

Field Emission Enhancement by Electric Field Activation in Screen-printed Carbon Nanotube Film

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Abstract

By applying a critical field treatment instead of the conventional surface treatments such as soft rubber roller, ion beam irradiation, adhesive taping, and laser irradiation, electron emission properties of screen-printed carbon nanotubes (CNTs) were enhanced and investigated based on the emission current-voltage characteristics through scanning electron microscopy. After nanotube emitters were activated at the applied electric-field of 2.5 V/um, the electron emission current density with good uniform emission sites reached the value of 2.13 mA/cm^2, which is 400 times higher than that of the untreated sample, and the turn-on voltage decreased markedly from 700 to 460 V. In addition, enhancement of the alignment of CNTs to the vertical direction was observed.

Keywords : carbon nanotube, surface treatment, field-emission, screen-printing

1. Introduction

High aspect ratios of carbon nanotubes (CNTs) with thermal conductivity, good chemical stability, and high mechanical strength may have a low threshold voltage and a stable field-emission source in field emission displays (FEDs) [1, 2]. FEDs using CNT emitters have been accomplished by the direct growth of [3, 4] within the submicron-sized gated holes or screen-printing method [4]. In particular, the screen-printing method has been proposed as a promising technology for large area panels and for low cost manufacturing. However, the printed CNT pastes generally have very poor electron emission characteristics due to the lack of alignment of CNTs or random distribution, and possible organic residues. Therefore, various surface treatment methods such as soft rubber roller [5], ion beam irradiation [5], adhesive taping [7], and laser irradiation [8] have been introduced to achieve a high electron emission current and a uniform emission site. The soft rubber roller and adhesive taping techniques are very simple and convenient processing methods for extracting the buried CNTs by removing the surface paste layer. But these techniques may cause detachment of CNTs or destruction of the patterned shape could result from these mechanical surface modification methods [5, 6] and thus still show problems related to nonuniform emission sites.

Recently, it was reported that the CNTs directly grown by chemical vapor deposition (CVD) could be controlled by using a strong electric field which is needed for electron field emission [9]. Through this approach, it may be possible to extract printed CNT emitters protruding in the field direction by higher biasing than the commonly applied voltage without other surface treatments. In this paper, we propose a new surface activation technique to improve field-emission characteristics without detaching CNTs by only applying a critical field after fitting firing condition. So far the surface treatment method by a simple biasing voltage for printed CNT paste has not been reported [5-8].

2. Experiments

In this experiment, double-walled carbon nanotubes (DWNTs) synthesized by thermal CVD were used. The CNTs dispersed in isopropyl alcohol by ultrasonic and were

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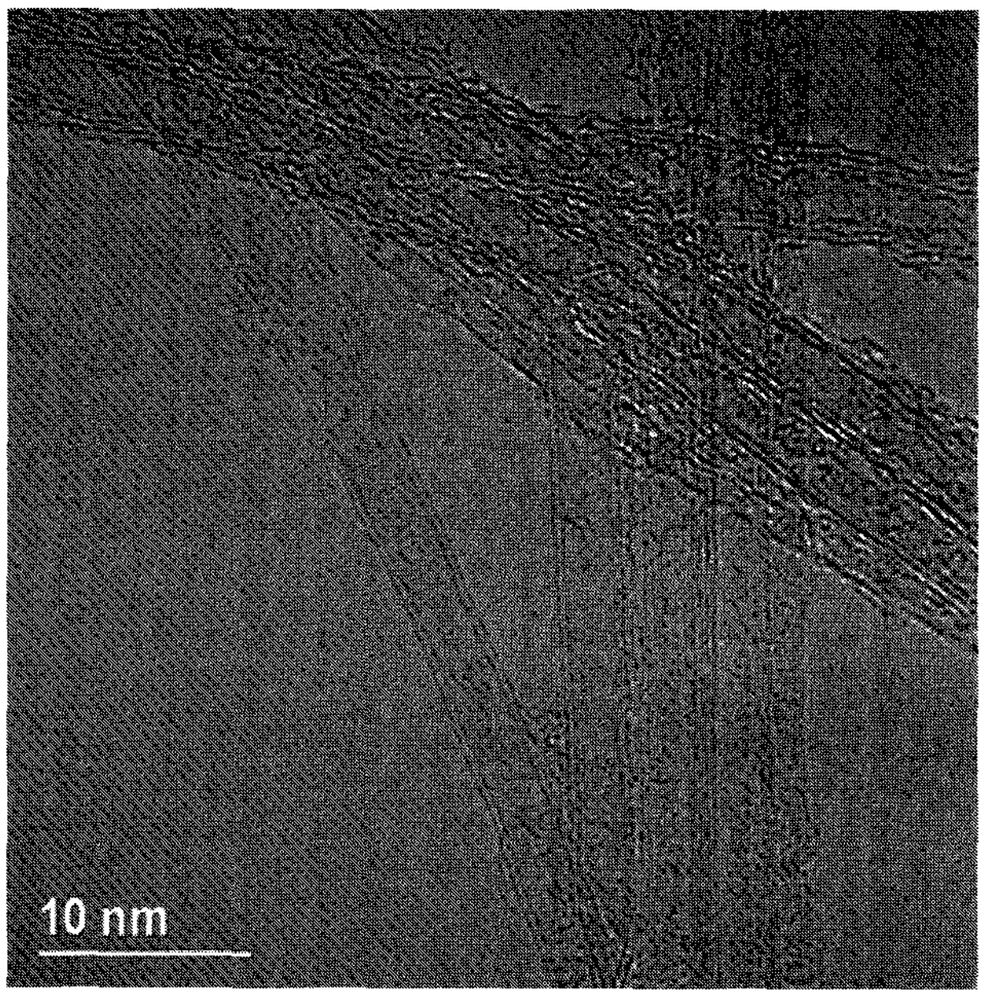

Fig. 1. TEM image of the DWNTs fabricated by thermal CVD deposition method.

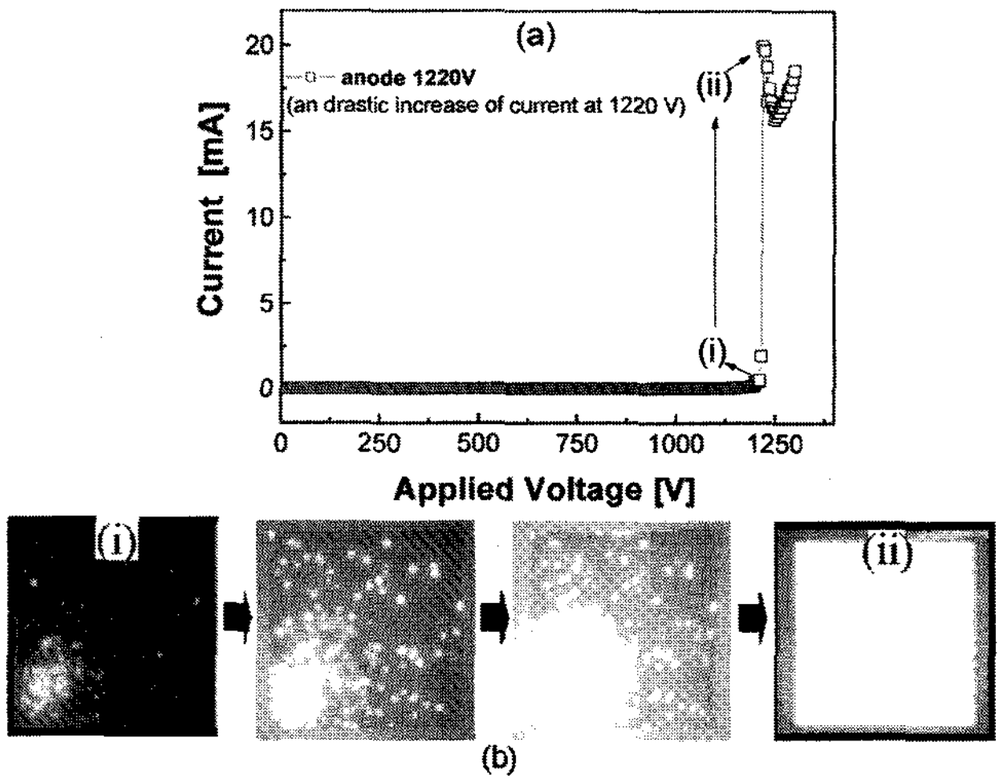

Fig. 2. *I-V* curve and the corresponding emission images of the nanotubes during activation procedure by only the critical bias.

mixed with glass frit, ethylcellulose, and terpineol and then were sufficiently stirred with ultrasonic for about 1h. Fig. 1 shows a high resolution transmission electron microscopy (HRTEM) image of the chemically purified DWNTs with diameter of 3-5 nm. The prepared CNT pastes were printed on an active area of 3 x 3 cm^2 of indium tin oxide (ITO)-coated soda lime glass substrate. Samples were dried at 120 °C for 1h in a conventional oven, and in order to remove the organic binders, They were fired at approximately 380 °C for 20 min under nitrogen ambient, and then naturally cooled down to room temperature. The base suitable sintering process was repeated once more at 380 °C for 20 min.

The field-emission properties of the screen-printed CNT layers were tested in a diode configuration under a vacuum of 5 x 10^{-6} Torr, with anode and cathode being spaced at 400 um. In order to image the electron emission site, we placed phosphor/ITO/glass at the anode side. The surface treatment by the critical electric field was directly performed on one of the specimens. Fig. 2(a) shows a typical emission current (*I*)-applied voltage (*V*) curve measured after surface treatment procedure. To understand the mechanism of the procedures occurring in nanotubes, we monitored systematically the change of emission characteristics as a function of voltage and were able to make the following observations. Firstly, at the relatively high voltage of 1.2 kV (3.05 V/um), the emission sites gradually increased in an edge region as shown in the images of Fig. 2 (b). Secondly, when maintaining the same voltage for a few seconds, the homogeneous emission pattern over the entire site was observed. The remarkable difference in emission current induced by the critical bias field of 3.05 V/um is clearly seen from the figure. The current increased drastically from 0.5 to 20 mA [see continuous parts of (i)-(ii) of Fig. 2(a)]. At the final stage, when the surface treatment process was completed, the stable field emission with the low turn-on voltage was observed.

3. Results and Discussion

By varying the firing temperate of the printed cathode layer, the applied electric field condition for treatment was changed. When the cathode layer was heated for 20 min at 380 °C, the critical bias condition used for the treatment was about 1.7 kV (4.25 V/um) and when one was heated for 40 min at 400 °C, the critical bias condition was 1.8 kV (4.5 V/um). After two fitting sintering cycles for 20 min at 380 °C, the specimen was treated by 1.22 kV (3.05 V/um). It is probable that the change in these applied voltages may be related to various parameters including adhesion of CNTs, the extent of CNTs on the surface, and organic residues remained after firing.

Fig. 3 shows *I-V* characteristics and emission images

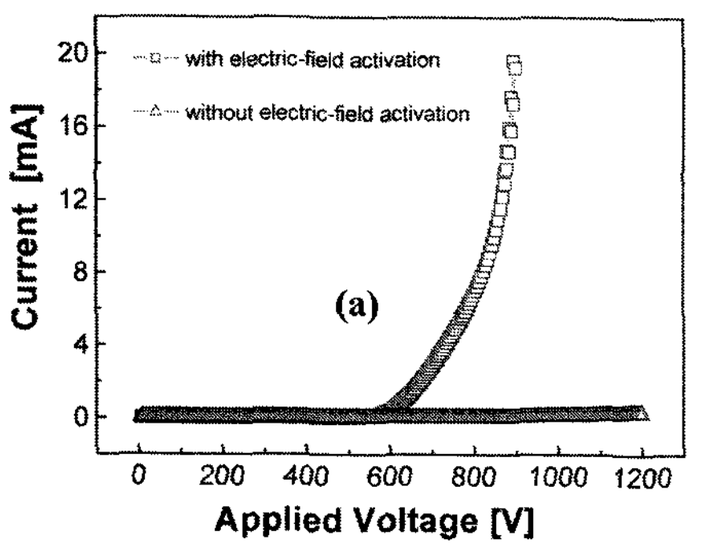

Fig. 3. *I-V* characteristics (a) and emission images (b) for CNT emitters with and without critical field activation.

for the screen-printed CNT emitters before and after surface treatment. Before surface treatment, with the applied voltage of 900 V, the emission current of the sample was 0.047 mA for the first measurement. During repetitious of *I-V* measurements, the emission current was almost the same. However, after treatment by a biasing condition, we can see an enhancement of field emission properties from the *I-V* curves shown in Fig 3(a). The turn-on voltage decreased from 700 V to 460 V and, for the same voltage, the emission current increased from 0.047 to 19.2 mA. As a result, the average emission current was about 400 times higher than that of the untreated sample. Fig. 3(b) shows the typical electron emission pattern of two specimens at the same applied voltage of 900 V (2.5 V/um). The image (i) of Fig. 3(b) was obtained without any surface treatments and with a repetitive applied voltage of 0-1.2 kV. As shown in the figure, only a few emission sites were observed, whereas the image (ii) of Fig. 3(b) was obtained with the critical bias treatment and a very homogenous emission pattern was achieved.

The treated cathode layer had a remarkably enhanced emission image compared with the untreated one. In the case of the untreated specimen, though the cathode emitter was experienced several times repeatedly in the field-emission cycles, the emission sites did not show any trace of the enhancement. This means that the field-emission characteristics can be enhanced by surface treatment under

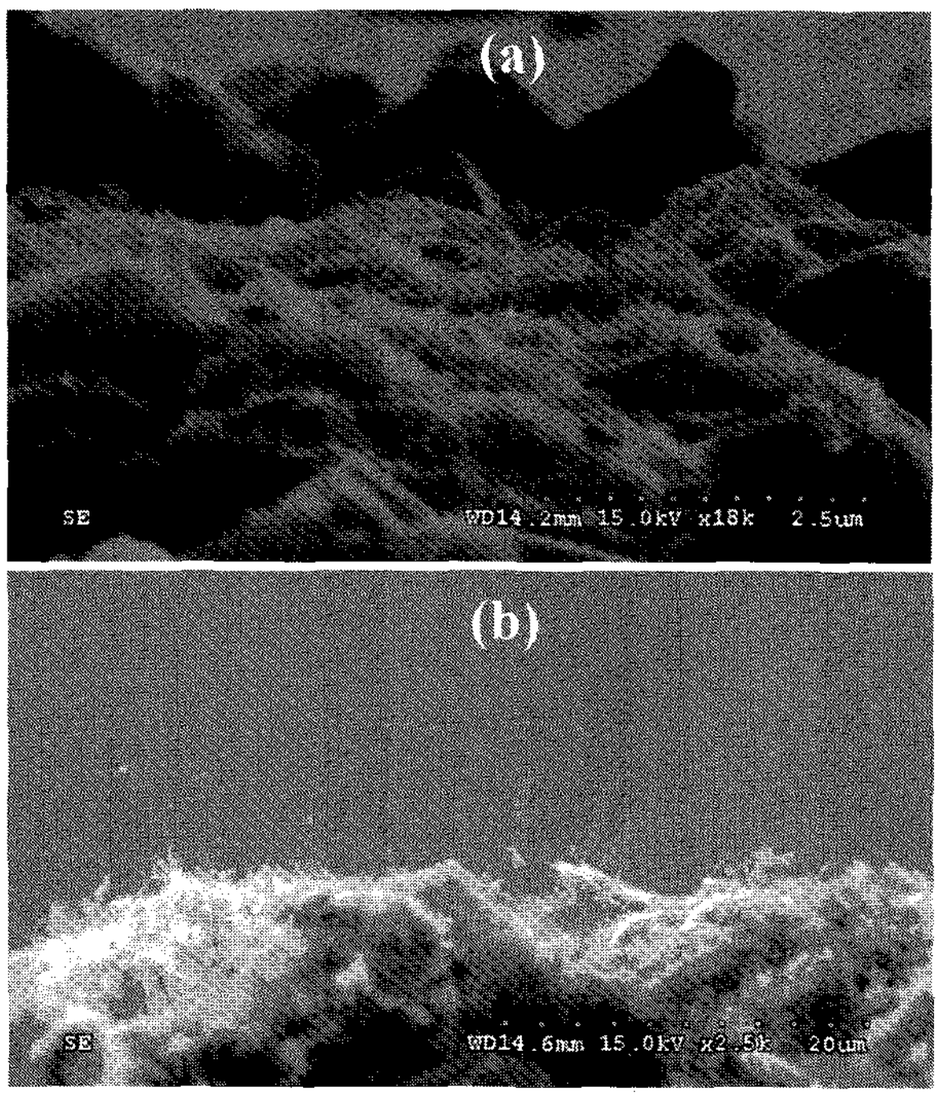

Fig. 4. Cross-sectional SEM images showing the morphological changes of CNT pastes: (a) as-deposited and (b) treated by the critical field.

a critical voltage condition of 1.22 kV (3.05 V/um). As mentioned earlier, this method is completely different from the mechanical surface treatment reported by others, so that no CNTs detachment or destruction of pattern shapes was generated.

The influence of an applied critical field effect on the printed CNTs was investigated thoroughly by using scanning electronic microscopy (SEM). Fig. 4 shows SEM images of the CNT emitters, indicating that the morphologies of the two surfaces are markedly different. This agrees well with the different electron emission characteristics of the two surfaces. As expected, for the sample with low field-emission current, parts of the nanotubes surrounded by organic residues and the entangled CNT bundles did not contribute significantly to field emission as shown in Fig. 4(a). In fact, prior to applying the critical bias for surface treatment, no (or very small) structure change was observed. Therefore, it is evident that degree of protrusion of the CNTs on the surface is influenced by the field condition. The specimen displaying an optimal electron emission pattern shows that the CNTs is well aligned in the vertical direction as shown in Fig. 4(b).

After high emission currents were extracted from the

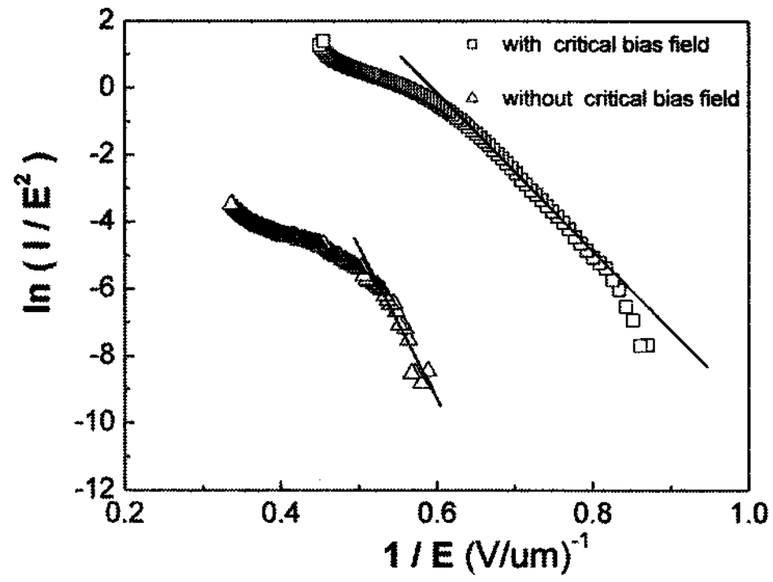

Fig. 5. Fowler- Nordheim (*F-N*) plots for CNT emitters with and without the critical field treatment.

nanotubes during treatment, although electric field was removed from the nanotubes, they were permanently deformed in the direction of the electric field. The improvement in emission characteristics can be explained in terms of surface morphology, especially the extent of protrusion of the CNTs under the critical bias condition.

Fig. 5 shows the Fowler-Nordheim (*F-N*) plots from the *I-V* result for the screen printed CNT emitters before and after surface treatment. The field-emission properties were also analyzed using the *F-N* model, [ln (I/V^2) vs $1/V$]. [10] As seen in this figure, the CNTs show a *F-N* type field-emission behavior in the low-field regime. The local electric field (E_1) can be related to the macroscopic electric field (E_m) by $E_1 = \beta E_m$, where β is the field-enhancement factor. The enhancement factor β can be derived from the slope of the *F-N* plot, under the assumption of a work function of 5 eV for CNTs. The field-enhancement factors of the CNTs with a treated sample and the untreated sample were calculated to be about $\beta = 3142$ and 1558, respectively. The field-enhancement factor of the CNTs with the critical bias is higher than the value of the untreated sample. The difference in β values suggests increase of the perpendicularly well-protruded CNTs by the surface treatment effect of the critical bias.

4. Conclusions

In summary, we have demonstrated that the screen-printed CNTs could be vertically aligned by the critical field without other surface treatments. The alignment of the CNTs by field treatment consequently resulted in a dramatic increase in the field-emission current, improved uniformity of the emission site, and a decrease in the turn-on voltage.

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