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Growth and Field-Emission Properties of Multiwalled Carbon Nanotubes Synthesized by a Pin-to-Plate-Type Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition

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In this study, carbon nanotubes (CNTs) were grown on sodalime glass substrates coated with NiCr (8 : 2) by using atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD), and their structural and electrical characteristics were investigated for possible applications as to the field emitters of field emission display (FED) devices. The substrate temperature was varied from 400 to 500 °C. The CNTs grown at 500 °C were multiwalled CNTs composed of 15 – 20 layers of carbon sheets with inner diameters of 10 ∼ 15 nm and outer diameters of 30 ∼ 40 nm. The ratio of the defective carbon peak to the graphite carbon peak of the CNTs grown at 500 °C, as measured by using Fourier transform (FT)-Raman, was 0.772. When the field-emission properties were measured, the turn-on field was 2.92 V/μm, and the emission field at 1 mA/cm^2 was 5.325 V/μm.

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I. INTRODUCTION

CNTs are being widely investigated for application to field emission tips of field emission display (FED) devices due to the excellent material and electrical properties. CNT emission tips can have one hundred times bigger electric field application factors than spindle-type emission tips due to the high aspect ratio of CNTs which have lengths of a few micrometers and diameters of a few tens of nanometers; therefore, field- emission voltage is reduced. Also, a stable emission current can be expected due to the strong physical properties of CNTs.

In general, when CNTs are applied as field emission tips, CNTs grown by various methods, such as arc discharge, laser sublimation, and thermal decomposition, are screen printed after mixing with a paste [1–3]. However, the screen printing of CNTs shows the problems such as paste residue on the CNT surface, outgassing from the paste, non-uniform dispersion of CNTs during the mixing with the paste, *etc.* [4]. Therefore, direct growth of CNTs on the FED glass substrate using chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), *etc.* in a vacuum chamber is being investigated [5]. However, a large area vacuum system for display substrates is very expensive, and, for the PECVD, the generation of a uniform plasma over a the large area substrate is very difficult.

In this study, AP-PECVD was used to grow CNTs [6], and the material and electrical properties of the CNTs were investigated for possible applications to field- emission tips for FED devices. The AP-PECVD was used to grow CNTs uniformly over a large area at a low temperature by in-line process using a pin-to-plate-type atmospheric pressure discharge system.

II. EXPERIMENTS

The pin-to-plate-type discharge system used to grow the CNTs at the atmospheric pressure is shown in Figure 1 [7–9]. The electrodes of the experimental pin-to-plate-type discharge system were made of aluminum. The

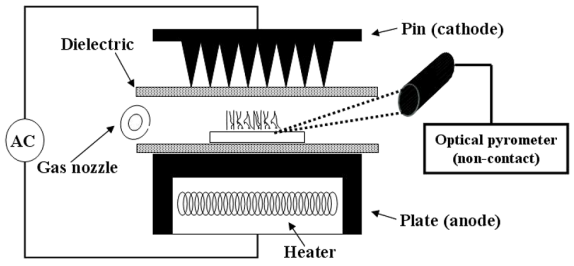

Fig. 1. Schematic diagram of the pin-to-plate type AP-PECVD system used in this study.

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powered electrode and the ground electrode were composed of pyramid-type multi-pins and a blank plate, respectively, and both electrodes were covered with dielectric plates to suppress arcing or filamentary discharge. On the multi-pin-type powered electrode, an alternating current (AC) power of 7.5 kV at 25 kHz was connected, and using the pin-type electrode, high-density plasmas could be obtained at a low voltage. The substrate temperature was varied from 400 °C to 500 °C by using a heating block located under the ground electrode, and the substrate temperature was measured by using an optical pyrometer (Luxtron, Model 100C - non-contact-type pyrometer)

NiCr(10 nm, Ni : Cr = 8 : 2)/Cr(100 nm) was sputter deposited on sodalime glass substrates before the AP-PECVD. The Ni in the NiCr was used as the catalyst for the CNT growth, and the Cr was used as an adhesion layer for the glass substrate. Before the growth of the CNTs, the glass substrate with NiCr(10 nm)/Cr(100 nm) was pretreated with a He(10 slm)/NH_3(150 sccm) plasma for 3 min. at the growth temperature to increase the surface area and to form nanosized Ni particles. To grow CNTs, we used He(10 slm)/ C_2H_2(210 sccm) was used with NH_3 (270 sccm) for hydrogen addition. The growth time was maintained at 3 min.

The growth characteristics were observed using field emission scanning electron microscop (Hitachi, S-4700), and Fourier-transform Raman spectroscopy (FT-Raman, Renishaw RM1000-InVia) was used to investigate the structure of the grown CNTs. Transmission electron microscopy (TEM; JEOL JEM-3011) was used for microstructural analysis of the grown CNTs, and the field emission characteristics of the grown CNTs were investigated using a homemade system equipped with a Keithley 2001 current meter.

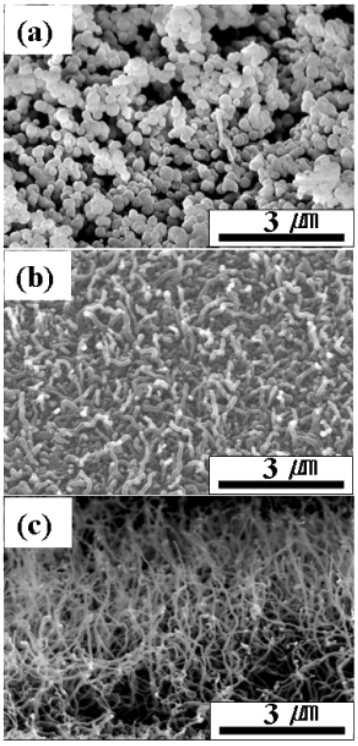

Fig. 2. SEM micrographs of the CNTs grown with He(10 slm)/C_2H_2(210 sccm) /NH_3(270 sccm) on the NiCr(10 nm)/Cr(100 nm)/glass substrates for 3 minutes at different substrate temperatures, after the He(10 slm)/NH_3(150 sccm) plasma pretreatment at 500 °C for 3 minutes: (a) 400 °C, (b) 450 °C, and (c) 500 °C.

III. RESULTS AND DISCUSSION

Figure 2 shows the effect of the substrate temperature during AP-PECVD on the growth of CNTs, as observed by FE-SEM. The growth temperature for (a), (b), and (c) were 400, 450, and 500 °C, respectively. To grow CNTs, we used He as the dilution and main discharge gas, C_2H_2 as the carbon source, and NH_3 as the additive gas for the promotion of CNT growth. NH_3 was also used during the pretreatment stage to form Ni nanoparticles before the CNT growth. The average length and diameter of the CNTs were measured by dispersing the CNTs in a solution by sonication and by measuring the dimensions using SEM. As Figure 2 shows, at 400 °C, no CNTs were grown on the substrate, and as the temperature was increased to 450 °C, CNTs with lengths of about 1 ± 0.5 μm was observed; at 500 °C, CNTs with lengths of about 3 ± 1 μm were observed. With increasing of substrate temperature, the diameters of the CNTs decreased from 80 ± 20 nm (450 °C) to 40 ± 10 nm (500 °C). The increase in the substrate temperature increased the length of grown CNTs due to the increased carbon reaction rate and increased of carbon diffusion into catalyst metal [10]. The diameter of the grown CNTs is known to be controlled by the size of the catalyst nanoparticles [11]. An increase in substrate temperature promotes agglomeration of Ni nanoparticles, thereby increasing the size of the catalyst nanoparticles. However, due to the NH_3 added during the pretreatment stage, with increasing substrate temperature, the catalyst surface is etched, so the size of the Ni nanoparticles is decreased; finally, the diameter of the grown CNTs is decreased [12].

Figure 3 (a)∼(c) show the TEM micrographs of CNTs grown at 500 °C by using AP-PECVD with a $He/C_2H_2/NH_3$ gas mixture. As Figure 3(a) shows, the grown material was multiwalled CNTs, not carbon nanowires. Also, as Figure 3(b) shows, the number of carbon layers of the CNT wall was $15 \sim 20$, and the distance between the carbon layers was 0.3 nm, which is similar to that of multiwalled CNTs grown by using other methods. The inside diameter of the grown CNTs was about $10 \sim 15$ nm, and the outside diameter was $30 \sim 40$ nm. Some crystallographic defects of the CNTs could be observed inside and outside the walls. At the tips of the CNTs, Ni nanoparticles were observed, as shown in

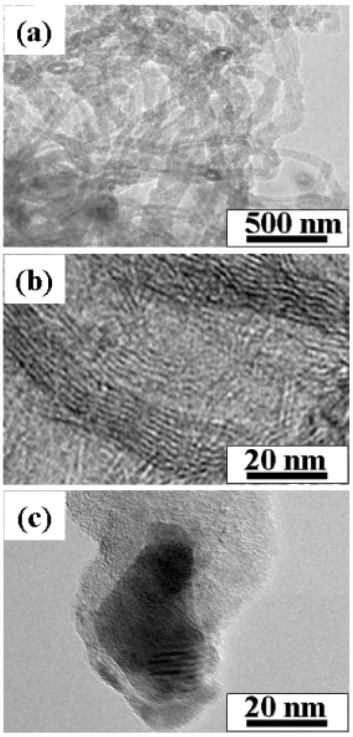

Fig. 3. TEM images of the CNTs grown at 500 °C by using AP-PECVD: (a) low magnification TEM image of CNTs , (b) HRTEM image of the CNT body, and (c) the tip of the CNT.

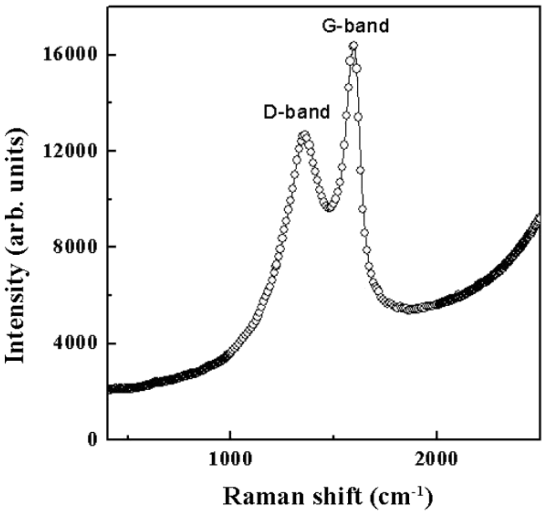

Fig. 4. FT-Raman spectrum of CNTs grown at 500 °C with He (10 slm)/C_2H_2(210 sccm)/NH_3 (270 sccm) for 3 min.

Figure 3(c), and the distance of graphite layers around the tip was also 0.3 nm.

Figure 4 shows FT-Raman spectrum of the CNTs grown at 500 °C by using AP-PECVD. In general, the peak near 1572.7 cm^{-1} is the G-band peak related to the typical graphite structure, and the peak near 1320 cm^{-1} is the D-band peak related to the graphite structure

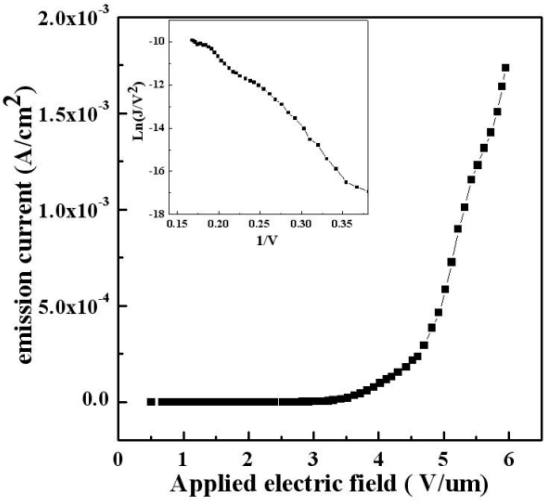

Fig. 5. Field-emission characteristics of the CNTs grown with He (10 slm)/C_2H_2(210 sccm)/NH_3(270 sccm) for 3 min. at 500 °C.

with defects and carbonous particles. As figure shows, two peaks,one near 1361 cm^{-1} and the other near 1591 cm^{-1}, related to the D-band and the G-band, respectively, could be observed. Also, in Figure 4, no peaks related to the single-walled CNTs were observed. The intensity ratio of the D-band to the G-band (I_D/I_G) was 0.772, which was lower than that found for the CNTs grown by other PECVD; methods, therefore, it is believed that stable CNTs can be grown by using AP-PECVD even though some defects can be observed when TEM is used.

The field-emission properties of the CNTs grown at 500 °C by using AP-PECVD were measured with a parallel diode-type configuration using a dc power supply in a vacuum chamber (5×10^{-6} Torr). The CNT emitter area was 1×1 cm^2, and the distance between the top anode electrode (glass coated with indium tin oxide) and the CNT layer was kept at 200 μm. Figure 5 shows the electric field (E) vs. current density (J) of the CNTs grown at 500 °C by using AP-PECVD. As figure shows, the turn-on electric field (defined as the electric field at 1 $\mu A/cm^2$ of the emission current density) of the CNTs grown at 500 °C was 2.92 V/μm, and a current density of 1 mA/cm^2 could be obtained with an electric field of 5.325 V/μm. The insert of Figure 5 shows the Fowler-Nordheim (F-N) plot of the field-emission curve. The emission current density (J) can be represented by the following F-N Equation [13,14]:

$$J = (AE^2/\Phi)\exp(-B\Phi^{3/2}/E), \quad (1)$$

where A = 1.54×10^{-6} $AeVV^{-2}$ and B = 6.83×10^9 $eV^{-3/2}$ Vm^{-1}. If the F-N plot shows a linear relationship, then the electrons are known to be emitted through field-emission characteristics. The plot in the insert a linear decrease, signifying that the electrons are emitted from the grown CNTs by field emission.

IV. CONCLUSIONS

In this study, CNTs were grown on NiCr(10 nm)/ Cr(100 nm)-coated sodalime glass at low temperatures (400 $\sim$ 500 °C which is lower than the glass softening temperature of 550 °C) by using pin-type AP-PECVD with He(10 slm)/ C_2H_2(210 sccm)/ NH_3(270 sccm). The CNTs were grown when the substrate temperature was higher than 450 °C, and increasing the substrate temperature increased the lengths of the grown CNTs and decreased the diameters of the CNTs. When the substrate temperature was 500 °C, multi-walled CNTs with inner diameter of 10 $\sim$ 15 nm and outer diameter of 30 $\sim$ 40 nm were grown. The number of graphite layers in the CNT wall grown at 500 °C was 15 $\sim$ 20, and the distance between the layers was 0.3 nm. When the field-emission characteristics of the CNT emitters grown at 500 °C were measured, a turn-on electric field of 2.92 V/μm and a current density of 1 mA/cm^2 at 5.325 V/μm could be obtained, which is appropriate for FED emitters.

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