Field emission properties of MWCNT film on graphite tip by electrophoretic deposition

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Abstract

We fabricated Multi-wall carbon nanotube (MWCNT) emitters by an electrophoretic deposition (EPD) method using a MWCNT-sodium dodecyl sulfate (SDS) suspension. MWCNT films were prepared on the graphite tip (CNTs-cathode) and prepated on the Ag-coated graphite tip (Ag-MCNTs cathode) using EPD. The Ag-layer makes low resistance between MWCNT film and graphite tip. The EPD deposited Ag-CNTs cathode was obtained a high emission current, field enhanced factor, and a good stability emission current than pristine MWCNT cathode.

1. Introduction

The most promising methods of carbon nanotube-based cold cathode fabrication are the screen-printing method[1], spray method[2] 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.[3-6]

Recently, a CNT-film has been EPD on a metallic electrode.[7-9] However, the main difficulty with this method is the weak adhesion of the MWCNT film to the substrate.

In this paper, we describe our fabrication of the MWCNT 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 like mechanical pencil and easy treatment.

To overcome adhesion between the CNTs and cathode (graphite tip), we coated Ag-paste layers on cathode. Then, we carry out EPD with coated graphite tip then apply heat treatment[10-11] to make the film adhere strongly to the substrate. The morphology and field emission characteristics of the MWCNT film emitters formed on Ag cathode using the EPD method were investigated.

2. Experimental

The MWCNTs used in our study, obtained from Iljin Nanotech Co. Ltd. Korea, were produced by chemical vapor deposition (CVD). The axial dimension of the MWCNTs is ~ m; the diameter ranges from 3 to 7 nm. 0.04 g of MWCNTs was mixed with 40 ml of de-ionized water and 0.08 g of sodiumdodeyl sulfate (SDS) (Aldrich). In order to disperse the MWCNTs, the mixture was sonicated using a tip-sonic for 25 min and then centrifuging (Vision Scientific, VS-15000N) was carried out at 113.4g (2500 RPM) for 15 min to remove some undissolved MWCNTs, and the supernatant was decanted carefully. Then electrophoresis deposition was carried out in the MWCNT dispersion to deposit MWCNT films onto graphite tip (diameter: 2 mm, length: 40 mm, degree of purity: 99.99%).

Ag-paste layer between graphite tip and MWCNT film is reduced resistance in order to increase emission current and stability. The Ag-paste were made by adding 1.5g Ag particle (Nanoplasma Co. Ltd., size: 800 nm) and 2 ml □-terpineol subsequently, where the viscosity substances include ethyl cellulose (0.05 g). The graphite tip was coated with Ag paste using a paintbrush.

Fig.1 shows schematic of a MWCNT film deposition on the graphite tip by EPD. Two electrodes were maintained at a distance of 2 mm. A constant dc 20 V was applied to the electrode for 3 min, and then, cathode is rinsed in water until bubble is not generated. This cathode was dried at room temperature for 2 hour and then was heated for 5 min by placing in furnace at 300oC 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 CNT film on graphite tip (diameter 2 mm) was 1 mm. The remaining solution of MWCNT-SDS was baked to dry and then was observed with thermogravimetric analysis (TGA). The morphology of the MWCNT film cathode was characterized by scanning electron microscopy (SEM,HitachiS4300).

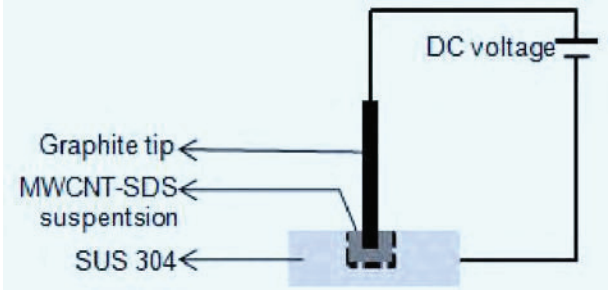

Fig. 1 A schematic of the deposition of an MWCNT film on the graphite tip by electrophoretic deposition.

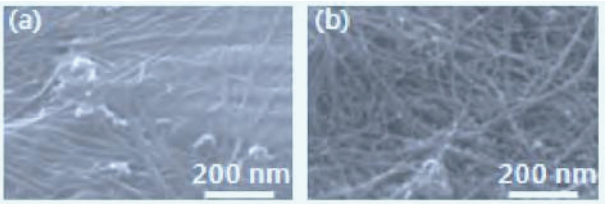

Fig. 2 The SEM images of (a) before heat treatment, (b) after heat treatment.

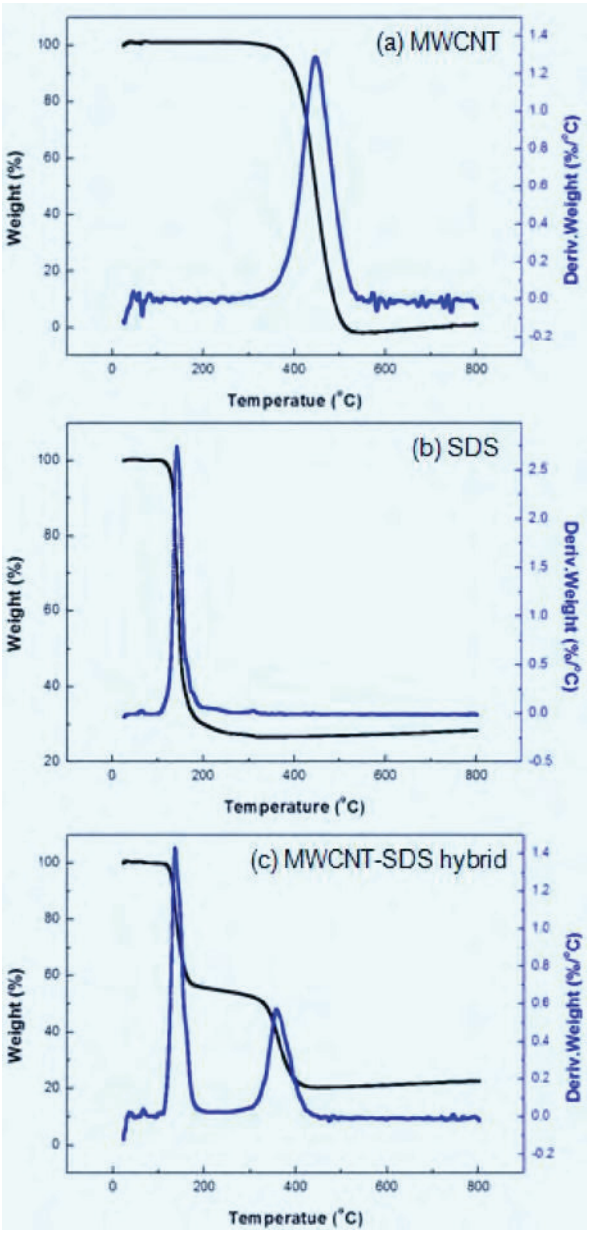

Fig. 3 The TGA profiles obtained with a ramp rate of 5oC min-1 for (a) the MWCNTs, (b) the SDS, and (c) the MWCNT-SDS hybrids; the derivative of the curve is in arbitrary units.

3. Results and discussion

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

Figs. 3a-c show the TGA profiles of the MWCNTs, the SDS, and the MWCNT-SDS films, along with the derivatives of these different curves. The samples start to burn off in air as the temperature is increased (5oC/min). The derivative of the MWCNTs showed a peak at 445oC, which can be attributed to the MWCNTs. The absence of the lower temperature peak (around 350oC) in the MWCNTs confirmed the removal of amorphous carbon owing to the low purity of MWCNTs. The TGA profile of the SDSs showed a slight reduction in weight in the temperature range of 130-200oC. This is weight loss of SDS due to the alky chain of the SDS is completely removed below 200oC12. The remaining residue (30 wt%) may be due to presence of the sulfate. The SDS gave one prominent peak at 190oC which are also seen in the MWCNT-SDS hybrid sample. The TGA also indicates that the MWCNTs at 450oC and MWCNT-SDS hybrid at 380oC.

Fig. 4a show the SEM images of (A) the CNT cathode (B) the Ag-CNTs cathode. The morphology of the film in (B) corresponds to a crater shape. After curing, the surface of the Ag-CNTs cathode was crater shaped. The MWCNT film was deposited at the edge parts of the crater shape because edge part is much high voltage than flat surface. Therefore, the MWCNT horizontally aligned on edge of crater shape.

Fig. 4b shows the field emission characteristics of the CNT cathode and Ag-CNTs cathode after heat treatment. The emission current versus the applied voltage (kV) plot and turn-on field to reach 1□A/cm2 were 1.1 and 1.3 kV/um, respectively. The emission current was also 9.44 and 1.2 mA at 2.0 kV, respectively. The turn-on fields differed little between the samples. The emission current value increased 8.24 mA in the MWCNT film on the Ag-CNTs cathode. Therefore, it is concluded that horizontally aligned CNT films have a good emission current as result of the geometry causing electron emission from the edge of crater shape.

Fig. 4b inset presents the Fowler-Nordheim (F-N) plots of the samples. The field emission properties also used the F-N model (ln (I/V2) versus 1/V). The values in the Ag-CNTs cathode and CNT cathode were determined to be 3902 and 1952 in the low voltage region, respectively. F-N plot which yields a line indicate good agreement with the F-N equation

Fig 4c shows the result of lifetime tests about the Pristine CNTs cathode and Ag-CNTs cathode. Here, the current decay is calculated by (Iinitial – Ifinal)/Iinitial, where Iinitialis the initial emission current and Ifinal is the emission current after 3 hour of measurement. The current of MWCNT film decreased 23.6 percent compared with the initial emission current and the current of Ag-CNTs cathode decreased 15 percent respectively. The electric field applied to measure the emission stability is approximately 4 V/□m. There are two reasons for decline. One is oxidation phenomena of anode (SUS) part. The oxidation phenomenon occurs due to high temperature and heat. After work long hours, anode plate is oxidized with soot. Accordingly, in order to solution of this problem, a good solution is to expand the thickness of anode

and use ceramic behind the anode plate. The ceramic absorbs heat of anode during field emission. The other is likely due to joule heating[13] produced by emission current that flowed through the most outer graphitic layers. Zhong L. Wand et al. reported the degradation of CNT[14]. We reduce the degradation of CNT by using Ag layer to reduce the resistance and enhance adhesion by Ag layer. P. C. Ma reported that Ag at CNT would have a beneficial effect on the electrical conductivity of CNT because the inherent electrical conductivity of Ag is much higher than that of the MWCNTs[15] .

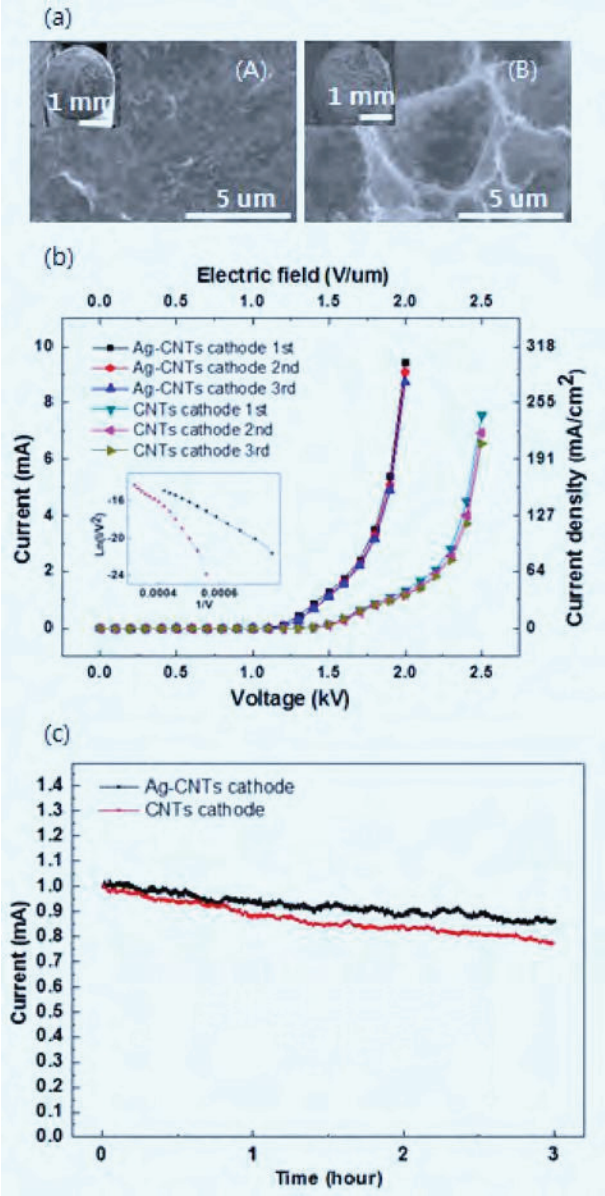

Fig. 4 (a) SEM images of the Pristine CNTs cathode (A) and Ag-CNTs cathode (B). (b) field-emission current versus the applied voltage for the MWCNT film prepared by our method. The inset shows the Fowler-Nordheim plot as In (I/V2) versus 1/V. (c) Emission stability of Ag-CNTs cathode and Pristine CNTs cathode prepared by EPD at same constant electric fields and a vacuum of 10-6 torr at room temperature with 3hour.

4. Conclusions

In summary, the field emission characteristics of EPD deposited Ag-CNTs cathode using MWCNT/SDS solution were investigated. The EPD deposited Ag-CNTs cathode were attributed as improving the field emission current and □ caused by the enhanced adhesion of CNT because Ag can reduce resistance between MWCNT and graphite tip, according to the Ag-CNTs cathode showed enhanced adhesion between the MWCNT and the Ag-particle substrates. The Ag-CNTs cathode showed a higher field emission current and better stability than the Pristine CNTs cathode.

7. Acknowlegements

This research were supported by Seoul Metropolitan Government though Seoul research and business development (Grant N. CR070054).

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