

TEM Observation of the Giant Carbon Nanotube Construction Using Langmuir-Blodgett Films

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Abstract— Langmuir-Blodgett (LB) films, which included Fe atoms as a catalytic metal material, were used for carbon nanotube (CNT) growth by chemical vapor deposition (CVD). A new form of localized nanotube growth was observed to result in a structure called a giant carbon nanotube construction (GNC). The GNC seems to be a self-assembled knitted structure formed by CNTs. The GNC is thin ($\sim 5 \mu\text{m}$ in diameter) and long ($\sim 100 \mu\text{m}$) and is quite different from a CNT bundle. A growth mechanism for the GNC was developed from the results of TEM, SEM, and Raman spectral analysis. The GNC might find applications for CNT sensors, synthetic fibers, and so on.

Index Terms— carbon nanotubes, chemical vapor deposition, Langmuir-Blodgett films, local growth

I. INTRODUCTION

Carbon nanotubes (CNTs) are key materials for nanotechnology, and many researchers have reported a variety of CNT growth methods, including arc discharge [1], thermal chemical vapor deposition (CVD) [2], hot-filament-assisted CVD [3], plasma CVD [4], and laser-assisted production [5]. For even the thermal CVD method alone, many different carbon sources can be used, such as hydrocarbons (acetylene, ethane, methane) [2], carbon monoxide [6], and alcohol [3]. Catalytic metals, such as iron, molybdenum, cobalt, and nickel, and their mixtures, also provide popular means of CNT CVD growth. Furthermore, the question of how to coat the catalytic metal onto the substrate is an important issue, resulting in the use of sputtered pure metal films, metal-complex solutions, and zeolite as support materials [7]. It is also important to control the diameter of CNTs, which strongly depends on the size of the catalytic metal particle, and therefore, on the thickness of the metallic thin films formed with sputtered metal atoms. It has been reported that the quality of CNTs mainly depends on the initial stage of nucleation [8]. Moreover, K. Hata et al. reported that ultrahigh-quality single-walled carbon nanotubes (SWNTs) could be formed by adding a little water [9]. All of these reports, however, related to controlling the growth of a single CNT.

We previously reported a simple mask method (with a SiO_2 mask film formed by plasma CVD) using a catalytic complex, which can control the local growth positions of

CNTs without requiring complicated lithographic techniques [10]. It is difficult, however, to control the film thickness of the catalyst layer used as a nucleation site for a relatively wide area ($\sim 1 \text{ cm}^2$). Therefore, in this work, we tried to control the film thickness of the catalyst layer by using Langmuir-Blodgett (LB) films of a stearic acid iron (III) salt (FeSt_3), which turned out to have the great advantage of enabling precise layer-by-layer control of the catalytic film thickness.

It is difficult to fabricate structures comprising large numbers of CNTs. Many researchers have reported on objects assembled using CNT bundles, but these are easily decomposed into single CNTs. Unlike these objects, we have discovered a self-assembled giant carbon nanotube construction (GNC) that looks like wool [11].

As the GNC has a complicated structure, we used transmission electron microscopy (TEM) to investigate the GNC more precisely. We also successfully observed the multi-walled CNTs (MWCNTs) forming the GNC, which included the Fe catalyst nuclei.

The GNC may find applications for new, functional CNT-based devices, such as CNT sensors [12-14] and synthetic fiber materials.

II. GNC FABRICATION USING LB FILMS

A. Substrate Preparation Procedure

A $10 \times 10 \text{ mm}$ silicon wafer (Cz-Si (100)) with a natural oxide layer was used as a substrate. We used LB films of FeSt_3 (TOKYO KASEI KOGYO Co., Ltd.) as a catalyst material for the CNT CVD process. The FeSt_3 molecules were allowed to distribute themselves over distilled water and then transferred onto the Si (100) wafer at a substrate-raising rate of 20 mm/min and a surface pressure of 20 mN/m . The vertical deposition method was used. We prepared FeSt_3 LB films consisting of 1 monolayer (ML), 3 MLs, and 5 MLs. A SiO_2 mask layer was deposited by plasma CVD (SAMCO International Corp. PD-240) at a process temperature of 600 K . The thickness of the deposited SiO_2 layer was about 300 nm .

B. CVD Growth of the GNC

CNT CVD was carried out using the apparatus previously shown in Ref. [10]. Acetylene (C_2H_2 , 99.99% pure) gas was used as the CNT source gas, and Ar gas (99.9999%) was used as the carrier gas. The flow rate of each gas was controlled with an electric mass flow system (KOFLOC Co., Ltd). The temperature of the sample was measured with a K-type thermocouple attached to the outside surface of the reaction chamber.

The sample was observed by scanning electron microscopy (SEM) (JEOL JSM-6500F) and Raman spectroscopy (JASCO NRS-1000) at room temperature. In the Raman spectroscopy observation, the 532.30-nm line from a semiconductor laser was used for excitation at a power of 10 mW, with a 100-power objective lens was used. The GNC sample was also observed by TEM (Hitachi H800). For the TEM observation, the GNC sample had to be transferred to the TEM sample holder without any adhesive materials. Because the GNC was sufficiently large to be viewed with an optical microscope ($\sim 50 \mu\text{m}$ in length and $20 \mu\text{m}$ in diameter), it was picked up with a W needle by using such a microscope. The needle, with the GNC attached, was then fixed to the TEM sample holder by using Ag paste. The orientation of the GNC (substrate (root) side, or opposite (tip) side) was identified from a video feed obtained via the optical microscope.

III. TEM AND SEM OBSERVATION

A. TEM Observation of the GNC

We previously reported the existence of the giant carbon nanotube construction (GNC) [11]. The GNC reported here has a more highly aligned structure than quasi-aligned MWCNTs [2]. Figure 2 shows a TEM image of the GNC sample. This GNC did not have a structure as highly ordered as that of the GNC that we reported previously [11]. The GNC shown in Fig. 1 was about $20 \mu\text{m}$ in diameter and about $50 \mu\text{m}$ long, and it partially decomposed when it was picked up from the Si substrate, though we observed the real-time video images obtained via the optical microscope during the transfer process. This TEM image indicates that the GNC had many catalytic Fe nuclei and much amorphous carbon on the side opposite from the Si substrate (tip side), but no Fe nuclei on the substrate side (root side).

Figure 3 shows a TEM image of the tip side of the GNC. As noted above, there were many catalytic Fe nuclei and much amorphous carbon here. This might indicate that this side included the growth tip of the GNC.

Figure 4 shows a TEM image of the root side. There is little evidence of catalytic Fe nuclei and amorphous carbon in this image. These TEM images thus suggest that this GNC grew

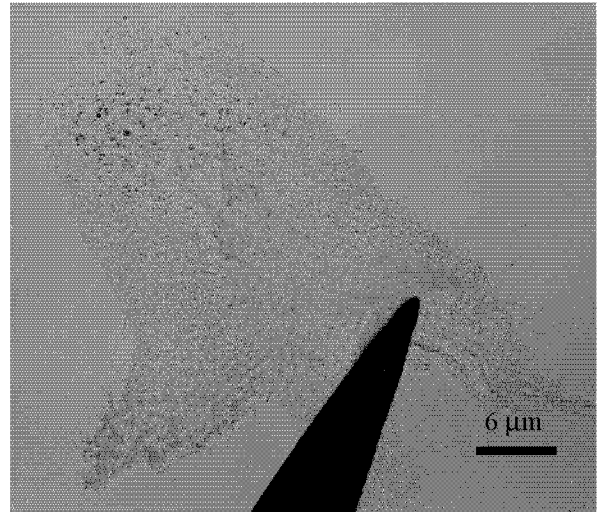


Fig. 1 Low-resolution TEM image of portion of the GNC sample. The sample was picked up from the Si growth substrate by using a W needle and an optical microscope, thus avoiding the need for any adhesive materials. The LB film for this sample consisted of 3 MLs

from the tip (grew from opposite side of the Si substrate), see fig. 6.

Other, the GNC grew only from locations where the SiO_2 layer had been removed. The mask SiO_2 layer is important to suppress the CNTs except GNC. Moreover, the quantity of CNTs increased as the FeSt3 LB film thickness was increased from 1 to 5MLs. This indicates that the thickness of the catalytic LB film could be used to control the quantity of CNTs. To gain more detailed information about the GNC, we will observe GNCs with an atomic force microscope. In particular, it will be important to obtain both 3-dimensional data and sectional data, but this remains for our future work.

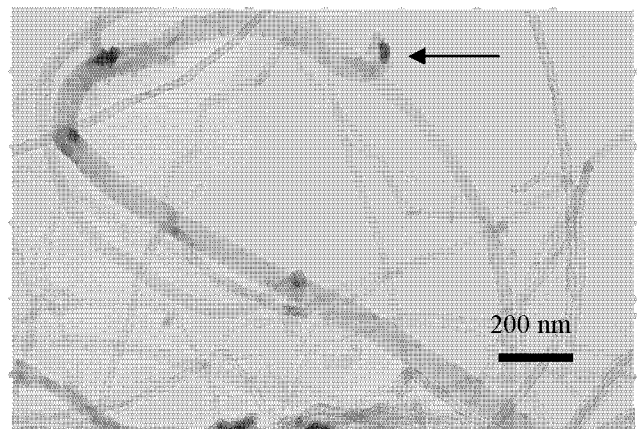


Fig. 2 High-resolution TEM image of the tip side (opposite from the Si substrate, i.e., the SiO_2 side). The catalytic Fe portion in the MWCNT can be observed.

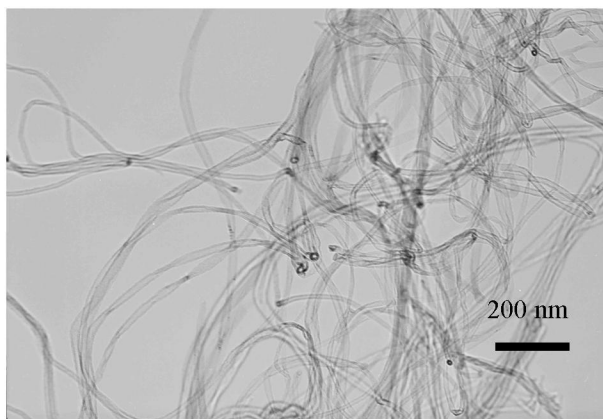


Fig. 3 High-resolution TEM image of the root side (i.e., the substrate side). No catalytic Fe nuclei can be observed. This may indicate that the growth side is opposite from the Si substrate, independently of the GNC diameter. Note that Figs. 2-4 show images of the same sample.

B. SEM observation of the disordered GNC without SiO₂ layer

It is important to investigate the growth mechanism of the GNC. In particular, since the LB films may easily decompose to increase the temperature (~ 500 K), we have to obtain the information of what was occurred to LB film under the plasma-CVD and CNT-CVD with high temperature. Figure 4 shows a low-magnification SEM image of a 3-ML sample after CNT CVD, without the SiO₂ layer. Many GNC-like structures appear on the substrate. Figure 5 shows a higher-magnification SEM image of the same sample shown in Fig. 4. This image indicates that these GNCs were almost the same as quasi-aligned MWCNTs [2]. We believe that these disordered GNCs grew from the decomposed LB film and then aggregated with LB molecules.

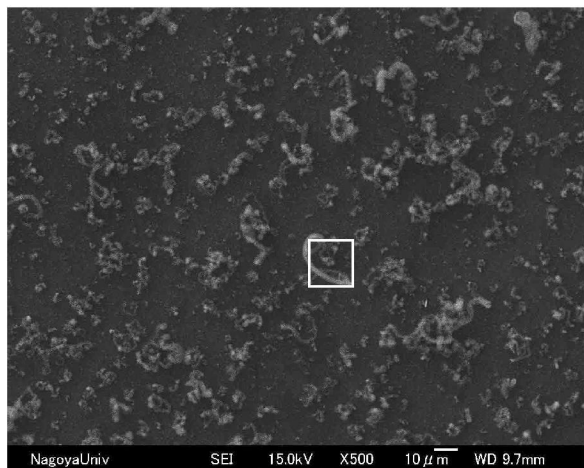


Fig. 4 SEM image of CNTs grown using a 3-ML LB (FeSt3) catalytic film, without the SiO₂ mask layer.

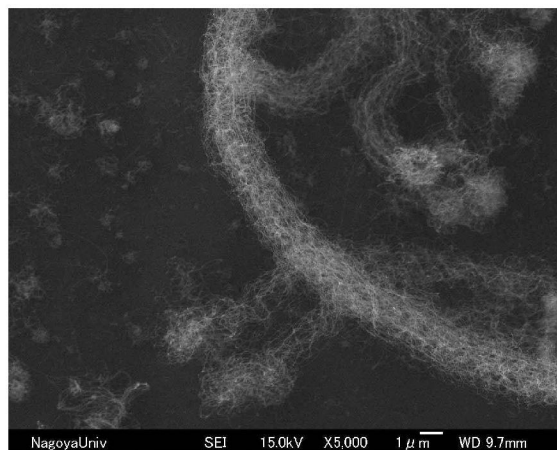


Fig. 5 SEM image of a disordered GNC. This is a blown-up image of the area in the white box in Fig. 5.

It is interesting that no highly ordered GNCs were found on this sample. Furthermore, the density of the disordered GNCs was very much higher than the density of GNCs obtained with the SiO₂ mask film. This may indicate that the highly ordered GNCs were grown at locations where the SiO₂ film was broken and the LB molecules aggregated. These results strongly suggest that rapid GNC growth occurred only with the presence of the SiO₂ mask layer. For localized growth, it is difficult to control the growth point of GNCs, but we expect that we can determine how to control the growth point. It is noted that the only GNC had grown and the isolated CNTs had suppressed using the mask SiO₂ layer.

From the Raman spectra of another disordered GNC sample (no figure), grown with a 3-ML StFe₃ film and no SiO₂ mask layer. The Raman measurement point was the middle of the GNC. The spectrum indicates that the G/D ratio was not very different from that of a highly ordered GNC (TSF). It is difficult to discuss the difference between the two types of GNC (disordered and highly ordered), because the substrate used for the disordered GNC (Si wafer + MWCNTs) was different from that used for the highly ordered GNC (plasma-deposited SiO₂, and locally grown). In the TEM images (not shown here) of both types, no significant difference was observed.

IV. PROPOSED GROWTH MECHANISMS OF THE GNC

Figure 6 shows a schematic diagram of the GNC growth mechanism. First, in the plasma CVD chamber, the LB film was heated to 600 K, at which point it simultaneously aggregated and partially evaporated. After depositing the SiO₂ layer, the sample was heated to 1050 K in the CNT CVD furnace. It can be seen that the SiO₂ mask layer was raised up by the growing CNTs. This suggests that the SiO₂ layer had been partially inflated by vaporization of aggregated StFe₃ molecules. That is, the aggregated FeSt₃ molecules were vaporized by CVD heating under the SiO₂

layer, so that the SiO₂ layer became partially inflated more easily. Where cracks occurred in the layer, sufficient C₂H₂ was supplied to construct GNCs. As a result, rapid CNT growth occurred (the CVD process time was only 2 minutes), finally producing a highly ordered GNC. In the case of growth without the SiO₂ mask layer before CNT CVD, disordered GNCs grew. This strongly indicates that the SiO₂ layer has an important role in GNC ordering.

Note that the CVD growth of GNCs was not stopped in order to investigate the growth processes. It is important to observe GNC growth *in situ*, by using high-pressure SEM with a video image recording system.

In addition, the growth position and direction of the GNC were not controlled in this work, but we will examine these aspects in the future by changing the thickness of the SiO₂ mask layer at the growth position and by applying an electric field to the substrate.

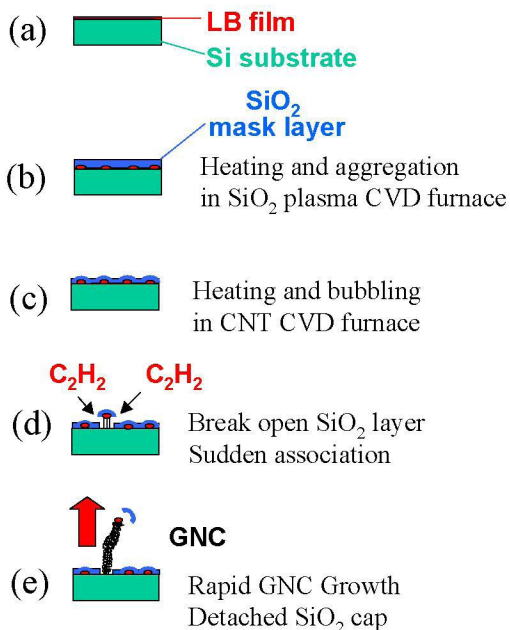


Fig. 6 Schematic drawing of the proposed growth mechanisms for the GNC.

V. CONCLUSION

GNCs were grown only on broken SiO₂ areas when FeS₁₃ LB films were used. The resulting GNCs consisted of large numbers of MWNTs. The quality (G/D ratio: ~1.5) of a disordered GNC formed from an LB film without a SiO₂ mask layer was almost the same as that of a GNC formed from an LB film with a SiO₂ layer (~1.3). From the results of our experiments, we have suggested a growth mechanism for the GNC. We believe that GNCs will be useful for applications such as CNT sensors and synthetic fibers.

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REFERENCES

- [1] Y. Saito, 'Carbon nanotubes produced by arc discharge', *New diamond and frontier carbon technology*, 9 (1999) 1-30.
- [2] K. Mukhopadhyay, A. Koshio, T. Sugai, N. Tanaka, H. Shinohara, Z. Konya, J. B. Nagy, 'Bulk production of quasi-aligned carbon nanotube bundles by the catalytic chemical vapor deposition (CCVD) method', *Chem. Phys. Lett.* vol.303, pp.117-124, April 1999.
- [3] T. Okazaki, H. Shinohara, "synthesis and characterization of single-wall carbon nanotubes by hot-filament assisted chemical vapor deposition", *Chem. Phys. Lett.*, vol.376, pp.606-611, July 2003.
- [4] Y. C. Choi, Y. M. Shin, Y. H. Lee, B. S. Lee, G. S. Park, N. S. Lee, J. M. Kim, "Controlling the diameter, growth rate, and density of vertically aligned carbon nanotubes synthesized by microwave plasma-enhanced chemical vapor deposition", *Appl. Phys. Lett.* vol.76, pp. 2367-2369, April 2000.
- [5] H. Kanzow, A. Schmalz, A. Ding, "Laser-assisted production of multi-walled carbon nanotubes from acetylene", *Chem. Phys. Lett.*, vol.295, pp.525-530, October 1998.
- [6] P. Nikolaev, M. J. Bronikowski, R. Kelley Bradley, F. Rohmund, D. T. Colbert, K.A. Smith, R.E. Smalley, "Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide", *Chem. Phys. Lett.* vol.313, pp.91-97, November 1999.
- [7] T. Sugai, T. Okazaki, H. Yoshida, H. Shinohara, "Synthesis of Single- and Multi-wall Carbon Nanotubes by the HTPAD and HFCVD methods", *New J. Phys.*, vol.6, pp.21-32, February 2004.
- [8] O. Suekane, T. Nagasaka, K. Kiyotaki, T. Nosaka, Y. Nakayama, "Rapid Growth of Vertically Aligned Carbon Nanotubes", *Jpn. J. Appl. Phys.* vol.43, pp. L1214-1216, September 2004.
- [9] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, "Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes", *Science*, vol.306, pp.1362-1364, November 2004.
- [10] Y. Imaizumi, Y. Arakawa, F. Arai, T. Fukuda, "Local growth of Carbon Nanotubes on the Cantilever by Chemical Vapor Deposition with Assist Etching", *Proc of Int. Conf. on IEEE-NANO2005*, CD-ROM, July 11-15, Nagoya, Japan (2005).
- [11] Y. Imaizumi, M. Kushida, Y. Arakawa, F. Arai, T. Fukuda, "Self-assembled Giant Carbon Nanotube Construction Using Langmuir-Blodgett Films", *Thin Solid Films*, 2006, in press.
- [12] F. Arai, C. Ng, P. Liu, L. Dong, Y. Imaizumi, K. Maeda, H. Maruyama, A. Ichikawa, T. Fukuda, "Ultra-small site temperature sensing by carbon nanotube thermal probes", *Proc. of Int. Conf. on IEEE-NANO2004*, CD-ROM, August 17-19, Munch, Germany (2004).
- [13] P. Liu, L. Dong, T. Fukuda, F. Arai, Y. Imaizumi, "Carbon Nanotubes Based Position Sensors", *Proc. of Int. Conf. on Intelligent Mechatronics and Automation (ICIMA2004)*, August 26-31, Chengdu, China (2004).
- [14] S. Ghosh, A. K. Sood, N. Kumar, "Carbon Nanotube Flow Sensors", *Science*, vol.299, pp. 1042-1044, February 2003.