Letter

Contact-driven deformation of metallic carbon nanotubes observed from an unconventional field effect

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Despite decades of intensive studies, some aspects of charge transport through carbon nanotubes (CNTs) remain poorly understood. Here, we explore the transport properties of field-effect devices based on metallic CNTs, where the density of states is supposed to be constant and a field effect is not anticipated. The observed current-voltage characteristics are qualitatively different from these expectations. The conductance of our devices shows significant modulation as a function of gate voltage. However, the minimal conductance does not show a temperature dependence, with the on/off ratio being constant in a wide temperature range. Still, when an axial magnetic field is applied, an Arrhenius temperature dependence of the minimal conductance is observed. The observed effects are naturally explained by the CNT's band-structure modifications under the metallic electrodes at the CNT edges. Our results provide experimental proof of the predicted structural deformations of CNTs in side-contacted devices.

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Single-walled carbon nanotubes (CNTs) have highly promising transport properties for next-generation nanoelectronics and optoelectronics [1,2]. Semiconducting CNT-based field-effect transistors (FETs) can achieve efficient gate electrostatics and superior transport characteristics [3]. Metallic CNTs demonstrate a high current density capacity for electrical interconnects [4], while small-gap quasimetallic CNTs can be used for THz optoelectronics [5]. Moreover, CNTs are fascinating objects because of their unique properties, such as the lack of backscattering in pristine CNTs with a perfect atomic structure. The transport properties of CNT-based devices are determined primarily by the nanotube's band structure. Electrostatic doping using a gate electrode allows for tuning the position of the CNT Fermi level. In the case of semiconducting nanotubes, it leads to a change in the conductance of a CNT device by several orders of magnitude even at room temperature [6], while for quasimetallic CNTs, the effect is not strong [7]. Minimum conductance as a gate voltage function occurs when the nanotube's CNP and Fermi levels coincide.

The band structure of a CNT is mainly defined by its geometry, that is, how the graphene's trigonal lattice is wrapped into a cylinder [8] forming the nanotube surface. The latter is described by the so-called chirality indices (n, m). It is well established that a CNT with a diameter above 1 nm is semiconducting with a band gap inversely proportional to its diameter when the difference $n - m$ is not a factor of 3. Whenever $n - m$ is not a factor of 3 but not 0, the CNT has a small band gap (so-called quasimetallic CNTs). CNTs with $n = m$ have a zero band gap and are truly metallic. In the case of smaller-diameter CNTs, the band structure is defined by $s - p$ hybridization and does not fall into the above classification.

Interaction of the carbon nanotube with its environment as well as Coulomb interactions between the carriers result in a modification of the CNT band gap. For example, it has been shown in Ref. [9] that an interaction with a substrate changes the band gap of a quasimetallic CNT, while in Ref. [10] the Mott insulating state has been demonstrated in zero-gapped ultraclean CNTs at low temperatures.

Importantly, transport phenomena in carbon nanotubes are affected by the interface between the nanotube and the metallic electrodes. In this Letter, we report on an unconventional gate voltage dependence of the conductance of metallic CNTs. The ratio of maximal to minimal conductance (on/off ratio) for the reported devices is about 2 at all temperatures studied (in the range of 4–300 K). The application of an axial magnetic field opens a band gap in the CNT spectrum and leads to a strong temperature dependence of the on/off ratio, similarly to Refs. [11–13]. This is direct evidence that there is no band gap in the CNT channel under a zero magnetic field. The observed on and off conductance values can be explained by a band gap opening near the CNT edges. This gap is explained as a consequence of the modification of the nanotube band structure under the metallic electrodes, which is caused by deformation and a related symmetry reduction [14]. A band gap opening in the case of a metallic (armchair) CNT was predicted recently in Ref. [15]. Our estimation of the induced CNT band gap value is a few hundred meV. The ability to open such a large band gap in a metallic CNT by deformation is promising for future applications.

This Letter is focused on the electrical transport in metallic carbon nanotubes in the field-effect transistor geometry. Nanotubes are synthesized by a chemical vapor deposition (CVD) method on a silicon wafer covered with a thermally grown silicon oxide layer. The thickness of the oxide layer t_{ox} ranges from 300 to 500 nm. Details of the CVD process are similar to Ref. [16]. The silicon wafer serves as a back gate. After

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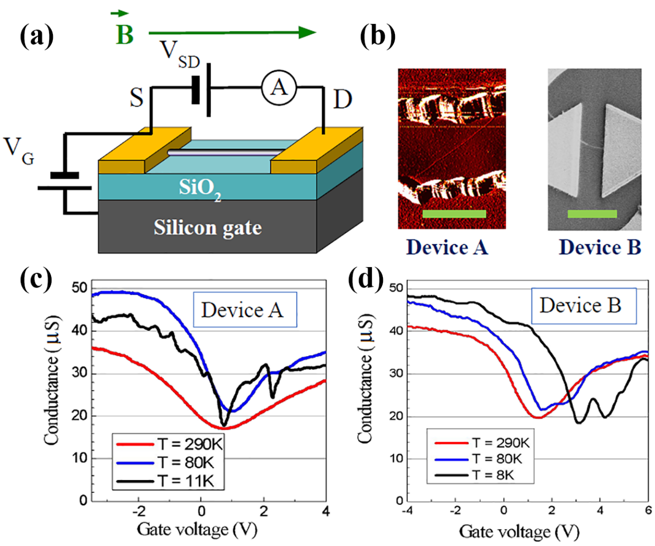

FIG. 1. (a) Schematics of the single CNT field-effect transistor. (b) AFM images of devices A and B. The scale bar corresponds to 3 μm. (c) and (d) show the temperature evolution of the transistor curves $G(V_g)$ in devices A and B correspondingly. We note that the minimal conductance is almost insensitive to temperature in the case of both devices.

a nanotube is located using a scanning electron microscope (SEM) with respect to alignment marks, two contacts are made to it using metal sputtering through an electron-beam-defined mask, followed by the lift-off. Palladium was used as the contact material in the case of device A [11] and gold with a thin vanadium adhesion layer in the case of device B [17]. CNT diameters of $d = 2.5 \pm 0.5$ nm for device A and 2.3 ± 0.5 nm for device B are obtained by atomic force microscopy (AFM) imaging; the length of the CNT channel was approximately 5 μm for device A and 1.5 μm for device B. Fabrication technology is presented, e.g., in Ref. [18].

Unconventional field-effect transistor behavior is illustrated in Fig. 1, which displays a gate voltage dependence on conductance $G(V_g)$ in two CNT-based devices, measured at a source-drain voltage of 10 meV at different temperatures. The minimal conductance of the two different-length devices is practically insensitive to temperature, which indicates that our devices are quasiballistic. Importantly, $G(V_g)$ curves that exhibit a decrease in conductance around the zero gate voltage are typical for the so-called quasimetallic CNTs that have a small curvature-induced band gap [7]. In the case of a finite band gap in the channel E_g [7], the minimal conductance is expected to follow the Arrhenius law $G \propto \exp(-E_g/2kT)$ [11]. The temperature evolution of the $G(V_g)$ curves in the case of devices A and B does not obey the Arrhenius law. Therefore, the dip in conductance around the zero gate voltage cannot be explained by the presence of a band gap in the nanotube conduction channel. We further note that not only the shapes of the $G(V_g)$ curves for devices A and B are similar, but also the conductance values of the devices are similar despite the different contact materials and lengths. Specifically, device A used a palladium metal contact, and device B used gold/vanadium. This suggests that our devices operate in a quasiballistic regime. Moreover, the ratio of maximal to minimal conductance (on/off ratio) for both devices is about a factor of 2 at all temperatures studied.

We have studied about 20 different devices with a quasimetallic CNT forming the conductance channel. All of them demonstrate a conductance minimum around zero gate voltage, with the on/off ratio ranging from 1.5 to 5 at room temperature. Among those, only two devices demonstrated temperature-independent minimal conductance. In all other cases, minimal conductance decreased with decreasing temperature [11,17], consistent with the results of other authors [7]. We here report such a temperature-independent on/off ratio in field-effect transistors with CNT channels.

The second conductance minimum at the $G(V\_G)$ curve shows the evolution at low temperature for both devices; we attribute it to the resonant scattering (see Ref. [19]).

Further evidence of a zero band gap band structure of the CNTs in devices A and B is obtained when an axial magnetic field is applied. The application of an axial magnetic field opens a band gap in such nanotubes, as has been shown in several works [11,13,20–22]. We used this effect to investigate how the appearance of a band gap in the CNT forming the conduction channel would affect the transport properties of our devices. As we see from Fig. 2, under moderate magnetic fields, the temperature dependence of the minimal conductance becomes pronounced (see Fig. 2), and a significant decrease of the minimal conductance is observed as the magnetic field is applied. We also note that the gate voltage value corresponding to the conductance minimum does not depend on the magnetic field. Minimal conductance is observed in a device with a CNT that has a band gap when the applied gate voltage places the Fermi level at the charge neutrality point (CNP) in the nanotube (see Fig. 3). We therefore conclude that the conductance minimum that we observe at zero magnetic field when the intrinsic band gap of the nanotube is zero is also observed when the Fermi level matches the CNP energy. Note that the band gap is proportional to the magnetic field, with a coefficient of proportionality of about 1 meV/T [11]. Therefore, for the highest magnetic field in our measurements, we anticipate a band gap opening below 20 meV. The above data obtained under an axial magnetic field indicate that the presence even of a small band gap with a value of a few meV in the CNT spectrum results in a strong temperature dependence of the minimal conductance in contrast to the data obtained under zero magnetic fields.

Our experimental results show unambiguously that (i) the transfer characteristics of two CNT-based devices show an on/off ratio of about 2 nearly independent of temperature (unconventional field effect), and (ii) that both devices A and B have a truly metallic CNT conduction channel (with a zero band gap). The latter circumstance rules out the band gap modification or opening as an explanation for the observed unconventional field effect. The band gap in truly metallic CNTs due to an electron-electron Coulomb interaction has been reported [10], but in our large-diameter CNTs the Coulomb interaction is suppressed. Similar considerations apply to the effect of the substrate demonstrated in Ref. [9], where the interaction with the substrate was shown to modify the CNT band gap.

We also want to stress the following: The diameters of our CNTs fall into the range from 2 to 3 nm. CNTs of 84

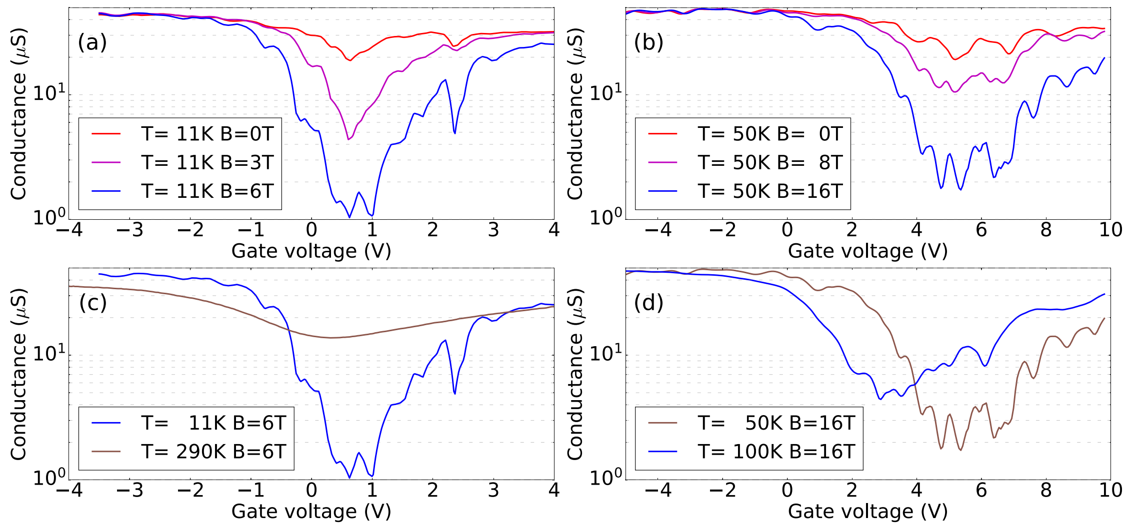

FIG. 2. Effect of a band gap opening in an axial magnetic field on the transport characteristics of a CNT FET. The upper panel shows suppression of minimal conductance for (a) devices A and (b) B as the axial magnetic field is increased; the lower panel shows how, in the presence of an axial magnetic field, the minimal conductance of (c) devices A and (d) B drops significantly as the temperature decreases.

different chiralities have diameters falling into that range. Among them 56 are semiconducting, 20 are quasimetallic, and 8 are armchair ones. This statistics explains why the transport properties of armchair CNT-based devices are not investigated as intensely as those of semiconductor nanotube-based devices.

We thus maintain that the unconventional field effect reported in this Letter is an intriguing observation. Theoretically, it was predicted recently in Ref. [15]. We note that the conductance of the section of the truly metallic CNT not in direct contact with the electrodes should not depend on the

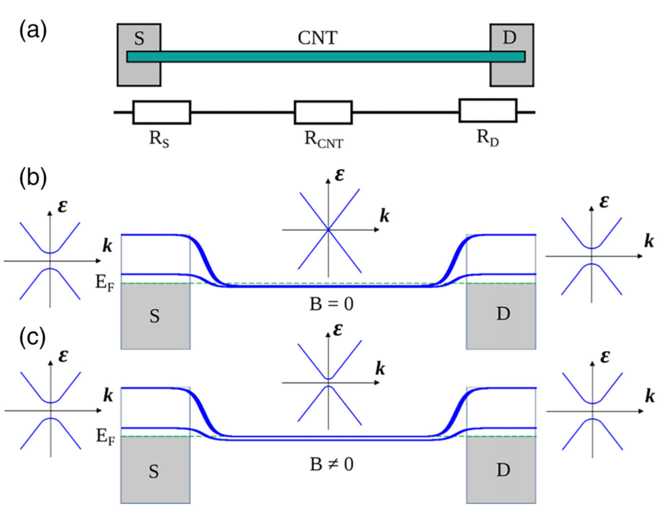

FIG. 3. (a) Schematics of the single CNT device and equivalent electric circuit. R_S and R_D represent the contact resistances of the source and drain correspondingly, while R_{CNT} represents the resistance of the CNT channel itself. (b) Qualitative band diagram for a single CNT device in zero magnetic field. No band gap is present for states inside the CNT channel, whereas the gap opens for states at the S and D contact areas. (c) Band diagram of the same device in an axial magnetic field. In this case, the band gap opens for states inside the CNT channel. The dashed line at E_F shows the position of the Fermi level in the system.

position of the Fermi level with respect to the band edges. The gate voltage can affect the transport properties of the CNT that is in direct contact with or in close vicinity of the metal electrode. The deformation of the CNT under the metallic electrode should result in a strong modification of its band structure [14]. The nanotubes probed in our experiments are armchair ones and have a high symmetry that should be lowered by deformation.

Ballistic CNT with transparent contacts would have conductivity $4h/e^2$ (owing to the $2 \times 2 = 4$-fold spin and valley degeneracy), which should be weakly dependent on temperature and gate voltage and corresponds to a resistance ≈6 kΩ (150 μS conductance). Observation of an order higher resistance in combination with the length independence of the conductance suggests that the contacts are not transparent for some reason. It is natural to suggest that the gate opens in the near-contact regions, probably due to the mechanical deformation of the nanotube. From an electrical point of view, this corresponds to the equivalent circuit shown in Fig. 3(a). As follows from the resistance value, the value of R_S is about several 10 kΩ. The band structure of the CNT at $B = 0$ is shown in Fig. 3(b). The transistor curves do not show a pronounced temperature evolution. It means that even at room temperature, the thermally activated transport contribution to conductance is much smaller than the tunneling transport through the barrier occurring due to the gap opening under the contacts. We can thus evaluate the band gap value from the tunneling integral,

$$R_S = \frac{4h}{e^2}\exp\left(\int\sqrt{\Delta(x)m}dx/\hbar\right),$$

where Δ is the value of the CNT band gap in the contact region. The value of R_S suggests that the integral under the exponent is about 1. For the Dirac dispersion in CNT, one has $\Delta \sim mc^2$, and one has an estimate for the Δ value,

$$\Delta\delta x/c \approx \hbar,$$

where δx is the approximate width of the near-contact gapped region. By substituting $c = 10^6$ m/s and $\delta x = 2.5$ nm (the diameter of the nanotube as the characteristic length scale of the deformation), one gets $\Delta \sim 400$ meV. Tunneling through the barriers occurring due to the band gap opening close to the electrodes explains the lack of temperature dependence as the band gap value is much larger than the thermal energy at room temperature. Interaction with the substrate considered in Ref. [9] will result in a band gap opening in the entire CNT that should result in a strong temperature dependence of the minimal conductance. A strongly inhomogeneous interaction with the substrate will result in the occurrence of multiple barrierlike defects and strongly suppress the CNT conductance, contradicting the measured values.

The band gap estimate based on our experimental data matches the one predicted in Ref. [15]. It is rough, yet very promising. It indicates the possibility of opening a relatively large gap sufficient for transistor applications in metallic CNTs by mechanical stress caused by the contact. One can imagine a future development of this work and gap opening, e.g., by insulating the top layer. It will allow the formation of electronic transistors on the basis of metallic CNT grids.

The band structure in the presence of a parallel magnetic field is shown in Fig. 3(c). It is in excellent agreement with the experimental data and further confirms our understanding of the system.

Thus, it is already clear that the unconventional field effect described in this Letter is a result of contact phenomena, and its further analysis will shed light on the interplay between the intrinsic and interface effects on the overall transport properties of CNT-based devices.

To conclude, we report on an unconventional gate effect observed in field-effect transistors with a conduction channel formed by a metallic nanotube. This phenomenon manifests itself as an absence of the temperature dependence of the off-conductance in a wide temperature range. The on/off ratio of our devices is equal to 2 and is strongly modified by applying an axial magnetic field that opens a band gap in the CNT spectrum. The qualitative interpretation of the experimental results is based on a band gap opening in the CNT deformed under the metallic electrodes. Further theoretical analysis of this effect will provide an advancement in understanding the interplay between intrinsic and contact phenomena in nanotube-based devices.

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