Multiprobe Transport Experiments on Individual Single-Wall Carbon Nanotubes

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Deposition of individual single-wall carbon nanotubes over multiple (up to seven) Pt nanoelectrodes is realized. Two-probe and four-probe transport measurements between adjacent pairs of electrodes show similar but not identical single-electron Coulomb charging signatures at low temperatures. The observations indicate that nanotubes can behave as a chain of quantum wires connected in series. We argue that the local barriers separating these islands may be caused by bending of the tube near the edges of electrodes. [S0031-9007(98)05997-3]

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Carbon nanotubes [1] are attracting much attention because of their unique electrical, mechanical, and capillary properties. The electrical properties of carbon nanotubes strongly depend on their diameter and the chiral angle of the atomic lattice: "Zigzag" or "chiral" nanotubes are predicted to be semiconductors with either a substantial ($\sim$1 eV) gap or a very low gap ($\sim$meV s), whereas "armchair" tubes are expected to be truly one-dimensional (1D) metals [2,3]. Recently, a high-yield method for the synthesis of single-wall carbon nanotubes (SWCNTs) was discovered [4], which enabled first experimental studies on the electronic properties of this model variety of nanotubes [3,5,6].

In our many experiments with *individual* SWCNTs between metallic electrodes, three types of behavior can be distinguished: (i) The current-voltage (*I-V*) characteristics are nonlinear already at room temperature, with a rather high ($>$10 MΩ) zero-bias resistance which increases upon cooling. These tubes are identified as large-gap semiconducting tubes [7]. (ii) *I-V* curves are linear at room temperature with a lower two-probe resistance (typically $\sim$1 MΩ). Upon cooling, this resistance is almost constant down to $\sim$100 K below which it rises due to Coulomb charging. A finite density of states is found even at mK temperatures [5], indicating that these tubes are metallic and presumably of the armchair variety. (iii) A third type of behavior is observed, where nanotubes display similar room-temperature characteristics and also a finite low-temperature density of states. However, the Coulomb charging signatures of these samples are quite different. In particular, a strong temperature dependence of the resistance is observed (increase of at least a factor of 20 from $\sim$100 to 4 K) which is absent in the second class of nanotubes. It is tempting to associate this third class with the low-band-gap semiconducting "quasimetallic" nanotubes. In this Letter we report on the investigation of this third class of nanotubes.

We succeeded in depositing individual SWCNT molecules on four or more metal leads [Fig. 1(a)], and investigating their two-probe and four-probe resistance versus length, temperature, and gate potential. The low-temperature properties appear to be determined by Coulomb blockade effects [8], where, in order to tunnel onto the nanotube, electrons should overcome the charging energy of the molecule with an integer number of electrons on it. The Coulomb charging signatures measured between adjacent pairs of electrodes are similar but not identical. A strong temperature dependence of the peak conductance is observed. Both features demonstrate that the nanotube internally consists of a small number of islands in series. Comparing with previous experiments [5] we thus find a different type of behavior, where a tube does not behave as one continuous quantum wire with extended quantum states. Instead it is electrically broken up into a chain of weakly coupled 1D quantum wires separated by local barriers. These barriers may

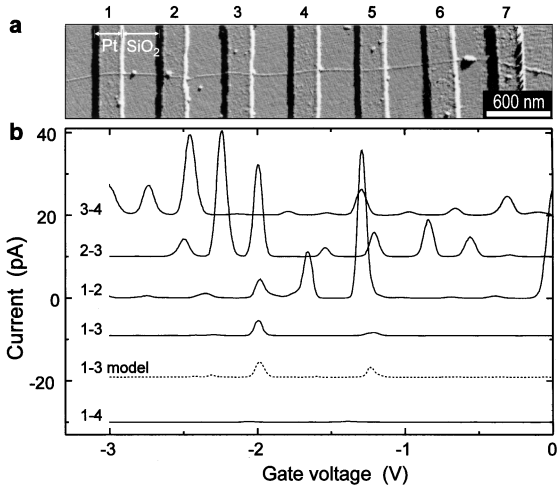

FIG. 1. (a) AFM image of the sample showing a single nanotube over seven Pt electrodes. The spacing between the leads is about 400 nm. The Pt gate electrode (not visible) is positioned at $\sim$10 μm from the tube. The apparent height of the SWCNT is $\sim$1.2 nm on top of the leads as well as in between them. (b) Two-probe measurements ($V_{\mathrm{bias}} = 1$ mV) of the current versus gate voltage between various pairs of leads *i-j* at 4 K. Curves are vertically offset for clarity. The curve "1-3 model" is the current calculated for electrodes 1-3 from the currents 1-2 and 2-3 under the assumption of a series connection of resistors (see text).

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be due to the bending of the tube that occurs when the molecule passes from an electrode to the substrate or vice versa. We thus have found a simple way to control electrical transport properties of nanotubes by means of the substrate relief.

To deposit individual nanotubes we ultrasonically disperse SWCNT soot in dichloroethane and spin dry it on an oxidized Si wafer with lithographically defined sets of Pt leads [Fig. 1(a)]. Each set includes seven leads (15 nm thick, 200 nm wide, and 10 μm long) and a gate electrode. By measuring the sample resistance at $T = 300$ K and imaging with atomic force microscopy (AFM), we are able to select those sets where four or more electrodes are connected to a single SWCNT [9]. Here we focus on one representative sample [Fig. 1(a)], where a single ~ 8 μm long SWCNT lies over all seven leads.

The multiple-electrode layout allows various types of measurements on the nanotube. The two-probe resistance ($R_{2\mathrm{pr}}$) can be measured between various pairs of neighbor electrodes (NE), as well as on separated (i.e., non-neighbor) electrodes (SE). Alternatively, one may measure the internal resistance of the tube between NE or SE in a four-probe configuration, i.e., measure the voltage drop (V) between two electrodes while biasing the tube with a current through two other leads near the ends of the tube. At room temperature the I-V traces are linear and the four-probe resistance ($R_{4\mathrm{pr}}$) measured on SE appears to be given by the sum of $R_{4\mathrm{pr}}$ between corresponding NE. For example, if electrodes 1 and 7 are current biased, then the voltage on electrodes 2 and 5 is the sum of voltages on the 2-3, 3-4, and 4-5 pairs. At 300 K, $R_{4\mathrm{pr}}$ measured between any pair of NE appears to always be the same (90 kΩ) within 10% accuracy. The contact resistance of the lead-tube connection (R_c) varies between 1 and 4 MΩ. $R_{4\mathrm{pr}}$ of all individual tubes increases monotonically upon cooling.

Below 70 K the conductance depends on the gate voltage (V_g). At 4 K [Fig. 1(b)] we observe an aperiodic sequence of sharp conductance peaks upon sweeping V_g with a fixed small bias voltage ($V_{\mathrm{bias}} = 1$ mV). From inspection of the curves 1-2, 2-3, and 3-4, it is clear that the patterns of conductance peaks are qualitatively similar (in terms of the peak height and spacing) but not identical when measured on various pairs of NE. Strongly different patterns are observed on SE (curves 1-3 or 1-4): The number of peaks and their heights are much smaller than for NE. The conductance between 1 and 3 has a well-defined peak *only if* peaks on pairs 1-2 and 2-3 coincide at the same V_g within the peak width. Since a coincidence of three peaks (1-2, 2-3, and 3-4) is unprobable, the 1-4 curve shows hardly any peaks at all. I-V_{bias} curves (two-probe, not shown) measured in valleys on NE at 4 K show a ~ 10 mV gap with a zero-bias resistance of $R_{2\mathrm{pr}} \sim 30$ GΩ. At certain values of V_g [corresponding to peaks in Fig. 1(b)] the gap is suppressed and the zero-bias resistance drops down to ~ 30 MΩ.

As the temperature is raised, a large increase of the two-probe conductance is observed [Fig. 2(a)]. At the peaks the conductance increases by a factor of ~ 20 in the temperature interval 4–80 K. In valleys between the peaks the increase can be larger than 10^4. At all V_g the conductance $G = I/V_{\mathrm{bias}}$ appears to follow an activation law at low temperatures [Fig. 2(b)]. Four-probe measurements were carried out only at $T \geq 20$ K where the sample resistance is finite at all V_g. Surprisingly, the two- and four-probe measurements show the same V_g dependence (Fig. 3), except that in two-probe the resistance is higher by a constant (~ 3 MΩ) representing the contact resistance.

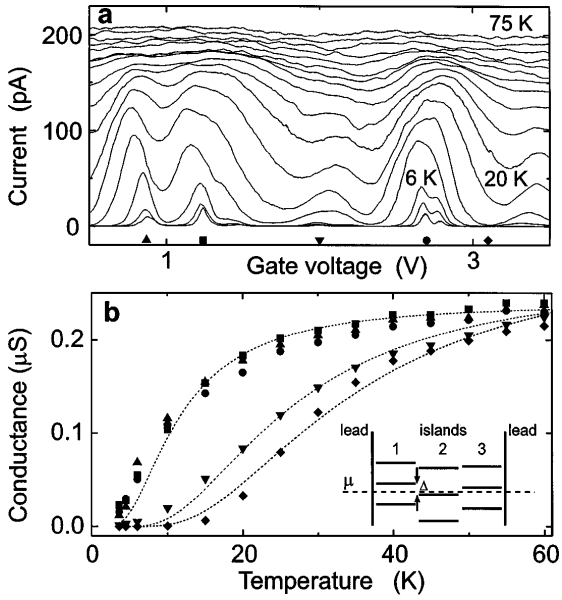

FIG. 2. (a) Temperature dependence of the Coulomb peaks (shown as current versus gate voltage at $V_{\mathrm{bias}} = 1$ mV; two-probe configuration) measured on leads 4 and 5 from 4 to 75 K ($T = 4$, 4.8, 6, and 10 to 75 in 5 K intervals). (b) Conductance $G = I/V_{\mathrm{bias}}$ [from (a)] versus temperature at various gate voltages. The temperature dependence is shown for three high-peak maxima (▲, ■, and ●), a low-peak maximum (▼), and a valley minimum (◆). The dashed lines are fits of $G \propto [T \sinh(\Delta/k_B T)]^{-1}$ that is predicted by the multiple-island model. The activation energy Δ is 2 meV for the three large peaks, 5 meV for the low peak, and 7 meV in the valley. Inset: Coulomb blockade energy diagram of three islands in series between leads with an electrochemical potential μ. The Coulomb charging energy has to be paid for each added electron on an island, which is represented by the vertical sequence of lines. Alignment of lines between adjacent island means that transport between the islands is possible. The largest misalignment between lines (Δ) represents an activation energy for transport to occur. The vertical line spacing of islands 1 and 3 is smaller than that of island 2, because islands 1 and 3 contact a Pt electrode which leads to a larger island capacitance and, thus, a smaller charging energy.

We now discuss the experimental findings. The gap in the low-temperature I-V_{bias} curves is suppressed at certain values of the gate voltage, which yields the conductance peaks in the gate scans [e.g., Fig. 1(b)]. This unambiguously indicates that the gap originates from Coulomb charging of the tube. Single-electron charging

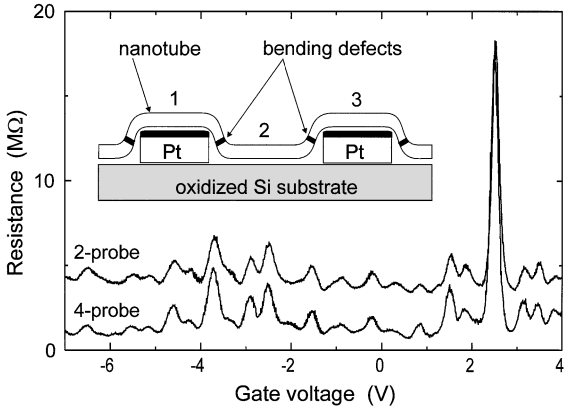

FIG. 3. Comparison between two-probe and four-probe resistance. $R = V/I$ is plotted versus gate voltage at 20 K. Two-probe data are taken between leads 3-4 at $V_{\text{bias}} = 1$ mV; four-probe data are taken at $I_{\text{bias}} = 200$ pA for current leads 2-5 and voltage leads 3-4. Inset is a schematic side view that shows the proposed breakup of the tube into a series of Coulomb islands due to the bending near the edges of the Pt leads. Black areas on top of the Pt leads are barriers that represent the large contact resistance (of unknown origin) observed in all our experiments. Black areas within the tube denote the internal bending barriers.

effects are not surprising because of the high electrode-nanotube contact resistance R_c ($R_c \sim 1\ \text{M}\Omega \gg R_Q$, with $R_Q \approx 25\ \text{k}\Omega$ the resistance quantum), and the low capacitance [10] of the tube $C \approx 2\pi\varepsilon_0 L/\ln(2L/d) \approx L \times 7.6\ \text{aF}/\mu\text{m}$, where $d = 1.4$ nm is the tube diameter, and L is its length (in μm). Moreover, in 1D conductors, unlike in 2D or 3D, a pair of local defects readily defines a quantum dot (or "island") with a quantized charge on it. The charging energy $E_c = e^2/2C \approx 10$ meV for $L = 1\ \mu$m is much larger than the thermal energy at 4 K. If the tube would be one uninterrupted island, the Coulomb peaks measured on different pairs of NE should appear at the same V_g. This is not observed experimentally [Fig. 1(b)]. We thus conclude that the tube consists of a number of 1D islands connected in series, and that each pair of NE is linked by its own island(s). The Coulomb peak patterns measured on SE can be explained by a simple series addition of NE resistances, i.e., $R_{13} = R_{12} + R_{23}$, or $I_{13} = V_{13}\,[(V_{12}/I_{12}) + (V_{23}/I_{23})]^{-1}$, with $V_{12} = V_{23} = V_{13} = 1$ mV in these two-probe measurements. This describes the SE current peaks quite well [compare curves 1-3 and 1-3 model in Fig. 1(b)]. This implies that electrons on an island do have the time to thermalize before they jump to the next island.

Which barriers does an electron have to pass on its way from one lead to the neighboring lead in a two-probe experiment? There always exists a barrier at each electrode-nanotube contact, as is evident from the observation of a high contact resistance ($R_c \sim 1\ \text{M}\Omega$) even at $T = 300$ K. There are also additional internal barriers inside the nanotube. Their presence is, for example, demonstrated from the fact that $R_{2\text{pr}}$ and $R_{4\text{pr}}$ versus V_g (Fig. 3) show identical Coulomb peaks [11]. In the absence of internal barriers such peaks should not be observable at all in $R_{4\text{pr}}$. The internal barriers electrically break the tube into a chain of weakly coupled islands connected in series.

The data indicate that electron transport occurs through *multiple* Coulomb islands. The simplest scenario one could propose is that each pair of NE is linked by one single island which extends from one lead to the other. While this can explain the observation of similar-but-not-coinciding peaks on different NE, this model *cannot* explain the aperiodicity of peaks in the gate scans and the temperature dependence. The orthodox theory for a single island predicts strictly periodic Coulomb peaks of an equal height which increases by only a factor of 2 upon raising the temperature [8,12]. These three features are not observed experimentally. The data *can*, however, be explained by the *multiple*-island model considered by Ruzin *et al.* [13]. These authors theoretically analyzed electrodes linked by two quantum dots connected in series. Such a system exhibits an aperiodic sequence of conductance peaks of different heights, with a thermally activated temperature dependence. Current peaks appear only at those V_g where the Coulomb blockade of both islands is suppressed. Since this suppression takes place in V_g regions of a finite width of $\sim k_B T$, the overlap is stronger at higher temperatures. This is the origin of the activation law for the conductance, $G \propto [(k_B T/\Delta)\sinh(\Delta/k_B T)]^{-1}$, which is predicted by theory [13] and observed experimentally [Fig. 2(b)]. The activation energy Δ appears to be small (2 meV) at peaks and large (7 meV) in valleys. Δ thus depends on V_g, with a high value when the system is in Coulomb blockade, as expected from the multiple-island model [cf. inset in Fig. 2(b)].

How large is the number of islands between neighbor electrodes [14]? We first note that this number should be the same for each pair of NE because (i) Coulomb peak patterns for all NE are very similar [15] [cf. curves 1-2, 2-3, and 3-4 in Fig. 1(b)], and (ii) $R_{4\text{pr}}$ between different pairs of NE at $T = 300$ K is the same. This implies the same number of internal barriers between each adjacent pair of electrodes. Consequently, the barriers are not some random defects, but appear to have been induced by the electrodes. In the previous paragraph we have shown that the number of islands between NE exceeds one. Can it be two? For example, one could imagine one internal barrier symmetrically located in the middle between NE, and, thus, two almost identical islands linking the electrodes. For two such very similar islands one inevitably would expect a beating pattern [13] in the current peaks. This has never been observed experimentally.

We finally conclude that each pair of NE is connected by three islands separated from each other by two internal barriers (not counting the tube-lead barriers); cf. inset in Fig. 3. For our sample geometry the logical location for the barriers is near the edges of the electrodes where

barriers may be induced by bending of the tube when it passes from the top of the 15 nm high Pt electrodes to the SiO_2 substrate. In this case, one island is located on top of each lead (islands 1 and 3 in the inset to Fig. 3), and one island is in between (island 2). Such a model is consistent with all our experimental data. Note that, due to the promixity of the electrodes, islands 1 and 3 will have a capacitance to the gate that is quite different from that of island 2, which prevents beating effects. Since the two internal barriers between NE define Coulomb blockade islands, their resistance has to be larger than R_Q. Since $R_{4\mathrm{pr}} = 90\ \mathrm{k}\Omega$ at $T = 300$ K [16], the intrinsic nanotube resistance must be (much) smaller than $R_{4\mathrm{pr}} - 2R_Q = 40\ \mathrm{k}\Omega$. This very low value for the upper limit for the intrinsic resistance suggests that the tube may act as a ballistic quantum wire even at room temperature.

It is of interest to compare our results to those obtained on a single tube [17] by Tans *et al.* [5]. From two-probe transport data they concluded that the electron wave function was spatially extended throughout the entire tube, i.e., not limited to the section between electrodes. They also obtained a much weaker temperature dependence [18], in agreement with the orthodox theory for transport through a single island [8,12]. We suggest that the multiple-island formation found in the present study is due to a nonzero chirality of our tubes [19]. This is in contrast with the tubes of Ref. [5], which are believed to be of the armchair type. We speculate that chiral tubes are affected by the bending which results in the formation of local barriers for electron transport [20], whereas nonchiral armchair tubes may survive the bending due to their higher symmetry [21] and accordingly these behave as long coherent quantum wires. More extensive measurements are needed to certify this, as well as theoretical work on electrical transport through mechanically deformed nanotubes of various chirality.

In conclusion, we have obtained first multiprobe measurements on individual single-wall carbon nanotubes. It is found that the tube can be considered as a chain of 1D quantum wires connected in series. The islands appear to be defined by local barriers induced by bending of the tube near the edges of the electrodes. Coulomb blockade on the islands determines the transport properties of the molecule.

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[8] *Single Charge Tunneling,* edited by H. Grabert and M. H. Devoret (Plenum Press, New York, 1992).
[9] The conclusion that there is only a single tube is based on (i) the height measurements with tapping-mode AFM which yield an apparent height of ~1.2 nm and (ii) on the absence of nonlocal voltages.
[10] For this estimate the tube is approximated by a prolate spheroid.
[11] The presence of high internal barriers is also confirmed by the observation of the series addition of *two-probe* resistances, $R_{13} = R_{12} + R_{23}$, at 4 K.
[12] P. Joyez *et al.,* Phys. Rev. Lett. **79**, 1349 (1997).
[13] I. M. Ruzin *et al.,* Phys. Rev. B **45**, 13 469 (1992).
[14] This number cannot be much bigger than unity, because the measured gap (~10 meV) is incompatible with the charging energy of islands, if they are much shorter than the distance between NE (400 nm).
[15] Note that the Coulomb patterns differ strongly when the leads are linked by an obviously different number of islands (cf. Fig. 1, curves 1-2, 1-3, and 1-4).
[16] From the 300 K data and the known spacing between the leads one may extract the tube 1D resistivity of $150\ \mathrm{k}\Omega/\mu\mathrm{m}$. This value is too high to be explained by electron-electron scattering or thermally activated twist deformations of the tube lattice (twistons) which could contribute only $\sim 5\ \mathrm{k}\Omega/\mu\mathrm{m}$; cf. C. L. Kane *et al.,* cond-mat/9704117. Instead, we attribute the observed resistance to local bending barriers within the tube.
[17] The sample geometry of their device was very similar. AFM showed that bending of the tube near the edges of electrodes also occurred.
[18] S. J. Tans *et al.* (unpublished).
[19] This is also consistent with the observed fraction of armchair and chiral tubes in the soot as found in recent STM experiments (Ref. [3]). The sample selection procedure of Tans *et al.* was such that only the most highly conducting (presumably armchair) nanotubes were studied in their mK experiments. In the present study, a wider range of nanotubes was investigated.
[20] Quasimetallic chiral tubes are one of the three classes of tubes [2,3] and are expected to have a small gap ~10 meV. The metal-like conductivity observed even at 4 K is likely due to a charge transfer from the Pt electrodes which leads to a shift of the Fermi energy into the valence band, i.e., away from the small gap [3].
[21] The strong effect of bending on the electronic properties of nanotubes may seem surprising. Indeed it has been argued by C. L. Kane and E. J. Mele [Phys. Rev. Lett. **78**, 1932 (1997)] that armchair tubes should be robust with respect to bending. Bending effects for chiral tubes were not considered, however.