FABRICATION OF ELECTRON FIELD EMITTERS USING CARBON NANOTUBES

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Carbon nanotube (CNT)-based field-emission displays (FEDs) have been fabricated using well-aligned nanotubes on substrates in situ grown by thermal chemical vapor deposition (CVD), and paste squeeze and surface rubbing techniques. Although the former seems to be an ultimate approach for CNT-based FED, a large area synthesis and uniform field emission over the entire area is yet to be not easily accessible. On the other hand, the latter is fully scalable on glass substrates and show 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 (23000-46000) 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 μm², which was confirmed by high-resolution scanning electron microscopy.

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. CNTs with extremely small diameters, hollowness, and chemical and mechanical strengths have provided a vast range of applications of nanotubes such as electron field emitters, room-temperature transistors, and vehicles for hydrogen storage. In particular, high aspect ratio and high chemical stability of CNTs have opened a possibility to use the CNTs 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 have sufficient electron field emissions. A suspension-filtering method, where CNTs are aligned on the polytetrafluoroethylene using the ceramic filters, has been first demonstrated for FEDs. Arc-discharge-generated CNTs/epoxy mixtures have also been used as a tip for FEDs. CNTs-

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based lamp operated at high voltage has been fabricated using core soot generated from arc discharge. Recently, vertically well-aligned CNTs have been grown by chemical vapor deposition (CVD). Although this approach may be an ultimate solution, a large area synthesis and uniform field emission have not been easily accessible. An FED in a diode type was recently tested in a vacuum chamber for the size of 10 mm x 10 mm, where CNTs were non-aligned. Yet, high brightness, uniformity, and high stability on a large area at low operating voltage have never been achieved in a fully integrated device level. Main difficulty in realizing FEDs using CNTs arises from the vertical alignment of a large number of CNTs on a large area at low processing temperature. Here we report two ways of fabricating FEDs using i) vertically aligned CNTs on a large area of Co-Ni codeposited Si substrates \textit{in situ} grown by the thermal CVD using C$_2$H$_2$ gas and ii) processes of fully sealed 4.5-inch CNTs adhered to a glass substrate by the paste squeeze and surface rubbing techniques.

2. \textit{In situ} growth of CNTs by thermal CVD

Co-Ni (Co: Ni=1:1.5) metal alloys with 100 nm in thickness were thermally evaporated on oxidized $p$-type silicon substrates at room temperature in a vacuum of $10^{-9}$ torr. Samples were dipped for 100-200 sec in HF solution (HF: DI water=3:12) and were then loaded on the quartz boat inside the CVD quartz reactor of 60 mm in diameter. Ar gas was flowed into the quartz reactor in order to prevent the oxidation of transition metal alloys while increasing the reaction temperature. Samples were pretreated using $\text{NH}_3$ gas with a flow rate of 80 secm for 5-20 min at 800-900 °C. CNTs were grown using C$_2$H$_2$ gas with a flow rate of 15-40 secm for 10-20 min at the same temperature. The reactor was cooled down slowly to room temperature in Ar ambient after the growth. The detail has been described elsewhere.

3. Diode fabrication

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 kept by 200 µm. CNTs were synthesized by a conventional arc-discharge. As-grown single-wall CNTs with a diameter of 1.4 nm were purified and cut into short pieces in a mixture of sulfuric and nitric acids (1:1) at 100 °C. Most carbonaceous particles were removed by the purification and typical lengths of CNTs were about 0.5-2 µm. The length of CNTs was shortened and impurities of carbonaceous and catalytic particles were removed during the purification process. 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 the metal mesh of 20 µm in size, and subsequently heat-treated at 300 °C for 20 min in order to burn out 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 on the uppermost surface, making CNTs protrude from the top surface.

For the anode plate, the Y$_2$O$_3$:Eu, ZnS:Cu,Al, and ZnS:Ag,Cl phosphors were deposited
with a thickness of 6-10 μm on the ITO-coated soda-lime glass for red, green, and blue colors, respectively. Following assembling of cathode and anode plates with spacers in-between, the panel was sealed at 415 °C using frit glass in an ambient of highly purified Ar gas. In order to avoid thermal reaction of CNTs, the processing temperature should be kept below 500 °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 hours, 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 by a luminance calorimeter (BM-7, Topcon).

4. Results and discussion

![SEM images](image_url)

Fig. 1. (a) SEM images of CVD-grown carbon nanotubes. Emission patterns from 1.4 cm × 1.6 cm in size with bias conditionings for (b) 30 min, (c) 90 min, and (d) typical I-V curve from (c).

Figure 1(a) shows the image of the scanning electron microscope (SEM) of CNTs grown by the thermal CVD. CNTs are well aligned vertically over the large area (20 mm × 30 mm) of the substrate. The surface morphologies of CNTs are clean and uniform with the length of about 5 μm and the diameter of about 200 nm. Note that top of the aligned nanotubes is terminated by transition-metal caps, the white spots. The density of nanotubes is about 3 × 10⁹ cm⁻², about 100 times larger than the typical density of microtips in conventional Spindt-type field emission arrays. We emphasize here that nanotubes can be aligned vertically on plain Si substrates using a simple surface treatment, in good contrast with the previous reports that nanotubes are aligned on catalyzed porous Si⁹ and CNTs are grown but not vertically aligned on catalyst-patterned Si substrates.¹⁴ The detail has been described elsewhere.⁹ Figure 1(b)-(c) illustrates emission patterns from vertically aligned CNTs. The anode, an ITO-phosphor-coated glass, was separated from the bottom layer of nanotubes by a spacer in size of 570 μm. The chamber was maintained at 1 × 10⁻⁵ torr. Although samples were clean, as seen in Fig. 1(a), they were annealed initially by repeatedly applying 100 V and 1000 V in order to burn unintentionally protruded nanotubes. This improves the emission patterns as shown in the figures. The turn-on voltage was about 1.2 V/μm with a current of 10 nA, which is much smaller than 4 V/μm obtained from patterned nanotubes-epoxy composite.⁵ For comparison, we have also fabricated patterned graphite powder-epoxy composite, which resulted in higher turn-on voltage, as shown
in Fig. 1(d). In spite of smaller effective emission area from CVD-grown samples, the emission current was much larger than that of graphite. The current increases sharply after turn-on voltage and saturates near 3 V/μm. The inset clearly shows that this field emission follows the Fowler-Nordheim (F-N) equation. The presence of metal particles at the top of nanotubes prohibited efficient emission and some protruded nanotubes gave rise to non-uniform emission patterns. A keen control with bias annealings is required to have large emission currents by removing metal caps and uniform emission patterns over a large area. Note that the present approaches are easily integrable within the current semiconductor process.

Figure 2(a) shows a red, green, and blue color bar image of the CNT-FED with 128 cathode lines that is matrix-addressable in a diode mode. A very uniform and stable emission image over the entire 4.5-inch panel was obtained. 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, compared to that (300 cd/m² at 6 kV) of Spindt-type FEDs. Such high and uniform brightness over a large area implies that the CNTs are well aligned, uniformly distributed with a high number density, and highly efficient in emitting electrons. The whole fabrication processes were 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 in Fig. 2(b) and 2(c) 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 chirality, iv) non-uniform distribution of CNTs, and v) non-uniform 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 non-uniform 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, the onset electric fields (for emission current of 10 nA) were quite low (1.5 ~ 3 V/μm) and the currents were saturated to about 1 mA. The anode currents strongly depend on the type of anode and preparation condition. 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 the bare ITO glass was around 1 V/μm. Emission characteristics were analyzed by applying the F-N equation, \[ I = A V^2 \exp(-b/V), \]
where \( a \) and \( b \) are constants. Figure 3(b) shows the F-N plots, \( \log(I/V^2) \) versus \( 1/V \), for the nine domains. The local electric field \( (E_i) \) can be related to the field enhancement factor \( \beta \) and macroscopic field \( (E_m) \) by \( E_i = \beta E_m \). The field enhancement factor can be calculated either from the slope of the F-N plot if the work function of the emitter is known or from measuring the geometry of a CNT tip. We measured emission currents by changing cathode-to-anode distances. The emission currents as functions of voltages 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 more suitable for the gap of 200 μm, instead of a plane-to-plane model. The field enhancement factor is \( \beta = 1/kr \) (r: tip radius, k ~ 10)\(^{17}\) for the point-to-sphere model, and is \( \beta = h/r \) (h: tip height, r: tip radius) for the plane-to-plane model.\(^{18}\) 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 investigated by the SEM observations as a form of bundle instead of a single nanotube. Assuming the work function of CNTs to be 5 eV, same as that of graphite or C\(_{60}\),\(^{19}\) \( \beta \) in the low field region \( S_1 \) were determined to be in the range of 23000 - 46000 for the different domains. These values are much larger than other reported values, probably due to smaller diameters of emitters of CNT bundles in our CNT-FEDs.\(^{17}\)

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

Emission stability of CNTs over the 4.5-inch cathode was tested by measuring the current fluctuation with time at a dc mode using the bare ITO glass in order to remove the voltage drop and/or degassing by phosphor layers. The current fluctuation at 0.1 mA, 0.5 mA, and 1.0 mA was found to be less than 10 % over the 4.5-inch panel. At a low voltage of 370 V, the current maintains nearly at the same level, whereas the currents fluctuate occasionally at the initial stage.
for higher voltages of 486 V and 540 V, probably due to the field stress effect. In the extended aging, however, the CNTs show negligible current deviations, indicating high stability in the electron emission.

5. Summary
We have shown the field emissions from in situ CVD-grown carbon nanotubes and well-aligned carbon nanotubes prepared by the paste squeezing and surface rubbing techniques. Although in situ grown nanotubes were easy to be applied for field emitters, the control of uniformity and large area synthesis was still difficult to achieve. The fully-sealed CNT-FEDs in 4.5-inch size were fabricated for the first time on glass at low temperature. The high luminance of 1800 cd/m² at 4 V/μm with stable electron emission was achieved. Large field enhancement factor was attributed to the vertically well-aligned nanotubes, which was achieved by our preparation processes. The degradation of nanotubes was small within 10 %.

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References