The Structure and Electrical Characteristics of CNTs Depending on the Hydrogen Plasma Treatment

*Hyung Soo Uh[1], Soo Myun Lee[1], Pil Goo Jeon[1], Byung Hwak Kwak[1], Sang Sik Park[1], Euo Sik Cho[2], Jong Duk Lee[2] and Sang Jik Kwon[3]

[1]Dept. of Electronics Eng. , Sejong Univ., 98 Kunja-dong, Kwangjin-gu, Seoul 143-747, Korea
*Phone : +82-2-3408-3728 , E-mail : hsuh@sejong.ac.kr
[2]School of Electrical Eng., Seoul Nat'l Univ., San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151-742, Korea
[3]Dept. of Electronics Eng., Kyungwon University, Seongnam-city, Kyunggi-do 461-701, Korea

Abstract

Carbon nanotubes (CNTs) were grown on Ni-coated TiN/Si substrate by microwave plasma chemical vapor deposition using mixture gas of H_2/CH_4 at low temperature of 500 ℃. Average diameter of CNTs could be easily controlled by H_2 plasma pretreatment time before CNTs growth. The turn-on voltages of CNT emitters were varied from 3.5 V/μm to 9 V/μm according to the hydrogen pretreatment conditions. The close relationship between electron emission characteristics and pretreatment time indicates that pretreatment condition can be a key process parameter in CNTs growth for field emission displays..

1. Introduction

Since the discovery of carbon nanotubes (CNTs)[1], CNTs have drawn much attention owing to their unique physical properties and wide variety of applications. One potential application is the electron source in field emission display (FED)[2]. The advantages of CNTs as field emitters include a small radius of curvature, high aspect ratio, high chemical inertness and mechanical strength[3,4]. Two different approaches can be applied to fabricate CNTs as FED cathode. One is the CNTs deposited in thick film pastes, and the other is the selective growth of CNTs onto patterned catalyst layers. While the former is simple and economical process, it requires post-activation process to kick off uniform and efficient electron emission and has some demerits in view of resolution and contamination. The latter can be highly selective and allow high resolution integration of CNTs. In addition, the selective CNTs growth is favorably the last step of the field emitter array (FEA) fabrication process with gate, leaving the CNTs free of any surface contamination due to post-processing. Among various methods for selective CNTs growth, chemical vapor deposition (CVD) method is eminently suitable for preparing CNTs as electron sources in FED owing to its controllability and reliability. However, more detailed understanding of growth mechanism and process parameters affecting the CNTs structure and electron emission properties is needed for the practical use of the method. In particular, small diameter CNTs with several micro-meters long are essential to achieve a low switching voltage and a high current density at HDTV resolutions.

In this paper, we study the CNTs grown on Ni-coated TiN/Si substrate at a low temperature of 500 ℃ using microwave plasma CVD (MPCVD). The influence of H_2 plasma pretreatment on the structural properties and field emission characteristics of CNTs is investigated.

2. Experimental

The starting material is a 120 nm-thick Ni coated TiN/Si substrate. Ni was deposited by rf magnetron sputtering process under a chamber pressure of 3.7 mTorr and substrate temperature of 183 ℃. The process for CNTs growth consists of two steps: (1) formation of metal catalyst in H_2 (100%) plasma pretreatment and (2) growth of CNTs in H_2 (20%) and CH_4 (80%). The H_2 pretreatment and the CNTs growth were carried out at microwave power, pressure and substrate temperature of 400 W, 10 Torr and 500 ℃, respectively. The pretreatment time was varied from 5 min to 15 min and the growth time was fixed at 30 min. Fig. 1 shows the schematic diagram of the MPCVD system. The growth temperature can be detected by two thermometers of pyrometer and thermocouple.

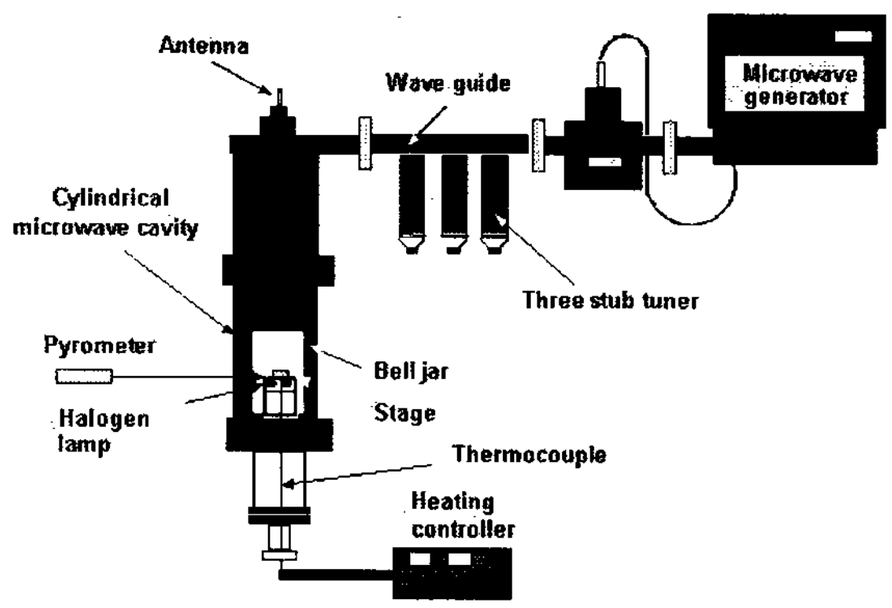

Fig. 1. Schematic diagram of MPCVD system used for CNTs growth.

3. Results and discussion

The growth morphology was observed by scanning electron microscope (SEM). Fig. 2 shows the typical SEM images of CNTs which are uniformly grown on substrate. Although the vertical alignment of CNTs has much room to improvement, the CNTs seem to be quite uniform in length. We measured TEM images of the CNTs to evaluate the wall structure and the CNTs diameter. As shown in Fig. 3, the TEM observation shows that these nanotubes have multiwalled structure with graphitic sheets and the tips of the CNTs are closed with cone-shaped catalytic metal particles. Fig. 4 shows the CNTs diameter versus H_2 pretreatment time. The diameter of CNTs linearly decreases with increasing pretreatment time, which is due to the reduction of Ni grain size caused by higher ion bombardment. As pretreatment time increases from 5 min to 15 min, the CNTs diameter decreases from 36 nm to 26 nm and thus CNTs with higher aspect ratio can be obtained at longer pretreatment time However, CNTs were rarely grown after longer H_2 plasma pretreatment than 25 min. This indicates that the optimum pretreatment time exists for the growth of CNTs.

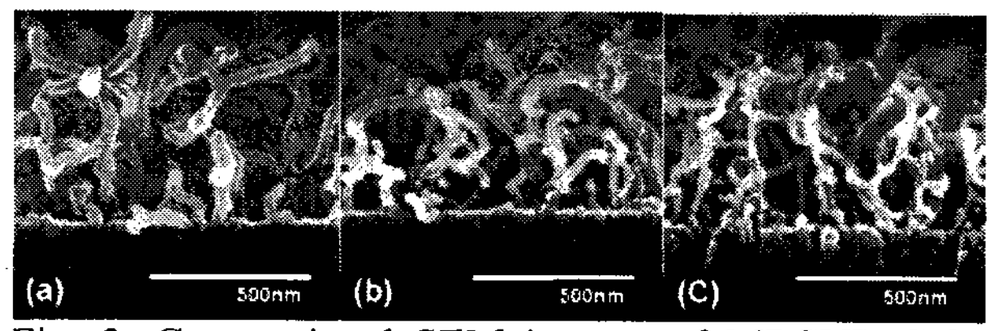

Fig. 2. Crossectional SEM images of MPCVD-CNT film with different pretreatment times of (a) 5 min, (b) 10 min, and (c) 15 min.

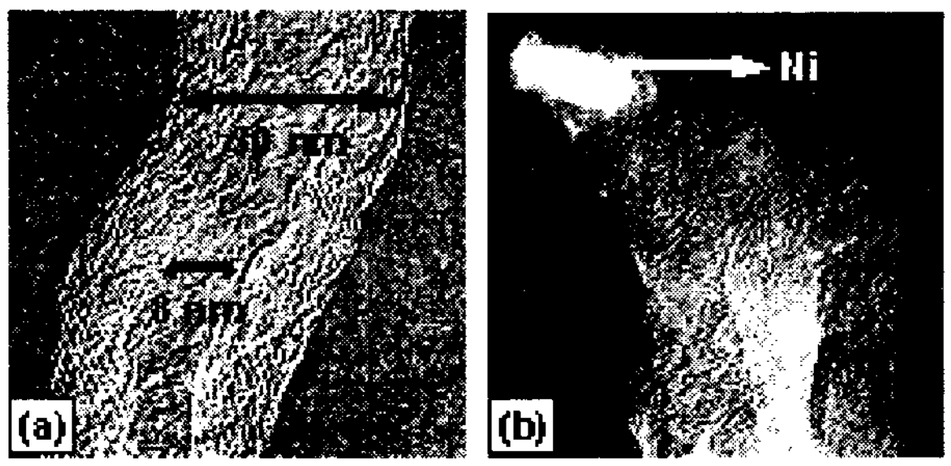

Fig. 3. HR-TEM images of multiwalled CNTs taken at (a) the middle and (b) the tip of the CNTs with the pretreatment time of 10 min.

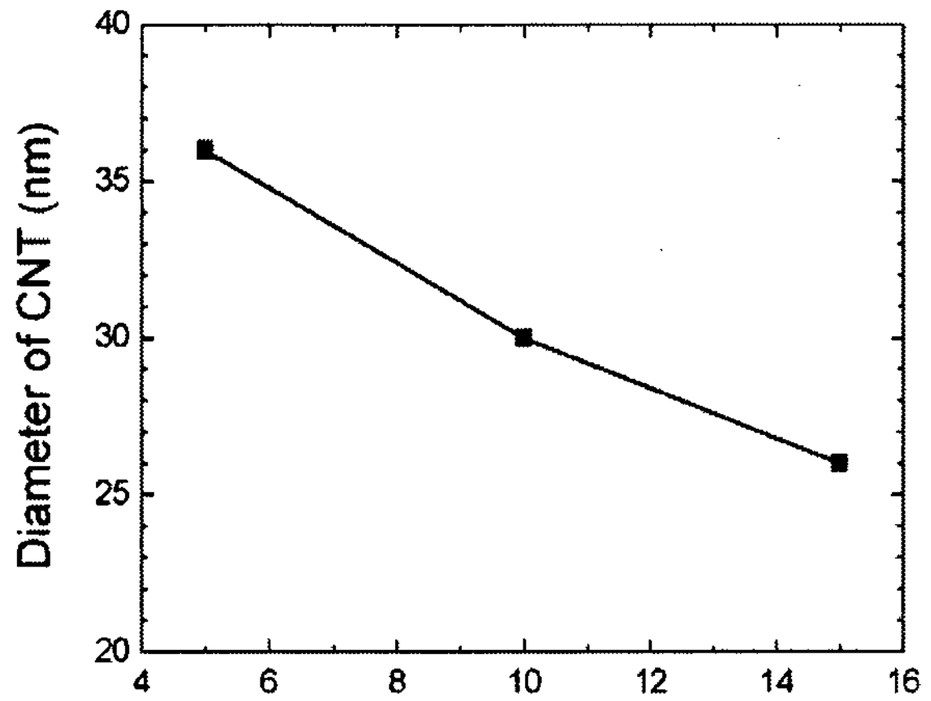

Fig. 4. Averaged diameter of CNTs as a function of H_2 pretreatment time.

Carbon nanotube films were also characterized by Raman spectroscopy. Fig. 5 is the typical Raman spectrum for the CNTs observed in Fig. 2(b). The difference in the spectra according to the pretreatment time variation was negligible. Only two peaks were observed in Raman spectrum. The strong peak at 1598 cm^{-1} (G-band) signifies the formation of graphitic CNTs. Another peak at 1350 cm^{-1}(D-band) indicates the carbonaceous particles adhered to walls of CNTs and the defective structure in the walls due to low growth temperature[5]. Larger intensity of D-band than that of G-band reveals that a large amount of carbonaceous particle and defects or imperfection in crystalline are contained in the CNTs.

Field emission properties of the grown CNTs were characterized using a diode-type configuration in a vacuum test station at a base pressure of 4.7×10^{-6} Torr. The distance between the anode and the CNT emitters

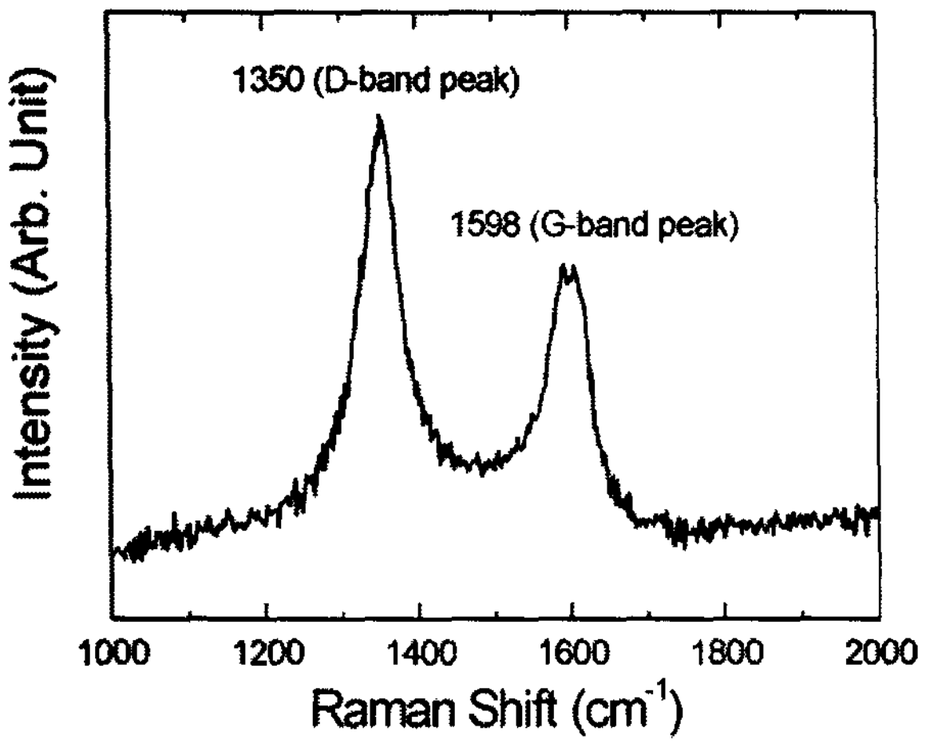

Fig. 5. Raman spectra of grown CNTs.

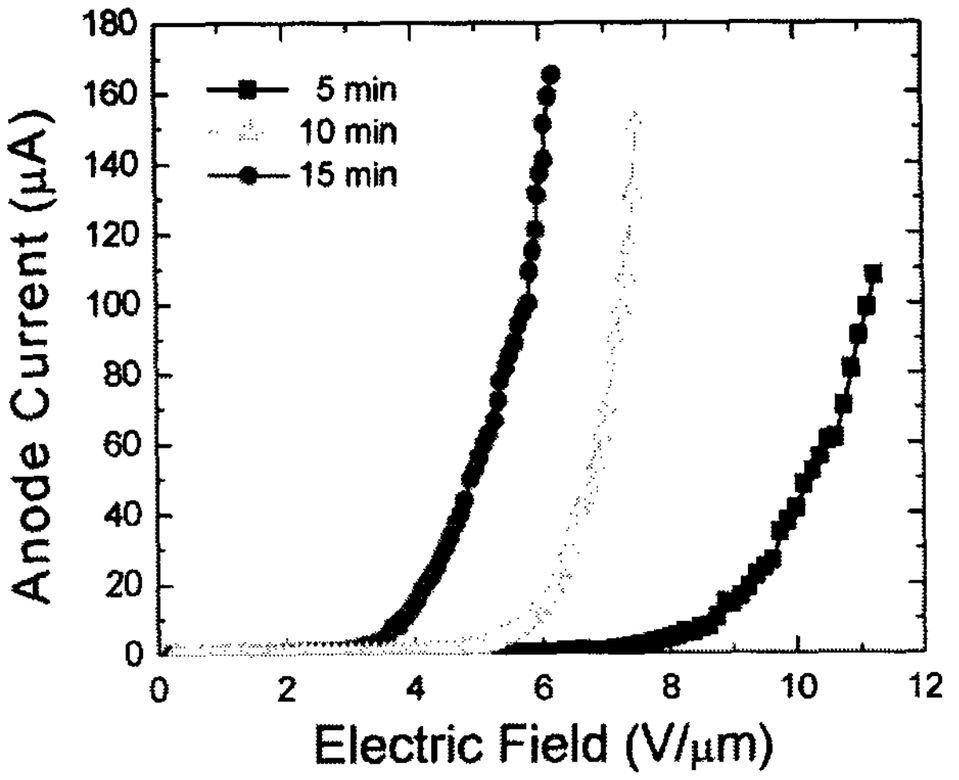

Fig. 6. Anode current as a function of macroscopic electric field for diode-type CNTs emitter structure with different hydrogen pretreatment time.

was kept at 160 μm throughout the measurement and the rectangular emission area was about 1 cm^2. Fig. 6 shows the anode current as a function of the macroscopic electric field for CNTs emitters observed in Fig. 2. The macroscopic electric field for the diode-type configuration is V_a/d, where V_a is the voltage between the anode and the CNTs emitter and d is the distance between the anode and the emitter surface. The turn-on field decreases from 9 V/μm to 3.5 V/μm with increasing pretreatment time from 5 min to 15 min, which suggests that the field emission characteristics of CNTs can be controlled via CNTs diameter by the pretreatment time because the CNT diameter affects the field enhancement factors β[6]. In fact, it is well known that the emission current is primarily dependent on the field enhancement factor, namely aspect ratio, of CNTs. Consequently, a slight variation of few tens percent of CNTs diameter causes a significant variation of the emitted current by several hundreds of percent.

Fowler-Nordheim (F-N) plots corresponding to the I-V curves of Fig. 6 are presented in Fig. 7. The experimental data are fitted well with a straight F-N lines. To gain a better understanding of electron field emission, field emission parameters can be extracted from the F-N plots by the simple slope-and-intercept method[7]. The emission current density J in A/cm^2 is generally expressed as the F-N equation[8]

$$J = \frac{1.4\times10^{-6}E_{loc}^2}{\phi}\exp\left(-\frac{6.53\times10^{7}\phi^{3/2}}{E_{loc}}\right) \qquad (1)$$

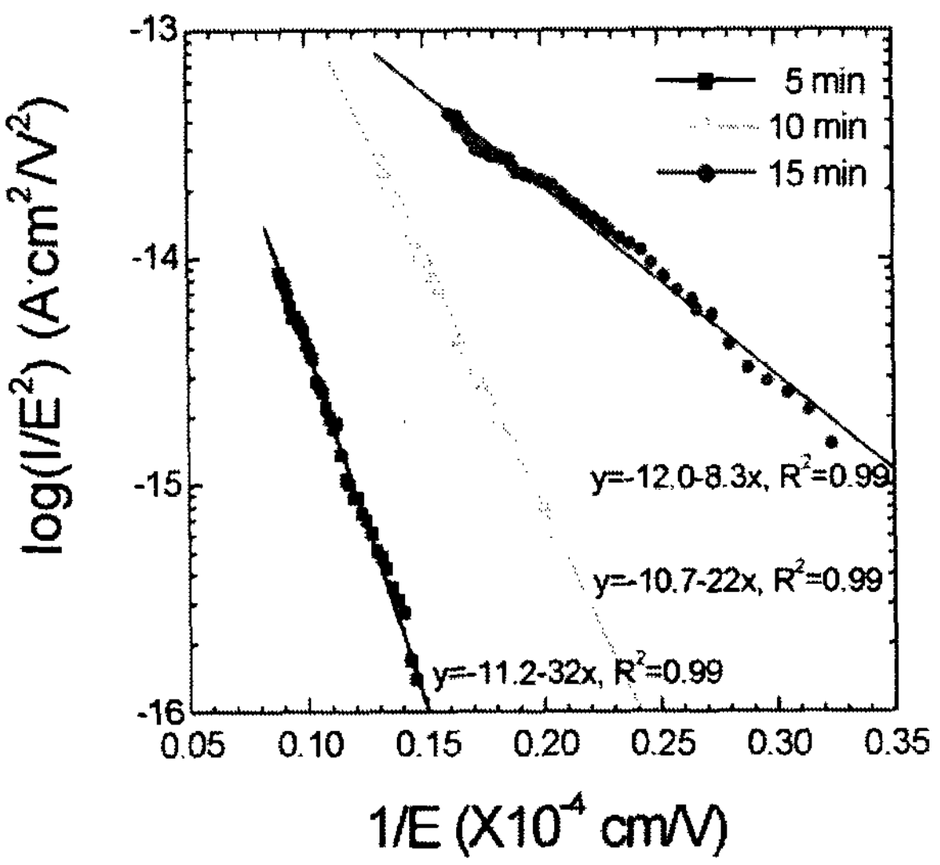

Fig. 7. Fowler-Nordheim plots corresponding to field emission curves of Fig. 6.

where ϕ is work function in eV, E_{loc} the microscopic local electric field near the CNT emitters in V/cm which can be given as $E_{loc} = \beta E$. β and E are the field enhancement factor and macroscopic electric field, respectively. From Eq., (1) and $J = I/\alpha$ where α denotes the emission area in cm^2, a linear relation of $\ln(I/E^2)$ and $1/E$ can be obtained as

$$\log\left(\frac{I}{E^2}\right) = \log\left(\frac{1.4\times10^{-6}\alpha\beta^2}{\phi}\right) - \frac{6.53\times10^{7}\phi^{3/2}\log e}{\beta E}$$
$$= C - \frac{S}{E} \qquad (2)$$

where C and S correspond to the intercept on I/E2-axis and the absolute value of slope of the F-N plot, respectively. With a work function given, field emission area and field enhancement factor can be calculated as

$$\beta = 2.84\times10^{7}\frac{\phi^{3/2}}{S}$$
$$\alpha = \frac{10^{C}\phi}{1.4\times10^{-6}\beta^2} \qquad (3).$$

The field emission parameters obtained from the simple F-N analysis and the assumption of ϕ= 5 eV[9] are listed in Table 1. The calculated field enhancement factors in Table 1 are something like the experimental results in previous results[10]. For example, if applied macroscopic electric field is 10 V/μm, then the field across the CNT emitter is 9.9×10^{7} ~ 3.8×10^{8} V/cm, which is sufficient to cause the field emission. Larger field enhancement factor of CNTs with 15 min pretreatment time than that with 5 or 10 min mainly results from larger aspect ratio due to smaller CNT diameter. Several reasons may account for very small emission areas including randomly aligned CNTs. Very high CNT density in our film may decrease the enhancement factor by field-shielding effect and also contribute smaller emission areas[11]. Large scale of well-dispersed and vertically-aligned CNTs will helpful to improve field emission characteristics.

Table 1. Field enhancement factor β and emission area α extracted from F-N plots for CNTs emitters with different pretreatment time of 5, 10, 15 min, respectively.

Sample / Parameters	5 min	10 min	15 min
β	992	1443	3826
α (x10^{-10} cm^2)	0.23	0.34	0.0024

4. Conclusion

We have successfully grown CNTs on Ni-coated TiN/Si substrate at 500 ℃ by MPCVD with mixed gas of CH_4 and H_2 after plasma pretreatment with H_2 gas. The CNTs were uniformly grown in high density. The increase of pretreatment time caused the decrease of CNTs diameter and thus improvement of electron emission characteristics owing to the higher aspect ratio. These results indicate that the optimization of the growth conditions for electron emitters is also necessary in the field of plasma pretreatment and still under way. We believe that the CNTs grown by the low temperature MPCVD process can be a promising candidate for the electron sources in the FEDs.

Acknowledgment

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