Electron-hole transport asymmetry in Boron-doped Graphene Field Effect Transistors

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***Abstract*— One of the main drawbacks of undoped graphene for digital electronics applications is its ambipolar behavior. Here we study the trasfer characteristics of transistors based on boron-doped graphene nanoribbons with atomic concentrations up to 0.6%, showing that the presence of doping generates a clear electron-hole transport asymmetry. In order to obtain these results, we introduce a method to accurately reproduce density functional theory (DFT) results using a self-consistent tight-binding (TB) model with a proper distribution of fixed charges.**

INTRODUCTION

In the last few years, graphene-nanoribbon field-effect-transistors (GNR-FETs) have been proposed as promising candidates for beyond-CMOS nanoelectronics, due to the high mobility and the one-atom thickness of graphene, which allow near-ballistic transport and effective gate control on the channel. However, in view of a possible application for digital electronic devices, graphene presents two main drawbacks [1]: the absence of an energy gap and an ambipolar behavior. The first one prevents the achievement of high ratios I_{ON}/I_{OFF} between the current of the device in the ON state and in the OFF state; the second one makes quite difficult to fabricate complementary logic circuits based on graphene. The absence of an energy gap cannot simply be overcome by strongly confining the channel, due to the limits of the present lithographic techniques. A particularly interesting method that has been suggested to mitigate these problems is to chemically dope graphene with boron or nitrogen.

Only a limited number of, often contradictory, experimental results exist in the literature for the electrical properties of doped graphene devices. For example, Tang *et al.* [2] prepared FETs based on graphene sheets obtained by mechanical exfoliation and boron-doped through reaction with a ion atmosphere of trimethylboron. They reached boron atomic concentrations up to 13.8% and measured an asymmetric p-type behavior with a I_{ON}/I_{OFF} ratio up to about 720. Analogously, Wei *et al.* [3] synthesized nitrogen-doped graphene flakes via a chemical-vapor-deposition (CVD) technique from CH_4 and NH_3. They obtained nitrogen atomic concentrations up to 8.9% and found an asymmetric n-type behavior, with I_{ON}/I_{OFF} ratios up to about 10^3. On the contrary, Brenner *et al.* [4] performed an *in-situ* doping by exfoliating graphene sheets in a nitrogen ambient, obtaining a I_{ON}/I_{OFF} of only few units. Jin *et al.* [5] prepared nitrogen-doped graphene layers by CVD from pyridine, reaching a nitrogen atomic concentration of about 2.4%, which however leads to a decrease of the I_{ON}/I_{OFF} ratio with respect to pristine graphene, with no significant improvement in terms of unipolarity.

Such a large discrepancy in the experimental results calls for further experimental and theoretical investigation. From this last point of view, it is necessary to develop a simple but reliable simulation

method, able to reproduce, in the case of isolated structures, the results of full *ab initio* calculations.

Attempts in this direction were recently made in Refs. [6] and [7], where DFT results on doped graphene structures were reproduced with properly fitted non-self-consistent nearest-neighbor TB calculations. However, both of these approaches suffer from a common drawback: since the TB model already mimics DFT self-consistency, it actually leads to an overscreening effect when this representation is used within a self-consistent Poisson-Schrödinger simulation of the complete boron-doped GNR-FET.

NUMERICAL METHOD

In order to solve this problem, we have developed an improved simulation approach to accurately reproduce the *ab initio* results with a TB model and to study a complete FET device.

We have first used the SIESTA code to make a DFT analysis (using the local density approximation and a double-ζ basis) of isolated graphene sheets and graphene nanoribbons with a single boron impurity in several substitutional positions. Then we have compared the DFT results, in terms of the impurity potential and transmission spectrum, with those achievable for the same structures with a self-consistent Poisson-Schrödinger calculation based on a nearest-neighbor TB description of the system, in which only the $2p_z$ atomic orbital of each atom is considered. In this TB scheme we have considered all the onsite energies ϵ null and all the transfer integrals equal to $t = -2.7$ eV, with the exception of edge dimers, for which $1.12\,t$ has been used [8]. We have observed that the DFT results are well-reproduced by introducing, into the self-consistent TB calculation, a proper distribution of fixed charges, corresponding, for each atom, to that of the nucleus and of all the electrons in orbitals different from the $2p_z$ ones, i.e. to $+e$ for the carbon atoms and 0 for the boron atoms (where e is the elementary charge, see Fig. 1). In the calculation this fixed charge adds up to that of the delocalized electrons deriving from the $2p_z$ atomic orbitals, which are the only orbitals that are considered in the TB scheme. In other words, if N_C (N_B) is the number of carbon (boron) atoms in an area A of the graphene flake, $LDOS$ is the local density of states deriving from the $2p_z$ atomic orbitals for unit area and energy, f is the Fermi-Dirac function, and E_F is the Fermi energy, the total charge inside A is

$$eN_C - e\int_A dA \int_{-\infty}^{+\infty} d\,E\,(LDOS(E)\,f(E-E_F))$$

where the second term accounts for the $2p_z$ electrons in the overall energy spectrum. This charge can be expressed also in terms of the electrons in the only conduction band (CB) and of the holes in the valence band (VB). In detail, we can rewrite the integral in energy as the sum of an integral from $-\infty$ to E_i and of one from E_i to $+\infty$, where E_i is the midgap energy. Then we can sum and subtract

$$e\int_A dA \int_{-\infty}^{E_i} d\,E\,(LDOS(E)) = e(N_C+N_B)$$

(since each of the N_C+N_B atoms of the area A has one $2p_z$ orbital and thus two electron states with different spin, the integral over the entire energy spectrum, which is twice this integral, would be $2\,e\,(N_C+N_B)$). Therefore, the charge in A is

$$\begin{aligned}&eN_C - e(N_C+N_B)\\&+e\int_A dA \int_{-\infty}^{E_i} d\,E\,(LDOS(E)(1-f(E-E_F)))\\&-e\int_A dA \int_{E_i}^{+\infty} d\,E\,(LDOS(E)f(E-E_F)) =\\&-eN_B + e\int_A d\,A\,(p-n)\ ,\end{aligned}$$

where p (n) is the concentration for unit area of holes (electrons) in the VB (CB). Thus the calculation can be equivalently performed considering the charge due to the holes in the VB and to the electrons in the CB, and a fixed charge equal to $-e$ at each boron atom and to zero at each carbon atom.

NUMERICAL RESULTS

In Fig. 2 we show the impurity potential obtained, for an isolated layer of graphene containing a boron atom, with a DFT calculation and with a self-consistent simulation based on the TB model with the described distribution of fixed charges.

In Fig. 3, instead, we report the results obtained using both numerical techniques (with Neumann boundary conditions) for the transmission, as a function of energy, of an isolated armchair nanoribbon with 35 dimer lines across its width and with a substitutional boron atom in two different positions.

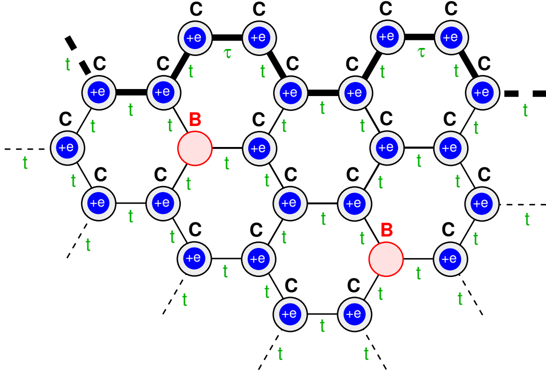

Fig. 1. Values of the TB parameters and distribution of fixed charges considered in our self-consistent TB calculations. The hopping parameter is equal to $t = -2.7$ eV inside the ribbon and to $\tau = 1.12\,t$ for edge dimers. The onsite energy ϵ is null for all of the atoms.

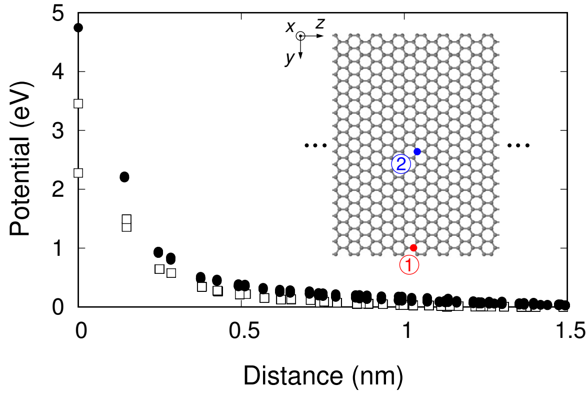

Fig. 2. Impurity potential obtained, for an isolated layer of graphene containing a boron atom, with a DFT calculation (empty squares) and with the self-consistent TB model (solid dots). Inset: positions of the boron atoms in the GNR for which we report the transmission in Fig. 3.

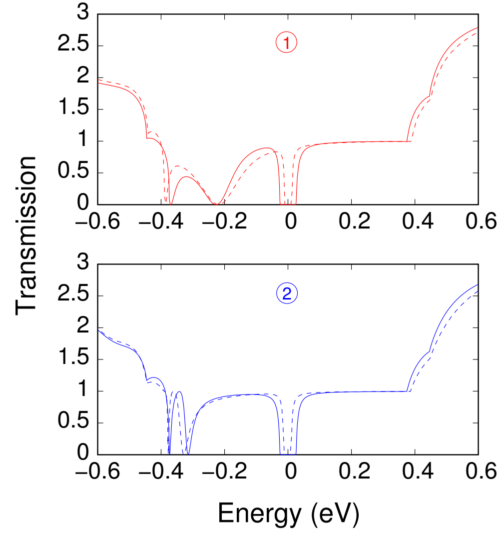

Fig. 3. Transmission, as a function of the injection energy, for an isolated 35 dimer-line wide armchair nanoribbon with a single boron dopant located in the positions indicated with 1 (upper panel) and 2 (lower panel) in the inset of Fig. 2.

A good agreement is reached between the two approaches. Looking at the transmission spectra, we notice dips on the hole side. These should be due to the presence of quasibound states localized around the boron atom, which give rise to anti-resonances in the transmission coefficient, analogously to what has been observed in carbon nanotubes [9].

Once validated, the proposed method has been applied to the study of the double-gate GNR-FET sketched in the inset of Fig. 4. The channel consists of a 20 nm long and 32 dimer-line wide boron-doped graphene armchair nanoribbon, separated from the bottom and top gates by 1 nm thick regions of silicon dioxide.

The previously described TB Hamiltonian and fixed-charge distribution have been included into the NanoTCAD ViDES code, which, for each value of the applied voltages, solves the Poisson and Schrödinger equations self-consistently, within the Green's Function formalism. Proper self-energies have been considered to model the Schottky contacts at the GNR ends. In Fig. 4 we show the transfer characteristics of the device, computed for $V_{DS} = 0.1$ V and for nanoribbons differing for the doping concentration or for the distribution of the randomly located dopant atoms. In particular, we show the characteristic of undoped graphene and, for the cases of 0.3% and 0.6% boron doping, those corresponding to 8 different distributions of the dopants along the channel. Due to the relatively small number of dopants, a large dispersion of the characteristics for different doping distributions is observed. Our results show that for our 32 dimer-line wide armchair nanoribbon (quasi-metallic in the absence of doping) the considered doping concentrations determine only a small improvement in the I_{ON}/I_{OFF} ratio, insufficient for logic applications. However, a clear electron-hole asymmetry and a mobility gap appear, dependent on the doping concentration, useful for the development of unipolar graphene devices.

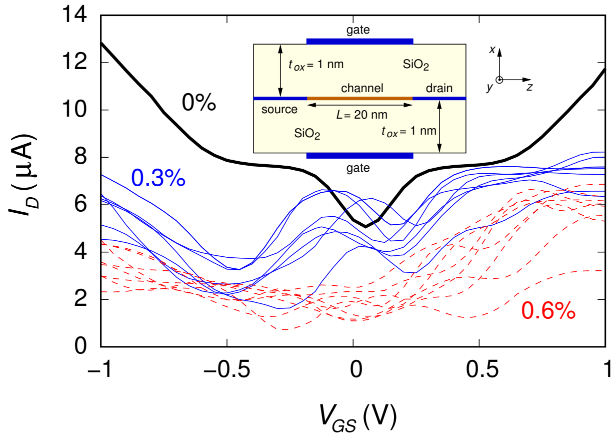

Fig. 4. Transfer characteristics computed at $V_{DS} = 0.1$ V for the considered GNR-FET. The thick solid line refers to an undoped nanoribbon, the thin solid (dashed) lines to 8 configurations of doped nanoribbons with a 0.3% (0.6%) boron atomic concentration. Inset: cross-section of the GNR-FET.

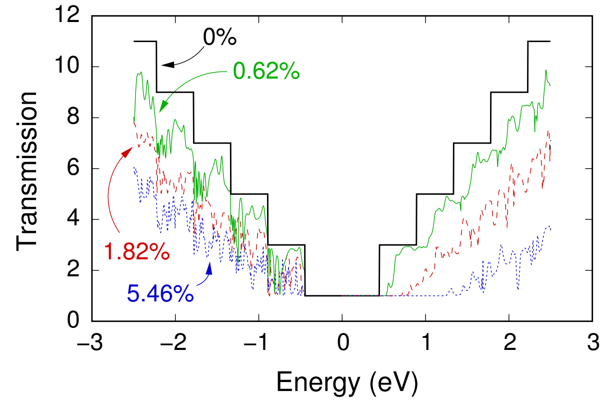

Fig. 5. Transmission, as a function of the injection energy, obtained from an envelope function simulation for an isolated 32 dimer-line wide armchair nanoribbon with different boron doping concentrations.

Due to numerical difficulties in achieving self-consistency, we have not investigated doping concentrations higher than 0.6%. However, for high concentrations the role of the backscattering generated by the quasibound states located around the boron impurities should progressively decrease with respect to the electrostatic action of the boron impurities. Thus the transmission suppression, which for low-doping affects mainly the hole branch (since the quasibound states appear at negative energies), at high doping should instead mainly impact electrons, which are electrostatically repelled by the negatively charged boron atoms (electron acceptors).

In Fig. 5 we report some transmission results obtained, using an envelope function approach [10], [11], for an isolated 32 dimer-line wide nanoribbon on which the screened potential corresponding to a boron impurity has been replicated in such a way to emulate ribbons with higher boron concentrations. Even though the envelope function approximation is not rigorously applicable in this case, where the potential is rapidly varying, these results provide some interesting hints on what should happen if the anti-resonance effect of the quasibound states is neglected (the adopted continuum approach, lacking atomic details, cannot properly include these effects). Actually, in this case it can be observed that electrons experience a stronger backscattering.

However, further numerical work would be necessary for high doping concentrations, in order to understand the physical origin (for example some ordering of the dopants) of the unexpectedly large I_{ON}/I_{OFF} ratios observed in some recent experiments. At the same time, it would be essential to gather more experimental data, both to obtain an independent verification of such measurements, and to accurately validate the numerical simulations.

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