

# Deposition of carbon nanotubes by capillary-type atmospheric pressure PECVD

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Available online 2 March 2006

## Abstract

In this study, the growth behavior of carbon nanotubes (CNT) deposited from  $C_2H_2$  by an atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) method was investigated. The deposition was performed at 400 °C using a modified dielectric barrier discharge using  $He/C_2H_2$  with additive gases such as  $N_2$  and  $NH_3$ . The effect of the pretreatment on the surface morphology of the Ni catalyst was also investigated. Treatment of the Ni catalyst surface with a He (6 slm)/ $NH_3$  (90 sccm) atmospheric pressure plasma for 5 min at 400 °C transformed the Ni surface into more uniformly agglomerated small Ni particles required for the enhanced carbon diffusion during the CNT formation. The CNTs grown by using He (6 slm)/ $C_2H_2$  (90 sccm) AP-PECVD with additive gases ( $NH_3$ ,  $N_2$ ) for 5 min at 400 °C after the pretreatment showed uniform 1.5–2  $\mu m$  long and 20–50 nm diameter multi-layer CNTs. By the application of –1.2 kV of dc bias to the substrate during the growth CNTs by the AP-PECVD, more vertical CNTs could be obtained. FT-Raman data showed the grown CNTs are multi-wall CNTs and have the intensity ratio of D-band/G-band was 0.8–0.9, so defects were involved in the grown CNTs. This study provides a new method growing CNTs at atmospheric pressure and at low temperature, which has special advantages for large scale applications using conventional glass substrates. © 2005 Elsevier B.V. All rights reserved.

*Keywords:* Atmospheric pressure PE-CVD; Carbon nanotube; dc bias; Pretreatment

## 1. Introduction

Many potential applications have been reported for carbon nanotubes (CNTs) including field emission displays (FEDs) [1], storage of hydrogen cells [2], SPM nanoprobe [3], sensors [4], etc. Among these potential applications, FEDs are one of the most commercially approached applications being developed by the industry due to the advantages of CNTs as a field emission tip such as low cost of tip fabrication, high emission efficiency, improved reliability, etc. [5]. FEDs have inherent advantages over thin film transistor liquid crystal displays (TFT-LCDs) such as low power consumption, a wide color reappearing range, high brightness, a wide viewing angle, a fast response rate, a wide operating temperature range, etc. Also, FEDs have higher power efficiency compared to plasma display panel (PDP) while the manufacturing cost is similar to PDP when the field emission tip is made of CNTs. Therefore, if low cost and reliable large field emission display panel is manufactured, it may take over the display panel market which is currently controlled by TFT-LCD and PDP.

Currently, CNTs are usually made by carbon-arc discharge [6], laser ablation of carbon [7], thermal-chemical vapor deposition [8], and plasma-enhanced chemical vapor deposition [9]. To apply CNTs as field emitters of FED, two different technologies are currently investigated. One method is to use organic paste containing CNTs and to form field emitters by screen printing it on the glass substrate followed by sintering [10]. The other method is to grow CNTs directly and selectively on the field emission area of FED using chemical vapor deposition [11]. The first method shows problems in making uniform CNT tips over large areas and making fine pixels for high-resolution display devices. The second method shows difficulty in growing CNTs at the temperature lower than the deformation temperature of sodalime glass substrates (550 °C) when chemical vapor deposition (CVD) methods are used. To reduce the growing temperature, the CNT growth using low temperature plasma enhanced chemical vapor deposition (PECVD) is currently investigated [12], however, due to the difficulty to form a uniform plasma over a large area and due to the use of vacuum in growing the CNTs, this method may not be applicable in the industry requiring continuous production of large area FED panel.

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In this study, one of the atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) systems was used to grow CNTs at the temperature lower than the glass softening temperature (about 550 °C). By using the AP-PECVD, if CNTs are successfully grown, the system can be fabricated at low cost and to a large size and the throughput could be increased because the AP-PECVD equipment does not require expensive vacuum equipments and can be processed in-line without using a loadlock. In fact, the growth of carbon nanotubes by the AP-CVD has already been studied by few researchers using conventional dielectric barrier discharge (DBD) systems [13] which are used to generate plasmas at the atmospheric pressure, but the growth of CNTs at the temperature lower than glass deformation temperature has not been reported yet possibly due to the low density of the plasma at the atmospheric pressure compared to low pressure plasmas. However, the atmospheric pressure plasma system used in this study is a high-density version of DBD using a capillary dielectric material instead of a conventional blank dielectric material and feed gas can be distributed more uniformly [14]. Using this plasma system, the carbon nanotubes were grown at a low temperature (400 °C) and their growth characteristics were investigated as a possible application to field emission tips. In addition, the effect of dc-biasing [15] during the growth of CNTs using AP-PECVD on the morphology of CNTs was also investigated.

## 2. Experiments

The capillary dielectric discharge system used in this study to grow CNTs at atmospheric pressure is shown in Fig. 1. The system is similar to a typical planar DBD system except for the dielectric material covered on the powered electrode. The powered electrode and the ground electrode were made of stainless steel. The top electrode was connected to an alternating current (ac) power supply (20–100 kHz, 3 kW) while the bottom electrode was grounded. The top electrode was covered with a 10-mm-thick aluminar plate with a

number of parallel small capillary holes (aspect ratio of the hole was 10:1). By using the dielectric barrier with capillary holes, a higher plasma density compared to conventional dielectric barrier discharges by forming a high-density plasma with an ion-beam like plasmas at the holes and more uniform reactive gas distribution through the capillary holes could be obtained. The distance between the two electrodes (air gap) was 5 mm. The ground electrode was heated using a heating block and was covered with a 3-mm-thick quartz. The substrate temperature was measured using a thermocouple located on the surface of the glass substrate and was maintained at 400 °C. To study the effect of substrate biasing, –1.2 kV of dc voltage was applied to the substrate during the growth of CNTs using a bipolar dc voltage supply with the voltage range of  $\pm 2$  kV.

5-nm-thick Ni thin films used for the catalyst in growing CNTs were deposited using RF-magnetron sputtering on the sodalime glass substrates after the deposition of 100-nm-thick Cr used to enhance the adhesion (buffer layer) of Ni films. Before the Cr/Ni deposition, the chamber was evacuated to a base pressure of  $1.0 \times 10^{-6}$  Torr. The deposition of Cr/Ni films was carried out at 10 mTorr Ar and at room temperature. The RF power density during the sputter deposition was  $1.27 \text{ W/cm}^2$ .

The morphology of the growing CNTs are related to the particle size and roughness of the deposited catalyst. Therefore, to control the particle size and the roughness of the Ni catalyst layer deposited, the effects of various pretreatment conditions were investigated. The pretreatment was carried out with/without He (6 slm)/NH<sub>3</sub> (90 sccm) atmospheric pressure plasmas and with/without heating of the Ni/Cr deposited substrate to 400 °C. The pretreatment time was generally maintained at 5 min. The details of the pretreatment conditions are described in Table 1. After the pretreatment, the morphologies of the Ni surfaces were observed using a field emission scanning electron microscope (FE-SEM; Hitachi S-4700) and using an atomic force microscope (AFM; Thero-Microscope CP Research). Using the FE-SEM, the particle diameters and

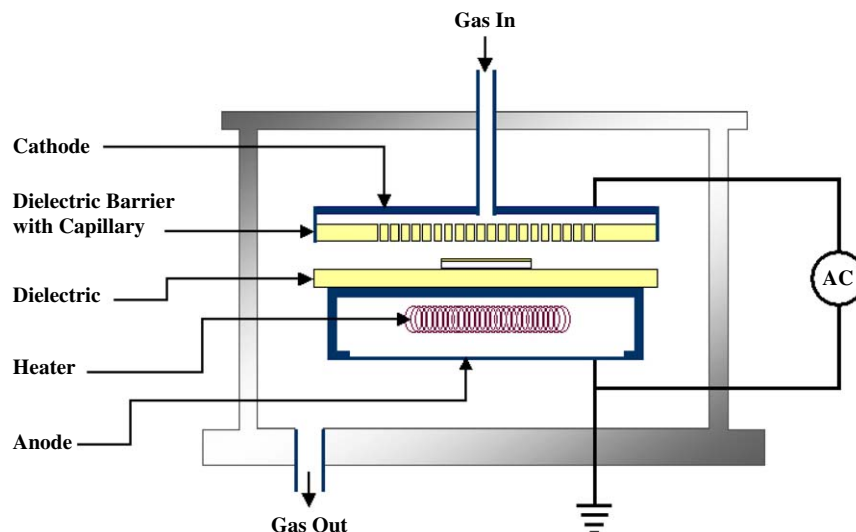


Fig. 1. Schematic diagram of the capillary dielectric discharge-type AP-PECVD system used in this study.

Table 1  
Pretreatment conditions for Ni catalyst before the growth of CNTs by the AP-PECVD system used in this study

Sample	Flow rate (sccm)		Plasma (kV)	Temp. (°C)	Time (min)
	He	NH <sub>3</sub>			
A	–	–	–	–	–
B	–	–	–	400	5
C	6000	90	4.0	25	5
D	6000	90	4.0	400	5

shapes were observed and, using the AFM, the rms surface roughness and height of Ni particles were measured. 20 samples were measured and averaged to obtain more accurate values.

The CNTs were grown on the Ni/Cr samples at 400 °C after the pretreatment using He (6 slm)/C<sub>2</sub>H<sub>2</sub> (90 sccm) AP-PECVD at 4 kV of rms voltage for 5 min. To study the effect of additive gases, 60 sccm of N<sub>2</sub> or NH<sub>3</sub> was added to the plasma during the growth of CNTs and compared with the CNTs grown without the additive gases. FE-SEM was also used to analyze the surface morphology of the grown CNT samples. FT-Raman spectroscopy (Renishaw RM1000-InVia) was employed to examine the binding states of the grown CNTs.

### 3. Results and discussion

It is well known that synthesis of CNT is dependent on the surface morphology of the catalyst and the formation of rough nanoparticle-shaped surface is required for the increased carbon diffusion through the catalyst. In fact, the surface morphology of the catalyst is partially dependent on the pretreatment condition before the growth of CNTs [16]. Fig. 2 shows the effect of various pretreatments on the surface morphology of the Ni catalyst observed by a FE-SEM. The

pretreatment time was 5 min. In the figure, (a) is the sputtered Ni surface (condition A in Table 1), (b) is the Ni surface after heating at 400 °C (condition B in Table 1), (c) is the Ni surface after a He/NH<sub>3</sub> atmospheric pressure plasma treatment at room temperature (condition C in Table 1), and (d) is the Ni surface after the plasma treatment while heating at 400 °C (condition D in Table 1). As shown in Fig. 2(b), when the Ni surface was maintained at 400 °C for 5 min without applying the plasma, some areas of the Ni surface were broken into small particles, however, large agglomerated particles were also observed. The average height of the particles on the Ni surface measured by AFM for twenty samples was 2450 nm with the standard deviation of 1498 nm. But when the He/NH<sub>3</sub> plasma was applied in addition to heating at 400 °C for 5min, as shown in Fig. 2(d), the particles were broken to more uniform and small particles. The height of the particles averaged for twenty samples was 71.4 nm with the standard deviation of 29.6 nm. When the samples were treated for 3 min with the condition in (d) instead of 5 min, large particles in addition to small particles were observed similar to the condition in (b), however, when the samples were treated for 10 min with the condition in (d), Ni particles appeared to be dissociated in full, therefore, no Ni particles could be observed by SEM. Also, when the surface composition was investigated for the sample treated for 10 min using an energy disperse X-ray spectrometer system (EDS) installed in the FE-SEM, less than 5% of Ni was remaining on the surface. Increased agglomeration to small particles with the He/NH<sub>3</sub> atmospheric pressure plasma in addition to the heating at 400 °C is similar to the results obtained with the NH<sub>3</sub> plasma treatment in a low pressure by other researchers, which is believed from the increased ion bombardment to the Ni surface, which enables increased surface diffusion of the Ni atoms [17]. Therefore, for the following experiments, the

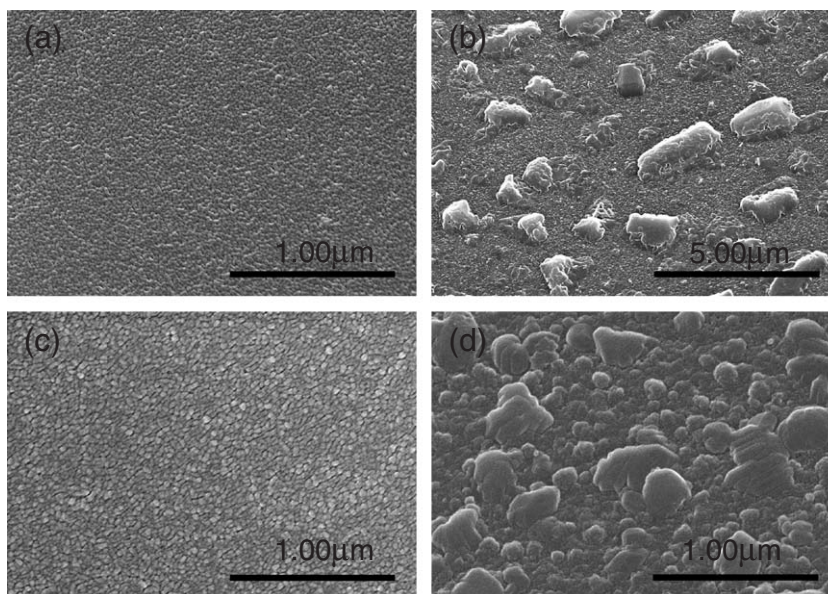


Fig. 2. Effect of various pretreatments in Table 1 on the surface morphology of the Ni catalyst observed by a FE-SEM. (a) The sputtered Ni surface (condition A in Table 1), (b) after heating at 400 °C (condition B in Table 1), (c) after a He/NH<sub>3</sub> atmospheric pressure plasma treatment at room temperature (condition C in Table 1), and (d) after the plasma treatment while heating at 400 °C (Condition D in Table 1).

pretreatment condition D in Table 1 was used for more uniform growth of CNTs.

Fig. 3 shows the SEM micrographs of the CNTs grown on the Ni (10 nm)/Cr (170 nm)/glass substrates after the He/NH<sub>3</sub> plasma pretreatment at 400 °C for 5 min (a) with a He/C<sub>2</sub>H<sub>2</sub> plasma, (b) with a He/N<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> plasma, (c) with a He/NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> plasma, and (d) with a He/NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> plasma under the bias voltage of –1.2 kV. All the samples were grown at 400 °C for 5 min. As shown in Fig. 3(a), by the application of a He/C<sub>2</sub>H<sub>2</sub> plasma, the growth of CNTs could be observed even though some amorphous carbon clusters are remaining on the top of the CNTs. The growth of CNTs by the application of the plasmas is from the increased dissociation of C<sub>2</sub>H<sub>2</sub> and increased surface diffusion through the Ni surfaces by the ion bombardment of the Ni surface. However, due to the difficulty with the He/C<sub>2</sub>H<sub>2</sub> plasma in removing the excessive carbon generated, carbon clusters were remaining on the top of the CNTs. By adding additive gases containing nitrogen such as N<sub>2</sub> and NH<sub>3</sub> to the He/C<sub>2</sub>H<sub>2</sub> plasma, as shown in Fig. 3(b) and (c), cleaner CNTs without having amorphous carbon clusters could be obtained. If the CNTs grown by the He/N<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> plasma are compared with those grown by the He/NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> plasma, the CNTs grown by the He/N<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> plasma were shorter and the top of the grown CNTs was thicker, and it appears to contain amorphous carbon. Fig. 3(d) shows the effect of dc biasing during the growth of CNTs and, to study the effect of dc biasing, the CNTs were grown by biasing of the substrate at –1.2 kV with the condition of Fig. 3(c). If the CNTs grown with and without the dc biasing are compared, as shown in Fig. 3(d) and (c), respectively, the CNTs grown with –1.2 kV of dc bias voltage appeared to have more vertical CNTs. In fact, the addition of –1.2 kV between the two electrodes having the distance of about 14 mm may not be sufficient to form an internal electric field to grow CNTs vertically by this additional field. However, it is believed that, if more dc electric field is

applied to the substrate, more vertical CNTs could be grown for the CNTs by our AP-PECVD.

The role of the nitrogen in the synthesis of CNTs has been described as the following four ways. (1) The increased carbon diffusion by the nitrogen ion bombardment to the Ni surface which has higher bombardment energy compared to other gases containing in the plasma [17,18]. (2) Supply of activation energy for the removal of excessive carbon from the Ni surface [19]. (3) Dilution gas for prohibiting excessive carbon dissociation and deposition [12,20]. (4) Increased dissociation of hydrogen from C<sub>2</sub>H<sub>2</sub> by nitrogen in the plasma [21]. In our experiment, as shown in Fig. 3(b) and (c), the benefit of nitrogen atom in the growth of CNTs could be also identified. Because the binding energy of N–N is 945 kJ/mol and that of N–H is 339 kJ/mol, more nitrogen atom concentration can be expected in the plasma by the addition of NH<sub>3</sub> compared to N<sub>2</sub>, therefore, cleaner growth of CNTs could be expected for the He/NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> plasma. However, the added N<sub>2</sub> or NH<sub>3</sub> percentage is very small (about 0.98%) in our atmospheric pressure plasma, the dilution effect will be negligible. Also, the effect of ion bombardment by N<sub>2</sub><sup>+</sup> should be greater than NH<sub>x</sub><sup>+</sup> and the ion bombardment energy itself appears not significant due to the extremely small collision mean free path at atmospheric pressure ( $\lambda_{\text{mfp}} \times 5/P$  (mTorr) cm, therefore, about 66 nm at atmospheric pressure) even though the operational voltage is higher (4 kV) compared to low pressure PECVD conditions. Therefore, the removal of excessive or loose carbon on the Ni surface by the formation of volatile compounds such as C<sub>2</sub>H<sub>2</sub> or HCN and/or the activation of Ni surface with the nitrogen atoms or NH<sub>x</sub> radicals formed by the atmospheric pressure plasma are believed more feasible in our experimental conditions. Also, the formation of more uniform small Ni particles with a He/NH<sub>3</sub> atmospheric pressure shown in Fig. 2(d) also appears more related to the increased surface diffusion through the activation of the Ni surface by the

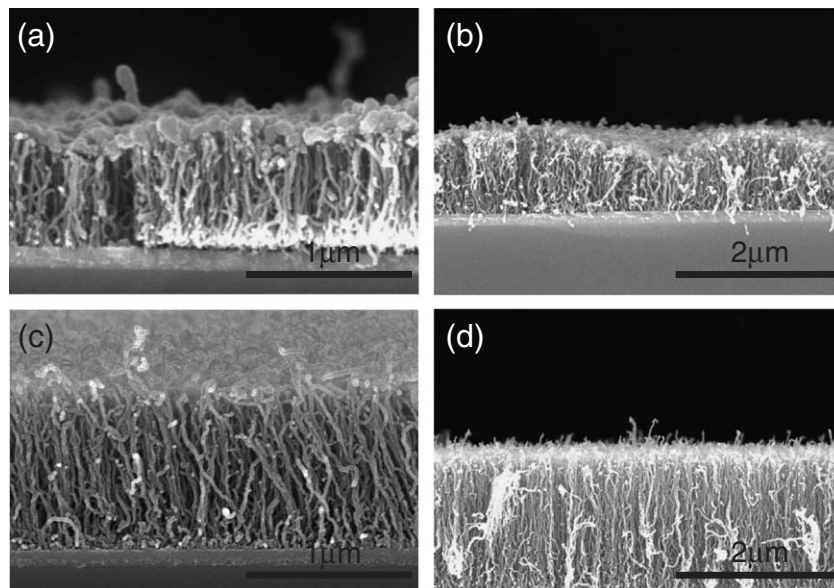


Fig. 3. SEM micrographs of the CNTs grown on the Ni (5 nm)/Cr (100 nm)/Si substrates after the He/NH<sub>3</sub> plasma pretreatment at 400 °C for 5 min: (a) with He/C<sub>2</sub>H<sub>2</sub> plasma, (b) with a He/N<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> plasma, (c) with a He/NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> plasma, and (d) with the condition (c) by biasing the substrate with the dc voltage of –1.2 kV.

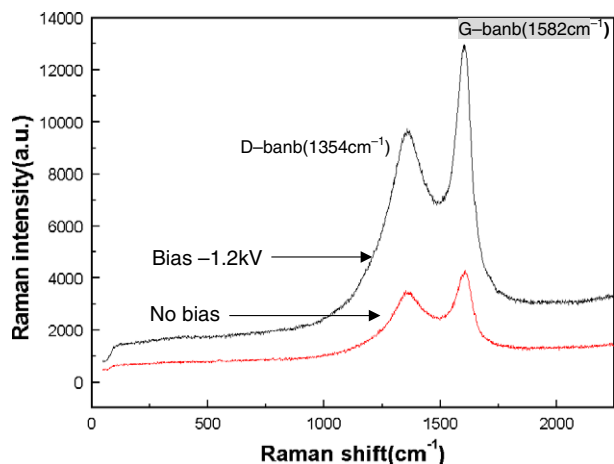


Fig. 4. Raman spectra of the CNTs grown with the condition in Fig. 3(c) and (d).

nitrogen atom or  $\text{NH}_x$  radicals rather than the nitrogen ion bombardment effect.

The CNTs grown in this study are multi-walled CNTs with the diameter in range from 20 to 50 nm and were curved as shown in Fig. 3(b) and (c). The curved CNTs contain defects in the CNT structure. To investigate the degree of defects in the CNTs grown in our experiment, the structures of grown CNTs were investigated for the conditions in Fig. 3(c) and (d) using FT-Raman and the results are shown in Fig. 4. All of the grown CNTs showed the G (graphite-like) band near  $1582\text{ cm}^{-1}$  originated from hexagonal carbon binding and the D (defect) band from  $1250$  to  $1350\text{ cm}^{-1}$  originated from the defects in the carbon binding. The measured relative intensities of these two bands ( $I_D/I_G$ ) for the conditions with and without the dc biasing were about 0.8 and 0.9, respectively, therefore, the dc biasing appeared to improve the crystallinity of the grown CNTs even though more systematic studies are required to convince the effect of dc biasing during the growth of CNTs using AP-PECVD.

The capillary dielectric discharge used in our experiment is a modified DBD-type plasma where the dielectric material covering the power electrode is perforated to have many long small holes (hole aspect ratio is 10). In this type of plasma, the electric field formed on the dielectric material is used to accelerate the electrons at the holes, therefore, ion beam-like high density plasma is obtained at each holes, therefore, higher plasma densities can be obtained compared to conventional DBDs used by other researchers to form uniform glow discharges at the atmospheric pressure. The details of the plasma characteristics are described elsewhere [14]. Previous researches on the growth of CNTs using atmospheric pressure plasmas had to use the substrate temperature higher than  $600\text{ }^\circ\text{C}$  possibly due to the low plasma density compared to the plasma density generated at low pressure. Therefore, to grow CNTs at the temperature lower than the glass softening temperature of  $550\text{ }^\circ\text{C}$ , a high-density plasma is required. It is believed that obtaining CNTs at  $400\text{ }^\circ\text{C}$  with our atmospheric pressure plasma is related to the increased dissociation of the species similar to low-pressure plasmas.

#### 4. Conclusions

In this study, the effects of capillary dielectric discharges operated at atmospheric pressure on the pretreatment of Ni catalyst layer with He/ $\text{NH}_3$  and the growth of CNTs with He/ $\text{C}_2\text{H}_2$  were studied for the application to the emission tip of FEDs. For the growth of CNTs, the effects of nitrogen containing gases such as  $\text{N}_2$  and  $\text{NH}_3$  to the He/ $\text{C}_2\text{H}_2$  and the addition of dc biasing to the substrate on the structure of CNTs were also investigated.

The pretreatment of the Ni surface using the He/ $\text{NH}_3$  atmospheric pressure plasma at  $400\text{ }^\circ\text{C}$  for 5 min promoted the agglomeration of the Ni catalyst layer into uniform and small particles required for the growth of CNTs by increasing the surface diffusion through the activation of the Ni surface by the nitrogen atom or  $\text{NH}_x$  radicals. Using the He/ $\text{C}_2\text{H}_2$  capillary dielectric discharges with additive gases such as  $\text{N}_2$  and  $\text{NH}_3$ , the CNTs could be successfully grown at  $400\text{ }^\circ\text{C}$  even though conventional DBD type atmospheric pressure plasmas are known to require higher than  $600\text{ }^\circ\text{C}$  for the growth of CNTs due to their low plasma densities. The successful growth of CNTs at  $400\text{ }^\circ\text{C}$  lower than glass softening temperature is believed from the increased dissociation of the gases by the increased plasma density because ion beam-like high density plasmas are obtained at the holes of dielectric in the capillary dielectric plasma system. The addition of  $\text{N}_2$  and  $\text{NH}_3$  to the He/ $\text{C}_2\text{H}_2$  plasma promoted the growth of CNTs possibly due to the removal of excessive or loose carbon on the Ni surface by the formation of volatile compounds such as  $\text{C}_2\text{N}_2$  or HCN and by the activation of Ni surface with nitrogen atom and  $\text{NH}_x$  radicals formed by the atmospheric pressure plasmas. The CNTs grown with He/ $\text{NH}_3/\text{C}_2\text{H}_2$  plasmas at  $400\text{ }^\circ\text{C}$  for 5 min were multi-wall nanotubes having the outside diameters in the range from 20 to 50 nm. The relative intensity ratio of D-band to G-band measured by FT-Raman was about 0.8–0.9, and the dc biasing of the substrate at  $-1.2\text{ kV}$  appeared to improve the crystallinity of CNTs even though more systematic studies are required to convince the effect of dc biasing.

#### Acknowledgments

This work was supported by National Research Laboratory (NRL) Program of Korea Ministry of Science and Technology.

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