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Investigation into Carbon Vacancies‘ Effects on The Band Gap of Single-Layer Graphene

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Abstract:

Since its first manufacture in 2010, Graphene has been a prevailing supermaterial, being considered to be promising in electrical engineering due to its high carrier mobility and great mechanical strength. However, Graphene lacks a band gap in its band structure, which is a determinant factor for semiconductors. This essay will aim to explore the possibility of harnessing structural defects, specifically carbon vacancies, to engineer the band structure of Graphene and thus create a band gap in single-layer graphene. The investigation will be conducted using Material Studio and the CASTEP module. Up to five carbon vacancies are to be created in a single-layer energy-minimised graphene structure and the electric structure will be calculated using density functional analysis (DFT). The information on the band gap will be extracted and displayed against the number of carbon vacancies. The result has shown the possibility of using carbon vacancies to engineer controllable band gaps from 0eV to 0.63eV in single-layer graphene. This has granted insight into the graphene engineering and semiconductor industry.

Keywords: Graphene, Electric Engineering, Band gap, DOS, Carbon Defect

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1. Introduction

As semiconductor was proposed in 1833, by Micheal Faraday, who‘s an electric engineer and physicist, it has gone through rapid development. Materials of the n and p-type semiconductors have been Silicon since 1954 [1]. Silicon is a tetravalent metalloid semiconductor. It has been widely used till today, however, some of its limitations have been revealed, one of them being its relatively low carrier mobility (σ), which limits the Silicon Metal-oxide-semiconductor Field-effect transistor’s (MOSFET) computational power [2].

Graphene, as a super material first made in the lab in 2010 by Hans Peter Boehm, has been one of the alternative materials of Silicon in electric devices. Electrons move faster in graphene than in Silicon, and therefore more information can be passed on. In this way, high carrier mobility grants a graphene MOSFET roughly 300 times greater computation power than a traditional silicon MOSFET [3]

However, according to the research on the electric properties of graphene, it also has a few drawbacks, which will be discussed below. The purpose of this essay is to investigate the possibility of using a type of intrinsic carbon defect - carbon vacancies - to engineer single-layer graphene's electric properties. The control of graphene's certain electric properties can suggest novel electronic and photonic applications based on graphene [4].

2. Investigation into carbon vacancies, band gap, and DOS

2.1 Graphene and Semiconductor

First of all, graphene will be introduced. Graphene is a 2D material that appears to be a single layer of carbon arranged in a hexagonal $P6_3/mmc$ lattice [5]. Each carbon atom in graphene bonds three nearest-neighbour carbon atoms with sp^2 the hybridisation of $2s, 2p_x, andsp_y$ orbitals, and $2p_z$ orbital forms delocalised π and π^* bands perpendicular to the graphene plane. The π and π^* bands cross the Dirac point.

That grants graphene unique physicochemical properties like high surface area, good biocompatibility, strong mechanical strength, excellent thermal conductivity, and fast electron transportation.

To be implemented into electric devices, the material needs to meet several properties. As mentioned in the introduction, carrier mobility σ characterizes how quickly an electron can move through a metal or semiconductor when pushed or pulled by an electric field. Graphene has a carrier mobility of around 256,000 cm2/Vs, which is much higher than other materials, for example, Silicon's 1000 cm2/Vs. Fast electron transportation in graphene has made it a viable choice to build super semiconductors at extremely high speed. It is estimated that the semiconductor transistor made from graphene may have around 300 times greater computational power [6, 7].

Besides, the structure of graphene makes it very suitable for electric applications. The conventional structure of single-layer graphene is shown in Figure 1, modelled by the author. Graphene's hexagonal lattice structure grants its great mechanical stability and thermal stability. Therefore, it is expected that graphene can sustain high temperatures up to 1000K, which is much higher than Silicon's 500K. A more stable structure enables graphene-made devices to operate in more extreme environments.

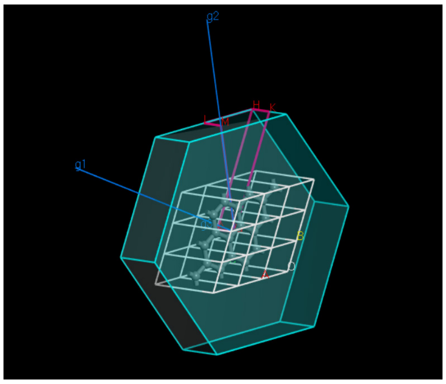

Figure 1. Conventional Graphene Structure [7]

However, research on graphene has revealed a disadvantage of graphene, which is graphene's zero band gap. The zero-band gap shows that graphene is a conductor instead of a semiconductor. The zero-band gap does not support the switching operation of graphene-based transistors with a sufficiently high on-off ratio, thus, pristine graphene cannot be used in electronic devices. Therefore, creating a band gap in graphene is a must. So far, there are mainly two methods to create a band gap: cutting out graphene nanoribbons or constructing bilayer graphene. The graphene nanoribbons are at a width of 16 to 320 nm, and then the band gap is created due to edge effects [8]. However, the engineering process is very costly due to the nano-scale cutting process. Bilayer graphene is another approach to engineering the electric properties of graphene. It has been found that when a displacement field D is applied, a band gap can be created. Nevertheless, it is also found that it's hard to apply a very precise displacement field is hard, and thus this approach is not very consistent. Thus, a new methodology needs to be investigated so that graphene can be engineered to be a useful semiconductor.

2.2 Band structure and electric properties of materials and fermi level

The energy band theory, namely the E-k dispersion theory, by Felix Bloch in 1928 can help indicate the electric properties of the material. It is proposed that within a crystal structure, electrons can interact with each other, thus causing changes in their energy levels, a group of possible energy levels will converge and cover a range of energy, forming energy bands [9].

When valence electrons' energy levels change, they also form a series of energy levels, namely an energy band, given the name of the valence band. The valence band contains the highest energy levels that the valence electrons can occupy. Furthermore, at higher energy levels than the valence band, there will sometimes be a forbidden band, where electrons are not able to take any energy levels within this range. The range of the forbidden band is the band gap. At even higher energy levels, there is the conduction band, which is another collection of energy levels that electrons can obtain. Electrons move from the valence band into the conduction band when the atom is excited [10].

The band gap in band structure is an important indicator, as it measures how much energy is needed to move an electron from the highest energy level in the valence band to the lowest energy level in the conduction band, namely how easy to conduct through the material. Materials are categorized based on the width of the band gap into insulators, semiconductors, and conductors. As mentioned above, the proper band structure of a semiconductor is usually between 0.5eV and 2.0 eV, and graphene's zero band gap doesn't fall into this range. The band gap will be taken as the variable in the following investigation.

2.3 Carbon Defects

Despite the verified approaches of carbon nanoribbons and bilayer graphene, engineering intrinsic carbon defects in single-layer graphene may successfully create a band gap in Graphene's electric structure. Intrinsic carbon defects refer to anomalous arrangements of crystal structures in nodes or adjacent microscopic regions. Intrinsic carbon defects include lattice distortion (topological defect), sp3 hybrid carbon defects (edge defects), and most commonly, carbon vacancy defects [11].

Based on research, it is believed that creating carbon vacancies can alter the uniform charge distribution of graphene surfaces and result in modifying the electronic structure and magnetic properties of graphene systems. A single vacancy (SV) defect is generated by a missing carbon atom. A multiple vacancy (MV) defect is the coalescence of multiple missing carbon atoms [12].

When a few atoms are missing in a periodic structure, the electric field inside the structure will be no longer uniform, and hence induces a difference in the potential of electrons when the electrons are in different regions. It has been investigated by Florian Banhart et al. that carbon vacancies give rise to localized states near the Fermi energy in sp2-bonded materials, "leading to the protrusions that appear in STM images, opening a local bandgap (up to 0.3 eV) in graphene." It is also found that significant band gaps are created in graphene with a single D_{3h} carbon vacancy [13, 14].

The following deduction tries to theoretically explain why electrons tend to form different energy bands when there are carbon vacancies. The potential as seen by an electron is defined to be,

$$V(x) = \sum_p V_p * e^{i*x*\frac{2*\pi*p}{a}} \tag{1}$$

$$V_p = \frac{1}{a}\int_0^a V(x) * e^{i*x*\frac{2*\pi*p}{a}} dx \tag{2}$$

Where, $V(x)$: The crystal potential function of a single electron. V_p: The Fourier Coefficient. a: Atomic spacing, specifically, the distance from the nucleus of carbon to the neighboring another's. In m. p: An integer.

After defining the potentials seen by an electron, Bloch function can be used to represent the influence of the crystal potential [9].

$$u(x) = \sum_n C_n e^{iG_n x} \tag{3}$$

Where, n: 0, ±1, ±2 …, G_n: $\frac{2\pi n}{a}$.

In the general form of the Schrodinger equation, the terms of $V(x)$ and $\psi(x)$ can be substituted by the $V(x)$ and $u(x)$ deducted here [9].

$$i\hbar\frac{\partial}{\partial t}\psi(x) = -\frac{\hbar^2}{2m}\nabla^2\psi(x) + V(x)\psi(x) \tag{4}$$

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi\sum_n C_n e^{(i(k+G_n)x)} &= -\frac{\hbar^2}{2m}n^2\sum_n C_n e^{(i(k+G_n)x)} \\ &+ \sum_p V_p * e^{i*x*\frac{2*\pi*p}{a}} * \sum_n C_n e^{(i(k+G_n)x)} \end{aligned} \tag{5}$$

Where, i: Imaginary number. $\hbar$: Reduced Planck's Constant. m: Mass of the particle. ∇^2: Laplacian operator. k: Space vector.

By solving this Schrodinger Equation for the value of C_n, a relationship equating E and k can be found out. In this way, E-k dispersion can be calculated. When the carbon vacancies are created in the structure, the atomic spacing will change for some potential regions, therefore, the coefficient of G_n will change. The solutions for the Schrodinger equation will change and thus the E-k dispersion will be altered.

2.4 Calculation using first principal methods

To investigate the effects of carbon vacancies on the band gap and DOS of single-layer graphene, Modelling and simulations of single-layer graphene are carried out via first principal methods, specifically, the program of CASTEP developed by Cambridge. The number of carbon vacancies in the graphene sheet will be modified in the range of 0-5, at the same time, the energy structure will be tested out by the simulation program. Analysis will then be performed to determine the band gap and DOS at the fermi level of the material. In this way, the relationship between the band gap and DOS of the graphene sheet and the carbon vacancies in the structure will be investigated [15, 16].

In the meantime, several parameters of the simulation will be controlled, including functional selection, spin polarisation, metal, energy cutoff, SCF tolerance, relativistic treatment, and pseudopotential. They will be presented in a table later.

A structure of single-layer graphene is set up in Material Studio Visualiser. The parameter has been set to be the dimension of a standard graphene: a:2.47 Å, b:2.47 Å, c:7.80 Å; α:90.00 º, β:90.00 º, ɣ:120.00 º. The intact graphene structure is present in Figure 2, using a supercell expansion of dimension: X :*4 units, Y :*4 units, Z :*1 unit.

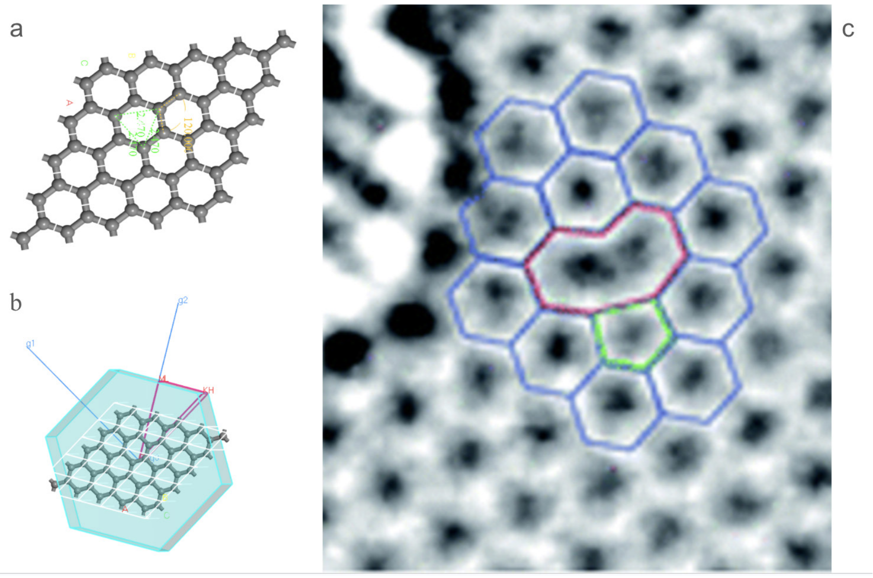

Figure 2. The graphene structure modeled with measurements is shown in graph a and graph b. In 2008, an experimental TEM image of graphene with single carbon vacancy was captured by J. C. Meyer et al. It is printed in Graph c [18]

The dimension is chosen to be medium size to ease the following simulation. After the intact graphene structure is constructed, carbon vacancies will be constructed in the structure.

In 2011, F. Banhart et al. looked into the theoretical structure of graphene with single carbon vacancy using DFT. The theory indicates the structure with the lowest energy, and it is shown in Figure 3.

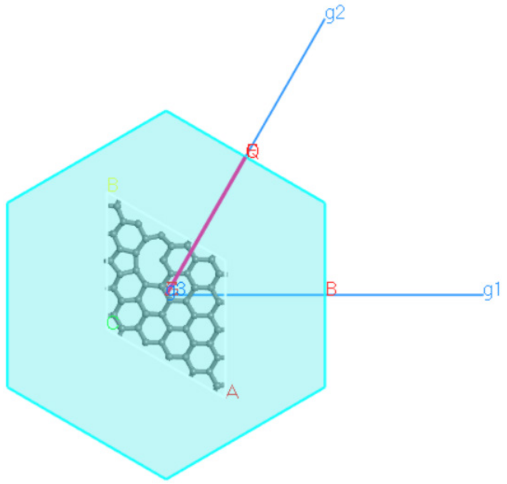

Figure 3. Structure with the lowest energy [19]

After constructing the structure of the intact and defective graphene, the calculation is conducted based on the program of CASTEP. The parameter of the simulation is set up in the fashion of the table 1 below.

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Table 1. Parameter of the simulation

Item	Variable	Selection	Justification
Task	Controlled	Energy	The task of energy will study the electron distribution and energy dispersion in the structure, which gives the most relevant results about the energy structure of graphene.
Quality	Controlled	Medium	Since more high-quality simulations will take significantly longer time, which is about one hour for each trial. Medium quality is chosen to ease the work. However, Ultra fine quality simulations are run for anomaly data, which will be specified later.
Functional	Controlled	GGA, PBE	The default choice of the two newest density functional analysis methodology
Spin polarisation	Controlled	Non-polarized	Graphene is spin-nonpolarized [20]
Metal	Controlled	Yes	Graphene is defined as a semi-metal and is usually treated as a metal in simulation. [21]
Charge	Controlled	0	Graphene has 0 charge
Energy Cutoff (eV)	Controlled	500	The cutoff energy of single-layer graphene with defects is conventionally set to be 500eV
SCF tolerance & tolerance per item	Controlled	Medium per atom	The default setting of metal
K-point set	Controlled	5*5*1	The k-point set determines the size of the graphene which the band structure is going to be calculated from. It is claimed that when the cutoff energy is set as 500 eV, the optimal K-points sets are 5 × 5 × 1 and 7 × 7 × 1. [22]
Pseudopotential	Controlled	OTFG Ultrasoft	OTFG Ultrasoft is especially suitable and convenient for structures with defects.
Relativistic Treatment	Controlled	Koelling-Harmon	The only available selection here.

And the Bar chart of band gap of graphene against the number of carbon vacancies is shown in Figure 4.

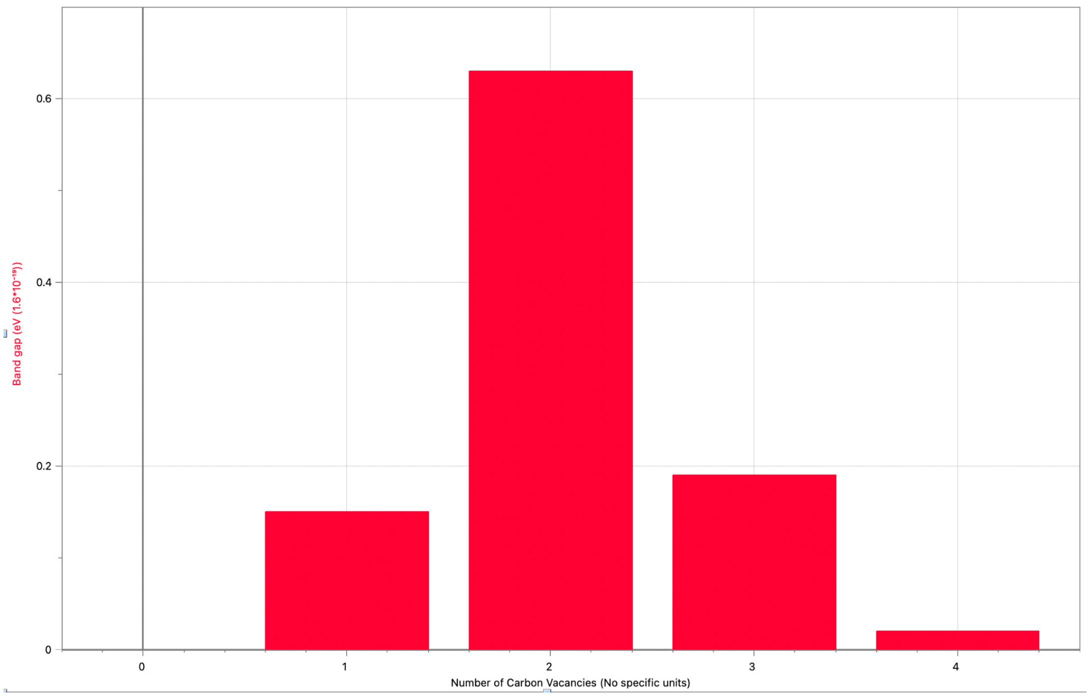

Figure 4. Bar chart of band gap of graphene against the number of carbon vacancies

A bar chart is plotted based on the data, to emphasize the discontinuity of the data and showcase that graphene with two carbon vacancies generally has the biggest band gap of 0.63 eV, then followed by the graphene with one and three carbon vacancies. More analysis will be included in the following conclusion.

3. Conclusion

The investigation into graphene with different numbers of carbon vacancies has matched the previous theoretical deductions. The creation of carbon vacancies in the structure can change the atomic spacings and therefore alter the band structure, opening up band gaps in the graphene structure. It is possible to monitor the band gap of graphene by creating carbon vacancies in it. That can be validated by the fact that all the graphene sheets with carbon vacancies simulated tested have significant band gaps bigger than 0.01eV.

Moreover, the results can show a certain correlation between the number of carbon vacancies, which means that it is viable to control the band gap of single-layer graphene by controlling the number of carbon vacancies created. It is indicated in the bar chart of Figure 4 that the band gap will be maximized and reach a value of roughly 0.63 ± 0.09 eV when two carbon vacancies are created in graphene, followed by three carbon vacancies in graphene, which gives a band gap of 0.19 ± 0.1 eV, and then one carbon vacancy graphene, which has a band gap of 0.15 ± 0.08 eV. An intact graphene and graphene with four carbon vacancies will have almost 0 band gap. By controlling the number of carbon vacancies, it is possible to engineer a certain band gap in single-layer graphene.

To look into the future of graphene applications, creating carbon vacancies in graphene can be a viable approach to engineer the band gap of the structure, thus better harnessing graphene as a semiconductor material. However, the relevant technologies are needed to ensure the operability of this approach. So far, only investigation into single-vacancy graphene has been done practically. Theoretical simulations can provide a profound insight into the relationship between carbon vacancies and band structure. However, further experiments can be conducted to validate this idea.

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