Impurity induced spin filtering in graphene nanoribbons

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Zigzag-edged graphene nanoribbons (ZGNRs) are used to build devices in which transport with high spin polarization is realized by first-principles simulations. At first, we dope the semiconducting ZGNRs with B atoms on both sides to obtain a metallic ribbon. Then, in one segment of this ribbon which acts as the scattering region, the B atoms at one edge are substituted by C atoms or by N atoms. It is found that such devices show very good spin filtering effect which originates from the interaction between the impurity atoms and the edge states. © *2009 American Institute of Physics*. [doi:10.1063/1.3237165]

Zigzag-edged graphene nanoribbons (ZGNRs), one dimensional stripes that are cut away from the strictly two-dimensional graphene,[1,2] are a kind of carbon nanostructures with very peculiar electronic structure. One of its peculiarities lies in the fact that localized edge states are formed on the two sides,[3–5] with the spins of the these states on the two sides antiferromagnetically (AF) aligned but with the energy degenerate. This results in local magnetism on the two edges and makes ZGNRs promising building blocks for spintronic devices, which has initiated great interest.

However, due to the spin degeneracy of the edge states, pristine ZGNRs cannot carry spin polarized transport, which can only be realized by breaking the spin degeneracy of the edge states by various ways.[5–10] Recently, there are a lot of investigations that are related to the edge states and magnetism of ZGNRs.[5–10] One of the most interesting results is the half-metallicity obtained by applying transverse in-plane external electrical field,[5] edge modification[6] or B–N chain substitutions.[7,8] The importance of half-metallicity lies in the coexistence of the metallic nature of electrons with one spin and an insulating nature for the other spin and thus results in a completely spin polarized current.[11–14] This is what has been sought with great efforts in spintronics in recent years.

In this letter, we build ZGNR-based devices by controlled doping in which very good spin filtering can be achieved. Chemical doping as one of the most frequently adopted ways for tuning the properties of graphene nanoribbons has been extensively reported.[7–10,15,16] We first obtain a metallic ZGNR still with spin degeneracy by doping symmetrically B atoms on the two sides of a 8-ZGNR (named by the convention in previous literature[4,5]). Both the leads and the scattering region are composed of such a ribbon. Each lead is described by a supercell with five repeated carbon unit cells along transport direction [see Fig. 1(d)] and the scattering region contains different number (n) of such supercells but with the B atoms at one edge substituted by C atoms (we call it C-scheme) or by N atoms (we call it N-scheme) to break the spin degeneracy (see Fig. 1).

Electronic structures and geometry relaxations are calculated by the well tested SIESTA package,[17] which employs norm-conserving pseudopotentials and linear combinations of atomic orbitals as basis sets. Transport calculations are performed by ATK program,[18,19] which is implemented in SIESTA and is capable of calculating the conductance and *I-V* characteristics of nanoelectronic devices by means of nonequilibrium Green's function technique. The wave function is expanded with a single zeta basis set to get a reasonable balance between computation and accuracy. This choice was also adopted in the calculations of carbon systems by many authors.[15,20,21] The fineness of real space grid is determined by an equivalent plane wave cutoff 200 Ry. The exchange-correlation potential is treated at the level of generalized gradient approximation, with the form of Perdew–Burke–Ernzerhof.[22] The Brillouin zone for the lead is sampled by a $1 \times 1 \times 20$ k-point grid.

Before computing transport properties, the structures of all the devices have been fully relaxed, with the force tolerance of 0.04 eV/Å being reached. It is found that AF is still the spin configuration with the lowest energy after doping. Figures 2 and 3 illustrate the conductance as a function of n for the C-scheme and N-scheme. It is clearly shown that with
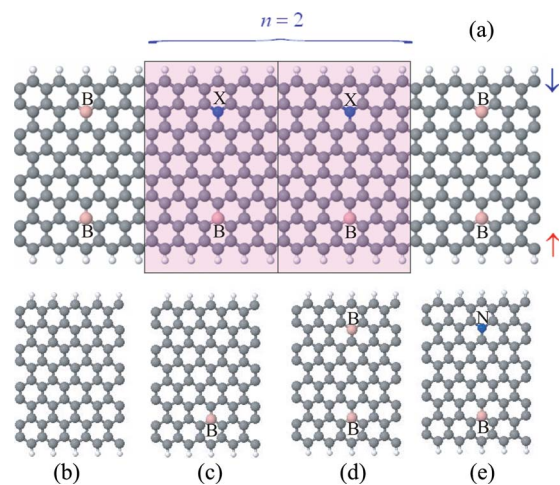

FIG. 1. (Color online) (a) The geometry structure of the device made from a 8-ZGNR. The scattering region (the shadowed area) contains different number (n) of lead supercells. This figure shows the n=2 case. The red and blue arrows indicate the AF aligned up (↑) and down (↓) spins of the valence edge states. The lower part shows four different doping situations: (b) no doping; (c) B doping; (d) B–B doping; and (e) B–N doping. The positions of the impurity atoms are shown in pink or blue and labeled by B, N, or X(=B,C,N).

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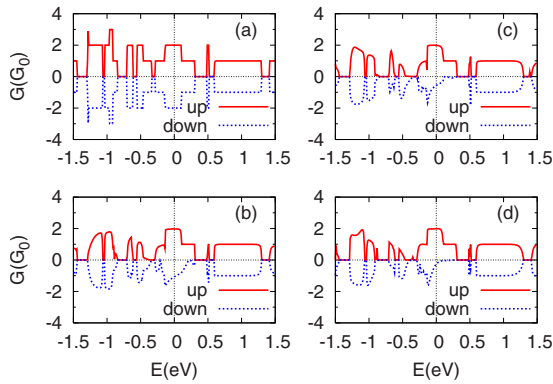[b] Electronic mail: zzeng@theory.issp.ac.cn.

FIG. 2. (Color online) Equilibrium conductance as a function of n for the C-scheme with: (a) $n=0$; (b) $n=1$; (c) $n=2$; and (d) $n=3$.

FIG. 4. (Color online) The DOS for: (a) no doping; (b) B doping; (c) B–B doping, and (d) B–N doping.

$n=0$ (a periodic system), around the Fermi level, both spin channels contribute $2G_0$ ($G_0=e^2/h$: half conductance quantum) conductance [see Figs. 2(a) and 3(a)]. We are interested in low bias transport in such devices since transport with possible high spin polarization can only be achieved through the edge states which lie at or very close to the Fermi level. Thus we will focus on changes of the conductance platforms around the Fermi level as a function of n, namely, the conductance in the energy range $[-0.30, 0.30]$ eV. When $n=1$, the conductance of the spin down channel in both the C-scheme and N-scheme is greatly reduced [see Figs. 2(b) and 3(b)] due to the scattering in the shadowed region in Fig. 1. However, comparatively, the conductance of the spin up channel almost keeps unchanged. With the increase in n in the C-scheme, the conductance of spin down channel above the Fermi level (in $[0.00, 0.30]$ eV) decreases rapidly and reaches zero when $n=3$, while the conductance of this channel below the Fermi level (in $[-0.30, 0.00]$ eV) still keeps a high value. In the meantime, the conductance in the spin up channel changes very little as n varying [see Figs. 2(c) and 2(d)]. Thus, a very good filtering effect is achieved above the Fermi level in the spin down channel.

What is more interesting is that, in the N-scheme, in the whole energy range $[-0.30, 0.30]$ eV, the spin down channel is rapidly suppressed with the increase in n and completely blocked when $n=3$, while the spin up channel always keeps a high value [see Figs. 3(c) and 3(d)]. Thus 100% spin polarization of the conductance is realized around the Fermi level.
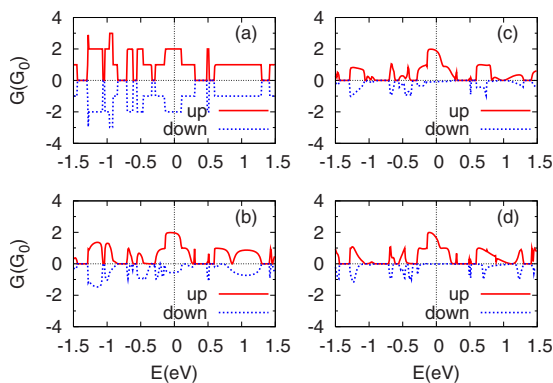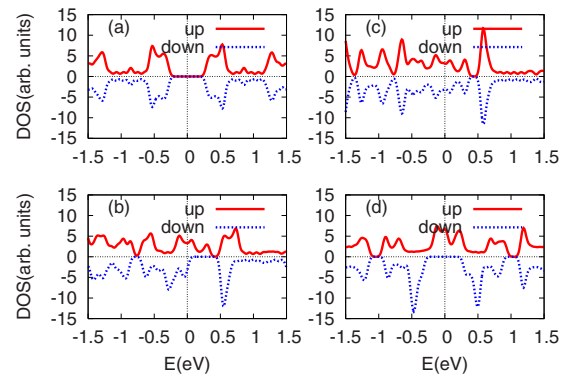
We now inspect the origins of the obtained full suppression of the transmission in the spin down channel. To this aim we have investigated the effects of B and N doping on the electronic structure of ZGNRs. Particularly, we consider the following doping situations [see Figs. 1(b)–1(e)]: (1) no doping; (2) doping one B atom at one edge (we call it B doping); (3) doping two B symmetrically on the two edges (B–B doping); and (4) doping one B and N on the two edges (B–N doping). The density of states (DOS) of these cases is shown in Fig. 4. We clearly see that without doping, the system is a semiconductor and the two spins are degenerate [see Fig. 4(a)].

It is well known that the edge states in ZGNRs are localized at the edges and decay exponentially into the center of the ribbon.[5] Furthermore, in pristine ZGNRs, the valence edge states with up spin are localized at one (the lower) edge, while those with down spin are localized at the other (the upper) edge, as shown by a cartoon in Fig. 5(a). However, it is an opposite case for the conduction edge states [see Fig. 5(b)].

When one B atom is doped at the lower edge, it introduces a hole and attracts one electron from the valence edge states with up spin [see Fig. 5(a)]; thus making the spin up channel of the valence band partially filled, while keeping the spin down channel in this band still fully occupied [see Fig. 4(b)]. When another B atom is doped at the upper edge, it also introduces a hole and consequently one electron from the valence edge states at the upper edge will transfer to the B atom, thus the spin down channel of the valence band also becomes partially filled [see Fig. 4(c)]. In contrast, when we dope B at the lower edge and N at the upper edge, B atom attracts one electron from the valence edge states with up spin, while the N atom donates an electron which goes to the conduction edge states with up spin. Thus the spin up channel both in the valence band and the conduction band tend to

FIG. 3. (Color online) Equilibrium conductance as a function of n for the N-scheme with: (a) $n=0$; (b) $n=1$; (c) $n=2$; and (d) $n=3$.
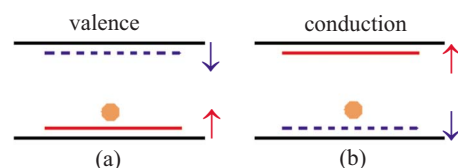

FIG. 5. (Color online) The cartoon representation of the positions of the edge states in: (a) the valence bands and (b) the conduction bands. The red solid (blue dashed) line shows the positions of the edge states with up (down) spin labled by the up (down) arrow. The red dot indicates one doping site.

be partially occupied. Meanwhile, the effects to the spin down channel are much smaller and this channel is still fully occupied or totally empty [see Fig. 4(d)]. Consequently, the spin down channel above the Fermi level in the C-scheme and the spin down channel both above and below the Fermi level in the N-scheme are completely suppressed when the length of the scattering region becomes long enough ($n \geq 3$) since there are no states that can mediate the transmission in these energy ranges. Even with $n \leq 2$, the transmission of spin down channel is also greatly reduced due to scattering.

Finally, we note that, in order to obtain good spin filtering effect, the positions of the B and N atoms in the scattering region are very important. Our study shows that the best positions are for the impurity atoms to be located at the second or third zigzag chains counted from the edges. In addition, we have done calculations for other ribbons with different width (7-ZGNR, 9-ZGNR, 12-ZGNR, and 18-ZGNR) and it is found that spin filtering effect is always achieved. Furthermore, in principle, spin filtering can always be observed when such a ribbon with finite length is attached to any metallic leads.

In conclusion, by using two different doping schemes, two different kinds of spin filtering are achieved. By doping B atoms only at one edge in the scattering region, the transmission above the Fermi level in one spin channel is completely suppressed. If we dope B at one edge and N at the other edge, fully spin polarized transport can be realized in energy range $[-0.30, 0.30]$ eV around the Fermi level and the scattering region is not required to be very long. The length of three supercells with about 40 Å is enough. This is very beneficial for practical realization of complete spin filtering using graphene nanoribbons. These findings open new possibilities of application of graphene nanoribbons in spintronic devices.

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