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Field emission properties of carbon nanotube film using a spray method

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Abstract

We fabricated carbon nanotube (CNT) emitters by a spray method using a CNT suspension with ethanol. Indium with a low melting pointing metal or indium tin oxide (ITO) was deposited on the glass substrate. The CNTs were sprayed on these layers and thermally annealed. The sprayed CNTs on an ITO were obtained a high emission current density, field enhancement factor, and a uniform emission pattern than the sprayed CNTs on an ITO layer. We found that the sprayed emitters on the indium layer had good field emission characteristics because of the strong adherence between the metal layer and CNTs.

PACS : 72.80.Rj; 79.70.+q

Keywords: Carbon nanotubes; Spray; Field emission

1. Introduction

One-dimension structures, such as carbon nanotubes (CNTs) are efficient cold field emission sources because of their large geometrical field enhancement factor, strong mechanical strength, and chemical stability. The CNT emitters are made by various methods such as direct growth [1], electrophoresis [2] and screen-printing [3]. The growth of CNTs, using a direct chemical vapor deposition (CVD) method, has had problems with low-throughput, a limited area cold cathode, and a high process temperature. On the contrary, a screen-printing method has advantages such as large area deposition of CNTs and low fabrication cost. However, there is damage of the nanotubes caused by an organic vehicle in the CNT paste during heat treatment (350–450 °C). Electrophoretic deposition using CNT suspension is disadvantageous in terms of the weak adhesion of the CNTs to the substrate and the limited panel size. The spray method to deposit CNTs is a simple process and can be fabricated into a large area cold cathode. However, poor adhesion of CNTs to the substrate is a drawback.

In this paper, we describe our fabrication of the CNT cathodes by a spray method using a CNT suspension without an organic binder. To overcome adhesion between the CNTs and the substrate, we deposited low melting temperature indium layers on a glass substrate using evaporation. The morphology and field emission characteristics of the CNT emitters formed on the indium layer and the indium tin oxide (ITO) coated glass using a spray method were investigated.

2. Experiment

Multiwalled carbon nanotubes (MWCNTs), with diameters that ranged form 3 to 7 nm, using a catalytic CVD, were used (Iljin Nanotech Co. Ltd.). The CNT suspension was dispersed, MWCNTs (10 mg) in an ethanol solution (100 mL), using ultrasonication. For good adhesion between the CNTs and the substrate, the indium metal layer was deposited on glass by E-beam evaporation. The deposition process of the CNT cathode using a spray gun is illustrated in Fig. 1. The CNT suspension was sprayed on the coated indium and the ITO coated glass. To remove the residual ethanol, the sample was dried at 120 °C for 1 h. The deposited CNTs were annealed at 200 °C for 20 min in a N_2 atmosphere. The indium metal (melting point of 156.61 °C) layer was melted resulting in strong adhesion between the CNTs and the glass substrate during the heat

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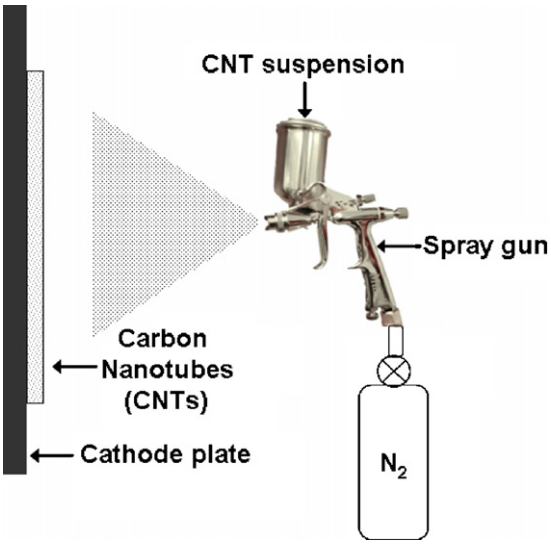

Fig. 1. A schematic diagram of the spray method for deposition of the CNT film.

treatment. The green phosphor was printed on the ITO glass of the anode plate. The distance between the anode and the cathode was 270 μm. The morphology of the MWCNT cathode was characterized by scanning electron microscopy (SEM, Hitachi S-4300). The field emission characteristics were investigated in a vacuum chamber with a pressure of 10^{-6} Torr.

3. Results and discussion

Fig. 2 shows the cross-sectional SEM images of the morphology sprayed CNT film on the indium-coated glass before and after the surface treatment. For the activation of field emission, surface treatment methods are the known laser irradiation, plasma treatment, a liquid polymer method, and mechanical treatment to protrusion of the CNT tips from the surface [4–7]. The vertically aligned CNTs are shown in Fig. 2(b) after a surface treatment using an adhesive taping. A surface treatment process using adhesive tape was adopted for the vertical alignment of CNTs. It was attached tape with a weak adhesion to sprayed CNTs on the substrate, and then adhesive tape was removed from the top part of the CNT film. In comparison to the untreated CNT film in Fig. 2(a), the differences of the morphological characteristics of the CNT film are clearly shown in Fig. 2(b). The emission current density and emission site uniformity were improved as more CNTs were revealed.

Fig. 3 shows the field emission characteristics of the CNT film on indium and the ITO layer cathode after the adhesive taping treatment, respectively. The emission current density (J) versus the applied voltage (V) plot and turn-on field to reach 1 μA/cm^2 were 1.13 and 1.17 V/μm, respectively, as shown in Fig. 3(a). The emission current density was also 2.11 and 1.33 mA/cm^2 at 540 V (2 V/μm), respectively. The turn-on fields differed little between the samples. The J value increased in the CNT film on the indium layer. Fig. 3(b)

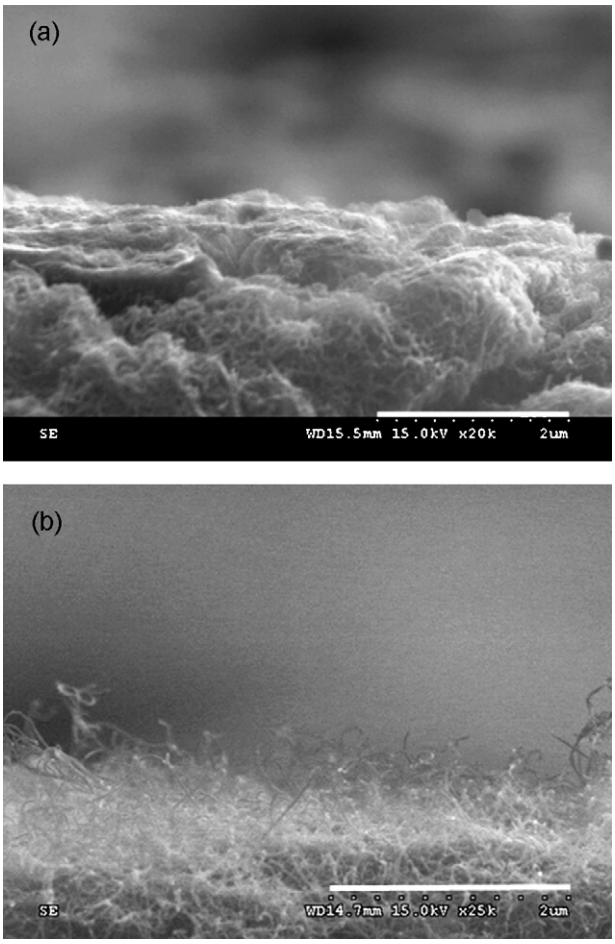

Fig. 2. (a) The tilted SEM images of the sprayed CNT film on indium metal coated glass at 200 °C and (b) the CNT film treated by an adhesive tape.

shows the Fowler–Nordheim (F–N) plots of the samples. The field emission properties also used the F–N model [$\ln(I/V^2)$ versus I/V], which described the electron tunneling though a vacuum under an applied voltage. The field enhancement factor (β) can be calculated from the slopes of the F–N plot under the assumption of a work function of 4.5 eV for the CNTs. The β values in the CNT film on the indium layer and the ITO layer after the adhesive taping treatment were determined to be 5941 and 5802 in the low voltage region, respectively. The β values of the CNT film on the indium layer and the ITO layer were found to be 19378 and 16150 in the high voltage regime, respectively. A wide range of applied voltage, the F–N plot, typical of metallic emitters, was a straight line. However, the plots deviated from the linearity, which were classified as two lines: a low and high voltage region. Deviations from the F–N behavior could be explained as the CNTs protruding from the substrate and gradually flexed to align themselves parallel to the electric field direction [8]. The sprayed CNTs on the indium layer were shown with higher β and J than that on the ITO layer. The β of the CNT film was related to geometrical properties such as emitter alignment and site density. Although the heated CNTs on an indium layer carried out an adhesive taping treatment, J was obtained relatively higher. We believe that the field

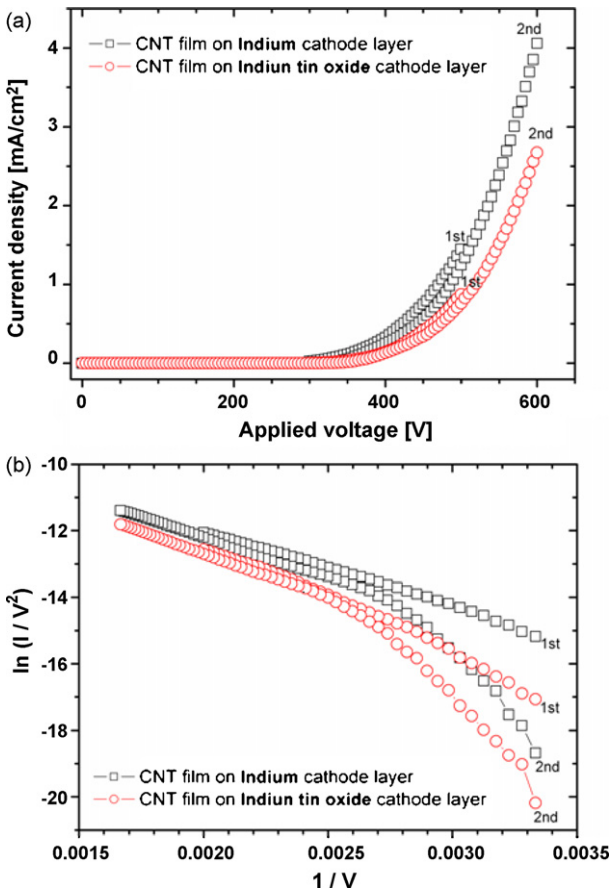

Fig. 3. (a) The J–V curves and (b) F–N plots of the CNT film on indium and the ITO layer after adhesive taping.

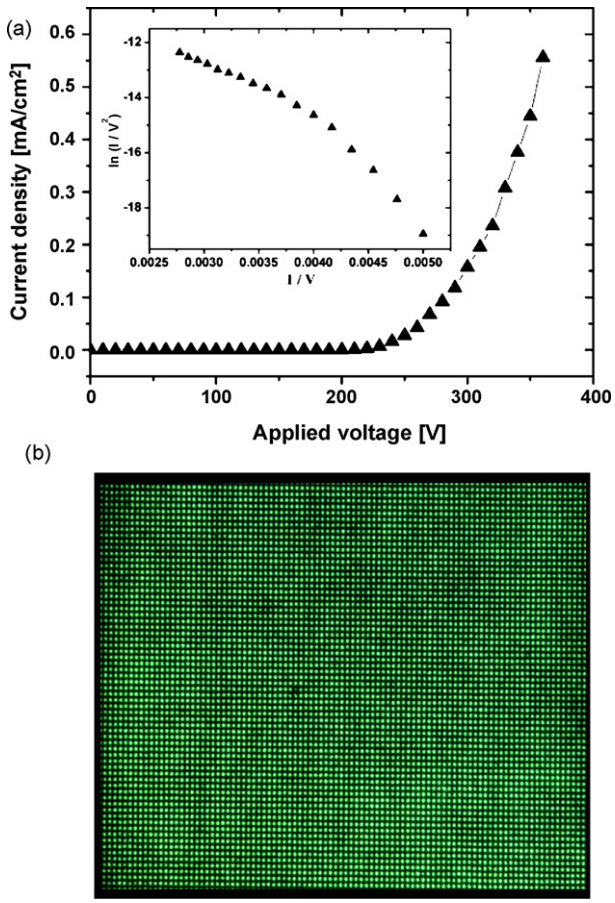

Fig. 4. (a) The J–V curves of the sprayed CNTs on the indium metal layer/ITO glass at 200 °C after adhesive taping and the corresponding F–N plots. (b) A photograph of emission pattern for sprayed CNT emitters with a size of 7 cm × 5 cm.

emission properties improve more than that of the ITO layer because of the interaction between the CNTs and substrate. The benefit of using an indium layer and the spray method is that it could be performed in a low temperature process without thermal damage to the CNTs. This method also has an advantage in that the heat treatment of high temperature to remove the organic binder is not needed because there is no binder containing in the CNT suspension.

Using an indium metal layer on ITO glass, we fabricated an emission pattern size of 7 cm × 5 cm as shown in Fig. 4. The green phosphor printed on the anode and cathode was spaced at 250 μm. The J–V curve is shown in Fig. 4(a); the corresponding F–N plot is given in the insert. The turn-on field was similar to Fig. 3(a) and the total J obtained 0.56 mA/cm^2 at 360 V. The β was 9673 and 24695 in the low and high voltage region, respectively. It was found that the β of the patterned sample (Fig. 4(a)) was much higher than Fig. 3(b) with the indium layer sample. This was the reason why the patterned sample had a much higher emission current density than that of Fig. 3. We believe that the high J originated from geometric field enhancement by a screening effect [9] such as the randomness of spacing between neighboring nanotubes. Fig. 4(a) shows the real emission image of the CNTs formed by spraying. The image was attributed to the uniform, without a hot spot-type in the entire area.

4. Conclusions

In summary, the field emission characteristics of sprayed CNTs on indium or ITO coated glass using a CNT/ethanol solution were investigated. Field emitters made of sprayed CNTs on an indium layer, such as a low temperature melting metal showed enhanced field emission properties compared to spray CNT emitters on an ITO layer. The sprayed CNTs were attributed as improving the field emission current density and β caused by the adhesion between the CNTs and the indium electrode by heat treatment (200 °C). Therefore, we expect that we can use the spray method to fabricate field emitters through a simple process with a flat light source at a large size.

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