

Field Emission Characteristics of Carbon Nanotube Cathode Using Ag Nano-Powder as Bonding Materials

Young-Je An¹, Sang-Hoon Ha¹, Young-Jun Choi¹, Jiho Chang²
Hong Chan Lee³, Young-Rae Cho¹

¹Dept. of Materials Science and Engineering, Pusan National University, Busan, Korea
TEL: 82-51-510-2389, e-mail: yescho@pusan.ac.kr.

²Major of Semiconductor Physics, Korea Maritime University, Busan, Korea

³Dept. of Mechatronics Engineering, Korea Maritime University, Busan, Korea

Keywords : Carbon nanotube, Field emission, Nano-Ag particle, Sintering, Bonding material

Abstract

Carbon nanotube (CNT) cathodes were fabricated using nano-sized silver powders as a bonding material. The effects of powder size on the field emission properties for the CNT cathode were investigated. The better emission properties of CNT cathodes using smaller particles are due to a low sintering temperature of the bonding materials.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention among materials scientists because of their unique physical properties and their potential for application in field emission displays (FEDs). Recently, a number of screen-printed FED prototypes with CNT emitters have been demonstrated [1-3]. However, the CNT-FEDs have severe problems that must be solved in order to develop marketable products. Two of the most important issues are a low current density of field emissions and the degradation of CNTs during high temperature sintering of bonding materials [4-9]. The major role of bonding material is to serve as an electrical connection between the CNTs and the cathode [5,6]. Another role is to increase the field enhancement effects of CNTs when a dielectric material is used for bonding [6]. Therefore, the design of an optimal bonding material for high-efficiency CNT cathode is very difficult. In this study, we tried to design and demonstrate an optimal bonding material for screen-printed CNT cathodes by the addition of different-sized Ag particles to frit glass. The effects of the addition of nano-sized Ag particles to their bonding material on the field emission properties of CNT cathodes were discussed in view point of electrical connection between CNTs and cathode.

2. Experimental

CNTs used were multi-walled carbon nanotubes. Fig. 1 shows a schematic representation of the fabrication and characterization procedure for CNT cathode. First, CNT particles were suspended in a solution of IPA (isopropyl alcohol). A CNT solution was prepared by strong sonicating of CNT particles in an organic solution of IPA. By mixing the CNT solution and binder materials, a CNT ink was prepared. A CNT paste for screen-printing was fabricated by adding the CNT ink and an inorganic bonding material (frit-glass paste and silver particle). CNT patterns were produced using a screen-printing technique on ITO electrodes. The procedure for CNT cathode in detail was published in a previous work [6]. In this study, two types of CNT cathodes were prepared: frit glass (4010-A1, Electro Science Laboratories; paste type) and a composite made by adding 25 wt.% Ag particles to the frit glass. The samples were heat treated at 390 °C in order to remove the organic vehicles, and adhesive tape was used for surface treatment of the samples [10].

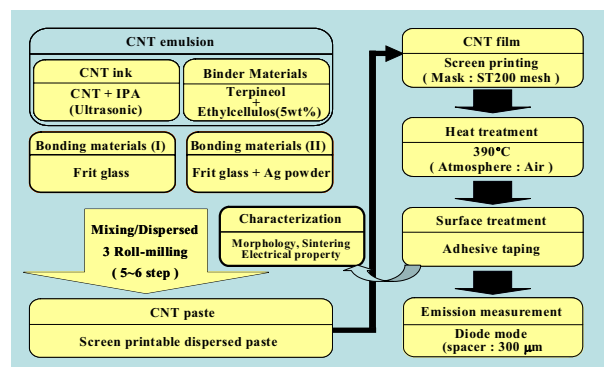


Fig. 1. A schematic diagram of the fabrication flow for carbon nanotube cathode.

For characterization of the CNT cathodes, the field emission properties and the surface morphologies of the bonding layers were investigated. The field emission properties of the CNT cathodes were measured in a diode mode using a high-vacuum chamber at a pressure of 1×10^{-6} Torr. The morphologies of CNT protrusion and the shapes of Ag particles after heat treatment were investigated using scanning electron microscopy (SEM). Furthermore, the sintering behavior of the bulk-type sample with nano-sized Ag particles, a shape of 10 mm in diameter and 2.4 mm in thickness by loading 120 bars, was characterized by means of SEM observation and 4-point probe measurement.

3. Results and discussion

Fig. 2 shows the current density of the CNT cathodes as measured in the diode mode in a vacuum chamber with respect to the different bonding materials. The emission current of the samples that contained only a frit glass in their bonding material showed about 0.7 mA/cm^2 at an electric field of $2.5 \text{ V}/\mu\text{m}$. However, the emission current for the samples that contained nano-sized Ag particles in their bonding material showed 0.85 mA/cm^2 and 1.1 mA/cm^2 , respectively. With respect to CNT-FEDs, the higher current density of CNT cathodes is a critical factor for high-brightness FEDs [5].

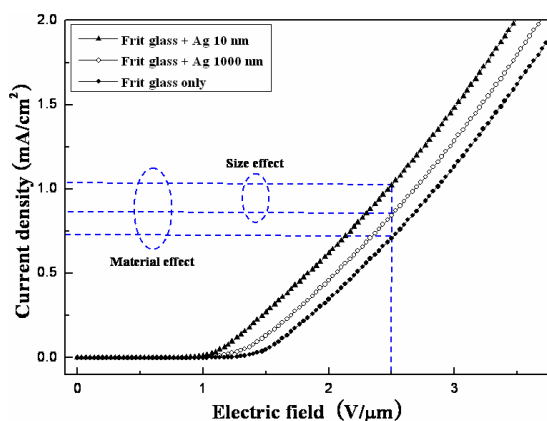


Fig. 2. Effects of bonding material on the field emission properties of screen-printed CNT cathodes measured in the diode mode of a high-vacuum chamber (distance between electrodes is $300 \mu\text{m}$).

Fig. 3 shows surface morphologies of samples after heat treatment at $390 \text{ }^\circ\text{C}$ and surface treatment by adhesive tape method. Fig. 3(a) and (c) represent the

SEM images from the sample for 10 nm sized-Ag particles. Fig. 3(b) and (d) are for the samples from 1000 nm sized-Ag particles. There is no distinct difference in microstructure as shown in Fig. 3. It is found that the thickness of screen-printed layer containing CNTs is measured about $10 \mu\text{m}$ as shown in Fig. 3(c) and (d). The composition of large particles (marked as F) and the small particles (marked as A) are characterized by using EDAX analysis. From the Fig. 4, the major component of the large particles (F) and the small particles (A) in Fig. 3 are identified as frit glass and Ag particles, respectively. The large peak of oxygen (O) may come from the several kind oxides such as PbO , SiO_2 and ZnO composing the frit glass. The weak peak of carbon (C) is probably due to an element composing CNTs.

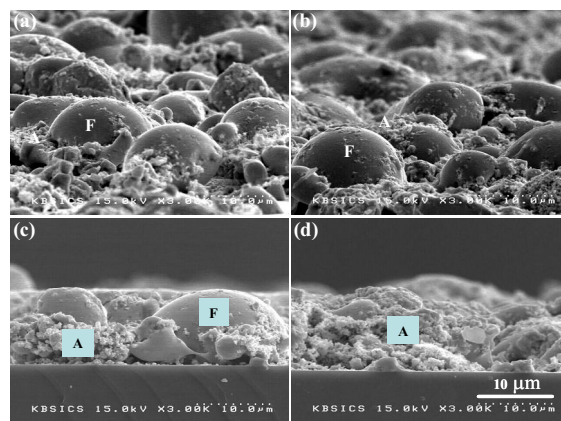


Fig. 3. SEM micrographs of surface morphology for CNT cathodes after heat treatment at $390 \text{ }^\circ\text{C}$ and surface treatment using a taping method : (a) and (c) with 10 nm Ag particles,

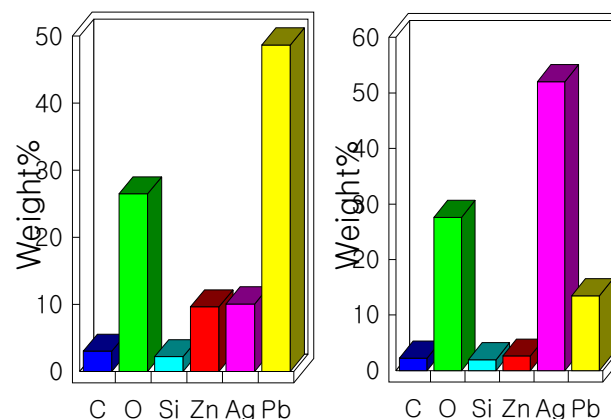


Fig. 4. Composition of the region F in Fig. 3 (c) and A in Fig. 3(d) with EDAX analysis.

Fig. 5 shows highly magnified SEM micrographs of samples for the region of A in Fig. 3(c) and (d). Though the composition of carbon in the region of A is very low as shown in Fig. 4(b), there exist a number of CNTs in the region of A. From this result, we can conclude that the CNTs are mixed with nano-sized Ag particles and the CNTs are protruded over the surface after surface treatment. Therefore, it is thought that the field emission property of CNT cathode is related to the density and height of protruded CNTs in the region of nano-sized Ag particles.

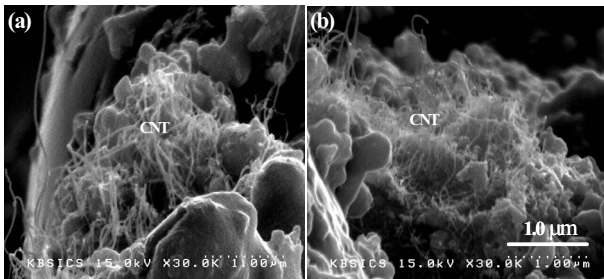


Fig. 5. SEM micrographs of samples for region A in Fig. 3 (c) and (d): (a) with 10 nm and at 390 °C, (b) with 1000 nm and at 390 °C.

As mentioned above, the major role of the bonding materials is to provide an electrical connection between the CNT and the cathode. To investigate the relationship between sintering temperature and particle size in a bonding material, the sintering behavior of nano-sized Ag particles was investigated using a disc-shaped (bulk-type) sample with observation by SEM image as shown in Fig. 6. The disc-shaped bulk sample was prepared via a pressing process and heat treatment using a paste formulation with Ag particles of 99 wt.% and an organic binder of 1 wt.%. Fig. 6(a) and (c) illustrate the SEM images of Ag samples 10 nm in diameter sintered at 290 and 390 °C, respectively. The sample heat-treated at 390 °C seemed to be sintered completely. However, the sample heat-treated at 290 °C showed only a partially sintered microstructure.

For the samples fabricated using 1000 nm sized-Ag particles, their microstructure when heat-treated at 290 °C clearly showed isolated Ag particles, as shown in Fig. 6(b). Though the sample heat-treated at 390 °C showed a mostly sintered microstructure, no sintered microstructure of Ag particles were also observed partly, as shown in Fig. 6(d). Many research groups have reported the effect of bonding material particle size on melting and sintering temperatures [6,11]. By comparing Fig. 6(a) and (b), it is obvious that the

sintering temperature of the 10 nm sample is much lower than that of the 1000 nm sample. A similar result was reported by Ide et al. while studying a metal-metal bonding process using Ag metallo-organic nano-particles [11].

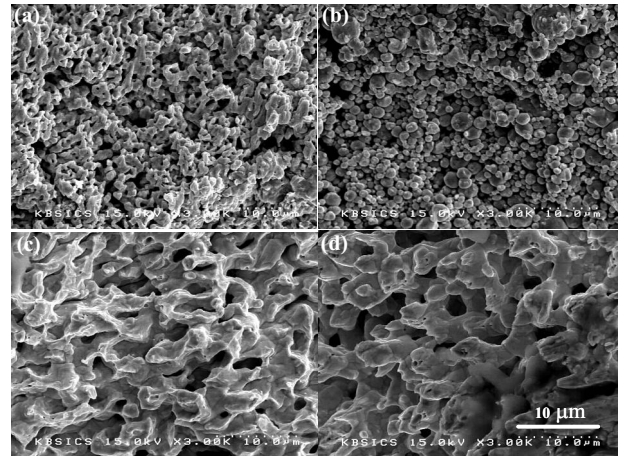


Fig. 6. SEM micrographs of bulked Ag samples fabricated by pressing with variable-sized particles at different temperatures: (a) with 10 nm and at 290 °C, (b) with 10 nm and at 390 °C, (c) with 1000 nm and at 290 °C and, (d) with 1000 nm and at 390 °C.

From the results in Fig. 2 and Fig. 3, it can be seen that the current density of CNT cathodes is dependent on the electrical conductivity of bonding materials after heat treatment at 390 °C. The reason samples made with 10 nm Ag particles have a higher current density is due to the higher electrical conductivity of binding materials. For the present study, a 4-point probe was used to measure the sheet resistance of 8 μm in thickness samples fabricated with the same composition using a similar fabrication procedure. The sheet resistance of the bonding material for the samples made from 10 nm and 1000 nm particles showed 0.5 kΩ/□ and 0.9 kΩ/□, respectively. Therefore, it is concluded that the higher current density of a CNT cathode using 10 nm particles is due to a lower sintering temperature and a better electrical contact between the protruded CNTs and the cathode.

4. Conclusions

Carbon nanotube cathodes (CNT Cathodes) were fabricated using frit glass and nano-sized silver (Ag) particles as a bonding material. The effects of particle

size on the sintering behavior, current density and emission image for a CNT cathode were investigated. As the diameter of an Ag particle decreases to as low as 10 nm, the sintering temperature also decreases due to a rise in the specific surface area of the Ag particle. Results from this study, we concluded that the better emission properties of CNT cathode using 10 nm particles is due to a better electrical contact between the protruded CNTs and the cathode.

Acknowledgement

This work was supported by grant No. (R01-2006-000-10436-0) from the Basic Research Program of the Korea Science & Engineering Foundation.

5. References

1. 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, 3129 (1999).
2. Y. Saito, S. Uemura, *Carbon* 38, 169 (2000).
3. P.S. Guo, T. Chen, Y.W. Chen, Z.J. Zhang, T. Feng, L.L. Wang, L.F. Lin, Z. Sun, Z.H. Zheng, *Soild State Electron.*, 52, 877 (2008).
4. 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, 1532 (2002).
5. Y. Qin, M. Hu, H. Li, Z. Zhang, Q. Zou, *Appl. Surf. Sci.*, 253, 4021 (2007).
6. H.Y. Shin, W.S. Chung, K.H. Kim, Y.R. Cho, B.C. Shin, *J. Vac. Sci. Technol. B*23, 2369 (2005).
7. J.H. Choi, S.K. Kang, J.H. Han, J.B. Yoo, C.Y. Park, J.W. Man, J.M. Kim, *Proceedings of IVMC'03 Digest*, p.223 (2003).
8. F. Ito, K. Konuma, A. Okamoto, *J. Appl. Phys.*, 89, 8141 (2001).
9. P. Yonathan, H.T Kim, D.H. Yoon, *Mater. Lett.*, 62, 2795 (2008).
10. Y.J. An, J.E. Lee, K.S. Kim, G.E. Cheon, H.C. Lee, J.H. Chang, Y.R. Cho, *Proceedings of ASID'06 Digest*, p.515 (2006).
11. E. Ide, S. Angata, A. Hirose, K.F. Kobayashi, *Acta Mater.*, 53, 2385 (2005).