Ab initio studies of isolated boron substitutional defects in graphane

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Abstract. We have systematically studied energetics, structural and electronic properties of different configurations of the B atoms substituting C-H pairs located on a single hexagonal ring in a graphane system using the first-principles density functional theory (DFT). A total number of 12 distinct B dopants configurations were identified and characterized. Based on the formation energy analysis, we found that relative stability of B dopants depends greatly on the defect configurations. Our results suggest that the B substitutions prefer to be distributed randomly but avoiding the formation of homo-elemental B-B bonds in a graphane system, at any concentration. Generally, the values of band gap decrease as the number of B dopants increases, but the low energy configurations have large band gaps compared to those that have homo-elemental bonds. As a result, the band gap of graphane can be fine tuned through the change in the structural arrangement of B atoms. The adequate control of the electronic structure of graphane through doping should be essential for technological device applications.

1. Introduction
A fully hydrogenated graphene monolayer (graphane) is a wide band gap semiconductor [1]. The previous density functional theory (DFT) studies reported a band gap of about 3.30 eV [2, 3, 4]. Graphane is likely to find its use in nanoelectronic technology owing to its relatively thin membrane [5]. On the other hand, graphane can be used as hydrogen storage template due to its extremely high hydrogen density [6].

The adequate control of the electronic properties of graphane through structural modification will be extremely important for technological device applications. For the fact that graphane has a low dimensionality, it can easily be modified at the atomic level. There are various techniques suggested [5] (for example, application of strain, creating vacancies etc.). For the latter, the hydrogen (H) vacancy and a pair of carbon and hydrogen (C-H pair) vacancy introduce a stable magnetism in a graphane system [5, 7, 8, 9, 10]. Foreign atom doping is another widely used method to alter electronic structure of a graphane system [5]. Substituting C atom with Boron (B) or Nitrogen (N) atom in a graphane monolayer surely causes the p-type or n-type system respectively and thereby causes a semiconductor-to-metal transition [11]. It has been reported that a graphane monolayer can be used as a base for creating new promising and nanotechnologically useful devices [12]. Experimentally, the B substitution in a graphane monolayer can occur through high energy ion implantation, as it was done in a free standing graphene [13]. In a graphane monolayer, this substitution or doping will affect the C atom as well as its bonded H atom (C-H pair). The creation of C-H pair vacancy leaves three C atom, each...
with dangling bond and therefore, the well know three valence electrons in a B atom should be able to saturate this vacancy induced dangling bonds through electronic pairing. Thus, understanding the effect of B atom on the electronic structure of graphane is important for its application in the nanotechnological devices.

In this work, we systematically investigated the energetics and electronic structure of B substituting C-H pairs (B$_{CH}$) on a single hexagonal ring in a graphane system using the first-principles DFT approach. To understand the role of B-B interactions in a graphane monolayer, the number of B dopants have been increased from 1 to 6, but restricted to a single hexagonal ring. At each number of B substitution dopants, different configurations where identified and examined. Firstly, our results show that the B substituting a C-H pair is more feasible than when substituting only a C atom in a graphane monolayer. The band gap of graphane can be fine tuned through the change in the structural arrangement as well as through the change in B atom concentrations. The adequate control of the electronic structure of graphane through doping should be essential for technological device applications.

2. Computational details

Our ground state electronic structure calculations were performed on the frame work of density functional theory implemented within the Vienna $ab$ initio simulation package (VASP) code [14, 15, 16, 17]. The generalized gradient approximations (GGA) parameterization of Perdew, Burke and Ernzerhof (PBE) was used for the exchange-correlation interactions [18]. The electronic spin was included for the start of each calculation. The projector augmented wave (PAW) method was employed for the generation of the atomic pseudopotentials [19]. For the plane wavefunctions expansion, an energy cut-off was set to 500 eV. For accurate sampling of the Brillouin zone, a $10 \times 10 \times 1$ k-meshes generated using Monkhorst-Pack scheme [20] were used. The total energies were allowed to converge to $10^{-7}$ eV.

To accurately populate electronic states in our calculations, the well known Methfessel-Paxton (MP) scheme [21] was used. The structure is allowed to fully relax until the inter-atomic forces is less than 0.01 eVÅ$^{-1}$. To eliminate the unwanted interlayer spurious interactions in the periodic system, the 15 Å spacing was set between the graphane layers.

3. Results and discussion

3.1. Identification of B configurations

In this study, the investigation of B atom substituting a C-H pair (B$_{CH}$) on a single hexagonal ring in a 7×7 supercell of a graphane monolayer was considered. To understand the role of B-B interactions in a graphane monolayer, the number of B dopants were increased from 1 to 6, but restricted to a single hexagonal ring. At each number of B substitution dopants, different configurations where studied. This study was carried out on a chair-like-graphane system which is a thermodynamically stable conformer of graphane [2].

The labels 1 to 6 in Fig 1 indicate the C-H pair sites which should be occupied by the B atoms. The labeling help us to name and distinguish the identified B configurations. All the identified configurations are presented in Table 1. Configuration c$_1$ is called B$_{CH_1}$ denoting a B dopant substituting C-H pair at site 1. For two B substitutions, we where able to identify three distinct configurations c$_1$, c$_2$ and c$_3$ namely, B$_{CH_{12}}$, B$_{CH_{13}}$ and B$_{CH_{14}}$, respectively. The configurations B$_{CH_{12}}$, B$_{CH_{13}}$ and B$_{CH_{14}}$ denote two B atom substituting C-H pairs at sites 1 and 2; sites 1 and 3, and at sites 1 and 4 respectively. In following this procedure, a total number of 12 unique B configurations on a single hexagonal ring of a graphane monolayer were obtained and shown in table 1. The energetics and electronic properties of each configuration where calculated and discussed.
Figure 1. The B adsorption sites in an unrelaxed state of a graphene monolayer supercell obtained from Ref [22]. The C-H pairs labeled 1 to 6 indicate the C-H pair sites which are occupied by the B atoms.

Table 1. The B atom configurations identified from a 7×7 supercell of a graphane monolayer.

| Configurations | B defects sites | No of B defects |
|----------------|-----------------|-----------------|
| c1             | B_{CH1}         | 1               |
| c2             | B_{CH12}        | 2               |
| c3             | B_{CH13}        | 2               |
| c4             | B_{CH14}        | 2               |
| c5             | B_{CH123}       | 3               |
| c6             | B_{CH124}       | 3               |
| c7             | B_{CH135}       | 3               |
| c8             | B_{CH1234}      | 4               |
| c9             | B_{CH1235}      | 4               |
| c10            | B_{CH1245}      | 4               |
| c11            | B_{CH12345}     | 5               |
| c12            | B_{CH123456}    | 6               |

3.2. Formation energies and structural properties

To evaluate the relative stability and formation possibility of the identified B substitutional configurations presented in table 1, their formation energies $E_f(B_{CH})$ are calculated as,

$$E_f(B_{CH}) = E_{tot}(B_{CH}) - E_{tot}(G) - n_B\mu_B + n_H\mu_H + n_C\mu_C,$$

in which $E_{tot}(B_{CH})$, $E_{tot}(G)$, $\mu_B$, $\mu_H$ and $\mu_C$ denote the total energy of the B doped graphane system, the corresponding pristine graphane monolayer, B in an orthorhombic structure, H molecule in a large box and C in a graphene monolayer respectively. The structure optimization was carried out with respect to atomic positions as well as cell parameters. The variables $n_B$, $n_H$ and $n_C$ denote the number of B dopants substituting the number of H and C atoms removed from a graphane monolayer.

The obtained $E_f(B_{CH})$ values of the identified B configurations are presented in Fig 2(a). The $E_f(B_{CH})$ value of a single B substituting a C-H pair $B_{CH1}$ (configuration c1) is 0.99 eV. Although
the positive formation energy indicates the thermodynamic instability of a defect, this value is far less than that for a B dopant substituting only a C atom in a graphene system of 4.51 eV calculated at the same level of accuracy. Although the B$_{CH}$ might not form spontaneously, can occur through ion implantation, with less energy compared to that of the B$_C$ defect in a graphene system. We measured the bond distances (C-B and C-C) to examine the influence of the B dopants on the structural properties of a graphene system. The C-B bondlength shown in Fig 2(b) suggests that the bonding between a B defect and its surrounding C atoms is the sp$^3$-like bond just like in a pristine graphene system. The C-B bondlength is found to be 0.02 Å lower than the homogeneous C-C bondlengths in the same system, revealing that an isolated B dopant in a graphene system does not induces a significant structural distortions.

To study the effects of B-B substitution interactions in a graphene system, the number of B dopants were increased to six on a single hexagonal ring in a graphene monolayer. For each number of dopants, different unique configurations are identified and presented in table 1. Fig 2 shows that the value of the formation energies increases as the number of dopants increases, although not monotonically. For two dopants concentration, three distinct configurations i.e. B$_{CH12}$ ($c_2$), B$_{CH13}$ ($c_3$) and B$_{CH14}$ ($c_4$) showing ortho, meta and para isomers are identified. For this concentration, the $E_f$(B$_{CH}$) follows an order of $c_3$ < $c_4$ < $c_2$. The $E_f$(B$_{CH}$) for $c_2$ is almost equal to that of $c_1$. Configuration $c_2$ to have high energy of 2.98 eV should be attributed to the formation of energetically unfavourable homo-elemental B-B bond of 1.66 Å in a graphene monolayer (shown in Fig 2(c)) as opposed to the formation of C-B bond. The formation of this relatively large B-B bond in ($c_2$) induces a significant structural distortion. As it is noted that C-B and C-C bond distances reduce to 1.51 Å and 1.49 Å respectively, as compared to those in $c_1$ (shown in Fig 2(b)) as well as in $c_2$ (shown in Fig 2(d)) and $c_3$ (shown in Fig 2(e)).

![Figure 2](image_url)

**Figure 2.** (a) The calculated formation energies of identified distinct configurations of B dopants in a graphene monolayer. Selected relaxed geometries of the identified configurations (b) $c_1$, (c) $c_2$, (d) $c_3$, (e) $c_4$ and (f) $c_7$ showing the significant variation in bondlengths due to the effect of B dopants.

In the case of three B dopants, three distinct configurations are noted i.e. $c_5$, $c_6$ and $c_7$. For this concentration, the $E_f$(B$_{CH}$) follows the order of $c_5$ = $c_6$ > $c_7$. The formation of B-
B bond should be a major driving force for relatively high formation energy in configurations \(c_5\) and \(c_6\) shown in Fig 2(a). Configuration \(c_7\) has three B dopants that do not form a B-B bond as shown in Fig 2(f), and thus has a relatively low \(E_f(B_{CH})\) of about 1.04 eV. We observe in Fig 2(a) that from configuration \(c_8\) to \(c_{12}\), the formation energy increases drastically, revealing that the substitution of B atoms in a contiguous sequence or in a compact sequence on a single hexagonal ring in a graphane monolayer is highly unstable. In summary, configuration \(c_7\) competes very well with configurations \(c_1\), \(c_3\) and \(c_4\) in terms of thermodynamic stability and are the lowest energy competing configurations. Therefore, experimental investigation of these B doped systems is required. In the next section, we investigated the influence of B dopants on the electronic structure of graphane.

3.3. Electronic properties

We further investigated how the effect of B dopant alters the electronic structures of graphane in all identified configurations using the density of states (DOS) plots shown in Fig. 3. We briefly discuss the DOS for a pristine graphane system shown in Fig. 3(a). A graphane monolayer is a non-spin polarized system, since its majority DOS (spin-up) are invertedly symmetrical to minority DOS (spin-down) for the entire plot. The valence band maximum (VBM) and conduction band minimum (CBM) are separated by a band gap of 3.35 eV. This band gap value is in good agreement with the values previously reported in Refs [2, 3, 23, 24, 25] revealing that graphane is a wide band gap semiconductor.

Figure 3. The density of states (DOS) for (a) a pristine graphane system, (b) \(c_1\), (b) \(c_2\), (d) \(c_3\), (e) \(c_7\) and (f) \(c_{12}\). The Fermi level is marked by the dashed line.

All the DOS plots show that the B doped graphane systems are non-magnetic, even if the spin is imposed before the calculations they turn out to be non-spin polarized after relaxation. The DOS plot for \(c_1\) shows that a B atom induces the non-spin polarized states with the sharp peaks just below the CBM, slightly reducing the band gap of graphane. Fig. 4 shows that doping a graphane system with a single B atom reduces a band gap to 2.98 eV. The DOS plot for \(c_2\) shows that the two B atoms that are bonded to together induce the non-spin polarized states in the vicinity of the band gap as shown in Fig. 3(c). Revealing that formation of a homo-elemental B-B bond in a graphane monolayer reduces a band gap from 3.35 eV to 1.19 eV.
However, for the same concentration, the DOS plot for $c_2$ shows that the two B atoms that are not bonded together but doped in the same hexagonal ring induce a non-spin polarized pronounced peak states at the CBM (see Fig. 3(d)). This configuration has a band gap of about 2.66 eV. Configuration $c_{12}$ that comprises of six B dopants forming a hexagonal ring in a graphene monolayer has a shortest band gap of 1.08 eV. This is because a hexagonal ring of B atoms doped in a graphene system induces the multiple non-spin polarized states in the band gap (see Fig. 3(f)).

![Graphene band gap diagram](image)

**Figure 4.** The calculated band gaps for all identified B dopants configurations in a graphene monolayer.

### 4. Conclusions

Using the first-principles density functional theory, we successfully studied energetics, structural and electronic properties of B doped graphene. To understand the role of B-B interactions in a graphene monolayer, the number of B dopants was increased from 1 to 6, but restricted to a single hexagonal ring in a graphene system. At each number of B substitution dopants, different configurations were studied. A total number of 12 distinct B dopants configurations were identified and examined. The lowest energy competing B dopants configurations such as $c_1$, $c_3$, $c_4$ and $c_7$ were noted, other structural configurations have high formation energies.

Our results suggest that the B substitutions would prefer to be distributed randomly but avoiding the formation of B-B bonds in a graphene system at any concentration. Although such kind of systems have positive formation energies, they should be plausible structures remembering that the zero temperature and pressure conditions assumed for our DFT calculations could also have a significant contribution on the obtained positive enthalpy of formation. Besides that, these configurations $c_1$, $c_3$, $c_4$ and $c_7$ should occur under high energy deposition techniques such as ion implantation.

Our results further show that the effects of B dopants reduce the maximum band gap of graphene. The low energy competing configurations such as $c_1$, $c_3$, $c_4$ and $c_7$ have a relatively wide band gap, whereas those that have energetically unfavourable homo-elemental B-B bond possess a small band gap. This suggests that the band gap of graphene can successfully be fine tuned through the variation in the B concentration. The adequate control of the electronic structure of graphene is essential for technological device applications. Experimental investigation of various dopants in a graphene system should be encouraged.

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