International Journal of Innovative Studies in Sciences and Engineering Technology (IJISSET)

ISSN 2455-4863 (Online) **www.ijisset.org** *Volume: 5 Issue: 8 | 2019*

A Comparative Study of the Electronic Structure Calculation of Ruthenium on Graphene Monolayer (CRu) using a Quantum ESPRESSO

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Abstract: *Since its first preparation by exfoliation graphene has become one of the most discussed topics in condensed matter due to its unusual properties. In this work the density functional theory (DFT) is been adopted. Using the DFT, we optimized the observed superstructures and found interfacial graphene-Ruthenium bonding of Ru atoms atop C atoms for the superstructure, which causes the monolayer graphene to form a periodic humps of about 7.3Å in hight within the monolayer sheet. From the band structure calculations the differences in energy between bottom of conduction band and top of valence band were found to occur at K indicating a direct band gap of Ruthenium on graphene of 0.75eV and these values shows an agreement with that of (David S.Sholl,2009) respectively.*

Keywords: *Graphene, Band gap, Density of State, Adsorption*

1. INTRODUCTION

Graphene has attracted increasing interest due to its remarkable properties both physical and chemical. However, the zero band gap of monolayer graphene limits it's further electronic and optoelectronic applications [1]. Thousands/hundreds/few layers of graphene are detached from the graphite lead of a pencil (invented in 1656 in England) it was used to write on a paper, a fact that went unnoticed, although graphite has been known to the mankind for centuries.

The detailed historical background and the status of graphene research as of December 2010, are given in the Nobel Lecture of Geim[2]. The term “graphene” was introduced by Boehm and his colleagues in 1986, by joining the term “graph” derived from the word “graphite” with the suffix “ene” that refers to polycyclic aromatic hydrocarbons. Now graphene is regarded as the basic building block of graphitic materials (i.e graphite = stacked graphene, fullerences = wrapped graphene, nanotube = rolled graphene).

These graphitic materials are classified as the allotropes of graphene (allotropes are different structural modifications of an element in the same phase of matter, e.g., different solid form).The basis vector that generates the graphene lattice is[3]:

$$\vec{a}_1 = a\cos 30^\circ\,\hat{x} + a\sin 30^\circ\,\hat{y} = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right) \tag{1}$$

$$\vec{a}_2 = a\cos 30^\circ\,\hat{x} - a\sin 30^\circ\,\hat{y} = \left(\frac{\sqrt{3}a}{2}, \frac{-a}{2}\right) \tag{2}$$

with

$$[\vec{a}_1] = [\vec{a}_2] = a = \sqrt{3}a_{c-c},\ \vec{a}_1\cdot\vec{a}_1 = \vec{a}_2\vec{a}_2 = a^2, \vec{a}_1\vec{a}_2 = a^2/2,$$

where $a_{c-c} \approx 0.142nm$ is the carbon-carbon bond length, A and B are the two atoms in the unit cell of graphene and these contribute to a total of two π electrons per unit cell to the electronic properties of graphene [4]. The primitive unit cell can be considered as equilateral parallelogram with side $a = \sqrt{3}a_{c-c}$ = 0.246 nm where a is the lattice constant of graphene.What makes graphene unique is first of all its band structure. Therefore, it is essential to generate a finite gap in the energy dispersion at Dirac point. Since the graphite is made of the stacking of many graphene plane, similar growth will be possible for graphene, if the graphene plane is supported mechanically with other certain material.Recent work [5]on the band gap opening for graphene-on-ruthenium reveals it was due to the symmetry breaking in the system.At the microscopic level, a hexagonal superstructure with repeating length of ~3.0*nm*has been observed by scanning tunneling microscopy (STM), and attributed to be a moire parttern caused by maching (12x12) graphene primitive cells to (11x11) Ru(0001) primitive cells[6][7][8] other models have been used to study the

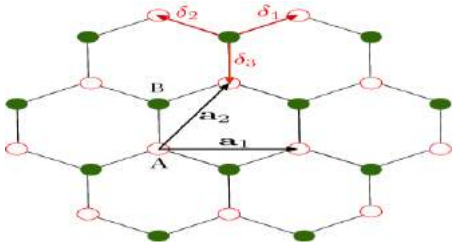

Figure 1 *Cayssol, Jerome*

electronic structure of graphene like the “tight-binding model”.

A simple TBM can be constructed to in-cooperate only the nearest-neighbor hopping of electrons between the adjacent A and B sub-lattices fig (1) of honeycomb lattice to study the low energy electron excitations and doping effect in pristine graphene[9]. Therefore, the study of electronic band structure of graphene is very important because it is the starting point for understanding of graphene’s solid state properties.

The origin of the band structure is simply related to the fact that un-hybridized P_Z overlap with nearest neighbors to form π – orbitals spread out in energy and give rise to band states extending over a range of energies [10][11].

2. THEORETICAL FORMULATION

In this work the density functional theory(DFT) is been adopted, for it allows the prediction and calculation of material behavior on the basis of quantum mechanical considerations, without requiring higher order parameters such as fundamental material properties. With DFT problem for a representative supercell of a material with n electrons can be studied as a set of n one-electron Schrodinger-like equations which are also known as Kohn-Sham equations[12][13] this Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed [13]in a work that proves two important theorems that later won them the Nobel Prize in chemistry and also lead to the development of DFT. The first theorem treats electron density $n(r)$ as a function of energy given as;

$$E[n(r)] = \langle \psi[n] | \hat{T} + V | \psi[n] \rangle \qquad (3)$$

In particular, the ground state energy is a function of n_0:

$$E_0 = E[n_0] = \langle \psi[n_0] | \hat{T} + V | \psi[n_0] \rangle \qquad (4)$$

Where $\hat{T}$ denotes the kinetic energy operator and V is an external effective potential in which the particles are moving. Kohn-Sham in 1965 reformulated the problem in a more familiar form having the same ground state charge density $n(r)$ and the Kohn-Sham orbital are the solution to the Schrodinger equation given as;

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_S(\vec{r}) \right] \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}) \qquad (5)$$

Which yields the orbitals φ_i that reproduce the density $n(\vec{r})$ of the original many-body system

$$n(\vec{r}) = n_s(\vec{r}) = \sum_i^N |\varphi_i(\vec{r})|^2 \qquad (6)$$

The effective single particle potential can be written in more detail as

$$V_s(\vec{r}) = V\left(\vec{r}) + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3 r' \right) + V_{XC}[n_s(\vec{r})] \qquad (7)$$

Where the second term denote the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term V_{XC} is called the exchange-correlation potential. This Hohenberg-Kohn theorems relate to any system consisting of electrons moving under the influence of an external potential.

3. COMPUTATIONAL METHOD

In this work, we employed the first-principles band calculation technique based on density functional theory[14]First principle total energy calculation have been performed using the program package “Quantum ESPRESSO” which is a software suite for *ab-initio* quantum methods of electronic structure calculation and materials modeling. The electron-ion interaction was treated by using the ultrasoft pseudopotential for carbon and Ruthenium (Vanderbilt, 1990).

We expanded the single-particle Kohn-Sham (Kohn&Sham,1965) wave functions using a linear combination of plane wave basis sets with a kinetic energy cutoff of 35Ry. The Kohn-Sham equations were self consistently solved by employing a 12 x 12 x 1 points Monkhorest-Pact set (Monkhorst & Pack, 1976) within the hexagonal Brillouin zone.Quantum ESPRESSO was able to do geometric optimization, self-consistent (SCF) and non-self-consistent (NSCF) total energy calculations. Band Calculation, Density of state.

4. RESULTS AND DISCUSSION

The optimized electronic structure of ruthenium-on-graphene (CRu) surface was computed by this powerful computational codes and was visualized using the GUI XCRYSDEN (fig2). The absorption site for the 3x3 super cell as in figure (2) are at the bridge site (B-site) positioned at the center of the C-C bond. The distance between the carbon-carbon bonds is about 1.42 Åwhich is smaller than the C-C bond lengths of diamond of 1.52Åand the distance between adatoms (Ru-C) is about 7.3Å. The C-C-C angle is measured to be 120^0 which is slightly larger than 109.5^0 in its diamond structure. The final potential is constructed self-consistently from eigenstates at 6 sampling K points in the Brillouin zone (BZ).

The minimal energy selected from each of the optimized parameter were set into the input file and calculation in the control of the input file was set to ‘relax’, calculation was done with the command ‘pw.x’ until the most stable final geometry coordinate were achieved and the structure was revealed fig (2).

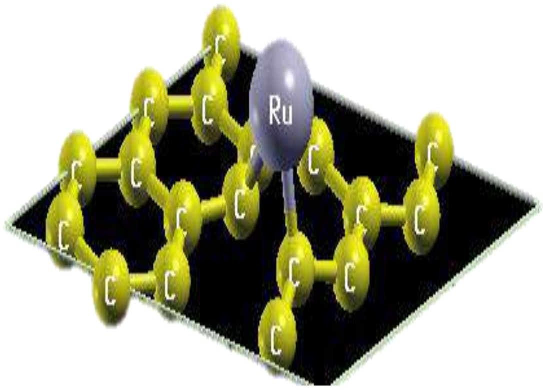

Figure (2) *Ruthenium-on-graphene surface*

5. ELECTRONIC PROPERTIES

5.1 Band structure

The electronic band structure of graphene is very important because it is the starting point for understanding of graphene's solid state properties.The calculation of electronic band structure is very important for describing the optoelectronic behavior. Here we performed an analysis of band structure, density (DOS) for ruthenium on graphene plane.

The electronic band structure of Ruthenium on graphene were computed within PBE approximation based on DFT. Fermi energy level scale at 0eV represented by dash line shown in **Fig (3).** From the band structure calculations the differences in energy between bottom of conduction band and top of valence band were found to occur at K indicating that is a direct band gap of Ruthenium on graphene 0.75eV and these values shows an agreement[15]

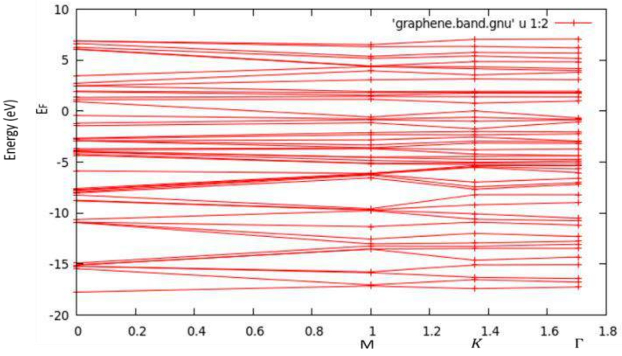

Figure 3 *Electronic band structure of Ruthenium on graphenesheet along the principal direction of the hexagonal Brillouin zone.*

5.2 Density of state (DOS)

The Density of state of a system describes the number of states per interval of energy at each energy level available to be occupied. DOS calculated result from **Fig (4)** shows the energy is 0.75eV with a dominant structure having the peak of energy level.

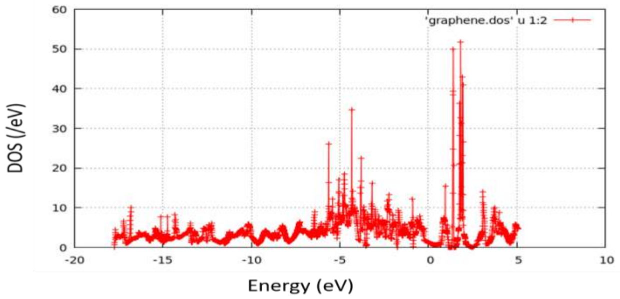

Figure.4 *Plot of the electronic density of state (DOS) of Ruthenium on graphene sheet*

The formation of the Ruthenium on monolayer graphene (on top of the buffer layer) leads to dramatic changes in the electronic structure of the system. The result obtained in this studies is in agreement with a previous study [16] and even higher than that of[17] shows that the Dirac energy ED in the Ru buffer layer on graphene.

6. CONCLUSION

Within the framework of local density approximation of the density functional theory and pseudopotential theory we have presented a comparative first principle calculation study for the adsorption of Ru on a pristine graphene using the Quantum ESPRESSO codes.Surprisingly, the energy gap for the π-states is found after intercalation of Ru atom on graphene monolayer. The appearance of such a gap in the electronic structure is assigned to the fact that the symmetry for two carbon sublattices is broken in the graphene/Ru system due to the geometry of the system.The band structure for GMO from the GGA and local-density approximation(LDA) calculations are obtained, and the corresponding band gap is 0.75 eV. The resultobtained is more close to the calculated result of (David S.Sholl 2009) which is attributed to that LDA underestimates the band gap of semiconductors.

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