First-principles calculation of X-ray photoelectron spectroscopy binding energy shift for nitrogen and phosphorus defects in 3C-silicon carbide

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We systematically investigated the formation energies and the core-level X-ray photoelectron spectroscopy binding energy (XPSBE) shifts of nitrogen (N) 1s and phosphorus (P) 2p for defects including N and P in 3C-SiC by a first-principles calculation using the generalized gradient approximation, whose reliability for n-type defects was confirmed by some tests using the HSE06 hybrid functional. XPSBEs were separated into the local potential average around the impurity and the relaxation energy of the wave function to analyze the relationship between the XPSBE shift and the defect structures. It is difficult to understand the relaxation energy intuitively. The electrons localized around the impurity atom, which have energy levels in energy gaps, make a large contribution to the relaxation energies. Considering the formation energies, we predicted some XPS peaks expected to be found.

1. Introduction
Silicon carbide (SiC) is a wide-band-gap semiconductor with high thermal conductivity and high breakdown voltage. SiC has various one-dimensional stacking sequences of Si-C pairs, called polytypes. Each polytype has different physical properties, such as the band gap and mobility of carriers. Among the over 200 kinds of polytypes, the most attractive properties, such as the band gap and mobility of carriers, pairs, called polytypes. Each polytype has different physical properties, such as the band gap and mobility of carriers. Among the over 200 kinds of polytypes, the most attractive

Generally, it is difficult to identify the structures of lattice defects in solids. There are two reasons for this difficulty. First, direct measurement of configurations is very difficult. Therefore, theoretical calculations are required. Second, the spectrum peaks from the defect of interest are weak since the amount of impurities in the crystal is quite small and the amount of impurity defects is even smaller. Recently, large synchrotron radiation facilities have enabled the measurement of core-level XPS of boron (B), P, and arsenic (As) in Si by using a high beam intensity to compensate for the weak signal. On the other hand, few reliable XPS calculations have been reported for defects. This is because reliable XPS calculations for defect models require large supercells to guarantee the convergence of binding energy.

We previously reported the XPSBE of p-type dopants B and aluminum (Al) in 3C-SiC. The XPSBE can be divided into two parts: the local potential contribution and the XPS relaxation energy (XPSRE). We analyzed them individually and found that the defects with localized electrons in the band gap or energy gap in the valence band have larger XPSRE than those without localized electrons. It is also found that the localized electrons after as well as before the photoelectron emission make a large contribution to the XPSBE, since large rearrangement of the electronic structure occurs after the electron emission. In contrast, spread electrons and electrons localized away from the core hole make a small contribution to the XPSBEs.

In this paper, we predict the XPSBE shifts of N 1s and P 2p for the defects in 3C-SiC and investigate the relationship between the XPS spectra and defects of n-type dopants in 3C-SiC. As a naive interpretation, the XPS spectra reflect the energy levels of the electrons before photoemission, that is, the potential to which the electrons are subjected. It is indicated by first-principles calculations that the relaxation of wavefunctions caused by the core hole remaining after photoelectron emission makes a large contribution to the XPS spectra. 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.\(^\text{15}\) The calculation code is xTAPP,\(^\text{16}\) which is a highly parallelized version of the plane-wave-based code TAPP (Tokyo ab initio program package).\(^\text{17}\) The interactions between ions and electrons are described by the norm-conserving pseudopotentials for Si and P\(^\text{18}\) and the ultrasoft pseudopotentials for N and carbon (C).\(^\text{19}\) 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 XPS binding energies.\(^\text{20}\) The atomic configurations are fully optimized for the total energy with a force criterion of less than \(1 \times 10^{-3}\) Hartree/Bohr. The calculated lattice constant is 4.37 Å and the experimental value is 4.3596 Å.\(^\text{21}\) The calculated band gap is 1.37 eV, which is much smaller than the experimental value of 2.417 eV,\(^\text{22}\) which is a well-known problem in the GGA.

For the core-level XPS calculation, we adopted the \(\Delta\)SCF method with screened core hole pseudopotentials (SCHPs).\(^\text{14}\) In the \(\Delta\)SCF method, the XPS binding energy 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. To evaluate the accuracy for the SCHPs, we calculated the relative XPS binding energies of N 1s and P 2p in some molecules, which are summarized in Table I. The experimental data are from Ref. 23. These calculations were performed using a cubic supercell with an edge of 8.4 nm. The difference between the calculated and experimental data is about 0.2 eV except for N\(_2\)O. Similar accuracy is expected in the present work.

There is a strong supercell size dependence in the XPS binding energy calculation, and the evaluation of the supercell size is important to obtain reliable values.\(^\text{24―26}\) Figure 1 shows the supercell size dependence of the XPS binding energy shifts of N 1s and P 2p for various 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 XPS binding energy 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.\(^\text{27}\) However, although the correction gives very accurate results for atoms and molecules, the correction is overestimated for the calculation of defects.\(^\text{28,29}\) In this study, we did not correct for charged states because we used relatively large supercells and obtained satisfactory convergence of the formation energies as shown above.

It is important to reproduce the band gap and electronic structure when the n-type impurity defects in semiconductors are calculated since they often have energy levels in the conduction band or in higher positions in the band gap. In particular, the localized orbitals in the band gap strongly affect the XPSBE. Therefore, it is necessary to confirm the reliability of the GGA PBE96, which underestimates the band gap. Hence, we performed test calculations using the HSE06 hybrid functional,\(^\text{30―32}\) which reproduces the band gap much more closely. The band gap calculated using HSE06 is 2.20 eV, which shows better agreement with the experimental value, 2.417 eV, than that calculated using PBE96, 1.37 eV. It is reported that the pseudopotentials generated with a conventional exchange correlation functional such as PBE96 can be adopted for the calculations using hybrid functionals.\(^\text{33}\) However, it is unclear whether the SCHPs can be adopted for the XPS calculations using the hybrid functionals. For this reason, we performed test calculations of the SCHPs using HSE06 in the molecular systems. After that, we compared PBE96 and HSE06 for the defects in 3C-SiC. In these test calculations, owing to the limitation of the code xTAPP for hybrid functionals, the norm-conserving pseudopotentials were used for all elements with a cutoff energy of 64 Rydberg in both HSE06 and PBE96 calculations.

For the same molecules as in Table I, the XPS binding energies calculated using PBE96 and HSE06, and the experimental values are summarized in Table II. Owing to the computational cost of HSE06, a smaller supercell with an edge of 2.1 nm was used. It was found that, for all molecular species, HSE06 reproduces the experimental values more closely than PBE96. However, the differences are approximately only a few percent except for N\(_2\)O, and PBE96 has sufficient reliability.

Table I. Relative XPSBE (eV) of N 1s and P 2p for some molecules. For nitrous oxide (N\(_2\)O), the XPS binding energies are calculated for the N atom with an asterisk in the molecular formula. Experimental data are from Ref. 23.

|                | Calc. | Exp. |                | Calc. | Exp. |
|----------------|-------|------|----------------|-------|------|
| N\(_1\)        | 0.00  | 0.0  | PF\(_1\)       | 0.00  | 0.0  |
| N\(_{2}\)      | 4.52  | 4.3  | PH\(_3\)       | 4.53  | 4.7  |
| N\(_{2}\)O     | 1.23  | 1.3  | PF\(_3\)       | 2.24  | 2.6  |
| NN\(_{2}\)O    | 2.32  | 2.6  | POF\(_3\)      | 1.20  | 1.2  |

Fig. 1. Dependence of the XPS binding energy shift of N 1s (a) and P 2p (b) in 3C-SiC on the supercell size. The horizontal axis refers to the number of atoms in each supercell. N\(_C\) and P\(_S\) are the energy reference for each supercell size. The circles, squares, triangles, and inverted triangles indicate X\(_{Si}\), X\(_{C}\), X\(_{SiO}\), and X\(_{C}\), respectively. The data points of P\(_{Si}\) and P\(_{C}\) completely overlap. For the notation of the defect types, see Sect. 3.
Table II. Relative XPS binding energies (eV) calculated using PBE06 and HSE06 for molecules. The binding energies of N 1s and P 2p were calculated for the same molecules as in Table I. For both functionals the norm-conserving pseudopotentials were used for all elements and the cutoff energy was 64 Rydberg. The calculations were performed in a cubic supercell with an edge of 2.1 nm, which is smaller than that in Table I owing to the computational cost of HSE06. Experimental data are from Ref. 23.

|            | PBE06 | HSE06 | Exp. |            | PBE06 | HSE06 | Exp. |
|------------|-------|-------|------|------------|-------|-------|------|
| N₂         | 0.00  | 0.00  | 0.0  | PF₃        | 0.00  | 0.00  | 0.0  |
| NH₃        | −4.19 | −4.32 | −4.3 | PH₃        | −4.20 | −4.44 | −4.7 |
| N’NO       | −1.40 | −1.27 | −1.3 | PF₃        | 2.36  | 2.52  | 2.6  |
| NN’O       | 2.29  | 2.79  | 2.6  | POF₃       | 1.10  | 1.17  | 1.2  |

Table III. Relative XPS binding energies (eV) of N 1s and P 2p for defects in 3C-SiC calculated using PBE06 and HSE06. N and P defects with relatively low formation energies were calculated using PBE06 (see Tables V and VI). For both functionals, the norm-conserving pseudopotentials were used for all elements and the cutoff energy was 64 Rydberg. The calculations were performed in a 216-atom supercell, which is smaller than those in Tables V and VI owing to the computational cost of HSE06.

|            | PBE06 | HSE06 | PBE06 | HSE06 |
|------------|-------|-------|-------|-------|
| N₅Si       | 2.30  | 2.23  | P₅Si  | 0.00  | 0.00  |
| NₛC        | 0.00  | 0.00  | PₛC   | −2.80 | −2.88 |
| NₛC-VₛSi   | −1.24 | −1.36 | PₛC-VₛSi | −1.83 | −1.92 |
| (001)(N-C)₅ | −1.57 | −1.79 | (001)(P-C)₅ | −1.93 | −2.12 |

HSE06. As test samples, we performed calculations for two substitutional defects: a vacancy-related defect and one with a relatively low formation energy as shown below. It was found that the calculated values agree within 10% for both functionals.

3. Models

In this section, we describe the defect models in the present study. The models are classified into five types.

First, an impurity atom is substituted at a lattice site. In SiC, Si and C are substituted and represented by X₅Si and X₅C, respectively, where X denotes the impurity element. Generally, this kind of defect is electrically active and stable in semiconductors.

Second, 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 tetrahedrally surrounded by four lattice sites of the same element. X₅TSi and X₅TC 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 X₅H.

Third, a pair of impurity and crystal atoms is located at a single lattice site. Such a defect is 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)₅Si. 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 X₅ is located at the bond center; this configuration is denoted as X₅C.

Fourth, an impurity atom is substituted at the nearest-neighbor site of a vacancy. This model has two variations: the impurity atom is substituted for a Si atom next to a C vacancy, X₅V₅C, or substituted for a C atom next to a Si vacancy, X₅V₅Si. Here, V denotes a vacancy.

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 X₅Si-T₅Si. We calculated the twelve models corresponding to the combinations of Si and C sites for X, and T₅Si, T₅C, and H sites for Si and C.

Figure 2 shows the optimized structures for some representative N defect models. In addition, some structures of the P defect model, which are not stable for N in 3C-SiC, are shown. To draw these figures, we used VESTA. Similar structures were obtained upon swapping N with P 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.

4. Results and discussion

For the charge-neutral states, the results of optimizing the structures introduced in Sect. 3 are summarized in Table IV, where “&” indicates that two defects exist apart from each other. The configurations including “&” are not considered, because these models are beyond the scope mentioned in the previous section. 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 the neutral state under the condition that the Fermi energy is set to the CBM. For substitutional defects, we examined the +1 charged state. For the defects with empty states below the CBM, we examined the electron-added states. For the defects with electrons close to the CBM, the ±1 charged states were considered. In such a case, the charged states show very similar formation energies, since the relevant electronic states are close to the Fermi energy (CBM) and widely spread in real space. Note that the difference in the formation energy between charged states whose charges differ by one is equal to the transition level measured from the CBM.

For all the stable structures, we calculated the formation energy, the local potential shift (ΔV) from the ideal 3C-SiC crystal at the vertex of the cubic supercells, the XPSBE, the local potential average (LPA) around the atom from which the photoelectron is emitted, and the relaxation energy. The results for N and P are summarized in Tables V and VI, respectively.

4.1. Formation energy

To discuss the energy stability of the defects, we introduce the formation energy (Eₙ) as follows:28,35

$$E_f = E_{tot} - n_{Si}μ_{Si} - n_{C}μ_{C} - n_{X}μ_{X} - n_{e}(μ_{e} + ΔV),$$  

(1)
Fig. 2. (Color online) Optimized structures of N and P defects in 3C-SiC. Yellow, gray, blue and pink spheres represent Si, C, N, and P, respectively. The horizontal direction is [110] and the vertical direction is [001]. See Sect. 3 for the abbreviations of the defect structures.
Table IV. Result of structure optimization of N and P impurities in SiC. X represents the symbol of impurities.

| Initial | N     | P     |
|---------|-------|-------|
| $X_{\text{Si}}$ | $N_{\text{Si}}$ | $P_{\text{Si}}$ |
| $X_{\text{C}}$ | $N_{\text{C}}$ | $P_{\text{C}}$ |
| $X_{\text{SiSi}}$ | $N_{\text{SiSi}}$ | $P_{\text{SiSi}}$ |
| $X_{\text{C}}$ | (001)$N_{\text{(C-C)}}$ | $P_{\text{C}}$ |
| $X_{\text{Si}}$ | (001)$N_{\text{(C-C)}}$ | $P_{\text{H}}$ |

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

$$E_f = E_{\text{tot}} - \frac{1}{2}(n_{\text{Si}} + n_{\text{C}})\mu_{\text{SiC}}^{\text{Bulk}} - \frac{1}{2}(n_{\text{Si}} - n_{\text{C}})(\mu_{\text{Si}}^{\text{Bulk}} - \mu_{\text{C}}^{\text{Bulk}} + \Delta \mu) - n_{\text{e}}\mu_{\text{e}} - n_{\text{e}}\mu_{\text{e}},$$

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

$$\mu_{\text{Si}} = \mu_{\text{Si}}^{\text{Bulk}} + \frac{\Delta H_f - \Delta \mu}{2},$$

$$\mu_{\text{C}} = \mu_{\text{C}}^{\text{Bulk}} + \frac{\Delta H_f + \Delta \mu}{2},$$

$\Delta H_f$ is the formation enthalpy and defined as $\Delta H_f = \mu_{\text{SiC}}^{\text{Bulk}} - \mu_{\text{Si}}^{\text{Bulk}} - \mu_{\text{C}}^{\text{Bulk}}$. From the above relations and the conditions $\mu_{\text{Si}} \leq \mu_{\text{Si}}^{\text{Bulk}}$ and $\mu_{\text{C}} \leq \mu_{\text{C}}^{\text{Bulk}}$, the range of $\Delta \mu$ is limited to $-\Delta H_f < \Delta \mu < \Delta H_f$. The experimentally obtained value of the enthalpy is 0.7 eV$^36$ 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. It is noted that the formation energies do not depend on $\Delta \mu$ under $n_{\text{Si}} = n_{\text{C}}$. We adopt the total energies of an isolated N$_2$ molecule and black phosphorus as the chemical potentials of the dopants, $\mu_{\text{N}}$ and $\mu_{\text{P}}$, respectively.

First, we discuss the formation energies of N defects. From Table V, it is found that N$_C$ has negative formation energy and is more stable than almost any other N defect including N$_{\text{Si}}$. The saturation of carriers occurs at a lower concentration of N atoms than of P atoms. This implies the formation of electrically inactive complexes containing N, which are more stable than N$_C$. According to the first-principles calculation by Ref. 37, more complexes of 4N$_C$-V$_{\text{Si}}$ than N$_{\text{Si}}$ defects are formed above a critical N concentration. 4N$_C$-V$_{\text{Si}}$ is electrically inactive and does not generate any carriers. As shown in the table, we also confirmed that 4N$_C$-V$_{\text{Si}}$ is very stable and inactive. The reason why 4N$_C$-V$_{\text{Si}}$ is very stable is that all the dangling bonds of C next to V$_{\text{Si}}$ are terminated by the substitution of N for C. Furthermore, 4N$_C$-V$_{\text{Si}}$ seems to have a similar structure to the stable compound $\alpha$-Si$_2$N$_3$. Many N$_C$ pairs, especially (001)(N-C)$_C$, are obtained as a result of total energy optimization. Reference 38 found by first-principles calculation that a (N-C)$_C$ pair diffuses in SiC and forms a N$_C$-V$_{\text{Si}}$ pair by meeting V$_{\text{Si}}$.

For P defects, the calculated results are summarized in Table VI. The donor levels of both P$_{\text{Si}}$ and P$_{\text{C}}$ are almost the same as 0.06 eV. Although P$_{\text{Si}}$ is more stable than P$_{\text{C}}$, the difference in formation energy between the two substitutional defects is much smaller than that in the case of N, which suggests that both P$_{\text{Si}}$ and P$_{\text{C}}$ may coexist, especially under a Si-rich condition. However, Greulich-Weber reported that only P$_{\text{Si}}$ was observed by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) measurements.$^{39)}$ The reason for this is that the samples he measured were prepared by neutron transmutation doping (NTD). In NTD, P is doped by the nuclear reaction of $^{30}$Si and neutrons. Thus, P appeared only in the Si site. From the first-principles calculation performed by Ref. 37, it is suggested that P$_{\text{C}}$ exists in 10% of P$_{\text{Si}}$ under a Si-rich condition. If a sample is prepared by ion implantation or CVD with phosphine gas, both P$_{\text{Si}}$ and P$_{\text{C}}$ can be observed. The P of P$_{\text{C}}$-V$_{\text{Si}}$ is unstable and becomes P$_{\text{Si}}$-V$_{\text{C}}$. The C site is too narrow for P. To release the strain, P moves to the Si site. P$_{\text{Si}}$-V$_{\text{C}}$ has relatively low formation energy compared with other interstitial defects, and was also observed by the above-mentioned EPR and ENDOR measurements.$^{39)}$

4.2. X-ray photoelectron spectroscopy binding energy

Before discussing the results, we introduce the XPS binding energy 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, 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 XPS binding energy ($E_{\text{bind}}^{\text{XPS}}$) 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 ($E^\text{HF}_{\text{core}}$) of the core electron. Thus, we can clearly define the relaxation energy as $E^\text{relax} = -E^\text{HF}_{\text{core}} - E^\text{XPS}_{\text{bound}}$. 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 ($\bar{\psi}_{\text{loc}}$) around the atom before photoelectron emission. We use the approximation $\Delta \bar{\psi}_{\text{loc}} \approx \Delta \bar{\psi}_{\text{loc}}$, 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 $\Delta E^\text{relax}_{\text{relax}}$ as

$$\Delta E^\text{relax}_{\text{relax}} = -\Delta \bar{\psi}_{\text{loc}} - \Delta E^\text{XPS}_{\text{bound}}.$$  

The spatial average around the atom was calculated within a sphere of radius $R_c$, which was set to double the peak position of the radial distribution function, $4\pi r^2 \rho(r)$, of the core electron in an isolated atom. For N 1s and P 2p, $R_c$ is 0.30 and 0.72 Bohr, respectively.

The XPSBE, LPA, and XPSRE of N and P defects in 3C-SiC are summarized in Tables V and VI, respectively. The reference defects used for the energies of N and P were set to N$_C$ and P$_{Si}$, respectively. Figures 3(a) and 3(b) show the relationship between the XPS level $\epsilon_{\text{XPS}}$ and the LPA for N and P defects in 3C-SiC, respectively. The XPS level is defined as the negative of the XPSBE. On the diagonal lines, XPS levels are equal to LPAs. Since $\Delta E_{\text{XPS}} = \Delta \bar{\psi}_{\text{loc}} + \Delta E^\text{DFT}_{\text{relax}}$ from Eq. (5), the XPSRE corresponds to the vertical shift from the diagonal line. A point on a diagonal line means that the defect has the same relaxation energy as the reference defect.

In terms of p-type dopants B and Al in 3C-SiC, we previously reported that the localized orbitals around the impurity atom before and/or after photoelectron emission have large effects on the XPSBE. The reason for this is considered to be that the change in the electron occupation of the localized orbital has a large effect on the LPA, and the core hole has a large relaxation effect on the localized orbitals. On the other hand, the change in the occupation of the spread orbital does not have a large effect on the LPA, and the core hole has a small effect on spread electrons. As an exception, there are some defects with the electrons which are spread before the emission and localized by the core hole left

| Structure        | Charged state | Formation energy (eV) | $\Delta \mu$ = 0 | $\Delta \mu$ (eV) | $\Delta V$ (eV) | XPSBE (eV) | LPA (eV) | XPSRE (eV) |
|------------------|---------------|-----------------------|-----------------|-----------------|----------------|------------|----------|------------|
| N$_{Si}$         | 0             | 6.07                  | 5.82            | 5.56            | 0.05           | 2.13       | -2.84    | 0.71       |
|                  | 1+            | 6.08                  | 5.83            | 5.57            | 0.06           | 2.77       | -2.85    | 0.08       |
| N$_C$            | 0             | -1.17                 | -0.91           | -0.66           | 0.04           | 0.00       | 0.00     | 0.00       |
|                  | 1+            | -1.15                 | -0.90           | -0.64           | 0.05           | 0.12       | -0.03    | -0.09      |
| N$_{Si}$         | 0             | 8.14                  | 8.14            | 8.14            | 0.01           | -2.46      | 0.92     | 1.54       |
|                  | 1+            | 7.44                  | 7.44            | 7.44            | -0.03          | -3.20      | 2.22     | 0.98       |
|                  | 2-            | 7.04                  | 7.04            | 7.04            | -0.09          | -4.04      | 3.54     | 0.50       |
|                  | 3-            | 6.94                  | 6.94            | 6.94            | -0.11          | -5.06      | 4.19     | 0.87       |
| (001)N-Si$_{01}$ | 0             | 6.19                  | 6.19            | 6.19            | 0.03           | -0.76      | 0.98     | -0.22      |
|                  | 1+            | 6.13                  | 6.13            | 6.13            | 0.02           | -0.90      | 1.05     | -0.15      |
| (001)N-Si$_{02}$ | 0             | 7.03                  | 7.54            | 8.05            | 0.06           | -1.95      | 2.26     | -0.31      |
|                  | 1+            | 7.02                  | 7.53            | 8.04            | 0.05           | -2.04      | 2.28     | -0.25      |
| (001)N-C$_{01}$  | 0             | 6.44                  | 5.93            | 5.42            | 0.02           | 0.00       | 0.30     | -0.31      |
|                  | 1-            | 6.33                  | 5.82            | 5.31            | 0.00           | -0.21      | 0.39     | -0.18      |
| (001)N-C$_{02}$  | 0             | 5.03                  | 5.03            | 5.03            | 0.05           | -0.94      | 1.28     | -0.54      |
|                  | 1+            | 4.72                  | 4.72            | 4.72            | 0.01           | -1.80      | 2.12     | -0.33      |
|                  | 1-            | 4.72                  | 4.72            | 4.72            | 0.01           | -2.17      | 2.19     | -0.02      |
| N$_{Si}$         | 0             | 4.80                  | 4.80            | 4.80            | 0.01           | -2.25      | 1.41     | 0.85       |
|                  | 1-            | 4.41                  | 4.41            | 4.41            | -0.03          | -3.14      | 2.75     | 0.39       |
| N$_{Si}$         | 0             | 6.66                  | 6.66            | 6.66            | 0.04           | 0.30       | -0.21    | -0.08      |
|                  | 0             | 6.65                  | 6.65            | 6.65            | 0.03           | 0.28       | -0.21    | -0.07      |
| N$_{Si}$         | 1-            | 6.64                  | 6.64            | 6.64            | 0.03           | 0.27       | -0.21    | -0.06      |
| N$_{Si}$         | 0             | 4.72                  | 4.72            | 4.72            | -0.02          | -1.67      | 1.88     | -0.21      |
|                  | 1-            | 4.23                  | 4.23            | 4.23            | -0.06          | -1.83      | 2.06     | -0.23      |
|                  | 2-            | 4.15                  | 4.15            | 4.15            | -0.07          | -1.99      | 2.15     | -0.16      |
|                  | 3-            | 4.13                  | 4.13            | 4.13            | -0.07          | -1.99      | 2.16     | -0.17      |
| 4N$_C$          | 0             | -5.71                 | -4.95           | -4.18           | 0.00           | -1.63      | 1.81     | -0.17      |
| 4N$_C$          | 1+            | 8.18                  | 8.69            | 9.20            | 0.11           | 0.21       | -0.83    | 0.62       |
| 4N$_C$          | 1-            | 8.09                  | 8.60            | 9.11            | 0.09           | 0.20       | -0.84    | 0.64       |
| 4N$_C$          | 1-            | 8.03                  | 8.54            | 9.05            | 0.07           | 0.20       | -0.86    | 0.66       |
| 4N$_C$          | 1+            | 7.69                  | 7.69            | 7.69            | 0.05           | -0.51      | 0.68     | -0.17      |
| 4N$_C$          | 1+            | 7.69                  | 7.69            | 7.69            | 0.05           | -0.51      | 0.68     | -0.17      |
| 4N$_C$          | 1-            | 7.69                  | 7.69            | 7.69            | 0.04           | -0.60      | 0.70     | 0.00       |
after the emission. In this case, a large rearrangement of electronic structure makes a significant contribution to the XPSRE. A similar discussion can be made for the n-type dopants N and P, although their detailed electronic structures are different from those of the p-type dopants B and Al.

First, we discuss the N defects. A characteristic feature of the electronic structure is that N defects have several localized electrons. Figures 4(a) and 4(b) show the density of states (DOS) for a pure 3C-SiC crystal and the projected DOS (PDOS) on N for NSi and NC, respectively. We can see that the localized orbitals that affect the XPSBE can exist in the energy region without bulk states, that is, below, inside, and above the valence band. These two substitutional defects do not have localized levels in the band gap but have two other regions. We investigated individual N defects we calculated and found that all the defects have localized levels, which are composed of N 2s, below the valence band. All the defect models have localized levels above the valence band (in the band gap) except NSi and NC. In the gap region inside the valence band, it is slightly complicated: all the defect models have localized levels except for NC, NC-VSi, and NTSi before photoelectron emission, and only NTSi does not have localized levels after photoelectron emission.

Table VI. Formation energy, P 2p XPS binding energy (XPSBE), local potential average (LPA), and P 2p XPS relaxation energy (XPSRE) of P defects in 3C-SiC. $\Delta V$ is the parameter of the stoichiometry of SiC. The Fermi energy is set to the conduction band bottom, and the chemical potential of P is set to the total energy of black phosphorus. The origins of the XPSBE and LPA are that of P$_{Si}$. $\Delta V$ 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.

| Structure | Charged state | Formation energy (eV) Si-rich | $\Delta V$ (eV) | XPSBE (eV) | LPA (eV) | XPSRE (eV) |
|-----------|---------------|-------------------------------|----------------|-------------|----------|-----------|
| P$_{Si}$  | 0             | 1.10                          | 0.04           | 0.00        | 0.00     | 0.00      |
|           | 1+            | 1.16                          | 0.04           | 0.00        | 0.00     | 0.00      |
| P$_{C}$   | 0             | 1.45                          | 0.05           | -2.72       | 2.04     | 0.68      |
|           | 1+            | 1.52                          | 0.06           | -2.64       | 2.01     | 0.63      |
| P$_{TSi}$ | 0             | 11.62                         | 0.10           | -0.46       | -0.82    | 1.29      |
|           | 1+            | 11.48                         | 0.08           | -0.45       | -0.79    | 1.24      |
| P$_{TC}$  | 1             | 11.39                         | 0.07           | -0.46       | -0.77    | 1.22      |
|           | 1+            | 11.67                         | 0.11           | -0.41       | -1.15    | 1.56      |
| P$_{H}$   | 1+            | 10.70                         | 0.10           | -1.66       | -0.13    | 1.79      |
|           | 1             | 10.54                         | 0.09           | -1.67       | -0.07    | 1.74      |
|           | 1+            | 10.46                         | 0.08           | -1.69       | 0.00     | 1.69      |
| (110)P-Si$_{Si}$ | 1+          | 8.95                          | 0.07           | -1.76       | 0.87     | 0.90      |
|           | 0             | 8.89                          | 0.07           | -2.27       | 0.94     | 1.33      |
| (001)P-Si$_{Si}$ | 1             | 8.83                          | 0.06           | -2.53       | 1.02     | 1.51      |
|           | 0             | 9.00                          | 0.03           | -2.89       | 1.81     | 1.08      |
| (001)P-C$_{Si}$ | 1             | 7.74                          | 0.02           | -2.86       | 1.96     | 0.90      |
|           | 1             | 6.98                          | 0.02           | -2.38       | 1.38     | 1.00      |
| (001)P-C$_{C}$ | 1             | 9.80                          | 0.06           | -2.69       | 1.56     | 1.13      |
|           | 0             | 9.72                          | 0.04           | -3.61       | 1.78     | 1.83      |
| P$_{Si}$-V$_{C}$ | 1+          | 9.68                          | 0.04           | -3.77       | 1.83     | 1.93      |
|           | 0             | 4.20                          | 0.04           | -1.83       | 1.48     | 0.35      |
| P$_{Si}$-Si$_{C}$ | 1             | 4.15                          | 0.04           | -1.85       | 1.48     | 0.37      |
|           | 1+            | 4.11                          | 0.04           | -1.86       | 1.47     | 0.39      |
| P$_{C}$-V$_{Si}$ | 1+          | 10.34                         | 0.12           | 0.03        | -0.69    | 0.67      |
|           | 0             | 10.12                         | 0.09           | 0.00        | -0.66    | 0.66      |
| P$_{C}$-Si$_{TSi}$ | 1+          | 9.96                          | 0.07           | -0.02       | -0.64    | 0.65      |
|           | 0             | 11.25                         | 0.11           | -2.34       | 1.41     | 0.93      |
| P$_{C}$-Si$_{TC}$ | 1             | 11.16                         | 0.11           | -2.37       | 1.44     | 0.93      |
|           | 1+            | 11.02                         | 0.11           | -2.30       | 1.45     | 1.75      |
| P$_{C}$-C$_{TSi}$ | 1+          | 10.51                         | 0.11           | -2.13       | 1.00     | 1.13      |
|           | 0             | 10.30                         | 0.11           | -2.16       | 1.03     | 1.13      |
| P$_{C}$-C$_{TSi}$ | 1             | 10.19                         | 0.11           | -2.19       | 1.06     | 1.13      |
|           | 1+            | 9.71                          | 0.02           | -2.92       | 2.00     | 0.92      |
| P$_{C}$-C$_{TSi}$ | 1             | 9.69                          | 0.01           | -3.23       | 2.11     | 1.12      |
Some defects above the diagonal line have localized electrons in the band gap in addition to those below the valence band, and show a higher XPSRE. For example, $N_{TSi}$ has three electrons in the triply degenerate levels in the band gap. Since the charged states are owing to the change in the number of electrons around N, the changes in the LPA and XPSBE of charged states become large.

Note that not all localized electrons strongly affect the XPSRE. The electrons localized far from the relevant impurity atom have a small effect on the XPSRE. For example, $N_{C-VSi}$, whose XPSRE and change in the LPA induced by a charged state are small, also has three electrons in the triply degenerate levels in the band gap. The triply degenerate orbitals are composed of dangling bonds of C next to $V_{Si}$ and are not localized around $N_{C}$.

For P defects, Fig. 5 shows the PDOS of $P_{Si}$ and $P_{C}$, which have the lowest two formation energies. $P_{Si}$ has a localized orbital below the valence band and $P_{C}$ does not have any localized orbitals. The reason for this is considered that, as shown in Table VII, the eigenenergies of P 3s and 3p are close to those of C 2s and 2p, whereas they are 3.1 and 1.4 eV lower than those of Si 3s and 3p, respectively. Only $P_{Si}$ and $P_{Si-VC}$ in the calculated P defect models do not have a localized orbital below the valence band. Considering that all N defects have localized levels below the valence band, the higher eigenenergy of P than of N is the reason that few P defects have localized levels below the band. In Fig. 3(b), almost all data points are distributed above the diagonal line and this distribution is similar to that of B and Al. This shows that the reference defect $P_{Si}$ has the lowest relaxation energy among all the model defects.

| Table VII. | Eigenenergies of 2s and 2p for isolated C and N, and 3s and 3p for isolated Si and P. |
|------------|----------------------------------|
| (eV)       | C  | N  | Si  | P   |
| s          | −13.74 | −18.56 | −10.77 | −13.90 |
| p          | −5.23  | −7.10  | −4.09  | −5.52  |

Fig. 3. Relationship between the XPS level and the local potential average (LPA) for (a) N defects in 3C-SiC, (b) P defects in 3C-SiC. The levels correspond to N 1s and P 2p. 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 $N_{C}$ and $P_{Si}$ for N and P, respectively. The XPS relaxation energy measured from that of the reference defects corresponds to the vertical shift from the diagonal line.

Fig. 4. (Color online) Projected density of states (PDOS) of (a) $N_{Si}$ and (b) $N_{C}$. 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. The blue line is the PDOS on N. The upper and lower panels show the PDOS before and after the core electron emission, respectively. The filled region implies that electrons are occupied. For comparison, the red lines show the same total DOS of pure 3C-SiC in both the upper and lower panels. The scales of the red and blue lines are different.
At the end of this section, we mention the observable XPS spectra for N and P defects in 3C-SiC. As far as we searched, there have been no reports on XPS spectra from N or P in SiC. As mentioned in Sect. 4.1, a high dose of N saturates the donor concentration. This is considered to be due to the formation of $4N_C$-$V_{Si}$. In our calculation, $4N_C$-$V_{Si}$ and $N_C$ have significantly lower formation energies than the other defects. For this reason, it is expected that two peaks separated by 1.6 eV will be observed from highly N-doped samples.

For P defects, the most favorable defect is $P_{Si}$ from the formation energy analysis. From the previous calculation by Ref. 37 and our results, $P_C$ probably exists to some extent. Thus, two peaks separated by 2.7 eV are expected to be observed for highly P-doped samples prepared by ion implantation or CVD with phosphine gas.

5. Summary

We systematically investigated the core-level XPS binding energy shifts and formation energies for defects of N and P, which are $n$-type dopants, in 3C-SiC by a first-principles calculation with the GGA. We confirmed the reliability of XPS calculations with the GGA PBE96 using the HSE06 hybrid functional, which reproduces the band gap much better than GGA functionals, since $n$-type dopants tend to have levels near the CBM. To analyze the relationship between the XPS binding energy shift and the defect structures, we separated the XPS binding energies into the depth of the core-level (the local potential average around the impurity) and the relaxation energy of the wave function after the emission of a photoelectron. The depth of the core-level gives an intuitive interpretation using the electrostatic potentials. On the other hand, the relaxation energy is not intuitive and an investigation of the electronic structure is required for its understanding. As we pointed out for the case of $p$-type defects, the electrons localized around an impurity atom, which have energy levels in energy gaps, also make a large contribution to the relaxation energy for $n$-type defects. We found from the analysis of the electronic structure that all the defects containing N have a localized level, which is composed of N 2$s$, below the valence band, which may cause N defects to have relatively similar relaxation energies. Considering the formation energies, two peaks of thermodynamically stable defects are expected to be found: $N_C$ and $4N_C$-$V_{Si}$, separated by 1.6 eV, for N, and $P_{Si}$ and $P_C$, separated by 2.7 eV, for P.

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