The Relation between Emission Properties and Growth of Carbon nanotubes with dc bias by RF Plasma Enhanced Chemical Vapor Deposition

Sun Hong Choi[a)*], Jae-Hee Han [a)]Tae Young Lee[a)], Ji-Beom Yoo[a)**], Chong-Yun Park [a)]

[a)]Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, 300 Chunchun-Dong, Jangan-Gu, Suwon, 440-746, Korea

Whikun Yi [c)], SeGi Yu[c)], Taewon Jung[c)], Junghee Lee [c)], and Jong Min Kim[c)]

[c)]Materials and Devices lab, Samsung Advanced Institute of Technology, P.O.Box 111, Suwon 440-600, Korea

Tel : +82-31-290-7413, [*]e-mail : **dokebl@mail.skku.ac.kr**

Abstract

The growth of carbon nanotubes (CNTs) was carried out using ratio frequency plasma enhanced chemical vapor deposition (rf PECVD) system equipped with dc bias for the directional growth. Acetylene and ammonia gas were used as the carbon source and a catalyst. The relation between gas flow rate and dc bias on the growth of CNTs was investigated. We studied the relation between emission properties and the directionality of CNTs grown under different dc bias voltage.

1. Introduction

In recent years, CNTs have been intensively studied because of their unique properties and applications. One of practical applications is an electron emitter in field emission display (FED) [1,2], which requires high current density at low operating voltage and large area growth. Up to now, many groups make efforts on the growth of CNTs by utilizing an arc discharge, laser vaporization, thermal chemical vapor deposition, and plasma enhanced chemical vapor deposition (PECVD) system [3-6]. Since these well-known techniques except PECVD were operated at higher temperature than 700 °C, growth of CNTs on the glass substrate was prohibited for application of FED. Growth of CNTs using direct current (dc) PECVD has been regarded as a promising candidate for low temperature growth of CNTs on glass substrate. However, dc PECVD has several limits, such as sample damage due to arcing and uniformity in large area growth.

In this study, we have been used radio frequency (rf) PECVD system for stabile and large area growth and low temperature growth of CNTs. Alignment of CNTs can be achieved by an additional dc bias during the growth of CNTs. We studied that the relation between emission properties and the directionality of CNTs grown under different dc bias voltage.

2. Experiment

The CNTs were grown in the rf PECVD system equipped with dc bias control. We

synthesized CNTs on nickel-coated glass substrate at low temperature below 500 °C. Acetylene and ammonia gas were used a carbon source and catalyst, respectively. Ar gas was used as a carrier gas. A Cr buffer layer of 200 nm and a Ni catalyst layer of 40 nm were sequentially deposited on the glass substrate by sputtering and an electron beam evaporation, respectively. The substrate was transferred to the chamber and chamber was pumped down below 2×10^{-5} Torr by a mechanical and a diffusion pump. And NH_3 was introduced into the chamber. After the working pressure had been stabilized, the rf power supply for plasma generation was turned on. The temperature of substrate was controlled by IR lamp heating system. The pre-treatment for morphology variation of surface of the nickel catalyst layer was conducted by NH_3 plasma at 330 °C for 5 min. The rf Power and flow rate of NH_3 for pre-treatment was 60 W and 240 sccm, respectively. After pre-treatment, C_2H_2 was introduced into the chamber. The rf power for CNTs growth was 130 W and the substrate temperature was 500 °C. The substrate temperature was measured using a thermocouple on substrate. We changed the various negative dc bias for the growth of CNTs. And the effect of gas flow rate on the CNTs growth was investigated. The morphology after pre-treatments and growth of CNTs were characterized by Field emission canning electron microscopy (FESEM). The Raman spectroscopy was used to evaluate the graphization of CNTs. Field emission was evaluated using phosphor coated anode in a vacuum chamber below 10^{-7} Torr.

3. Results and Discussion

Figure 1 typical FESEM images of the CNTs films synthesized using different flow ratio of the carbon source to NH_3 gases for 15 minute. Figure 1 (a) shows that the short stub CNTs were sparsely grown when the flow rate of NH_3 and C_2H_2 were 240 and 60 sccm, respectively. When the flow rate of NH_3 and C_2H_2 were 260 and 40 sccm, more sparsely short stub CNTs was compared. It may suggest that the growth of CNTs was limited due to the shortage of carbon supply. The flow rate of C_2H_2 increased form 60 to 75 sccm, and the morphology of CNTs was shown in Fig. 3 (b). Growth of CNTs with larger flow rate of C_2H_2 was enhanced. However, the growth of CNTs was inhibited with an additional increase in C_2H_2 supply of 100 sccm. It may be attributed to over supply of C_2H_2 and lack of NH_3 gas prohibited the growth of CNTs.

Figure 2 is a series of FESEM micrographs showing the effect of dc bias on the growth of CNTs for 10 minute. As shown in Fig. 2 (a), with the plasma power 130 W (without dc bias), the CNTs were rarely grown because of shortage of carbon source in the growth of CNTs. Figure 2 (b) and 2 (c) shows morphology of CNTs with negative 30 and 50 V, respectively. The growth of CNTs was promoted compared to that of CNTs without dc bias. It is considered that negative dc bias improved carbon source supply to the substrate. When the dc bias increased form 50 V to70 V, CNTs was not grown because of too much carbon supply to the substrate. Too much carbon source came to be deposited on the carbon atom left on Ni surface after carbon diffusion via surface or bulk of the metal particle [7]. Deposited

carbon on surface of catalyst would be interfered CNTs growth, resulting in the formation of carbon layer instead of CNTs.

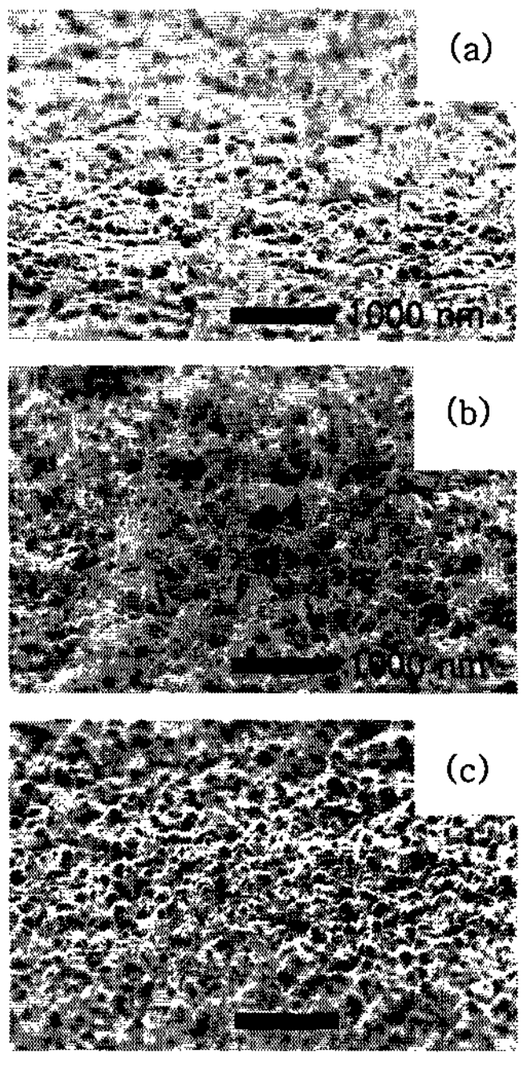

Figure 1 Typical FESEM images of the CNTs films synthesized under different growth condition. (a) NH_3 : C_2H_2 = 240 : 60 sccm (b) NH_3 : C_2H_2 = 225 : 75 sccm (c) NH_3 : C_2H_2 = 200 : 100 sccm. The plasma power was 130 W.

Figure 3 shows a typical Raman spectrum for the CNTs observed in Fig.2. Raman spectra represent the formation of graphitized CNTs. The spectrum peak at D-band indicates that carbonaceous particles exist near CNTs or adhere to the wall of CNTs. As the dc bias increased for 0 to 50 V, total intensity of spectrum increased, and D/G intensity ratio increased. When the intensity of D-band is larger than G-band, that CNTs grown contain a large amount of carbonaceous particle and defects [8]. Addition negative dc bias

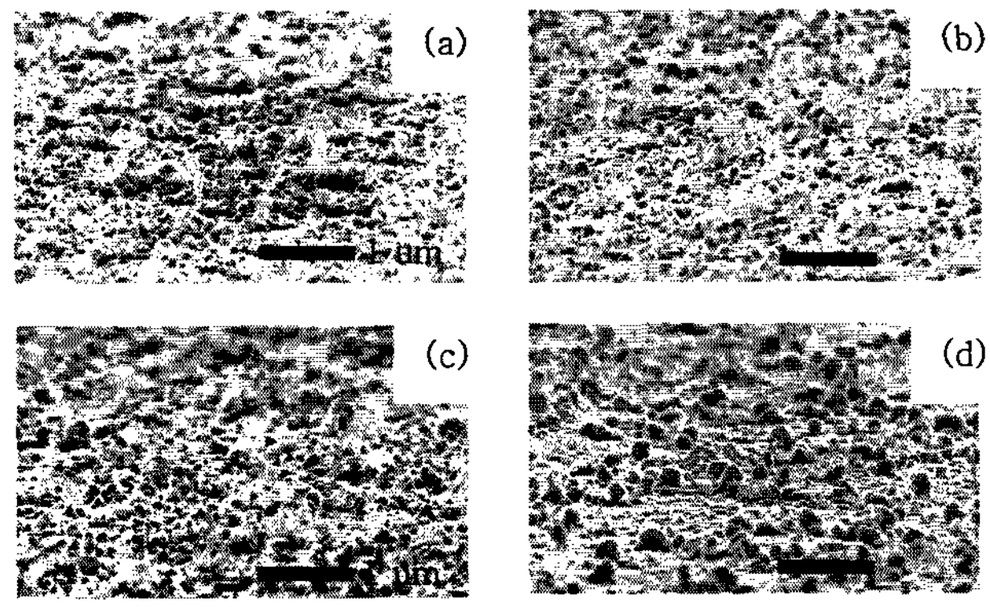

Figure 2 FESEM micrographs of CNTs grown at the power of 130W for 10 min. (a) without bias (b) bias voltage of 30V (c) 50 V (d) 70 V

enhanced carbon source supply to the substrate. We assumed that excess carbon source act as defects. Dc bias enhanced carbon source supply also crystallinity of CNTs becomes poor.

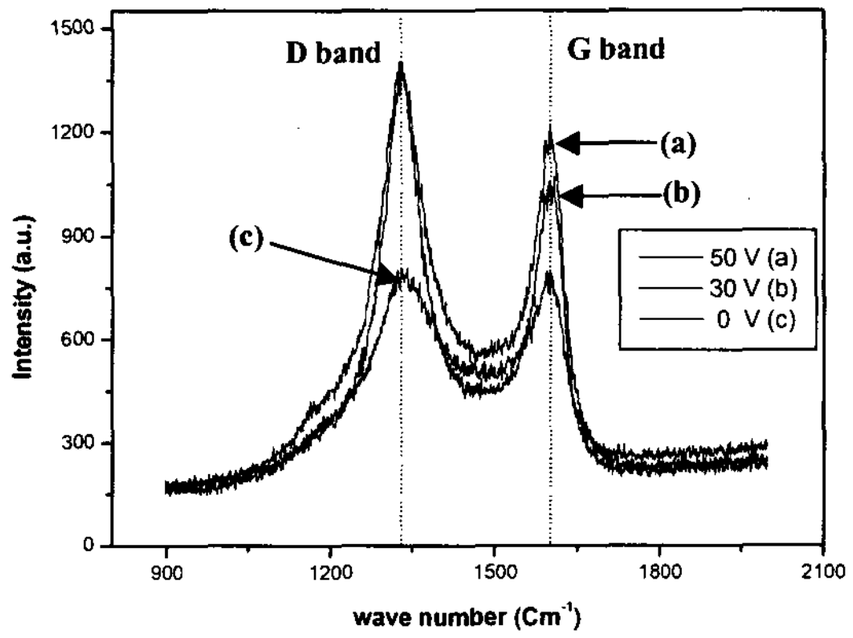

Figure 3 Raman spectra of CNTs grown at the different bias conditions (a) without bias (b) 30 V and (c) 50 V.

The emission current was measured at room temperature in a vacuum chamber at 10^{-7} Torr. The distance between the anode and the

substrate was kept at 170 μm throughout the measurement. Figure 4 shows emission properties of CNTs observed in fig.2. The insert shows the Fowler-Nordheim plot. We found that emission properties of grown CNTs with dc bias were enhanced.

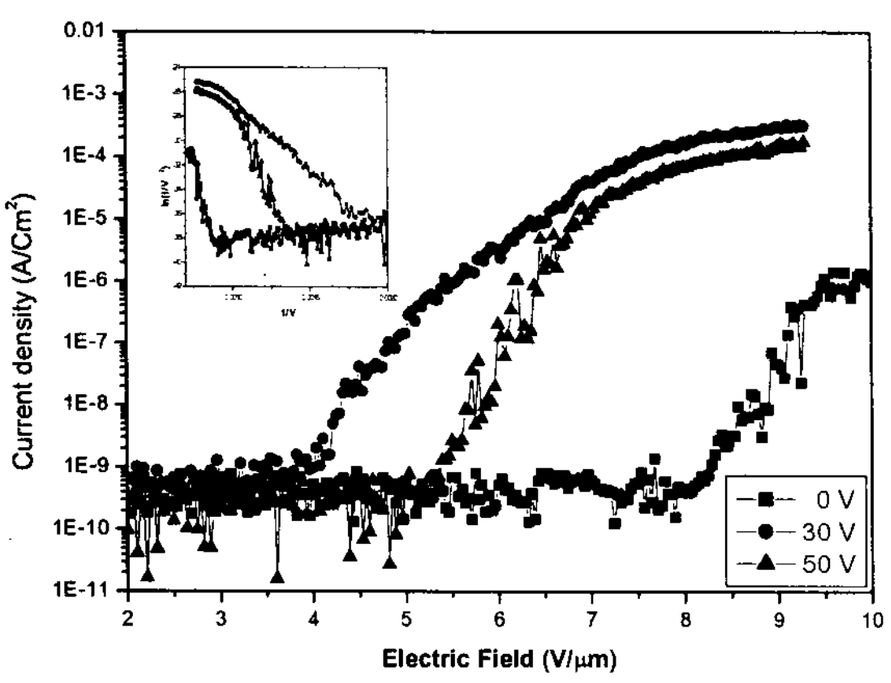

Figure 4 Field emission current vs. electric field plot (insert plot) Fowler-Nordheim plot (a) without bias (b) 30 V and (c) 50 V.

4. Conclusion

We used radio frequency (rf) PECVD system equipped with dc bias control for the growth of CNTs at below 500°C. Growth of CNTs with larger flow rate of C_2H_2 was enhanced. However, the growth of CNTs was inhibited with an additional increase in C_2H_2 supply of 100 sccm. Negative dc bias improved carbon source supply to the substrate, and the growth of CNTs was more promote than that of CNTs without dc bias. When the dc bias increased form 30V to 50V, crystallinity of CNTs was degraded. Slope in F-N plot decreased with dc bias indicated higher β.

5. Referance

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