Improvement of field emission from printed carbon nanotubes by a critical bias field

H. J. Lee, S. I. Moon, and J. K. Kim
Korea Institute of Science and Technology, Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Korea

Y. D. Lee and S. Nahm
Division of Materials Science and Engineering, Korea University, Anam-dong Seongbuk-gu, Seoul 136-7011, Korea

J. E. Yoo and J. H. Han
Iijin Nanotech Co. Ltd., Seoul 157-810, Korea

Y. H. Lee
Department of Physics, Korea University, Anam-dong Seongbuk-gu, Seoul 136-701, Korea

S. W. Hwang
Department of Electronics and Computer Engineering, Korea University, Anam-dong Seongbuk-gu, Seoul 136-701, Korea

B. K. Ju
Department of Electrical Engineering, Korea University, Anam-dong Seongbuk-gu, Seoul 136-701, Korea

(Received 21 January 2005; accepted 24 May 2005; published online 14 July 2005)

By applying a critical bias field instead of conventional surface treatments, the electron emission properties of screen-printed nanotubes were investigated through scanning electron microscopy and emission current-voltage characteristics. After the surface treatment, at the bias field of 2.5 V/μm, the electron emission current density with good uniform emission sites reached the value of 2.13 mA/cm², which was 400 times higher than that of the untreated sample, and the turn-on voltage decreased markedly from 700 to 460 V. In addition, the enhancement of the alignment of carbon nanotubes to the vertical direction was observed, resulting in an increase in the field-enhancement factor. © 2005 American Institute of Physics. [DOI: 10.1063/1.1953889]

High aspect ratios of carbon nanotubes (CNTs) with thermal conductivity, good chemical stability, and high mechanical strength have a possibility of a low threshold voltage and a stable field-emission source in field-emission displays (FEDs). Recently, it was reported that the CNTs directly grown by chemical vapor deposition (CVD) could be controlled with the assistance of a strong electric field needed for electron field emission. This approach provided a possibility that the printed CNT emitters could be protruded to the field direction by higher biasing than the commonly applied voltage without other surface treatments. In this paper, we have provided a new surface treatment technique to improve the field-emission characteristics without detaching CNTs by only applying a critical bias field. Until now, in the case of printed CNT paste, the surface treatment method by a simple biasing voltage has not been reported.

In this experiment, double-walled carbon nanotubes (DWNTs) synthesized by thermal CVD were used. The prepared CNT pastes were printed on an active area of 3 × 3 cm² of indium tin oxide (ITO)-coated soda lime glass substrate. Two samples were dried at 120 °C for 1 h in a conventional oven and, in order to remove the organic binders, were fired at approximately 380 °C for 20 min under N₂ ambient, and then naturally cooled down to room temperature. The sintering 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 the vacuum of 5 × 10⁻⁶ torr, with the anode and cathode being spaced at 400 μm. In order to image the electron emission site, we placed phosphor/ITO/glass at the anode side. The surface
treatment by a critical electric field was directly performed on one of the specimens. Figure 1(a) shows a typical emission current ($I$)-applied voltage ($V$) curve measured after the 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 observed as follows. Firstly, at a relatively high applied voltage of 1.2 kV (3.05 V $\mu$m$^{-1}$), the emission sites gradually increased in a solid line of an edge region as shown in the image of Fig. 1(b). Secondly, when maintaining the same voltage for a few seconds, the homogeneous emission pattern over the entire site is observable. The remarkable difference in emission current induced by the critical bias field of 3.05 V $\mu$m$^{-1}$ is clearly seen from the figure. The current increases drastically from 0.5 to 20 mA [see encircled parts of (c) and (d) of Fig. 1(a)]. At the final stage, when the surface treatment process was completed, the stable field emission with the low turn-on voltage was observed.

Figure 2 shows the typical electron emission pattern of two specimens at the same applied voltage of 900 V (2.5 V $\mu$m$^{-1}$). The image of Fig. 2(a) was obtained without any surface treatments and with a repetitive applied voltage of 0–1.2 kV. As shown in Fig. 2(a), only a few emission sites were observed, whereas the image of Fig. 2(b) was obtained with a critical bias treatment. 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 by the field-emission cycles, the emission sites did not show any trace of enhancement. Therefore it was proven that the field-emission characteristics can be enhanced as a result of surface treatment by a critical voltage condition of 1.22 kV (3.05 V $\mu$m$^{-1}$). As mentioned earlier, this method is completely different from the mechanical surface treatment reported by others, so that no CNT detachment or destruction of the patterned shape was generated.

The influence of an applied critical field effect on the printed CNTs was investigated microscopically by using scanning electronic microscopy (SEM). Figure 3 shows the SEM images of the CNT emitters, indicating that the morphologies of the two surfaces are markedly different, which agree well with the different electron emission characteristics of the two surfaces. As expected, for the sample with a low field-emission current, as shown in Fig. 3(a), the part of the nanotubes surrounded by organic residues could not contribute significantly to field emission. It is noticeable, in fact, that prior to applying the critical bias for surface treatment, no (or very small) structure change was induced. Therefore it is clear that the particular field conditions could make CNTs protrude on the surface. The specimen displaying an optimal electron emission pattern has the carbon nanotubes well aligned to the vertical direction, as shown in Fig. 3(b). After high emission currents were extracted from the nanotubes during treatment, although the electric field was removed from the nanotubes, they were permanently deformed in the direction of the electric field. We can explain the improvement in emission characteristics in terms of surface morphol-
ogy, especially the extent of protrusion of the CNTs under a critical bias condition.

Figure 4 shows the $I-V$ characteristics and estimates the Fowler-Nordheim (FN) plots from the $I-V$ result for the screen-printed CNT emitters before and after surface treatment. Before the surface treatment, with an applied voltage of 900 V, the emission current of the sample was 0.047 mA for the first measurement. During the repetition of $I-V$ measurements, the emission current was almost the same. After treatment by a biasing condition, the enhancement of field-emission properties is also obvious from the $I-V$ curves shown in Fig. 4(a). The turn-on voltage decreased from 700 V (1.75 V $\mu$m$^{-1}$) to 460 V (1.15 V $\mu$m$^{-1}$) 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 the current of the untreated sample. The field-emission properties were also analyzed using the Fowler-Nordheim model, $\ln(I/V^2)$ vs $1/V$. Figure 4(b) shows the Fowler-Nordheim-type field-emission behavior of the carbon nanotubes in the low-field regime. The local electric field ($E_l$) can be related to the macroscopic electric field ($E_m$) by $E_l = \beta E_m$, where $\beta$ is the field-enhancement factor. The enhancement factor $\beta$ is derived from the slope of the FN plot under the assumption of a work function of 4.5 eV for CNTs. The field-enhancement factor of the carbon nanotubes with the critical bias is higher than the value of an untreated sample. The difference in these $\beta$ values was explained as an increase of perpendicularly well-protruded CNTs by the surface treatment effect of the critical bias.

In summary, we have demonstrated that the printed carbon nanotubes were vertically aligned only by the critical bias field without other surface treatments. Consequently, a drastic increase in the field-emission current, the excellent uniformity of the emission site, and the decrease in the turn-on voltage were obtained.

This work was supported by the Ministry of Commerce, Industry, and Energy of Korea through a Components and Materials Technology Development project.