Field Emission properties of photosensitive carbon nanotube paste with different inorganic binders

Jae-Hong Park, Jin-San Moon, Jin-Soo Jeong, Ji-Beom Yoo[a)], and Chong-Yun Park

Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon, Korea

Joong- Woo Nam, Jong Hwan Park, and Deok Hyeon Choe

Corperate R&D Center, Samsung SDI, Yongin, Korea

[a)] Corresponding author; Tel: +82-31-290-7396, E-mail: jbyoo@skku.ac.kr

Abstract

We report effects of inorganic binder on the emission properties of CNT paste for low cost and high low-cost and large area field emission devices or displays. Two types of photosensitive carbon nanotube (CNT) paste were formulated by using of glass frit and spin on glass (SOG) as an inorganic binder and investigated their emission properties according to inorganic binders and firing conditions.

Introduction

Carbon nanotube (CNT) paste has been proposed as a capable technology for low-cost and large area field emission display (FED) [1]. The screen-printing of CNT paste has been adopted to form the large area cold cathode panel due to low cost, simple process, uniform emission site, and mass production [2].

For high resolution FEDs, the development of micro-patterning process is necessary. The screen-printing process has some limitations in terms of obtaining fine-pitched patterns due to the inherent paste rheology. When a photosensitive CNT paste and photolithography technique such as backside exposure and development is used, however, a much smaller pattern size can be obtained [3,4]. Photosensitive CNT paste is typically synthesized by mixing of CNT powders, inorganic binders, organic vehicles, photosensitive monomers, photosensitive oligomers and photo initiators.

Inorganic binder affects adhesion and film formation of CNT paste after firing. The selection of binder materials is very important for stable and uniform field emission. In this study, we focused on the suggestion of a suitable inorganic binder for photosensitive CNT paste.

Experiments

To investigate emission properties depending on the inorganic binders, two types of photosensitive CNT paste were formulated by using of glass frit and spin on glass (SOG) as an inorganic binder. Multi-walled CNTs (MWNTs) powders grown by CVD and acryl based organic solution were used as an electron emission source and organic vehicle, respectively. To form photosensitive organic vehicle, acryl was dissolved in terpineol and mixed with photosensitive additives such as photosensitive monomers, photosensitive oligomers and photo initiators. The glass frit is glass powder with diameter of a few μm and typically used as inorganic binder. SOG is a type of glass that can be applied as a liquid and cured to form a layer of glass similar to SiO_2. SOG is originally employed in the planarization coating as smoothing layer, and dielectric materials for integrated circuit manufacturing.

The mixture of CNT powders, organic vehicles and inorganic binder was pre-mixed through solder paste softener for 15 min. Then the three-roll mill process was carried out for mixing and dispersion of CNT powders in organic vehicle as polymer matrix. The mechanically well-dispersed CNT pastes were screen-printed onto an indium tin oxide (ITO) coated glass through a metal mesh and subsequently dried at 90 °C for 15 min in a forced convection oven. For uniform thickness and patterning of CNT emitter, backside ultraviolet (UV) exposure and organic solvent development techniques were applied. After the UV exposure process, CNT paste films were etched away by a spraying process (development) using organic solvents. The CNT paste was simply patterned because of the difference in solubility between UV exposed region and unexposed region. The residue of organic vehicle leads to problems such as out-gassing and arcing during a field emission measurement. Organic materials in paste have to be removed in order to obtain the stable emission characteristics. Therefore, CNT emitters were fired at 400 ~ 450 °C in air or nitrogen (N_2).

Field emission scanning electron microscopy (FESEM) was employed for the characterization of CNT paste and the emission characteristics of screen-printed CNT FEA were measured in a vacuum chamber with a parallel diode-type configuration at a base pressure of 5×10^{-6} Torr.

Results and discussion

Figure 1 shows FESEM images of screen-printed photosensitive CNT paste films after firing under different firing conditions. The firing temperature for photosensitive CNT paste changed from 400 to 450 °C under air or N_2 ambient. The CNT paste films easily formed a uniform thick film after backside exposure and firing process. The thickness of CNT paste films is under 2 μm. In our previous report [5], we confirmed that the CNT paste with a glass frit showed poor uniformity of the cathode layer and lower density of CNTs after firing at 450 °C in an air ambient. In case of the photosensitive CNT paste with a glass frit, however, uniform cathode layers were obtained although firing was carried out at relatively high temperature of 450°C in an air ambient. It may be suggested that the photosensitive CNT paste has better oxidation resistance and thermal stability than that of conventional paste because organic vehicle and photosensitive additives were strongly cross-linked by photo polymerization during the UV exposure process.

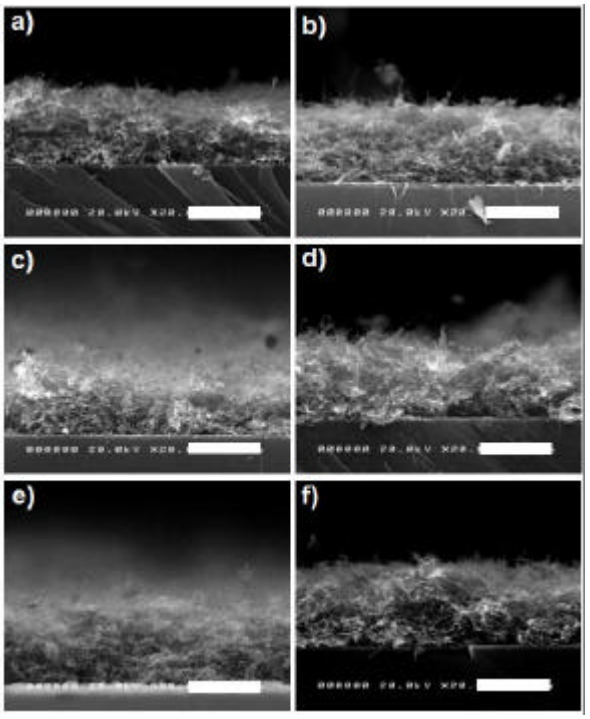

Figure 1. SEM images of screen-printed CNT paste films with different inorganic binder after firing at (a), (b) 400°C in air, (c), (d) 450°C in air, and (e), (f) 450°C in N_2. (a), (c) and (e) are CNT paste with frit. (b), (d) and (f) are CNT paste with SOG. All scale bars represent 1.5 mm equally.

Emission properties of printed CNT emitters with different inorganic binders depending on firing conditions were evaluated. For current-voltage (I-V) characteristics, five different samples were prepared. The I-V characteristics of CNT emitters were measured in a high vacuum chamber ($< 5 \times 10^{-6}$ Torr) with a parallel diode-type configuration. We have adopted pulsed voltage supply with a duty cycle of 1/500. An ITO coated glass was used as the anode and the distance between anode and cathode was maintained at 200 μm using a glass spacer. As-prepared CNT emitters showed very poor emission characteristics because of insufficient CNT emitter density. Therefore special surface treatments, called surface activation, was required using different methods such as adhesive taping, soft rubber rolling, focused ion beam, laser irradiation, ion irradiation, etc [6-9]. To protrude the buried CNTs on surface by the removal of covered layer, we applied the adhesive tape technique.

The emission properties from activated samples were shown in Figure 2. Figure 2(a) and (b) indicated an applied electric field to obtain the current density of 300 μA/cm^2 and a current density when applied the electric field was 5 V/μm, respectively. The emission properties from photosensitive CNT paste with SOG were better than those of photosensitive CNT paste with a glass frit. Two types of CNT pastes have similar emission properties when fired at 400 °C in an air ambient or 450 °C in a N_2 atmosphere. However, when fired at 450 °C under an air atmosphere, there are some differences in the emission properties between two types of photosensitive CNT pastes. When inorganic binder was changed from frit to SOG, an electric field at the emission current of 300 μA/cm^2 was decreased from 6.2 to 5.34 V/μm. A current density when an electric field was 5 V/μm increased from 104 to 192.5 μA/cm^2 as inorganic binder changed from frit to SOG. The maximum emission current densities were obtained from CNT emitters fired at 450 °C in an N_2 ambient. When firing temperature decreased from 450 to 400 °C in an air ambient, the emission property of CNT paste was enhanced. The reason for enhanced emission is that the effective emission sites for field emission were increased after firing because of decrease in thermal damage and oxidation of CNTs. In other words, high temperature firing over 450 °C in air can degrade CNTs, resulting in decrease in the emission site density and increase in defects on the surface of CNTs.

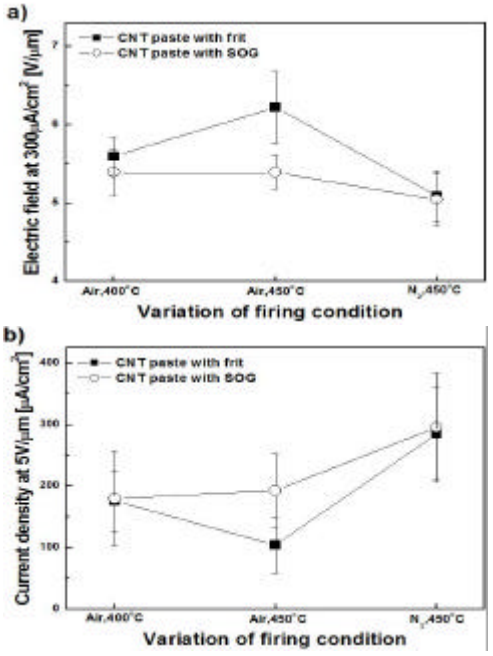

Figure 2. Variations of emission properties of CNT paste with different firing condition depending on the inorganic binders : (a) an applied electric field to obtain the current density of 300 μA/cm^2 and (b) a current density when applied the electric field of 5 V/μm.

Conclusions

CNT paste films with different inorganic binders were prepared and their emission properties were evaluated depending on firing condition. The emission properties of CNT emitters with SOG were better than those of CNT emitters with a glass frit. Particularly, the emission properties of photosensitive CNT pastes with SOG were stable and uniform after firing at relatively high temperature of 450 ^{o}C under N_2. It is concluded that SOG is more suitable inorganic binder than glass frit for photosensitive CNT paste.

Acknowledgment

This research was funded by the Ministry of Industry and Energy of Korea and Korea Science and Engineering Foundation (KOSEF) through the Center for Nanotubes and Nanostructured Composites (CNNC) at Sungkyunkwan University.

Reference

[1] N. S. Lee, D. S. Chung, I. T. Han, J. H. Kang, Y. S. Choi, H.Y. Kim, S. H. Park, Y. W. Jin, W. K. Yi, M. J. Yun, J. E. Jung, C. J. Lee, J. H. You, S. H. Jo, C. G. Lee, J. M. Kim, *Diamond Relat. Mater.*, **10**, 265 (2001).

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

[3] Y. R. Cho, J. H. Lee, C. S. Hwang, Y. H. Song, H. S. Uhm, D. H. Kim, S. D. Ahn, C. H. Chung, B. C. Kim, K. I. Cho, *Jpn. J. Appl. Phys.*, **41** (2002) 1532.

[4] Y. S. Choi, Y. S. Cho, J. H. Kang, Y. J. Kim, I. H. Kim, S. H. Park, H. W. Lee, S. Y. Hwang, S. J. Lee, C. G. Lee, T. S. Oh, J. S. Choi, S. K. Kang, and J. M. Kim, *Appl. Phys. Lett.*, **82** (2003) 3565.

[5] J. H. Park, J. H. Choi, J. S. Moon, D.G. Kushinov, J. B. Yoo, C. Y. Park, J. W. Nam, C. G. Lee, J. H. Park, D. H. Choe, *Carbon* **43** (2005) 698.

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

[7] Y. C. Kim, K. H. Sohn, Y. M. Cho, E. H. Yoo, *Appl. Phys. Lett.* **84** (2004) 5350.

[8] W. Zhao, N. Kawakami, A. Sawada, M. Takai, *J. Vac. Sci. Technol.* B **21** (2003) 1734.

[9] D. H. Kim, C. D. Kim, H. R. Lee, *Carbon* **42** (2004) 1807.