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In-situ electrical characterisation of suspended multiwalled carbon nanotubes

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Abstract. Room temperature electrical transport measurements have been made on suspended multi-walled carbon nanotubes (MWNTs) using a remote controlled manipulation system within a scanning electron microscope. It is shown that the current-voltage characteristics of the MWNTs are symmetric with respect to voltage and that the conductance improves with multiple cycling of the voltage. Estimations of the semiconducting sub-bands and the contact transmission coefficients of the MWNTs have also been made.

1. Introduction
Experimental and theoretical studies of carbon nanotubes (CNTs) have shown that they have remarkable electrical, thermal and mechanical properties. In particular they are the most ideal one-dimensional structure to have been discovered so far and depending on their atomic structure, they may be either metallic or semiconducting, [1] with a band gap that decreases as the diameter increases. Hence CNTs are one of the most high profile materials to have been investigated recently and their use in novel devices needs to be investigated. For example, semiconducting single-walled carbon nanotubes have been used as the channel of field-effect transistors, [2] while multi-walled carbon nanotubes (MWNTs) have been used in field emission applications. [3]

CNTs also have a strong covalent structure which means that they have a reduced phase space for scattering and it is possible for them to exhibit ballistic conduction. This proposition was first confirmed by Frank et al. [4] who lowered arc-discharge MWNTs into a liquid metal and measured the conductance as a function of depth. They found that when a single nanotube was in contact with the metal it produced conductance plateaus very close to the quantum of conductance, 1G₀. These results are consistent with those of a ballistic conductor of uniform width and strongly suggest that the tube is a quantized conductor. In 2002, Poncharal et al. [5] expanded this experiment and showed that the conductance of the CNTs increased linearly with voltage by ~0.3G₀/V and that the conduction of the nanotubes was related to the density of states of the nanotubes.

In this paper the electrical properties of suspended, arc-discharge MWNTs that have been embedded in a polymer matrix are characterized using a two-probe manipulation system operated within a scanning electron microscope (SEM). [6] This experiment utilizes a grounded MWNT and one of the probes, as shown in figure 1, to explore the role of the contact in this arrangement.
2. Experimental Method
The experimental work was carried out on MWNTs embedded in a polymer matrix that were produced as described in ref. [7] The composites had a nanotube to polymer ratio of 1:3 and were cleaved to expose the MWNTs. High-resolution transmission electron microscope images of the CNTs showed that they had an exposed length of 2 -12 μm, an outer diameter of ~13 nm and a polymer coating of ~30 nm. These composites were investigated in a Cambridge Instruments Stereoscan 250, MK3 SEM in which a custom manufactured, remote controlled manipulation system was installed. An electrical feed-through was used to connect a Keithley 238 Source-Measurement Unit to the probes. This allowed for single suitable MWNTs to be located and contacted to as shown in figure 1. Once a good mechanical contact had been achieved, the electron beam was turned off in order to minimize its affect on the properties of the MWNTs and conventional current-voltage measurements were performed.

Figure 1. Scanning electron microscope image of a protruding polymer coated MWNT, which is attached to a sharpened metal tungsten tip. The nanotube has been enhanced in this image for clarity.

3. Results and Discussion
Initial investigations into the nanotubes showed that repeated cycling of the voltage improved their resistance. From here on this shall be referred to as conditioning. Figure 2(a) shows an I-V characteristic of a typical 5 μm polymer coated MWNT, where the current limit was raised for each cycle from 16 μA up to 40 μA. This graph also shows that the I-V characteristics for this nanotube are symmetric with respect to voltage polarity.

Figure 2. (a) I-V characteristics of a 5 μm MWNT for current limits between 16 and 40 μA. (b) Conductance-voltage characteristics of a 10 μm MWNT for current limits of 2 μA, 8 μA and 16 μA.
This behavior may be further analyzed by considering the conductance characteristics of the nanotubes. Figure 2(b) shows the conductance \((G/G_0)\) characteristics for three different voltage cycles that were run on a 10 \(\mu m\) nanotube. The graph shows how the gradient increases from \(1.5 \times 10^{-3} G_0/V\) to \(2.8 \times 10^{-3} G_0/V\) and the conductance at near zero voltage, \(G_{min}\) increases from 0.0036\(G_0\) to 0.01\(G_0\) by repeated cycling of the voltage. The majority of nanotubes tested followed this behavior and had \(G_{min}\) and gradient values of \(1.1 \times 10^{-3} G_0\) to \(0.1G_0\) and \(1.1 \times 10^{-4} G_0/V\) to \(0.05 G_0/V\) respectively.

The conductance of the nanotubes may be understood by considering the electronic band structure of metallic CNTs, which consists of two metallic sub-bands that cross at the Fermi level and a number of occupied and unoccupied semiconducting sub-bands. The band-gap between the first set of semiconducting sub-bands is proportional to the diameter, \(D\), of the nanotube and is given by:

\[
\Delta E = \frac{6\gamma_0 a}{D} \propto \frac{1}{D},
\]

where \(\gamma_0\) is the energy overlap integral (3 eV) and \(a\) is the carbon-carbon lattice spacing (0.14 nm) [8]. For a metallic MWNT with a typical diameter of 13 nm, as found by the TEM images, \(\Delta E = 0.19\) eV. As this value is greater than \(kT\) at room temperature, at voltages below this only the metallic sub-bands contribute to the transport and produce a plateau near \(V=0\). The size of this plateau is determined by Landauer’s equation and is dependent on the scattering at the contacts \((T_c)\) and in the metallic sub-bands \((T_m)\), such that

\[
G_{min} = 2G_0T_mT_c,
\]

where \(G_0 = (2e^2)/h\). For voltages above \(\Delta E\), the semiconducting sub-bands start to conduct one at a time and produce a series of steps in the conductance characterstic. The width of the steps is equal to half the value of the sub-band separation \(\Delta E\), [8] while the height is set by Landauer’s equation, which is dependent on scattering at the contacts and in the semiconducting sub-bands \((T_s)\), such that

\[
\text{height of step } (dG) = 2G_0T_sT_c.
\]

Hence, the gradient of the conductance can be described by the equation:

\[
\frac{dG}{dV} = \frac{2G_0T_sT_c}{0.5\Delta E}
\]

This explanation indicates that the variation in the values for \(G_{min}\) and the gradient in figure 2(b) may be due to either different amounts of scattering occurring in the conducting sub-bands or due to the fact that each contact has a different resistance. To determine which of these factors dominate the results, the conductance may be normalized by dividing the gradient (eq. 4) by \(G_{min}\) (eq. 2) This removes the effects of the contacts, and if \(T_m\) is also assumed to equal one, as only minimal scattering should occur in the metallic sub-bands, [8] then the normalized gradient is only dependent on scattering within the semiconducting sub-bands and the diameter of the MWNT being investigated, such that:

\[
\frac{dG/dV}{G_{min}(V=0)} = \frac{T_s}{0.5\Delta ET_m} \quad T_m = 1
\]

Figure 3 shows the normalized gradient of a 10 \(\mu m\) MWNT. It exhibits a small difference in the gradient over all cycles, with an average value of 0.265 V\(^{-1}\), which may be attributed to a small variation in \(T_c\). Repetition of this analysis for all of the nanotubes studied produced normalized gradient values between 0.1 and 0.46 V\(^{-1}\). This conclusion may be reinforced by calculating \(T_s\) and \(T_c\) for the MWNT investigated in figure 3 and assuming a diameter of 13 nm. \(T_s\) was calculated using
equation (5) and had values between 0.017 and 0.036. $T_c$ was calculated by substituting these values into equation (4) and had values between $2 \times 10^{-3}$ and $8 \times 10^{-3}$. The smaller values of $T_c$ indicate there is more scattering at the contacts than in the semiconducting sub-bands, while the larger range of values of $T_c$ indicate there is a large variation in the scattering at the contacts. Therefore the contacts dominate the scale of the electrical characteristics, while the MWNTs themselves dominate the overall shape of the characteristics. A more detailed analysis of this work is given in reference [6].

**Figure 3.** The normalized gradient of a 10 µm long MWNT at different current limits. The current is increased by 2 µA every four voltage cycles from an initial limit of 4 µA to a final limit of 18 µA.

This data has few similarities to the results published by other groups and is thought to be due to the type of contacts that are made. For example, Poncharal et al. [5] used a low resistance, liquid metal to form their contacts, while here a high resistance contact was formed using a tungsten probe. Therefore, the differences in the results may be due to differences in the experimental set-up and the same normalization procedure applied to other results should result in similar normalized gradients.

4. Conclusions
In summary, the electrical characteristics of polymer coated MWNTs have been examined using a custom designed manipulation system within an SEM. The results show that the size of the conductance characteristics is dependent on the contacts that are formed. However, as the contact resistances are assumed to be independent of the voltage, the contacts do not control the overall shape of the characteristics. Therefore, it may be concluded that the conditioning seen in these devices is dependent on the contacts and the changes they experience over successive voltage cycles.

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