Nonlinear Resistance versus Length in Single-Walled Carbon Nanotubes

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In this work fundamental properties of the electrical transport of single-walled carbon nanotubes as a function of their length are investigated. For this purpose, we have developed a new technique that allows us to characterize electronic transport properties of single-walled carbon nanotubes by probing them at different spots. This technique uses scanning force microscopy to make mechanical and electrical nanocontacts at any selected spot of a given image. We have applied this technique to molecules with high intrinsic resistance. The results show a nonlinear resistance vs distance behavior as the nanotube is probed along its length. This is an indication of elastic electronic transport in one-dimensional systems.

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Molecular wires should present a number of new transport properties [1–4] such as ballistic transport, quantized resistance, or Coulomb blockade, among others. Since the discovery of carbon nanotubes in 1991 [5] their potential use as molecular wires [6] became clear. Several devices have already been proposed with carbon nanotubes: nanotweezers [7], chemical noses [8], and field emitters [9]. In addition, tight-binding calculations show that carbon nanotubes present different current vs voltage characteristics (IV) that evolve from linear to nonlinear, depending on the nanotube chirality [10]. This theoretical prediction has been confirmed by different authors (see, for instance, [11] for a review).

Many of the previous studies have been performed in systems where the contact resistance of the nanotube to the macroscopic electrodes was very high [12]. More recently the contact resistance was lowered by covering both ends of the carbon nanotubes with metal electrodes [13,14]. In a recent work by W. Liang *et al.* [15] the authors were able to find up to 15 samples with resistances below 15 kΩ. The lowest resistance found by these authors was 7 kΩ, approaching the theoretical lower limit of 6.5 kΩ. Those samples presented clear evidence of quantum transport as expected from the theory. The authors also find that a high number of metallic nanotube samples ($\approx$85%) exhibited greater resistances, in the range of 100 kΩ. These high resistances are usually explained in terms of the combination of the contact resistances with the electrodes and the intrinsic resistance of molecule. The aim of the present work is, first, to discriminate between contact resistances and intrinsic resistances of the molecules and, second, to show that even for the high-resistance samples, quantum transport is present in the system. We use the term quantum transport when electron scattering mechanisms preserve the electron wave function phase in the system, and consequently the classical Drude model is not valid any longer [6].

We have developed a new technique to obtain IV characteristics in carbon nanotubes using scanning force microscopy (SFM). Our work extends a previous experiment [16] performed with multiwalled carbon nanotubes (MWNTs) where SFM images, taken in contact mode, showed a current map of MWNTs connected to a gold electrode on an insulating substrate. From those images, the resistance of the nanotubes could be obtained. In our present work, not only the resistance, but also the IV characteristics in single-walled carbon nanotubes (SWNTs) have been obtained. This allows for the first time a full electrical characterization of the SWNT along its length.

SWNTs used in the present experiment were prepared using nonintrusive methods [17]. Our specific procedure for sample preparation is described in [18]. The resulting sample is a 5 μm wide insulating line of SiO_2 with a random distribution of SWNTs between two macroscopic parallel gold electrodes. By inspecting with SFM near the gold edges, molecules partially covered with gold are easy to locate. Thus, following the gold electrode edge we can obtain IV characteristics on several SWNTs with the same SFM tip. It is also feasible to measure IV curves on different positions along a chosen SWNT. This is a major advantage with respect to other experimental setups where IV curves can only be acquired on one SWNT and for a unique SWNT length. In addition, our sample preparation does not need any lithography facility and thus samples are by nature free of possible contamination coming from the etching procedure.

Figure 1 shows the topography of a typical sample prepared as described above. In the image, the gold borders and several SWNTs partially covered with gold can be clearly seen. Images are taken in noncontact dynamic mode [19]. This mode is not required to image MWNTs [16] since those are more strongly anchored to the surface than SWNTs [20]. That is the reason why in the case of MWNTs current maps showing the resistance of the molecules can be easily obtained. The microscope is controlled using a digital signal processor that allows sophisticated and flexible data acquisition [21]. Commercial cantilevers with a resonance frequency of 80 kHz and a

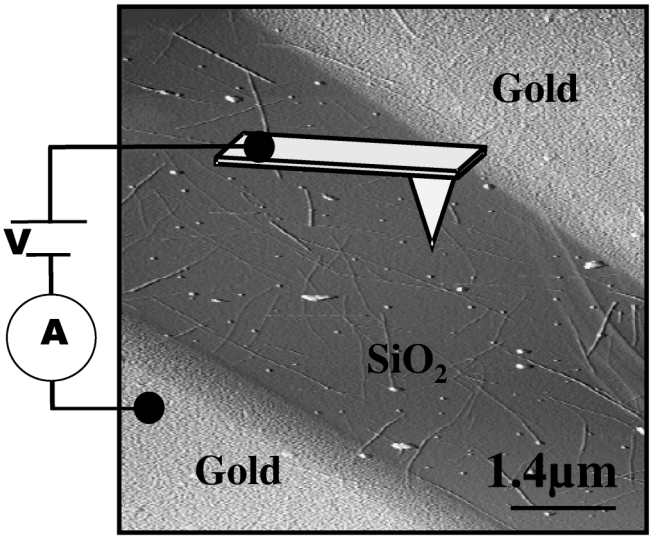

FIG. 1. 6 μm $\times$ 6 μm dynamic mode SFM image showing a general view of the sample. The gold electrodes, silicon oxide region, and carbon nanotubes can be clearly seen. Some molecules are partially covered with gold. The schematic of the experimental circuit is also shown.

force constant of 1 N/m are consecutively covered with titanium and gold.

In order to acquire the IV plots we have modified the software procedure that controls the acquisition of force vs distance curves in such a way that IVs can be taken at the maximum tip indentation. The quality of the contact does not critically depend on the loading force of the lever [18]. The current was measured using a commercial preamplifier [22].

After taking an overview image, the scanning area is reduced while keeping the target nanotube in the center of the image. Only SWNTs with a diameter of about 2 nm are selected to perform the experiments. We should remark that at the moment it is impossible to determine whether the rope selected is formed by one or several SWNTs with SFM [23,24]. The slow-scan motion is then stopped but keeping the scanning along the fast direction. Using a trace image we can observe and correct the drift motion due to piezoelectric creep or thermal effect. We keep the carbon nanotube right at the center of our trace image by slightly changing the X and Y offset positions. Once the nanotube is centered we proceed to acquire a combined force vs distance curve together with an IV as follows: the software stops the lateral motion at the center of the image and sends a voltage ramp to the Z piezoelectric element. At its maximum extension an IV is acquired. Figure 1 shows a schematic representation of the circuit used in the experiments. A similar setup has been used with λ-DNA molecules [25].

In previous studies we have shown that mechanical and electrical contact in nanotubes using a metallized SFM tip are almost simultaneous [18]. We thus conclude that in the case of nanotubes, the electrical contact to the SFM tip is specially good and reproducible. We remark that this is not the case on usual conducting samples, as for instance gold or high oriented pyrolytic graphite (HOPG). Using the method described above, we have obtained linear IV plots of a 2.3 nm high rope with a resistance as small as 10 kΩ [26] for a contact experiment near the electrode edge. If the experiment is repeated on the same molecule, but 500 nm away from the electrode, a similar IV is obtained with a resistance of 10.5 kΩ. The small resistance of the molecule (near the theoretical prediction) and the extremely low dependence of the resistance vs distance suggest ballistic transport, in good agreement with previous studies [15]. In order to assess whether the resistance and shape of the curve is affected by the tip-nanotube contact, the following experiment has been performed. First an IV plot is taken on a nanotube showing a linear behavior, then another IV is taken on a different nanotube having a semiconducting character. Finally, when returning to the first nanotube, the same linear IV characteristic is reproduced within the precision of the experiment. From this, as well as from many similar experiments, we conclude that the present technique is very reproducible for the formation of controlled tip-molecule contacts.

The total resistance R of a contact measurement is a combination of three different contributions R_e, R_t, $R_n(L)$, where R_e and R_t are the contact resistances of the nanotube to the gold electrode and to the SFM tip, respectively, and $R_n(L)$ is the intrinsic resistance of the nanotube that depends on its length (L) and the density of defects along the nanotube. The resistance R_e to the gold electrode may vary from one nanotube to another but is constant for a given nanotube, whereas R_t may fluctuate between two contact experiments but as stated above, this fluctuation is small. In any case, neither of those two factors depends on the distance. In the case described previously, where the SWNT showed a well-defined ballistic behavior, the contact resistance was of the order of the total resistance. If a perfect SWNT is assumed, the total contact resistance is about 4 kΩ. We notice that low resistance SWNTs are rather exceptional. A large percentage of our experimental measurements reveals that the resistance is far from being constant for nanotubes longer than 1 μm. These samples are not usually considered as candidates to show well-quantized transport properties. These high resistance SWNTs are the main focus of the present study devoted to establish the origin of the length dependence of the resistance. We calculate the resistance value $R(L)$ using the linear part of the IV curve near 0 V. We note that for voltages $\geq$200 mV our IV plots present a clear tendency to saturation [27–29] as can be seen in Figs. 2(b) and 3(b).

Hence we proceed to investigate the electronic properties of molecules with a marked change in $R_n(L)$ as a function of their length. Figure 2(a) shows a SFM image of a SWNT of $\sim$1.5 nm diameter contacting with the gold electrode. Figure 2(b) presents the IV characteristics of the SWNT at different distances. The IVs present

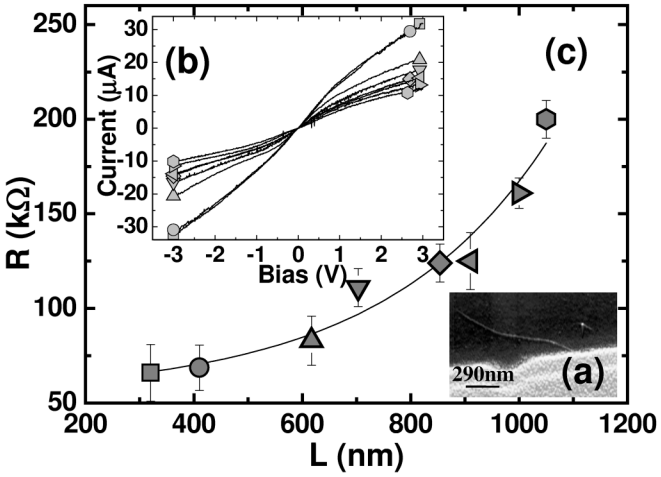

FIG. 2. (a) SWNT of 1.5 nm diameter contacting the gold electrode is shown. (b) several IV curves taken along the nanotube. They present a linear region around 0 V. For large voltages a saturation effect is observed. (c) Resistance vs nanotube length shows a nonlinear behavior. From this plot a contact resistance of 54 kΩ is extrapolated.

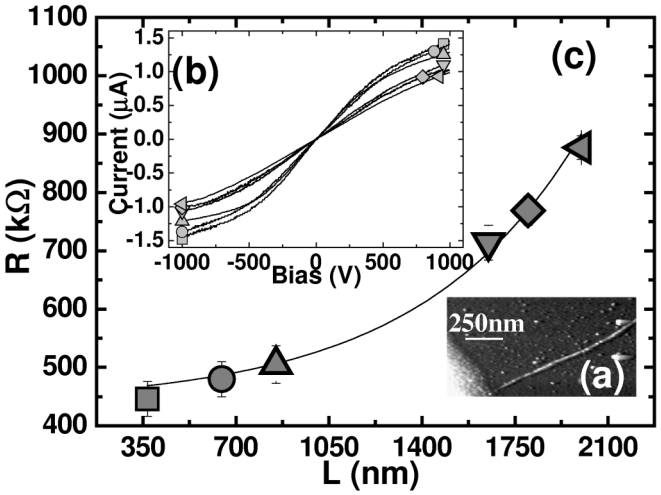

FIG. 3. (a) SWNT of 1.7 nm diameter partially covered with gold is shown. (b) IV curves taken along the nanotube. They present a linear region around 0 V. For large voltages a saturation effect is again observed. (c) Resistance vs nanotube length shows a nonlinear behavior. Note that the extrapolated resistance (350 kΩ) is much higher than the 54 kΩ of Fig. 2.

a linear behavior near 0 V [30]. For larger voltages the conductivity decreases as expected from the saturated behavior of the IVs. Figure 2(c) presents the evolution of the resistance taken as the average slope of several IVs acquired between −200 mV and +200 mV as a function of the length of the molecule. The data show that the resistance increases with length from 70 kΩ at 300 nm from the gold edge to about 200 kΩ at the free end of the nanotube (1000 nm away from the gold electrode). We start the IV acquisition at the nanotube free end in order to avoid possible changes due to tip-induced nanotube modifications [26]. We have tentatively fitted the data to the expression $R(L) = R_0 + A\exp(L/L_0)$. The best fitting has been obtained for $R_0 = 54$ kΩ, $A = 4.2$ kΩ, and $L_0 = 305$ nm. The low deviation of the data along the exponential fit of the resistance vs SWNT length again proves that tip-nanotube contact is well defined and reproducible. If the tube is probed reversing the direction, from the gold electrode to the free end, the same IV vs length plot is obtained. In other cases, the contact resistance can be much larger, but the nonlinear dependence on the nanotube length is again present. Figure 3(a) shows a second SWNT with ∼1.7 nm diameter in contact with the gold electrode. Figure 3(b) shows the IVs characteristics taken at several distances from the gold electrode. The IVs again present a linear behavior near 0 V with a tendency to saturate at larger voltages. Finally, Fig. 3(c) depicts resistance vs length evaluated as in Fig. 2(c). In this case the measured resistance at the nearest point to the gold electrode (350 nm) is as high as 450 kΩ but again the data can be fitted to an exponential with good accuracy. The following values have been obtained from this fit: $R_0 = 440$ kΩ, $A = 16.8$ kΩ, and $L_0 = 600$ nm. Now the contact resistance is almost 6 times larger than in the previous sample. In both cases the value L_0 indicates the length where the resistance deviates from the linear behavior.

In our opinion, the good exponential fitting is incidental. What we would like to stress here is that the resistance vs length plots are nonlinear and that this dependence is intrinsic to each SWNT. The nonlinear increase indicates that the electronic transport through the tube is not Ohmic. Each and every conducting wire that follows Ohm's law always presents a linear dependence of the resistance upon its length. Ohm's law is a consequence of dissipative transport caused by inelastic scattering (due to phonons, for instance). However, our experimental data describe a different situation, where each nanotube has its own nonlinear characteristic curve $R(L)$. This situation is compatible with a different explanation: In the absence of inelastic scattering the electrons may still suffer elastic scattering events with defects inside the conductor. In addition, the resulting effects due to elastic scattering are noticeable assuming that the transport is coherent inside the nanotube. Since the defect distribution is random, each nanotube will present a different resistance vs length pattern. Only a statistical treatment of the conductance vs length curves will reveal the electron transport regime characteristics of the SWNTs ensemble. The average of many experiments should then give a linear dependence in the so-called semiballistic regime [31], a nonlinear dependence in the diffusive regime, and an exponential dependence for electron localization [6].

Here we are presenting only two different tubes, therefore statistics cannot be obtained yet, and hence the precise transport mechanism is still unclear. What we know for certain is that for each experiment the resistance increases faster than linearly with nanotube length. This is a clear sign of nondissipative behavior and is consistent

with elastic electronic transport along the nanotube. From a theoretical point of view the exponential dependence of resistance on length is compatible with a situation where many consecutive scatterers act on the electron, each decreasing the probability amplitude by a given factor T_s [6]. Also the presence of fluctuations in resistance for increasing lengths should be observable as a consequence of interference effects. In this respect, the number of points available in our experiments do not allow such resistance fluctuations to be resolved. It is worth pointing out that coherent transport is not only present in SWNTs with low resistance, as the one with 10 kΩ, or as those considered by W. Liang *et al.* [15], but also in SWNTs with high intrinsic resistances.

In summary, we have presented a new experimental procedure to acquire IVs in SWNT molecules, allowing us for the first time to characterize the electrical properties of a SWNT along its length. Using this technique we can probe several carbon nanotubes with the same SFM tip obtaining a variety of reproducible IV characteristics. We have found that the tip-molecule contact is reproducible, showing that molecule metal contacts of a few square nanometers can be performed in a reliable way. By probing the SWNT at different distances from the macroscopic gold electrode we have obtained the evolution of the IV characteristic with the nanotube length. From these IVs a nonlinear resistance vs nanotube-length behavior is found. We suggest that this is due to the presence of nondissipative scattering centers. This effect is strong evidence for coherent electron transport along the nanotubes, even for those with high intrinsic resistances.

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