Berseneva, N.; Gulans, A.; Krasheninnikov, A.V.; Nieminen, R.M.

Electronic structure of boron-nitride sheets doped with carbon from advanced first-principles calculations

Published in:
Physical Review B

DOI:
10.1103/PhysRevB.87.035404

Published: 01/01/2013

Please cite the original version:

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Electronic structure of boron nitride sheets doped with carbon from first-principles calculations

Natalia Berseneva,1 Andris Gulans,1 Arkady V. Krasheninnikov,1,2 and Risto M. Nieminen1
1COMP Centre of Excellence and Department of Applied Physics, P.O. Box 11100, FI-00076 Aalto University, Espoo, Finland
2Department of Physics, University of Helsinki, P.O. Box 43, FI-00014, Finland

(Received 15 May 2012; published 2 January 2013)

Using density functional theory with local and non-local exchange and correlation (XC) functionals, as well as the Green’s function quasiparticle (GW) approach, we study the electronic structure of hexagonal boron nitride (h-BN) sheets, both pristine and doped with carbon. We show that the fundamental band gap in two-dimensional h-BN is different from the gap in the bulk material, and that in the GW calculations the gap depends on the interlayer distance (separation between the images of the BN layers within the periodic supercell approach) due to the non-local nature of the GW approximation, so that the results must be extrapolated to infinitely large separations between the images. We further demonstrate by the example of carbon substitutional impurities that the local and hybrid XC functionals give a qualitatively correct picture of the impurity states in the gap. Finally, we address the effects of many important parameters, such as the choice of chemical potential, and atom displacement cross sections for the substitutional process during electron-beam-mediated doping of h-BN sheets with carbon atoms. Our results shed light on the electronic structure of pristine and doped h-BN and should further help to optimize the post-synthesis doping of boron nitride nanostructures stimulated by electron irradiation.

I. INTRODUCTION

Isolation of single sheets of graphene,1 a truly two-dimensional (2D) material, and the discovery of its unique properties2 have given rise to vigorous research of other 2D systems.3–5 Among them, a structural analog of graphene, a single sheet of hexagonal boron nitride (h-BN) comprised of alternating boron and nitrogen atoms, has received particular attention.6–9 Similar to graphene, h-BN has excellent mechanical properties and high thermal conductivity, while its electronic structure is different: in comparison to semimetallic graphene with zero band gap, 2D electronic structure is different: in comparison to semimetallic graphene, h-BN is a wide (more than 5 eV) band gap semiconductor (see Ref. 10 for an overview of the properties of BN nanostructures).

Both graphene1,11–14 and 2D h-BN15,16 can be grown using the chemical vapor deposition (CVD) technique. Keeping in mind the similarities between the atomic structures of these systems (the mismatch between the lattice constants of the materials is only 2%) and the radically different electronic properties, the growth of doped BN and hybrid boron carbon nitride (BCN) materials with tunable electronic characteristics has been attempted.17 However, although the growth of N-doped graphene has been successfully demonstrated, the hybrid BCN material has proven to be thermodynamically unstable with regard to segregation to graphene and h-BN, so that the growth of homogeneous structures has not been achieved. At the same time, CVD does not provide enough spatial control over the growth of the structures, making impossible the development of well-defined graphene and BN regions within a single sheet, the composite structures which have been predicted to have peculiar electronic and magnetic properties.

A different approach to the development of hybrid BCN materials was recently demonstrated.28,29 The method was based on the post-synthesis substitutional carbon doping of h-BN sheets29 and BN nanotubes28 via in situ electron-beam irradiation inside a transmission electron microscope (TEM). It was found that carbon atoms coming from the decomposition of hydrocarbon molecules (intentionally added to the TEM chamber) under the 300 keV electron beam take the positions of boron atoms; see Fig. 1(a). Using essentially the same technique, C impurities were also introduced into BN sheets at electron energies of 60 keV.30

It was later theoretically shown that the main driving force for the substitution is the energetics of the system, as it costs less energy to substitute a B atom than an N atom, especially when the system is becoming charged due to the electron-beam irradiation. The kinetic effects (the displacement rates for B and N atoms) could not fully explain the preferential substitution of B atoms, as at an acceleration voltage of 300 kV the rates are roughly the same for B and N atoms.32 Considering the possibility of creating triangular holes in the h-BN sheet, shown in Fig. 1(b), it was also suggested that a focused electron beam could be employed to create triangular carbon islands or straight ribbons embedded into the BN matrix, as schematically shown in Fig. 1(c), either through beam-mediated substitution reactions or by “filling up” the holes. The theoretical analysis of the substitution process was based on first-principles calculations of formation energies of various substitutional carbon impurities in the h-BN matrix. The formation energies of defects in finite supercells were computed for different charge states as functions of electron chemical potentials within the framework of density functional theory (DFT), using local and hybrid exchange and correlation (XC) functionals. The simulation setup and its adequacy for describing the experimental conditions were discussed later on, eventually giving rise to a question of how well the DFT approach describes the electronic structure of h-BN with carbon impurities.

The main goal of this paper is to study the electronic structure of an h-BN sheet with carbon substitutional impurities using advanced techniques such as DFT with hybrid functionals and Green’s function quasiparticle (GW) methods. We first carefully simulate the electronic structure of the pristine 2D h-BN material and study the convergence of the
results with regard to the most important parameters. We show that due to the non-local nature of the GW approximation, the calculated fundamental band gap in 2D h-BN depends on the interlayer distance in the simulation supercell (that is the separation between the images of the h-BN sheet within the periodic supercell approach), and that the results must be extrapolated to infinitely large separation between the images. We also show, that contrary to what has been assumed in many papers, the band gaps of bulk and 2D h-BN systems differ by more than 0.5 eV. We further demonstrate, by the example of single- and four-carbon-atom substitutional impurities, that the local and hybrid XC functionals give a qualitatively correct picture of the impurity states in the gap. Finally, we address the effects of many important parameters such as the choice of chemical potential, interlayer distance, displacement cross section of electron-beam-mediated substitution process, and the charge state of the system.

II. COMPUTATIONAL METHODS

We carried out first-principles spin-polarized plane-wave electronic-structure calculations within density functional theory, as implemented in the VASP code. We used projector-augmented wave potentials to describe the core electrons and the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) to account for the exchange-correlation energy of interacting electrons. As the PBE approach normally underestimates the band gap and thus may give rise to incorrect positions of the impurity levels, more accurate results were obtained with the use of the hybrid Heyd-Scuseria-Ernzerhof (HSE) functional. To confirm the results, we carried out even more rigorous GaW6, GW0, and GW (Refs. 38,39) calculations on top of the PBE data. Structural optimizations of all geometries were performed by the conjugate-gradient scheme until the maximum allowed force acting on each atom was less than 0.02 eV/Å. In most of the calculations, the one-electron Kohn-Sham wave functions were expanded over a plane-wave basis with a kinetic energy cutoff of 400 eV. We further studied the dependence of the results on the kinetic energy cutoff, as described in Sec. III A.

In this work, we investigate both neutral and charged states of the h-BN system with impurity atoms. Supercells of different sizes (2, 18, 32, and 72) with different numbers of B and N atoms substituted with C atoms were employed. In order to prevent spurious interlayer interaction within the periodic supercell simulation scheme, we used a vacuum spacing between adjacent 2D h-BN layers (in the direction normal to the sheet) of 10 Å. The dependence of the results on vacuum spacing was tested, as described in Secs. III A and III B. In the total-energy calculations, k points in the Brillouin zone (BZ) were generated by the Monkhorst-Pack scheme with a Γ-centered grid. The optimal number of k points used to sample the BZ was determined by a series of convergence tests. Particularly, we used 6 × 6 × 1, 4 × 4 × 1, and 6 × 6 × 3 Γ-centered k-point meshes for computing, respectively, the 3 × 3 (18 atoms), 4 × 4 (32 atoms), and bulk h-BN with AB stacking. Such a simulation setup has been demonstrated to be adequate for the modeling of defects and impurities in 2D systems with covalent bonding. DFT molecular dynamics (MD) simulations of atom dynamics after electron impacts were carried out as in Refs. 32 and 42.

III. RESULTS AND DISCUSSION

A. Electronic structure and band gap of the pristine h-BN sheet

Although the electronic structure of bulk and 2D h-BN materials has been studied at length, both experimentally and theoretically, the reported results differ considerably from each other. Theoretical estimates of the gap for an isolated h-BN sheet vary from 4.6 to 7.1 eV depending on the simulation method used. Experimental data also vary from 4.6 to 7.0 eV. Moreover, it was assumed in many works that the gap of 2D h-BN is the same as in bulk 3D material. Interestingly enough, in spite of a large number of experiments on the electronic properties of bulk h-BN (see Refs. 50 and 51 and references therein), neither the direct nor indirect band gap is accurately known: the values reported in the literature range from 3.6 to 7.1 eV; see Ref. 51. Putting aside uncertainties in the stacking order of the layers affecting the electronic structure, different experimental techniques (optical/transport measurements) used to measure the gap, and strong excitonic effects in h-BN (which should decrease the gap by nearly 1 eV), it is desirable to have the accurate theoretical value for a single h-BN sheet obtained from the GW calculations. Although such calculations have already been carried out, the convergence of the results with regard to the most important parameters, such as the amount of vacuum between the images of the sheet (within the periodic supercell approach) and the number of empty states accounted for, has not been studied before.

In order to accurately assess the gap of the isolated h-BN sheet and get further insight into the electronic properties...
ELECTRONIC STRUCTURE OF BORON NITRIDE SHEETS ... PHYSICAL REVIEW B 87, 035404 (2013)

Fig. 2. (Color online) (a) PBE, (b) HSE, and (c) $G_0W_0$ band structure for pristine $h$-BN sheet (2-atom unit cell) with 10 Å vacuum layer thickness. The top of the valence band within the PBE is taken as zero energy. The edges of the PBE band gap are indicated by black dashed horizontal lines. The Greek letters stand for high-symmetry points in the BZ of the supercell.

Fig. 3. (Color online) The band gap extrapolated to the complete-basis limit as a function of the number of unoccupied states accounted for at different plane-wave cutoff energies calculated using $G_0W_0$ for $h$-BN with 10 Å vacuum layer thickness. The labels stand for different plane-wave cutoff energies used for the representation of the Kohn-Sham eigenstates.

Fig. 4. (Color online) The band gap as a function of the inverse interlayer distance (1 Å) for bulk $h$-BN (AB stacking) are 6.07, 6.41, and 6.90 eV, respectively. The band gap increases with each level of self-consistency, and this observation is in agreement with the trends observed in Refs. 38 and 39.

Apart from purely numerical issues, we also considered how the band gap depends on the thickness of the vacuum layer between the images of the $h$-BN sheet. As the separation between $h$-BN layers increases, the PBE/HSE band gap quickly saturates to the monolayer limit, as shown in Fig. 4.

The numerical reliability of existing many-body studies of bulk and single-layer BN is unclear in light of recent GW calculations done by Friedrich et al. and Shih et al. They considered quasiparticle spectra of ZnO and showed that the calculated band gap is very sensitive to the number of available unoccupied states and perform the extrapolation to the complete basis limit in further $G_0W_0$, $GW_0$, and GW calculations.

The obtained $G_0W_0$, $GW_0$, and GW quasiparticle gaps for bulk $h$-BN (AB stacking) are 6.07, 6.41, and 6.90 eV, respectively. The band gap increases with each level of self-consistency, and this observation is in agreement with the trends observed in Refs. 38 and 39.

Apart from purely numerical issues, we also considered how the band gap depends on the thickness of the vacuum layer between the images of the $h$-BN sheet. As the separation between $h$-BN layers increases, the PBE/HSE band gap quickly saturates to the monolayer limit, as shown in Fig. 4.

The obtained $G_0W_0$, $GW_0$, and GW quasiparticle gaps for bulk $h$-BN (AB stacking) are 6.07, 6.41, and 6.90 eV, respectively. The band gap increases with each level of self-consistency, and this observation is in agreement with the trends observed in Refs. 38 and 39.

Apart from purely numerical issues, we also considered how the band gap depends on the thickness of the vacuum layer between the images of the $h$-BN sheet. As the separation between $h$-BN layers increases, the PBE/HSE band gap quickly saturates to the monolayer limit, as shown in Fig. 4.
TABLE I. Calculated and experimental results for bulk and planar (2D) BN.

<table>
<thead>
<tr>
<th>Structure</th>
<th>(E_{\text{G0W0}}) (eV)</th>
<th>(E_{\text{GW0}}) (eV)</th>
<th>(E_{\text{GW}}) (eV)</th>
<th>Expt. value (eV)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>6.07</td>
<td>6.41</td>
<td>6.90</td>
<td>3.6–7.1</td>
<td>50, 51</td>
</tr>
<tr>
<td>2D</td>
<td>7.40</td>
<td>7.83</td>
<td>8.43</td>
<td>4.6–7.0</td>
<td>49</td>
</tr>
</tbody>
</table>

The situation is different in the GW calculations. The \(G_0W_0\), \(GW_0\), and GW band gaps for an isolated \(h\)-BN sheet (at 10 Å vacuum separation) are 6.60, 7.00, and 7.60 eV, respectively. The \(G_0W_0\) value agrees well with the results reported in Ref. 47. However, it is evident from Fig. 4 that the band gaps calculated at 40 Å of the interlayer separation in \(h\)-BN are different from the values calculated at 10 Å and still differ from the limit of infinite separation. This behavior contrasts with the PBE and HSE data, where a separation of 15 Å is sufficient to obtain a converged band gap.

Such a difference between PBE/HSE and all three quasiparticle methods can be explained by non-local screening effects, which are described with the GW formalism, but cannot be captured with PBE and HSE. For a detailed discussion of the physics behind this effect, we refer to Refs. 60 and 61. In the limit of large separations \(d\) between \(h\)-BN layers, the GW band gap converges as \(1/d\), and we use this dependence for extrapolation. Truncation of the Coulomb interaction in the direction perpendicular to the sheets may also be a solution to this problem.

The \(G_0W_0\), \(GW_0\), and GW band gaps for an isolated \(h\)-BN sheet (at infinite separation) are 7.40, 7.83, and 8.43 eV, respectively. It is obvious that the band gaps for bulk and monolayer \(h\)-BN differ by more than 0.5 eV (see also Table I).

B. Electronic structure and band gap of the \(h\)-BN sheet with carbon impurities

Having analyzed the electronic structure of the pristine \(h\)-BN sheet, we calculated the band structures of doped BN sheets with triangular-shaped substitutional carbon defects. Examples of investigated configurations are shown in Fig. 5. Throughout this paper, we use the following notations: \(C_B\) means that a single B atom was substituted with a C atom, while \(4C_{3B1N}\) stands for a triangular island formed by substituting three B and one N atoms with four C atoms, etc.

In Fig. 7, we present PBE and HSE band structures for 32-atom supercells with substitutional defects composed from one to four carbon atoms (\(C_B\), \(C_N\), \(4C_{3B1N}\), \(4C_{1B3N}\)) inserted into the \(h\)-BN host matrix. The PBE and HSE pictures are qualitatively the same, which explains the good agreement between the HSE and PBE formation energies of the defects reported earlier. New states associated with defects appear in the gap, either deep states close to the middle of the gap or shallow states close to the band edges. It is obvious that the larger the defect size, the more new states appear in the band gap (Fig. 6). Defects with the preferential substitution of B atoms (e.g., \(4C_{3B1N}\)) give rise to occupied states (for zero electron chemical potential), while those with the preferential substitution of N atoms (e.g., \(4C_{1B3N}\)) structure give rise to empty states.

We also carried out quasiparticle \(G_0W_0\) calculations for single-atom impurities. The band structures for a 18-atom system (at 10 Å interlayer separation) with \(C_B\) and \(C_N\) defects are shown in Fig. 8. The positions of the impurity levels qualitatively agree well for PBE, HSE, and \(G_0W_0\) calculations. In addition, we considered the band structure dependence on the thickness of the vacuum layer between the images of the \(h\)-BN sheets. Due to the high computational cost, only calculations with 12.5 and 15 Å vacuum layer separation were carried out for an 18-atom system with \(C_B\) and \(C_N\) defects. We conclude that with increasing the interlayer distance, the impurity level moves up in energy (towards the conduction band edge).

C. Defect formation energies: The role of chemical potential

The substitutional carbon defects can appear in various charge states \(q\). The formation energy \(E_f\) of a defect composed of \(K_C\) carbon atoms inserted to replace \(K_B\) boron and \(K_N\) nitrogen atoms (\(K_B + K_N = K_C\)) in the \(h\)-BN
Electrical conductivity of B and C sheets is measured as a function of temperature. The results show that the conductivity of B sheets is higher than that of C sheets at room temperature. The conductivity of B sheets decreases with increasing temperature, while the conductivity of C sheets remains relatively constant. The activation energy for the conductivity of B sheets is found to be lower than that of C sheets, indicating a stronger bond strength in B sheets. The observed behavior is consistent with theoretical predictions based on the electronic structure of these materials. Analysis of the band structures and density of states further supports the experimental findings. Overall, the study demonstrates the potential of B sheets for applications requiring high electrical conductivity at moderate temperatures.
The horizontal lines stand for the $E_f$ atoms with C for the neutral charge states as functions of $\mu$ in the supercell (at 10 Å vacuum separation) where a B or N atom is substituted with a C atom. Calculations are done involving PBE (blue lines) and G0W0 (red lines) approaches. Green dotted lines emphasize the impurity levels. Spin-up and spin-down results are presented. The top of the valence band within the PBE is taken as zero energy. The displacement difference between the reference system and a configuration shown on the right side from the arrow. $q$ stands for the charge. It is evident that positive charge decreases the formation energy of substitutional C impurity in the position of the B atom.

The complete understanding of the substitution process under the electron beam is not possible without the microscopic knowledge of the dynamical effects. To estimate the role of kinetics in the process of carbon substitution, molecular dynamics simulations of electron impacts onto the h-BN monolayer were carried out. Since we are interested in the growth of carbon islands under electron-beam irradiation, displacement thresholds of C substitutional impurity (in the B- and N-atom position) as well as its nearest-neighbor B and N atoms were calculated. The displacement threshold ($T_d$) is the minimum kinetic energy that should be delivered to the atom to remove it from its position without immediate recombination. The corresponding electron threshold energy can be estimated when $T_d$ is known. In addition, when the displacement threshold is known, the estimation of the displacement rate ($\sigma$) can be done using the McKinley-Feshbach...
formalism for Coulomb scattering of relativistic electrons. In the simulations, the \( h \)-BN sheet is oriented perpendicularly to the incident electron direction and thus maximum energy transfer from the incident electron to the atom is considered. Kinetic energy was instantaneously assigned to the recoil atom, and DFT molecular dynamics was used to investigate if the amount of energy was sufficient to take the atom away from the system. We neglected the effects of temperature on the displacement thresholds, as they give rise to a tail just below the threshold only and do not change the shapes of the curves at higher voltages.

We found that \( T_d \) for the C atom (independent of the B or N atom substitution) is 1.5 eV less than for a B atom in the pristine system, giving a rise to a 30% increase in the displacement rate (for 300 keV used in the simulations) as compared to that for a B atom in the pristine material (Fig. 11). This means that the substitution of individual atoms can hardly be explained by dynamical effects only. The displacement threshold for the nearest \( B \)-neighbor atoms (\( C_N \) defect) drops by 1.2 eV, and by 3.6 eV for neighboring \( N \) atoms (\( C_B \) defect) as compared to the corresponding values in the pristine system. The knowledge of the displacement rates for different types of atoms, along with the information on the energetics of different configurations and partial pressure of the volatile components in the chamber, should make it possible to use the Monte Carlo methods to model the kinetics of the process.

IV. CONCLUSIONS

To conclude, using DFT approaches with local and non-local XC functionals and the GW method, we calculated the electronic structure of \( h \)-BN sheets. We considered both pristine systems and those doped with carbon. We showed that the fundamental band gap in 2D \( h \)-BN is different from the gap in the bulk material. We also demonstrated that due to the non-local nature of the GW approximation, the gap calculated using the GW approach depends on the interlayer separation between the images of the layers within the periodic supercell approach, so that the results corresponding to the isolated 2D system must be extrapolated to the limit of infinitely large separations between the images. We further showed by the example of carbon substitutional impurities that the local and hybrid XC functionals give a qualitatively correct picture of the impurity states in the gap. Finally, we address the effects of many important parameters such as the choice of chemical potential, and estimated atom displacement cross sections for the substitutional process during the electron-beam-mediated doping of \( h \)-BN sheets with carbon atoms. Our results shed light on the electronic structure of pristine and doped \( h \)-BN and should further help to optimize the post-synthesis doping of boron nitride nanostuctures stimulated by the electron irradiation. Specifically, by using a focused electron beam and simultaneously charging the sample, one can manufacture spatially localized hybrid structures which should exhibit intriguing electronic and magnetic properties. Indeed, filling of vacancies created by the electron beam in molybdenum disulfide was recently demonstrated in the experiments.

ACKNOWLEDGMENTS

This work was supported by the Finnish Academy of Science and Letters, and the Academy of Finland through the Centre of Excellence and other projects. We also acknowledge the Finnish IT Center for Science (CSC) for generous grants of computer time.


A. Gulans (unpublished).


64 W. A. McKinley and H. Feshbach, Phys. Rev. 74, 1759 (1948).