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Published in:
Physical Review B Condensed Matter

Link to article, DOI:
10.1103/PhysRevB.85.184426

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Saha, K. K., Blom, A., Thygesen, K. S., & Nikolic, B. K. (2012). Magnetoresistance and negative differential resistance in Ni/graphene/Ni vertical heterostructures driven by finite bias voltage: a first-principles study. Physical Review B Condensed Matter, 85(18), 184426. https://doi.org/10.1103/PhysRevB.85.184426
Magnetoresistance and negative differential resistance in Ni/graphene/Ni vertical heterostructures driven by finite bias voltage: A first-principles study

Kamal K. Saha,1 Anders Blom,2 Kristian S. Thygesen,3 and Branislav K. Nikolić1,*

1Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716-2570, USA
2QuantumWise A/S, Lersø Parkallé 107, DK-2100 Copenhagen, Denmark
3Center for Atomic-Scale Materials Design (CAMD) and Center for Nanostructured Graphene (CNG), Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

(Received 29 March 2012; published 25 May 2012)

Using the nonequilibrium Green’s function formalism combined with density functional theory, we study finite bias quantum transport in Ni/Gr/Ni vertical heterostructures where n graphene layers are sandwiched between two semi-infinite Ni(111) electrodes. We find that the recently predicted “pessimistic” magnetoresistance of 100% for n ≥ 5 junctions at zero bias voltage Vb → 0 persists up to Vb ≃ 0.4 V, which makes such devices promising for spin-torque-based device applications. In addition, for parallel orientations of the Ni magnetizations, the n = 5 junction exhibits a pronounced negative differential resistance as the bias voltage is increased from Vb = 0 V to Vb ≃ 0.5 V. We confirm that both of these nonequilibrium transport effects hold for different types of bonding of Gr on the Ni(111) surface while maintaining Bernal stacking between individual Gr layers.

DOI: 10.1103/PhysRevB.85.184426

PACS number(s): 72.25.Mk, 73.43.Qt, 75.47.—m, 72.80.Vp

I. INTRODUCTION

A magnetic tunnel junction (MTJ) consists of an ultrathin insulating barrier which separates two metallic ferromagnetic layers with variable magnetization direction. The MTJs based on transition metals or their alloys and an epitaxial MgO barrier1 are the present workhorse of both commercial and basic research spintronics. For example, MgO-based MTJs are the core elements of read heads in hard drives or in basic research spintronics. For example, MgO-based MTJs

1098-0121/2012/85(18)/184426(6) ©2012 American Physical Society
FIG. 1. (Color online) (a) Schematic view of Ni/Gr/Ni junction where Gr represents five layers of graphene and Ni is (111) fcc nickel. The device extends to infinity along the transverse directions, while the Ni electrode (orange) is semi-infinite in the longitudinal (transport) direction. The two investigated types of bonding (Refs. 11, 12, and 20) for Gr on the Ni(111) surface are illustrated in panel (b), as the AB configuration where the two carbon atoms in the graphene unit cell cover Ni atoms in layers A (surface) and B (second layer), and in panel (c) as the AC configuration in which carbon atoms are placed directly above the Ni atoms in layers A (surface) and C (third layer). Here, ABC refers to three close-packed layers within a fcc crystal.

has to compute the charge redistribution\textsuperscript{15} due to the current flow by evaluating the nonequilibrium density matrix \( \rho \), a procedure which ensures the gauge invariance\textsuperscript{16} of the current-voltage \( I-V \) characteristics. On the other hand, the nonequilibrium Green’s function formalism combined with density functional theory (NEGF-DFT),\textsuperscript{15,17,18} where the DFT part of the calculations is implemented in the basis of local orbitals, makes it relatively straightforward to obtain \( \rho \).

Here, we show how to use efficiently spin- and \( k_\parallel \)-resolved NEGF-DFT framework to understand nonequilibrium transport through two Ni/Gr/Ni junctions depicted in Fig. 1 for parallel (P) or antiparallel (AP) orientation of the Ni magnetizations. Our principal results are shown in Figs. 2 and 3. In Fig. 2(a), we first confirm the result of Refs. 11 and 12 about the zero bias “pessimistic” MR reaching 100% for barriers composed of \( n \geq 5 \) graphene layers and, moreover, in Fig. 2(b) we predict that such maximized MR would persist even at finite \( V_b \lesssim 0.4 \) V. Figure 2(b) also suggests that the bias voltage dependence of MR can be employed experimentally to determine the type of bonding configuration [illustrated in Figs. 1(b) and 1(c)] for Gr on the Ni(111) surface.

Furthermore, Fig. 3(c) shows that the Ni/Gr/Ni junction with P orientation of the Ni magnetizations will exhibit pronounced negative differential resistance (NDR), where total charge current first increases and then decreases as the bias voltage is increased from \( V_b = 0 \) V to \( V_b \gtrsim 0.5 \) V (or symmetrically in the opposite direction). The origin of NDR is explained in Fig. 5 by plotting the position-dependent local density of states (LDOS) across the junction.

The paper is organized as follows. In Sec. II, we discuss the vertical Ni/Gr/Ni heterostructure setup and how to tune the spin- and \( k_\parallel \)-resolved NEGF-DFT framework in order to describe properly magnetism around its interfaces. Section III discusses the magnetoresistance at finite bias voltage, as well as the unusual conduction properties of general vertical graphene heterostructures, the fabrication of which has been initiated recently,\textsuperscript{19} which make Ni/Gr/Ni junctions different from either conventional MTJs or spin valves. In Sec. III, we
discuss NDR in Ni/Gr/Gr/Ni junctions driven by finite bias voltage. We conclude in Sec. V.

II. VERTICAL HETEROSTRUCTURE SETUP AND TUNING OF NEGF-DFT FRAMEWORK FOR ITS MODELING

The disorder-free junction shown in Fig. 1(a) consists of up to seven graphene layers arranged in Bernal stacking, which serve as the barrier separating the two semi-infinite Ni electrodes. The junction is infinite in the transverse direction, so that its transverse periodicity requires \( k \)-point sampling. The spin injection and spin filtering in ferromagnetic multilayers depends not only on the properties of the ferromagnetic electrodes, but also on the geometry, bonding, and electronic and magnetic structure of the contact region, as emphasized by the studies of MgO-based MTJs. Therefore, we consider two different Gr on the Ni(111) surface bonding configurations illustrated in Figs. 1(b) and 1(c).

We note that DFT calculations employing different approximations for the exchange-correlation functional (such as the local density approximation, or the generalized gradient approximation), and van der Waals density functionals (SZP basis for C atoms and DZP basis for Ni atoms), have yielded contradictory conclusions about the AC bonding configuration being the most stable energetically and the corresponding binding distance. The recent random phase approximation (RPA) calculations have resolved this controversy and demonstrated that the conflicting results are due to a delicate interplay between covalent and dispersive interactions, which is not captured by the DFT functionals. Also, the scanning tunneling microscopy imaging shows that perfectly ordered epitaxial graphene layers can be prepared by elevated temperature decomposition of hydrocarbons where domains are larger than the terraces of the underlying Ni(111) surface.

The NEGF-DFT framework was originally developed to treat quantum transport through small molecules attached to metallic electrodes. Its application to modeling of charge and spin transport in MTJs requires careful tuning of pseudopotentials and basis sets in order to obtain an accurate description of the band structure near the Fermi level, which is particularly important for the studies of spin-polarized transport. For example, pseudopotentials and localized basis sets that reproduce the electronic structure of the ferromagnetic electrode and barrier material when treated separately do not necessarily reproduce the electronic structure of the more complicated ferromagnetic-electrode/barrier interfaces.

In order to capture accurately the electronic and magnetic structure around interfaces, we first compute the band structure of a periodic superlattice ...Ni/Gr/Gr/Ni/Gr/Gr ... using DFT based on the projector augmented wave (PAW) methodology with a wave-function representation on uniform real-space grids as implemented in the GPAW code where we choose a grid spacing of 0.18 Å. Within the PAW formalism, one works implicitly with the all-electron wave functions and has access to the (frozen) core states, which makes the method applicable to a broad range of systems (including materials with strongly localized \( d \) or \( f \) electrons that can be problematic to describe with pseudopotentials). The same band structure is then recomputed using DFT where the wave functions are represented in terms of a linear combination of atomic orbitals (LCAO) and the behavior of the core electrons is described by norm-conserving Troullier-Martins pseudopotentials, as implemented in the ATK code. In the ATK-based calculations, we choose a single \( \zeta \) polarized (SZP) basis on C atoms and a double \( \zeta \) polarized (DZP) basis on Ni atoms. The Brillouin zone of the superlattice was sampled by \( 12 \times 12 \times 100 k \)-point grid, and the charge density and potentials were determined on a real-space grid with a mesh cutoff energy of 150 Ry. This was sufficient to achieve a total energy convergence of better than 0.01 meV/unit cell in the self-consistent loop.

The excellent agreement we achieve in Fig. 4 between the real-space grid PAW and LCAO pseudopotential DFT calculations, where the Perdew-Burke-Ernzerhof (PBE) parametrization of the spin-polarized generalized gradient approximation (GGA) for the exchange-correlation functional has been used in both cases, also selects the correct parameters to be used for LCAO pseudopotential part of NEGF-DFT analysis of the two-terminal Ni/Gr/Ni junctions discussed below. The active region of the device in Fig. 1(a) simulated by the NEGF-DFT code consists of seven Ni(111) layers on the left, \( n \) layers of Gr, and six layers of Ni(111) on the right. This active region is first relaxed until the maximum force component goes below 0.02 eV/Å per atom, and then attached to two semi-infinite ideal Ni electrodes.

The NEGF formalism for steady-state transport operates with two central quantities, the retarded \( G(E) \) and the lesser Green’s functions \( G^{-}(E) \), which describe the density of available quantum states and how electrons occupy those states, respectively. In the NEGF-DFT framework, the Hamiltonian is not known in advance and has to be computed by finding the converged spatial profile of the electron charge distribution via the self-consistent DFT loop for the density matrix \( \rho = \frac{1}{\pi} \int dE G^{+}(E) \), the diagonal elements of which give the charge density. The Hamiltonian matrix...
H in the local orbital basis \( \{ \phi_i \} \) is composed of elements \( H_{ij} = \langle \phi_i | \hat{H}_{KS} | \phi_j \rangle \), where \( \hat{H}_{KS} \) is the effective Kohn-Sham Hamiltonian obtained from the DFT self-consistent loop and the overlap matrix \( S \) has elements \( S_{ij} = \langle \phi_i | \phi_j \rangle \).

In the coherent transport regime (i.e., in the absence of electron-phonon or electron-electron dephasing processes), only the retarded Green’s function

\[
G^\sigma_{k_i} = \left[ E - H^\sigma_{k_i} - \Sigma^\sigma_{L,k_i} - \Sigma^\sigma_{R,k_i} \right]^{-1}
\]

(1)
of the active device region is required to post-process the result of the DFT loop by expressing the current between the left \((L)\) and the right \((R)\) electrodes as

\[
I^\sigma(V_b) = \int_{\text{BZ}} \frac{dE}{2\pi} \int dE' \frac{dE}{2\pi} T^\sigma(k_i,E,V_b)[f(E - \mu_L) - f(E - \mu_R)].
\]

(2)
The electrodes are assumed to be attached to macroscopic reservoirs at infinity characterized by the Fermi function \( f(E - \mu_L) \), so that the bias voltage driving the nonequilibrium transport is given by \( \mu_L - \mu_R = eV_b \). Here, we resolve all quantities in minority and majority spin channels \((\sigma = \text{min}, \text{maj})\) while neglecting spin-orbit coupling or spin-flip scattering. The spin- and \( k_z \)-resolved transmission function for coherent transport is given by

\[
T^\sigma(k_z,E,V_b) = \text{Tr} \left\{ G^\sigma_{R,k_z}(E) G^\sigma_{L,k_z}(E) \Gamma^\sigma_{L,k_z}(E) \Gamma^\sigma_{R,k_z}(E)^\dagger \right\},
\]

(3)
where the level broadening matrices \( \Gamma^\sigma_{L,R,k_z}(E) = i[\Sigma^\sigma_{L,R,k_z}(E) - \Sigma^\sigma_{L,R,k_z}(E)^\dagger] \) are expressed in terms of the retarded self-energies \( \Sigma^\sigma_{L,R,k_z}(E) \) of the semi-infinite ideal Ni electrodes. In order to converge the integration over the (conserved in the absence of disorder) transverse wave vector \( k_z \) in Eq. (2), we find it necessary to use a dense grid of \( 301 \times 301 \) of \( k \) points in the corresponding 2D Brillouin zone (BZ). This procedure yields the bias-dependent transmission function \( T(E,V_b) = \int_{\text{BZ}} dE k_z T(k_z,E,V_b) \) plotted in Figs. 3(a) and 3(b).

### III. MAGNETORESISTANCE AT FINITE BIAS VOLTAGE

The Ni/Gr\(_{\text{r}}\)/Ni multilayered heterostructure is not a conventional MTJ. Unlike MgO-based MTJs where the linear-response \((V_b \to 0)\) conductances \( G_p^\text{min} = I^\text{min}/V_b \) and \( G_p^\text{maj} = I^\text{maj}/V_b \) decay exponentially \(^1\) with increasing number of MgO layers, in the case of Ni/Gr\(_{\text{r}}\)/Ni junction, \( G_p^\text{min} \) is independent of \( n \) for \( n > 4 \) (apart from an even-odd oscillation as a function of the thickness \( n \)).\(^{11,12} \) On the other hand, Gr\(_{\text{r}}\) acts as a tunnel barrier for majority spin electrons causing \( G_p^\text{maj} \) to decay exponentially with \( n \). The spin-resolved linear-response conductances for Ni/Gr\(_{\text{r}}\)/Ni junctions are compared in Table I with the same conductances for Fe/MgO/Fe MTJs containing an MgO barrier of similar thickness as our Gr\(_{\text{r}}\) barrier.

The recent first-principles analysis \(^{27} \) of different metal/Gr\(_{\text{r}}\)/metal junctions for \( n \leq 4 \), assuming reasonable metal-graphene epitaxial relationships, has delineated conditions for Gr\(_{\text{r}}\) to behave effectively as a tunnel barrier causing an exponential decay of the conductance with increasing \( n \), which requires a crystal momentum mismatch between the bulk Fermi-level states in the metallic electrode and those in the Gr\(_{\text{r}}\) barrier. Furthermore, recent experiments \(^{19} \) measuring \( I-V \) characteristics of metal/Gr\(_{\text{r}}\)/metal vertical junctions (with Ti/Pt used as top and bottom metal electrodes) have demonstrated the feasibility of applying a bias voltage up to \( |V_b| \leq 1 \text{ V} \) without encountering catastrophic breakdown while showing transitions from Ohmic \( I \propto V_b \) (at very low bias) to power-law \( I \propto V_b^m \) \((m > 2)\) characteristics.

In conventional MTJs, tunneling rates are higher if there are similar or identical states on both sides of the barrier. Therefore, the tunneling electrons need not only get through the barrier, but there must be a state of the correct symmetry on the other side to accept them.\(^1 \) This effect is part of the reason for the commonly observed decrease in TMR with \( V_b \), since, as the bias increases, the states on opposite sides of the barrier for P orientation differ more.\(^{9,10,14} \) On the other hand, “our pessimistic” MR in Ni/Gr\(_{\text{r}}\)/Ni remains 100% up to \( V_b \leq 0.4 \text{ V} \) for Gr barriers of thickness \( n \approx 5 \), as shown in Fig. 2(b).

### IV. NEGATIVE DIFFERENTIAL RESISTANCE

Figures 3(c) and 3(d) plot the \( I-V \) characteristics for P and AP orientations of the Ni magnetizations where the total charge current is \( I = I^\text{min} + I^\text{maj} \). Since in the AP orientation the bias-dependent transmission \( T(E,V_b) \) in Fig. 3(b) is nearly flat around the Fermi level, the \( I-V \) characteristics in Fig. 3(d) is linear up to the voltage \( V_b \approx \pm 0.6 \text{ V} \). However, in P orientation, the total charge current \( I \) sharply increases to reach its maximum value at \( V_b \approx \pm 12 \text{ V} \) and then drops, thereby exhibiting a pronounced NDR. This feature can be explained using \( T(E,V_b) \) curves plotted for the AC configuration in Fig. 3(a). At lower \( V_b \), the transmission resonance (around \( E_E - E_F = 0.0 \text{ eV} \) falling into the bias window (marked by dashed wedge) contributes to the peak in the \( I-V \) characteristics. However, this resonance gets diminished with increasing \( V_b \), which eventually shuts off the current flow when \( V_b \approx 0.5 \text{ V} \) is reached. The current is allowed to flow again when the new resonance around \( E_E - E_F \approx -0.45 \text{ eV} \) enters the bias window \( V_b \approx -0.7 \text{ V} \).

Further insight into the microscopic mechanism behind the NDR in P orientation of magnetizations in Ni/Gr\(_{\text{r}}\)/Ni junctions can be explained by examining the position-dependent...
FIG. 5. (Color online) The position-dependent LDOS from left to right electrodes in Ni/Gr$_5$/Ni junction, in AC bonding configuration at the Ni(111)/Gr interface and P orientation of the Ni magnetizations, at different bias voltages $V_b$. The electrochemical potentials $\mu_L$ and $\mu_R$ of the two Ni electrodes are marked by dashed horizontal lines, while the zero of energy is set at $(\mu_L + \mu_R)/2$. The LDOS exhibits high values in the Ni electrodes (white regions), while the central colored region corresponds to the Gr$_5$ barrier. The dashed ovals indicate the position of the resonant states which contribute to transport. Note that a strong coupling of the resonant states of the electrodes and the Gr barrier at a given energy level is required for large transmission $T(E, V_b)$ through the junction.

LDOS

$$N(z, E) = -\frac{1}{\pi} \int d\mathbf{k}_\parallel \sum_{ij, \sigma} \text{Im} \langle \phi_i(z) | G_{ij, \mathbf{k}_\parallel}^\sigma(E) | \phi_j(z) \rangle,$$  \hspace{1cm} (4)

from the left to the right Ni electrode. The LDOS is plotted in Fig. 5 where we choose four bias voltage values ($V_b = 0.0, -0.1, -0.5, -0.9$ V) at which the magnitude of the total charge current differs significantly.

V. CONCLUDING REMARKS

In conclusion, we have demonstrated that perfect spin filtering in Ni/Gr$_n$/Ni, with $n \geq 5$ layers of graphene sandwiched between two (111) fcc Ni electrodes, characterized by a “pessimistic” TMR $= 100\%$ at zero bias voltage$^{11,12}$ would persist even at finite bias voltage $V_b \lesssim 0.4$ V. This feature is markedly different from conventional MgO-based MTJs where TMR drops sharply$^9,10$ with increasing bias voltage. Thus, it could play an important role in spintronic devices based on STT$^2,4$ Furthermore, we predict that the Ni/Gr$_n$/Ni junction with P orientation of the Ni magnetizations would exhibit negative differential resistance as the bias voltage is increased from $V_b = 0$ V to $V_b \simeq 0.5$ V due to a transmission resonance which is formed at zero bias voltage, which is then gradually pushed outside of the bias window.

ACKNOWLEDGMENTS

We thank K. S. Novoselov and J. Q. Xiao for illuminating discussions. K.K.S. and B.K.N. were supported by DOE Grant No. DE-FG02-07ER46374 through the Center for Spintronics and Biodetection at the University of Delaware. K.S.T. was supported by the Danish National Research Foundation’s Center for Nanostructured Graphene (CNG). The supercomputing time was provided in part by the NSF through XSEDE resource TACC Ranger under Grant No. TG-DMR100002 and NSF Grant No. CNS-0958512.

*bnikolic@udel.edu

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