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FIELD EMISSION PROPERTIES OF CARBON NANOTUBES AND THEIR APPLICATION TO DISPLAY DEVICES

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Field emission microscopy (FEM) of carbon nanotubes (CNTs) revealed that the adsorption and desorption of gas molecules on the tip were responsible for stepwise increases and decreases in the emission current, respectively. Long-term emission experiments under various ambient gases (such as H_2, He, N_2, O_2, H_2O, CH_4, CO_2, Ar) have shown that the degradation of emission current occurred most sensitively in O_2, H_2O and CH_4 atmosphere. Electron emission from CNT films prepared by spray-deposition of preformed CNTs was also measured as a function of the distance (d) between the nanotube cathode and an anode plate, and the macroscopic field strength E_{av} (voltage divided by distance between the cathode and the anode) that sustain a certain constant current was found to rise steeply with the decrease of d, for a small gap region ($d <$ ca. 40 μm) while the E_{av} slowly decreases with increasing d for a large gap. Finally, we report our recent fabrication of nanotube-based ultra-high luminance light sources that provide intense light of 10^6 cd/m^2 for green at 30 kV dc-driving voltage.

1. INTRODUCTION

Carbon nanotubes (CNTs) are now attracting great interest from researchers because of their intrinsic scientific richness and diverse application potential. Nanotubes as electron emitters [1–7], scanning-type

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microscope probes [8,9] and energy storage materials [10,11] are now under intense scrutiny. Of the various applications proposed, CNTs as field emission electron sources are the most promising. When a high electric field on the order of 10^7 V/cm is applied to a solid surface with negative electrical potential, electrons inside the solid are emitted into vacuum by a quantum mechanical tunneling effect. This phenomenon is called field emission of electrons. An extremely high field can be obtained on a sharp tip of a very thin needle, because the electric field concentrates at the sharp point. CNTs possess the following advantages as field emitters: (1) needle-like shape with a sharp tip, (2) high chemical stability, (3) high mechanical strength, and (4) low carbon atom mobility.

In 1995, field emission (FE) from an isolated single multiwall nanotube (MWNT) was first reported by Rinzler *et al.* [1], and FE from a MWNT film was reported by de Heer *et al.* [2]. We began a field emission microscopy (FEM) study of CNTs in 1997 [3,4], and experimentally manufactured cathode-ray tube (CRT) type lighting elements and field emission display (FED) panels with CNT cold cathodes. In 2001, Ise Electronic Corp. fabricated a 14.5 inch CNT based-FED panel with a triode structure [12]. In 1999 Samsung SDI reported the experimental fabrication of a 4.5 inch color FED panel [7], and also demonstrated a 9 inch FED displaying color moving pictures. Recently, Samsung developed a triode-type FED panel with an 8 bit gray scale control and demonstrated full color moving pictures [13].

In this report, we describe three topics. First, a FEM study was carried out under controlled ambient gas atmosphere to reveal the effects of adsorbed molecules on the electron emission and the CNT cap structure. Second, current-voltage characteristics of CNT films prepared by spray deposition were measured as a function of the distance between the nanotube cathode and the anode plate, and the gap-dependent macroscopic electric field required to sustain a fixed current was determined. Finally, we describe our recent development of CNT-based ultra-high luminance light source devices, in which special MWNTs called "nanografibers" [14] were employed as cold cathodes.

2. FIELD EMISSION PROPERTIES OF CARBON NANOTUBES

CNTs used for field emission measurement were produced by the arc discharge method. The shapes of the CNT emitters were either a needle-like bundle fixed on the apex of a hairpin shaped tungsten filament or as films spread on a metal substrate. The former emitter was used for field emission microscopy (FEM), while the latter was for the parallel-plate diode apparatus.

2.1. Electron Emission in Various Gas Atmospheres

Multiwall nanotubes (MWNTs) with clean surfaces give FEM images exhibiting 6 bright pentagonal rings (Fig. 1a), which are considered to originate from carbon pentagons at the CNT tip, indicating preferential electron tunneling through the pentagons [15]. The CNT caps could stay clean for several minutes in an ultra-high vacuum (UHV) with a pressure of 10^{-10} Torr. Even in UHV, residual gas molecules adsorb on the nanotube tip several minutes after electron emission from a clean cap starts. Figure 1b shows a FEM pattern of the CNT cap with an adsorbate. The adsorbate is observed as a bright spot as indicated by an arrow, showing that electron emission is enhanced through adsorbed molecules. Flash heating of the emitter desorbs the adsorbates, and the nanotube emitter recovers its original clean surfaces. Thus we have shown that the adsorption and desorption of gas molecules were responsible for stepwise increases and decreases in the emission current, respectively [16].

The influence of ambient gases on long-term emission current variation (or emitter life time) was examined. Ambient gases studied were H_2, He, N_2, O_2, H_2O, CH_4, CO_2 and Ar at pressures from 10^{-7} to 10^{-5} Torr, and the CNT emitters used were bulk bundles of MWNTs. The initial total current was set at 50 μA, and the resulting variation of the current was recorded under a constant applied voltage. The time-traces of the emission current obtained under various atmospheres at 10^{-5} Torr are shown in Figure. 2. The degradation of emission current was most sensitive to O_2, H_2O, CO_2 and CH_4 atmosphere. N_2 and Ar also degraded the emission, but their effects were small compared with more reactive gases. For He and H_2, no serious degradation was observed.

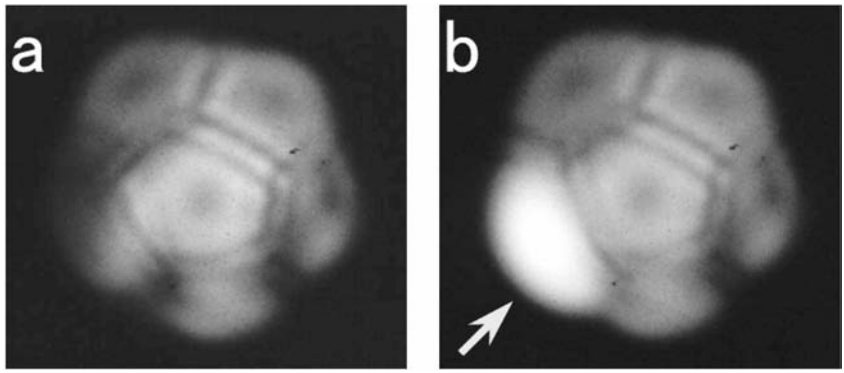

FIGURE 1 FEM patterns of a MWNT. (a) Clean surface, and (b) surface with an adsorbate (indicated by an arrow).

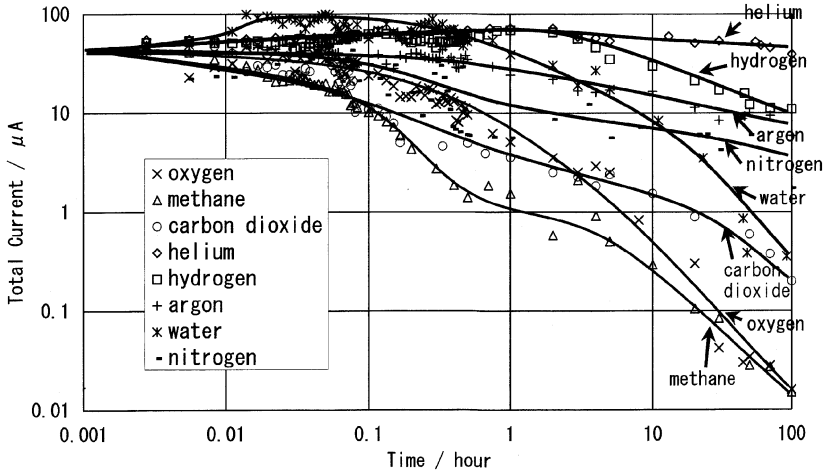

FIGURE 2 Variations in emission current with time under various atmospheres at 10^{-5} Torr.

2.2. Field Emission from Spray-Deposited CNT Films

2.2.1. Preparation of CNT Films

MWNTs used for film emitters were produce by arc discharge, and not subjected a purification process. However, SWNTs used for films were purified by acid (HCl) and centrifugation treatment. MWNTs and SWNTs were dispersed in ethanol, and then film samples for field emission experiments were prepared by spraying the suspended solution onto the top flat surface of cylinders (5 mm diameter by 6 mm height) made of stainless steel. The edge of the flat plane on which nanotubes were deposited was rounded to a radius of 0.5 mm. Thus a flat region with diameter 4 mm is left at the tip of the cylinder.

Figures 3 (a) and (b) show scanning electron microscope (SEM) images of spray-deposited MWNT and SWNT films, respectively. Since the MWNTs used in this study are pristine (i.e., no purification process was performed), carbon debris such as graphitic nanoparticle exists on the film. In the SWNT film, bundles of SWNTs typically 20–30 nm in diameter and many microns long are entangled.

A diode consisting of a CNT film cathode and an anode plate was studied. The anode was a disk of stainless steel of 40 mm diameter. The emission current versus voltage (I–V) characteristics were measured at various anode-cathode distance (d) from 10 to 1000 μm.

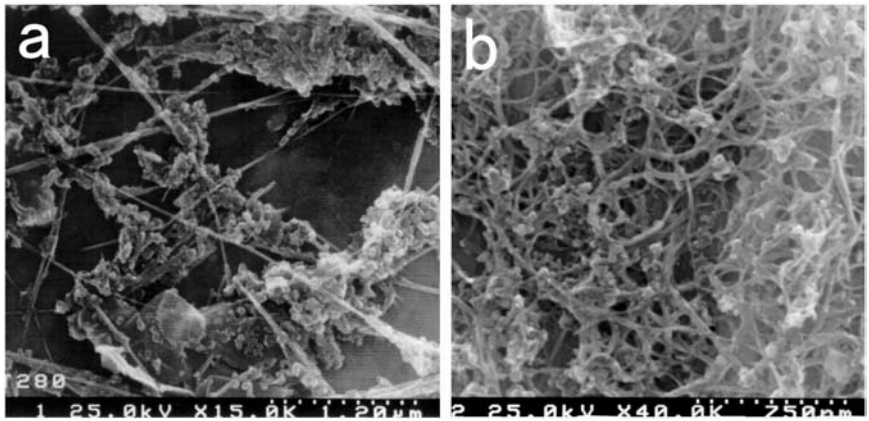

FIGURE 3 SEM images of spray-deposited CNT films: (a) MWNTs and (b) SWNTs.

2.2.2. Effect of Cathode-anode Gap on Current-voltage Characteristics

From the measured $I-V$ characteristics at various d's, the voltage (V) and the corresponding average electric field ($E_{av} = V/d$) giving the same emission current density was plotted as a function of d. The effective emission area used to calculate the current density (J) is the area of a circle of 4 mm diameter. Figure 4 shows the E_{av}-d characteristics at $J = 1\,\text{mA/cm}^2$ for MWNTs and SWNTs. It is obvious that the average electric field E_{av} necessary to obtain a certain fixed current depends on the size of the gap; i.e., E_{av} increases steeply with the decrease of d for small gaps while E_{av} is only weakly dependent on d for large gaps.

If the actual electric field on the emitter surface is independent of the gap distance as it is between parallel flat plates, the E_{av}-d curves should be constant irrespective of d (parallel to the axis). However, Figure 4 shows that the E_{av}-d curves are not straight lines parallel to the axis. In the present case, the electron emitter does not have a flat surface but a rugged surface consisting of needle-like materials (carbon nanotubes). The field distribution around a needle tip should be affected by the anode-cathode distance when the gap is small. Since the actual field strength on the emitter surface required for field emission is on the order of 1 V/nm (i.e., $10^3\,\text{V/}\mu\text{m}$), the E_{av}-value should be close to this magnitude in the small gap limit ($d \cong 0$). On the other hand, the field around a tip is only determined by the curvature of the tip when the gap distance is large enough. In the large gap limit, usually encountered in field emission microscopy, the

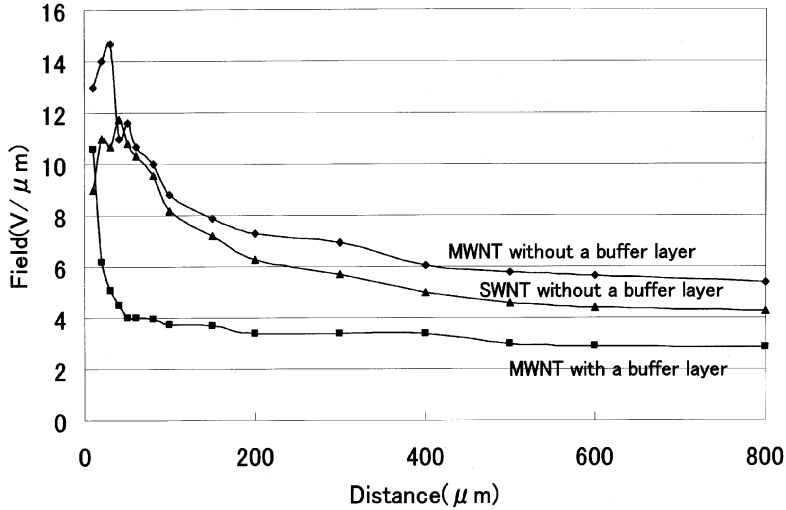

FIGURE 4 E_{av}-d characteristics at a constant current density of 1 mA/cm^2 from three kinds of CNT films: MWNT (◆) and SWNT (▲) films without buffer layer, and a MWNT film (■) with an iron buffer layer.

electric field at the tip of a needle is well approximated by V/r, where V is the voltage applied to the emitter and r is the radius of curvature of the tip. That is to say, the value of E_{av} approaches zero asymptotically for large d. From these considerations, it is expected that the E_{av} is not constant with d but increases as d decreases. Actually, in the small gap region ($d <$ ca. 100 μm) the E_{av}-d curve shows a steep rise with decreasing d, and in a large gap region ($d >$ ca. 100 μm) the curve shows a slowly descending behavior with increasing d.

The difference in the E_{av}-values between MWNT and SWNT films is probably due to the small diameter of nanotubes. As far as operating voltage is concerned, SWNTs seem to be superior to MWNTs as electron sources.

2.2.3. Improvements with a Metal Buffer Layer

An Fe buffer layer was used to improve the electrical and mechanical contact between CNTs and the substrate. After spray-deposition of the CNT suspension onto the Fe-coated substrates, the films were heated to 600°C for 10 min in vacuum (0.01 Torr). Current-voltage characteristics were measured as a function of the distance (d) between the CNT cathode and an anode plate. As shown in Figure 4, the E_{av}-d curve of the film emitter

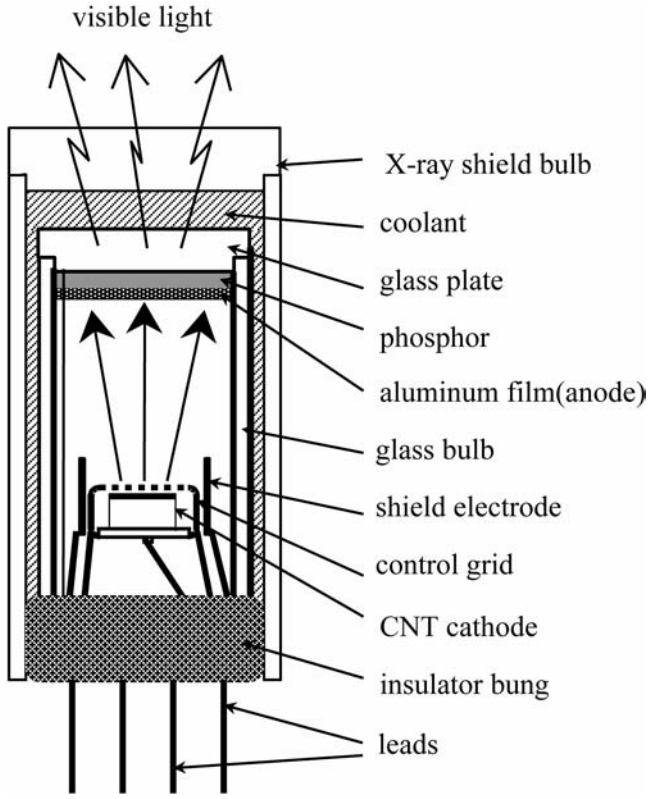

FIGURE 5 Schematic drawing of a CNT-based ultra-high luminance light source [17].

with the buffer layer lies below (about half of the value of E_{av}) that without the buffer layer, clearly showing the improvement of electron emission.

3. CARBON NANOTUBE-BASED VACUUM TUBES

As one of the applications of CNT emitters, our recent development of ultra-high luminance light source is described here. Nanografibers [14], special MWNTs, were used as a cold cathode to fabricate ultra-high luminance light sources [17], the structure of which is shown in Figure 5. A high current density of ca. 100 mA/cm^2 was obtained at a grid voltage of 2.9 kV with the cathode-grid distance of ca. 1.5 mm. The light source device showed 10^6 cd/m^2 in the green at a dc-driving voltage of 30 kV and was expected to emit a luminous flux of more than 1000 lm.

REFERENCES

[1] Rinzler, A. G., Hafner, J. H., Nikolaev, P., Lou, L., Kim, S. G., Tomanek, D., Nordlander, P., Colbert, D. T., & Smalley, R. E. (1995). *Science*, *269*, 1550.

[2] de Heer, W. A., Chatelain, A., & Ugarte, D. (1995). *Science*, *270*, 1179.

[3] Saito, Y., Hamaguchi, K., Nishino, T., Hata, K., Tohji, K., Kasuya, A., & Nishina, Y. (1997). *Jpn. J. Appl. Phys.*, *36*, L1340.

[4] Saito, Y., Hamaguchi, K., Hata, K., Uchida, K., Tasaka, Y., Ikazaki, F., Yumura, M., Kasuya, A., & Nishina, Y. (1997). *Nature*, *389*, 554.

[5] Saito, Y., Uemura, S., & Hamaguchi, K. (1998). *Jpn. J. Appl. Phys.*, *37*, L346.

[6] Uemura, S., Nagasako, T., Yotani, J., Shimojo, T., & Saito, Y. (1998). *SID '98 Digest*, 1052.

[7] Choi, W. B., Chung, D. S., Kang, J. H., Kim, H. Y., Jin, Y. W., Han, I. T., Lee, Y. H., Jun, J. E., Lee, N. S., Park, G. S., & Kim, J. M. (1999). *Appl. Phys. Lett.*, *75*, 3129.

[8] Dai, H., Hafner, J. H., Rinzler, A. G., Colbert, D. T., & Smalley, R. E. (1996). *Nature*, *384*, 147.

[9] Nishijima, H., Kamo, S., Akita, S., Nakayama, Y., Hohmura, K. I., Yoshimura, S. H., & Takeyasu, K. (1999). *Appl. Phys. Lett.*, *74*, 4061.

[10] Dillon, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S., & Haben, M. J. (1997). *Nature*, *386*, 377.

[11] Gao, B., Kleinhammes, A., Tang, X. P., Bower, C., Fleming, L., Wu, Y., & Zhou, O. (1999). *Chem. Phys. Lett.*, *307*, 153.

[12] Uemura, S., Yotani, J., Nagasako, T., Kurachi, H., Yamada, H., Ezaki, T., Maesoba, T., & Saito, Y. (2001). *Proc. Asia Display/IDW'01*, 1201–1204.

[13] Kim, J. M. *et al.*, Demonstration at the Tsukuba Symposium on Carbon Nanotube (Tsukuba, Oct. 3–5, 2001).

[14] Saito, Y., Mizushima, R., Kondo, S., & Maida, M. (2000). *Jpn. J. Appl. Phys.*, *39*, 1468.

[15] Saito, Y., Hata, K., & Murata, T. (2000). *Jpn. J. Appl. Phys.*, *39*, L271.

[16] Hata, K., Takakura, A., & Saito, Y. (2001). *Surface Sci.*, *490*, 296.

[17] Yotani, J., Uemura, S., Nagasako, T., Kurachi, H., Yamada, H., Ezaki, T., Saito, Y., Ando, Y., & Zhao, X. (2001). *Proc. SID'01.*, pp. 312–315.