Formulation of Carbon Nanotube Paste and Its Optimization for Field Emission Display Applications

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Abstract

Of the emissive display technologies, field emission displays using pasted carbon nanotubes offer several advantages over other competing cathode materials such as low driving voltage, possible large-area and low-cost processes. In this study, formulation of carbon nanotube paste and its electron field emission properties are characterized. Also the effects of additive powders and surface morphology on electron emission are reported.

1. Objectives and Background

Carbon nanotube (CNT)-paste is a promising technology for a large area field emission display (FED)[1] and paste formulation is its key technique for cold electron source with low turn-on voltage and high emission current. In addition, CNT-paste should be fine patterned for micro-precise patterns. The selection of additive fillers and frit glass powders for CNT-paste strongly affects the electron field emission properties and surface morphology.

In this report, some experimental results are given for the formulation of CNT-paste focused on the effects of additive powders and improvement of field emission characteristics induced by surface crack modification.

2. Results

For CNT-paste formulation, arc-discharged single-walled nanotubes (SWNTs) were pre-dispersed in isopropyl alcohol (IPA) by high speed homogenizer (~ 30 000 rpm). Organic mixtures of cellulose or acrylate were then mixed with the pre-mixed CNT/IPA solution. Intensive 3-roll milling was finally processed. Various powders such as oxides, metals, and frit glasses were added for fillers and adhesion improvement, respectively.

The paste of well-dispersed CNTs was printed onto Cr-deposited low-sodium glass (155x155 mm^2) through metal meshes with 20 μm in size. The optical microscopic image of

the printed CNT dots is shown in Fig. 1.

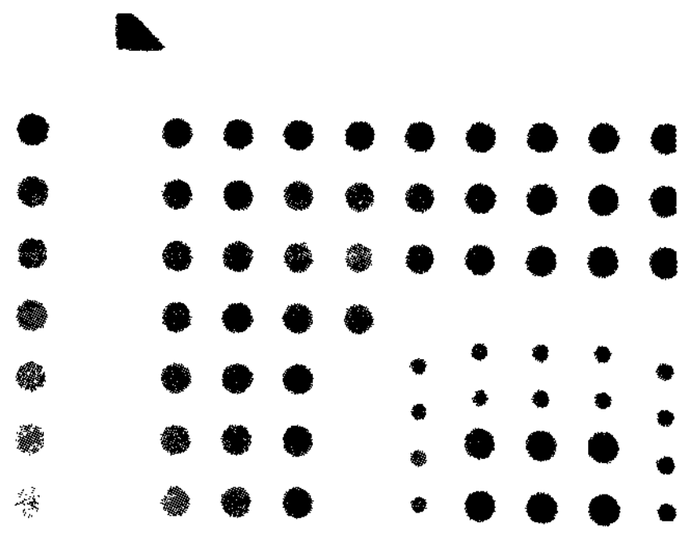
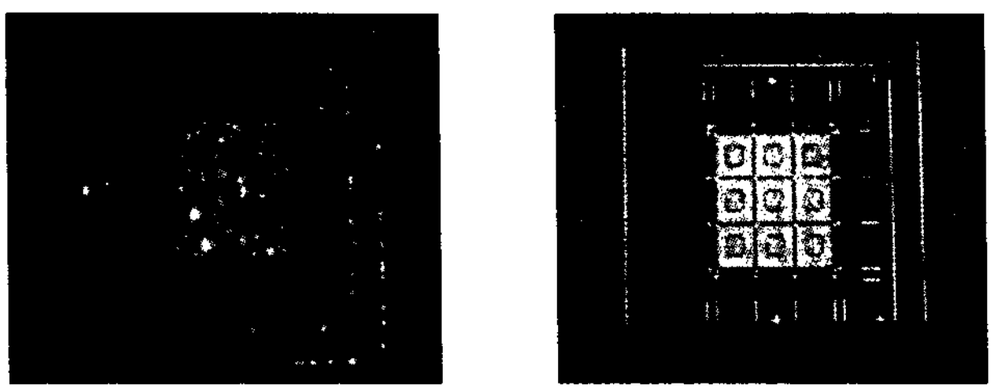


Figure 1. An optical microscopic image of printed dots with 100 ~ 400 μm in diameter

After 2-step firing at 350 °C in air and 400 ~ 450 °C in N_2 each for 30 min, electron emission characteristics were observed in a vacuum chamber at 5 x 10^{-6} Torr. The anode was 80 x 100 mm^2 phosphor coated on the ITO/glass substrate. The cathode-anode gap was spaced at 500 μm.

In general, pasted CNTs are poor electron emitters without special post-treatment. Adhesive taping [2] is a simple technique to activate CNT paste for electron emission. Fig. 2 shows the effect of taping treatment on the CNT cathode.



(a) (b)

Figure 2. Phosphor images from cathodes: (a) before and (b) after adhesive tape treatment.

After taping, the emission current was increased noticeably and most of the CNT dots contributed to electron emission.

The filler materials examined in the present study were indium tin oxide (ϕ 17 ~ 250 nm), SiO_2 (ϕ 800 nm), TiO_2 (ϕ 250 nm) and Ag (ϕ 2 μm). Effects of fillers on the emission current – applied voltage (I-V) are summarized in Fig. 3.

Conductive fillers showed more efficient electron emission than insulator ones. Nevertheless the powder size effect is not apparent from this result we believe that the optimal fillers are conductive and spherical-shaped sub-micron oxide powders.

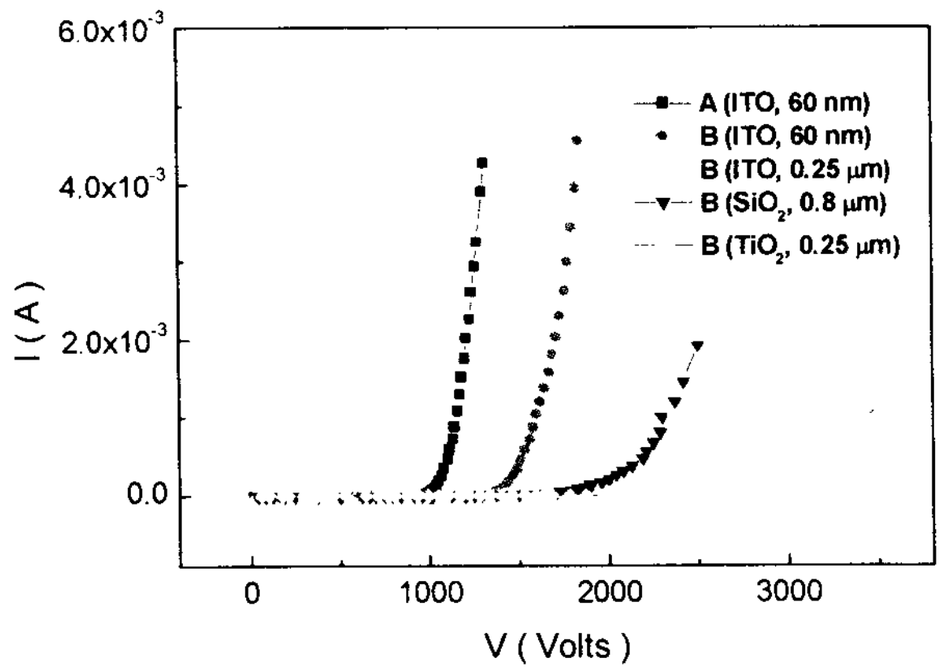
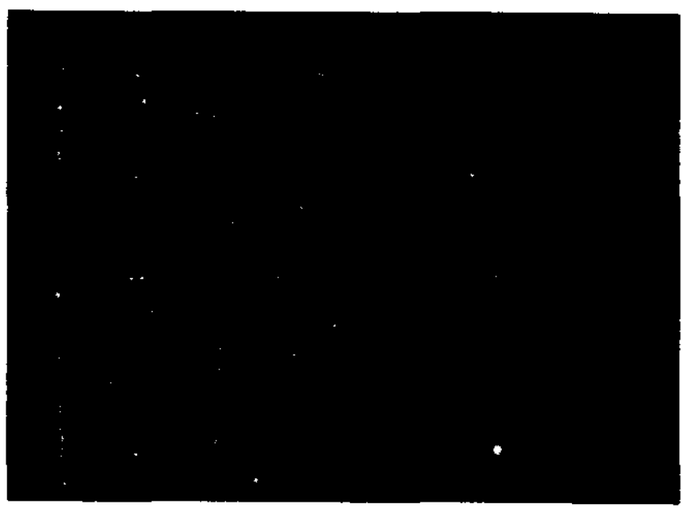


Figure 3. Additive filler effect on electron field emission. (Proportion of the fillers are fixed constant to organic binder: 20 wt%)

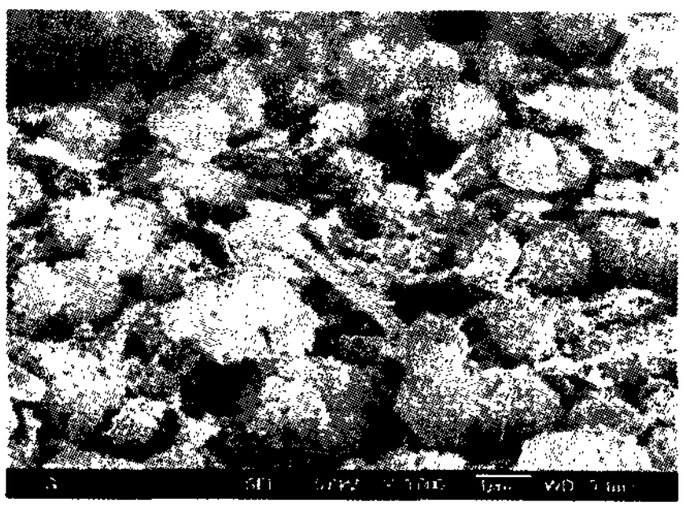
Too small sized (under 100 nm) fillers resulted in self-coagulation by themselves after thermal treatment, from which we could not obtain uniform surfaces. We also tested Ag powders to improve the contact resistance.

However, as shown in Fig. 4 (a), the emission image was very poorly demonstrated in the case of Ag addition. Analysis of scanning electron microscopy confirmed that most of the CNTs were disappeared after paste sintering process.[Fig. 4 (b)] From this result, it is thought that Ag can acts as an oxidizing agent of CNTs, thereby degrading the CNTs during thermal process in air environment at as low as 300 °C for organic binder burn-out.

During burn-out process, surface micro-crack occurred on the cathode surfaces, and from which, without other special post-treatment such as taping, an excellent emission image was obtained from them.[Fig. 5 (a)]



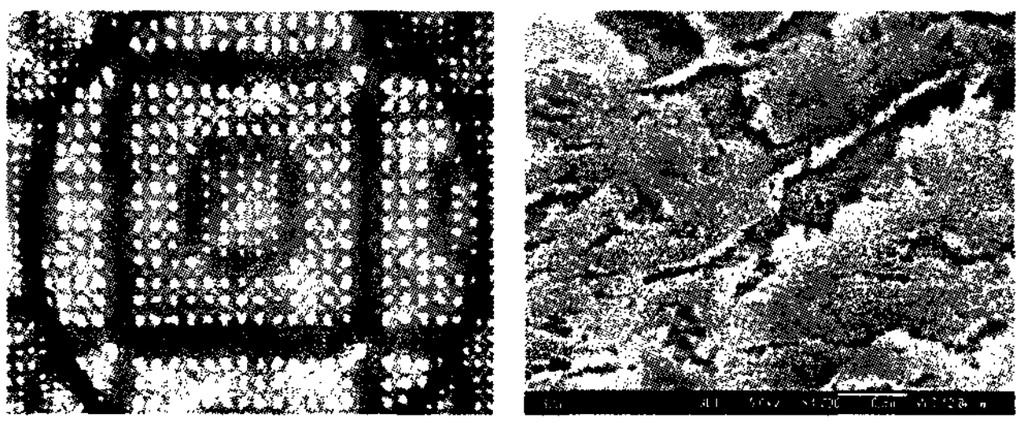
(a)



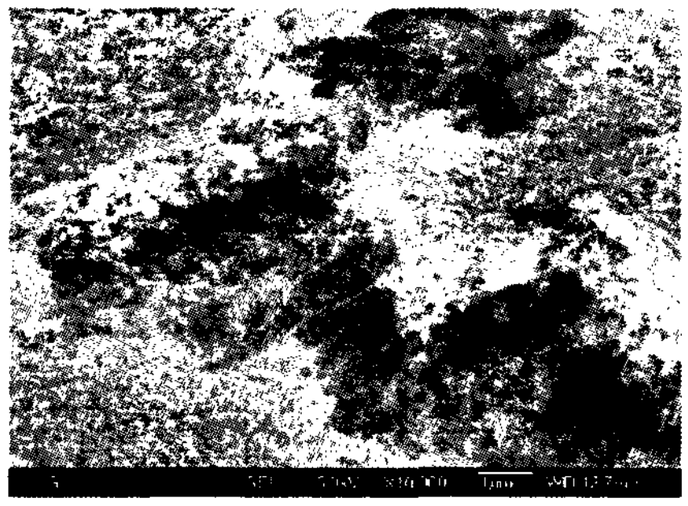
(b)

Figure 4. Electron emission degradation by Ag addition. (b) Scanning electron microscopic image confirms CNT degradation.

This remarkable improvement is caused by surface outcrop of CNTs between micro-cracks and these cracks are formed during thermal process of CNT paste; A kind of thermal shock by temperature rising or falling. The length and width of the surface micro-cracks are dependent on the filler size/shape/material, temperature cycling, and ramp-rate during thermal process.



(a) (b)



(c)

Figure 5. Enhanced electron emission image from a CNT cathode (a), which is due to the surface micro-cracks (b). Magnified image of a micro-crack revealed that large number of CNTs pop their head out of the cracks (c).

3. Conclusion

We have investigated the effects of additive

fillers for the formulation of CNT formulation. It was found that the electron emission properties were remarkably enhanced by surface micro-crack formation without any post-treatment.

References

[1] C. G. Lee, *et al.*, "32-inch Under-Gate CNT Cathode for Large TV Applications.", IVMC' 02.

[2] T. J. Vink, M. Gillies, J. C. Kriege, and H. W. J. J. van de Laar, Appl. Phys. Lett. **83**, 3552 (2003).