Multiwalled carbon nanotube films as temperature nano-sensors

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ABSTRACT

Most of the basic research on the electrical behavior of CNTs has been carried out on individual or bundle nanotubes. More recently random or oriented CNT networks (CNTN) are emerging as new material for electronic application. We present the fabrication of thick and dense CNTNs, in the form of freestanding films, and the study of their electric resistance as a function of the temperature, from -200 to +150 °C. A non-metallic behavior has been observed with a monotonic R(T). A good long-term stability and a behavioral accordance with the temperature measured Si or Pt thermistor are demonstrated. We underline that a transition from non-metallic to metallic can take place at few degrees below 0°C. A model involving regions of highly anisotropic metallic conduction separated by tunneling barrier regions can explain the non-metallic to metallic crossover, based on the competing mechanisms of the metallic resistance rise and the barrier resistance lowering.

Keywords: carbon nanotubes, bucky paper, temperature nano-sensor, non-metallic behavior

1 INTRODUCTION

The temperature dependence of the electric resistance of carbon nanotubes is an important topic for technological applications. A through understanding of it is relevant for the utilization of carbon nanotube networks as sensing element in temperature nano-sensors. A sensor of nanometric size can provide local accurate measurements of a rapidly changing temperature, while reducing the possibility of disturbing the neighboring environment. In addition, the small size sensor implies a very low power consumption.

For single and multi-wall CNTs, both a non-metallic (with negative dR/dT) and a metallic (with positive dR/dT) temperature dependence of the electric resistance has been reported [1-6] as well as a mixed behavior with a transition from non-metal to metal occurring a few tens degree below 0 °C [7-10]. A remarkable similarity between the temperature behavior of CNTNs and of highly conducting polymers (as for example blends of polyaniline dispersed in non conducting PMMA) has been pointed out and attributed to a common feature in the conduction mechanism, namely the presence of metallic conducting regions separated by insulating barriers. A heterogeneous model involving regions of highly anisotropic metallic conduction separated by tunneling barrier regions can explain the non-metallic to metallic transition by competing mechanism of the metallic resistance augmentation and the barrier resistance lowering [11].

Since most of the basic research on the electrical behavior of carbon nanotubes has been carried out on individual or bundle nanotubes, it is interesting to study other forms of interacting nanotubes, such as random or oriented networks in freestanding thick films.

In this paper we present the fabrication of thick and dense multiwalled carbon nanotube (MWCNT) freestanding films (often referred as bucky paper) and the study of their electric resistance as a function of the temperature, from -200 to +150 °C. been sometimes observed.

2 EXPERIMENTAL

2.1 CNT fabrication process

MWCNTs have been synthesized by ethylene catalytic chemical vapour deposition (CCVD) on Co/Fe-Al_2O_3 catalyst, prepared by wet impregnation of gibbsite (γ-$Al(OH)_3$) powder with cobalt acetate (2.5 wt%) and iron acetate (2.5 wt %) ethanol solution [12]. The catalyst was dried at 393 K for 720 min and preheated before synthesis at 70 K/min up to 973 K under N_2 flow. For the CNT synthesis a mixture of ethylene 10% v/v in helium was fed to a continuous flow microreactor at 973 K, with a runtime of 30 min. Gas flow rate and catalyst mass were 120 (stp)cm^3/min and 400 mg. The nanotubes were obtained by a very effective synthesis, yielding more than 95% conversion of the injected carbon.

The MWCNTs selectivity was about 100%, while to remove catalyst impurities the sample was treated

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with HF (46% aqueous solution), and the solid residue was washed with distilled water, centrifuged and finally dried at 353 K for 12 h. High purity multiwalled carbon nanotubes (>97%) were obtained.

To prepare a BuckyPaper free-standing sheet, 0.5 g of MWCNTs were suspended in 100 g of water in presence of 0.1 mg of sodium dodecyl sulfate, sonicated and then vacuum filtered onto a membrane support. After drying, a bucky paper was removed from the support as MWCNT films of different thickness and density.

The paper can be folded and cut with scissor and was sufficiently robust to let stable silver paint contacts to be formed and to withstand long thermal stresses.

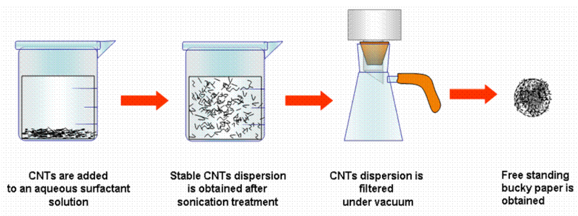

Figure 1: Scheme of the different steps for the production of the CNTNs.

2.2 Setup for electrical measurements

A 4-probe method was adopted to measure the low resistance of the CNT films, typically of ~1 Ω, and to overcome the problem of the comparatively high contact resistance. The electrical contacts were improved by making pads with smeared silver paint. Films of different but approximately rectangular shape, dimensions up to 3mm × 6mm and thicknesses between 300 and 500 µm, were measured by forcing a current of 1-10 mA through the outer probes and measuring the voltage thus developed between the inner ones. For this purpose a Keithley 4200 SCS was used as source and measurement unit (SMU). The temperature was monitored through a fast silicon temperature sensor (Infineon KT–11-6) and/or a platinum PT100 thermistor, mounted very close to the bucky paper and read by additional SMUs of the same Keithley 4200 SCS. The temperature cycles, with warming or cooling sweeps, were performed while operating the device in constant current mode and with a power consumption as low as 1 µW.

The temperature of the air-filled and high thermal capacity chamber, which was housing the sample, was varied by means of an external resistive heater; the measurements below ambient temperature were performed by flowing nitrogen vapours in the chamber or by inserting the sample in a dewar containing liquid nitrogen or helium.

Since considerably room temperature resistance drift was observed in non-treated samples, before systematic measurements, a few stabilising thermal annealing cycles, from room temperature up to about 100 °C, were performed. Thermal annealing is believed to make the connections between the CNTs and of the CNTs with the silver paint more robust and to evaporate adsorbates.

3 RESULTS AND DISCUSSION

3.1 Bucky Paper Characterization

Figure 2a shows a typical SEM picture of the as produced bundle of nanotubes grown from the catalyst, with a length in the range 100-200 µm. Bundle organisation, constituted of entangled nanotubes, is more clearly visible in the SEM picture of Figure 2b, and in TEM Figure 2c. Nanotubes are multiwalled with a diameter ranging from 10 to 30 nm, while the internal diameter varies between 5 and 10 nm (see Figure 2d).

In Figure 3 a SEM image of a final film is shown.

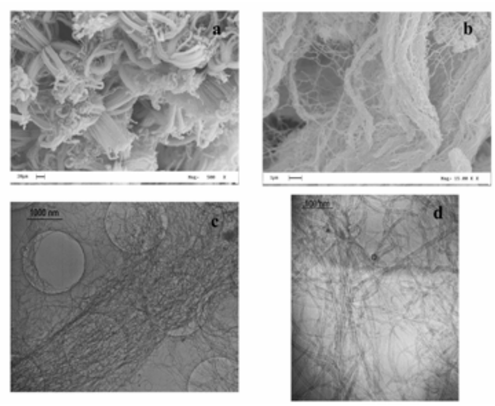

Figure 2: SEM image of as produced CNT bundles (a), of a particular of a bundle (b); TEM image of an as produced bundle (c), of CNTs at high resolution (d).

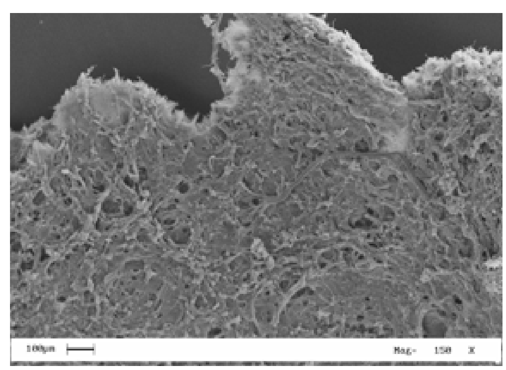

Figure 3: SEM image of the bucky paper

3.2 Electrical characterization

As expected, all the MWCNT freestanding films were highly conductive with a resistance around 1 Ω.

Figure 4 shows a typical result with a linearly decreasing resistance for raising temperature on the whole range investigated (from -40°C to +150°C). Several temperature sweeps, corresponding to warming up and cooling down cycles, were measured. A good reproducibility and a low hysteresis were obtained. These measurements also demonstrate that the CNT sensor and its contacts are not damaged by the temperature variations, as a consequence of a possible mismatch of the coefficients of thermal expansion at the interfaces of the device.

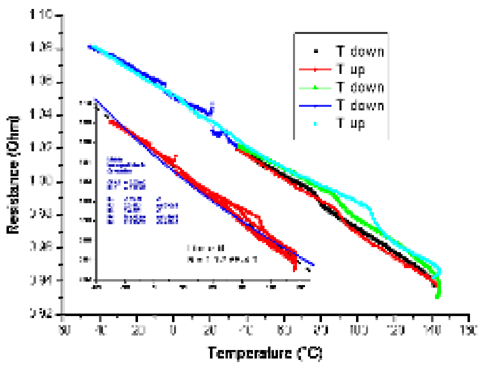

Figure 4: R-T characteristics of a bucky paper. The sample was heated and cooled down several times in the range -50 to 145 °C. The fits in the insert considers all the data together.

A linear fit to the data of figure 4, taken all together, can be used to estimate the temperature coefficient of resistance (TCR), defined as TCR = $1/R_0 \cdot dR/dT$ (where R is the resistance at temperature T and R_0 is the resistance at the standard temperature of 0°C). A negative TCR = -0.0007 is obtained and is consistent with values reported by other authors [6,13-15]. Such behavior is expected when the CNT network becomes thinner and less denser, i.e. with reduced metallic percolating paths, making a barrier tunneling mechanism dominant (see following).

The behavior of the bucky paper at lower temperatures was further tested with a different experimental setup, consisting of a Keithley 2400 used as source and meter unit connected to an insert that was slowly driven in or out of a dewar containing liquid helium. The curve shown in figure 5 confirms the non-metallic behavior, with lesser linearity.

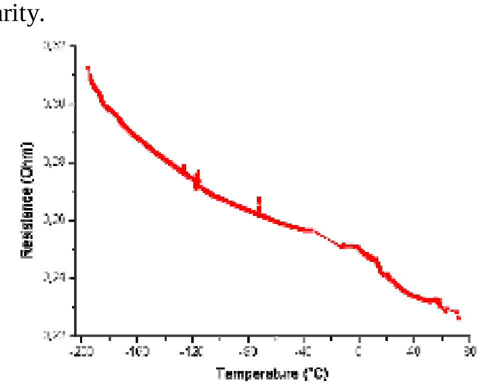

Figure 5: R-T characteristic of a CNTN at low temperature.

A different behavior is shown in figure 6. A sample, from the same batch of that used in the measurements of figures 4/5 was slowly heated from -45 till +140 °C (in a time of more than three hours). The curve obtained shows a non-metallic behavior at low temperatures which turns into a metallic one at T=-15°C.

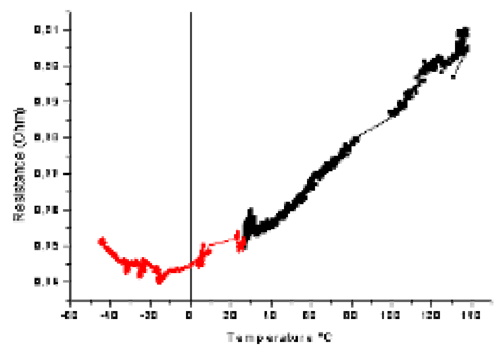

Figure 6: R-T characteristic of a bucky paper sample from the same batch of that used in the measurements of figures 4/5 and slowly heated from -45 to +140 °C.

A model of interrupted metallic conduction, with temperature dependent tunneling through thin electrical barriers separating metallic regions, has been suggested to account for the mixed non metallic-metallic behavior in quasi one-dimensional conductors, in which carriers cannot circumvent defects or other barriers to conduction [9,11]. If the barriers between metallic regions, intertube or inter-rope contacts or due to tubule defects are thin, a substantial conductance can still be seen in the absolute zero-temperature limit. As temperature increases, thermal fluctuations assist the tunnel and reduce the resistance (yielding a negative sign for the temperature coefficient, $dR/dT<0$). At higher temperatures, the usual increase in resistivity due to scattering of carriers by phonons may dominate the T dependence, thus leading to a change of behavior with a crossover and a valley in the R(T) curve. Backscattering by phonons is the main cause of the changeover to a metallic sign of dR/dT.

Such model can easily fit R-T experimental data with a non-metallic to metallic crossover.

3.3 CNTNs thermal response

Samples with a monotonic R(T) can be used to realize miniaturized temperature sensors, with fast response, repeatability, durability, etc. For an ideal sensor repeatability means to recover the same minimum/maximum resistance when temperature reaches the same minimum/maximum values.

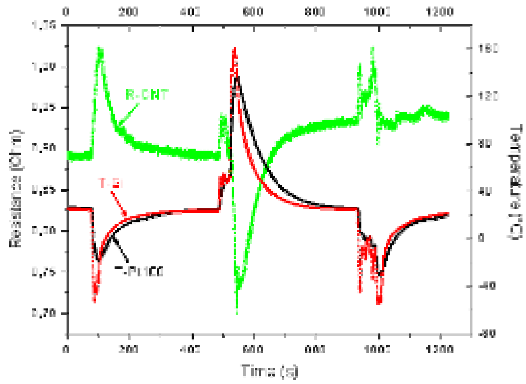

Figure 7: CNTN resistance and Si/Pt temperature vs time for a sample under heating/cooling fast cycles.

From figure 7 it is clearly seen that the resistance of our CNT sensor returns back to the same minimum/maximum value, with the same or an higher speed than the Si/Pt sensors.

To check the reliability of our MWCNT freestanding film we monitored its long-term stability by measuring the room temperature for a time of 24 hours. The result is shown in figure 8.

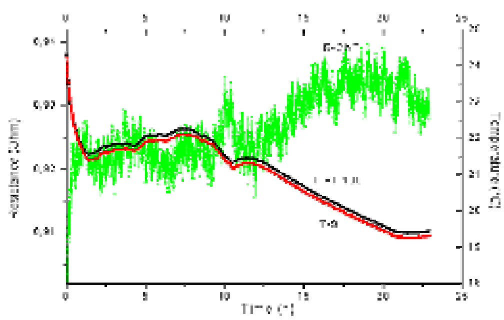

Figure 8: Room temperature monitored by the CNT film and Si/Pt thermistors.

A good accordance with the measurements performed by the Si/Pt thermistor are observed. The CNTN resistance fluctuation have successively discovered to be reduced by increasing the operating current.

4 CONCLUSIONS

In this paper, a study of the electric resistance vs temperature of freestanding MWCNT films has been reported in the aim of a possible application of carbon nanotubes as sensing element in temperature nano-sensors. A monotonic R(T) has been demonstrated, making the CNT films suitable as temperature sensors. Once protected from moisture and contaminants in an operational environment, CNTN films would have wide operating range, fast time response, low size and power consumption.

The temperature coefficient of resistance may not be so good as compared with the ones for platinum temperature sensors. However the nano-size of CNTNs can result in a very high sensitivity to the environmental temperature change and in an excellent time response, which is highly desirable for local measurements in systems with very rapid temperature variations and where the perturbation introduced by the thermometer has to be reduced as much as possible.

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