Characteristic of carbon nanotubes synthesized by pin-to-plate type atmospheric pressure plasma enhanced chemical vapor deposition at low temperature

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CNTs have been widely investigated as the emitting tips for field emission display (FED) applications. Even though the screen printing of the CNTs are widely applied for FED, direct growth of CNTs on the FED glass substrate using plasma enhanced chemical vapor deposition (PECVD), etc. in vacuum is preferred due to the problems of the screen printing such as paste residue, non-uniform dispersion, etc. However, the large area vacuum system for the display substrates is very expensive and, for the PECVD, the generation of a uniform plasma over the large area substrate is very difficult in addition to the low throughput [1–3].

In this letter, an atmospheric pressure PECVD (AP-PECVD) has been used to grow CNTs and the characteristics of the CNTs were investigated in view of their possible application as field emission tips for FED. The AP-PECVD was applied to grow CNTs uniformly over a large area at low temperature and by in-line process for flat panel display processing [4,5].

The pin-to-plate type discharge system used to grow CNTs at the atmospheric pressure is shown in Fig. 1. The powered electrode and the ground electrode were composed of pyramid type multi-pins and a blank plate, respectively, and both electrodes were covered by dielectrics. On the multi-pin-type powered electrode, an alternating current (AC) power supply of 7.5 kV at 25 kHz was connected. Before the growth of 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 450 °C to increase the surface area and to form nanosize NiCr alloy particles. The composition of NiCr was Ni(80%)Cr(20%).

SEM micrographs of the CNTs grown at different substrate temperatures of 400–500 °C are shown in Fig. 2. He(10 slm)/C_2H_2(210 sccm)/NH_3(210 sccm) was used. The growth time was 3 min. As shown in Fig. 2(a)–(c), CNTs were grown at the substrate temperature higher than 450 °C. Also, the increase of the substrate temperature increased the length of the CNT from 1 ± 0.5 μm (450 °C) to 3 ± 1 μm (500 °C) and decreased the diameter of the CNT from 80 ± 20 nm (450 °C) to 40 ± 10 nm (500 °C).

SEM micrographs of CNTs grown at 500 °C for 3 min with different NH_3 flow rates of 150–270 sccm in He(10 slm)/C_2H_2(210 sccm) are shown in Fig. 3(a)–(c), and the TEM micrograph of the CNT grown at 500 °C with 210 sccm NH_3 is shown in Fig. 3(d). The lengths of the grown CNTs were 1.5 ± 0.7 μm (150 sccm NH_3), 3 ± 1 μm (210 sccm NH_3), and 3.5 ± 1 μm (270 sccm NH_3) and the diameters were 100 ± 20 nm (150 sccm NH_3), 40 ± 20 nm (210 sccm NH_3), and 35 ± 8 nm (270 sccm NH_3). Therefore, with increasing NH_3, the length of the grown CNTs was increased and the diameter was decreased. The increase of CNT length and the decrease of CNT diameter with increasing NH_3 flow rate are believed to be related to the removal of amorphous carbon dissociated on the Ni catalyst surface by hydrogen from NH_3. As shown in Fig. 3(d), the CNT grown at 500 °C was multi-walled CNT with 40–45 nm of outside diameter and 10–15 nm of inside diameter.

FT-Raman data are shown in Fig. 4 for the growth temperature of 450 and 500 °C and for the NH_3 flow rate of 210 and 270 sccm. Two FT-Raman peaks located at 1354 and 1595 cm^{-1} could be observed which correspond to defective carbon (I_D) and graphite carbon (I_G) of multi-walled CNT, respectively. The I_D/I_G was generally lower than 1.0 and the increase of substrate temperature and NH_3 flow rate decreased the I_D/I_G. At 500 °C and 270 sccm of NH_3, the I_D/I_G was about 0.772. Since the amount of impurities appears to be quite low from the SEM and TEM images, the decrease of I_D/I_G with increasing substrate temperature and NH_3 is related to the improved quality of the well structured CNTs. Using the CNTs grown at 500 °C for 3 min in He(10 slm)/C_2H_2(270 sccm)/(NH_3 210 or 270 sccm), the field emission characteristics

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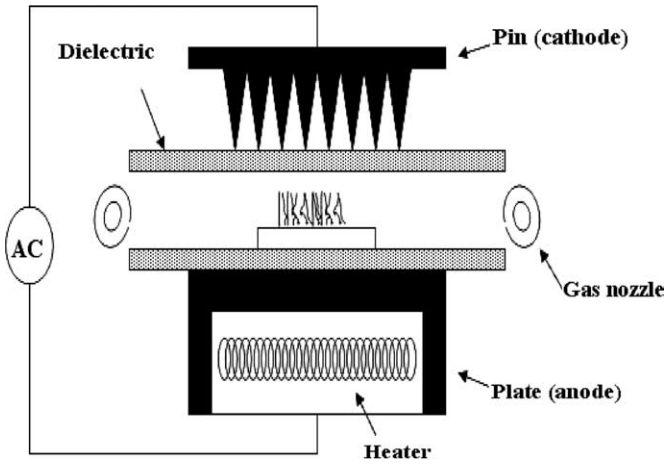

Fig. 1. Schematic diagram of the pin-to-plate type AP-PECVD system used in this study.

of the CNTs were measured and the results are shown in Fig. 5. In the figure, the Fowler–Nordheim (F–N) plots ($\ln I/E^2$ vs. $1/E$) are also shown in the insert. The emission fields for 210 and 270 sccm of NH_3 were 4.15 and 3.5 V/μm, respectively. The emission current density required for the application to FED is known to be 1 mA/cm^2 [6]. The CNTs grown at 500 °C in our AP-PECVD with

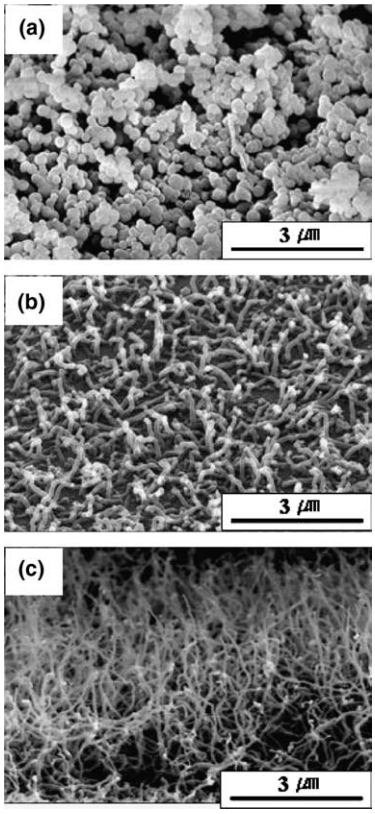

Fig. 2. SEM micrographs of the CNTs grown with He(10 slm)/C_2H_2(210 sccm)/NH_3(210 sccm) on the NiCr(10 nm)/Cr(100 nm)/glass substrates for 3 min at different substrate temperatures after the He(10 slm)/NH_3(150 sccm) plasma pretreatment at 450 °C for 3 min. (a) 400 °C, (b) 450 °C, and (c) 500 °C.

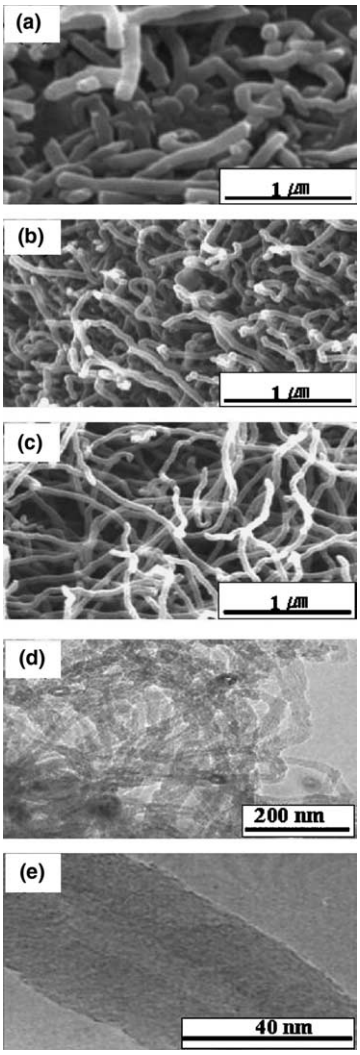

Fig. 3. SEM micrographs of the CNTs grown at 500 °C on the NiCr(10 nm)/Cr(100 nm)/glass substrates for 3 min with different NH_3 flow rates in He(10 slm)/C_2H_2(210 sccm)/NH_3 after the He(10 slm)/NH_3(150 sccm) plasma pretreatment at 450 °C. The NH_3 flow rates were (a) 150 sccm, (b) 210 sccm, and (c) 270 sccm. (d), (e) TEM micrograph of the CNTs grown at 500 °C and with 210 sccm of NH_3.

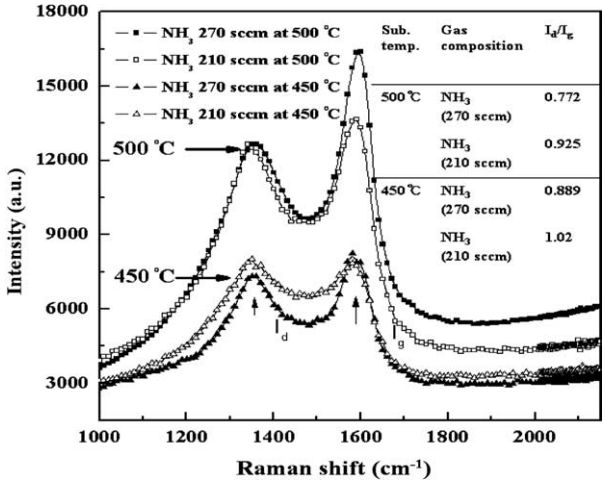

Fig. 4. FT-Raman spectra of CNTs grown at 450 and 500 °C and with the NH_3 gas rate of 210 and 270 sccm in He(10 slm)/C_2H_2(210 sccm)/NH_3 for 3 min.

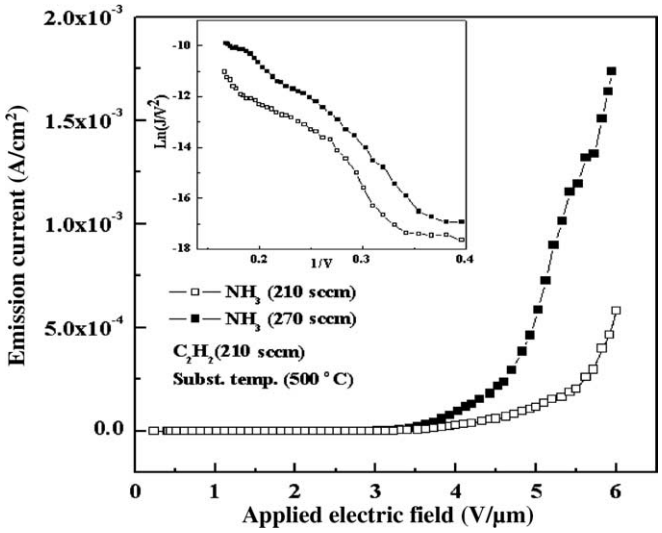

Fig. 5. The field emission characteristics of the CNTs grown with the NH_3 gas flow rate of 210 and 270 sccm in He(10 slm)/C_2H_2(210 sccm)/NH_3 for 3 min at 500 °C.

He(10 slm)/C_2H_2(210 ccm)/NH_3(270 sccm) showed 1 mA/cm^2 at 5.25 V/μm possibly due to the high quality of the grown CNTs. The F–N plot showed the almost linear slopes suggesting that the above emissions are related to the field emission by tunneling of electrons from the CNTs.

In summary, CNTs were successfully grown in He/C_2H_2/NH_3 by AP-PECVD using a multi-pin-to-plate type discharge system at the substrate temperature higher than 450 °C. FT Raman data showed the decrease of I_D/I_G to 0.772 with increasing substrate temperature and NH_3 suggesting the improved quality of grown CNTs. When the field emission properties were measured for the CNTs grown at 500 °C for 3 min with He(10 slm)/C_2H_2(210 sccm)/NH_3(270 sccm), the turn-on field was 3.5 V/μm and the field emission field at 1 mA/cm^2 was 5.25 V/μm.

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Supported carbon nanofibers for the fixed-bed synthesis of styrene ☆

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The styrene synthesis is one of the ten largest industrial processes. This monomer is involved in several polymer syntheses, and is industrially produced by the direct dehydrogenation of ethylbenzene at 873–953 K over a potassium promoted iron oxide catalyst [1]. This strongly

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