Modeling the Charge Transport through Graphene Nano Ribbon (GNR) Between Electrodes of Different Materials

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ABSTRACT: In this paper, we analyzed the influence of changing the material of electrodes on the transport properties of single junction comprising GNR (Graphene Nano Ribbon) stringed to two semi-infinite electrodes using semi empirical model. The investigation of electron transport through GNR was accomplished by linking it to different metallic electrodes (Pt, Au and Ag) under different bias voltages within Keldysh's non- equilibrium Green Function formulism (NEGF) using Extended Huckel (EHT) semi empirical approach. The simulated results revealed that among different electrode, the metallic electrodes showed maximum conductance of the order of 10^{-5}nS. By comparing the I-V curves obtained using different metallic electrodes , we perceived that platinum showed maximum conductance and silver showed transmission of current amidst strongest coupling and thus affirmed to be the most effective material for electrodes for nanometer scale molecular junctions, when compared with other metallic electrodes.

KEYWORDS: Non equilibrium Green's Function (NEGF), Extended Huckel Theory (EHT), GNR, Self-Assembled Mono layers (SAM), ATK 12.2.0, Virtual Nano Lab,

1. INTRODUCTION

Since the report of the preparation of graphene by Novoselov et al. [1] in 2004, there has been an enormous and rapid growth in interest to the semiconductor industry because this material is compatible with planar technology. Graphene has attracted intensive interest due to its fundamental properties and potential applications in future electronic devices.

The advancements in the semiconductor fabrication techniques led to the study of electron transport through hetero junctions comprising of single organic molecule stringed to side electrodes, which alleviated into an important area of research called molecular electronics. Molecular electronics, or Moletronics established itself as a key area of research for many physicists, engineers, quantum chemists and many more researchers due to following reasons [2].

The size of the molecule is inherently in the range of 1nm to 100nm, so the nanostructures of all dimensions can be implemented with these molecules, which would have the advantage of low cost, low power dissipation and technological superiority.Certain molecules have several isomers and thus having different geometries. These variations in geometry cause significant variations in electrical properties of molecules which has been the field of interest for many researchers.

The self- assembled mono layers (SAM) will be the active components in electronic circuits as intermolecular interactions can be studied, thus providing varying transmission behavior leading to both switching and sensing capability.Moreover molecular electronics finds applications in processing and storage of information and biological applications as well. The molecular devices can interact directly with the molecules within the cell, and thus can be used for studying various processes within the cell [3].The instability at high temperatures and the lack of robustness associated with the organic molecule based electronic devices are the two biggest causes of concern for implementation in real time applications

2. THEORETICAL BASIS AND COMPUTATION METHOD

Both theories Density Functional Theory (DFT) and Extended Huckel Theory (EHT) had been worked upon by the various researchers for elucidating the electronic transport through single molecule junctions. Our computational approach has been based upon Hartree –

Fock (HF) method approximation for the determination of the ground-state wave function and ground-state energy of a quantum many-body system along with Keldysh's Non Equilibrium Green's Function (NEGF) Formalism combined with Ronald Hoffmann's tight binding approach Extended Huckel Theory (EHT). No doubt Density functional theory had been comprehensively used by researchers in the past, but EHT due to its simplicity and speed has gained much attention. EHT has been effectively employed to determine the molecular orbitals and relative energy of different geometrical configurations neglecting certain non-elastic scattering like electron-electron repulsions and expressing energy just as the sum of terms for each electron in the molecule. The off-diagonal Hamiltonian matrix elements are calculated using Wolfsberg and Helmholtz approximation that relates them to the diagonal elements and the overlap matrix element

$$Hij = KSij (Hii + Hjj)/2 \quad (1)$$

K is the Wolfsberg-Helmholtz constant, and generally has a value of 1.75.

The results produced using semi-empirical EHT were accurate enough to explain the electron transport phenomenon through single molecular junction. The NEGF [4-8] combined with EHT forms the basis for our model in this research work.

In our suggested model based on two probe method, a Graphene Nano Ribbon (GNR) is stringed to two semi-infinite electrodes. The commercial simulation package for nano scale electron transport adopted for our modeling and simulation is Atomistix Toolkit ATK 12.2.0 [9] which is based on self-consistent field method (SCF) along with Density Functional Theory (DFT) and Non-Equilibrium Green's Function (NEGF) techniques. ATK and its metamorphic user interface Virtual Nano Lab was employed to calculate the electron transport properties of GNR by first defining coupling between the molecule and the other atoms of electrodes using Green's Function approach [10] as given by

$$G(E) = 1/[ES - F - \sum_L(E) - \sum_R(E)]. \quad (2)$$

Where F is the Fock matrix of the molecule, S is the overlap matrix, and $\sum_L(E)$, $\sum_R(E)$ are self-energies that explain the couplings to the contacts [10]. The self-energies are given by the following equation

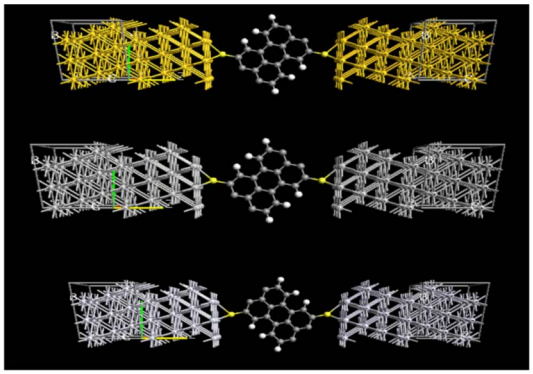
$$\sum(E) = \tau\, T\, gs(E)\, \tau \quad (3)$$

Where τ is the matrix that defines the coupling between the molecule and the atoms of the contacts, gs(E) is a matrix representing surface green's function for semi-infinite bulk metal. Then transmission spectrum and I-V curves can be assimilated.

3 MODELING & SIMULATION

The modeling setup is based upon two-probe model consisting of left and right semi-infinite electrodes that acts as source and drain of a conventional transistor and the scattering region constituting of the Graphene Nano Ribbon (GNR). In this case, we sandwiched GNR molecule by connecting it to the various metallic electrodes (Au, Ag, Pt) one by one (figure1) all having different chemical properties. Gold electrodes had been commonly used in single molecule junctions previously because of their stability in air. Both gold and platinum are highly non-reactive metals, while other metals like silver form their metal oxides which affect the conductance up to a large extent and offers large resistance to the transmission of current [11].

We optimized the geometry using Guassian-03, till the maximum stress as well as the force on the constraint atoms becomes 0.01eV ,then further modeling was done using Atomistic Toolkit ATK 12.2.0[9] and its graphical user interface Virtual Nano Lab and then finally enumerated the self- consistent approach for harmonizing transmission spectrum under variegated bias voltages ranging from -2V to 2 V with a step size of 0.5V as zero bias characteristics were not ample to figure out the quantum transport of electrodes through GNR. So Device, transmission spectra and I-V curves were obtained with each above mentioned electrodes under bias voltages ranging from -2 V to 2 V with a step size of .5V.



GNR sandwiched between a)gold b)silver c)platinum

The table (1) below shows values of various parameters that were defined before commencing the simulations.

sampling: nA: nB: nC	1:1:100
Absorption height	1.5 Å
Miller h:k:l	1:1:1
Length of left surface	7 Å
Length of right surface	7 Å

Table 1: Geometry optimization parameters

Electrode material	Average Fermi level(eV)
Au	-9.815937
Ag	-5.070062
Pt	-1.117746e+01

Table 2: Fermi levels for different electrodes at zero bias

4. RESULTS AND DISCUSSIONS

In this paper, we inspected the conduction properties of GNR by coupling it to different metallic contacts. Our objective for this research work was to compare the overall impact of metallic electrodes on nanometer scale electron transport through these molecular junctions and suggesting the optimal material of electrode to predict the transport properties of grapheme nano ribbon stringed to different metallic electrodes -gold, silver, platinum electrodes. We simulated I-V curves, transmission spectra, and conductance curves at various applied bias ranging from -2V to 2V with each electrical contact.

I-V curves

According to Landauer, the current through the junction occurs due to the elastic scattering of electrons between two electrodes. Thus the current calculated by the Landauer- Buttiker formalism [12, 13] is given by

$$I(Vb) = \frac{2e^2}{h}\int_{\mu L}^{\mu R} T(E, Vb)\,dE \ldots\ldots\ldots (4)$$

Where 2e2 / h is the quantum unit of conductance, T (E, Vb) is the transmission function, μL (Vb) = μL (0) + eVb/2and μR (Vb) = μR (0) + eVb/2 are the chemical potentials of the left/right electrodes, with μL, R (0) being the average Fermi level of the system without bias and Vb = (μL − μR)/e being the bias voltage.

The figure 2 shows the plots for the transmission current with respect to the applied bias voltage.

The maximum value of current was observed as 39.243μA for silver which stepped down to 33.654μA for platinum, whereas this value reduced to 27.201μA for gold (figure 2).

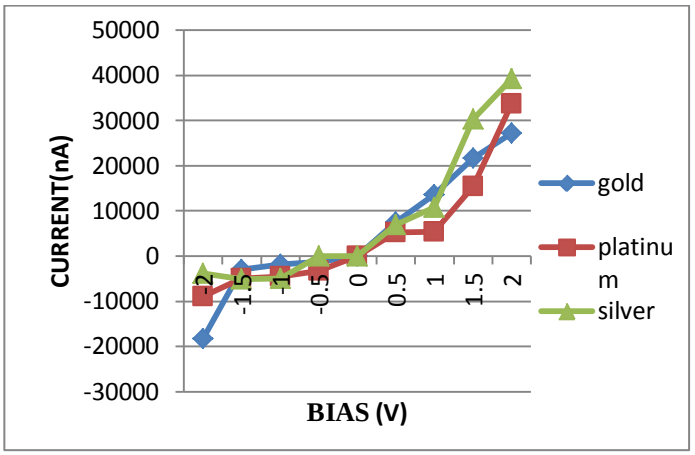


Figure 2: I-V Curves comparingdifferent metallic electrodes

a) Platinum: The I-V curves in (Figure 2) clearly demonstrated that this metal contact shows variations in the amplitude of current transmitted. The current remains approximately constant from -1.5v to -1v and 0.5 v to 1v, elsewhere it continues to increase with highest value of 33.654 μA . The current - voltage characteristics are dependent largely on the GNR and the electrodes. The Fermi levels, current transmission and band lining up of electrons change on changing the material of 2 semi-infinite electrodes.

b) Gold electrodes: Initially, the current increased with increase in bias, then with a slight negative differential resistance, the current again started increasing(figure 2 (b)). The linearity in I-V curve is observed till the current reaches value of 27.201μA.

c) Silver electrodes: Among metallic electrodes the most transmission of current is noticed with silver with highest value of 39.243μA.

According to Landauer, the total conductance of a ballistic constriction is equal to the quantized conductance G0 (=2e2/h) times the transmittance of all the Eigen channels present in the constriction, where the number of channels can be calculated by the chemical valence of the atom in the junction and the transmittance is proportional to the coupling between the atom and the electrode.

At -2V, gold electrodes depicted maximum value of conductance as 12.3μS which is 0.159G0,Platinum electrodes exhibited maximum conductance of 43.6 μS which is 0.56G0 (figure 3).
The maximum conductance recorded for silver was just 10.6 μS (0.14 G0) at the same voltage (figure 3).
So G/G0 < 1 in case of gold, platinum and silver indicated weak coupling of sulphur atom with these metallic contacts , so these electrodes are tunnelling contacts where electron transmission is non- coherent.

The conductance was scrutinized as a function of displacement current for each electrode (figure 3). The conductance initially decreased from approximately 1.00E-05 S to 1.00E-06 S with gold electrodes, increases from 1.00E-07 to 1.00E-05 S with platinum electrodes, from 1.00E-07 to 1.00E-06 for silver electrodes. So maximum conductance of 0.56 G 0 was recorded with platinum, 0.16G0 for gold ,while silver exhibited maximum conductance of 0.14G0 which justifies our result that platinum has more potential to be used as electrodes , than gold and silver.

There are many factors that influence the conductance of the molecular junction such as bonding of the molecule to the contacts and the geometry of molecule that has been used in the central region. The electronic bonding of the molecule to the contacts alters the orbital energy levels of the molecule.

TRANSMISSION SPECTRA

In the molecular junctions, coupling between the electrode and the molecule leads to overlapping of the hybridized orbitals and a change in HOMO-LUMO gaps leading to energy dissipation in the electrodes but no energy dissipation occurs in the molecule. So the electronic transport is affected by the coupling between the electrode and the molecule. In order to know which bias voltages supports strongest peaks or least HOMO-LUMO gaps, the transmission spectrum is plotted against bias voltages with energy ranging from -2eV to 2eV, 101 points and the energy zero parameter is adjusted as average fermi level.

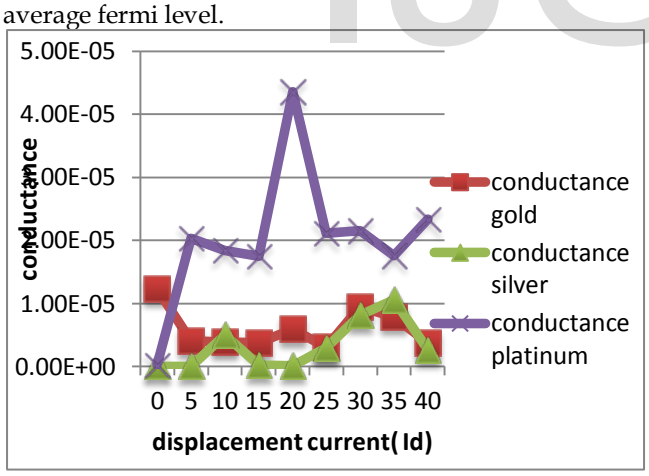


Figure-3: Conductance as function of displacement current comparing different metallic electrodes.

The transmission coefficient T(E) strongly associates the density of states between HOMO and LUMO. A significant change in the molecular orbitals, the occupied and gap states are noticed at different bias voltages. Different contacts showed significant variations in peaks and gaps at varying voltages. Sharp peaks in the transmission spectra correspond to the maximum transmission of electrons whereas flatness in the curves depicts large HOMO-LUMO gaps.

Platinum: Large number of peaks were observed at energies ranging from -2eV to 0.5eV whereas outside this range less perturbations were seen resulting into flatness in the curves corresponding to large band gaps beyond this bias range. The clustering of transmission peaks indicated strong to moderate coupling for these electrodes. So the platinum electrodes can selectively participate in conduction as well as tunneling under different bias conditions (figure 4(a)).

Silver: Large HOMO-LUMO Gaps were noticeable at all energies from -1.5eV to 1.5eV.peaks are observed between these levels, the transmission of electrons began and peaks were observed between -2eV and -1eV indicating narrowing of HOMO-LUMO gaps and hence the probability of tunneling. (figure 4 (b)).

Gold: GNR with gold electrodes showed maximum peaks for negative energy from -2eV to -1eV (figure 4(c)) as well as for positive bias 1eV to 2eV. Gold electrodes exhibited maximum transmission coefficient of above 2 which points towards the fact that anchoring atoms of GNR were strongly coupled to the gold electrodes. The regular appearance of transmission peaks indicated that Gold electrodes formed metallic contacts with the molecule under observation and hence conduction was possible virtually at every bias.

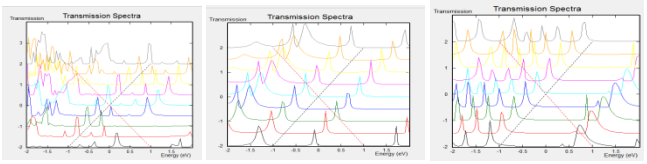


Figure 4: Transmission Spectrum for a) platinum b) silver c) gold

5. CONCLUSION

The variations in the electron charge transport properties of GNR were studied when the GNR is sandwiched between two metallic electrodes. The material of the electrodes was varied for different simulations. The order of the transmission of current with different metallic (Au, Ag, Pt) electrodes is: gold < platinum <silver and for conductance is: silver<gold<platinum. Among metallic electrodes, gold and platinum have great potential as choice for electrodes to be implemented in single molecule junctions.

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