In-situ rf treatment of multiwall carbon nanotube with various post techniques for enhanced field emission

*Kyoung Soo Ahn, Jun Sik Kim, Ji Hoon Kim, Chae Ok Kim, and Jin Pyo Hong**
New Functional Materials and Device Lab, Department of Physics, Hanyang University
Seoul 133-791, Republic of Korea jphong@hanyang.ac.kr

Abstract

Well-aligned multiwall carbon nanotubes (MWCNTs) were prepared at low temperature of 400 ℃ by utilizing a radio frequency plasma-enhanced chemical vapor deposition (rf-PECVD) system. The MWCNTs were treated by an external rf plasma source and an ultra-violet laser in order to modify structural defect of carbon nanotube and to ablate possible contamination on carbon nanotube surface. Structural properties of carbon nanotubes were investigated by using a scanning electron microscopy (SEM), Raman spectroscopy, Fourier transformer Infrared spectroscopy (FTIR) and transmission electron microscope (TEM). In addition, the emission properties of the MWNTs were measured for the application of field emission display (FED) in near future. Various post treatments were found to improve the field emission property of carbon nanotubes.

1. Introduction

Carbon nanotube (CNT) is increasingly becoming a significant electron emission source for field emission displays (FED) or vacuum microwave devices due to its potential for long life, high emission current, and low-voltage operation [1]. The CNT emitters with small diameters are crucial in order to significantly reduce the operation voltage. In addition, the CNT has distinct advantages, such as a superior aspect ratio, electrical conductivity, and mechanical stiffness over conventional emitters in the FED application [2]. In this letter, the as-grown MWCNTs were *in-situ* treated with external rf plasma sources (Ar, H_2, NH_3, C_2H_2) and an ultra-violet laser in order to obtain efficiently structural purification of the MWCNTs and to ablate possible contaminants of the MWCNTs without producing any destructive transformation of the MWCNTs. [3]

2. Experimental, results and discussion

Fig. 1 shows typical SEM images of the MWCNTs before and after Ar plasma treatment and UV-laser treatment. As shown in Fig. 1a, the as-grown MWCNTs clearly had an average height and diameter of about 3.8 μm and about 50 nm, and Fig. 1b shows an optimum condition of Ar plasma treatment, also, Fig 1c, d show the as-grown and an optimum condition of UV-laser treatment, respectively. The upper portion of Fig. 1a, c exhibited the presence of disordered carbons and other phase particles on the as-grown

MWCNTs' surface. These unwanted particles or phases were mainly attributed to the low temperature growth of the MWCNTs at 400 °C. Fig. 1b displays a SEM view of the MWCNTs after 5 min Ar plasma exposure time. As shown in this figure, the disordered carbons of the as-grown MWCNTs were etched off from the MWCNTs' surface. It was primarily due to Ar ion bombardment effect on the MWCNTs during this short exposure time. At a longer exposure time beyond 25 min, the MWCNTs were significantly damaged and had more highly disordered phases on the the MWCNTs' surface again. As shown in Fig. 1d, the MWCNTs after UV-laser treatment by an optimum condition of a laser scan speed. The optimum laser scan speed is 30 mm/s. The effects resemble Ar plasma treatment. Therefore, longer exposure time and slow laser scan speed were expected to generate highly strong effect on the MWCNTs. In these conditions, Ar plasma irradiation would influence only structural purification of the MWCNTs, also, laser exposure would influence decrease disordered MWNTs. [4]

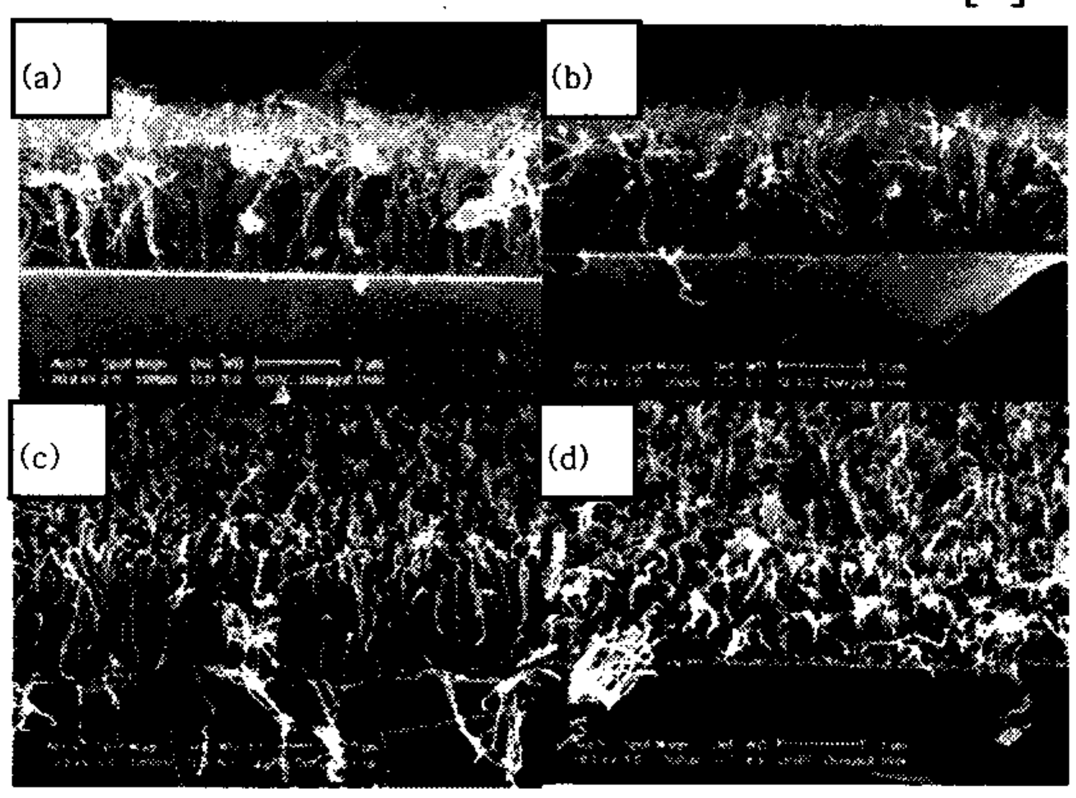

Figure 1 SEM images of (a) and (c) as-grown MWCNTs. (b) and (d) indicate MWCNTs after treatments, repectively.

Fig. 2 reveals typical TEM images of the MWCNTs before and after Ar plasma exposure, laser exposure, respectively. As shown in Fig. 2a, the as-grown MWCNTs were clearly encapsulated by pear-shaped Ni catalytic particles on the edges. Figs. 2b and 2c exhibit typical TEM images of the MWCNTs treated at various post-treatments, respectively. As shown in Fig. 2b and c, only catalyst particle at the tip disappeared, without causing any damage to the main crystal structure of MWCNTs.

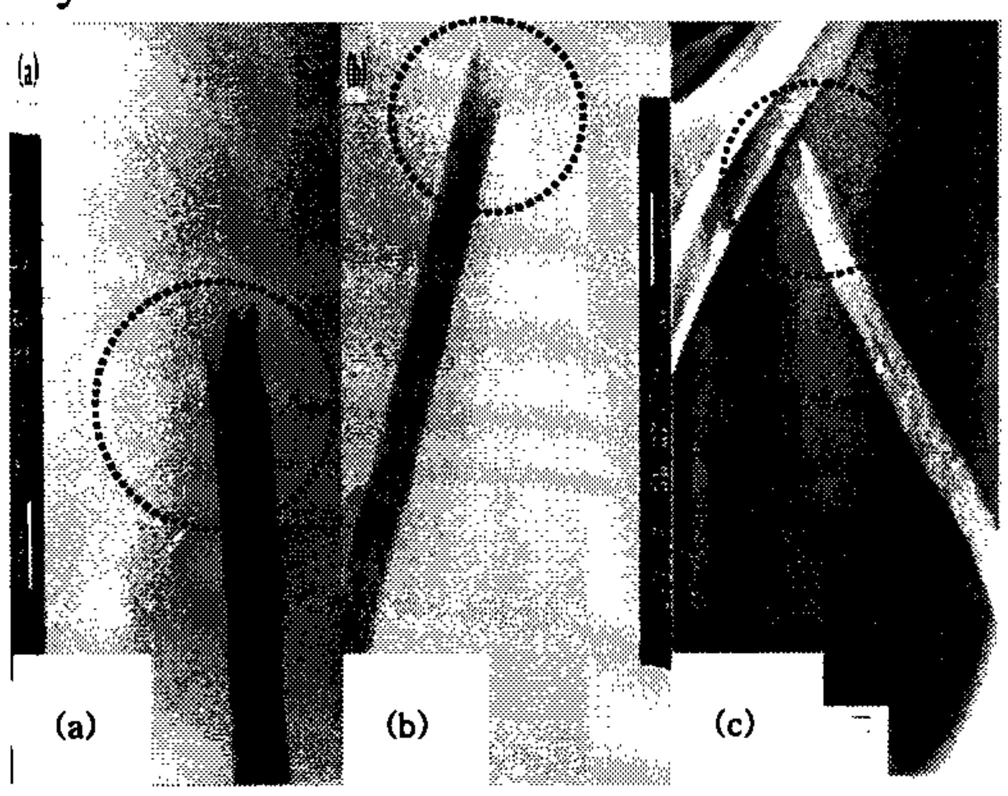

Figure 2 TEM images before and after treatments.

In-situ rf Ar plasma of the MWCNTs were at first investigated by utilizing various gases plasma. A primary experimental parameter of plasma exposure time was mainly examined to promote simple treatment procedure of the MWCNTs without affecting any structural transformation by Ar plasma treatment. Previous treatments with other reactive plasma have various chemical bindings to carbon atoms. But these chemical bindings could be controlled and purified by our method with an inert Ar gas. In addition, post-laser treatment of MWCNTs was carried out using an Nd-YAG pulse laser. The optimum conditions induced the structural improvement of the MWCNTs by effectively removing Ni catalytic particles and reducing the amorphous phases of the as-grown MWCNTs. Therefore, simple Ar gas and laser exposure on the MWCNTs leads to significant improvement in the emission property and turn-on field.

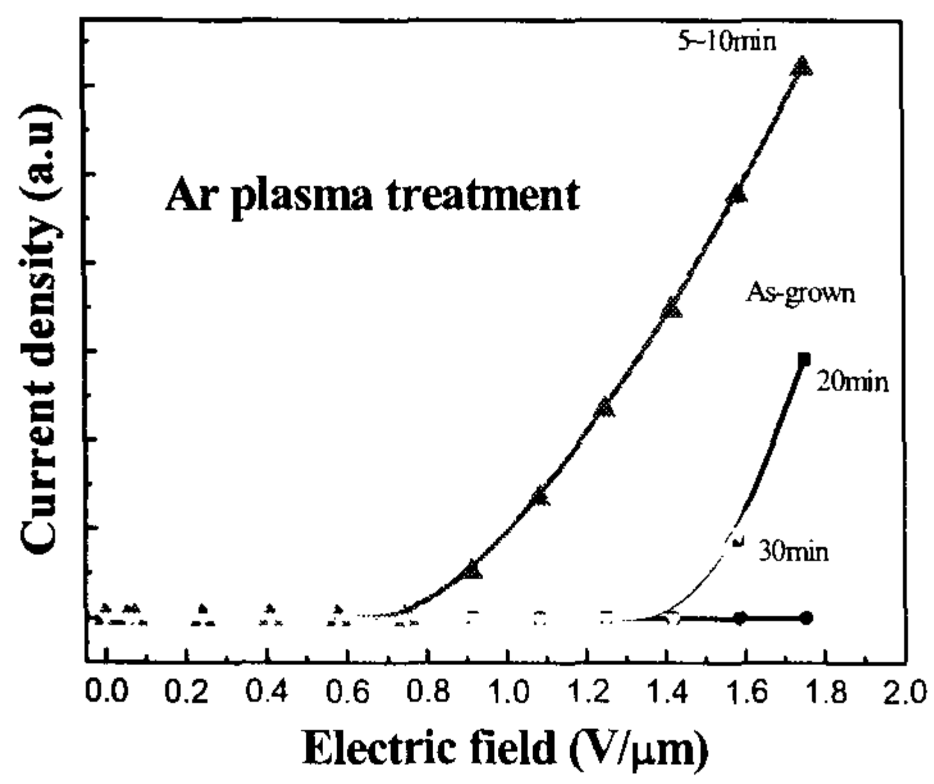

Figure 3 I-V Typical results of emission current density versus electric field for the MWCNTs before and after plasma post-treatments.

Fig. 3, 4 shows typical I-V characteristics of the MWCNTs before and after the plasma and laser treatments. The emission measurement was performed in a vacuum chamber below 10^{-7} torr at room temperature. The spacing distance between the cathode and the anode was 300 μm. The measured field emitting area was 1.0 cm^2. An indium-tin-oxide glass was used as on anode plate. As shown in this Fig. 3, the structural enhancement of the MWCNTs after the Ar plasma treatment improved the field emission ability of the MWCNTs, The turn-on field (E_t) was decreased from 1.65 V/μm to 0.93 V/μm for the Ar plasma duration of 5~10 min. However, there was no detectable emission current after the plasma exposure more than 30 min because the MWCNTs were significantly damaged for longer rf exposure time. Fig. 4 displayed the field emission capability of MWCNTs after UV-laser treatment. The same as Ar plasma treatment result the structural enhancement of MWCNTs. The E_t was decreased from 1.00 V/μm to 0.50 V/μm for the laser scan speed of 30 mm/s. However, there was increased E_t after the laser scan speed more than 20 mm/s.

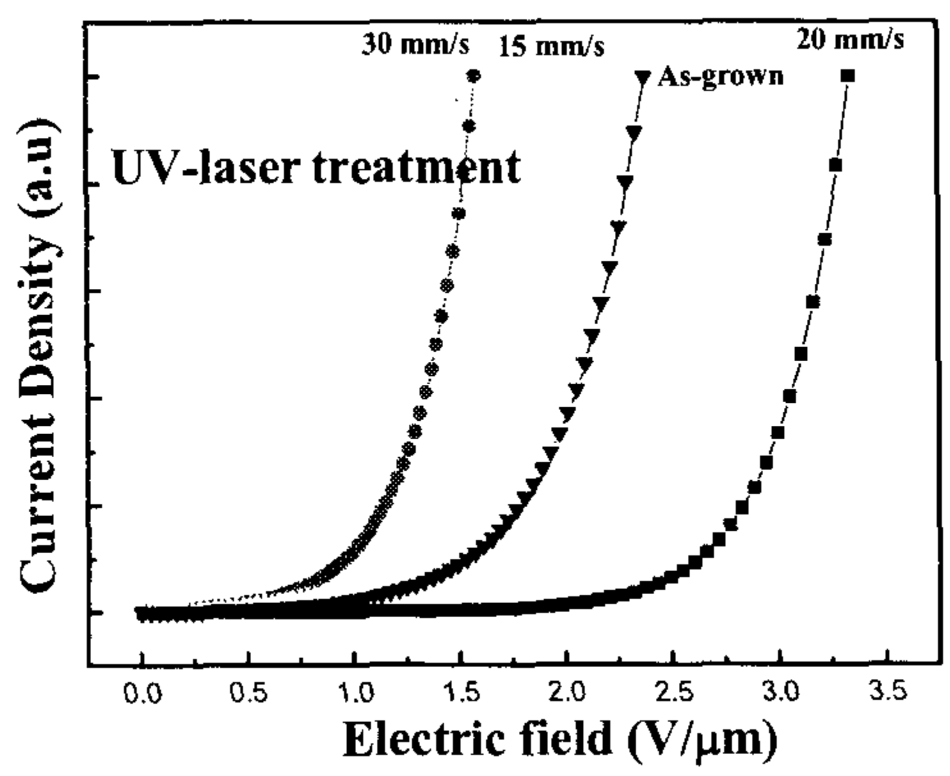

Figure 4 I-V Typical results of emission current density versus electric field for the MWCNTs before and after UV-laser post-treatments.

3. Conclusion

The improvement in the turn-on field and emission current was responsible for the fact that Ar plasma and laser treatments produced open-ended MWCNTs and also generated a uniform inter-tube distance of the MWCNTs by prominent effects on the top surface of the MWCNTs after the optimum plasma and laser exposure [5]. Also these treatments improved structure and field emission properties of MWNTs after post-treatments. These MWNTs would be applied to high power electron emitting devices, in near future

4. Acknowledgements

This work is supported by Samsung Electronics Co., LTD.

5. References

[1] W. A. Deheer, A. Chatelain, D. Ugarte, Science 1995; 270:1179-1180.

[2] E. W. Wong, P. E. Sheehan, C. M. Lieber, Science 1997; 277:1971-1975.

[3] J. S. Kim, K. S. Ahn, C. O. Kim, J. P. Hong, Appl. Phys. Lett. 2003; 82(10):1607-1609.

[4] C. Y. Zhi, X. D. Bai, E. G. Wang, Appl. Phys. Lett. 2002;81(9):1690-2.

[5] L. Türker, Ş. Erkoç, Journal of Molecular structure (Theochem) 2002; 577:131-135.