Effect of Boron and Oxygen Doping to Graphene Band Structure

Siti Fazlina bt Fauzi* and Syarifah Norfaezah bt Sabki

School of Microelectronic Engineering, Universiti Malaysia Perlis (UniMAP), Kampus Pauh Putra, 02600 Arau, Perlis

ABSTRACT

Graphene band structure can be modulated when dopant atoms are introduced into graphene sheets. As a result, there is flexibility in design and optimisation of electronic devices. In this study, the effects of atomic doping to graphene band structure were investigated by using boron and oxygen as dopant atoms. Different dopant concentrations and dopant locations in graphene sub lattices were studied by using a 4x4 graphene sub lattice which consists of 32 carbon atoms. Results show that both dopants cause opening of energy band gap of mono layer graphene. The highest energy band gap (Eg) value for graphene doped with boron is 0.52 eV and the highest Eg value for graphene doped with oxygen is 1.67 eV, in which both results are obtained for highest dopant concentration and farthest dopant's distance in a graphene sheet. This shows that higher dopant concentration and farther dopant's location in a graphene sheet lead to higher energy band gap.

Keywords: Graphene, band structure, band gap, boron, oxygen, atomic doping

INTRODUCTION

Graphene is a carbon allotrope arranged in a honeycomb lattice with an atomically thin layer. It has attracted interest among researchers due to its excellent physics properties as well as its electrical and mechanical properties. Due to this, a lot of new applications have been explored using graphene, especially as an alternative to replace silicon based transistor. However, monolayer graphene is a zero bandgap material, which means the conduction band and the valence band of graphene meet at one point. It is known that band gap is the difference of energy between the lowest point of conduction band and the highest point of valence band. Band gap also refers to the amount of energy needed to excite the electron in the valence to the conduction band so that electricity can be conducted. Due to that, a band gap is needed in a respective

value so that there will be a clear state where the device can be turned on and off. Therefore, a lot of measures have been taken in order to open a band gap in graphene. For instance, there are studies that had been carried out by applying electric field to bilayer graphene which have resulted in band gap due to the breaking of inversion symmetry between two layers (McCann, 2006; Castro et al., 2007, Oostinga et al., 2008). However, this method reduced the mobility carrier of graphene (Oostinga et al., 2008), in which high mobility carrier can only be obtained in monolayer graphene. Carrier mobility is often observed in determining performance of devices. Maintaining high carrier mobility in monolayer graphene as well as creating a band gap are crucial. Few methods that have been carried to open a band gap in monolayer graphene. Modifying the edge structures such as quantum dots /antidotes (Fujita et al., 1996, Nakada et al., 1996, Son et al., 2006) and nano ribbons (Singh et al., 2010; Fü¨rst et al., 2009) have shown that band gap can be opened in monolayer graphene. However, tuning the band gap magnitude by using this method is difficult due to the complexity in controlling the edge structure (Takahashi et al., 2014). Another method that has been proposed to open a band gap in monolayer graphene is by applying uniaxial strain to the graphene sheet (Ni et al., 2008, 2009). However, this method requires a very strong strain in order to open a band gap in monolayer graphene. Doping graphene sheets with heteroatoms (Denis et al., 2009, Dai et al, 2009) is found to be better in creating band gap in monolayer graphene whilst maintaining its high carrier mobility and with better control.

This paper examines the effect of boron and oxygen doping in graphene band structure. Both atoms are known to have the ability to increase the energy band-gap of graphene, Boron is recognised as a P-type dopant when it is included in graphene (Rani et al., 2013) and oxygen is chosen as the dopant due to its atom size which is quite similar to the size of carbon atom and the ability of its valence electrons to make bonds with carbon atoms. In this paper, boron and oxygen atoms are introduced in monolayer graphene sheets in graphene band structure.
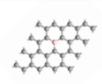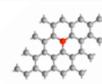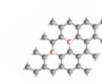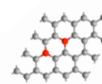
METHODOLOGY

The simulation has been performed using the Atomistix Tool Kit (ATK) simulator by Quantumwise. The band structure of the monolayer graphene sheet is calculated using the semi-empirical Huckel (SE Huckel) calculator. The SE Huckel is able to calculate the band structure of doped graphene faster than the density functional theories (DFT) calculator because it uses simpler models. However, the results from the SE Huckel are similar to the results obtained from DFT calculator.

To perform the simulation, initially, a graphene sheet of 4 x 4 lattices with 32 carbon atoms is made. Boron and oxygen atoms 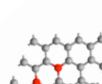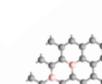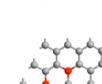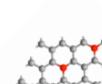in the graphene sheet are added in different concentrations. The dopant atoms are inserted in the graphene sub lattices in 1, 2 and 3 atoms, which provide 3%, 6% and 9% dopant concentration respectively. The dopant atoms are also arranged in such a way that they are in the same and different sub lattices.

As shown in Table 1, boron atom in the same graphene sub lattice is labelled B1. Boron atoms in different sub lattices are divided into two different positions, which are represented by boron in sub lattice 2 and 3, labelled as B2 and B3 respectively. The same position and

concentration arrangement are also applied for oxygen atoms, and labelled as O1, O2 and O3. The dopant atoms in sub lattice 2 involves the inclusion of dopant atoms in two neighbouring sub lattices, while the dopant atoms in sub lattice 3 separates the dopant atoms in the farthest distance. The dopant atoms arrangement in the graphene sheet is shown in Table 1 below.

Table 1
Structure of monolayer graphene doped with boron (B) and oxygen (O) atoms at different concentrations and different locations

Dopant concentration	Boron in same sub lattice (B1)	Oxygen in same sub lattice (O1)	Boron in different sub lattice 1 (B2)	Oxygen in different sub lattice 1 (O2)	Boron in different sub lattice 2 (B3)	Oxygen in different sub lattice 2 (O3)
3 %						
6 %						
9 %						

RESULTS AND DISCUSSION

Monolayer graphene doped with boron

The inclusion of boron in the graphene sheet changes the properties of graphene into p-type. This is due to the lower number of electron valence in boron compared with carbon that results in the Fermi level of graphene shifting below the Dirac point (or also known as K point). With the Fermi level, the band gap opening is also expected to occur with the inclusion of boron in graphene. As shown in Figure1 for graphene doped with boron in the same sub lattice (B1) (refer Table 1), the opening of band gap is observed for all 3 different concentrations, with energy gap of 0.16 eV for 3%, 0.21 eV for 6% and 0.37 eV for 9% boron concentration. The linear increment of this energy gap is in agreement with previous studies (see for example, Rani et al., 2013); however, it is slightly different in terms of value. It is suggested that this band gap opening at the K point of monolayer graphene with the inclusion of boron atoms is caused by the broken symmetrical hexagonal structure in the graphene sub lattices (Rani et al., 2013).
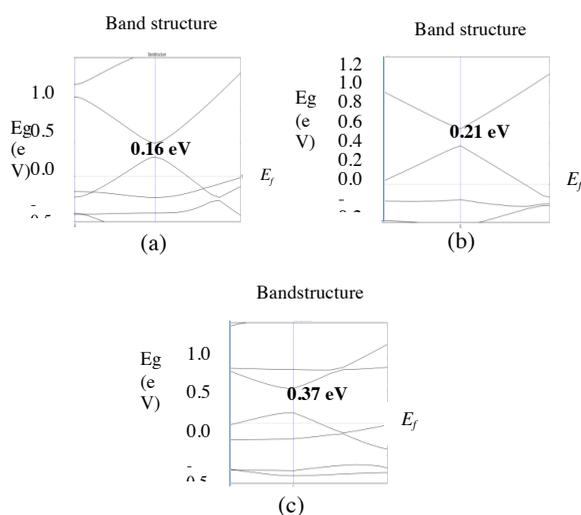
Figure 1. Band structures of graphene doped with boron in the same sub lattice (B1). The boron concentrations are at (a) 3 %, (b) 6% and (c) 9%

The effect of dopant atoms at different graphene sub lattice 1 (B2) is shown in Table) at the same concentration of boron at 6% and 9%. Boron concentration of 6% produces 0.38 eV energy bandgap and 9% produces 0.5 eV energy bandgap, which are higher than energy gap shown in Figure 1. This shows that different locations of boron atoms in the graphene sub lattices plays an important role in altering the graphene band gap at K point. This may happen due to the symmetry in the triangular sub-lattices of graphene formed by the hetero-atoms.

For boron doped in different sub lattice 2 (B3), the energy band structures are shown in Figure 3(a). The energy band gap for 6 % of boron concentration gives the highest value of 0.40 eV compared to 6% boron concentration doped in the same sub lattices (B1) and in different sub lattice 1 (B2). This shows that the distance between each boron atom affects the value of energy bandgap. This result is consistent with the findings of Rani et al. (2013). The same trend is also observed for 9 % of boron concentration doped in different sub lattice 2 (B3) with energy band gap of 0.52 eV, which is also the highest value compared with the 9% boron concentration doped in same sub lattice (B1) and in different sub lattice 1 (B2). The band structures for graphene doped with boron atoms caused the Fermi level to be lower than the top of valence band. This could be because the boron atom has 3 valence electrons, which introduces more holes in the valence band than electrons in the conduction band. The Fermi level shows the probability of holes to occupy lower energy levels in the valence band. The complete results for energy bandgap of boron doped graphene are shown in Table 2.
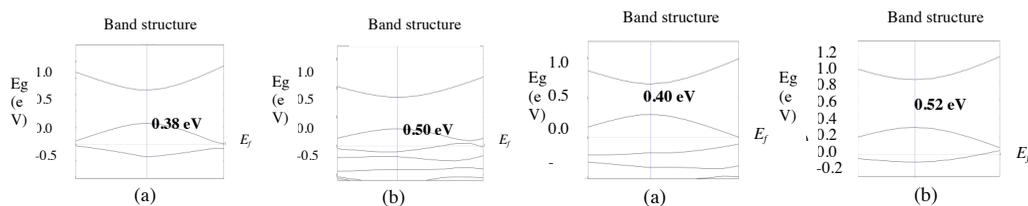
Figure 2. Band structures of graphene doped with boron in different sub lattice 1 (B2). The boron concentrations are at (a) 6% and (b) 9%

Figure 3. Band structures of graphene doped with boron in different sub lattice 2 (B3). The boron concentrations are at (a) 6% and (b) 9%

Monolayer graphene doped with oxygen

As shown in Figure 3 for graphene doped with oxygen in the same sub lattice (O1) (Refer Table 1), the opening of band gap is observed for all three different concentrations, with energy gap of 0.40 eV for 3%, 0.50 eV respectively for 6% and 0.63 eV for 9% boron concentration. The linear increment of this energy gap is also consistent with findings of previous study (Rani et al., 2013) though it is slightly different in the value. The energy gaps for graphene doped with oxygen atoms are larger compared with graphene doped with boron atoms. This may be suggested by the excitation energy for electrons in oxygen that is higher than boron. The number of valence electrons in oxygen and boron also may give rise to this effect. As mentioned earlier, this band gap opening at the K point of monolayer graphene with the inclusion of oxygen atoms is also caused by the broken symmetrical hexagonal structure in the graphene sub lattices (Rani et al., 2013).

For dopant atoms at different graphene sub lattice 1 (O2) (refer Table 1) in Figure 4, boron concentration of 6% produces 0.67 eV energy band gap and 9% produces 0.71 eV energy band gap, which are higher than energy gaps obtained in Figure 4 and also higher than energy gaps for graphene doped with boron as in Figure 2.

For boron doped in different sub lattice 2 (O3) (refer Table 1), the energy band structures are shown in Figure 5. The energy band gap for 6% of oxygen concentration gives the value of 0.93 eV which is higher than 6% oxygen doped in the same sub lattices (O1) and in different sub lattice 1 (O2). The same trend is also observed for 9% of oxygen concentration doped in different sub lattice 2 (O3) with energy band gap of 1.67 eV, which is also higher than 9% oxygen doped in the same sub lattice (O1) and in different sub lattice 1 (O2). The band structures for graphene doped with oxygen atoms caused Fermi level to be higher than the minimum level of conduction band. This happens due to the 6 valence electrons in oxygen that introduce higher number or electrons in the conduction band. The Fermi level shows the probability for electrons to occupy higher levels in the conduction band. The complete results for energy band gap of graphene doped with oxygen are shown in Table 2.
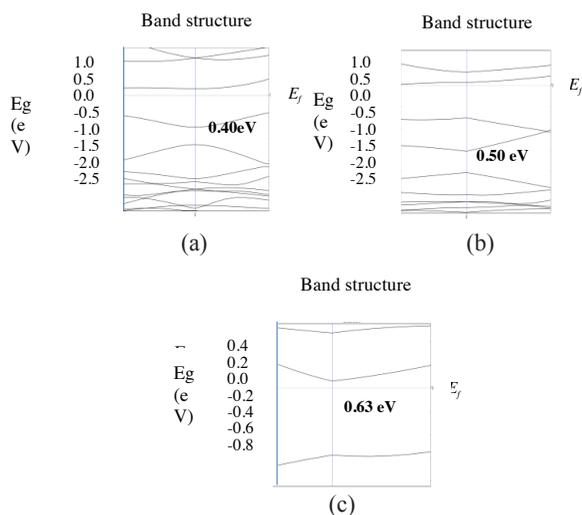
Figure 4. Band structure for graphene doped with oxygen in the same sub lattice (O1). The oxygen concentrations are at (a) 3 %, (b) 6% and (c) 9%
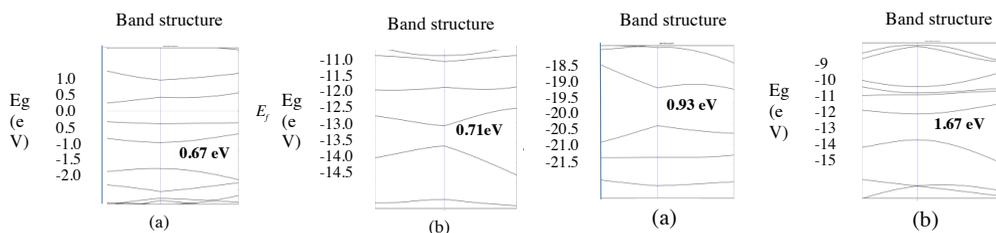

Figure 5. Band structures for graphene doped with oxygen in different sub lattice 1 (O2). The oxygen concentrations are at (a) 6% and (b) 9%
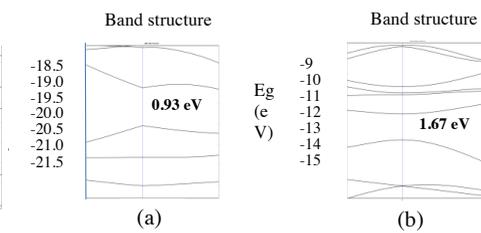
Figure 6. Band structures for graphene doped with oxygen in different sub lattice 2 (O3). The oxygen concentrations are at (a) 6% and (b) 9%

Table 2

Energy band gap for monolayer graphene doped with boron (B) and oxygen (O) at different dopant concentrations and different locations

Dopant concentration [%]	B1	O1	B2	O2	B3	O3
	[Electron Volt - eV]					
3 %	0.16	0.40	0.21	0.40	0.21	0.40
6 %	0.21	0.50	0.38	0.67	0.40	0.93
9 %	0.37	0.63	0.50	0.71	0.52	1.67

CONCLUSION

The band structure of graphene doped with boron and oxygen atoms are investigated and the energy band gaps of graphene are observed. For graphene doped with boron atoms, the Fermi

level is lower than the top of the valence band, which suggests that there is a probability that majority of holes are occupying the valence band. For graphene doped with oxygen, the Fermi level is higher than the bottom of the conduction band, which suggests that there is a probability that majority of electrons are occupying the conduction band. This suggests the mobility carriers (electrons) in graphene doped with oxygen is higher than graphene doped with boron. It was also observed that higher dopant concentration contributes to larger energy band-gap. The location of dopant atom in a graphene sheet also affect the energy band-gap, whereas the farther the distance between dopant atoms the higher the energy gap. This work shows that graphene band gap is tunable and can be easily controlled using dopant atoms. This tunable band gap is crucial for the design and optimisation of high performance electronic devices.

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