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Characteristics of Carbon Nanotubes Deposited by Using Low-Temperature Atmospheric-Pressure Plasma-Enhanced Chemical Vapor Deposition

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In this study, carbon nanotubes (CNTs) were grown using a capillary dielectric barrier discharge (DBD)-type atmospheric-pressure plasma-enhanced chemical vapor deposition (AP-PECVD) system at a low temperature of 400 °C, and their growth characteristics were investigated. The CNTs grown using He (6 slm)/C_2H_2 (90 sccm) AP-PECVD with additive gases (NH_3, N_2) for 5 minutes at 400 °C after a pretreatment were multi-layer CNTs with diameter of 20 – 50 nm and uniform lengths of 1.5 – 2 μm. FT-Raman spectroscopy showed that the grown CNTs were multi-wall CNTs with a D-band/G-band intensity ratio of 0.9. Transmission electron microscopy of the AP-PECVD-grown CNTs showed that the CNT had a 30-nm outer diameter and a 7-nm hollow inner diameter with a Ni particle on the top of the tube.

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Keywords: Carbon nanotube, Atmospheric-pressure plasma, Dielectric barrier discharge, AP-PECVD

I. INTRODUCTION

Among the many potential applications [1–4] field emission displays (FEDs) are one of the most commercially approached applications being developed by industry due to the advantages of using carbon nanotubes (CNTs) as field emission tips [5]. These advantages include a low cost of tip fabrication, a high emission efficiency, improved reliability, *etc.* One of the methods for applying CNTs as FED field emitters is to use chemical vapor deposition to grow the CNTs directly and selectively on the field emission area of the FED/citeR6. Currently, there is difficulty using this method to grow CNTs at temperatures lower than the deformation temperature of the sodalime glass substrates (550 °C), so CNT growth using low-temperature plasma-enhanced-chemical vapor deposition (PECVD) is currently under investigation [7]. However, this method may not be applicable to industries requiring continuous production of large-area FED panels due to the difficulties in forming a uniform plasma over a large area and the difficulties associated with growing CNTs in a vacuum.

II. EXPERIMENTS AND DISCUSSION

In this study, an atmospheric-pressure plasma PECVD (AP-PECVD) system was used to grow CNTs at temperatures lower than the glass softening temperature (approximately 550 °C). Even though the growth of carbon nanotubes using atmospheric-pressure CVD has already been examined using conventional dielectric barrier discharge (DBD) systems [8], the growth of CNTs at temperatures lower than the glass deformation temperature has not yet been reported. This is possibly due to the low density of atmospheric pressure plasmas compared to low-pressure plasmas. However, the atmospheric- pressure plasma system used in this study is a high-density version of a DBD system [9] using a capillary dielectric material instead of a conventional blank dielectric material, and the feed gas can be distributed more uniformly [10]. Using this plasma system, the CNTs were grown at a low temperature (400 °C), and their growth characteristics were examined for possible applications to field emission tips.

Figure 1 shows the capillary dielectric discharge system used to grow the CNTs at atmospheric pressure. The system is similar to a typical planar DBD system except for the dielectric material covering 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 (Al_2O_3) with a number of parallel small capillary holes (the aspect ratio of the holes was 10 : 1) to form an ion-beam-like high-density plasma in the hole and to distribute the reactive gases) The diameter of the ground electrode was 130 mm, and the ground electrode was heated using a heating block and was cov-

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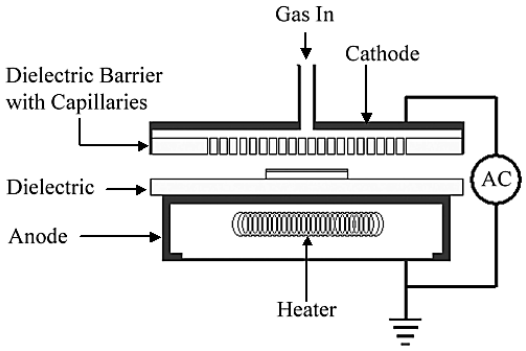

Fig. 1. Schematic diagram of the capillary dielectric discharge-type AP-PECVD system used in this study.

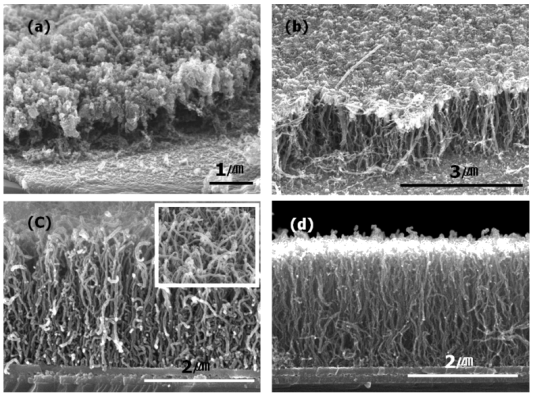

Fig. 2. SEM micrographs of the CNTs grown on Ni(10 nm)/Cr(170 nm)/glass substrates after the He(200)/NH_3(3) plasma pretreatment at 400°C for 5 minutes: (a) with He(200)/C_2H_2(3) without a plasma, (b) with a He(200)/C_2H_2(3) plasma, (c) with a He(200)/N_2(2)/C_2H_2(3) plasma, and (d) with a He(200)/NH_3(2)/C_2H_2(3) plasma.

ered with a 3-mm-thick quartz plate. The temperature of the substrate was measured directly by locating and attaching a thermocouple on the surface of the glass substrate. Due to the noise to the thermocouple on the glass substrate during the plasma operation, the temperature of the substrate was maintained by using the thermocouple in the heater. The temperatures measured on the glass substrate before and after the plasma operation for 5 minutes were similar to each other.

A 10-nm-thick Ni layer was deposited on a 170-nm Cr buffer layer deposited on a sodalime glass substrate by rf sputtering. The morphology of the grown CNTs was related to the Ni thickness and the pretreatment conditions. The pretreatment was carried out using a He(6 slm)/NH_3(90 sccm) atmospheric pressure plasma while heating the Ni/Cr coated substrate to 400 °C for 5 minutes. The CNTs were grown on the Ni/Cr samples at 400 °C. In order to examine the effect of the additive gases, we added 60 sccm of N_2 or NH_3 to the plasma during CNT growth and compared those CNTs with those grown without the additive gases. Field-emission scanning electron microscopy (FE-SEM) was used to analyze the surface morphology of the grown CNT samples, and transmission electron microscopy (TEM; JEOL JEM-3011) was used to study the microstructures. FT-Raman spectroscopy (Renishaw RM1000-InVia) was used to examine the binding states of the grown CNTs.

Figure 2 shows SEM micrographs of the CNTs grown at 400 °C for 5 minutes (a) with He(200)/C_2H_2(3) without plasma, (b) with a He(200)/C_2H_2(3) plasma, (c) with a He(200)/N_2(2)/C_2H_2(3) plasma, and (d) with a He(200)/NH_3(2)/C_2H_2(3) plasma. As Fig. 2(a) shows, when a Ni/Cr sample was exposed at 400 °C without a plasma, clean CNTs were not grown, and only amorphous carbon clusters could be seen. However, as Fig. 2(b) shows, the growth of CNTs could be observed after applying a He/C_2H_2 plasma even though some amorphous carbon clusters were observed on top of the CNTs. The growth of CNTs after applying the plasmas is the result of increased C_2H_2 dissociation and increased surface diffusion through the Ni surface. However, due to the difficulties associated with a He/C_2H_2 plasma, removing the excessive carbon generated, carbon clusters remained on top of the CNTs. The amorphous carbon on top of the CNTs is believed to be generated by the deposition of the residual carbon during the plasma-off period. After we added nitrogen containing gases such as N_2 and NH_3 to the He/C_2H_2 plasma, as shown in Figs. 2(c) and (d), cleaner CNTs without amorphous carbon clusters were obtained. If the CNTs grown by using the He/N_2/C_2H_2 plasma are compared with those grown by using the He/NH_3/C_2H_2 plasma, the CNTs grown by using the He/N_2/C_2H_2 plasma were thicker and the tops of the grown CNTs appeared to contain amorphous carbon.

The benefits of the nitrogen in the synthesis of CNTs have been described by other researchers. These include nitrogen-ion bombardment, dilution of the carbon-containing gas, a reduction of the activation energy for enhanced diffusion, increased dissociation of hydrogen molecules, *etc.* [11–15]. In our experiments, as Figs. 2(c) and (d) show, the benefit of nitrogen atoms in the growth of CNTs was also identified. Because the binding energy of N-N is 945 kJ/mol and that of N-H is 339 kJ/mol, more nitrogen atoms can be expected in a plasma with added NH3 compared with N_2 in addition to hydrogen atoms from NH_3. Hydrogen atoms can remove amorphous carbons on the Ni surface by forming volatile CH_x compounds. Therefore, a cleaner growth of CNTs can be expected for the He/NH_3/C_2H_2 plasma. However, the percentage of added N_2 or NH_3 was very small (about 0.98 %) in the atmospheric pressure plasma. Therefore, the dilution effect was negligible. In addition, the effect of ion bombardment by N_2^+ should be greater than that by NH_x^+, and the ion bombardment energy itself does not appear to be significant due to the extremely small collision mean free path at atmospheric pressure ($\lambda_{mfp} \cong 5/\mathrm{P(mTorr)}$ cm, approximately 66 nm at atmospheric pressure). This is despite the fact that the operational voltage was higher (4 kV) than it was in low-

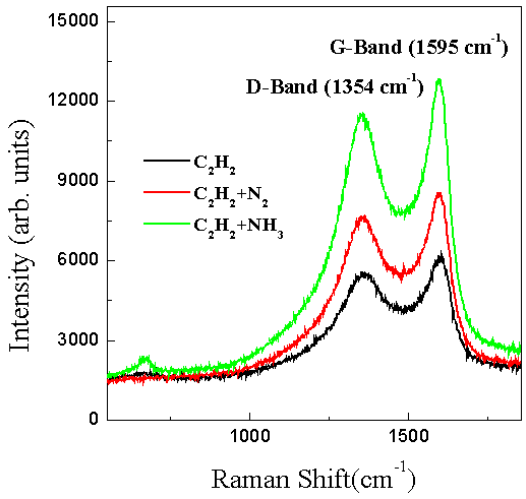

Fig. 3. FT-Raman spectra of CNTs for the conditions in Fig. 2.

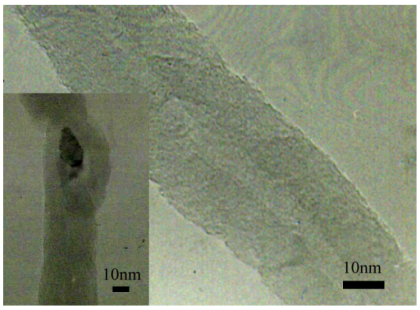

Fig. 4. TEM images of the multi-wall CNTs grown under the conditions of Fig. 2(d).

pressure PECVD. Hence, the removal of excess or loose carbons on the Ni surface as a result of the formation of volatile compounds such as C_2N_2, CH_x, or HCN and/or the activation of the Ni surface with nitrogen atoms or NH_x radicals formed in the plasma is believed to be the reason for these observations.

The CNTs grown in this study had diameters ranging from 20 to 50 nm and were curved. The curved CNTs obtained in these experiments appear to be related to the use of an AC plasma with no DC bias. The curved CNTs contained defects in the CNT structure. The structures of the grown CNTs were investigated using FT-Raman in order to investigate the degree of the defects in the CNTs grown under the conditions in Figs. 2(b), (c), and (d), and the results are shown in Fig. 3. All the grown CNTs showed a G(graphite-like) band near 1582 cm^{-1}, which originated from hexagonal carbon binding, and a D(defect) band from 1250 to 1350 cm^{-1}, which originated from defects in the carbon binding. The measured intensity ratio of these two bands (I_D/I_G) were approximately 0.9 and did not differ significantly with the experimental conditions. In order to identify the structure of the CNTs obtained in this study, we observed the microstructures of the CNTs obtained under the conditions shown in Fig. 3(d) by using TEM, and the result is shown in Fig. 4. The CNTs obtained were hollow multi-wall CNTs with an outer diameter of 30 nm and an inner diameter of 7 nm.

III. CONCLUSIONS

In this study, the effects of capillary dielectric discharges at atmospheric pressure on the growth of CNTs with He/C_2H_2 were examined for applications to the emission tips of FEDs. For the growth of CNTs, the effects of adding nitrogen-containing gases, such as N_2 and NH_3, to the He/ C_2H_2 on the structure of the CNTs were also investigated. Using He/C_2H_2 capillary dielectric discharges with additive gases such as N_2 and NH_3, we could successfully grown CNTs at 400 °C even though conventional DBD-type atmospheric-pressure plasmas are known to require more than 600 °C for the growth of CNTs due to their low plasma densities. The successful growth of the CNTs at 400 °C, which is less than the glass softening temperature, is believed to result from increased dissociation of the gases due to the increased plasma density. This is because ion beam-like high-density plasmas were obtained at the holes of the dielectric in the capillary dielectric plasma system. The CNTs grown using $He/NH_3/C_2H_2$ plasmas at 400 °C for 5 minutes were multi-walled nanotubes with outer diameters ranging from 20 to 50 nm and inner diameters of 7nm.

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