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Nanoscale electronic devices on carbon nanotubes

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Abstract. Conductivity measurements were performed on bundles of single-walled carbon nanotubes with the aid of a scanning tunneling microscope (STM). Semimetallic current–voltage (I–V) characteristics generally indicated the bundles to be electronically similar to graphite. However, by moving the STM tip along the length of the nanotubes, sharp deviations in the I–V characteristics could also be observed. Well-defined positions were found at which the nanotube transport current changed abruptly from a graphitic response to one that is highly nonlinear and asymmetric, including near-perfect rectification. This abrupt change in the nanotube transport suggests that the STM tip had passed a region of the nanotube which acts less like a wire than it does a Schottky barrier or other heterojunction. Similar on-tube nanodevices have been theoretically predicted for point defects in individual carbon nanotubes and are consistent with our observations.

1. Introduction

Carbon nanotubes [1] are a fascinating new class of materials from both theoretical and applied standpoints. Theoretical models have predicted that nanotubes could behave electronically as ideal one-dimensional 'quantum wires' with either semiconducting or metallic behaviors [2–4]. Careful study of transmission electron micrograph (TEM) images, however, has indicated that the nanotubes also incorporate kinks and defects into their walls. Recent theoretical attention to defect-containing nanotubes suggests a rich variety of heterojunction behaviors [5–8] may be possible in these one-dimensional wires. Such junctions could provide electronic elements with sizes inaccessible by lithographic manufacturing.

Experimental work with multiwalled carbon nanotubes has not identified these quantum wire or heterojunction behaviors. Room-temperature measurements generally reported metallic characteristics [9–12] for nanotubes, and in a sliding contact measurement [13] a nanotube was found to have uniform resistivity throughout its length. These findings are partly understood as a result of the nanotube morphology, since the large diameter, multiwalled nanotubes are structurally and electronically quite similar to graphite and so exhibit a two-dimensional metallic or semimetallic characteristic, rather than the quantization of a true one-dimensional material.

Progress in nanotube synthesis has now yielded single-walled nanotubes (SWNTs) with well-defined diameters [14, 15], bringing the experimental situation much closer to that of the theoretical models. Recent measurements indicate that these materials do behave like one-dimensional wires [16–20]. The SWNTs should also be more sensitive to defects, to the extent that defects may dominate the transport characteristics. In this work, a scanning tunneling microscope (STM) tip was used as a sliding electrical contact to probe the length dependence of SWNT conductance. Although atomic defects were not directly imaged, sharp conductance transitions and heterojunction behaviors in the nanotube conductances are suggestive of the signatures of nanotube defects.

2. Experiment

The SWNTs were synthesized using both a laser-assisted process as previously reported [14], and an arc-plasma method [15]. The samples were subsequently burned in oxygen at 750 °C to remove the bulk of the amorphous and graphitic material. The resulting material was observed under TEM to be made up of no less than 90% nanotubes. A large proportion of the nanotubes have 1.3 nm diameters and zero chirality (so-called 'armchair' tubes) as indicated by x-ray and TEM studies, and have uniform diameters over micrometer lengths.

The individual SWNTs typically align and close pack into crystalline 'ropes' which can have diameters as large as 30 nm [12, 14]. Presumably, the small volume-to-surface area ratio of the nanotubes allows for strong van der Waals bonding among each other and to flat surfaces. The same forces which bind the SWNTs together into ropes allow the ropes to loosely adhere to a clean metal probe, a fact exploited in the following experiments.

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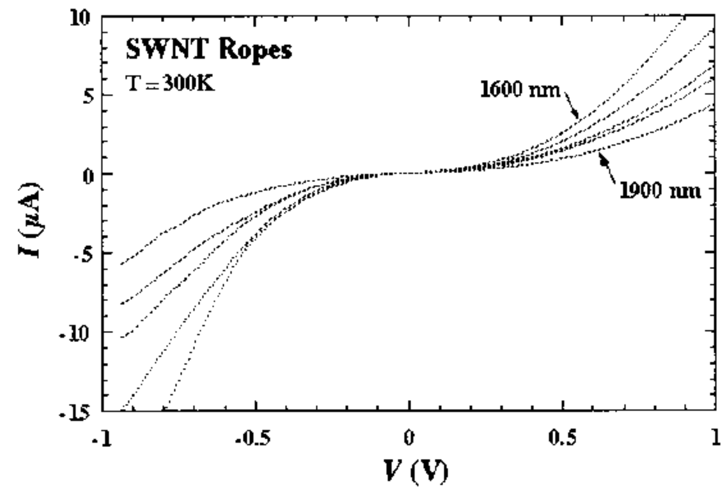

Figure 1. I–V characteristics obtained for contact points at different heights along a carbon nanotube rope.

We produced a thick film of randomly aligned nanotubes by pressing the purified nanotube material onto a gold-coated glass substrate. Using a specially constructed STM, a sharpened platinum wire was then brought within tunneling distance of the disordered surface. With certainty the sample was not suitable for normal STM imaging, but in this case the STM was merely used as a precise local-probe micromanipulator. From a position of stable tunneling, the STM tip was driven forward into the nanotube film approximately 100 nm, or until a metallic contact was formed. Upon retraction of the tip well beyond the normal tunneling range, continuous electrical contact indicated that nanotube material now spanned the gap between tip and sample. Even several hundred nm above the original tunneling position, material stuck to the tip for nearly 5% of the trials. This success rate could not be achieved with nanotubes which do not have the tendency to form ropes, namely multiwalled nanotubes or contaminated nanotubes. This fact indicates that adhesion between a SWNT rope and the tip, as opposed to nanotube entanglement, is the source of the physical connection.

Current–voltage (I–V) characteristics for the nanotubes could be acquired while in this conducting state. Furthermore, a fine stepper motor allowed further mechanical retraction of the tip from the surface in steps averaging 2 nm. Starting with the STM tip retracted by its full range of 300 nm, I–V characteristics were acquired in 2 nm increments of tip–substrate separation until electrical contact was irreparably broken. After losing contact, current could only be obtained by returning the STM tip to approximately the original surface height. The continuous increase of the tip-to-sample distance allowed measurement of different lengths of nanotube material. For some samples, retraction of more than 2 μm occurred before electrical contact was lost, in agreement with the observed free length of SWNTs. Although repeating the experiment on the exact same nanotube was impossible after losing contact, further measurements by the same technique showed qualitatively similar behaviors.

The precise nature of the electrical contacts between tip, SWNT rope, and surface are experimentally difficult to determine. Only measurements with 500 nm or more of retraction are reported here, since in these cases electrical transport is unambiguously from the STM tip to the surface through a SWNT rope. Based on the morphology of the starting material, the nanotube rope is probably entangled at the surface, resulting in a number of good physical as well as electrical contacts at that end. The connection at the STM tip, on the other hand, is presumably a weakly bound one. Based on the continuous electrical connection even 2 μm from the sample surface, it is clear that the adhesion between the nanotube rope and the STM tip is strong. Even so, the lateral forces, or friction, between the two may be quite weak. This intuitive picture of the physical contact is in accord with a sliding electrical contact. We argue that as the tip pulls a nanotube rope away from the surface, the STM tip-to-nanotube connection forms a sliding contact, providing for a length-dependent measurement of electrical transport through the nanotube rope.

3. Results

Figure 1 depicts several I–V curves obtained at varying positions along a nanotube rope. Each curve was found to be highly reproducible for a given tip position. As the tip moved, however, the overall magnitude of each I–V curve varied non-monotonically over as much as an order of magnitude, even for tip displacements of merely a few nm. This variation in magnitude, but not shape, of the I–V characteristics is a primary indicator of the sliding contact between the tip and a SWNT rope: after each successive tip movement, the slightly altered electronic coupling at the interface merely rescales the dominant I–V characteristic. In fact, the curves displayed in figure 1 are exactly identical if each is normalized to its current magnitude at $V = 1$ V.

Thousands of I–V characteristics were obtained from different samples, many of which showed the same general, nonlinear, symmetric shape. This dominant characteristic can be understood as related to graphitic properties [21], as expected for a large rope of nanotubes at room temperature. Slight asymmetries were also generally observed and are

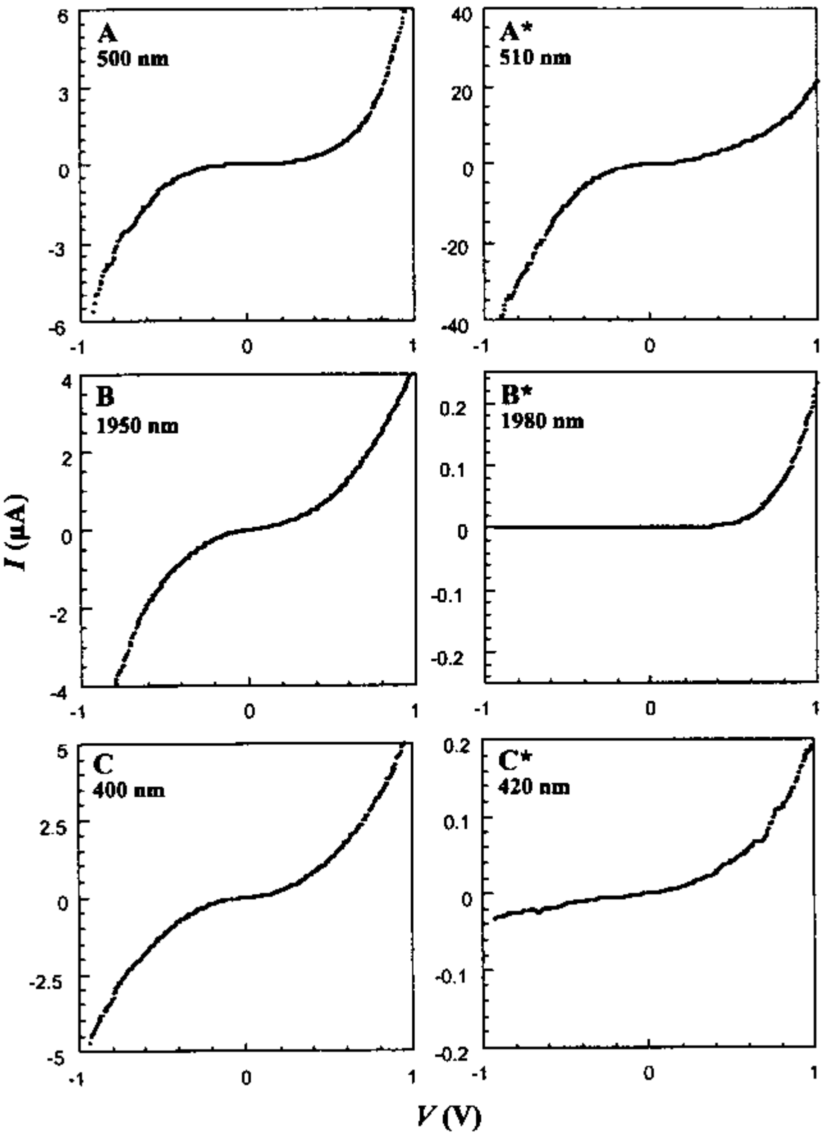

Figure 2. I–V characteristics from three different samples, each of which displayed an abrupt deviation from the dominant semimetallic characteristic. The I–V curve obtained from the beginning of the experiment until the transition point is shown in the left-hand figures; on the right-hand figures is the I–V curve obtained from after the transition point until contact was lost.

apparent in figure 1, but could be due either to the tubes themselves or to the STM tip-to-nanotube contact and will not be analyzed further.

Figure 2 displays pairs of curves from three different samples indicating departures from the dominant transport characteristics. For each sample, the first I–V characteristic was stable and reproducible over hundreds of nm of tip motion (figures 2(a^*)–(c^*)). After a particular tip movement, however, a significantly changed I–V characteristic was recorded (figures 2(a)–(c)). The transition from one type to the other occurred over mere nm of tip motion near tip heights of 500, 1950, and 400 nm for samples (a), (b), and (c), respectively. After these transitions, the new characteristics were equally stable and reproducible, again over hundreds of nm or until a rope broke free from the STM tip. Small scaling changes attributed to the sliding contact were evident both before and after the transition point. Based on these observations, it is credible that the measured changes in conductivity arise from the nanotube rope itself and not the nature of the contact.

Although sample (a) showed an interesting transition from an asymmetric to a more symmetric I–V characteristic, samples (b) and (c) showed a much more dramatic change. In these two samples, the I–V characteristic has the familiar shape for positive tip biases but is then rectified for negative tip biases. Similar rectification was never observed in the opposite direction for positive biases, but this missing effect may be an artifact of the experimental procedure. After each original movement of the tip into the gross nanotube film we checked for a connecting rope only under positive tip bias conditions, when in fact a rope may have been physically connected but conductive only for negative biases.

4. Analysis and discussion

Due to the observed nonlinear I–V characteristic, there exists no true linear resistivity for the nanotube rope. Most

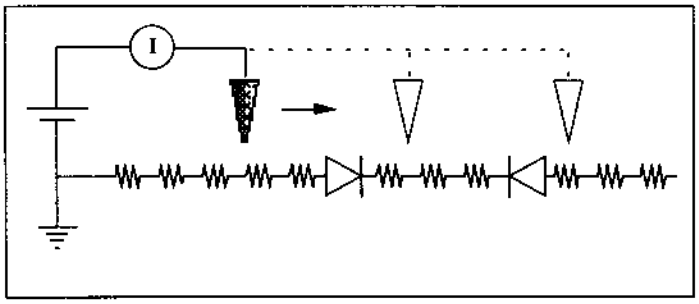

Figure 3. Schematic model of a defect-including nanotube. Depending on the position of current injection by the STM tip, the nanotube behavior can be semimetallic, rectifying, or insulating.

transport measurements in the literature, however, quote resistance values for various measurement configurations. Calculation of a nominal resistance is therefore instructive, since a comparison with other measurements can indicate how many ropes span the micrometer-scale gap between the STM tip and the surface in the present experiment. In figure 1, the dominant I–V characteristics for our samples give a low-bias resistance of 100 kΩ. For a single rope with a typical diameter of 10–30 nm, this implies a nanotube resistivity of $10^{-2}\Omega$ cm^{-1}. This value is consistent with others reported in the literature [11, 12, 14], supporting the suggestion that only a single rope electrically connects the STM tip to the surface. However, the electrical contact area is, by the nature of the experiment, poorly defined. This precludes a quantitative comparison of the data with specific theories, since the tip-to-tube junction may form a tunneling barrier, a point contact, or a large area contact.

We argue that the distinct changes in conductivity are due to the incorporation of a nanotube defect at the transition contact point. The random spacing and infrequent occurrences of the observed transitions are in accord with a low density of defects on the nanotube ropes. Such defects could be expected to cause extreme changes in the transport behavior as the tip passes through a nm-sized region. After passing the region, the transport should not relax but should remain in its altered state, exactly as we have observed.

Qualitatively our observations of rectification by the nanotube rope are in excellent agreement with recent theoretical treatments of defects in carbon nanotubes [5–8]. A nanotube defect alters the local electronic density of states $N(E)$, both on the nanotube and possibly for a local area of the rope. For example, the existence of pentagon–heptagon pairs in the otherwise perfectly hexagonal carbon lattice introduces sharp discontinuities in $N(E)$ which have been theoretically shown to completely block transport currents [5]. Nanotube defects essentially behave as seamless junctions between otherwise disparate materials, joining for example a metallic nanotube to a semiconducting one to produce a Schottky barrier. Depending on the exact geometry of the nanotubes on each side of the defect, a variety of pure-carbon nanoscale junctions have been proposed, including the Schottky barrier example given.

Figure 3 depicts a schematic network for the observed behavior based on this interpretation. A defect on a nanotube rope, modeled as a nonlinear element, might produce unusual transport properties as we have measured. Before the STM tip reaches the defect, the nanotube rope exhibits a graphitic response, as modeled by a purely resistive network. As the contact slides further along the nanotube rope, the nonlinear element is incorporated into the current path, rectifying all further responses. In this way, the local graphitic response of the rope is dominated by a defect which, at least physically, can be hundreds of nm from the contact point. A second defect, as shown in the figure, will simulate the loss of physical contact to the nanotube rope. With our present apparatus, we are unable to distinguish between an insulating rope and the loss of physical contact.

It is important to consider other tip-related artifacts which could be causing the abrupt transitions between a symmetric I–V characteristic and a rectifying one. TEM studies of the SWNT ropes indicate that the ropes tend to twist, suggesting that the contact area may actually jump from nanotube to adjacent nanotube within the same rope. However, this type of slippage of the tip contact point should produce conductivity changes as frequent as the overall twisting. Experimentally, we observe no such periodic jumps, but rather a smooth and continuous variation in the I–V characteristic leading up to a transition. Similar effects could be caused by contamination or disconnected material interfering with the tip-to-nanotube contact. However, under TEM observation the outer walls of the SWNT ropes are completely free of such materials after the purification treatment.

5. Conclusions

The nonlinear nanotube I–V characteristics presented here hint at a viable source of nanosized electronic components for future applications. Because of their size, nanotube devices can be expected to operate with unusually high speed, high element density, and excellent thermal dissipation characteristics. If indeed the nonlinear characteristics are the effects of single point defects, then the question at hand is how to incorporate defects and their electronic effects into useful electronic devices. Two possible paths towards this goal are currently under investigation [22].

In one scenario, defects are created in pristine, defect-free nanotubes in predetermined positions. After positioning a nanotube on metallic contacts or in a network of other nanotubes, one employs the local action of an STM tip to damage or chemically functionalize a section of the tube. With the development of proper techniques, it may become possible to choose from the variety of nanotube-based devices which are theoretically possible.

In a second, less determinate model, the equilibrium thermodynamic density of defects is employed. The as-grown sample of entangled tubes will inevitably contain a high density of randomly arranged device elements, perhaps orders of magnitude higher than in state-of-the-art Si technology. In this approach, multiple connections are made to a sample and characterized, ultimately determining algorithms which can exploit the functions already existing within the sample. Such a sample might form the basis of a useful machine, perhaps a computer [22], with high-speed characteristics.

In conclusion, reproducible electronic conductivities have been measured on a number of different single-walled nanotube bundles. We have measured distinct changes in the conductivity as the active length of the nanotube was increased, suggesting that different segments of the nanotube exhibit different electronic properties. The changes occur over very short lengths, suggestive of point defects in the tube wall itself. As such, the nanotubes constitute molecular-scale nonlinear electronic devices. The controlled production or manipulation of nanotubes with these characteristics could allow for the utilization of these features in ultraminiature electronic devices and circuits.

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