Field emission properties of carbon nanotubes synthesized by capillary type atmospheric pressure plasma enhanced chemical vapor deposition at low temperature

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Abstract

Carbon nanotubes (CNTs) were grown using a modified atmospheric pressure plasma with NH_3(210 sccm)/N_2(100 sccm)/C_2H_2(150 sccm)/He(8 slm) at low substrate temperatures ($\leqslant 500\,°C$) and their physical and electrical characteristics were investigated as the application to field emission devices. The grown CNTs were multi-wall CNTs (at 450 °C, 15–25 layers of carbon sheets, inner diameter: 10–15 nm, outer diameter: 30–50 nm) and the increase of substrate temperature increased the CNT length and decreased the CNT diameter. The length and diameter of the CNTs grown for 8 min at 500 °C were 8 μm and 40 ± 5 nm, respectively. Also, the defects in the grown CNTs were also decreased with increasing the substrate temperature (The ratio of defect to graphite (I_D/I_G) measured by FT-Raman at 500 °C was 0.882). The turn-on electric field of the CNTs grown at 450 °C was 2.6 V/μm and the electric field at 1 mA/cm² was 3.5 V/μm.
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1. Introduction

Many potential applications have been reported for carbon nanotubes (CNTs) including transparent conductive thin film, high-strength composites, energy storage, energy conversion devices, field emission electron sources for flat panel displays, etc. Among these, one of the important CNT applications being developed by industry is field emission display (FED) due to the advantages of CNTs in emitting electrons by electric field and due to the advantage of the FED over liquid crystal display (LCD) such as low power consumption, high brightness, wide viewing angle, fast response rate, and wide operating temperature range.

In general, two different methods are being developed to apply CNTs as field emitters of FED. One is to screen-print the CNTs mixed with organic vehicles, and the other is to directly grow the CNTs onto patterned catalyst layers at low pressure by chemical vapor deposition (CVD) [1–3]. The screen-printed CNTs are more useful in terms of simple process and low cost than the CNTs grown by the CVD which has several problems such as higher growth temperature, lower throughput, higher cost of ownership, etc. But the former is also encountering problems including difficulties in non-uniform dispersion of CNTs, bad adhesion, low resolution integration of CNT emitters, etc. By using plasma enhanced CVD instead of thermal CVD, the growth temperature can be lowered even though the quality is known to be worse than those grown by thermal CVD. However, the problems such as low throughput, expensive cost of ownership, etc. are still remained due to the use of vacuum.

By using atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) in the growth of CNTs

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instead of low pressure PECVD, it is believed that higher throughput, lower process equipment cost, etc. could be realized by continuous in-line processing at the atmospheric pressure without using an expensive vacuum equipment. Therefore, in this study, as one of the direct growth methods of CNTs for FED to improve the above mentioned problems of CVD, an AP-PECVD method has been used and the physical and electrical characteristics of the grown CNTs have been investigated. Even though the growth of CNTs using an AP-PECVD has been investigated previously using a modified tip-plate configuration [4], low temperature growth characteristics and the electrical characteristics of the grown CNTs have never been reported.

2. Experiment

The AP-PECVD system used in this experiment is a modified planar DBD system using a capillary type dielectric plate instead of a blank dielectric plate as the dielectric plate covering the power electrode [5,6]. The two parallel electrodes of the system was made of stainless steel. The top electrode (power electrode) was connected to an alternating current (AC) (20–100 kHz, 3 kW) power supply while the bottom electrode was grounded. The power electrode was covered with a capillary type dielectric plate composed of a 10 mm thick aluminar plate having a number of parallel small capillary holes (aspect ratio of the holes was 10:1) to form an ion beam-like high density plasma in the hole and to distribute reactive gases. The distance between the two electrodes (air gap) was 4 mm. The substrate temperature was varied from 350 °C to 500 °C using a heating block located under the ground electrode and the substrate temperature was measured by an optical pyrometer (Luxtron, Model 100 C-non contact).

NiCr (10 nm thick) was deposited as the catalyst for the CNT growth on the ITO glass substrates after the deposition of 100 nm thick Cr to enhance the adhesion of NiCr films. The growth conditions of CNTs are listed in Table 1. The growth of CNTs was consisted of two steps: (1) NH_3 plasma treatment step: the formation of catalyst metal nanoparticles using a NH_3(150 sccm)/He(8 slm) plasma for 15 min in the AP-PECVD chamber [7] and (2) CNT growth step: the growth of CNTs using a NH_3(210 sccm)/N_2(100 sccm)/C_2H_2(150 sccm)/He(8 slm) plasma for 8 min.

Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700) was used to analyze the growth character-

istics and FT-Raman spectroscopy (Renishaw RM1000-InVia) was used to analyze the structure of the grown CNTs. The field emission characteristics of the grown CNTs were measured with a parallel diode-type configuration using a home-made system equipped with a Keithley 2001 current meter.

3. Results and discussion

Fig. 1 shows the scanning electron microscopic (SEM) images of the CNTs grown as a function of temperature ((a) 350 °C, (b) 400 °C, (c) 450 °C, and (d) 500 °C) using the AP-PECVD. The conditions for the NH_3 plasma treatment step and the CNT growth step are described in Table 1. The temperature of the plasma treatment step was the same as the temperature of the CNT growth step. Among the gases used for the CNT growth, He was used for the dilution and for maintaining glow discharge and C_2H_2 was the carbon source for the CNT growth. NH_3 and N_2 were used for the Ni surface activation and Ni nanoparticle formation [7]. As shown in Fig. 1 with increasing the substrate temperature from 350 °C to 500 °C, the length of the CNTs was increased and the diameter of the CNTs was decreased.

Fig. 2(a) shows the average length and average diameter of the grown CNTs measured as a function of temperature from 350 °C to 500 °C using the AP-PECVD with the process conditions shown in Table 1. To measure the average length and diameter of the CNTs, the grown CNTs were dispersed in a solution by a ultrasonic and measured by SEM as shown in the insets of the graph. As shown in Fig. 2(a) the measured average lengths of CNTs grown at 350 °C, 400 °C, 450 °C and 500 °C were 1 ± 0.5 μm, 2.5 ± 0.5 μm, 5.5 ± 1 μm, and 8 ± 1 μm, respectively, and the diameters were 100 ± 10 nm, 75 ± 10 nm, 55 ± 5 nm, and 40 ± 5 nm, respectively. The increase of CNT length

Table 1
CNT growth conditions for the capillary type AP-PECVD system

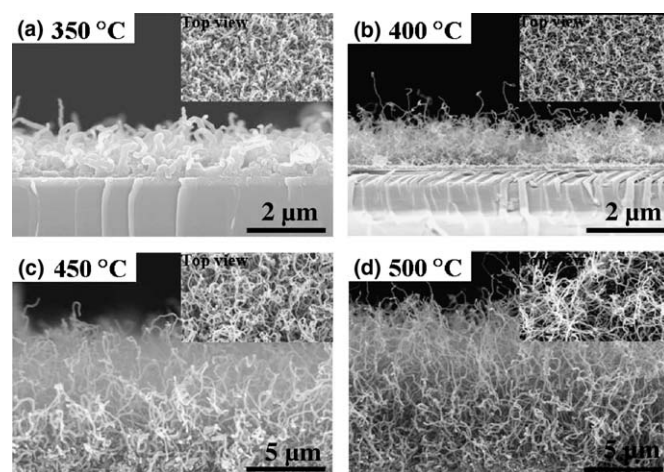| Process	Condition					Time (min)
	AC power (kV)	Gas flow rate (sccm)				
		NH_3	C_2H_2	He	N_2	
NH_3 plasma treatment	3.0	150	0	8000	0	15
Carbon nanotube growth	5.0	210	150	8000	100	8

Fig. 1. SEM micrographs of CNTs grown as a function of substrate temperature by a modified AP-PECVD with He(8 slm)/C_2H_2(150 sccm)/NH_3(210 sccm)/N_2(100 sccm) on the NiCr(10 nm)/Cr(100 nm)/ITO glass substrates for 8 min after He(8 slm)/NH_3(150 sccm) plasma pretreatment for 15 min. (a) 350 °C, (b) 400 °C, (c) 450 °C, and (d) 500 °C.
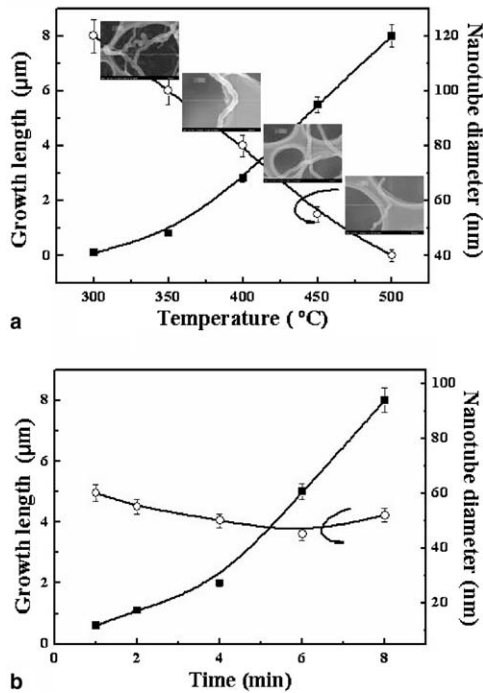
Fig. 2. (a) The length and diameter of the CNTs grown as a function of the substrate temperature for the process condition in Table 1. (b) The growth length and diameter measured as a function of growth time at 500 °C.

with increasing growth temperature is related to the increase of carbon reaction rate and the increased carbon diffusion to Ni catalyst similar to the conventional CNT growth by conventional CVD. Also, the decrease of CNT diameter with increasing substrate temperature appears to be related to the increased Ni surface roughness and the formation of smaller nanosize Ni particles by the increased NH_3 reaction with Ni catalyst layer during the NH_3 plasma treatment step at the higher temperature as investigated by other researchers [7,8]. Fig. 2(b) shows the length and diameter of CNTs grown at 500 °C as a function of growth time. The process condition was same as the conditions shown in Fig. 2(a). As shown in Fig. 2(b), the length of CNTs were increased almost linearly with increasing growth time at about 1.0 ± 0.1 µm/min. During the growth, the diameter of the grown CNTs was remained the similar at 45 ± 5 nm. Therefore, the length and diameter of the CNTs could be controlled by changing the growth time and the growth temperature.

Fig. 3 shows the FT-Raman spectra observed to characterize the structure of the CNTs grown as a function of temperature by the AP-PECVD. As shown in Fig. 3, the graphite peak (G-band) near 1582 cm^{-1} originated from the Sp^2 structure of the rolled graphite sheet and the defect peak (D-band) at 1300–1350 cm^{-1} from the Sp^3 structure of amorphous carbon could be observed. However, the radial breathing mode (RBM) peak known to exist at 100–300 cm^{-1} for the single-wall nanotubes (SWNTs) could not be observed (not shown), therefore, the CNTs grown in this experiment appeared to be multi-wall CNTs.
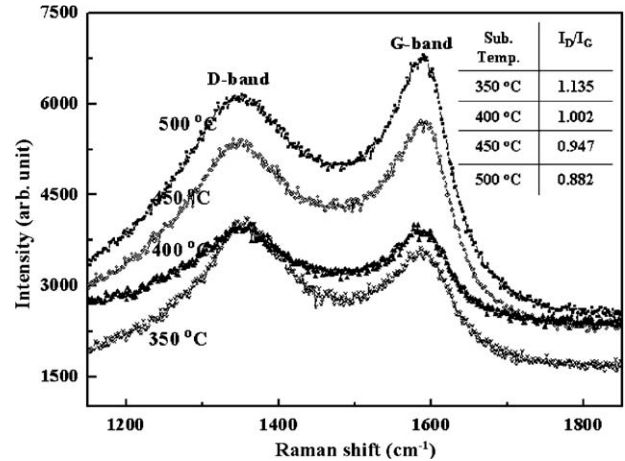

Fig. 3. FT-Raman spectra of the CNTs grown by the AP-PECVD at 350 °C, 400 °C, 450 °C and 500 °C.

If the relative intensities of the two bands (I_D/I_G) are compared, as shown in the inset, with the increase of substrate temperature from 350 °C to 500 °C, the I_D/I_G was decreased from 1.135 to 0.882 indicating the decrease of defect in the grown CNTs.

The field emission properties of the CNTs grown by the AP-PECVD was measured with a parallel diode-type configuration in a vacuum chamber (5×10^{-6} Torr) using a direct current(DC) power supply. The measured CNT emitter area was 1×1 cm^2 and the distance between the top ITO plate and the bottom CNT/NiCr/Cr/ITO glass plate was 200 µm. Fig. 4 shows (a) the electric field (E) versus current density (J) and (b) turn-on field intensity and the electric fields measured at 1 mA/cm^2 of the CNTs grown at various substrate temperatures. The turn-on field was defined as the electric field at 1 µA/cm^2 of the emission current density. As shown in Fig. 4(b), the turn-on electric fields were 2.4 V/µm at 400 °C, 2.6 V/µm at 450 °C, and 3.7 V/µm at 500 °C. For the electric fields measured at 1 mA/cm^2 were 3.5 V/µm for 450 °C and 5.54 V/µm for 500 °C. The lower turn-on field observed at the CNTs grown at the lower substrate temperature appears to be related to the increase of the defect in the grown CNTs because it is known that the CNTs with the more defects tend to show the lower turn-on voltage [9–11]. However, in the case of the CNT field emitter grown at 400 °C, it was difficult to obtain 1 mA/cm^2 possibly due to too much defects in the grown CNTs.

The inset of Fig. 4(a) shows the Flower–Nordheim plots of the field emission curves in Fig. 4(a). As shown in the inset of Fig. 4(a), the plots show nearly linear shapes indicating the electron emission is originated from the field emission [12–15]. The emission current density J (A/cm^2) in Fig. 4 can be expressed as the following equation:

$$J = \frac{1.56 \times 10^{-6} E_{\mathrm{loc}}^2}{\varphi} \times \exp\left(-\frac{6.83 \times 10^7 \varphi^{3/2}}{E_{\mathrm{loc}}}\right) \quad (1)$$

where, φ is work function ($\varphi = 5$ eV for the multi-wall CNTs), E_{loc} is the local electric field at the CNT emitting
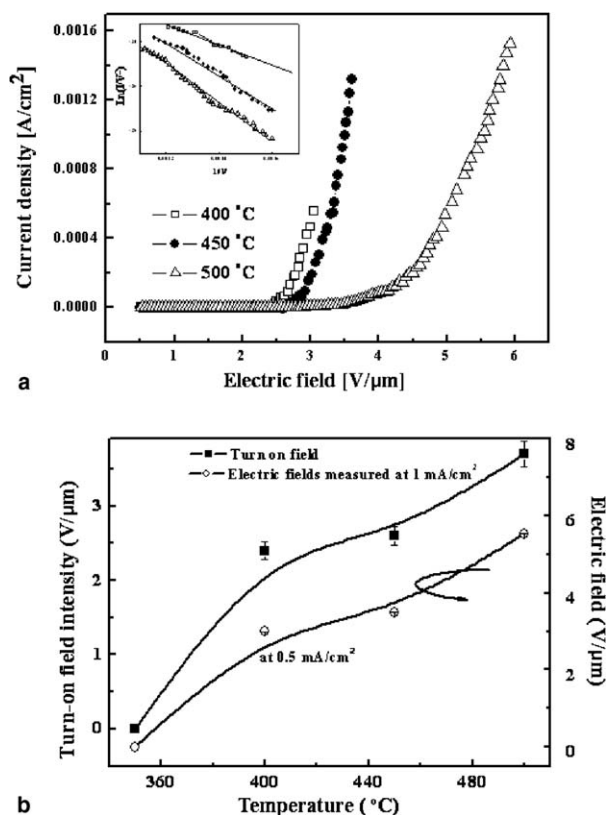
Fig. 4. (a) The field emission characteristics of the CNTs grown by the AP-PECVD at 400 °C, 450 °C and 500 °C. (b) Turn-on electric field and the electric fields measured at 1 mA/cm² of the CNT field emitter grown at various temperatures.

Fig. 5. HRTEM images of the CNTs grown at 450 °C by the AP-PECVD. (a): the tip of the CNTs, (b) and (c): the body of the CNTs.

tip ($E_{loc} = \beta E$), and β is field enhancement factor expressed as following Eq. (2):

$$\beta = 2.84 \times 10^7 \frac{\varphi^{3/2}}{S} \tag{2}$$

where, S is the slope of (J/E^2) versus $1/E$ modified from Eq. (1). The field enhancement factor (β) calculated for the CNTs grown at 400 °C, 450 °C, and 500 °C were 1069, 1374, and 1527 cm^{-1}, respectively. Wang et al. [16] observed the linear increase of field enhancement factor of CNT emitters with the increase of CNT aspect ratio and reported that the aspect ratio of the CNT is the most important factor of CNT field enhancement. The increase of field enhancement factor with the increase of growth temperature obtained in our experiment appears to be also related to the increase of aspect ratio of the grown CNTs by increasing CNTs length and by decreasing CNT diameter with increasing growth temperature even though the turn-on voltage of CNT emitter was lower for the CNTs grown at the lower growth temperature possibly due to the increase of defect density on the CNT surface.

Fig. 5 shows the HRTEM images observed for the CNTs grown at 450 °C by the AP-PECVD. As shown in Fig. 5(a), the CNTs grown by the AP-PECVD showed a Ni catalyst particle on the top of the CNT and the Ni p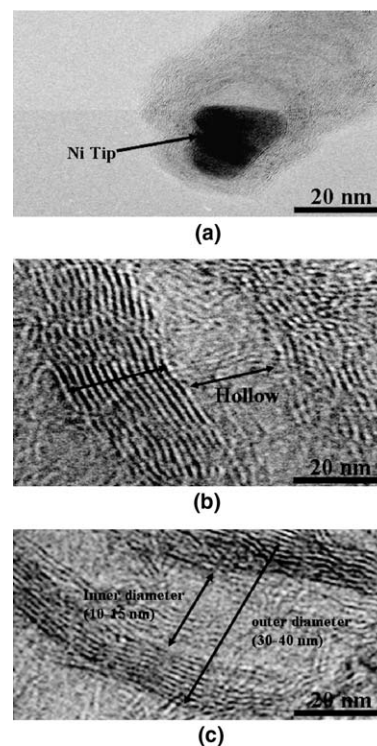article was covered with layers of graphite shells. The graphite shells were made of 15–25 graphite sheets with the wall-to-wall distance of 0.3 nm as can be seen from Fig. 5(b) and (c). The inner diameter and the outer diameter of the grown CNTs were 10–15 nm and 30–50 nm, respectively.

4. Conclusions

In summary, CNTs were grown using a capillary type AP-PECVD with NH$_3$(210 sccm)/N$_2$(100 sccm)/C$_2$H$_2$(150 sccm)/He(8 slm). The CNTs grown at the temperature range from 350 °C to 500 °C at the atmospheric pressure for 8 min were multi-wall CNTs with the length and the diameter in the range from 1 μm to 8 μm and from 100 ± 10 nm to 40 ± 5 nm, respectively. The increase of substrate temperature increased the CNT length and decreased the CNT diameter. With increasing the substrate temperature, the I_D/I_G measured by the FT-Raman decreased from 1.135 at 350 °C to 0.882 at 500 °C. The turn-on field of the grown CNT field emitter was increased with increasing CNT growth temperature possibly due to the decrease of defects in the CNTs grown at the higher temperature. The electric fields measured at 1 mA/cm² were 3.5 V/μm for 450 °C and 5.54 V/μm for 500 °C.

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