Journal of the Korean Crystal Growth and Crystal Technology
Vol. 15, No. 5 (2005) 198-201

Control the growth direction of carbon nanofibers under direct current bias voltage applied microwave plasma enhanced chemical vapor deposition system

Sung-Hoon Kim†

Department of Nano Chemistry Materials & Engineering, Silla University, Busan 617-736, Korea

(Received September 1, 2005)
(Accepted October 7, 2005)

Abstract Carbon nanofibers were formed on silicon substrate which was applied by negative direct current (DC) bias voltage using microwave plasma-enhanced chemical vapor deposition method. Formation of carbon nanofibers were varied according to the variation of the applied bias voltage. At −250 V, we found that the growth direction of carbon nanofibers followed the applied direction of the bias voltage. Based on these results, we suggest one of the possible techniques to control the growth direction of the carbon nanofibers.

Key words Carbon nanofibers, Growth direction, Microwave plasma, Negative bias voltage

1. Introduction

Carbon nanofilaments, called carbon nanotubes if hollow and carbon nanofibers if filled, have regarded as the promising material candidate for interconnection lines of transistors and cold electron emission sources, due to their unique geometries [1].

For the application of carbon nanofilaments to interconnection lines, lateral growth is required because this direction makes connection plausible [2, 3]. To apply carbon nanofilaments to the electron emitter, however, achievement of a vertical alignment is preferential [4, 5]. Therefore, the control of the growth direction of carbon nanofilaments is indispensable to such applications.

Recently, the application of a negative bias voltage during plasma reaction has been known to facilitate well-aligned carbon nanofilaments in the vertical direction to the substrate surface [6, 7]. In addition, to enlarge the application area of vertically well-aligned carbon nanofilaments to the various shapes, such as convex and concave, the control of the vertical growth direction of carbon nanofilaments would be required.

For the control of the carbon nanofilaments growth direction, Jang *et al.* reported that multi-walled carbon nanotubes (MWCNTs) were laterally aligned by an electric field [8]. They selectively grew MWCNTs between lateral sides of the catalytic metals on predefined electrodes. Then, they found that the electric field direction at the vicinity of catalyst and nanotubes-substrates interactions were principal factor in aligning MWCNTs laterally. Zhu et al. reported the different growth direction of carbon nanotubes on the substrate according to the gravity factor [9].

Despite these efforts, the manipulation of carbon nanofilaments growth direction is still required to maximize their applicable purpose.

In this work, we observed the different growth behavior of the carbon nanofilaments on the substrate according to the different substrate positions with respect to the counter electrode. Based on these results, we suggest the promising methods to control the growth direction of the carbon nanofilaments.

2. Experimental Section

We deposited carbon nanofilaments films on the nickel layer-coated $10.0 \times 10.0\ mm^2$ Si substrate in a horizontal-type microwave plasma-enhanced chemical vapor deposition (MPECVD) system as shown in Fig. 1. 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 100 nm film thicknesses after 5 min sputtering reaction.

Before the carbon nanofilaments deposition reaction, we cleaned the substrate with H_2 plasma for a few minutes. CH_4 and H_2 were used as source gases. Bias voltage value was maintained at −250 V. The detailed experimental conditions of the carbon nanofilaments formation using

†Corresponding author
Tel: +82-51-999-5619
Fax: +82-51-999-5176
E-mail: shkim@silla.ac.kr

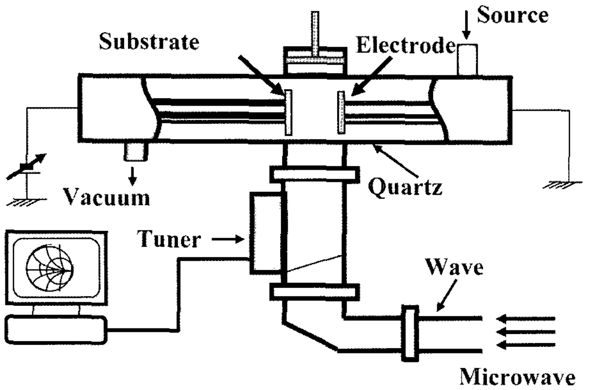

Fig. 1. Systematic diagram of a horizontal-type microwave plasma-enhanced chemical vapor deposition (MPECVD) system.

MPECVD were shown in Table 1.

The morphologies of carbon nanofilaments were investigated by field emission scanning electron microscopy (FE-SEM). The nanostructures of carbon nanofilaments were examined by transmission electron microscopy (TEM). The samples for TEM were prepared by dispersing the carbon nanofiaments 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 carbon nanfilaments were investigated.

3. Results and Discussion

After 5 min carbon nanofilaments deposition as a function of the applied bias voltage, we investigated the surface morphology of the substrate, as shown in Fig. 2. We could observe the randomly orientation of the carbon nanofilament formation below –50 V bias voltage application condition (see Fig. 2a). With increasing the bias voltage (at –150 V and –250 V), we could observe the vertical growth of the carbon nanofilaments (see Figs. 2b and c). At high bias voltage (–300 V) in this work, the bundle formation of the vertically-aligned carbon nanofilaments could be observed as shown in Fig. 3. As shown in the inset in Fig. 3, these bundles were composed by the respective carbon nanofilaments. And each carbon nanofilaments incorporates Ni at the top position of the nanofilaments. The existence of Ni at the top position of the nanofilaments was confirmed by electron probe micro analysis (EPMA) (see Table 2).

To identify whether these carbon nanofilaments are carbon nanotubes or carbon nanofibers, we carried out TEM study. Figure 4 shows the detailed structure of the carbon nanofilaments. From the stacking lattices, the protrusions of the lattices to the outside of the filaments and the filled image at the inside of the filaments, we confirmed that these filaments were carbon nanofibers. The diameters of the carbon nanofibers in this work were measured in the range of between 20 and 70 nm.

From the combined results of Figs. 2~4, we suggest that the well-aligned vertical growth of the carbon nanofibers could be formed with increasing the applied negative bias voltage.

Table 1
Experimental conditions of carbon nanofibers formation

Microwave power	Source gases	Flow rates of source gases	Sub. temp.	Total pressure	Reaction time	Bias voltage (V)
600 W	CH_4, H_2	CH_4: 2.5 sccm H_2: 57.5 sccm	950°C	85 Torr	5 min	–50~–300 V

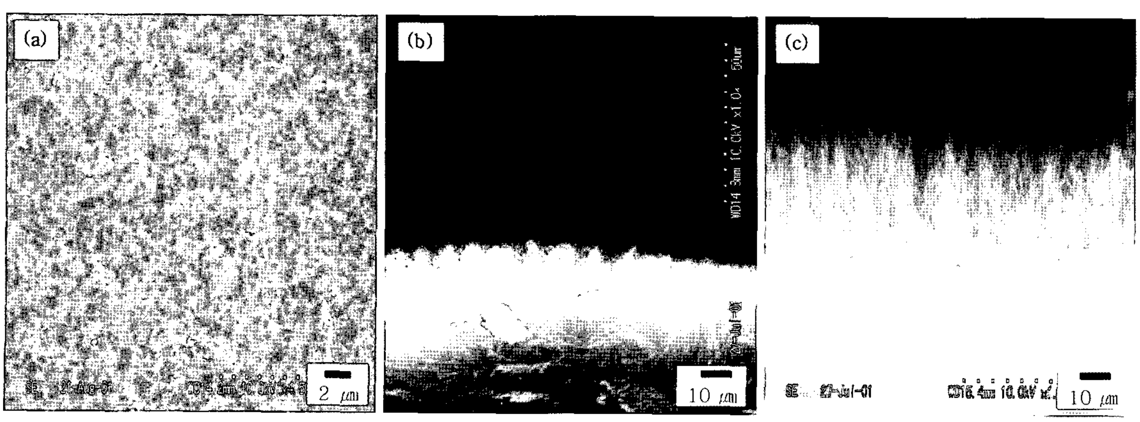

Fig. 2. FESEM images of the carbon nanofilaments as a function of the applied bias voltage: (a) –50 V, (b) –150 V and (c) –250 V.

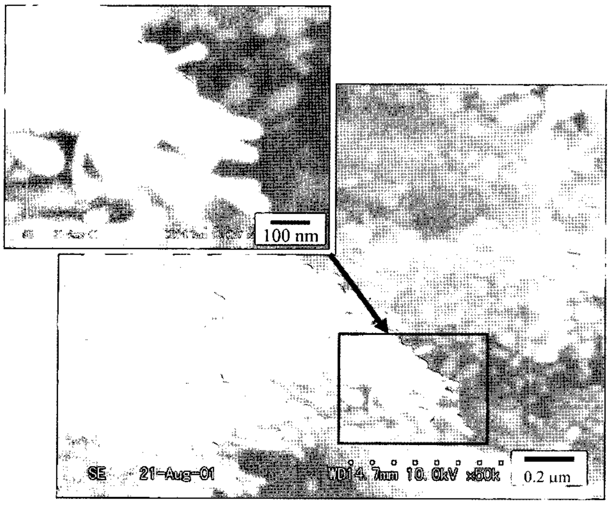

Fig. 3. FESEM image of the carbon nanofilaments at −300 V. The inset shows the bundles of these carbon nanofilaments composed by the respective carbon nanofilaments. It also shows the incorporation of Ni at the top position of the each carbon nanofilament.

Table 2
Compositions of the nickel-catalyzed carbon nanofilaments measured by EPMA

Elements	Compositions [%]
C	84.57
Ni	0.51
Mg	1.98
O	12.94

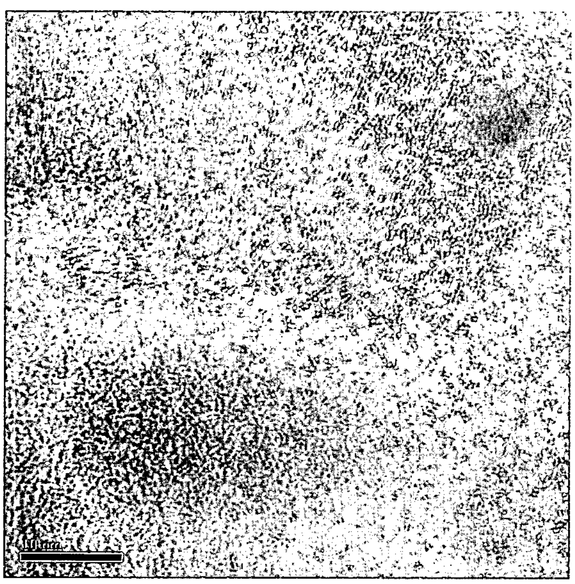

Fig. 4. TEM images of the individual carbon nanofiber.

To control the growth direction of the carbon nanofibers, we intentionally made the different positions between the counter electrode and the substrate as shown in Figs.

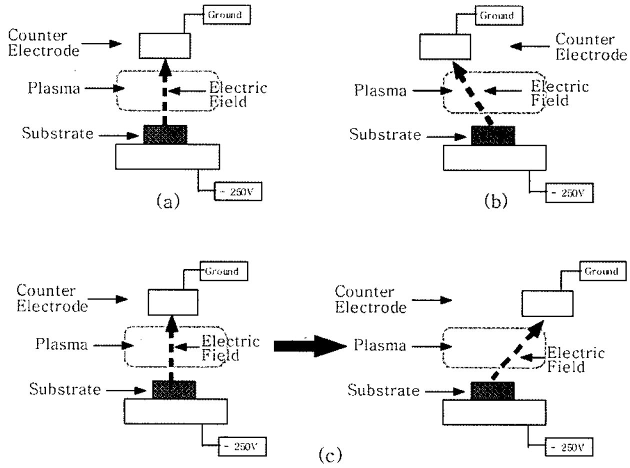

Fig. 5. The systematic diagrams according to the different positions between the counter electrode and the substrate: (a) the face to face position, (b) the face to slipped face position and (c) the position moving from the face to face position into the face to slipped face position.

5a, b, and c. Figure 5a shows the face to face position between the substrate and the counter electrode. Figure 5b shows the face to slipped face position between the substrate and the counter electrode. And the Fig. 5c shows the position moving from the face to face into face to slipped face. Indeed, this moving was carried out in situ process during the reaction. Namely, 2 minute's face to slipped face position was set after 3 minute's face to face position.

In the face to face position, the growth direction of the carbon nanofibers was vertical straight from the substrate to the counter electrode as shown in Fig. 6a. On the other hand, in the face to slipped face position the growth direction of the carbon nanofibers was slant straight following the direction from the substrate to the counter electrode as shown in Fig. 6b. In the face to slipped face position after 3 minute's face to face position, interestingly, the growth direction of the carbon nanofibers was initially vertical straight from the substrate to the counter electrode and then slanted toward the counter electrode as shown in Fig. 6c. These results reveal that the growth direction of the carbon nanofibers would follow the applied direction of the bias voltage.

Therefore the growth direction of the carbon nanofibers seems to be controlled simply by varying the position between the counter electrode and the substrate. Based on these results, we suggest that the growth direction of carbon nanofibers may follow the electric field direction from the substrate to the counter electrode.

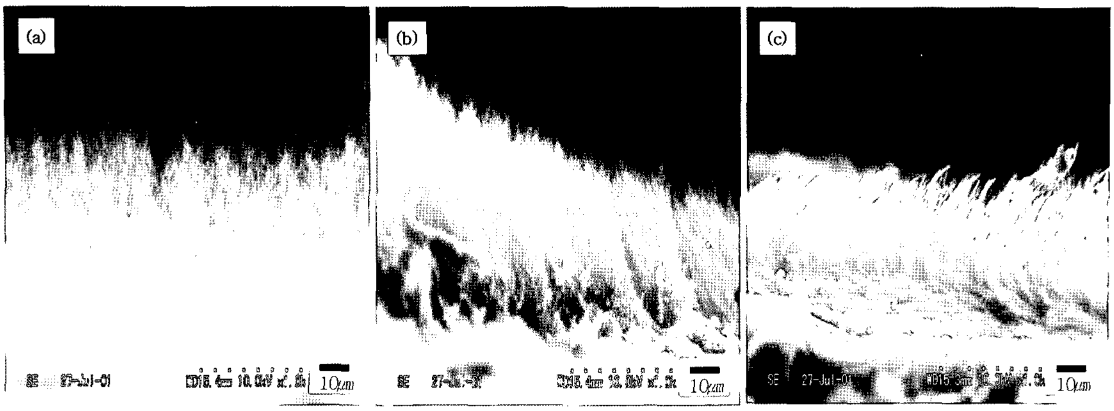

Fig. 6. FESEM images of the as-grown carbon nanofibers as a function of the different positions between the counter electrode and the substrate: (a) the face to face position, (b) the face to slipped face position and (c) the position moving from the face to face position into the face to slipped face position.

4. Conclusions

The well-aligned vertical growth of the carbon nanofibers could be formed with increasing the applied negative bias voltage. By varying the position between the counter electrode and the substrate, the growth direction of the carbon nanofibers could be controlled. The electric field direction seems to be the cause to determine the growth direction of carbon nanofibers.

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 (1998) 1105.
[2] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs and C. Dekker, "Individual single-wall carbon nanotubes as quantum wires", Nature 386 (1997) 474.
[3] L. Marty, V. Bouchiat, A.M. Bonnot, M. Chaumont, T. Foutnier, S. Decossas and S. Roche, "Batch processing of nanometer-scale electrical circuitry based on in-situ grown single-walled carbon nanotubes", Microelectronic Engineering 61-62 (2002) 485.
[4] J.-M. Bobard, H. Kind, T. Stöckli and L.-O. Nilsson, Solid-State Electronics, "Field emission from carbon nanotubes: the first five years", 45 (2001) 893.
[5] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao and G. Wang, "Large-scale synthesis of aligned carbon nanotubes", Science 274 (1996) 1701.
[6] C. Bower, W. Zhu, J. Sungho and O. Zhou, "Plasma-induced alignment of carbon nanotubes", Appl. Phys. Lett. 77 (2000) 830.
[7] Y. Avigal and R. Kalish, "Growth of aligned carbon nanotubes by biasing during growth", Appl. Phys. Lett. 78 (2001) 2291.
[8] Y.-T. Jang, J.-H. Ahn, B.-K. Ju and Y.-H. Lee, "Lateral growth of aligned multiwalled carbon nanotubes under electric field", Solid-state Communications 126 (2003) 305.
[9] S. Zhu, C.-H. Su, J.C. Cochrane, S. Lehoczky, Y. Cui and A. Burger, "Growth orientation of carbon nanotubes by thermal vapor deposition", J. Cryst. Growth 234 (2002) 584.