## **Electrical Switching in Metallic Carbon Nanotubes**

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We present first-principles calculations of quantum transport which show that the resistance of metallic carbon nanotubes can be changed dramatically with homogeneous transverse electric fields if the nanotubes have impurities or defects. The change of the resistance is predicted to range over more than two orders of magnitude with experimentally attainable electric fields. This novel property has its origin that backscattering of conduction electrons by impurities or defects in the nanotubes is strongly dependent on the strength and/or direction of the applied electric fields. We expect this property to open a path to new device applications of metallic carbon nanotubes.

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Are single-walled carbon nanotubes (SWNTs) suitable for future nano-electronic device applications? The answer depends on whether the electrical properties of carbon nanotubes are changeable by applied gate voltages or electric fields [1]. Carbon nanotubes are either semiconducting or metallic, depending on their atomic geometry (diameter and chirality). Semiconducting carbon nanotubes are well suited for nano-electronic device applications [2, 3, 4, 5] because their electrical resistance is controllable by the gate voltage just as in silicon-based field-effect transistors. On the other hand, metallic nanotubes reportedly have electrical resistances which are not sensitive to the gate voltage or homogeneous transverse electric fields [6, 7, 8, 9] and this insensitivity has discouraged device applications of the metallic ones. The previous reports on metallic nanotubes, however, are limited to clean ones with electric fields [8, 9, 10, 11, 12] or to defective ones without electric fields [13, 14, 15, 16] even though impurities or structural defects under the transverse electric field may produce exotic effects because of the low dimensionality of the nanotubes.

A clean armchair-type SWNT is metallic with two linear bands intersecting at the Fermi energy  $(E_F)$  regardless of its diameter [17] (Fig. 1(a)). The tube's electrical resistance is determined by its electronic structure. A clean metallic SWNT should have an electrical resistance of 6.5 k $\Omega$  in two-probe measurements with perfect electrical contacts [17, 18]. This results from the resistance quantum, 12.9 k $\Omega$  [19, 20] (which is  $h/2e^2$  with h = Planck's constant and e = charge of an electron) divided by the number of bands at  $E_F$ . The resistance of a clean metallic carbon nanotube is insensitive to a homogeneous transverse (i.e., perpendicular to the tubular axis) electric field. Although the applied electric field polarizes the nanotube along the field direction [21] and the band dispersion is modified near  $E_F$  (Fermi velocities are slightly decreased as shown in Fig. 1(b)), electric fields

of moderate strength do not change the number of bands at  $E_F$  [8, 9, 10, 11] which is the only material parameter that determines the resistance of a clean one dimensional sample. Contrary to the clean tube case, however, a defective metallic carbon nanotube, as will be shown in this Letter, will have an electrical resistance which is very sensitive to transverse electric fields, and this property may be exploited for switching device applications.

Our study of the resistance of defective metallic SWNTs in transverse electric fields (Fig. 2) is based on first-principles calculations [22]. We introduce either impurities or structural defects into metallic nanotubes and describe their atomic and electronic structures using norm-conserving pseudopotentials [23] with Kleinman-Bylander's nonlocal projectors [24] and the local density approximation for the exchange-correlation potential. The wavefunction is expanded with a single zeta basis set [22] to produce the similar relaxed geometric

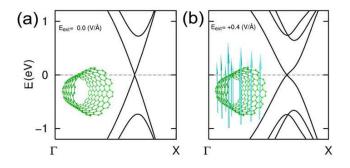


FIG. 1: Electronic structure of a clean SWNT with and without a transverse electric field ( $E_{\rm ext}$ ). The Fermi level is set to zero in all figures. (a) Band structure near the Fermi level of a clean (10, 10) SWNT with  $E_{\rm ext} = 0$ . The inset is the atomic structure of the (10, 10) SWNT. (b) Band structure of a clean (10, 10) SWNT with  $E_{\rm ext} = 0.4$  V/Å. The inset shows the nanotube and the applied electric field perpendicular to the tubular axis.

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configurations with the defect and the electronic structures compared with the result using plane-wave basis set [13]. A periodic saw-tooth-type potential perpendicular to the direction of the tube axis is used to simulate the applied transverse electric field in a supercell having 420 carbon atoms for (10.10) nanotube and 576 atoms for (18,0) tube respectively and such a potential is homogeneous along the tube axis as shown in the inset of Fig. 1(b). By calculating the scattering wavefunctions of electrons around the defects, we obtain the quantummechanical probability for an electron near  $E_F$  to transmit through the defects [25, 26]. The two-probe resistance of the sample is inversely proportional to the obtained transmission probability as well as the number of bands [27]. Our calculational results show that the resistance of defective metallic SWNTs is very sensitive to the strength and/or direction of the applied transverse electric field (Figs. 2-4).

Impurities or structural defects in metallic nanotubes produce quasibound states which backscatter conducting electrons resonantly near the quasibound-state energies. In case of a nitrogen and a boron doped (10, 10) nanotube (Fig. 2(a)), the electrical resistance shows maximum values at the electric field of 0.4 V/Å and -0.5 V/Å, respectively (Fig. 2(b)). Without electric fields, the nitrogen (boron) impurity produces resonant backscattering dips in the transmission associated with donor-like (acceptorlike) quasibound states above (below)  $E_F$  as shown in the middle panels (denoted by  $E_{\text{ext}} = 0.0$ V/Å) of Fig. 2(c-d) [13].

When transverse electric fields are applied, the fieldinduced change of the screened electrostatic potential near the impurity sites changes the quasibound-state energies and thereby the resonant backscattering and the resistance of the nanotubes (Fig. 2(c-d)). With an electric field, the dips move in the same direction in energy both for the nitrogen and for the boron impurity. The shapes of the dips are distorted when the dips approach the Fermi level or subband edges. The maximum resistances are about twice of the zero-field resistance because, at the corresponding electric fields, half of the conducting electrons at  $E_F$  are backscattered by the impurities. Since the resonant backscatterings are shifted energetically by the field-induced potential change at a defect site, the effect of the electric field scales as  $|E_{\text{ext}}| \cos \theta$  approximately when the electric field  $(E_{\text{ext}})$  has an angle  $\theta$ with the normal direction of the tubular surface at the defect site. So, the effect is maximized if  $\theta = 0$  as shown in Fig. 1(a). We have also examined, by first-principles calculations, electrical properties of single-impurity doped semi-metallic (3n, 0) carbon nanotubes which have very small energy gaps due to the curvature effect [28]. Our calculation results show that, with transverse electric fields, the resistance of a doped (18,0) SWNT, which is measured at either the conduction or the valence band edge, has almost the same tunable behavior (not shown

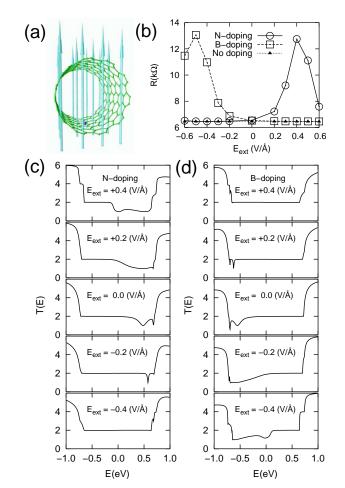


FIG. 2: Electrical resistances of single-impurity doped SWNTs in transverse electric field  $E_{\text{ext}}$ . (a) A ball-and-stick model of a nitrogen- or boron-doped SWNT in a transverse electric field. The impurity is denoted by a darker atom. The direction of the arrows (from the impurity-doped side to the other) corresponds to  $E_{\text{ext}} > 0$ . (b) Calculated two-probe electrical resistances (R) of a nitrogen-doped (10,10) SWNT, a boron-doped one and a clean one. Transmission spectra T(E) of (c) a nitrogen-doped and (d) a boron-doped (10,10) SWNT in various transverse electric fields.

here).

By adding up the effects of the nitrogen and the boron impurity in a single nanotube, we can produce much larger variation of the resistance so that with nitrogen and boron co-doping, a metallic carbon nanotube shows an "on-to-off" switching behavior as a function of the applied electric field (Fig. 3(b)). When two carbon atoms on opposite sides of a (10, 10) nanotube are replaced by a nitrogen and a boron atom (Fig. 3(a)), the resistance of the nanotube is slightly (3%) increased when no transverse electric field is present (Fig. 3(b)). It remains in the low-resistive "on-state" (6.7 k $\Omega$ ). When an electric field of 0.4V/Å pointing from the nitrogen-doped side to boron-doped side (Fig. 3(a)) is applied, the resistance of the nanotube increases to 221 k $\Omega$ , switching to a high-

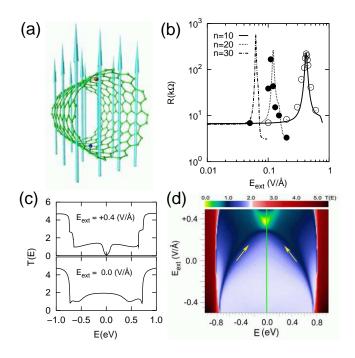


FIG. 3: (color online) Electrical resistance of nitrogen and boron co-doped SWNTs in transverse electric field  $E_{\text{ext}}$ . (a) A schematic diagram of a nitrogen (blue dot) and boron (red dot) co-doped SWNT in a transverse electric field. The direction of the arrows corresponds to  $E_{\text{ext}} > 0$ . (b) Calculated two-probe electrical resistances (R) of nitrogen and boron co-doped (n, n) SWNTs (n=10, 20, 30). Empty and filled circles are results from *ab-initio* calculations for (10,10) and (20,20) SWNTs, respectively, and lines are results from tightbinding approximations. (c) Transmission spectra T(E) of the nitrogen-and-boron co-doped (10,10) SWNT in electric fields of 0.0 and 0.4 V/Å. (d) Color-scale plot of transmission spectra T(E) as a function of energy E and electric field  $E_{\text{ext}}$  for the nitrogen-and-boron co-doped (10,10) SWNT. The color-scale bar is placed on top of the plot.

resistive "off-state" (Fig. 3(b)). With further increase in the strength of the electric field, the resistance decreases back to 20 k $\Omega$ . When the direction of the electric field is reversed, the doped nanotube remains in the low-resistive "on-state" (less than 10 k $\Omega$ ) at all values of field strength.

The high-resistive "off-state" of the N and B co-doped metallic nanotubes originates from the impurity-induced resonant backscatterings which reflect most of the conducting electrons at  $E_F$ . With no electric field, resonant scatterings due to the N and the B impurity occur above and below  $E_F$ , respectively, reflecting half of the conducting electrons at their respective resonant energies (Fig. 3(c)). With nonzero  $E_{\text{ext}}$ , the field-induced potential shifts are of the opposite sign near the two impurities since the two impurities are placed at opposite sides of the tube. This makes resonant backscatterings by the two impurities move in opposite directions in energy (toward  $E_F$ ) and, with a specific  $E_{\text{ext}}$ , they meet at  $E_F$ , causing almost complete reflection of the conducting electrons (Fig. 3(c)) and thereby the large increase of the resistance. In Fig. 3(d), it is shown that with electric fields, resonant backscattering dips (dark blue) associated with the boron and the nitrogen impurity move in opposite directions (denoted by yellow arrows) in energy because they are located on opposite sides of the nanotube. With  $E_{\text{ext}} \simeq 0.4 \text{V/Å}$  in Fig. 3(d), the two dips merge, making transmission almost zero (yellow region) at  $E_F$  (green vertical line).

The relative position of the boron and nitrogen impurities on the tubular surface affects the magnitude of the maximum resistance at the "off-state". Let z be the distance of the two impurities along the tubular axis, and  $\phi$  be their polar-angle difference. When  $\phi = 180^{\circ}$  and  $z = (3n \pm 1) \times L$  for integral n (as shown in Fig. 3(a)), the maximum resistance at the "off-state" is about 221 k $\Omega$ . Here, L is the unit-cell length of the armchair-type nanotube. If  $\phi = 0^{\circ}$  and  $z = 3n \times L$ , only one conduction channel is blocked at the maximal resistance condition, resulting in the maximal resistance of about 13 k $\Omega$ . These features are coherent effects of the two impurity scatterings, which occurs if the two impurities are closer than the phase coherence length of the electrons.

In a larger-diameter SWNT, the electrical switching is possible with a weaker electric field. First-principles calculations are preformed for different diameter defective tubes up to the (20, 20) carbon nanotubes, and we adopt tight-binding calculations to even larger-diameter nanotubes such as (30, 30) and (40, 40) tubes (Fig. 3(b)). The tight-binding approximation here adopts the standard one  $\pi$ -electron model with the nearest-neighbor hopping interaction [30]. A nitrogen (boron) impurity is represented by an attractive (repulsive) Gaussian onsite potential and the applied electric field is expressed with the onsite-energy variation screened with a dielectric constant. Parameters for impurity potentials and the dielectric constant are fit to reproduce our first-principles calculations of the doped (10,10) nanotubes. The required field strength to maximum resistance is found to be approximately inversely proportional to the square of the diameter of the nanotube. This scaling is due to the product of two effects: the field-induced potential drop across the tube diameter increases linearly and the subband energy interval decreases linearly with the increase of the diameter of the nanotubes [29]. For example, the "off-state" for a nitrogen-boron co-doped (30, 30) nanotube can be reached by a field of 0.06 V/Å (Fig. 3(b)). Thus, the switching behavior will be more easily achieved in experiments with larger-diameter nanotubes.

An "off-to-on" switching behavior occurs when considering a carbon nanotube with a vacancy. A recent observation on graphene layers and SWNTs [31] by transmission electron microscopy reveals stable intrinsic vacancy defects under strong electric field. When four adjacent carbon atoms are removed in a (10, 10) SWNT (shown in the inset of Fig. 4(a)), for example, the nanotube is in a

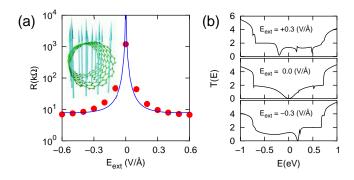


FIG. 4: (a) Calculated two-probe resistance of a (10,10) SWNT with a vacancy in transverse electric fields ( $E_{\text{ext}}$ ). Filled circles result from *ab-initio* calculations while the solid line from a tight-binding approximation. The direction of the electric field in the inset represents  $E_{\text{ext}} > 0$ . (b) Transmission spectra (T(E)) of the (10, 10) SWNT with the vacancy as a function of energy (E). From the top to the bottom panel, the applied fields are +0.3, 0.0, and -0.3 V/Å, respectively.

high-resistive "off-state" with no electric field. Resonant backscatterings are at  $E_F$  and the resistance is 1.2 M $\Omega$ (Fig. 4(a)). As a transverse electric field is applied, regardless of the sign of the field, the resonant backscatterings move away from  $E_F$  (Fig. 4(b)) and the nanotube switches to a low-resistive "on-state" having the resistance less than 20 k $\Omega$  for  $|E_{\text{ext}}| \geq 0.12$ V/Å (less than 100 k $\Omega$  for  $|E_{\text{ext}}| \geq 0.04$ V/Å) [32].

In summary, we have shown theoretically that the resistance of SWNTs is tunable up to three orders of magnitude by both defects and transverse electric fields, even if the SWNTs are metallic. Such a result may open a new way to make electronic devices by exploiting the variation of the resistance in metallic and semiconducting nanotubes simultaneously as a function of the electric field. The possible randomness of size of defects and those distributions and the stability of defects under the electric fields will require future works [33]. We anticipate that this interesting property of the defective metallic SWNTs can be tested by suitable experimental setup, e.g., isolated nanotube in a nanoelectromechanical system [34] or in a split-gate configuration [35].

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