Electronic Properties of Boron and Nitrogen doped graphene: A first principles study

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Abstract

Effect of doping of graphene either by Boron (B), Nitrogen (N) or co-doped by B and N is studied using density functional theory. Our extensive band structure and density of states calculations indicate that upon doping by N (electron doping), the Dirac point in the graphene band structure shifts below the Fermi level and an energy gap appears at the high symmetric K-point. On the other hand, by B (hole doping), the Dirac point shifts above the Fermi level and a gap appears. Upon co-doping of graphene by B and N, the energy gap between valence and conduction bands appears at Fermi level and the system behaves as narrow gap semiconductor. Obtained results are found to be in well agreement with available experimental findings.

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I. INTRODUCTION

Graphene has been a topic of intensive investigation since the pioneering work on synthesis of this unique two-dimensional material by Geim, Novoselov and co-workers [1-3]. Recently, various attempts have been made to fabricate graphene devices by engineering their band gaps by doping [4-6]. Investigations on doped graphene nano-ribs [4, 5] indicate that upon doping by N or B n-type or p-type semiconducting graphene can possibly be obtained. It has been experimentally established that upon N doping of graphene [4], the Dirac point in the band structure of graphene tends to move below the $E_F$ and an energy gap appears at high-symmetric K-point.

Very recently, Ci et al. [6] have been able to synthesize a novel two-dimensional nanomaterial where a few Carbon atoms on a graphene sheet is replaced by equal number of B and N atoms. The concentration of the dopant atoms can be controlled by keeping B/N ratio same. This novel BNC nanomaterial was found be semiconducting with a very small gap between the valence and conduction bands. Synthesis of similar BNC materials have also been reported by Panchakarla et al. [7]. The electronic properties of N and B doped graphene nanoribbons with armchair edges also has been reported [8]. N introduces an impurity level above the donor level, while an impurity level introduced by B is below that of the acceptor level. In contrast to single wall carbon nanotubes, the impurity level is neither donor nor acceptor in their systems. The donor and acceptor levels are derived mainly from the lowest unoccupied orbital and the highest occupied orbital.

Theoretically, there are various possibilities to introduce gap in graphene, i.e. by oxidation of monovacancies in graphene [9], graphene/boron nitride heterobilayers [10, 11], F-intercalated graphene on SiC substrate [12], and bilayer graphene-BN heterostructures. Experimentally, substitutional carbon doping of boron nitride nanosheets, nanoribbons, and nanotubes has been reported [13]. Experimentally, it has been observed that the $sp^2$ hybridized BNC nano-structure, with equal number of B and N atoms, can open finite band gap [6].

Motivated by these current experimental and theoretical reports, we investigated in this paper the effect of doping of Boron and Nitrogen and also of their co-doping on the electronic properties of the graphene systems using first-principles electronic structure calculations based on density functional theory. Our results indicate that due to the presence of B or
N atoms Graphene is more stable as compared to pristine h-BN. This suggests that the h-BNC domains are more likely to form in h-CBN nanomaterial. The electronic properties of Graphene with single substitutional B or N atoms, indicative of a p (n)-doping, can be tuned easily as reported recently [14]. Furthermore, we have carried out extensive band structure calculations [8] in the framework of the local spin-density formalism (LSDA) using first-principles pseudopotentials [15] and examined the effect of B and N doped multilayers graphene. To best of our knowledge, the stability and electronic properties of such a system has not been well understood. We believe our results explain the formation of h-BNC nanomaterials as it has been proven experimentally [6]. These new form of hybridized h-BNC nanomaterial enables for the development of band gap engineering applications, in particular, in nano-electronics and nano-optics that are distinct from those of pristine graphene and pristine h-BN.

II. CALCULATION METHOD

The calculations were performed using Quantum Espresso code [15]. The code has already been used successfully for graphene and h-BN systems [11, 16–18]. The atomic positions and cell parameters are fully relaxed in all cases, until an energy convergence of $10^{-7}$ eV and a force convergence of 0.04 eV/Å is reached. First, we obtained the total energy of pristine graphene using self-consistent calculation and then the band structure, densities of states (DOS), partial density of states (PDOS) and charge densities [21]. We have checked different sets of pseudopotentials and find von Barth [19] pseudopotentials is reasonable good for our present calculations. Hence, we used von Barth with wave function and charge-density cut-offs of 60 Ryd and 600 Ryd, respectively and obtained quite accurate vales of in-plane and out-of-plane lattice constant $a$ and $c$, respectively by the process of the total energy minimization.

After getting the relaxed structures, we performed self consistent calculations with a Monkhorst-Pack [20] $8 \times 8 \times 8$ k-mesh followed by the non-self consistent calculations for band structures, DOS/PDOS and charge density separately. We have used $61 \times 61 \times 61$ k-points mesh along the path $\Gamma - K - M - \Gamma$ in the irreducible Brillouin zone to obtain the band structure with very fine mesh points. Next, the doping of graphene was carried out using a $2 \times 2$ supercell of graphene with one atom replaced by B or N and the band structure
FIG. 1: A $2 \times 2$ unit cell of graphene codoped with equal number of B and N atoms with carbon concentrations of 75\% (left), 50\% (middle) and 25\% (right) used in the calculation.

was obtained without changing the lattice constant. However, ionic relaxation has been taken into account and finally, we performed band structures and DOS/PDOS calculations. Turning in to the multilayered structure, we first considered B or N doped two-layer (ABAB stacked) graphene with different concentrations of B and N atoms. Thereafter, we performed band structures and DOS/PDOS calculations as similar as discussed above. Finally, we have performed the relaxation, band structures and density of states calculations for three-layers of B or N doped graphene with similar stacking as above by keeping the interlayer spacing same as in graphite calculated earlier \cite{21}. Based on Löwdin population analysis,
it is confirmed that in B-doped case the charge is concentrated on the C sites whereas, in N-doped case the charge is concentrated in N site.

Thereafter, we carried out calculations for co-doping of B and N using a $2 \times 2$ supercell of graphene by replacing C atoms by one, two or three B and same number of N atoms, yielding a concentration of 75%, 50% or 25% of C atoms and corresponding concentration of 25%, 50% and 75% of BN atoms, respectively. The lattice was allowed to relax and the in-plane lattice constant was obtained self-consistently by minimizing the total energy for each of these configurations. The cut-off energies in this case for wave function and charge-density were 100 Ryd and 1000 Ryd respectively. The band structure was obtained for $(61 \times 61 \times 61)$ $k$-points along the path $\Gamma - K - M - \Gamma$ exactly similar process as mentioned above. Similar kinds of study was also performed for multilayers (ABAB-stacked) of such BNC sheet with interlayer separation 3.29 Å, which is average of the interlayer separations of pristine graphite and pristine $h$-BN calculated using same pseudopotentials as discussed above [10].

III. RESULTS AND DISCUSSION

In the Fig. 2, we show the calculated band structure of undoped, B-doped and N-doped graphene for a single-layer, two-layers and three-layers, respectively. We clearly observe that the Dirac point for undoped graphene moves above (below) the $E_F$ upon doping by B (N). B ($2s^22p^2$) has one valence electron less whereas N ($2s^22p^3$) has one more than Carbon ($2s^22p^2$). Therefore, doping by B (N) results as hole (electron) doping of graphene resulting into shifting of the bands to accommodate extra hole (electron). For B doped graphene, we show the band structure together with the DOS(PDOS) in left panel of the Fig. 3. The Dirac cone shifts above at $E_F$ by 2 eV with finite splitting and the linear dispersion of pristine graphene disappears. Above the $E_F$ the $\pi$ band contributed from the $p_z$ orbital of the B and $\pi^*$ band contributed from the $p_z$ orbital of C. However, for N doped graphene we obtain the band structure together with the DOS(PDOS) as shown in right panel of the Fig. 3. The Dirac cone shifts below the $E_F$ by 1.5 eV with finite splitting. Below the $E_F$ the $\pi$ band contributed from the $p_z$ orbital of the C and $\pi^*$ band contributed from the $p_z$ orbital of N. In the electron doping more states are pulled below the $E_F$ whereas for hole doping the reverse is the case.
FIG. 2: Calculated band structure of undoped (green), B-doped (red) and N-doped (blue) graphene calculated using LSDA, for single layer (left panel), two-layers (middle panel) and for three-layers (right panel), shown near the high-symmetric K-point of hexagonal Brillouin zone.

FIG. 3: Calculated band structure, DOS and PDOS for Boron-doped (left panel) and for Nitrogen-doped graphene (right panel).
FIG. 4: Calculated band structure of graphene co-doped with B and N atoms at three different concentration of C atoms: 75% (left panel), 50% (middle panel) and 25% (right panel), respectively. Results for single layer (blue), two layers (red) and three layers (green) are given.

In the Fig. 4, we show the band structure of graphene co-doped with both B and N. The number of B and N atoms were kept same and calculations were performed for three configurations with concentration of C atoms to be 75%, 50% and 25%, respectively. We clearly observe the appearance of a band gap (summarized in Table I) at the high-symmetric K-point in the Brillouin zone, which depends sensitively on the doping-concentration and also on the thickness of the layers. We find for each C concentration, the band gap decreases with increasing number of layers. Also, with increasing B and N atom concentration the band gap increases. The calculated band gaps for 75% C concentration are 1.06 eV, 0.6 eV and 0.46 eV; for 50% C concentration are 1.8 eV, 1.36 eV and 0.45 eV; and for 25% C concentration are 3.05 eV, 2.49 eV and 0.44 eV; for one-layer, two-layers and three-layers samples respectively. The gap occurs due to mixed hybridization of valence states of B and N with that of C atoms. These results are found to be in qualitative agreement with experimental measurement. The calculated value of band gap presented in Table I shows
that such nano-materials may have potential application in nano-scale semiconducting and nano-scale optoelectronic devices.

We have examined the origin of the gap in the band structure due to B or N doping by calculating the PDOS on different atomic sites, which is not shown here. We have found that the DOS near the gap is essentially of $p_z$ character occurring from the anti-bonding (bonding) $p_z$ B (N) states hybridizing with those of bonding (anti-bonding) $p_z$ states of Carbon. The position of the energy gap due to such hybridization is very crucial such that upon co-doping of graphene by equal number of B and N the energy gap occurs at the $E_F$. Thus a band gap may be engineered in graphene by doping in equal amount of electron and hole.

IV. CONCLUSION

In summary, we used ab-initio density functional theory to investigate the effect of the B and N doped graphene. Shifting and splitting of the Dirac cone below and above the $E_F$ by N and B doping is observed. The band structures, DOS/PDOS and charge density for $h$-BCN hybrid structures are explicitly studied. We found that the band gap energy increases quadratically with respect to the BN concentrations in the range 25% to 75% keeping B to N ratio same. These results may provide guidance in practical engineering applications, specially to tune the band gap in graphene. Finally, our results are useful to provide an explain of the formation of $h$-BNC nano-materials [6]. These new form of hybridized $h$-BNC material enables for the development of band gap engineering and applications, in particular, in nano-electronics and nano-optics. A further study should be performed in order to shed light on this issue, in particular energy path and activation barrier.

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| Concentration (%) | Gap$_1$ (eV) | Gap$_2$ (eV) | Gap$_3$ (eV) |
|------------------|--------------|--------------|--------------|
| 75               | 1.06         | 0.60         | 0.46         |
| 50               | 1.80         | 1.36         | 0.45         |
| 25               | 3.05         | 2.49         | 0.44         |

**TABLE I:** Concentration of C atoms and the calculated band gap in $h$-CBN: one layer (Gap$_1$), two layers (Gap$_2$) and three layers (Gap$_3$).