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We studied the energetics and the properties of impurity states that result from doping cubic silicon–carbide (3C–SiC) with aluminum (Al), boron (B), and nitrogen (N) atoms using the tight-binding linear combination of muffin-tin orbital atomic sphere approximation method. For Al doping, it is only favorable to substitute Al for Si atoms. The corresponding hole states contribute to a partially filled weak peak near the Fermi energy. For B doping, it is possible to replace either Si or C atoms in the crystal. When a B atom is at a Si site, the hole states exhibit behavior similar to the case of Al doping. However, when a B atom is at a C site, the hole states form a partially filled strong peak above the Fermi energy. This localized feature is explained in terms of the screening effect of the neighboring atoms. For *n*-type doping, a N atom can enter either the Si or C site. The latter site is more energetically favorable. Furthermore, the corresponding donor states form deep impurity states within the gap. In contrast, when a N atom is at a Si site, shallow donor states are formed. © *1999 American Institute of Physics.* [S0003-6951(99)01027-X]

One of the wide gap semiconductors, silicon–carbide (SiC), has long been of interest for potential technological applications.[1] It is a polytype material with the 6H and 4H structures, which are hexagonal, more commonly grown than the cubic (3C) SiC. Some of their attractive properties include large hole mobility and high breakdown voltage. In addition, boron (B)-doped samples show high resistivity and the doping concentration of aluminum (Al) in SiC can be as high as 10^{20}/cm^3. Recently, 3C–SiC has been shown to be an excellent microwave device operating above room temperature ($\sim 400\,°$C)[2] and having an output power density of 67 kW/cm^2, which is about 30 times larger than the output of devices made from GaAs.[2] Furthermore, devices using 3C–SiC can now be fabricated by heteroepitaxial methods on a Si substrate.[2] Thus, it is important to understand the features relevant to the doping of this material, such as which atoms can be used as dopants and what are the properties of the impurity states.

In this letter, we use the self-consistent, supercell approach to study the energetics and the electronic properties of three different dopants: aluminum (Al), B, and nitrogen (N) doped in 3C–SiC. We shall discuss the binding energies of the respective dopants, and use the density of states to illustrate the properties of the impurity states. Other details, such as the charge densities of the impurity states, will be given elsewhere.

Doping in 3C–SiC is modeled by a 64-atom supercell formed by stacking eight cubic conventional cells. The lattice constant of the supercell a_s is 8.696 Å, which is twice the lattice constant of the conventional cell ($a = 4.348$ Å).[3] We used the tight-binding linear combination of muffin-tin orbitals atomic sphere approximation (TBLMTO-ASA) method[4,5] with the local density approximation (LDA)[6] of density functional theory.[7] The exchange-correlation func-

tional of Hedin–Lundqvist[8] is used in the LDA.

In Fig. 1(a), the total density of states of pure 3C–SiC is plotted against energy. The gap is 2.0 eV, which is smaller than the measured value of 2.2 eV. This is the typical result of using the LDA. It is an indirect gap with the top of the valence band at the Γ ($\mathbf{k}=0$) point in the first Brillouin zone of the fcc structure and the bottom of the conduction band at the $X[\mathbf{k}=(2\pi/a,0,0)]$ point. These qualitative results agree with earlier results.[9] The characters of the states near the fundamental gap are analyzed using the angular momentum decomposed density of states. We found that the states at the valence band edge have contributions from both the Si $3p$ [Fig. 1(b)] and the C $2p$ states [Fig. 1(c)]. The states at the conduction band edge also have the character of the Si $3p$ and the C $2p$ states. In order to compare the doping energetics, we calculated the binding energies of a Si and a C atom in our model. The total energy of this 64-atom (Si$_{32}$C$_{32}$) model is $-20\,949.096$ Ry. The energies of Si$_{32}$C$_{31}$ and Si$_{31}$C$_{32}$ with a vacancy at the center of the unit cell are $-20\,870.528$ and $-20\,367.777$ Ry, respectively. The energy of a Si free atom is -578.131 Ry, and the corresponding value for a C atom is -75.093 Ry. The binding energy of a Si atom in this model is 3.188 Ry, which is 0.286 Ry less than the energy to bind a C atom.

To simulate a dopant in a 3C–SiC crystal, we fill the vacancy at the center of the supercell with an atom of Al, B, or N for both Si$_{32}$C$_{31}$ and Si$_{31}$C$_{32}$. Thus we consider a total of six cases. The corresponding dopant concentration is 1.56%. When an Al atom replaces a Si atom, the total energy is $-20\,851.938$ Ry, while the energy is $-21\,353.930$ Ry, when it is at a C atomic site. When a B atom replaces a Si or C atom the total energy is $-20\,417.434$ or $-20\,930.222$ Ry, respectively. The corresponding energies for the N atom replacement are $-20\,476.804$ and $-20\,980.088$ Ry, respectively. The energies of the free atoms are -483.985 Ry for Al, -48.875 Ry for B, and -108.359 Ry for N. The binding

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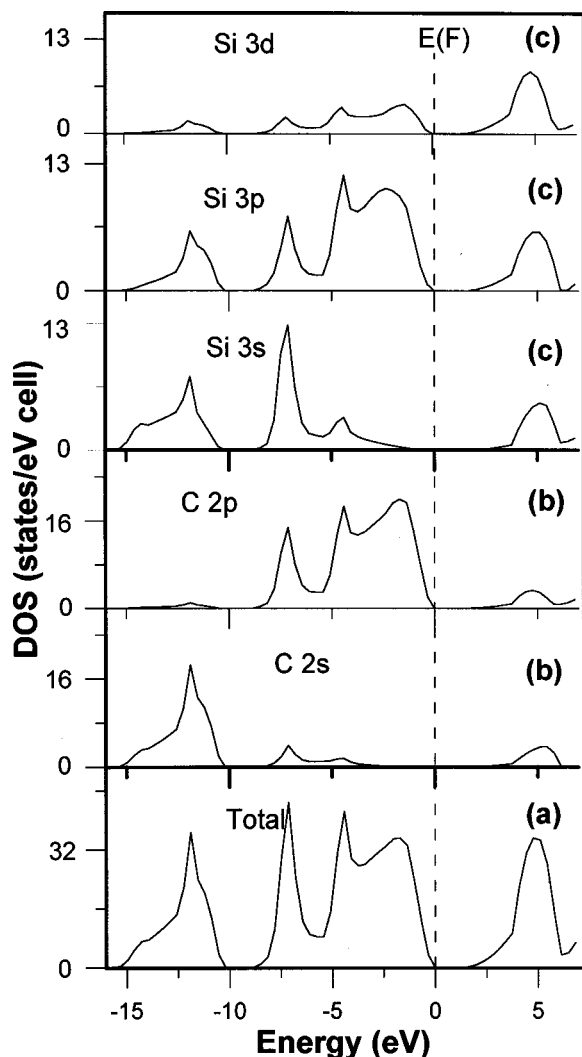[a)]Electronic mail: vgubanov@msn.com

FIG. 1. (a) Total density states of 3C–SiC, (b) partial density of states for C, and (c) partial density of states for Si contribute to the states of the valence band and the conduction band edge.
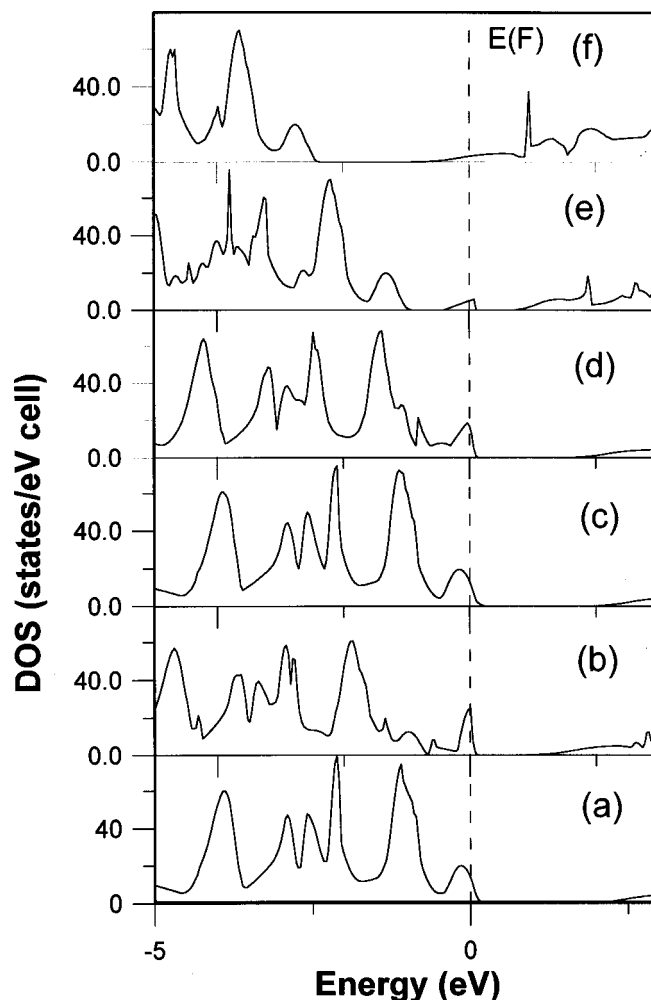

FIG. 2. Total density of states (a) for an Al atom at a Si site, (b) for an Al atom at a C site, (c) for a B atom at a Si site, (d) for a B atom at a C site, (e) for a N atom at a Si site, and (f) for a N atom at a C site.

energies for the six cases are summarized in Table I. Based on our results, the most favorable doping is the n-type doping with N atoms substituting for C atoms. The p-type dopings are possible for both Al and B atoms replacing a Si atom. However, it will be difficult to dope an Al atom into a C site. This last result is quite reasonable because it is less likely that the Al atom will form strong bonds with neighboring Si atoms.

We next compare the hole properties of doping Al or B at the central Si or C sites. The total density states for the four cases are shown in Figs. 2(a)–2(d). The hole states, which are above zero energy (the Fermi energy of the system) for the Al [Fig. 2(a)] or B atom [Fig. 2(c)] at the Si vacancy, are quite similar. This similarity persists for each of the two impurity atoms at the C site [Fig. 2(b) for Al and Fig. 2(d) for B]. The dominant contribution to the hole states

TABLE I. The binding energies of Al, B, and N at Si and C sites.

	Si site (Ry)	C site (Ry)
Al	0.176	−0.583
B	0.782	0.819
N	0.668	1.200

comes from the p-like states of the dopant. The difference arises, however, when one compares the site at which the dopant, be it Al or B, is located. A narrow, partially filled peak appears at the Fermi energy for the cases of either impurity atom at the C site, as compared to a broad and shallow peak for the cases at the Si site. By examining the local density of states (not shown), we found that when the impurity atom substitutes a C atom, the hole states have contributions from the states up to the second nearest neighbor only. On the other hand, when a Si atom is replaced by an impurity atom, the states above the Fermi energy have contributions from the third neighbor Si and fourth neighbor C atoms. The localization for the impurity at the C site cannot be interpreted as the impurity atom and its nearest neighbor Si atoms forming strong bonds. Because of the less tightly bound $3p$ states of the Si atoms, the effect of the missing electron of the impurity atom (valence 3) is easily screened by the neighboring Si atoms. The situation is different when the dopant is at the Si site. In this case, the first neighbor C atoms try to fill their tightly bound $2p$ orbitals. However, because of the tightly bound orbitals, each neighboring C atom will not share its electrons with other C atoms, so that each C atom tries to fill its $2p$ shell by taking electrons from second neighbor Si atoms. This effect is in fact felt by the

second shell (third neighbor) C atoms. The more tightly bound $2p$ states of C provide less screening effect. Consequently, the hole states for dopings at the Si site are in fact more dispersed in space.

The total density of states for a N atom occupying the vacancy of either $Si_{32}C_{31}$ or $Si_{31}C_{32}$ model are given in Figs. 2(e) and 2(f). The significant difference between the two cases is the presence of gap states for the N atom at the Si site. For the N atom substituting for a C atom, the donor states merge into the tail of the conduction band. This is due to the size effect of the nearest neighbor atoms. Our results suggest that N atoms doped at Si sites can provide deep impurity states while the impurity states formed by substituting N atoms for C atoms should exhibit shallow donor behavior. Combine this last result with the result of N having the largest binding energy among the three dopants, N doping N should produce an excellent material for making n-type devices.

In summary, we have studied the energetics and the properties of impurity states for doping Al, B, and N in 3C–SiC using the self-consistent LMTO-ASA method. Our results suggest that: (1) when doping with Al, the Al atoms will only substitute for the Si atoms in the host crystal. (2) In B doping, replacement of the C atoms is favored. Furthermore, the corresponding hole states contribute to a narrow, partially filled peak near the Fermi energy. (3) Shallow hole states are formed by both Al and B dopings when the impurity atom occupies a Si site in 3C–SiC. (4) For n-type doping, it is most energetically favorable for the C atom to be replaced by N. The corresponding donor states form deep impurity states within the gap.

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