A Simulation Study of the Effect of Platinum Contact on CNT Based Gas Sensors Using Self-Consistent Field with NEGF Method

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Abstract—**The electronic structure of the π electrons of the CNT is highly affected by the presence of foreign molecules. This property can be utilized in CNT based gas sensing applications. In this work, we study bare zigzag CNT, NO_2 adsorbed zigzag CNT, and Pt contacted NO_2 adsorbed zigzag CNT to find the effectiveness of zigzag CNT and Pt in making a NO_2 gas sensor. We find that bare zigzag CNT is a good material for NO_2 detection and platinum make Schottky contact with zigzag CNT which can be used for gas sensing applications.**

Keywords-carbon nanotube; gas sensor; contact; ballistic; band-bending

I. INTRODUCTION

With technological advancements, several nanostructures and nano-scale devices hold the promise of a variety of novel applications. CNTFET devices, which employ carbon nanotubes (CNT) as the material for the channel region of a FET, have the potential of detecting various gas and biological agents. The target molecules bind with the CNT channel changing its conductance, by measuring change of conductance the amount of target molecule can be determined.

Due to the nanometer sized tubular structure CNTs have a large surface area, which gives them higher chance of getting bound with gas molecules. High concentration of gas molecules results in large change in the conductance of the channel due to the accumulated effects of all individual gas molecules. Experimentally, the conductance of single wire nanotube (SWNT) has been shown to change linearly as a function of NO_2 concentration [1].

For a particular gas adsorption, the change in conductance depends on the bandstructure of the CNT with attached gas molecule. For semiconducting SWNT of 1.8 nm diameter, exposure to NO_2 gas causes the conductance to increase three orders of magnitude as the tube becomes more p-type. However, after NH_3 adsorption, the conductance of the same tube drops by 100 times as the tube become more intrinsic, as in [2].

It is important to obtain the current-voltage relationship of CNT devices, for better understanding of conduction through such devices or to model the behavior of such devices. Currently, no experimental data is available for the dependence of current on the bias voltage across only the CNT channel.

In short-channel CNT devices, the contact resistance affects the overall resistance significantly due to the shortening of the channel length. A mismatch between simulation and measured subthreshold slope of 9 nm CNTFET indicates the lack of understanding of the theory of conduction through metal-CNT interface [3]. Reports of different metal contacted CNT have shown that upon gas adsorption the contact resistance also changes in addition to the channel resistance. In some cases, the change in the contact resistance may be the dominant one [4].

In this work, we study the current-voltage relationship of bare zigzag (10,0) CNT, NO_2 adsorbed (10,0) zigzag CNT and platinum contacted NO_2 adsorbed (10,0) zigzag CNT. The study is aimed at understanding effect of adsorption of NO_2 and Pt contact on the I-V characteristics. Ballistic transport is assumed by ignoring all scattering of electrons. We have chosen (10, 0) zigzag CNT as it is a semiconducting nanotube with 0.94 eV bandgap. Having a considerable amount of bandgap, this nanotube is expected to be very sensitive to NO_2 and platinum.

II. SIMULATION MODEL AND PARAMETERS

We have used ATOMISTIX TOOLKIT package for the simulation [5]. This tool calculates electronic wavefunction using either Density Functional Theory (DFT) or extended Hückel Theory (EHT), which are two self-consistent field methods and uses Non-Equilibrium Green's Function (NEGF) to obtain the density matrix. The current is calculated from the electronic wavefunction using Wave-Function Matching (WFM) technique.

Density Functional Theory (DFT) is an *ab initio* method to calculate electronic wavefunction with some approximations [6]. Since the exact exchange-correlation (XC) of electrons is not known, the local density approximation (LDA) is used as the best option in its place. Moreover, Kohn-Sham one electron wavefunctions are used which cannot describe many body effects in the system.

The work was sponsored by Defence Research and Development Organisation, India, through grant no. DRD-587-ECD

ISBN 978-0-615-71756-2

Extended Hückel Theory (EHT) is a semi-empirical approach to calculate electronic wavefunction using a model Hamiltonian and basis set with adjustable parameters as discussed in [7]. As all the parameters are consistent with the experimental data, EHT often gives result which agrees well with the experiments.

In Wave-Function Matching (WFM) technique, the transmission and reflection coefficients are calculated by matching the left or right going wavefunctions of boundary layers of device with the bulk modes of the electrodes, as in [8]. To obtain the transmission coefficient, the wavefunction of the layer before the right electrode is equated to the right going bulk modes of the right electrode multiplied by transmission coefficient. To obtain the reflection coefficient, the wavefunction of the layer after the left electrode is equated to the sum of right going bulk modes of the left electrode multiplied by right going Bloch factor and the left going bulk modes of the left electrode multiplied by reflection coefficient. From the transmission coefficient of each modes we can calculate the transmission spectrum $T_n(E)$.

Now, we can use Landauer-Buttiker formulism [9] to calculate the current from left to right electrodes,

$$I_{LR} = -\frac{e}{\pi h}\int_{-\infty}^{+\infty}\left(\sum_n [f_L(E) - f_R(E)]T_n(E)\right)dE \quad (1)$$

where $f_L(E)$ and $f_R(E)$ are Fermi functions of left and right electrodes respectively.

The Density Functional Method is used to simulate bare Zigzag (10,0) CNT with double zeta polarized (DZP) basis set and local density approximation (LDA). The structure simulated is shown in Fig. 2a has four unit cells long (17.05 Å) and the diameter of nanotube is 7.84 Å. The extended Hückel theory is used to simulate NO_2 adsorbed Zigzag (10,0) CNT and Pt contacted NO_2 adsorbed Zigzag (10,0) CNT. The equilibrium adsorption distance between NO_2 and CNT is simulated and found to be 2 Å. We have used (111) face of fcc Pt as the contact. The Pt contact has three layers of Pt atoms and the total width of the contact region is 6.79 Å. The distance between Pt contact and CNT end is 1.84 Å. The length of the contact is sufficient to avoid truncation of wave-function as the interaction radius for Pt basis set is shorter than contact length. The basis set used for carbon is cedra graphite, and that used for nitrogen, oxygen and platinum are Hoffman basis set. Wave-function matching technique is used for the calculation of transmission spectrums for each bias point.

III. Results and Discussion

The density of states of bare zigzag CNT is shown in Fig. 1. It has a very high bandgap of 0.94 eV between the π orbitals in the valence band and the π* orbitals in the conduction band. In Fig. 2b, the I-V characteristic of bare zigzag CNT is shown. In the structure the carrier density is very low due to its high bandgap and small current flows. At significantly high bias (nearly 1V), the band bending across the structure is high enough to allow direct tunneling from conduction to valence band and significantly high current flows.

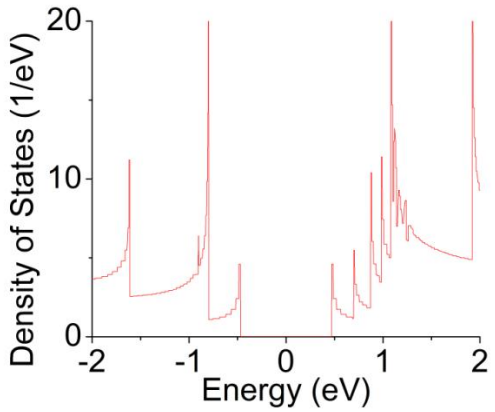

Figure 1. Density of states of bare zigzag (10, 0) CNT.

It is important to investigate how the current depends on the channel length. In the absence of gate electrode, for fixed bias across it, a homogenous CNT channel will have equal amount of band-bending for equal lengths. The slope of the bands will be given by,

$$\text{slope} = \frac{qV}{L} \quad (2)$$

where V is the applied bias and L is the length of the channel. Thus, if length is scaled by 2, the applied voltage will scale by 0.5. From this relationship, we can obtain the current-voltage relationship of any length of CNT given the relationship for a particular length.

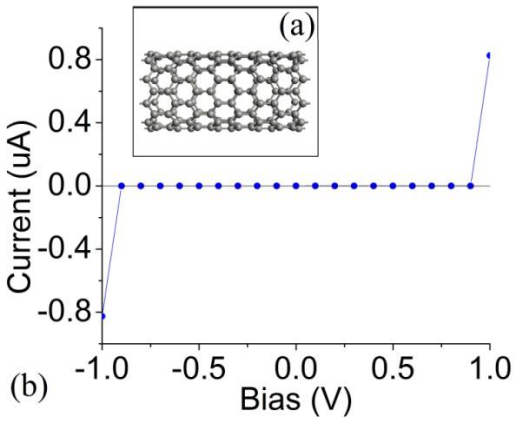

Figure 2. (a) Structure of bare zigzag (10, 0) CNT, and (b) I-V characteristics of bare zigzag (10, 0) CNT.

The density of states of NO_2 adsorbed zigzag CNT shown in Fig. 3 has a state lying exactly on top of the Fermi energy.

This state appears due to the weak bonding orbital between NO_2 and CNT.

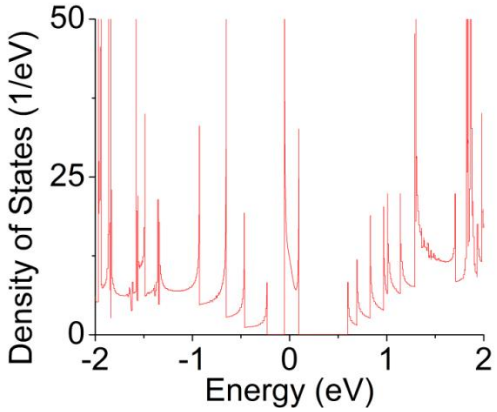

Figure 3. Density of states of NO_2 adsorbed zigzag (10, 0) CNT.

At different biases, this state can spatially couple with other electronics states. As shown in Fig. 4a, it couples with another CNT-NO_2 boding state. In Fig. 4b and Fig. 4c, it couples with bonding π orbitals, anti-bonding π* orbitals of CNT respectively. In Fig. 4d, it does not couple with any orbital at all.

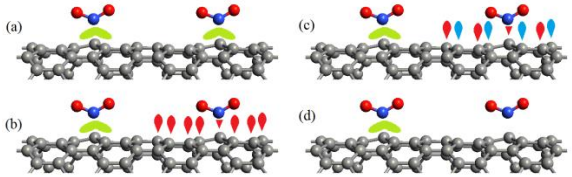

Figure 4. The CNT-NO_2 bonding state coupling to (a) other CNT-NO_2 bonding state, (b) bonding π orbital, (c) anti-bonding π* orbital, and (d) no other state.

The coupling of CNT-NO_2 state with other state depends on the applied bias across the structure. Whenever the CNT-NO_2 bonding state can couple with other states at some particular bias, finite conduction occurs through it at that bias. But when it cannot couple with any other states no conduction occurs through it for the corresponding bias. In Fig. 5b, the I-V characteristics of NO_2 adsorbed zigzag CNT is shown. Thus, we see negligible current in the range 0.1 V – 0.3 V. We also see a negative differential conductivity region in 0.4 V – 0.6 V range due to diminishing conduction peaks. At the high bias range, current increases again due to high amount of tunneling.

When Pt forms contact with the CNT, it is expected to form maximum number of bonds with the carbon atoms to make a good contact. The (111) face of Pt has maximum number of Pt atoms on its surface and thus is suitable for making contact with CNT. However, only one layer of this Pt surface is not sufficient, as the carbon wavefunctions may go past the position of one layer Pt atoms.

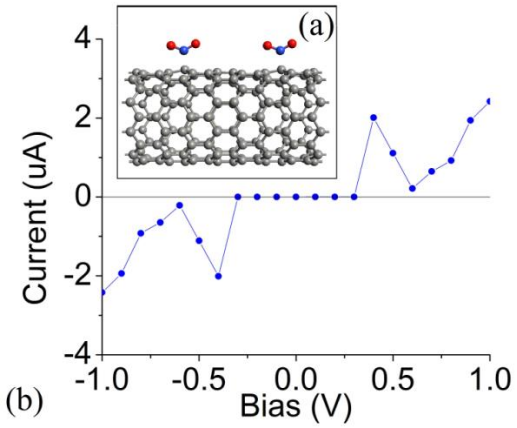

Figure 5. (a) Structure of NO_2 adsorbed zigzag (10, 0) CNT, and (b) I-V characteristics of NO_2 adsorbed zigzag (10, 0) CNT.

The I-V characteristics of Pt contacted NO_2 adsorbed zigzag CNT is shown in Fig. 6b. The I-V characteristics of this junction are similar to the I-V characteristics of a Schottky barrier diode and Pt acts like an anode.

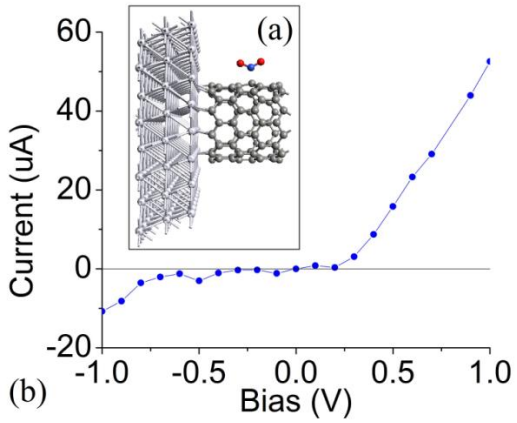

Figure 6. (a) Structure of Pt contacted NO_2 adsorbed zigzag (10, 0) CNT, and (b) I-V characteristics of Pt contacted NO_2 adsorbed zigzag (10, 0) CNT.

The Pt d orbitals form both σ and π bonds with the nanotube. However due to the difference in the work function, CNT bands are realigned with respect to Pt bands and a potential barrier appears at the metal-CNT junction. However, in ballistic transport scenario, carriers cannot change their energy while propagating through a structure. Thus conduction through this metal-CNT contact is not a Schottky effect i. e. thermionic emission over the barrier. Rather, it is a tunneling phenomenon where electrons from one allowed energy level tunnels across the potential barrier to another allowed energy level. The transmission spectrum of the same structure, as shown in Fig. 7, indicates large hole current in forward bias and a small electron current in the reverse bias.

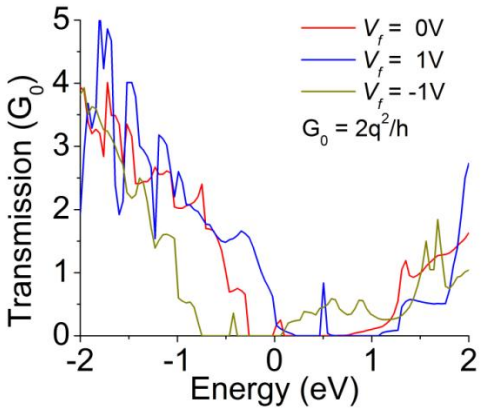

Figure 7. Transmission spectrum of Pt contacted NO_2 adsorbed zigzag (10, 0) CNT at bias V_f = 0V, 1V and -1V.

IV. CONCLUSIONS

In this study the band structure and transport properties of zigzag CNT for gas sensing applications are investigated. The study shows that the bare zigzag CNT remains almost non-conducting upto very high bias. However, after NO_2 adsorption, its conductance increases significantly, turning it p-type. Thus, bare zigzag CNT is a very good material to use as the channel for NO_2 sensor. The introduction of Pt contact makes the structure to have exponential I-V characteristics like a diode. But, due to high tunneling current through the contact region, it will have very small voltage drop across it. So, Pt can easily be used as the contact material.

ACKNOWLEDGMENT

The authors would like to thank Dr. Murlidharan and Dr. P K Chaudhary of SSPL New Delhi for useful discussion and their support during this work.

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