Using dopping and adsorption to introduce energy band gap into graphene ; a DFT study.

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Abstract . It is essential introducing and tuning an energy band gap to graphene for the promising electronic and optoelectronic application of this 2D carbon nanostructure.In the natural state, graphene cannot be used in electronic nanoscale applications because graphene is a semiconductor with a nearly zero band gap energy, which behaves like a semi-metal, as it is necessary to open the band gap energy values of graphene for use in various nanoscale applications as a semiconductor material with different band gap.Investigate the co-doping method .Materials Studio simulation tool ,based on Density Functional TheoryDFT and Local Density Approximation (LDA) to study doping and adsorption large unit cell (4x4x1) for graphene to opening different values of band gap energy . We have been observed different band gap energy between (0.084 eV – 0.77 eV), These values of band gap energy converting graphene from a semiconductor with a gap almost zero to semiconductor with different values of band gap energy.

Key word: Energy band gap, Graphene, Doped, Adsorption,Band structure, Density of state.

Introduction

Graphene is one –atom-thick layer of sp^2 bonded carbon atoms, which forms a two dimensional (2D) honey comb lattice .This nanomaterial was first synthesized by Novoselov and Geim[1]Due to its electronic properties, nowadays it is believed that graphene would be a promising candidate in the field of nano electronics as well as in material science [2].Graphene has offer many useful properties ,such as low weight, high electrical conductivity and novel combination of these properties [3].Graphene based devices, such as filed –effect transistors ,often demand a nonzero band gap to function. Therefore, creating a bandgap in graphene and controlling its magnitude is an important technology advance[4].

Graphene hybridized orbitals form strong σ-bonds in the plane and un-hybridized p-orbitals overlap with neighboring atoms to form π-bond. While the σ-bond is responsible for the most of the structural integrity of graphene, the π-bond determines electronic and optical properties[5]. In this study mainly focus on the local changes of the graphene by broken symmetry ,we using two method doping and adsorption. We used different considering of doping B and N atom in the graphene, at doping concentrations (3.125 %,6.25%,9.375%) .After that adsorption this sheets with

hydrogen atom. We have been observed different values of band gap energy ranging (0.084 – 0.77 eV), these values of energy band gap converting graphene from a semiconductor with a gap of almost zero to a semiconductor with a gap of different values. In this study we using large unite cell (4×4×1) Which equals 32 carbon atoms for pristine graphene and have been used First principle calculations by Density Functional Theory(DFT) method and Local Density Approximation(LDA) have been described Band Structure and Density Of State (DOS) to find out different values of band gap energy for graphene plates, Which are suitable for various applications.

Computational Details

The calculation has been done using Density Functional Theory (DFT) in DMOI^3 based study was performed using Local Density Approximation (LDA). Periodic boundary condition has been applied to the large cell unit (4×4×1) that consists of 32 carbon atom and lattice parameter was (a,b,c) where (a=b) is equal 9.838 A˚ and c=30 A˚. Stapes of calculations included Geometry optimization of graphene sheet and after that has been calculation electronic structures (band structure and density of state).

Results and Discussion

Band structure, density of state and energy band gap has been calculated of doped graphene and adsorption graphene. Band structure are placed along high symmetry points (G-M-K-G).

Doped graphene: Boron and nitrogen are two natural options to doping the graphene due same size of the carbon atoms. Doping in boron atoms give p-type doping and the nitrogen atoms n-type doping or any of them accepter and the other donor the electrons**.** When doping graphene with boron atoms (figure1)**,** observed band structure shifted above the fermi level because the electronegativity of boron atoms is higher with respect to carbon atoms. Dirac con show E_f lie in valence band (Figure 3b) and above fermi level opening band energy gap between (0.084 eV -0.375 eV) that due to breaking of the symmetry of graphene and graphene sheets turn to semiconductor p- type with different values of band gap energy (Table 1) . Large value of energy band gap has been observed at(3B(b)) As shown in band structure and density of state (Figure2).
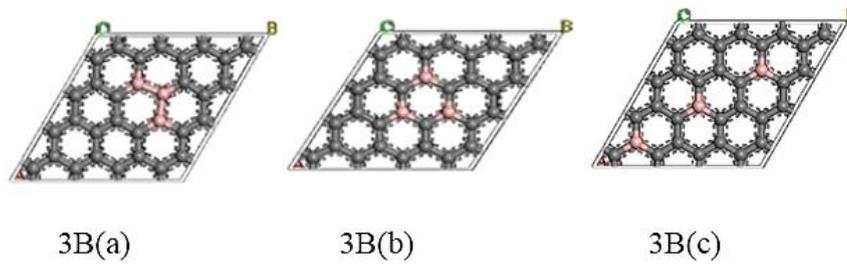
Figure (1) graphene sheets with doping boron atoms.

| 1B | 2B(a) | 2B(b) | 2B(c) |

3B(a)　　　　　3B(b)　　　　　3B(c)
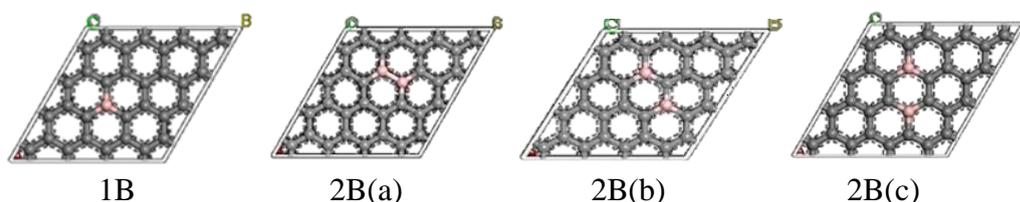
Figure (2) Band structure and density of state of highest energy band gap observed doping at case 3B (b).
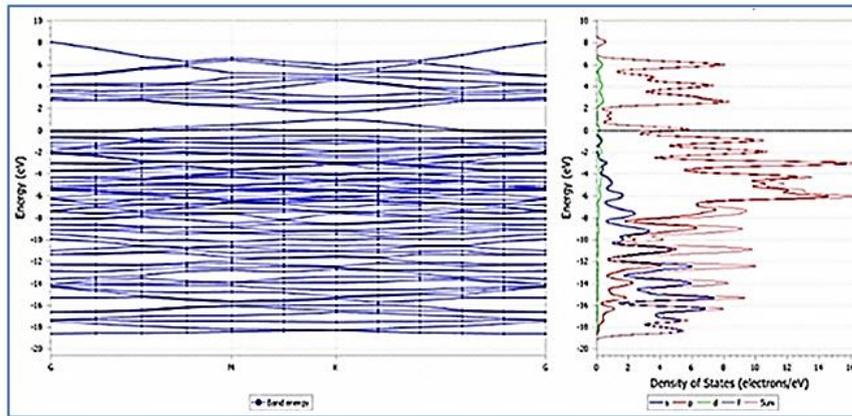

Table (1) Values and type of energy band gap of doping graphene doped with boron atoms.

Type of band gap	Band gap(eV)	Configuration	Concentrations	Doped atoms
	0.00		3.125 %	1B
Direct	0.265	a		
	0.00	b	6.25%	2B
	0.00	c		
Indirect	0.084	a		
Indirect	0.375	b	9.375%	3B
	0.00	c		

Figure (3) Dirac cons: Schematic band structures of graphene. (a) Band structure of pristine graphene with zero bandgap. E_f is at the cross-over point. Band structures of
 (b) p-type and (c) n-type graphene with the bandgap. E_f lies in valence and conduction band,respectively[6]
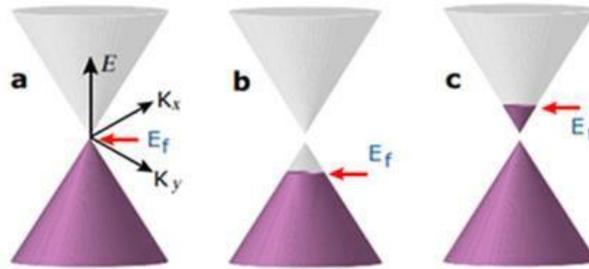
When graphene is doped with nitrogen atoms (figure 4)**,** Band structure shifted below the fermi level Because the electronegativity of carbon atoms is higher with respect to nitrogen atoms. Dirac con show E_f lie in conduction band (Figure3(c)) and below fermi level energy band gap ranging (0.174 eV -0.4 eV),This is due to breaking of the symmetry of graphene and graphene sheets turn to semiconductor n-type with different values of band gap energy (Table 2) . The highest value of energy band gap has been observed at case (2N(b)) as shown in band structure and density of state (Figure 5).

Figure (4) Graphene sheets with doping nitrogen atoms.

1N   2N(a)   2N(b)   2N(c)

3N(a)   3N(b)   3N(c)

Figure(5) Band structure and density of state of highest energy band gap observed doping at case 2N(b).

Table (2) values and type of energy band gap of doping graphene with nitrogen atoms.
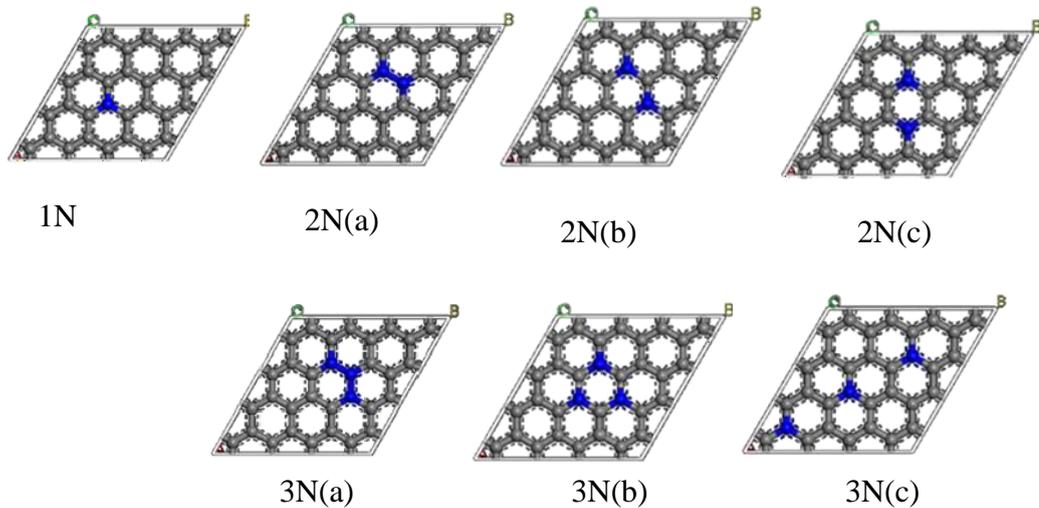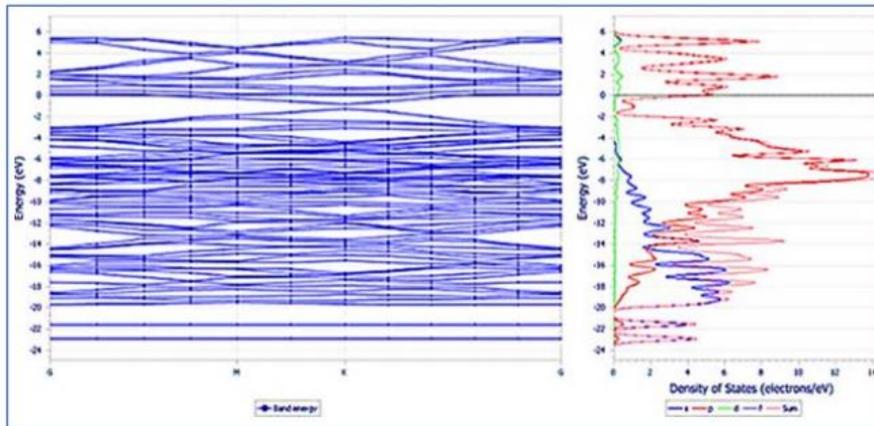
| Type of bandgap	Band gap(eV)	Configuration	Concentrations	Doped atoms
Direct	0.2		3.125 %	1N
Direct	0.231	a		
Direct	0.4	b	6.25%	2N
Direct	0.174	c		
Indirect	0.343	a		
	0.00	b	9.375%	3N
	0.00	c		

Graphene adsorption: In this step we add hydrogen atom on graphene sheets doped with boron and nitrogen atoms. The interaction between the hydrogen atom and the graphene layer is nonlocal, as they are not covalently bonded. In the adsorbed the graphene observed the bands be down the fermi level due below the fermi level the π band contributed from the pz orbital of carbon atoms and *π band contributed from the pz orbital of adsorption atom (H). The binding energy(Eb) for adsorption atom on the graphenesheets doped was calculated by this equation:

$$E_b = -\frac{[E_{graphene+metal} - (E_{graphene} + nE_{metal})]}{n}$$

$E_{graphene+metal}$: total energy of adsorbed graphene sheet, $E_{graphene}$: total energy of graphene sheet, E_{metal}: total energy of adsorbed atoms ,n: number of adsorbed atoms]7[.when we add one atom of hydrogen on surface of graphene sheets doped with boron atoms(figure 6) , The results showed clear band gap energy ranging(0.088eV-0.645 eV) and large binding energy is has been observed (2.872eV),

as shown at (Table 3), Highest energy band gap has been observed at case (3B(a)-G-H), As shown in band structure and density of state (Figure7).

Figure (6) Adsorption hydrogen atom on the   surface of graphene sheets doped with boron atoms.

B-G-H   2B (a)- G-H   2B(b)-G-H

2B (c)- G-H   3B (a)- G-H   3B (b)- G-H

3B (c)- G-H
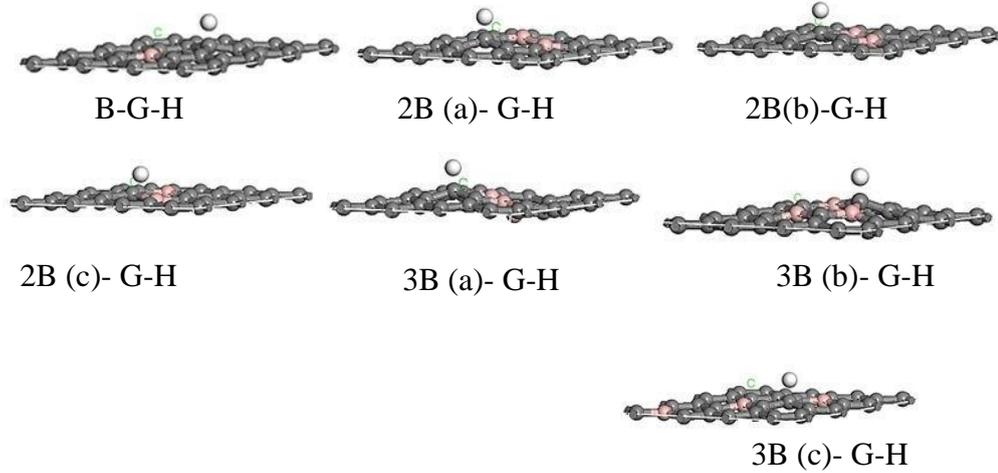
Figure(7) band structure and density of state of largest energy band gap has been observed at(3B (a)- G-H).
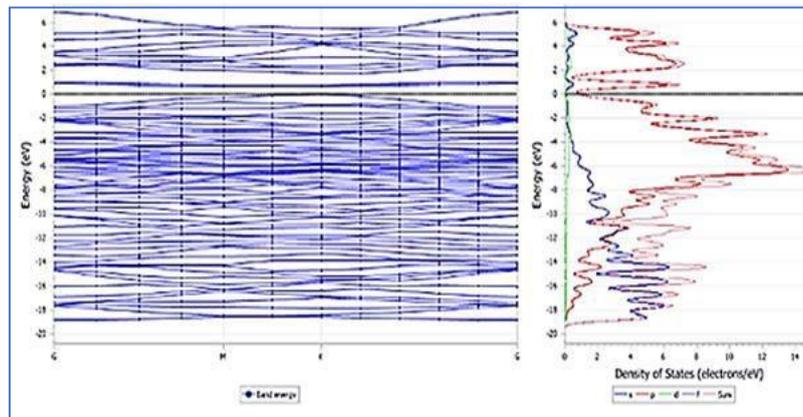

Table (3) Values ,type of energy band gap and binding energy of adsorption hydrogen atom on the surface of graphene sheets doped with boron atoms.

E_b (eV)	Type of band gap	Band gap(eV)	Configuration	Type of structural
1.749	Indirect	0.640		B-G-H
1.774	Indirect	0.215	a	
1.495	Indirect	0.088	b	2B-G-H
1.668		0.00	c	
2.872	Indirect	0.645	a	
2.616		0.00	b	3B-G-H
1.761		0.00	c	

When we add one atom of hydrogen on surface of graphene sheets doped with nitrogen atoms (figure8) , The results showed clear band gap energy ranging (0.316V-0.77 eV) and big binding energy is (1.127 eV)(Table 4), largest of energy band gap has been observed at case (3N(b)-G-H), As shown in band structure and density of state (Figure9) .

Figure (8) Adsorption hydrogen atom on the surface of graphene sheets doped with nitrogen atoms.

N -G-H   2N (a)-G-H   2N(b)-G-H

2N (a)-G-H   3N (a)-G-H   3N (b)-G-H
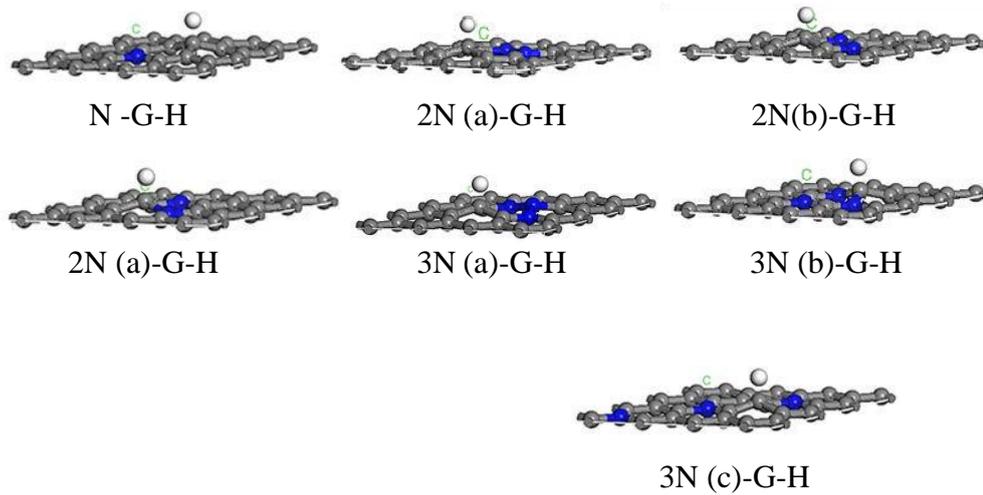
3N (c)-G-H

Figure (9) Band structure and density of state of largest energy band gap has been observed at case (3N (b)- G-H).
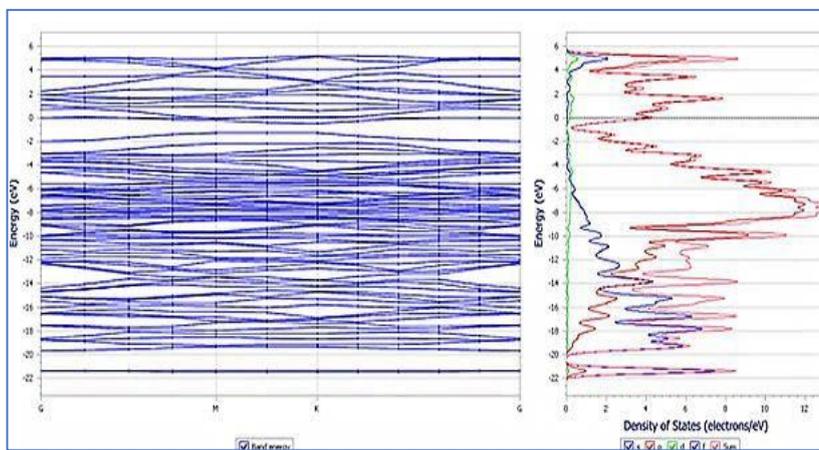

Table (3) Values ,type of energy band gap and binding energy of adsorption hydrogen atom on the surface of graphene sheets doped with nitrogen atoms.

E_b (eV)	Type of band gap	Band gap(eV)	Configuration	Type of structural
0.768	Indirect	0.536		N-G-H
0.838	Indirect	0.525	a	

0.796	Indirect	0.316	b	2N-G-H
0.877	Indirect	0.344	c	
0.786	Indirect	0.544	a	3N-G-H
1.127	Indirect	0.77	b	
0.744	Indirect	0.389	c	

Conclusions

Density functional theory was used to study geometry, electronic structure and energy band gap for graphene doped with B,N and adsorbed with H. The redistribution of surface charge which breaks the local symmetry of graphene is main reason for band gap opening of graphene on case B or N doping ,which leads to the separation of the valence and conduction band of graphene at the direct points. Hence, B doping leads to band gap opening above the fermi level between (0.084 eV -0.375 eV) and converting graphene into a semiconductor p- type .Also ,N doping below the fermi level between (0.174 eV -0.4 eV) and convert graphene into a semiconductor n- type, As nitrogen atoms open larger bandgap energy values compared to boron atoms. When adsorping hydrogen atom on the surface graphene sheets doping with boron has been observed highest energy band gap is (0.645 eV) and adsorping on nitrogen atoms is (0.77 eV) ,We observed graphene sheets doping with nitrogen opening band gap energy wider than graphene sheets doping with boron. binding energy for adsorption hydrogen on graphene sheets doping with boron equal to (2.872 eV) while for adsorption hydrogen on graphene sheets doped with nitrogen equal to (1.127 eV), We conclude from this that boron atoms Increases surface stability of graphene More than nitrogen atoms upon adsorption .This study investigated to open the band gap energy of graphene for use in various nanoscale applications as a semiconductor material with different band gap values.

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