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)/NH3(150 sccm) plasma for 3 min at 450 °C.

SEM micrographs of the CNTs grown at different substrate temperatures of 400–500 °C are shown in Fig. 2. 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 NH3 flow rates of 150–270 sccm in He(10 slm)/C2H2(270 sccm) are shown in Fig. 3(a)–(c), and the TEM micrograph of the CNT grown at 500 °C with 210 sccm NH3 is shown in Fig. 3(d). The lengths of the grown CNTs were 1.5 ± 0.7 μm (150 sccm NH3), 3 ± 1 μm (210 sccm NH3), and 3.5 ± 1 μm (270 sccm NH3) and the diameters were 100 ± 20 nm (150 sccm NH3), 40 ± 20 nm (210 sccm NH3), and 35 ± 8 nm (270 sccm NH3). Therefore, with increasing NH3, 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 NH3 flow rate are believed to be related to the removal of amorphous carbon dissociated on the Ni catalyst surface by hydrogen from NH3. 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 NH3 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 (ID) and graphite carbon (IG) of multi-walled CNT, respectively. The ID/IG was generally lower than 1.0 and the increase of substrate temperature and NH3 flow rate decreased the ID/IG. At 500 °C and 270 sccm of NH3, the ID/IG was about 0.772. Since the amount of impurities appears to be quite low from the SEM and TEM images, the decrease of ID/IG with increasing substrate temperature and NH3 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)/C2H2(270 sccm)/NH3 (210 or 270 sccm), the field emission characteristics were very difficult in addition to the low throughput [1–3].
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 \( \text{NH}_3 \) were 4.15 and 3.5 V/\( \mu \text{m} \), 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
He(10 slm)/C₂H₂(210 ccm)/NH₃(270 sccm) showed 1 mA/cm² at 5.25 V/lm 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/C₂H₂/NH₃ 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 NH₃ 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)/C₂H₂(210 ccm)/NH₃(270 sccm), the turn-on field was 3.5 V/µm and the field emission field at 1 mA/cm² was 5.25 V/µm.

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References


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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