

Growth model of bamboo-shaped carbon nanotubes by thermal chemical vapor deposition

Cheol Jin Lee^{a)}

School of Electrical Engineering, Kunsan National University, Kunsan 573-701, South Korea

Jeunghee Park

Department of Chemistry, Korea University, Jochiwon 399-700, South Korea

(Received 3 July 2000; accepted for publication 7 September 2000)

Vertically aligned carbon nanotubes were grown on iron-deposited silicon oxide substrate by thermal chemical vapor deposition of acetylene. The carbon nanotubes have no encapsulated iron particles at the closed tip and a bamboo structure in which the curvature of compartment layers is directed to the tip. A base growth model is suggested for the bamboo-shaped carbon nanotubes grown under our experimental conditions. © 2000 American Institute of Physics.

[S0003-6951(00)00944-X]

Synthesis of carbon nanotubes (CNTs) using various methods such as arc discharge,^{1–3} laser vaporization,⁴ pyrolysis,⁵ plasma-enhanced⁶ or thermal chemical vapor deposition (CVD),^{7,8} etc., has been extensively investigated by a number of research groups. 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. However, despite great progress in CVD growth of CNTs, the growth mechanism has still not been completely understood.

Given the different synthetic techniques, it is likely that a variety of mechanisms play a role in the growth of CNTs. Two growth models, i.e., the base growth and tip growth models, were early proposed for the catalytic growth of carbon filaments.⁹ These growth models have been frequently adopted to explain the growth mechanism of CNTs. In the case of CNTs synthesized using plasma-enhanced CVD (Refs. 6, 10, and 11) and pyrolysis,¹² the catalytic particles usually remain at the tip, which was rationalized by the tip growth models. In contrast, Dai and co-workers proposed a base growth model for the vertically aligned CNT growth on iron (Fe) patterned porous silicon substrates using thermal CVD.⁸

In the present experiment, we found no encapsulated catalytic particles at the closed tip from the CNTs grown by thermal CVD of acetylene (C₂H₂). The vertically aligned CNT grown on Fe-deposited plane silicon oxide at temperatures over the range 750–950 °C were carefully investigated using high-resolution transmission electron microscopy (HRTEM). All CNTs have a bamboo structure irrespective of the growth temperature. Based on the HRTEM images, we suggest a base growth model for the bamboo-shaped CNTs grown using the thermal CVD method.

A 20 mm×30 mm size *p*-type Si(100) substrate with a resistivity of 15 Ω cm was thermally oxidized. The thickness of the silicon oxide (SiO₂) layer was estimated to be approximately 300 nm. A 100-nm-thick Fe film was thermally

deposited on the SiO₂ layer under a pressure of 10⁻⁶ Torr. The substrates were dipped in a diluted HF solution for 200 s. Then, the catalytic film was pretreated by NH₃ gas with a flow rate of 100–200 sccm for 20–40 min at 750–950 °C in order to form the catalytic particles in nanometer size, which is a crucial step for controlling the size and the vertical alignment of CNTs.¹³ The CNTs were grown using C₂H₂ with a flow rate of 40–80 sccm for 10 min at 750–950 °C. A scanning electron microscope (SEM) (Hitachi S600) and a transmission electron microscope (TEM) (Philips CM20T, 200 kV) were used to investigate the CNTs.

Figure 1 is SEM micrographs for the CNTs grown at 950 °C. Figure 1(a) shows the vertically well-aligned CNTs with a uniform length of 100 μm. A magnified top view, as shown in Fig. 1(b), reveals that the diameter is in the range from 100 to 200 nm. The CNTs have a closed tip and a very clean surface without any carbonaceous particles. Most of the tips are tilted from the vertical direction within 10°.

TEM analysis was performed on the CNTs dispersed on a carbon TEM microgrid after separating from the substrate by ultrasonic treatment in acetone. Figure 2 is the TEM images showing that all CNTs consist of hollow compartments, looking like bamboo. Figure 2(a) reveals the closed tips with no encapsulated catalytic particles (see arrows ①), an open root separated from the Fe particle (see arrow ②), and the compartment layers with a curvature directed toward the tip

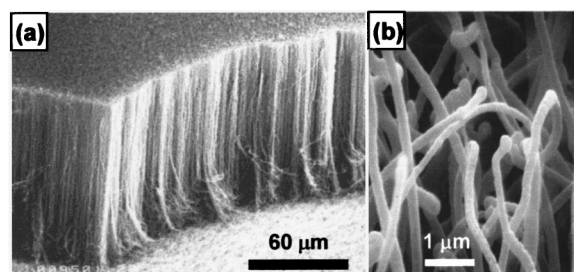


FIG. 1. SEM micrographs of vertically well-aligned CNTs grown on an Fe-deposited SiO₂ substrate, under the condition that C₂H₂ flows with a rate of 40 sccm for 10 min at 950 °C. (a) Uniformly grown CNTs with a length of 100 μm. (b) A top view showing the diameter distribution in the range of 100–200 nm.

^{a)}Author to whom correspondence should be addressed; electronic mail: cjlee@ks.kunsan.ac.kr

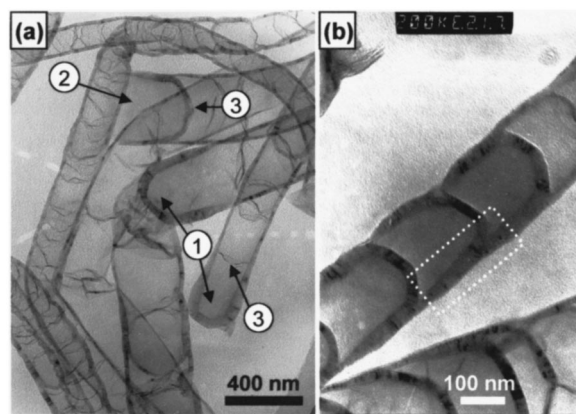


FIG. 2. TEM images of the CNTs grown at 950 °C, dispersed on a carbon microgrid after stripping from the substrate. (a) All CNTs have a bamboo structure. There are closed tips with no encapsulated catalytic particles (see arrows ①), an open root (see arrow ②), and compartment layers with a curvature directed to the tip (see arrows ③). (b) The CNT has the compartment layers regularly at a distance of about 200 nm. The wall thickness increases by the joint of the compartment layers (see the dotted box).

(see arrows ③). A CNT with an outer diameter of about 200 nm, shown in Fig. 2(b), has the compartment layers regularly at a distance of about 200 nm. The wall thickness increases due to the connection with the compartment layer (see the dotted box), but the outer diameter remains about the same for the entire tube. This periodic change of wall thickness can be also found from the CNTs grown on a cobalt-deposited SiO₂ substrate, which was previously reported by our group.¹⁴

Figure 3(a) is a HRTEM image for the joint between the wall (see arrow ①) and the compartment layer (see arrow ②). Following the downward direction (see the arrow-marked positions), the wall with a thickness of 8 nm becomes as thin as 6 nm and then as thick as 9 nm after the joint. The crystalline graphite sheets of the wall combine with those of the compartment without any defects, as indi-

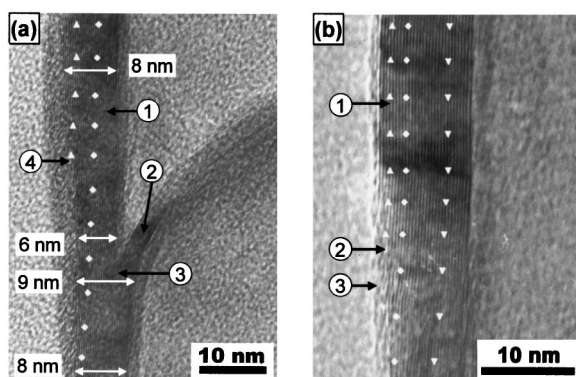


FIG. 3. (a) HRTEM image of a bamboo-shaped CNT, showing a joint between the wall (see arrow ①) and the compartment (see arrow ②) graphite sheets. Following the downward direction (see arrow-marked positions), the wall thickness changes from 8 to 6 nm, again to 9 nm by the joint of the compartment layer, and finally, to 8 nm. The crystalline graphite sheets of the wall combine with those of the compartment without any defects (see arrow ③). The graphite sheets are aligned with a tilted angle of about 5° toward the tube axis (see the Δ and \diamond). The graphite sheets at the outside disappear, as indicated by arrow ④. (b) HRTEM image for the wall of a CNT. The graphite sheets are tilted toward the tube axis (see the Δ , \diamond , and ∇). A crystalline graphite sheet (marked by Δ) becomes defective, and finally, vanishes as indicated by arrows ①, ②, and ③.

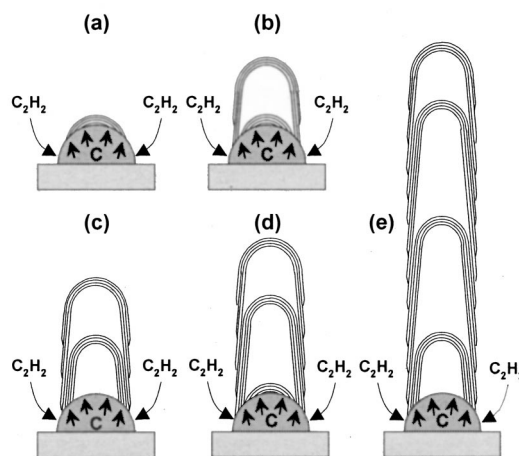


FIG. 4. Schematic diagrams of the base growth model.

cated by arrow ③. The graphite sheets of the wall are aligned with a tilted angle of about 5° toward the tube axis (see the Δ and \diamond). The graphite sheets at the outside disappear, as indicated by arrow ④. Figure 3(b) is a HRTEM image of the wall of another CNT, revealing that the graphite sheets are aligned to the tube axis with a tilted angle of about 2° (see the Δ , \diamond , and ∇). The graphite sheet marked by Δ is crystalline (see arrow ①), becomes defective (see arrow ②), and finally vanishes (see arrow ③).

All CNTs grown in the temperature range of 750–950 °C have the same characteristics such as no encapsulated catalytic particles and a bamboo structure. Saito and co-workers reported the bamboo structure of CNTs grown using arc discharge.^{15,16} The bamboo structure has been found in the CNTs grown using microwave plasma-enhanced CVD (Ref. 10) and pyrolysis.¹² Therefore, we can conclude that the formation of the bamboo structure can be possible regardless of the growth method. However, the curvature of the compound layer in the bamboo-shaped CNTs grown using plasma-enhanced CVD and pyrolysis is directed to the root, which is opposite to that of our CNTs. As we mentioned previously, those CNTs grown using plasma-enhanced CVD or pyrolysis have an encapsulated catalytic particle at the tip, which is also different from our results. The tip growth model is inappropriate to justify no encapsulated catalytic particles at the tip. Here, we propose a base growth model to explain the bamboo-shaped CNTs grown under our experimental conditions.

Our growth model comprises the following structural features of CNTs obtained from HRTEM images. (i) There is no encapsulated metal particle at the closed tip and (ii) a bamboo structure with a compartment curvature directed to the tip. (iii) The graphite sheets of the wall are aligned toward the tube axis with an angle of few degrees and the outer graphite sheets vanish continuously. (iv) The wall joints with the compartment layer without any defects, resulting in the formation of a thick wall. (v) The number of graphite sheets at the wall changes, but the outer diameter remains almost the same.

The schematic diagrams of our model are shown in Fig. 4. Carbons produced from the decomposition of C₂H₂ molecules adsorb on a catalytic particle. The carbons diffuse via the surface and/or bulk of the metal particles, forming graph-

ite sheets as a cap on the catalytic particles, as illustrated by Fig. 4(a). Once the formation of the graphite sheet starts, the diffusion of carbons probably accelerates into the reaction zone of the catalytic particle, thus the carbons are continuously added to the edge of the cap. As the cap lifts off the catalytic particle, a closed tip with the inside hollow is formed [Fig. 4(b)]. The motive force departing from the catalytic particle may be the stress accumulated under the graphite cap. The wall would grow toward the vertical direction with a certain angle and the outer graphite sheets disappear. The accumulation of carbons at the inner surface of the catalytic particle occurs mainly via bulk diffusion, which produces the compartment graphite sheets. The compartment graphite sheets grow by forming the joint with the wall, as shown in the TEM image of Fig. 3(a). As the wall grows further, the compartment layer departs from the catalytic particle due to stress [see Fig. 4(c)]. Next, the compartment layer grown on the catalytic particle is again connected with the wall [see Fig. 4(d)]. The shape of the compartment layers is probably influenced by the surface geometry of the catalytic particle. When the carbons are supplied continuously under steady-state condition, the compartment layers can appear periodically [see Fig. 4(e)], which is consistent with Fig. 2(b).

In summary, we have reported the growth of vertically aligned CNTs on an Fe-deposited SiO₂ substrate by thermal CVD of C₂H₂ at 750–950 °C. All the CNTs have no encapsulated catalytic particles at the closed tip and a bamboo structure. The curvature of the compartment layers is always directed to the tip. HRTEM images provide information whereby the bamboo-shaped CNTs grow by forming a joint

between the wall and compartment. We propose a base growth model to explain the structure of the CNTs. Our model would provide insight into understanding the growth mechanism of CNTs.

- ¹S. Iijima, *Nature (London)* **354**, 56 (1991).
- ²D. S. Bethune, C. H. Kiang, M. S. deVries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature (London)* **363**, 605 (1993).
- ³C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer, *Nature (London)* **388**, 756 (1997).
- ⁴A. 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, and R. E. Smalley, *Science* **273**, 483 (1996).
- ⁵M. 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).
- ⁶Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, *Science* **282**, 1105 (1998).
- ⁷W. Z. Li, S. S. Xie, L. X. Qain, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, *Science* **274**, 1701 (1996).
- ⁸S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, *Science* **283**, 512 (1999).
- ⁹R. T. K. Baker, *Carbon* **27**, 315 (1989).
- ¹⁰H. Murakami, M. Hirakawa, C. Tanaka, and H. Yamakawa, *Appl. Phys. Lett.* **76**, 1776 (2000).
- ¹¹Y. Chen, D. T. Shaw, and L. Guo, *Appl. Phys. Lett.* **76**, 2469 (2000).
- ¹²D.-C. Li, L. Dai, S. Huang, A. W. H. Mau, and Z. L. Wang, *Chem. Phys. Lett.* **316**, 349 (2000).
- ¹³C. 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, and S. C. Yu, *Appl. Phys. Lett.* **75**, 1721 (1999).
- ¹⁴C. J. Lee, J. H. Park, and J. Park, *Chem. Phys. Lett.* **323**, 560 (2000).
- ¹⁵Y. Saito and T. Yoshikawa, *J. Cryst. Growth* **134**, 154 (1993).
- ¹⁶Y. Saito, *Carbon* **33**, 979 (1995).