Hybrid functional with semi-empirical van der Waals study of native defects in hexagonal BN

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The formation energies and transition energy levels of native defects in hexagonal BN have been studied by first-principles calculations based on hybrid density functional theory (DFT) together with an empirical dispersion correction of Grimme’s DFT-D2 method. Our calculated results show that the interstitial B is the most stable defect in BN under N-rich and p-type conditions, followed by the N vacancy. While the B vacancy and interstitial N become the dominate defects when the electron chemical potential near the conduction band maximum of host. Nevertheless, the calculated ionization levels of these native defects are ultra deep, indicating that they will not act as effective charge compensating defects under both p- and n-type conditions.

I. INTRODUCTION

Hexagonal boron nitride (h-BN) is a promising material for the realization of compact ultraviolet laser devices,[8,9] high-temperature and high-pressure device.[10] Because it has high temperature stability, a low dielectric constant, high mechanical strength, a large thermal conductivity, high hardness, and high corrosion resistance. Furthermore, it also can be well integrated with graphene to design new novel devices as they have small mismatch (1.6%) and the same hexagonal structure.[11] It exists in various phases, including cubic (c-BN), wurtzite (w-BN), hexagonal (h-BN) structures. Similar to graphite, h-BN consists of stacked BN layers with equal numbers of boron and nitrogen atoms. Within each h-BN layer, alternating boron and nitrogen atoms form a honeycomb sheet by \(sp^2\) hybridization, while the interlayer attractive forces are mediated by pseudodelocalized out-of-plane \(\Pi\) orbital and weak van der Waals interactions. In contrast to the semimetallic behavior of graphite, h-BN is a wide gap semiconducting material due to its partially ionic character of the BN bond.

h-BN is commonly synthesized through mechanical[12] or liquid-phase[13] exfoliation, chemical vapor deposition (CVD)[14,15] During the process of BN growth, native defects are thus readily formed as result of the regular synthesis processes in an uncontrolled way, and they can be unintentionally generated to modify the conductivity of h-BN. Recently, Shi et al. synthesized h-BN films with the thickness up to 20 \(\mu\)m on the Ni surface by CVD. They pointed that the B/N ratio reaches to be 1:1.12 detected by X-ray photoelectron spectroscopy.[16] A detailed investigation on the stability and conductivity of native defects in h-BN becomes necessary. Previous theoretical studies have investigated the native defects in h-BN based on traditional density functional theory (DFT) within generalized gradient approximation (GGA) or local density approximation (LDA).[13,14] The native defect properties of hexagonal BN bilayer and monolayer have also been studied in our earlier DFT-GGA calculations.[16] However, the severe underestimation of traditional DFT on the band gap of semiconductors, especially in the wide-gap semiconductors, results in large uncertainties in the position of defect levels and the stability of defects.[13,16,21]

The recent development of hybrid density functional theory[22] provides an accurate description of band structures of semiconductors and insulators.[23] It is therefore necessary to use hybrid density functional that overcome the band gap problem in order to correctly describe the electronic properties of native defects in h-BN. Hybrid functionals, which mix a fraction of Hartree-Fock (HF) exchange with the LDA or GGA exchange and correlation potentials, can correct the band gap and, in principle, allow for a better description of formation energies and transition levels. In this paper, we have systematically revisited the formation energies and transition energies of native defects in h-BN using hybrid density functional theory. Our results show that the calculated transition energies of all native defects are ultra deep and thus neither of them cannot contribute or compensate specific conductivity by extrinsic doping. The remainder of this paper is organized as follows. In Sec. II, the details of the computation are described. Sec. III presents our calculated formation energies and single particle energy levels of native defect in bulk hexagonal BN. Finally, a short summary is given in Sec. IV.

II. METHODS

Our total energy and electronic structure calculations were based on spin-polarized Kohn-Sham theory with the hybrid functional as proposed by Heyd, Scuseria, and Ernzerhof (HSE) as implemented in the VASP code employing the projector augmented wave potentials.[22] In the HSE approach, a screening parameter of 0.2 Å\(^{-1}\) was used as suggested for the HSE06 functional.[22,23] We found that a proportion of \(\alpha=33\%\) HF exchange with 67% GGA of Perdew, Burke and Ernzerhof (PBE) exchange produces an accurate value of the band gap for h-BN. The week van der Waals interaction...
between the layers plays a key role in determining the interlayer distance for materials with layered structure. We incorporated the van der Waals interactions through employing an empirical correction scheme of Grimme’s DFT-D2 method, which has been proven to be successful in describing the geometries of layered materials.

The hexagonal BN structure has four atoms per unit cell with five possible phases. More details about the effects of stacking behavior can be found in Refs. 31 and 32. The most stable AB-like stacking sequence with each boron atom on top of a nitrogen atom is adopted in our current study. The DFT-D2 (global scaling factor \(s_g=0.40\)) plus HSE06 (\(\alpha=0.33\)) scheme gives the calculated optimized lattice constants are \(a=2.50\) Å and \(c=6.42\) Å respectively, in good agreement with the experimental values of \(a=2.50\) and \(c=6.66\) Å.

The defect systems were modeled by adding (removing) an atom to (from) in a \(4\times4\times2\) \(h\)-BN supercell consisting of 128 atoms, resulting in the separation between defect reaching to \(\sim 10\) Å. The wave functions were expanded by plane waves up to a cutoff energy of 300 eV. The integrations over the Brillouin zone were performed using Γ-centered \(2\times2\times2\) k-point mesh generated by Monkhorst-Pack scheme. The internal coordinates in the defect supercells were relaxed to reduce the residual force to less than 0.02 eV·Å\(^{-1}\). In the charged-defect calculations, a uniform background charge is added to keep the global charge neutrality of supercell. The formation energy of a charged defect is defined as:

\[
\Delta E_f^D(\alpha, q) = E_{tot}(\alpha, q) - E_{tot}(0) - \sum n_{\alpha} \mu_\alpha + q(\mu_e + \epsilon_e + \Delta V_{align}[q]),
\]

where \(E_{tot}(\alpha, q)\) and \(E_{tot}(0)\) are the total energies of the supercell with and without defect \(\alpha\). \(n_{\alpha}\) (\(n_{\alpha}=1\)) is the number of species \(\alpha\) (\(\alpha=B, N\)) needed to create the defect \(D\), and \(\mu_\alpha\) is the corresponding atomic chemical potential. \(q\) is defect charge state, and \(\mu_e\) is electron chemical potential in reference to the valence band maximum (VBM, denoted as \(\epsilon_e\)) of bulk \(h\)-BN. The electron chemical potential varies between zero and the band-gap \(E_g\). The potential offset \(\Delta V_{align}[q]\) is determined by the difference of the atomic-sphere-averaged electrostatic potentials around host atoms farther away for the defect, relative to the atomic-sphere-averaged electrostatic potentials around host atoms in the defect-free supercell.

The chemical potential \(\mu_\alpha\) depend on the experimental growth conditions. The chemical potentials of boron and nitrogen are subject to their lower bounds satisfied by the constraint \(\mu_{B\alpha}(bulk)=\mu_B+\mu_N\), where \(\mu_{B\alpha}(bulk)=\) is the total energy of \(h\)-BN (per formula unit). The HSE06 calculated formation energy of \(h\)-BN is \(-2.95\) eV, slightly unstable 0.35 eV than the value obtained by the previous GGA-based calculation. The \(\mu_N\) is subject to an upper bound given by the energy of N (-10.34 eV) in a \(N_2\) molecule, corresponding to extreme N-rich/B-poor growth conditions. Similarly, the upper bound of the \(\mu_B\) is limited by the energy of one B atom (-7.65 eV) in bulk boron, corresponding to extreme B-rich/N-poor growth conditions.

The defect transition energy level \(\epsilon_\alpha(q/q')\) is the Fermi energy in Eq. (1) at which the formation energy \(\Delta E_f^D(\alpha, q)\) of defect \(\alpha\) with charge \(q\) is equal to that of another charge \(q'\) of the same defect. In practice, the charge state of defects will be determined by both the position of the transition levels and the Fermi level in the material:

\[
\epsilon_\alpha(q/q') = \frac{\Delta E_f^D(\alpha, q) - \Delta E_f^D(\alpha, q')}{(q'-q)}.
\]

### III. RESULTS AND DISCUSSION

#### A. Pristine bulk \(h\)-BN

Despite the larger number of experiments and theoretical calculations devoted to the study of the electronic properties of bulk \(h\)-BN, both direct and indirect band gap are not yet accurately determined; the band gap energies ranging from 3.2 to 5.97 eV have been reported in the previous studies. For example, Watanabe et al. showed that \(h\)-BN has a direct band gap of 5.97 eV by experiments. However, this results is in contradiction with the most recent quasiparticle theoretical calculations. Liu et al. attributed such disagreement between experiment and theory to the coexistence of the substable structure with a direct band gap in bulk \(h\)-BN. Before proceeding to the results for the native defects in \(h\)-BN, it is worthwhile to investigate the band structure of \(h\)-BN using HSE06 functional. The HSE06 calculated band structure of \(h\)-BN is shown in Fig. 1(a). Our calculations predict that the VBM is situated at the H point, with the conduction band minimum (CBM) located at M point, resulting in a indirect band gap of 5.92 eV, slightly larger ~0.4 eV than the direct band gap at the H point. Analysis of the HSE06 calculated partial density of state (DOS), Figure 1(b) shows that the upper valence band is dominated by N-2p states, with the lower conduction band comprised mostly of B-2p ones. In fact, as it will be shown in latter, the highest occupied band (HOB) and the lowest unoccupied band (LUB) of bulk \(h\)-BN mainly derive from the N-2p\(z\) and B-2p\(z\) respectively.

#### B. Native defects in \(h\)-BN

In semiconductors and insulators, defects typically introduce levels in the band gaps of the host materials. We first examine the defect induced DOS in the band gap of the systems with neutral single B vacancy (\(V_B\)), N vacancy (\(V_N\)), interstitial B (\(B_i\)) and interstitial N (\(N_i\)), respectively. The HSE06-calculated defect DOS are plotted...
It is expected that the possible charge states \( \epsilon \) occupied defect state at \( \epsilon \) defect level(s) in the spin-up (-down) component around the Fermi level is labeled by using a blue vertical line. The Fermi level is set to zero.

In Fig. 2, in comparison with the DOS of defect-free system, we note that the \( V_B \) introduce one (two) unoccupied defect level(s) in the spin-up (down) component around \( \epsilon_v+3.0 \) eV above VBM into the fundamental band gap of host. It is expected that the possible charge states of \( V_B \) can range from 0 to 3-. The \( V_N \) introduce one occupied defect state at \( \epsilon_v+3.0 \) eV as well as one unoccupied one \( \epsilon_v+5.9 \) eV in the spin-up component, and one unoccupied state \( \epsilon_v+5.0 \) eV in the spin-down component. Thus, its possible charge states can range from 1+ to 2-. As shown in Fig. 2(e), three occupied defect states and three unoccupied ones are introduced by the \( B_1 \). It is noteworthy that there are double-degenerate states occupied by four electrons just above CBM originating from the N 2p\(_x\), instead of the introduction by the \( B_1 \). The reason is attributed to the interaction between the \( B_1 \) and the N atoms in the adjacent BN layer. A wide range of the possible charge states from 3+ to 3- can be expected for the \( B_1 \). Finally, we note that one occupied defect state at \( \epsilon_v+0.1 \) eV and one unoccupied state at \( \epsilon_v+1.5 \) eV in the band gap of host with \( N_i \). Therefore, the 1+ charge state is the lowest achievable charges state of \( N_i \). Adding one, and two electrons into the \( N_i \) defect state in the spin-down component results in the 0 and 1- charge states. Previous theoretical study reports the formation energies as a function of charge state for all native defect. However, based on the HSE06-calculated defect DOS, we find that not all native defects can in the charge states ranging from 3+ to 3-. Nitrogen vacancy is an example.

For the neutral \( V_B \) with a calculated total magnetic moment of 1 \( \mu_B \), we find that its wave functions localize symmetrically over all three N neighbors and show a \( sp^2 \)-like hybridized character [Fig. 3(a)]. No significant John-Teller distortion is observed, namely, the average N-N distances between these three nitrogen atoms are practically equal and are about 2.70 Å. The N-N distances equably reduce to 2.55 Å when the \( V_B \) in the charge state of 1-, closing to the ideal N-N distance of 2.5 Å. We attribute the decrease of N-N distance to the repulsion between B atoms and the neighboring N ones of \( V_B \). It is expected that N-N distances further reduce when the \( V_B \) capture more extra electrons. On the other hand, the strong Coulomb repulsion between the negatively charged N atoms results in the out-of-plane distortion for one (denoted as \( N_{out} \)) of the three N neighbors in the case of \( V_B^{-2} \). Bader charge analysis estimate that the \( N_{out} \) and the other two N atoms neighboring the \( V_B \) (\( N_{in} \)) capture about 0.95 \( e \) and 0.44 \( e \) per \( N \) respectively due to the existence of symmetry breaking. The \( N_{out} \) is found to attract and bond with the nearest neighbor B locating the next to BN layer in turn, as shown in Fig. 3(c). Based on the defect levels induced by \( V_B \), the total magnetic moments of the systems consisting of \( V_B^{-2} \), \( V_B^{-1} \), \( V_B^{+1} \), \( V_B^{+2} \) and \( V_B^{+3} \) are expected to 2 \( \mu_B \), 1 \( \mu_B \) and 0 \( \mu_B \).

In contrast to the behavior of \( V_B \), the wave functions of defect states induced by \( V_N \) mainly localize on two of the three B neighbors and show a B \( p_z \) character, as displayed in Fig. 7. The B-B distances between these B neighbors shorten from 2.44 Å for \( V_B^{+3} \) to 2.07 Å for...
The changes of B-B distances almost undergo in the same BN layer plane when the VN in different charge states except for the 2− state. In the latter case, a slightly out-of-plane distortion is observed for VN neighbors. As shown in Fig. 2 (d), the occupied defect state at 3.0 eV above VB results in the the total magnetic moment of 1 µB for the system with neutral VB. Therefore, the VN1+, VN−1 and VN2− will contribute 0 µB, 0 µB and 1 µB to system respectively, according to the electron filling in defect levels.

There are three possible interstitial sites for B or N atoms occupying, namely, the hollow site above the center of the space decided by the directly opposite the two BN hexagon in adjacent two BN layer, the top site directly over a B atom (below a N atom in the above adjacent layer) and the bridge site above (below) the middle of a B-N bond (the above adjacent layer). This is similar to the case of transition-metal adsorbed on graphene layer investigated in our previous studies [2]. The optimized local structures of Bi under different charge states are more complicated than the B and N vacancies discussed above. As typical models, we display the relaxed local structures as well as the calculated band decomposed charge-density of B3+ and B3− in Fig. 3 (a) and (b). First, we note that the Bi always favor the top site. It is found that a N-B-B-N vertical chain forms when the Bi in the 3+ charge state. In contrast, the B3+ with three neighboring lattice B atoms bond tetrahedrally. The wave functions of defect levels are found to localize on the Bi atom. We can also deduce the magnetic moment of Bi in any possible charge state from the calculated value of 1 µB in the charge-neutral state.

Since the extreme B-rich growth conditions is probably not experimentally accessible which corresponds to very low nitrogen partial pressures. In our present study, we only show the formation energies of native defects under N-rich conditions. The VB, VN, Bi and Ni formation energies as a function of electron Fermi level are plotted in Fig. 4. Under p-type condition EF near VBM, the Bi3+ with a formation energy of around -0.78 eV is found to be the most stable defect. The solubility of Bi3+ is expected to be high under equilibrium conditions. The Bi acts as a donor-like defect, but its calculated transition level of (3+/0) is 3.4 eV with respective to VBM. This is a rather deep level, indicating that it will not compensate accep-
tor formation for \( p \)-type doping. On the other hand, the formation of the other defects (\( V_B \), \( V_N \), and \( N_i \)) is high, at least 4.54 eV. This suggests that the concentration of these defect will be negligibly under equilibrium conditions. When the \( E_F \) is close to CBM, the \( V_B \) and \( N_i \) become more stable with respect to the \( V_N \) and \( B_i \). This is consistent with the experimental observation of higher concentration of nitrogen than boron.

Similar results were found in the case of \( n \)-type doping, the shallowest donor levels \((1-/2-)\) and \((2-/3-)\) are occurring at the 2.0 eV and 3.0 eV below the CBM for the \( N_i \) and \( V_B \), respectively. Thus, the dominating electron killer \( N_i \) and \( V_B \) are ineffective under \( n \)-type conditions.

**IV. SUMMARY**

In summary, we have systematically studied the native defects in hexagonal BN using first-principles calculations based on hybrid density functional theory. The van der Waals interactions between BN layer are described via Grimme’s DFT-D2 method. We first investigated the defect levels induced by the neutral native defects to determine the possible charge states of these defects. Then we calculated the formation energies and local structures of various native defects as a function of their possible charge states. We found that \( B_i \) is the most stable in \( n \)-BN under \( N \)-rich and \( p \)-type conditions, followed by the \( V_N \). While the \( V_B \) and \( N_i \) become more energetically stable when the electron chemical potential near the conduction band maximum of host. The relaxed structures of native defects were found to be strongly dependent on their charge states. Finally, based on the calculated transition energies, it is found that the energetically favorable defects will not act as effective charge compensating defects under both \( p \)- and \( n \)-type conditions due to their ionization levels are ultra deep.

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