text{host}) - \varepsilon = [e_{CBM}^\Gamma(\text{host}) - e_D^\Gamma] + [E(\alpha) - (E(\alpha) - qe_D^k)], \quad (1)$$

$$\Delta H_f(\alpha, q) = E(\alpha, q) + \sum n_i \mu_i + qE_F. \quad (2)$$

Here,  $\varepsilon_g^\Gamma(\text{host}) - \varepsilon$  is the ionization energy,  $\Delta H_f$  is the defect formation energy, and  $E(\alpha, q)$  is the total energy for a supercell containing defect  $\alpha$  in a charge state of  $q$ . The formation energy also depends on the atomic chemical potentials  $\mu_i$  and the electron Fermi energy  $E_F$ . In this paper, we will only discuss the formation energies of Al-O complexes in the charge neutral state as calculated using Eq. (2).

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### III. RESULT AND DISCUSSION

It is known that individual Al atoms prefer energetically at substitutional sites and act as shallow acceptors in Si. Individual O atoms prefer energetically at the bond center interstitial sites, acting as neutral dopants without strong influence on the electronic properties of Si [Fig. 1(a)]. However, when the concentration of O is high, multiple O atoms can aggregate together or combine with other impurities, such as B and Al atom, and result in different electronic properties than individual O atoms. In our work, all structures considered for B-O complex<sup>11</sup> are considered for Al-O complexes. Furthermore, we examine several more configurations for Al-O complexes as described in Fig. 1.

#### A. O thermal donors

An isolated O atom prefers occupying a bond center interstitial site that has the similar configuration in silicon dioxide and has not much influence on the electronic

property of bulk Si.<sup>17,18</sup> However, at high O concentration, several O atoms will aggregate together and form the thermal donor.<sup>19–22</sup> The configurations of O thermal donors are critical for studying B- or Al-related O defect complexes in Si. An individual O atom and a thermal donor consisting of 4 O atoms are shown in Figs. 1(a) and 1(b), respectively. The key feature of the configuration of this thermal donor is the rhombohedra ring formed by two O and two Si atoms and the breaking of one Si-Si bond. The Si-Si bond breaking causes large atomic distortions around the defect core region. Without considering other impurities, the O rhombohedra ring must have at least four O atoms to become stable. To show the effects of individual  $O_i$  atoms and thermal donors, the calculated band structures for the supercells without O atom, with one  $O_i$  and one thermal donor of four O atoms are shown in Figs. 2(a)–2(c), respectively. In Figs. 2(a) and 2(b), the highest occupied band is at the top of the valance band of the supercell as indicated by the lower dotted line. The  $O_i$  does not introduce any states in the band gap. In Fig. 2(c), the level indicated by the arrow is slightly below the conduction band minimum (CBM) of Si. The highest occupied state is indicated by  $E_f$ . Therefore, the thermal donor composed by four  $O_i$  atoms is a shallow donor and can be ionized by thermal energy at elevated temperatures. However, if acceptor dopants such as B or Al are present, the O thermal donor can be stable with only two O atoms.

#### B. $Al_{Si}$ and $O_i$ complexes in Si

Due to the strong ionic Al-O bonding, an  $Al_{Si}$  atom and an  $O_i$  atom favor to combine together, forming an  $Al_{Si}-O_i$  complex, which acts still as a shallow acceptor. Under O-rich condition, an  $Al_{Si}$  atom can combine with multiple  $O_i$  atoms. Such kind of defect complex was previously studied for B-O complexes by Sanati and Estreicher.<sup>11</sup> For (B,  $2O_i$ ), it was reported that the configuration shown in Fig. 1(d) [note: the configuration of  $B_{Si}-O_i$  complexes are adopted for  $Al_{Si}-O_i$  complex in our paper] is a more stable structure than the one shown in Fig. 1(c). Our results for the stability of the (B,  $2O_i$ ) configurations are consistent with that reported by Sanati and Estreicher.<sup>11</sup> The total energy of configuration shown in Fig. 1(d) is about 0.23 eV lower than that of the configuration shown in Fig. 1(c). However, we find that the trend is different for  $Al_{Si}-O_i$  complex. Our results reveal that the total energy of the configuration named {a- $Al_{Si}$ ,  $2O_i$ } shown in Fig. 1(c) is about 1.66 eV less than that of the configuration named {b- $Al_{Si}$ ,  $2O_i$ } shown in Fig. 1(d). The total energies of these two different complexes are listed in Table I. Therefore, an  $Al_{Si}$  atom prefers at the nearest site of an O atom, while a  $B_{Si}$  atom favors the second nearest site of an O atom.

The different trend could be explained by the different electronegativity of Al and B elements; Al element has a stronger metallicity than B element. Therefore, the direct Al-O bonding is energetically more favorable than the direct B-O bonding. The total density of state (TDOS) of the two  $Al_{Si}-O_i$  complexes shown in Figs. 1(c) and 1(d) are given in Figs. 3(a) and 3(b), respectively. It is seen that the two  $Al_{Si}-O_i$  complexes are shallow donors and no deep gap state are

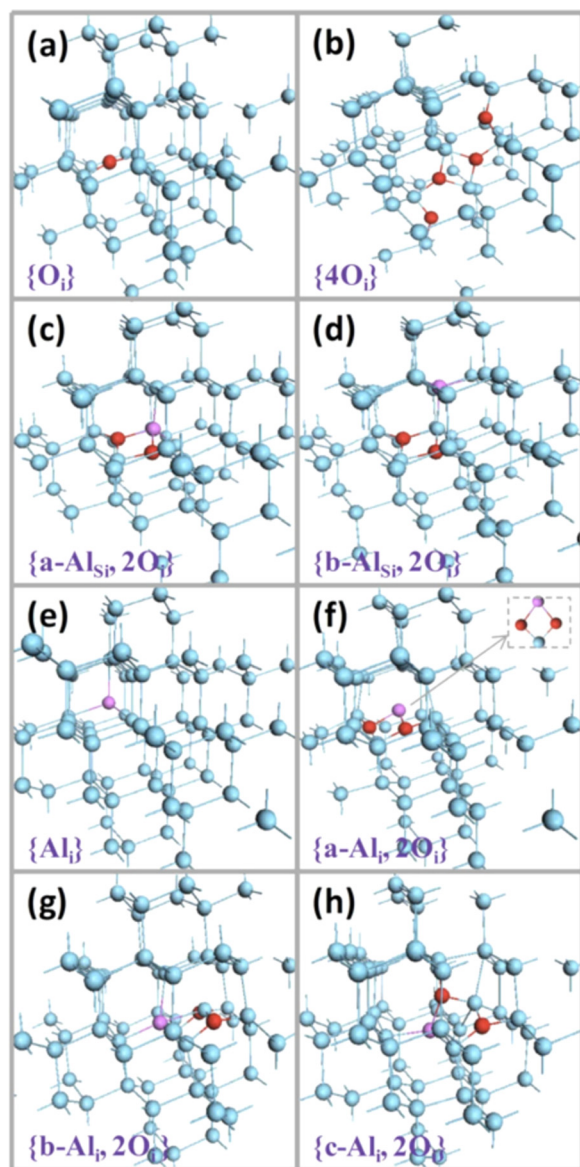


FIG. 1. Defect structures of Al-O complexes in Si considered in this paper.

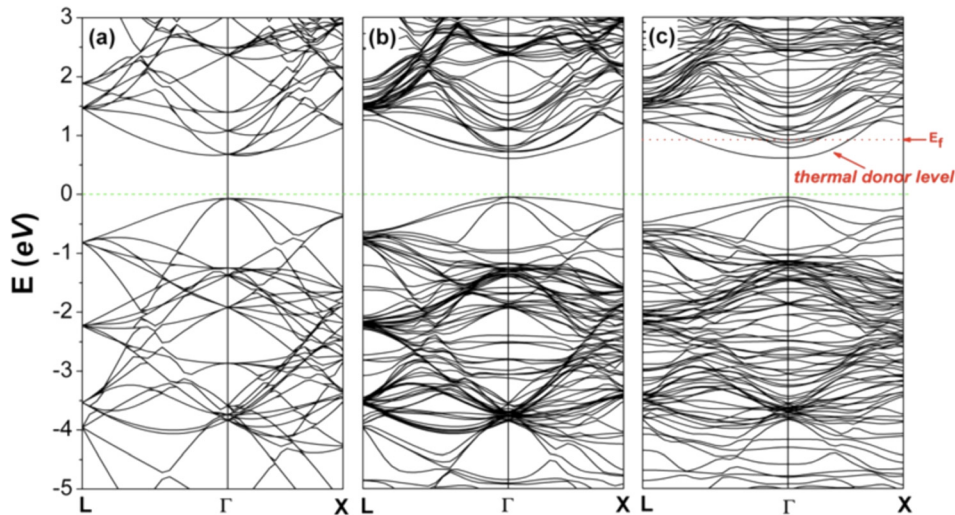


FIG. 2. Calculated band structures of supercells containing (a)  $\{\text{Si}_{64}\}$ , (b)  $\{\text{Si}_{64}, \text{O}_i\}$ , and (c)  $\{\text{Si}_{64}, 4\text{O}_i\}$ .

observed. The behavior of shallow donor can be easily understood because these  $\text{Al}_{\text{Si}}\text{-O}$  complexes include the O ring configuration. Each O ring is a double shallow donor, which donates two electrons to the  $\text{Al}_{\text{Si}}$  atom. As a result, the  $\{\text{Al}_{\text{Si}}, 2\text{O}_i\}$  complexes are single shallow donors. It was reported that the stable  $\{\text{a-B}_{\text{Si}}, 2\text{O}_i\}$  configuration create deep level of 0.45 eV below the CBM of bulk Si.<sup>11</sup> However, our results indicated that both  $\{\text{a-Al}_{\text{Si}}, 2\text{O}_i\}$  and  $\{\text{b-Al}_{\text{Si}}, 2\text{O}_i\}$  are shallow donors. Therefore, unlike  $\text{B}_{\text{Si}}\text{-O}$  defect complexes,  $\text{Al}_{\text{Si}}\text{-O}$  defect complexes do not introduce deep gap states and therefore they are not responsible for the reduction of carrier lifetime observed in Al and O co-existed Si.

### C. $\text{Al}_i$ and $\text{O}_i$ complexes in Si

The structures of  $\text{Al}_i$  and  $\text{O}_i$  complexes are depicted in Figs. 1(f) ( $\{\text{a-Al}_i, 2\text{O}_i\}$ ), 1(g) ( $\{\text{b-Al}_i, 2\text{O}_i\}$ ), and 1(h) ( $\{\text{c-Al}_i, 2\text{O}_i\}$ ). The structures of  $\{\text{b-Al}_i, 2\text{O}_i\}$  and  $\{\text{c-Al}_i, 2\text{O}_i\}$  are constructed based on the B-O complexes reported by Sanati and Esteicher.<sup>11</sup> We find that the new structure of  $\{\text{a-Al}_i, 2\text{O}_i\}$  shown in Fig. 1(f) has a lower energy than the configurations of  $\{\text{b-Al}_i, 2\text{O}_i\}$  and  $\{\text{c-Al}_i, 2\text{O}_i\}$ . Typically, an Al atom in Si prefers energetically at a substitutional site rather than at an interstitial site, because the formation energy of an  $\text{Al}_i$  is much higher than that of an  $\text{Al}_{\text{Si}}$ . Therefore, the concentration of  $\text{Al}_i$  atoms is typically much lower than that of  $\text{Al}_{\text{Si}}$  atoms. However, the situation changes significantly when both Al and O atoms are available because Al atoms bind O atoms forming Al-O complexes shown in Figs. 1(f)–1(h). The calculated TDOS of the three different

configurations of  $\text{Al}_i\text{-}2\text{O}_i$  defect complexes are shown in Fig. 3. We find that the configuration of  $\{\text{a-Al}_{\text{Si}}, 2\text{O}_i\}$  shown in Fig. 1(f) introduces obvious deep levels in the band gap of Si, as indicated by the red arrow in Fig. 3. However, other two configurations shown in Figs. 1(g) and 1(h) do not show clear deep gap states, which is consistent with the previous work that predicts the shallow-donor feature of  $\text{B}_i\text{-}2\text{O}_i$  defect complexes with the same structures.<sup>11</sup>

To understand the origin of the deep gap state of the  $\{\text{a-Al}_i, 2\text{O}_i\}$  complex shown in Fig. 1(f), we have calculated the

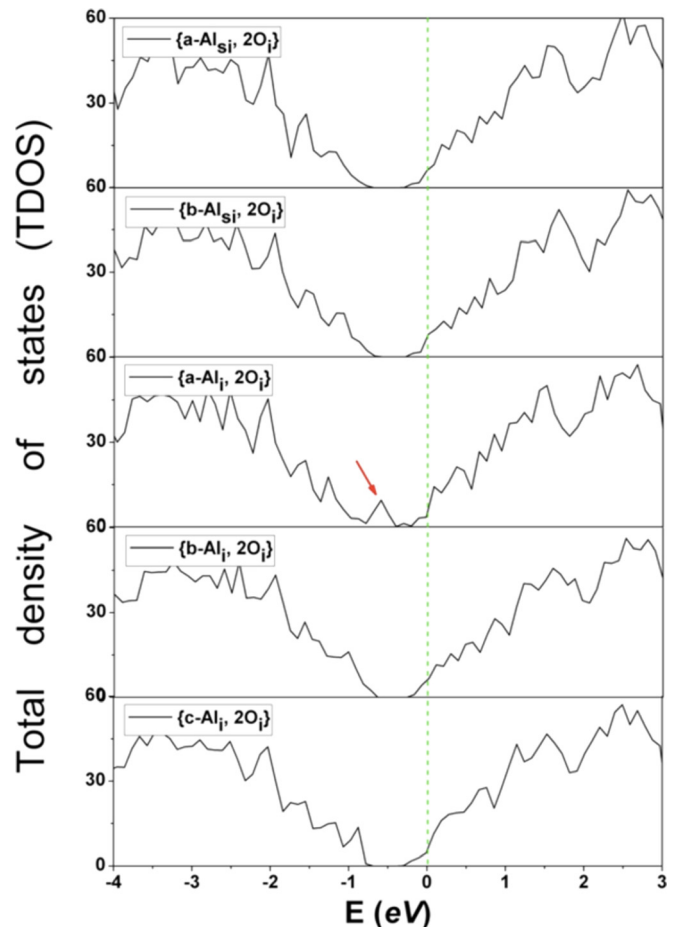


FIG. 3. Calculated TDOS of supercells with various Al-O complexes.

TABLE I. Calculated total energies of supercells containing various Al-O complexes.

Complexes of Al-O in Si	Total energy (eV)
$\{\text{a-Al}_{\text{Si}}, 2\text{O}_i\}$	-360.562
$\{\text{b-Al}_{\text{Si}}, 2\text{O}_i\}$	-358.989
$\{\text{a-Al}_i, 2\text{O}_i\}$	-363.701
$\{\text{b-Al}_i, 2\text{O}_i\}$	-362.136
$\{\text{c-Al}_i, 2\text{O}_i\}$	-362.968



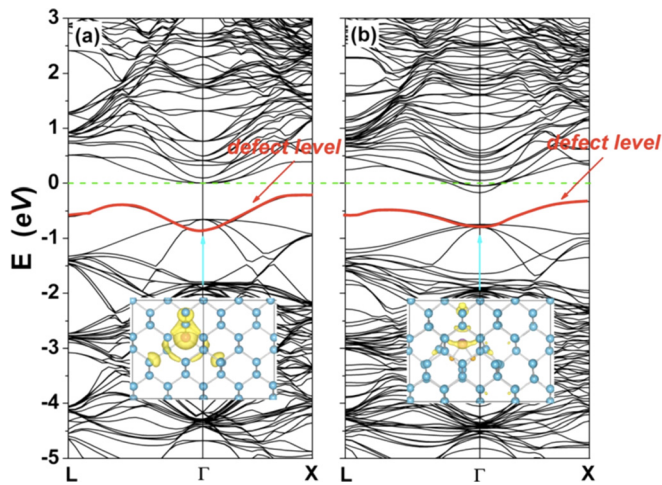


FIG. 4. Calculated band structures of supercells containing (a)  $\{Al_i\}$  and (b)  $\{a-Al_i, 2O_i\}$ . The insets are partial charge densities corresponding to the defect levels.

band structures for supercells containing an individual  $Al_i$  and a  $\{a-Al_i, 2O_i\}$  complex. As shown in Fig. 4, the deep levels (indicated by the arrows) introduced by the individual  $Al_i$  atom and the  $\{a-Al_i, 2O_i\}$  complex are very similar, indicating that the deep level created by the  $\{a-Al_i, 2O_i\}$  complex is also due to the  $Al_i$  atom in the complex. The calculated ionization energy for the  $\{a-Al_i, 2O_i\}$  complex using Eq. (1) is about 0.466 eV. The calculated partial charge densities associated with the deep gap states are given as the insets in Fig. 4. It is seen that at both cases, the partial charge densities located around the  $Al_i$  atoms confirm that the deep gap states are originated from the  $Al_i$  atoms. Compared with the configuration of complex  $\{a-Al_i, 2O_i\}$ , the structural characters of complexes  $\{b-Al_i, 2O_i\}$  and  $\{c-Al_i, 2O_i\}$  are very different. Complexes  $\{b-Al_i, 2O_i\}$  and  $\{c-Al_i, 2O_i\}$  have the split interstitial Al configuration, in which the Al atom is at the substitutional site and the Si is pushed to the interstitial site ( $Si_i$ ). Therefore, the Al atom does not introduce deep gap states. Because the s-orbit of Si is much lower in energy than the s-orbital of Al, the defect levels created by the  $Si_i$  are much lower in energy than that created by  $Al_i$ . Therefore, the levels created by complexes  $\{b-Al_i, 2O_i\}$  and  $\{c-Al_i, 2O_i\}$  are inside the valence band of Si and therefore no gap states are observed.

#### D. The effects of O chemical potential

We now discuss how the formation of the  $Al-2O_i$  complexes may be influenced by the O chemical potentials. It is known that without O, an Al atom favors a substitutional site and act as a shallow acceptor. An individual  $Al_i$  atom is expected to have much higher formation energy than an  $Al_{Si}$ . However, for  $Al-2O_i$  complexes, their formation energies depend also on the chemical potentials of O. As indicated by Eq. (2), the formation energies of  $Al-2O_i$  complexes should decrease as the chemical potential of O increases. Therefore, the formation energies of  $Al_i-2O_i$  complexes could be lower than that of an  $Al_i$ . If a high density of  $\{a-Al_i, 2O_i\}$  complex is formed, the carrier lifetime will be reduced due to the deep gap states created by the  $\{a-Al_i, 2O_i\}$  complexes. Fig. 5

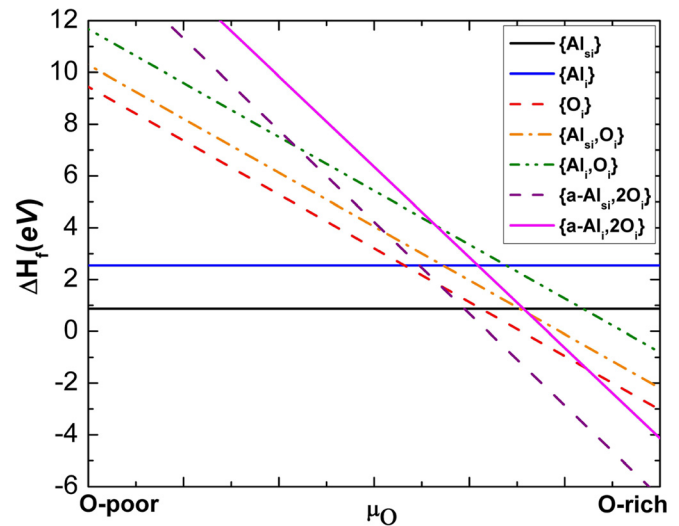


FIG. 5. Calculated formation energies of Al-O complexes as a function of the O chemical potential.

shows the calculated formation energies for various complexes as a function of the O chemical potential. The chemical potentials of Al and Si are obtained from the chemical potential of their corresponding bulk. It is seen that the formation energies of Al-O complexes depend strongly on the atomic chemical potential of O. As the O chemical potential increases, the formation energies of the Al-O complexes decrease quickly. For the complexes with more O atoms, the formation energies decrease even more. However, the formation energy of the individual  $Al_i$  does not depend on the O chemical potential. As a result, at O-rich conditions, the formation energy of the  $\{a-Al_i, 2O_i\}$  complex that creates deep gap states can be significantly lower than that of  $Al_i$  and become comparable to that of  $Al_{Si}$ . Therefore, O will assist the formation of Al-O defect complexes including the detrimental  $\{a-Al_i, 2O_i\}$  complex. Our results therefore suggest that the formation of the  $\{a-Al_i, 2O_i\}$  complex could be the reason why when Al and O co-exist, the minority carrier lifetime of Si is reduced significantly. Our results also reveal that the formation energy of the  $\{a-Al_{Si}, 2O_i\}$  complex has even lower formation energy at O-rich conditions. However, an  $\{a-Al_{Si}, 2O_i\}$  complex is a shallow donor and is not responsible for the reduced carrier lifetime. The formation of  $\{a-Al_{Si}, 2O_i\}$  complexes will compensate the p-type conductivity. At extreme O-rich conditions, the presence of Al and O is also expected to reduce the p-type conductivity of Si.

#### IV. CONCLUSION

Using first-principles DFT calculations, we have studied the structure and electronic properties of Al-O complexes in Si. Due to their different electronegativity, Al and B form different configurations when they combine with O atoms. We found that the  $\{a-Al_i, 2O_i\}$  complex produces deep levels in the band gap of Si. The co-existence of O promotes the formation of all Al-O related complexes including the  $\{a-Al_i, 2O_i\}$  complex. Our results suggest that the formation of this Al-O complex could be responsible for the experimentally observed carrier life reduction of Si when Al and O co-exist.

## ACKNOWLEDGMENTS

Y.Y. acknowledges the support from the Ohio Research Scholar Program (ORSP). Work at NREL was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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