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Quantum Capacitance and Fermi Level Change in Graphene Nanoribbons Due to Gas Sensing

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***Abstract:** Here we used semiempirical computations to examine the property of nanoribbon of Graphene as a gas sensor with interaction of H_2O gas molecule for both pure and defective GNRs which has been generated in Atomistix Toolkit (ATK) software. Density of States GNR before and after the interaction is shown in a (DOS) diagram with gas particles was discovered to be different which has been observed in MATLAB software. It's vital to look at the quantum capacitance when examining Graphene's electrical properties. So, this study looked at change in quantum capacitance and Fermi Level of Graphene before and after gas sensing and the results were produced with necessary equations. Using a three-electrode electrochemical setup, we are able to directly quantify Graphene's quantum capacitance as a function of gate potential. If Graphene is used in a highly sensitive capacitive circuit, the change in Fermi energy was determined from experimental data of changed Density of States (DOS). Although this research has some limitations and future scopes, we can propose that the change in Fermi Energy level can be approximately 9.5 eV with respect to the quantum capacitance of fabricated Graphene interacting with H_2O which is used as a MOSFET in this work.*

***Keywords:** Graphene, Nano ribbon, Density of States, Quantum Capacitance, Fermi Level.*

1. INTRODUCTION

Since its successful production, Graphene, a 2-D single layer hexagonal structure of Carbon, has piqued attention. Grapheme offers potential in nanoelectronics applications for its unique electrical, structural and mechanical features.

Graphene Nanoribbon (GNR) is graphene strip which can have any length, and because of its high aspect ratio, they are classified as mono dimensional (1-D) Nano materials. GNRs are members of new family of Nano materials with semiconducting or metallic characteristics

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that are now being studied for intriguing quantum-mechanical properties which can be implied in electrical features [1].

Because GNR is a allotrope in a plane of Carbon, which means that all of the atoms of Carbon in it create covalent connections in a single plane as opposed to in numerous planes as is the case with normal carbon, GNR is more stable than normal carbon. To reach a level of sensitivity that is capable of resolving variations between individual quantities of a chemical that is being measured should be the ultimate goal of any method of detection. The quantity that is being measured is often represented by a single atom or molecule. Up to this time, detection technologies such as solid-state gas sensors have not been successful in obtaining such a degree of resolution

Nanosensors constructed out of graphene have the ability to detect specific events, such as when a gas particle adheres to or separates from the surface of the substance. The local concentration of graphene's carriers can be altered by adsorbed molecules, which leads to fluctuations in graphene's resistance that are step-like. Graphene is a particularly noise-free electronic component so it is an intriguing choice for use in chemical detectors because of the high level of sensitivity that can be attained with it [2].

The prospective of GNR as a sensor has been proven in a number of practical and theoretical analysis [3-5]. All varieties of GNRs have a finite band gap. As a result, gas molecule adsorption is projected to have a greater impact on changing the electrical characteristics of GNRs. As a result, GNR is expected to be more sensitive to gases and performs better as electrical device.

Because of its crucial electrical characteristics, organic electrical devices like Organic Field-Effect Transistors (OFET), Organic Light Emitting Diodes (OLED) can use graphene [6-9]. The interaction among the graphene surface and particularly the tiny adsorbed gas molecules are the emphasis here (H_2O, H_2, O_2, CO, NO_2, NO, and NH_3). The topic then moves on to graphene-based gas sensor technologies. In analyzing the research on the effects of molecule adsorption on graphene, it is clear that p and n doping can significantly alter graphene's electrical structure, increasing the Quantum Capacitance of the material.

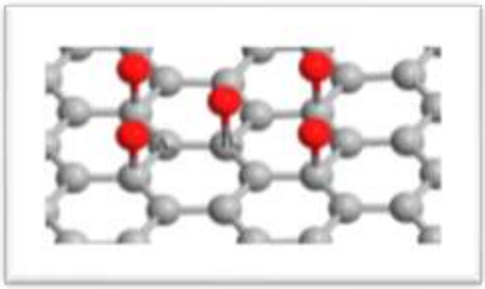

Fig.1 Gas molecules are adsorbing on unit cells of graphene[12]

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After doping with impurity molecules, the GNR band gap can alter, resulting in variations in the –band. After absorbing gas molecules onto the GNR surface, the band gap shifts, modulating the electrical and physical properties [10-11]. This occurrence demonstrates that graphene is extremely sensitive to its surroundings, and that even a single gas molecule can modify its electrical properties.

The quantum capacitance effect is one of the most important characteristics of graphene which can define the property, specially the electrical property of a graphene. Quantum Capacitance of the single layer graphene nanoribbon is used to assess the effect of gas sensing or gas molecule adsorption. This capacitance is a function of carrier density which has been established through experiments. Changes density of charge carriers generated by the adsorption of gas molecules in graphene nanoribbon (which will eventually be referred to as DOS) may increase or decrease Quantum Capacitance.
Quantum Capacitance Cq can be calculated in the form of following expression:

$$C_q = e^2.\frac{\partial n}{\partial E} \dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Here, $\partial Q = e \cdot \partial n$ and Q is the charge (Coloumbs), e is the value of charge and $\partial V = \partial E/e$ is the voltage applied to the device. To calculate the Quantum Capacitance, the grapheme nanoribbon's charge carrier density model must be developed. The number of energy-carrying carriers (electrons) has been calculated to be, $DOS(E) \cdot f(E) \cdot dE$ [12]

Changing of carrier concentration can be used to describe density of states (DOS), which represents the amount of possible energy states at each energy level of graphene that can be filled by carriers. The graphene nanoribbon's carrier concentration value is n = 2.5* 10^{11} cm^2. Some important features of the Current–Voltage characteristics that are analyzed to gain a better understanding of the quantum capacitance of GNRFET-based sensors. As a result, it's critical to track variations in quantum capacitance as a function of DOS in a gas-sensing Graphene. The gas adsorption impact is evaluated using the quantum capacitance characteristic of monolayer graphene nanoribbons in the nanoscale regime [12].

A traditional plate capacitor is made up of two well-conducting plates that are laid out in parallel to each other and are separated by a layer of dielectric material with a specific thickness. It is possible to compute its capacitance by taking into account the material and geometric parameters of the system. The objective of this piece is to produce a comprehensive analytical answer to the Quantum Capacitance problem, which will make use of no mathematical approximations and will be based on the assumption of a known DOS function. We are going to derive the quantum capacitance by applying a few straightforward definitions. The electrostatics that are used to describe the system can be used to derive the total capacitance that is present between the gate and the electron gas for the Quantum Capacitance given a known DOS function [13].

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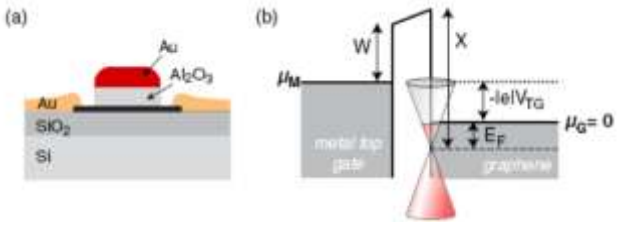

Fig.2 a)schematic representation of a cross-section through a sample of top-gated graphene.

The graphene flake, depicted in black, is connected to gold electrodes depicted in orange, and it is partially covered by an alumina and gold top gate, depicted in gray and red, respectively. (b) A schematic representation of the structure's electrostatics, illustrating the difference in electrochemical potential between the graphene sheet and the top-gate electrode[14].

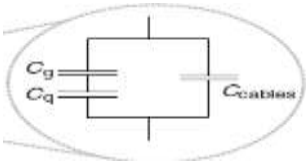

Fig.3 Circuit connection for the system being measured [14]

The majority of study has focused on gas molecule adsorption on graphene and how it affects the electrical characteristics of the material. The analytical potential of GNR for gas sensing applications, on the other hand, has yet to be thoroughly explored. GNR changes in a different way than graphene when exposed to gas molecules. Understanding interactions between gas molecules that have been adsorbed and GNR is essential for getting the most out of GNR-based gas sensors. Gas adsorption alters not just the concentration of carriers (electron/hole) in the GNR, but also the energy band-gap, altering properties such as density of states and quantum capacitance, which is what we're after.

If a GNRFET consists of gas effected Graphene, the carrier concentration will change so that the change in Fermi energy causes changed density of states and changed quantum capacitance.

Research Elaborations

We chose armchair-edged GNR to use as a gas sensor in our simulation. We're not going to recommend a particular device structure here. Instead, we'll look at GNR on its own to see how varied gas adsorption affects its Density of States (DOS). Changes in the DOS, particularly at the Fermi-energy level, are anticipated to result in noticeable changing of electrical characteristics.

The number of lateral chains can be used to indicate the width of the Na-aGNRs. The bandgap (which is denoted by Eg) of Armchair graphene is inverse proportional to the thickness and also relies on the number of armchair chains. This relationship can be expressed using a handy first-order semi-empirical equation.

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The values of 'Density of States (DOS)' and band structure of armchair-edged GNR with sensing of gas molecule and without sensing of gas molecules were obtained from the simulator's (Virtual Nanolab) output.

We estimated the armchair GNR's bandgap using the simulated DOS shown in Fig. 4 as a quick way to assess whether or not the output that was generated was accurate. The DOS team has determined that the bandgap is 0.13 eV [13].

Hence, Bandgap of this armchair grapheme, Eg=0.13 eV which is shown in fig. 3.

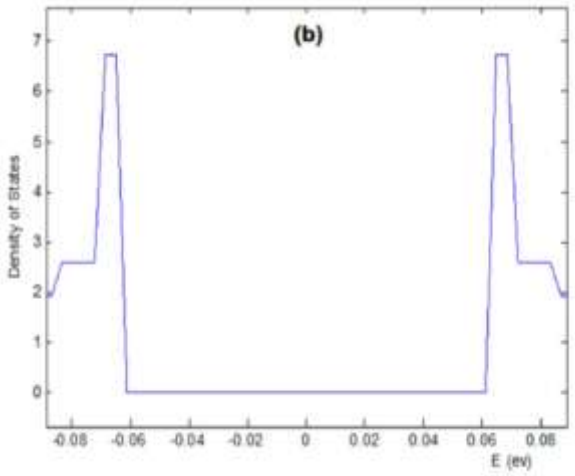

Fig.4 Bandgap of an extended graphene[13]

The values of 'Density of States' have been observed for armchair graphene with sensing of gas and without sensing of gas which were extracted from the software's (virtual nanolab) result.

This analysis clearly shows that changed DOS from the simulation of Virtual Nanolab adheres to anticipated structure, at the Fermi level (zero) [15].

When it is obvious that the new values of density of states of defective graphene fluctuates after touching the molecule of gas under examination. Resulting fluctuation differs depending on the gas [15].

for T = 298 K considering the Fermi level, Boltzmann constant used for all numerical computations and for all plots is k_B = 8.61733030 × 10^{-2} meV^{-1} K [12].

The calculation of DOS:

$$DOS^2 = \pm \frac{(t'^2+t^2+4t^2\,\beta+4t^2\,\beta^2+2t^2\,\beta k_x^2 a^2)}{4\pi t^2 \beta a^2\, kx} \quad \text{.....(2)[12]}$$

where *kx* is the wave vector in the *x* direction which is calculated as:

$$E = (Eg - x)k_BT \quad \text{.....(3)}$$

with normalized Fermi energy, $\eta = E_F - Eg/\, k_BT$ .....(4)

and $x = E - Eg/k_BT$ .....(5)

$$Cq = \pm e^2 * DOS^2 * \left(\frac{1}{1+e^{x-\eta}}\right) \quad \text{.....(6)}$$

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After using equation (6), we will observe that, the more the quantum capacitance increases, the more the carrier concentration changes [12]. The results will be shown in the tabular form in Table I, II, III and IV.

The methodology presents a quantitative description of the quantum capacitance of graphene in terms of Fermi velocity, carrier density temperature and other fundamental physical characteristics.For the graphene potential,

$$V_{ch} = \frac{V_g C_i}{(C_i + C_g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)[16]$$

$$C_q = C_Q\,(V_{TG}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where Vg is the gate potential. The geometric capacitance of the top-gate to be *C*g = 6 fFμm^{-2}. where V_g is the gate potential and C_i = 20 mF cm^{-2} is the double layer capacitance of the ionic liquid[16].

2. RESULTS

Quantumwise Atomistix ToolKit (ATK), version 13.8.2 software can do atomic scale modelling and simulation of nanosystems. In this research, this software has been used for observing changed DOS with respect to Graphene Energy Level. We got our result which has been shown below.

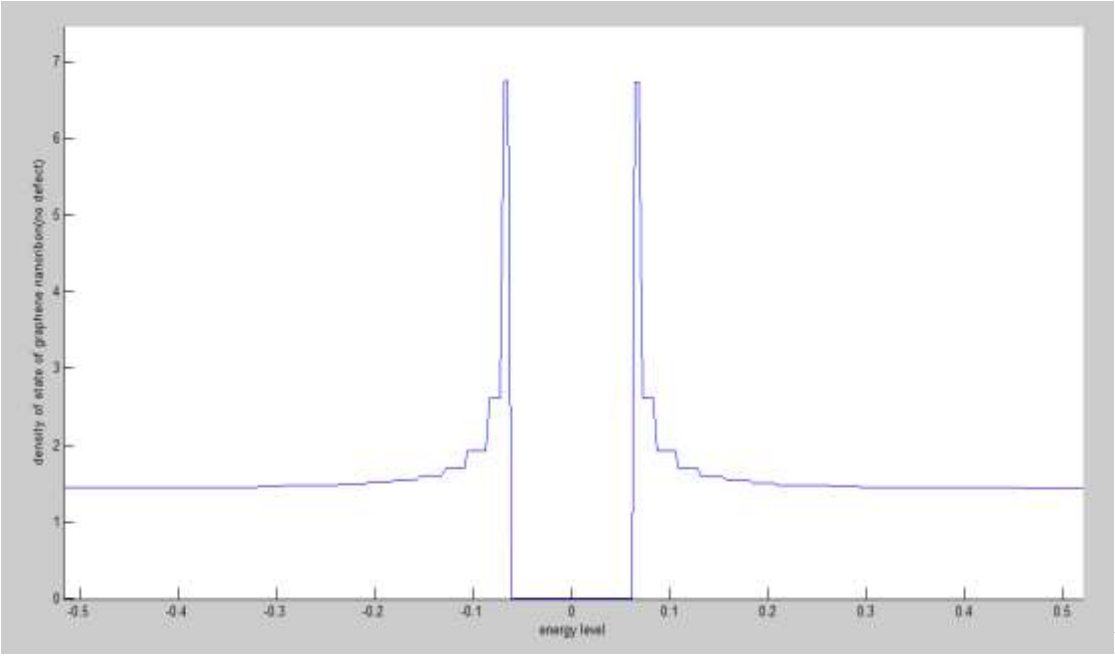

Fig.5 DOS of defect free GNR after sensing H_2O

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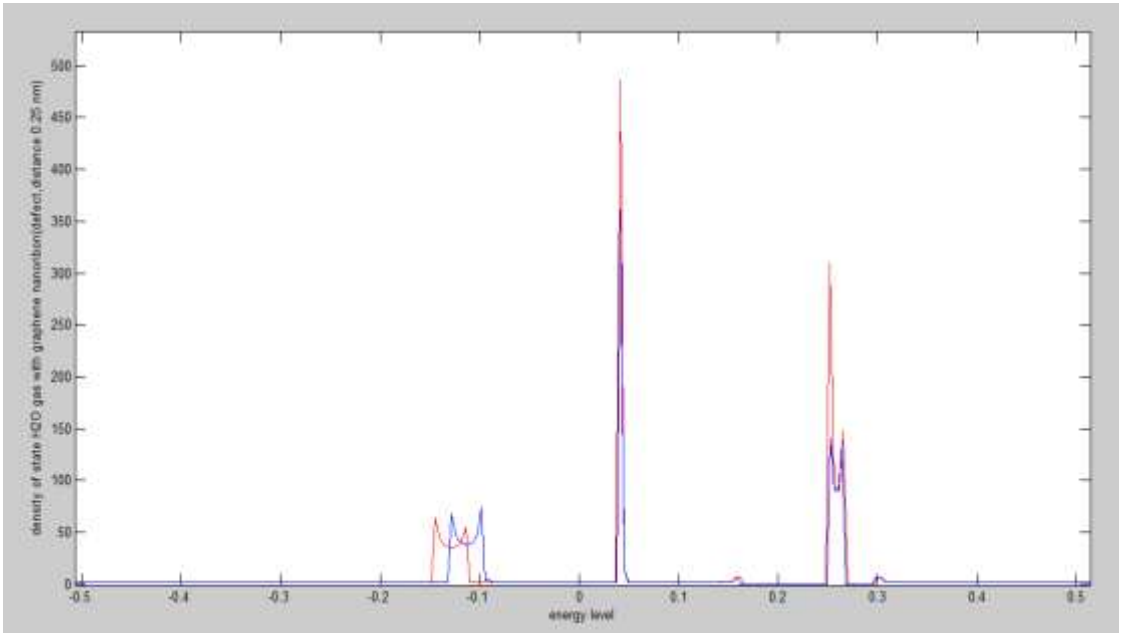

Fig.6 Defected GNR with H_2O

In Fig. 6, Energy level in DOS of GNR (defect) with H_2O (far, distance=0.25nm) (red) shifted left than Energy level in DOS of GNR with defect (blue). This shifting causes change in band gap. This represents the response of GNR due to gas molecules.

In Fig. 7 , for Graphene energy level, the quantum capacitance changes slightly with respect to changed DOS in the case of defect free GNR(blue curve of Fig. 5). In Fig. 8 , for Graphene energy level, the quantum capacitance changes slightly with respect to changed DOS in the case of defect free GNR(blue curve of Fig. 5).

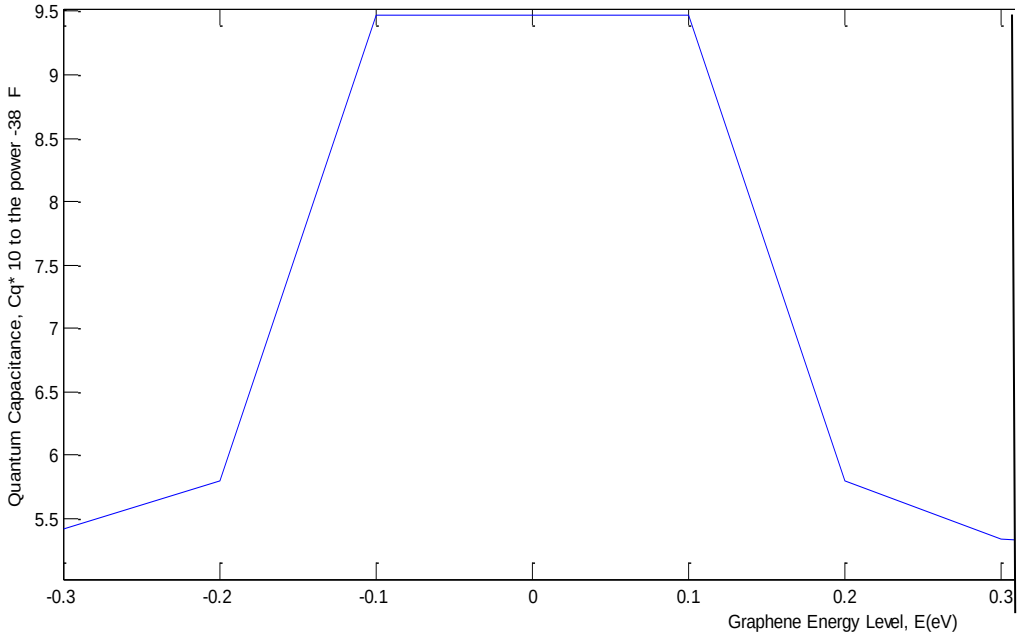

Fig.7 Energy Level vs Quantum Capacitance of defect free Graphene

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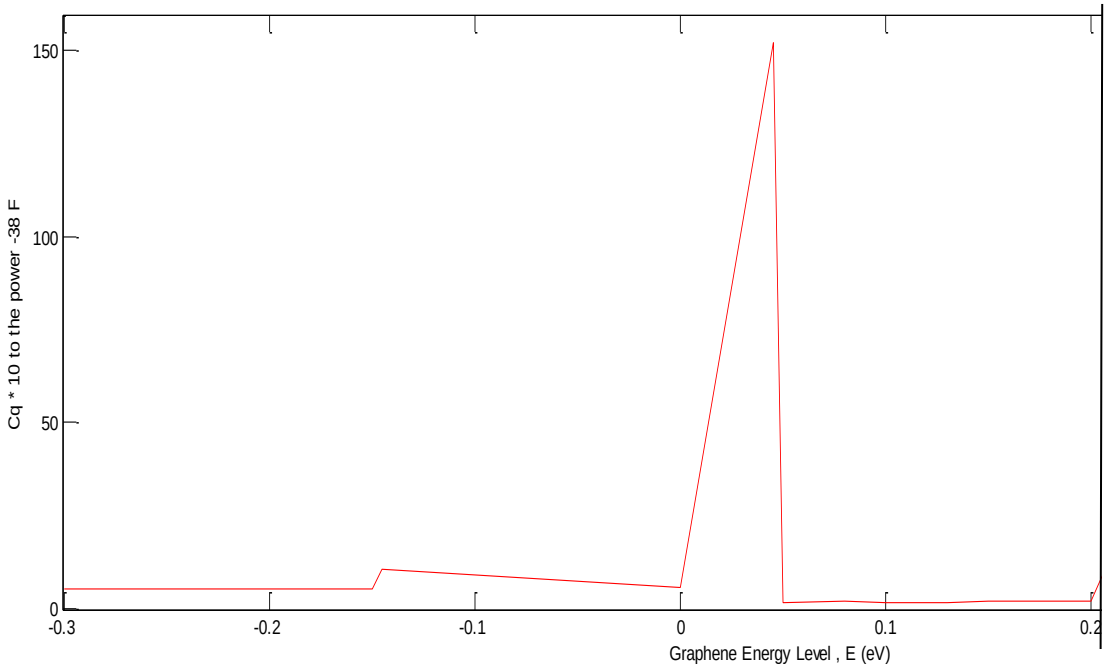

Fig.8 Energy Level vs Quantum Capacitance of Graphene(H_2O sensed)

In Figure 8, for defected GNR (after sensing H_2O), the red curve shows energy level vs changed quantum capacitance ($Cq*10^{-38}$ F) which we have got from the simulation result of ATK 13.8.2. The blue curve shows the result of defect free GNR.

The change in Fermi energy regarding above mentioned analysis is,

$$\frac{\partial E_F}{\partial V_G} = |e|\left[1 + \frac{C_q(V_{TG})}{C_g}\right]^{-1} \text{.....(6)[12]}$$

$$= 9.58\, Volt\ (for\ H_2O\ defected\ GNR)$$

Using above equation, the increase of Fermi energy with respect to gate voltage is 9.58 eV (for reference value of Graphene energy) 0.145 eV.

3. CONCLUSIONS

We have measured the capacitance and transport on a single-layer graphene sheet that has been locally gated. The carrier concentration changes in proportion to the quantum capacitance. The quantum capacitance corresponding to gate voltage can change the Fermi level of energy which has been calculated in our work.

In the above work measurements of graphene's quantum capacitance have been made. with the changed value of DOS of graphene which sensed gases. It refers to non-ideal graphene that contains an acceptor (H_2O) gas molecule. Quantum capacitance increases linearly with potential, resulting in a completely different Fermi Level for non-ideal, defective graphene with gas sensing and doping properties.

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