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# *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 were 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.

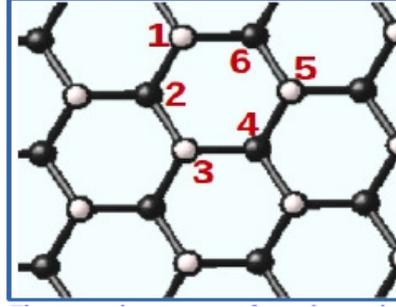
To accurately populate electronic states in our calculations, the well known Methfessel-Paxton (MP) scheme [21] was used. The structure is allowed to fully relax until the inter-atomic forces is less than  $0.01 \text{ eV}\text{\AA}^{-1}$ . To eliminate the unwanted interlayer spurious interactions in the periodic system, the  $15 \text{ \AA}$  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  $7 \times 7$  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 were 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 were 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 were 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  $7 \times 7$  supercell of a *graphene* monolayer.

Configurations	B defects sites	No of B defects
c <sub>1</sub>	B <sub>CH<sub>1</sub></sub>	1
c <sub>2</sub>	B <sub>CH<sub>12</sub></sub>	2
c <sub>3</sub>	B <sub>CH<sub>13</sub></sub>	2
c <sub>4</sub>	B <sub>CH<sub>14</sub></sub>	2
c <sub>5</sub>	B <sub>CH<sub>123</sub></sub>	3
c <sub>6</sub>	B <sub>CH<sub>124</sub></sub>	3
c <sub>7</sub>	B <sub>CH<sub>135</sub></sub>	3
c <sub>8</sub>	B <sub>CH<sub>1234</sub></sub>	4
c <sub>9</sub>	B <sub>CH<sub>1235</sub></sub>	4
c <sub>10</sub>	B <sub>CH<sub>1245</sub></sub>	4
c <sub>11</sub>	B <sub>CH<sub>12345</sub></sub>	5
c <sub>12</sub>	B <sub>CH<sub>123456</sub></sub>	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,

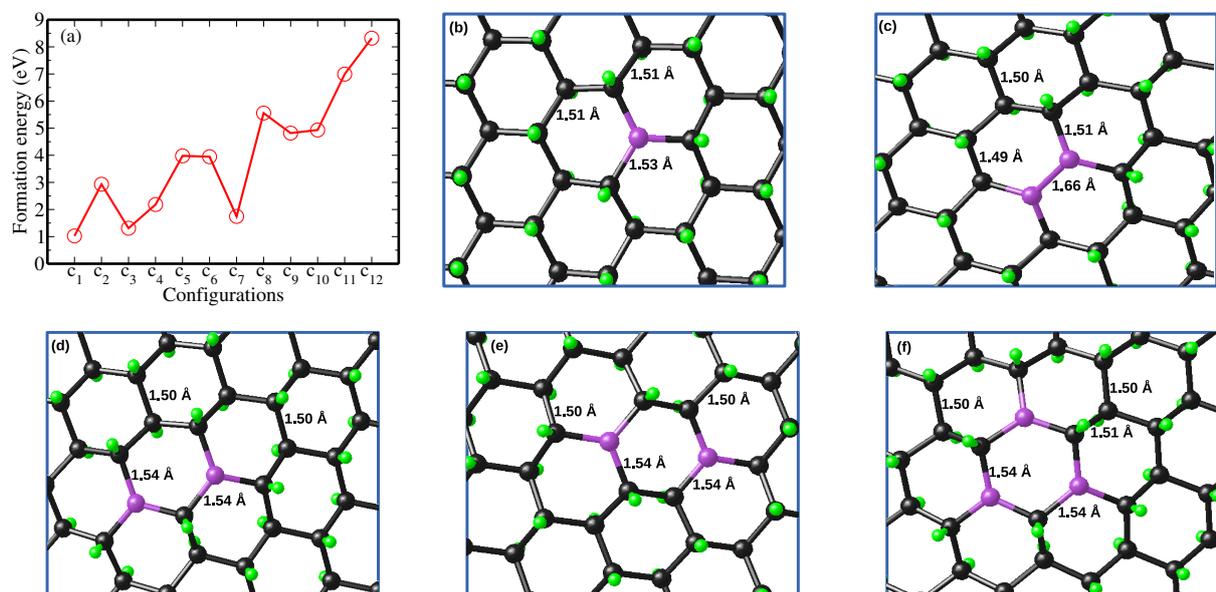
$$E_f(B_{CH}) = E_{tot}(B_{CH}) - E_{tot}(G) - n_B \mu_B + n_H \mu_H + n_C \mu_C, \quad (1)$$

in which  $E_{tot}(B_{CH})$ ,  $E_{tot}(G)$ ,  $\mu_B$ ,  $\mu_H$  and  $\mu_C$  denote the total energy of the B doped *graphene* system, the corresponding pristine *graphene* 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 *graphene* 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<sub>CH<sub>1</sub></sub> (configuration c<sub>1</sub>) 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 *graphane* 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 *graphane* 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 *graphane* 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 *graphane* 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 *graphane* system does not induce a significant structural distortions.

To study the effects of B-B substitution interactions in a *graphane* system, the number of B dopants were increased to six on a single hexagonal ring in a *graphane* 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.  $B_{CH_{12}}$  ( $c_2$ ),  $B_{CH_{13}}$  ( $c_3$ ) and  $B_{CH_{14}}$  ( $c_4$ ) 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  $c_3$  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 *graphane* 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)).



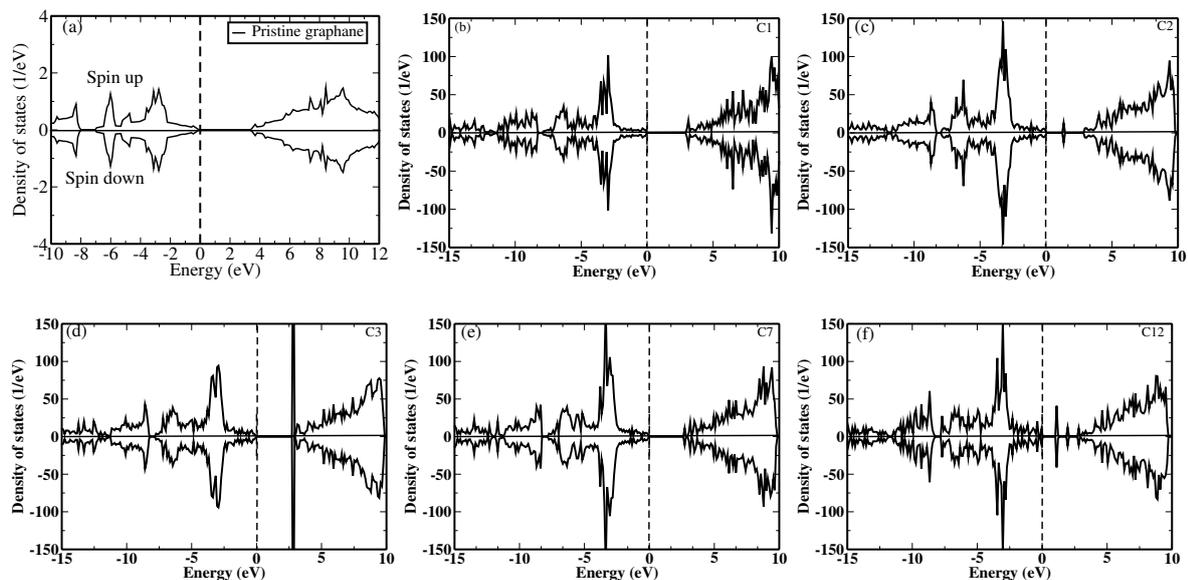
**Figure 2.** (a) The calculated formation energies of identified distinct configurations of B dopants in a *graphane* monolayer. Selected relaxed geometries of the identified configurations (b)  $c_1$ , (c)  $c_2$ , (d)  $c_3$ , (e)  $c_4$  and (f)  $c_7$  showing the significant variation in bondlengths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

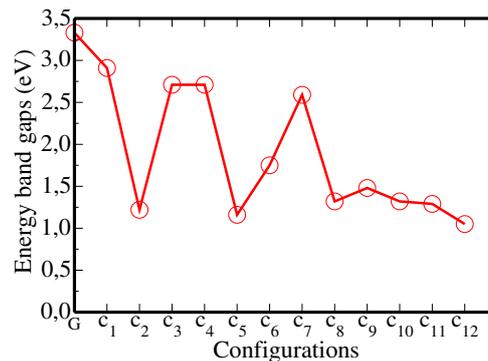
We further investigated how the effect of B dopant alters the electronic structures of *graphane* in all identified configurations using the density of states (DOS) plots shown in Fig. 3. We briefly discuss the DOS for a pristine *graphane* system shown in Fig. 3(a). A *graphane* monolayer is a non-spin 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 *graphane* monolayer has a shortest band gap of 1.08 eV. This is because a hexagonal ring of B atoms doped in a *graphane* system induces the multiple non-spin polarized states in the band gap (see Fig. 3(f)).



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

#### 4. Conclusions

Using the first-principles density functional theory, we successfully studied energetics, structural and electronic properties of B doped *graphane*. To understand the role of B-B interactions in a *graphane* monolayer, the number of B dopants was increased from 1 to 6, but restricted to a single hexagonal ring in a *graphane* 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 *graphane* 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 *graphane*. The low energy competing configurations such as  $c_1$ ,  $c_3$ ,  $c_4$  and  $c_7$  have a relative 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 *graphane* can successfully be fine tuned through the variation in the B concentration. The adequate control of the electronic structure of *graphane* is essential for technological device applications. Experimental investigation of various dopants in a *graphane* system should be encouraged.

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