Field emission from 4.5 in. single-walled and multiwalled carbon nanotube films

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Field emission properties of 4.5 in. flat panel displays in a diode type panel using single-walled (SWNTs) and multiwalled carbon nanotube tips (MWNTs) were characterized and compared. The panel, fabricated by a slurry squeezing and surface rubbing technique, enables the generation of more emission sites by removing materials on the surface. The turn-on field of MWNTs decreased from 6.4 to 3 V/μm by treatment of the surface, and that of SWNTs also decreased, from 4.5 to 2 V/μm. The density of aligned MWNTs is approximately 2/μm², whereas the aligned SWNTs were uniformly distributed, with densities of 5–10/μm². As a result, SWNT films show higher emission uniformity than MWNT films. A gradual degradation over time was observed in both MWNTs and SWNTs. The current stability curve of the SWNTs decreased about 20%, while that of the MWNTs decreased less than 10%. © 2000 American Vacuum Society. [S0734-211X(00)05302-6]

I. INTRODUCTION

The carbon nanotube (CNT) is a new form of carbon phase with unique electrical and structural properties.1–2 The high aspect ratios and small tip radii of curvature of carbon nanotubes, which result from the folding of graphite layers into long carbon cylinders, have especially received great attention for electron field emission. Several results have been reported on field emission from multiwalled CNTs (MWNTs) and single-walled CNTs (SWNTs).3–5 Bonard et al. have demonstrated electron field emission from CNT films by drawing a suspension through a 0.2 μm pore ceramic filter and transferring the films to copper or brass covered with a Teflon film.6 Wang et al. reported a row-column matrix display based on arc-produced CNTs.7 They fabricated carbon nanotube films on photosensitive glass (the microchannel of which was etched by HF solution) and a polished plate to expose the channels. Uemura et al. fabricated cathode ray tube (CRT)-lighting element using bundles of MWNTs that operated at 10 kV anode voltage.8 We have already presented a fully sealed large area SWNT field emission display.9 High brightness at a turn-on field as low as 1 V/μm with uniform emission was reported. In this study, the effect of surface treatment and emission properties of a 4.5 in. SWNT and a MWNT panel are presented.

II. EXPERIMENT

MWNTs and SWNTs were synthesized in a conventional dc arc-discharge system under a helium environment of 360 Torr.10 CNTs were formed in the core of the cathode side. The resulting tubes were ground for 2 h in ethanol, followed by sonification for 20 min in 80 °C water. After evaporation of the ethanol, the sample was placed in distilled water and boiled to break the nanotube clusters by bubbling of the ethanol. After breaking the nanotube clusters, amorphous and graphitic particles were purified by annealing. Annealing was carried out in the rolling tube for effective catalysis with air for 40 min at 760 °C. SWNTs were purified in a solution of sulfuric and nitric acid (1:1) at 100 °C. The purified SWNTs were dispersed in isopropyl alcohol (IPA) by sonification. The SWNTs were cut into pieces 0.5–2 μm long.

For a large area flat panel display, a CNT cathode was fabricated by the slurry squeeze technique. For good electric-

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Fig. 1. Experimental setup of field emission measurements using a diode structure. The anode covered with green phosphor is more than 200 μm from the cathode. (a) Anode structure of the ITO electrode and 3–7 μm phosphor; (b) cathode structure of a 4 μm Ag electrode and the nanotubes.
Fig. 2. HRTEM images of (a) a MWNT and (b) a SWNT.

Fig. 3. (a) Raman spectra taken with 632.8 nm excitation MWNT of (a) and (b) SWNT samples.

$\text{In}_2\text{O}_3$ was mixed into the phosphor to reduce the effect of charging. Figure 1 is a schematic of the experimental setup for field emission characterization. The spacing between the anode and cathode was maintained by a 200 $\mu$m alumina spacer and the emission current was characterized in the range of 0–1600 V by dc mode. The MWNTs and SWNTs were characterized using scanning electron microscopy (SEM) (Hitachi S-4700) and high-resolution transmission electron microscopy (HRTEM). Micro-Raman spectroscopy (Renishaw micro-Raman 2000) was also used with 632.8 nm excitation wavelength of a He–Ne laser.

III. RESULTS AND DISCUSSION

Figure 2 shows a HRTEM picture of the MWNTs and SWNTs. The MWNTs are 1–2 $\mu$m in length with a 20 nm outer diameter and the SWNTs are formed as bundles with 1.5 $\mu$m diameters. Figure 3 shows the Raman spectra of MWNTs and SWNTs. The $G$ lines near 1581 cm$^{-1}$ for the MWNTs and 1590 cm$^{-1}$ for SWNTs, indicating the formation of a graphitic sheet, are clearly seen. The peak near 1300 cm$^{-1}$ originates from either carbonaceous particles or defective carbon from the graphite sheet.$^{12,13}$ Prominent low energy peaks at 169 and 181 cm$^{-1}$ for the SWNTs are radial breathing modes, whereas these peaks are greatly suppressed in the case of MWNTs. The peak at 1780 cm$^{-1}$ results from
second order Raman scattering of the breathing modes and G lines. Peaks ranging from 400 to 1000 cm\(^{-1}\) are usually observed in SWNTs and could be related to the finite length of the nanotubes.\(^{13}\) Figures 4(a) and 4(b) show SEM images of MWNTs before and after surface treatment. Micrometal powder 0.1–0.2 \(\mu\)m in size has mixed with MWNTs on the film surface before treatment, as shown in Fig. 4(a). The micrometal powder on the uppermost film surface was roughly removed and the MWNTs are exposed following a specific surface treatment, as shown in Fig. 4(b).\(^{9}\) The density of aligned MWNTs is approximately 2/\(\mu\)m\(^2\). Figures 5(a) and 5(b) show SEM images of SWNTs before and after surface treatment. The micrometal powder was clearly removed and aligned perpendicular to the anode by a special surface treatment, shown in Fig. 5(b). It seems that the SWNT tips, having been under the micrometal powder, became erect as a result of their elastic property after the metal powder was removed. Although the exact number of tips per unit area was not counted, it was observed that the aligned SWNT tips were uniformly distributed, with densities of 5–10 \(\mu\)m. On the other hand, the distribution of aligned MWNTs was less uniform than that of SWNTs. Figure 6 shows emission current as a function of the applied voltage of MWNTs. The onset electric field of MWNTs decreased from 6.4 to 3 V/\(\mu\)m through surface treatment. Removing metal powder from the uppermost surface and aligning the CNTs increased the emissivity and, moreover, reduced the turn-on field. The inner diagram in Fig. 6 is a Fowler–Norheim (FN) plot before and after surface treatment. Tips

**Fig. 4.** SEM micrographs of cross-sectional of a MWNT sample (a) before and (b) after surface treatment.

**Fig. 5.** Cross-sectional SEM micrographs of a SWNT sample (a) before and (b) after surface treatment.

**Fig. 6.** \(I–V\) characteristics of a MWNT sample using a diode structure. The Fowler–Norheim curve is plotted inside the \(I–V\) curve. The linearity at low current shows that the emission property follows the Fowler–Norheim equation.
Figure 4. Emission image of as-fabricated 4.5 inch CNTs-FED (a) and it’s field emission characteristic. Uniform emission image of surface treated 4.5 inch CNT-FEDs (c).
MWNTs has more fluctuation than SWNTs. This may come from the difference in shape and the number of emitting sites. In the case of SWNTs, an electric field was applied to one point of the tube end. However, MWNTs could have multipoints in the tip end along each wall, therefore, there could be fluctuation in the current stability curve. This also gives rise to twinkling of the luminescence in the emission. A gradual degradation over time was observed in both MWNTs and SWNTs which is different from our previous result. 17 We attributed the degradation to the ion bombardment of degassed ions. Under comparable initial experimental conditions, SWNTs degraded faster than MWNTs. SWNTs are susceptible to ion bombardment in single emitting regions, whereas MWNTs are more rigid through ion bombardment for multiemitting regions. Figure 9 shows emission images of a 4.5 in. MWNT and a SWNT panel. SWNT films have better emission uniformity than MWNT films. The difference in emission uniformity comes from the density of aligned tips per unit area. It depends on each CNT's properties and the degree of dispersion of the nanotubes, as verified by SEM observations. In order to obtain an image of uniform emission of MWNT films, additional experiments for dispersion of MWNTs will be done.

IV. CONCLUSION

CNT field emitters having good uniformity were developed using a slurry squeezing and surface rubbing technique. Removing metal powder from the uppermost surface and aligning the CNTs by a surface treatment enhanced the emissivity; moreover, it reduced the turn-on field to half the value. SWNTs showed better emission properties than MWNTs: lower turn-on voltage and higher emissivity. The low turn-on field of SWNTs was attributed to the stronger local electric field on the small tip radius. SWNT films show higher emission uniformity than MWNT films. This results from the fact that the aligned SWNT tips were more uniformly distributed than those of the MWNTs, as verified by SEM observations. SWNT films show less emission stability than MWNT films. We attributed this to the tip degradation.

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