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Diameter-controlled growth of carbon nanotubes using thermal chemical vapor deposition

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Abstract

The diameter and the growth rate of vertically aligned carbon nanotubes (CNTs) are controlled by modulating the size of catalytic particles using thermal chemical vapor deposition (CVD). The size of iron catalytic particles deposited on silicon oxide substrate is varied in a controlled manner by adjusting the condition of ammonia pretreatment. We found an inverse relation between the diameter and growth rate of carbon nanotubes. As the diameter increases, the compartment layers of bamboo-shaped carbon nanotubes appear more frequently, which is suitably explained by the base growth mechanism. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs), since their first discovery in 1991 [1], have been considered for many potential technological applications because of their extraordinary electrical and mechanical properties. Various methods have been developed for the synthesis of CNTs, including arc discharge [2,3], laser vaporization [4], pyrolysis [5], plasma-enhanced chemical vapor deposition (CVD) [6], and thermal CVD [7,8]. The CVD method has attracted much attention because of the advantage that the growth of CNTs can be achieved with high purity, high yield, and vertical alignment. The growth of vertically aligned CNTs in a controlled manner is necessary for many applications. A number of research groups reported that the diameter of CNTs is controllable by the size of catalytic particle which can be varied with the growth parameters of CVD, i.e., plasma intensity, thickness of catalyst film, composition of precursors, etc. [6,9–12]. Ren et al. [13] announced that the diameter of CNTs depends on the catalyst particle size. They controlled the catalyst particle size by changing the thickness of stainless steel film. However, not much systematic diameter control has been demonstrated for thermal CVD growth of CNTs.

In this work, we report a diameter-controlled growth of vertically aligned CNTs using thermal CVD of acetylene (C_2H_2) gas at 950°C. The diameter of CNTs is in the range 60–240 nm simply by altering the condition of ammonia (NH_3) pretreatment for iron (Fe)-deposited silicon oxide (SiO_2) substrate. As the diameter increases, the growth rate decreases approximately with the

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inverse dependence. As the diameter increases, the compartment layers of bamboo-shaped CNTs have a shorter distance. We suggest that the diameter, growth rate, and structure of CNTs can be easily controlled by changing the NH_3 pretreatment condition.

2. Experimental

The 20 mm $\times$ 30 mm size p-type Si(1 0 0) substrate with a resistivity of 15 Ω cm was thermally oxidized. The thickness of SiO_2 layer was estimated approximately as 300 nm. A 50 nm thick Fe film was thermally deposited on a SiO_2 layer using a thermal evaporator under a pressure of 10^{-6} Torr. The Fe-deposited SiO_2 substrates were loaded with facedown direction on a quartz boat in the CVD reactor. Argon (Ar) gas was flowed into the CVD reactor in order to prevent the oxidation of Fe while raising the temperature. The Fe-deposited SiO_2 substrates were pretreated by NH_3 gas with a flow rate in the range 100–300 sccm for 20–240 min at 950°C, in order to form the Fe particles in nanometer size [14]. C_2H_2 gas was supplied with a flow rate of 30 sccm for 3–30 min at 950°C to grow the CNTs. The Fe particles and CNTs were examined by a scanning electron microscope (SEM) (Hitachi S-800, 30 kV). A transmission electron microscope (TEM) (Philips, CM20T, 200 kV) was used to investigate the structure of CNTs.

3. Results and discussion

Fig. 1 shows SEM micrographs for vertically aligned CNTs grown on Fe-deposited SiO_2 substrate. The C_2H_2 gas for CNT growth is fixed to the flow rate of 30 sccm for 10 min at 950°C but

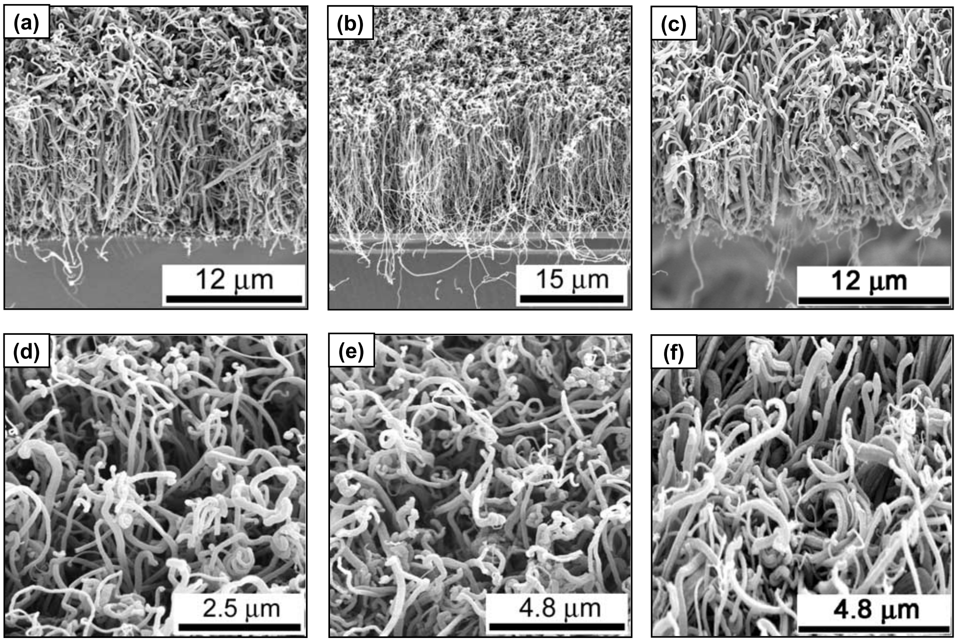

Fig. 1. SEM micrographs for vertically aligned CNTs grown on Fe-deposited SiO_2 substrate. The C_2H_2 gas for CNT growth is fixed to the flow rate of 30 sccm for 10 min: (a) SEM image of vertically aligned CNTs with a length of 12 μm. The flow rate of NH_3 gas is 100 sccm for 20 min. (b) SEM image of vertically aligned CNTs with a length of about 18 μm. The flow rate of NH_3 gas is 300 sccm for 120 min. (c) SEM image of vertically aligned CNTs with a length of about 8 μm. The flow rate of NH_3 gas is 300 sccm for 240 min. (d) Magnified top view of (a) revealing the average diameter of CNTs with 130 nm. (e) Magnified top view of (b) showing the average diameter of CNTs with 60 nm. (f) Magnified top view of (c) showing the average diameter of CNTs with 240 nm.

the NH_3 pretreatment condition is changed to manipulate the size of Fe catalytic particles. Fig. 1a,d are SEM micrographs of vertically aligned CNTs grown on the Fe particles. The flow rate of NH_3 gas is 100 sccm for 20 min. We measured the size and density of catalytic particles before the CNT growth. The average size of Fe particles is about 200 nm and their density is about 2×10^9 cm^{-2}. As shown in Fig. 1a, the high density CNTs with a length of about 12 μm are vertically grown on a large area substrate. Fig. 1d shows that the average diameter of CNTs is 130 nm, which is in a narrower range than that of catalytic particles.

Fig. 1b,e are SEM micrographs for the vertically aligned CNTs grown on the Fe particles in which the flow rate of NH_3 gas is 300 sccm for 120 min. In this condition, the Fe particles with an average diameter of 130 nm are formed with a density of $\sim 4 \times 10^9$ cm^{-2}. The NH_3 pretreatment with a higher flow rate and a longer time etches efficiently the Fe catalyst, resulting in the smaller size Fe particles. Highly purified CNTs with a length about 18 μm are distributed on the substrate and the average diameter of CNTs is about 60 nm.

Fig. 1c,f are SEM micrographs for the vertically aligned CNTs grown on the Fe particles. The flow rate of NH_3 gas is 300 sccm for 240 min. When the NH_3 pretreatment is carried out using a flow rate of 300 sccm for 240 min, the average size of Fe particles becomes approximately 400 nm and the density is about 1×10^9 cm^{-2}. The longer pretreatment time results in the larger catalytic particles due to the agglomeration of catalytic particles. The length of CNTs is 8 μm and the average diameter of CNTs is about 240 nm. The growth conditions of CNTs and the results are listed in Table 1. It shows that the size of Fe particles is controlled by the NH_3 flow rate and pretreatment time, which determine the diameter of CNTs. As the average diameter of CNTs increases from 60 to 240 nm, the length decreases from 18 to 8 μm, corresponding to a 2.3 time decrease.

Fig. 2a is a plot of the growth rate of CNTs as a function of average diameter. The average growth rates are 1.8, 1.2, and 0.8 μm/min for the average diameters 60, 130, and 240 nm, respectively. The growth rate can be fitted by an inverse function of average diameter shown as a curve. Recently, Bower et al. [10] reported that the growth rate is inversely proportional to the nanotube diameter for the CNTs grown on cobalt (Co) catalyst using microwave plasma-enhanced CVD, which is consistent with our results. Choi et al. [9] showed that the growth rate of CNTs increases with decreasing the size of catalytic particles for microwave plasma-enhanced CVD. Baker [15] reported that the growth rate of carbon filaments has an inverse of square root dependence on the particle size. As some of the workers [9,15] pointed out, it could imply that the diffusion of carbons is mainly operative in the growth of CNTs. As the size of particles decreases, the diffusion time for carbons to arrive at the growth site would become short, resulting in accelerating the growth rate of CNTs. We measured the length of CNTs as a function of growth time. The experimental data are listed in Table 1 for the CNTs with an averaged diameter of 130 nm. Fig. 2b displays the length vs. the growth time for the CNTs with a diameter of 130

Table 1
The average diameter and growth rate of CNTs depending on the growth condition

Number of experimental runs	NH_3		C_2H_2		Average Fe particle diameter (nm)	Average CNT diameter (nm)	CNT length (μm)	Growth rate (μm/min)
	Flow rate (sccm)	Time (min)	Flow rate (sccm)	Time (min)				
4	100	20	30	10	200	130	12	1.2
3	300	120	30	10	130	60	18	1.8
2	300	240	30	10	400	240	8	0.8
2	100	20	30	3	200	130	3.6	1.2
2	100	20	30	20	200	130	20	1
2	100	20	30	30	200	130	28	0.9

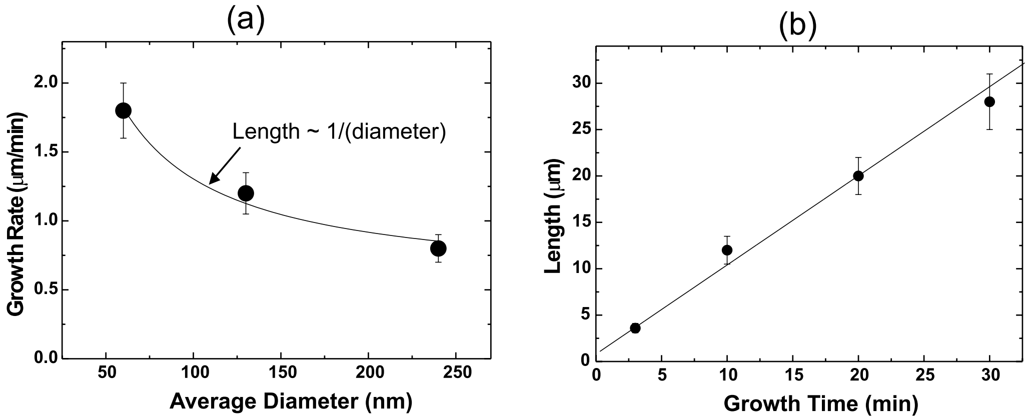

Fig. 2. Dependence of CNT growth on the average diameters and growth time: (a) The growth rate of CNTs as a function of average diameter. The data points are fitted by an inverse function of average diameter shown as a curve. (b) The length vs. the growth time for the CNTs with a diameter of 130 nm.

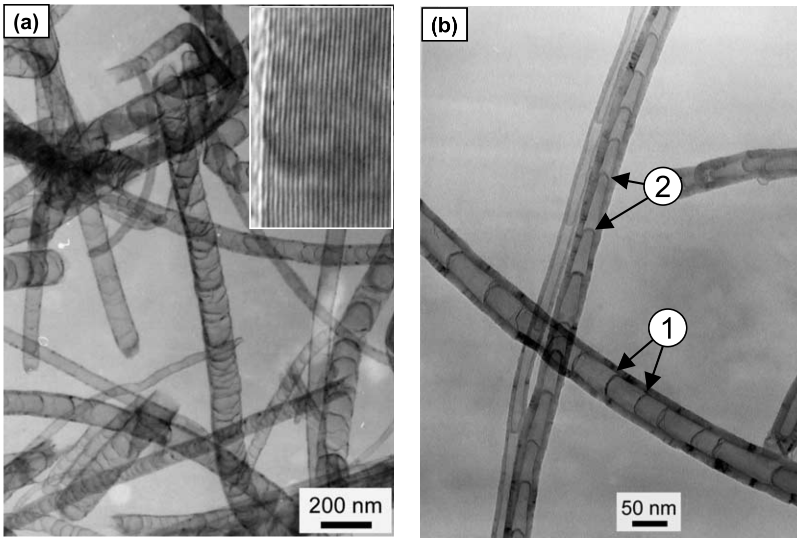

Fig. 3. TEM images showing that all CNTs have bamboo-shaped structure: (a) TEM image for bamboo-like structured CNTs, revealing the closed tips without encapsulated Fe particles and compartment layers with a curvature directed toward the tip. The inset in Fig. 3a shows that high-resolution TEM image, revealing that graphite sheets have a good crystallinity. (b) TEM image showing that compartment layers appear at a longer distance as the diameter of CNTs decreases (see arrows ① and ②).

nm. The length of CNTs increases linearly with the growth time during 30 min, indicating that the growth rate is about constant. We observed that the growth rate decreases significantly over 40 min because carbon atoms cannot be adsorbed to the surface of Fe particles due to the carbonaceous particles covering the surface of Fe particles.

To investigate the structure of CNTs, the CNTs were separated from the substrate using an ultrasonic treatment in acetone, and then dispersed on a carbon TEM microgrid. Fig. 3a is the TEM image showing that all CNTs have bamboo-like structures. The tips of CNTs are closed and free of the encapsulated catalytic particles and compartment layers are directed toward the tips. Catalytic particles which are attached to the root of CNTs are separated during the ultrasonic treatment in acetone. The inset in Fig. 3a shows that high-resolution TEM image, revealing that graphite sheets have a good crystallinity without defects. We also found that the diameter of CNTs is strongly correlated to the size of Fe catalytic particles. Fig. 3b shows that the compartment layers of bamboo-shaped CNTs appear at a longer distance as the diameter of CNT decreases (see arrows ① and ②). The base-growth mechanism can be adopted to explain our experimental results in which the growth of CNTs depends on the diameter of catalytic particles [16–18]. Carbons generated from the decomposition of C_2H_2 diffuse into the catalytic particles and then form the graphitic sheets on the surface of the catalytic particle. The accumulation of carbons at the inside surface of the catalytic particle occurs probably mainly via bulk diffusion, which produces a compartment layer. If the carbons are regularly supplied to the catalytic particles, the growth rate would be constant and thus the compartment layers of CNTs can also appear periodically. The size of catalytic particle limits the diameter of the growing tube. When the size of catalytic particles is smaller, the diameter of CNTs becomes narrower and the growth rate increases proportionally to the inverse of CNT diameter. The increased growth rate of CNTs on the smaller catalytic particle may be due to a reduced arrival time of carbons at the growth site. As the growth rate increases, the compartment layers of CNTs would take place less frequently.

In summary, we have grown the vertically aligned CNTs on Fe-deposited SiO_2 substrates using thermal CVD of acetylene gas at 950°C. The size of Fe particle is controlled by the flow rate of NH_3 gas and pretreatment time, which leads to control the diameter of CNTs. The size of catalytic particle limits the diameter of CNTs. As the diameter of CNTs decreases, the growth rate is enhanced with an inverse dependence of the CNT diameter. The growth rate of CNTs increases linearly as the growth time increases until 30 min but is rapidly decreased over 40 min. As the diameter of CNTs increases, the compartment layers of bamboo-shaped CNTs appear in more frequent periods. A base-growth model is suitable to explain the dependence of growth rate and structure of CNTs on the diameter size of catalytic particles.

Acknowledgements

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References

[1] S. Iijima, Nature 354 (1991) 56.
[2] D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature 363 (1993) 605.
[3] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, Nature 388 (1997) 756.
[4] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fisher, R.E. Smalley, Science 273 (1996) 483.
[5] M. 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, D.R.M. Walton, Nature 388 (1997) 52.
[6] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science 282 (1998) 1105.
[7] W.Z. Li, S.S. Xie, L.X. Qain, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
[8] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, Science 283 (1999) 512.
[9] Y.C. Choi, Y.M. Shin, Y.H. Lee, B.S. Lee, G.-S. Park, W.B. Choi, N.S. Lee, J.M. Kim, Appl. Phys. Lett. 76 (2000) 2367.
[10] C. Bower, O. Zhou, W. Zhu, D.J. Werder, S. Jin, Appl. Phys. Lett. 77 (2000) 2767.
[11] S.B. Sinnott, R. Andrews, D. Qian, A.M. Rao, Z. Mao, E.C. Dickey, F. Derbyshire, Chem. Phys. Lett. 315 (1999) 25.
[12] I. Willems, Z. Kónya, J.-F. Colomer, G. Van Tendeloo, N. Nagaraju, A. Fonseca, J.B. Nagy, Chem. Phys. Lett. 317 (2000) 71.
[13] W.Z. Li, D.Z. Wang, S.X. Yang, J.G. Wen, Z.F. Ren, Chem. Phys. Lett. 335 (2001) 141.
[14] C.J. Lee, D.W. Kim, T.J. Lee, Y.C. Choi, Y.S. Park, W.S. Kim, Y.H. Lee, W.B. Choi, N.S. Lee, J.M. Kim, Y.G. Choi, S.C. Yu, Appl. Phys. Lett. 75 (2000) 1721.
[15] R.T.K. Baker, Carbon 27 (1989) 315.
[16] C.J. Lee, J. Park, Appl. Phys. Lett. 77 (2000) 3397.
[17] C.J. Lee, J.H. Park, J. Park, Chem. Phys. Lett. 323 (2000) 560.
[18] C.J. Lee, J. Park, S.Y. Kang, J.H. Lee, Chem. Phys. Lett. 326 (2000) 175.