Carbon-Nanotubes for Full-Color Field-Emission Displays

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A 4.5-inch fully sealed carbon-nanotube field-emission display with a 200-μm narrow gap was fabricated on glass using paste squeezing and surface rubbing techniques. The fabricated displays were fully scalable at low temperatures below 415°C and showed very high luminance of 1800 cd/m² at 4 V/μm. The degradation of emission currents for single-wall carbon nanotubes was less than 10% in electrical aging tests. Large field-enhancement factors and low turn-on voltages (1.5–3 V/μm) were attributed to well-aligned carbon nanotubes on substrates and a large number density of carbon nanotubes of 5–10/trμm², which was confirmed by high-resolution electron microscopy. Although localized states exist for various tip morphologies, which was calculated by density-functional tight-binding calculations, the contribution from such states was found to be negligible.

KEYWORDS: full-color field-emission display, carbon nanotubes, SEM image, Fowler–Nordheim plot, local density of states, display

1. Introduction

Carbon nanotubes (CNTs), originally produced as by-products of fullerene synthesis, have remarkable mechanical, electronic, and magnetic properties that can be tailored in principle by varying diameters and chirality of CNTs and the number of concentric shells.¹ CNTs with extremely small diameters, hollowness, and chemical and mechanical strengths have provided a vast range of applications of nanotubes such as in electron field emitters,² room-temperature transistors,³ and vehicles for hydrogen storage. In particular, the high aspect ratio and high chemical stability of CNTs have enabled the CNTs to be used as strong electron emitters. There have been tremendous efforts in developing field emission displays (FEDs) using CNTs. The key issue here is to align CNTs vertically on substrates in order to achieve sufficient electron emissions. A suspension-filtering method by which CNTs are aligned on the polytetrafluoroethylene using ceramic filters has been demonstrated for FEDs.⁴ An arc-discharge-generated CNTs/epoxy mixtures has also been used as a tip for FEDs. A CNTs-based lamp operated at high voltage has been fabricated using core soon generated from the arc discharge.⁵ Recently, vertically well-aligned CNTs have been grown by chemical vapor deposition.⁶–¹⁰ Although these approaches may lead to an ultimate solution, large area synthesis and uniform field emission have not been easily accessible.

CNT-FEDs have a strong potential to be applied in emissive devices including flat panel displays, cathode-ray tubes, backlighting for liquid-crystal displays, outdoor displays, and traffic signals. A FED in a diode-type of the size of 10 mm × 10 mm was recently tested in a vacuum chamber, where the CNTs were non-aligned.⁶ Yet, high brightness, uniformity, and high stability on a large area at a low operating voltage have never been achieved at the level of a fully integrated device. The main difficulty in realizing FEDs using CNTs arises from the vertical alignment of a large number of CNTs on a large area at a low processing temperature. Here, we report the integration processes of fully sealed 4.5-inch full-color CNT-FEDs on glass using paste squeezing and surface rubbing techniques. High brightness and uniformity with high stability are achieved.

2. Diode Fabrication

The CNT-FED in a diode-type is shown in Fig. 1. The panel structure consists of two glass plates: stripes of CNTs on the patterned cathode glass and phosphor-coated indium tin oxide (ITO) stripes on the anode glass. The cathode and anode stripes are arranged perpendicular to each other, resulting in the formation of pixels at their intersections. The spacing between two glass plates is maintained at 200 μm. CNTs were synthesized by conventional arc-discharge as described elsewhere.¹¹ As-grown single-wall CNTs with a diameter of 1.4 μm were purified and cut into short pieces in a mixture of sulfuric and nitric acids (1:1) at 100°C.¹² Purified CNTs were rinsed with distilled water, followed by drying, and then further dispersed in isopropanol alcohol by sonication. Scanning electron microscope (SEM) images showed that most carbonaceous particles had been removed by purification, and typical lengths of CNTs were about 0.5–2 μm. After drying at 150°C, the CNTs were mixed with slurry of metal powders and organic vehicles. The paste of well-dispersed CNTs was squeezed onto the metal-patterned soda-lime glass through a metal mesh of 20 μm in size, and subsequently heat-treated at around 300°C for 20 min, in order to burn off the organic binders. Finally, the mixture of CNTs and metal powders was strongly adhered onto the...
metal-patterned stripes. A subsequent surface rubbing process removed metal powders from the uppermost surface, causing the CNTs to protrude from the top surface. For the anode plate, Y_{2}O_{3}:Eu, ZnS:Cu, Al, and ZnS:Ag, Cl phosphors were deposited to a thickness of 6–10 μm on the ITO-coated soda lime glass for red, green, and blue colors, respectively. Following the assembly of cathode and anode plates with spacers between them, the panel was sealed at 415°C using frit glass in an ambient of highly purified Ar gas. The result of thermal analyses of our CNTs revealed that the dissociation of CNTs started at 500°C in an inert gas, and the weight loss from dissociation was over 40% at 800°C. The panel was evacuated down to the pressure level of 1 × 10^{-7} Torr. Non-evaporable getters of a Ti–Zr–V–Fe alloy were activated during the final heat-exhausting procedure at 330°C for 6 h, finally leading to the complete fabrication of 4.5-inch fully sealed CNT-FEDs. Emission currents were measured in dc and pulse modes at voltages up to 800 V. The resultant brightness was measured using a luminance calorimeter (BM-7, Topcon).

3. Results and Discussion

Figure 2(a) shows a red, green, and blue color bar image of a CNT-FED with 128 cathode lines that is matrix-addressable in diode mode. An image with a highly uniform and stable emission was obtained over the entire 4.5-inch panel. The brightness of 1800 cd/m² at 800 V or 4 V/μm (duty: 1/4, frequency: 15.7 kHz) was achieved on the green phosphor. The fabricated CNT-FED showed unusually high brightness at the low operating voltage, which is attributed to the good alignment, uniform distribution with a high number density, and high efficiency in emitting electrons. All the fabrication processes are fully scalable and reproducible.

In order to analyze the emission uniformity, the 4.5-inch screen was divided into nine domains. Brightness and current density were measured in the nine different domains at the anode voltage of 700 V using green phosphor. The brightness and current density shown in Figs. 2(b) and 2(c), respectively vary from domain to domain by about 50%. Such variation may be attributed to i) different lengths of CNTs protruding from the surface, ii) different degree of alignment on the surface, iii) various chiralities, iv) nonuniform distribution of CNTs, and v) nonuniform deposition of phosphor layers from domain to domain. The fluctuation of the brightness does not necessarily coincide with that of the current density of the corresponding domains, due to the nonuniform thickness of phosphor layers. Nevertheless, the resultant fluctuation of brightness even at the current stage is acceptable for low-end display applications.

Emission current–voltage (I–V) curves from the nine different domains of the CNT-FED are shown in Fig. 3(a). Currents start increasing at 1.5–3 V/μm and saturate near 3–5 V/μm, which varies from domain to domain. Despite the fact that currents were measured with phosphor layers, as listed in Table I, the onset electric fields (for emission current of 10 nA) were quite low (1.5–3 V/μm) and the currents were saturated at about 1 mA. The anode currents strongly depend on the type of anode and preparation conditions. A bare ITO glass and a phosphor-deposited ITO glass were used in this experiment. We found that the turn-on field for the phosphor-deposited ITO glass was around 1.5–3 V/μm, whereas that for

Fig. 2. (a) Emission image of the fully sealed 4.5-inch CNT-FED. A red, green, and blue color bar image is shown with high brightness at the applied voltage of 700 V ac. Half of the cathode lines are biased in this display. (b) Brightness distribution of a 4.5-inch CNT-FED at different areas. The 4.5-inch screen is divided into nine sectors on the green phosphor anode for the purpose of area-by-area analysis. (c) Current density distribution of a 4.5-inch CNT-FED at different areas.
of the F–N plot if the work function of the emitter is known or by measuring the geometry of a CNT tip. We measured emission currents by changing cathode-to-anode distances. The emission currents as a function of voltage were insensitive to distance variation below 200 μm, while the emission currents increased linearly with the gap greater than 200 μm. Therefore, a point-to-sphere electric-field model is suitable for the gap of 200 μm, where the field enhancement factor is $\beta = 1/k r$ (unit: cm$^{-1}$, $r$: tip radius, $k \sim 10^{15}$) for the point-to-sphere model. The tip radii $r$ were obtained to be 30–60 nm by the relation of $r = 1/(k\beta)$. The calculated tip radii were in the same order as the measured ones, which were shown in the TEM and SEM observations in the form of bundles instead of a single nanotube, as given in Fig. 4. Assuming the work function of CNTs to be 5 eV, same as that of graphite or $C_{60}$,$^{15}$ the field enhancement factors in the low-field region $S_i$ were determined to be in the range of 17000 to 53000 for the different domains. These values are much larger than other re-

![Figure 3](image1.png)

**Fig. 3.** (a) Emission $I$–$V$ curves and (b) Fowler–Nordheim plots of the nine different sectors of the 4.5-inch CNT-FED.

![Figure 4](image2.png)

**Fig. 4.** (a) Cross-sectional SEM image of CNT cathode. CNTs are aligned perpendicular to the substrate and firmly embedded into the metal electrode. (b) TEM image of SWNTs.

| Field enhancement factor ($\beta$) and turn-on field of carbon nanotubes. $S_i$ and $S_2$ are the slopes of F–N plot in Fig. 3(b) and $\beta$ is the field enhancement factor. $F_{\text{ITO}}$ and $F_{\text{phosphore}}$ are turn-on fields on ITO and on phosphor/ITO anode, respectively. |
|-------------------------------------------------|--------------------------------------------------------|
| Our CNTs                                         | Other CNTs                                             |
| $\beta$                                         | 17000–33000                                           |
|                                                | 1300$^2$                                               |
|                                                | 2500–10000$^{18}$                                      |
|                                                | 600$^{22}$                                             |
| $S_1$                                          | 23000–40000                                           |
| $S_2$                                          | 1000–5000                                              |
| $F_{\text{ITO}}$ (V/μm) (at $I = 10$ nA)         | 1.0–1.5$^1$                                            |
|                                                | 2700                                                  |
|                                                | 840$^{23}$                                             |
| $F_{\text{phosphor}}$ (V/μm) (at $I = 10$ nA)     | 1.5–4.5$^{18}$                                         |
|                                                | 2.6 (at 10 $\mu$A/cm$^2$)$^{18}$                     |

the bare ITO glass was around $\pm$ V/μm.

Emission characteristics were analyzed by applying the Fowler–Nordheim (F–N) equation, $I = aV^2 \exp(-b/V)$, where $a$ and $b$ are constants.$^{14}$. Figure 3(b) shows the F–N plots, $\log(I/\sqrt{V})$ versus $1/V$, for the nine domains. The local electric field ($E_0$) can be related to the field enhancement factor ($\beta$) and macroscopic field ($E_m$) by $E_0 = \beta E_m$. The field enhancement factor can be calculated either from the slope
ported values (Table 1), probably due to the smaller diameters of emitters and/or field strengthening at the electrode in our CNT-FEDs. At the high field region of \( S_2 \) in Fig. 3(b), the slopes of the \( I^2 - N \) plots decrease, exhibiting a different emission behavior from that of the low field region \( S_1 \). It has been suggested that the deviation from the \( I^2 - N \) law at the high field region is due to the space charge effect and/or burning-out.\(^{15} \)

It has also been argued that localized states at CNT tips play a role in suppressing the electron emission, which is supported by the light emission from CNTs.\(^{19} \) There is a possibility that various types of chirality and different diameters exist among the CNTs.

In order to investigate the effect of such localized states, we performed a density-functional tight-binding calculation.\(^{18} \)

Figure 5 shows the local densities of states of typical armchair and zigzag nanotubes with various tip morphologies. We used 200 carbon atoms for a (5,5) nanotube with 30 cap atoms at the tip end, and open end at the other end. The local densities of states are calculated by choosing 30 atoms at the cap and 10 edge atoms with dangling bonds at the open edge. The ideal (5,5) nanotube shows metallic behavior.\(^{20} \)

Both capped and open edges revealed localized states. The open-edged nanotube is more strongly localized due to dangling bonds, where pentagons in the cap still contribute to the localized states, as shown in Fig. 5(a). Similar calculations were performed for (9,0) nanotubes. A (9,0) zigzag nanotube is a zero-gap semiconductor.\(^{20} \) The behaviors are similar to those of armchair nanotubes. More deeply localized states exist in the zigzag edges. Although the ideal (5,5) and (9,0) nanotubes are metallic and zero-gapped, respectively, in our density-functional tight-binding calculations, both CNTs with an open edge and a cap show localized states at top valence bands and bottom conduction bands. The capped CNTs might be formed during the synthesis but can easily be attacked by oxygen during the purification process, leaving eventually open-edged CNTs. Oxygen atoms could be adsorbed at the edge during the cutting procedure in sulfuric and nitric acids. However, these oxygen atoms can be easily removed during the electric field treatment. Therefore, open edges are expected in any case during electron field emission. Our photoluminescence measurement of CNTs did not find any light emission in the visible region. On the other hand, the light emission from CNTs on the transparent ITO glass anode was observed with the brightness of \( 2 \text{ cd/m}^2 \), but at a much higher field region (5 V/\( \mu \text{m} \)), which seems to be attributable to the thermionic effect of CNT edges as observed in another study.\(^{21} \) Therefore, the suppression of electron emission by the localized states appears to be negligible and the main contribution is still under investigation.

Figure 4 shows a cross-sectional SEM image of a CNT cathode. It clearly shows that CNT bundles are firmly adhered onto the metal electrode and aligned mostly perpendicular to the substrate. The density of CNT bundles as determined by the SEM measurements was 5–10/\( \mu \text{m}^2 \), about 100 times larger than the typical density of microtips in conventional Spindt-type FEDs.\(^{22} \) It was estimated that the average emission current from a single nanotube bundle was on the order of pico-amperes at 3 V/\( \mu \text{m} \). The CNTs were well aligned over the entire patterned area of the 4.5-inch panel. Vertical alignment of CNTs was solely achieved by i) squeezing paste through the metal mesh, ii) surface rubbing, and/or iii) conditioning by an electric field. The former aligned CNTs have been grown by chemical vapor deposition at high temperatures over 700°C.\(^{3,8} \) However, display applications using soda-lime glass require low-temperature processing below 500°C. During our CNT-FED fabrication processes, the temperatures were maintained below 415°C.

Emission stability of CNTs over the 4.5-inch cathode was tested by measuring the current fluctuation with time in dc mode using bare ITO glass in order to prevent the voltage drop and/or degassing by phosphor layers. In Fig. 6, the data were acquired by averaging 10 data points per second. The inset shows the \( I \sim V \) curve of CNTs measured with the bare ITO anode glass, which exhibits a much lower turn-on field (less than 1 V/\( \mu \text{m} \)) compared to that of the \( I \sim V \) curves measured with the phosphor-coated glass of Fig. 3(a). The current fluctuations at 0.1 mA, 0.5 mA, and 1.0 mA were found to be less than 10% over the 4.5-inch panel.

At a low voltage of 210 V (1.05 V/\( \mu \text{m} \)), the current remains nearly at the same level, whereas the currents fluctuate occasionally in the initial stage at higher voltages of 236 V (1.15 V/\( \mu \text{m} \)) and 310 V (1.5 V/\( \mu \text{m} \)), probably due to the field stress effect. With extended aging, however, the CNTs show negligible current deviations, indicating high stability in the electron emission.
Fig. 6. Current stability of the 4.5-inch CNT cathode at three different voltages (dc mode). A bare ITO glass anode was used for this experiment in order to avoid the voltage drop and/or outgassing by phosphor layers. The inset shows the effect of phosphor layers on ITO glass.

The inset clearly shows the effect of phosphor layers on ITO glass. The deposition of phosphor layers increases the turn-on voltages by several factors as listed in Table I, and further decreases the stability by degassing. This can be prevented by introducing getters during the sealing of CNT-FEDs in the final heat-exhausting procedure.

4. Summary

The fully-sealed 4.5-inch CNT-FEDs were fabricated for the first time on glass at low temperature, where CNTs were vertically aligned using the paste squeezing technique. The resultant high luminance of 1800 cd/m² at 4 V/µm with stable electron emission was achieved. All processes are scalable and cost-effective in fabricating CNT-FEDs. The fabrication of larger CNT-FEDs with moving images is currently under investigation.

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