ELSEVIER

Diamond and Related Materials 10 (2001) 1947–1951

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

Synthesis of high-density carbon nanotube films by microwave plasma chemical vapor deposition

U. Kim[a,*], R. Pcionek[a], D.M. Aslam[a], D. Tománek[b]

[a] *Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI 48824, USA*
[b] *Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA*

Received 1 August 2000; accepted 19 January 2001

Abstract

Nanotubes with diameters ranging from 20 to 400 nm and densities in the range of 10^8–10^9 cm^{-2}, produced on metal-coated silicon by microwave plasma chemical vapor deposition, show various shapes depending upon: (i) growth conditions; and (ii) pre- or post-growth treatment of the samples. Presence of nitrogen in the growth or pre-growth atmosphere increases the density and vertical growth rate of nanotubes. The growth rate on an iron-coated substrate is higher than on a nickel-coated substrate. A cleaning procedure, consisting of ultrasonic treatment of nanotubes in methanol, is demonstrated.

Keywords: Carbon nanotube; Microwave plasma chemical vapor deposition (MPCVD)

1. Introduction

Since their discovery [1] using arc discharge evaporation, carbon nanotubes have been the subject of numerous investigations [2–6] because of their unique electronic and mechanical properties. A precise control of the fabrication method including patterning is required for potential applications in electronics [7,8], field emission displays [9–12], biomedical devices and nanoelectromechanical systems (NEMS) [13]. Aligned carbon nanotubes have been obtained using chemical vapor deposition (CVD) on flat substrates [4], and by pyrolysis of acetylene on cobalt within a nano-channel alumina template [14]. Bower et al. [15] showed that aligned carbon nanotubes can be grown perpendicular to the local substrate surface, regardless of the surface tilt or shape, using microwave plasma CVD (MPCVD). The alignment is induced by the electrical self-bias field imposed on the substrate surface from the plasma environment.

In the present study, we make use of the many control parameters accessible in an MPCVD reactor to selectively grow nanotubes with particular morphologies. Similar to all other nanotube synthesis techniques, incorporation of defects cannot be avoided during the growth. A post-growth cleaning process is usually required before using the nanotubes in device structures. In this article, we report: (i) a uniform, high-density growth; and (ii) a cleaning procedure for carbon nanotubes.

2. Experimental

The flexibility of the MPCVD system, which permits a contamination-free processing and a modification of plasma shape through tuning of the cavity, allows syn-

* Corresponding author. Tel.: +1-517-353-6329; fax: +1-517-353-1980.
E-mail address: kimungsi@egr.msu.edu (U. Kim).

0925-9635/01/$ - see front matter
PII: S0925-9635(01)00384-3

thesis of a wide variety of carbon allotropes, ranging from nano-diamond [16] to nanotubes. Nanotubes in the present study are fabricated by MPCVD using iron (Fe) or nickel (Ni) as transition metal catalysts on titanium coated silicon substrates. A thin film of Ni (100 nm) is sputter deposited, or ferric nitrate [$Fe(NO_3)_3$] dissolved in methanol is coated (100–300 nm) on the substrate. Typical parameters varied in this study are: (i) growth temperature (450–850°C), growth time (0.5–120 min) and atmosphere ($N_2/H_2/CH_4$), and (ii) pre- and post-growth treatment (N_2/H_2). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize nanotube properties such as diameter, length, orientation, uniformity and density.

3. Results and discussion

Fig. 1 shows an overview of nanotube structures grown under varying deposition parameters as detailed in Table 1. A very uniform growth is achieved at temperatures between 650 and 750°C. Both vertical and horizontal growth of nanotubes was observed. A pre-growth treatment in nitrogen plasma enhances vertical growth. As shown in Fig. 1a, clusters are formed on top of the nanotubes during deposition at 650°C. The diameters of tubes grown under these conditions are in the range of 20–100 nm, implying multi-wall nanotubes. Energy-dispersive spectroscopy (EDS) indicates the presence of carbon in these clusters. Increasing the deposition temperature to 750°C reduces the size of these clusters, but increases the diameter of the tubes to 100–400 nm as shown in Fig. 1b. We interpret this diameter increase by improved growth kinetics at higher temperatures, in agreement with the conclusions of Thess et al. [2]. As seen in Fig. 1c, the build-up of clusters is strongly suppressed if nanotubes are grown by placing the metal-coated substrate upside down, leaving a gap between the growing surface and the substrate holder. In this case, tubes are grown downward and the plasma has to reach the growing surface. At the growth temperature of 650°C, the tube lengths are found to increase from approximately 1 μm to 50

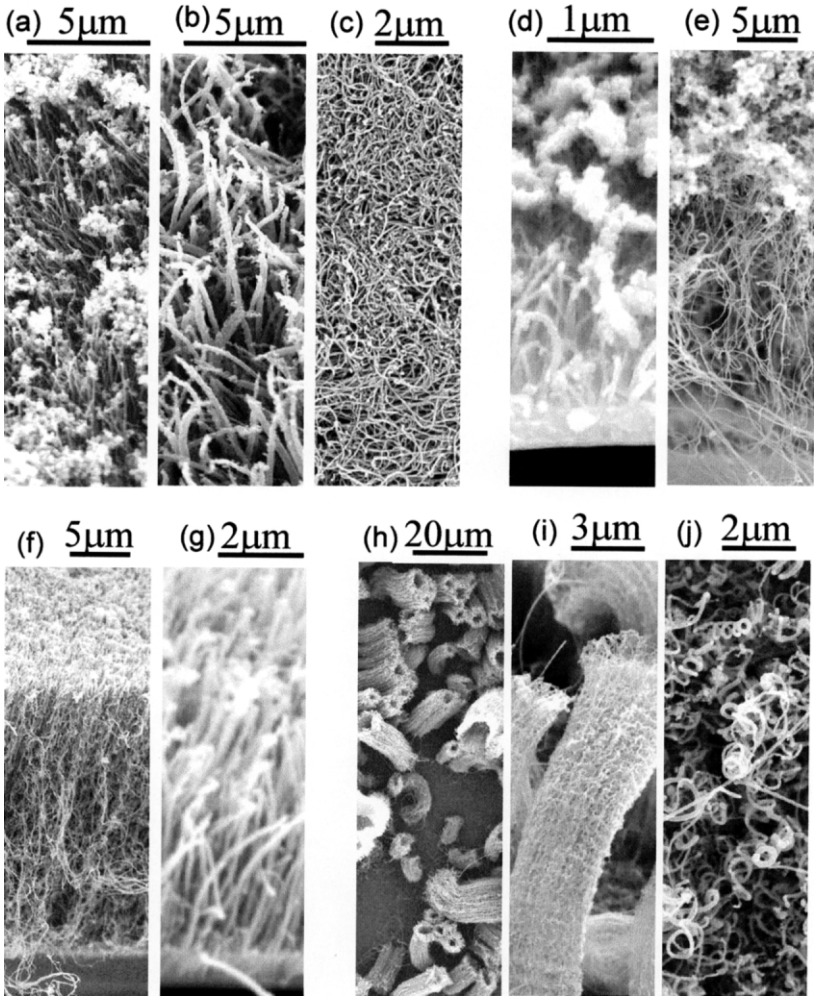

Fig. 1. Scanning electron microscopy (SEM) images of carbon nanotube films grown under the conditions described in Table 1.

Table 1
Growth conditions and tube diameters shown in Fig. 1

Specimen	Growth parameters				Tube diameter (nm)
	Temp. (°C)	Growth time (min)	Reaction gases	Substrate	
Fig. 1a	650	15		Fe/Ti/Si	20–100
Fig. 1b	750	15		Fe/Ti/Si	100–400
Fig. 1c	650	15		Si/Ti/Fe	30–50
			H_2 (90 sccm)		
Fig. 1d	650	0.5		Fe/Ti/Si	20–100
			N_2 (10 sccm)		
Fig. 1e	650	120		Fe/Ti/Si	20–100
			CH_4 (6 sccm)		
Fig. 1f	650	15		Fe/Ti/Si	20–100
Fig. 1g	650	15		Ni/Ti/Si	60–100
Fig. 1h,i,j	650	15		Fe/etched Ti/Si	20–80

μm, if the growth time is increased from 30 s to 120 min, as seen in Fig. 1d,e. The tube diameter is not affected by the growth time. Also in this case, terminating clusters can be clearly seen. In another experiment, the effect of Fe and Ni as a catalyst was investigated, while keeping the growth parameters the same. Although the growth on Fe or Ni yields similar ranges of diameters, density and orientation (vertical or horizontal), the growth rate is faster for Fe than that for Ni, consistent with the higher catalytic activity of Fe. Morphology of nanotube films grown on Fe and Ni is shown in Fig. 1f,g, respectively.

Different nanotube shapes can be obtained if the substrate is etched using different acids before applying the Fe coating (Fig. 1h–j). This treatment, leading to a very thin (20–80 nm) layer of Fe coating, can be used to create 'macaroni' shapes with a hollow core, which appear to be woven out of very fine nanotubes, as seen in Fig. 1i. This technique has the potential of creating different types of 'fibers' made of nanotubes.

Transmission electron microscopy (TEM) was used for accurate measurements of the tube diameter. As seen in Fig. 2a,b, TEM images of nanotubes grown at 650°C show two distinct features, namely a straight hollow and a repeating arrowhead shape. For straight hollow tubes, the width of hollow region is in the range of 11–55 nm, with a wall thickness in the range of 20–38 nm depending on the tube diameter. The tip of the arrowhead is in the range of 8–12 nm, while the wide side of arrowhead is in the range of 15–30 nm. It is interesting to know that the average tube diameter is different from the hollow structures. The tubes with a straight hollow core are approximately 20 nm larger in diameter than the ones with an arrowhead shape. The tip of the tubes is tapered and closed. The black spots on the walls seem to be the structural defects generated during growth.

As shown in Fig. 3, patterned substrates are used to deposit nanotubes selectively. The substrate is treated in H_2/N_2 plasma at 650°C for 5 min, followed by exposure to CH_4.The growth lasts for 15 min. SEM observations indicate that the alignment and orientation of nanotubes in Fig. 3 are uniform across the deposited area.

In addition to the above observed structures, we report two new findings based on our experiments, namely the etching of nanotubes by plasma and post-growth detachment of the carbon clusters from the tubes. For growth temperatures in the range of 800–900°C, etching of carbon nanotubes was observed. At the lower end of this range, tubes grown during short growth times (less than 5 min) can be etched if longer growth times (greater than 15 min) are used.

Previously reported purification methods [17,18], designed to remove clusters and other undesirable structures from the nanotube material, involve laborious steps such as refluxing, centrifugation, sedimentation

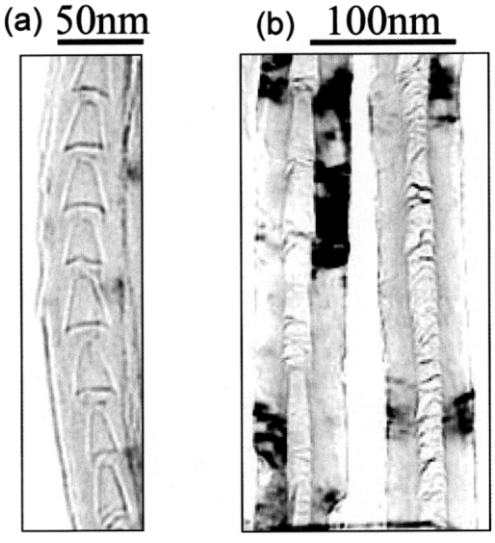

Fig. 2. Transmission electron microscopy (TEM) images of carbon nanotube films grown under various conditions.

and filtration, or boiling in an acid bath. We have demonstrated an alternate, less laborious way to purify CVD grown nanotubes, which involves treatment of as-grown nanotubes in methanol in an ultra-sonic bath for 15 min. Tubes cleaned in this way, shown in Fig. 4, become free of the cluster residue. We find that CVD-grown nanotubes adhere well to the substrate, thus suggesting their application as field electron emitters. It may be pointed out that an ultrasonic cleaning procedure has also been reported for single-wall nanotubes grown by laser-vaporization [19].

4. Conclusions

A comparison between the growth conditions described in Table 1 and the nanotube morphologies of Fig. 1 suggests that the higher temperature used to synthesize the sample in Fig. 1b yields tubes that are fatter and straighter. At lower temperatures, associated with the system depicted in Fig. 1j, the commonly forming pentagon–heptagon defects cannot be annealed easily, causing the tubes to bend. We note that nanotube coils, when anchored firmly in a substrate, could be used to make strong interconnects between surfaces [20], in vague analogy with the Velcro® closure, thus harnessing the unusually high tensile strength of 30 GPa found in carbon nanotubes [21].

In summary, we report formation of dense carbon nanotube films with different morphologies that were synthesized by varying the conditions in a MPCVD reactor. We found optimum growth in presence of an iron catalyst and nitrogen in the atmosphere. A cleaning procedure, consisting of ultrasonic treatment of nanotubes in methanol, has been found to efficiently remove any amorphous residue formed during the synthesis.

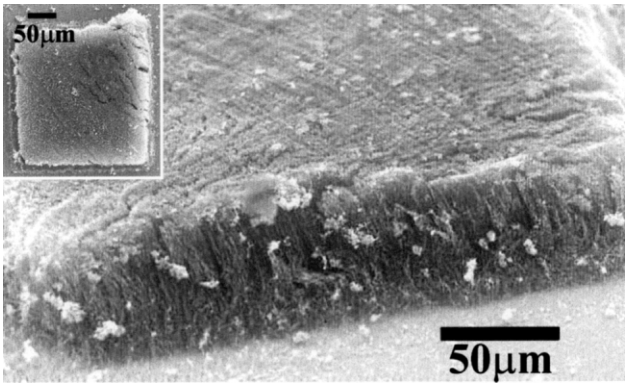

Fig. 3. SEM micrographs show the patterned nanotubes (250×250 μm^2).

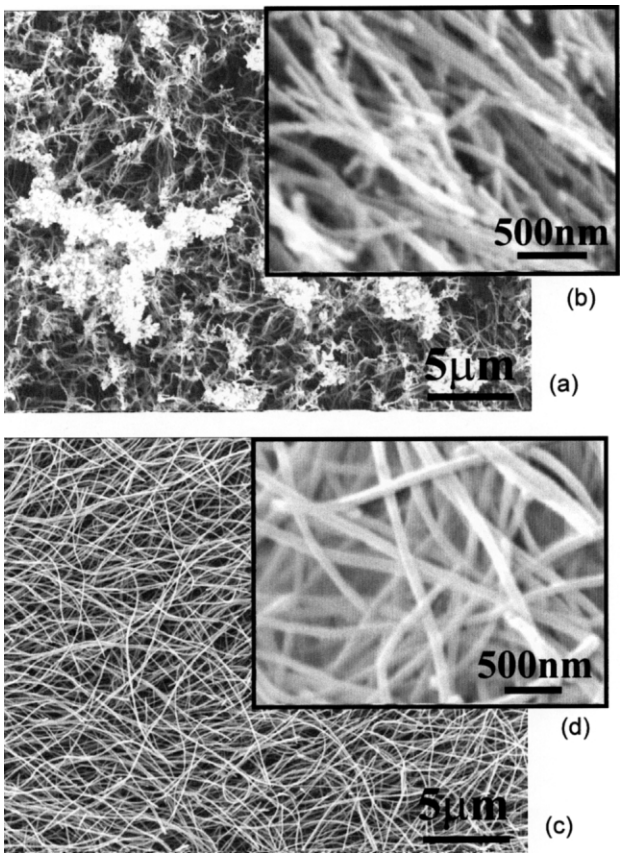

Fig. 4. SEM images of as-grown nanotube films (a and b) and films that have been subjected to ultrasonic treatment in methanol (c and d), resulting in removal of carbon clusters.

Acknowledgements

Financial support for this research has been provided by NASA Grant Number NAG5-9276. D.T. acknowledges financial support from ONR/DARPA under Grant Number N00014-99-1-0252.

References

[1] S. Iijima, Nature (London) 354 (1991) 56.
[2] A. Thess, R. Lee, P. Nikoaev et al., Science 273 (1996) 483.
[3] W.Z. Li, S.S. Xie, L.X. Qian et al., Science 274 (1996) 1701.
[4] Z.F. Ren, Z.P. Huang, J.W. Xu et al., Science 282 (1998) 1105.
[5] L.C. Qin, D. Zhou, A.R. Krauss, D.M. Gruen, Appl. Phys. Lett. 72 (1998) 3437.
[6] X. Xu, G.R. Brandes, Appl. Phys. Lett. 74 (1999) 2549.
[7] C. Dekker, Physics Today, May (1999) 22.
[8] P. Poncharal, Z.L. Wang, D. Ugarte, W.A. de Heer, Science 283 (1999) 1513.
[9] W. Zhu, C. Bower, O. Zhou, G. Kochanski, S. Jin, Appl. Phys. Lett. 75 (1999) 873.
[10] K.A. Dean, B.R. Chalamala, J. Appl. Phys. 85 (1999) 3832.
[11] Y. Saito, K. Hamaguchi, R. Mizushima et al., Appl. Surf. Sci. 146 (1999) 305.
[12] P.G. Collins, A. Zettl, Phys. Rev. 55 (1997) 9391.
[13] D. Srivastava, Nanotechnology 8 (1997) 186.
[14] J. Li, C. Papadopoulos, J. Xu, M. Moskovits, Appl. Phys. Lett. 75 (1999) 367.

[15] C. Bower, W. Zhu, S. Jin, O. Zhou, Appl. Phys. Lett. 77 (2000) 830.
[16] G.S. Yang, M. Aslam, K.P. Kuo, D.K. Reinhard, J. Asmussen, J. Vac. Sci. Technol. B 13 (1995) 1030.
[17] J. Liu, A.G. Rinzler, H. Dai et al., Science 280 (1998) 1253.
[18] L. Forro, J.P. Salvetat, J.M. Bonard et al., in: D. Tománek, R.J. Enbody (Eds.), Science and Application of Nanotubes, Kluwer Academic/Plenum Publishers, New York, 2000.
[19] K.B. Shelimov, R.O. Esenaliev, A.G. Rinzler, C.B. Huffman, R.E. Smalley, Chem. Phys. Lett. 282 (1998) 429.
[20] Micro-Fastening System and Method of Manufacture. U.S. patent application of D. Tománek, Richard J. Enbody, Young-Kyun Kwon.
[21] M.F. Yu, B.S. Files, S. Arepalli, R.S. Ruoff, Phys. Rev. Lett. 84 (2000) 5552.