MEASUREMENTS OF THE CONDUCTIVITY OF INDIVIDUAL 10 NM CARBON NANOTUBES

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ABSTRACT

Catalytically grown carbon fibers approximately 10 nm in diameter and several microns long were characterized by transmission electron microscopy and determined to be multiple-walled nanotubes, and a technique was developed to measure the conductivity of an individual nanotube. Nanotubes were dispersed in solvents and precipitated onto lithographically defined gold contacts to make a 'nano-wire' circuit. Non-contact AFM was used to image the nano-wires, and a resistance of 11.4 (± 1.0) MΩ was measured through a single nanotube at 23° C. A resistivity of 9.5×10^{-5} Ω m was estimated for carbon conducting along the axis of a fiber. Local heating of nanotubes appeared to occur at high current densities. The nanotubes could sustain currents on the order of 10 μA per fiber, but application of currents on the order of 100 μA per fiber resulted in rapid decomposition in air and breaking of the circuit.

INTRODUCTION

A circuit was designed, consisting of two gold contacts separated by approximately 5 μms and connected by a carbon nanotube, and current was passed through the circuit. To our knowledge no other measurements of the conductivity of individual carbon nanotubes with comparably small diameters have been reported, although some theoretical predictions have been advanced regarding electronic properties of nanotubes [1-3]. Conductivity measurements of much larger carbon fibers of several types [4-8] and recently of carbon nanotube bundles [9,10] are also documented. Electrical resistivity in catalytically grown nanofibers is difficult to determine by conventional means because of their small size [11]. The 'nano-wires' were imaged by non-contact AFM. Related images of nanotubes and nanotube bundles have been reported using other scanning probe techniques [12-14].

Carbon nanotubes are interesting for the purpose of building nano-scale devices because of their size. Our research group has an interest in the development of new lithographic techniques for the patterning of surfaces [15], and one of the reasons for developing such techniques is to find better ways of fabricating small (less than 30 nm) features. Various non-classical phenomena such as single electron tunneling [16], which might be exploited to build new devices, are observed at increasingly high temperatures as feature sizes decrease. A complementary approach to building nano-electronic devices might be to chemically build up structures from colloidal or molecular pieces such as carbon nanotubes in addition to relying on lithographic techniques.

EXPERIMENTAL

A sample of catalytically grown carbon nanotubes was obtained from Hyperion Catalysis International. We imaged the carbon nanotubes by transmission electron microscopy (TEM), and the carbon in the material consisted mostly of fibers (figure 1). TEM was performed on a Phillips EM 420 microscope. The carbon nanotubes were dispersed in ethanol or xylenes with sonication and pipetted onto TEM grids from Structure Probes Inc. The fibers had diameters of approximately 10 nm and lengths of several μms.

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N-doped silicon (100) wafers were obtained from Silicon Sense Inc. These wafers were oxidized in air at 1000 ^{o} C for 24 hours. The oxidized wafers were mounted in a dual source e-beam evaporator containing a gold source and either a titanium, nickel, or chromium source to be used as an adhesion promoter. 10 Å of adhesion promoter followed by 200 Å of gold were deposited on the wafers. The gold coated wafers were patterned through a mask using photolithography, then the exposed gold was etched for 2 sec in Gold Etchant TFA supplied by Transene Inc. The oxide layer insulated the gold contacts from each other and from the silicon substrate. The resist remaining on the gold contacts was stripped off, and PMMA was then spin-coated onto the wafers for e-beam patterning.

E-beam patterning was performed on a JEOL JSM-640 Scanning Microscope. A window pattern was written in the PMMA resist, and it consisted of a rectangular box with dimensions of 10 μm x 20 μm. The window area was scanned with a 35 kV 400 pA e-beam using a line dose of 8 nC/cm for best results. Upon development, the PMMA completely insulated the gold contacts except inside of this window.

The development of these windows and the number of nano-wires present inside of them were assessed by AFM on a Topometrics Scanning Probe Microscope. The fibers were imaged in air on the AFM using low resonant frequency 1660-00 silicon tips from Topometrics. The tips oscillated at approximately 150 kHz, and amplitude detection was used to collect the signal.

Currents were applied to the gold contacts using a Princeton Applied Research Model 273 Potentiostat/Galvanostat operated in the galvanostatic mode. The current source was connected to the gold substrate via wires planted into indium solder.

RESULTS

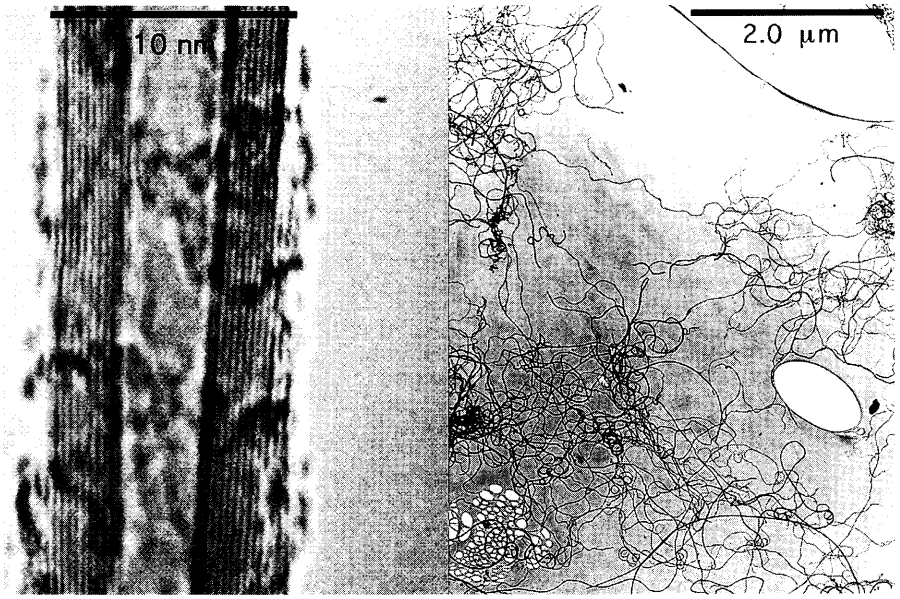

Figure 1: Typical nanotubes have diameters of about 10 nm and lengths of several μms. The high resolution image on the left was recorded by Y. Lu at the Harvard MRL Central Facility.

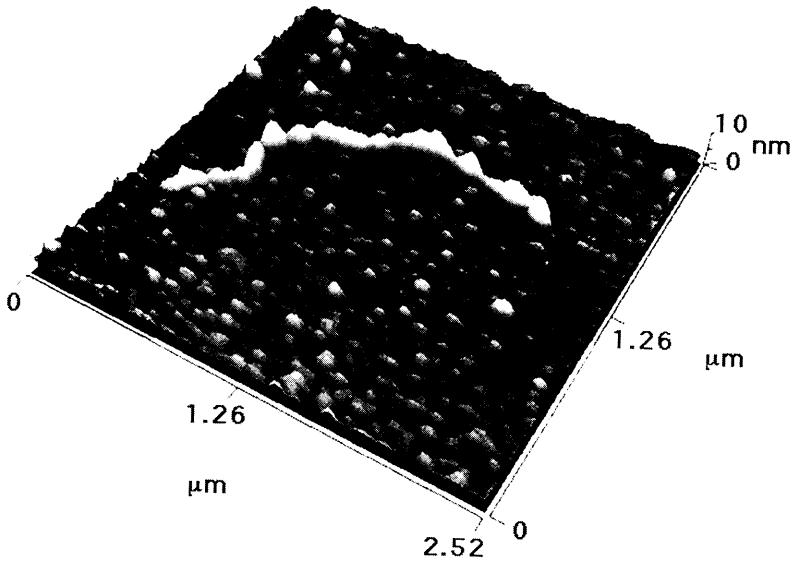

Figure 2: A non-contact AFM image of a nanotube precipitated onto a gold film is depicted.

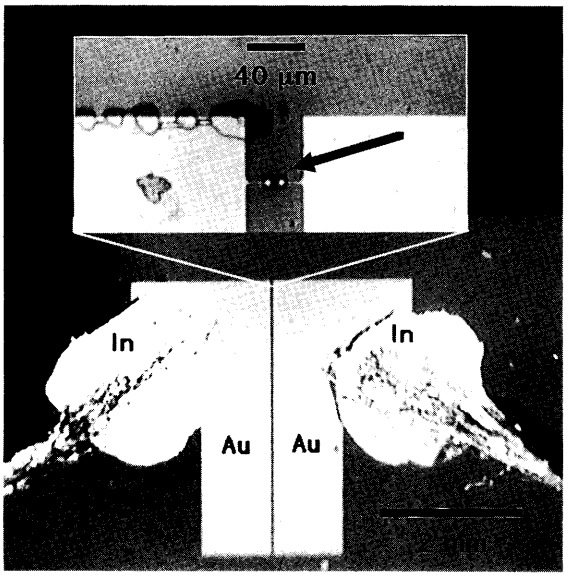

Figure 3: Lithographed gold contacts on an oxidized silicon substrate are connected to wires via indium solder. A rectangular window in PMMA is centered where the contacts make their closest approach at a separation of approximately 5 µm (see arrow). E-Beam exposures along the top left contact occurred during positioning of the e-beam for the window exposure. The inset of this visual image is a view through an optical microscope.

We mounted the carbon fibers on lithographically defined gold contacts so that we could measure their conductivity, and non-contact atomic force microscopy (AFM) was used as a method for imaging these fibers on a circuit. Comparison of the AFM images with TEM images showed that the lateral thickness of fibers erroneously appeared to be approximately ten times wider than the correctly scaled vertical thickness in the AFM images (figure 2).We were able to scan over individual fibers reproducibly because the weak interaction between the AFM tip and the fibers did not cause them to move.

Dispersions of carbon nanotubes were sonicated in ethanol to make dispersions of $4x10^{-3}$ or $4x10^{-4}$ mg/ml and precipitated onto thermally oxidized silicon (100) substrates patterned with lithographed gold features (figure 3). The gold features had been previously coated with insulating poly(methyl methacrylate) (PMMA) except within a 200 μm^2 area where PMMA was subsequently removed using e-beam lithography. The solvent was either allowed to dry in air or to evaporate quickly under a stream of argon. A 100 pA current was typically applied across two gold contacts. A voltage greater than 1.0 V between the contacts was measured and observed to rise capacitatively prior to the deposition of fibers. The occurrence of one or more nanotubes lying across the gap between the two gold contacts resulted in a dramatic and sustained decrease in the voltage that was measured, and drops of the dispersion were pipetted repetitively onto the substrate until a potential drop was realized. The nanotubes precipitated onto an area of approximately 1 cm^2, but the PMMA layer prevented them from making electrical contact with gold except inside of the 200 μm^2 window. The window area was small enough to be scanned with an AFM tip so that we could observe the number of fibers bridging the two gold contacts inside of it.

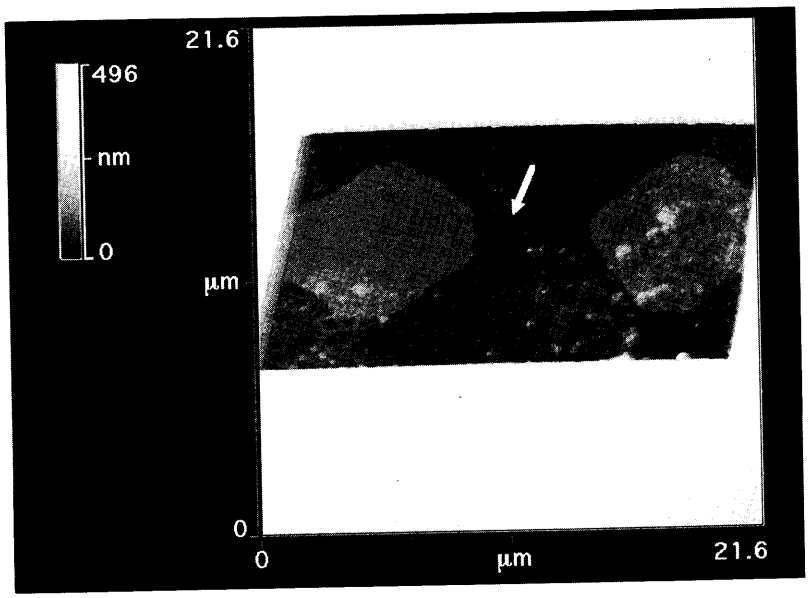

Figure 4: The gold contacts in this image were thought to be bridged via a single fiber. The vertical height of the nanotube was between 8 and 10 nm. The hollow inner diameter was assumed to be 1/3 of the total diameter based upon TEM images of similar fibers, and the cross-sectional area of carbon was therefore estimated to be 57 (± 16) nm^2. The length of the fiber was 7.5 (± 1.0) µm.

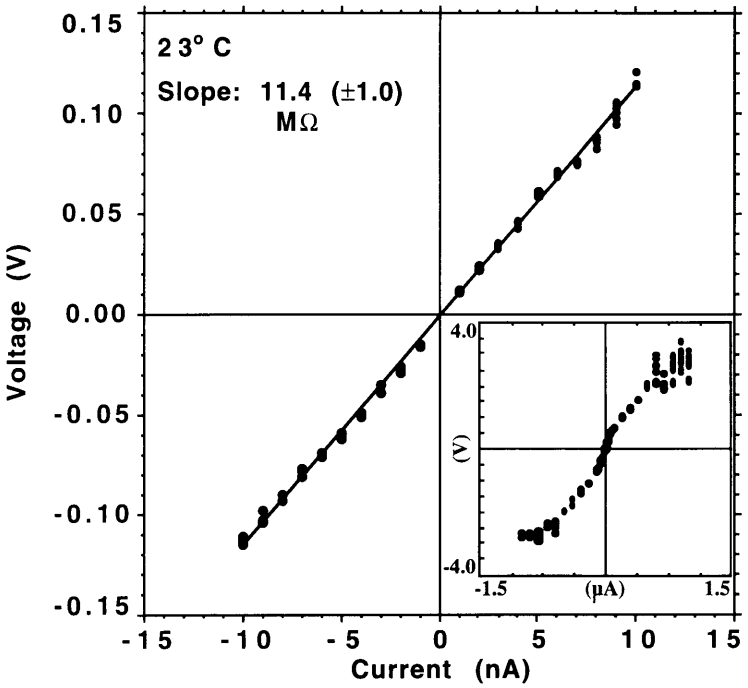

Figure 5: The voltage vs. applied current plot corresponding to the image in figure 4 is depicted.

The d. c. conductivity was measured at room temperature (23 ^{o} C) using a galvanostat to apply currents in forward and reverse directions through the nanotubes that connected the gold contacts. In our initial experiments no attempt was made to thermostat the circuit or correct for self-heating of the nanotubes. Since the conductivity was derived from the limiting slope of a voltage vs. applied current curve at low currents, self-heating is not likely to have been a problem. Often, more than one fiber or an aggregate of fibers was observed to be bridging the contacts. Our best example of gold contacts bridged by a single fiber is shown in figure 4. Aggregates of carbon fibers were also present, but only one nanotube was observed to be bridging the contacts.

The voltage vs. applied current plot that we attribute to this single bridging fiber is shown in figure 5. The resistance of the fiber was obtained from a linear fit to the plot at low magnitudes of applied current, and it is 11.4 (± 1.0) MΩ. This measurement correlates well with some other measurements that we have made in which more than one connecting fiber was observed and the measured resistance was correspondingly lower. By measuring the length and cross-sectional area of the nanotube from its AFM image the resistivity of carbon along the fiber axis could be estimated to be 9.5×10^{-5} Ω m. This estimated resistivity is more than an order of magnitude higher than reported resistivities in the basal plane of ordered pyrolytic graphite [17]. The resistivity in carbon nanotube bundles synthesized by arc discharge has been been estimated by others to vary between 10^{-4} and 10^{-5} Ω m [9] and to be 6.5×10^{-5} Ω m at 300 K [10]. The room temperature resistivity of methane-derived carbon fibers was shown to be 10^{-5} Ω m or less depending on heat treatment temperature [7]. The resistivity of benzene-

derived carbon fibers was shown to be on the order of 10^{-6} Ω m after heat treatment at 3500°C, and it increased as the diameter of the fiber decreased between 34 and 1.6 μms [8].

At currents above 1 μA the voltage vs. applied current curve in figure 5 deviates significantly from linearity and the measured voltage becomes more uncertain. The reason for the lowering of the resistance at high currents may be local heating of the nanotubes. We observed that the nanotubes were capable of supporting on the order of 10 μA of applied current per fiber without being damaged. Application of currents on the order of 100 μA per fiber resulted in rapid decomposition of the fibers in air and breaking of the circuit.

We wish to thank Dr. D. Moy at Hyperion for providing the carbon fibers and for advice.

CONCLUSIONS

These carbon fibers show promise as materials for building nano-scale electronic devices. They can be imaged individually and reproducibly on a circuit by non-contact AFM. Our estimate of the resistivity of carbon in a single nanotube parallel to its axis is much higher than resistivities that have been reported for ordered pyrolytic graphite [17]. The resistivity is similar to resistivity measurements of nanotubes of similar diameter in coaxial bundles [9,10]. The resisitivity is an order of magnitude or more higher than the resistivity of individual vapor grown fibers with diameters greater than 1 μm [7,8]. The contribution of contact resistance to our measurement is still unclear, but some information about contact resistance may be obtainable from a. c. conductivity measurements. A four-point probe measurement of a single nanotube would be desirable, but also difficult to accomplish. We will also attempt in future experiments to better control and detect local heating that is probably occurring when we apply high currents to the nano-wires.

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