Energetics of carbon and oxygen impurities and their interaction with vacancies in cubic boron nitride

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We investigate, through first-principles calculations, the energetics of substitutional carbon and oxygen impurities as well as complexes involving these impurities and vacancies in cubic boron nitride (c-BN). The formation energies and the electronic and structural properties of these defects in their various charge states are investigated. We find that, under a boron-rich condition, both the carbon and the oxygen impurities at the nitrogen site (C_N and O_N) have formation energies comparable to or lower than those calculated for the vacancies, which are the lowest-energy intrinsic defects. Regarding defect complexes, we find that the donor character observed for the nitrogen vacancy (V_N) can be compensated by the C_N impurity in the formation of a V_N-C_N complex which has low formation energies. We also find that the V_B-O_N complex has low formation energies under n-type conditions. In contrast to the above mentioned complexes, we find that the V_B-C_B complex has high formation energies under a boron-rich condition, and shall only occur under a nitrogen-rich condition.

I. INTRODUCTION

Cubic boron nitride (c-BN), the widest band-gap III-V compound, exhibits interesting properties like hardness and thermal conductivity very similar to those observed in diamond. More interesting, however, is that c-BN can be doped p type as well as n type,[1,2] in contrast to diamond which resists to n-type doping. These characteristics make c-BN a very promising material for applications in high-temperature microelectronic as well as optoelectronic devices.

Recently, considerable efforts have been made in the synthesis of c-BN thin films using a variety of ion-beam-assisted processes[3–10] and several plasma-, ion-, and laser-assisted chemical vapor deposition methods.[11–13] These investigations have established that the c-BN formation requires an initial sp^2-bonded boron nitride layer (amorphous and turbostratic) grown onto the substrate surface. The transition from sp^2- to sp^3-bonded material is attained by low-energy ion bombardment (e.g., Ar^+ and ${N_2}^+$) during boron deposition at about 700 K, suggesting a stress-induced mechanism for the growth of c-BN thin films which would be intermediated by point defects.[14] Recently, near-edge x-ray-absorption fine structure measurements[15] have shown that the c-BN formation is accompanied by nitrogen vacancies in the initial hexagonal phase and interstitial nitrogen in the final cubic phase, supporting the current model of defect-intermediated c-BN growth.

Given the growth conditions necessary to attain c-BN thin films, high concentrations of native defects are expected in the as-grown materials. Electron paramagnetic resonance studies[16] have shown that the nitrogen vacancy is the dominant paramagnetic center in BN films. In addition to native defects, unintentional impurities are known to occur on c-BN thin films. Recently, a significant amount of carbon and oxygen impurities has been detected in c-BN thin films by x-ray photoelectron spectroscopy[17] showing that these impurities are common contaminants. Other recent experimental investigations have reported n-type conductivity[13] attributed to carbon contamination during deposition as well as p-type conductivity[8] in intentionally carbon-doped films. Also, it has been pointed out that this impurity could have an important role in the stabilization of paramagnetic defects, e.g., the nitrogen vacancy.[16]

The study of native defects and impurities in c-BN is a subject of considerable interest due to the reasons described above. In a previous study, we have shown through first-principles calculations that nitrogen and boron vacancies have lower formation energies than antisites[18] and self interstitials,[19] exhibiting donor and acceptor characters, respectively. In the present work we examine the energetics of carbon and oxygen impurities at substitutional sites and complexes involving these impurities with neighboring vacancies in c-BN, employing total-energy pseudopotential calculations. The formation energies and the electronic and structural properties of these defects in their various charge states are investigated. Growth-induced deviations of stoichiometry are considered. The aim of this work is to obtain the energetics of the incorporation of carbon and oxygen in c-BN and their role in the experimentally observed n- and p-type conductivities. We also investigate the stability of complexes involving these impurities and vacancies.

We find that the substitutional impurities C_B and O_N are single donors while C_N is a single acceptor. We also find that, under a boron-rich condition, these impurities have formation energies comparable to or lower than those calculated for vacancies. In addition, we find that the donor character observed for the nitrogen vacancy (V_N) is compensated by the C_N impurity in the formation of a V_N-C_N complex which

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has low formation energies. We also find that the V_B-O_N complex has low formation energies under n-type conditions. In contrast to the above mentioned complexes, we find that the V_B-C_B complex has high formation energies, and shall not occur under a boron-rich condition. The energetics of point defects and complexes under a nitrogen-rich condition are also investigated.

II. THEORETICAL METHOD

Our self-consistent total-energy calculations are based on the density-functional theory[20] and first-principles pseudopotential approach. For the exchange-correlation potential we use the generalized-gradient approximation.[21] We make use of normconserving soft pseudopotentials generated by the scheme of Troullier and Martins.[22] All calculations have been performed with a supercell of 64 atomic sites in the zinc-blende structure and a plane-wave energy cutoff of 60 Ry. The Brillouin zone sampling is performed by a single **k** point (the Γ point). Tests with defect systems using denser **k**-point sets (four points) show that variations in the total energies are less than 0.04 eV/atom. All atoms are fully relaxed according to the calculated Hellmann-Feynman forces on ions until these forces are negligible (less than 0.05 eV/Å) and assuming no symmetry constraints.

The formation energies of the substitutional impurities in c-BN are calculated using a widely established method,[23] in which the parameters are the chemical potentials of each atomic species (e.g., μ_B, μ_N, μ_C, and μ_O) and, for charged systems, the electron chemical potential or Fermi level (μ_e). For instance, in the case of a carbon atom occupying a nitrogen site in c-BN in the charge state q, the formation energy is given by

$$E_f(C_N{}^q)=E_t(C_N{}^q)-n_N\mu_N-n_B\mu_B-\mu_C+q(\mu_e+\epsilon_v), \tag{1}$$

where E_t is the total energy and n_N (n_B) the number of N (B) atoms in the supercell calculation. The Fermi level μ_e is measured relative to the top of the valence band ϵ_v. The chemical potential of B and N atoms vary over a range given by the heat of formation of c-BN, defined as $H_f=E_{B(bulk)}+E_{N(bulk)}-E_{cBN}$, which we calculate in 3.0 eV (the experimental value is 2.77 eV).[24] Additionally, the atomic chemical potentials are constrained by the equilibrium conditions $\mu_B+\mu_N=\mu_{cBN}$. Upper bounds for μ_N and μ_B are assumed to be the precipitation limits on bulk phases, $\mu_N\leqslant\mu_{N(bulk)}$ and $\mu_B\leqslant\mu_{B(bulk)}$, which are calculated from solid nitrogen (α-N_2) and metallic boron (α-B), respectively. For c-BN, we find an equilibrium lattice constant $a_0=3.617$ Å and a bulk modulus $B=3.80$ Mbar,[25] that are in good agreement with the experimental values ($a_0=3.615$ Å and $B=3.69$ Mbar).[26] Details of bulk structure calculations can be found in Ref. 18.

The incorporation of substitutional carbon and oxygen impurities in c-BN and the formation of stable chemical compounds involving these impurities with B or N atoms are competitive processes during growth procedure. Therefore, for the solubility limits of carbon and oxygen impurities in c-BN we considered the formation of boron carbide (B_4C) and boron oxide (B_2O_3) compounds. In fact, B_2O_3 is commonly found as a residual material in several growth techniques.[12] We calculate the total energy at the equilibrium geometry for B_4C and B_2O_3 applying the same method and plane-wave basis set used for the impurity system. However, we consider an appropriate **k**-point set according to the metallic character of B_4C and the insulating character of B_2O_3. Thus, the upper bounds for μ_C and μ_O can be obtained from the stoichiometric relations $4\mu_B+\mu_C=\mu_{B_4C}$ and $2\mu_B+3\mu_O=\mu_{B_2O_3}$.

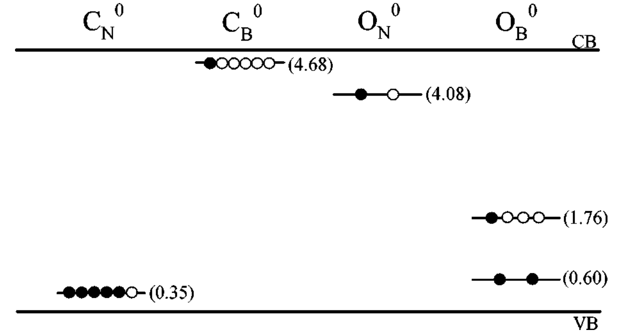

FIG. 1. Schematic representation of the single-particle energy levels inside the band gap induced by substitutional carbon and oxygen impurities in c-BN in neutral charge state. The filled dots indicate electrons and the open dots indicate holes. Numbers in parentheses give energies, in eV, representing level positions with respect to the top of the valence band (VB).

III. RESULTS AND DISCUSSION

In Secs. III A and III B, we present our results for the isolated carbon and oxygen impurities occupying both anion and cation sites in c-BN. The electronic and structural properties of some of these centers have been previously investigated by tight-binding,[27] cluster,[28] and more recently by linear muffin-tin orbital[29] methods. However, the emphasis of our calculation is on the energetics of the isolated carbon and oxygen impurities as well as complexes formed by these impurities with vacancies. We have considered the relevant charge states for each defect and the entire range of the band gap for the Fermi level variation. In previous studies, using the same calculational method, we showed that the nitrogen and boron vacancies have the lowest formation energies among native defects in c-BN.[18,19] In order to compare the formation energies of carbon and oxygen impurities with those of vacancies, we have included those previous results in the present work. The comparison of formation energies between vacancies and impurities indicates which ones are the most favorable defects that can be formed for a specific growth condition. In Sec. III C, we discuss the energetics of complexes formed by neighboring vacancies and the impurities that, in certain cases, would be favorable to occur according to the available experimental data.[16]

A. Substitutional carbon in *c*-BN

Our results for the electronic structure of a carbon atom occupying either a nitrogen or a boron site in the neutral charge state ($C_N{}^0$ and $C_B{}^0$, respectively) are represented schematically in Fig. 1. We find that both defects induce threefold-degenerated (t_2) levels close to an edge of the band gap. In the figure, the width of the gap corresponds to

TABLE I. Stable configurations of substitutional carbon and oxygen impurities in c-BN for different charge states. Δd represents the mean variation on the bond length between the impurity and the first-neighbor atoms, units are in percent with respect to the B-N bond length of bulk c-BN. E_r is the gain in energy due to the atomic relaxation.

Defect	Symmetry	Charge	Δd (%)	E_r (eV)
C_N	T_d	1+	0.5	0.18
		0	−0.1	0.17
		1−	−1.0	0.20
C_B	T_d	1+	−3.8	0.41
		0	−3.6	0.35
		1−	−3.6	0.30
O_N	T_d	1+	5.8	0.65
		0	7.3	0.98
		1−	8.8	1.46

the theoretical value (4.8 eV). For C_N^0, the t_2 level is occupied by five electrons and located at 0.35 eV above the valence band maximum (ϵ_v), while for C_B^0 the t_2 level is occupied by one electron and located at $\epsilon_v+4.68$ eV. This shows that C_N acts as a shallowlike acceptor (considering the large band gap of c-BN) while C_B is a shallowlike donor, implying that carbon is an amphoteric impurity as previously suggested by theoretical and experimental results.[29,27,5] The amphoteric nature of the carbon impurities can be explained qualitatively by a vacancy-impurity model. In this model the dangling bonds surrounding an undistorted vacancy form molecular orbitals of a_1 and t_2 symmetry. The s function of the impurity couples with the a_1 state of the vacancy creating a_1-*bonding* and a_1-*antibonding* orbitals. The p functions of the impurity couples with the t_2 vacancy orbitals creating t_2-*bonding* and t_2-*antibonding* orbitals. In the undistorted nitrogen vacancy, the a_1 and t_2 states are occupied by two electrons and one electron, respectively. A carbon atom, with four valence electrons, placed at the vacancy site results in a bonding a_1 resonance in the valence band and a bonding t_2 state in the gap occupied by five electrons, as seen in Fig. 1. In the undistorted boron vacancy, the a_1 and t_2 states are occupied by two electrons and three electrons, respectively, where the t_2 state is found in the lower part of the band gap while the a_1 state lies as a resonance in the valence band. A carbon atom placed at the vacancy site results in fully occupied bonding a_1 and t_2 resonances and a singly occupied antibonding t_2 state, as also seen in Fig. 1.

The distortions induced by substitutional impurities in c-BN can be divided into two types, those that preserve the tetrahedral symmetry (T_d) of the crystal by breathing relaxation, and those that reduce the T_d symmetry. Our results for the equilibrium geometries and relaxation energies for the C_B, C_N, and O_N impurities in their relevant charge states are listed in Table I. For neutral C_B we observe an inward breathing relaxation of the first-neighbor N atoms of about 0.06 Å (3.6%) with respect to the unrelaxed positions. Similar relaxation is observed for the other charge states investigated. For C_N we find a smaller breathing relaxation of the

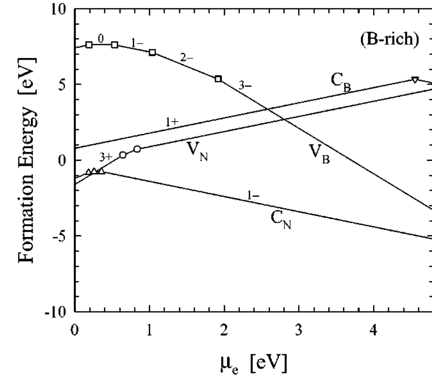

FIG. 2. Formation energies as a function of the Fermi level (μ_e) for substitutional carbon and vacancies in c-BN for a boron-rich condition. The symbols indicate the transition states or ionization levels and the numbers on the lines indicate the respective defect charge states.

first-neighbor B atoms, less than 1%, which is inward or outward depending if the charge state of the impurity is positive or negative, respectively. For the neutral impurity there is essentially no distortion. This behavior is consistent with the similarity between the ionic radii of N and C atoms.

The electronic structure of both C_N^0 and C_B^0 impurity systems suggest that they should undergo symmetry lowering Jahn-Teller (JT) distortions. We have searched for such distortions moving the C atom from the tetrahedral equilibrium position along [111] and [100] directions. However, our results show that going along both directions the total energy increases. We thus conclude that JT distortions for these impurity systems must be too small to be detected within the accuracy of our calculations.

We now discuss the energetics of substitutional carbon in c-BN. For this, we consider a boron-rich growth condition ($\mu_B=\mu_{B(bulk)}$), which appears to be common in several c-BN growth methods.[17,8] Figure 2 shows our results for the formation energies of C_N and C_B impurities as a function of the Fermi level (μ_e). We also include the formation energies of nitrogen and boron vacancies.[18] The range of variation of μ_e is chosen to be the theoretical gap (4.8 eV), where $\mu_e=0$ represents the energy of the valence-band maximum (ϵ_v). In the figure, the slopes of the line segments represent charge states of the respective defects and impurities. The values of the Fermi level at which competing charge states intersect, indicate transition states or ionization levels.

Figure 2 shows that C_N has the lowest formation energies among the intrinsic defects for almost the entire range of the Fermi level. Therefore, it should be easily incorporated under a B-rich condition. This result suggests that C_N shall be considered as a potential source of p-type conductivity in c-BN, in agreement with recent experimental results.[8] In addition, the present calculation indicates three transition states for C_N (2+/0), (1+/0) and (0/1−) with ionization levels at $\epsilon_v+0.19$, $\epsilon_v+0.26$, and $\epsilon_v+0.36$ eV, respectively. Thus, in heavily doped p-type c-BN, C_N could also act as a donor impurity.

In contrast with C_N, Fig. 2 shows that C_B has formation energies larger than those of the intrinsic defects. Only for p-type c-BN (Fermi level close to the top of the valence band) can their formation energies be considered relatively

low. This result suggests that in semi-insulating and n-type c-BN (Fermi level in the middle of the gap and close to the bottom of the conduction band, respectively), n-type conductivities shall not be associated to the C_B impurity. Figure 2 also shows that C_B could act as a single acceptor for a heavily doped n-type material. Further, we note that the neutral charge state is never stable showing that this impurity forms a negative-U system. From the $(1+/0)$ and $(0/1-)$ transitions states with ionization levels at $\epsilon_v+4.56$ and $\epsilon_v+4.55$ eV, respectively, we find that $U=\epsilon(1+/0)-\epsilon(0/1-)\approx-0.01$ eV. However, the uncertainty of the ionization levels due to the supercell approach, which we estimated in 0.1 eV, prevents a definitive conclusion about this negative-U term.

The above results were obtained by considering a boron-rich growth condition. For a nitrogen-rich condition ($\mu_N=\mu_{N(bulk)}$), the formation energies of C_B are shifted by 3.0 eV to lower energies with respect to the B-rich calculations (this shift corresponds to the calculated heat of formation of c-BN). However, the formation energies of C_N are shifted to higher energies in the same quantity. As a consequence, C_B and C_N have similar formation energies which are relatively low for any Fermi level position. Therefore, under a N-rich condition both impurities would be equally favorable to be incorporated inducing simultaneous p-type and n-type conductivities in c-BN.

B. Substitutional oxygen in c-BN

The electronic structure of the neutral O_N (Fig. 1) shows a single-occupied nondegenerated a_1 level located at $\epsilon_v+4.08$ eV, suggesting that this impurity behaves as a deep donor. The impurity state induced in the gap by O_N can be explained qualitatively by the vacancy-impurity model. In the undistorted nitrogen vacancy, the a_1 and t_2 states are occupied by two electrons and one electron, respectively. An oxygen atom, with six valence electrons, placed at the vacancy site results in bonding a_1 and t_2 fully occupied resonances in the valence band and a singly occupied antibonding a_1 state lying in the upper part of the band gap, as seen in Fig. 1.

The equilibrium geometry of this defect (see Table I) shows an onsite impurity which preserves the T_d symmetry. For $1+$, neutral and $1-$ charge states, the neighboring B atoms suffer large outward breathing relaxations, of about 0.09, 0.11, and 0.14 Å with respect to their unrelaxed positions. However, consider that oxygen occupying an anion site in GaAs shows offcenter distortions with C_{2v} symmetry for negative charge states.[30] We therefore investigated possible off-center distortions with C_{2v} or C_{3v} symmetries for $O_N{}^0$ and $O_N{}^{1-}$ in c-BN. These calculations were performed considering four special **k** points for the Brillouin zone sampling. Our results show that the O atom tends to return to its tetrahedral equilibrium position after being displaced along [111] or [100] directions. These results confirm our previous calculation considering one **k** point.

For the neutral O_B impurity, we find remarkably large off-center distortions for the O atom, which can occupy two nearly degenerate equilibrium positions with C_{2v} and C_{3v} symmetries. In one of these configurations, the O atom moves from the tetrahedral site towards one first-neighbor N atom, along the [111] direction, breaking three O-N bonds. The resulting equilibrium structure shows oxygen strongly bound to one N atom with O-N bond length of 1.37 Å, while the remaining first-neighbor N atoms relax outward by about 0.13 Å from their ideal positions. This triple-broken-bond (TBB) configuration has C_{3v} symmetry. However, in the second equilibrium configuration, the O atom binds to two first-neighbor N atoms forming a bridge structure with equal O-N bond lengths of 1.56 Å and a N-O-N bond angle of 122°. This double-broken-bond (DBB) configuration has C_{2v} symmetry and its total energy is about 0.1 eV higher than the TBB total-energy configuration. In Table II we summarize the equilibrium geometries and relaxation energies of the O_B impurity in the TBB and DBB configurations for their relevant charge states. We find that both nearly degenerate equilibrium geometries are stable for different charge states exhibiting similar relaxation energies. We also find that for the neutral defect, the TBB and DBB configurations are separated by an energy barrier of 0.8 eV. The finding of two bonding structures for oxygen occupying a boron site in c-BN is consistent with the existence of distinct types of N-O bonds in the NO and N_2O molecules. In fact, our results for the TBB configuration show a strong O-N bond, which resembles a NO molecule weakly bonded with the lattice.

TABLE II. Stable configurations for oxygen occupying a boron site in c-BN for different charge states. The triple-broken-bond (with C_{3v} symmetry) and the double-broken-bond (with C_{2v} symmetry) configurations are considered. d_{ON} represents the bond length between oxygen and the first-neighbor N atoms and θ the angle between the N-O-N bonds. E_r is the gain in energy due to the atomic relaxation.

Defect	Symmetry	Charge	d_{ON} (Å)	θ (deg)	E_r (eV)
O_B	C_{2v}	1+	1.60	116.2	2.48
		0	1.57	122.3	4.41
		1−	1.55	125.6	6.51
O_B	C_{3v}	1+	1.50		2.51
		0	1.37		4.49
		1−	1.36		6.75

The undistorted O_B defect (with T_d symmetry) gives rise to two states inside the band gap, a single-occupied t_2 level at $\epsilon_v+3.70$ eV and a fully occupied a_1 level at $\epsilon_v+1.61$ eV. The electronic structure of this defect can also be explained by the vacancy-impurity model. In the undistorted boron vacancy, the a_1 and t_2 states are occupied by two electrons and three electrons, respectively. An oxygen atom, with six valence electrons, placed at the vacancy site results in fully occupied a_1 and t_2 bonding resonances, a fully occupied antibonding a_1 state in the gap, and a singly occupied t_2 bonding state in the band gap. The single occupied t_2 degenerate level found for the undistorted O_B impurity suggests that the offcenter configurations originate from JT distortions.

The positions of gap levels for the TBB configuration (with C_{3v} symmetry) are show in Fig. 1. The t_2 level splits into an empty singlet (a_1) and a single-occupied doublet (e), lying into the conduction band and at $\epsilon_v+1.76$ eV, respectively, while the fully occupied a_1 level stabilizes at

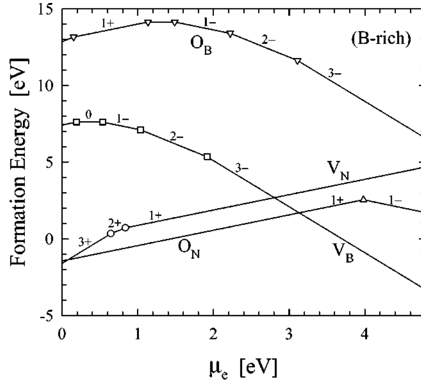

FIG. 3. Formation energies as a function of the Fermi level (μ_e) for substitutional oxygen and vacancies in c-BN for a boron-rich condition.

$\epsilon_v+0.60$ eV. According to Fig. 1, the the electronic structure for O_B^0 in the TBB configuration suggests a second JT distortion for this center. However, in the present calculation no other lower symmetry distortion is detected. The electronic structure for the DBB configuration (with C_{2v} symmetry) shows three a_1 levels inside the band gap, a fully occupied at $\epsilon_v+0.81$ eV, a semioccupied at $\epsilon_v+1.62$ eV, and an empty level at $\epsilon_v+2.98$ eV.

Our results for the formation energies of the substitutional oxygen in c-BN are shown in Fig. 3. We observe that the $O_N{}^{1+}$ impurity has lower formation energies than $V_N{}^{1+}$ for any Fermi level position. Therefore, this impurity is favorable to be incorporated under a B-rich condition. For p-type and semi-insulating c-BN, O_N behaves as a single donor while in n-type c-BN it is a single acceptor. Hence, this impurity might be considered an important candidate for dopant compensation. We also note that the neutral charge state of O_N is never stable, which indicates that this impurity also forms a negative-U system. From $(1+/0)$ and $(0/1-)$ transition states with ionization levels at $\epsilon_v+3.98$ and $\epsilon_v+3.92$ eV, respectively, we find that $U=\epsilon(1+/0)-\epsilon(0/1-)\approx-0.06$ eV. In the same way as for the C_B impurity, the accuracy of the present calculation prevents a definitive conclusion about this negative-U term.

Low formation energies of O_N impurities have also been reported in GaN and AlN,[31,32] suggesting that oxygen is one of the main contaminants in III-V nitrides. However, for the case of O_B impurity in the most stable configuration (TBB), we find relatively high formation energies for any Fermi level position. Therefore, this impurity would be unlikely to occur in significant concentrations.

For a nitrogen-rich condition, the formation energies of O_N are shifted by 3 eV to higher energies with respect to the B-rich calculations. As a result, this impurity exhibits relatively low formation energies only for p-type c-BN, where it behaves as a single donor. On the other hand, the formation energies of O_B are shifted by 3 eV to lower energies. However, they are still too high as compared with those of vacancies, showing that O_B is an energetically unfavorable defect also under a N-rich condition.

C. Vacancy-impurity complexes in c-BN

In this section we discuss the energetics of complexes formed by vacancies and substitutional carbon and oxygen impurities in c-BN. The possible existence of such complexes is supported by the low formation energies exhibited by the V_N and V_B vacancies and by the C_N, C_B, and O_N impurities. In the present work, we initially guided ourselves in a search for possible low-energy complexes by assuming that the formation of vacancy-impurity complexes is partly induced by electrostatic interactions between positively charged donors and negatively charged acceptors. Therefore, according to our previous results on the formation energies of the point defects, possible complexes suitable to form would be the second-neighbor pairs V_N-C_N and V_B-C_B, and the first-neighbor pair V_B-O_N. We investigate the electronic and structural properties of these complexes as follows.

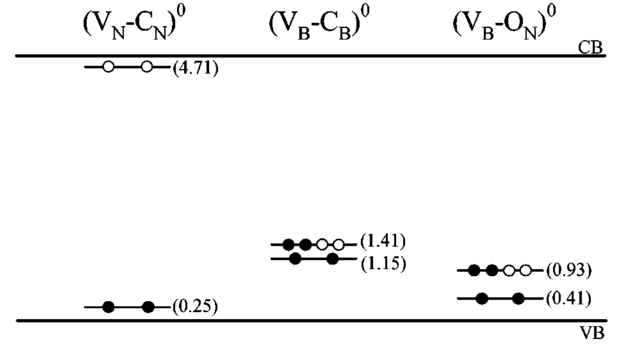

FIG. 4. Schematic representation of the single-particle energy levels inside the band gap induced by vacancy-impurity complexes in c-BN in neutral charge state.

Figure 4 shows the electronic structure of the complexes under study in the neutral charge state. For V_N-C_N, we find two a_1 levels inside the band gap, one fully occupied located at $\epsilon_v+0.25$ eV, and the other one empty at $\epsilon_v+4.71$ eV. Therefore, the donor and acceptor character observed for V_N and C_N are mutually compensated in the formation of the V_N-C_N complex. Only for strong p-type or n-type c-BN, could this complex act as a double donor or double acceptor, respectively. On the other hand, the V_B-C_B and V_B-O_N complexes have very similar electronic structures, as shown in Fig. 4. In the neutral charge state, both complexes show a fully occupied singlet and a semioccupied doublet in the lower part of the band gap, so that they act as double acceptors, as expected from the coupling of a triple acceptor (V_B) (Ref. 18) and a single donor (C_B, O_N).

The impurity states induced by the V_N-C_N complex can be qualitatively described as originating from the V_N and the C_N states. In such a description, the electron in the e-like resonance of the neutral V_N (see Ref. 18) is transferred to the acceptor state of the neutral C_N. Part of the e-like resonance is split into an empty state inside the band gap, and the fully occupied $V_N\,a_1$ state remains in the band gap. In a similar way, the impurity states induced by the V_B-C_B complex can be described as originating from the V_B and the C_B states. In such a qualitative description, the electron at the donor state of the neutral C_B is transferred to the p-like t_2 state of the neutral V_B, which is split into a fully occupied a_1 state and a half occupied e state inside the band gap.

In the V_N-C_N complex, V_N and C_N are second-neighbor defects, both surrounded by B atoms. One of these B atoms is a mutual first neighbor to V_N and C_N. The equilibrium

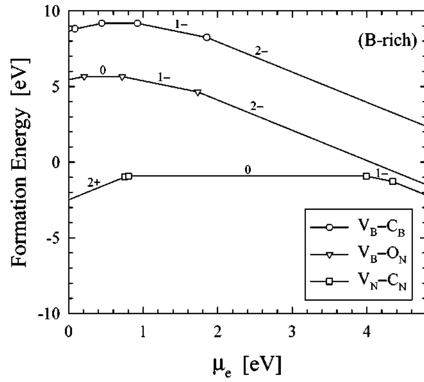

FIG. 5. Formation energies as a function of the Fermi level (μ_e) for vacancy-impurity complexes in c-BN for a boron-rich condition.

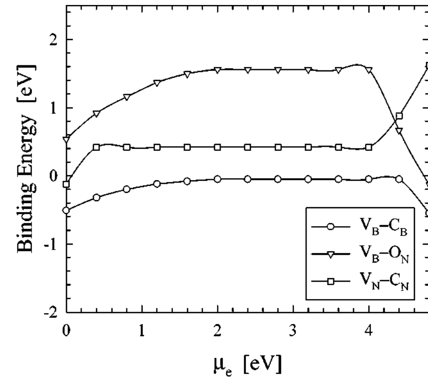

FIG. 6. Binding energies as a function of the Fermi level (μ_e) for vacancy-impurity complexes in c-BN.

geometry of this complex shows an outward relaxation of the B atoms first neighbors to V_N, about 8.3% with respect to their ideal positions, and a small outward relaxation of the B atoms first neighbors to C_N, about 0.7%, exhibiting B-C bond lengths of 1.58 Å. The B atom first neighbor to V_N which is also bonded to C_N shows a larger outward relaxation from its ideal position by 10.8%, and a shorter B-C bond length of 1.51 Å.

Similar to V_N-C_N, the V_B-C_B complex is also formed by second-neighbor V_B and C_B defects, showing equivalent equilibrium geometries. The N atoms first neighbors to V_B relax outward by 10.3% from their ideal positions, while the N atoms first neighbors to C_B relax inward by 1.4%, exhibiting N-C bond lengths of 1.54 Å. The N atom which connects both V_B and C_B defects shows a larger outward relaxation from its ideal position by 11.5%, and a shorter B-C bond length of 1.42 Å.

In contrast to the above complexes, V_B-O_N is formed by first-neighbor V_B and O_N defects. The equilibrium geometry in neutral charge state shows an outward relaxation for the three neighboring N atoms and the O impurity by 10.4% and 11.1%, respectively. We find that the O atom is threefold coordinated showing equal O-B bond lengths of 1.53 Å.

Figure 5 shows the formation energies for the vacancy-impurity complexes in c-BN under a B-rich condition. We find that V_N-C_N has significant low formation energies for any Fermi level position, suggesting a favorable situation for the complex formation. Our calculations indicate four transition states for this complex $(2+/1+)$, $(1+/0)$, $(0/1-)$ and $(1-/2-)$ with ionization levels at $\epsilon_v+0.75$, $\epsilon_v+0.80$, $\epsilon_v+3.99$, and $\epsilon_v+4.34$ eV, respectively. As previously pointed out, for p-type or n-type conditions V_N-C_N can act as a double donor or double acceptor, respectively. For V_B-O_N we find relatively low formation energies only for n-type c-BN. The relevant transition state is $(1-/2-)$ which has an ionization level at $\epsilon_v+1.73$ eV. Therefore, this complex would be favorable to form only for n-type conditions, acting as a double acceptor. Our results for the formation energies of V_B-C_B show a similar trend as those found for V_B-O_N, but shifted to higher energies by about 4 eV. The relatively high formation energies suggest that this complex is unlikely to occur for any Fermi level position under a boron-rich condition.

For a N-rich condition, the formation energies of V_N-C_N and V_B-C_B are shifted to higher and lower energies, respectively, by about 6 eV with respect to the B-rich calculations. However, the formation energies of V_B-O_N remain unchanged. As a consequence, V_B-C_B is now the complex with significant low formation energies in semi-insulating and n-type c-BN where it would be favorable to form, acting as a double donor. On the other hand, V_N-C_N is now a high-energy complex being unlikely to occur.

Finally, in Fig. 6 we show the calculated binding energy of the complexes as a function of the Fermi level. These binding energies are calculated by the difference in the formation energies between the complex and the respective point defects for different Fermi level positions. We find that V_B-O_N shows the higher binding energies, as expected for a complex formed by first-neighbor V_B and O_N defects. The V_B-O_N binding energy increases from 0.5 eV for p type to 1.6 eV for semi-insulating c-BN, indicating an exothermic process for the complex formation which would be stable against dissociation. However, for n-type c-BN, its binding energy decreases drastically suggesting that the complex becomes unstable under such conditions. For V_N-C_N we also find a stable complex for semi-insulating c-BN with binding energies of about 0.4 eV, which can increase to 1.6 eV going for n-type c-BN, becoming a very stable complex under such condition considering that it is formed by second-neighbor V_N and C_N defects. However, V_B-C_B shows negative binding energies for p-type and n-type c-BN, therefore being unstable against dissociation into V_B and C_B defects.

IV. SUMMARY

We have investigated the electronic structure, atomic geometry, and formation energies of substitutional carbon and oxygen impurities as well as complexes formed by these impurities and vacancies in c-BN, using pseudopotential total-energy calculations. We find that, under a B-rich condition, both C_N and O_N have formation energies comparable to or lower than those calculated for the vacancies, which are the lowest-energy intrinsic defects. The low formation energy of C_N and the fact that it exhibits an acceptor state close to the valence band edge (a quantitative description of shallow states is presently beyond first-principles calculations[33]) suggests that this impurity might be related to observed p-type conductivities in c-BN.

Based on our results on the formation energies for the point defects, we considered the following complexes which shall be suitable to form: V_N-C_N, V_B-C_B, and V_B-O_N. We find that the donor character of V_N and the acceptor character of C_N mutually compensate in the formation of the neutral V_N-C_N complex which is stable for semi-insulating c-BN, as supported by experimental observation.[16] This complex can also act as a donor or as an acceptor for p-type or n-type conditions, respectively. For the neutral V_B-C_B and V_B-O_N complexes we find similar electronic structures, both acting as double acceptors. For a B-rich condition, the V_N-C_N complex has low formation energies for any Fermi level positions, being favorable to form, while V_B-O_N has low formation energies only for n-type c-BN. These characteristics make them strong candidates for dopant compensation under such conditions. However, for V_B-C_B we find an energetically unfavorable complex, unlikely to form under a B-rich condition.

Our calculations suggest that oxygen impurities, either as an isolated substitutional defect or associated with a boron vacancy, might negatively affect the conductivity characteristics of c-BN samples. Under B-rich conditions, the O_N defect has low formation energies for any Fermi level position, and can be either an acceptor or a donor impurity (depending on the position of the Fermi level). Therefore, it should be considered as a source for either electron or hole compensation. Also, the V_B-O_N defect has low formation energies for n-type conditions, where it is a deep double acceptor. These results indicate that oxygen contamination might reduce carrier concentrations or even induce semi-insulating characteristics on c-BN.

For a N-rich condition, the C_B and C_N defects have low formation energies for any Fermi level position which are close in energy. Therefore, they would be equally favorable to be incorporated inducing simultaneous p-type and n-type conductivities. Finally, for the same sublattice-defect complexes we find an opposite behavior for the formation energies as observed under a B-rich condition. V_B-C_B has low formation energies for semi-insulating and n-type c-BN acting as a double acceptor, while V_N-C_N is an energetically unfavorable complex unlikely to form.

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