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Simulations of Propane and Butane Gas Sensor Based on Pristine Armchair Graphene Nanoribbon

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Abstract. Over the last decade graphene and its derivatives have gained a remarkable place in research field. As silicon technology is approaching to its geometrical limits so there is a need of alternate that can replace it. Graphene has emerged as a potential candidate for future nano-electronics applications due to its exceptional and extraordinary chemical, optical, electrical and mechanical properties. Graphene based sensors have gained significance for a wide range of sensing applications like detection of biomolecules, chemicals and gas molecules. It can be easily used to make electrical contacts and manipulate them according to the requirements as compared to the other nanomaterials. The intention of the work presented in this article is to contribute in this field by simulating a novel and cheap graphene nanoribbon sensor for the household gas leakage detection. QuantumWise Atomistix (ATK) software is used for the simulations of propane and butane gas sensor. Projected device density of the states (PDDOS) and the transmission spectrum of the device in the proximity of gas molecules are calculated and discussed. The change in the electric current through the device in the presence of the gas molecules is used as a gas detection mechanism for the simulated sensor.

1. Introduction

The discovery of graphene has quickly sparked the interest of researchers due to its tremendous promising and unique attributes. The exceptional properties and nontoxic nature of graphene are making it a potential candidates for future electronics applications [1]. Graphene is a single layer of carbon atoms having thickness of 0.35-1.6 nm with a honeycomb lattice structure of sp²-bonded carbon atoms. It is a two dimensional material with Dirac cones. In graphene lattice, C-C bond length is 1.42 Å and the lattice constant is 2.46 Å. The electronic structure of graphene can be explained by tight-binding approach [2]. Graphene is so called a zero-gap semiconductor [3] which has the possibility to tune its band gap [1]. The unique band structure of graphene give rise to exceptional high electron mobility. It has been reported that the charge carrier transport in the graphene remains ballistic up to 0.3 μm at 300 K. It is highly sensitive to any chemical change in its surrounding environment. Every carbon atom in graphene provides the greatest surface per unit volume and makes mobility of the charge carriers highly sensitive to the adsorbed molecules. Another interesting quality of graphene is its intrinsically low electrical noise due to high quality of crystal lattice. This property makes it highly suitable for ultra high sensitive chemical detection applications [4].



Graphene is being used for high frequency electronic application, field effect transistors, and transparent conductors. Recently graphene based biological and chemical sensor has gained significant importance [5]. Graphene is also emerging as a potential candidate for sensor applications in nano-electronics. Graphene is being used for the detection of gases, biomolecules and heavy metal ions. The adsorption and desorption of gas molecules change the conductivity of the graphene. These gas molecules act as acceptors or donors when they approach the graphene and ultimately they change the conductance of the graphene. The change in the electrical conductance of the graphene nanoribbon is taken as a detection signal for the gas molecules. Molecules of different gases affect the conductance of the graphene differently. So a large number of gases can be detected by using graphene [6]. In this paper pristine armchair graphene nanoribbon based sensor has been simulated for the detection of household alkane group gases like propane (C_3H_8) and butane (C_4H_{10}). To the best of author's knowledge only one closest reference [7] has been found that deals with the usage of the nanotubes for the detection of natural gases that are detected in this paper. In the presence of these gases, change in current through the armchair nanoribbon has been used as a gas detection signal. These simulations are to estimate the device behaviour before physical fabrication experiments of household gas leakage detection sensor.

1.1. Graphene nanoribbons

Different synthetic techniques are being used to synthesize a versatile family of graphene based materials with distinct properties. Graphene nanoribbons belong to the graphene materials family that are highly suitable for sensor applications. The electronic properties of the graphene nanoribbons change from semiconductors to spin-polarized half metals. Graphene nanoribbons are obtained from the unzipping of carbon nanotubes (CNTs) [8]. Depending on the termination pattern of the edge, graphene nanoribbons are divided into two types: armchair edge graphene nanoribbon (AGNR) and zigzag edge graphene nanoribbon (ZGNR). GNRs tend to repeat their geometric sequence to form periodic structures as shown in figure 1 [3].

It has been reported that the bandgap of GNRs changes with the number of carbon atoms constituted by them. It means that the electronic and the magnetic properties of nanoribbons are a function of the length of the ribbons. The bandgap of armchair nanoribbons gradually decreases as the number of carbon atoms increase in the ribbon as shown in figure 2(a). The bandgap of zigzag nanoribbon also tends to decrease gradually for odd and even number of carbon atoms differently in the ribbon as shown in figure 2(b) [9].

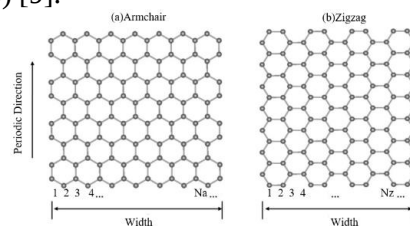


Figure 1. Armchair and zigzag graphene nanoribbons.

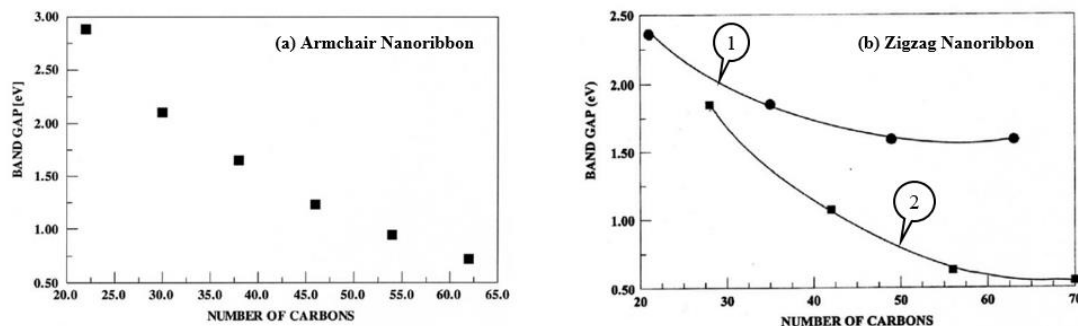


Figure 2. Plots of bandgap energies vs number of carbon atoms for armchair and zigzag graphene nanoribbons where curve 1 is for odd and 2 is for even number of electrons.

Many theoretical studies such as density functional theory (DFT), tight-binding calculations and many-electron Green's function approach have been done for the investigation of the electronic properties of the graphene nanoribbons. Most of the theoretical studies have been done by using DFT calculations method [3]. In order to enhance the sensing capabilities of graphene, usually it is functionalized by a functional group. Mostly hydroxyl (-OH) and carboxylic (-COOH) groups are used as functional groups for the graphene. In addition, many kinds of chemical moieties such as hydroxyl or alkyl groups can be introduced onto graphene surfaces by adding oxidizing agents. Furthermore, amino groups (-NH₂) and sulfonate (-SO₃) groups can also be introduced into the graphene. These functional groups act as a chemical handlers to graft different polymers and proteins by creating covalent bonds with them. Hence, in this manner the sensing capabilities of the graphene is increased by covalent bonding [5]. In spite of the stability and the effectivity of covalent strategies, this method is avoided. Because, it unavoidably changes the inherent electronic properties of the graphene by converting sp² hybridization of carbon atoms to sp³ hybridization. So, in order to preserve the intrinsic electronic properties of the graphene; non-covalent modifications to graphene are commonly used [5].

2. Methodology

QuantumWise Atomistix (ATK) software package has been used for the simulations of the gas sensor based on pristine armchair graphene nanoribbon. ATK software package has a graphical user interface called virtual nano lab (VNL). VNL has been used to simulate the structure of graphene based nano sensor as shown in figure 3.

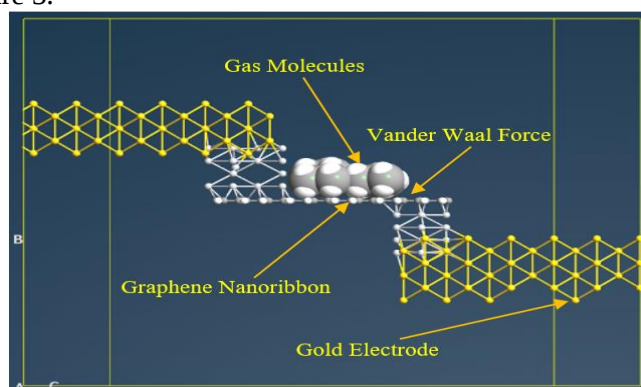


Figure 3. Simulated structure of armchair graphene Nanoribbon based propane and butane gas sensor.

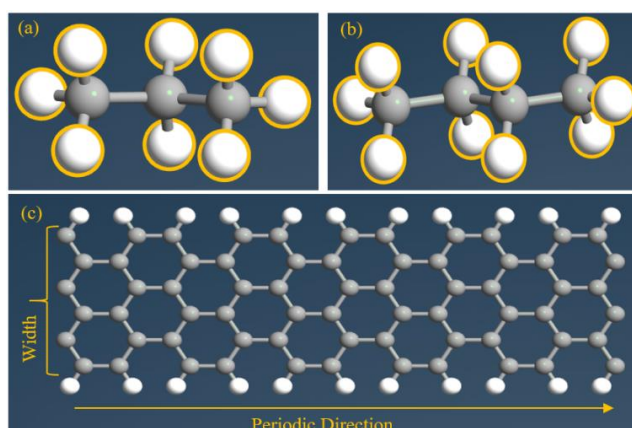


Figure 4. Simulated structure of (a) propane; (b) butane; (c) armchair graphene nanoribbon in ATK.

The Gas molecules are interacting with the armchair graphene nanoribbon by Van der Waal Forces in these simulations. Whereas gold electrodes have been deposited on the nanoribbon for

characterization of the sensor by applying external voltages. In order to reduce computational time in the simulator; four molecules of the propane gas, four molecules of the butane gas, and two-two molecules of both propane and butane gases are detected by the graphene nanoribbons in three individual experiments. The length of armchair graphene nanoribbon in the simulated device along the periodic direction is 21.31 Å and width is 8.05 Å in figure 4(c). The white balls indicate hydrogen atoms and black balls represent carbon atoms in figure 4(a), (b) and (c).

2.1. Calculation methodology of the ATK-DFT calculator

ATK software has different types of inbuilt calculators to solve Schrödinger equation. ATK-DFT calculator has been used for the simulations presented in this paper. Mathematical formalism [10] used by the ATK-DFT calculator has been explained in this subsection. ATK is a nano-level device simulator that is used to model open and closed systems within the domain of the density functional theory (DFT). Density matrix is the key parameter for the calculations of the Kohn-Sham equations. This density matrix defines the electron density. A non-equilibrium Green's Function (NEGF) is used to calculate the density matrix for open system. Whereas for closed systems diagonalisation of the Kohn-Sham Hamiltonian equation is used to calculate the density matrix. The effective potential set up by the electron density is given by the Hartree, the external potential and the exchange correlation. Then effective potential is used to get the Kohn-Sham Hamiltonian. Electronic structure of a system can be given by one-electron Kohn-Sham Hamiltonian as follows:

$$H1e = -\frac{\hbar^2}{2m}\nabla^2 + V^{eff}[n](r) \quad (1)$$

In equation (1), the first term indicates the kinetic energy of electron whereas the second term indicates the potential energy of electrons moving in the electrical field created by the external potential. Total electron density can be given by, $n = n(r)$. After this one-electron Schrödinger equation is solved to get the eigen-functions of the Kohn-Sham Hamiltonian as:

$$H1e\Psi_\alpha(r) = \varepsilon_\alpha\Psi_\alpha(r) \quad (2)$$

Equation (2) is called a Kohn-Sham equation with the density functional theory (DFT). This is solved by expanding eigen-functions in a set of basis function, Φ_i :

$$\Psi_\alpha(r) = \sum_i c_{\alpha i} \Phi_i(r) \quad (3)$$

Now the differential equation can be represented as a matrix equation to determine the expansion coefficients, $c_{\alpha i}$:

$$\sum_j H_{ij}c_{\alpha j} = \varepsilon_\alpha \sum_j S_{ij}c_{\alpha j} \quad (4)$$

In equation (4), the Hamiltonian matrix H_{ij} and the overlap matrix S_{ij} are given by the multiple integrals with respect to the electron coordinates. Now finally the electron density of many-electron system can be given by the eigenstates of the Kohn-Sham Hamiltonian, thus:

$$n(r) = \sum_\alpha f_\alpha |\Psi_\alpha(r)|^2 \quad (5)$$

In equation (5), f_α is the occupation of level which has been denoted by α . Then finally the electron density can be given in terms of the density matrix as follows:

$$n(r) = \sum_{ij} D_{ij} \Phi_i(r) \Phi_j(r) \quad (6)$$

3. Results and discussion

This section contains the results and discussion of the simulations of gas sensor. The transmission spectrum and projected density of states of the device at zero bias condition are given and discussed. Furthermore, the graphs for the change in the current through the device in the proximity of the propane and the butane gases are also discussed in this section.

3.1. Projected density of the states of the device

The projected density of the states (PDOS) versus energy of the graphene nanoribbon based gas sensor is shown in figure 5. It can be clearly observed from these plots that many energy states are available to be occupied below and above the fermi level. The Projected density of the states are indicating the presence of many energy states around the fermi level. Comparison of the density of the states (DOS) with respect to corresponding energy values of the device reveals a considerable difference in DOS.

Figure 5(a) is the density of the state of the sensor in the absence of any gas while (b) is the DOS in the presence of the propane gas. It can be seen in figure 5(a) that there are three sharp peaks appearing at the energy levels of approximately 1.2 eV, 1.7 eV and 2.4 eV. Whereas in figure 5(b) the presence of propane gas has influenced the DOS of the device. Hence, there is only one sharp peak is appearing at the energy level of 1.2eV in this graph as compared to figure 5(a).

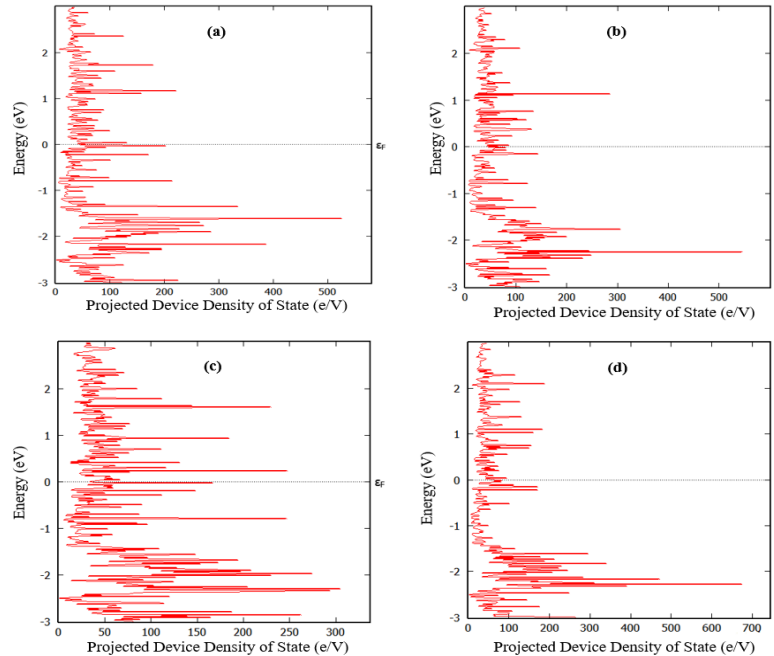


Figure 5. Projected density of the states of the simulated sensor vs. energy where (a) graphene sensor without gas; (b) sensor with propane gas; (c) sensor with the butane; (d) sensor with propane and butane gas.

Comparison of the DOS of the device in the presence of butane gas in figure 5(c) with the sensor in the absence of gas in figure 5(a) reveals that a lots of energy states have been added by the butane gas. Many sharp peaks of the density can be seen above and below the Fermi level as compared to figure 5 (a) and (b). Finally the density of the states of the device under the joint influence of the propane and the butane gases are shown in figure 1(d). It can be observed in this graph that the energy states have been modified differently as compared to figure 1(b) and (c). These modifications in the density of the states by these gases have a strong influence on the electrical conduction properties of graphene based gas sensor.

3.2. Transmission spectrum of the device

Transmission spectrum of the device is calculated to analyse the contribution of different energy levels in the total transmission of the charge carriers through the device [11]. The plots of the transmission as a function of the energy are shown in figure 6 and 7. It can be seen in figure 6 that for the same energy levels, the value of the transmission is different for the different gases. In the absence of any gas at energy level of $E = -1.32$ eV, the value of transmission is 0.606 for the sensor as shown in figure 6(a). Whereas for the same energy level, the value of the transmission for the device in the proximity of the propane gas is 0.0046, as shown in figure 6(b).

Similarly in figure 6(c); the value of transmission as a function of the same energy level is 0.00034 in the presence of butane gas. This value of transmission is quite different from the values that are shown in figure 6 (a) and (b). At $E = -1.32$ eV, in the presence of the propane and the butane gases the transmission value is 0.0486 as shown in figure 6(d). So, it is clear from these results that the presence of different gases alters the value of the transmission of the charge carrier through the device for the same energy levels.

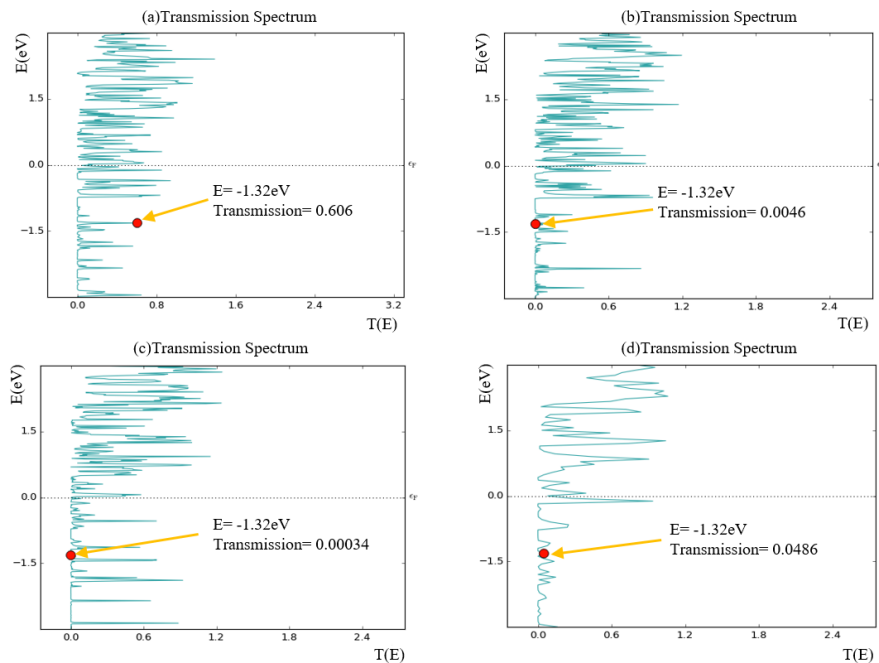


Figure 6. Transmission spectrum as a function of energy of simulated sensor at different energy levels (a) in the absence of gas; (b) with propane gas; (c) with the butane gas; (d) with the propane and butane gas.

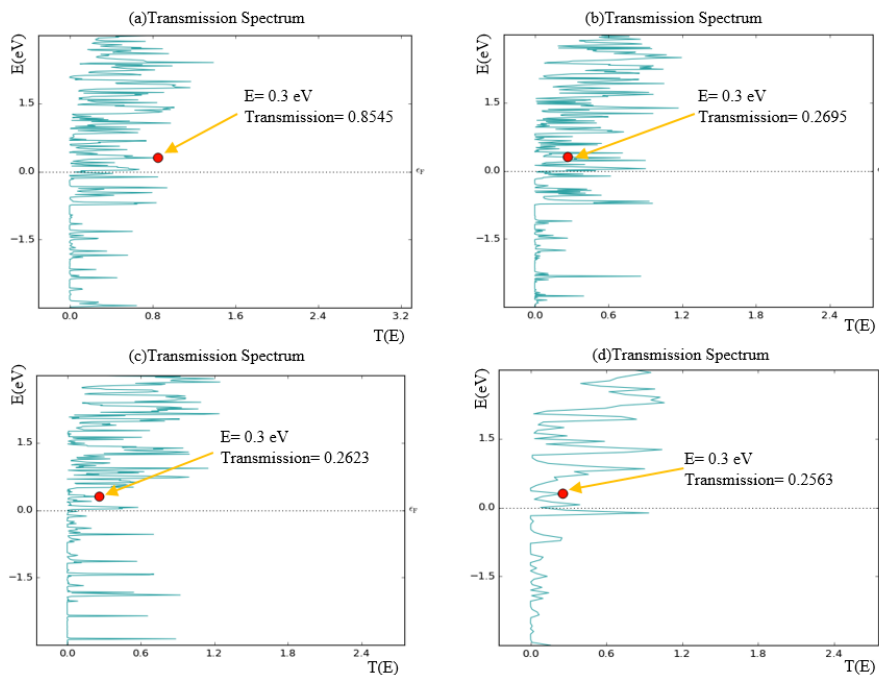


Figure 7. Transmission spectrum as a function of energy of simulated sensor at different energy levels (a) in the absence of gas; (b) with the propane gas; (c) with the butane gas; (d) with propane and butane gas.

Furthermore, the transmission spectrum at different energy levels of the same device in the presence of the same gases is also presented in figure 7. It can be observed in figure 7 (a) that at energy level $E = 0.3$ eV, the value of transmission is 0.8545 in the absence of any gas. While, for the same energy level for the propane gas the value of transmission is 0.2695 in figure 7(b). For the same energy level, in the presence of the butane gas transmission is 0.2623 as shown in figure 7(c). Whereas

the transmission is 0.2563 at the same energy level in the presence of the butane and the propane gases as shown in figure 7(d).

3.3. Current-voltage curves of the device

The electrical conductivity of the majority of the graphene based gas sensors changes in the presence of foreign gas molecules. This change in the conductivity is used as a gas detection mechanism in the graphene based gas sensors [4]. The same principle has been used to develop the propane and the butane gas sensor based on the armchair graphene nanoribbon in our simulations. DC bias voltages are applied at the electrodes of the simulated sensor to obtain the current-voltage (IV) curves. These simulations are done in the absence of any gas, in the presence of the propane gas, in the presence of the butane gas and in the presence of both propane & butane gases to obtain different IV-curves. These IV-curves are shown in figure 8. The Curve 1 in figure 8 is representing the current through the simulated device when there was no gas in the proximity of the sensor. It can be observed that the device is showing almost resistive behaviour in all cases. Curve 1 is revealing that the device starts to conduct immediately even at a very low bias voltage. In the absence of any gas, the IV-curve of the device is almost linear with the high current flowing through the device.

Curve 2 in figure 8 is obtained in the presence of the propane gas molecules. It can be observed in this curve that the presence of the propane gas molecules has reduced the current through the device as compared to curve 1. The adsorbed gas molecules act as donors or acceptors for the graphene and change its conductivity [4]. Graphene shows ultrahigh sensitivity in the presence of the foreign gases because the pristine graphene is inherently a low noise material. The presence of gases near the graphene introduce electrical noise and disturbs its electronic cloud. As the conductivity of the charge carriers through the device depends on the number of charge carriers and their mobility. So, the presence of the propane gas may have changed the number of the charge carriers or their mobility in the graphene nanoribbon. Due to which Curve 2 is showing a decrease in current through the device. The change in charge carriers concentration, changes the current through the device and acts as a governing mechanism for the conductivity of the device [4, 5].

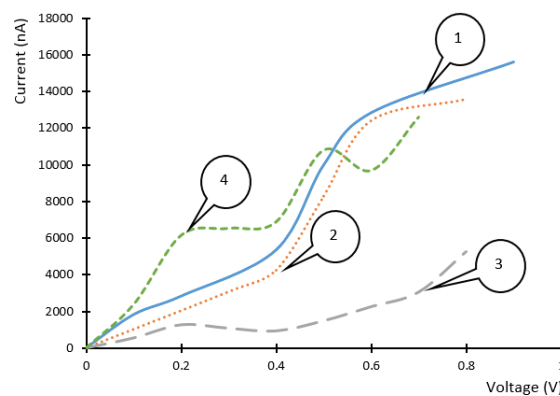


Figure 8. Current-voltage curves of simulated armchair graphene Nanoribbon based gas sensor where curve (1) in the absence of gas; (2) with propane gas; (3) with butane gas; (4) with propane and butane gas.

Furthermore, in the presence of the butane gas a significant reduction in the current through the sensor is observed as shown in Curve 3 in figure 8. The possible reason of this reduction in the current can be the decrease in the number of the majority charge carriers and their scattering by the butane gas molecules [8]. An interesting behaviour of IV-curve is observed in Curve 4 in figure 8 when the both propane & butane gases were in the proximity of the device. It can be observed from this curve that the current through the device has increased significantly. In addition to the electric current, the nonlinearities in this IV-curve 4 are also increased. The reason of this increase in the electric current up to a certain voltage level and then decrease could be due to the joint influence of the scattering process provoked by these both gases.

4. Conclusion

The objective of the current work is to simulate the graphene nanoribbon based sensor for the leakage detection of household gases and estimate device behaviour before physical fabrication. The nanoscale simulations of the gas sensor are done successfully with the QuantumWise Atomistix software. The results of these simulations revealed that the graphene is highly sensitive to the change in its surrounding environment. The presence of the gases in the proximity of the graphene device strongly influenced its density of the states, the transmission spectrum and the electric current, when propane and butane gases were in its proximity. The reasons of this change in the conductivity are an increase or decrease in the charge carriers and/or their mobility caused by the adsorbed gas molecules on the surface of graphene. A decrease in the current through the sensor is observed when propane and butane gases are interacting with it individually. But when both gases are interacting simultaneously with the graphene, an increase in the current and the nonlinearities are observed. This change in the conductivity through the device can be used as a gas detection signal for sensor applications. Although the graphene is a potential candidate for sensor applications in future electronics, but there are still a large number of technical challenges that need to be addressed. These challenges are the selectivity of graphene to detect the specific gases, reliability and the cost of the device. Further investigations are required to improve the performance of our simulated graphene based gas sensor. For this purpose, more than one detection mechanisms can be used simultaneously (i.e. change in optical and electrical properties) to avoid errors in the sensor readings due to the contamination of undesired particles and the effect of the temperature in the sensing environment.

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