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A Novel Carbon Nanotube FED Structure and UV-Ozone Treatment

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Abstract

A 10″ carbon nanotube field emission display device was fabricated with a novel structure with a hopping electron spacer (HES) by screen printing technique. HES plays a role of preventing the broadening of electron beams emitted from carbon nanotubes without electrical discharge during operation. The structure of the novel tetrode is composed of carbon nanotube emitters on a cathode electrode, a gate electrode, an extracting electrode coated on the top side of a HES, and an anode. HES contains funnel-shaped holes of which the inner surfaces are coated with MgO. Electrons extracted through the gate are collected inside the funnel-shaped holes. They hop along the hole surface to the top extracting electrode. In this study the effects of the addition of HES on emission characteristics of field emission display were investigated. An active ozone treatment for the complete removal of residues of organic binders in the emitter devices was applied to the field emission display panel as a post-treatment.

Keywords : carbon nanotubes, field emission display, screen printing, hopping electron spacer, UV-ozone cleaning

1. Introduction

Flat panel display devices have been significantly developed to overcome the bulky and heavy cathode ray tube (CRT) display [1-3]. Among them, the field emission display (FED) device is very similar to CRT in principle, and many developers have shown significant interests in FED devices due to its superior image quality as in CRT. Recently, carbon nanotubes (CNTs) have been regarded as a good candidate as field emitter materials for the application of FED because CNTs have sharp tips and then can easily emit electrons even at low voltage [4-5]. The screen printing method is mostly employed by major worldwide companies for the fabrication of a large FED panel using CNTs, because of its large scalability at low cost and through a simple process [6-7].

However, the pixel image is non-uniform since it is formed by the point emissions from CNTs instead of area emission. High anode voltage (about over 5 kV at the gate-anode distance of 1 mm) can directly turn on the electron emission from CNTs even without gate voltage, unless some kinds of shield from electrical field are applied to CNT emitters. It makes the gate control (i.e. emission or brightness control) difficult.

The CNT paste for screen printing technique is prepared by mixing organic binder and inorganic powders such as glass frits, indium tin oxide (ITO), CNTs, etc. This paste should be burned out after printing to remove organic vehicles, because organic residues are the source of contamination during electron emissions, degrading the emission characteristics of CNTs. Normally, burning-out is not enough to completely remove organic residues and thus other post-treatments are needed.

In this study, a hopping electron spacer (HES) was employed to collect the scattered electron beams from many CNT sources to ensure good uniformity and to shield CNTs emitters from high anode voltage. These FED panels using CNTs were fabricated by screen printing and were characterized for different processing conditions such as additives in CNT pastes and different kinds of CNTs. The effects of ultraviolet (UV)-ozone gas for the complete removal of organic residues on the emission characteristics of CNT emitters were investigated.

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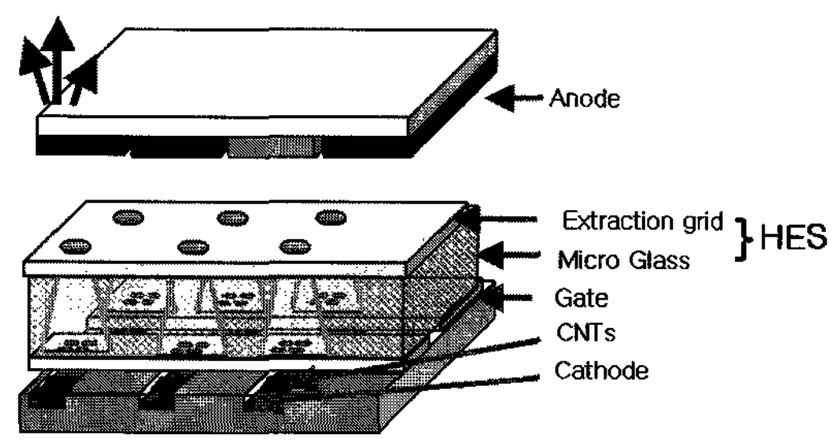
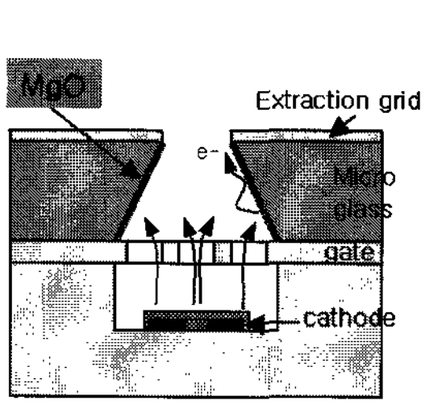
2. Experiments

Fig. 1 shows the schematic view of CNT field emitters having a tetrode structure. 10″ panels (152 gate lines × 27 cathode lines) were fabricated and the emission characteristics of the panels were investigated in a vacuum chamber at a pressure of ~10^{-8} Torr. A novel tetrode FED panel consists of a cathode electrode which includes CNT field emitters, a gate electrode, an extracting electrode coated on top side of a HES, and an anode electrode as shown in Figs. 1(a) and 1(b). Note that a borosilicate substrate glass plate is periodically grooved (depth: 40 μm) by the photolithographic and etching technique. An advantage of this method is that it keeps a constant and uniform distance of cathode-gate electrode. In this study, CNT emitters as well as Ag cathode electrodes were screen-printed inside the grooves and then dried and fired at 150 °C for 20 min and 400-500 °C for 60 min, respectively. Each cathode electrode consists of two lines and CNTs were printed on the cathode electrode as dots as shown in Fig. 1(c). Gate sheet metal electrodes having 9 holes/subpixel were placed on the grooved glass plate at the cathode-gate distance of 40 μm and gate-anode distance of 2900 μm. The gate holes were well-aligned to CNT dots. The reason for the 2 cathode lines and 9 gate holes is that the more edge lines there are, the larger the electrical field on the edge and the more emission of electrons.



(a)



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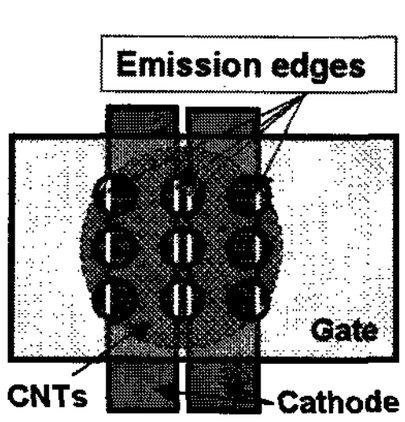
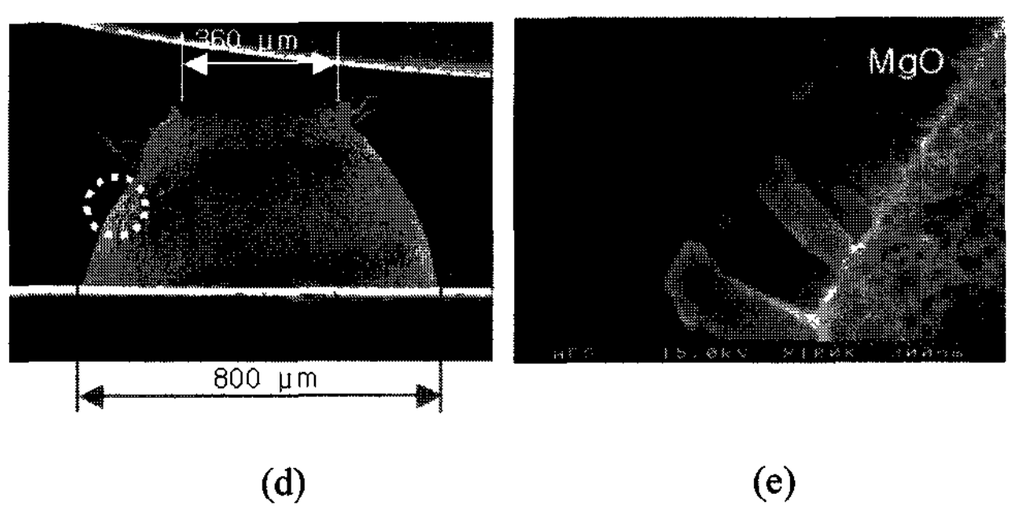


(c)



(d) (e)

Fig. 1. Schematic view of a novel FED structure.
(a) 3-D view, (b) cross-sectional view, (c) design geometry of gate and cathode, (d) cross-sectional image of HES, and (e) magnified view of circle in (d).

HES, an insulating plate with an extraction electrode, was placed over the gate sheet electrode. The top of HES was coated with a conductive metal film as an extraction electrode for extracting electrons coming through gate holes. HES contains funnel-shaped holes whose inner surfaces are coated with MgO as shown in Figs. 1(d) and 1(e). The MgO material was adjusted to make its secondary electron yield value unity [6, 8]. When a surface material of funnel-shaped holes collides with electrons coming through gate holes with a certain energy, the surface material having larger or smaller secondary electron yield value than unity will produce or consume more electrons, making the hole surface electropositive or electronegative, respectively. The continuous accumulation of charge on the surface induces discharge, i.e. causes operation failure. This accumulation at a charge can be prevented by using a material with secondary yield value of unity. Electrons extracted through gate holes are collected inside the funnel holes of HES and hop along the hole surface to the top extracting electrode. Through this HES structure, more electrons can be collected and evenly distributed in each subpixel.

The CNT pastes for screen printing were formulated with 0.4-1.0 wt% of CNTs (multi-walled carbon nanotubes (MWNTs) or single-walled carbon nanotubes (SWNTs)) and 0-1 wt% of frit glass powders in an ethyl cellulose-terpineol binder.

After Oxygen was introduced into a chamber and irradiated by UV using a mercury vapor lamp (λ=185 & 256 nm) to form reactive ozone and atomic oxygen, making organic residues or amorphous carbons in CNTs volatile hydrocarbon gases [9]. The UV treatment was applied to FED panels for 0-30 min to completely remove the residues

of organic binders in the emitter devices, and the physical property of CNTs was investigated as a function of UV exposure time using Raman spectra.

3. Results and Discussion

For the better and more uniform emission of FED panels, an electrical aging treatment (anode aging and gate aging) was applied. Anode voltage was increased to 2.4 kV at a rate of 400 V/hr and kept at 2.4 kV for 18 hrs with no voltage to gate electrode. Gate voltage was also applied up to 240 V at a rate of 5 V/hr with a pulse mode of 1 Hz and duty of 20 %. Current-voltage (I-V) characteristics of FED panel were measured with sweep of gate voltage from 0 to ~200 V at a rate of 5 V/sec and an anode voltage of 2 kV.

Fig. 2 shows I-V curves of 10" FED panels with and without an addition of frit glass powders in CNTs. With an addition of frits, the turn-on field was increased from 3.3 to 4.2 V/μm^2 and the emission current density was decreased from 436 to 117 μA/cm^2 at 5 V/μm. Here, the turn-on field for the electron emission from CNTs is defined as the electric field (V/μm) acquiring the current density of 10 μA/cm^2. Although the addition of frits to CNTs enhances the adhesiveness of CNT powders to cathode electrode, the emission characteristics of the panels worsened due to increase in resistivity of emitters. The emission images of the 10" FED triode panels with and without frit addition are shown in Fig. 3.

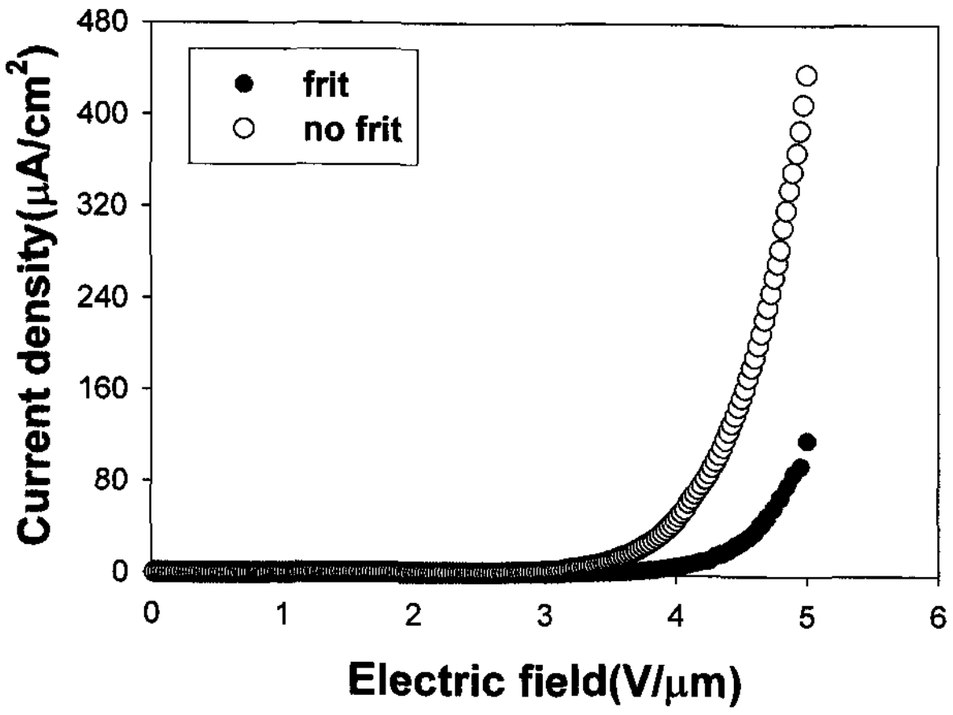
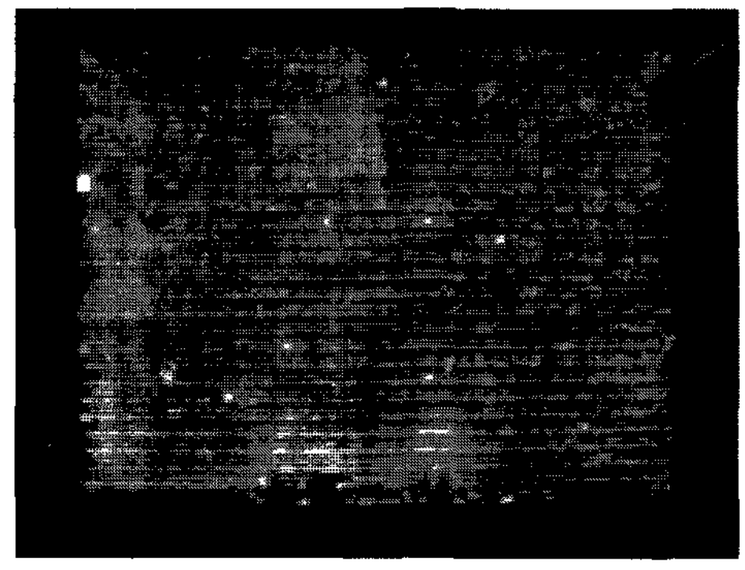
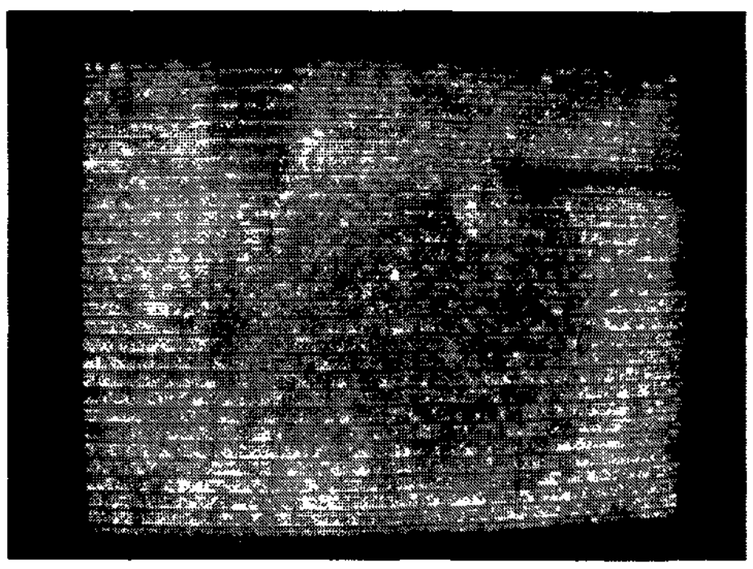


Fig. 2. I-V curves of 10" FED triode panels with and without frit (0.4 wt%) additions (0.8 wt% SWNT in ethyl cellulose-terpineol binder).



(a)



(b)

Fig. 3. Emission images of 10"FED triode panels (a) with or (b) without frit (0.4 wt%) addition.

To prevent the broadening of electron beams from CNT emitters and to collect electrons without loss, the HES with funnel-shaped holes was placed immediately above the gate holes. The gate, anode, and HES currents were measured as a function of gate voltage at different HES voltages as shown in Fig. 4 and Table 1. The inset in Fig. 4 shows a magnified image of the I-V curve. The emission efficiency of this tetrode structure was found to be around 12-14 %, depending upon the HES voltage. As HES voltage increased, more electrons were extracted from the gate. It is noteworthy that although HES current was negligibly small, it was interestingly negative contrary to our expectation. It is possible that the MgO coated inside HES holes may have a secondary electron yield value slightly larger than unity. Therefore, when electrons emitted from CNTs collide with MgO, it produces secondary electrons, causing the MgO surface to remain electropositive (Fig. 5). The top electrode of HES might supply electrons back along the MgO surface for the charge

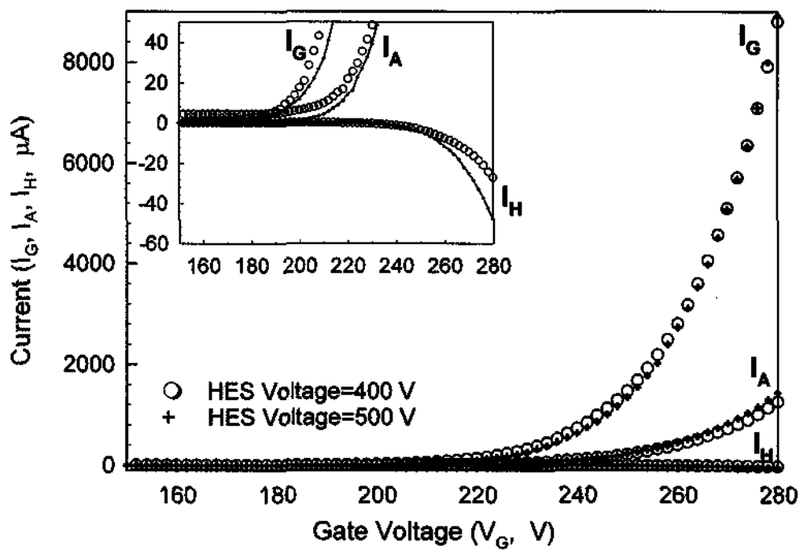


Fig. 4. I-V curves of a FED tetrode panel depending upon the HES voltage (0.4 wt% SWNT in ethyl cellulose terpineol binder, no frit)(The inset is the magnified scale).

Table 1. Electrode current data as a function of HES voltage

Gate Voltage=280 V	HES Voltage	
	400 V	500 V
Gate Current, I_G	8,796 μA (87.8 %)	8,917 μA (86.5 %)
Anode Current, I_A	1,258 μA (12.5 %)	1,437 μA (13.9 %)
HES Current, I_H	-27 μA	-45 μA
Total Current	10,028 μA	10,306 μA

( ) : efficiency

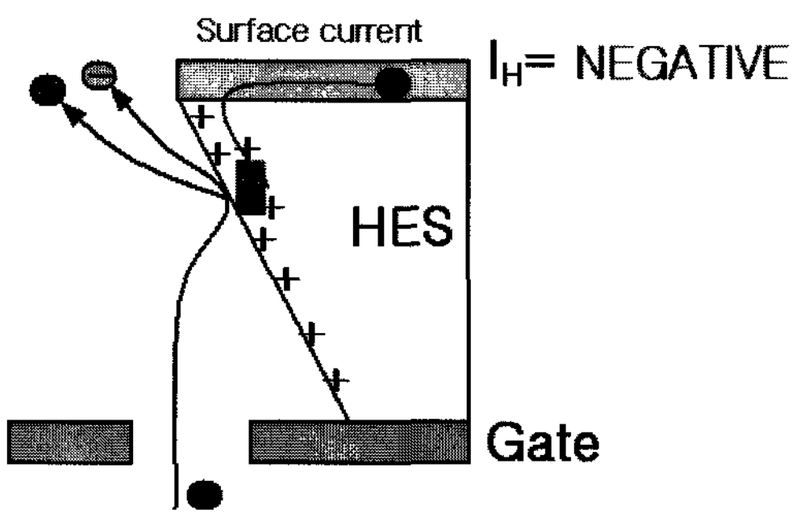
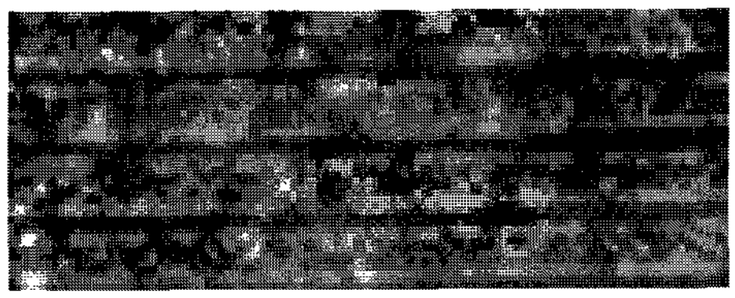


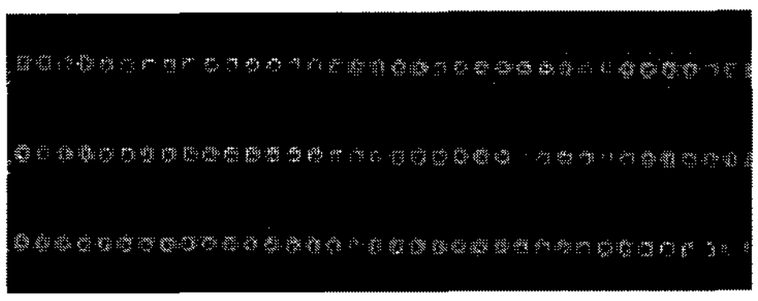
Fig. 5. Expected model for the negative current of extraction electrode in HES.

neutralization. This is still a matter that need to be clarified.

Fig. 6 shows the emission images of cathode lines with and without HES. In case where HES was not used [Fig. 6(a)], it was difficult to distinguish emission images between each subpixel. They showed blurry images. When HES was used [Fig. 6(b)], the broadened electron beams were successfully focused and each subpixel was clearly defined.

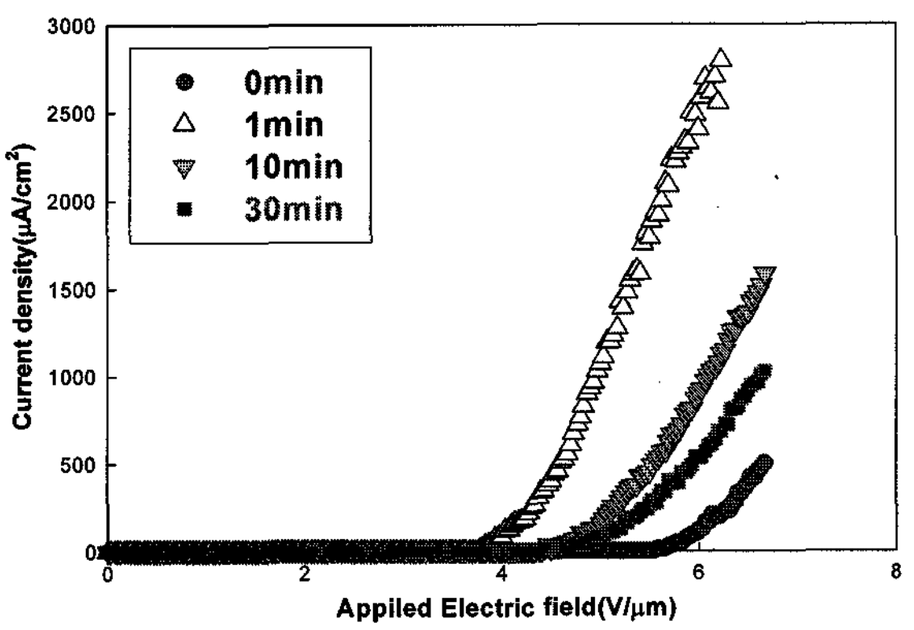


(a)

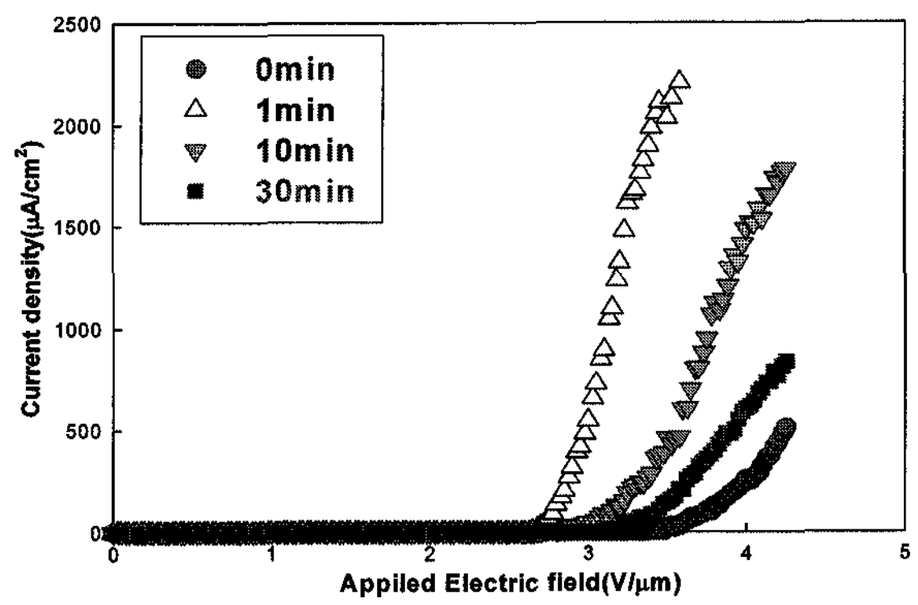


(b)

Fig. 6. Emission images of cathode lines in FED tetrode panel (a) without and (b) with HES (0.4 wt% SWNT in ethyl cellulose-terpineol binder, no frit).



(a)



(b)

Fig. 7. I-V curves of (a) MWNTs (2 wt% MWNT ethyl-cellulose + terpineol binder, no frit) and (b) SWNTs (0.4 wt% SWNT in ethyl-cellulose + terpineol binder, no frit) for different ozone treatment time.

As CNT paste for the screen printing is used, it is quite difficult to remove organic binder residues from CNT paste by simply firing at 400 °C. Therefore, the UV-ozone treatment on both SWNTs and MWNTs was tried for 0-30 min after burning-out of CNT pastes to remove residual contaminants. As shown in Fig. 7, the ozone treatment effectively improved the emission characteristics of CNTs compared to the non-treated CNTs. When the ozone treatment was continued for 1 min, the emission characteristics of CNTs were found to be significantly improved. However, the further increase in treatment time over 1 min decreased electron emission. From the scanning electron microscope (SEM) images for CNTs as a function of ozone treatment time (Fig. 8), little difference in images of MWNTs was observed. MWNTs are, in general, known to be chemically-strong compared to SWNTs because MWNTs have several layers of carbons. In contrast, SWNTs were severely damaged when ozone treatment was continued for 30 min [Fig. 8(f)].

Fig. 9 shows the Raman spectra of MWNTs as a function of ozone treatment time. Among these Raman spectra, "MWNT (as-received)" is CVD-grown original carbon nanotubes and "MWNT (0min)" indicates the screen-printed/burned-out carbon nanotubes without any UV-ozone treatments. In our study there were D- and G-peaks in Raman spectra ranging from 1337-1359 cm^{-1} and 1575-1596 cm^{-1}, respectively, depending upon ozone treatment time. In order to observe the change in crystallinity of CNTs as a function of ozone treatment time, the integrated intensity ratio of D-peak to G-peak (I_D/I_G) was calculated (Fig. 10) from Raman peaks in Fig. 9 where

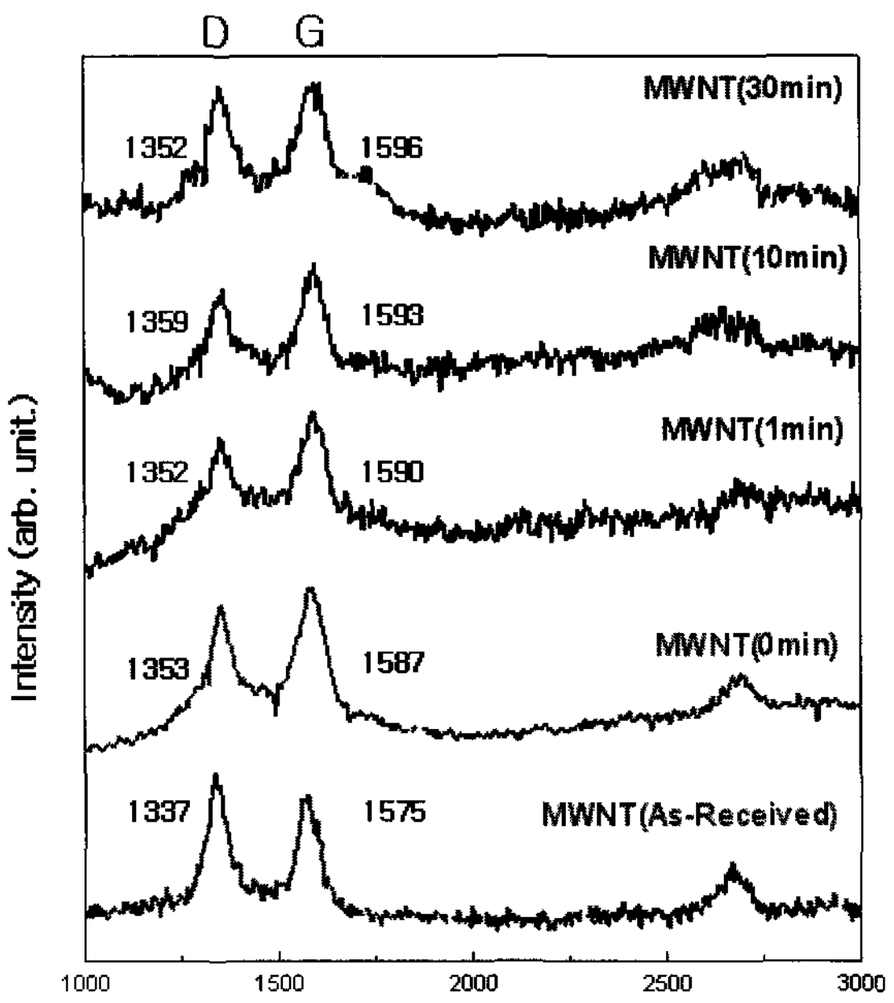


Fig. 9. Raman Spectra of MWNTs (2 wt% MWNT ethyl-cellulose + terpineol binder, no frit) for different ozone treatment time (as-received : CVD-grown CNTs, 0 min: screen-printed and burned-out CNTs with no UV treatment).

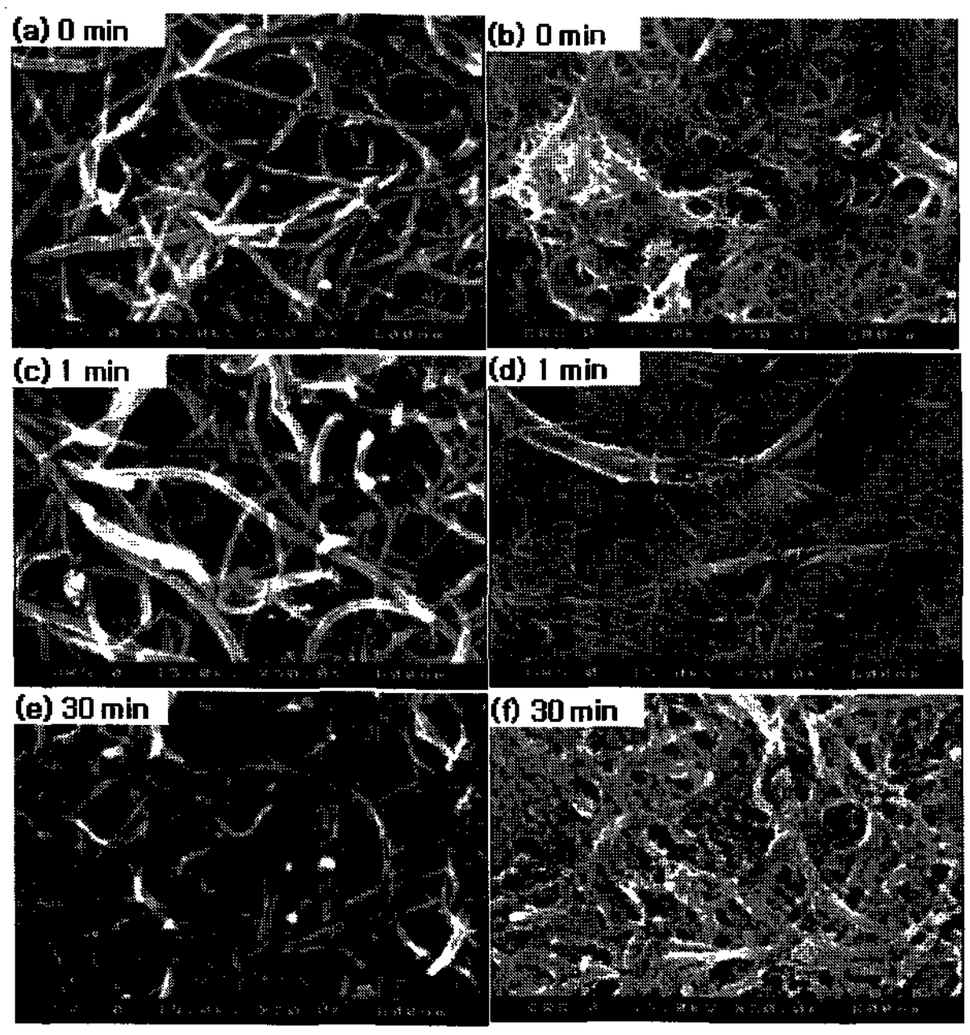


Fig. 8. SEM images of MWNTs (2 wt% MWNT ethyl-cellulose + terpineol binder, no frit) and SWNTs (0.4 wt% SWNT in ethyl-cellulose + terpineol binder, no frit) with ozone treatment time of 0 min (a, b), 1 min (c, d), and 30 min (e, f), respectively.

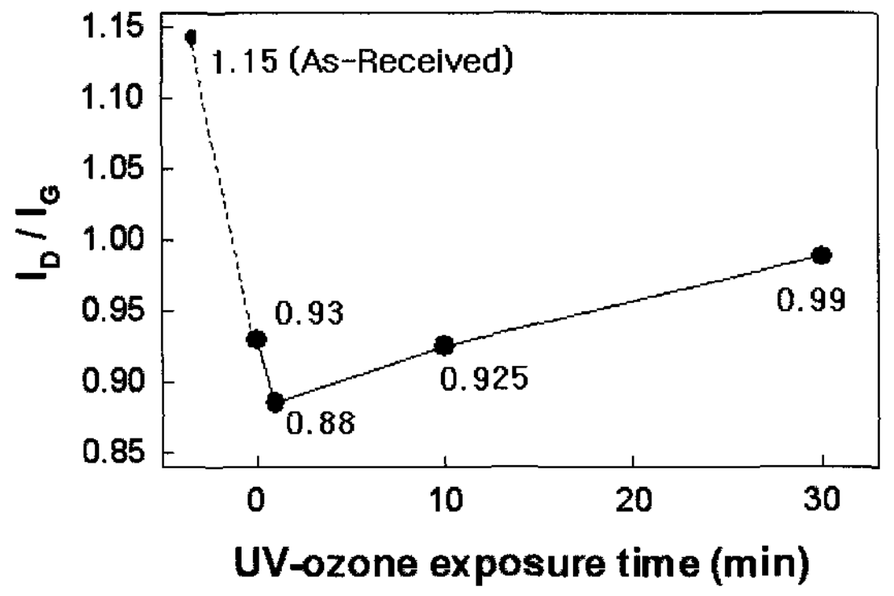


Fig. 10. Integrated intensity ratio of I_D/I_G in Raman spectra of MWNTs (2 wt% MWNT ethyl-cellulose + terpineol binder, no frit) for different ozone treatment time.

D-peak means that there are amorphous carbons or carbonaceous impurities, and G-peak indicates the crystallinity of graphite. From Fig. 10, it matches well the emission characteristics in Fig. 7(a). After the ozone treatment is run for 1 minute, the intensity ratio of I_D/I_G reached a minimum, which means that carbonaceous impurities such as organic residues and defects inside CNTs were substantially removed. Further ozone treatment damaged the crystallinity of CNTs. This shows that a short ozone treatment of not longer than 1 min is better for the emission characteristics of the panels.

4. Conclusion

In this study, we successfully fabricated of a 10" FED panel using CNTs. Applying the HES structure to the conventional FED triode to collect and focus the emitted electrons from CNTs showed to improve the emission characteristics of FED. Furthermore, a short ozone treatment time of not more than 1 min on a FED panel helped to remove contaminants of the CNT surface, leading to better emission results.

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