Graphogrowth of Carbon Nanotubes by Chemical Vapor Deposition

Takayuki Arie, Seiji Akita, and Yoshikazu Nakayama

Department of Physics and Electronics,
College of Engineering,
Osaka Prefecture University
1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

(Received: 15 January 1998; accepted: 16 March 1998)

Abstract

Self-aligned carbon nanotubes have been synthesized by catalytic decomposition of benzene using the substrate with grooves. The nanotubes typically with ~500 nm in length and 30-50 nm in diameter are grown from the top edge of grooves toward the center of grooves and parallel to the substrate surface. They have a straight form, which is quite different from nanotubes produced by conventional catalytic chemical vapor deposition. The growth mechanism of nanotubes is discussed in terms of the feeding of precursors guided by the wrinkles which were formed at the edge of the main grooves when the grooves were made by scratching using a scriber.

I. Introduction

Since the discovery of carbon nanotubes [1] which are only a few nanometers in diameter and a few micrometers in length, their applications to mechanical and electronic nanometer-scale devices have been expected. Electrical conductivity measurements on the bulk material [2,3], on individual multi-walled [4,5] and single-walled [6] nanotubes and on bundles of single-walled nanotubes [7,8] have revealed that they have a function as metallic, insulating or semiconducting nanowires, which is probably depending on the helicity and the diameter as theoretically predicted [9-11]. Conventional methods used to generate nanotubes, such as carbon-arc discharge techniques [1,12], catalytic pyrolysis of hydrocarbons [13], catalytic and condensed phase electrolysis [14], generally suffer from drawbacks that polyhedral particles are coincidently formed and/or the dimensions of the nanotubes are highly variable. Therefore, the methods for purification and individual handling of nanotubes have been investigated (see e.g., Ref. [15]), which is important for further progress of their fundamental and application studies. There have also been several attempts of the position controlled growth of nanotubes by controlling the position of catalytic material in catalytic chemical vapor deposition (CVD) [16]. In this paper, we demonstrate a graphogrowth of nanotubes, which is a self-aligned growth of nanotubes on the grooved substrate by catalytic CVD.

II. Experiments

Substrates were quartz plates with and without grooves. The grooves were formed by scratching using a scriber and had ~10 μm width. Fine and almost straight wrinkles also appeared near the edge of the main grooves with angles of 110-115° from the scratching direction. The wrinkles were several nanometers in height and their spacing was ~ 500 nm. An 8 nm thick Ni film was evaporated as a catalyst on the substrates. The substrates were set on a substrate holder of graphite positioned in a quartz reactor tube (28 mm outside diameter, length 50 cm) and Helium gas was introduced at the flow rate of 50 sccm as shown in Fig. 1. The substrate surface was

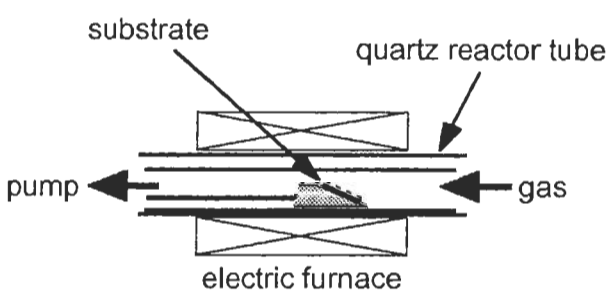

Fig. 1 Schematic diagram of the CVD system.

placed face downwards. The temperature was raised at 120℃/min up to 700℃ and maintained it for 30 min in order to change the thin film of Ni to round particles with diameter of 10-300 nm. The operating pressure was 120 mTorr. After that, a source gas of benzene was fed into the reactor at the flow rate of 50 sccm

for an hour to form nanotubes under the condition of the pressure of 2 Torr and temperature of 700℃.

The products were observed using a field emission scanning electron microscope (FESEM, HITACHI S-4500).

Ⅲ. Results and Discussion

Figure 2 shows the SEM image of nanotubes

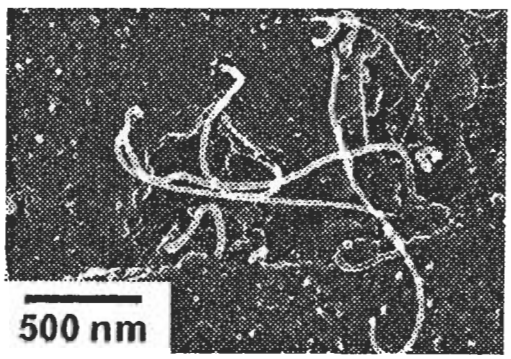

Fig. 2 SEM image of the typical nanotubes grown of the flat surface.

prepared on the substrate without grooves. The shape of the resultant nanotubes is typical of that (not straight) by catalytic CVD. The diameter and length of nanotubes are ~25 nm and several micrometers, respectively. The role of the catalyst in this CVD process has been considered to be dehydrogenation of benzene to produce precursors [17]. This result suggests that it is difficult to control the tube direction, although there have been several reports (see e.g., Ref. [16]) on the growth position control by positioning catalytic metals.

Figure 3 shows the SEM image of nanotubes

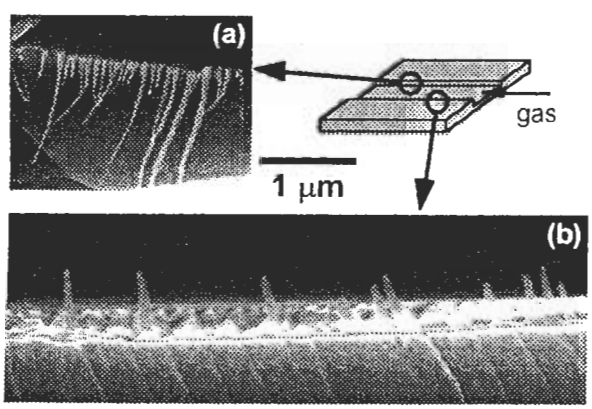

Fig. 3 SEM images of the nanotubes at the edge of the groove. The direction of the source gas is also indicated.

prepared on the grooved substrate, where the direction of the source gas flow is also indicated. The aligned nanotubes are grown from the top edge of grooves toward the center of grooves and parallel to the substrate surface. Moreover, none of the nanoparticles, polyhedral particles usually formed in an arc discharge method and bundled nanotubes is observed. The nanotubes have a straight form typically with 0.5-1 μm in length and 30-50 nm in diameter. This shape is quite different from that of nanotubes on the flat surface shown in Fig. 2. It is obvious that not only the growth position but also the tube direction can be controlled. It is also observed that nanotubes are grown with the same direction as the wrinkles formed near the edge of the groove. This is much more clearly seen in Fig. 3(b).

Figure 4 shows the SEM image of the

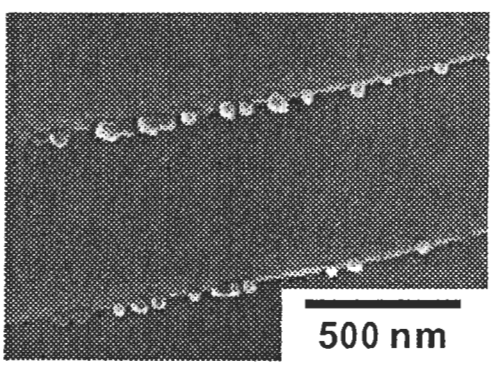

Fig. 4 SEM image of the Ni particles after the heat treatment of the Ni film.

wrinkles after the thermal treatment of Ni thin films. As seen in the figure, the Ni particles with diameter of ~40 nm gather along the wrinkles. This suggests that the Ni particles formed from thin films migrate to be trapped at a step. Taking account of the role of the Ni particles in CVD, we have a growth model described below. Source gas molecules reaching the wrinkles adsorb with its ring parallel to the Ni surface, and then are dehydrogenated by Ni catalysis to produce precursors. The precursors are guided by the wrinkles and move to the top edge of grooves to form nanotubes there. Here Ni round particles might cause the graphite sheets adsorbing Ni surface to transform into the carbon nanotubes [18].

The feeding of precursors with a certain direction is believed to grow the straight nanotubes. It is found in Fig. 3(b) that a

nanotube does not always grow where a wrinkle intersects the top edge of grooves. This might be caused by the fluctuation of the line density of Ni particles on a wrinkle.

We have confirmed that the growth of aligned nanotubes does not depend on whether the substrate is placed face downwards (described here) or upwards.

IV. Conclusion

The aligned growth of nanotubes has been achieved on the grooved substrate by catalytic CVD. This graphogrowth has been explained by the feeding of precursors with a certain direction which is guided by the wrinkles where Ni particles of a catalyst gather. This result gives us a key to control not only the growth position but also the growth direction of nanotubes.

References

1. S. Iijima, Nature **354**, 56(1991).
2. W. A. de Heer, W. S. Bacsa, A. Châtelain, T. Gerfin, R. Humphrey-Baker, L. Forro, and D. Ugarte, Science **268**, 845(1995).
3. Y. Nakayama, S. Akita, and Y. Shimada, Jpn. J. Appl. Phys. **34**, L10(1995).
4. H. J. Dai, E. W. Wong, and C. M. Lieber, Science **272**, 523(1996).
5. T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, Nature **382**, 54(1996).
6. S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, and C. Dekker, Nature **386**, 474(1997).
7. M. Bockrath, D. H. Cobden, P. L. McEuen, N. G. Chopra, A. Zettl, A. Thess, and R. E. Smalley, Science **275**, 1922(1997).
8. 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. Tománek, J. E. Fischer, and R. E. Smalley, Science **273**, 483(1996).
9. J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631(1992).
10. N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579(1992).
11. R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204(1992).
12. T. W. Ebbesen, and P. M. Ajayan, Nature **358**, 220(1992).
13. S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov, and J. B. Nagy, Science **265**, 635(1994).
14. W. K. Hsu, J. P. Hare, M. Terrones, H. W. Kroto, D. R. M. Walton, and P. J. F. Harris, Nature **377**, 687(1995).
15. K. Yamamoto, S. Akita, and Y. Nakayama, Jpn. J. Appl. Phys. **35**, L917(1996).
16. W. 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).
17. M. Yudasaka, R. Kikuchi, T. Matsui, K. Tasaka, Y. Ohki, S. Yoshimura, and E. Ota, J. Vac. Sci. Technol. A **13**, 2142(1995).
18. M. Yudasaka, R. Kikuchi, T. Matsui, Y. Ohki, S. Yoshimura, and E. Ota, Appl. Phys. Lett. **67**, 2477(1995).