CHANGE IN DENSITY OF STATES AND QUANTUM CAPACITANCE OF GRAPHENE NANORIBBON BECAUSE OF GAS SENSING PROPERTY

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Abstract

This research uses a simulation based on semiempirical computations to examine the property of graphene nanoribbon (GNR) as a gas sensor. GNR's interactions with two gas molecules (mithane, and water) have been thoroughly studied (both pure and defective). The adsorbtion of that two gas molecules was significantly higher in the case of malfunctioning GNR. The "Density of States (DOS)" diagram of graphene nanoribbon (GNR) before and after the interaction with gas molecules was discovered to be different. It's vital to look at the quantum capacitance when examining Graphene's electrical properties in order to comprehend the band structure and I–V characteristics. This study looked at quantum capacitance before and after gas sensing, and the results were produced with the help of simulation tools and equations.

Keywords: Density of States, Quantum Capacitance, Fermi level, Graphene Nanoribbon

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1. INRODUCTION

Graphene nanoribbons (GNRs) are a family of one-dimensional (1D) materials with a graphitic lattice structure. GNRs possess high mobility and current-carrying capability, sizeable bandgap and versatile electronic properties, which make them promising candidates for quantum electronic applications. In the past 5 years, progress has been made towards atomically precise bottom-up synthesis of GNRs and heterojunctions that provide an ideal platform for functional molecular devices, as well as successful production of semiconducting GNR arrays on insulating substrates potentially useful for large-scale digital circuits. With further development, GNRs can be envisioned as a competitive candidate material in future quantum information sciences. In this Perspective, we discuss recent progress in GNR research and identify key challenges and new directions likely to develop in the near future.
As cut-outs from a graphene sheet, nanographenes (NGs) and graphene nanoribbons (GNRs) are ideal cases with which to connect the world of molecules with that of bulk carbon materials.

Two different edge geometries, namely zigzag and armchair, arising from the finite termination of graphene, control the electronic properties of graphene nanoribbons. Here we attempt to give an overview of their interesting electronic, magnetic, optical, conduction properties and explore possible ways of enhancing their device applicability by a number of ways including external perturbations, doping and chemical modifications.

Graphene, with its characteristic high permittivity, has been demonstrated to possess remarkable EM dissipation abilities (e.g., converting EM into heat). However, the intrinsically high thermal conductivity, low Seebeck coefficient, and zero bandgap structure prevent heat–DC conversion[14,15]. Element doping and the creation of graphene nanostructures (e.g., nanoribbons) have been widely used to alter graphene's electronic and phononic structure by covalently tuning the intralayer atomic bonding[1]

Graphene nanosensors can detect events like the attachment and detachment of gas molecules to and from the material's surface. Adsorbed molecules can affect the local concentration of graphene's carriers, leading to step-like oscillations in the material's resistance. Graphene's remarkable level of sensitivity in chemical detectors [2] results from the fact that it is an incredibly low-noise electronic material.

Several empirical and theoretical studies have established GNR's potential as a sensor. There is a definite band gap in all GNR types. Therefore, it is predicted that the adsorption of gas molecules will have a more significant effect on altering the electrical properties of GNRs. Therefore, GNR is predicted to have enhanced gas sensitivity and improved electrical performance.[3-5]

Graphene's advantageous electrical properties allow it to be used in a wide variety of organic electrical devices [6-9], including Organic Field-Effect Transistors (OFET) and Organic Light Emitting Diodes (OLED). The discussion then shifts to gas sensor systems that make use of graphene. Research into graphene's adsorption effects reveals that p- and n-doping can drastically modify the material's electrical structure, boosting its quantum capacitance.

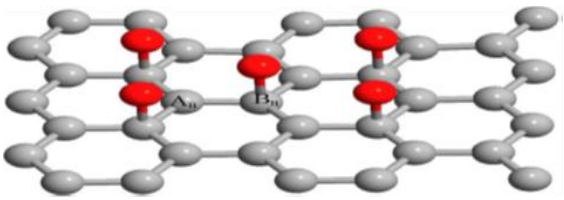

Figure 1. Gas molecules are adsorbing on unit cells of graphene

The band of a GNR can shift after being doped with molecules of impurity. When gas molecules are absorbed by the GNR surface, they cause a change in the band gap, which in turn affects the material's electrical and physical characteristics [10, 11]. That one gas molecule can alter the electrical characteristics of graphene reveals how sensitive it is to its environment.

Effective carrier doping would be expected to enhance the electrical conductivity and further improve the quantum capacitance (C_q) of graphene. [12] The quantum capacitance effect is one of the most important characteristics of graphene which can define 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. Changes of 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. The lower Cq is determined by the lower DOS near the E_F of graphene. Thus, it is crucial to modulate the DOS near the E_F of graphene so as to effectively increase its carrier density and Cq.

Quantum capacitance Cq can be calculated in the form of following expression:

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

Here, $\partial Q = e \cdot \partial n$ and Q is the charge (Coloumbs), e is the electron charge and $\partial V = \partial E/e$ is the voltage applied to the device. In order to estimate the quantum capacitance, a model of the charge carrier density of the graphene nanoribbon must be developed. The number of energy-carrying carriers (electrons) has been calculated to be, DOS(E) · f (E) · dE [12]

Density of states (DOS) is a measure of the number of potential energy levels in graphene at each energy level, and it may be described in terms of changes in carrier concentration. The graphene nanoribbon has a carrier concentration of n = 2.5*1011 cm2. In order to learn more about the quantum capacitance of GNRFET-based sensors, it is necessary to evaluate certain aspects of the Current-Voltage characteristics. Consequently, monitoring quantum capacitance changes as a function of DOS in a gas-sensing Graphene is essential. Quantum capacitance of monolayer graphene nanoribbons at the nanoscale is used to assess the effect of gas adsorption [13].

Most research has focused on how the adsorption of gas molecules on graphene modifies its electrical properties. However, GNR's analytical potential in gas sensing applications has not been fully investigated. When exposed to molecules of gas, GNR shifts in a way that graphene does not. To get the most out of GNR-based gas sensors, it is crucial to understand the interactions between adsorbed gas molecules and GNR. What we want is for gas adsorption to change the energy band-gap in the GNR, which in turn changes features like the density of states and the quantum capacitance.

The objective of this research is to provide a full analytical solution for the quantum capacitance for a specified DOS function. From these elementary definitions, the quantum capacitance can be derived.

2. METHODOLOGY

As a gas sensor, we simulated with armchair-edged GNR. It is anticipated that significant modifications to the DOS, especially at the Fermi level, will cause corresponding modifications to the electrical properties.

2.1. Observing Density of States

The width of the Na-aGNRs can be inferred from the total number of lateral chains. The bandgap (Eg) of a-GNRs is dependent on the total number of armchair chains and decreases with decreasing width. This connection can be written as a convenient semi-empirical equation of the first order.

The simulator's (Virtual Nanolab) output provided armchair-edged GNR's "Density of States (DOS)" and band structure with and without gas molecule sensing.

As a fast check to see if the generated output was accurate, we approximated the bandgap of the armchair GNR using the simulated DOS displayed in Fig. 4. The bandgap has been calculated by the DOS group to be 0.13 eV. By applying Equation (2), we can determine

that the length of the particular 5-aGNR that was used in this instance is,
ω= 0.492 nm.

Hence, from Eqn (2), Bandgap of this a-GNR, E_g=0.13 eV which is shown in fig. 4.

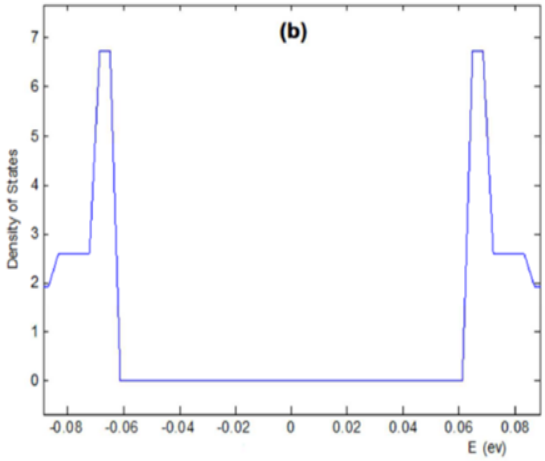

Figure 2. Bandgap of an extended graphene

This gives the result of α to be 0.26. This result of α is valid as α ranges from 0.2 to 1.5 .

3. RESULTS

Extracted from the output of the simulator (virtual nanolab), the values of 'Density of States' have been observed for both ‘with gas’ and ‘without gas’ armchair graphene.

This analysis unequivocally demonstrates that the modified DOS in the Virtual Nanolab simulation follows the predicted structure at the Fermi level (zero).

When the new values of graphene's density of states change dramatically after touching the molecules of the gas under study, and when the shape of this fluctuation varies from gas to gas.

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 [13].

The calculation of DOS:

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

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

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

with normalized Fermi energy,

η= E_F−Eg/ k_BT…….....(4)
and x =E−Eg/k_BT……...(5)
$Cq = \pm e^2 * DOS^2 * (\frac{1}{1+e^{x-\eta}})$……....(6)

Using equation (6), we can see that there is a correlation between the quantum capacitance and the subsequent change in carrier concentration [13]. Tables I through IV will display the tabulated results. After doing a paper simulation, we were able to obtain the revised DOS.

Table1. Table of calculation of Quantum Capacitance C_q(defect free GNR with CH_4)

GrapheneEnergy Level,E(eV)	**Changing Quantum Capacitance with DOS**				
	Gate Voltage,Vg	***DOS***	***x***	e^{x-n}	C_q *10^{-38}***(F)**
-0.5	-0.48	1.44	-0.0206	0.006266	5.27
-0.4	-0.38	1.45	-0.0206	0.006266	5.27

-0.3	-0.28	1.46	-0.016	0.006244	5.42
-0.2	-0.18	1.51	-0.012	0.006269	5.8
-0.1	-0.08	1.93	-0.001169	0.006333	9.47
-0.000177	$-1.6*10^{-4}$	0.00	-0.00505	0.0063	5.64
0	0	0.00	-0.0050	0.0063	5.64
0.000177	$-1.6*10^{-4}$	0.00	0.00507	0.0063	5.64
0.1	0.158	1.93	-0.001169	0.006333	9.47
0.2	0.25	1.5	-0.001167	0.006338	5.72
0.3	0.28	1.45	0.002723	0.006375	5.34
0.4	0.38	1.44	0.006613	0.006387	5.27
0.5	0.48	1.43	0.010	0.006409	5.27

Table 2. Table of calculation of Quantum Capacitance C_q(defected GNR with CH_4**)**

Graphene Energy Level ,E(eV)	**Changing Quantum Capacitance with DOS**				
	V_g	***DOS***	***x***	e^{x-n}	C_q ****10^{-38}(F)***
-0.5	-0.48	1.46	-0.0206	0.006266	5.42
-0.4	-0.38	1.54	-0.0206	0.006266	6.033
-0.3	-0.28	7.05	-0.016	0.006244	125
-0.2	-0.18	1.44	-0.012	0.006269	5.27
-0.1	-0.08	43.2	-0.001169	0.006333	4740
-0.00036	$-2.58*10^{-4}$	1.49	-0.00542	0.006339	5.64
0	0	1.49	-0.0050	0.00634	5.64
-0.00036	$-2.58*10^{-4}$	1.49	0.00542	0.006349	5.64
0.159	0.158	7.06	0.0015	0.0073	126
0.252	0.25	141	0.002569	0.0082	5040
0.3	0.28	1.45	0.002723	0.006375	125
0.4	0.38	1.44	0.006613	0.006387	6.05
0.5	0.48	1.43	0.010	0.006409	6.07

In table I, it can be observed that, for -0.0017 eV, the quantum capacitance Cq changes slightly with respect to the changed values of DOS. Approximately at point -0.00017 eV, the quantum capacitance C_q= $5.64*10^{-38}$ F and at 0.00017eV, C_q= $9.47*10^{-38}$ F (comparing with previous).

In the same case for the defected and CH_4 sensed GNR(table-II), at -0.1 eV, quantum capacitance C_q is $4740*10^{-35}$F and at 0.252 eV, C_q is $5040*10^{-38}$ F which are much more higher than that of non-CH_4 defected GNR, for the changed values of DOS .

Table 3. Table of calculation of Quantum Capacitance C_q(defect free GNR with H_2O**)**

Graphene Energy Lev ,E(eV)	**Changing Quantum Capacitance with DOS**				
	Gate Voltage, Vg (V)	***DOS***	***x***	e^{x-n}	C_q****10-^{38} (F)***
-0.5	-0.48	1.44	-0.0206	0.006266	5.27
-0.4	-0.38	1.45	-0.0206	0.006266	5.27
-0.3	-0.28	1.46	-0.016	0.006244	5.42
-0.2	-0.18	1.51	-0.012	0.006269	5.8
-0.1	-0.08	1.93	-.001169	0.006333	9.47
0.1	0.158	1.93	-.001169	0.006333	9.47
0.2	0.25	1.5	-.001167	0.006338	5.8
0.3	0.28	1.45	.002723	0.006375	5.34
0.4	0.38	1.44	.006613	0.006387	5.27
0.5	0.48	1.43	0.010	0.006409	5.27

Table 4. Table of calculation of Quantum Capacitance C_q(defected GNR with H_2O)

Graphene Energy Level,E(eV)	**Changing Quantum Capacitance with DOS**				
	Gate Voltage, Vg (V)	***DOS***	***x***	e^{x-n}	C_q*10^{-38} ***(F)***
-0.5	-0.48	1.44	-0.0206	0.006266	5.27
-0.4	-0.38	1.45	-0.0206	0.006266	5.27
-0.3	-0.28	1.46	-0.016	0.006244	5.27
-0.2	-0.18	1.51	-0.012	0.006269	5.28
-0.145	-0.087	64.7	-0.00889	0.006289	10050
-.000216	$-1.3*10^{-4}$	1.49	-.0065073	.006313	5.64
.000216	$1.3*10^{-4}$	1.49	-.0065075	.006314	5.65
-0.114	-0.087	55.6	-.00090	0.006315	7860
-0.1	-0.08	1.93	-.001169	0.006333	5.95
0.1	0.158	1.93	-.001167	0.006338	1.72
0.2	0.25	1.5	.002723	0.006375	0.00
0.3	0.28	7.05	.006613	0.006387	126
0.4	0.38	1.44	0.010	0.006409	6.03
0.5	0.48	1.43	0.0144	0.006435	5.42

In table III, for Graphene energy level -0.1 eV, the quantum capacitance changes slightly with respect to changed DOS in the case of defected GNR(blue curve). In Table III approximately at point -0.1 eV, the quantum capacitance C_q= $9.47*10^{-38}$ F and at 0.1eV, C_q= $9.47*10^{-38}$ F. In the same case for the defected and H_2O sensed GNR, the quantum capacitance at -0.145 eV, C_q is $10050*10^{-38}$F and at 0.3 eV, C_q is $126*10^{-38}$ F which are much more higher than that of non-H_2O defected GNR. The density of states (DOS) was highest at -0.1 eV and 0.25~0.26 eV.

Hence, it is clear that, quantum capacitance increases with respect to DOS while Graphene can sense gas[14].

4. CONCLUSION

As the quantum capacitance varies, so does the carrier concentration. Future studies will concentrate on determining whether or not gas-molecule doping can enhance electronic aspects like I-V characteristics.

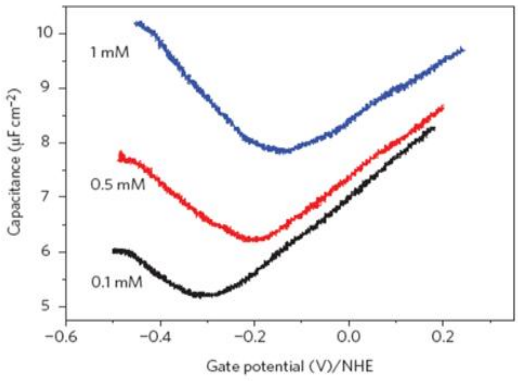

Figure 3. Capacitance of GNRFET[13]

The quantum capacitance corresponding to gate voltage is plotted in Fig. 3 using the capacitance model that was obtained.
In order to better understand the quantum capacitance of GNRFET based sensors, certain significant properties of the C-V characteristics can be explored in the future employing faulty Graphene that can sense gases (CH4, H2O) and obtain changed DOS.

Quantum capacitance of graphene sensing gases has been studied in the aforementioned work by varying the DOS of graphene. A donor (CH4) and an acceptor (H2O) gas molecule are present in this type of non-ideal graphene. The quantum capacitance has a linear dependence on potential on either side of the minimum, leading to a significantly different and enhanced value (for non-ideal, defective graphene) with gas sensing and doping features.

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