International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:5, No:2, 2011

Field Emission Properties of Multi-wall Carbon Nanotube Field Emitters using Graphite Tip by Electroporetic Deposition

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***Abstract*—**We fabricated multi-walled carbon nanotube (MCNT) emitters by ~~an~~ electroporetic deposition (EPD) method using a MCNT-sodium dodecyl sulfate (SDS) suspension. MCNT films were prepared on graphite tip using EPD. We observe field emission properties of MCNT film after heat treatment. Consequently, The MCNT film on graphite tip exhibit good electron emission current.

***Keywords*—**Field emission, Multi-wall carbon-nanotube (MCNT), Electrophoretic deposition (EPD)

I. Introduction

THE carbon nanotubes (CNTs) have attracted much interest due to chemical stability, their geometrical field enhancement factor[1], strong mechanical strength [2, 3], thermal [4], and electronic properties [5]. In comparison to the conventional field emitters, CNTs have with low emission threshold fields, large emission current densities and long emitter stability [6].

The most promising methods of carbon nanotube-based cold cathode fabrication are the screen-printing method [7], spray method [8] and electrophoretic deposition (EPD). Compared with other processing methods, EPD offers advantages of low costs, process simplicity and fast, uniformity of deposition, well control of deposit thickness, microstructure homogeneity, and deposition on complex shaped substrates.[9-11]

Recently, a CNT-film has been fabricated through EPD on a metallic electrode [12-14]. However, the main difficulty with this method is the weak adhesion of the MCNT film to the substrate.

In this paper, we describe our fabrication of the MCNT cathodes by an EPD method using a CNT suspension on graphite tip. The advantages of using graphite tip have good conduct electricity, mass produced at low cost.

II. Experimental

The MCNTs used in our study, obtained from Iljin Nanotech CO. Ltd. Korea, were produced by chemical vapor deposition (CVD). The axial dimension of the MCNTs is ~μm; the diameter ranges from 3 to 7 nm. 0.04 g of MCNTs was mixed with 40 ml of deionized water and 0.08 g of sodium dodeyl sulfate (SDS) (Sigma Aldrich). In order to disperse the MCNTs, the mixture was sonicated using a bath-sonic for 15 min and then centrifugation (Vision Scientific, VS-15000N) was carried out at 113.4g (2500 RPM) for 15 min to remove some undispersed MCNTs, and the supernatant was decanted carefully. Then EPD was carried out in the MCNT dispersion to deposit MCNT film onto graphite tip (diameter: 2 mm, length: 40 mm, degree of: 99.999%).

Fig. 1 shows schematic of a MCNT film deposition on the graphite tip by EPD. Two electrodes were maintained at a distance of 2 mm. A constant dc 25 V was applied to the electrode for 3 min, and then, cathode is rinsed in water until bubbles are not generated. This cathode was dried at room temperature for 2 hour and then was heated for 5 min by placing in furnace at 300^{o}C under air.

Field emission properties were measured inside a vacuum chamber with diode-type configuration at a pressure 10^{-6} torr using a high voltage DC power supply. The distance between an anode (304 stainless-steel plate) and the MCNT film on graphite tip was 2 mm. The morphology of the MCNT film cathode was characterized by scanning electron microscopy (SEM, Hitachi S-4300).

III. Results and Discussion

Fig. 2 shows the SEM images, (a) before and (b) after being heated, MCNT film deposited on the graphite tip by EPD. In (a) surface before heat treatment, MCNTs are difficult to find because the impurities thoroughly covered the MWCNT from the SEM image. However, (b) surface after heat treatment are observed that the SDS was removed.

Fig. 3 indicates the Raman spectroscopy of MCNT/SDS film before heat treatment and after heat treatment. The graphite crystal structure of the MWCNTs has a characteristic peak at 1580 cm^{-1} (G band) which indicates a good arrangement of the hexagonal lattice of graphite. The peak at 1320 cm-1 (D band) indicates the level of disorder of the carbon. The G and D modes of MCNTs at about 1580 and 1320 cm-1 are clearly observed from fig. 3. The peak at 1580 cm-1 (G) results from the graphite sheet of MCNT wall, which consists of carbon atoms all arranged in the form of hexagon, while the peak at 1322 cm-1 (D) represents the impurity and the effects of atomic structure in the MCNT sample. The MCNT was evaluated by UV-visible Raman spectroscope, in order to compare the before and after effects of heat treatment. The results show that before heat treatment and after heat treatment, I_d / I_g ratio remains at 0.4. The heat treatment did not change the value. This reflects the MCNT film is not affected by heat treatment at 300^{o}C.

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Fig. 4 shows the field emission characteristics of before heat treatment and after heat treatment. The emission current versus the applied voltage (kV) plot and turn-on field to reach 1μA/cm^2 were 4.0 and 3.4 kV/um, respectively. The emission current was also 0.7 and 2.4 mA at 6 kV, respectively. The turn-on field differed little between the samples. The emission current value increased 2.3 mA in the MCNT film on graphite tip after heat treatment.

Fig. 4 inset presents the Fowler-Nordheim (F-N) plots of samples. The field emission properties also used the F-N model [ln (I/V^2) versus 1/V].

Assuming that the work function of graphene is the same as that of graphite (~ 5eV), the field-enhancement factor (β) of before heat treatment and after heat treatment were determined to be 2875 and 4071 in 6 kV voltage region, respectively, F-N plot which yields a line indicate good agreement with the F-N equation.

Fig. 5.Field emission scanning electron microscope (FESEM) Hitachi-4300 was also used to analyze the surface morphology of the MCNT film. Fig. 5 (a) shows the FESEM images of the MWCNT film deposited on a graphite tip substrate by EPD and after heat treatment.

In order to get the image of the surface, the sample stage of the SEM has been tilted 30^o. Fig. 3 (b) shows the enlarged image of the MWCNT film surface after heat treatment. In Fig. 3 (b), some of MWCNTs are clearly protruding on the surface of the MCNT films after heat treatment. Most of the MCNTs in the film have bonded together. The SDS acts as a bonding material when the film is heating in the furnace.

The heat treatment process removes the SDS completely at 200^{o}C temperature. L. Sicard et al. reported that the alky chain of the surfactant is completely removed below 200^{o}C whereas the sulfate head group is lost in the region between 400^{o}C and 550^{o}C in MCNT-SDS sample.[15] The emission properties enhanced emission current because of removed SDS.

IV. Conclusion

The field emission characteristics of EPD deposited MCNT film on graphite tip using MWCNT/SDS solution were investigated. EPD deposited MCNTs film showed improved the field emission current and β caused by the enhanced adhesion of the MCNT because of the enhanced bonding between MCNT and the protruding morphology on the surface. The MCNT-graphite cathode showed a higher field emission current and better enhance factor than MCNT of before heat treatment.

Acknowledgment

This research was supported by Seoul Metropolitan Government though Seoul research and business development (Grant N. CR070054). This work was supported by the Industrial Core Technology Development Program funded by the Ministry of Knowledge Economy (No. 10037379, Development of Multi X-ray Source and Tomosynthesis System based on Nano Materials).

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Table I Summarized Emission Characteristics Of MCNT Films Formed By EPD And Heat Treatment

Samples	Turn on voltage [μA/cm^2]	β (enhancement factor)	Peak current (mA)
Before heat treatment	4.0	2875	0.7
After heat treatment	3.4	4071	2.4

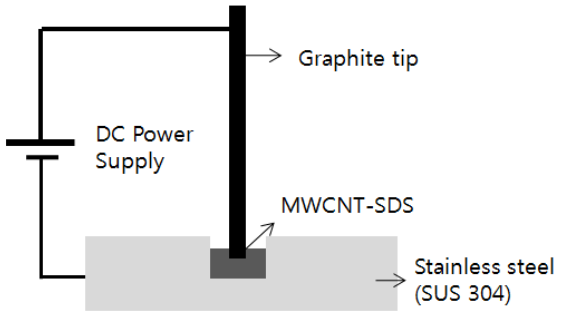

Fig. 1 A schematic of the deposition of an MWCNT film on the graphite tip by electrophoretic deposition

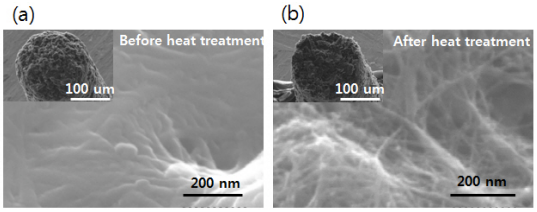

Fig. 2 SEM images of before heat treatment (a), after heat treatment (b)

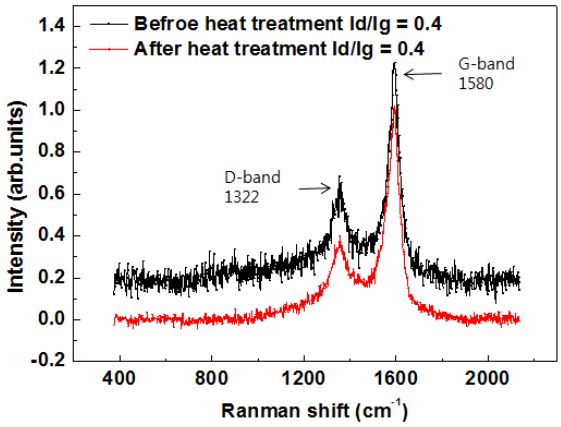

Fig. 3 Raman spectra of the MWCNT-SDS samples before and after heat treatment

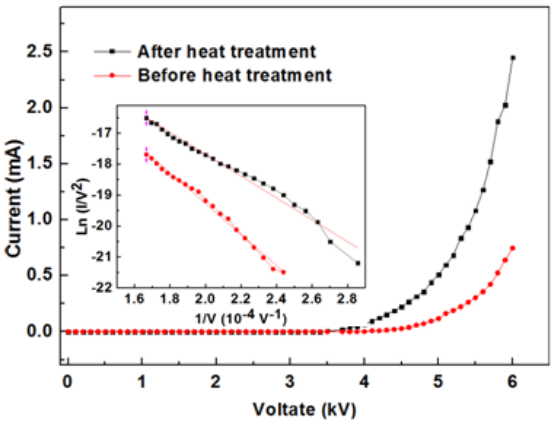

Fig. 4 field-emission current versus the applied voltage for the MWCNT film prepared by our method. The inset shows the Fowler-Nordheim plot as In (I/V^2) versus 1/V

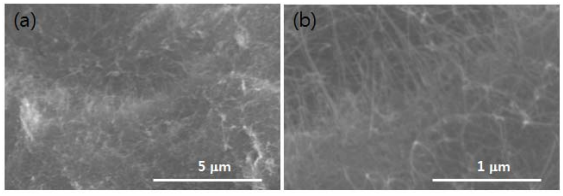

Fig. 5 SEM images of the MCNT film prepared by electrophoretic deposition (EPD) of MCNTs on a graphite tip substrate and heated after emission.