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Vertically aligned carbon nanotubes grown on various substrates by plasma enhanced chemical vapor deposition

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Abstract – Vertically well aligned multiwall carbon nanotubes were grown on nickel coated different substrates by plasma enhanced hot filament chemical vapor deposition at low temperatures below 650°C. Acetylene and ammonia gas were used as the carbon source and a catalyst. The surface roughness of nickel layer increased as NH_3 etching time increased. The diameters of the nanotubes decreased and the density of nanotubes increased as NH_3 etching time increased. Diameter of nanotube was 30 to 70 nm. Nickel cap was observed on the top of the grown nanotube and very thin carbon amorphous layer was found on the nickel cap.

I. Introduction

Since the first discovery of carbon nanotubes in 1991 [1], there has been increasing interest in carbon nanotube because of its unique electrical, chemical and mechanical properties and many potential applications. Therefore, numerous papers have been reported on the growth characteristics and the properties of carbon nanotube such as growth mechanism [2-5], structure, alignment [6-9], and electron emission properties [10-13]. Carbon nanotubes are especially promising candidates for cold cathode field emitter because of their unique electrical properties, their high aspect ratios and small radius of curvature at their tips. Various studies on the electron field emission have been reported including electron emission from a single carbon nanotube [14, 15] and a carbon nanotube matrix [10]. These results show that carbon nanotube films are extremely suitable as field emitters for field emitting devices. For applications such as flat panel displays and vacuum microelectronics, large area films of nanotubes or nanofibers producing uniform field emissions are required. Particularly, alignment of the carbon nanotubes is important to both fundamental studies and applications.

Recently, aligned carbon nanotubes have been grown above 700°C on mesoporous silica embedded with iron nanoparticles by thermal decomposition of acetylene gas in nitrogen gas [6]. The growth of well aligned carbon nanotubes on nickel-coated glass over areas up to several square centimeters below 660°C has been reported using plasma enhanced hot filament chemical vapor deposition (PEHFCVD) with a gas mixture of ammonia and acetylene [16].

In this study, we report the growth of vertically aligned, multiwall carbon nanotubes on nickel coated different substrates over large areas at low temperatures (<650°C) using the plasma enhanced hot filament chemical vapor deposition (PEHFCVD). We investigate the effect of growth parameters on the growth characteristics of carbon nanotubes.

II. Experiments

The experiments were carried out in a plasma enhanced hot filament chemical vapor deposition (PEHFCVD) system. Growth system with reactor configuration is schematically shown in Fig. 1. Acetylene (C_2H_2) gas was used as the carbon source and ammonia (NH_3) gas was used as a catalyst and dilution gas. The flow rate of acetylene was 80

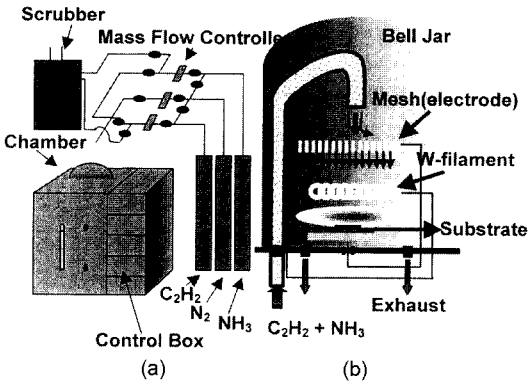

Fig. 1. Schematic diagram of PEHFCVD (plasma enhanced hot filament chemical vapor deposition) (a) System configuration (b) Reactor.

sccm and that of ammonia was 160 sccm. A dc plasma was employed in this work to deposit vertically aligned carbon nanotubes. A thin nickel layer was deposited on glass with and without Indium Tin Oxide (ITO) and silicon (100) by dc magnetron sputtering. The nickel film was deposited under the condition that the base pressure of a chamber was below 7×10^{-5} Torr, the operating pressure was 5×10^{-3} Torr, the operating current was 0.3 A, the flow rate of argon gas was 10 sccm, and the operation temperature was room temperature. The deposition rate of nickel film was 200 Å/min. Prior to carbon nanotube growth, the substrate was cleaned in TCE, acetone, methanol for 10 min., and rinsed in deionized water to remove organic contaminants. The substrate was transferred to a chamber and pumped down below 2×10^{-5} Torr by a mechanical and a diffusion pump. After the chamber pressure reached 2×10^{-5} Torr, NH_3 was introduced into the chamber in order to maintain a working pressure of 1 to 5 Torr. After the working pressure had been stabilized, the power to the tungsten filament coil and to the dc power supply were turned on to generate heat and plasma. The bias voltage for plasma generation was kept from 480 to 600 volts. The pre-treatment (surface etching) was conducted by NH_3 plasma for 1 to 5 min. And then C_2H_2 was introduced into chamber for the growth of carbon nanotubes.

The grown carbon nanotubes were characterized by scanning electron microscopy (SEM) to investigate the effect of growth parameters on the morphology of carbon nanotubes. Transmission electron microscopy (TEM) was used for microstructure analysis of nanotube.

III. Results and Discussion

In order to study the initial growth of carbon nanotubes, the growth of carbon nanotubes were carried out for 2 to 5 min.. The SEM images of carbon nanotubes were shown in Fig. 2. Prior to the growth of carbon nanotube, surface etching was performed using NH_3 for 4 min.. The pressure of chamber was 3.2 Torr. The flow rate of NH_3 was 160 sccm, the filament current was 16 A, and the plasma intensity was 522 V and 0.11 A. After nickel etching with NH_3, C_2H_2 was introduced for carbon nanotubes growth. The flow rate of C_2H_2 was 80 sccm. The plasma intensity was 563V and 0.18A. As shown in Fig. 2, uniform carbon particles were formed on the substrate and a size of carbon particles increased as the growth time increased. This result shows that many nuclei were produced on nickel layer at the initial stage of carbon nanotubes growth and these nuclei grew as the growth time increased. It seems that the nuclei do not agglomerate each other. It

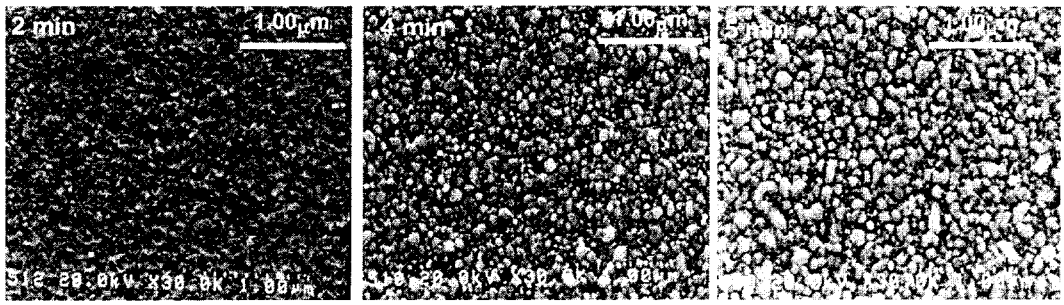

Fig. 2. Initial growth of carbon nanotubes with different growth.

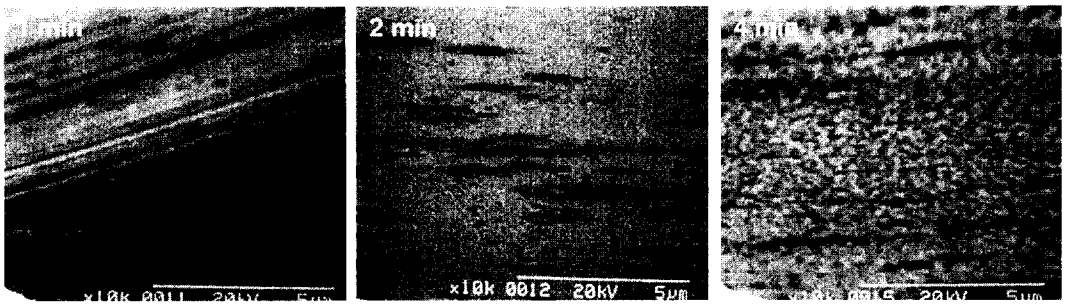

Fig. 3. Effect of etching time with NH_3 on the surface of Ni layer.

implies that the density and distribution of carbon nanotubes are determined at the initial stage of nucleation. The effect of NH_3 etching of nickel layer on the growth characteristic of carbon nanotubes was investigated. Figure 3 shows a surface morphology of nickel layer etched by NH_3 for different time. The etching was performed under the condition that the working pressure was 1.4 Torr, the flow rate of NH_3 was 160 sccm, the filament current was 9A, the plasma bias voltage and current were 460V and 0.01A respectively. A surface scratch (Fig. 3 in 1 min, upper left) is due to the peeling operation with tweezers. As shown in Fig. 3, the surface roughness of nickel layer increased as etching time increased.

We studied the effect of surface etching on the growth characteristics of carbon nanotubes. The growth time was 14 min.. The rest of the growth conditions were same as conditions previously used. As shown in Fig. 4, well aligned carbon nanotubes were obtained. The diameters of the nanotubes decreased and the density of nanotubes increased as NH_3 etching time increased. This result may be due to the fact that the nucleation of nanotubes on the nickel surface increased as NH_3 etching time increased.

Carbon nanotubes were grown on nickel coated substrates such as silicon (100), and ITO coated glass. The effect of substrates on the growth characteristics of nanotubes was investigated and was shown in Fig. 5. The growth conditions of carbon nanotubes were same as the condition mentioned above. As shown in Fig. 5, the diameter of the grown nanotubes on nickel coated glass (as shown in Fig. 5. (a)) was nearly same as that of nanotube on the nickel coated silicon (as shown in Fig. 5. (b)). In case of nickel coated glass with ITO, adhesion between ITO layer and nickel layer caused problem. ITO layer was peeled off. But, the carbon nanotubes were also found in the separated nickel layer that remained on the substrate. This indicates that the growth of carbon nanotubes can be observed on any substrates if nickel layer exists and the growth conditions are satisfied.

Figure 6 is TEM cross-sectional views showing the interior and wall structures of the carbon nanotubes grown on nickel coated glass substrate. The outer diameter of carbon nanotube is almost 70 nm, and the inner diameter of tube is 7.5 nm approxi-

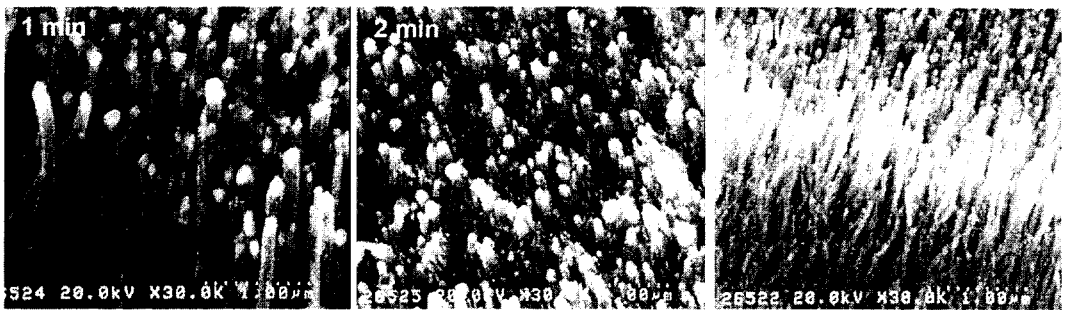

Fig. 4. Variation of diameter and density of carbon nanotubes with etching time.

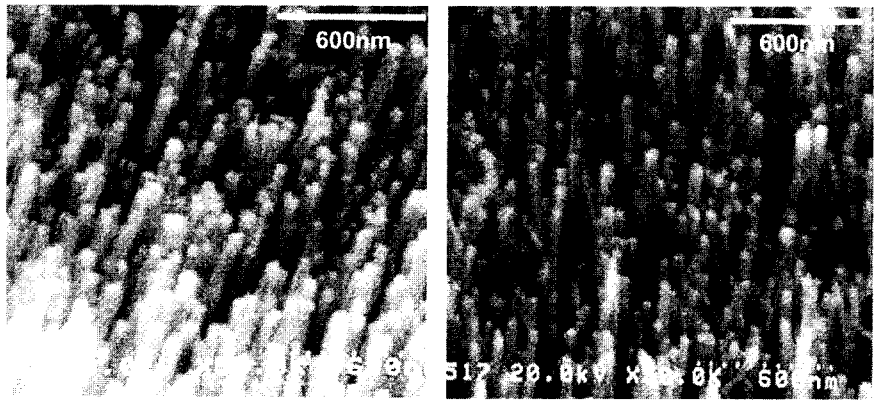

Fig. 5. Effects of substrate on the growth of carbon nanotube: (a) glass, (b) Si (100).

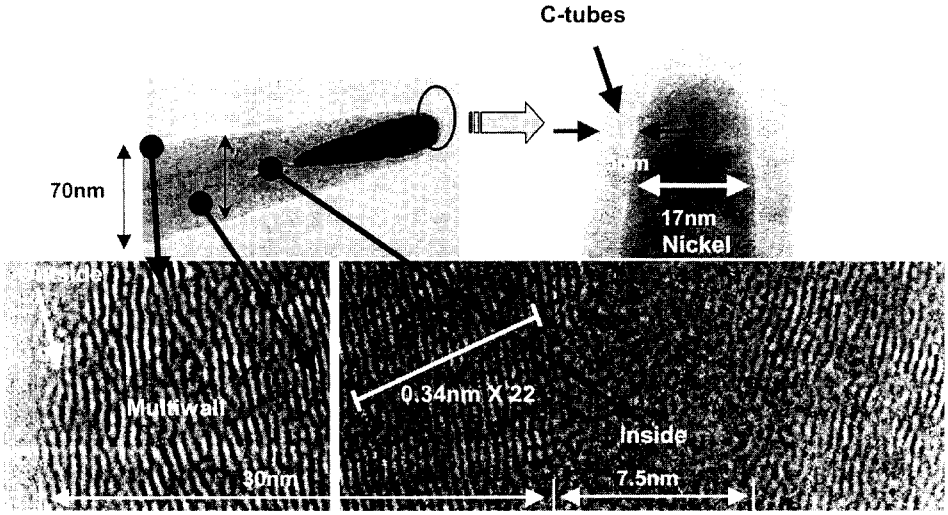

Fig. 6. TEM images of carbon nanotubes grown on Ni-coated glass layer.

mately. It shows that the nanotube is a multiwall tube that has a central hollow. The fringes in a multiwall are individual cylindrical graphitic layers. In the lower-right image of Fig. 6, the lined part is nearly 7.5 nm and this has 22 graphitic walls. This is clearly consistent with the fact that the graphite spacing is C/2 = 0.34 nm. The graphitic walls running across the diameter of the nanotube looks like having some cut-off-like defects. The lighter contrast part in the lower right of Fig. 6 indicates the inside of the nanotube that has the hollow structure. A nickel cap was observed at the end of each carbon nanotubes as shown in the upper left image of Fig. 6. The shape of the nickel cap is like long ellipsoid with sharp end. The nanotube has a narrow appearance at the end of nanotube. As shown in the upper right image of Fig. 6, the diameter of the nickel cap is about 17 nm, 5 nm thickness of carbon amorphous layer was deposited on the nickel cap.

IV. Conclusions

Vertically aligned carbon nanotubes on nickel coated glass substrates were obtained at low temperatures below 650°C by plasma enhanced hot filament chemical vapor deposition using acetylene gas as the carbon source and ammonia gas as the dilution gas and catalyst. The surface roughness of nickel layer increased as NH_3 etching time increased. The diameters of the nanotubes decreased and the den-

sity of nanotubes increased as NH_3 etching time increased. The growth characteristics of carbon nanotubes are dependent on under layer such as glass, ITO and silicon. Nickel cap was observed on the top of the grown nanotube. Very thin carbon amorphous layer was found on the nickel cap from transmission electron microscopy. Highly oriented carbon nanotubes obtained in this work can be applied to the field emission display (FED).

References

[1] S. Iijima, Nature (London) **354**, 56 (1991).

[2] T. W. Ebbesen, *Carbon Nanotubes: Preparation and Properties* (Chemical Rubber, Boca Raton, 1997).

[3] J. C. Charlier, A. De Vita, X. Blasé, R. Car, Science **275**, 646 (1997).

[4] M. Yudasaka, R. Kikuchi, Y. Ohki, E. Ota and S. Yoshimura, Appl. Phys. Lett. **70**, 1817 (1997).

[5] S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov and J. B. Nagy, Science **265**, 635 (1994).

[6] 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).

[7] P. M. Ajayan, O. Stephan, C. Colliex and D. Trauth, Science **265**, 1212 (1994).

[8] W. A. de Heer, W. S. Bacsa, A. Châtelain, T. Gerfin, R. Humphrey-Baker, L. Forro, and D. Ugarte, Science **268**, 845 (1995).

[9] M. Terrones *et al.*, Nature (London) **388**, 52 (1997).

[10] P. G. Collins and A. Zettl, Phys. Rev. B **55**, 9391 (1997).

[11] H. Schmid and H. W. Fink, Appl. Phys. Lett. **70**, 2679 (1997).

[12] A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. Colbert and R. E. Smalley, Science **269**, 1550 (1995).

[13] W. A. de Heer, A. Chatelain and D. Ugarte, Science **270**, 1179 (1995).

[14] J.-M. Bonard, J.-P. Salvetat, T. Stöckli, W. A. de Heer, L. Forró and A. Châtelain, Appl. Phys. Lett. **73**, 918 (1998).

[15] Y. Saito, K. Hamaguchi, T. Nishino, K. Hata, K. Tohji, A. Kasuya and Y. Nishina, Jpn. J. Appl. Phys., Part 2 **36**, L1340 (1997).

[16] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal and P. N. Provencio, Science **282**, 1105 (1998).