Theoretical Investigation of Electronic Properties of Armchair Graphene Nanoribbon

Ritin Jhamb[1], Deep Kamal[2], Kaur Randhawa[3], Aseem Sharma[4]

Department of Electronics and Communication Engineering,
Guru Nanak Dev University, Regional Campus, Jalandhar, Punjab, India.
ritin.jhamb94@gmail.com

Abstract: **Graphene nanoribbons (GNRs) are prospective material for nanoelectronics. The current-voltage (I-V) characteristics and the transmission spectra of armchair graphene nanoribbon with different width configurations are investigated. It is shown that the I-V curve and the transmission spectra strongly depend upon the width of the nanoribbon. Thus it shows both metallic as well as semiconducting nature depending upon the width of the nanoribbon. The energy band gap between the valence and conduction band of the nanoribbon varies inversely with the width of the nanoribbon.**

1.   INTRODUCTION

Carbon is an abundantly available chemical element with atomic number 6. As a member of group 14 on the periodic table, it is nonmetallic and tetravalent—making four electrons available to form covalent chemical bonds. Carbon exists in everything from crude oil to DNA. There are about sixteen million compounds of carbon, more than for any other element. It is an incredible element. The single isolated carbon atom has ($1s^2 2s^2 2p^2$) configuration. 1s and 2s states are filled and two electrons are present in the 2p state. The two neighboring carbon atoms can form strong bonds through sp^2 hybridization involving the σ and π states with the latter involving the p_z orbitals which are directed perpendicular to the intersection line between the atoms[1]. Due to the high π - bonding energy, graphite is energetically slightly more stable than sp^3-bonded diamond-like structures under ambient pressure and temperature. The elements to the left and right of carbon in the periodic table (nitrogen and boron) can also form strong π bonds. But carbon is the only atom that has exactly four electrons in its valence shell and needs four bonds to attain a closed shell. Also, carbon has the ability to form anisotropic and stable 2D structures as compared to the other elements which form clusters in 3D.

Carbon has almost infinite number of allotropes. Diamond (3D) and Graphite (2D) are two of the most famous allotropes. Discovery of C60 [2] has opened a new family of carbon allotropes, known as "Fullerenes" which includes C60, C70, C82, ... [3]. Fullerenes are usually composed of pentagons

and hexagons. One of the most significant discoveries of recent times is a carbon allotrope called Carbon Nanotubes [4, 5]. Carbon nanotubes mostly contain hexagons. These include multi-walled nanotubes, single–walled nanotubes, double walled, few-walled, with open ends or closed ends. The carbon nanotubes can have either semiconducting or metallic properties depending on the diameter and chirality.[6-9] The another form of carbon is graphene nanoribbbons (GNRs) which have recently been proposed as one of the potential candidate for use as material in electronic circuits. [10]-[12]. Since each GNR can be considered as an unrolled single wall carbon nanotube (SWCNT), most of GNR electronic properties are similar to those of SWCNT. Depending on its geometry, GNR can be either metallic or semiconducting [13-15].

2.   GRAPHENE NANORIBBONS(GNRS)

The fundamental 2D carbon structure is graphene, a honeycomb atomic layer (Fig. a) representing the basic structural constituent of graphite. Graphene can be conceptually viewed as an indefinitely extended, 2D aromatic macromolecule. The graphene can be used both as a metal with vanishing Fermi surface and as a semiconductor with a vanishing band gap which can be easily confirmed through its electronic- band structure. The charge carriers in graphene behave like massless Dirac fermions[16].
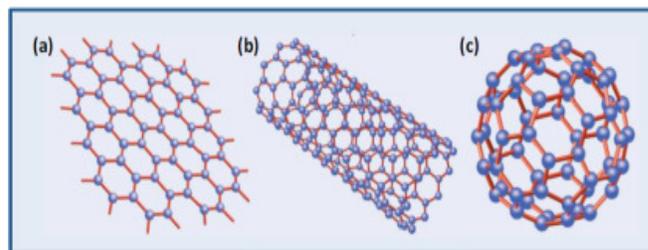

Fig.1 Three forms of carbon nanomaterials : (a) graphene sheet, (b) carbon nanotube (CNT) and (c) fullerene.

Graphene nanoribbons are quasi 1D structures cut from graphene sheet in particular orientations.They are categorized by the alignment of the edge atoms, namely zigzag (ZGNR) and armchair (AGNR). Virtue their various edge structures, GNRs present different electronic properties ranging from normal semiconductors to spin-polarized half metals, which open the possibility of GNRs as electronic devices. Adopting the standard convention, the width of armchair GNRs is classified by the number of dimer lines (N_a) across the ribbons. Zigzag GNRs are classified by the number of zigzag chains (N_z) across the ribbons. Perpendicular to the direction of defined width, GNRs repeat their geometric structures, and form one-dimensional periodic structures.

Density Functional Theory (DFT) calculations show that armchair nanoribbons can be either semiconducting or metallic with an energy gap scaling with the inverse of the GNR width [17]. Experiments verified that energy gaps increase with decreasing GNR width [18]. Zigzag nanoribbons present spin polarized edges. Their gap opens an unusual antiferromagnetic coupling between the magnetic moments at opposite edge carbon atoms. This gap size is inversely proportional to the ribbon width.[16-19]. For the ZGNR, scanning tunneling microscope(STM) images revealed a high density of edge states near the Fermi level along its edges[20], which is important for spintronics applications. In addition, we can tune the properties of ZGNR, by introducing defects[21, 22], by application of gate voltage[23, 24], by absorption[25], by doping[26-31], by chemical functionalization[32, 33], and by various shaped molecular junctions based on GNRs[34-40]. In this paper we investigate the current voltage (I-V) characteristics and the transmission spectra of armchair graphene nanoribbon with varying GNR width. We observe that the I-V curves and transmission spectra strongly vary by varying the width of the armchair GNR.
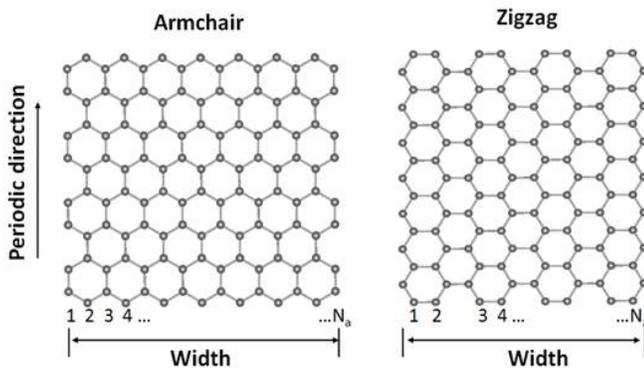

Fig. 2. Types of Graphene nanoribbons

3. COMPUTATIONAL METHODOLOGY

To study the electronic properties of armchair graphene-nanoribbon, GNR samples have been inserted between two infinite electrodes (leads). The scattering region has the same structure as the electrodes. The I-V curves and transmission spectra are calculated by using the density-functional theory(DFT)and non- equilibrium Green's function (NEGF) formalism which is applied in the ATOMISTIX TOOLKIT with Virtual NanoLab package(version 2014.2)[41, 42]. In the calculation, the exchange correlation potential is described by the Perdew–Zunger local density approximation (LDA.PZ). A single-zeta (SZ) basis set is used and in order to save computational time, a mesh cutoff is taken to be 150 Ry. The temperature of the electron is taken to be 300 K. The Brillouin zone is sampled with 1 x 1 x 50 k-points.

The transmission function of the system as per NEGF theory is a sum of transmission probabilities of all then channels available at energy under external bias voltage V_b [43],

$$T \quad T(E, Vb) = Tr[\Gamma_L(V_b)G^R.(E, V_b)\Gamma_R(V_b)G^A(E, V_b)], \quad (1)$$

here $G^{R, A}$ is the retarded and advanced Green's function.[44] The coupling function $\Gamma_{L, R}$ is the imaginary parts of the left and right self-energies, respectively.

The Landauer formula gives the I-V characteristics as follows,

$$I(V_b) = \frac{2h}{e} \int_{-\infty}^{\infty} [f_L(E, V_b) - f_R(E, V_b)]dE \qquad (2)$$

where h is Planck's constant, e is the electron charge, $f_{\frac{L}{R}}(E, V_b)$ is the Fermi–Dirac distribution function for the left (L)/right (R) electrode, and the difference in the electrochemical potentials is given by eV_b with the applied bias voltage V_b, i.e. $\mu_L(V_b) = \mu_L(0) - eV_b/2$ and $\mu_R(V_b) = \mu_R(0) + eV_b/2$.

4. RESULTS AND DISCUSSIONS

GNR samples of various ribbon widths were investigated for their electronic properties. Nanoribbons being studied have widths of 3, 5, 6, 8, 9, 11, 14 atoms. The width of the scattering region is 11.9119 angstrom, while the left and right electrodes are 4.2658 angstrom wider. The GNR assemblies are shown in Fig1. A bias voltage sweep of -2V to +2V applied to the nanoribbons with a step size of 0.1 V. Corresponding current voltage curves obtained are shown in Fig.4. The curves obtained show a very symmetric behavior in the positive and negative bias regimes. This is probably due to the highly symmetric structure of the nanoribbons. For the applied bias range GNR with width of three atoms did not show any conduction. So the bias voltage sweep was extended -3V to 3 V for GNR with width of three atoms so as to further investigate its behavior. From the curves obtained it is observed that the graphene nanoribbons exhibit an interesting behavior. The ribbons with width of 3, 6, 9 atoms are semiconducting in nature. For low bias voltages current flow is negligible. As the voltage bias is increased, at a particular

voltage(cut-in voltage), conduction starts and a linear curve is obtained thereon. The value of the cut-in voltage is 2V for nanoribbon that is 3 atoms wide; while the cut-in voltage is1.3V for nanoribbon that is 6 atoms wide and that for width 9 atoms is 0.9V.This semiconducting behavior is due to the gap present in between the valence and conduction band of the graphene nanoribbon. This gap varies inversely with the width of the armchair graphene nanoribbon.hence the cutin voltage also reduces as width of the nanoribbon increases .However the structure shown in the figure 4(b) shows nearly metallic properties which can be observed from its I-V characteristics which are almost linear. The current in this curve goes to zero for only small values of applied bias near to the zero. This zero-bias value of current is again due to the almost negligible band gap between the valence and conduction band of the nanoribbon. The metallic nature of the nanoribbon increases with the increase in the width of the nanoribbon as the band gap becomes almost zero at larger width of nanoribbons. This can be observed in the figures 5(b), 5(d), 5(f), 5(g). A very conspicuous pattern is observed in the conductivity of various nanoribbons being studied. The GNRs with a width of 3+3n (n=0, 1, 2..) atoms exhibit semiconducting properties. The GNRs with a width of 5+3n (n=0, 1, 2..) atoms exhibit metallic nature.This can be clearly understood from the transmission spectrum of the below structures.
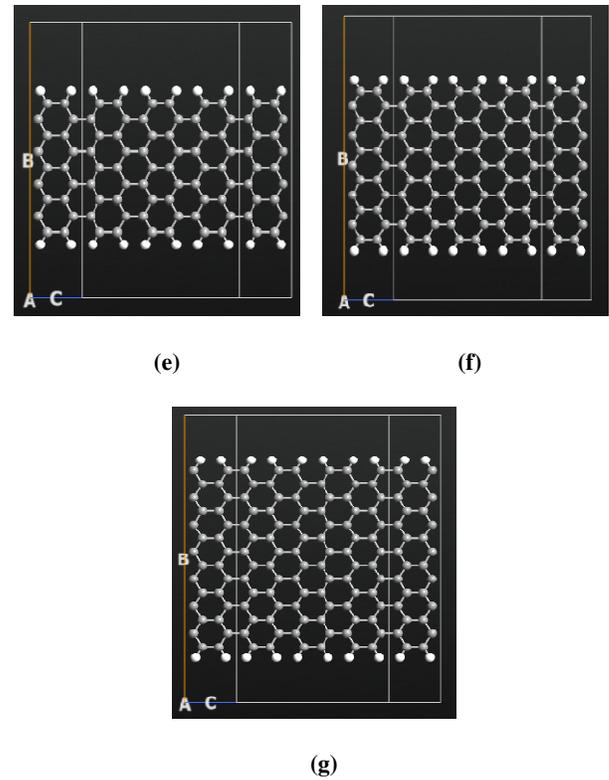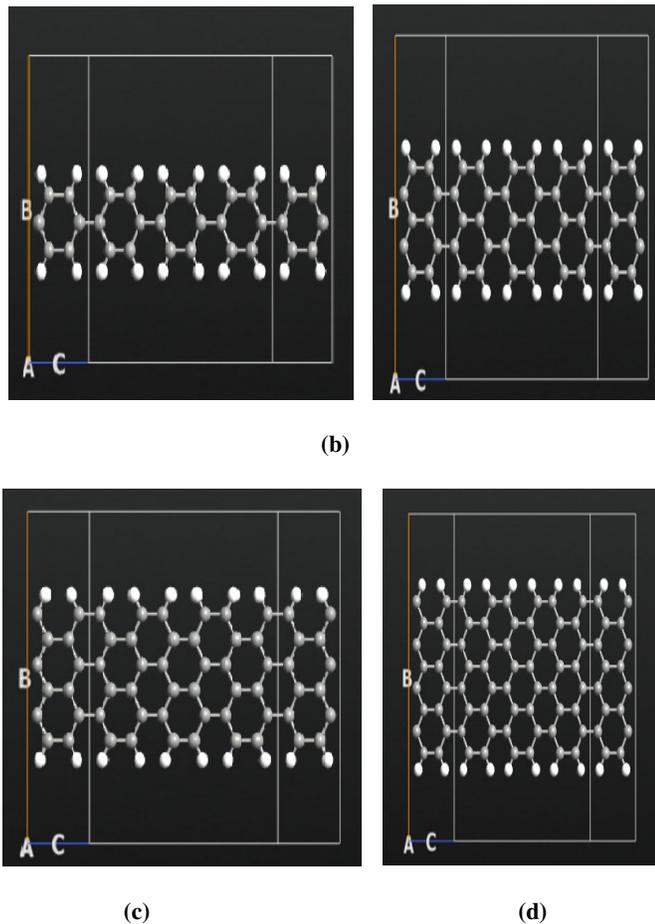

**(e)**   **(f)**

(g)

Fig. 3. 6 Armchair nanoribbons, terminated by hydrogen atoms with varying width. Here (a), (b), (c), (d), (e), (f), (g) are respectively, Armchair GNRs having width of 3, 5, 6, 8, 9, 11, 14 atoms.

(b)

The transmission properties are a function of the band structure near the Fermi energy. The calculated zero bias transmission spectra for the six structures are shown in the figure 5. For the structure displaying semiconducting behaviour, the transmission spectra shows a zero-bias transmission gap around E_f which states that there is an energy band gap between the valence and conduction band of the armchair nanoribbbon. Therefore the I-V curve for this structure is semiconducting. The transmission coefficient remains at one unit for the higher values of energy thus showing that the curve is linear after the knee voltage. For the structure displaying metallic behaviour it is observed from the transmission spectra that the zero-bias transmission gap for this structure is very less as compared to the figure 5(a). At very high values of energy the transmission coefficient reaches the value of 2, which implies the tunneling of electrons across the energy barrier between conduction and the valence band of the nanoribbon. At this very high energy, the current will flow at any condition. The transmission spectrum of the structure shown in fig 5(c) corresponding to the fig.3(c) is again showing the semiconducting behavior of the nanoribbon of width 6 atoms. The zero transmission gap is less in this figure as compared to the figure 5(a), which shows that the knee voltage for this curve will be less than that of the structure with width of 3 atoms. The transmission spectra
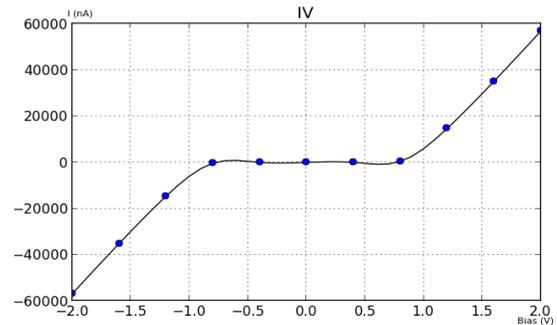

(c)   **(d)**

corresponding to the structures shown in figs. 3(b), 3(d), 3(f), 3(g) have the zero transmission gap around the E_f decreasing in order of increasing width of nanoribbon correspondingly the metallic character of the nanoribbons increases.
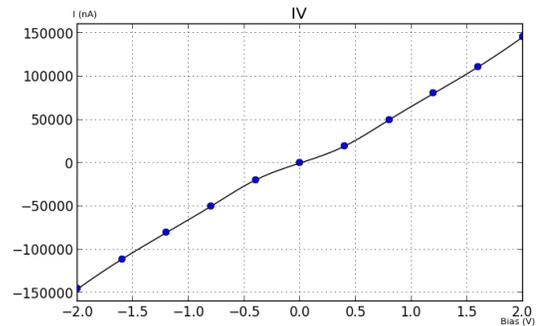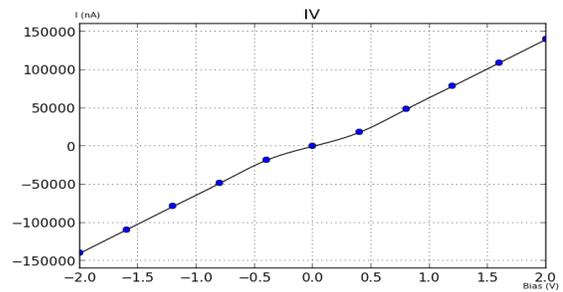

(a)

(b)
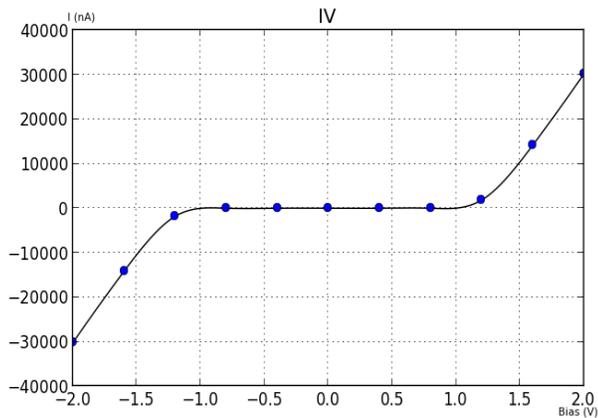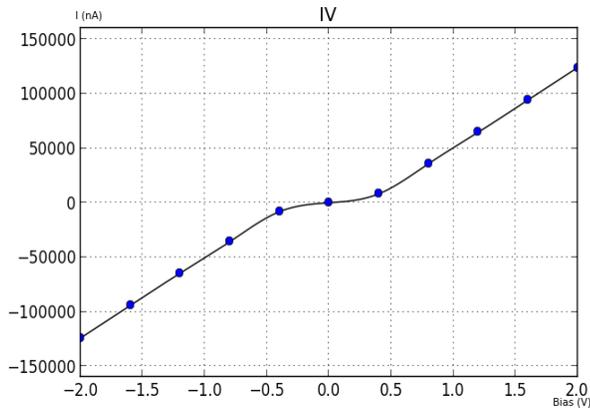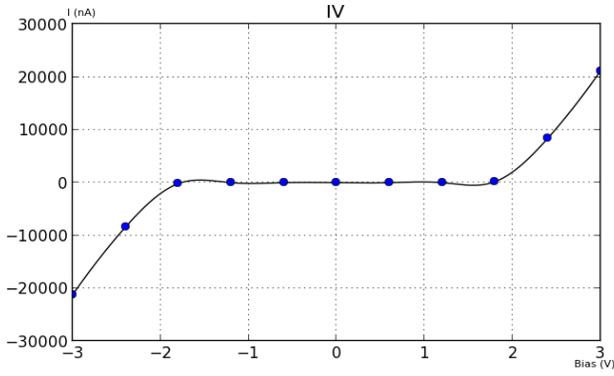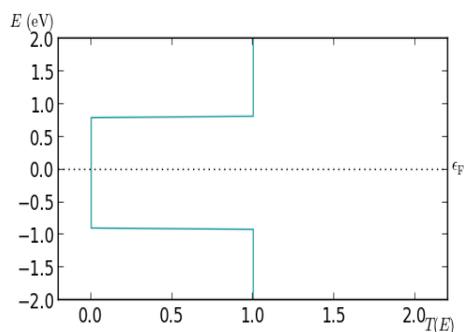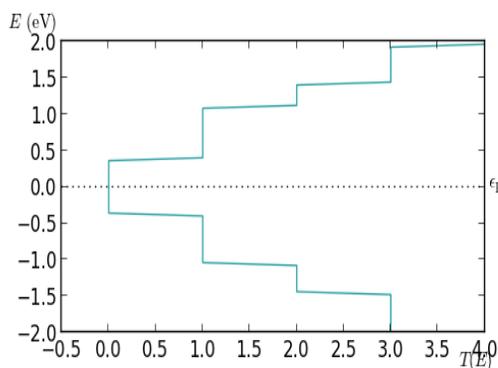

(c)
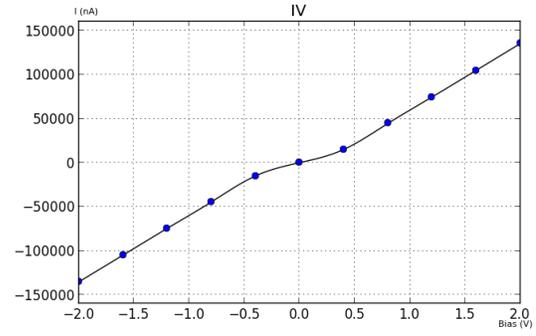
(d)

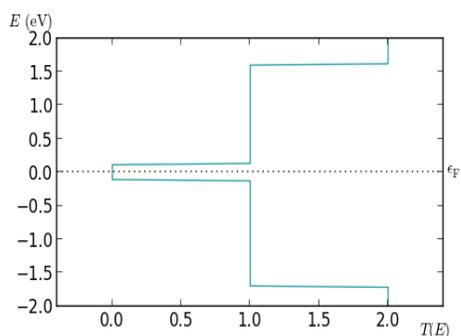**(e)**

(f)

(g)

Fig. 4. I-V curves for the seven structures with different widths of nanoribbons, corresponding to the structures shown in Figs 1(a)-1(g)
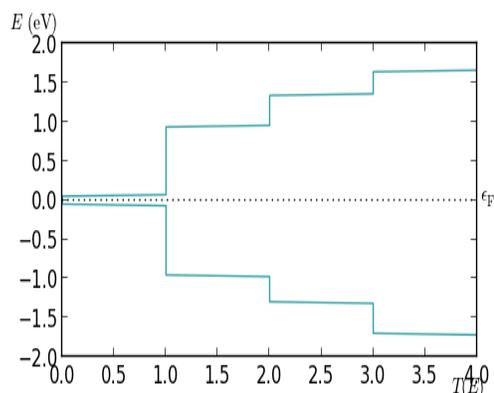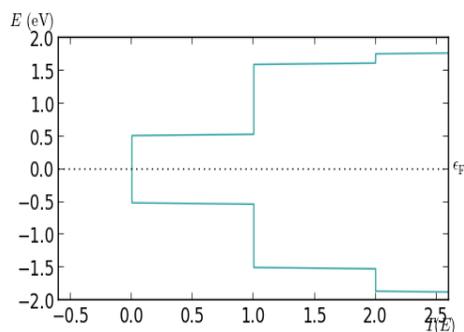
(a)

(b)

(c)

(d)

(e)

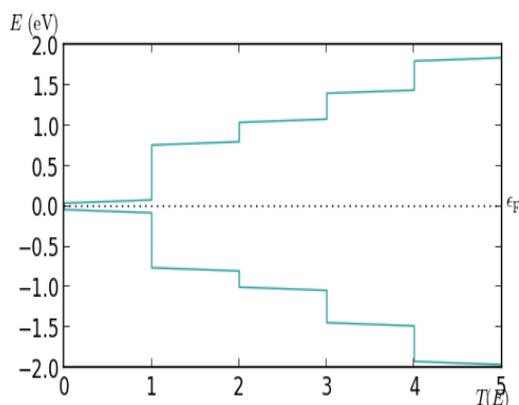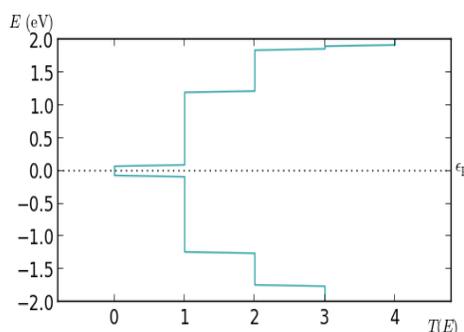**(f)**

(g)

Fig. 5. Transmission spectra for the seven structures with different widths of nanoribbons, corresponding to the structures shown in Figs 1(a)-1(g)

5. CONCLUSION

In this paper graphene nanoribbons have been investigated for conductivity so as to predict their electronic behavior. It has been observed that these nanoribbons exhibit a varied

conductivity pattern In some cases it has metallic nature while in some cases it behaves like a semiconductor. A unique pattern was observed during the analysis of the results obtained. The GNRs with a width of 3+3n (n=0, 1, 2..) atoms exhibit semiconducting properties, while the ones with a width of 5+3n (n=0, 1, 2..) atoms exhibit metallic nature. It is also seen that conductivity increases as the width of GNR increases as band gap is reduced. The cutin voltage for semiconducting GNRs also reduces as the width of the nanoribbons increases

ACKNOWLEGMENTS

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