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First principles investigation of electronic properties of graphene doped with Al and N atoms

Elham A. Mohamed,[a,*], Afnan Z. Mohamed,[a], Fadl M. Abou El-Ela,[a] Samy H. Aly, [b]

[a]*Physics Department, Faculty of Women for Arts, Science and Education, Ain shams University, 11757, Cairo, Egypt.*
[b]*Physics Department, Faculty of Science, Damietta University, New Damietta, Egypt.*

Abstract

The geometry optimizations and electronic structure calculations were performed for graphene sheet doped with aluminium (Al) and nitrogen (N). The effect of doping has been examined by changing the concentrations of dopants from 2 % (one atom of the dopant in 50 host atoms) to 12 % (six dopant atoms in 50 host atoms). All the calculations have been performed by using the Burai Graphical user interface that used the Quantum Espresso code based on density functional theory, plane waves, and pseudo potentials. By Al and N doping, p-type and n-type doping are induced respectively in the graphene sheet. The results showed that the planar structure of the graphene sheet remains unaffected on doping. However, the electronic properties were changed from semimetal to semiconductor with an increasing number of dopants. These interesting results provide the possibility of tuning the bandgap of graphene as required and therefore extend its application in electronic devices.

Keywords: Graphene; Graphene derivatives; DFT; Electronic properties; Band gap energy; Density of states.

1. Introduction

Graphene is the name given to a single layer of graphite where three of the valence electrons of carbon atoms are used [1, 2]. It has a two-dimensional crystalline structure and is densely packed in a regular sp2-bonded atomic-scale hexagonal pattern in graphene. Based on the literature, it's explicit that, graphene and other structures which are two dimensional in nature (2D), has recently been recognized as potentially very important materials for multiple applications in optoelectronics, chemical sensing, battery fabrication, supercapacitor, and transparent semiconductor production [3–5]. Graphene has been an extremely focused-upon topic since the start of the pioneering work on the synthesis of this unique two-dimensional material by Geim, Novoselov, and co-workers [6, 7].

Graphene has important properties including high-strength, light weight, and an excellent conductivity of both heat and electricity. The band gap energy of pure graphene was found to be zero, (as a result of the electrons in their transitions between the highest of the valence band and the bottom of the conduction band meet at the Dirac points at the Fermi level). Moreover, the development of graphene-based electronics is based mainly on our ability to open a tunable band gap [8]. The determination of the electronic band structures of graphene and therefore the effects of dopant atoms on the electronic band structures are examined in numerous studies [9-15].

Some studies show that doping graphene with different atoms element such as Boron, Nitrogen, Sulphur, Phosphorus, and Gold change the electronic and optical properties to become more useful in

*Corresponding author e-mail: elham.atef@women.asu.edu.eg.; (Elham A. Mohamed).
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optoelectronic devices applications compared to pure graphene [12-15].Another study also shows that the opening band gap of graphene doped with Gallium, Germanium, Arsenic, and Selenium Atoms, varied from 0.3 to 1.3 eV [16]. Opening the band gap into the strip structure of the 2D sheet is possible by cutting the graphene into thin ribbons [17, 18].

This study deals with the effects on the electronic properties of doping graphene with Al and N by increasing the concentration of the individual dopants. Doping graphene with Al makes it a p-type semiconductor whereas, with N doping it becomes an n-type semiconductor [19, 20]. It has been established through an experiment upon the doping of graphene [8], the Dirac point in the band structure of graphene shifts below the Fermi level, and an energy gap appears at high symmetric K-point.

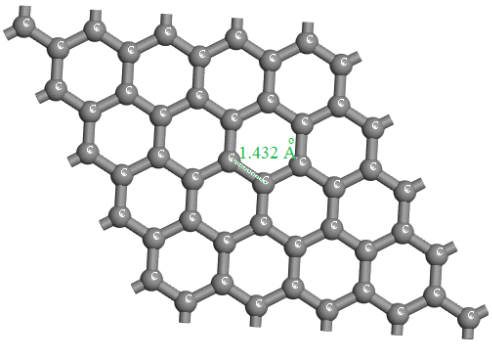
2. Computational Methods

In this work, we conducted a first principle investigation on the band structure properties and density of states of graphene sheet that are uniformly doped by various dopants including nitrogen and aluminum atoms. We unveiled that a doped graphene remains gapless at the Dirac point, which is dependent on the density of the dopant atoms. The electronic structure and density of state calculations were carried out using Burai software code[21] which is a remarkable Graphical User Interface (GUI) system for Quantum Espresso code [22] implemented of first-principle density functional theory (DFT), within the generalized gradient approximation (GGA) [23], for the exchange correlation energy of electrons. In the DFT method, we used Ultra-Soft- Pseudo potential of the nuclei and core electrons of atoms. The energy cutoff of the plane wave basis set was 350 eV, which has been tested to give the best-converged results for all properties studied in this work.

A vacuum slab higher than 15 Å was used between the graphene layers to avoid layers interactions. The convergence tolerance for the various structure geometry optimization calculations was set to the maximum values of displacement 0.002 A, energy change 2.0×10-5 eV/atom, and the maximum force on every atom lower than 0.001 eV/A. A 6×6×1 group point centered Monkhorst-Pack grid was used in the first Brillion Zone for the calculations of band structure density of states (DOS) to calculate the symmetric path of Γ-K-M-Γ. In our model, the 5×5×1 graphene supercell has been used (Figure 1). For this supercell, lattice parameters are a = b = 12.3 Å, γ =120◦, and C-C bonds length is 1.42Å.

Fig. 1. Optimized geometry supercell 5×5x1 for pure graphene.

3. Results and Discussions



Most of our calculations were done based on Burai software code which is a GUI for Quantum Espresso code. If the objective is to complete a calculation of band structure that is accomplished by calculating an integral over the crystal Brillion zone. Quantum Espresso does the numerical integration in an earlier step, so the main requirements are election of the points desired for plotting. The Brillion zone of graphene is a two-dimensional hexagon. In which a perfect one is known to be semi-metallic, where the Fermi level is aligned with the Dirac point and there is no free electron in the conduction band at zero Kelvin [24].

The electronic band structure and density of states (DOS) for pure graphene sheet is presented in figure 2. As we see in this figure, the conduction band and valence band intersect with each other at the Fermi level at zero band gap which is consistent with other researches [25, 26]. Unlike the conventional two-dimensional semiconductor with a parabolic linear dispersion relation at the bottom of the conduction band and the top of the valence band, graphene shows a good linear dispersion relation near the Dirac point.

Subsequently, pure graphene is doped with Al and N atoms with a concentration of 2%, 4%, 6%, 8%, 10%, and 12%. The Optimized geometry calculations of Al and N doped graphene are shown in figure 3 for concentration 2%. After geometry optimization, the bond lengths belong to Al -C and N -C atoms are equal to 1.710 Å and 1.414 Å, respectively.

For Al doping graphene, the bond lengths of Al-C are larger than those of C-C for pure graphene. It can be due to the larger covalent radius of the Al atom (1.21 Å) than that of C atom (0.73 Å). This large radius of Al leads to ~~an~~ increase of the bond length of Al-C and ~~the~~ decrease of bond lengths of C-C next to the Al-C bond.

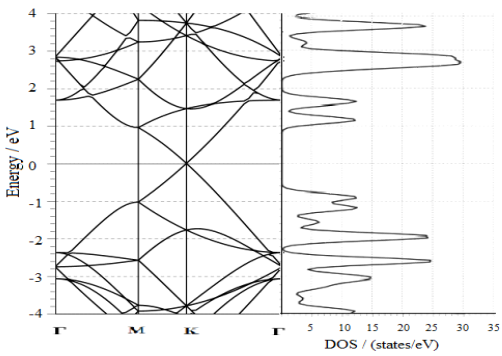


Fig. 2. The electronic band structure and DOS for pure graphene sheet.

The bond lengths of N-C are close to those of C-C bonds for pure graphene, in an experimental work. Zheng et al. [27] demonstrate that the N-C bond length is 1.41 Å where this result is align with our work, which can be due to the similar covalent radii of a carbon atom and nitrogen atom (0.71 Å).

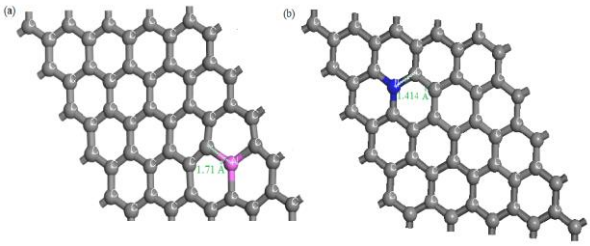


Fig. 3. Optimized geometry for (a) single Al atom doped graphene and (b) single N atom doped graphene.

Using the computational procedure as mentioned above, the electronic properties, especially the band structure and DOS, could be calculated. Figure 4 shows the band structures of graphene doped with Al with the previous doping concentrations. In the presence of Al dopant, the fermi level is lowered to its valence band which is attributed to the fact that the Al atom has one electron less than a C atom and hence acts as a p-type doping. This result is consistent with previous theoretical results and experimental works [12–15, 27]. Fermi level shifts significantly by about 0.8 eV below the Dirac point resulting into a p-type doping. This changes the behavior of graphene. When a graphene sheet is doped with one Al atom, the Al atom undergoes sp2 hybridization.

The doping of Al in the graphene leads to an opening gap. The increasing of doping percentage increases the existing energy difference between the valence band and the conduction band. We obtained the band gap ranging from 0.233eV to 0.969eV, a significant gap value was mentioned for 12%; this is due to a charge transfer between the p orbital of Al and carbon.

The Total density of state (DOS) and the projected density (PDOS) of states for both carbon and Aluminum curves of graphene doped with Al for various concentrations are given in figure 5. The analysis from the DOS closing to the Fermi level could give consistent results with the band structures as shown in figure 4. As a result of the electron disfiguring defacing in the Al in compassion to C atom, the Fermi level of Al-doped graphene moves below the Dirac point showing a p-type semiconductor. This indicates that doping Al atom induces acceptor states in graphene, thus enhancing its extrinsic conductivity.

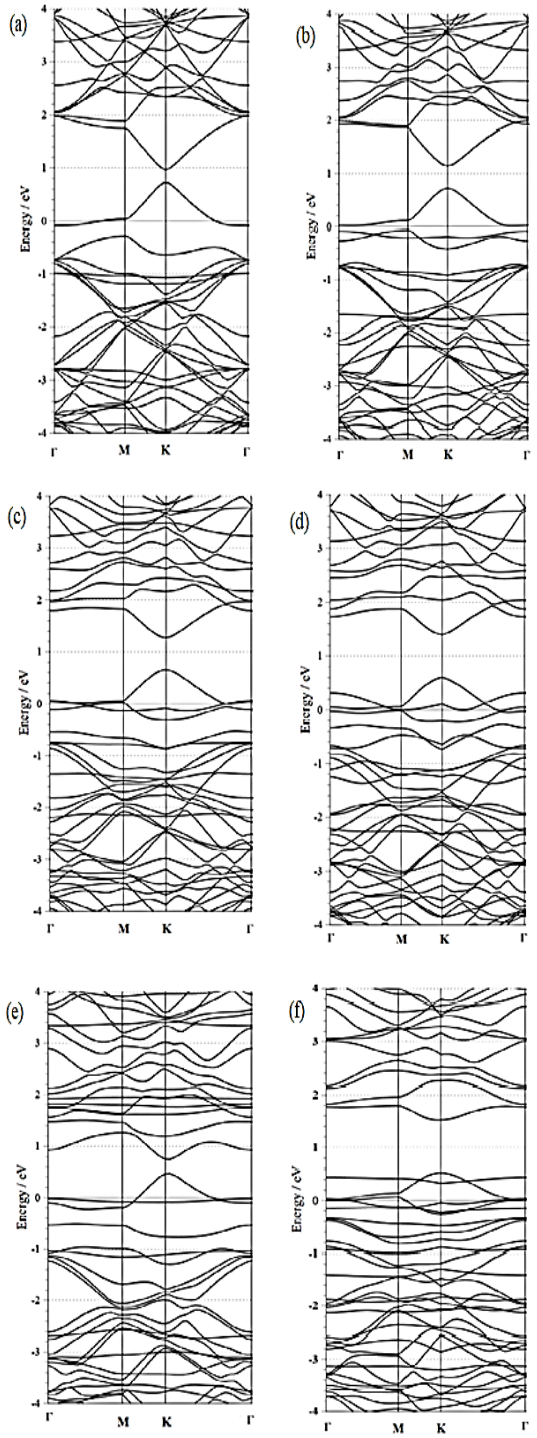


Fig. 4. Band structure of Al doped graphene for various concentrations (a) 2%, (b) 4%, (c) 6%, (d) 8%, (e) 10% and (f) 12%

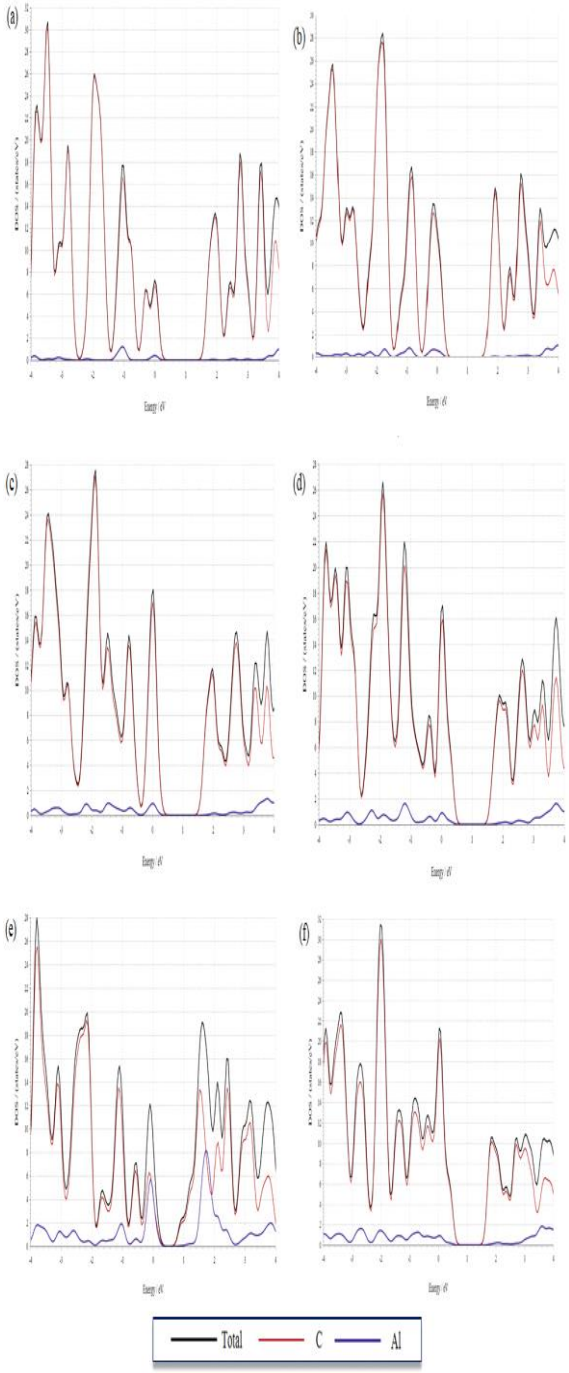


Fig. 5. Density of state of Al doped graphene for various concentrations (a) 2%, (b) 4%, (c) 6%, (d) 8%, (e) 10% and (f) 12%

The electronic structure analysis shows an increase of band gap with concentration of Al doping. Figure 6 summarized the variation of band gap with concentration of Al in our model system.

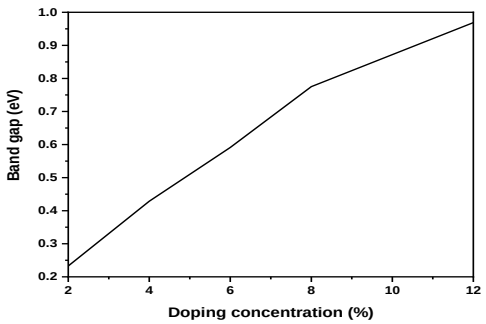


Fig. 6. Band gap in increasing order of doping concentrations for Al doped graphene

On contrary to introducing the Al atoms, N atoms make the graphene sheet behaves like n-type semiconductors; this is because Nitrogen atom has one electron more than a carbon atom. We present in figure 7 and figure 8 the electronic band structure and density of states respectively obtained by various N doped atoms. The structural properties of N-doped graphene geometries do not show any remarkable change due to the close size of the covalent radius of carbon and nitrogen atoms. As shown in figure 8, the Fermi level of our model system moves above the Dirac point in pure graphene display that N-doped graphene behaves as an n-type semiconductor.

The Total density of state (Dos) and the projected density (PDOS) of states for both carbon and nitrogen curves of graphene doped with N for various concentrations are displayed in figure 8. Comparing the band structure and the density of states of different concentrations of N doped graphene disclose that the band gap of graphene is opened after the N atoms were doped.

The analysis from the DOS closing to the Fermi level could give consistent results with the band structures shown in figure 7. We would like to report that both the doped models investigated in this work are heavily doped. Therefore, the Fermi level crosses the valence band in the case of the Al-graphene model system in figures (4, 5) and the conduction band in case of N-graphene model system in figures (7, 8). The position of the Fermi level shows that these system models exhibit metallicity.

The energy gaps of different concentrations of (a) 2%, (b) 4%, (c) 6%, (d) 8%, (e) 10% and (f) 12% are 0.11305, 0.22937, 0.39154, 0.42293, 0.5174 and 0.57505 respectively propose that higher the Al doping concentrations the higher band gap. A plot of variation of band gap with doping concentration presented in figure 9.

The present computational work indicated that modeling graphene is an important step toward functionality and possible applications of graphene. This finding is in good agreement with those obtained earlier [28-30]

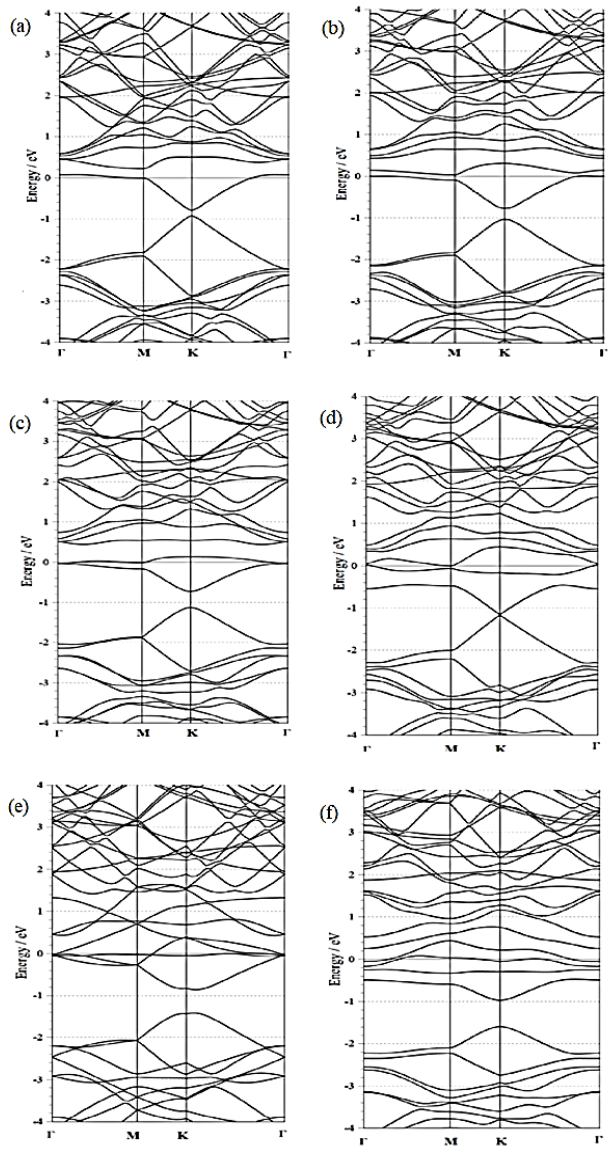


Fig. 7. Band structure of N doped graphene for various concentrations of (a) 2%, (b) 4%, (c) 6%, (d) 8%, (e) 10% and (f) 12%

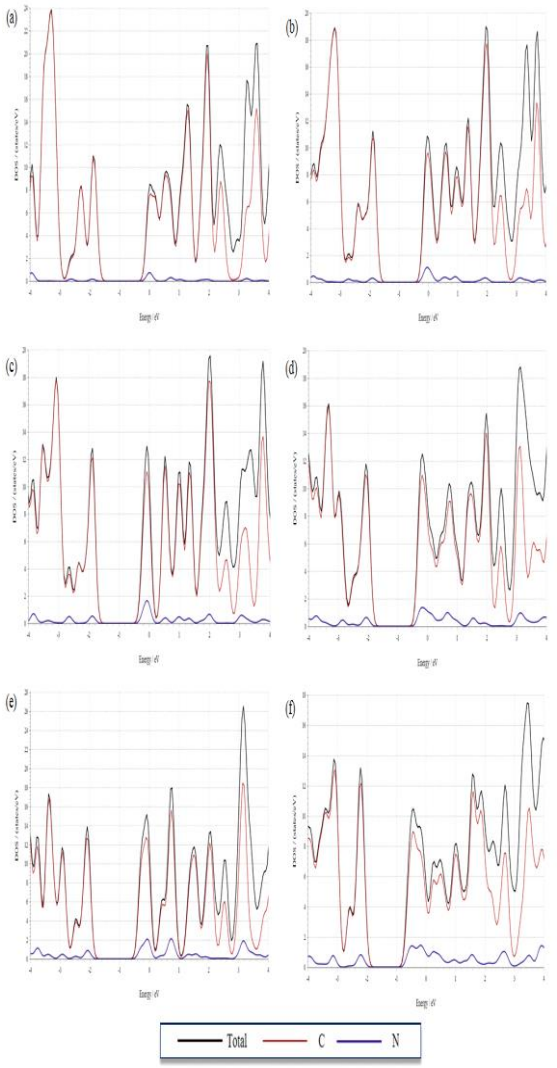


Fig. 8. Density of state of N doped graphene for various concentrations of (a) 2%, (b) 4%, (c) 6%, (d) 8%, (e) 10% and (f) 12%

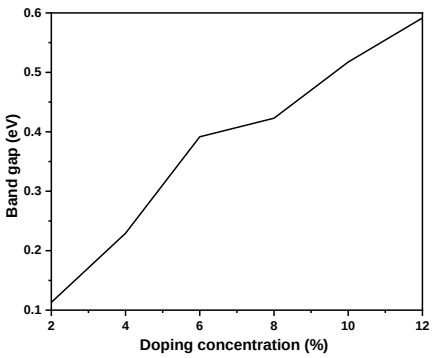


Fig. 9. Band gap in increasing order of doping concentrations for N doped graphene

4. Conclusions

This study investigates the effect of doping Al and N on the electronic properties of graphene-based on the structure optimization calculations by using DFT theory. The effect of doping was studied by varying concentrations of dopants from 2 % (one dopant atom) to 12 % (six dopant atoms). Al and N doping induced p-type and n-type semiconductors respectively in the graphene sheet. We observe the transition of graphene from semimetal to semiconductor with an increasing number of dopants. These exciting results provide the possibility of designing the band gap of graphene as desired allowing application in a wide range of electronic devices.

5. References

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Arabic abstract

تم إجراء التحسينات البلورية وحسابات البنية الإلكترونية للجرافين المطعم بذرتي الألومنيوم (**Al**) والنيتروجين (**N**). تم فحص تأثير التطعيمات عن طريق تغيير تركيز االتطعيمات من 2٪ (ذرة واحدة من المطعم في 50 ذرة من الجرافين) إلى 12٪ (ست ذرات من المطعم في 50 ذرة من الجرافين). تم إجراء جميع الحسابات باستخدام كود **BURAI** الذي استخدم **Quantum Espresso** وتستند إلى نظرية وظيفية الكثافة والموجات المستوية والإمكانات الزائفة. باضافه ذرتي **Al** و **N** ، يتم انتاج اشباه موصلات من النوع **p** والنوع **n** على التوالي في شريحه الجرافين. أوضحت النتائج أن الهيكل المستوي لشريحه الجرافين لم يتأثر بالتطعيمات. ومع ذلك ، تم تغيير الخصائص الإلكترونية من شبه معدن إلى شبه موصل مع زيادة عدد الذرات المطعمه .توفر هذه النتائج المثيرة للاهتمام إمكانية ضبط فجوة الطاقه من الجرافين كما هو مطلوب وتطبيقه في الأجهزة الإلكترونية.