Effect of Liquid Surface Treatments on Field Emission Properties of Carbon Nanotube Cathodes

Ji-Eon Lee, Young-Je An, Heon-Cheol Shin, Won-Sub Chung and Young-Rae Cho*
School of Materials Science and Engineering, Pusan National University,
Busan 609-735, Korea
TEL: 82-51-510-2389, e-mail: yescho@pusan.ac.kr

Keywords : surface treatment, liquid method, field emission, CNT emitter, screen print.

Abstract

Carbon nanotube (CNT) cathodes having a trench structure similar to the structure of the gated triode-type cathode were successfully fabricated by a screen-printing method with multi-walled carbon nanotubes. We observed that a liquid method not only readily removes the organic residues on the CNT films, but also satisfactorily protrudes the CNTs out of the electrode surface. The CNT cathodes prepared by the liquid method showed a turned-on field of 1.4 V/μm. The emission current density of them was about 3.1 mA/cm^2 at the electric field of 3 V/μm. The liquid method appears to be a promising surface treatment of CNT cathode for gated triode-type FEDs applications.

1. Introduction

CNTs (carbon nanotubes) have attracted considerable attention among the modern materials scientists because of their unique physical properties and potential applications to the field emission displays (FEDs) [1-4]. Recently, fully-sealed FED prototypes with CNT emitters have been fabricated using a screen-printing process. The CNT emitters made by screen-printing have several advantages such as low cost and simplicity in manufacturing process for large diagonal displays. However, they have some problems to be solved for commercial use such as low emission current density and uneven uniformity in CNT cathode due to entangled CNT bundles and the lack of CNTs protrusion from the surface of cathode.

To overcome this task, several surface treatment methods such as laser irradiation [5], ion irradiation [6], adhesive taping [7] and rolling [8] methods have been carried out for screen-printed CNT cathode. For the diode-type cathode, showing a flat surface morphology in cross sectional view of cathode, the adhesive taping and rolling methods are effective on surface treatment. For the triode-type structure, however, only the laser or ion irradiation had an effect to modify surface morphology of the CNT film. The most serious problem in the laser or ion irradiation is the difficulty in area selection and low throughput of them in the surface treatment [9].

In this study, the effects of surface treatment of CNT cathodes on field emission properties were investigated using the liquid elastomer for the use in triode-type FED applications. The results were compared to the conventional adhesive taping and rolling methods, from the viewpoint of emission uniformity and high process reproducibility.

2. Experimental

Figure 1 shows the experimental flow chart for this work. The CNTs were multi-walled carbon nanotubes with a micro-range powder. The CNT powders were suspended in a solution of IPA (isopropyl alcohol).

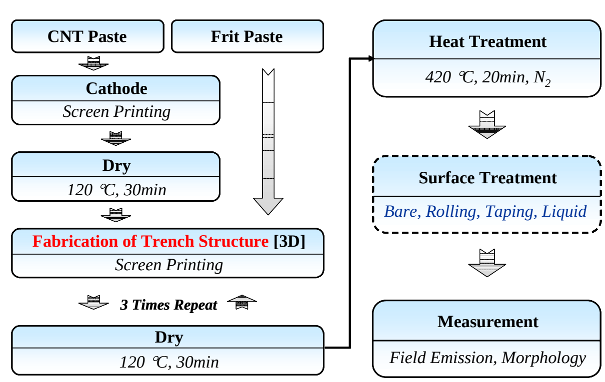

Fig. 1. A schematic experimental procedure describing this work.

A CNT ink was prepared by ultrasonic dispersion of CNT powders and an organic solution of IPA. A CNT paste for screen-printing was fabricated by mixing the CNT ink, an organic binder and inorganic bonding materials using a three-roll mill for 1 h. The CNT films for electron emission were synthesized by screen-printing on the ITO (indium tin oxide) coated soda-lime glass through 500-mesh of metal mask [10,11]. The trench structures, which have the function of gated structure in triode-type FEDs, were screen printed on the area where between the lines of CNT patterns using a dielectric frit paste.

After firing the organic binder in the CNT paste at 420 °C in nitrogen atmosphere, a series of surface treatment was carried out. In this study, a liquid-phase elastomer was used as an adhesive agent for the surface treatment. For comparison, conventional adhesive taping and rolling methods in the surface treatment were also carried out.

Figure 2 shows detailed process steps of the surface treatment process using a liquid-phase elastomer method. Generally, CNTs are buried in inorganic bonding materials, ash and some kinds of residues of the organic binder after the firing process. Surface treatments in this study can be divided into 3 steps. In first step, the liquid-phase elastomer was poured onto the screen printed CNT film. In second step, the liquid-phase elastomer is converted to a gel-type elastomer layer during the thermal curing process. Finally, the gel-type elastomer layer is removed from the surface of CNT cathode. In the detachment process, some parts of inorganic films burying CNTs and ash covering CNTs will be removed.

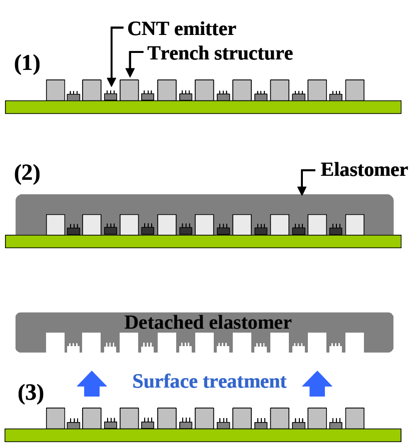

Fig. 2. Schematic describing liquid surface treatment; (a) fabricated trench-type CNT cathode, (b) covered elastomer and (c) cured and removed elastomer.

The field emission properties of the CNT films were characterized in diode mode with the anode and cathode being spaced at 300 μm in a high vacuum chamber at a pressure of $1x10^{-6}$ Torr. For the emission image describing the uniformity of emission sites in the pixel, we used phosphor coated anode plate. The scanning electron microscope (SEM) observation was carried out to examine CNT protrusions and morphology of CNT films.

3. Results and discussion

Figure 3 shows SEM images of CNT cathodes having trench structure after heat treated at 420 °C in N_2 atmosphere. As shown in Fig. 3(a), CNT emitter layer is located lower than top of the trench structure. It is noted that the shape of trench structure is similar to the gate structure of triode-type cathodes. The maximum height of trench and CNT film before surface treatment was 40 μm and 5 μm, respectively. It seems that the configuration of trench and CNT film in Fig. 3 (b) is very similar to the case of gated structure for triode type cathode. Theoretically, the residues and ash covering the CNTs on the CNT films should be removed in the surface treatment process.

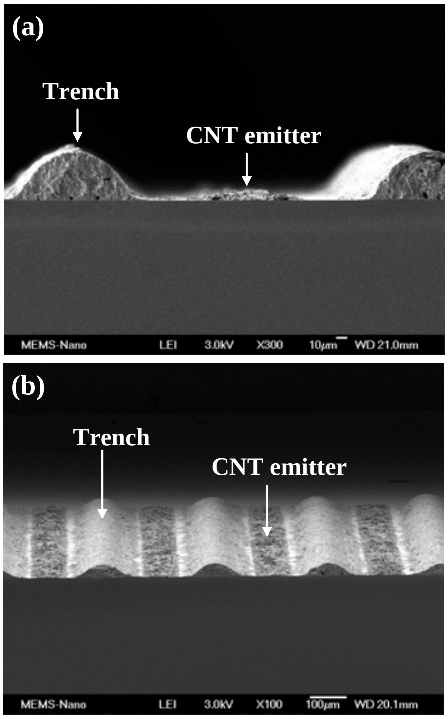

Fig. 3. (a) Cross-sectional and (b) tilted views of trench-type CNT cathode structure, observed by scanning electron microscopy.

Figure 4 shows the SEM images of the CNT films after different surface treatments. Fig. 4 (a) is the CNT film that is not done in surface treatment. As shown in Fig. 4(b) and Fig. 4(c), the CNTs films, surface treated by rolling and adhesive taping methods, are similar to that of none treatment. However, the liquid surface treatment gave rise to vertical alignment and protrusion of CNT emitters to the surface of CNT films, as shown in Fig. 4(d). It can be seen that a sol-type elastomer can be uniformly cover the entire screen-printed CNTs film, regardless of a shape of the cathode and surface morphology. Furthermore, the gel-type elastomer has an appropriate adhesion strength to the CNTs film after dry process it can provide uniform surface treatment even if the morphology of the CNT films have stepwise roughness.

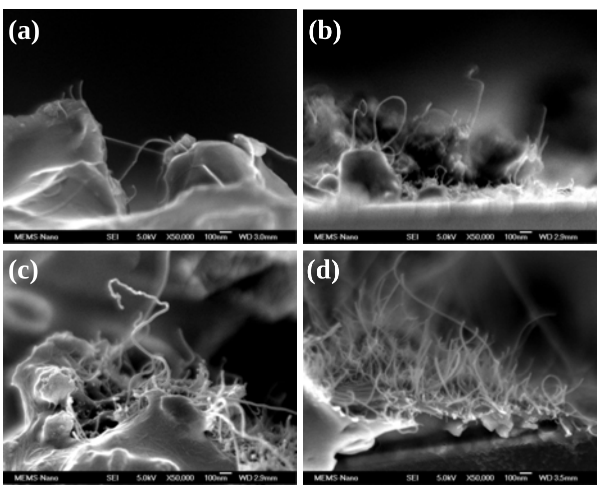

Fig. 4. SEM images after different surface treatments; (a) none treatment, (b) rolling method, (c) taping method and (d) liquid method.

Figure 5 shows the field emission characteristics of CNT cathodes measured by a diode-type mode in a vacuum chamber for the different surface treatments. The field emission current densities of samples surface-treated using the rolling method, the adhesive taping method and the liquid method are 1.4 mA/cm^2, 1.0 mA/cm^2 and 3.1 mA/cm^2, respectively, at an electric field of 3 V/μm. Compared to the taping and rolling methods, the liquid method resulted in a relatively higher field emission current. The reason of different values is due to micro-morphology of carbon nanotube bundles after each surface treatment [6,12].

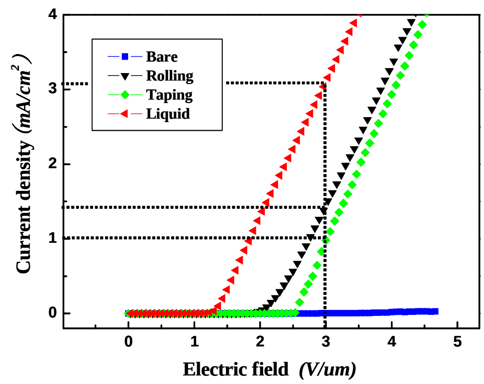

Fig. 5. Field emission characteristics of CNT cathodes having trench structure with different surface treatments.

Figure 6 shows the field emission images for samples that were heat treated at 420 °C in an atmosphere of N_2 using different surface treatments. As is known, the emission images of the sample treated with rolling and adhesive taping method are not uniform and poor. However, the sample surface treated with a liquid elastomer method shows a homogeneous emission image over the whole pixel area compared to the samples surface treated using conventional rolling and adhesive taping methods. Furthermore, the liquid method is simple and is also a low cost process.

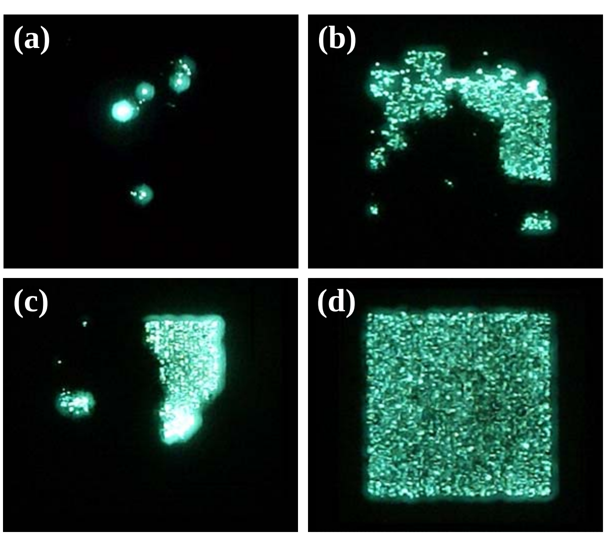

Fig. 6. Field emission images after different surface treatments; (a) none treatment, (b) rolling method, (c) taping method and (d) liquid method.

From this study, we conclude that the liquid method is more efficient than the conventional mechanical method for achieving the CNT cathode with uniform surface treatment regardless of a shape of the cathode and surface morphology.

4. Conclusion

Carbon nanotube (CNT) cathodes having a trench structure were successfully fabricated by a screen-printing method with multi-walled carbon nanotubes. The sample surface treated by a liquid elastomer method showed a homogeneous emission image over the whole pixel area compared to the samples surface treated using conventional rolling and adhesive taping methods. From this study, it is proposed that the liquid method leads to high current density and high uniformity, implying that this can be the useful method of surface treatment of CNT cathodes for gated triode-type FEDs applications.

5. Acknowledgements

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

6. References

1. W. I. Milne, K. B. K. Teo, M. Chhowalla, P. Legagneux, G. Prio and D. Pribat, *SID 2002 Dig. Tech. Pap.*, 1120 (2002).
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 and J. M. Kim, *Appl. Phys. Lett.*, **75**, 3129 (1999).
3. S. Kang, C. Bae, W. Son, M. H. Kim, J. Yi, S. T. Lee, A. Chang, J. J. Kim, C. R. Lee, J. H. Moon, S. H. Lim, H. S. Kim and J. Jang, *SID 2003 Dig. Tech. Pap.*, 802 (2003).
4. J. C. Ho, Y. Y. Chang, J. H. Liao, H. C. Cheng, J. R. Sheu, M. C. Hsiao, C. D. Lee, S. M. Huang, C. S. Cho, W. K. Huang, W. Y. Lin and C. C. Lee, *SID 2002 Dig. Tech. Pap.*, 372 (2002).
5. W. J. Zhao, A. Sawada and M. Takai, *Jpn. J. Appl. Phys.*, **41**, 4314 (2002).
6. D. H. Kim, C. D. Kim and H. R. Lee, *Carbon*, **42**, 1807 (2004).
7. T. J. Vink, M. Gillies, J. C. Kriege and H. W. J. J. van de Laar, *Appl. Phys. Lett.*, **83**, 3552 (2003).
8. Y. C. Kim, K. H. Sohn, Y. M. Cho and E. H. Yoo, *Appl. Phys. Lett.*, **84**, 5350 (2004).
9. H. J. Lee, Y. D. Lee , S. I. Moon, W. S. Cho, Y. H. Lee, J. K. Kim, S. W. Hwang and B. K. Ju, *Carbon*, **44**, 2625, (2006).
10. J. Li, W. Lei, X. Zhang, X. Zhou, Q. Wang, Y. Zhang and B. Wang, *Appl. Surf. Sci.*, **220**, 96 (2003).
11. Y. S. Shi, C. C. Zhu, W. Qikun and L. Xin, *Diamond Relat. Mater.*, **12**, 1449 (2003).
12. 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 and K. I. Cho, *Jpn. J. Appl. Phys.*, **41**, 1532 (2002).