Dual Spin Filter Effect in a Zigzag Graphene Nanoribbon

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Abstract

By first principle calculations, a dual spin filter effect under finite bias voltages is demonstrated in an antiferromagnetic junction of symmetric zigzag graphene nanoribbon (ZGNR). Unlike conventional spin filter devices using half metallic materials, the up- and down-spin electrons are unidirectionally filtered in the counter direction of the bias voltage, making the junction a dual spin filter. On the contrary, asymmetric ZGNRs do not exhibit such a spin filter effect. By analyzing Wannier functions and a tight-binding model, we clarify that an interplay between the spin polarized band structure of $\pi$ and $\pi^*$ states near the Fermi level and decoupling of the interband hopping of the two states, arising from the symmetry of the wave functions, plays a crucial role in the effect.

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I. INTRODUCTION

The graphenes have been recently attracting much attention as a candidate material for spintronics devices because of its peculiar electronic structures, while so far most of promising materials in developing the devices have been found in ferromagnetic (FM) metals and FM semiconductors such as GaMnAs. In fact, recent experiments have achieved spin injection into graphene layers at room temperature for the first time among molecular materials, and observed the magnetoresistance (MR) effect. In addition, several intriguing transport properties have been theoretically predicted especially for zigzag graphene nanoribbons (ZGNRs). For instance, it is shown that ZGNRs can be utilized even for generation of a spin polarized current in which an external electric field applied across ZGNR along the lateral direction may induce a half-metallic band structure being responsible for the spin polarized current. Also an extraordinary large MR and generation of spin-polarized current are also theoretically found in a spin valve device consisting of ZGNR. The unique properties in the electronic transport properties of ZGNRs can be attributed to the characteristic band structures of ZGNR and the symmetry of wave functions near the Fermi level. Along this line, the family of graphenes related to ZGNR might be anticipated to exhibit unexpected electronic properties which can be useful in developing spintronics devices. However, transport properties of ZGNRs under finite source-drain bias voltages $V_{bias}$ have not been fully explored even from the theoretical points of view. For development of future device applications it is highly important to fully understand intrinsic behaviors in the transport properties of ZGNRs under a wide range of finite bias voltages.

In this paper we present a novel and intrinsic electronic transport property of ZGNR under finite bias voltage $V_{bias}$, based on first principle calculations, that a symmetric ZGNR with an antiferromagnetic (AFM) junction exhibits a dual spin filter effect under finite $V_{bias}$, namely, the up- and down-spin electrons are unidirectionally filtered in the counter direction of $V_{bias}$. Based on an analysis using Wannier functions (WFs) and a tight-binding (TB) model, we further clarify that the spin filter effect arises from an interplay between the band structure and absence of the interband hopping of the $\pi$ and $\pi^*$ states near the Fermi level.
II. COMPUTATIONAL DETAILS

At each bias voltage $V_{\text{bias}}$ the electronic structure of ZGNR shown in Fig. 1(a) is self-consistently determined under a temperature of 300 K by means of a non-equilibrium Green function (NEGF) method\textsuperscript{15,16} coupled with a local spin density approximation (LSDA)\textsuperscript{17} in the density functional theory (DFT)\textsuperscript{18}. The equilibrium density matrix (DM) is evaluated by a contour integration method\textsuperscript{19} while the non-equilibrium DM is numerically computed on a line with an imaginary part of 0.01 eV which is parallel to real axis in complex plane\textsuperscript{20}. The conductance and current are calculated by the Landauer formula\textsuperscript{21}. Norm-conserving pseudopotentials are used in a separable form with multiple projectors to replace the deep core potential into a shallow potential\textsuperscript{22}. Pseudo-atomic orbitals (PAOs) centered on atomic sites are used as basis functions. The PAO basis functions, generated by a confinement scheme\textsuperscript{23}, are specified by H5.5-s2 and C4.5-s2p2, where the abbreviation of basis functions, such as C4.5-s2p2, represents that C stands for the atomic symbol, 4.5 the cutoff radius (Bohr) in the generation by the confinement scheme\textsuperscript{23}, and s2p2 means the employment of two primitive orbital for each of s- and p-orbitals. The real space grid techniques are used with the energy cutoff of 120 Ry as a required cutoff energy in numerical integrations and the solution of Poisson equation using FFT\textsuperscript{24}. In addition, the projector expansion method is employed in the calculation of three-center integrals for the deep neutral atom potentials\textsuperscript{25}. The geometrical structures used are optimized with a criterion of $10^{-4}$ hartree/bohr for forces on atoms under the periodic boundary condition. All the calculations were performed by an \textit{ab initio} DFT code, OpenMX\textsuperscript{26}.

III. RESULTS

$n$-ZGNRs are characterized by the number of carbon atoms, even (symmetric) or odd (antisymmetric), in the sublattice being across ZGNR along the lateral direction, while Fig. 1(a) shows the case of eight carbon atoms abbreviated as 8-ZGNR. For ZGNRs we focus a spin configuration with an AFM junction as shown in Fig. 1(a). Considerable magnetic moments are found at both the zigzag edges which can be attributed to the existence of the flat band near $X$-point\textsuperscript{24}. Although the AFM coupling between the zigzag edges is favored by about 10 meV per edge carbon atom compared to the FM coupling, we consider the
spin configuration consisting of the FM coupling between the zigzag edges and the AFM junction at the central region. The spin configuration is crucial for the spin filter effect we discuss, and might be realized by a magnetic field applied in a spin valve device or chemical modifications for ZGNRs. It should be noted that the effect does not appear in the other spin configurations. The current-voltage (I-V) characteristics for 8-ZGNR with the spin configuration depends on intriguingly not only spin, but also the direction of $V_{\text{bias}}$ as shown in Figs. 1(b) and (c). Interestingly, the up-spin electron substantially flows only in the negative regime of $V_{\text{bias}}$, while the down-spin electron flows only in the positive regime. The ratio of the spin dependent currents, $I_{\text{up}}/I_{\text{down}}$, turns out to be 44.3 at $-0.4$ V, and the value is equivalent to the rectification ratio for each spin-dependent current because of the I-V characteristics. The I-V characteristics of other even cases, $n$ =6 and 10, are also found to be nearly equivalent. Thus, a symmetric ZGNR plays dual roles as a unidirectional spin filter for each spin state under finite $V_{\text{bias}}$. The effect can also be regarded as a dual spin diode effect due to the unidirectional nature of the spin dependent current. In contrast, the current for 7-ZGNR with the spin configuration is almost independent of spin, and proportional to $V_{\text{bias}}$ within the regime, leading to $I_{\text{up}}/I_{\text{down}}$ of a nearly one. Thus, it should be emphasized that the parity in the geometrical structure of $n$-ZGNR is the key factor even for the behavior of the spin polarized current as in the spin unpolarized current.

The I-V characteristics for 8-ZGNR is understood by examining the dependency of the conductance on $V_{\text{bias}}$. It is found in Fig. 2(a) that there is a conductance gap of about 0.4 eV for both the up- and down-spin states around the chemical potential at $V_{\text{bias}} = 0$ V. The gap for the up-spin state decreases as $V_{\text{bias}}$ increases toward the negative direction, and approaches zero at about $V_{\text{bias}} = -0.4$ V as shown in Fig. 2(b), while the zero gap is kept up to $V_{\text{bias}} = -0.55$ V. From then onwards the gap increases as illustrated in Fig. 2(c). On the other hand, the gap for the down-spin state monotonically increases as $V_{\text{bias}}$ increases toward the negative direction. The conductance gaps for the up- and down-spin states are shown as a function of $V_{\text{bias}}$ in the inset of Fig. 2(a). We see that the behavior of the gaps is opposite for the up- and down-spin states in the regime of the positive direction of $V_{\text{bias}}$ in contrast with that in the negative direction. The shaded regions in Fig. 2(b) and (c) correspond to the regime in between two chemical potentials of the left and right leads, where the electron transmission can contribute to the current flow. Thus, it is confirmed that in the regime of the negative $V_{\text{bias}}$, $|I_{\text{up}}|$ increases up to around $V_{\text{bias}} = -0.55$ V, where the gap opening
occurs again, and from then onwards saturated. Also it turns out that $|I_{\text{down}}|$ should be nearly zero in the regime of the negative $V_{\text{bias}}$, since the shaded region is always inlying in the conductance gap for the down-spin state. In the regime of the positive $V_{\text{bias}}$, the $I$-$V$ characteristics can be explained in the same way by considering the reversed roles of up- and down-spin states. Note that the reversal of the roles arises only in the spin configuration with the AFM junction.

The opening and closing of the conductance gap can be attributed to the band structure near the Fermi level of 8-ZGNR with the FM coupling between the zigzag edges. The exchange splitting $\Delta_x$ is found to be 0.553 eV at $X$-point from Fig. 3(a). The right blue and pink shades denote the conductance gaps for the up- and down-spin states in Fig. 2. It is clearly seen that the conductance gap corresponds to an energy regime where the $\pi(\pi^*)$ state in the left panel overlaps with only the $\pi^*(\pi)$ state with the same spin in the corresponding right panel. The $\pi^*$ up-spin state in Fig. 3(a) overlaps with only the $\pi$ up-spin state in Fig. 3(d) in the conductance gap. Once the overlap regime fades away at the situation given by Figs. 3(b) and (e), and then onward it turns out that the $\pi$ up-spin state in Fig. 3(c) overlaps with only the $\pi^*$ up-spin state in Fig. 3(f) in the regime of the conductance gap. On the other hand, for the down-spin state the energy regime, where the $\pi$ state in the left panel overlaps with only the $\pi^*$ state in the right panel, linearly increases as the energy shift increases toward the negative direction as shown in Figs. 3(d), (e), and (f). The same idea except for reversing of the roles of the $\pi$ and $\pi^*$ states can apply to the case of the energy shift toward the positive direction. Since the band structures in the left and right panels can be regarded as those of the left and right leads in Fig. 1(a), the correspondence implies that the electron transmission from the $\pi(\pi^*)$ to $\pi^*(\pi)$ states is forbidden. In fact, it is shown that the Bloch function of the $\pi (\pi^*)$ state is antisymmetric (symmetric) with respect to the $\sigma$ mirror plane which is the mid plane between two edges.\textsuperscript{4,5} Thus, the electron transmission should be forbidden in the energy regime where the $\pi (\pi^*)$ overlaps with only the $\pi^* (\pi)$ states. The band structure of 7-ZGNR with the FM coupling between the zigzag edges is very similar to that of 8-ZGNR so that the above analysis can also apply to the case. However, as discussed later the transmission is allowed even for the energy regime, where only the overlap between the $\pi (\pi^*)$ and the $\pi^* (\pi)$ states survives, due to the absence of the mirror plane in 7-ZGNR, leading to the linear $I$-$V$ characteristics as shown in Figs. 1(b) and (c).
To further verify the physical origin, explained above, of the peculiar $I$-$V$ curves which can be determined by the characteristic band structure of ZGNRs and the symmetry of wave functions, we construct WFs for the $\pi$ and $\pi^*$ states for 7- and 8-ZGNRs with the non-magnetic state $^{27}$ and evaluate tight-binding (TB) parameters using WFs. It is confirmed that WFs of 7-ZGNR is neither symmetric nor antisymmetric (not shown), and that the absolute value of the nearest neighbor hopping integral between the $\pi$ and $\pi^*$ states is $0.485$ eV which is comparable to the nearest neighbor hopping integral for the $\pi$ ($\pi^*$) state of $-0.777$ ($0.784$) eV. On the other hand, WFs for the $\pi$ and $\pi^*$ states of 8-ZGNR are antisymmetric and symmetric with respect to the $\sigma$ mirror plane, and localized in three unit cells along the ribbon direction as shown in Figs. 4(a) and (b). We confirm that the hopping integrals between WFs for the $\pi$ and $\pi^*$ states are nearly zero (not shown). Also it turns out that the next nearest neighbor hopping integral and more, $h_n (n = 2 - 4)$, are one order smaller than $h_1$ as shown in Table I. Thus, we can construct a simple TB model determined by a fitting, containing the essence of the spin filter effect, which consists of only the on-site energy, the nearest neighbor hopping integral, and the exchange splitting $\Delta_x$. The fitted parameters in Table I are determined so that the band width and the degeneracy of the $\pi$ and $\pi^*$ states at X-point can be reproduced. It should be noted that the two band TB model can be decomposed into two decoupled one band models due to the decoupling of the $\pi$ and $\pi^*$ states. The fact allows us to evaluate a spin polarized current for the $\pi (\pi^*)$ state using the Landauer formula $^{21}$ for the one band TB model and the fitted parameters as:

$$I = \int dE (f_L - f_R) T(E),$$

where $f_L$ and $f_R$ are the Fermi functions with the chemical potentials for the left and right leads, respectively. The transmission $T$ is given by an analytic formula:

$$T(E) = \frac{4S_L(E)S_R(E)}{[S_L(E) + S_R(E)]^2}$$

with

$$S_L(E) = \sqrt{4h_1^2 - \left[ E - (\varepsilon - \frac{1}{2} \Delta_x) \right]^2},$$

$$S_R(E) = \sqrt{4h_1^2 - \left[ E - (\varepsilon + \frac{1}{2} \Delta_x + V_{bias}) \right]^2},$$

where $S_L$ and $S_R$ are not zero only if the number in the square root is larger than zero, and therefore the transmission is finite within the energy range where both $S_L$ and $S_R$ survive. It
is emphasized that the behaviors of the conductance gap in Fig. (2) can be easily traced by the model. Using Eq. (1) we evaluate the gate voltage dependency of the $I$-$V$ characteristics for the up-spin state as shown in Fig. 4(c), where $\Delta_x$ of 0.553 eV, being that of the spin polarized 8-ZGNR, is used, and the gate voltage $V_{\text{gate}}$ is taken into account by adding $V_{\text{gate}}$ to the on-site energy. The proposed TB model can be validated by the fact that the $I$-$V$ characteristics at $V_{\text{gate}} = 0.0$ V is quite similar to that in Fig. 1(b) calculated by the NEGF method. In addition, it is found that the $I$-$V$ characteristics does not largely change as long as $V_{\text{gate}}$ lies in between $\pm \frac{1}{2} \Delta_x$, while the absolute threshold voltage at which the current starts to flow can be tuned. However, once $|V_{\text{gate}}|$ exceeds $\frac{1}{2} \Delta_x$, the originally suppressed current starts to leak in the positive $V_{\text{bias}}$ regime. The leak current is due to the fact that one of the chemical potentials is located at the outside of the conductance gap. In case that ZGNR contacts with a metallic substrate, the Fermi level of ZGNR might be shifted by charge transfer between them. For such a case the gate voltage dependency apparently suggests that the Fermi levels must be adjusted within the energy regime of the exchange splitting by applying a proper gate voltage in order to keep the high $I_{\text{up}}/I_{\text{down}}$.

IV. CONCLUSIONS

In summary, we demonstrate based on the NEGF method coupled with DFT that the symmetric ZGNRs with an AFM junction possess intrinsically a peculiar $I$-$V$ characteristics which can be regarded as a dual spin filter effect. It is shown by analyzing the band structure, WFs of the $\pi$ and $\pi^*$ states, and a TB model that the physical origin of the spin filter effect can be attributed to the spin polarized band structure of the symmetric ZGNR and the symmetry of wave functions of the $\pi$ and $\pi^*$ states near the Fermi level. The dual spin filter effect might initiate a novel avenue in developing spintronics using graphene based devices.
Acknowledgments

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Table:

TABLE I: Tight-binding parameters (eV) evaluated by WFs denoted by WF, and a fitting, denoted by fitted, for the $\pi$ and $\pi^*$ states of the non-spin polarized 8-ZGNR, where $\varepsilon$ is the on-site energy, and $h_1, h_2, \cdots$ the nearest and the second nearest neighbor hopping integrals, and so on. The Fermi level is set to zero.

|        | $\varepsilon$ | $h_1$   | $h_2$   | $h_3$   | $h_4$   |
|--------|---------------|---------|---------|---------|---------|
| $\pi$  (WF) | -1.3609      | -0.7660 | 0.0076  | 0.0529  | -0.0352 |
| $\pi^*$ (WF) | 1.4486       | 0.7708  | -0.0400 | -0.0513 | 0.0269  |
| $\pi$  (fitted) | -1.4165      | -0.7083 | 0       | 0       | 0       |
| $\pi^*$ (fitted) | 1.4135       | 0.7067  | 0       | 0       | 0       |
Figure captions:

Fig. 1
(a) 8-ZGNR, terminated by hydrogen atoms, with an AFM junction together with the spatial distribution of the spin density at $V_{bias} = 0$ V, where the red and blue colors stand for positive and negative signs, and $L$, $R$, and $C$ means the left and right leads, and the central scattering region. $I$-$V_{bias}$ curves for (b) the up-spin and (c) the down-spin states of 7- and 8-ZGNRs with the AFM junction.

Fig. 2
Conductance of 8-ZGNR with the AFM junction with $V_{bias}$ of (a) 0.0, (b) $-0.4$, and (c) $-1.0$ V. The inset in (a) shows the conductance gap near the chemical potentials.

Fig. 3
(a)-(c) Band structures of 8-ZGNR with a FM coupling corresponding to the left lead region in Fig. 1(a). Band structures shifted with (d) 0.0, (e) $-0.4$, and (f) $-1.0$ eV of 8-ZGNR with a FM coupling corresponding to the right lead region in Fig. 1(a). The blue and red shades show the conductance gap for the up- and down-spin electrons, respectively. The horizontal dot line indicates the chemical potential, being position dependent, of 8-ZGNR shown in Fig. 1(a).

Fig. 4
Wannier functions for (a) the $\pi$ and (b) $\pi^*$ states of the non-spin polarized 8-ZGNR. (c) $I$-$V_{bias}$ curves of the up-spin state calculated by the simple TB model with the AFM junction for a series of the gate voltage $V_{gate}$. 