First-principles X-ray photoelectron spectroscopy binding energy shift calculation for boron and aluminum defects in 3C-silicon carbide

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1. Introduction

Silicon carbide (SiC) is expected to be used in power devices owing to its wide band gap, high thermal conductivity, and high breakdown voltage. SiC has more than 200 stable structures, which are characterized by one-dimensional stacking sequences of Si–C pairs. Such different structures are called polytypes and show different physical properties such as their band gap and mobility of carriers. Among the polytypes, the most attractive polytype for application is 4H-SiC (hexagonal structure). Although 3C-SiC (zincblende structure) has a narrower band gap than 4H-SiC, 3C-SiC has the advantage of forming an inversion layer at a lower voltage. It has also been reported that the n-channel mobility in the metal-oxide-semiconductor structure of 3C-SiC is higher than that of 4H-SiC, although, in the bulk, the electron mobility of 3C-SiC is lower than that of 4H-SiC.\(^4\)\(^5\)\) This is considered to be due to the band gap as follows. The defect levels in the vicinity of the SiC/SiO\(_2\) interface, which scatter carriers, exist below the conduction band bottom of 4H-SiC. On the other hand, in 3C-SiC, the levels are buried in the conduction band.\(^3\) In this paper, we considered 3C-SiC, which has a simple and symmetric structure, and performed an X-ray photoelectron spectroscopy (XPS) calculation as a first step to classifying the defects in SiC. SiC is a VI–VI compound semiconductor, and group III elements such as boron (B) and aluminum (Al) can be used as \(p\)-type dopants in SiC as well as in Si. Al has a shallower acceptor level than B and is commonly used as a \(p\)-type dopant in SiC. B is used to form the edge termination structure in high-voltage devices.\(^7\) B diffuses rapidly in SiC, the mechanism of which has been reported in many studies.\(^6\)\(^\text{–}\)\(^8\) We reported preliminary results about B in 3C- and 4H-SiC using small supercell of about 500 atoms.\(^9\)

Generally, it is difficult to identify defect structures in solids. There are two reasons for this. First, it is difficult to measure atomic configurations directly in the bulk. Instead, we can obtain spectra including information of the defect structures, and numerical simulations are required to associate the spectra with the structures. Second, the spectra from the defects of interest are very weak since the population of impurities is much smaller than that of the crystal matrix and the defects of interest are much fewer. Recently, however, large synchrotron radiation facilities such as SPring8 have enabled the core-level XPS measurement of B, phosphorus (P), and arsenic (As) defects in Si by using a strong beam to amplify the weak signals.\(^9\)\(^\text{–}\)\(^11\) On the other hand, few reliable XPS calculations have been reported for defects. One reason is that the reliable calculation of the XPS binding energy (XPSBE) shift requires careful evaluation of the model boundary condition, which leads to a large supercell size.

In this study, we predicted the XPSBE shifts of B 1s and Al 2p for the defects in 3C-SiC, and investigated the relationship between the XPS spectra and the defects of \(p\)-type dopants in 3C-SiC. As a naive interpretation, the XPS spectra reflect the energy levels of the electrons before photoemission, i.e., the potential the electrons are subjected to. It is pointed out by first-principles calculations that the relaxation of wavefunctions caused by the core hole left after photoelectron emission makes a large contribution to the XPS spectra.\(^12\) We also discuss this relaxation energy in detail.

2. Method

The calculations are based on density functional theory (DFT) with the generalized gradient approximation (GGA) PBE96.\(^13\) The interactions between ions and electrons are described by the norm-conserving pseudopotentials for Si and Al\(^14\) and the ultrasoft pseudopotentials for B and carbon (C).\(^15\) Unless otherwise mentioned, the calculation model is a cubic supercell with a side of approximately 2.62 nm, corresponding to a crystal containing 1728 atoms \((6 \times 6 \times 6\) eight-atom unit cells). The sampled \(k\)-point is the single \(\Gamma\) point and the cutoff energy is 30.25 Rydberg, which shows satisfactory convergence for formation and XPSBEs. To check the cutoff energy dependence, we calculated the formation and XPS binding energy shifts for the defect structures \(X_{\text{Si}}\), \(X_{\text{C}}\), \(X_{\text{TC}}\), and \(X_{\text{TSi}}\) \((X = B, Al)\) using cutoff

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energies of 30.25 and 42.25 Rydberg and found that the maximum change in energy for the two cutoff energies is 0.05 eV, and most of the energy changes are less than 0.03 eV. The atomic configurations are fully optimized for the total energy with a force criterion of less than $1 \times 10^{-3}$ Hartree/Bohr. The calculation code is xTAPP,\textsuperscript{16} which is a highly parallelized version of the plane-wave-based code TAPP.\textsuperscript{17} The calculated lattice constant is 4.37 Å, and the experimental value is 4.3596 Å.\textsuperscript{18} The calculated band gap is 1.37 eV, which is much smaller than the experimental value of 2.417 eV,\textsuperscript{19} which is a well-known issue in the GGA.

For the core-level XPS calculation, we adopted the $\Delta$SCF method with screened core hole pseudopotentials (SCHPs).\textsuperscript{12} In the $\Delta$SCF method, the XPSBE is obtained as the difference in the total energy between the system where one electron in the relevant core-level is removed and that in the ground state. As a test of accuracy for the SCHPs, we calculated the relative XPSBEs of B 1$s$, S$i^2$p, and P 2$p$ in some molecules, which are summarized in Table I. The experimental data are from Ref.\textsuperscript{20}. These calculations were performed using a cubic supercell with an edge of 8.4 nm. For Al 2$p$, no experimental data were available. Instead, using the same procedure as that for Al 2$p$, we prepared SCHPs for Si 2$p$ and P 2$p$, which follow Al in the periodic table, and calculated the XPSBE shifts. It was found that the agreement between the calculated and experimental data is excellent for molecules that consist of the same kind of elements as the boranes. On the whole, the difference between the calculated and experimental data is about 0.1 eV. Similar accuracy was expected in the present work.

The supercell size dependence is large in the XPSBE calculation, and the evaluation of the supercell size is important to obtain reliable values.\textsuperscript{21–23} Figure 1 shows the supercell size dependence of the XPSBE shifts of B 1$s$ and Al 2$p$ in some defect models. The sampling k-point for all models is the single $\Gamma$ point. In the figures, the horizontal axis is the number of atoms for the ideal 3C-SiC corresponding to the supercell used in this calculation, and the vertical axis is the XPSBE measured from the substitutional defect at the Si site in the electrically neutral state. Using a 1728 atom supercell, we can expect an accuracy of about 0.1 eV.

For the charged state calculation, the Makov–Payne correction is well-known in this field.\textsuperscript{24} However, while the correction gives very accurate results for atoms and molecules, the correction is overestimated for the calculation of defects.\textsuperscript{25,26} In this study, we did not make corrections for charged states because we used relatively large supercells and obtained satisfactory convergence of the formation energies as shown above.

### Table I. Relative XPS binding energies in eV of B 1$s$, Si 2$p$, and P 2$p$ for some molecules. Pentaborane(9) (B$_5$H$_9$) has a pyramidal B-atom skeleton. Experimental data are from Ref. 20.

|        | Calc. | Exp.  | Calc. | Exp.  | Calc. | Exp.   |
|--------|-------|-------|-------|-------|-------|--------|
| B$_2$H$_6$ | 0.00  | 0.0   | SiH$_4$ | 0.00  | 0.0   | PF$_3$ | 0.00 | 0.0   |
| B$_5$H$_9$(apex) | -2.29 | -2.3  | SiF$_4$ | 4.38  | 4.5   | PH$_3$ | -4.53 | -4.7  |
| B$_3$H$_9$(base) | -0.42 | -0.4  | Si$_2$H$_6$ | -0.53 | -0.4  | PF$_5$ | 2.42  | 2.6   |
| PO$_3$F$_3$ | 1.20  | 1.2   |        |       |       |        |
impurity atom is substituted for a Si atom next to a C vacancy, $X_{Si}-V_{C}$, or substituted for a C atom next to a Si vacancy, $X_{C}-V_{Si}$. Here, V denotes a vacancy.

Third, an impurity atom occupies an interstitial site. We carried out calculations for a tetrahedral site (T-site) and a hexagonal site (H-site). A T-site is a position tetrahedrally surrounded by four lattice sites of the same element. $X_{TSi}$ and $X_{TC}$ denote T-sites surrounded by Si and C lattice atoms, respectively. An H-site is the center of a six-membered ring of Si and C atoms and is denoted as $X_{H}$.

Fourth, a pair of impurity and crystal atoms is located at a single lattice site. Such a defect is known as a split interstitial. For example, an X and Si pair occupying a Si lattice site in the (110) direction is denoted as $(110)(X-Si)_{Si}$. We considered eight patterns of this type of defect, that is, the eight combinations of $X$–Si and $X$–C pairs, (110) and (001) directions, and Si and C sites. In addition, the impurity atom X is located at the bond center; this configuration is denoted as $X_{bc}$.

Finally, combinations of a substitutional impurity and self-interstitial are considered. For instance, the pair comprising an X atom substituting at a Si site and Si substituting at the nearest TSi site is denoted as $X_{Si}-Si_{TSi}$. We calculated the twelve models corresponding to the combinations of Si and C sites for X, and TSi, TC, and H sites for Si and C.

Figure 2 shows the optimized structures for some representative B defect models. To draw these figures, we used VESTA. Similar structures were obtained upon swapping B with Al and Si with C. We optimized the energy with respect to the atomic structure for the models introduced above in a neutrally charged state. For charged states, we also optimized the total energy under the condition that the Fermi energy is set to the valence band top (VBT).

Fig. 2. (Color online) Optimized structures of B defects in 3C-SiC. Yellow, gray, and green spheres represent Si, C, and B, respectively. The horizontal direction is [110] and the vertical direction is [001]. See Sect. 3 for the abbreviations of the defect structures.
Table II. Results of the structure optimization of B and Al impurities for the charge-neutral states. X represents the symbol of impurities.

| Initial | B     | Al    |
|---------|-------|-------|
| XSi     | BSi   | AlSi  |
| Xc      | BC    | AlC   |
| Xa-Vc   | Bva-Vc| Aka-Vc|
| Xc-Vsi  | Bcs-Vsi| Aks-Vsi|
| Xfesi   | Bfesi | Alfesi|
| Xch     | Bhi   | Alrc  |
| Xal     | BAl   | AlAl  |
| (110)X-Si3Si | (110)B-Si3Si | (110)Al-Si3Si |
| (001)X-Si3C | (001)B-Si3C | (001)Al-Si3C |

For the charge-neutral states, the results of optimizing the structures introduced in Sect. 3 are summarized in Table II.

The results for B and Al are summarized in Tables III and IV.

4. Results and discussion

For the charge-neutral states, the results of optimizing the structures introduced in Sect. 3 are summarized in Table II. Approximately half of them were stable and the others changed into different structures from their initial configurations. Many of the split interstitials and the pairs comprising a substitutional impurity and self-interstitial were unstable. For the stable structures, we also considered charged states with energy less than or nearly equal to that of a lower charged state under the condition that the Fermi energy is set to the VBT. For example, we adopted $X^{n+}$ as the energy of $X^{n+}$ is less than or nearly equal to that of $X^{n-1+}$ for positive integer $n$. Note that difference in the formation energy between charge states whose charges differ by one is equal to the transition level measured from the VBT.

For all the stable structures, we calculated the formation energy, the local potential shift ($\Delta V$) from the ideal 3C-SiC crystal at the vertex of the cubic supercells, XPSBE, the local potential average (LPA) around the atom from which the photoelectron is emitted, and the relaxation energy. The results for B and Al are summarized in Tables III and IV. The column “Removed/added” indicates where an electron is removed (added) when the charge state transits from the state in the upper row. For example, V for $B_{Si}$ means that an electron is added to the state in the valence band. Likewise, C for ($B_{Si}$-V)$_c$ and G for ($B_{C}$-V)$_Si$ mean that electrons are removed from the states in the conduction band and the band gap, respectively.

4.1. Formation energy

To discuss the energy stability of the defects, we introduce the formation energy ($E_f$) as follows:

$$E_f = E_{\text{tot}} - n_{Si} \mu_{Si} - n_{C} \mu_{C} - n_{X} \mu_{X} - n_{e} \mu_{e},$$

where $E_{\text{tot}}$ is the total energy of the system including a defect, $n_{Si}$, $n_{C}$, and $n_{X}$ (X = B, Al) are the numbers of atoms for each element, and $\mu_{Si}$, $\mu_{C}$, and $\mu_{X}$ are the chemical potentials for each element. $n_{e}$ is the number of electrons added to the neutral state. $\mu_{e}$ is the chemical potential of electrons. Considering that B and Al are p-type dopants in SiC, $\mu_{C}$ is set to the VBT corrected by $\Delta V$. Equation (1) can be rewritten as

$$E_f = E_{\text{tot}} - \frac{1}{2} \left( \mu_{Si} + \mu_{C} \right) \delta_{\text{Bulk}} - \frac{1}{2} \left( \mu_{Si} - \mu_{C} \right) \delta_{\text{Bulk}} + \Delta \mu,$$

$$= n_{X} \mu_{X} - n_{e} \mu_{e},$$

where $\mu_{Si} \delta_{\text{Bulk}}$, $\mu_{C} \delta_{\text{Bulk}}$, and $\Delta \mu$ are the chemical potentials of bulk 3C-SiC, Si, and diamond, respectively. These chemical potentials are approximated by the total energy. The relation $\mu_{Si} \delta_{\text{Bulk}} = \mu_{Si} + \mu_{C}$ holds in equilibrium. $\Delta \mu$ is a parameter of the stoichiometry of SiC and defined as

$$\mu_{Si} = \mu_{Si} \delta_{\text{Bulk}} + \frac{\Delta H_{f} - \Delta \mu}{2},$$

$$\mu_{C} = \mu_{C} \delta_{\text{Bulk}} + \frac{\Delta H_{f} + \Delta \mu}{2}.$$

$\Delta H_{f}$ is the formation enthalpy and defined as $\Delta H_{f} = \mu_{Si} \delta_{\text{Bulk}} - \mu_{Si} \delta_{\text{Bulk}} - \mu_{C} \delta_{\text{Bulk}}$. From the above relations and the conditions $\mu_{Si} \leq \mu_{Si} \delta_{\text{Bulk}}$ and $\mu_{C} \leq \mu_{C} \delta_{\text{Bulk}}$, the range of $\Delta \mu$ is limited to $-\Delta H_{f} \leq \Delta \mu \leq \Delta H_{f}$. The experimentally obtained value of the enthalpy is 0.7 eV$^{28}$ and the calculated value is 0.51 eV. The upper and lower limits of $\Delta \mu$ correspond to the Si-rich and C-rich limits, respectively. We adopt the total energies of $\alpha$-boron and metallic aluminum as the chemical potentials of the dopants, $\mu_{B}$ and $\mu_{Al}$, respectively.

First, we discuss the formation energies of B defects. The formation energies of $B_{C}$ and $B_{Si}$ are similar and $B_{C}$ is more stable than $B_{Si}$ under the condition $\Delta \mu = 0$ (midway between the Si-rich and C-rich conditions). The acceptor levels of $B_{C}$ and $B_{Si}$ are obtained as 0.24 and 0.07 eV, respectively, from the difference in the total energy between the charged and neutral states. $B_{Si}$ has a shallower acceptor level than $B_{C}$, which is in good agreement with a previous study. $^{29} (B_{Si}-V_{C})$ has a stable formation energy, similar to those of substitutional defects, and, in particular, is the most stable defect under the condition $\Delta \mu = 0$. This defect emits one electron, compensates acceptors, and decreases electrical activity. Reference 30 reported a similar result. Most of the other defects have much higher formation energies and occupy energy levels higher than the VBT in the neutral state. The most stable interstitial defect in the neutral state is $B_{H}$. In the 3+ charge state optimization, $B_{H}$ changes into $B_{TC}$, which returns to $B_{H}$ in the 2+ charge state optimization. On the other hand, although $\langle 100 \rangle (B-Si)_{Si}$ also changes into $B_{H}$ in the 2+ charge state optimization, $B_{H}$ does not return to $\langle 100 \rangle (B-Si)_{Si}$ in the 1+ charge state optimization.

For Al defects, it is shown in Table IV that Al in a Si substitutional site (Al$_{Si}$) is approximately 5–6 eV more stable...
The formation energy of B is XPS binding energy (XPSBE), local potential average (LPA), and B XPS relaxation energy (XPSRE) of B defects in 3C-SiC. \( \Delta \mu \) is the parameter of the stoichiometry of SiC. The Fermi energy is set to the valence band top and the chemical potential of B is set to the total energy of \( \alpha \)-boron. The origins of the XPSBE and LPA are that of B\(_{\alpha} \). \( \Delta V \) is the difference in the LPA around the atom at the vertex of the supercell between the system including a defect and the pure 3C-SiC crystal. The column “Removed/add” indicates the energy level where an electron is removed (added) when the charge state changes from that in the row immediately above to that in the present row. C, V, and G indicate the energy levels in the conduction band, valence band, and energy gap, respectively.

| Structure | Charged state | Formation energy (eV) | \( \Delta \mu = 0 \) | \( \Delta V \) (eV) | XPSBE (eV) | LPA (eV) | XPSRE (eV) | Removed /added |
|-----------|---------------|------------------------|-----------------|----------------|-----------|---------|---------|--------------|
| B\(_{\alpha} \) | 0              | 2.57                   | 2.31            | 2.06           | 0.00      | 0.00    | 0.00    | V            |
|            | 1–             | 2.64                   | 2.38            | 2.13           | 0.04      | 0.03    | 0.10    | –0.12        |
| B\(_C \)   | 0              | 1.98                   | 2.24            | 2.49           | 0.02      | –3.42   | 2.21    | 1.21         |
|            | 1–             | 2.22                   | 2.48            | 2.73           | 0.06      | –3.57   | 2.98    | 0.59         |
| B\(_{3v}–\) | 0              | 3.37                   | 3.37            | 3.37           | 0.04      | 0.33    | –1.00   | 0.67         |
| B\(_C–\)   | 0              | 2.04                   | 2.04            | 2.04           | 0.05      | 0.84    | –1.01   | 0.16         |
|            | 1+             | 7.52                   | 7.52            | 7.52           | 0.06      | –1.32   | 0.15    | 1.18         |
| B\(_{TSi} \) | 0              | 7.66                   | 7.66            | 7.66           | 0.04      | 1.23    | –3.96   | 2.72         |
|            | 1              | 6.33                   | 6.33            | 6.33           | 0.04      | 1.45    | –3.97   | 2.51         |
|            | 2+             | 5.97                   | 5.97            | 5.97           | 0.10      | 2.08    | –4.65   | 2.57         |
|            | 3+             | 5.64                   | 5.84            | 5.84           | 0.14      | 2.88    | –5.03   | 2.15         |
| B\(_{TC} \) | 0              | 6.00                   | 6.00            | 6.00           | 0.08      | 3.37    | –3.89   | 0.52         |
|            | 1+             | 4.74                   | 4.74            | 4.74           | 0.08      | 3.37    | –3.89   | 0.52         |
|            | 2+             | 3.59                   | 3.59            | 3.59           | 0.13      | 3.46    | –3.96   | 0.49         |
|            | 3+             | 2.49                   | 2.49            | 2.49           | 0.15      | 3.98    | –4.02   | 0.04         |
| B\(_H \)   | 0              | 5.63                   | 5.63            | 5.63           | 0.05      | 0.62    | –1.39   | 0.77         |
|            | 1+             | 4.32                   | 4.32            | 4.32           | 0.06      | 0.64    | –1.39   | 0.76         |
|            | 2+             | 3.50                   | 3.50            | 3.50           | 0.11      | 1.86    | –2.71   | 0.84         |
| \( \rightarrow \)B\(_{TC} \) | (110)/(B–)Si\(_{3s} \) | 0.63                   | 6.63            | 6.63           | 0.01      | –0.10   | –0.99   | 1.09         |
| (001)/(B–)Si\(_{3s} \) | 0              | 5.62                   | 5.62            | 5.62           | 0.06      | 0.51    | –1.57   | 1.06         |
| (110)/(B–)C\(_{3s} \) | 0              | 5.24                   | 5.24            | 5.24           | 0.11      | 0.88    | –2.19   | 1.31         |
| (001)/(B–)C\(_{3s} \) | 0              | 5.16                   | 5.16            | 5.16           | 0.15      | 1.26    | –2.59   | 1.33         |
| B\(_{3v}–\) | 0              | 6.08                   | 6.08            | 6.08           | 0.03      | –1.30   | 0.09    | 1.21         |
| B\(_3Si–\)TC | 0              | 5.43                   | 5.43            | 5.43           | 0.05      | –0.39   | –0.01   | 0.40         |
| B\(_{3v}–\)Si\(_{TSi} \) | 0              | 5.43                   | 5.43            | 5.43           | 0.05      | –0.39   | –0.01   | 0.40         |
| B\(_C–\)Si\(_{TSi} \) | 0              | 6.44                   | 6.44            | 6.44           | 0.11      | 1.64    | –2.06   | 0.42         |
| B\(_C–\)Si\(_{3s} \) | 0              | 5.29                   | 5.29            | 5.29           | 0.13      | 1.77    | –2.14   | 0.38         |
| B\(_C–\)Si\(_{TC} \) | 0              | 4.22                   | 4.22            | 4.22           | 0.16      | 2.10    | –2.21   | 0.11         |
| B\(_C–\)Si\(_{TSi} \) | 0              | 8.88                   | 9.39            | 9.90           | 0.05      | –1.66   | 1.03    | 0.63         |
| B\(_C–\)Si\(_{3s} \) | 0              | 7.57                   | 8.08            | 8.59           | 0.06      | –1.62   | 1.01    | 0.61         |
| B\(_C–\)C\(_H \) | 0              | 6.89                   | 7.40            | 7.91           | 0.11      | –1.40   | 0.82    | 0.58         |
|            | 2+             | 6.39                   | 6.90            | 7.41           | 0.16      | –1.15   | 0.60    | 0.55         |
|            | 3+             | 6.45                   | 6.45            | 6.45           | 0.05      | –1.36   | 0.87    | 0.48         |
| B\(_C–\)C\(_H \) | 0              | 6.25                   | 6.25            | 6.25           | 0.10      | –1.10   | 0.41    | 0.69         |
|            | 3+             | 5.94                   | 5.94            | 5.94           | 0.14      | –0.63   | –0.05   | 0.68         |

than that in a C substitutional site. Al\(_{3s} \) has an acceptor level of 0.09 eV and Al\(_C \) has deep levels occupied by electrons, which compensate acceptors. The formation energy of (Al\(_{3v}–\)V\(_C \))^\(^{-3}\), which compensates acceptors, is relatively low and similar to that of (B\(_{3v}–\)V\(_C \))^\(^{-3}\), but it is higher than that of Al\(_{3s} \) in a wide range of \( \Delta \mu \). This might be one of the reasons why Al is a more favorable \( p \)-type dopant in SiC than B. As shown in Table II, Al\(_C–\)V\(_C \) is unstable. In the optimization, Al of Al\(_{C–}\)V\(_{3s} \) moves into the Si vacancy site and changes into Al\(_{3s}–\)V\(_C \). In the case of Al, only two split intermediates in the Si substitutional site [(110)/(Al–)Si\(_{3s} \) and (001)/(Al–)C\(_{3s} \)] are stable, and all those in the C site are not stable. It is considered that the reason why Al has a smaller variety of structures than B is that the atomic size of Al is larger than that of B.
Table IV. Formation energy, Al 2p XPS binding energy (XPSBE), local potential average (LPA), and Al 2p XPS relaxation energy (XPSRE) of Al defects in 3C-SiC. $\Delta \mu$ is the parameter of the stoichiometry of SiC. The Fermi energy is set to the valence band top and the chemical potential of Al is set to the total energy of metallic aluminum. The origins of the XPSBE and LPA are that of $\Delta \mu$. $\Delta V$ is the difference in the LPA around the atom at the vertex of the supercell between the system including a defect and the pure 3C-SiC crystal. The column “Removed/added” indicates the energy level where an electron is removed (added) when the charge state changes from that in the row immediately above to that in the present row. C, V, and G indicate the energy levels in the conduction band, valence band, and energy gap, respectively.

| Structure | Charged state | Formation energy (eV) | $\Delta V$ (eV) | XPSBE (eV) | LPA (eV) | XPSRE (eV) | Removed/added |
|-----------|--------------|-----------------------|----------------|------------|----------|-------------|---------------|
| SiTSi     | 0            | 1.87                  | -0.04          | 0.00       | 0.00     | 0.00        | V             |
|           | 1-           | 1.96                  | -0.05          | 0.00       | 0.14     | -0.14       |               |
|           | 1+           | 6.94                  | -1.40          | -0.04      | 1.44     |              |               |
|           | 2+           | 6.22                  | -0.64          | -0.86      | 1.50     |              |               |
|           | 3+           | 5.68                  | 0.56           | -2.20      | 1.64     |              |               |
| Al$_{2}^{+}$V$_{C}$ | 0          | 3.28                  | 1.14           | -1.14      | 0.00     |              |               |
|           | 1+           | 1.94                  | -1.14          | -0.33      | 0.00     |              |               |
| AlTSi     | 0            | 8.26                  | 2.16           | -3.17      | 1.01     |              |               |
|           | 1+           | 7.03                  | 2.16           | -3.22      | 1.06     |              |               |
|           | 2+           | 5.89                  | 2.16           | -3.30      | 0.74     |              |               |
|           | 3+           | 4.82                  | 2.33           | -3.43      | 0.21     |              |               |
| Al$_{2}^{+}$SiTSi | 0          | 6.12                  | 2.28           | -2.76      | 0.47     |              |               |
|           | 1+           | 4.88                  | 2.39           | -2.81      | 0.43     |              |               |
|           | 2+           | 3.76                  | 2.53           | -2.89      | 0.36     |              |               |
|           | 3+           | 2.69                  | 2.76           | -3.00      | 0.24     |              |               |

\[
\begin{align*}
(110)/&(Al-Si)$_{3}\mu \quad 0 &\quad 8.00 &\quad 8.00 &\quad 8.00 &\quad 0.05 &\quad 1.64 &\quad -2.40 &\quad 0.77 &\quad C \\
1+ &\quad 6.70 &\quad 6.70 &\quad 6.70 &\quad 0.06 &\quad 2.21 &\quad -2.46 &\quad 0.25 &\quad C \\
2+ &\quad 6.05 &\quad 6.05 &\quad 6.05 &\quad 0.11 &\quad 2.54 &\quad -2.74 &\quad 0.19 &\quad G \\
3+ &\quad 4.81 &\quad 4.81 &\quad 4.81 &\quad 0.15 &\quad 3.21 &\quad -3.42 &\quad 0.20 &\quad G \\
(001)/&(Al-C)$_{3}\mu \quad 0 &\quad 8.00 &\quad 7.49 &\quad 6.98 &\quad 0.02 &\quad 0.74 &\quad -1.15 &\quad 0.41 &\quad C \\
1+ &\quad 6.80 &\quad 6.29 &\quad 5.78 &\quad 0.05 &\quad 1.11 &\quad -1.34 &\quad 0.23 &\quad G \\
2+ &\quad 6.55 &\quad 6.04 &\quad 5.53 &\quad 0.10 &\quad 1.63 &\quad -2.03 &\quad 0.40 &\quad G \\
3+ &\quad 6.42 &\quad 5.91 &\quad 5.40 &\quad 0.16 &\quad 2.45 &\quad -2.53 &\quad 0.08 &\quad G \\
Al$_{2}^{+}$SiTSi | 0          | 8.63                  | 1.94           | -2.30      | 0.35     |              |               |
|           | 1+           | 7.33                  | 2.03           | -2.32      | 0.30     |              |               |
|           | 2+           | 6.70                  | 2.26           | -2.42      | 0.16     |              |               |
|           | 3+           | 6.21                  | 2.53           | -2.50      | -0.03    |              |               |
| Al$_{2}^{+}$SiTC | 0          | 7.28                  | 1.45           | -1.53      | 0.09     |              |               |
|           | 1+           | 6.08                  | 1.53           | -1.58      | 0.05     |              |               |
|           | 2+           | 4.95                  | 1.65           | -2.03      | 0.00     |              |               |
|           | 3+           | 3.92                  | 1.75           | -2.15      | -0.08    |              |               |
| Al$_{2}^{+}$CTSi | 0          | 8.52                  | 1.85           | -2.27      | 0.40     |              |               |
|           | 1+           | 7.20                  | 2.14           | -2.29      | 0.14     |              |               |
| Al$_{2}^{+}$CCTS | 0          | 13.84                 | -0.73          | -0.58      | 1.31     |              |               |
|           | 1+           | 12.53                 | -0.68          | -0.60      | 1.28     |              |               |
|           | 2+           | 11.91                 | -0.48          | -0.77      | 1.25     |              |               |
|           | 3+           | 11.44                 | -0.23          | -0.97      | 1.20     |              |               |
| Al$_{2}^{+}$SiTC | 0          | 12.04                 | -0.00          | 1.33       | 1.33     |              |               |
|           | 1+           | 10.83                 | 0.12           | 1.36       | 1.24     |              |               |
|           | 2+           | 9.68                  | 0.16           | 1.46       | 1.15     |              |               |
|           | 3+           | 8.61                  | 0.31           | 1.46       | 1.15     |              |               |
| Al$_{2}^{+}$CH | 0          | 8.28                  | 1.30           | -1.26      | -0.04    |              |               |
|           | 1+           | 6.96                  | 1.36           | -1.27      | -0.09    |              |               |
|           | 2+           | 6.88                  | 1.36           | -1.60      | -0.04    |              |               |
|           | 3+           | 6.76                  | 1.88           | -1.82      | -0.05    |              |               |

4.2. X-ray photoelectron spectroscopy binding energy

Before discussing the results, we introduce the XPSBE of core electrons and related quantities. As a naive interpretation, XPS spectra reflect the depth of the eigenenergies of photoelectrons before emission, in other words, the depth of the potential. However, it is well-known that the relaxation energy, which is the reduction in energy caused by the relaxation of wavefunctions due to core holes remaining after photoelectron emission, makes a non-negligible contribution. Therefore, in this study, we separate the XPSBE ($E_{\text{XPS}}$) into the energy of the core electron before its emission and the relaxation energy. In Hartree–Fock theory, the removal energy of a core electron without the relaxation of the remaining electrons is the negative of the eigenenergy ($\epsilon_{\text{core}}^{\text{HF}}$) of the core electron. Thus, we can clearly define the relaxation energy as $E_{\text{relax}} = -\epsilon_{\text{core}}^{\text{HF}} - E_{\text{XPS}}$. However, since such a relation for the removal energy without relaxation does not exist in DFT, we adopt the spatial average of the local potential ($\bar{V}_{\text{loc}}$) around the atom before photoelectron emission. We use the approximation $\Delta \bar{V}_{\text{loc}} \approx \Delta \bar{V}_{\text{loc}}$, where $\Delta$ indicates that all values to be discussed are relative to that of the reference defect. Here, it is expected that the remaining contributions to the eigenenergy such as the kinetic energy...
and exchange correlation energy will cancel. Assuming that the change in the potential within the core region is constant, the above approximation will be valid. We can define the relative relaxation energy $E_{\text{relax}, \text{DFT}}$ of the originating XPS energy $E_{\text{DFT}}$ as 

$$E_{\text{relax}, \text{DFT}} = E_{\text{DFT}} - E_{\text{loc}}^\text{bind}.$$ 

The spatial average around the atom was calculated within a sphere of radius $R_c$, which was set to the double the peak position of the radial distribution function, $4\pi r^2 \psi^2(r)$, of the core electron in an isolated atom. For B $1$s and Al $2p$, $R_c$ is 0.44 and 0.86 Bohr, respectively.

The XPSBE, LPA and XPS relaxation energy (XPSRE) of B and Al defects in SiC are summarized in Tables III and IV, respectively. The reference defects used for the energies of B and Al were set to B$_{\text{Si}}$ and Al$_{\text{Si}}$, respectively. From the tables, we can derive some characteristics for the LPA. Considering the different charge states of the same defect, the LPA is decreased and increased, when an electron is removed and added, respectively. If C or V is in the column “Removed/added”, then the change in the LPA is small since the electron is removed from or added to the spread orbital. In contrast, if G in the column, the change in the LPA becomes large since the electron is removed from or added to the orbital localized around the impurity.

Figures 3(a) and 3(b) show the relationship between the XPS level $\varepsilon_{\text{XPS}}$ and the LPA for B and Al defects in 3C-SiC, respectively. The XPS level is defined as the negative value of the XPS binding energy. The origins of the XPS levels and LPA are set to those of B$_{\text{Si}}$, Al$_{\text{Si}}$, and substitutional B (B$_s$) for B in 3C-SiC, Al in 3C-SiC, and B in Si, respectively. The XPS relaxation energy measured from that of the reference defects corresponds to the vertical shift from the diagonal line.

Fig. 3. Relationship between the XPS level and the local potential average (LPA) for (a) B defects in 3C-SiC, (b) Al defects in 3C-SiC, and (c) B defects in Si. The results for all calculated defect models are shown for 3C-SiC and those of some characteristic defects are indicated. The XPS level is the negative value of the XPS binding energy. The origins of the XPS levels and LPA are set to those of B$_{\text{Si}}$, Al$_{\text{Si}}$, and substitutional B (B$_s$) for B in 3C-SiC, Al in 3C-SiC, and B in Si, respectively. The XPS relaxation energy measured from that of the reference defects corresponds to the vertical shift from the diagonal line.
energies. It is considered that the electronic structures of substitutional sites are similar to that of the pure crystal; thus, the rearrangement of electrons caused by core electron emission is small. Actually, the XPSRE slightly decreases when the valence band of the substitutional model is filled by an ionization to the −1 charged state. As will be mentioned below, it is also the reason for the small relaxation energy that the reference defects do not have orbitals localized around the impurity.

Thus, let us compare B defects in the compound semiconductor 3C-SiC [Fig. 3(a)] and B in the Si monoelemental semiconductor [Fig. 3(c)]. Whereas the range of the LPA is around 4 eV in Si, that in SiC is extended to around 9 eV. Since SiC is constituted of two different elements and has ionic bonding, the variation of the local potential in SiC is larger than that in Si.

Investigating the LPA and XPSRE in detail, we found that the electrons localized around the impurity before and after photoelectron emission have a significant effect on the LPA and XPSRE. The occupation of the spread orbital does not have a large effect on the LPA, and the core hole remaining after the emission has a small effect on the spread electrons. On the other hand, localized electrons have a large effect on the LPA, and the core hole has a large relaxation effect on the localized electrons.

In the following, we give some characteristic examples of the effect on the XPSRE.

B\textsubscript{H} has two localized electrons in the band gap and one electron in the conduction band. Figure 4(a) shows the density of states (DOS) for pure 3C-SiC crystal and the projected DOS (PDOS) for B\textsubscript{H} around the band gap. The upper and lower panels represent the DOS before and after B 1s core electron emission, respectively. The red and blue lines refer to the DOS of 3C-SiC and the PDOS on B atoms, respectively. The filled region denotes the occupation by electrons. The PDOS in the conduction band is not filled, which means that the electron in the conduction band has a small amplitude around the B atom. Thus, the LPA of B\textsubscript{H} is hardly changed from that of the neutral state. For B\textsubscript{H}\textsuperscript{2+}, the localized electron is removed from B\textsubscript{H}; thus, the LPA and XPSRE are significantly changed.

Localized electrons have a small effect on the XPSRE when they have a small amplitude around the impurity atom. The localized electrons of B\textsubscript{C}–Si\textsubscript{Si} have a large amplitude around Si\textsubscript{Si}, but not around B\textsubscript{C}. Consequently, the XPSREs of B\textsubscript{C}–Si\textsubscript{Si} with 2+ and 3+ charged states are not changed.

Figure 4(b) shows the DOS of ⟨001⟩(B–C)\textsubscript{C} around the band gap. Before photoelectron emission from B 1s, there is an electron in the conduction band and no states in the band gap. After photoelectron emission, the conduction band electron transfers to the localized states newly generated by the core hole in the band gap. This electron transfer makes a large contribution to the XPSRE. As a result, whereas the LPAs of ⟨001⟩(B–C)\textsubscript{C} and ⟨001⟩(B–C)\textsubscript{C} are similar, their XPSREs are considerably different.

The XPSBE and LPA in B\textsubscript{C} are markedly different from those in B\textsubscript{Si}. B\textsubscript{C} attracts electrons from nearest-neighbor Si atoms; thus, the core-level becomes shallower and the XPSBE becomes small. These two defects act as acceptors in SiC and receive an electron. Receiving an electron, the two substitutional defects with the −1 charge state, whose valence bands are filled up and difficult to rearrange by applying an external potential, exhibit smaller XPSREs than those in the neutral state.

Different from Si, SiC is a compound semiconductor with an energy gap region in the valence band. Some impurity defects form localized levels, which affect the XPSRE, in this region before and/or after the photoelectron emission. B\textsubscript{Si} does not have levels in the gap region both before and after emission. B\textsubscript{C} has a localized level in this region after emitting a core electron, which explains its much larger XPSRE than that of B\textsubscript{Si}.

From the above-mentioned analysis, we find some trends of the relaxation energy as follows. Defect structures with localized electrons before photoelectron emission have a large XPSRE. If the defects have no localized electrons before the emission, the defects have a large XPSRE, when they have localized electrons after the emission. On the other hand, a structure with a valence band that is not fully occupied sometimes has a relatively large XPSRE. The defects with a fully occupied valence band and no occupied localized levels before and after photoelectron emission have a small XPSRE. Conduction band electrons whose amplitude is extended and remote from the core hole remaining after the emission tend to have a small XPSRE.
Fig. 5. (Color online) Projected density of states (PDOS) of AlC. The horizontal axis is the energy level and the origin of the energy is set to the valence band top. The vertical axis is the DOS. Blue and green lines are the PDOS on Al 3s and 3p states, respectively. The filled region implies that the states are occupied by electrons. For comparison, red lines show the total DOS of pure 3C-SiC. The scales of the total and partial DOS are different.

We can discuss the LPA and XPSRE for Al in 3C-SiC in a similar manner to those for B. AlC shows the most characteristic feature among Al defects. Although this defect is a substitutional one, in the neutral state it has five electrons in the band gap levels. These orbitals are triply degenerated and mainly composed of Al 3p orbitals. Figure 5 shows the PDOS of AlC on Al 3s and 3p. The origin of the deep levels occupied by five electrons may be shallow Al 3p eigenenergy. We calculated isolated Al and B atoms and found that the eigenvalue of Al 3p is higher than that of B 2p by 0.89 eV. Fukumoto reported that AlC formed deep acceptor level, the ionization energy of which is 1.13 eV.29) Fukumoto used small supercells of 32 and 64 atoms, which cause large dispersion. Thus, probably, the occupied deep levels were not identified. We calculated the above ionization energy as 1.07 eV, which is not shown in Tables IV.

At the end of this section, we mention the observable XPS spectra for B and Al defects in 3C-SiC. Some defects have a very high formation energy; thus, we do not consider that the spectra of all defects will be found. According to the formation energy, B_{Si}, B_{C}, (B_{Si}–V_{C})^{–}, and B_{C}^{+} are expected to be observed, whose relative XPSBEs are 0.0, −3.42, 0.84 and 3.98 eV, respectively. On the other hand, the experimental spectra of B 1s are reported as 188.7 and 188.9 eV for SiC powder, whose polytypes are not described,31) 189.7 eV for 6H-SiC, which suggests B–C bond,32) and 187.6 eV for 3C-SiC films, which suggests B–Si bond.33) Correspondence between such experimental spectra and the present calculation is not clear. A possible reason is that the polytypes of SiC are different in each experiment and the conditions of the chemical potential are not clear.

For Al in 3C-SiC, it is expected that the peaks of Al_{Si} and (Al_{Si}–V_{C})^{+}, which have relatively low formation energies, can be observed 1.16 eV apart from each other. Oswald et al. reported that XPS spectra of Al 2p in 6H-SiC are observed at 74.4 and 73.9 eV for as-implanted and annealed samples. Assuming that 3C- and 6H-SiC have similar defect properties, and that the peak of the annealed sample is due to energetically stable defect Al_{Si}, the candidates for the peak of the as-implanted sample are the defects with XPSBE near +0.5 eV such as AlC^{3+} (0.56 eV), (001)(Al–C)_{Si} (0.74 eV), and (AlC–SiC)_{Si}^{3+} (0.31 eV), where the figures in parentheses are XPSBE shift.

5. Summary

We systematically investigated the core-level XPSBE shifts and formation energies for defects including B and Al in 3C-SiC by first-principles calculation, and predicted the observable peaks of the defects. To analyze the relation between the XPSBE shift and the defect state, we separated the XPSBEs into the depth of the core-level (the LPA around the impurity) and the relaxation energy of the wave function caused by the emission of the photoelectron. It was found that the defects with localized electrons in the band gap or energy gap in the valence band have larger XPSBEs than those without localized electrons. The localized electrons before or after photoelectron emission make a large contribution to the XPSBEs. On the other hand, spread electrons and electrons localized away from impurities make a much smaller contribution. It was found that such localized electrons also have a large effect on the LPA.

Further, we compared the XPS spectra of B and Al in SiC and B in Si to analyze the dependence on crystal matrices, that is, elemental and compound semiconductors. The variation of the local potential of SiC is larger than that of Si since SiC has two different elements and ionic bonding. However, it was found that the ranges of the XPSBEs of B in SiC and Si were comparable.

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