Synthesis and Properties of Carbon Nanotube Paste with Different Inorganic Binders for Field Emission Display

Jae-Hong Park[1], Jin San Moon[1], Joong-Woo Nam[1, 2], Jonghwan Park[2], A.S. Berdinsky[1, 3], Ji Beom Yoo[1*], C.G. Lee[2] and Chong Yun Park[1]
[1]Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Korea;
[2]Technology Development 3, Corperate R&D Center, Samsung SDI, Korea;
[3]Novosibirsk State Technical University, Russia
Phone : +82-31-290-7413 , E-mail : jbyoo@skku.ac.kr

Abstract

CNT pastes with different inorganic binder such as glass frit and spin on glass (SOG) were synthesized by using multi-walled nanotube (MWNT) grown by CVD. The uniformity of cathode layer after firing was enhanced and the emission current density at an applied field of 7.95V/µm increased from 133µA/cm² to 265µA/cm² when inorganic binder changed from glass frit to SOG. The emission properties of CNT pastes with SOG were stable and uniform although firing was carried out at relatively high temperature of 450°C under air. It is concluded that SOG is more suitable inorganic binder than glass frit for field emission application.

1. Introduction

Field emission displays (FEDs) has characteristics of superior display performances such as fast response time, wide viewing angles, wide temperature range of operation, cathode ray tube-like colors, ultra slim features, low cost and low power consumption, etc [1]. CNTs have been one of the most actively studied materials for cold cathode emitter. Due to their geometrical properties (e.g. high aspect ratios and small tip radii of curvature) and good chemical and thermal stability, CNTs exhibit excellent field emission characteristics [2-5]. Recently, the direct growth method such as chemical vapor deposition (CVD) and the screen-printing method using CNT powders were used for fabrication of field emission array (FEA)[6-9]. However, CVD techniques have problems in controlling each CNTs, complicated process, high cost and high growth temperature. Therefore, the screen-printing process using CNT paste has been adopted to form the large area cold cathode due to low cost, simple process, uniform emission site and mass production. In order to enhance adhesion between CNT paste film and substrate after firing process, various inorganic binders were used. In this study, CNT pastes were prepared by using different inorganic binder such as glass frit and SOG. Then we compared the microstructures of CNT pastes with different inorganic binders and their field emission characteristics.

2. Experimental

CNT paste for FED is composed of CNT powder, inorganic binder and organic vehicle. MWNT powders produced by CVD were used as electron source. Glass frit of solid phase and SOG of liquid phase were used as inorganic binder to enhance adhesion of cathode layer. And organic vehicle was prepared by mixing of ethyl cellulose and terpineol. Mixture of CNT powders, organic vehicles and SOG were pre-mixed through solder paste softener for 20 min. then CNT paste dispersed in organic matrix by three-roll milling processing for 3 times. Mechanically well-dispersed CNT paste was printed to form patterned size of 1 × 1 cm² on an indium thin oxide (ITO) coated soda lime glass. Organic vehicle plays an important role in printing characteristic and viscosity of CNT paste. In order to remove the organic vehicles in CNT paste, heat treatment was performed in a tube furnace in an air atmosphere. A surface treatment using adhesive tape was used to make the CNT protrude from the surface. The emission characteristics were measured in a vacuum chamber with a parallel diode-type configuration at 5 x 10^{-6}Torr. Field emission scanning electron microscopy (FESEM) was employed for the analysis of the morphology of CNT paste after firing.

3. Results and discussion

Figure 1 shows FESEM images of CNT paste with different inorganic binder. When we changed inorganic binder from glass frit to SOG, the morphology of cathode layer showed a big difference between glass frit and SOG after firing at 450℃ under air atmosphere. Figure 1 (a) and (b) are top and cross-sectional view of CNT paste with glass frit. We can observes small amount of CNTs and partially melted glass frit.

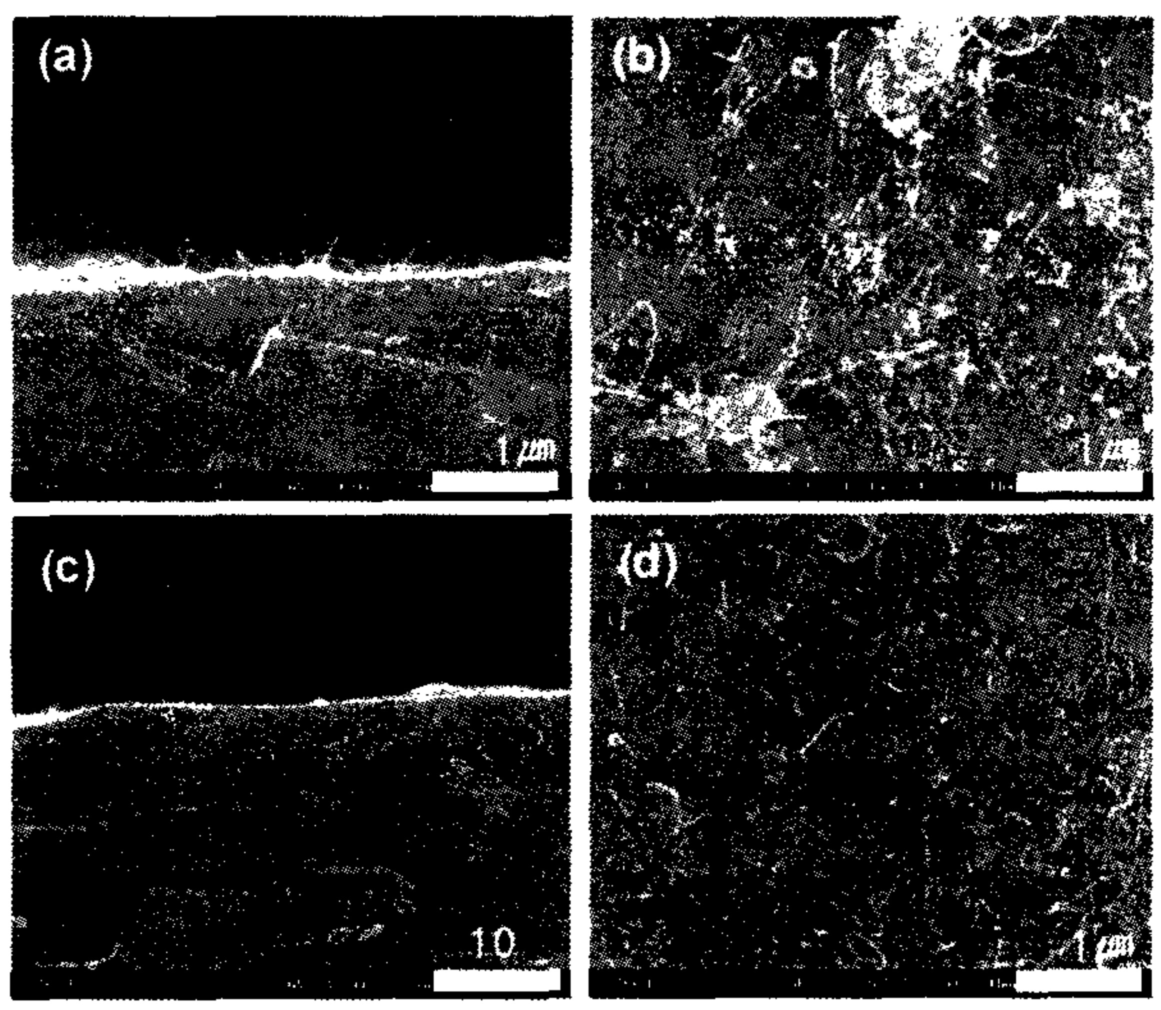

Figure 1. FESEM images of CNT paste with different inorganic binder; (a) top and (b) cross sectional view of CNT paste with frit, (c) top and cross-sectional view of CNT paste with SOG

Because not only organic materials but also CNT powder were mostly burned out during heat treatment, the cathode layer has shown the poor uniformity. Therefore, in case of glass frit, the optimization of firing condition such as inert gas atmosphere and relatively low temperature was required to get uniform cathode layer. However, CNT paste with SOG formed easily uniform thick film without optimization of firing condition. Figure 1 (c) and (d) are top and cross-sectional view of CNT paste with SOG. Film thickness is about 7.1µm.

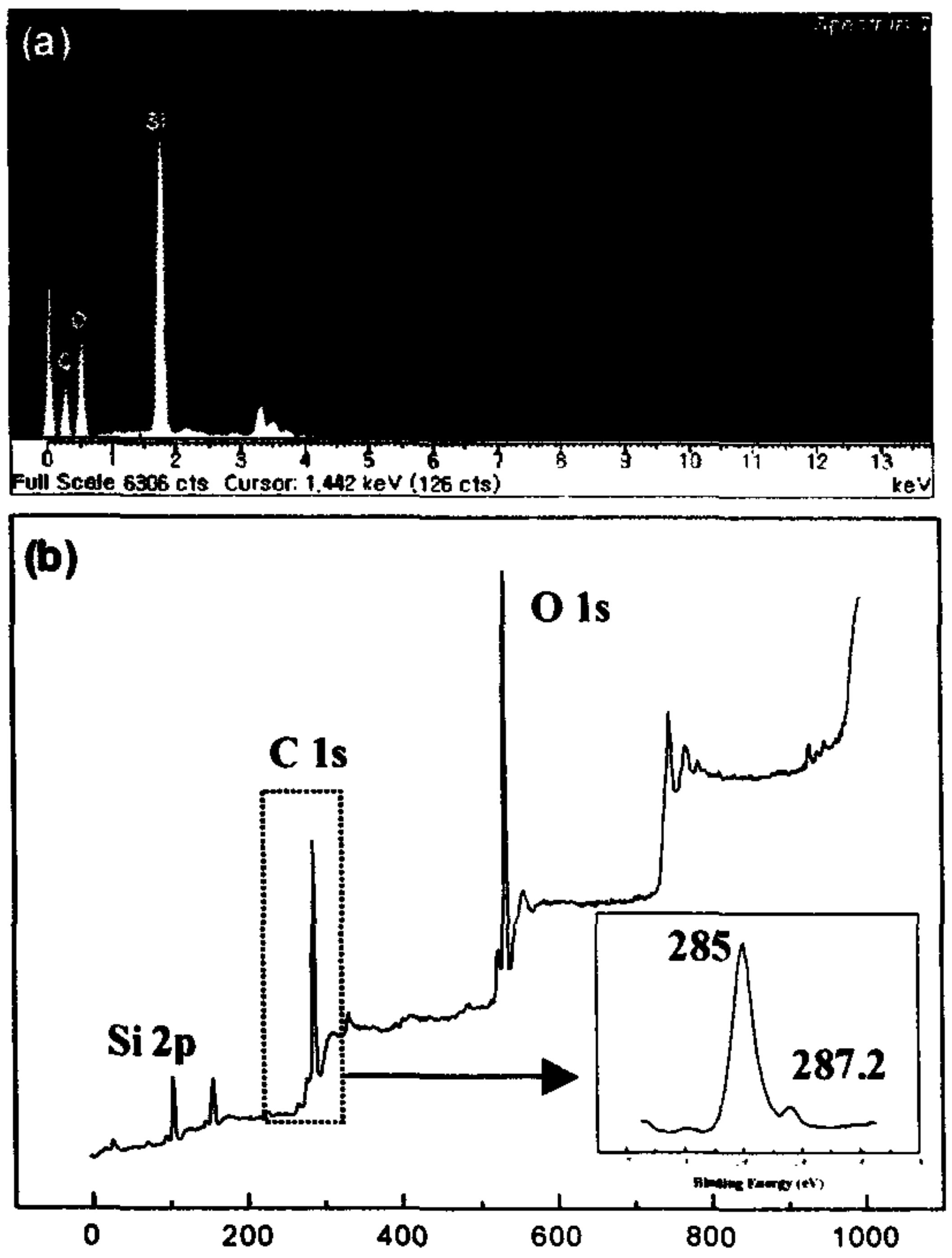

Figure 2. EDX data and XPS spectrum of CNT paste after sintering. Inset of (b) was magnification of the peak of C 1s.

For analysis of chemical composition and bonding state in the surface of CNT paste film, EDX and XPS were employed. Si (K_α, 1.74 keV), O (K_α, 0.52 keV) and C (K_α, 0.28 keV) peaks were clearly appeared in an EDX spectrum, in Figure. 2 (a). Compositions of the top and bottom part of CNT paste film were almost same (not shown here). The peak of Si and O were uniformly existed in the whole of paste film. It was shown that SOG was more easily dispersed in matrix than frit due to liquid phase.

Figure. 2 (b) indicate a wide XPS spectrum from surface of CNT paste. The peak of Si 2p, C 1s and O 1s was clearly shown. The pick at 103.7 (Si 2p) and 533.2 eV (O 1s) indicate bonding energy of Si-O. The curve was fitted using of Gaussian function. Two peaks at 285 eV and 287.2 eV in C 1s position indicate the bonding state of $C_6H_5CH_3$ (C^*-H) and CH_3C^*N formed by remained resins, respectively. There are no C bonding states such as sp^2 and sp^3. Therefore, we confirmed that the surface of paste layer was covered with mixture of remained resin and silica after heat treatment at 450℃. In other words, SOG and residue of organic vehicle generated a shielding layer to prevent main component from being oxidized int the CNT paste film surface. To obtain protrusion of CNT from matrix, for the high emission current and uniform emission site, screen printed CNT-FEA needs a special surface treatment such as laser irradiation, ion irradiation and surface rubbing [7-9]. We carried out activation treatment using adhesive tape for good emission and removal of shielding layer. Then, the emission characteristics of CNT paste were measured in a high vacuum chamber with a parallel diode-type configuration at pressure of 5×10^{-6} Torr. We have adopted pulsed DC with a duty cycle of 1/500. Emission area was 2cmx2cm and spacing between cathode and anode was 200µm. Figure 3 shows I-V curve and F-N plot of activated CNT paste films containing glass frit and SOG. The emission current density at an applied field of 7.95V/µm increased from 133µA/cm^2 to 265µA/cm^2 when inorganic binder changed from glass frit to SOG. Because oxidation of CNT was decreased and uniformity of cathode layer was increased due to effect of the shielding layer, the emission property of CNT paste with SOG was better than that of glass frit.

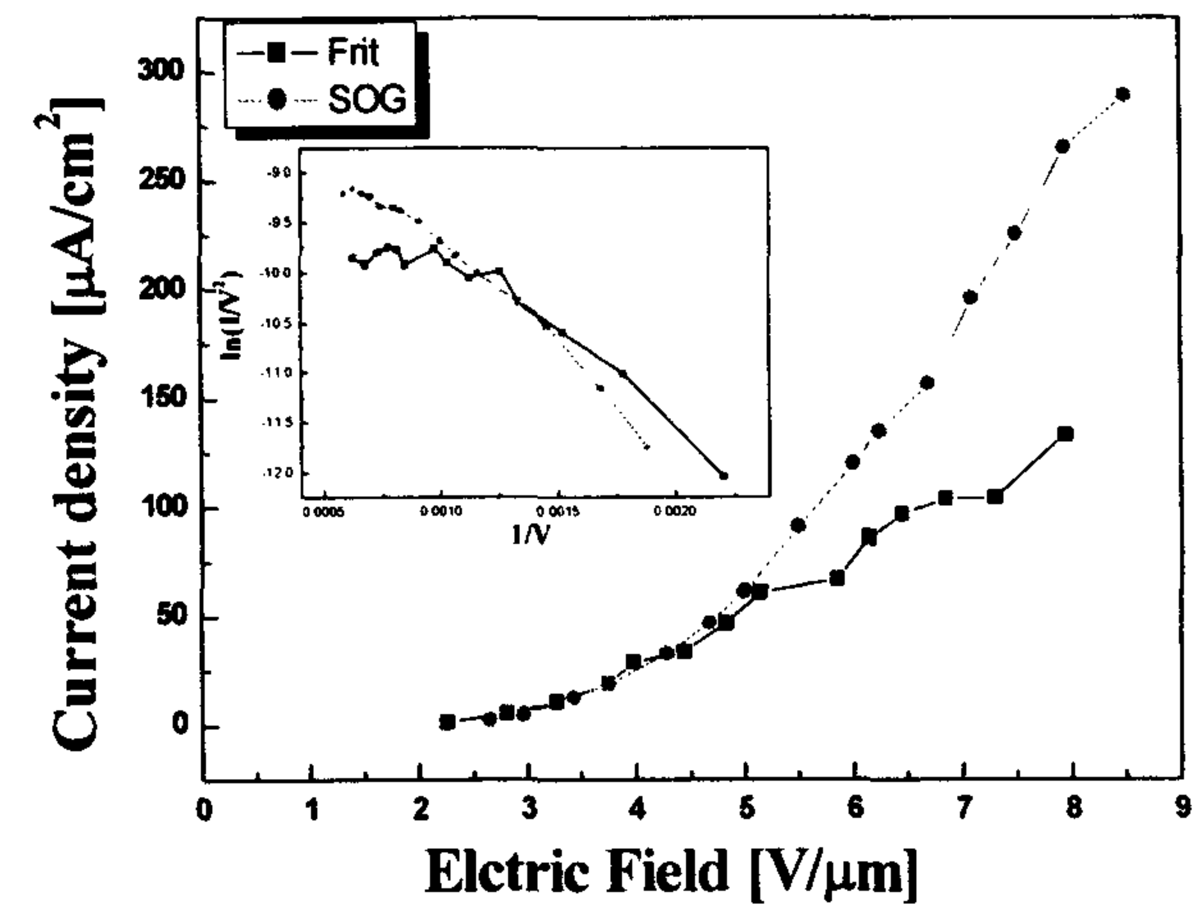

Figure 3. I-V characteristics of CNT paste with different inorganic binder. Inset indicates the Fowler-Nordheim plot.

4. Conclusion

CNT paste was synthesized by using SOG as inorganic binder instead of glass frit. The SOG, as an inorganic binder, has many advantages, which assist to get uniform cathode layer, good dispersion and adhesion of CNT. Emission current density of CNT paste with SOG was also improved. The emission current density was increased to 265µA/cm^2 at an applied field of 7.95V/µm. Our experiments have shown that SOG can be used as an efficient inorganic binder of CNT paste for field emission display. The emission properties of CNT pastes with SOG were stable and uniform although firing was carried out at relatively high annealing temperature of 450℃ under air. It is concluded that SOG is more suitable inorganic binder than glass frit for FED application.

5. Acknowledgment

This research was supported by a grant (M1-02-KR-01-0001-02-K18-01-016-1-2) from Information display R&D Center, one of the 21st Century Frontier R&D program funded by the Ministry of Science and Technology of Korea government and KOSEF through CNNC.

6. References

[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, and J.M. Kim. Diamond and Related Materials, vol. 10, 265 (2001)

[2] Baughman, R. Science 297, 787 (2002)

[3] X. Zhang, R. Liu, T. V. Streekumar, S. Kumar, V. C. Moore, R. H. Hauge and R. E. Smalley. Nano Lett 3, 1285 (2003)

[4] 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, and J. M. Kim. Appl. Phys. Lett 75, 3129 (1999).

[5] S. J. Tan, A. R. M. Verschueren, and C. Dekker. Nature (London) 393, 49 (1998)

[6] Jean-Marc Bonard, Kenneth A. Dean, Bernard F. Coll and Christian Klinke. Phys. Rev. Lett 89, 197602 (2002)

[7] W. J. Zhao, N. awakami, A. Sawada, and M. Takai. J. Vac. Sci. Technol. B 21, 1734 (2003)

[8] Do-Hyung Kim, Hoon-Sik Jang, Chang-Duk Kim, Dong-Soo Cho, Hee-Dong Kang, Hyeong-Rag Lee. Chem. Phys. Lett 378, 232 (2003)

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