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Investigation on effect of boron and nitrogen substitution on electronic structure of graphene

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ABSTRACT

Necessity of opening of energy gap in the band structure of, otherwise a zero gap semiconductor, graphene, is a must for its use in fabrication of high speed electronic devices. One such technique, for opening of energy gap in graphene, is by way of doping the pristine graphene with boron or nitrogen. Besides many important applications, to which B- and N-doped graphene has been put, the one very important for solving the global energy crisis is by way of its capacity for hydrogen storage. In this paper electronic structure of B- and N-doped graphene has been studied by using Density Functional Theory, as implemented in WIEN2K code. PBE-GGA (Perdew–Burke–Ernzerhof 96) pseudo-potential is used for solving the Schrodinger equation in self-consistent manner and to account for the exchange and correlation effects through the use of Generalized Gradient Approximation. The band structure calculations reveal that whereas a band gap opens at the symmetry point K both for B- and N-doped graphene, the center of the gap (i.e., the Dirac point in pristine graphene) is shifted above the Fermi level by about 2.20 eV for B-doped graphene, and shifted down the Fermi level by about the same amount for N-doped graphene, when the doping level was kept 25% in each case. The energy gap opened was found to be about 0.30 eV for B-doped graphene and 0.45 eV for N-doped graphene. The linear dispersion characteristics obtained at Dirac point for pristine graphene, almost vanish for B-/N-doped graphene, due to symmetry breaking and opening of energy gap. The band structure and Density of States of B-/N-doped graphene are found also to depend on the choice of cell parameters.

1. Introduction

Successfully peeled off for the first time as a two dimensional (2D) single layer of carbon from a graphite crystal by Novoselov et al. [1], graphene is made of sp^2 hybridized carbon atoms arranged in a honeycomb lattice. In pristine graphene, three valence electrons of a carbon atom form strong σ bonds with three nearest neighbors in the plane of graphene layer and the fourth electron forms π bond perpendicular to the plane of the graphene sheet. In graphite or bilayer graphene the electrons forming π bonds are responsible for binding between two layers by means of weak Vander Walls forces, whereas in monolayer graphene the π bonds are not complete and the electrons forming such bonds behave as almost delocalized electrons, associated with the graphene sheet by means of dangling bonds. The experimental value of the lattice constant of pristine graphene is 2.46 Å and C–C bond length in it has been reported to be 1.42 Å [1]. There are two carbon atoms per primitive cell, which contribute two π electrons in the conduction band of graphene. The E-k diagram for pristine graphene is linear in the vicinity of the K- points (the so called Dirac points) of the Brillouin zone, the band gap being zero and electrons behaving as mass less particles at these points. The pure graphene, therefore, behaves as a semi metal.

The high charge carrier mobility due to linear dispersion at the Dirac points, excellent electrical conductivity, good thermal conductivity, high mechanical strength and unusual flexibility make graphene an excellent material for energy applications and for next generation electronics by overcoming limitations of Si–based electronics [2–6]. The potential applications to which graphene has been put or are in the process of development, include: super capacitors, lithium-ion batteries, fuel cells, solar cells, electrochemical sensors, bio-sensors, pesticide sensors etc. [7,8].

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However, the zero band gap in pristine graphene makes it unsuitable for most of the electronic applications, since it will be difficult to switch off such a device. One of the methods used for opening a band gap in graphene, is by way of doping it with hetero atoms. In this method, the B and N atoms are the natural candidates for doping of graphene, their atomic sizes being quite close to that of C atom and because of their hole acceptor and electron donor characters respectively. As a result of B- (or N-) doping, band gap opens in graphene and Fermi level lies in the valence band (or conduction band), showing ideal p- type (or n-type) semiconducting properties in the doped graphene [5]. Thus, as a result of hetero atom doping, graphene changes its character from semi-metal to semi-conductor.

The method of B- and N-doping for opening the band gap in graphene is novel in the sense that the gap opened is stable and the Fermi level also can be adjusted as per requirements of a particular application by controlling the doping level of the impurity. When we substitute some of the C atoms in graphene by B atoms, three valence electrons of B atom form σ bonds with three nearest neighbor C-atoms, but since there is no other valence electron on B atom to form a π bond, as in case of C atoms in graphene, it effectively gives rise to p-type character to the B-doped graphene. This is because of the deficiency of electrons in the conduction band and shifting of dangling bonds from C-atoms to B-atoms, which gives rise to creation of holes in the valence band of the parent lattice. As a consequence of it, the Fermi level shifts down to pass through the valence band. On the other hand, if we substitute some of the C atoms in graphene by N atoms, three of five valence electrons of N atom form σ bonds in the plane of graphene with three nearest neighbor C-atoms and the remaining two valence electrons on N atom form π bonds at right angles to the plane of graphene sheet. Thus, an N-impurity atom contributes one excess electron to the conduction band of graphene as compared to C atoms, with the result that the Fermi level shifts upwards to pass through the conduction band and gives rise to n-type character to N-doped graphene.

In addition to their applications for electronic devices, the B- and N-doped graphenes have also been found to be useful for several other important applications. Liu et al. [9] reviewed the research and development on graphene based materials for energy applications and found them useful for advanced energy conversion devices, such as solar cells, fuel cells etc. and for energy-storage devices, like super-capacitors, lithium-ion batteries etc. Zhu et al. [10] also observed that the graphene based materials are useful for energy storage applications and owing to their unique properties of high mechanical flexibility, large surface area, chemical stability, superior electric and thermal conductivities, they stand great potential for being used as alternative electrode materials for electrochemical energy storage systems.

Tokarev et al. [11] found boron substituted graphene decorated with Potassium metal atoms to be a novel material for hydrogen storage. They used DFT theory calculations to model key properties of this material, like geometry, hydrogen packing and hydrogen adsorption capacity and found that the new material has extremely high hydrogen storage capacity: 22.5 wt%. Xie et al. [12], on the other hand, explored its other dimension, related to hydrogen generation from solar light driven water splitting by using graphene based materials.

Wang et al. [13] examined various techniques used for synthesis and characterization of nitrogen doped graphene and various configurations that can be obtained by doping graphene with nitrogen, viz., pyridinic-N, pyrrolic-N and graphitic-N. Doping of graphene by an impurity also results in distortion of the graphene sheet in the vicinity of the impurity atoms, because of the difference in core sizes and charge carried by the impurity atoms [14].

Panchakarla et al. [15] have studied synthesis, structure and properties of B- and N-doped bi-layer graphene. They reported that in B-substituted graphene B-C bond is about 0.5% longer than the C–C bond, whereas in N-substituted graphene the N–C bond is of about the same length as C–C bond, resulting in significant relaxation of the structure of B-doped graphene. The energy of formation of doped graphene from pristine graphene and dopant atoms in gaseous form was found by them to be 5.6 and 8.0 eV/atom respectively for B- and N-doping, suggesting that the synthesis of B- and N-doped graphene should be quite possible. They also observed that the linearity in the dispersion of the electron energy bands, observed in pristine graphene at Dirac points, is maintained for B- and N-doped graphene as well within 1 eV of the Fermi energy.

Joucken et al. [16] observed that for carbon-based materials, the incorporation of nitrogen in the lattice is a natural choice because of its ability to form covalent bonds with carbon atoms and to modify the electronic properties of sp^2 carbon locally, with minor structural perturbations. They also observed that the substitution of some carbon atoms by nitrogen atoms gives rise to localized donor states in the electronic density of states of the substituted nitrogen atoms. For a 0.6% substitution of carbon atoms by nitrogen atoms, they estimated a charge transfer of 0.8 electron per dopant atom from nitrogen to carbon atoms.

Rani and Jindal [17] made a detailed analysis of density of states of B- and N-doped graphene by using VASP code [18]. They considered the graphene honeycomb lattice to be made of two interpenetrating triangular sub-lattices and observed that by B and N doping graphene acquires p-type and n-type characteristics, respectively. They consider that while on doping graphene with B or N, the planar structure of the graphene sheet remains unaffected, the electronic properties change from semimetal to semiconductor with increasing number of dopants. Through calculation of Density of States (DOS) for different concentration of dopants at different sites of graphene lattice, they concluded that the band gap opening is maximum when dopants are placed at the points of the same sub-lattice of graphene, because of the combined effect of symmetry breaking of the two sub lattices, and the band gap opening is minimum when dopants lie at adjacent positions (i.e., on alternate sub lattice positions).

Wu et al. [19] made first principle calculations to study the geometry, electronic structure and magnetic properties of graphene doped with light non-metallic atoms (B, N, O, F). They observed that the planar structure and quasi-linear energy dispersion near the Dirac points obtained in pristine graphene are retained through the doping of graphene with B and N atoms. For O doping, a band gap of about 0.5 eV was observed by them and geometrically O atoms were also found to reside in the plane of graphene sheet.

In view of the applications mentioned as above, B- and N-doped (p-type and n-type) graphene stand great potential for device fabrication and in energy applications. While designing a practical application of these materials, it is rather a pre-requisite to investigate changes in electronic structure of pristine graphene on being doped with boron or nitrogen and to fairly understand functioning of two types of materials. In this paper the results obtained for charge density, density of states and band structure of pristine graphene are compared with the relevant results obtained for B- and N-doped graphene, at the doping level of 25% in each case. The new features obtained in the electronic structure of B-doped (p-type) and N-doped (n-type) graphene are highlighted. The doping level for this study was based on the observation made by Patra [20] on the basis of density of states analysis that in B- doped graphene the band gap opens at about 3% B-impurity, which increases with the increase in doping level and stabilizes for doping of about 50%, beyond which it does not change. On the other hand in N-doped graphene, the gap opens at about 3% N-impurity, increases with the doping level, becomes maximum for some N-concentration and then decreases