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Competitive Growth of Carbon Nanotubes versus Carbon Nanofibers

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ABSTRACT

Carbon nanofilaments were formed on silicon substrate using microwave plasma-enhanced chemical vapor deposition method. The structures of carbon nanofilaments were identified as carbon nanotubes or carbon nanofibers. The formation of bamboo-like carbon nanotubes was initiated by the application of the bias voltage during the plasma reaction. The growth kinetics of bamboo-like carbon nanotubes increased with increasing the bias voltage. The growth direction of bamboo-like carbon nanotubes was vertical to the substrate.

Key words ***: Carbon nanofibers, Carbon nanotubes, Competitive growth, Bias voltage***

1. Introduction

Recently, carbon nanofilaments which were classified as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been regarded as the promising candidate materials for the diverse nanoelectronic applications, such as the nanowiring to the nanoelectronic devices, hydrogen storage media, field emitter, catalyst supporting media and so forth.[1-6] For the crystal structure point of view, CNF basically has a vertical stacking lattice structure to the principal axis of the nanofiber.[7] On the other hand, CNT shows a parallel lattice structure to the principal axis of the nanotube.[3,8] There are a number of reports regarding the structural transformations between CNTs and CNFs known as follows; CNTs transform into CNFs by the sonication.[9] Recently, a new structural transformation from CNFs into CNTs-like morphology was developed by the thermal annealing.[10, 11]

This work presents the competitive formation between CNTs and CNFs by the applied bias voltage during the plasma reaction. We confirmed the initiation of bamboo-like CNTs by the application of the bias voltage. The extents of CNTs and CNFs were investigated as a function of the bias voltage and their detailed morphology and nanostructure were also examined. Based on these results, the effect of the bias voltage during the plasma reaction on the competitive formation between CNTs and CNFs was discussed.

2. Experimental

CNTs and CNFs films were deposited on the nickel layer-coated 1.0×1.0 cm^2 Si substrate in a horizontal-type Microwave Plasma-Enhanced Chemical Vapor Deposition (MPECVD) system. Nickel coating could be achieved by Radio Frequency (RF) sputtering system. In RF-sputtering experiment, we used Ar gas with 30 mTorr total pressure under 500 W RF power condition. We obtained around 50 nm film thicknesses after 5 min sputtering reaction. Before the CNTs and CNFs deposition reaction, the substrate has been cleaned with H_2 plasma for a few minutes. CH_4 and H_2 were used as source gases. The detailed experimental conditions were described in Table 1.

The morphologies of carbon nanostructures were investigated using Field Emission Scanning Electron Microscopy (FESEM) and the compositions of carbon nanostructures were analyzed by Electron Probe Micro-Analysis (EPMA). The samples for TEM were prepared by dispersing CNTs and CNFs using acetone in an ultrasonic bath. A drop of suspension was placed onto a carbon film supported by a Cu grid; then, Cu grid was placed into TEM chamber and the detailed morphologies of CNTs and CNFs were investigated via Transmission Electron Microscopy (TEM) study.

3. Results and Discussion

We first investigated the surface images of CNTs or CNFs deposited substrates as a function of the applied bias voltage. Fig. 1(a)~(c) show FESEM synthesized CNTs or CNFs images on the nickel coated Si substrates after deposition reaction under –50 V (Fig. 1(a)), –200 V (Fig. 1(b)), and –400 V (Fig. 1(c)) bias voltage. Fig. 2(a)~(c) show the magnified images of Fig. 1(a)~(c), respectively. As shown in Fig. 1(b) and (c), we could observe the formation of the nanostructure including the conventionally grown nanostructure (A-type) and the linearly well-developed nanostructure (B-type) morphologies. The number density of B-type nanostructure on

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Table 1. Experimental Conditions of Carbon Nanotubes and Carbon Nanfibers Formation

Microwave power	Source gases	Flow rates of source gases	Reaction time	Total pressure	Bias voltage	Sub. Temp.
600 W	CH_4, H_2	CH_4 : 2.5 sccm H_2 : 47.5 sccm	5 min	60 Torr	–50 V –200 V –400 V	920°C, 990°C, 1070°C

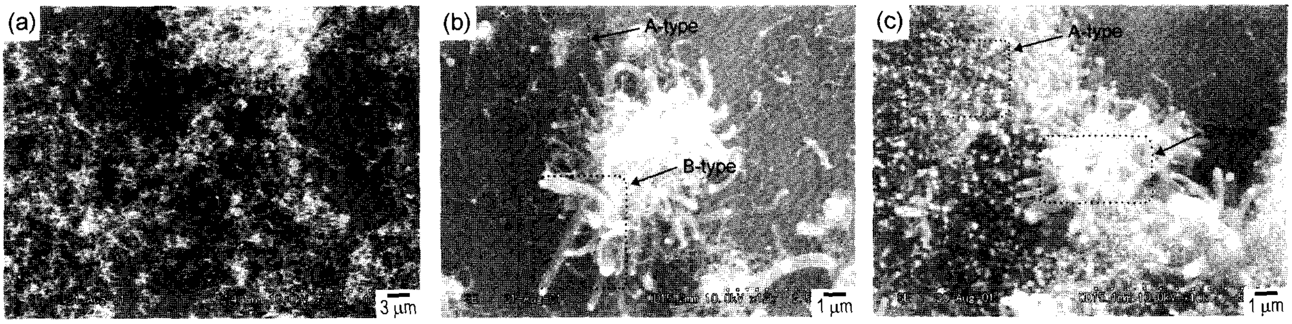

Fig. 1. FESEM images of the CNFs-deposited Si substrates under (a) –50, (b) –200, and (c) –400 V bias voltage conditions.

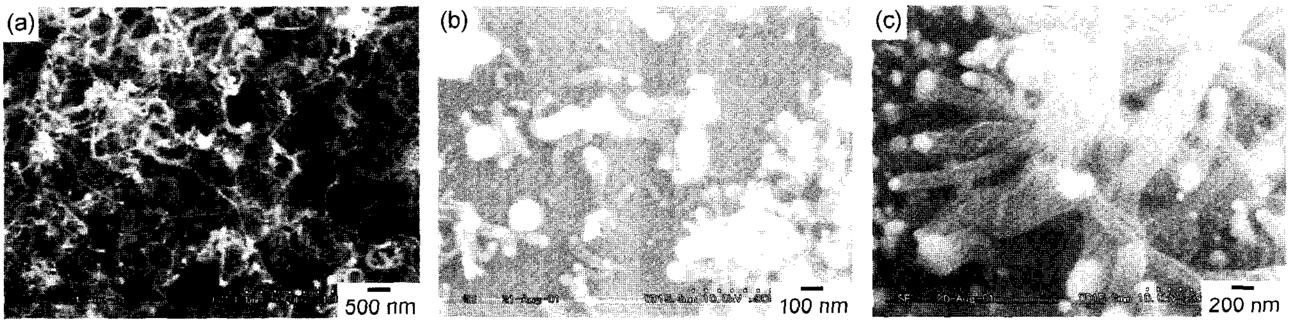

Fig. 2. The magnified FESEM images of Fig. 1.

the substrate seems to increase with increasing the applied bias voltage (see Fig. 1(a)–(c)). Indeed, A-type nanostructure was mostly observed under the low bias voltage (–50 V) condition. However, we could observe the well-developed vertical growth of B-type nanostructure onto the substrate surface at the high negative bias voltage (–400 V) (see the growth direction of the nanostructure in Fig. 2(c)).

To identify the detailed nanostructures of A and B-type morphologies, we carried out a TEM study. Fig. 3 shows the filled and the hollow spaces inside the nanostructures. These features were more pronounced under the high negative bias voltage (–400 V) condition. For the hollow nanostructures, we clearly observed the parallel-developed lattice structure at the wall of the nanostructure (see P position in Fig. 3) and the crossing lattice structure across the inside of the nanostructure (see C position in Fig. 3). These results reveal that B-type morphology would follow the nanostructure of bamboo-like carbon nanotubes.[12, 13] On the other hand, the stacking lattices (see the horizontal lines at H position in Fig. 3), the protrusions of the lattices to the outside of the nanostructure (see O position in Fig. 3) and the filled image at the inside of the nanostructure confirmed that this material would follow the nanostructure of carbon nanofibers.[3,11] The B-type morphology could be well-developed with increasing the applied bias voltage. Indeed, we

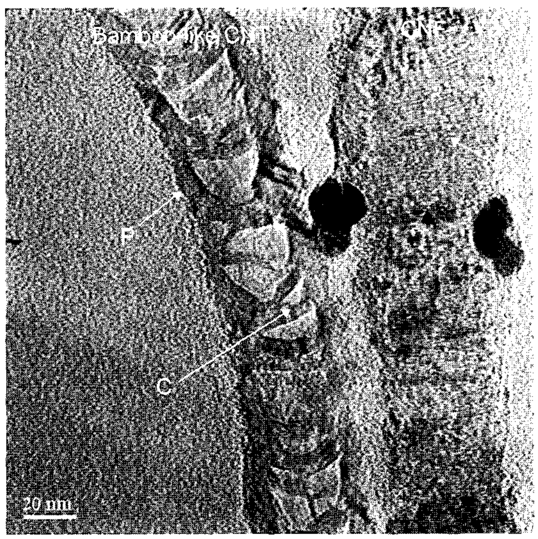

Fig. 3. TEM image for one of the bamboo-like carbon nanotubes and the carbon nanofibers under 400 V bias voltage condition.

rarely observed the nanostructure having hollow space under the low bias voltage (–50 V) application. Instead, the formation of the nanostructure having filled space was more pronounced. Fig. 4 shows TEM image of the frequently

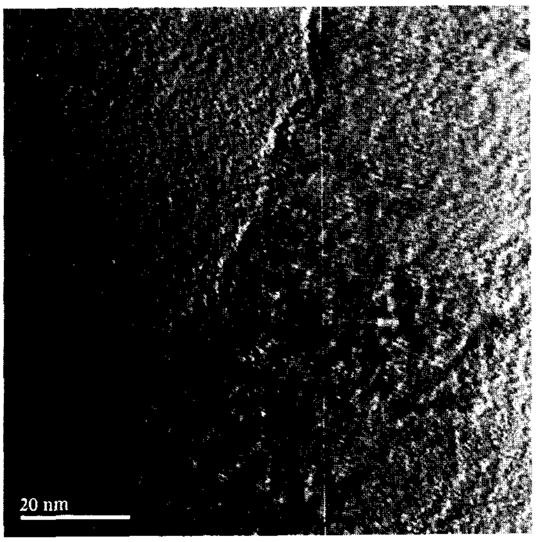

Fig. 4. TEM image for one of the carbon nanofibers under –50 V bias voltage condition.

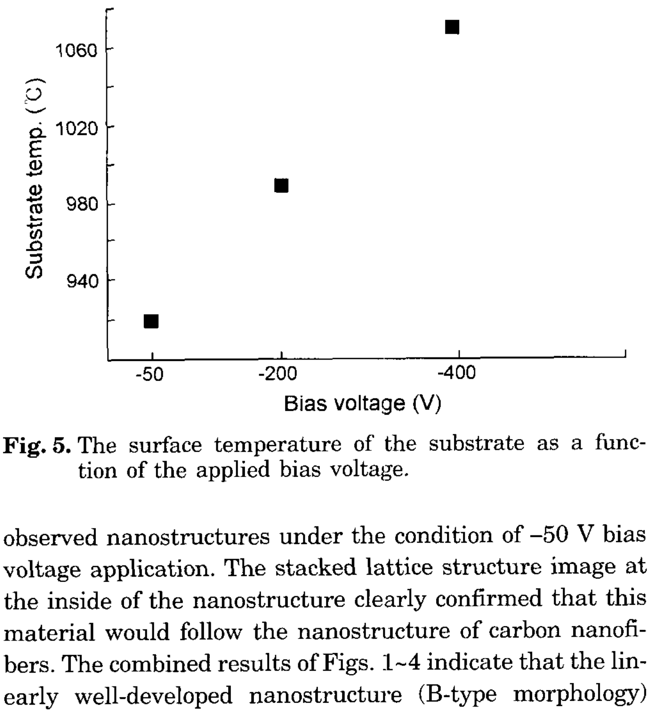

Fig. 5. The surface temperature of the substrate as a function of the applied bias voltage.

observed nanostructures under the condition of –50 V bias voltage application. The stacked lattice structure image at the inside of the nanostructure clearly confirmed that this material would follow the nanostructure of carbon nanofibers. The combined results of Figs. 1~4 indicate that the linearly well-developed nanostructure (B-type morphology) would be the bamboo-like carbon nanotubes. In addition, we may suggest that the number density of the bamboo-like carbon nanotubes increases with increasing the applied bias voltage.

The cause for the enhancement of bamboo-like carbon nanotubes density under the high bias voltage application condition may be attributed to the variation of the induced temperature of the substrate surface caused by the applied bias voltage. Fig. 5 shows the variation of the substrate temperature as a function of the application of the negative bias voltage. As shown in Fig. 5, the high bias voltage application induces high temperature of the substrate surface. Previously, it was reported that a new structural transformation from CNFs into CNTs-like morphology was developed by the high temperature thermal annealing.[10,11] So, we suggest that the formation of the bamboo-like carbon nanotubes seems to originate from the higher induced temperature of the substrate surface.

4. Conclusions

The bias voltage application during the plasma reaction gave rise to the formation of the bamboo-like carbon nanotubes under the carbon nanofibers formation condition. The ratio of the number density of the bamboo-like carbon nanotubes to that of the carbon nanofibers increases with increasing the applied bias voltage. The well-developed vertical growth of the bamboo-like carbon nanotubes onto the substrate surface could be observed by the high negative bias voltage (–400 V) application.

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REFERENCES

1. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Sirgal, and P. N. Provencio, "Synthesis of Large Arrays of Well-aligned Carbon Nanotubes on Glass," *Science*, **282** 1105-07 (1998).
2. S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Casell, and H. Dai, "Self-oriented Reqular Arrays of Carbon Nanotubes and their Field Emission Properties," *Science*, **283** 512-13 (1999).
3. M. J. Ledoux, R. Vieira, C. Pham-Huu, and N. Keller, "New Catalytic Phenomena on Nanostructured (fibers and tubes) Catalysis," *J. of Catalysis* **216** [1-2] 333-42 (2003).
4. S. Iijima, "Helical Microtubules of Graphite Carbon," *Nature*, **354** 56-8 (1991).
5. M. S. Kim, W. J. Woo, H. S. Song, Y. S. Lim, and J. C. Lee, "Characterization of Nanostructure and Electronic Properties of Catalytically Grown Carbon Nanofiber," *J. Kor. Ceram. Soc.*, **37** [4] 345-53 (2000).
6. M. S. Kim, S. W. Jung, W. J. Woo, and Y. S. Lim, "Preparation of Porous Carbon Support using Carbon Nanofiber and its Catalytic Activity," *J. Kor. Ceram. Soc.*, **36** [5] 504-12 (1999).
7. T. Ikuno, J.-T. Ryu, T. Oyama, S. Ohkura, Y.-G. Baek, S. Honda, M. Katayama, T. Hirao, and K. Oura, "Characterization of Low Temperature Growth Carbon Nanofibers Synthesized by Using Plasma Enhanced Chemical Vapor Deposition," *Vacuum* **66** [3-4] 341-45 (2002).
8. H. K. Yu, H. Ryu, F. Saito, and B. Lee, "The Effect of Mechanochemical Treatment of the Catalyst in the Preparation of Carbon Nanotubes and their Electrical Properties" *J. Kor. Ceram. Soc.*, **38** [12] 1110-14 (2001).
9. K. Mukhopadhyay, C. D. Dwivedi, and G. N. Mathur, "Conversion of Carbon Nanotubes to Carbon Nanofibers by Sonication," *Carbon*, **40** [7] 1373-76 (2002).
10. M. Endo, Y. A. Kim, T. Hayashi, T. Yanagisawa, H. Mura-

matsu, M. Ezaka, H. Terrones, M. Terrones, and M. S. Dresselhaus, "Microstructural Changes Induced in "Stacked Cup" Carbon Nanofibers by Heat Treatment," *Carbon,* **41** [10] 1941-47 (2003).

11. G.-B. Zheng, H. Sano, and Y. Uchiyama, "New Structure of Carbon Nanofibers after High-temperature Heat-treatment," *Carbon,* **41** [4] 853-56 (2003).
12. Y. Huh, J. Y. Lee, J. H. Lee, T. J. Lee, S. C. Lyu, and C. J. Lee, "Selective Growth and Field Emission of Vertically Well-aligned Carbon Nanotubes on Hole Patterned Silicon Substrates," *Chem. Phy. Lett.*, **375** [3-4] 388-92 (2003).
13. X. Wang, W. Hu, Y. Liu, C. Long, Y. Xu, S. Zhou, D. Zhu, and L. Dai, "Bamboo-like Carbon Nanotubes Produced by Pyrolysis of Iron(II) Phthalocyanine," *Carbon,* **39** [10] 1533-36 (2001).