Band-Structure Modulation in Carbon Nanotube T Junctions

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We show that the band structure of metallic carbon nanotubes can be dramatically altered by the local electrostatic field. This is realized by coupling chemically functionalized nanotubes to form T junctions. The bar of the T is the conducting channel and the leg of the T is used for local gating. Transport measurements reveal that an energy gap develops upon application of a local electric field in both devices with or without linker molecules at the junction. We propose that the mechanism of the band gap modulation in the T junctions without linker molecules is the field effect, with the linker molecules introducing additional electromechanical and chemical effects.

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The electronic structure of carbon nanotubes is crucially dependent on their diameter and chirality. The existence of different chiralities gives both metallic and semiconducting nanotubes [1,2]. It is also known that mechanical deformation [3] and a high electrostatic field [4,5] can remarkably affect a tube's electronic properties and could be used for band gap engineering in nanotube-based molecular scale electronics. Previous experiments have focused on strain-induced conductance changes mainly based on a scanning probe technique where the loading is applied by an atomic force microscope (AFM) tip on a suspended nanotube [6–8]. Stress is exerted throughout the tube and causes different deformation modes: bending in the tip-contacted region and stretching along the axial direction in the straight parts. It was found in these experiments that the conductance could drop by a factor of 2 [7,8] or even by 2 orders of magnitude [6] in metallic nanotubes under various strains.

Here we present measurements to demonstrate that the band structure of metallic nanotubes can also be modulated by a *local electrostatic field.* Both metallic (on) and insulating (off) states are accessible by changing the field strength, resembling a molecular switch. To achieve this, we interconnect two tubes in "end-to-side" configuration via bifunctional amide groups as linker molecules, forming a T-shape junction as illustrated in Fig. 1(a). The bar of the T is the conducting channel and the leg of the T is used for gating the channel.

Carbon nanaotube T junctions (CNTJs) used in the present study were fabricated by functionalizing nanotubes on the defect sites [9]. The carbon gate is capacitively coupled to the channel via an insulating molecule (tripropylentetramin) bridging the two tubes. The long molecular chain and perpendicular linkage keep the nanotubes in proximity without allowing contact. Devices were subsequently made by dispersing CNTJs randomly on a Si substrate with degenerate doping, followed by *e*-beam lithography for contacting CNTJs. Figure 1(b) shows a typical AFM image of such a CNTJ embedded in four AuPd electrodes. The tube between $E1$ and $E2$ is defined as the conducting channel and the tube between $E2$ and $E3$ is used only for diagnostic purposes. A dual gate configuration is designed in our devices: the Si chip with 100 nm oxide acts as a back gate, and the leg of the T is used as an in-plane carbon gate. To gain insight into the modulation mechanisms, we have investigated the electrical transport along two different kinds of CNTJs. The first type (CNTJ-I) was made as described above, whereas the bridging molecule was destroyed by heat treatment in the second type (CNTJ-II).

Shown in Fig. 2 is the conductance of a metallic channel in CNTJ-I as a function of the back gate voltage V_{bg} at 4 K. Figures 2(a)–2(c) correspond to different

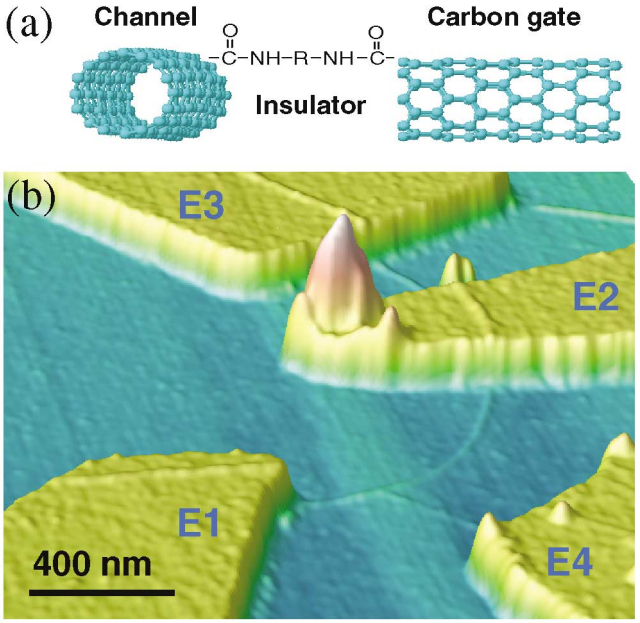

FIG. 1 (color). (a) A schematic diagram of a CNTJ via a single molecule as linkage, where $R = (CH_2)_3NH(CH_2)_3NH(CH_2)_3$. (b) An AFM image of a CNTJ embedded in AuPd electrodes (channel $d_{ch} = 1.6$ nm; carbon gate $d_{cg} = 1.3$ nm).

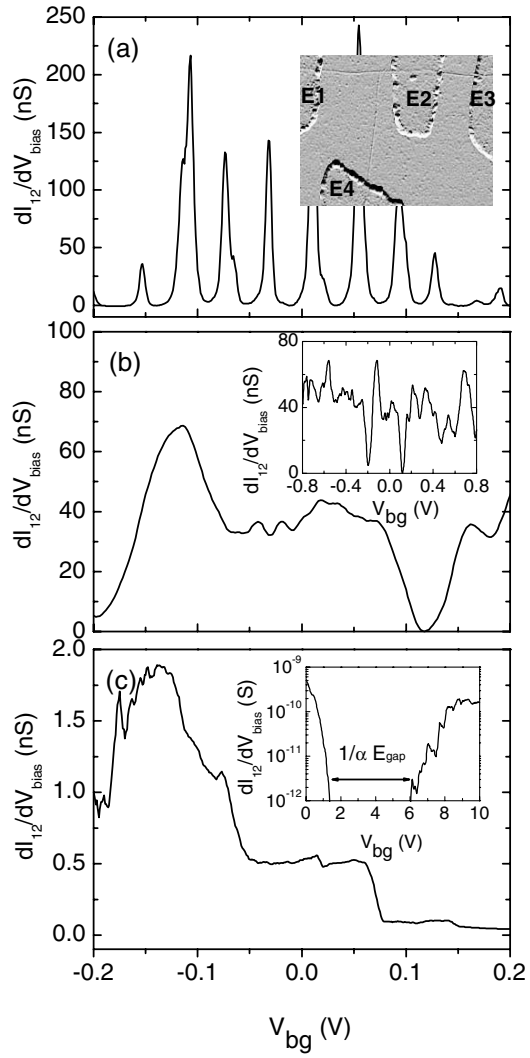

FIG. 2. Evolution of V_{bg} dependent conductance in a metallic channel of CNTJ-I at 4 K. The data were taken at $V_{bias} = 6$ mV with (a) $E_{cg} = 0$, (b) $E_{cg} = 4 \times 10^3$ V/cm, and (c) $E_{cg} = 1 \times 10^4$ V/cm. The inset to (a) is the AFM image of the junction investigated (channel $d_{ch} = 1.0$ nm; carbon gate $d_{cg} = 2.8$ nm). The distance from the junction to the closest neighbor lead is $L_r = 70$ nm. Both insets to (b) and (c) show the conductance in extended voltage scale.

fields applied through the carbon gate. The bias across the channel is kept constant at 6 mV and the channel current I_{12} is measured. At $E_{cg} = 0$ [Fig. 2(a)], regular conductance oscillations are seen in the dI_{12}/dV_{bias}-V_{bg} plot. They originate from the quantum confinement on the metallic channel by the two contact barriers. These conductance peaks appear when a new quantized excitation becomes energetically accessible, opening a tunneling pathway between the confined nanotube and the electrodes. The peak spacing is constant, implying that a single quantum dot is defined between the two confining electrodes.

Applying field strength of 4×10^3 V/cm on the carbon gate [Fig. 2(b)] dramatically distorts the Coulomb blockade (CB) oscillations. A new oscillation pattern, shown in Fig. 2(b) and its inset, emerges with average peak spacing broadening from $\Delta V_{bg} = 40$ mV to $\Delta V'_{bg} = 140$ mV. The increasing peak spacing and the irregular amplitude indicate that the electric field acts as a local perturbation to the 1D quantum structure. The channel is energetically split into two islands which are connected in series with length $L_l \approx 4L_r$. This change can be confirmed from $\Delta V'_{bg}/\Delta V_{bg}$ obtained from the self-capacitance of the split channel. ΔV_{bg} corresponds to a change of one electron in the island and can be expressed as $e\Delta V_{bg} = (E_{n+1} - E_n)C_\Sigma/C_{bg} + e^2/C_{bg}$, where C_{bg} is the gate capacitance and C_Σ is the total capacitance of the defined quantum dot. It is assumed that the energy spectrum for the greater split island can be regarded as continuous at 4 K [10]. In the approximation of vanishing energy splitting in the smaller island $E_{n+1} - E_n \approx 0$, we obtain $\Delta V'_{bg}/\Delta V_{bg} \approx C_{bg}/C'_{bg} = L\ln(2L_r/d_{ch})/L_r\ln(2L/d_{ch}) = 3.8$ with $d_{ch} = 1.0$ nm being the tube diameter and $L = L_l + L_r$ being the channel length. This is in good agreement with the observed ratio $\Delta V'_{bg}/\Delta V_{bg} = 3.5$ in the dI_{12}/dV_{bias}-V_{bg} plot shown in Fig. 2(b) and its inset.

Interestingly, if we further increase E_{cg} to 10^4 V/cm, the CB oscillations vanish and a steplike conductance shows up in Fig. 2(c). The dI_{12}/dV_{bias}-V_{bg} curve now shows ambipolar transport with hole conduction at $V_{bg} < 1.5$ V and electron conduction at $V_{bg} > 6$ V [inset to Fig. 2(c)]. In contrast to $E_{cg} = 0$, here the channel conductance has dropped by 2 orders of magnitude in the conducting state. This change occurs only *locally* in the channel where the carbon gate is attached. The electrical transport in a diagnostic segment next to the channel is not affected upon application of the E_{cg}. This result shows that the increasing E_{cg} progressively modifies the electronic structure of the metallic tube locally. At $E_{cg} = 10^4$ V/cm, an energy gap E_{gap} is induced in the metallic channel. The energy gap E_{gap} can be estimated by multiplying a gate efficiency factor $\alpha \approx 10$ meV/V to the insulating region spanning $\Delta V_{bg} \sim 4.5$ V, yielding $E_{gap} \sim 45$ meV.

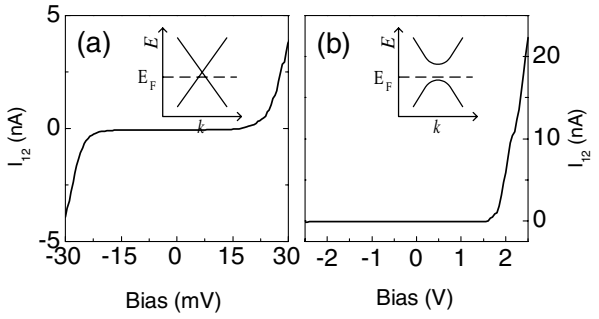

FIG. 3. I_{12}-V_{bias} curves of CNTJ-I at (a) $E_{cg} = 0$ and (b) $E_{cg} = 1 \times 10^4$ V/cm. Both data were taken at $V_{bg} = 0$. The insets to (a) and (b) show the dispersion relation near Fermi level at corresponding E_{cg}.

In Fig. 3 we show the I_{12}-V_{bias} curves of CNTJ-I at $E_{\text{cg}} = 0$ [panel 3(a)] and at $E_{\text{cg}} = 10^4$ V/cm [panel 3(b)]. The nonlinear I_{12}-V_{bias} curve in panel 3(a) is due to the CB effect where the conductance gap corresponds to a charging energy of $E_c = e^2/2C_\Sigma \approx 20$ meV. In striking contrast, the I_{12}-V_{bias} curve under $E_{\text{cg}} = 10^4$ V/cm is highly nonlinear and asymmetric, resembling that of a Schottky diode. The rectifying behavior as a signature for metal-semiconductor (MS) junctions is explicitly associated with the gap opening. Additional transmission barriers develop at the MS interfaces. This gives rise to a reduction of the turn-on voltage by 2 orders of magnitude at $V_{\text{bias}} > 0$, consistent with the conductance drop in the dI_{12}/dV_{bias}-V_{bg} plot shown in Fig. 2. Notably, the I_{12}-V_{bias} curve under $E_{\text{cg}} = 10^4$ V/cm is very similar with that in nanotube MS intrajunctions observed by Yao *et al.*, where an asymmetric barrier is induced by a kink defect [11]. In our case the origin of the asymmetric barriers could be attributed to the asymmetric defect structure (e.g., pentagon-heptagon pair), which serves as an anchor group for linkage.

The mechanism(s) governing the gap opening observed in Figs. 2 and 3 is (are) presently unsettled. Different scenarios can be speculatively proposed to explain this effect.

We first discuss the "field effect" since the carbon gate is capacitively coupled to the channel and can apply a local perturbation to the charge distribution in the vicinity of the junction by electrostatic field. For such a nanotube contacted only at one end by a metal lead, the application of the voltage on the tube will result in charge injection from the source ($E4$). The extra charges accumulate considerably at the very end (within 3 Å) instead of being uniformly distributed along the tube [12]. This gives rise to substantial charge density at the tube end. Additionally, accumulating charges will enhance the local electric field and are delicately influenced by the aspect ratio and the edge geometries [13]. This field enhancement factor can be estimated by using $\eta \sim 1.2(L_{\text{cg}}/R_{\text{cg}} + 2.15)^{0.9}$ [14], where $L_{\text{cg}} = 550$ nm and $R_{\text{cg}} = 1.4$ nm are the length and the radius of the carbon gate, yielding an η value ranging from 10^2 to 10^3. The local field at the end of the carbon gate is then modified to be about 10^6–10^7 V/cm. As predicted [5], at low field strength ($\ll 3 \times 10^8$ V/cm), the field-induced polarization in metallic channel is negligible, but the electric field could cause the redistribution of the charge density in the highest occupied molecular orbital and the lowest unoccupied molecular orbital. It was suggested for metallic nanotubes that a nonzero transmission barrier appears as the local electric field reaches the order of 10^7 V/cm and eventually results in a gap opening of tens of meV in the local density of electronic states for a higher electric field ($> 2 \times 10^7$ V/cm) [4]. If we take η into account, then the field-effect picture will be in reasonable agreement with the experimental results. However, in accumulating the experimental statistics of CNTJ-I so far ($\sim$15 devices) we found two additional issues that remain uncertain: jerkylike conductance changes in most of the devices upon application of a similar order of E_{cg} and rather poor reversibility of the conductance changes in both metallic and semiconducting channels (i.e., the gating occurs only in one way, either $E_{\text{cg}} > 0$ or $E_{\text{cg}} < 0$).

We, therefore, propose another mechanism which could contribute to the band structure modulation in CNTJ-I. The length of the carbon gate could be changed due to the charge injection and, consequently, the mechanical force of lattice expansion/contraction in the carbon gate exerted on the circumference of the channel via the single molecular linkage. The sidewall of the channel could hence be twisted, giving rise to the change of local helicity near the junction. Prior to the twisting deformation, k_F of the metallic tube sits on the allowed subband. Upon twisting, the wrapped graphite structure rotates, shifting k_F away from the original state. This gives rise to a nonzero shortest distance $|k'_F - k_F|$, which is proportional to the induced energy gap at the Fermi surface of a metallic tube [3].

To compare quantitatively the experimental results with theories based on the "electromechanical effect", we consider the model suggested by Yang *et al.* [3], in which the band gap under strain in the circumference of the channel varies as

$$dE_{\text{gap}}/d\gamma_{\text{ch}} = \text{sgn}(2p + 1)3t_0 \sin 3\phi, \tag{1}$$

where $t_0 \approx 2.7$ eV is the tight-binding overlap integral, ϕ is the chiral angle, $p = 0, \pm 1$ is the remainder in $n_1 - n_2 = 3q + p$ with (n_1, n_2) being nanotube indices and q being an integer. If it is assumed that the whole length change on the carbon gate due to hole injection is transmitted to the transversal carbon channel, then the strain in the channel is given as [15]

$$\begin{aligned}\gamma_{\text{ch}} &\equiv \delta R_{\text{ch}}/R_{\text{ch}} \approx \delta L_{\text{cg}}/R_{\text{ch}} \\ &= (\gamma_0 + 0.2p \cos 3\phi) f l/R_{\text{ch}},\end{aligned} \tag{2}$$

where $l = 3$ Å and $\gamma_0 = 0.07$ is a chirality-independent lattice displacement factor. The doping level in the tube can be written as

$$f = \frac{C_{\text{cg}} V_{\text{cg}} - \delta q}{n_{\text{cg}}} \approx \frac{2\pi\varepsilon L_{\text{cg}} V_{\text{cg}} - \delta q}{n_{\text{cg}} \ln(2L_{\text{cg}}/d_{\text{cg}})}, \tag{3}$$

where $\delta q \approx 0.04$ is the charge transferred from the amine group of the linker molecule [16], ε is the dielectric constant, d_{cg} is the tube diameter, and n_{cg} is the number of carbon atoms within 3 Å [12]. It leads to $f \approx 8.4 \times 10^{-4}$ and corresponds to $6.6 \times 10^{-5} \leq \gamma_{\text{ch}} \leq 1.3 \times 10^{-4}$ strain at the end of the carbon gate, depending on the tube chiral angle. A gap ranging from 0.52 to 1.1 meV is then expected under such strain in the circumference of the channel. This value is somehow too small to explain the

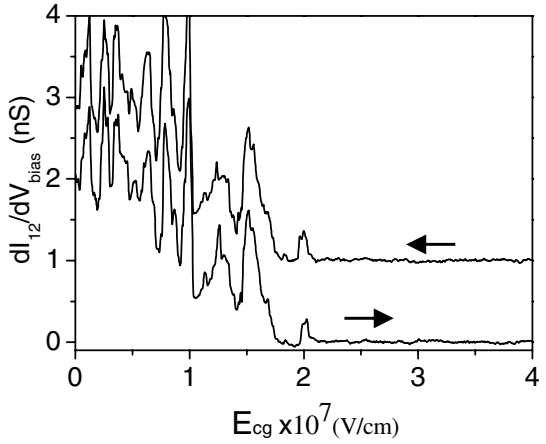

FIG. 4. dI_{12}/dV_{bias}-E_{cg} curves of CNTJ-II under $V_{\text{bg}} = -251$ mV and $T = 4$ K. The sample in question is shown in Fig. 1(b). The upper curve showing the sweep with decreasing field is offset by 1 nS for clarity.

experimental results, but it is sufficient to address the jerkylike conductance changes observed in most of the CNTJs with linker molecules [17].

The third scenario which cannot be ruled out is the "chemical effect." The linker molecule used in connecting two nanotubes has zigzaglike linear conformation and the motion of the carbon gate might be damped a lot by the molecule, leading to an overestimation of the electromechanical effect discussed above. The adsorption of partial δL_{cg} by the linker molecule results in changes in the molecular conformation and accordingly an electronic charge redistribution on the molecule and the attached nanotube edge. This resembles an application of electrostatic field on nanotubes.

To clearly separate the possible electromechanical and chemical effects from the field effect in CNTJ-I, we have produced a second type of CNTJ, in which a linker molecule between the conducting channel and the carbon gate was burned out (or broken) by heat treatment in air at 150 °C after constructing the device by a lift-off technique. Figure 4 shows the dI_{12}/dV_{bias}-E_{cg} curve of a metallic channel in CNTJ-II measured at 4 K. Sitting on a back gate voltage of $V_{\text{bg}} = -251$ mV (single electron tunneling regime) the channel conductance first oscillates as a function of E_{cg} and then drops to an immeasurable state (<picoamp). This behavior is fully reversible in repeated measurement cycles. The conductance fluctuation could be due to the interference effect [18], in which the transmission probability for the two conducting subbands is additionally modified by the applied carbon gate. Beyond a field of $E_{\text{cg}} > 2 \times 10^7$ V/cm the metallic channel in the vicinity of the junction turns into an insulating state, in excellent agreement with the predicted value [4]. It is interesting to note that at $E_{\text{cg}} < 0$ the field-effect modulation in the channel conductance is not symmetric to that at $E_{\text{cg}} > 0$; a steplike conductance is observed instead (not shown). Disregarding the edge geometry of the carbon gate and the induced enhancement of the electric field, a local field of over 10^7 V/cm is required for opening a gap in metallic tubes.

In summary, we have investigated the conductance of metallic carbon nanotubes, locally gated by another nanotube. The channel can be reversibly switched to the off state at $E_{\text{cg}} > 2 \times 10^7$ V/cm in case the linker molecule at the junction is removed. In contrast, the channel conductance is strongly perturbed by the existing linker molecule when a lower E_{cg} is applied. In addition to the pure field effect, the electromechanical and the chemical contributions are discussed in CNTJs with linker molecules. At this early stage of investigation, different scenarios cannot be excluded either. Further experimental and theoretical efforts will be needed, especially for some open issues such as the reversibility and the asymmetry of conductance change upon the application of E_{cg}.

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