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Citation: Applied Physics Letters 97, 263114 (2010); doi: 10.1063/1.3533643
View online: http://dx.doi.org/10.1063/1.3533643
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Gyubong Kim1,2 and Seung-Hoon Jhi2,3,a

1Computational Science Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea
2Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
3Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

(Received 26 October 2010; accepted 13 December 2010; published online 30 December 2010)

Electronic and magnetic properties of bilayer zigzag graphene nanoribbon (bZGNR) are studied using pseudopotential density functional method. The edge atoms in the top and bottom layers of bZGNR make a weak hybridization, which leads to electronic structures different from monolayer ZGNR. For asymmetric bZGNR, where the top and bottom layers have different widths, one edge is pinched by the interlayer bonding and the other sustains antiferromagnetic ordering. A small amount of charge transfer occurs from narrower to wider layer, producing spin-polarized electron and hole pockets. External electric field produces asymmetric energy-gap opening for each spin component, inducing half-metallicity in bZGNR. © 2010 American Institute of Physics.

[doi:10.1063/1.3533643]

Low dimensional graphitic materials such as graphenes and carbon nanotubes have drawn a great deal of interests for their potentials in future nanoelectronics.1 Their electric and transport properties can essentially vary by chemical doping or morphology. For example, graphene nanoribbons (GNRs) have been reported to possess intriguing electric/magnetic features depending on their edge atomic structures.2−4 Metallic zigzag edged GNRs (ZGNRs) become small-gap semiconductor due to antiferromagnetic ordering in the edge atoms as their width decreases.3 Edge-localized states in ZGNRs have a ferromagnetic spin-polarization along the edge and antiferromagnetic ordering across the edges.3−8 This peculiar magnetic property of ZGNRs has been actively studied because of potential importance in spintronic applications. It was shown that transverse external electric field or chemical doping can control the spin-current by inducing half-metallicity in ZGNRs.3,6−8 Another issue in graphene research critical for device applications is to produce energy gap. Bilayer graphene was shown to have energy gap when external electric fields are applied.12,13 Depending on the stacking and the width together upon applying electric fields, bilayer graphene nanoribbons are thus expected to exhibit rich magnetic and electronic properties.

In this paper, we study electronic and magnetic properties of bilayer ZGNRs (bZGNRs) using pseudopotential density functional methods. We were particularly interested in half-metallic characters of unbalanced bZGNRs that have top and bottom ZGNRs of different widths. This type of configuration is frequently observed in step edges of multilayer graphene.14−17 All calculations were performed with the spin-polarized first-principles total energy methods as implemented in the Vienna ab initio simulation package.18 The projector augmented wave pseudopotentials were used as provided in this package.19 The electron exchange-correlation was treated within local spin-density approximation.20 The cutoff energy for the planewave-basis expansion was chosen to be 400 eV and the atomic relaxation was carried out until Helmann–Feynman forces acting on atoms are less than 0.02 eV/Å. The supercell method is employed with the edge-to-edge and the distance between bZGNRs in the supercell set to 15 Å. Following the convention,3,8 we designate ZGNRs by the number of the zigzag carbon chains across the ribbon width. For example, the ZGNR shown in Fig. 1 is 16-ZGNR.

We considered two common stacking geometries of bZGNRs, AA- and AB-stackings (Fig. 1). In monolayer ZGNRs, there exist two edge-localized states (termed edge states).3−8 We observed relatively strong bonding (compared to interlayer weak van der Waals interaction) between such edge-localized orbitals in the top and bottom ZGNRs, which leads to a bending of the two layers at the edge, as shown in Fig. 1 (the layer distance is shorter at the edge). It was found that the AB-stacking is more stable than AA-stacking by about 3 meV/atom. The additional energy gains from edge coupling between top and bottom layers are about 0.17 and 0.09 eV/Å for the bZGNRs in Fig. 1 with AB- and AA-stackings, respectively.

Figure 2 shows calculated band structure and bonding character of edge states of bZGNR with AB-stacking. The most contrasting feature in the band structure of bZGNR compared to monolayer ZGNR is observed near the Fermi level. Narrow monolayer ZGNRs have small energy gaps due to antiferromagnetic coupling between the edges and show very flat band dispersion near the gap.3,5,8 For bZGNR, the magnetic ordering disappears and the edge states exhibit a larger band dispersion due to the edge coupling between top and bottom layers. The band structure has rather a large energy gap of ~1.45 eV at X point due to such enhanced dispersion. The charge density plot of top of the valence band and bottom of the conduction band at X point [states marked by small dark (red) squares in Fig. 2(a)] shows clearly the antibonding and bonding characters [Figs. 2(b) and 2(c)]. One interesting observation here is that the magnetic ordering at ZGNR edges disappears, and thus the bond-
ing between upper and lower edges leads to the spin singlet states.

The bZGNRs can be aligned asymmetrically if top and bottom layers have different widths. In such a case, the edges in one side are pinched by the interlayer coupling and do not have magnetic ordering. The states at the unmatched edges in the other side are still spin-polarized [Fig. 3(a)]. The band structure of each spin component is different from what was observed in monolayer ZGNRs. Interestingly, we found that a small amount of charge transfer occurs from narrower ZGNR [here 8-ZGNR in Fig. 3(a)] to wider ZGNR (16-ZGNR), and the transferred electrons are localized at the weakly bonded edges. The charge transfer is due to an enlarged difference in work function between the two ZGNRs; calculated work functions of 8- and 16-ZGNRs, which are isolated but having the same atomic structure as in asymmetric bZGNR structure, are 4.39 and 4.48 eV, respectively. We note that the work functions for isolated and flat 8- and 16-ZGNRs are 4.41 and 4.39 eV, respectively. The increase in work function of 16-ZGNR is due to the effect of strain induced by the bending of the edge in 16-ZGNR.21 Near the Fermi level, the energy gap for \( \alpha \)-spin electrons is indirect whereas that for \( \beta \)-spin bands is direct energy gap.

The half-metallicity is an intriguing phenomenon observed in ZGNR and zigzag carbon nanotubes.8,9,11,22 Two opposite spin states that are geometrically separated in ZGNRs can be manipulated by external electric fields.8,9,11,22 Here we applied external electric field \( (E_{\text{ext}}) \) perpendicular to the ZGNR layer to investigate how the electronic structure of each spin component is affected by the field. As shown in Figs. 3(c) and 3(d), the energy-gap asymmetry for each spin is clearly visible at \( E_{\text{ext}} \sim 0.3 \ \text{V/A} \). The semimetallic nature of \( \beta \)-spin (with a small energy gap of \( \sim 10 \ \text{meV} \)) does not change even if very strong \( E_{\text{ext}} \) is applied [see Figs. 3(c) and 3(d)] whereas the energy gap of \( \alpha \)-spin increases. Thus the spin transport of asymmetric bilayer graphene will be essentially different from what was observed in monolayer ZGNRs.8,9 We note that the half-metallicity in asymmetric bZGNR is an intrinsic property, not specific to a particular combination of the two ZGNRs considered here. The narrow ZGNR is on top of the wide ZGNR and can be considered as a part of bilayer graphene whereas the edge of the bottom (wide) ZGNR does not feel the potential from the top layer.

![Fig. 1. (Color online) Optimized geometries of (a) AA- and (b) AB-type stacked zigzag graphene nanoribbon bilayers with a width of 16 zigzag carbon chains (16-ZGNR). The AB-stacking is energetically more stable than the AA-stacking by about 3 meV/atom. The cyan (small gray) balls denote the passivating hydrogen atoms. The nearest atomic distances (in angstrom unit) between top and bottom layers are indicated at the center and edge atoms. Due to different atomic arrangements at the edge for the two stackings, we observe a slightly different bending of the ZGNRs at the edges that have a weak coupling between the layers.](image)

![Fig. 2. (Color online) (a) Calculated band structures of AB-stacking bZGNR shown in Fig. 1(b). (b) and (c) show the side view of the squared wave functions for the states in the conduction and the valence bands as marked by small dark (red) squares in (a), respectively. The contour interval is 0.1 e/Å³ and the light-grey (yellow) balls denote the edge carbon atoms at top and bottom ZGNR layers. We observe weak antibondinglike and bondinglike coupling between the edge atoms.](image)
The different response of $\alpha$- and $\beta$-spin states to $E$-field comes from the difference in screened potentials for top and bottom layers in this respect. The electric potential screened by the Hartree and exchange-correlation terms is comparably nonuniform around the edge of the top layer ($\alpha$-spin states). It is known that bilayer graphene develops a gap when external electric field is applied. The same behavior occurs for the $\alpha$-spin states in asymmetric bZGNRs since the edge of the top layer is in similar chemical environment as in the bilayer graphene. To confirm explicitly the half-metallicity of asymmetric bZGNRs, we calculated another asymmetric pair (4-ZGNR+32-ZGNR) and found the same behavior to $E$-field. Our results indicate that spin-polarized currents can be generated with small bias voltages in asymmetric bZGNR.

In conclusion, we studied the electronic and magnetic properties of bilayer ZGNR using first-principles calculations. Due to the coupling of edge states in the top and bottom layers, the band dispersion of bilayer ZGNR exhibits contrasting features compared to monolayer ZGNRs, and also the magnetic ordering at the edge atoms disappears. When the width of top and bottom layers is different, the edges at one side are pinched by weak coupling between top and bottom layers whereas the edges at the other side still have antiferromagnetic coupling between top and bottom layers just like the coupling between the opposite edges in monolayer ZGNRs. For these asymmetric bilayer ZGNRs, it was shown that external electric fields perpendicular to the layer can induce half-metallicity in bilayer ZGNR. With external gate electric field, the energy gap of one spin component can be controlled whereas the other spin component remains metallic. This study demonstrated that an asymmetric bilayer ZGNR can be an interesting platform as spintronic devices with unique electronic and magnetic properties.

This research was supported by the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (Grant No. 2009-0087731 and WCU Program No. R31-2008-000-10059-0). Computational time was provided by Korea Institute of Science and Technology Information (Grant No. KSC-2009-S01-0002).