Four-point resistance of individual single-wall carbon nanotubes

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We have studied the resistance of single-wall carbon nanotubes measured in a four-point configuration with noninvasive voltage electrodes. The voltage drop is detected using multiwalled carbon nanotubes while the current is injected through nanofabricated Au electrodes. The resistance at room temperature is shown to be linear with the length as expected for a classical resistor. This changes at cryogenic temperature; the four-point resistance then depends on the resistance at the Au-tube interfaces and can even become negative due to quantum-interference effects.

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Transport measurements are a powerful technique to investigate electronic properties of molecular systems [1]. Most often, individual molecular systems are electrically attached to two nanofabricated electrodes. However, such two-point experiments do not allow the determination of the intrinsic resistance that results from scattering processes involving e.g. phonons or disorder. Indeed, the resistance is mainly dominated by poorly defined contacts that lie in series. A solution to eliminate the contribution of contacts has been found with scanning probe microscopy techniques [2, 3, 4, 5], which enable the measurement of resistance variations along long systems such as nanotubes, but these techniques have only been applied at room temperature. The standard method to determine the intrinsic resistivity of macroscopic systems is the four-point measurement. The application of this technique to molecular systems is challenging however, since the electrodes used so far have been invasive. For example, nanofabricated electrodes were shown to divide nanotubes into multiple quantum dots [6].

We report four-point resistance measurements on single-wall carbon nanotubes (SWNT) using multiwalled carbon nanotubes (MWNT) as noninvasive voltage electrodes (Fig. 1(a)). We find that SWNTs are remarkably good one-dimensional conductors with resistances as low as 1.5 kΩ for a 95 nm long section. The nanotube resistance is shown to linearly increase with length at room temperature, in agreement with Ohm’s law. At low temperature, however, the resistance can become negative and the amplitude then depends on the resistance at the Au-SWNT interfaces. In this regime, four-point measurements can be described by the Landauer-Büttiker formalism taking into account quantum-interference effects.

Before discussing these measurements, we briefly review the basic physics of four-point measurements (Fig. 1(b)). In the diffusive incoherent limit, the four-point resistance $R_{4pt}$ of SWNTs, characterized by 4 conducting channels, is given by

$$R_{4pt} = \frac{h}{4e^2} \frac{L}{l_e}$$

with $l_e$ the elastic mean-free path and $L$ the separation between the voltage electrodes. Equation 1 describes the intrinsic resistance generated by the electronic backscattering along the nanotube.

We next remind how $R_{4pt}$ can deviate from equation 1. The transmission to the voltage electrodes should be made weak to suppress an additional resistance contribution that results from electrons entering the voltage electrodes. Such electrons are replaced by electrons that scatter into either direction of the tube, enhancing the resistance $R_{4pt}$.

By introducing quantum-interference effects, four-point measurements can give striking results such as negative $R_{4pt}$. This is best seen using the Büttiker formula [10, 11, 12], which is convenient for the description of multi-terminal conductors. The current $I_o$ in each electrode is related to the electrochemical potential $\mu_\beta$ of
other electrodes by

\[ I_\alpha = \frac{4e^2}{h} \sum_\beta T_{\alpha\beta} \mu_\alpha - T_{\alpha\beta} \mu_\beta \]  

with \( T_{\alpha\beta} \) the total transmission between the \( \alpha \) and \( \beta \) electrodes (Fig. 1(c,d)). The condition \( I_3 = 0 \) for a voltage probe gives \( \mu_3 = (T_{31} \mu_1 + T_{32} \mu_2)/(T_{31} + T_{32}) \). The transmission between electrodes 3 and 4 has been neglected since it corresponds to a second-order process. The potential of the voltage electrode \( \mu_3 \) can thus take any value between \( \mu_1 \) and \( \mu_2 \). Since the same holds for \( \mu_4 \), \( R_{4pt} \) can be negative (see Fig. 1 (c,d)). Using \( R_{2pt} = (\mu_1 - \mu_2)/I \) and \( R_{4pt} = (\mu_3 - \mu_4)/I \), we find that \( R_{4pt} \) takes any value between \( \mu_1 \) and \( \mu_2 \).

\[ -R_{2pt} \leq R_{4pt} \leq R_{2pt} \]  

Previous work on ballistic one-dimensional conductors fabricated in semiconductors showed that \( R_{4pt} \) can become slightly negative \([12, 14, 15]\). However, large negative modulations of \( R_{4pt} \) remain to be observed.

We have fabricated nanotube circuits with a new layout for four-point measurements. First, \( \sim 1 \) nm diameter SWNTs grown by laser-ablation \([16]\) or chemical-vapor deposition \([17]\) are selected with an atomic force microscopy (AFM). Voltage electrodes are then defined by positioning two MWNTs above the SWNT using AFM manipulation. We choose such voltage electrodes since the electric transmission between two nanotubes is known to be low \([13, 16]\). Then, Cr/Au electrodes are patterned for electric connection with standard electron-beam lithography techniques (see Fig. 1(a)).

We now look to the length dependence of \( R_{4pt} \) measured at 300K. Fig. 2(a,b) shows that \( R_{4pt} \) linearly increases with the length, in agreement with Ohm’s law and eq. 1. Two types of measurements have been carried. In

![FIG. 2: Length dependence of \( R_{4pt} \) at room temperature and \( V_g = 0 \). (a) SWNT contacted by 2 MWNTs. One MWNT is displaced back and forth with an AFM tip. Points are numbered to describe the measurement sequence. Point 1 has been acquired one week before in the cryostat. (b) SWNT contacted by 6 MWNTs.](image)

![FIG. 3: Temperature dependence of \( R_{4pt} \) measured at zero \( V_g \). The inset shows \( G_{4pt} \) as a function of \( V_g \) for Device 4.](image)

Fig. 2(b), 6 MWNTs have been placed on a long SWNT, enabling the resistance measurement of multiple portions \([20]\). In Fig. 2(a), an AFM tip has been used to change the separation between two MWNTs. Most points have been recorded while decreasing \( L \), so that the resistance enhancement with the length is not due to a structural degradation during the manipulation. However, the manipulation might well stretch the tube, deposit or remove some molecules adsorbed on the SWNT, or modify the pressure applied by the MWNT on the SWNT. Those modifications may account for the scattered \( R_{4pt} \) points in Fig. 2(a).

The measurements above also show that \( R_{4pt} \) tends to zero as the length is reduced. This suggests no (or little) additional contribution to the resistance from the MWNT contacts. Our device layout thus allows for the first direct measurement of the intrinsic resistance of a nanotube. The lowest resistance that we obtained is 1.5 kΩ for a 95 nm long section (Fig. 2(a)). Such a low resistance is remarkable, since the resistance of quasi one-dimensional conductors is expected to be dramatically enhanced with the presence of disorder or phonons. This agrees with previous two-point measurements \([21, 22, 23, 24]\) since \( R_{4pt} \) was shown to approach the quantum resistance \( h/4e^2 = 6.5 \) kΩ, which suggests low intrinsic resistance.

Further insight into transport properties is obtained by decreasing the temperature \( T \). Figure 3 shows that \( R_{4pt} \) does not change for \( T \) above \( \sim 80 \) K, suggesting that the intrinsic resistance is related to some static disorder and not to phonons. At lower \( T \), however, the inset of Fig. 3 shows that \( G_{4pt} \) fluctuates with sweeping of the backgate voltage \( V_g \).

We now discuss the possible origin of these fluctuations. They may originate from low-transmission barriers created by the MWNTs or some static disorder that form quantum dots along the tube. The transport may then be dominated by Coulomb blockade (CB). However, the conduction stays mostly constant with \( T \) above \( T^* \sim 60 \) K, the temperature at which fluctuations appear. This is in opposition to CB theory \([25]\) that predicts...
\[ G = G_0(1 - \frac{1}{2}E_c/kT) \] for temperatures larger than the charging energy \( E_c \), expected to be close to \( kT^* \). Moreover, the best fit between this model and measurements above \( T^* \) gives \( E_c/k \approx 5 \text{ K} \), which is much lower than \( T^* \). Another mechanism is thus needed to account for the fluctuations.

The presence of disorder is expected to generate a complicated interference pattern along the tube that should vary with the Fermi level. This results in aperiodic conductance fluctuations around the classical conductance when sweeping \( V_g \) \cite{27}, which is consistent with our measurements. Such fluctuations appear when effects of thermal averaging and phase decoherence are weak enough so that the thermal length \( L_T = \hbar v_F/kT \) and the coherence length \( L_c \) are larger than the elastic mean-free path. Interestingly, \( L_T \) at \( T^* = 60 \text{ K} \) is comparable to \( L_c \) that is determined using Eq. 1 (see Table 1). This suggests that thermal averaging is here at least as detrimental as decoherence. Note, moreover, that the amplitude of the fluctuations approaches \( e^2/h \) at \( \approx 40 \text{ K} \). This is expected \cite{20} when the lower of \( L_T \) and \( L_c \) is comparable to the separation between the voltage electrodes, which is again consistent with measurements since \( L_T = 150 \text{ nm} \) and \( L = 140 \text{ nm} \). Overall, our measurements suggest that quantum-interference effects start to modify the classical resistance given by eq. 1 around a few tens of Kelvin.

We turn now our attention to two-point measurements at the much lower temperature of 1.4 K. Figure 4(a) shows a series of CB peaks, which appear at the same gate voltages for measurements between different pairs of electrodes. This indicates that Au and MWNT electrodes probe the same nanotube quantum dot. The peak occurrence is quite regular with a spacing of \( V_g \approx 75 \text{ mV} \). Coulomb diamonds measurements (not shown) give that the charging energy \( E_c \) \approx 5 \text{ meV}. It has been shown that \( E_c \approx \frac{5\text{ meV}}{L_p[nm]} \) for similarly prepared samples \cite{22}, so that the dot length is \( \approx 1 \text{ \mu m} \), which is consistent with the 600 nm separation between Au electrodes. These measurements suggest that MWNTs are sufficiently noninvasive to not divide the SWNT in multiple quantum dots, in opposition to nanofabricated electrodes \cite{7}.

Having shown that the SWNT is a single quantum dot over its length at 1.4 K, we now look at the four-point measurements. The inset of Fig. 4(b) shows that \( R_{4pt} \) becomes \(-29 \text{ M}\Omega \) near zero \( V_g \). However, \( R_{4pt} \) significantly drops to 0 for \( V_g \) between -0.05 and -0.1 V when the two-point conductance between Au electrodes increases, in agreement with Eq. 3. Figures 4(b,c) show that the modulations of \( R_{4pt}/R_{2pt} \) are significant, with absolute values that reach as high as 0.6.

We now discuss the origin of the negative \( R_{4pt} \). It could arise from voltage electrodes that differently couple to the left and the right moving states inside the tube \cite{12,13,14}. However, such a classical effect should persist at higher temperature, which is not the case since \( R_{4pt} \) is only positive at \( T \gtrsim 10 \text{ K} \).

The resistance ratio \( R_{4pt}/R_{2pt} \) is given by \cite{11}

\[ \frac{R_{4pt}}{R_{2pt}} = \frac{T_{31}T_{42} - T_{32}T_{41}}{(T_{31} + T_{32})(T_{41} + T_{42})} \]  

Part of the fluctuations are expected to come from
the Coulomb blockade observed at 1.4 K that leads to oscillations in $T_{ij}$ transmissions. However, regular $V_g = 75$ mV CB oscillations cannot alone account for the rapid $V_g \sim 10$ mV fluctuations of $R_{4pt}/R_{2pt}$ in Fig. 4(b). We rather attribute those fluctuations to quantum-interference terms that are contained in $T_{ij}$ transmissions and that may arise from the superposition of different electronic paths between $i$ and $j$ electrodes. Indeed, the disorder along the SWNT leads to different possibilities in the pathway between 2 electrodes (see the inset of Fig. 4(c)). It is also likely that the sign change originates from those interferences. Variations of $T_{ij}$ transmissions with $V_g$ are then uncorrelated, enabling the sign reversal of the numerator in Eq. 4.

$R_{4pt}/R_{2pt}$ goes to zero when the temperature is increased to $5$ K (Fig. 4(b)). This is expected when the nanotube is no longer phase-coherent over its length, so that the quantum-interference term of the transmissions vanishes. Another possibility is that the quantum-interference term is washed out due to thermal averaging, since $kT$ enhances the number of electron paths between two electrodes that contribute to transport. Interestingly, the 510 nm thermal length at 5 K is comparable to the 600 nm separation between Au electrodes of Device 4. $L_T$ is $(\hbar v_F L_e/kT)^{1/2}$ since the transport is here diffusive. This points to the same finding observed at higher temperature that the thermal length apparently is the relevant parameter for quantum-interference phenomena in SWNTs.

In conclusion, we have shown that quantum-interference effects dramatically modulate the four-point resistance of SWNTs, so that $R_{4pt}$ can even become negative. This happens when the thermal length is longer than the dimension of the system. The thermal length is 20 nm long at room temperature; hence it is likely that inclusion of these quantum-mechanical interference effects will ultimately be required in the design of practical multi-terminal intramolecular devices.

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