Available online at www.sciencedirect.com
ScienceDirect
Optical Materials 29 (2006) 122–125
OPTICAL Materials
www.elsevier.com/locate/optmat

Electrical properties of carbon nanofibers synthesized using carbon disulfide as precursor

D. Mendoza *

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, 04510 México DF, Mexico

Available online 2 May 2006

Abstract

Electrical characterization of carbon nanofibers synthesized by a thermal chemical vapor deposition technique using carbon disulfide as the source of carbon is reported. Electrical resistance of mats and thin films samples of carbon nanofibers has been measured in the range of temperatures of 100–430 K. The electrical behavior of the mats can be explained within the Luttinger liquid model, but thin films show an anomaly around 273 K that may be related to charge trapping enhanced by the presence of water molecules.

Keywords: Carbon nanotubes and nanofibers; Electrical properties; Luttinger liquid; Thin films; Sulfur

1. Introduction

Carbon nanotubes and nanofibers are unique nanostructures owing to their transport properties. In the case of metallic single wall carbon nanotubes (SWNT), their transport properties are explained in terms of one-dimensional conductor within the so called Luttinger liquid theory (LL) in which the electron–electron interaction leads to the suppression of the tunneling density of states [1]. In experimental measurements this effect is usually observed at low temperatures as a depletion in the conductance at zero bias, and as power laws of the conductance as a function of temperature and bias voltage [2,3]. Nevertheless, in the case of multi wall carbon nanotubes (MWNT), there is controversy whether their transport properties can be explained within the LL model [4] or if other microscopic model is necessary to explain the observed experimental behavior [5,6].

On the other side, it is also interesting to study the transport properties of carbon nanofibers because their structure is different to both SWNT and MWNT. Carbon nanofibers have several tens of nanometer diameters and it has been suggested that subtle differences are expected between their physical properties relative to the corresponding properties in MWNT [7].

In this work we present experimental results of electrical measurements made on carbon nanofibers in the range of temperatures of 100–430 K. It is found that the temperature dependence of the electrical resistance of nanofiber mats can be fitted using the LL model along with a linear contribution. Electrical characterization of nanofiber films is also presented.

2. Experimental

Carbon nanofibers were synthesized by a thermal chemical vapor deposition technique, using carbon disulfide as the source of carbon and iron as the catalyst on fused quartz substrates. As the source of the iron catalyst a 120 mM solution of $Fe(NO_3) \cdot 9H_2O$ in ethanol was prepared and spin-coated on the substrates. These substrates were loaded at the center of an horizontal quartz tube furnace. The tube was purged with argon and the temperature was raised to 900 °C under an argon flow of 126 sccm, then the flow of argon was switched-off and replaced by pure hydrogen (450 sccm, 5 min) directly into the tube furnace.

* Tel.: +52 5622 4735; fax: +52 5616 1251.
E-mail address: doroteo@servidor.unam.mx

0925-3467/$ - see front matter
doi:10.1016/j.optmat.2006.03.019

After this process, the hydrogen flow is reduced to 88 sccm and passed through a bubbler containing 20 ml of carbon disulfide during a period of 60 min. At the final of this stage, the flow of hydrogen through the bubbler is switched off and pure argon (126 sccm) is introduced directly into the tube furnace. Finally, the furnace is switched off and cooled to room temperature under the argon flow.

For the electrical characterization two kind of samples were prepared: in one kind the as grown nanofibers were gently scratched off from the substrate in a form of a mat and transferred to a glass substrate using a drop of acetone to compact the sample. Silver paste was used as electrodes for two terminal electrical measurements. For the second kind of samples, a clean glass substrate was placed on the quartz substrate where the nanofibers were grown and pressed gently together. With this procedure a thin film of nanofibers is attached to the glass substrate. In this case, silver paste or evaporated silver thin films were used as electrodes.

Electrical characterization was made in an evacuated chamber ($P \sim 5 \times 10^{-5}$ Torr) equipped with a heater and a cold stage for cooling below room temperature using liquid nitrogen. Firstly the sample temperature was raised to 160 °C and then the electrical current through the sample was measured in the cooling process with a fixed bias voltage.

3. Results and discussion

Scanning electron microscopy (SEM) images of the samples prepared for electrical characterization are shown in Fig. 1. SEM observations show carbon nanofibers with diameters in the range of 50–500 nm and lengths up to 500 μm. In the limit of resolution of the used SEM, we did not observe the existence of other particles than the nanofibers, but an EDS analysis on the mat sample shows the presence of small quantities of sulfur (in the order of 0.25 at.% compared to carbon). Note the random position of the nanofibers in both the mat sample (a) and in the film (b).

In Fig. 2(a) a graph of the experimental results of the resistance against temperature of the mat of nanofibers is presented. Here we can note a semiconductor-like behavior as a function of temperature, but the data can not be fitted to an activated transport model with the form $R(T) = R_0 \exp(C/T)$. We also tried other models for conduction described by the general expression $R(T) = R_0 \exp(T_0/T)^n$, that includes the variable-range hopping mechanism [8] and the model where the MWNT are considered as a disordered quasi-one-dimensional conductor, in the last case $n = 1/2$ [9]. We tried to fit the experimental data using $n = 1/2$, 1/3 and 1/4 but deviations with any of these values are found. Exploring the possibility that the nanofibers might follow a Luttinger liquid behavior, as has been reported for SWNT and MWNT, with the form $R(T) = R_0 T^{-\alpha}$, in Fig. 2(b) a plot of Log(R) versus Log(T) is presented. We can see in this figure that the experimental

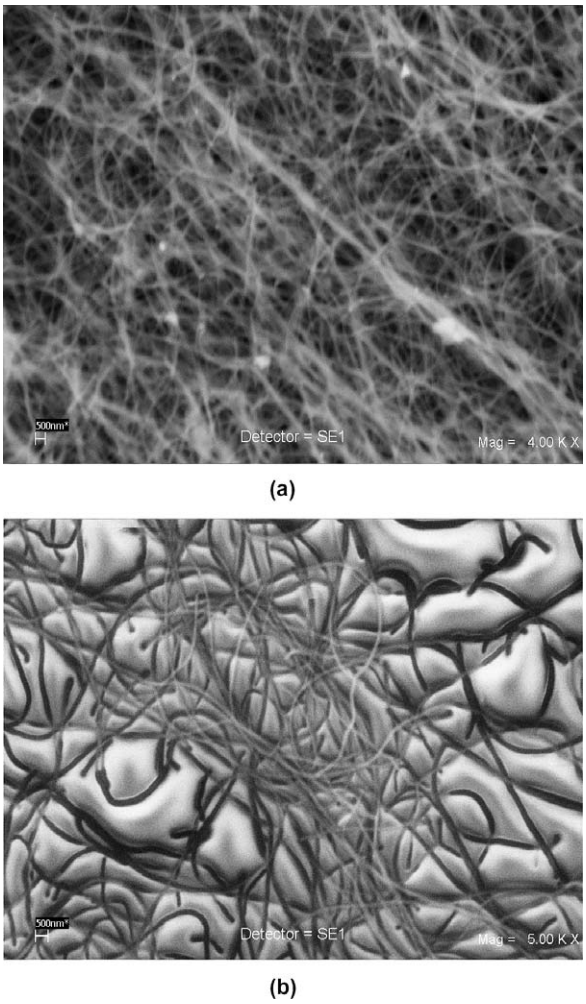

Fig. 1. SEM photographs of the carbon nanofibers samples used for the electrical characterization (electrodes not shown): mat sample (a) and thin film (b). The bright zones in (b) are artifacts due to the charging effect of the glass substrate. The scale bar in both images is 500 nm.

data can not be fitted to this model. Finally, considering that the sample consists of a mat of interconnected nanofibers, forming a random network of junctions (see Fig. 1(a)), we add other term to the resistance to take in account the junctions resistance: $R(T) = R_0 T^{-\alpha} + R_1 T$. This model has been successfully used to explain transport properties of SWNT [10] as well as MWNT [11] where the effective resistance of the sample is considered as series resistor formed by the Luttinger liquids (carbon nanotubes) and Fermi liquids (junctions). Thus the linear temperature contribution to the resistance is attributed to a Fermi liquid behavior of the junctions in the mat of nanotubes. In Fig. 3 a very good fit of the experimental data to this model is observed with $\alpha = 0.224$. It has been found experimentally that the values of the exponent α within the Luttinger liquid model ranges between 0.3–0.6 [2] up to 2.2 [3] for SWNT and 0.36–0.95 for MWNT [4]. The somehow small value for the parameter α found in our experiments might be related to structural differences of the nanofibers compared to SWNT and MWNT structures.

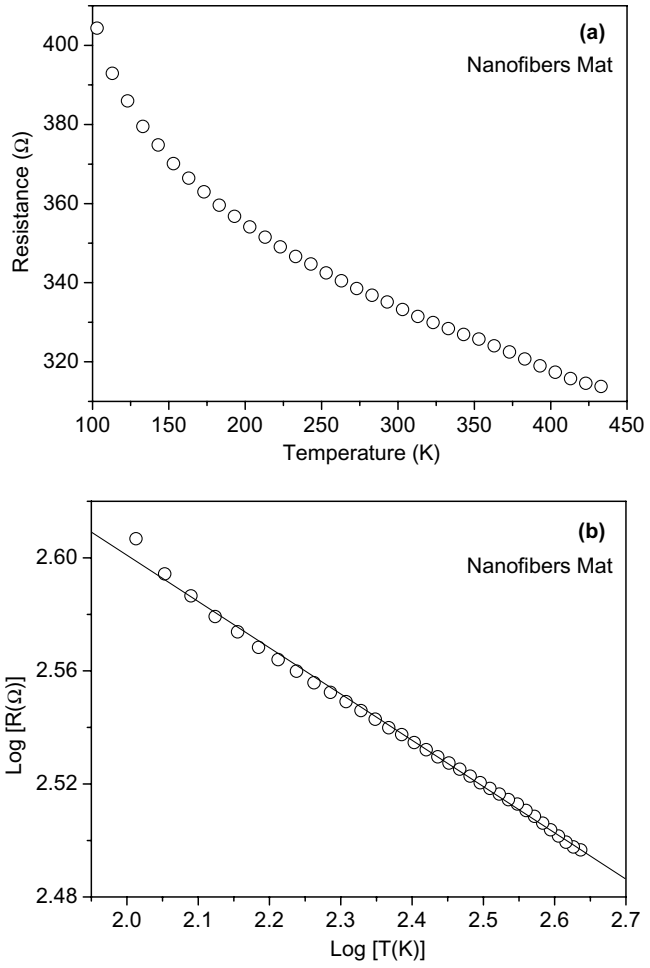

Fig. 2. Electrical resistance against temperature for the mat sample in a linear (a) and in a log–log scale (b). The straight line in (b) is a fit to the experimental data using the model $R(T) = CT^{-\alpha}$.

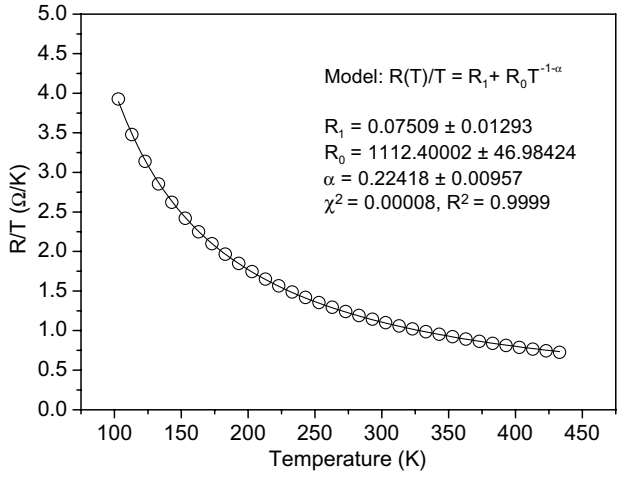

Fig. 3. Same experimental data of the mat shown in Fig. 1(a) but plotting $R(T)/T$ against temperature. The continuous line corresponds to a fit using the model $R(T) = R_0T^{-\alpha} + R_1T$ divided by the temperature, the corresponding value for α is 0.224 (see text).

Then we conclude that the transport properties of the carbon nanofibers studied in this work can be explained within the Luttinger liquid model, although a linear contribution to the resistance must be included to take into account Fermi liquid interactions, which is relevant mainly at higher temperatures.

As a final part of this report, in Fig. 4 the electrical resistance against temperature of two films is presented. Here we can observe a great difference compared to the electrical behavior of the mat (Fig. 2(a)). This is an intriguing result because being the same material, the only difference in both cases is the procedure to prepare the sample for electrical characterization (see Fig. 1). In the case of the films, in the cooling process a semiconductor-like behavior and a small jump is observed around $T = 273$ K, but in the heating process a maximum in the electrical resistance is observed around the same temperature.

To date we do not have a clear explanation of that phenomenon. We believe it may be related to an intimate interaction of the nanofibers and the substrate, which is enhanced in the form of thin film compared to the case

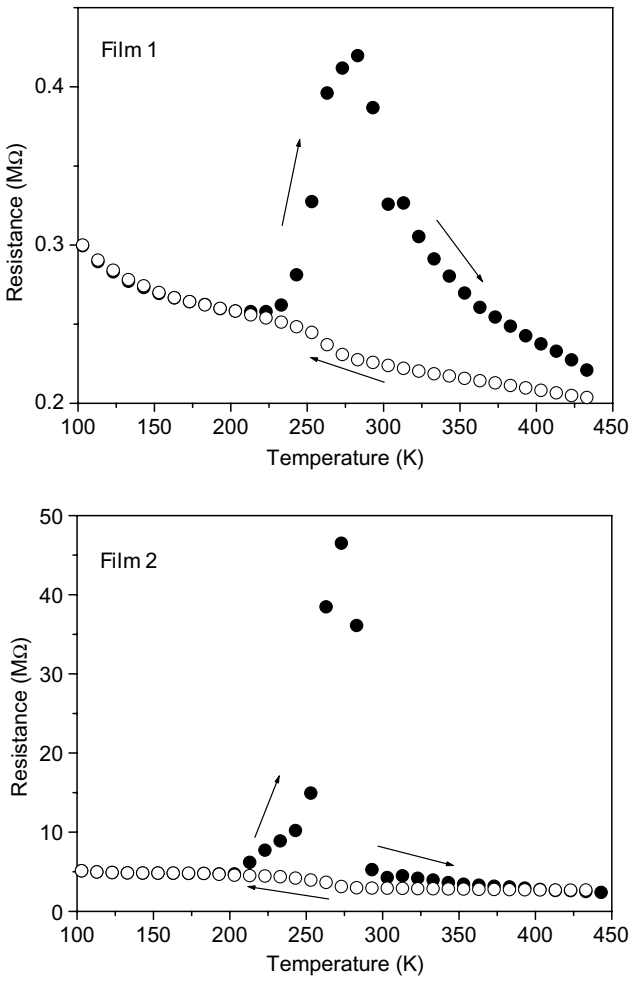

Fig. 4. Plot of resistance against temperature for two thin films of carbon nanofibers. The two films were made in similar conditions, but for the electrical measurements silver paste (film 1) and evaporated silver thin films (film 2) were used as electrodes. The arrows indicate the direction in which the temperature was varied in the measurements beginning at the highest temperature.

of the mat sample. Careful measurements around $T = 273$ K in the mat sample did not reveal the existence of the anomaly observed in thin films. On the other hand, it has been reported hysteresis in the electrical characteristics of field-effect transistor made with carbon nanotubes and the phenomenon has been attributed to the charge trapping by the nanotubes [12,13]. It is proposed that charge trapping is enhanced by the presence of water molecules adsorbed in the nanotube-substrate vicinity and by the strong interaction of OH radicals with silicon oxide surface [12]. We are unaware of the existence of any report related to the presence of hysteresis in the electrical resistance as a function of temperature in carbon nanotubes, but we believe that the charge trapping enhanced by the presence of water molecules may be related to the effect we observe in nanofiber thin films. This possibility is reinforced because the anomaly in the electrical resistance (the jump and the maximum) is located around the freezing temperature of water, but this phenomenon deserves further investigation.

4. Conclusions

Electrical resistance as a function of temperature of carbon nanofibers has been measured for two kind of samples: mats and thin films. In the case of mats, a very good fit to the experimental data is found if one assumes that the body of the nanofiber behaves as a Luttinger liquid system, but it is necessary to add a linear temperature contribution to the electrical resistance to take into account the interconnections between the nanotubes in the mat. In the case of films, hysteresis in the electrical resistance against temperature and an anomaly around 273 K are observed. We believe that this phenomenon may be related to charge trapping enhanced by the presence of water molecules, but more work is necessary to clarify this issue.

Acknowledgements

I thank P. Santiago for useful discussions related to the structural properties of carbon nanofibers and to J. Guzmán (IIM-UNAM) for SEM characterization.

References

[1] H. Ishii, H. Kataura, H. Shiozawa, H. Yoshioka, H. Otsubo, Y. Takayama, T. Miyahara, S. Susuki, Y. Achiba, M. Nakatake, T. Narimura, M. Higashiguchi, K. Shimada, H. Namatame, M. Taniguchi, Nature 426 (2003) 540.
[2] M. Bockrath, D.H. Cobden, J. Lu, A.G. Rinzler, R.E. Smalley, L. Balents, P.L. McEuen, Nature 397 (1999) 598.
[3] Z. Yao, H.W. Postma, L. Balents, C. Dekker, Nature 402 (1999) 273.
[4] E. Graugnard, P.J. de Pablo, B. Walsh, A.W. Ghosh, S. Datta, R. Reifenberger, Phys. Rev. B 64 (2001) 125407.
[5] V. Krstic, S. Blumentritt, J. Muster, S. Roth, A. Rubio, Phys. Rev. B 67 (2003) 041401.
[6] D. Mendoza, F. Morales, R. Escudero, Solid State Commun. 130 (2004) 317.
[7] M.S. Dresselhaus, M. Endo, in: Carbon Nanotubes: Synthesis, Structure, Properties, and Applications. Topics in Applied Physics, vol. 80, Springer, Berlin, 2001.
[8] N. Mott, Conduction in Non-Crystalline Materials, Clarendon Press, Oxford, 1987.
[9] E.G. Mishchenko, A.V. Andreev, L.I. Glazman, Phys. Rev. Lett. 87 (2001) 246801.
[10] D.J. Bae, K.S. Kim, Y.S. Park, E.K. Suh, K.H. An, J. Moon, S.C. Lim, S.H. Park, Y.H. Jeong, Y.H. Lee, Phys. Rev. B 64 (2001) 233401.
[11] L. Valentini, I. Armentano, P. Santilli, J.M. Kenny, L. Lozzi, S. Santucci, Diamond Relat. Mater. 12 (2003) 1524.
[12] W. Kim, A. Javey, O. Vermesh, Q. Wang, Y. Li, H. Dai, Nano Lett. 3 (2003) 193.
[13] S. Wang, P. Sellin, Appl. Phys. Lett. 87 (2005) 133117.