Half metallic transition in silver-adsorbed zigzag graphene nanoribbons

Pankaj Srivastava[1*], Subhra Dhar[1], Neeraj K Jaiswal[2]

[1]*Nanomaterials Research Group, ABV-Indian Institute of Information Technology and Management (IIITM), Gwalior 474015, M P, India*
[2]*Discipline of Physics, PDPM-Indian Institute of Information Technology, Design and Manufacturing (IIITDM), Jabalpur 482005, M P, India*

[*]Corresponding author. E-mail: pankajs@iiitm.ac.in

ABSTRACT

We investigate Ag atom bonding to zigzag graphene ribbons and properties of these systems to increase the understanding of spin transport. Results concerning the total energies preferred binding sites, equilibrium distances, and electronic character for Ag adatoms on ZGNR are predicted in this study. The study also provides insight into the diffusion kinetics of adsorbed Ag atoms on zigzag edged graphene nanoribbons. The ribbons considered in the present work have an antiferromagnetic ground state and undergoes transition from semiconducting to half-metallic on spin polarization. DOS profiles of Ag-adsorbed ZGNR at the bridge site reveals low DOS across the Fermi level ensuring its semiconducting character, validated from the unpolarized spin calculations. Though nonlinear at biases less than 1V in the FM and AFM calculations, the spin current of atop adsorbed ribbon increases rapidly with the increase of the bias voltage beyond 1V. Copyright © 2016 VBRI Press.

Keywords: Zigzag graphene nanoribbon; silver; spin; adsorption; current.

Introduction

Graphene is a zero bandgap semiconductor with linear dispersion of bands near the Fermi level. Besides its unusual properties, graphene is a candidate for a large number of applications and has the potential to offer new concepts in materials research and fundamental science. Extensive research has indicated that an electronic gap in graphene systems can be opened by carving ribbons of a finite width from graphene sheets. The electronic structure of graphene nanoribbons (GNRs) and band gap value can be controlled by edge shape, as edge reconstructions lower the energy of the system, so that in principle one can obtain metals or semiconductors with the desired gap. More interestingly, zigzag GNRs (ZGNRs) are known to have localized edge states, which are antiferromagnetically coupled between the two edges [1]. The edge state, in the zigzag graphene ribbons, has a large local density of states in the edge region and is spin polarized, plays an important role in giving electronic, magnetic and chemical activities to zigzag edges [2].

Significant efforts have been done to study the effects of transition metal (TM) atoms embedded in single and double vacancies on the electronic and magnetic properties of graphene [3]. Carbon p_z orbitals were found to hybridize strongly with the d orbitals of the adsorbed TM atoms. Though the outermost s orbitals of the transition metals are completely filled, because of their partially filled inner d orbitals, diverse adsorption characteristics for different atoms can be expected. Chan *et al.* have analyzed the structural and electronic properties of 12 different metal adatoms on graphene [4]. Rigo *et al.* have studied the

structural, magnetic, and transport properties of a single Ni atom adsorbed on ZGNRs [5]. Pt impurity concentrations have explained the transition from semiconductor to metal to half-metal through the interaction of Pt impurity and ribbon edge states in [1].

Silver (Ag) possesses excellent electrical, thermal and optical properties, making them indispensable in various kinds of fields. It has been also demonstrated that the combination of Ag nanoparticles with nanocarbon materials like carbon nanofibers and graphene can enhance their field electron emission, electrical, and photo response properties [6]. However, Ag-adsorbed zigzag ribbons have not been investigated, yet. So, the central objective of the work involves the geometry structures and study of electronic properties of 24-ZGNRs (3 zigzag chains) with Ag-adsorption done at various plausible sites. Though the variations in electronic and magnetic properties upon TM atom adsorption are analyzed depending on the adsorbate concentration, adsorption site, and the species of the adsorbent [7] our investigation focuses on spin polarized and unpolarized results of embedded Ag atom in the ZGNRs. All the ZGNRs considered are those passivated with hydrogen. The novelty of this work lies in Ag atom bonding to zigzag graphene ribbons and understanding of spin transport in these ribbons. Results concerning the total energies preferred binding sites, equilibrium distances, and electronic character for Ag adatoms on ZGNR are predicted in this study. The study also provides insight into the diffusion kinetics of adsorbed Ag atoms on zigzag edged graphene nanoribbons. DOS profiles of Ag-adsorbed ZGNR at the bridge site reveals low DOS across the Fermi level ensuring its semiconducting character, validated from

the unpolarized spin calculations. Further, transitions are observed in the electronic character of the ribbon as we show that it is possible to obtain half metallicity through Ag atom adsorption in the ZGNRs. Details of computational methodology are described in Sec. 2. Our results and discussion on the structural, electronic and spin transport properties of Ag adatom adsorbed ZGNR are presented in Sec. 3. Conclusions and a summary are given in Sec. 4.

Experimental

We perform DFT based first principles calculations to explore the spin dependent electronic and transport properties of Ag doped ZGNR. Atomistix Tool Kit Virtual NanoLab (ATK-VNL) simulation package [**8**] is used for the present calculations.
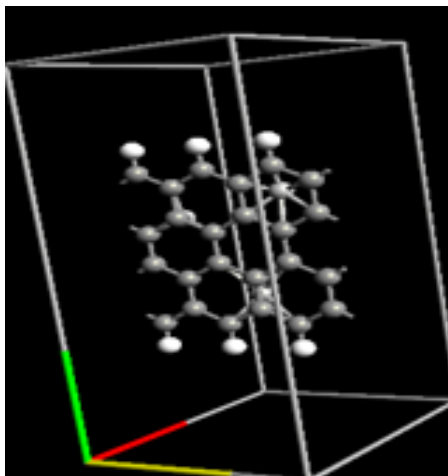
Fig. 1. Adsorption sites atop, hole and bridge investigated in the super cell of the 24-ZGNR (Ag atoms in steel gray, carbon atoms in dark gray and hydrogen atoms in white colour).

We consider the binding of the adatom on three sites of high symmetry: the hole (H) site at the center of a hexagon, the bridge (B) site at the midpoint of a carbon–carbon bond, and the atop (T) site at directly above a carbon atom [**9**] as shown in **Fig. 1**. To model the ribbons, supercell method is used and the cut off energy of 150 Ryd is selected.
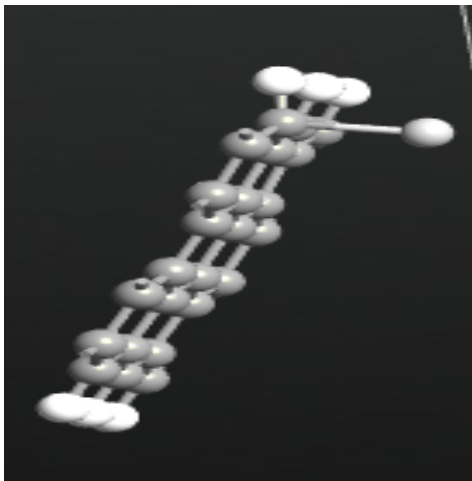

Fig. 2. The optimized geometry of ZGNR due to Ag adsorbed in atop site.

The supercells of the 24-ZGNR under study contained 24 carbon atoms and one adsorbed Ag atom. The edges were terminated by hydrogen atoms to form C–H bonds for neutralizing valencies of all the carbon atoms. Ribbons were allowed to grow along z axis whereas rests of the two directions were confined. All the ribbons are optimized self consistently and all the atoms are fully relaxed so that the maximum force component on all atoms is less than 0.05 eV/Å. The optimized geometry of ZGNR due to Ag adsorbed in atop site and the two probe model of H-passivated ZGNR with Ag adsorbed at atop site are shown in **Fig. 2** and **3** respectively. Upon full geometry optimization, Ag favors bonding on all sites of the graphene layer. The adsorption of Ag atom does not yield any significant distortion or stress on the graphene lattice unlike in [**10**].
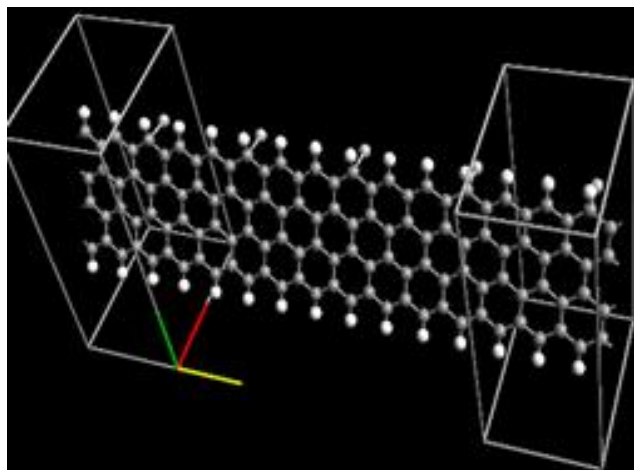

Fig. 3. The two probe model of H-passivated ZGNR with Ag adsorbed at atop site.

We also carried out structural optimization with spin-polarized DFT for all the above mentioned sites of the ZGNR, where the same tendency is found with small difference in the total energies. To calculate the transport properties, we used two probe models. The calculation of the complete system is obtained from calculations of the two electrode regions, and a central scattering region. The spin-dependent current through the system is obtained from the Landauer - Buttiker formula [**11**]

$$I_\sigma = \int_{-\infty}^{+\infty} T_\sigma\,(E,V_b)\big[\,f_L\big(E-\mu_L\big) - f_R\big(E-\mu_R\big)\big]dE \qquad (1)$$

where, $f_{L/R}$ (E, V_b) is the Fermi Dirac distribution function for the left (L)/right(R) electrode, $\mu_{L(R)}$ are electrochemical potentials of the left and right electrodes and the difference of them is given by eV_b with the applied bias voltage V_b and T_σ is the transmission coefficient from left (L) lead to right (R) lead, which can be expressed as

$$T_\sigma = T_r(\Gamma_R G^R_C \Gamma_L G^A_C) \qquad (2)$$

where, G^R_C and G^A_C are the retarded and advanced Green's functions of the conductor, respectively, and $\Gamma_{L(R)}$ is the coupling matrices from the conductor to the left (right)lead.

Results and discussion

Adsorption of metal atoms is an effective way of functionalizing nanostructures. In this section, we present our results concerning the total energies, preferred binding sites, equilibrium distances, and electronic character for Ag adatoms on 24-ZGNR. We expect that this systematic study will increase the understanding of *3d* Ag atom bonding to the graphene ribbon and the behavior and properties of these systems, such as spin transport.

Table. 1. Unpolarized structural and electronic properties of Ag adsorbed 24-ZGNR.

S.No	Dopant site	Total energy (eV)	Bond length (A°)	Band gap (eV)	B.E (eV)	Electronic character
1.	1 Ag atom atop site of 24 C ZGNR	-5201.9982	2.112	1.9	-1.878	Semi conducting
2.	1 Ag atom bridge site of 24C ZGNR	-5201.5584	2.053	2.0	-1.445	Semi conducting
3.	1 Ag atom hole site of 24 C ZGNR	-5201.9832	2.141	2.0	-1.872	Semi conducting

On spin polarizing the Ag-adsorbed ribbons, we arrive at encouraging results from all the dopant sites. The effect of adsorption done at atop, hole and bridge sites with an Ag atom and increased dopant concentration at the above said sites are presented systematically in this section. Unpolarized structural and electronic properties of Ag adsorbed 24-ZGNR of all the investigated adsorption sites are listed in **Table 1**.

Though Ag adatom is exceptional [12], significant interaction can be seen as the doped ribbon turns semiconducting in nature as predicted by the band gaps in **Table 1**. To start with, the atomic structure and geometry of Ag adsorbed 24-ZGNR at various identified sites is carried out. Though our total energy calculations imply that all the Ag-doped systems are stable, the top site is confirmed to be most stable in case of Ag-adsorption. The favored adsorption site indicates the main chemical bond between Ag adsorbate and ZGNR. We find that the values of bond lengths are close to each other and are strongly bound to the carbon atom as suggested by the binding energies. In the case of full optimization, the *m- c* bond lengths reported here are in good agreement with the previous study done in [13], whereas the binding energies are suggestive of more stability than those reported in [13]. As Ag adatoms can diffuse almost unrestrictedly on the graphene sheet, the diffusion energies [14, 15] reported as the difference between the most stable site and the second most stable site is calculated to be 0.015 eV, thus confirming the stability of the Ag adsorbed ZGNR.

Ag is purely physisorbed on the GNR, and the distortion of the graphene sheet by Ag is negligible for equilibrium distances, calculations predict that the top site is more favorable than the bridge and hole sites, in accordance with [15]. Ag doped nanoribbons are significant as electronic interaction [16] between Ag nanoparticles with graphene in [17] confirms appropriate tuning of carriers concentration can result in placing the Fermi energy in the gap region, and behave as semiconductor. The flat bands observed in

the electronic band structures of spin unpolarized ribbons near the Fermi level arise from the localized electronic states of the Ag adsorbed ZGNRs also validate similar behavior in the present study. Though zigzag silicene nanoribbons (ZSiNR) undergoes a transition from semiconductor to half-metal with the increasing electric field [18, 19], and has an antiferromagnetic (AFM) ground state much similar to Ag adsorbed ZGNR, the ribbons considered in the present work undergoes transition from semiconducting to half-metallic on spin polarization.
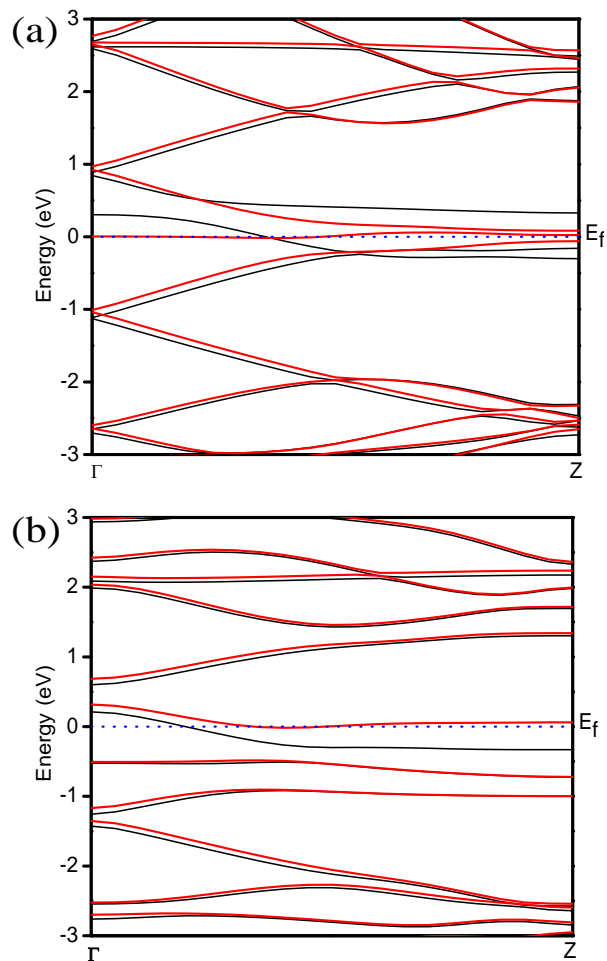

Fig. 4. The spin dependent band structures due to Ag adsorbed 24-ZGNR at bridge site (a) FM (b) AFM. Fermi level E_f is set at 0. Spin up is represented in red and spin down in black.

All the systems in the present work are magnetic and the Ag-atop site at the ground state (AFM) is the most stable site. The spin polarized electronic band structures of ZGNR due to Ag adsorption at bridge site shown in **Fig. 4** are highly encouraging as they present half metallic characteristics [20]. The spin polarization of the Ag-adsorbed ZGNR confirms that the 3d electrons of the adatom and C atom around the Fermi surface cause polarization.

The total density of states (TDOS) of Ag-hole site adsorbed ZGNR are plotted in Fig. 5. In contrast to the DOS of FM setup in **Fig. 5(a)**, the spin polarization of AFM in **Fig. 5(b)** is more prominent. We find that the DOS profiles of Ag-adsorbed ZGNR at the bridge site due

to FM state reveals more number of states available for conduction, whereas AFM state resulted in lower DOS across the Fermi level. The low DOS across the Fermi level ensures its semiconducting character, which is also validated through the spin unpolarized calculations of this configuration. This work was conducted on similar ZGNRs by increasing the dopant concentration two times, though no change was noticed in its structural properties, the band structures differed distinctly as the flat bands vanish and band gaps were reduced significantly.
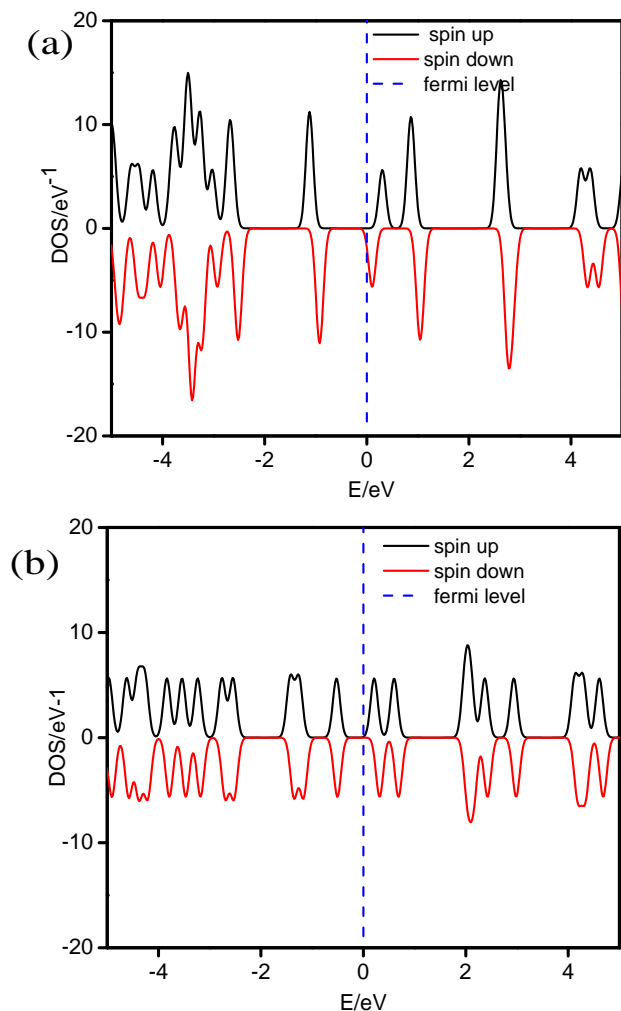
Fig. 5. The spin dependent TDOS profiles of Ag-adsorbed 24-ZGNR at hole site (a) FM and (b) AFM. Spin-up and spin-down contributions are presented along the positive and negative y axes, respectively. Along the vertical axis, the zero corresponds to the Fermi level.

I-V curves

Chemical modification plays an important role on the electronic properties and spin transport properties of GNRs [21]. Recently, transport calculations done to adsorb Fe and Co atoms through an extended line defect in the graphene lattice presented significant results at less than 0.6V in [22]. In the present work, to understand the transport mechanism in the Ag-adsorbed ZGNRs, we undertake spin transport calculation on the Ag-adsorbed systems. Our spin polarized transport calculations done on the ZGNRs with Ag-adsorbed at atop site reveals that the two probe device

produces fully spin-polarized current. We understand the variation of total currents in FM and AFM configurations from the **Fig. 6**.

The calculated total current highlights the fact that the current is increased in the FM setup beyond a bias voltage of 1V in the two probe device. On increasing the bias further to 2V, the total current increases appreciably. For AFM setup, the total current remains relatively small when the bias is 1V. Along with the increase of the bias voltage beyond 1V, the current increases rapidly, however, the difference between two states is not much obvious from the outset as both the currents exhibits nonlinear behavior. Adsorbed by vanadium, the spin current through the zigzag ribbon behaves nonlinearly against low bias voltage [**11**].
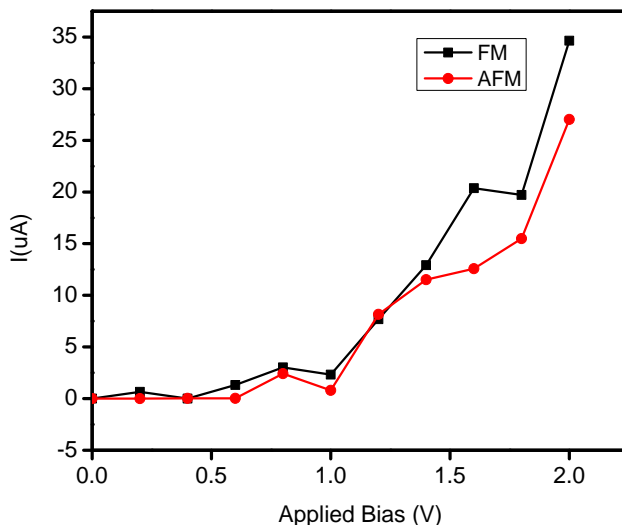

Fig.6. The total currents in FM and AFM state of the ribbons of Ag-atop adsorbed 24-ZGNR.

This is in similarity to the present observations, which leads to further probing through spin unpolarized current – voltage characteristics in the Ag-adsorbed systems. The authors come across interesting results in this case. The NDR phenomena observed at voltages below 1V in case of Ag atop and hole site doped is lifted in non-spin calculations when Ag is doped at the bridge site. Also, the Ag-bridge adsorbed ZGNR presents higher currents along with linear variation with the increase in bias voltage.

Conclusion

WSC Spin polarized DFT calculations have been performed to study the structural, energetic, electronic and transport properties of Ag adsorbed ZGNRs. It is evident that the electronic and magnetic properties of the ZGNRs are influenced after Ag adatom treatment. On spin polarization, semiconducting ZGNR changes to half metallic upon adsorption of Ag adatoms. Band structure calculations reveal half metallicity in all Ag-adsorbed ribbons at all doping sites. The Ag-bridge adsorbed ZGNR presents higher currents along with linear variation with the increase in bias voltage in the spin unresolved calculations. Along with the increase of the bias voltage beyond 1V, the current increases rapidly, however, the difference between two states is not much obvious from the outset as both the
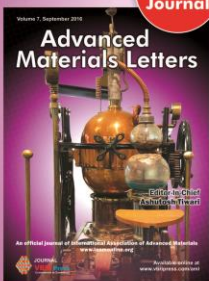
currents exhibits similarity in its nonlinear behavior. These findings open new prospects for the design of ZGNR-based spin-valves for integration in nanoelectronic devices. Our results suggest a huge possibility in spintronics device applications for achieving half-metallicity in the ZGNRs without the excessively high external electric fields.

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