

Band Gap Engineering in the 2D Wonder Material Graphene A Review of our Computational approach

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Abstract: Band gap engineering of graphene is an important technological challenge for device applications. Different techniques like doping, vacancy creation, strain engineering are tried to open a gap in the bandstructure of graphene and in some cases the gap opened up, but when the gap opens up the Dirac cones disappeared. Graphene, without Dirac cones, loses all its novelty. As a result, opening a gap in graphene retaining Dirac cones has become a challenging task. Through first principles study, using Density Functional theory, we have done band gap engineering/tuning investigations. We have succeeded in opening the band gap, retaining the Dirac cones. In surface doping (adsorption) various elements are tried and finally surface doping of sulphur is found to induce band gap opening in graphene. We also have done ab-initio study on the band gap opening in graphene through vacancy, adding impurity atom in the vacancy and substitutional co-doping. The Dirac cones are retained and the graphene is now a semiconductor with fast moving massless Dirac Fermions. In this article, we present a review of our work done in this technologically important area.

1 Introduction

Graphene, one of the allotropes of carbon, was discovered after carbon nanotube (CNT), another allotrope of carbon. Even though it is less popular than CNT in the application side, the Nobel prize was given for graphene discovery, because it brought in new physics. It is now the mother material for all the allotropes of

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carbon. Because of strange electron - electron interaction in graphene, its electrons attain very high velocity, resulting in Dirac fermions. In the bandstructure of graphene which is dominated by Dirac description, there is no gap, it is a zero gap semiconductor or a semimetal with zero density of states. To have applications in nanoelectronics a suitable band gap is essential. In the past [1-12], several methods are suggested for band gap opening in graphene. Due to the strong sp² bonding the graphene surface has maximum robustness and it is very hard for the foreign atoms to replace the carbon atoms or get adsorbed. Substitutional doping, surface doping (physisorbed adsorbates), defects and co-doping on graphene lead to a different situations. We have tried surface doping for modifying the electronic structure of graphene.

The surface doped atoms are physisorped. In our first study [13], we have functionalized graphene with oxygen atoms with different coverages and have demonstrated the change in the structural and electronic properties of graphene. For a single O atom a gap of 0.08 eV opens up and the Dirac cones made of single bands separated at their tips appear. For more number of surface doped O atoms the gap is large and the Dirac cones are completely destroyed. Taking this as a clue, we have surface doped graphene with ‘oxygen-like atoms’ and looked at the band structure [14]. There are several works on vacancy defects in graphene systems and a reasonable amount of theoretical work has also been done on substitutional covalent bonding in carbon (C)/nitrogen (N), carbon/boron (B), and carbon/boron/nitrogen systems [7-12]. We also considered opening the band gap by modifying the graphene by introducing vacancy defects and impurities. We also explored the influence of point defects on the geometric and electronic structure of graphene using DFT calculations. The creation of vacancies, the inclusion of foreign atoms, and the coexistence of both and their effects on the band structure of graphene are investigated [15].

2 Computational Details

The computations are carried out using DFT based plane wave code, VASP [16]. The PW 91 exchange functional [17], GGA and projector augmented wave (PAW) potentials are used in the calculation. The usual convergence criteria for an accurate calculation is prescribed for the present calculation. By surface doping, the band gap engineering can be controlled in different ways. The surface doping of graphene with oxygen atom led to band gap opening. But the band gap was very small and the Dirac cones are retained to some extent. In order to increase the band gap and at the same time retain the Dirac cones, which is the manifestation of mass less Dirac fermions, We have surface doped graphene with oxygen like atoms F, Cl, P, N & S [14,8]. The creation of vacancies, the inclusion of foreign atoms, and the coexistence of both and their effects on the band structure of graphene are investigated by means of total energy and band structure calculations.

3 Band gap engineering

3.1 Surface doping with oxygen-like atoms

The relaxed structure of 96-atom slab graphene (G96) and its band structure are given in Fig.1 and Fig.2.

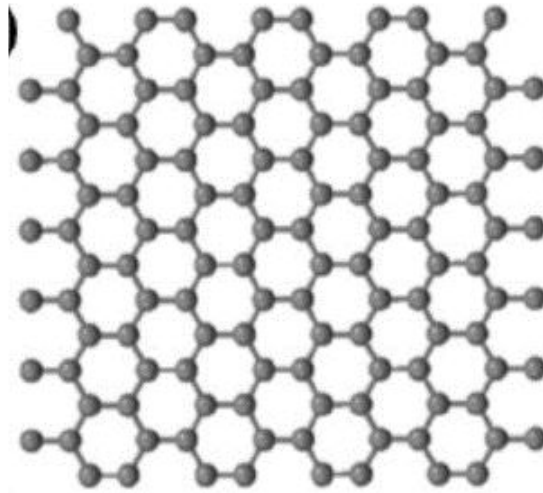


Figure 1: Relaxed structure of 96-atom slab graphene (G96)

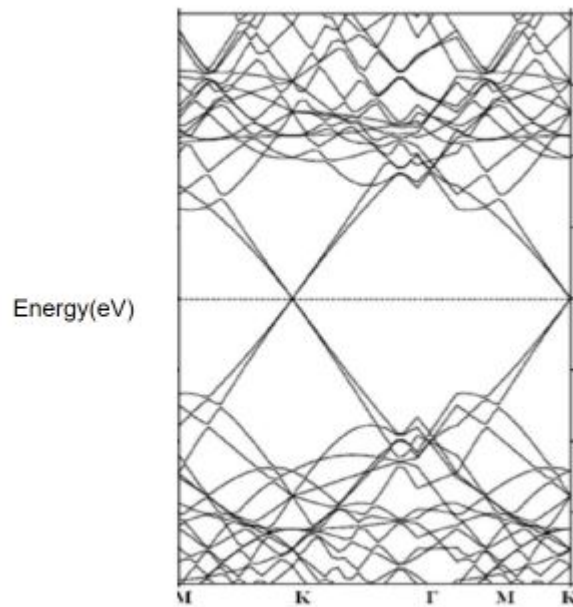
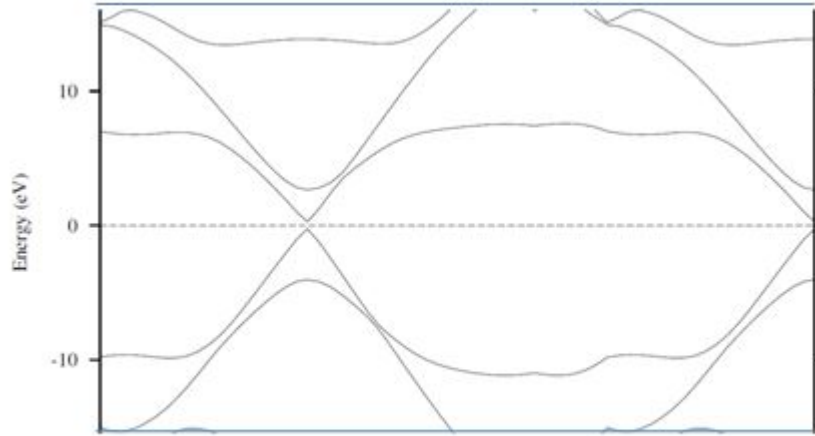


Figure 2: Band structure of graphene (G96)

The surface doping of graphene with oxygen-like atoms F, Cl, P, N & S are done, one by one. In all the cases except S, the Dirac cones are shifted above the Fermi level (FL). The dopant bands lie near and parallel to the FL and no gap at the FL. But the surface doping with sulphur (S) atom alone leads to gap opening in the bandstructure of graphene. If we look at the electronic configuration of the above surface adsorbed atoms, N : $1s^2 2s^2 2p^3$; O : $1s^2 2s^2 2p^4$; F : $1s^2 2s^2 2p^5$; P : $1s^2 2s^2 2p^6 3s^2 3p^3$; S : $1s^2 2s^2 2p^6 3s^2 3p^4$; Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$, we can note the similarity between the electronic configurations of O and S. p4 electrons interact with the pz electron of carbon in graphene leading to the band gap opening at the junction of the Dirac cones and at the FL. Out of the four Dirac cones (two below and two above the FL) two cones (one above and below the FL) lose their cone shape and move away from the FL. But the remaining two Dirac cones (one above and below the FL) are in tact retaining their linear portions.

Due to the surface doping of G96 with s, a direct band gap of about 1.0 eV opens up at the K-point (Fig.3).



e) Close view of the Band gap

Figure 3. Close view of the band structure, band gap and Dirac cones

The band gap arises due to the interaction of p electrons of S with the pz electrons of graphene. As a result the doubly degenerate cone shaped bands are pulled apart leading to the opening of gap. Out of the four Dirac cones pulled apart, two of them retain their shape and stop moving further apart after the gap opening. The other two cone-shaped bands lose their shape and become parabolic in shape and move away (below and above) further from the cone tips. Finally the graphene surface doped with S is a semiconductor with massless Dirac fermions and electrons contributing to its carrier mobility the Dirac cones are in better shape than the case

with G24. This graphene semiconductor is better than the ordinary semiconductor because of the presence of Dirac cones and massless Dirac Fermions. This will have a lot of application in device industry compared to a pristine graphene because of the presence of a gap and Dirac cones.

3.2 Tuning the band gap

Next we tried to modify the surface doping so that we will have control over the band gap. We increased the number of surface doped sulphur atom. We surface doped with two sulphur atoms [14]. For one orientation of the two sulphur atoms a large gap (12 eV) opens up in the graphene bandstructure. The bandstructure is completely modified. The Dirac cones disappear, and doped graphene loses all its special features. For the other orientation of the two sulphur atoms, in the bandstructure of doped graphene, no gap opens up, the Dirac cones are shifted up above the Fermi level through 5.0 eV. The sulphur bands mixes with the graphene bands near the Dirac cones. As a result, there is discontinuity in the lower portion of the lower Dirac cone. The sulphur bands lie across the lower cones parallel to the Fermi level and extends on either side of the cones. The two sulphur atoms are at a distance of 3.94 Å from G24 and the planar nature of graphene is not disturbed and as a result, there is no band gap opening but only a shifting of bands. We surface doped two S atoms on G96 for two different distances between the two S atoms. In the relaxed structures the two S atoms are at distances 1.921 Å and 1.946 Å from G96. Here also the planar nature of G96 is not disturbed, that means no band gap opening will occur for surface doping of two S atoms.

3.3 Co-doping

To further improve and control band gap opening through surface doping using sulphur as the surface dopant, we added a co-dopant along with S. Since we have already effected band gap opening, retaining Dirac cones, using O [13] and S separately, we tried simultaneous surface doping of graphene with S and O. The best way, we thought, is surface dope graphene with SO₂. Surprisingly the surface doping of graphene with SO₂ does not effect any band gap opening. The Dirac cones intersection point is shifted slightly above the FL and the flat SO₂ bands lie parallel to the Fermi level.

Next, we surface doped graphene with CO₂. This bandstructure looks exactly like the bandstructure of pristine graphene. Since the CO₂ molecule is a little far away from G24, neither C nor O atoms have any effect on graphene. Now we surface co-doped S along with CO₂ (Fig.4). The bandstructure looks similar to the bandstructure of graphene surface doped with S alone. Here also a band gap of ~ 1.4 eV opens up, the two Dirac cones are retained with rounded off cone tips [14].

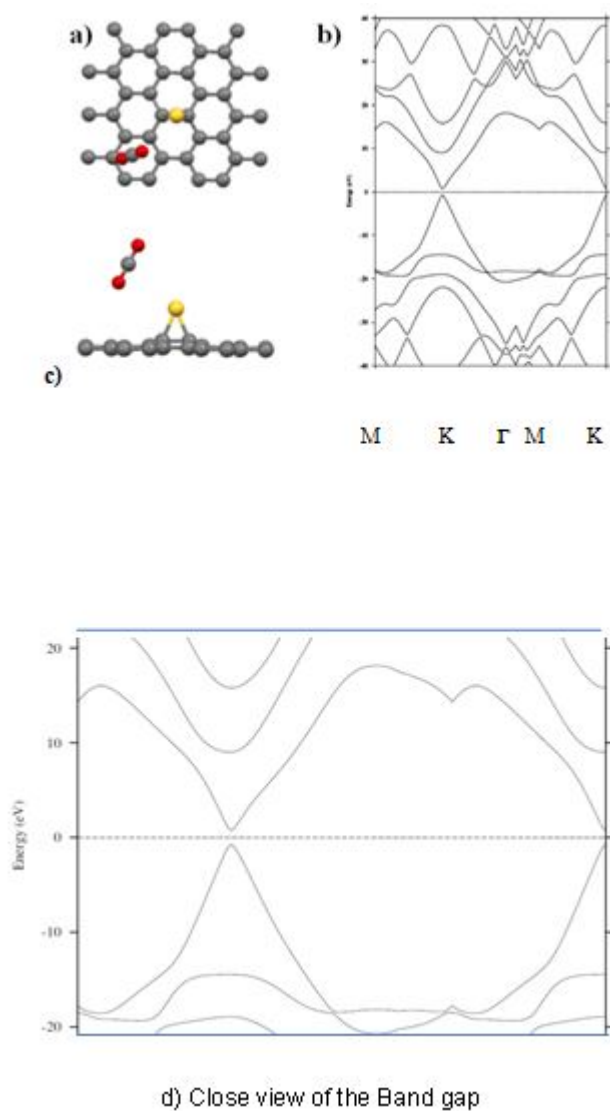
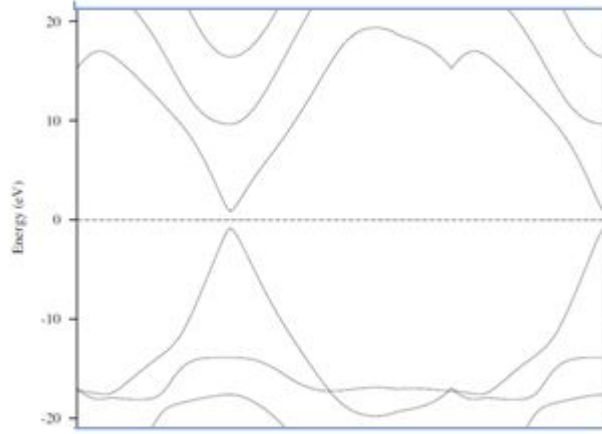


Figure 4. (G24+CO2+S): a) relaxed structure, b) band structure, c) relaxed structure-side view and d) Close view of the band gap and Dirac cones

It is also known that when N is doped substitutionally in graphene, it leads to n type graphene. No gap opens up. When we surface doped graphene with N and NN, we come across some interesting features in the band structure of graphene. With a single N, the two Dirac cones are shifted up above the Fermi level and a small gap opens up. The nitrogen band mixes with the graphene bands near the inverted V Dirac cones. The nitrogen bands lie across the lower cones parallel but below the Fermi level and extends on either side of the cones. When one more N is added, we get a band structure similar to a pristine graphene (Fig.2). The nitrogen

bands are well below and above the Dirac cones. Here we come across a different type of complementary doping similar to the complementary substitutional doping of N and B in graphene. To engineer a band gap, along with NN we doped different elements like P,S [14].



e) Close view of Band gap

Figure 5. (G24+NN+S) : Close view of the band gap and Dirac cones.

When P is added to G24+NN system the band structure is completely modified. No gap opens up, the Dirac cones are shifted up above the Fermi level but without any distortion, the linearity of the bands is fully retained. The nitrogen and P bands mixes with the graphene bands near the Dirac cones, as a result there is discontinuity in the lower portion of the lower Dirac cone. The N and P bands lie across the lower cones parallel and just below the Fermi level and extends on either side of the lower cones. When we surface doped S instead of P in G24+NN, the bandstructure (Fig.5) looks similar to the bandstructure of G24+S or G24-CO₂+S, but now the band gap value has increased to ~ 1.5 eV. It is reflected in the density of states. The nitrogen atoms are at a distance of about 5 Å and there is a very weak interaction between graphene and them where as S atom is at a distance of 1.92 Å and a strong interaction is established between S and G24 [14].

3.4 Vacancies in Graphene

The structural and band structure modification caused by the creation of single, double and trivacancies (three monovacancies) in the basal plane of graphene are investigated methodically. The removal of one, two and three carbon atoms from graphene leads to the above mentioned vacancies. While mono and divacancies have

been investigated in G24 [15], we have included those vacancies in G96 along with trivalent sites and added impurities in them.

3.4.1 Monovacancy

The monovacancy is created by removing a carbon atom and the system is relaxed. We can identify the void space in the stabilized structure. Now, it is evident that the vacant site is stable and there is no reconstruction. The carbon atoms surrounding the vacancy buckle. There is small amount of charge in the vacant site. There is a charge transfer from the neighbouring sites to the carbon atoms near the vacancy. As a result, a small amount of electron charge is leaking into the vacancy site. In the band structure of graphene with single vacancy (Fig.6), we can observe the separation of the tips of the Dirac cones at the "K" point. The presence of vacancy affects the electron-hole symmetry of the two Dirac cones (out of the 4 Dirac cones) and localized band states appear near the Fermi level (FL). The Dirac cones are shifted up. Non-dispersing flat band and quadratically dispersing bands are introduced. They are responsible for the magnetism induced in the graphene with mono-vacancy [3]. The flat band in the gap arises due to the localized states of the vacancy.

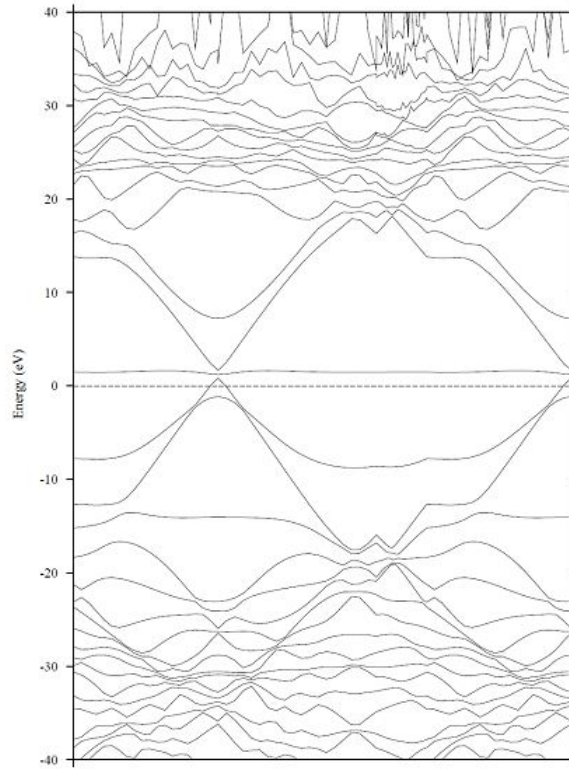


Figure 6 : Band structures of graphene with single vacancy.

In Fig. 6, one can see a direct band gap of ~ 1.0 eV and with this band gap the graphene can be tailored for device applications. The band gap opening due to vacancy, according to Dvorak and Wu [4], arises because the defect structure vary on the scale of the inter-atomic distance inducing inter-valley scattering between the Dirac points and cause a gap opening at the "K" point. They also claim [4] that the inter-valley scattering mechanism has a strong resemblance to the prevention of merging of the Dirac points, leading to a topological phase transition in both cases.

3.4.2 Divacancy and Two Single Vacancies

In a work [15] on graphene G24, the case of divacancy is reported. Its characteristics are completely different from that of the single vacancy. The introduction of divacancy results in a band gap of ~ 0.5 eV [15]. To see the effect of two single vacancies compared to a divacancy, researchers have investigated the G96 system with two monovacancies (G94+2Vac) [15]. There is buckling (protrusion and depression) of carbon atoms near the vacant site. The doubly degenerate cone shaped bands are pulled apart leading to the opening of a different type of gap. Out of the four Dirac cones (2 above and 2 below the FL) pulled apart, two of them (inner most) retain their shape and stop moving further apart after the gap opening. The other two cone shaped bands lose their shape and become parabolic. Two flat bands due to localized charge states of the two vacancies lie in the band gap between the separated tips (one V shaped tip and another rounded tip) of Dirac cones parallel to the FL and extends on either side of the cones (Fig. 7). Effectively, there is an indirect band gap (pseudo gap) of ~ 1 eV. The shape of the Dirac cone below the FL is almost retained except its rounded tip. This semiconducting graphene with two monovacancies is better than the ordinary semiconductor because of the presence of linear bands and massless Dirac Fermions in addition to the gap.

The vacancy formation energy for a single vacancy (G96-G95) is 7.7 eV. This value is in good agreement with the previously reported value in a DFT calculation. The vacancy formation energy for two single vacancies (G95-G94) is 15.8 eV. The vacancy formation energy for the second vacancy with the presence of a single vacancy (G95-G94) is 8.2 eV. We have performed spin-polarized calculations. The ground state energy is 0.038 eV lower than the nonspin-polarized calculation. It is found that the top of the fully occupied spin up band crossed the Fermi level and the system turns out to be a ferromagnetic metal. The magnetic moment of the system is about 0.29 B.

3.4.3 Impurity atoms in the vacancy

In the vacant site there is charge accumulation and distortion. This will cause the adsorption of foreign molecules. Now, the vacant sites are acting as trapping centres and adsorb the foreign atoms/molecules. The system, graphene, may get

reconstructed. In order to further improve the band gap opening in the graphene we introduced impurity atoms in the vacancies and investigated the changes in the band structure, mainly the band gap opening.

3.4.4 Hydrogen in multiple vacancies

Firstly, we created three monovacancies in the G96 slab and relaxed it. We come across some interesting features in the band structure of this graphene.

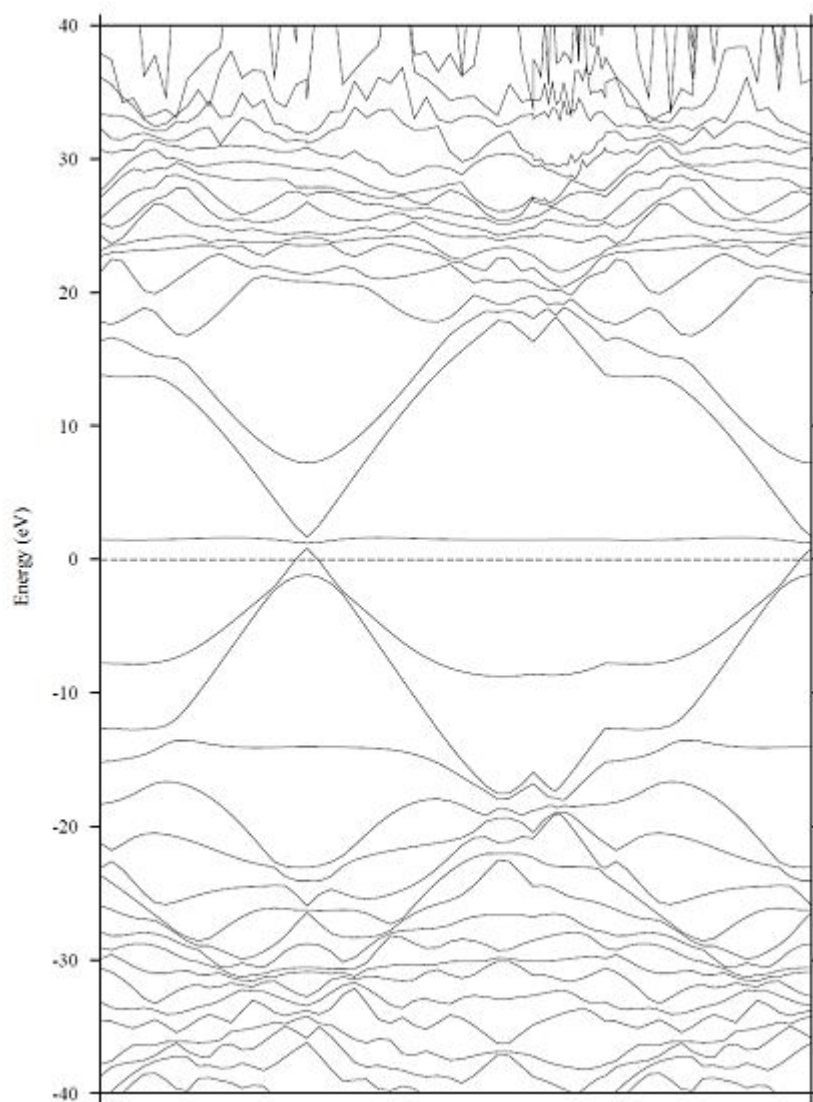


Figure 7: Band structures of graphene with two single vacancies (G94+2Vac)

Two Dirac cones are shifted up above the FL and a small gap opens up. In the gap lies the H band. Now, out of the four Dirac cones two outer cones have turned into a quadratically dispersing parabolic band (above and below the FL). The bands corresponding to the vacancy states mixes with the graphene bands near the bottom of the inverted V Dirac cone and lie across the lower cones parallel but below the FL and extends on either side of the cones. Apparently, there is no band gap opening near the FL. However, well above the FL, as mentioned, there is a small gap. To make use of this gap, we have to tune the system so that the gap moves closure to the FL. We have introduced one more H atom in one of the remaining two monovacancies.

The H atoms in the vacancies are projecting out of the plane and there is buckling of carbon atoms. In the band structure the Dirac cones and the gap have moved down towards the FL, but not much. To get further movement of the gap, we have added the third H atom in the third monovacancy. The H atoms in the vacancies are projecting out of the plane and there is buckling of carbon atoms around the H atoms. In the band structure the Dirac cones and the gap have moved up away from the FL.

Tuning the band gap with multiple monovacancies and gradual filling them with H atoms has not given the desired result. May be the interaction of H atom with the graphene is strong enough to spilt the Dirac cones and move them above the FL. Also there is no reconstruction of the sites around the vacancies.

3.5 Substitutional doping in graphene

On substitution of boron (B) and nitrogen (N) atoms, FL is shifted in opposite directions in the band structure. The acceptor and donor bands are formed below and above FL in B-doped and N-doped graphene and obtain p-type and n-type graphene with B and N doping respectively. Since both B and N are non-metals, they form covalent bonds with carbon atoms of G95. Even after the doping, the structure of graphene is not distorted except the change in inter-atomic bond lengths. The formation energy of boron doping is more than that of N atom. Therefore, doping of graphene by N is thermodynamically favorable. In this case there is no band gap opening; only bands shift for the doping of N and B individually.

The co-substitution of B and N leads to equal concentrations of p-type and n-type impurities [18]. Here also no band gap opens. The touching of the distorted Dirac cones at the Fermi point can be a check mark for presence of equal concentration of p-type and n-type impurities in graphene. With the co-substitution of B and N, a third suitable dopant element which will induce a small gap upon substitution, has to be identified. In this process, the percentage of N and B is increased to check the effect on band gap. The systems investigated are G93+NBB and G93+BNN.

Since the B-N pairs are isoelectronic to C-C pairs, in the relaxed structures there are no buckling or any other distortions. In the band structure also, we did not observe any major changes. The band structure of G93+NBB looks similar to the B doped graphene band structure and G93+BNN band structure mimics the N doped graphene band structure.

In the above tri-doping, we want to change the third dopant that it will lead to band gap opening in graphene. From our experience in band gap engineering using surface doping of various atoms [14], we reason out that the third dopant could be sulphur (S) only. In the above systems, G93+NBB and G93+BNN, we have replaced the second B/N by S. The relaxed structures G93+BNS are shown in Fig.8.

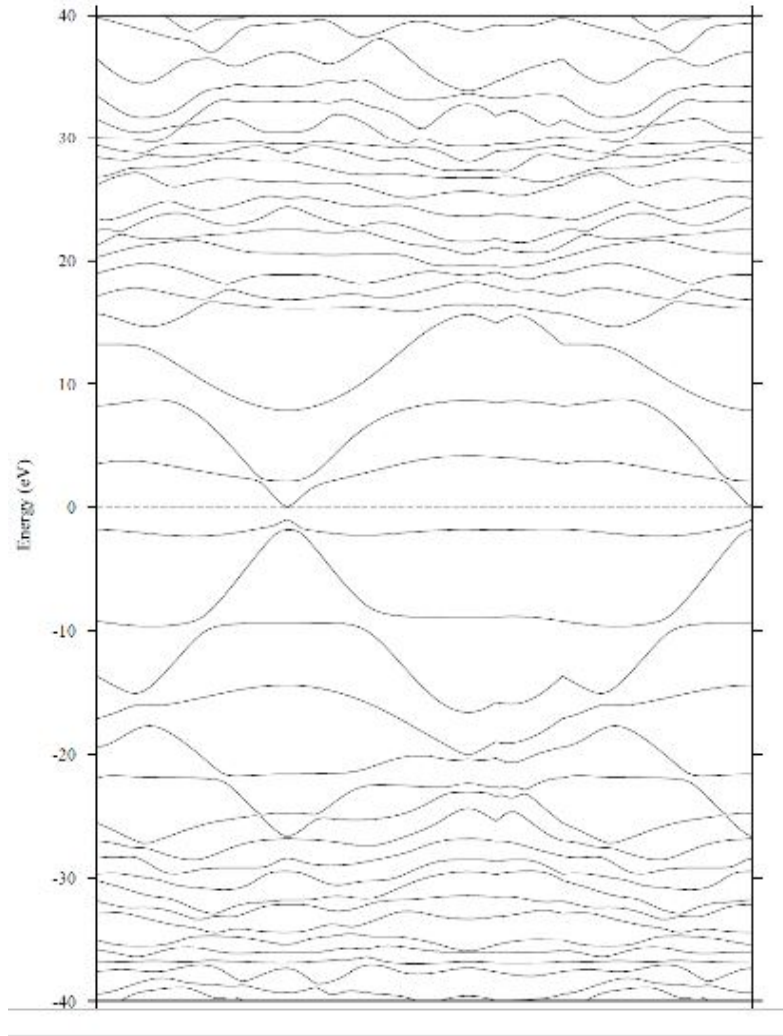


Figure 8 : The band structure of Graphene doped with B,N,S (G93+BNS).

This interaction of S atom with graphene has altered the electronic band structure of (G93+NBB) / (G93+BNN). The doubly degenerate cone shaped bands are pulled apart leading to the opening of gap. Out of the four Dirac cones pulled apart, two of them retain their shape and stop moving further apart after the gap opening. The other two cone shaped bands lose their shape and mixes with the S bands and lie in the band gap between the rounded tips of the less distorted Dirac cones parallel to the FL and extends on either side of the cones. Effectively there is a direct gap of ~ 1 eV and the shape of the Dirac cone below the FL is almost retained except its rounded tip. As a result, the graphene substitutionally co-doped with S atom has turned into a semiconductor.

4 Summary and Conclusion

Out of the different cases of surface doping of graphene with various atoms and molecules, the cases involving Sulphur turn out to be useful leading to band gap opening. Sulphur interaction with graphene surface is unique. It moderately distorts the surface atoms and the interaction is limited such that a band gap opens without much distorting the Dirac cones. With single S a band gap of ~ 1.4 eV opens up. Also when S is co-doped along with CO₂ or with NN similar band gap opening occurs but the bands are less distorted compared to S doping alone and the gap has slightly increased. The calculation of surface doping of graphene with S is repeated with 96 atom simulation cell. The band gap value is ~ 1.0 eV. The value of band gap can be tuned to the required value by varying the distance of S atom of the co-dopants from the surface of graphene, which can be achieved by proper ion implementation technique or by atomic layer deposition directly using remote oxygen plasma surface pretreatment.

In the case of graphene with single vacancy a direct band gap of ~ 1 eV is obtained. This is a spin polarized state. The graphene system with two monovacancies gives rise to an effective indirect band gap (pseudo gap) of ~ 1 eV. This is not observed earlier. The graphene substitutionally doped with B and N is co-doped (tri-doped) with S. This tri-doped (B, N, S) graphene has turned into a semiconductor (band gap ~ 1 eV). In all the cases, where we have induced a band gap, the massless Dirac fermions and electrons are contributing to the carrier mobility of the semiconducting systems. This graphene semiconductor is better than the ordinary semiconductor because of the presence of Dirac cones and massless Dirac Fermions. This will have lot of application in device industry compared to a pristine graphene because of the presence of a gap and Dirac cones.

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