Density functional theory investigation of negative differential resistance and efficient spin filtering in niobium-doped armchair graphene nanoribbons

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Using density functional theory calculations in combination with a non-equilibrium Green’s function method, we explore the transport properties of a niobium-doped (~3.57%) armchair graphene nanoribbon of dimer length 7 in a two-terminal device configuration. The band structure of the supercell with niobium atoms showed spin splitting near the Fermi level. The spin-dependent transport properties and spin-resolved band structure of electrodes with applied bias values were calculated to understand the spin filter and the negative differential resistance (NDR) effect. The spin filter efficiency of the device was found to be more than 95% in the applied voltage range of 0.15 V to 0.5 V for the antiparallel configuration, and the device is suitable as an efficient spin filter at room temperature. The parallel configuration has a higher range, 0 V to 0.5 V, with an efficiency more than 70%. The peak-to-valley ratios in the parallel configuration for spin-up and spin-down currents were 4.5 and 17.8, respectively, while in the antiparallel configuration, the values were 4.57 and 37.5, respectively. The combined NDR characteristic showed figure of merit with a peak current density of ~6 mA μm⁻¹ and a PVR of ~4.6, useful for logical application. Our findings open a new way to produce multifunctional spintronic devices based on niobium-doped armchair graphene nanoribbons.

1. Introduction

Graphene, a two-dimensional material, has attracted a lot of interest because of its unique electronic and mechanical properties for applications in nanoelectronic devices. High electron mobility, spin injection capability and long spin relaxation times and lengths make it a promising material for spintronic applications, such as spin valves, spin filters, spin qubits, and spin field-effect transistors. Chisholm et al. found that graphene can prevent the oxidation of incorporated single atoms and small nanoclusters of atoms, thus facilitating catalytic applications. By incorporating appropriate single atoms in graphene, electronic and magnetic devices are possible. Krasheninnikov et al., using density functional theory (DFT), calculated bond lengths, binding energies and magnetic moments in graphene embedded with transition metal atoms. Enhanced catalytic activities for the CO oxidation and oxygen reduction reactions by Cu, Fe, Pt, Nb and Co-doped graphene sheets have been reported. Nb acts as a p/n-dopant on the graphene surface depending upon separation, stress and other factors. Nb–graphene contact resistivity has been experimentally found to be around 25 kΩ μm. Nb has a critical temperature of 9.25 K and acts as a superconductor in its bulk phase at lower temperatures. Nb/Ti contacts show a high critical magnetic field (4 T at 2 K) and can be used as a superconductor interconnecting monolayer graphene. Banerjee et al. demonstrated superconducting properties in the Ni₈₀Fe₂₀/Ho/Nb/Ho/Ni₈₀Fe₂₀/FeMn heterostructure. The thickness of the Nb layer was adjusted to achieve superconductivity in the range of 2–7 K, and the structure showed the spin selective properties useful for spintronic devices. Wei et al. reported the electrical spin injection and detection of spin-polarized carriers into Nb-doped strontium titanate (SrTiO₃) by the Hanle technique. Zhang et al. reported that a single Nb atom substituted in defective graphite layers induced local structural asymmetry and a permanent electric dipole. A two-dimensional single layer of MoS₂ doped with Nb showed spin splitting characteristics near the Fermi level.

Graphene nanoribbons (GNRs) show tunable electronic properties depending on the edge structure, chemical doping, geometrical deformation, structural defects, and external electric and magnetic fields. According to the crystallographic orientation of the edge structure, two types of GNRs exist: zigzag-edge graphene nanoribbons (ZGNRs) and armchair graphene nanoribbons (AGNRs). In the presence of a transverse electric field, spin splitting occurs in ZGNRs, which have edge states, while AGNRs do not show spin selective behavior. Spin filters, spin...
valves and spintronic logic gates have been theoretically studied for GNRs having edge structures like sawtooth, phosphorus-doped, oxygen-terminated and voltage-driven GNRs.\textsuperscript{22–25} Recently, Zhang et al. found spin filtering, rectifying and negative differential resistance (NDR) properties in the special edges of B- and N-doped hydrogenated 7AGNRs (dimer length of 7) with 100% spin filter efficiency.\textsuperscript{26} Graphyne nanoribbons doped with transition metals were found to be half-metal with 100% spin polarization at the Fermi level.\textsuperscript{27} Computational studies suggest that the central position of the AGNR is most stable for substitutional doping.\textsuperscript{28} The edge modification of AGNRs by Mn and F (AGNR–Mn–F$_2$) introduces half-metallic properties and 100% spin polarization.\textsuperscript{29} However, Nb doping in AGNRs has not been reported yet.

The fabrication of GNRs down to a width of 20 nm has been reported by using e-beam lithography.\textsuperscript{20,30} GNRs with smooth edges and a width of sub-10 nm can be produced by the sonication of exfoliated graphite flakes.\textsuperscript{31} The scanning tunneling microscopy (STM) technique has been used for cutting graphene up to a width of 1.7 nm with potential applied on the STM tip.\textsuperscript{32} 7AGNRs have been chemically derived on the Au(1 1 1) surface.\textsuperscript{33} All these studies have experimental challenges in chemical doping, absorption and manipulation.

The negative differential resistance (NDR) properties in devices are the basis for many electronic circuits, such as frequency multipliers, memories, fast switching circuits and high-frequency oscillators. NDR properties can be introduced and modified by adjusting strain, chirality, defects, doping and oxidation in two-terminal and three-terminal graphene devices.\textsuperscript{34–36} Doping in GNRs can form an impurity band near the Fermi level and introduce NDR properties. The peak-to-valley ratio (PVR) depends on the separation of the impurity band from the valence and conduction bands. In this article, we present current–voltage ($I$–$V$) characteristics of a two-terminal Nb-doped 7AGNR device with Nb substituted at the central position and show the clear NDR behavior of the device.

2. Computational methods

Electronic structural calculations were performed using the \textit{ab initio} based software package, ATK, based on the self-consistent non-equilibrium Green’s function (NEGF) and DFT.\textsuperscript{37,38} We optimized all the structures with the spin-polarized local density approximation (LSDA).\textsuperscript{39–41} A force tolerance of 0.05 eV Å$^{-1}$ and a cutoff energy of 75 Hartree with a Monkhorst–Pack $k$-mesh of 1 $\times$ 1 $\times$ 100 were chosen, where the 100 $k$-point is employed in the transport direction. A single-$\zeta$-polarized basis set was used for electron wave function.\textsuperscript{39,40,42} For transport calculations, we varied the bias from 0 V to 0.5 V. The spin-dependent current through a two-terminal device with a scattering region was calculated using the Landauer–Buttiker formula:\textsuperscript{43}

$$I^{(1)}(V_b) = \frac{e}{h} \int T^{(1)}(E, V_b)[f_l(E - \mu_l) - f_r(E - \mu_r)]dE$$

where $T^{(1)}(E, V_b)$ is the spin-resolved transmission coefficient at energy $E$ and bias voltage $V_b$, $\mu_l$ and $\mu_r$ are the electrochemical potentials of the left and right electrodes, and $\mu_l - \mu_r = eV_b$.

3. Results and discussion

The band structures for hydrogen saturated 7AGNR converges to spin-unpolarized characteristics, as shown in Fig. 2(a), and the band gap at the $\tau$ point is 1.37 eV. DFT calculations underestimate the band gap for low-dimensional semiconductors.\textsuperscript{44,45} The band structure for the supercell of Nb–7AGNR given in Fig. 2(b) shows the splitting of spin-up and spin-down subbands. The spin–orbit splitting is 95 and 34 meV for the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively, at the $\tau$ point in the band structure of Nb–7AGNR. The addition of the Nb atom in the supercell introduces impurity states near the Fermi level. The splitting of spin-up and spin-down subbands and intermediate spin-resolved band states near the Fermi level yields the spin-dependent transport properties in Nb–7AGNR.

To study the spin-polarized transport properties of the devices, parallel (P) and antiparallel (AP) spin configurations are used. In the P configuration, the spin orientations for both left and right electrodes are up, while they are up (down) in the AP configuration. The current and voltage ($I$–$V$) characteristics from the spin-polarized transport calculations for the P and AP
configurations of the Nb–7AGNR two-port devices, for the applied bias voltages from 0 to 0.5 V, are shown in Fig. 3. We applied the high bias in the left electrode for all the calculations in the remaining article. Since our structure is symmetrical in both the electrodes, the results will be identical for both negative and positive bias. The $I–V$ characteristics of the P configuration in Fig. 3(a) show the NDR properties. The spin-up current increases as the bias increases from 0 V to 0.13 V and reaches a maximum of 5.671 $\mu$A. Beyond 0.13 V, the spin-up current decreases and reaches a local minimum of 1.256 $\mu$A at 0.35 V. The peak-to-valley ratio (PVR) for the spin-up current is 4.5. The spin-down current magnitude is comparatively lower; however, its PVR is 17.8, about eight times the PVR of the spin-down current, as shown in the inset of Fig. 3(a). $V_P$ and $V_V$ for the total current in the AP configuration are 0.18 and 0.45 V, respectively, with a PVR of 4.59 in the voltage range of 0.18–0.45 V having a peak current density of 6.3 mA $\mu$m$^{-1}$.

The performance parameters of the PVR of current, voltage range and peak current density obtained for Nb–7AGNR are compared with other reported studies of the graphene-based NDR in Table 1. In the present case, the current density of Nb–7AGNR is a moderate value with respect to other reported results, and this emphasizes that medium power can be provided by this NDR device. We find that our result is quite comparable with the reported studies. In particular, the peak current density of Nb–7AGNR is better than the N-doped AGNR.$^{34}$ We observe that the voltage range is little less in the present case. Earlier reports suggest that the N-doped 7AGNR has a very high (50) PVR with low current density (0.9 mA $\mu$m$^{-1}$),$^{34}$ while the P-doped 7AGNR shows a low (3.9) PVR with moderately high current density (19 mA $\mu$m$^{-1}$).$^{35}$ The left and right electrodes doped with N and B atoms, respectively, in 7AGNR showed the p–n type NDR device with low (4.5) PVR with very high (54 mA $\mu$m$^{-1}$) current density.$^{48}$ Experimental studies of dual-gated graphene FETs show NDR properties under optimized source, drain and gate potential.$^{35}$ The device channel length varying from 200 nm to 5 $\mu$m shows the PVR of 1.07 and 2.2 with current densities of 0.7 and 1.01 mA $\mu$m$^{-1}$ in the bias range of 2.0–2.6 V and 2.0–2.45 V respectively.$^{35,36}$ However, no experimental results have been reported yet on the doped AGNR.

Next, we calculated the spin filtering efficiency (SFE) of Nb–7AGNR with SFE = $(I_{\uparrow} - I_{\downarrow})/(I_{\uparrow} + I_{\downarrow})$, where $I_{\uparrow}$ and $I_{\downarrow}$ are the $I–V$ characteristics of the AP configuration in Fig. 3(b) also show NDR properties. The spin-down current increases as the bias voltage increases from 0 V to 0.18 V, and reaches a maximum of 5.868 $\mu$A. Beyond 0.18 V, the spin-down current decreases and reaches a local minimum of 1.285 $\mu$A at 0.45 V. The PVR for the spin-down current is 4.57. The spin-up current magnitude is comparatively lower; however, its PVR is 37.5, about eight times the PVR of the spin-down current, as shown in the inset of Fig. 3(b).

Fig. 3 Spin–resolved $I–V$ characteristics of Nb–7AGNR for the (a) parallel and (b) antiparallel spin configurations.
spin-up and down currents, respectively. At zero bias, we calculated the SFE from the formula \( SFE = \frac{T_{up}(E_f) - T_{down}(E_f)}{T_{up}(E_f) + T_{down}(E_f)} \), where \( T_{up}(E_f) \) and \( T_{down}(E_f) \) are the transmission coefficients of the spin-up and spin-down current, respectively, at the Fermi level. Fig. 4 shows the SFE as a function of applied bias voltage. The SFE for the P configuration of Nb–7AGNR, as in Fig. 4, is greater than 70% in the bias range of 0 to 0.5 V. The AP configuration shows greater than 95% SFE in the bias range from 0.15 to 0.5 V. So both P and AP configurations can act as a good spin filter device.

Nb–7AGNR has a high SFE with a large voltage range. Table 2 shows the comparison of the SFE of Nb–7AGNR with that of other GNR-based spin filter devices. The voltage range for Nb–7AGNR in the P and AP configurations is comparable to the reported results of other theoretical studies.\(^{22,24,26,40} \) For Nb–7AGNR, a wide bias window (BW) of 0–0.5 V for the P and 0.15–0.5 V for the AP configuration is available for spin filtering applications.

Electrical transport performance is closely related to the electronic structure of the electrodes and scattering regions. To understand the transport phenomena, the spin-polarized transmission coefficient of Nb-doped 7AGNR versus the energy level of the left (right) electrodes and the bias voltage is plotted. Bias voltages influence the shapes and positions of the transmission coefficients. Previous research found that the transmission channel will be open only in the case of overlapping of similar bands in the BW of the left (right) electrodes.\(^{46} \) If opposite bands are present, the transmission channel will be closed for that particular band. We consider the condition of applied bias (0, 0.1, 0.2, 0.3 and 0.4 V) and the magnetization configurations P and AP. The band structures for the left and right electrodes are represented as the BSL and the BSR respectively, and the spin configuration is represented as spin-up (SU) and spin-down (SD) in the figure of the following discussion.

In the P configuration, the spin orientations of both left and right electrodes are up and the band structures are the same for the left/right electrodes at a bias of 0 V, as shown in Fig. 5(a). Due to a similar spin-resolved subband, the same band is present in symmetry to each other for both electrodes. Around the Fermi level, the spin-up bands are present in the left (right) electrodes, so the spin-up transport channel is open with a high transmission coefficient. The spin-down bands are present above the Fermi level in both electrodes, but they do not cross the level, so the spin-down transport channel is closed and has a zero transmission coefficient.

![Fig. 4 The spin filter efficiency (SFE) of Nb–7AGNR for the P and AP configurations.](image-url)
In the AP configuration, the spin orientation of the left (right) electrode is up (down) and the spin-resolved band structures are reversed for the left (right) electrodes at a bias of 0 V as in Fig. 5(b). Due to different band structures around the Fermi level, the spin-up (spin-down) bands are present in the left (right) electrode. So, there is no possibility of any overlapping of the spin band, and thus the transmission channel is closed for the up (down) spin and has a zero transmission coefficient.

When a bias is applied to the two-port device, a positive (negative) bias shifts the band structure of the left (right) electrodes downward (upward). Our device is positively biased, so the left (right) electrode band structure will shift downward (upward). The down (up) movement of the band structure leads...
to a variation in the spin band overlapping in the BW for the left (right) electrodes. For the P configuration, the transmission spectrum and the band shifting of the left (right) electrodes are displayed in Fig. 6. As the bias increases, the current integral area increases due to an increase in the transmission coefficient up to 0.13 V. Further increase in bias shifts the spin band away from the BW, which results in the decrease of transmission, and as a consequence, causes the spin-polarized NDR characteristics. When the bias is 0.3 V, the transmission coefficient decreases due to the decrease in the overlapping band for transmission from the left electrode to the right electrode. At a bias of 0.4 V, current starts increasing again due to an increase in the spin band overlapping in the BW. The spin-down transmission spectrum has a low coefficient initially, increases up to 0.1 V and decreases further for 0.2, 0.3 and 0.4 V.

In the AP configuration, the transmission spectrum and the band shifting of the left (right) electrode are shown in Fig. 7. Initially, at a bias of 0 V, as shown in Fig. 5(b), no symmetrical spin band is available for the transmission of the spin-up (down) current. As the bias increases to 0.1 V, down (up) shifting of the spin band in the left (right) electrodes opens the transmission channel for the spin-down current (see Fig. 7(a)). A small transmission coefficient observed for spin-up, which gives rise to the small current, also follows a similar behavior. As the bias voltage increases, the current integral area increases up to 0.18 V bias due to the increase in the transmission coefficient and then decreases to a minimum at 0.45 V. It again rises up to 0.3 V as more spin-down band dispersion is coming in the BW. These characteristics show the spin-polarized NDR characteristics. When the bias is near 0.5 V, the transmission coefficient decreases due to less overlapping band being available for transmission from the left electrode to the right electrode. The spin-down transmission spectrum has a low coefficient, which also increases up to 0.1 V and decreases to near zero at 0.2 V and remains negligible up to 0.5 V. So, we observe a significantly high spin-up current from 0 V to 0.5 V.

Altogether the calculated spin-polarized transmission spectrum, which determines the NDR, originates from the corresponding electronic band structure and its variation with the applied bias at the Fermi level. These results are consistent with the reported literature. From a combined analysis of the spin-resolved transmission spectrum and the band structure, we came to a conclusion that the presence of the spin-dependent contribution of the Nb atom in the plane of the AGNR to the orbitals close to Fermi energy make it a good spin filter with NDR properties.
4. Conclusion

We investigated the NDR and spin polarization properties of an Nb-doped 7AGNR using DFT and Green’s functional methods. Doping induced spin splitting near the Fermi energy indicates spin-polarized currents. In the parallel spin configuration of the electrode, the spin-up current is dominant, while in the antiparallel configuration, the spin-down current is dominant. The transmission coefficient in the P and AP configurations was determined from the Landauer–Buttiker formula. For the applied bias voltage range of 0.15 V to 0.5 V in AP configuration, spin filter efficiency is extremely high (>95%), and the device can act as a perfect spin filter. In the P configuration, spin filter efficiency is in the range of 70–98%. In addition, the plots of current vs. bias voltage for the P and AP configurations show the NDR properties. The PVR for the spin-up and spin-down currents is 4.5 and 17.8, respectively in the P configuration, while the values are 4.57 and 37.5, respectively, in the AP configuration. In general, an Nb–7AGNR device shows a high spin polarization ratio with NDR over a broad range of bias voltage. In practice, undesirable environmental effects such as substrate effect, temperature and contact resistance may limit the performance. The theoretical results in this article can be considered as the ideal limit of experimental studies. As nanofabrication methods, techniques and protocols for graphene manipulation are developing rapidly, we consider that graphene nanoribbon devices with precise doping may lead the way for future spintronic devices.

Conflicts of interest

There are no conflicts to declare.

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References