

Electronic properties of B and Al doped *graphane*: A hybrid density functional study

R.E. Mapasha^{a,*}, E. Igumbor^a, N.F. Andriambelaza^a, N. Chetty^{a,b}

^a Department of Physics, University of Pretoria, Hatfield campus, Pretoria 0002, South Africa

^b National Institute for Theoretical Physics, Johannesburg, 2000, South Africa

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ABSTRACT

Using a hybrid density functional theory approach parametrized by Heyd, Scuseria and Ernzerhof (HSE06 hybrid functional), we study the energetics, structural and electronic properties of a *graphane* monolayer substitutionally doped with the B (B_{CH}) and Al (Al_{CH}) atoms. The B_{CH} defect can be integrated within a *graphane* monolayer at a relative low formation energy, without major structural distortions and symmetry breaking. The Al_{CH} defect relaxes outward of the monolayer and breaks the symmetry. The density of states plots indicate that B_{CH} doped *graphane* monolayer is a wide band gap semiconductor, whereas the Al_{CH} defect introduces the spin dependent mid gap states at the vicinity of the Fermi level, revealing a metallic character with the pronounced magnetic features. We further examine the response of the Al dependent spin states on the multiple charge states doping. We find that the defect formation energy, structural and electronic properties can be altered via charge state modulation. The +1 charge doping opens an energy band gap of 1.75 eV. This value corresponds to the wavelength in the visible spectrum, suggesting an ideal material for solar cell absorbers. Our study fine tunes the *graphane* band gap through the foreign atom doping as well as via defect charge state modulation.

1. Introduction

Recently, two-dimensional (2D) material systems such as the graphene [1], *graphane* [2], hexagonal boron nitride [3] and transition metal dichalcogenides [4] monolayers have attracted great research interests owing to their peculiar electronic properties. A relatively high charge carrier mobility indicated by the linear dispersion-like at the Dirac-point in the electronic spectrum of a graphene monolayer exposes its semi-metallic character [1,5–8]. The absence of the band gap is a setback for the direct integration of the graphene thin films into the electronic devices. To make graphene electronically viable, alteration of its electronic structure and prediction of other new graphene-related 2D material systems have become intensive topics. The *graphane*, hexagonal boron nitride and transition metal dichalcogenides monolayers are amongst those predicted, and are wide band gap semiconductors [2,3,9–12].

The *graphane* thin films were experimentally synthesized by Elias et al. [13] under hydrogen plasma surrounding as free standing materials. It was reported that the experimental characterization of the *graphane* samples reveals that they are thermodynamically stable at room temperature and possess insulating features, although the

magnitude of the band gap was not quantified [13]. Based on this and also considering its relatively thin membrane [14], *graphane* may be suitable for current nanoelectronic technology. Depending on the type of exchange-correlation functional employed, the density functional theory (DFT) calculations predict *graphane* to have the direct band gap of 3.40 eV [15] using a Perdew, Burke and Ernzerhof generalized gradient approximation (PBE-GGA) [16] functional and 4.38 eV [17] for a Heyd, Scuseria and Ernzerhof (HSE06) [18] hybrid functional. The underestimation of the band gap by a PBE-GGA functional is due to its self-interaction leading to underbinding of localized states. A HSE06 functional reduces this by mixing a 25% fraction of Hartree-Fock exchange with 95% fraction of a PBE-GGA functional for the short-range exchange potential part [18]. A HSE06 functional has been known to accurately predict the band gap of semiconductors [18] and the defects charge state transition levels [19].

Modulating the electronic properties of the nanostructure materials is essential for the technological device operations. Since *graphane* belongs to the class of the 2D systems which have low dimensionality [14], it can be modified at an atomic level without difficulty. In a *graphane* monolayer, every C atom is in the sp^3 hybridization with its nearest neighbour three C atoms and one H atom. Ideally, *graphane* is

* Corresponding author.

E-mail address: edwin.mapasha@up.ac.za (R.E. Mapasha).

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fully saturated, and it is not expected to possess any valuable magnetic features. To alter the electronic structure of *graphane*, vacancies and dopants are the possible options. The hydrogen (H) vacancy is a simple defect one can create [20,21]. Pujari et al. [22] reported that the C-H vacancy pair is also a possible defect, and can form with a lower energy than the H vacancy.

The B and N atom substitutions create the p-type and n-type doping in a *graphane* monolayer respectively, and also causes the semiconductor to metallic transition [23,24]. It was suggested that a *graphane* monolayer can be a useful base for creating new nanotechnological devices. These recent DFT studies focused on replacing the C atom in a *graphane* monolayer i.e. B_C , N_C , Al_C and P_C [23,24]. The information on replacing a C-H pair with foreign atoms has not been reported before, and is worth to be investigated. The substitution of a C-H pair with solid atoms such as B and Al although has not yet reported can be achievable experimentally through ion implantation. Considering the fact that creation of the C-H pair leaves its three nearest neighbour C atoms dangling, each with an unpaired electron, therefore an introduction of the B atom having three excited valence electrons at this vacancy site should cause saturation through electron pairing. Thus, influence of the B_{CH} defect should be structural instead of chemical in this case.

In this work, we study the thermodynamic stability, structural and electronic properties of B_{CH} and Al_{CH} defects in a *graphane* monolayer using a HSE06 hybrid DFT approach. Considering the inability of the standard DFT functionals to accurately predict the band gap, a HSE06 functional is employed. Our results reveal that the B_{CH} doped *graphane* monolayer is a wide band gap semiconductor, whereas the Al_{CH} defect induces spin dependent states crossing the Fermi level, showing a metallic character. We further examine the influence of the intrinsic charge doping on the Al induced spin dependent states. This study fine tunes the band gap of *graphane* through the foreign atom doping as well as via changing the charge state of the defect.

2. Computational details

Our first-principles electronic structure calculations are performed using the DFT approach implemented within the Vienna ab initio simulation package (VASP) code [25]. These calculations are carried out with the projector augmented wave (PAW) pseudopotential plane-wave method [26]. For the exchange-correlation interactions, a HSE06 functional is employed [18]. For energetics comparison, a GGA-PBE functional is also employed. For the start of each calculation, the electronic spin is tuned on. The energy cut-off was set to 500 eV for expanding the plane wavefunctions. The structural geometries are allowed to relax until each atomic force is less than $0.01 \text{ eV}\text{\AA}^{-1}$ and the total energies are converged to 10^{-7} eV .

The defect formation energy is defined as;

$$E_{form}(X) = E_X - E_{graphane} + \mu_C + \mu_H - \mu_X + q[E_F + E_V] + \Delta_{MP}^q. \quad (1)$$

The first two terms E_X and $E_{graphane}$ are the total energies of B or Al doped *graphane* and pristine *graphane* respectively. The μ_C and μ_H terms are the chemical potentials of the host C atom (obtained as the total energy per C atom from the unit cell of graphene monolayer) and H atom (obtained as the total energy per H atom from the hydrogen molecule), whereas the μ_X term is the chemical potential of the B defect (obtained as the total energy per B atom from α rhombohedral B structure) or Al defect (obtained as the total energy per Al atom from the Al face centered cube structure) respectively. E_F is the Fermi level position referenced to the valence band maximum (VBM) in the pristine *graphane* structure, whereas E_V is the energy corresponding to the VBM of the defect. The Makov-Payne [27] correction term (Δ_{MP}^q) is added to Eq. (1) to eliminate the energy errors that might arise due to the effects of the spurious electrostatic interactions of the doped charge with its periodic image. The complete expression of Δ_{MP}^q can be found in reference [27].

The following supercell convergence tests are carried out to reduce the fictitious defect-defect interactions from the periodic images along the xy plane. The B and Al atoms individually substituting the C-H pair in the 4×4 , 5×5 , 6×6 , 7×7 and 8×8 *graphane* supercell sizes are considered on the formation energy analyses employing a PBE-GGA functional. The formation energy for the B defect obtained using Eq. (1) is 0.48 eV (4×4), 0.89 eV (5×5), 0.94 eV (6×6), 0.97 eV (7×7) and 0.99 eV (8×8). The formation energy difference ΔE between the next and previous supercell is 0.42 eV, 0.04 eV, 0.03 eV and 0.02 eV. This trend agrees very well with that of Leenaerts et al. [28] for B atom replacing C atom in a fluorographene monolayer. The formation energy for the Al defect is 2.09 eV (4×4), 3.19 eV (5×5), 3.49 eV (6×6), 3.50 eV (7×7) and 3.51 eV (8×8) with the ΔE of 1.10 eV, 0.30 eV, 0.01 eV, 0.01 eV. For both defects, ΔE indicates that the 6×6 supercell size is sufficient to correctly describe the properties of the defect. For this supercell size, the $2 \times 2 \times 1$ k-point meshes generated using the Monkhorst-Pack scheme [29] are used for structural relaxation, and increased to $10 \times 10 \times 1$ for the density of states (DOS) calculations. The converged 20 \AA spacing was set to isolate the *graphane* layers along the z axis.

Graphane can appear in different H isomers such as boat, chair, armchair etc. An overview of all the *graphane* isomers are found in the review paper of Sahin et al. [14]. Amongst all the isomers mentioned, the chair isomer is the most thermodynamically stable structure [14], and it was accomplished spontaneously during the graphene hydrogen plasma exposure [13]. Based on this, all our calculations are performed using the *graphane* chair isomer depicted in Fig. 1(a). The ground state

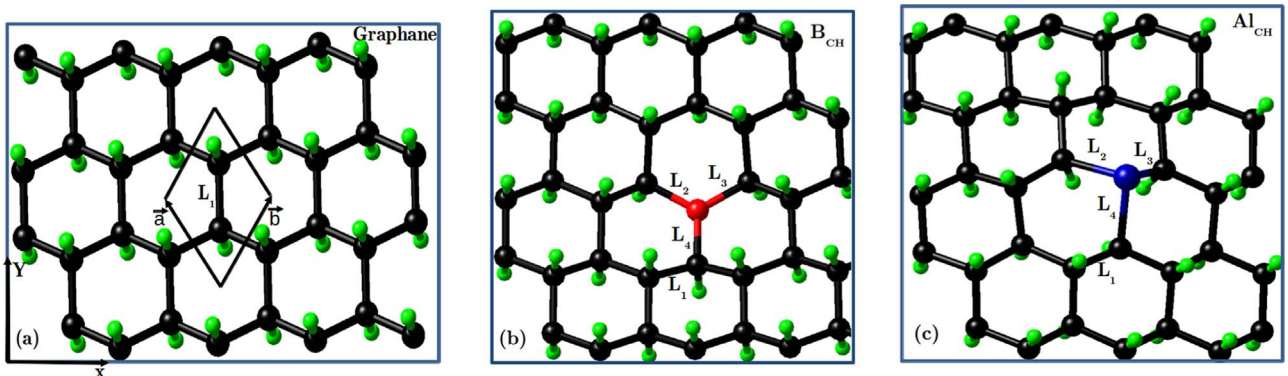


Fig. 1. (a) The relaxed geometry of a pristine *graphane* chair isomer monolayer. The parallelogram shape indicates the unit cell of a *graphane* monolayer having the two C atoms and two H atoms, where \vec{a} and \vec{b} are the lattice vectors which their magnitudes are equal to a_0 presented in Table 1. The relaxed geometries of (b) B doped *graphane* (B_{CH}) and (c) Al doped *graphane* (Al_{CH}) defects. The C and H host atoms are indicated by the black and light green spheres, whereas the B and Al defects are indicated by the red and blue spheres respectively. The C–C bondlength (d_{C-C}) is represented by the variable L_1 , whereas the three C–B/Al bondlengths are represented by the variables L_2 , L_3 and L_4 . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

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