

Spin-valve effect in zigzag graphene nanoribbons by defect engineeringSankaran Lakshmi,¹ Stephan Roche,^{1,2} and Gianaurelio Cuniberti¹¹*Institute for Materials Science and Max Bergmann Center of Biomaterials,
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We report on the possibility for a spin-valve effect driven by edge defect engineering of zigzag graphene nanoribbons. Based on a mean-field spin-unrestricted Hubbard model, electronic band structures and conductance profiles are derived, using a self-consistent scheme to include gate-induced charge density. The use of an external gate is found to trigger a semiconductor-metal transition in clean zigzag graphene nanoribbons, whereas it yields a closure of the spin-split band gap in the presence of Klein edge defects. These features could be exploited to make charge- and spin-based switches and field-effect devices.

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The recent fabrication of single and few layers graphene has sparked considerable expectations in the field of all-carbon nanoelectronics.^{1,2} Although two-dimensional graphene is a semimetal, the possibility to pattern graphene nanoribbons (GNRs) with widths of few tens of nm, has enabled band-gap engineering³ and the development of efficient GNRs-based field-effect transistors (FETs).⁴ However, the further optimization of GNRs-based devices or the design of device functionalities demand for more understanding and control of not only unavoidable structural disorder and defects but also edge geometry and chemical functionalization. Experimental characterization either with Raman studies, scanning tunneling microscopy, or high-resolution transmission electron microscopy (HR-TEM) has revealed a large spectrum of topologically different edge profiles, which can exhibit either an armchair or a zigzag symmetry,⁵ as well as a range of edge imperfections.⁶ In particular, individual pendent atoms named Klein defects have been predicted^{7,8} and more recently observed.⁹ In principle, such edge disorder is unsuitable for keeping good conduction properties of otherwise clean GNRs. As a matter of fact, several experimental¹⁰ and theoretical¹¹ reports evidence the enlargement of the transport gap and strong fluctuations of low-temperature conductance.

A pioneering work by Son *et al.*¹² predicted half-metallic behavior in clean zigzag GNRs (ZGNRs) in the presence of a transverse electric field, opening up avenues for the design of spin-dependent switching devices.¹³ Several recent studies have also reported on the possibility for half metallicity in ZGNRs using chemical doping,¹⁴ whereas the application of an external magnetic field was shown to trigger a transition from parallel to antiparallel magnetic edges, resulting in giant magnetoresistance phenomena and efficient spintronics devices.¹⁵

In this Brief Report, we investigate the electronic and conductance properties of gated ZGNRs with and without the presence of Klein edge defects. The energetics of the GNRs is described by a mean-field Hubbard Hamiltonian which has been shown to well reproduce density-functional theory results in the spin local-density approximation.^{16,17} The gate-injected charge density is also self-consistently included in the band structures and transport calculations. For clean zigzag GNRs, the external gate is shown to tune the

electronic structure from a semiconducting state to a purely metallic state, thus switching on current through the device, whereas in presence of Klein defects, the spin-split gap is closed, resulting in a transition from a pure spin-current to a spin-degenerate charge current, close to the Fermi energy.

ZGNRs are very peculiar in the sense that they have a magnetic ground state, with each edge having electrons aligned ferromagnetically with each other, albeit antiferromagnetically with respect to the other edge.¹² The ground state is entirely dominated by these magnetic edge states,⁵ which generate a semiconducting band gap.¹² The introduction of a Klein edge profile (with additional π -electron hopping bonds) in the ZGNR, is known to produce a flat band over the entire Brillouin zone,⁷ within a tight-binding description. However, with the incorporation of electron correlations, a ground state with a net magnetization and a spin-split band-gap emerges.^{18,19} Kusakabe *et al.* have theoretically discussed a Klein edged situation by dihydrogenating one of the edges of the ZGNR, validating the occurrence of a spin-polarized band at the Fermi energy.¹⁹ Very recently, these edges were observed, although locally, in graphene using HR-TEM.⁹

Here, it is our interest to study the effect of an external gate on the band gaps of these two categories of bipartite semiconducting systems, one of which has a antiferromagnetic ground state (ZGNR), and the other ferromagnetic (ZGNR with a Klein edge defect). We model GNRs using the spin-unrestricted mean-field Hubbard Hamiltonian,

$$H = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_{i, \sigma} \langle n_{i-\sigma} \rangle n_{i\sigma}, \quad (1)$$

where $c_{i\sigma}^\dagger$, $c_{i\sigma}$, and $n_{i\sigma}$ are the creation, annihilation, and number operators for an electron of spin σ in the π orbital of the i th C atom in the ribbon, with $t=2.6$ eV and $U=2.75$ eV.²⁰ The unit cell of the ZGNR has width 20 (40 atoms) and that of the Klein edged ZGNR has an extra C atom at one edge. When the system is nongated, its Fermi energy (E_F^0) is obtained by integrating the charge density up to half filling.

One common way to tune the device conductance is to use an external metallic gate for monitoring the depletion or accumulation of charges in the conducting channel.⁴ The

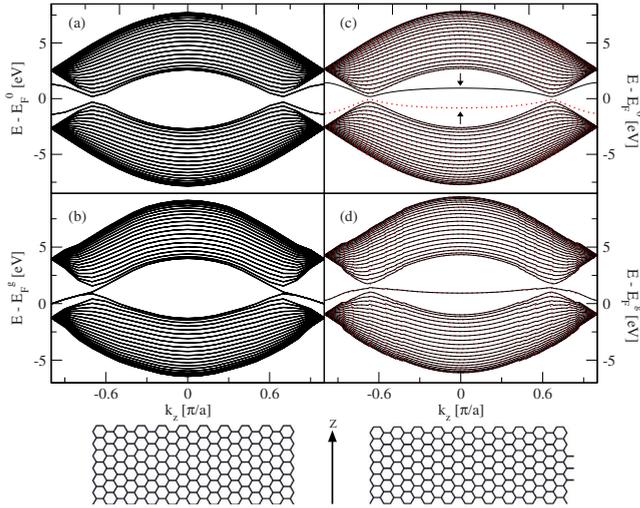


FIG. 1. (Color online) Band structures of the clean ZGNR with (a) $V_g=0$ and (b) $V_g=1.5$ V for both up and down (degenerate) spins. Band structures of the ZGNR with one Klein edge when (c) $V_g=0$ and (d) $V_g=1.5$ V for up (red dotted) and down (black solid) spins. The schematic shows few unit cells of the clean ZGNR on the left. On the right, three Klein defect edges in an otherwise clean ZGNR have been shown for clarity.

presence of such a gate terminal is numerically simulated by shifting the on-site energies by eV_g , where V_g is the gate voltage. The modified charge-density distribution up to E_F^0 at every V_g is further self-consistently computed. To do so, the excess charge carriers introduced by the gate are obtained as $n(E_F^g) - n(E_F^0)$, where $n(E_F^g)$ is the charge density at the Fermi energy in the presence of the gate and $n(E_F^0)$ is that in the absence of the gate [$n(E_F) = \int_{-\infty}^{E_F} \rho(E) dE$ with $\rho(E)$ the density of states]. The modified charge density at every V_g is then incorporated into the Hamiltonian and solved self-consistently to obtain the new band structure of the gated GNR with the associated Fermi level (E_F^g).

The coherent transport through the system is then calculated using the well-known Landauer's formalism. The source-drain electrodes for simplicity are assumed to consist of the same GNRs. The retarded Green's function of the device is computed as $G = (E - H - \Sigma_L - \Sigma_R)^{-1}$, where Σ_L and Σ_R are the self-energies of the GNR electrodes, calculated as $\Sigma = \tau g_s \tau^\dagger$, where τ contains the device-source/drain interactions and g_s is the surface Green's function of the electrodes, calculated using standard recursive Green's-function techniques.²⁰ The conductance of the device is finally obtained as $G_D(E) = \frac{e^2}{h} T(E)$, where $T(E)$, the transmission probability at energy E is given by $\text{Tr}[\Gamma_L G \Gamma_R G^\dagger]$, Tr is the trace and $\Gamma_{L,R} = i(\Sigma_{L,R} - \Sigma_{L,R}^\dagger)$. Basically, this formalism would keep count of the number of conducting channels of different spins in the GNR.

Electronic band structures of ZGNR with or without a Klein edge, and as a function of applied external gates can be seen in Fig. 1. First, as observed in Fig. 1(a), when $V_g=0$, the ground state is characterized by a band gap, resulting from its oppositely spin-polarized edges. With the application of a positive gate voltage channeling holes into the system, the electron density at the edges ($2/3 \leq |k| \leq 1$) gradually dimin-

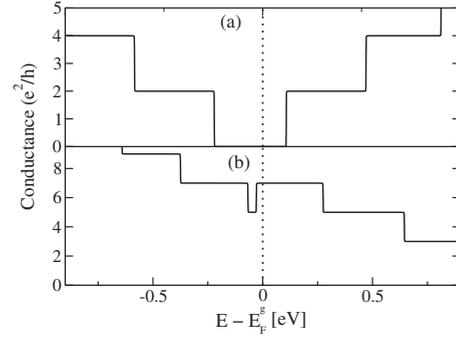


FIG. 2. Spin-degenerate (up and down) conductance of the ZGNR with respect to the incident energy of the electrons (E) scaled by E_F^g for (a) $V_g=0$ and (b) $V_g=1.5$ V.

ishes, which results in a completely nonmagnetic, metallic system. A closing of the band gap is seen in Fig. 1(b) for $V_g=1.5$ V. Previous studies on gatelike effects on ZGNRs also validate this result.^{21,22} The effect of gate voltage on the low-energy conductance can be appreciated in Fig. 2. Given that the GNRs are disorder free, the conductance remains quantized and is fixed by the number of available conduction channels at the relevant Fermi level. At injection energies close to E_F^g , a current switch is driven by the gate voltage increase, indicating a transistor-type behavior.

In contrast, the situation for the ZGNR with one Klein edge shows some marked differences. First by looking at the band structure at zero gate voltage [Fig. 1(c)], it is clear that the highest-occupied band is made up entirely of one spin (dotted) and the lowest-unoccupied band, of the other (solid). The ground state of the system shows some ferromagnetism with both edges displaying high electron density of the same (majority) spin. This is explained by the finite sublattice imbalance which favors the appearance of midgap states and magnetic properties.^{16,17,23}

When a positive gate voltage is applied, the majority-spin (up) band shifts upward, reducing the electron (up-spin) density, as seen in Fig. 3(b), which eventually meets the minority-spin (down) density to make the system completely nonmagnetic and metallic. This is also characterized in Fig. 3(a) by the slow reduction in the spin-split gap, which eventually disappears beyond $V_g=1.5$ V. The band structure of

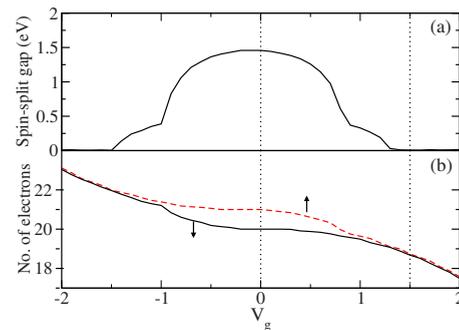


FIG. 3. (Color online) (a) Variation in the band gap over the entire Brillouin zone with V_g . (b) The total number of up (red dashed) and down electrons (black solid) with respect to V_g . Dotted lines are marked at $V_g=0$ and $V_g=1.5$ V for clarity.

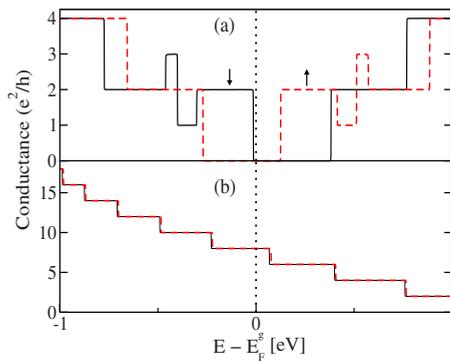


FIG. 4. (Color online) Conductance of the Klein-edged ZGNR with respect to the incident energy of the electrons (E) scaled by E_F^g for (a) $V_g=0$ and (b) $V_g=1.5$ V. Dashed (red) lines refer to the spin-up conductance and solid (black) lines refer to the spin-down conductance.

the GNR at $V_g=1.5$ V, shown in Fig. 1(d), clearly exhibits spin-degenerate bands. When a negative gate bias injecting excess electrons into the device is applied, a similar situation follows. The down-spin band gets pushed into the occupied states, diminishing the total magnetization and hence the spin-split gap. Here, the down-spin density increases to meet its up-spin counterpart as seen in Fig. 3(b).

In Fig. 4 at $V_g=0$, the transmission probability of the majority spin close to E_F^g is very high, as it is the only band available in the energy range. As the gate voltage is increased, the system transmits only the majority spin until ≈ 1.0 V, after which it turns nonmagnetic with both spins having identical transmissions. This indicates that it is possible to tune the current in the system from one which is

completely spin polarized to an unpolarized charge current just with the help of an external gate.

The origin for such transitions from semiconducting to metallic in the gated ZGNRs and from a spin-polarized to a spin-degenerate response in the Klein-edged ZGNRs can be rationalized as follows. The ground state of both systems are entirely composed of magnetic edge states, which produce their respective band gaps. An external gate voltage does break the spin polarization of the system due to the change in the charge number at the edges. As a consequence, a controlled switch from a spin-splitting gap to metallicity is observed. One notes that the application of an external magnetic field in clean ZGNR also yields a similar effect and giant magnetoresistance.¹⁷

In summary, we have studied the effect of gate voltage on the band-structure and conductance profiles of a ZGNR and a Klein-edged ZGNR, based on the mean-field spin-unrestricted Hubbard model. The gate-injected charge density was obtained self-consistently and conductance calculations were performed using the Landauer's formalism. We have found that an external gate could tune the spin-induced band gap in clean ZGNRs or in Klein-edged ZGNR. In the former case, this leads to a switching on of the charge current, whereas in the latter case, a transition from a pure spin current to a completely unpolarized charge current is achieved. These features could eventually help in designing GNR-based charge and spin switches and FETs in future all-carbon circuits.

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