First-principles calculations of boron-related defects in SiO₂

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We report first-principle total-energy calculations that provide stable and metastable geometries and diffusion mechanisms of boron in SiO₂ with point defects which contain O vacancies and O interstitials. We find that a B atom forms various stable and metastable geometries in SiO₂ with point defects, depending on its charge state and surrounding environments. We also perform calculations that clarify the chemical feasibility of bonding configurations between a B atom and constituent atoms in SiO₂. It is found that wave function distribution around the impurity and its occupation are essential to determine the geometry for each charge state. Binding energies of a B atom with constituent atoms in SiO₂ are decisive factors to the bond configuration around the B atom. In the case of B in SiO₂ with an O interstitial, a B atom forms a very stable B-O complex in which the B atom is bound to the O interstitial. Once the B-O complex is formed, the B atom diffuses via the SiO₂ network keeping this B-O unit with unexpectedly small activation energies of 2.1–2.3 eV. The calculated activation energies agree well with the data experimentally available.

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I. INTRODUCTION

Atomic diffusion in materials is one of the fundamental phenomena. Particularly in the semiconductor industry, dopant diffusion in semiconductors during fabrication processes is essential to realize designed performances of devices. Hence a much of effort has been devoted to clarifying mechanisms of the atomic diffusion in semiconductors, mainly in Si. Along with the recent trend of miniaturization of metal oxide semiconductor (MOS) devices, ultrathin silicon oxide films are demanded for use as gate oxide films for MOS and other devices. As the thickness of the films is decreased, the problem of impurities, e.g., B atoms diffusing into the SiO₂ film from the gate electrode and further penetrating into the silicon substrate, becomes serious. Experimentally, it is reported that H, F, and Cl atoms accelerate the penetration of B atoms, while oxinitride films decrease their penetration. A model for B diffusion in SiO₂ is proposed by compiling thermochemical data. In that model the B atom diffuses in SiO₂ via a peroxy linkage (PL) defect, -Si-O-O-Si-. However, the suppression mechanisms of the B penetration and the diffusion mechanisms of B atoms in SiO₂ have not been clarified yet. Theoretically Fowler et al. investigated B diffusion models using semiempirical quantum chemical calculations and proposed a model in which the B atom diffuses by exchanging its position to the Si atom. To increase the reliability of ultrathin gate oxide films, it is essential to clarify both stable geometries of B atoms and atomistic mechanisms of B diffusion in SiO₂. Recently, we have clarified both stable geometries and the diffusion mechanisms of B in defect-free SiO₂ using first-principle total-energy calculations. The results showed that a B atom forms various stable and metastable geometries depending on its charge state. In addition, we have clarified that the B atom diffuses by breaking and forming bond configurations in SiO₂ networks, and that the diffusion mechanism also differs depending on the charge state. The calculated activation energies agree well with those obtained experimentally.

II. CALCULATION

Density-functional theory (DFT) is used within the generalized-gradient approximation (GGA). Norm-conserving pseudopotentials for Si (Ref. 20) and ultrasoft pseudopotentials for O and B (Ref. 21) are adopted to describe the electron-ion interaction. The cutoff energy of the plane-wave basis set is 25 Ry. We use the Γ point for the Brillouin zone (BZ) sampling. Geometries are optimized...
for all atoms until the remaining force on each atom is less than 5 mRy/Å.

Network former impurities such as B, P, and As, are known to diffuse by reacting with the SiO₂ network. Thus diffusion barriers are likely to be dominated by local bonding effects. Though the actual oxide films have an amorphous structure, it consists of a continuous network of corner-sharing SiO₄ tetrahedra. In this study, we employ a supercell containing 72 atoms in a α quartz as a representative of containing a network of corner-sharing SiO₄ structure. To simulate a B atom diffusion in the oxide films we calculate with a constraint in the (N-1)-dimensional space into a structural optimization problem with a constraint in the (N-1)-dimensional space. Here, N is the degrees of freedom of atoms contained in a unit cell.

The formation energy of a structure with defect α is defined by

\[ E_f(\alpha, Q, \mu_e, \mu_B) = E_{tot}(\alpha, Q) - Q \mu_e - \sum_{\beta} n_{\beta} \mu_{\beta}, \]

where \( E_{tot}(\alpha, Q) \) is the total energy of the supercell containing the defect α with a charge state Q, \( \mu_e \) is the electron chemical potential, i.e., Fermi level in the energy gap, \( n_{\beta} \) is the number of β atoms (β = Si, O, B) in the supercell, and \( \mu_{\beta} \) is the chemical potential of a β atom. For the charged state Q, we consider +1 (Q = 1, neutral (Q = 0), and −1 (Q = −1) charged state. The value of \( \mu_e \) when \( E_f(\alpha, Q, \mu_e, \mu_B) = E_f(\alpha, Q + 1, \mu_e, \mu_B) \) is defined as \( \mu_{\beta}(Q + 1) \). This value is called the thermodynamic level, which determines the stability of the charged states with Q and (Q + 1). The chemical potentials of bulk Si and O molecules are chosen as the maximum values for \( \mu_{\text{Si}} \) and \( \mu_{\text{O}} \), respectively, and satisfy the relation \( \mu_{\text{Si}} + 2 \mu_{\text{O}} = \mu_{\text{SiO}_2} \), where \( \mu_{\text{SiO}_2} \) is the total energy per molecule in SiO₂. Under these conditions, the range of values for \( \mu_{\text{Si}} \) is \( \mu_{\text{Si}}^{(\text{bulk})} \leq \mu_{\text{Si}} \leq \mu_{\text{Si}}^{(\text{bulk})} \).

For the analysis of the structural deformation of a SiO₄ tetrahedron, we have introduced a tetrahedral distortion parameter \( t \). The tetrahedral distortion is defined by way of the sum of angles of three Si-O-Si bonds. A regular tetrahedron consisting of \( sp^2 \) hybridization has a total angle of 328.5°, whereas a planar trigonal structure consisting of \( sp^2 \) hybridization has the total angle 360°. We define the tetrahedral distortion as one when the total angle corresponds to the \( sp^2 \) hybridization, and we define it as zero when that corresponds to the \( sp^3 \) hybridization. The tetrahedral distortion is then defined as \( t = (360 - \sum_{i=1,3} \alpha_i)/31.5 \), where \( \alpha_i \) is an angle of Si-O-Si bond.

III. STABLE GEOMETRIES OF B ATOM IN SiO₂

A. B atom in defect-free SiO₂

Figure 1 shows a part of atomic geometries of SiO₂ and B₅Si₃(3) for each charge state. As shown in Fig. 1(a), the atomic geometry of SiO₂ is continuation of corner-sharing SiO₄ tetrahedra, with twofold coordinated O atoms in the Si-O-Si bridge form. In the neutral charge (0) state, B₅Si₃(3) [Fig. 1(b)] is the most stable geometry [Fig. 1(a) in Ref. 15]. A B atom is threefold coordinated with Si and two O atoms, whereas the bond configurations of Si³⁺ are changed from fourfold to threefold coordinated. We have found that the B₅Si₃(3)(0) has a localized state originated from a silicon dangling bond in the gap. To clarify the spatial distribution of the localized state, we have shown isosurfaces of the wave functions in Fig. 2. As seen from Fig. 2(a), the wave function of the highest occupied state is localized on the undercoordinated Si³⁺ atom as well as on the B-Si³⁺ bond. An electron is accommodated in the localized state so that the spin is 1/2. In the negatively charged (−1) state, B₅Si₃(3)(−) [Fig. 1(c)] is the most stable geometry [Fig. 1(c) in Ref. 15]. B₅Si₃(3)(−) [Fig. 1(c)] is a metastable geometry and is higher than B₅Si₃(3)(0) in total energy by 0.77 eV. The main structural relaxation of the B₅Si₃(3)(−) relative to the B₅Si₃(3)(0) results in the strong tetrahedral distortion on the undercoordinated Si³⁺ atom. To accommodate an additional electron in the half occupied localized state of B₅Si₃(3)(0), Si³⁺ forms a new bond (so-called floating bond [24]) with Si³⁺ associated with structural deformation. Hence, the Si³⁺ atom becomes fivefold coordinated. The wave function of the highest occupied state is thus distributed mainly on the Si³⁺-Si³⁺ floating bond and on the B-Si³⁺ bond around the B atom [Fig. 2(b)]. In the positively charged (+1) state, B₅O₃O(3) is the most stable geometry [Fig. 1(e) in Ref. 15]. When an electron is removed from B₅Si₃(3)(0), a positively charged state B₅Si₃(3)(+) [Fig. 1(d)] is obtained, which is found to be a metastable geometry of which energy is 0.50 eV higher than the B₅O₃O(3) geometry.
In +1 charged state the localized state of B$_3$Si$_3$($0$) [Fig. 2(a)] is empty. The planar $sp^2$-like bonding configuration is clearly shown in Fig. 1(d). The spatial distribution of the wave function of the lowest unoccupied state is a little larger than that in neutral charge state. Thus Si$^1$ atom forms the $sp^2$ hybridized configuration in +1 charged state.

The bond length and the distortion of the tetrahedron $t$ for B$_3$Si$_3$($3$) geometry are listed and compared for various charge states in Table I. We have also shown the bond length and $t$ for SiO$_2$ as a reference. The distance between Si$^1$ and Si$^1'_2$ atoms drastically increases as an electron is removed from the localized state as described in Table I, namely, the floating bond is stable only for the negatively charged state. The decrease in occupation number of the defect state also causes the B-Si$^1$ bond length is slightly longer than that in the negatively charged state. In the +1 charged state, since an electron is removed from the localized state [Fig. 2(c)], the B-Si$^1$ bond strength becomes weaker than that in other charged states. As seen from the bond configuration of Si$^1$ in Fig. 1, the tetrahedral distortion may be different for each charge state. Though Si$^1$ is fourfold coordinated in the −1 charged state, the tetrahedral distortion is slightly smaller than 1. This is indicative of forming the floating bond with Si$^1$ atom associated with structural deformation. In the neutral state, the tetrahedral distortion is slightly larger than 1, which is typical for the dangling bond on undercoordinated silicon atom. Due to the absence of an electron in the localized state in the +1 charged state, the bonding configuration of Si$^1$ is stabilized by forming $sp^2$-like bond configuration. Hence the tetrahedral distortion of the +1 charged state decreases close to zero.

**TABLE I. Interatomic distances ($\AA$) and tetrahedral distortion parameter $t$ (see text) of the geometries in Fig. 1. The name of atoms with/without Greek superscript in the first column correspond to the symbols of the atoms in Fig. 1.**

<table>
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<th></th>
<th>SiO$_2$</th>
<th>B$_3$Si$_3$($3$)($-$)</th>
<th>B$_3$Si$_3$($3$)($0$)</th>
<th>B$_3$Si$_3$($3$)($+$)</th>
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<td>1.672</td>
<td>1.649</td>
<td>1.579</td>
</tr>
<tr>
<td>Si$^1$-Si$^1'_2$</td>
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<td>1.641</td>
<td>1.662</td>
<td>1.581</td>
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<td>2.554</td>
<td>2.883</td>
<td>2.899</td>
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<tr>
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<td>3.038</td>
<td>2.918</td>
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<tr>
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<td>1.360</td>
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<tr>
<td>B-O$^1$</td>
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<td>1.358</td>
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<td>1.005</td>
<td>0.882</td>
<td>1.282</td>
<td>0.209</td>
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</table>

**B. B atom with O vacancies**

We have found that a B atom takes a variety of stable and metastable geometries depending on its charge state in defect-free SiO$_2$. Yet the thermal oxidized SiO$_2$ films might have various defects, we further elucidate the stable and metastable geometries of a B atom which is binding with the various defects in SiO$_2$. Here, we clarify the stable and metastable geometries of the B atom in SiO$_2$ containing O vacancies in the neutral state ($Q = 0$). Figure 3 shows a part of the atomic geometries of the O vacancy, and the stable and the metastable geometries for the B atom binding with the O vacancy. First, we have explored the stable geometry including the single O vacancy in SiO$_2$ in the neutral state and found that the two dangling bonds on Si$^1$ and Si$^1'_2$. It has also been found that a new Si$^1$-Si$^1'_2$ bond is formed with structural deformation as shown in Fig. 3(a). This stable geometry corresponds to that obtained in previous calculations. When a B atom is bound with an O vacancy, the stable geometry is B$_5$Si$_3$($2$) [Fig. 3(b)], in which the B atom is substituted into the O vacancy site and forms a twofold coordinated geometry with Si$^1$ and Si$^1'_2$. In B$_5$Si$_3$($2$) geometry the Si$^1$ atom maintains the Si-O-Si bond with O$^1$ and Si$^1'_2$. In a metastable geometry, on the other hand, B$_5$Si$_3$($3$) [Fig. 3(c)] is obtained. The B atom is substituted into an O vacancy site, as in the case of B$_5$Si$_3$($2$), however, it breaks the Si$^1$-O$^1$ bond and forms a threefold coordinated (Si=B) geometry with nearby Si atoms. The total energy of B$_5$Si$_3$($3$) geometry is higher by 2.11 eV than that of B$_5$Si$_3$($2$) due to the higher binding energy of Si-O bond compared to that of the Si-B bond.

Secondly, we have calculated the stable geometries of a B atom in the case where an O$^1$ site shown in Fig. 3(a) is replaced by a vacancy, namely, two O vacancies exist in SiO$_2$. The stable geometry B$_5$Si$_3$($3$)O$_2$ and the metastable geometry B$_5$Si$_3$O$_2$ are shown in Figs. 3(d) and 3(e), respectively. In B$_5$Si$_3$O$_2$ geometry, the Si$^1$-B bond is broken and...
Si IV is bound with Si III; the total energy for B S(2) O V is higher by 0.66 eV than that of B S(3) O V. Basically a B atom prefers a threefold coordinated geometry to a twofold one. Although both B S(3) and B S(3) O V geometries have Si=Si bonds, B S(3) is a metastable geometry in SiO 2 with a single O vacancy, whereas B S(3) O V is the most stable geometry in SiO 2 with double O vacancies. This can be understood as follows. In B S(3) geometry the Si III-O I bond is broken and then a new bond between B and Si III atoms is formed. The Si-O bond, however, is stronger than the Si-B bond in energy by 5.3 eV. Consequently, B S(3) geometry becomes metastable due to the energy consuming bond recombination. On the other hand, in the case of the conversion from B S(2) O V to B S(3) O V, the bond length of Si III-Si IV is 2.48 Å, which is longer than that in bulk Si of 2.37 Å; hence, the Si III-Si IV bond is a weak bond. Thus the bond is easily broken and the energy loss is small. Therefore, B S(3) O V is the most stable configuration.

C. B atom with an O interstitial

Next, we have performed an extensive search for the stable and the metastable geometries of a B atom with an O interstitial. Among various geometries of the O interstitial, we have found that the PL geometry [see Fig. 4(a)] is the most stable geometry for the neutral charge state. This stable geometry was also found in previous calculations. In B (2) O I [Fig. 4(b)], which is metastable geometry, the B atom intervenes between O I and O III and is twofold coordinated (-O I-B-O III). Furthermore, we have found another stable geometry B (3) O I, which is lower than B (2) O I in total energy by 0.65 eV. The B atom breaks the Si III-O III bond and forms a new B-O III bond to take B=O geometry (B (3) O I). This structural transformation results in that a dangling bond remains on Si I. This is due to the fact that a B atom prefers the threefold coordinated geometry and that the B-O bond is stronger than the Si-O bond; this dangling bond configuration is also seen in the stable geometry of B in defect-free SiO 2, B S Si (3) [Fig. 1(a)].

D. Formation energies of various B-related defects

The results presented above clearly show that a B atom takes a variety of the stable and the metastable geometries depending on the atomic geometries around the B atom. Therefore it is important to clarify the relative stability among the stable geometries presented above. The concentrations of O vacancies and O interstitials depend on the oxygen concentration in SiO 2. In other words, they depend on the Si concentration, i.e., the chemical potential of Si. To clarify the possible stable geometries of a B atom depending on the chemical potential of Si, we have calculated the formation energy for each geometry when the chemical potential \( \mu_{Si} \) of Si, i.e., the stoichiometry of Si, is changed. The results are shown in Fig. 5. In the Si rich limit (\( \mu_{Si} \approx 0 \)), B S Si (3) geometry in which the B atom is bound to two O atoms and Si atom is stable. In the O rich limit (\( \mu_{Si} \approx -8.8 \), i.e., \( \mu_{O} \approx \mu_{O(mol)} \), on the other hand, B (3) O I geometry in which the B atom is threefold coordinated with

![FIG. 3.](image1.png)

![FIG. 4.](image2.png)

![FIG. 5.](image3.png)
forming and breaking bond configurations in SiO$_2$ with an O interstitial are shown in Figs. 6. The defect-free SiO$_2$ and SiO$_2$ with an O interstitial have similar geometrical characteristics in the sense that a dangling bond remains on the Si atom. We have explored the diffusion mechanisms and the activation energy of the B diffusion in SiO$_2$ containing an O interstitial.

IV. B DIFFUSION IN SiO$_2$ CONTAINING O INTERSTITIAL

A. Stable geometries in charge states

In atomic diffusion in semiconductor, charge states of the defect greatly affect the diffusion mechanism and the activation energy. Thus, we first elucidate the charge-dependent multi-stability of a B atom in SiO$_2$ with an O interstitial. In the neutral charge state, we have found the stable geometry for a B atom in the defect-free SiO$_2$ and in SiO$_2$ with an O interstitial [Figs. 1(b) and 4(e)]. $\text{B}_3\text{Si}(3)$ and $\text{B}_3\text{O}_1$ have similar geometrical characteristics in the sense that a dangling bond remains on the Si atom. We have explored the stable geometries of the B atom with an O interstitial for charged ($-1$ and $+1$) states. It has been revealed that there are close analogies in the stable geometries of the B atom for each charge state between defect-free SiO$_2$ and SiO$_2$ with an O interstitial. Figure 6 shows the stable geometries. In the $+1$ charged state, the stable geometry of the B atom in the defect-free SiO$_2$ [Fig. 1(e) in Ref. 15] and that in SiO$_2$ with an O interstitial are shown in Figs. 6(a) and 6(b), respectively. Since an electron is missing on the B atom in the positively and negatively charged state are stable, whereas the neutral state is metastable for any value of $\mu_e$, the relative stability among the different charge states in the equilibrium. In general, the charge state of the impurity changes depending on the chemical potential of the electron: For instance, in the case of a B atom in the defect-free SiO$_2$, the positively and negatively charged state are stable, whereas the neutral state is metastable for any value of $\mu_e$ in the energy gap. This relative stability results in a negative-U system associated with structural transformation which takes place at the value of $\mu_e$ at the Si mid gap. Figure 7 shows the formation energies of $\text{B}_3\text{O}_2$ as a function of $\mu_e$ for the positive ($+1$; $Q=1$), neutral (0; $Q=0$), and negative ($-1$; $Q=-1$) charge states. As shown in Fig. 7, similar to the B atom in defect-free SiO$_2$, the neutral state is the metastable geometry for any value of $\mu_e$ over the entire region of the SiO$_2$ energy gap. In addition, we have also found that B in SiO$_2$ with an O interstitial has negative-U character associated with structural transformation. The value of $\mu_e$ is in

![FIG. 6. (Color online) Geometric structures of total-energy minimized (a) $\text{B}_3\text{O}_2(3)(+)$ [Fig. 1(e) in Ref. 15], (b) $\text{B}_3\text{O}(+)$, (c) $\text{B}_3\text{Si}(5)(-)$ [Fig. 1(c) in Ref. 15], and (d) $\text{B}_3\text{O}_1(-)$. Only a part of the atoms in a unit cell are shown to avoid visual complexity.](image-url)
the Si band gap, however, the positively charged state is stable except for when $\mu_c$ is located below the Si conduction band bottom.

**B. Diffusion mechanism of B atoms**

We have found the stable geometry of B in SiO$_2$ with an O interstitial for each charge state. Next, we have calculated the diffusion pathways and its activation energies. We start with the most stable geometry and explore a variety of possible diffusion pathways toward the final geometry using our constrained minimization technique. We obtained the final geometries from the corresponding starting geometry by a threefold rotation followed by a 2$\sqrt{3}$ nonprimitive translation. Here $c$ is a lattice parameter of the supercell. The most favorable pathways and corresponding activation energies determined by the present calculations are shown in Fig. 8.

As mentioned previously, if a B atom diffuses along the SiO$_2$ networks leaving an O interstitial alone, it costs more than 6 eV to break the strong B-O bond and diffuse via the SiO$_2$ networks. Surprisingly, as is obvious from Fig. 8, the calculated activation energies are lower than 6 eV for all the charge states. The activation energies are 2.3 eV for +1 charged state, 2.1 eV for −1 charged state, and 1.1 eV for the neutral state as shown in Fig. 8. These values are comparable to those for the diffusion of B in defect-free SiO$_2$. $^{15}$

This activation energy lowering can be understood as follows. Careful analyses of the diffusion process have indicated that for all the charge states, the B atom is threefold coordinated with nearby O atoms during diffusion. Thus, in oxygen rich SiO$_2$, the B atom diffuses through the SiO$_2$ networks with an O interstitial atom by forming a “B-O complex.” An O atom in the B-O complex is not the same O atom in the diffusion process, but a different O atom is used to maintain the B-O complex. One of the O atoms (O$^1$) in the B=O bonds is kicked to the next -Si-O$^2$-Si- bond with a B atom and then O$^0$ is kicked to the next stable site with a B atom. During this process, the B atom can diffuse by keeping the B=O bonds without forming the Si-B bond. Once the B atom formed the Si-B bond, the activation energy for the B diffusion should be higher than this diffusion mechanism due to the fact that the B-O bond is much stronger than the Si-B bond. In the present diffusion processes, however, Si-B bonds are not formed. Thus the activation energies are remarkably suppressed. Consequently we have found that in an equilibrium condition the B atom diffuses in SiO$_2$ with activation energies of 2.1–2.3 eV irrespective of the presence or absence of an O interstitial.

Variation of atomic geometries and bond configurations during the diffusion are extremely interesting and further clarify the specific characteristics of the charge states. Figure 9 shows the geometries near the saddle points S1, S2, and S3 shown in Fig. 8. In the saddle-point geometry of S1 [Fig. 9(a)] for the +1 charged state, a nonbonding orbital of the O atom is bound to the $sp^2$-hybridized orbital of the B atom. In other geometries on the diffusion pathways, the $sp^2$-hybridized orbital of the B atom always binds to the nonbonding orbital of the O atom, and diffuses via the SiO$_2$ networks with the O interstitial. In the saddle-point geometry of S2 [Fig. 9(b)] for the −1 charged state, many floating bonds are formed to accommodate an additional electron. In the −1 charged state, an additional electron is continuously accommodated in the floating bond, and the B atom diffuses by forming and breaking that bond with the O interstitial. In the neutral state, the saddle-point geometry is S3 [Fig. 9(c)].
We have presented first-principle calculations that clarify the stable geometries and the diffusion mechanisms of a B atom in defect-free SiO$_2$ and SiO$_2$ with point defects. We have found that the B atom takes various stable and metastable geometries in SiO$_2$, depending on its charge state and the local network around the B atom. In the case of a B atom in defect-free SiO$_2$, B$_2$Si$_3$ geometry becomes stable for the neutral state. Only a part of atoms in a unit cell are shown to avoid visual complexity.

As seen from the figure, there is a dangling bond on the Si atom. Furthermore the dangling bond is also present on the Si atom in defect-free SiO$_2$ and SiO$_2$ with point defects. We have found that the activation energies of the B-O complex are 2.1–2.3 eV. Since the activation energies of the B atom in defect-free SiO$_2$ were found to be 2.2–2.3 eV, the activation energies of the B atom are 2.1–2.3 eV irrespective of the presence or absence of the O interstitial. These values agree well with those obtained experimentally.

V. SUMMARY

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19 The inclusion of spin degree of freedom is important: The total energy gain due to spin-polarization is typically 0.2–0.5 eV, and the spin splittings of Kohn-Sham levels are 1.5–2.0 eV.


22 The convergence of the calculational parameters are examined by using the cutoff energies of 25, 49, and 64 Ry, and the Γ point and the eight k point samplings in BZ. The calculated total energy differences are found to converge within 0.02 eV.


