

Carbon nanotube field emission display



Won Bong Chil

The National Creative Research Initiatives Center for Electron Emission Source, Samsung Advanced Institute of Technology, P.O.Box 111, Suwon 440-600, Korea Phone : 82-331-280-9316 Fax : 82-331-280-9349 Email : wbchoi@sait.samsung.co.kr Department of Physics, Jeonbuk National University, Jeonju 561-756, Korea



Jong Min Kim

The National Creative Research Initiatives Center for Electron Emission Source, Samsung Advanced Institute of Technology, P.O.Box 111, Suwon 440-600, Korea Phone : 82-331-280-9316 Fax : 82-331-280-9349 Email : wbchoi@sait.samsung.co.kr Department of Physics, Jeonbuk National University, Jeonju 561-756, Korea

Abstract

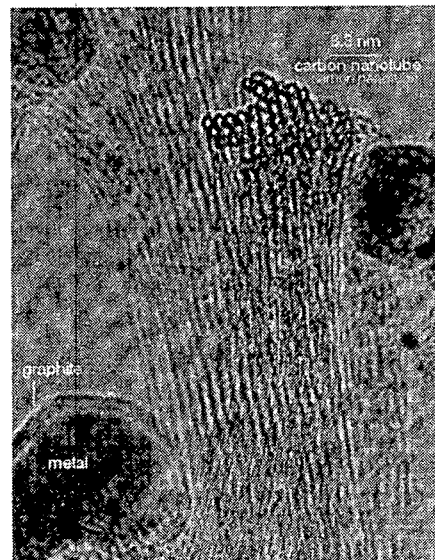
Fully sealed field emission display in size of 4.5 inch has been fabricated using single-wall carbon nanotubes-organic vehicle composite. The fabricated displays were fully scalable at low temperature below 415°C and CNTs were vertically aligned using paste squeeze and surface rubbing techniques. The turn-on fields of 1V/ μm and field emission current of 1.5mA at 3V/ μm ($J=90\mu\text{m}/\text{cm}^2$) were observed. Brightness of 1800cd/ m^2 at 3.7V/ μm was observed on the entire area of 4.5-inch panel from the green phosphor-ITO glass. The fluctuation of the current was found to be about 7% over a 4.5-inch cathode area. This reliable result enables us to produce large area full-color flat panel display in the near future.

Carbon nanotubes (CNTs) have attracted much attention because of their unique elec-

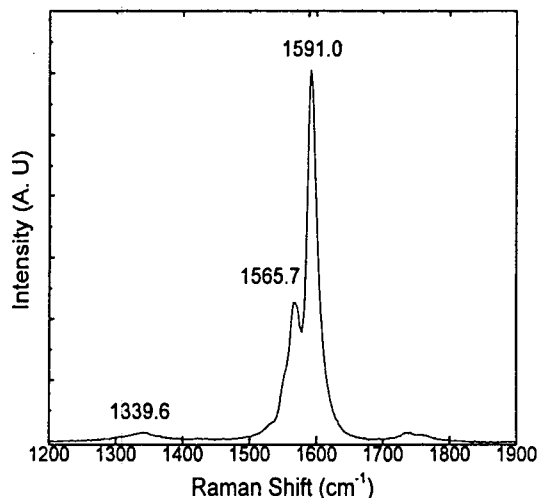
trical properties and their potential applications [1, 2]. Large aspect ratio of CNTs together with high chemical stability, thermal conductivity, and high mechanical strength are advantageous for applications to the field emitter [3]. Several results have been reported on the field emissions from multi-walled nanotubes (MWNTs) and single-walled nanotubes (SWNTs) grown from arc discharge [4, 5]. De Heer et al. have reported the field emission from nanotubes aligned by the suspension-filtering method. This approach is too difficult to be fully adopted in integration process. Recently, there have been efforts to make applications to field emission devices using nanotubes. Saito *et al.* demonstrated a carbon nanotube-based lamp, which was operated at high voltage (10KV) [8]. A prototype diode structure was tested by the size of 10mm \times 10mm in vacuum chamber [9]. The difficulties arise from the arrangement

of vertically aligned nanotubes after the growth. Recently vertically aligned carbon nanotubes have been synthesized using plasma-enhanced chemical vapor deposition (CVD) [6, 7]. Yet, control of a large area synthesis is still not easily accessible with such approaches. Here we report integration processes of fully sealed 4.5-inch CNT-field emission displays (FEDs). Low turn-on voltage with high brightness, and stability clearly demonstrate the potential applicability of carbon nanotubes to full color displays in near future.

For flat panel display in a large area, carbon nanotubes-based field emitters were fabricated by using nanotubes-organic vehicles. The purified SWNTs, which were synthesized by dc arc discharge, were dispersed in iso propyl alcohol, and then mixed with an organic binder. The paste of well-dispersed carbon nanotubes was squeezed onto the metal-patterned sodalime glasses through the metal mesh of $20\mu\text{m}$ in size and subsequently heat-treated in order to remove the organic binder. The insulating spacers in thickness of $200\mu\text{m}$ are inserted between the lower and upper glasses. The $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$, $\text{ZnS}:\text{Cu}$, Al, and $\text{ZnS}:\text{Ag}$, Cl, phosphors are electrically deposited on the upper glass for red, green, and blue colors, respectively. The typical sizes of each phosphor are 2~3 micron. The assembled structure was sealed in an atmosphere of highly purified Ar gas by means of a glass frit. The display plate was evacuated down to the pressure level of 1×10^{-7} Torr. Three non-evaporable getters of Ti-Zr-V-Fe were activated during the final heat-exhausting procedure. Finally, the active area of 4.5-inch panel with fully sealed carbon nanotubes was produced. Emission currents were characterized by the DC-mode and pulse-modulating mode at the voltage up to 800 volts. The brightness of field emission was measured by the Luminance calorimeter (BM-7, Topcon).



(a)



(b)

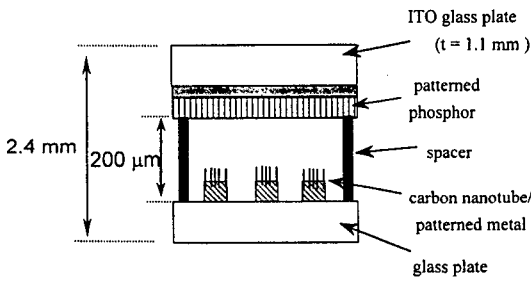
Fig. 1. (a) TEM image of SWNTs. It shows that the SWNTs are formed as a rope type and carbonaceous particles are attached on the SWNTs. (b) Raman spectra of SWNTs sample obtained using 514.5 nm excitations.

Figure 1(a) shows transmission electron microscopy (TEM) images of as-fabricated SWNTs. Bundles of SWNTs with diameters

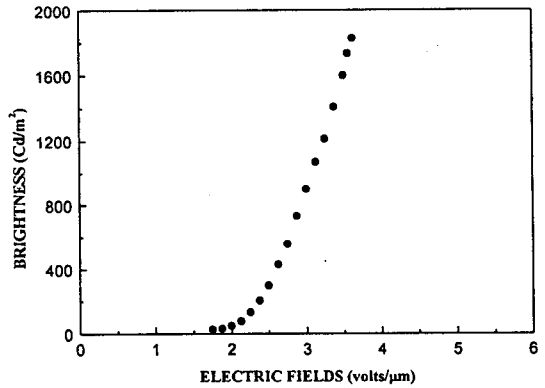
of about 1.6nm are clearly seen. Metal particles were attached at the edge of the SWNT bundles. Figure 1(b) shows the Raman spectrum of SWNTs by using Ar excitation ($\lambda=514.5\text{nm}$). The Raman spectrum clearly shows the G-line at 1591cm^{-1} which originates from the graphitic sheets, with extra peak near 1566cm^{-1} , indicating the general trends of SWNTs [10, 11]. The broad peaks near 1750cm^{-1} result from the second order Raman scatterings, coupled between the breathing modes near 180cm^{-1} and G-lines [11]. The broad peaks near 1340cm^{-1} indicate the existence of defective

graphitic layers and/or some carbonaceous particles, which remain even after the purification procedure.

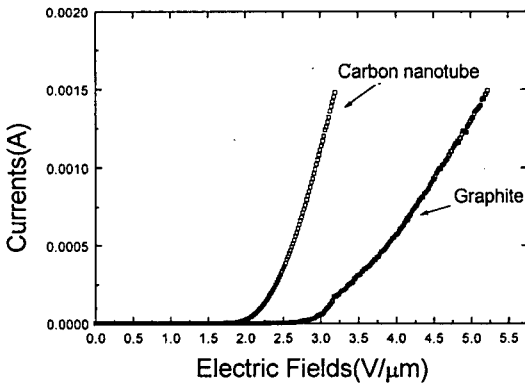
The panel structure of carbon nanotubes-based diode-type flat panel display is shown in Fig. 2(a). This structure consists of two sets of glass plates : SWNTs stripes on the patterned cathode glass and phosphor-coated ITO stripes on the anode glass. The spacing between two sets of glass plates is kept by $200\mu\text{m}$ spacers, and the pixels are formed at the intersection of cathode and anode stripes. Figure 2(b) shows I-V characteristics of a 4.5-in. panel, in which



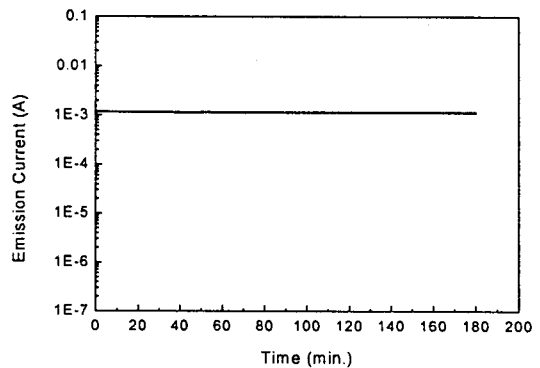
(a)



(c)



(b)



(d)

Fig. 2. (a) Schematic structure of the fully sealed 128 lines matrix-addressable carbon nanotube flat panel display. The pixels are formed at the cross section of cathode and anode. (b) Emission current of carbon nanotube and graphite as a function of electric fields. (c) Brightness of the SWNT-FED as a function of electric fields. (d) Fluctuations of the 4.5-inch SWNTs-FED at constant voltage (electric fields of $2.5\text{V}/\mu\text{m}$).

SWNTs/metal on glass was patterned to form stripes of $300\mu\text{m}$ wide with a pitch size of $325\mu\text{m}$. A graphite-powder cathode was also prepared by the same method, and compared to the properties of SWNTs. The turn-on field was less than $1\text{V}/\mu\text{m}$ and the total currents was 1.5mA at $3\text{V}/\mu\text{m}$ (current density, $J = 90\mu\text{A}/\text{cm}^2$), which is much better than that of the graphite cathode and that of previously reported values with similar approaches [9]. Figure 2(c) shows the brightness of the 4.5-in. panel as a function of electric field. The brightness of $1800\text{cd}/\text{m}^2$ at $3.7\text{V}/\mu\text{m}$ (duty 1/4, frequency 15.7KHz) was achieved on the green phosphor. The fabricated CNT-FED showed unusually high brightness at the low operating voltage, compared to that of Spindt-type FEDs ($300\text{Cd}/\text{m}^2$ at 6KV) [13]. The emission stability of SWNTs before and after sealing was tested by measuring the current fluctuation with time at a fixed voltage (DC-mode). The fluctuation measured in the vacuum chamber was found to be less than 7% over a 4.5-in. Fig. 2(d). Figure 3(a) shows the emission image of the carbon nanotubes-based 128 lines matrix-addressable diode display

at color mode with red, green, and blue color phosphor. An In_2O_3 conducting powder is added to reduce the phosphor's resistivity. A very uniform and stable emission images were obtained following the current-conditioning procedure [12]. 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 from the SEM measurements was $5\sim 10/\mu\text{m}^2$, about 100 times larger than the typical density of microtips in conventional Spindt-type FEDs [13]. It was estimated that the average emission current from a single nanotube bundle was an order of pico-amperes at $3\text{V}/\mu\text{m}$. 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) paste squeezing through the metal mesh, ii) surface rubbing, and/or iii) conditioning by electric field. The former aligned CNTs have been grown by chemical vapor deposition at high temperatures over 700°C [6,7]. The display applications using sodalime glass, however, require low-tem-

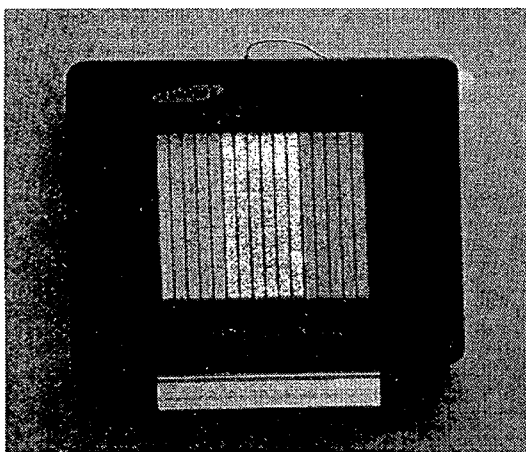


Fig. 3. Emitting image of fully-sealed SWNT-FED at color mode with red, green, and blue phosphor columns.

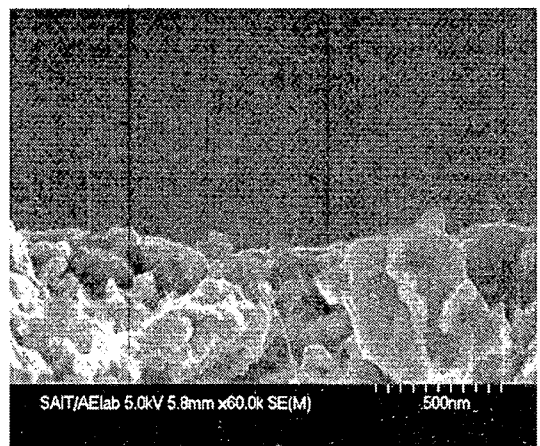


Fig. 4. Cross-sectional SEM image of CNT cathode. CNTs are aligned perpendicular to the substrate and firmly embedded into the metal electrode.

perature processing below 500°C. During our processes of CNT-FED fabrication, the temperatures were kept below 415°C.

In summary, fully sealed 4.5-inch CNT-FEDs have been successfully fabricated using single-wall carbon nanotubes-organic vehicle composite. The fabricated displays were fully scalable at low temperature below 415°C and CNTs were vertically aligned using paste squeeze and surface rubbing techniques. The turn-on field of less than 1V/μm and emission currents of 1.5mA at 3V/μm (current density, $J=90\mu\text{A}/\text{cm}^2$) were achieved. Brightness of 1800cd/m² at 3.7V/μm with fluctuation of around 7% was observed. These reliable results enable us to produce carbon nanotube-based large area full-color FEDs in the near future.

Acknowledgement

The authors would like to thank Y.H Lee at Jeonbuk National University, and S. H. Park, D. S. Chung, J. H. Kang, H. Y. Kim, N. S. Lee and J. E. Jung for their help in fabricating device. Dr. S. A. Song at AE lab is appreciated for his TEM work.

References

- [1] Walt A. de Heer, A. Chatelain, and D. Ugarte, *Science* **270**, 1179(1995).
- [2] S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603(1993).
- [3] Thomas W. Ebbesen, "Carbon Nanotubes", CRC Press, Inc. (1997).
- [4] Y. Saito, K. Hamaguchi, T. Nishino, K. Uchida, Y. Tasaka, F. Ikazaki, M. Yumura, A. Kasuya, and Y. Nishina, *Nature (London)* **389**, 554(1997).
- [5] J. Bonard, J. Salvétat, T. Stockli, W. A. de Heer, L. Forro, A. Chatelain, *App. Phys. Lett.* **73**, 918(1998).
- [6] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, H. Dai, *Science* **283**, 512(1999).
- [7] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, *Science* **282**, 1105(1998).
- [8] Y. Saito, S. Uemura, and K. Hamaguchi, *Jpn. J. Appl. Phys.* **37**, L346(1998).
- [9] Q. H. Wang, A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, E. W. Seelig, and R. P. H. Chang, *Appl. Phys. Lett.* **72**, 2912(1998).
- [10] S. L. Fang, A. M. Rao, P. C. Eklund, P. Nikolaev, A. G. Rinzler, and R. E. Smalley, *J. Mater. Res.* **13**, 2405(1998).
- [11] C. J. Lee, D. W. Kim, T. J. Lee, Y. C. Choi, Y. S. Park, W. S. Kim, W. B. Choi, N. S. Lee, J. M. Kim, Y. G. Choi, S. C. Yu, and Y. H. Lee, submitted to *Appl. Phys. Lett.* April (1999).
- [12] R. Latham, "High voltage vacuum insulation", Academic Press, p. 34, 1995.
- [13] B. R. Chalamala et al., *IEEE Spectrum*, April **42**(1998).