Improvement of emission reliability of carbon nanotube emitters by electrical conditioning

J.H. Park, S.Y. Jeon, P.S. Alegaonkar, J.B. Yoo *

School of Advanced Materials Science and Engineering and Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon, 440-746, South Korea

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Abstract

We have investigated the effect of electrical aging to improve emission reliability of carbon nanotube (CNT) emitter. The CNT emitters were prepared by the screen-printing of the CNT paste. The electrical aging treatment was carried out in a high vacuum chamber by applying the pulsed dc voltage. The field emission measurements and lifetime tests were performed on the CNT emitters depending on the electrical aging time and current density. After the electrical aging treatment, emission properties of CNT emitter were suppressed but the half lifetime was dramatically improved.

Keywords: Carbon nanotube; Field emission; Reliability; Electrical aging

1. Introduction

Carbon nanotubes (CNTs) have been regarded as a promising cathode material for flat panel displays and vacuum electronic devices [1–5]. The use of CNTs with high field enhancing structures could bring numerous advantages such as low threshold field for emission, high and uniform density of emission sites and low-cost production technology in contrast to the Spindt type micro-tip. To incorporate in real devices, however, the emission characteristics of the CNT paste emitters should be stable at their operational condition over a long period of time. Previously, the stability and reliability of CNT emitters was found to be strongly dependent on the vacuum level and residual gas [6,7]. Gradual degradation and abrupt failure of CNT emitter under the extreme field emission condition have been also reported [8–11]. It is expected that wide band gap materials coating and post-treatments can enhance the environmental stability and reliability of CNT emitter [12,13]. However, these approaches have serious limitations. They need expensive equipment and are not applicable for the CNT emitter with gated structure. In this study, we suggested the electrical aging as a simple way to improve emission reliability of CNT emitters. We have investigated the effective parameters for the electrical aging.

2. Experimental details

Among various technologies, CNT paste has been proposed as a capable technology for large area field emission displays (FED) due to excellent emission properties, low cost, simple process, and mass production [4]. In this study, the CNT emitters were prepared by the screen-printing of the CNT paste. CNT paste was prepared by mixing of CNT powders, organic vehicle and inorganic binder. Generally, single-walled CNTs (SWCNTs) have been studied to obtain low threshold electric field and high emission current density, but abrupt degradation of emission current becomes a serious obstacle for field emission applications. In contrast to SWCNTs, multi-walled CNTs (MWCNTs) have shown better emission reliability, however, a small field enhancement factor attribute low emission current. To overcome these limitations, thin MWCNTs that have intermediate structural properties between SWCNTs and MWCNTs were employed. We have used commercially available thin multiwall carbon nanotubes (CMP-320F, Iljin Naotech, Korea), which were synthesized by the chemical vapor deposition technique. The number of tube walls is between 3 and 6, and the corresponding outer diameter is less than 7 nm.

* Corresponding author.
E-mail address: jbysub@skku.edu (J.B. Yoo).
Spin on glass (SOG, Honeywell Electronic Materials Aucuglass 512B) was used as an inorganic binder instead of conventional glass frit. The SOG is a type of glassy material that has liquid-like properties and can be cured to form layers of glass similar to SiO$_2$.

For uniform film thickness and fine-pitched patterns, we applied a photosensitive CNT paste and photolithography. To form photosensitive organic vehicle, acryl was dissolved in terpineol and mixed with photosensitive additives such as monomers, oligomers and photo initiators.

The mixture of thin MWCNT powders, organic vehicles and inorganic binder was pre-mixed through solder paste softener for 15 min. After this, the three-roll mill process was carried out for mixing and dispersion of CNT powders in organic vehicle. The mechanically well-dispersed thin MWCNT pastes were screen-printed onto an indium tin oxide (ITO) coated glass through a metal mesh and subsequently dried at 90 °C for 15 min in a forced convection oven.

After the backside-ultraviolet (UV) exposure process, CNT paste films were etched out by a spraying process (development) using organic solvents. The CNT paste was simply patterned because of the difference in solubility between UV exposed region and unexposed region. The residue of organic vehicle leads to problems such as out-gassing and arcing during a field emission measurement. Organic materials in paste have to be removed in order to obtain the stable emission characteristics. Therefore, CNT emitters were annealed at a temperature ~450 °C for 10 min in the nitrogen atmosphere.

The field emission characteristics and reliability of the CNT emitters were measured in a high vacuum chamber with a working pressure below 5 × 10$^{-6}$ Torr. The emission area was ~1 × 1 cm$^2$ and the distance between cathode and anode electrodes was maintained at 200 μm.

![Fig. 1. Cross-sectional SEM micrographs for (a) as-prepared, (b) activated and (c) electrically treated (at 300 μA/cm$^2$ for 5 h) CNT emitter cathode layers.](image)

![Fig. 2. The current density and electric field plot of CNT emitters depending on the electrical aging time: (a) un-treated and electrical aging at 300 μA/cm$^2$ for (b) 10 min, (c) 5 h and (d) 20 h. The inset shows the corresponding F–N plots.](image)

![Fig. 3. The current density and time characteristics of CNT emitters depending on the aging time: (a) un-treated and electrical aging at 300 μA/cm$^2$ for (b) 10 min, (c) 5 h and (d) 20 h.](image)
3. Results and discussion

Fig. 1(a) shows the cross sectional field emission scanning electrons microscopy (FESEM) image of the screen-printed CNT emitter after the annealing process. The CNT paste films easily formed a uniform layer. The thickness of CNT film was \(\sim 4.3\ \mu\text{m}\), approximately. It was difficult to observe the protruded CNTs at film surface. As-prepared CNT emitters showed very poor emission characteristics because of insufficient CNT emitter density at the surface. Special surface activation treatment was required for the modification of surface morphology. The buried CNTs on the surface have been protruded by the removal of covered layer, by applying the adhesive tape technique [14]. The surface morphology of protruded CNTs at film surface. As-prepared CNT emitters activation treatment was required for the modification of surface density protruded to the surface was found to be greatly increased.

The activated CNT emitters were transferred to a high vacuum camber for electrical treatment. The electrical aging treatments were carried out by applying a pulsed dc voltage with duty factor of \(1/100\). After electrical aging, the field emission characteristics and reliabilities of CNT emitter depending on electrical aging condition were evaluated without a vacuum break. For these, a pulsed dc voltage with duty factor of \(1/1000\) was used.

To study aging time effect, preferentially, the current density for electrical aging was adjusted to \(300\ \mu\text{A/cm}^2\) and the aging time was varied from \(10\) min to \(20\) h. Fig. 2 shows the current density and electric field characteristics of electrically treated CNT emitters. Fig. 2(a) indicated the un-treated CNT emitter. The turn-on electric field \((E_{\text{on}})\), which was defined as the electric field to obtain a current density of \(10\ \mu\text{A/cm}^2\), was \(2.3\ \text{V/}\mu\text{m}\) and the current density of \(1\ \text{mA/cm}^2\) \((E_{J=1}\ \text{mA})\) was obtained at the applied electric field of \(4.7\ \text{V/}\mu\text{m}\). As increasing of the aging time from \(10\) min to \(20\) h, the \(E_{\text{on}}\) and the \(E_{J=1}\ \text{mA}\) was significantly increased from \(3.2\) to \(4.42\ \text{V/}\mu\text{m}\) and from \(5.1\) to \(6.65\ \text{V/}\mu\text{m}\), respectively.

In order to evaluate the emission reliability, we performed the current density and time characteristics and compared the half-lifetime of CNT emitters depending on the aging time. The half-lifetime is defined as the time required to reduce the magnitude of current density half of its initial value (in our case \(1\ \text{mA/cm}^2\)). Fig. 3 shows the current density variation of CNT emitters as function of time. In case of un-treated sample (Fig. 3(a)), the emission current density was rapidly decreased at the initial stage of the reliability measurement. This current degradation was gradually reduced with degradation rate from \(12\) to \(1.25\ \mu\text{A/cm}^2\) per hour, as time passes. The half-lifetime was \(12.1\ \text{h}\), approximately. After the electrical aging, CNT emitters showed small current degradation rate and longer half-lifetime as contrasted with un-treated one. As increasing of the aging time from \(10\) min to \(20\) h, the half-lifetime of CNT emitters was increased from \(29.9\) to \(149.5\ \text{h}\), approximately. We carried out the FESEM observation for the CNT emitter before and after electrical aging to understand this enhancing behavior. No considerable change has been observed, related to the surface morphology of the un-treated and electrically aged samples, however, the overall height and density of the CNTs protruded on the cathode surface was slightly decreased after the electrical aging, as seen in Fig. 1(c). It means that long CNTs at the film surface were preferentially destructed during the electrical aging. The high emission current (electric field) induced structural degradation and failure of SCWNTs and

<table>
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<tr>
<th>Table 1</th>
<th>The field emission characteristics and factors of CNT emitter depending on electrical aging conditions.</th>
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<tr>
<td></td>
<td>(E_{\text{on}}) (V/(\mu\text{m}))</td>
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<tr>
<td>Un-treated</td>
<td>2.3</td>
</tr>
<tr>
<td>300 (\mu\text{A/cm}^2), 10 min</td>
<td>3.2</td>
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<tr>
<td>300 (\mu\text{A/cm}^2), 5 h</td>
<td>3.5</td>
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<tr>
<td>300 (\mu\text{A/cm}^2), 20 h</td>
<td>4.42</td>
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<tr>
<td>500 (\mu\text{A/cm}^2), 5 h</td>
<td>3.9</td>
</tr>
<tr>
<td>1000 (\mu\text{A/cm}^2), 5 min</td>
<td>4.85</td>
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Fig. 4. The current density and electric field plot of CNT emitters depending on the current density for electrical aging: (a) 300, (b) 500 and (c) 1000 \(\mu\text{A/cm}^2\). The inset shows the corresponding \(F-N\) plots.

Fig. 5. The current density and time characteristics of CNT emitters depending on the aging current: (a) 300, (b) 500 and (c) 1000 \(\mu\text{A/cm}^2\).
MWCNTs during field emission have been reported by the in-situ observation [8–11].

According to the Fowler–Nordheim ($F$–$N$) model [15], moreover, the field enhancement factor ($\beta$), i.e. local field divided by potential, and the emitting area ($A$) of as- and aged CNT emitter were calculated from the slope and the intercept of the $F$–$N$ plots in the inset of Fig. 2. The work function of thin MWCNTs was assumed 5 eV, similar to graphite. The calculated $\beta$ and $A$ values of the CNT emitter depending on electrical aging condition were summarized in Table 1.

As shown in Table 1, the $\beta$ values of electrically aged CNT emitters were much smaller than that of un-treated one and slightly decreased as increasing of aging time. The corresponding $A$ values of CNT emitter before and after aging treatment were dramatically increased from $10^{-17}$ to $10^{-12}$ m$^2$ ranges (without the 20 h aged one). From these results, it is suggested that the increased emitting area is attributed to removal of weak and extremely sharp CNTs from their local positions due to resistive heating of the individual tube which provide instability during the electrical aging, resulting in the improvement of half-lifetime [11,16].

The effects of current density for electrical aging also investigated. Current density was varied from 300 to 1000 $\mu$A/cm$^2$ by controlling the applied electric field and the aging time was maintained 5 h. Fig. 4 shows the current density and electric field characteristics of the CNT emitters depending on the aging current. The details of the field emission properties and factors of CNT emitters were also presented in Table 1. The $E_{\infty}$ and the $E_Jm$–$V$ were increased from 3.5 to 4.85 and from 5.5 to 6.9 V/μm, respectively. The $\beta$ values, calculated from the $F$–$N$ plots in the inset of Fig. 5, were decreased with the current density increase. But the corresponding $A$ values were $10^{-12}$ m$^2$ ranges, similar to previous results. As increase in current density for the electrical aging, the emission properties of CNT emitter were suppressed but the half-life was significantly improved. Fig. 5 indicated the current density variation of CNT emitters as function of time depending on the aging current. As increasing of the aging current density, the half-lifetime of CNT emitters was increased from 68.9 to 137.8 h, approximately. These results show that the current density also an important parameter of the electrical aging as well as aging time and the higher current density can effectively reduce the aging treatment time.

4. Conclusions

The field emission measurements and reliability tests were performed on the CNT emitters to evaluate the electrical aging effects. After the electrical aging treatment, emission properties of CNT emitter were suppressed but the half lifetime was dramatically improved. The improvement of emission reliability is attributed to the removal of relatively weak CNT emitters caused by resistive heating during the electrical aging at a high voltage. We expect that the CNT emitters can show much longer lifetime if the electrical aging conditions will be optimized.

Acknowledgements

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