Impurity doping in SiO$_2$: Formation energies and defect levels from first-principles calculations

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(Received 7 June 2010; revised manuscript received 22 September 2010; published 22 October 2010)

Substitutional doping properties of silicon dioxide are investigated systematically with \textit{ab initio} calculations. The dopants include a range of elements from group-III, group-V, and group-VII. We find that SiO$_2$ has a relatively symmetric doping profile in terms of its ionization energies, i.e., relatively shallow acceptor levels and donor levels are both predicted, despite its wide experimental band gap of 9.65 eV. The best candidates for \textit{p}-type and \textit{n}-type doping are Al$_{\text{Si}}$ and P$_{\text{Si}}$ with calculated ionization energy of 0.86 eV and 0.74 eV, respectively, both being less than 10% of the total band gap. Larger doping asymmetry exists in terms of the impurity formation energy: under optimum (O-rich) growth conditions, the shallowest acceptor, Al$_{\text{Si}}$, and donor, P$_{\text{Si}}$, have formation energies of 1.75 eV and 3.05 eV, respectively. These results provide theoretical insights on how to make this previously considered absolute insulator work as a wide-gap semiconductor.

DOI: 10.1103/PhysRevB.82.155132 PACS number(s): 61.72.J−, 71.55.−i

I. INTRODUCTION

Silicon dioxide (SiO$_2$), an abundant resource in nature, holds an important status in various applications due to its excellent optical and electrical properties.\textsuperscript{1} For instance, glass fiber is regarded as the basis of modern communication.\textsuperscript{2,3} In the metal-oxide-semiconductor (MOS) glass fiber is regarded as the basis of modern properties.\textsuperscript{4–17} For example, cationic impurities, such as aluminum or boron have been studied by optical absorption spectra.\textsuperscript{13,18} While it is generally accepted that these impurities would produce a series of distinct electronic levels in the band gap, other dopants have been found to significantly enhance the photosensitivity of SiO$_2$. Phosphorus is a case. With phosphorus doping the efficiency of rare-earth based optical fiber amplifier is greatly increased. Furthermore, phosphosilicate glass is considered to be a good candidate for radiation sensors due to its near linear response to radiation dose.\textsuperscript{9,19,20} Yet other impurities have been studied with regard to improvement of the dielectric characteristics in the usage of the MOS devices, for instance, nitrogen substituting oxygen as a Si-O-N alloy can substantially enhance its dielectric constant.\textsuperscript{14,21}

Until now efforts on SiO$_2$ doping focus on improving the application-demand characteristics. Due to the very large band gap of SiO$_2$ (9.7 eV), it is generally accepted that SiO$_2$ is exclusively an insulator. However, diamond was also commonly believed to be an insulator due to its relatively large band gap of 5.5 eV before the achievement of \textit{p}-type doping.\textsuperscript{22} As a matter of fact, the boundary between semiconductors and insulators is becoming more and more difficult to define, in light of recent success in doping wide-gap materials such as AlN and ZnMgO for future ultraviolet optoelectronic devices.\textsuperscript{23,24} This raises an interesting and important question: can SiO$_2$ also be doped to become a semiconductor? Since SiO$_2$ is known to be the largest-gap inorganic solid, it is an excellent test case for doping wide-gap insulators.

In this paper, we address this question through systematic calculations of the doping properties of substitutional impurities in SiO$_2$. The acceptors include group-III elements (B$_{\text{Si}}$, Al$_{\text{Si}}$, and Ga$_{\text{Si}}$) and group-V elements (N$_{\text{O}}$, P$_{\text{O}}$, and As$_{\text{O}}$), whereas the donors include group-V elements (N$_{\text{Si}}$, P$_{\text{Si}}$, and As$_{\text{Si}}$) and group-VII elements (F$_{\text{O}}$, Cl$_{\text{O}}$, and Br$_{\text{O}}$). We find that, in general, the group-III-on-group-IV impurities have shallower acceptor levels and the group-VII-on-group-VI impurities have shallower donor levels. These can be understood because a group-III-on-group-IV site would not directly perturb the valence-band maximum (VBM) which is oxygen derived. Similarly, a group-VII-on-group-VI site would not directly perturb the conduction-band minimum (CBM) which is silicon derived. However, there is an important exception; namely, P-on-Si has by far the shallowest donor level, being 0.74 eV below the CBM. In contrast, the shallowest acceptor level, Al-on-Si, is 0.86 eV above the VBM. The corresponding impurity formation energies, at the most favorable oxygen rich growth condition, are 3.0 eV and 1.7 eV, respectively. We can estimate the solid solubilities at the SiO$_2$ melt temperature of 1650 °C to obtain $10^{15}$ cm$^{-3}$ and $10^{18}$ cm$^{-3}$ for phosphor and aluminum doping, respectively. With today’s doping techniques, one may boost the doping level considerably from the solid solubility level by nonequilibrium doping. These results thus suggest that doping SiO$_2$ for electronic and optoelectronic applications may be possible at least at elevated temperatures.

II. CALCULATION METHODS

We perform first-principles calculations based on the density-functional theory (DFT),\textsuperscript{25,26} as implemented in the
such, it cannot accurately describe the local configuration for DFT possesses residual self-interaction for electrons. As their transition levels. The formation energy of a dopant in a bulk crystal is obtained from \[ \frac{\Delta H(\text{SiO}_2)}{2} \leq \mu(0) \leq 0 \] (O-poor condition), \[ \mu(0) \leq \Delta H(\text{SiO}_2) \] (O-rich condition).

From the calculated formation energies, which for charged defects explicitly depend on \( E_F \), we determine the thermodynamic transition levels of the defects. The transition level, defined as the value of \( E_F \) where the different charge states have the same formation energy, can be written as follows:

\[ \varepsilon(q/q') = \left[ \frac{\Delta E(X^q_Y)}{q'} - \frac{\Delta E(X^{q'}_Y)}{q} \right] \]

where \( q \) and \( q' \) are the two different charge states of the substitutional dopant, e.g., an acceptor transition level, \( \varepsilon(0/-1) \), is the Fermi energy at which the acceptor defect has equal energy in the two different charge states, \( q = 0 \) and \( q' = -1 \), whereas a donor transition level, \( \varepsilon(+1/0) \), is the Fermi energy at which the donor defect has equal energy in the two different charge states, \( q = 1 \) and \( q' = 0 \).

While Eq. (5) yields the transition energy within the calculated band gap of 6.54 eV, there exists a substantial deviation from the experimental gap of 9.65 eV. This large discrepancy, of over 3 eV, is of particular concern in the determination of whether a defect is shallow or deep, so care must be taken in order to determine how the defect levels shift as the gap is opened. In this work, we make an effort to overcome this problem with the wave-function-projection method (WFM). That is that when we raise the conduction band to meet the experimental gap the transition levels are modified according to the projected ratio of the defect state on the VBM and CBM at the \( \Gamma \) point of the Brillouin zone. This method has been shown to give reasonable results.

**III. RESULTS AND DISCUSSIONS**

**A. Atomic geometry**

In \( \alpha \) quartz, each Si atom and its four neighboring O atoms form a \( \text{SiO}_4 \) tetrahedron with \( C_2 \) symmetry. For most impurities, the tetrahedron for the neutral substitutional impurity \( X^q_y \) (\( X \) refers to every dopant) is preserved in LDA calculations. In contrast, our GGA+U calculations destroy the \( C_2 \) symmetry of the tetrahedron. Most of our calculations are consistent with electron paramagnetic resonance (EPR) or electron spin resonance experiment, including both local structure and spin electron distribution. The only exception being \( N_{50}^0 \), where it is difficult to find an experiment result of an \( \text{NO}_4 \) tetrahedron in quartz. That, however, can be attributed to its high formation energy, which will be discussed later. Figures 1(a) and 1(b) show the relaxed local configuration of Si-substituted impurities and their corresponding bond lengths. For group-III acceptors, one of the X-O bonds elongates significantly. Compared to the remaining three, the elongated bond is increased by 44.7%, 10.6%, and 12.7% for B, Al, and Ga, respectively. For group-V donors, N has the similar bond-length variation that one bond (N-O^3) is 54.4% longer than the other three, whereas P and As maintain the \( C_2 \) symmetry. For P and As, two pairs of bonds are elongated (X-O^2 and X-O^3), leaving a shorter pair
of bonds (X-O$^-$ and X-O$^3$). The spin electron density distributions [see Fig. 1(a)] clearly reveal the origin of the local distortion, which could be classified as Jahn-Teller distortion. For group-III dopants, their spin charge is mainly localized in the 2$p$ orbital of the elongated-bond oxygen atom. Due to the $C_2$ symmetry of the SiO$_4$ tetrahedron in bulk (one pair of long bonds and one pair of short bonds) the 2$p$ orbital of O is doubly degenerate. When a group-III dopant (three valence electrons) replaces Si (four valence electrons), the structure is stabilized when the hole occupies the local orbital, with the degeneracy removed, rather than the nonlocal degenerate orbital [see Fig. 1(a)]. This hole weakens the Coulomb binding between the dopant and one of the oxygen, elongating their distance. For the N impurity of group-V, the extra unpaired electron does not occupy the bonding states but antibonding state overlapped by one O(2$^6$)2$p$ orbital and N sp$^3$ hybrid orbital. Hence this antibonding state weakens the covalent bond of N-O$^-$, leading to a substantial extension of the N-O$^-$ bond. However, it is quite different for case of P and As which should be attributed to the existence of unoccupied $d$ orbital. For the P dopant, the antibonding state, which is occupied by the unpaired electron, is made up of its 3$d$ orbital and the 2$p$ orbital of the related O (O$^2$ and O$^3$). This is why the spin charge dominates the region around the extended P-O$^3$ bond and P-O$^3$ bond. Moreover, the increased angle of O$^{2-}$-P-O$^3$ shows more or less the characteristics of $d$ orbital bonding. The local structure for As is similar to that for P, the only difference being that each of the As-O bonds are slightly longer than the corresponding P-O bonds. Chemically, the only difference is that the occupied antibonding state is made up of 4$d$ orbital of As and 2$p$ orbital of two related O (O$^2$ and O$^3$).

**B. Formation energy**

Growth conditions can greatly affect the formation energies of defects. In SiO$_2$, further considerations must be made due to the number of secondary compounds, which can limit the range of growth conditions. To avoid the formation of the secondary compound $X_nZ_m$ (where Z is a host atom, O or Si), the chemical potential must also satisfy $m\mu(X)+n\mu(Z) = \Delta H(X_nZ_m)$, where $\Delta H(X_nZ_m)$ is the formation enthalpy of the secondary compound. From the equations above, the formation energy is greatly limited by the formation enthalpies of the secondary compounds. Table I shows the calculated formation enthalpies of SiO$_2$ and the possible secondary compounds. From the comparison with experiment, it can be seen that while the formation enthalpies for the nonoxides are quite reasonable, those of the oxides have a relatively large error. This error for the oxides is mainly due to the $U$ parameter for energy calculation. However, as we detailed in Sec. II, the $U$ parameter is critical for reproducing reasonable

**TABLE I.** Calculated and experimental formation enthalpies, $\Delta H_f$, for SiO$_2$ and the possible secondary compounds. For the calculation of formation enthalpy, we add $U$ parameters ($U=7$ eV) both on O 2$p$ orbital of oxides and O$_2$ molecule which is consistent with our procedure for geometry relaxation.

<table>
<thead>
<tr>
<th>Compound (phase)</th>
<th>$\Delta H_f$ (Calc.) (eV)</th>
<th>$\Delta H_f$ (Expt)$^a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (s)</td>
<td>−7.72</td>
<td>−9.47</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (s)</td>
<td>−13.90</td>
<td>−17.40</td>
</tr>
<tr>
<td>As$_2$O$_3$ (s)</td>
<td>−5.33</td>
<td>−9.25</td>
</tr>
<tr>
<td>B$_2$O$_3$ (s)</td>
<td>−10.94</td>
<td>−13.07</td>
</tr>
<tr>
<td>Ga$_2$O$_3$ (s)</td>
<td>−7.98</td>
<td>−11.29</td>
</tr>
<tr>
<td>P$_2$O$_5$ (s)</td>
<td>−11.55</td>
<td></td>
</tr>
<tr>
<td>Si$_3$N$_4$ (s)</td>
<td>−7.73</td>
<td>−7.73</td>
</tr>
<tr>
<td>SiF$_4$ (g)</td>
<td>−15.63</td>
<td>−16.77</td>
</tr>
<tr>
<td>SiCl$_4$ (g)</td>
<td>−6.43</td>
<td>−6.82</td>
</tr>
<tr>
<td>SiBr$_4$ (g)</td>
<td>−4.64</td>
<td>−4.31</td>
</tr>
</tbody>
</table>

$^a$Reference 41.
localized geometries of the defect structures. While this leads to some unavoidable error in the domain of the allowable chemical potentials, which is reflected in the formation energies, it should be noted that this in no way affects the defect transition levels.

For charged defects, the formation energy is also a function of Fermi energy ($E_F$) as defined in Eq. (1). The $E_F$ varies from the VBM to the CBM according to the band gap of $\alpha$ quartz. Here, we directly apply the calculated band gap with GGA+$U$ to define the variation in $E_F$. The formation energies of the substitutional dopants, as a function of $E_F$, are shown in Fig. 2. For neutral impurities, we can clearly see that the Si-substituted dopants have lower formation energies at the O-rich condition [see Fig. 2(a)], whereas the O-substituted dopants have lower formation energies at Si-rich condition [see Fig. 2(d)]. In fact, it makes sense that at the O-rich condition the low concentration of O vacancy hinders the O-substituted doping but the high concentration of Si vacancy facilitates the Si-substituted doping and vice versa at Si-rich condition. From the calculated results shown in Fig. 2, the formation energies of the neutral group-III acceptors (BSi, AlSi, and GaSi) are fairly low under O-rich conditions, being 1.44 eV, 1.75 eV, and 2.23 eV, respectively. In contrast, acceptors are much more difficult to form at the Si-rich condition; the lowest formation energies for neutral acceptors being the group-V acceptors (NO, PO, and AsO) with formation energies of 3.01 eV, 2.68 eV, and 3.11 eV, respectively. For the case of donors, the lowest formation energy of the neutral group-V donors (NSi, PSi, and AsSi) are 4.92 eV, 3.05 eV, and 1.97 eV, respectively, at O-rich condition and the lowest ones for the neutral group-VII (FO, ClO, and BrO) donors are 2.75 eV, 3.39 eV, and 3.92 eV, respectively, at Si-rich condition. In fact, the formation energy for the dopants in SiO$_2$ exhibits a broad variation region. It can be traced back to the wide band gap of SiO$_2$ and the relatively large formation enthalpy of SiO$_2$. Based on the formation energy, acceptors (group-III at the Si site) should be quite easy to dope, with group-V at the O site being more difficult. The doping of donors is more problematic due to the generally higher formation energies. However, most donors formation energies are less than 3.4 eV except NSi and BrO. Adequate doping concentrations may thus be attained with modern nonequilibrium doping techniques.

C. Transition level

The transition levels of the substitutional dopants are shown in Fig. 3. A comparison of the results with and without the WPM correction shows that the impurity levels with respect to the respective band edges do not change due to the correction. For example, the acceptor levels relative to the VBM increase typically by less than 0.01 eV; the donor levels relative to the CBM decrease typically by less than 0.03 eV. The only exception is NSi for which the decrease is 0.33 eV (more discussion on this exceptional and relatively large shift will be given below). The virtually null result of the projection is quite informative given the relative deepness of all the impurity levels (>0.9 eV). It suggests that for SiO$_2$ with a 9.65 eV band gap, a state 2–3 eV deep inside the band gap is predominantly a band edge state, most likely with physical properties similar to those of its parent states.

For acceptors, the transition levels of group-VI donors (BSi, AlSi, and GaSi) are substantially lower than that of group-VI donors (NO, PO, and AsO) (2.34 eV, 3.73 eV, and 4.02 eV above the VBM, respectively). This can be understood by noting that the VBM is mainly derived from the Si-O bond compared to B and Ga. For the group-V impurity acceptors (O substituted), the transition
The value of transition levels are shown with respect to VBM. U of AsSi, and hence becoming markedly deeper than that of section, leading to a substantial deepening of the donor level goes local structural distortion, as indicated in the geometry dopants tively, are generally shallower than those of the group-V being 1.43 eV, 1.46 eV, and 1.36 eV below the CBM, respec-
tive N, P, and then As, the corresponding defect level be-
level is more simply related to their electronegativity, it be-
ing easier to put an electron on a more electronegative atom. Hence, as the substitutional atom becomes less electronega-
A similar result is found for the case of donors. The transition levels of the group-VII dopants (F\textsubscript{O}, Cl\textsubscript{O}, and Br\textsubscript{O}), being 1.43 eV, 1.46 eV, and 1.36 eV below the CBM, respectively, are generally shallower than those of the group-V dopants (N\textsubscript{Si}, P\textsubscript{Si}, and As\textsubscript{Si}), being 4.23 eV, 0.74 eV, and 2.97 eV below the CBM, respectively. The explanation for this behavior is similar to the acceptors but here it is the O-substituted donors which perform only a small perturba-
tion on CBM, mainly yielding shallower donor levels than the Si substituted donors. The notable exception is P\textsubscript{Si}, which has the shallowest level of all the donors investigated, at only 0.74 eV below the CBM. The position of the donor levels of group-V dopants at the Si site (much like as acceptors at the O site) are primarily determined by their atomic levels and subsequent relaxation. From their behavior in crystalline Si, one might expect both P and As to introduce shallow donor levels.\textsuperscript{45} While this is true for the case of P\textsubscript{Si} (which retains the crystal symmetry with very little relaxation), As\textsubscript{Si} undergoes local structural distortion, as indicated in the geometry section, leading to a substantial deepening of the donor level of As\textsubscript{Si}, and hence becoming markedly deeper than that of P\textsubscript{Si}. N\textsubscript{Si}, on the other hand, is quite deep; this is not only due to the large ionization energy of the N atom but also due to the broken N-O bond, as shown in Fig. 3(a).

In the light of the transition levels for the considered dop-
ants, the best candidate for \textit{n}-type doping and \textit{p}-type doping are predicted to be P\textsubscript{Si} (0.74 eV below CBM) and Al\textsubscript{Si} (0.86 eV above VBM), respectively, for the substitutional impurities. With a clear charge-transfer mechanism of Al\textsubscript{Si}, there have been experimental reports on the level position of Al\textsubscript{Si} in SiO\textsubscript{2} to be 1.96 eV above the VBM.\textsuperscript{8,15} Since this is an optical measurement, it does not include the relaxation effect of the final state, and therefore, one cannot compare directly with our calculated transition energy level, which should be thermally excited instead. To facilitate a direct comparison with the experiment, we have calculated the energy associated with the structural relaxation of Al\textsubscript{Si} after it is charged to be 1.06 eV. We can then approximate the optical transition level (thermodynamic level+relaxation energy) to be 1.92 eV, which is in surprisingly good agreement with experiment. Similarly, for the P\textsubscript{Si} case, it is approximated that the optical transition level (0.74 eV of thermodynamic level +3.05 eV of relaxation energy) to be 3.79 eV. While the experimental situation is more complicated in phosphate glass, the phosphorous-oxygen-hole center has been fitted to three absorption bands at 2.3, 2.89, and 3.82 eV.\textsuperscript{12}

In general, \textit{n}-type doping needs the CBM far away from the vacuum level whereas the \textit{p}-type doping needs VBM close to the vacuum level.\textsuperscript{43,44} Therefore, a complete success for both \textit{p}-type and \textit{n}-type doping is quite difficult for materials with wide band gap, such as ZnO and diamond.\textsuperscript{45,46} It is, therefore, encouraging to see that SiO\textsubscript{2}, a very wide band-gap material, possesses both relatively shallow donor and acceptor transition levels. Although we refer to these levels as “shallow,” it is important to note that we mean relative to the very large gap of SiO\textsubscript{2}. In an absolute sense, 0.8 eV is still quite deep in that it is very difficult to ionize at room temperature.

IV. CONCLUSION

Our systematic investigation of the doping properties of SiO\textsubscript{2} reveals no obvious doping asymmetry in the donor and acceptor level position, and only modest asymmetry in the impurity formation energy. With a GGA+U approach, we achieve a description of the local configuration of substituting impurities in SiO\textsubscript{2} which is quite consistent with EPR spectroscopy. It is found that SiO\textsubscript{2} can have both relatively shallow (with respect to the band gap) acceptor and donor

FIG. 3. (Color online) The calculated thermodynamic transition levels for substitutional defects before and after modification in SiO\textsubscript{2}. The value of transition levels are shown with respect to VBM. (a) The position of the transition levels and the calculated band gap with GGA+U. (b) The transition levels after application of the wave-function-projection method and the experimental band gap.
transition levels. Our predicted best candidates for $p$-type and $n$-type doping are Al$_{0.86}$ (0.86 eV above the VBM) and P$_{0.74}$ (0.74 eV below the CBM), respectively, both of which are consistent with previous experiments. These findings point out that this generally accepted insulator would have potential applications on forming an active layer for semiconductor devices. To utilize such new character for SiO$_2$, some critical problems must necessarily be solved, such as the migration of free carriers. Fortunately, the hopping-transfer mechanism of holes in disordered SiO$_2$ has been predicted.\textsuperscript{47} Furthermore, the great success of the organic/polymer on electronic devices provides a good example for an insulating material being used as semiconductor. We expect some procedures,\textsuperscript{48,49} such as codoping\textsuperscript{50} or band-gap reduction,\textsuperscript{51} would further lower the acceptor/donor levels to meet the ultimate acquirement of practical applications.

ACKNOWLEDGMENTS

We acknowledge the High Performance Computing Center (HPCCC) of Jilin University and the Computational Center for Nanotechnology Innovations (CCNI) of Rensselaer Polytechnic Institute for supercomputer time. Works at JLU and RPI were supported by the National Science Foundation of China under Grant No. 90923037 and the U.S. Department of Energy under Grant No. DE-SC0002623. We gratefully thank W. Q. Tian, Q. D. Chen, Z. G. Chen, X. Meng, H. Yang, and H. Wang for their helpful discussions and technical support.


