Ab-intio investigations on pure and B-Mg atom co-doped monolayer graphene

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Abstract

The structural, electronic and optical properties of individual Boron (B) and B-Mg(Magnesium) co doped system has been investigated through first principles density functional theory method.

It is found that, After B-Mg co-doping the Dirac cone moves to conduction Band and a Band gap of 0.6ev appears at high symmetric K-point. A shift in Fermi level forward and valence band. Optical properties specifically absorption and reflectivity were calculate as well .it is found that ,B-Mg co-doping produces rise in absorption in 0-2ev energy range and a red-shift also appear in absorption coefficient static reflectivity parametric is increased , and reflectivity parametric shows rise in lower energy range

Key words:

Graphene; B-Mg doping; Absorption; Doping; Material studio.

1. Introduction

The discovery of graphene[1-3], has ignited intense research in the field of two dimensional (2D) materials. Hexagonal boron nitride (h-BN)[4] and phosphorene[5] are paradigms of 2D materials that, like graphene attract scientific and technological appeal. The band structure of graphene depicts linear energy dispersion near the Fermi energy level, this unique behavior is mainly responsible for its many interesting properties including high-electron mobility approximately 105 cm2 V-1s-1, which can be very useful for obtaining high-speed and high-performance transistors having properties exceeding the conventional semiconductors. However the major obstacle for graphene being used in engineering world is the lack of band gap at the Fermi level, which is the imperative concept for semiconductors and essential for controlling the conductivity by electronic means. Therefore band gap tuning is very important for graphene for its applications in the real engineering world. Hexagonal boron nitride (h-BN) has similar structure like graphene and have approximately same lattice parameters. However graphene has zero band gap at Dirac point but h-BN is wide band gap semiconductor[6]. Hence doping of boron and nitrogen is a natural proposition to introduce band gap in graphene. Since we know that optical properties depend upon the band gap and Fermi energy, thereby tuning the band gap can alter the optical properties of graphene.

Earlier, attempts have been made to open band gap in graphene by hydrogenation[7] and adsorption[8]. Hydrogenation causes change in hybridization of graphene from sp2 to sp3 and creates buckling effect. However, graphene nanoribbons containing edges terminated with hydrogen atoms produce band gap due to quantum confinement[9]. Individual boron and magnesiam-doped graphene[10, 11] as well as BMg co-doped graphene[12, 13] have been investigated vastly in past. Boron and magnesiam atoms substituting carbon atoms in graphene layer at the same concentration does not have a unique chemical composition and morphology. As a result, the electronic and optical properties of graphene can be tuned by changing the growing conditions in which graphene and BMg layers are formed[14]. Various experimental studies[15, 16] on controlled amount of BMg doping in graphene indicate the possibility of band gap opening. The band gap of BMg doped graphene structure vary over a wide range[17], which may lead to applications in optoelectronics. Since graphene in pure form is transparent in the visible part of the spectrum, so in order for graphene based optoelectronic devices to be useful, it is beneficial if they can be tailored to absorb specific wavelength region of the spectra. Previously experimental spectroscopy of graphene in conjunction to ab-initio calculations[18] is carried out to calculate the loss function of graphene and effects of ripples on optical properties[19] of graphene are investigated. However no in-depth study using first-principles calculations has been attributed to find the effect of foreign atom substitution on optical properties of graphene so far.

Motivated by these theoretical and experimental discoveries, in this paper we tried to investigate the effect of doping B and Mg atoms and also BMg co-doping on the electronic and optical properties of the single layer graphene system by first-principles calculations based on density functional theory (DFT) technique.

Our work is organized as following; First we study the electronic and optical properties of individual B and Mg-doped graphene and the obtained results are compared with the electronic and optical properties of pure graphene, then we examine the influence of change in concentration

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of doping atoms on these properties. Next, we explore the effect of BMg co-doping in the form of BMg ring inside the graphene sheet, similarly we vary the concentration of BMg rings to determine the effect on above mentioned properties thereby reporting the results in detail for mentioned properties.

2. Computational Method

The calculations were performed using the with plane wave basis set [20, 21]. Projector-augmented-wave (PAW) pseudo-potential (PP) [22, 23] method and generalized gradient approximation [24] (GGA) approach was adopted for exchange-correlation energy. An energy cut-off of 400 eV is used for plane-wave expansion of the PAW. For all our calculations, the system is modeled by a 4 × 3 graphene supercell containing 24 atoms and a vacuum space of 12 Å in the Z-direction is introduced to eliminate the interaction between adjacent layers. A 7 × 7 × 1 Γ-centered k-point grid is used for sampling of the Brillouin zone. The shape and size of 2D supercell model and atomic positions are optimized until the Hellmann–Feynman forces were less than 0.005 eV/Å and the total energy is converged within 10-6 eV. All the calculations were performed in spin-polarized mode.

In order to calculate the optical properties, we used DFT within the Random Phase Approximation (RPA) [28] approach in which local fields effects are omitted. Only interband transitions are included, so there can be some inaccuracy in dielectric function at low energies. Firstly Dielectric constant 'ε' was calculated using material studio software. Since dielectric constant is the sum of real and imaginary part i.e. ε = ε' + i ε" together. The imaginary part is obtained by the summation of empty states using following equation.

$$\varepsilon''_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q\to 0} \frac{1}{q^2} \sum_{c,v,k} 2\omega_k\, \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \langle u_{ck+e_\alpha q} | u_{vk} \rangle \langle u_{ck+e_\beta q} | u_{vk} \rangle \qquad (1)$$

Where the indices α and β are the Cartesian components, $\mathbf{e}_\alpha$ and $\mathbf{e}_\beta$ are the unit vectors along the three directions, c and v refers to conduction and valence band respectively. ϵ_{ck} and ϵ_{vk} describe the energy of conduction and valence band respectively and u_{ck} is the cell periodic part of the orbital at the k-point k.

The real part of dielectric tensor was calculated by using Kramers-Kronig transformation

$$\varepsilon'_{\alpha\beta}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon''_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta} d\omega' \qquad (2)$$

Where P denotes the principle value. This method is explained in detail in Reference [28].

From the values of real and imaginary part of dielectric tensor we can easily get refractive index **'n'** and extinction coefficient **'k'** by using the following equations,

$$n(\omega) = \left[\frac{\sqrt{\varepsilon'^2 - \varepsilon''^2} + \varepsilon'}{2}\right]^{\frac{1}{2}} \qquad (3)$$

$$k(\omega) = \left[\frac{\sqrt{\varepsilon'^2 - \varepsilon''^2} + \varepsilon'}{2}\right]^{\frac{1}{2}} \qquad (4)$$

With the calculated refractive index **'n'** and extinction coefficient **'k'** we can obtain absorption coefficient **'α'** and reflectivity 'R' by [19],

$$\alpha(\omega) = 4.\pi.k(\omega).\omega \qquad (5)$$

$$R(\omega) = \frac{(n(\omega) - 1)^2 + k(\omega)^2}{(n(\omega) + 1)^2 + k(\omega)^2} \qquad (6)$$

3. Result and discussion

Firstly we investigated pure graphene sheet and its geometry was fully optimized, the lattice constant was found to be 2.4589 Å which is nearly same as the experimental value of 2.46 Å and the C - C atoms bond length was found to be 1.418 Å which is in agreement with the previous work[25]. The optimized geometry of 4 × 3 pure graphene supercell is shown in Fig. 1

We calculated the band structure of pure graphene and is shown in Fig. 2, and the result is found to be in complete agreement with the literature[2].

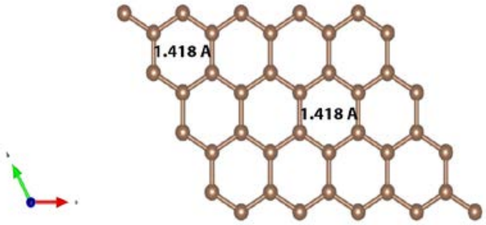

Fig. 1 pure graphene

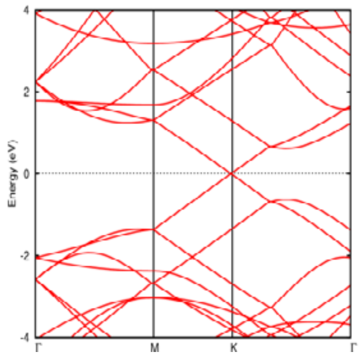

Fig. 2 Band structure of pure graphene

Figure 1. (a) Optimized structure of pure graphene (b) Band structure of pure graphene

Afterwards, pure graphene is doped with boron and magnesium atoms concentration is. Lattice constant of graphene sheet increases in case of B-Mg co- doping and decreases in case of B-Mg co-doping, because the covalent radius of boron/Mg is larger than carbon atom and the covalent radius of B-Mg is smaller than carbon atom, this prediction is in agreement with the previous literature available

3.1 B-Mg co-doping

Similar to B-doped graphene, we investigate B-Mg codoping system. In this configuration we substituted two Boron and two Magnesium atoms in pure graphene lattice.

When graphene is doped with Boron and magnesium atoms, similar cases as in case of boron doping appear , only the difference is that in case of Mg doping than MgC bond length is increased as compared to B-C bond length , it is due to the larger covelent radii of Mg atom than C atom. However both atom goes through sp2 hyberdization process same like carbon atom.

Bandlength of Mg-C atom was found 1.82A and bandwidth between B-C atom is found to be 1.4A.

1.398A

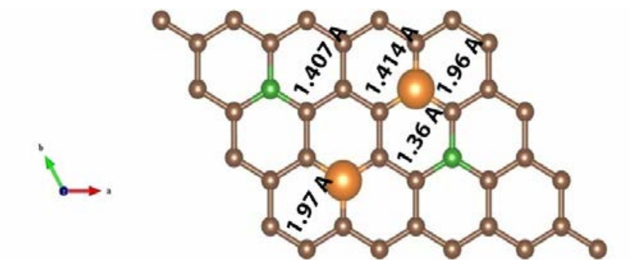

Fig. 3 B-Mg co-doped graphene structure

3.1.1 Band structure and density of states

Band structure diagrams of B-Mg doped graphene sheet are shown in fig . since we know that B atom contains one extra hole than host carbon atom and magnesium contains two extra electron . The system displays electron doping properties there by causing shift in dirac point above the Fermi level approximately 1.2 ev as presented in fig. however B-Mg doping preserves the linear energy dispersion close to dirac point and a band gap of approximately 0.6ev appears at high symmetric K-point due to breaking of extra symmetry of graphene sub lattice because of B-Mg doping process[27].

DOS and PDOS plot is shown in Fig. 8(c) for B-Mg co-doped graphene and comparison is made between two plots to understand the change in DOS of graphene after B-Mg co-doping. Comparsion in the plot indicates that when B-Mg is doped in the graphene layer it causes the shift in Dirac cone into the conduction band and Fermi level moves to the valence band with a finite splitting and linear dispersion of graphene disappears.

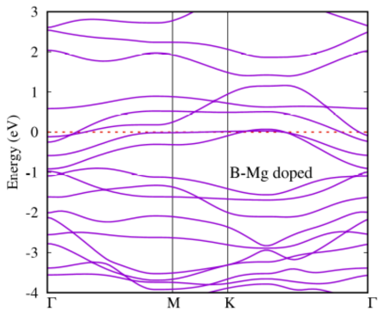

Fig. 4

Comparison between plots

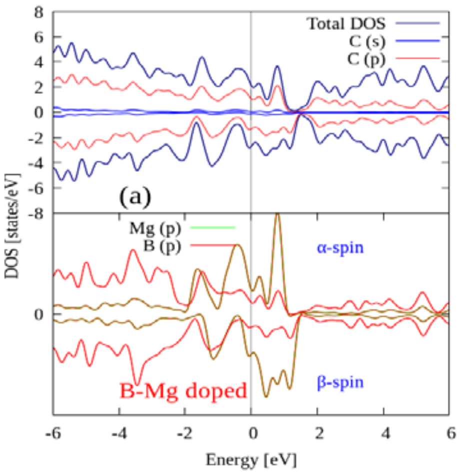

Fig. 5

3.1.2 Optical properties

The absorption coefficient and reflectivity plots for B-Mg co-doped graphene are shown in fig . After B-Mg doping the absorption coefficient peak at 15ev reduces to 8500 . the absorption coefficient between 0-2ev appears which was not present in case of pure graphene ,absorption peak at 0.5ev increases to 500 in case of B-Mg co-doping and a red shift appears in absorption coefficient after B-Mg co-doping.

The static reflectivity (i.e reflectivity at 0ev) energy rises to 0.37 in comparison to 0.19 of pure graphene . moreover , the reflectivity parameter increases in low energy range and shows decreasing values in high energy range.

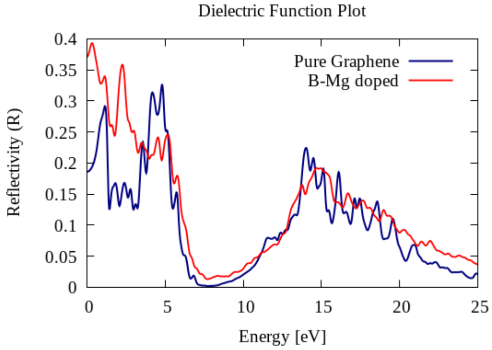

Fig.6 Absorption coefficient

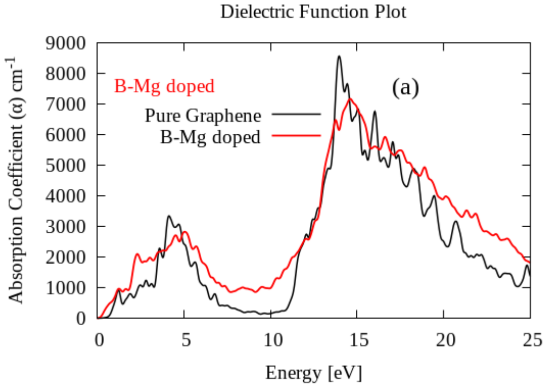

Fig.7 Reflectivity plots of B-Mg doped graphene

4. Summary and conclusions

In summary, the structural electronic and optical properties for pure graphene and B-Mg co-doped system were calculated through FPS-DTF method

After B-Mg atom substitute the lattice constant of graphene increase due to increase in C-C , C-Mg and C-B bond lengths

B-Mg co-doping converts zero band gap semiconductor graphene to half metal graphene .In addition a band gap of 1.2ev appears at high symmetric-point.

B-Mg co-doping shifts Dirac cone to conduction band and Fermi level moves down to valence band

In terms of absorption coefficient ,B-Mg co-doped impurities absorption in lower energy range and also produces a red shift towards visible range .

The static reflectivity parameter rises after B-Mg co-doped

In general it can be concluded , that B-Mg co-doping is an efficient way to tune .The electronic and optical properties of graphene for practical engineering applications those are distinctive to pure graphene.

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