Making a field effect transistor on a single graphene nanoribbon by selective doping

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Using first-principles electronic structure calculations, we show a metal-semiconductor transition of a metallic graphene nanoribbon with zigzag edges induced by substitutional doping of nitrogen or boron atoms at the edges. A field effect transistor consisting of a metal-semiconductor-metal junction can then be constructed by selective doping of the ribbon edges. The current-voltage characteristics of such a prototype device is determined by the first-principles quantum transport calculations. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2826547]

Graphene nanoribbons (GNRs) have attracted intensive interest because of their unique electronic properties and vast potential for device applications.[1–12] In particular, the GNR-based devices could behave like molecule devices, such as those based on carbon nanotubes (CNTs),[13–15] but with some inherent advantages, including more straightforward fabrication processes by using lithography technique and better control of crystallographic orientation in constructing device junctions.[6,8,9,12] Different from CNTs, the existence of edge structures endows GNR with some novel physical and chemical properties, such as the high edge reactivity[16] and unique edge states around the Fermi level.[1] These may offer key advantages in realizing various electronic applications via edge chemical functionalization, such as *doping*.

It is well known that nitrogen (N) and boron (B)atoms are typical substitutional dopants in carbon materials (such as CNTs[17]), and their binding with the C atom is covalent and quite strong, comparable to that of host C–C bond. The incorporation of N or B atoms into the carbon materials will influence the electronic and transport properties of the C host by introducing extra carries and/or new scattering centers.[18] In this letter, we theoretically show that a metal-semiconductor transition (MST) can be induced in an "armchair" GNR (with zigzag edges)[6] by substitutional doping of N or B atoms on the edges. Based on this finding, we propose a field effect transistor (FET) made from a single armchair GNR via selective edge functionalization (doping), and demonstrate that the characteristics of such a FET is comparable with that of the CNT-FETs.

Our electronic structure calculations are performed using the Vienna *ab-initio* simulation package,[19] which implements the formalism of plane wave ultrasoft pseudopotential based on density functional theory (DFT) within local density approximation. The plane wave cutoff energy is set as 350 eV. Structural optimization was first carried out on all doped systems until the residual forces on all ions were converged to below 0.01 eV/Å. The quantum transport calculations were performed using the ATOMISTIX TOOLKIT2.0 package,[20,21] which implements DFT-based real-space, nonequilibrium Green's function formalism. The mesh cutoff of carbon atom is chosen as 100 Ry to achieve the balance between calculation efficiency and accuracy.

A (2,2) armchair GNR with H termination [Fig. 1(a)] is chosen as a model system to study the effect of substitutional doping of N and B atoms in armchair GNRs. Herein, the armchair GNRs are denoted using a nomenclature in analogy to armchair carbon nanotubes that would unfold into corresponding ribbons with zigzag edges.[6] Our calculations show that the zero-temperature ground state of armchair GNRs is spin polarized in agreement with the previous calculations.[4] The energy of the spin-polarized state is only 20 meV per edge atom lower than the spin-unpolarized state. However, the spin-polarized state would become unstable with respect to the spin-unpolarized state in the presence of a ballistic current through the GNRs.[10] Moreover, the magnetization was shown theoretically to be forbidden in one-dimensional and two-dimensional systems at finite temperatures,[22] while most transistors work at finite temperature (room temperature). Therefore, we will only consider the spin-unpolarized state of armchair GNRs for our investigation of GNR-based devices. In this case, pristine (2,2) GNR is metallic with partially flatbands at the Fermi energy (the so-called "edge states"[1]) localized at the ribbon edges [Fig. 1(b)].

Doping is achieved in the supercell made of the 4 unit cells by substituting a N or B atom for a C atom in the GNRs. Four different doping sites are considered, as shown in Fig. 1(a), and the corresponding total energies are calculated to determine the most energy-favorable site. For N doping, the calculated substitution energy of site 1 is much lower than those of site 2 (by 1.07 eV), site 3 (by 1.00 eV), and site 4 (by 1.32 eV). While for the case of B doping, the corresponding energy differences are 0.69, 0.60, and 0.97 eV, respectively. This clearly indicates that the edge (site 1) of GNR is the most energetically favorable site for N or B substitution. Furthermore, it is found that the substitution of N or B atoms for C atoms does not affect the stability of overall configuration, consistent with the previous experimental results.[23] The local structural distortion induced by B-doping is more pronounced than N-doping, like the case in CNTs,[17] which can be related to the atomic radius difference between N (or B) and C atom.

Since both edges of a GNR are identically active for doping and it is difficult in practice to realize selective doping merely on one edge while keeping another edge un-

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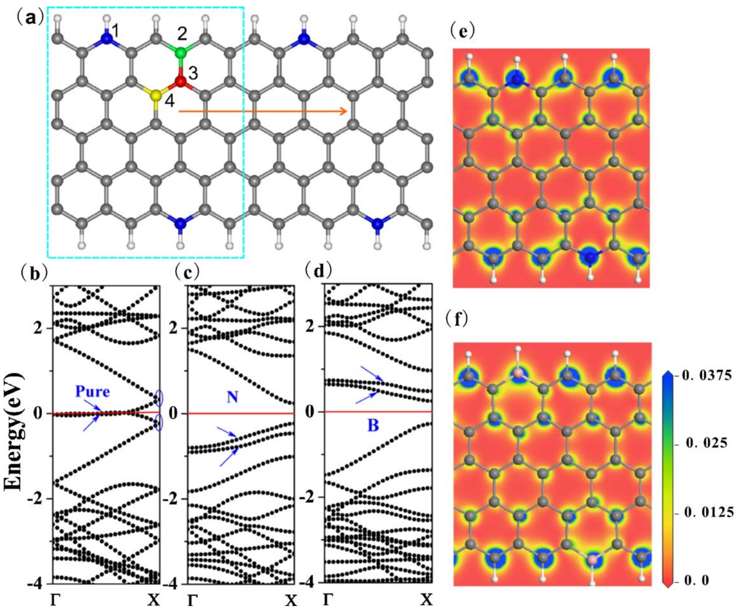

FIG. 1. (Color online) (a) Atomic structure of the armchair (2,2) GNR, where the arrow shows the periodic direction. The edges are terminated by H atoms (denoted by small white spheres). Four different substitutional sites are considered. (b) Band structure of pure (2,2) GNR. The Fermi energy is set to zero and the edge states are indicated by the arrows. (c) Band structure of the N-doped (2,2) GNR. (d) Band structure of the B-doped (2,2) GNR. The partial charge density of two bands labeled by the two arrows of the N-doped and B-doped GNRs are shown in (e) and (f), respectively. The scale bar is in units of e Å^{-3}.

changed, we will focus our study on the cases where two carbon atoms (one per edge) in the supercell are simultaneously substituted by two N or B atoms. The two substitutional edge sites are determined by minimizing the total energy of the system, which are indicated by blue atoms in Fig. 1(a). Figures 1(c) and 1(d) show the band structures of the N-doped and B-doped (2,2) GNRs, respectively. From the partial charge density analysis [shown in Figs. 1(e) and 1(f)], we find that the energy states [indicated by two arrows in Figs. 1(c) and 1(d)] near the Fermi energy are mainly localized at two zigzag edges and are derived from the original edge states. Most importantly, the substitutional doping of the N (or B) atoms has removed the degeneracy of the eigenvalues at X point and, thus, open an energy gap. The N (B) substitution consequently changes the original band filling [the two states denoted by the arrows are now fully occupied (unoccupied)] and eventually induces a transition of the armchair GNR from metallic to semiconducting. This phenomenon is rather interesting and somewhat unexpected since impurity doping, in general, results in a transition of semiconducting to metallic. We have examined the cases for different substitutional sites of two N (B) atoms in GNRs and observed similar MST in the system. It should be noted that our above calculations correspond to a uniform impurity distribution since the conventional periodic boundary condition is adopted and there is only one impurity at each edge in the unit cell. To clarify the effect of random substitution, we have also studied electronic structure of GNRs using a larger supercell containing two impurities at each edge, where the "nonperiodic" substitution could be partially considered with different configurations of the impurities. It is found that compared with the periodic substitution mentioned above, such nonperiodic substitution is energetically unfavorable and, importantly, does not change the MST of GNRs in essence. The above results show that the edge doping-induced transition could be general in armchair GNRs.

Next we will investigate the effect of the doping concentration and nanoribbon width on the electronic properties of the doped GNRs. Herein, we define the linear doping concentration as $n_l = N_{\text{dopant}}/L$, where N_{dopant} is the number of dopants per supercell and L is the length of the supercell along the nanoribbon. Figure 2(a) shows the band gaps of N-doped and B-doped (2,2) GNRs as a function of the linear doping concentration n_l. Note that the configuration we studied at each doping concentration is always chosen as the energetically most favorable one. Interestingly, it is found that the band gap first increases with increasing n_l until it reaches the maximum (0.77 and 0.82 eV for N doping and B doping, respectively) at n_l of 0.1365 Å^{-1}, and then decreases with further increasing n_l. The GNRs with B substitution have slightly larger band gaps than those with N substitution. In addition, the band gap of the GNR decreases with increasing ribbon width and eventually diminishes when the width is too large [Fig. 2(b)].

Among many challenges for the use of graphene or nanoribbon in FETs, an important and practical issue is to fabricate semiconducting channel with large enough band gap, which is crucial for effectively reducing the leakage current and improving the critical performance parameters such as on/off current ratio. However, until recently it is still very hard to experimentally fabricate semiconducting GNRs with the energy gap larger than 0.2 eV.[8,9] The doping-induced MST we report here may be used to provide another way to fabricate transistor semiconducting channels in future graphene-based devices. Below we will demonstrate the characteristics and performance parameters of the N-doped GNR-FET by first-principles quantum transport calculations. It should be noted that both the electrodes and the conduction channel are integrated on a single GNR in such a device [Fig. 3(a)]. Such a linear configuration can also be advantageous to increase the device density in an electronic circuit

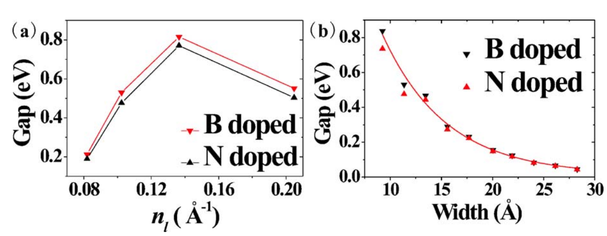

FIG. 2. (Color online) (a) The dependence of the band gap on the linear doping concentration for the N- and B-doped (2,2) GNR. (b) The dependence of the band gap on the GNR width with the linear doping concentration of 0.1024 Å^{-1}.

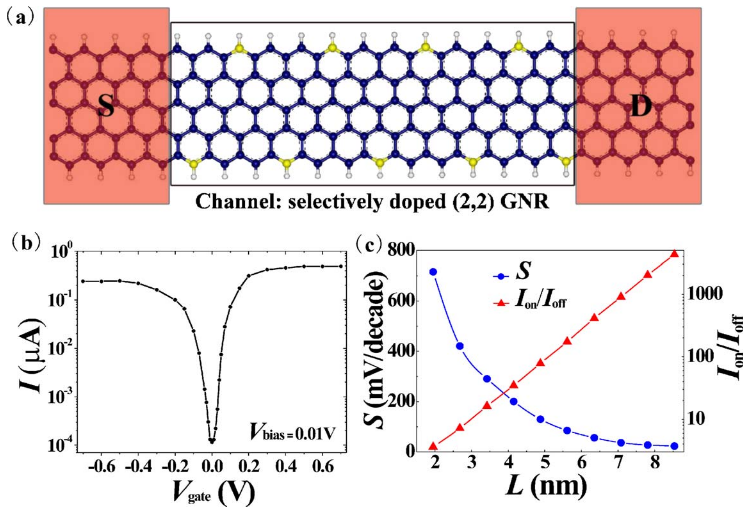

FIG. 3. (Color online) (a) The schematic structure of the field effect transistor (FET) made from a single (2,2) GNR. The semiconducting channel is obtained by edge doping of N in a finite-length region (the center region). (b) Simulated I-V_{gate} curves of N-doped GNR-FETs under V_{bias}=0.01 V. The channel length is 8.54 nm and the linear doping concentration is 0.1365 Å^{-1}. (c) The dependence of the subthreshold swing S (blue line) and the on/off current ratio (red line) on the channel length L.

as well as to simplify the fabrication process.

Figure 3(b) shows the typical I-V_{gate} curves for the N-doped GNR-FET (with the channel length of 8.54 nm) at the bias voltage V_{bias}=0.01 V. In the voltage window of −0.7–0.7 V, the doped FET exhibits ambipolar characteristics with the on current (I_{on}) of ~1 μA. The minimum leakage current is limited to a rather small value ($\sim 1.2 \times 10^{-4}$ μA), and a high on/off current ratio ($I_{on}/I_{off} > 2000$) is achieved in such N-doped GNR-FETs. The large on/off current ratio manifests the "perfect" atomic interface between the metal-semiconductor GNR junctions with a minimum contact resistance. It increases the possibility of experimental operation between on and off states. Moreover, such a device exhibits an excellent "theoretical" switching characteristics with a subthreshold swing $S = \ln(10)[dV_{gate}/d(\ln I)]$ ~40 mV/decade. This is comparable to that of high performance CNT-FET (60–80 mV/decade) (Refs. 14 and 15) and reaches the theoretical limit of S (~60 mV/decade) for Si-based FET at room temperature.[24] The switching mechanism here can be understood in terms of a semiclassical band bending mechanism.[6]

We further studied the relationship between the device performance and the channel length by calculating I-V_{gate} curve of N-doped GNR-FETs as a function of the doped channel length from 0.49 to 8.54 nm while keeping the bias voltage V_{bias} at 0.01 V. As shown in Fig. 3(c), the subthreshold swing S of these doped GNR-FETs decreases and the on/off current ratio increases exponentially. Our calculations show that in order to obtain good device performance with small S value (e.g., below 100 mV/decade) and high on/off current ratio (e.g., above 100), the doped channel length needs to be longer than 5 nm. The minimum leakage current of those FETs with the doped channels shorter than this critical length will be greatly enhanced by direct tunneling, which lowers the device performance.

In conclusion, using first-principles calculations, we have studied the electronic and transport properties of armchair GNRs with substitutional edge doping of N or B atoms. It is found that the edge doping will greatly modify the band structure (especially the edge states) of the system, and induce a metal-semiconductor transition. The band gap of the doped GNR exhibits a strong dependence on both the linear doping concentration and the nanoribbon width. It is demonstrated that electronic devices, such as FETs, could be integrated on a single GNR by selective edge doping/chemical functionalization, which avoids the need to connect/integrate the GNRs with different orientations. Simulated I-V_{gate} curves indicate that such FETs exhibit ambipolar on-off characteristics with excellent performance parameters.

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