Single Electron Transport in Ropes of Carbon Nanotubes

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We have measured the electrical properties of individual bundles, or ”ropes” of single-walled carbon nanotubes. Below 10 K, the low bias conductance is suppressed for voltages below a few millivolts. In addition, dramatic peaks are observed in the conductance as a function of a gate voltage that modulates the number of electrons in the rope. We interpret these results in terms of single electron charging and resonant tunneling through the quantized energy levels of the nanotubes comprising the rope.

In the last decade, transport measurements have emerged as a primary tool for exploring the properties of nanometer-scale structures. For example, studies of quantum dots have illustrated that single electron charging and resonant tunneling through quantized energy levels regulate transport through small structures [1]. Recently, a great deal of attention has been focused on a new class of nanometer-scale systems: carbon nanotubes [2]. The conducting properties of these nanotubes, which are essentially tubular sheets of graphite, are predicted to depend upon the diameter and helicity of the tube, parameterized by a rollup vector (n,m). One type of tube, the so-called (n,n), or armchair, tube is predicted to be a novel 1D conductor with current carried by a pair of one dimensional subbands [3], whose dispersion relations near $E_f$ are indicated in the right inset to Figure 1. A recent breakthrough has made it possible to get large quantities of one particular armchair nanotube, the (10,10) tube, which is approximately 1.4 nm in diameter [4]. This, coupled with recent successes in performing electrical measurements on individual multiwalled nanotubes [5] and nanotube bundles [6], makes possible the study of the electrical properties of this novel 1D system.

In this Report, we describe our measurements of transport through bundles, or ropes, of nanotubes bridging contacts separated by 200-500 nm. We find that a gap (suppressed conductance at low bias) is observed in the $I-V$ curves at low temperatures. Further, dramatic peaks are observed in the conductance as a function of a gate voltage $V_g$ that modulates the charge per unit length of the tubes. These observations are consistent with single electron transport through a segment of a single tube with a typical addition energy of $\sim$10 meV and an average level spacing of $\sim$3 meV.

The device geometry is shown in the inset to Figure 1. It consists of a single nanotube rope to which lithographically defined leads have been attached. The tubes are fabricated as described in Ref. [4] and consist of ropes made up of 1.4 nm diameter single-walled tubes. Nanodiffraction studies [7] indicate that approximately 30 - 40 % of these are (10,10) tubes. Contacts are made to individual ropes as follows. First, the nanotube material is ultrasonically dispersed in acetone and then dried onto an oxidized Si wafer upon which alignment marks have been previously defined. An atomic force microscope (AFM) operating in the tapping mode is used to image the nanotubes. Once a suitable rope is found, its position is noted relative to the alignment marks. Resist is then spun over the sample, and electron beam lithography is used to define the lead geometry. A metal evaporation of 3 nm Cr/500 nm Au followed by liftoff forms the leads. An AFM image of a completed device is shown in the left inset to Figure 1. This device has four contacts, allowing different segments of the rope to be measured and four-terminal measurements to be performed. The rope is clearly seen underneath the metal layer, although it is not visible in between the contacts due to the contrast of the image. The device is mounted on a standard chip carrier, contacts are wire bonded, and the device is loaded into a He cryostat. A dc bias can be applied to the chip carrier base to which the sample is attached. This gate voltage $V_g$ modifies the charge density along the length of the rope. A number of samples have been studied. All of the data presented here, however, were measured on a single 12 nm diameter rope which should contain roughly 60 single-walled nanotubes.

Figure 1 shows the current-voltage characteristics of the nanotube rope section between contacts 2 and 3 as a function of temperature. The most notable feature is the appearance of a strong suppression of conductance near $V = 0$ for temperatures below 10 K. Gaps of a similar magnitude were obtained for a number of nanotube ropes with diameters varying from 7 nm to 12 nm, and lengths from 200 to 500 nm. There was no clear trend in the size of the gap or the high-bias conductance with the rope length or diameter. We note that measurements of multi-walled nanotubes by us and others...
displayed no such gap in their $I-V$ curves. These results are in rough agreement, however, with those reported previously by Fischer et al. and similar, but longer, ropes of single-walled nanotubes. In their experiments, the linear-response conductance also decreased at low temperatures.

Figure 2 shows the linear response conductance $G$ of the rope segment as a function of $V_g$, measured at a temperature $T = 1.3$ K. Remarkably, the conductance consists of a series of sharp peaks separated by regions of very low conductance. The separation between peaks varies significantly, but has a typical period of $\sim 1.5$ V. The peak amplitudes vary widely, with the maximum amplitude of isolated peaks approaching $e^2/h$. The peaks are reproducible, although sudden changes ("switching") in the positions sometimes occur, particularly at larger voltages. The left inset to Figure 2 shows the temperature dependence of a selected peak. The peak width increases linearly with increasing $T$ (Figure 2: right inset) and the peak amplitude decreases. The most isolated peaks remain discernible even up to 50 K.

Figure 3 shows the differential conductance $dI/dV$ as a function of both $V$ and $V_g$ for the rope segment between contacts 2 and 3. The data are plotted as an inverted grayscale, with dark corresponding to large $dI/dV$. The linear response peaks in $G$ (e.g. point A in the figure) correspond to the centers of the crosses along the horizontal line at $V = 0$. The gap in $dI/dV$ corresponds to the white diamond shaped regions between the crosses (such as the region containing point B). These crosses delineate the point of the onset of conduction at finite $V$ (point C). Since the application of large biases led to significant switching of the device, our sweeps were limited to 8 mV, and only the centers of the diamond regions are visible. Additional features (point D) are also observed above the gap.

We now discuss our interpretation of these results. We note that they are very reminiscent of previous measurements of Coulomb blockade transport in metal and semiconductor wires and dots. In these systems, transport occurs by tunneling through an isolated segment of the conductor or dot that is delineated either by lithographic patterning or disorder. Tunneling on or off this dot is governed by the single-electron addition and excitation energies for this small system. The period of the peaks in gate voltage, $\Delta V_g$, is determined by the energy to add an additional electron to the dot. In the simplest model that takes into account both Coulomb interactions and energy-level quantization, which we refer to as the Coulomb blockade (CB) model, the peak spacing is given by:

$$
\Delta V_g = (U + \Delta E)/e\alpha
$$

where $U = e^2/C$ is the Coulomb charging energy for adding an electron to the dot, $\Delta E$ is the single-particle level spacing, and $\alpha = C_g/C$ is the rate at which the voltage applied to the substrate changes the electrostatic potential of the dot. In the above, $C$ is the total capacitance of the dot and $C_g$ is the capacitance between the back gate and the dot.

To understand the dependence on $V$ and $V_g$ in more detail, consider the energy level diagrams for the dot shown in the lower part of Figure 3. They show a dot filled with $N$ electrons, followed by a gap $U + \Delta E$ for adding the $(N + 1)th$ electron. Above this, additional levels, separated by the $\Delta E$, are shown, which correspond to adding the $(N+1)th$ electron to one of the excited single-particle states of the dot. At a gate voltage corresponding to a Coulomb peak, the electrochemical potential of the lowest empty state aligns with the Fermi energy of the leads and single electrons can tunnel on and off the dot at $V = 0$ (Figure 3A). At gate voltages in between peaks (Figure 3B), tunneling is suppressed due to the single electron charging energy $U$. As $V$ is increased so that the electrochemical potential of the right lead is pulled below the energy of the highest filled state, an electron can tunnel off the dot, resulting in a peak in $dI/dV$ (Figure 3C). Further increasing $V$ allows tunneling out of additional states, giving additional peaks in $dI/dV$ (Figure 3D). Similar processes occur for negative bias, corresponding to tunneling through unoccupied states above the Coulomb gap. At its largest, the required threshold voltage for the onset of conduction of either type is:

$$
V_{max} = U + \Delta E.
$$

To apply this model to our system, we must postulate that transport along the rope is dominated by single electron charging of a small region of the rope or perhaps a single tube within the rope. We will return to this issue later. For now, we will use the Coulomb blockade model to infer the properties of this isolated region. Further, we initially restrict ourselves to the data of Figures 2 and 3, which corresponds to the central rope segment.

The temperature dependence of Coulomb blockade oscillations can be used to infer the parameters in equation (1). In the CB model, the width of the Coulomb oscillation is given by: $d(\Delta V_g)/dT = 3.5k_B/e\alpha$. Comparison with the data in the right inset to Figure 2 gives $\alpha = 0.01$. From this, and the measured spacing between peaks of 1-2 V, we infer a typical addition energy: $U + \Delta E = 10-20$ meV. Also note that the disappearance of the oscillations above $\sim 50$ K yields a similar estimate for the addition energy.

The amplitude of the conductance peak increases with decreasing temperature at low temperatures. Within the extended CB model, this indicates that $\Delta E >> k_BT$ and that transport through the dot by resonant tunneling through a single quantum level. The peak height decreases as $T$ is increased for temperatures up to roughly 10 K. This sets a lower bound on the energy level splitting of $\Delta E \sim 1$ meV. In addition for some peaks, such as
those in the center of Figure 2, the intrinsic linewidths of the peaks are clearly observable. Fitting the peak shapes (not shown) reveals that they are approximately Lorentzian, as expected for resonant tunneling through a single quantum level \( \text{(1)} \).

The nonlinear \( I-V \) measurements confirm the addition and excitation energies given above. The maximum size of the Coulomb gap \( V_{\text{max}} \) in Figure 3 is a direct measure of the addition energy - for the two peaks in the figure, it is \( \sim 14 \) meV. Tunneling through excited states is also visible above the Coulomb gap for some peaks, and the level spacing to the first excited state is found to range between 1-5 meV \( \text{(1)} \). For example, in Figure 3, the level spacing between states labeled by C and D is \( \Delta E = 1 \) meV.

We now discuss how these parameters compare with expectations. Consider a single \((n,n)\) nanotube. The tube is predicted to be metallic \( \text{(3)} \), with two 1D subbands occupied at \( E_f \). The order of magnitude of the average level spacing should be related to the dispersion \( dE/dk \) at the Fermi level \( \text{(12)} \):

\[
\Delta E \sim \frac{dE}{dk} \frac{\Delta k}{2} \sim \frac{dE}{dk} \frac{\pi}{L} \sim \frac{0.5eV}{L[\text{nm}]},
\]

where the 2 arises from non-degeneracy of the two 1D subbands (see Fig. 1, right inset.) The charging energy is more difficult to estimate accurately. The actual capacitance of the dot depends on the presence of the leads, the dielectric constant of the substrate, and the detailed dielectric response of the rope \( \text{(13)} \). For an order of magnitude estimate, however, we take the capacitance to be given by the size of the object, \( C = L \). We then have:

\[
U = \frac{e^2}{C} = \frac{e^2}{L} = \frac{1.4eV}{L[\text{nm}]}. \quad \text{(4)}
\]

Note the remarkable result that in 1D, both (3) and (4) scale like \( 1/L \), and hence the ratio of the charging energy to the level spacing is roughly independent of length. This means that the level spacing will be important even in fairly large dots, unlike in 3D systems. Using a length of tube \( L \sim 200 \) nm (the spacing between the leads) gives \( U = 7 \) meV and \( \Delta E = 2.5 \) meV. These are consistent with the observed values. To relate these theoretical results for a single tube to the measurements of rope samples, we first note that current in the rope likely flows along a filamentary pathway \( \text{(4)} \) consisting of a limited number of single tubes or few-tube segments. This is because, first, 60-70% of the tubes are not \((10,10)\), and hence the majority of the tubes in the rope will be insulating at low \( T \) \( \text{(14)} \). Second, the inter-tube conductance is small compared to the conductance along the tube, inhibiting inter-tube transport. Finally, the metal likely only makes good contact to the metallic tubes which are on the surface of the rope, further limiting the number of tubes involved in transport.

Disorder along a filamentary pathway will effectively break it into weakly coupled localized regions. This disorder may result from defects \( \text{(14)} \), twists \( \text{(14)} \), or places where inter-tube hopping is necessary along the pathway. Generally, the conductance would be expected to be determined by single electron charging and tunneling between a few such localized regions. For other rope segments that we have measured, the characteristics are consistent with transport through a few segments in series/parallel, each with different charging energies. For the particular rope segment we have focused on here, however, a single well-defined set of Coulomb peaks is observed, indicating that transport is dominated by a single localized region. Further, since the amplitude of isolated peaks approaches the theoretical maximum for single-electron transport of \( e^2/h \), there is no other significant resistance along the pathway. We believe that this single region dominating transport is a section of a single tube or at most a few-tube bundle.

While the above interpretation explains the major features in the data, many interesting aspects of this system remain to be explored. First one would like to establish absolutely that transport is indeed occurring predominantly along a single tube. Second, it should be determined whether all details of the data can be explained within the simple Coulomb blockade model discussed above, since Coulomb interactions may significantly modify the low-energy states from simple 1D non-interacting levels \( \text{(18)} \). Of great interest would be measurements of disorder-free tubes, where the intrinsic conducting properties of the tube can be measured without the complications of single-electron charging. To address these issues, experiments on individual single-walled tubes are highly desirable, and both our group and others \( \text{(19)} \) are making progress in this direction. Yet another important experiment would be to measure directly the inter-tube coupling by making separate electrical contact to two adjacent tubes.

In conclusion, we have measured transport in single nanotube ropes at low temperatures. We find that a Coulomb gap appears in the \( I-V \), Coulomb oscillations are observed as a function of an external gate voltage, and structure is observed in the \( I-V \) curve above the Coulomb gap. We interpret these results as evidence for single-electron transport through the quantized energy levels of the nanotubes comprising the rope.

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The level spacing can be determined from the data in D. Bernaerts, et al. preprint (1996); J.M. Cowley, P. Niloli, L. X. Benedict, S. G. Louie, and M. L. Cohen, Phys. Rev. 76, 971 (1996).

Other measurements on these samples also support the notion that transport is through individual decoupled tubes. In four terminal measurements of the ropes at different contacts make contact to different tubes and the opposite-handed twins. The gap of the (7,13) tube is small and likely does not survive intertube interactions, but the gaps of the (9,11) and (8,12) tubes are about 0.5 eV, which is probably large enough to maintain semiconducting behavior within the rope.

FIG. 1. Left inset: Atomic Force Microscope (AFM) micrograph of a completed device. The bright regions are the lithographically defined metallic contacts, labeled 1-4. The rope is clearly visible as a brighter stripe underneath the metallic contacts. In between the contacts (dark region), it is difficult to see the rope because of the image contrast. Note that the width of the rope in the AFM image reflects the convolution of its actual width with the AFM tip radius of curvature. The actual thickness of the rope is experimentally determined by the measuring its height with the AFM and assuming that the rope is cylindrical. Main: The $I - V$ characteristics at different temperatures for the rope segment between contacts 2 and 3. Right inset: Schematic energy-level diagram of the two one-dimensional subbands near one of the two Dirac points [3], with the quantized energy levels indicated. The k-vector here points along the tube axis.

FIG. 2. Conductance versus gate voltage at $T = 1.3$ K for the segment between contacts 2 and 3. Left inset: Temperature dependence of a peak. Note that this peak was measured on a different run from the data in the main panel and does not directly correspond to any of those peaks. Right inset: Width of the peak in the left panel as a function of temperature.

FIG. 3. Top: gray scale plot of the differential conductance $dI/dV$ of the rope segment between contacts 2 and 3, plotted as a function of $V$ and $V_g$. To enhance the contrast of the image, a smoothed version of the data was subtracted from the differential conductance. Bottom: Schematic energy-level diagrams of the device within the Coulomb blockade model at the points indicated in the upper panel. Panel A shows the linear-response ($V = 0$) transport possible at a Coulomb peak. Panel B shows the blocked regime between peaks; indicated are the addition energy $U + \Delta E$ and the level spacing $\Delta E$. Panels C and D show the diagram at two different applied voltages corresponding to transport through the first and second occupied states, respectively.
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