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B and N codoping effect on electronic transport in carbon nanotubes

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We present here an analysis of the electronic-quantum properties of B and N codoping of carbon nanotubes. We show that BN pairs are transparent for conduction electrons. Localized transport phenomena, observed for isolated B or N doping, are recovered when B and N atoms are far apart. We also analyze the effect of BN nanodomains on the quantum conductance and demonstrate the drastic effect of the B-N "parity" and of the shape of the domain. Our simulations have been performed at the density-functional-theory level and within Green's function Landauer approach. However, we show that a one-parameter (on-site energy) model could catch the main features of the transport properties of BN codoping effect on electronic transport

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The modification of the intrinsic electronic, optical, mechanical, and transport properties of nanomaterials by defects, doping, or an external field is a key for the engineering of new devices. In the recent years, carbon nanotubes (CNTs) and nanoribbons have been extensively studied as one of the most promising materials for one-dimensional (1D) nanoelectronics. Beside the fundamental understanding of quantum transport in truly low-dimensional systems,[1] the tuning of their intrinsic electronic properties by encapsulation,[2] chemical substitution,[3–5] π stacking,[6] or covalent functionalization[7] reinforced their technological interest. Moreover, chemical reactivity[8] and optical properties[5] can be modified together with conduction characteristic, opening the route to application in selective nanosensing, new polymer composite, transparent films, or nanoelectronic switching devices. Localized charge transfer in NT could also play a significant role in large-scale fuel cells device.[9]

For example, it has been established that nitrogen (boron) substitution in carbon nanotubes not only transfer electrons (holes) to the graphitic network but also gives rise to quasibound impurity states.[3] As a consequence, the electronic-quantum conductance is reduced and shows evidence of strong localization: the mean-free path of electrons is drastically damped around the corresponding quasibound state (QBS) energies whereas pristine nanotubes display ballistic behavior.[10] Similar effects have been recently predicted for carbon nanoribbons with a dependence on the transverse position of the dopant.[11] Doping effect on the conductance of semiconducting nanotubes has been less extensively studied[12] even if, for practical applications, the tuning of electronic properties of nonmetallic tube is of prime importance. A deep understanding of the interplay between the QBS energy position, *n* or *p* type of doping, tube metallicity, or reactivity is obviously necessary for further development of the above-mentioned applications. We show in this paper that BN codoping is a possible route toward a control of those parameters.

Much progress has been made in the recent years concerning the production of B- and N-doped CNT.[13,14] Fingerprints of local electronic and vibrational modification have been tracked down by Raman spectroscopy[15] and scanning tunneling microscopy (STM).[14] Earlier, heteroatomic BNC compounds have been produced.[16–18] Simulation[19–21] and more recent electron-energy-loss spectroscopy (EELS) measurements[22] tend to demonstrate a phase segregation and the formation of BN nanodomains in BN-doped single-wall carbon nanotubes (SWNT). In multi-wall carbon nanotubes (MWNT), a radial segregation has also been reported.[23] Very recently, the production of graphene sheet with BN domain have been reported.[24]

At the best of our knowledge, no detailed study on transport properties of BN nanodomains in a carbon nanotubes have been reported yet. In this Brief Report, we focus on the quantum transport of boron and nitrogen codoping of metallic and semiconducting carbon nanotubes. We show that the substitution of a BN pair in the carbon network does not modify significantly the quantum transport of the nanotube at low gate voltage whereas impurity states reduce the conductance by half when B and N atoms are far apart. For larger BN nanodomains and rings, the conductance plateau decreases quasilinearly as a function of the density of BN pairs and localization phenomenon could be observed or not depending on the geometry of the domain.

We have performed *ab initio* simulations of the electronic properties of such systems[25] and obtained the quantum-transport conductance for a wide range of gate voltage by means of Green's functions formalism.[26] The Hamiltonian and the overlap matrices are obtained from the *ab initio* calculation in a similar manner than in Refs. 12 and 27. The systems we have considered [(10,10) metallic and (17,0) semiconducting nanotubes] are connected to leads consisting of perfect semi-infinite nanotubes on both sides. The size of the supercell ensures that the localized electronic states centered on the doping site has no effect on the lead.

On Fig. 1, the quantum conductances for the metallic and semiconducting carbon nanotubes with different doping configurations are presented. The simple N substitution curve reproduces data published on metallic nanotubes [Figs. 1(a) and 1(f)].[3,12] The resonant backscattering by the QBS located 0.50 eV above E_F reduces the transmission of metallic nanotubes by one quantum of conductance ($G_0=e^2/\hbar$). The transmission of the N-doped (17,0) semiconducting nanotube, is affected by the presence of a state very close to the bottom of the conduction band, turning the nanotube into a *n*-doped

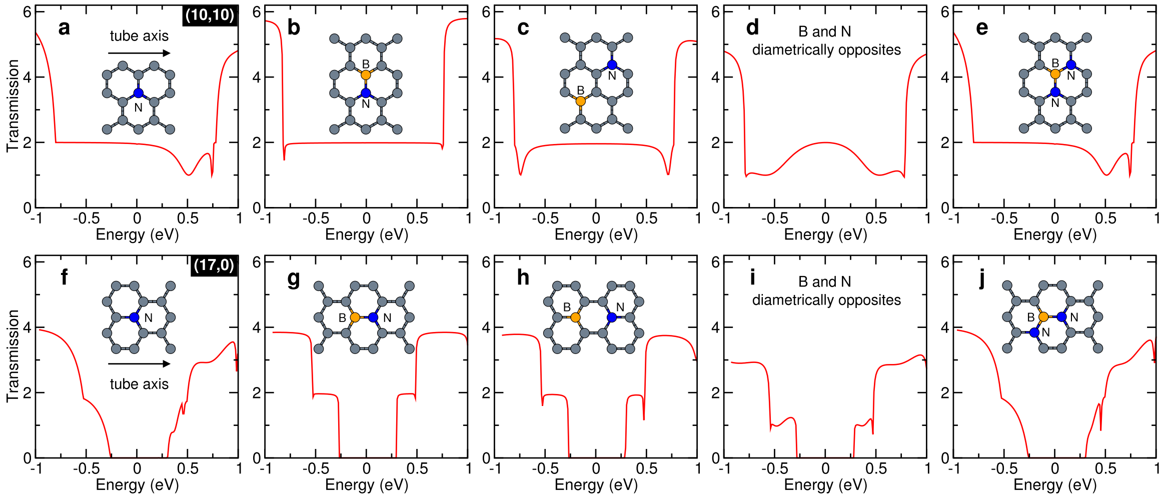

FIG. 1. (Color online) Calculated conductance of metallic (upper frames) and semiconducting (lower frames) nanotubes containing B and N codoping. The simple nitrogen substitution (a) and (f) induces a damping of the conductance created by the quasibound state located at $E_N \simeq 0.50$ eV whereas a pair of adjacent B and N atoms [(b) and (g)] is mainly transparent for conducting electrons close to E_F, and only two narrow dips in the transmission are predicted, close to the VHS. When B and N dopants are separated, like in a BCCN case [(c) and (h)] the two dips become broader and move closer to E_F. At last, when B and N atoms are far from each other [(d) and (i)] effect of back scattering is intense, and is reminiscent of both the N and the B substitutions. The doping by the more complex NBN group of atoms, shown in [(e) and (j)], exhibit a transmission curve very similar to the single N substitution.

semiconductor.[28] Transmission of the valence band remains mainly unaffected, edge steps are smoothed however. Substitutional doping by boron atoms gives rise to the same behavior for the valence band, mirrored respect to E_F (Refs. 3 and 10) (not shown).

In contrast with the single doping substitution, the quantum-conductance curves of nanotubes containing a BN pair show a symmetric shape with respect to E_F, for both metallic or semiconducting cases [Figs. 1(b) and 1(g)]. The BN bond orientation has almost no effect on the results (not shown). Moreover, a drastic dependence on the distance between B and N atoms is predicted. Indeed, for a pair of adjacent BN atoms the transmission curves of both (10,10) and (17,0) tubes remain similar to what it is observed for pristine case (ballistic transport), except the presence of small dips close to the Van Hove singularities (VHS), as plotted on Figs. 1(b) and 1(g). Increasing the B-N distance within the hexagonal network enhances the backscattering, as illustrate in the BCCN case where the doping atoms are third neighbors [Figs. 1(c) and 1(h)].[29] The dips are larger and deeper than in the previous situation, and they move closer to the Fermi level of the metallic tube. The global scattering however remains weak, and it appears that the codoping of B and N atoms preserve the transmission much more than a single dopant substitution.

To explain and rationalize this nonintuitive behavior, we have examined the effective potential seen by electrons in the vicinity of the defect. Like in Ref. 12 we have extracted the Hamiltonian matrix from a DFT ground-state calculation of a graphene supercell containing boron and/or nitrogen substitutions. The local electrostatic potential felt by the electron can be modeled by the on-site energy relative to the first zeta channel of the p_z orbital (left frame of Fig. 2). The N (respectively, B) atom creates a well (respectively, a barrier) of potential, and localized QBSs appear in the electronic density of states. The QBS responsible for the electron backscattering is the closest to the Fermi level, located above E_F for the nitrogen, and below E_F for the boron substitution. They are sketched on the right frame of the 2.

For B and N atoms in the carbon network, the effective potential of the doped system is surprisingly very well represented by the sum of the potential of the singly substituted B and N atoms (2). This implies that the depth of the well

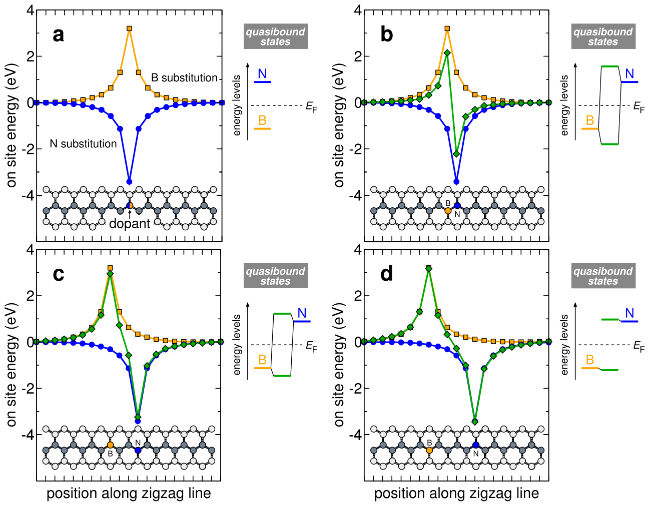

FIG. 2. (Color online) Effective potential (on-site energy) created by substitutions in a graphene sheet (see text). (a) single N (blue circles) (or B—green squares) substitution. (b) BN pair (adjacent). (c) B and N located as third neighbors (BCCN). (d) B and N located as fifth neighbors. Codoping [(a), (b), and (c)]: orange diamonds. The codoping effective potential is well represented by the sum of the isolated N (or B) substitution. For each doping configuration, a schematic representations of the corresponding QBS created by the effective potential is plotted and compared with the isolated N and B substitution.

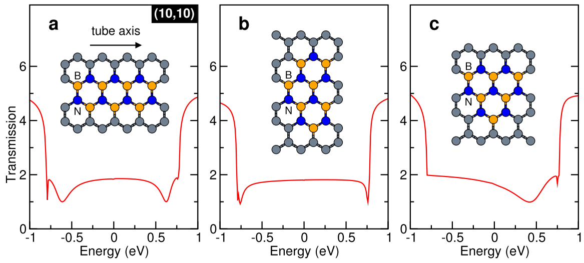

FIG. 3. (Color online) Quantum conductance of BN nanodomains. Nanodomains made of 7N and 7N with (a) hexagon aligned and (b) perpendicular to the tube axis. Example of a domain with a break of parity (7N, 6B) is represented (c).

(created by N) and the height of the barrier (created by B) are strongly reduced when B and N are nearest neighbors, whereas total potential is recovered when B and N are further apart. As a consequence, in the case of the BN pair, the QBSs repulse each other and move far from E_F. The absence of bound impurity states for BN pair have been reported previously.[30] Increasing the distance between the doping atoms will reduce this effective interaction. At last, when B and N atoms are far apart, the original QBSs tend to be recovered, explaining why the transmission is much more affected when B and N atoms are diametrically opposites, as shown in Figs. 1(d) and 1(i).

The exact position of all the QBSs on the energy scale is of course dependent of the electron density of the carbon network, then on the nanotube geometry. The B and N related QBS act as quantum levels, dressed by the electronic density of the honeycomb lattice. We have however checked that the B and N effective potential spatial dependence is very similar for planar graphene and for both metallic and semiconducting carbon nanotubes. An important conclusion at this point is that we have demonstrated the possibility to describe DFT-based calculations for the B and N doping and codoping for several sp^2 carbon network with a single spatial variation in electrostatic potential (on-site energy of localized orbitals).

Let us now explore the effect of more complex codoping geometries. The transmission of a nanotube containing a NBN defects exhibit a curve very similar to the simple N substitution [Figs. 1(e) and 1(j)]. As seen before, it happens that the effect of the boron annihilates the one of the nitrogen. The three QBSs (one from B atom, two from the N atoms) mix up and result onto a state located exactly at the energy of the single N-substitution QBS, and two new QBSs located further below and above E_F (not in the energy range of Fig. 1). The quantum conductance of nanotubes containing larger BN domains are shown on Fig. 3. We observe that the energies of the localized states depend drastically on the domain shape. Explanation of this phenomenon can also rely on the description of the effective potential of the domain as the sum of the effective potential of the single N- and B-substituted system, similarly than atomic states mix up onto molecular states.[31] Nanodomains made of 7B and 7N give QBSs close to the VHS. The energy separation of the localized states is smaller when the domain has linear shape [antracenelike molecule shape, Fig. 3(a)] and larger when the domain is C shaped [phenanthrenelike molecule shape, Fig. 3(b)].[31] Figure 3(c) shows the conductance of a nanotube containing a BN domain with odd parity (7N and 6B). The curve is no longer symmetric respect to E_F, and, like for the NBN case, one state is located at very similar energy than the original N-substitution QBS.[31]

We can also observe that the conductance plateau around the Fermi level is lower for domains (Fig. 3) than for BN pair (Fig. 1). BN pair presents a conductance very close to $2G_0$ (for ballistic transport for pristine tubes) where the conductance is lower by $0.15G_0$ for 7B-7N domains. The lowering of this conductance plateau does not present any resonant effect and is not related to any QBS. It can then be directly related to a conventional diffusive process due to the presence of disorder in the systems, rather than to a specific electronic localized state. This behavior is further analyzed in Fig. 4 where we have considered BN hexagon (with a B and N parity) lying perpendicular to the tube, forming eventually a ring of BN hexagons in a otherwise pure carbon nanotube.

For this particular configuration, the localized state effects are located at the VHS energies (similarly to the BN pair case investigated above). The quasilinear decrease in the conduction plateau is clearly evidenced (Fig. 4). This behavior is typical of a tunneling effect of the conduction electron through a larger and larger BN domains (BN crystal compound has a 6 eV gap). We also note that only a small decrease is observed when a complete ring of BN pairs is formed (20 BN units). This is in agreement with the 1D conductance behavior of carbon nanotubes. The BN domains do perturb the conduction channel even if a "carbon path" is topologically available.

In conclusion, we have investigated the B and N codoping effect on quantum transport of both metallic and semiconducting carbon nanotubes. We have shown that our DFT-based calculations could be explained by a one-parameter model (spatial variation in the on-site energy of the localized orbitals) and, consequently, more complex doping situations could be handled.

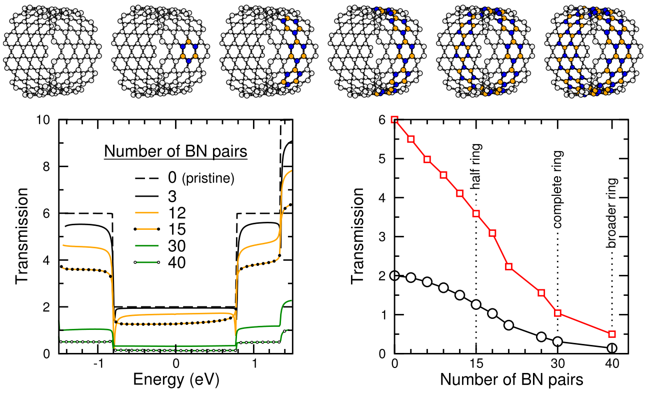

FIG. 4. (Color online) Top: schematic representation of the BN domain forming ring of hexagons. From pristine tube (left) to broad ring (right). Left: conductance of a BN-doped carbon nanotube for different number of BN pairs forming hexagons perpendicular to the tube axis. 20 BN pairs correspond to a complete ring of BN hexagons. Right: conductance (G_0 unit) at the plateau as a function of the number of BN pairs. Both plateau around the Fermi level and after the first Van Hove singularity (0.8 eV) are considered

We have first demonstrated that a BN pair exhibits a transparency behavior for conduction electron and that localization phenomenon is recovered when B and N atoms are no more adjacent. Larger BN domains transport properties have been shown to depend on the nanodomain shape. However, a monotonic decrease in the conductance plateau is observed for single domain as the concentration of BN increases. Interesting resonant tunneling effects could be foreseen when two (or several) BN domains are separated by a few carbon hexagons. Furthermore, the codoping of carbon nanotube could also modify the chemical reactivity of the nanotube and the catalytical activity for oxygen reduction.[9] Local probes (EELS, Raman, STM) have also been shown to be able to track down doped defects.[14,15,22] The production of controlled BN codoping in CNT is still a real challenge (BN domain size has however been shown to be dependent on the production methods[22]) but our study predicts that the electronic transport properties of CNT can be modified (or not) by tuning the BN composition and domains geometry and, together with the availability of local probe, opens new possibilities for sensing and switching devices.

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