

Growing carbon nanotubes by microwave plasma-enhanced chemical vapor deposition

L. C. Qin,^{a)} D. Zhou,^{b)} A. R. Krauss, and D. M. Gruen

Materials Science and Chemistry Divisions, Argonne National Laboratory, MSD/CHM 200, Argonne, Illinois 60439

(Received 4 November 1997; accepted for publication 27 April 1998)

A processing route has been developed to grow bundles of carbon nanotubes on substrates from methane and hydrogen mixtures by microwave plasma-enhanced chemical vapor deposition, catalyzed by iron particles reduced from ferric nitrate. Growth takes place at about 900 °C leading to nanotubes with lengths of more than 20 μm and diameters on the nanometer scale. © 1998 American Institute of Physics. [S0003-6951(98)01826-9]

The extraordinary properties of carbon nanotubes¹ have made this allotrope of nanocarbon the most studied nanomaterial for the past few years. Mechanical measurement of the axial Young's modulus of multiwalled carbon nanotubes² obtained extremely high values of about 1800 GPa, which suggest that carbon nanotubes are the stiffest material known to date. Electronically, a carbon nanotube can behave either as a semiconductor or as a metal, depending on its diameter and helicity.³ This unique electronic property makes carbon nanotubes a novel material that allows tuning of its electronic properties by manipulating its atomic structure in order to fabricate electronic devices. Carbon nanotubes have also been investigated for applications as electric-field-induced electron emitters^{4–6} and a very low onset field of 0.8 V/ μm has been observed from multiwalled carbon nanotubes produced by arc discharge.⁶ Recent experimental studies have demonstrated that carbon nanotubes possess quantum wire behavior⁷ and electronic property enhancement can be achieved by chemical doping.⁸

One of the challenging issues has been the synthesis of this form of nanocarbon on large scales ever since it was first observed at the cathode in an electric arc evaporation experiment where the anode had been consumed.¹ In addition to the refinement of the arc discharge technique,^{9,10} subsequent developments have led to the realization of many alternative processing techniques, such as laser evaporation,^{11,12} pyrolysis of hydrocarbon gases using benzene (C_6H_6),¹³ acetylene (C_2H_2),¹⁴ methane (CH_4);^{15,16} etc.^{17,18} However, given the sensitive relationship between the atomic structure and the properties of the tubules, in order to make carbon nanotubes of practical importance, the criteria for assessing any synthesis technique must include the feasibility and potentiality for scaled-up production at low cost as well as the ability to control structure. In this regard, gas phase deposition methods have received a great deal of attention since they can be conveniently scaled up in production levels, while growth takes place at moderate temperatures (around 1000 °C), well below the operating temperature for the arc-discharge

method (estimated to be 5000–20 000 °C) or the laser evaporation method (4000–5000 °C). It also seems that for growing well-aligned nanotube arrays^{16,19} on solid substrates for potential nanodevice applications, chemical vapor deposition (CVD) methods appear to be most promising.

In this letter we report a method that enables growth of carbon nanotubes of large aspect ratios on supporting solid matrices by microwave plasma-enhanced chemical vapor deposition. The apparatus is of the same type that has been widely employed to grow nanocrystalline diamond thin films.²⁰ However, different conditions have been identified that allow the deposited carbon to grow into graphitic tubules. For example, the growth of carbon nanotubes requires higher methane-to-hydrogen ratios compared with the conditions under which micro- or nanodiamond thin films are grown.

Alumina substrates (Al_2O_3) used for growing the carbon nanotubes in our system were first coated with ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] solution. The coating of such an iron-containing compound has been found to be necessary as the iron catalyst particles are essential for both the initial nucleation and the subsequent growth of carbon nanotubes. Growth takes place in a vacuum chamber in which the substrate can be heated to about 850–900 °C. The substrate temperature was kept constant throughout the deposition process. A mixture of methane (CH_4) and hydrogen (H_2) gases were admitted to the deposition chamber through mass flow controllers. The total pressure in the chamber was kept constant at 15 Torr while the flow rates were 15 and 10 sccm for CH_4 and H_2 , respectively. The microwave plasma input power was 600 W. A schematic of the experimental setup is given in Fig. 1. The lower edge of the plasma was in contact with the substrate surface during the deposition process. The deposited film was studied by scanning electron microscopy (SEM) to examine the structure of the as-grown material prior to any postdeposition treatment.

A typical as-grown morphology of the carbon deposits taken with a SEM is shown in Fig. 2, where large bundles of tangled carbon nanotubes can be seen. A striking feature is that the as-grown nanotubes have quite a uniform diameter of about 10–50 nm, while the typical length is well beyond 20 μm , resulting in a high aspect ratio of about 1000 or larger. Two major components are identified: carbon nano-

^{a)}Present address: IBM Corp., Department MXQ/014, 5600 Cottle Road, San Jose, CA 95193. Electronic mail: qin@ibm.net

^{b)}Present address: Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, FL 32816.

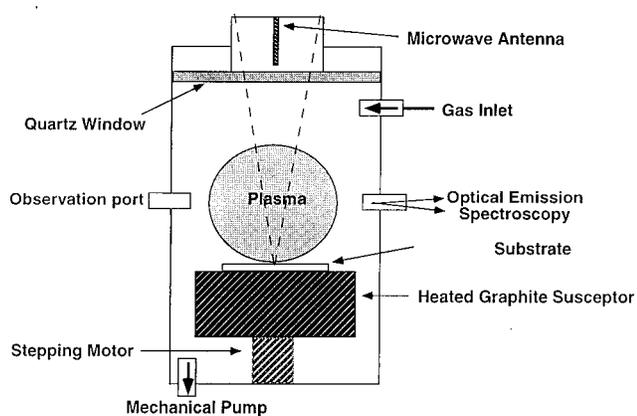


FIG. 1. Schematic of the microwave plasma-enhanced CVD apparatus. Methane and hydrogen gases enter the chamber (with 1 mTorr base pressure) where a coated substrate can be heated to elevated temperature (370–950 °C). The plasma is excited above the substrate on which carbon nanotubes are grown.

tubes and soot. It is interesting to note that the carbon nanotubes appear superficially very similar to those produced by electric arc-discharge evaporation, despite the fact that the two processes operate in vastly different temperature regimes. The similarity is displayed in Fig. 3, which gives a SEM image of carbon nanotubes deposited at the cathode in an arc-discharge experiment.²¹ It should also be emphasized that in our experiment the nanotubes are quite evenly distributed over the total surface of the substrate, which measures $25 \times 50 \text{ mm}^2$; while in the arc-discharge method, they occupy only a small portion of the central region of the cathode. The large-area uniformity of the deposition in the present study has important practical implications for array fabrication and other applications.

We propose that the growth mechanism is catalyst assisted. Figure 4 depicts a two-step model for the nucleation and growth of carbon nanotubes by catalytic reaction in plasma-enhanced CVD. Nucleation is assumed to occur at the surfaces of the iron catalyst particles, as indicated in the Fe–C phase diagram. The decomposition of hydrocarbons at a particle surface would result in carbon deposition at its surface. In the meantime, the plasma formed above the substrate would enhance diffusion of carbon species into the

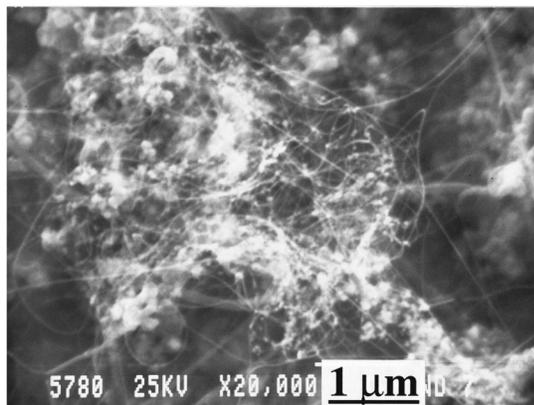


FIG. 2. SEM image of tangled carbon nanotubes of uniform diameter grown on an alumina substrate by microwave plasma-enhanced CVD. Typical diameters of the shown carbon nanotubes are 10–50 nm, while their lengths go well beyond $20 \mu\text{m}$.

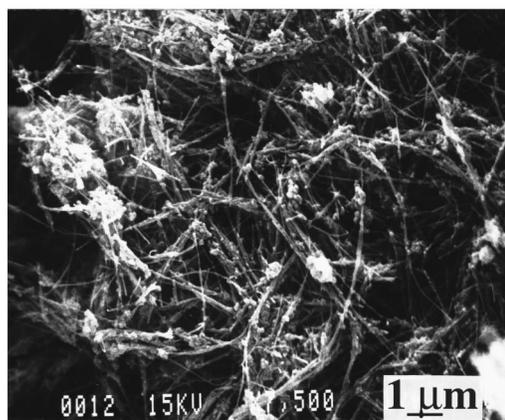


FIG. 3. SEM image of tangled carbon nanotubes produced by the electric arc-discharge technique. Note the striking resemblance in morphology of the arc-produced nanotubes with those produced by microwave plasma-enhanced CVD shown in Fig. 2.

catalyst particles while the continued heating of the substrate would quickly bring the iron particles back to thermal equilibrium. Since the temperature of the substrate is kept constant, the bottom of the catalytic particle should be hotter than the top. This should result in the growth of carbon tubules from the iron particle while the catalyst particles stay on the surface of the supporting substrate. The presence of atomic hydrogen in the plasma should also enhance the decomposition of ferric nitrate associated with the initial coating into iron particles on the substrate surface, in addition to enhancing the diffusion of carbon into the iron particles.

The growth rate of carbon nanotubes in the microwave plasma-enhanced CVD described here has been found to be much slower than that in the pyrolytic growth reported earlier.^{15,16} We believe that the difference in growth rate is caused by the temperature difference between the two cases, noting that the pyrolytic deposition was performed at about $1200 \text{ }^\circ\text{C}$. The growth of the nanotubes has been observed to occur in both axial and radial directions. Although the nanotubes appear to be closely associated with the catalytic particles, it is not yet clear what effect the size of the iron catalyst particles has on the diameter of the carbon nanotubes.

The significance of the present results is twofold: (1)

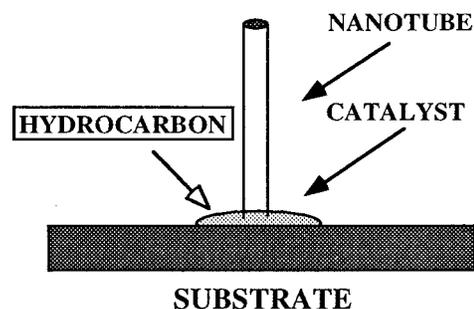


FIG. 4. Growth model for the formation of carbon nanotubes in microwave plasma-enhanced CVD. The catalyst particle (coated onto the substrate surface as indicated by a solid arrow) can contain larger amount of carbon in equilibrium while temperature is raised; the heat needed to decompose methane molecules (moving towards the catalytic particle as indicated by the open arrow) at the catalytic particle surface lowers the temperature, resulting in the particle being supersaturated, and therefore, precipitation of excess carbon occurs—forming graphitic tubules at the surface.

appropriate physical conditions have been identified for the growth of carbon nanotubes by microwave plasma-enhanced CVD, and (2) the successful growth on solid substrates opens potentially new processing routes for growing well-aligned carbon nanotubes. The latter should be of great technological interest as carbon nanotubes have shown excellent electric-field-induced electron emission properties. In particular, this method should allow more precise control over the growth of carbon nanotubes than pyrolysis carried out in an electric tube furnace.^{15,16} As mentioned above, the ultimate purpose should be a scaled-up production of carbon nanotubes either in three-dimensional tangle, well-sorted parallel bundles, or well-aligned arrays grown on selected substrates. Although alumina substrates have been used in the present study, it appears that the substrate material does not affect the growth process; it is, therefore, anticipated that the process discussed here may be used for the controlled growth of carbon nanotubes on a wide variety of substrates. It is possible that lithographically produced grids can be fabricated for positioning the catalyst material, resulting in the growth of carbon nanotube arrays of uniform length and diameter for device applications.

In conclusion, we have established a processing route to synthesize carbon nanotubes by using microwave plasma-enhanced CVD. This method produces carbon nanotubes on supporting solid matrices over large areas with quite even distribution, and allows potentially for more precise control over the growth of carbon nanotubes.

This research was supported by the U.S. Department of Energy, BES–Materials Sciences under Contract No. W-31-109-ENG-38.

- ¹S. Iijima, *Nature (London)* **354**, 56 (1991).
- ²M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, *Nature (London)* **381**, 678 (1996).
- ³N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992).
- ⁴A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colbert, and R. E. Smalley, *Science* **269**, 1550 (1995).
- ⁵W. A. de Heer, A. Chatelain, and D. Ugarte, *Science* **270**, 1179 (1995).
- ⁶Q. H. Wang, T. D. Corrigan, J. Y. Dai, R. P. H. Chang, and A. R. Krauss, *Appl. Phys. Lett.* **70**, 3308 (1997).
- ⁷S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, and C. Dekker, *Nature (London)* **386**, 474 (1997).
- ⁸R. S. Lee, H. J. Kim, J. E. Fisher, A. Thess, and R. E. Smalley, *Nature (London)* **388**, 255 (1997).
- ⁹T. W. Ebbesen and P. M. Ajayan, *Nature (London)* **358**, 200 (1996).
- ¹⁰S. Seraphin and D. Zhou, *Appl. Phys. Lett.* **64**, 2087 (1994).
- ¹¹T. Guo, P. Nikolaev, A. G. Rinzler, D. Tomanek, and R. E. Smalley, *J. Phys. Chem.* **99**, 10 694 (1995).
- ¹²L. C. Qin and S. Iijima, *Chem. Phys. Lett.* **269**, 65 (1997).
- ¹³M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, and H. W. Kroto, *J. Phys. Chem. Solids* **54**, 1841 (1993).
- ¹⁴V. Ivanov, J. B. Nagy, Ph. Lambin, A. Lucas, X. B. Zhang, X. F. Zhang, D. Bernaerts, G. Van Tendeloo, S. Amelinckx, and J. Van Landuyt, *Chem. Phys. Lett.* **223**, 329 (1994).
- ¹⁵L. C. Qin, *J. Mater. Sci. Lett.* **16**, 457 (1997).
- ¹⁶L. C. Qin and S. Iijima, *Mater. Lett.* **30**, 311 (1997).
- ¹⁷M. Terrones, N. Grobert, J. Olivares, J. P. Zhang, H. Terrones, K. Kordatos, W. K. Hsu, J. P. Hare, P. D. Townsend, K. Prassides, A. K. Cheetham, H. W. Kroto, and D. R. M. Walton, *Nature (London)* **388**, 52 (1997).
- ¹⁸Y. L. Li, Y. D. Yu, and Y. Liang, *J. Mater. Res.* **12**, 1678 (1997).
- ¹⁹W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, *Science* **274**, 1701 (1996).
- ²⁰D. M. Gruen, S. Liu, A. R. Krauss, and X. Pan, *J. Appl. Phys.* **75**, 1758 (1994).
- ²¹S. Seraphin, D. Zhou, and J. Jiao, *Carbon* **31**, 1212 (1993).