Correlating electrical resistance to growth conditions for multiwalled carbon nanotubes

C. Lan P. B. Amama

T. S. Fisher R. G. Reifenberger

Correlating electrical resistance to growth conditions for multiwalled carbon nanotubes

Chun Lan[a)]
Department of Physics, Purdue University, West Lafayette, Indiana 47907
and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907

Placidus B. Amama
Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907

Timothy S. Fisher
School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907
and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907

Ronald G. Reifenberger
Department of Physics, Purdue University, West Lafayette, Indiana 47907
and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907

(Received 18 May 2007; accepted 5 August 2007; published online 28 August 2007)

A correlation between growth temperature and electrical resistance of multiwalled carbon nanotubes (MWNTs) has been established by measuring the resistance of individual MWNTs grown by microwave plasma-enhanced chemical vapor deposition (PECVD) at 800, 900, and 950 °C. The lowest resistances were obtained mainly from MWNTs grown at 900 °C. The MWNT resistance is larger on average at lower (800 °C) and higher (950 °C) growth temperatures. The resistance of MWNTs correlated well with other MWNT quality indices obtained from Raman spectra. This study identifies a temperature window for growing higher-quality MWNTs with fewer defects and lower resistance by PECVD. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2776022]

Plasma-enhanced chemical vapor deposition (PECVD) offers a reliable method of producing graphitized, vertically aligned multiwalled carbon nanotubes (MWNTs).[1,2] A distinguishing feature of the PECVD process is the presence of a highly reactive plasma environment, which enhances the decomposition of the hydrocarbon feedstock during carbon nanotube (CNT) growth. This results in a significant decrease in the activation energy,[1] allowing the growth of CNTs over a wide temperature range (200–950 °C).[1,2]

The dissociation of the carbon feedstock, carbon diffusion in the catalyst particles, and the crystallinity of CNTs all critically depend on temperature. On the basis of the vapor-liquid-solid model,[3,4] the diffusion of carbon in the catalyst is generally considered to be the rate-determining step.[5] The driving force for carbon diffusion in the catalyst could be either a temperature or a concentration gradient.[4] It has been suggested that higher growth temperature (>800 °C) improves the quality of CNTs.[6] However, growth temperatures higher than ~1050 °C seem to be detrimental to the quality of CNTs, as judged by the increase of bamboo structures, amorphous carbon, and carbon particulates.[7]

Although electrical transport in CNTs has been studied extensively,[8–10] a systematic electrical characterization of individual CNTs grown at different temperatures has not yet been reported. Typically, electrical characterization involves bundles of CNTs,[11–13] providing little information about the properties of individual CNTs. In what follows, we present resistance measurements of individual MWNTs randomly selected from MWNTs grown at 800, 900, and 950 °C. Our data indicate a statistically significant correlation between the resistance of MWNTs and growth temperature. The work also reveals a temperature window that produces MWNTs with relatively low electrical resistance.

The MWNT samples were grown from Fe_2O_3 nanoparticles at 800, 900, and 950 °C in a SEKI AX5200S microwave PECVD reactor. A detailed description of the PECVD system and the relevant CNT growth conditions has been reported elsewhere.[14] The catalyst fabrication process followed a procedure previously described.[15]

MWNT samples were characterized using a field emission scanning electron microscope (FESEM) (Hitachi S4800) and a Raman spectrometer (Renishaw Raman imaging microscope) with a 785 nm (1.58 eV) laser as the excitation source. The diameters of the MWNTs grown at the various temperatures are in the range of 50–250 nm. MWNTs ~30 μm long were intentionally selected to minimize the contact resistance which scales roughly with inverse contact area.

Representative Raman spectra are presented in Fig. 1(a). A least-squares deconvolution[16] of the G band (~1590 cm^{-1}) and the D band (~1310 cm^{-1}) was carried out, as shown in the figure. Raman spectra at four different places from each of four separate growth runs were analyzed. The ratio of the integrated intensity of the deconvoluted G band relative to the D band (I_G/I_D) provides an index to evaluate the quality of the MWNTs. The full width at half maximum (FWHM) of the deconvoluted G band provides a second measure of the degree of graphitization of CNTs.[17] The average values of the FWHM of the G band and the I_G/I_D ratios of MWNTs are plotted in Fig. 1(b). The error bars represent the standard deviations of the fitting parameters obtained from the Raman spectra from four samples at four locations per each sample. The highest I_G/I_D and the lowest FWHM are observed for MWNTs grown at 900 °C,

[a)]Electronic mail: lan0@physics.purdue.edu

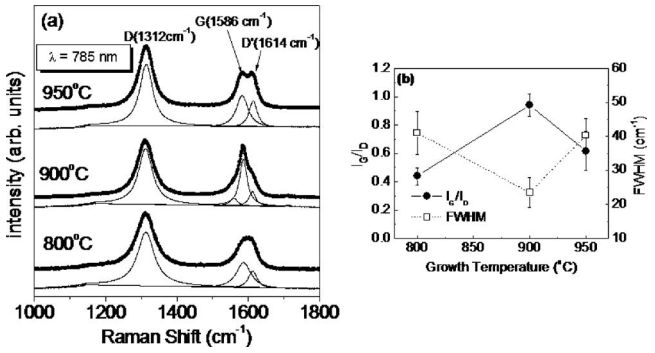

FIG. 1. In (a), a plot of representative Raman spectra (solid dots) from MWNTs grown at 800, 900, and 950 °C. The least squares deconvolution of the Raman spectra (thin line) is also plotted. In (b), average values of the I_G/I_D ratio and the FWHM of the deconvoluted *G* band of MWNTs obtained from Raman spectra.

suggesting that this growth temperature yielded well graphitized MWNTs of the highest purity with the fewest defects. The degree of graphitization and the purity of MWNTs decreased at lower (800 °C) and higher (950 °C) temperatures.

Individual MWNTs were randomly selected from the samples for characterization by two-probe *I-V* measurements. The MWNTs were placed onto a glass substrate and were masked by manipulating a 4 μm diameter W wire using techniques described previously.[18] Using this wire shadow mask, Ti/Au electrodes were then thermally evaporated onto both ends of an individual MWNT. The contact length under each electrode was approximately 1/2 of the total length of the MWNT minus the 4 μm length in the middle. We prepared 34 samples in total. Similar sample preparation techniques were used for all samples to ensure the same separation between the two electrodes. The contact resistance is controlled by following the same evaporation procedure for each sample. Low bias (±0.1 V) *I-V* measurements revealed a linear behavior for all the prepared MWNTs. After electrical measurements, each MWNT sample was further examined by FESEM to estimate diameters and to evaluate whether any structural damage occurred.

When measuring the resistance of MWNTs longer than the coherence length, the measured resistance should reflect the average number of defect sites in the MWNT. In our studies, the MWNT growth temperature is the dominant variable. Thus, it is possible that our *I-V* data contain information about the MWNT defects introduced by growth temperature.

When current flows through a MWNT, it favors the outermost shells because these shells are in direct contact with the deposited electrode.[19,20] Under these conditions, the resistance will be approximately given by

$$R = \rho \frac{L}{\pi d t^*},$$

where d is the diameter of the outermost shell, L is the length, ρ is an intrinsic resistivity of the MWNT, and t^* (which is difficult to determine accurately) is the effective thickness through which the current flows. From our resistance data, the ratio ρ/t^* of individual MWNTs at each growth temperature can be determined.

Histogram plots show the distribution of ρ/t^* from all the measured samples in Fig. 2. We infer that the values of

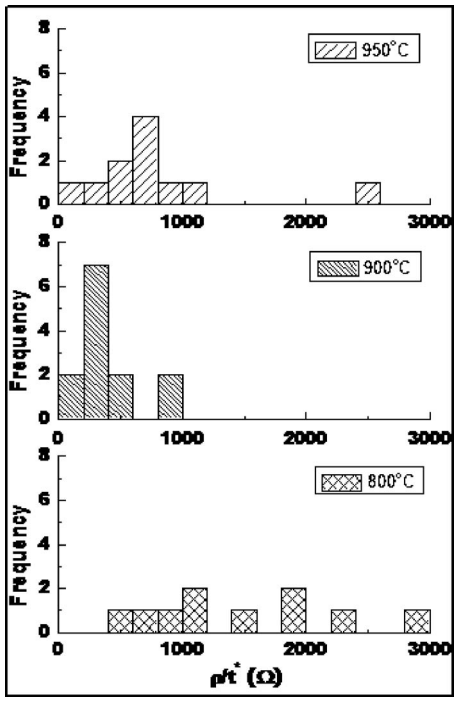

FIG. 2. Histograms showing the distribution of resistivity divided by effective shell thickness t^* at growth temperatures of 800, 900, and 950 °C for the 34 MWNTs investigated in this study.

ρ/t^* obtained from MWNTs grown at temperatures of 800, 900, and 950 °C have different distributions. Student *t* tests indicate that at the 85% confidence level, the mean of each distribution with respect to any other does not overlap, indicating that the growth temperature affects ρ/t^* significantly. The lowest ρ/t^* values appear more frequently at 900 °C. Assuming that the ρ/t^* reflects the average number of defects in the MWNTs, the data suggest that the most favorable growth temperature for producing low-defect MWNTs by PECVD is near 900 °C. This conclusion is also consistent with the Raman results discussed previously.

We find that MWNTs grown at 900 °C can exhibit both high and low ρ/t^* values. For example, two MWNTs from the same growth run have ρ/t^* of 252 and 836 Ω. What might account for this increase in ρ/t^* by a factor of 3.3 after taking into account any variation in average diameter? To answer this question, FESEM characterization of the two MWNTs were carried out, as shown in Figs. 3(a) and 3(b). The FESEM images indicate that the MWNT with low resistance possesses a well defined diameter that varies by ~2% along its length, while the higher-resistance MWNT has a diameter that varies by as much as ~12% over its length. This result suggests that at low bias, any significant variation

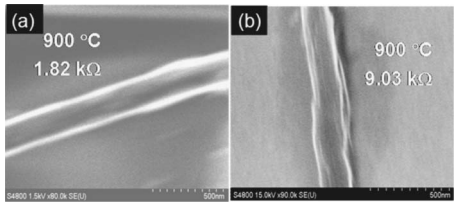

FIG. 3. FESEM images of two individual MWNTs grown under identical conditions at 900 °C. (a) A FESEM image of an individual MWNT with a measured resistance is 1.82±0.01 kΩ. (b) A FESEM image of another MWNT with a larger resistance. In this case, the measured resistance is 9.03±0.01 kΩ.

in diameter is likely to add additional resistance. This suggestion provides further insight into the nature of the defects that influences the electrical properties of MWNTs at low bias.

A few published studies report electrical measurements on a statistically significant number of CNT samples. Dohn *et al.* found from measurements of 39 MWNTs grown by CVD (length of 3 μm, diameters ranging from 30 to 100 shells) an average four-probe resistance of 4.7 kΩ.[21] Wakaya *et al.* found from measurements of 11 MWNTs grown by the arc discharge method (lengths between 0.66 and 2.82 μm, diameters not specified) values of resistance ranging from 30 kΩ to 8.8 MΩ.[22] These results can be compared to our average value of 3.5 ± 2.6 kΩ obtained for the PECVD MWNTs grown at 900 °C.

In summary, we have conducted a study that characterizes the properties of MWNTs by measuring *I-V* for randomly selected individual MWNTs grown at 800, 900, and 950 °C by PECVD. The data suggest that MWNTs grown at 900 °C contain the fewest defect sites on average, as evidenced by the majority of the low resistance (specifically, the ρ/t^* ratio) amongst all the measured MWNTs. The measured resistances correlate well with the quality of MWNTs based on the I_G/I_D ratios and the FWHM of the *G* band obtained from Raman spectra. The main benefit of this work is the identification of a favorable temperature window that enhances the PECVD growth of high-quality MWNTs with superior electrical transport properties.

The authors gratefully acknowledge the funding from the NASA-Purdue Institute for Nanoelectronics and Computing (INaC) and the Birck Nanotechnology Center. The authors are grateful to Lynne Taylor at the Department of Pharmacy, Purdue University for access to the 785 nm excitation Raman system. TSF gratefully acknowledges support from the National Science Foundation (CBET–0646015).

[1] S. Hofmann, C. Ducati, J. Robertson, and B. Kleinsorge, Appl. Phys. Lett. **83**, 135 (2003).
[2] M. Meyyappan, L. Delzeit, A. Cassell, and D. Hash, Plasma Sources Sci. Technol. **12**, 205 (2003).
[3] G. W. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
[4] A.-C. Dupuis, Prog. Mater. Sci. **50**, 929 (2005).
[5] S. Hofmann, G. Csányi, A. C. Ferrari, M. C. Payne, and J. Robertson, Phys. Rev. Lett. **95**, 036101 (2005).
[6] S. B. Sinnott and R. Andrews, CRC Crit. Rev. Solid State Mater. Sci. **26**, 145 (2001).
[7] W. Z. Li, J. G. Wen, and Z. F. Ren, Appl. Phys. A: Mater. Sci. Process. **74**, 397 (2002).
[8] E. Graugnard, P. J. de Pablo, B. Walsh, A. W. Ghosh, S. Datta, and R. Reifenberger, Phys. Rev. B **64**, 125407 (2001).
[9] K. Molhave, S. B. Gudnason, A. T. Pedersen, C. H. Clausen, A. Horsewell, and P. Boggild, Nano Lett. **6**, 1663 (2006).
[10] P. J. de Pablo, S. Howell, S. Crittenden, B. Walsh, E. Graugnard, and R. Reifenberger, Appl. Phys. Lett. **75**, 3941 (1999).
[11] M. Nihei, A. Kawabata, D. Kondo, M. Horibe, S. Sato, and Y. Awano, Jpn. J. Appl. Phys., Part 1 **44**, 1626 (2005).
[12] L. Langer, L. Stockman, J. P. Heremans, V. Bayot, C. H. Olk, C. Vanhaesendonck, Y. Bruynseraede, and J. P. Issi, J. Mater. Res. **9**, 927 (1994).
[13] M. Radosavljevic, J. Lefebvre, and A. T. Johnson, Phys. Rev. B **64**, 241307 (2001).
[14] M. R. Maschmann, P. B. Amama, A. Goyal, Z. Iqbal, R. Gat, and T. S. Fisher, Carbon **44**, 10 (2006).
[15] P. B. Amama, M. R. Maschmann, T. S. Fisher, and T. D. Sands, J. Phys. Chem. B **110**, 10636 (2006).
[16] A. M. Rao, A. Jorio, M. A. Pimenta, M. S. S. Dantas, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. Lett. **84**, 1820 (2000).
[17] A. Yoshida, Y. Kaburagi, and Y. Hishiyama, Carbon **44**, 2333 (2006).
[18] P. J. dePablo, E. Graugnard, B. Walsh, S. Datta, and R. Reifenberger, Appl. Phys. Lett. **74**, 323 (1999).
[19] P. G. Collins, M. S. Arnold, and P. Avouris, Science **292**, 706 (2001).
[20] C. Schönenberger, A. Bachtold, C. Strunk, J.-P. Salvetat, and L. Forró, Appl. Phys. A: Mater. Sci. Process. **69**, 283 (1999).
[21] S. Dohn, K. Mølhave, and P. Bøggild, Sens. Lett. **3**, 300 (2005).
[22] F. Wakaya, K. Katayama, and K. Gamo, Microelectron. Eng. **67-68**, 853 (2003).