Effects of Bonding Material and Surface Treatment on Properties of Carbon Nanotube Cathode for Field Emission Display

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Abstract: *The effects of bonding materials and surface treatment on CNT cathodes used in field emission displays were investigated. A liquid method using a polymer-based organic solution and a mechanical method were applied. The liquid method, using PVA (polyvinyl alcohol) showed high potential compared to the mechanical adhesive taping and rolling method used in the fabrication of CNT cathodes. However, the liquid method could only be applicable when the CNT films have good adhesion on the cathode after heat treatment.*

Keywords: field emission; carbon nanotube; surface treatment; bonding material; CNT cathode.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention among materials scientists because of their unique physical properties and their potential for applications in field emission displays (FEDs). The reason why CNTs can be used as materials for field emitters is the intense local electric fields caused by both the intrinsic needle-like shape of the CNTs and the fact that they protrude over the surface of the bonding materials. The use of a screen-printing process for preparing, fully-sealed FED prototypes with CNT emitters has recently been demonstrated. However, CNT-FEDs have some severe problems that must be solved in order to realize marketable products. One of the most important issues is the uniformity of field emission [1]. In this study, the effects of bonding materials and surface treatment of CNT-cathodes on field emission properties for use in high efficiency field emission displays were investigated. A polymer-based organic solution method was used for the surface treatment [2-5] and the results were compared to the conventional adhesive taping and rolling method, from the view point of emission uniformity and high process reproducibility.

2. Experiments

Figure 1 shows the experimental flow chart for this work. The CNTs were multi-walled carbon nanotubes. CNT powders were suspended in a solution of IPA (isopropyl alcohol). A CNT solution was prepared by strongly sonicating of CNT powders in an organic solution of IPA. By mixing the CNT solution and binder materials (terpineol and ethylcellulos or acrylate), a CNT ink was prepared. A CNT paste for screen-printing was fabricated by adding the CNT ink and inorganic bonding material (frit-glass paste or ITO powder). CNT patterns were produced by a screen-printing technique on ITO electrodes [6-7]. After firing the organic binder in the CNT paste at 350°C in air or 430°C in nitrogen (N_2) atmosphere, a special surface treatment was carried out. For the surface treatment, the PVA solution was poured on the surface of a screen printed CNT film. The PVA solution was converted to a PVA film during the drying process. When the PVA film was removed from the ITO glass, the ash attached to the CNTs could be removed successfully.

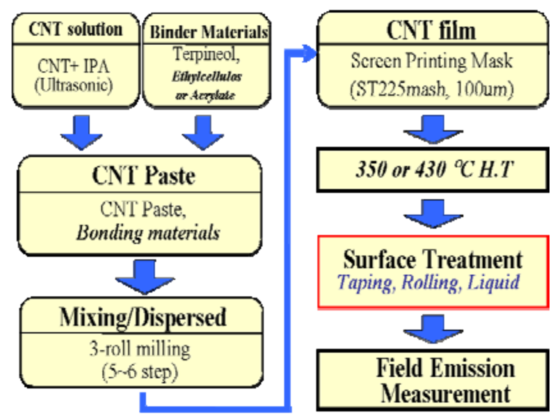

Figure 1. Schematic diagram of the experimental procedure used in this work.

In this study, two types of CNT cathodes were prepared according to the bonding material. One is frit glass based bonding material and the other is ITO (indium tin oxide) powder based bonding material. For the samples that were processed a heat treatment between 350°C and 430°C a polymer-based organic solution was used in the surface treatment. For comparison, a conventional adhesive taping [8] and rolling [9] methods were also carried out. The field emission properties of the CNT films were characterized with a diode-mode in a high vacuum chamber at a pressure of $1x10^{-6}$ Torr. Optical microscope (OM) observation was carried out to examine CNT protrusions and CNT films.

3. Results and discussion

3.1 Frit glass based bonding material: Figure 2 show the OM photos for samples that were prepared by using frit glass based CNT paste and heat treated at 350°C in air. Fig. 2(a) shows the sample before surface treatment, clearly showing a thick CNT film on the ITO electrode. Fig. 2(b) shows the sample with a PVA film on the CNT film. It can be seen that the CNT pattern is completely covered with PVA film. Fig. 2(c) and Fig. 2(d) show samples after removal of the PVA film for different concentration ratios of PVA powder to DI (deionized) water. Compared to Fig. 2(d), Fig. 2(c) showed thicker lines of CNT film on the ITO electrode. This is due to the stronger adhesive strength of the PVA film made from 5 wt. % PVA over a PVA film made using 3 wt.% PVA.

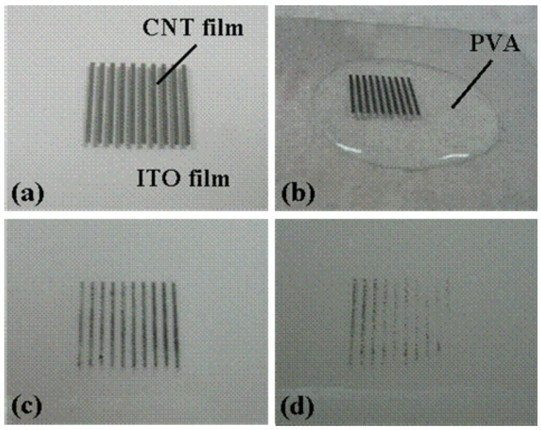

Figure 2. Optical microscopic photos of samples before and after surface treatment: (a) before surface treatment, (b) after applying the PVA solution, (c) after surface treatment using 3 wt. % PVA, (d) after surface treatment using 5 wt. % PVA.

Figure 3 shows OM images and field emission images for samples that were heat treated at 350 °C in an atmosphere of air using different surface treatments. As is known, the surface of the sample treated with a polymer-based organic solution using 5 wt.% PVA shows a poor emission image. However, the sample surface treated with a polymer-based organic solution containing 3 wt.% PVA showed an emission image comparable to the samples surface treated using conventional adhesive taping and rolling methods.

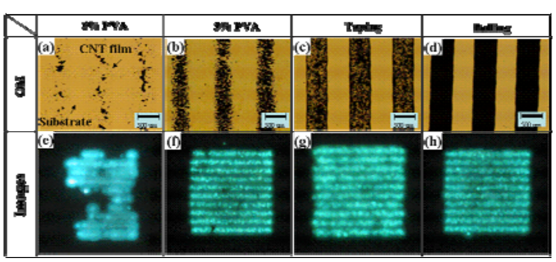

Figure 3. Optical microscopic photos and emission images for samples after different surface treatments: (a), (e) 5 wt.% PVA, (b), (f) 3 wt.% PVA, (c), (g) taping method, (d), (h) rolling method.

Figure 4 shows the field emission characteristics of CNT cathodes measured in the diode mode in a vacuum chamber, heat treated at 350 °C in air atmosphere, for the different surface treatments. The emission currents of the sample surface treated using the rolling method, the adhesive taping method and the liquid method at an electric field of 2.5 V/μm are 440 μA, 370 μA and 330 μA, respectively. Compared to the rolling method, the liquid method resulted in a slightly smaller emission current. However, the liquid method is very simple and is also a low cost process. From this study, we conclude that the liquid method is more efficient than the mechanical method for achieving a uniform surface treatment for CNT cathode.

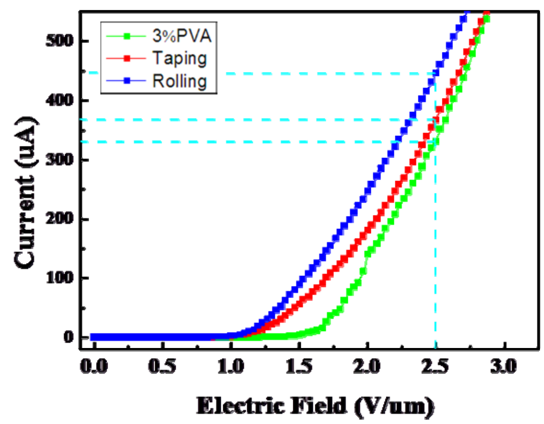

Figure 4. Effects of surface treatment on the field emission properties of screen printed CNT cathodes measured in the diode mode in a high vacuum chamber.

3.2 ITO powder based bonding material: Figure 5 shows OM images and field emission images for samples that were heat treated at 430 °C in an atmosphere of nitrogen (N_2) using different surface treatments such as taping or rolling method. As shown in Fig. 5(c) and Fig. 5(d), the CNT cathodes fabricated by using ITO powder based bonding materials showed very uniform emission images. However, the CNT cathode surface treated by liquid method showed undetectable emission current because the CNT patterns were detached almost by PVA film during surface treatment. From this result, it is concluded that the liquid method is not applicable for the CNT cathodes fabricated by using ITO powder based bonding materials. For the application of liquid method, the bonding materials should be relatively sintered and have fairly good adhesion between CNT film and cathode.

Figure 6 shows the field emission characteristics of CNT cathodes measured in the diode mode in a vacuum chamber, heat treated at 430 °C in N_2 atmosphere, for the different surface treatments. The emission currents of the samples surface treated by using the rolling method and the adhesive taping method at an electric field of 2.5 V/μm are 280 μA and 220 μA, respectively. Compared to the rolling method, the taping method resulted in a slightly smaller emission current.

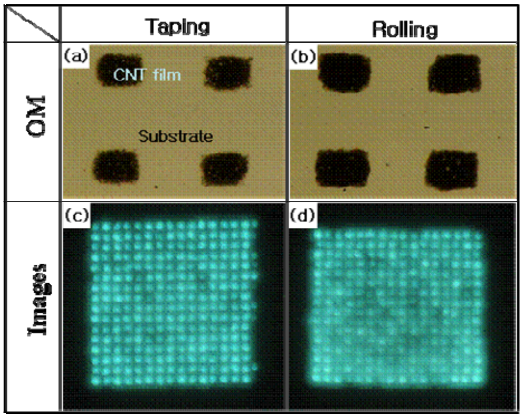

Figure 5. Optical microscopic photos and emission images for samples fabricated by ITO powder based bonding material after different surface treatments: (a), (c) taping method, (b), (d)

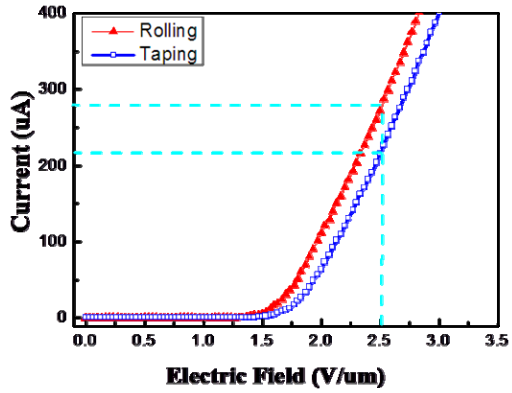

Figure 6. Effects of surface treatment on the field emission properties of screen printed CNT cathodes fabricated by ITO powder based bonding material.

The most important application of liquid method in surface treatment for CNT cathode should be the bottom of hole or trench which has high aspect ratio. For the fabrication of triode type CNT cathode, the CNT films should be positioned in the deep hole. In this case, the application of taping method and rolling method is impossible. However, the liquid method for surface treatment is applicable because PVA solution has high fluidity. This suggests that the liquid method could only be applicable when the CNT films have good adhesion on the cathode after heat treatment. From this result, we can conclude that the bonding material of ITO powder was almost not preceded a sintering during the heat treatment of 430 °C in an atmosphere of N_2.

4. Conclusions

We found that the emission current in a screen-printed CNT cathode is dependent on the methods used in the surface treatment after the firing process. We also propose that the liquid method is one of the best surface treatments for CNT cathodes with triode structure, resulting in a high uniformity. The liquid method could only be applicable when the CNT films have good adhesion on the cathode after heat treatment. This result can be used as the criteria for choosing the surface treatment method for fabricating high-efficient and large-sized CNT-cathodes.

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. Shin, H. Y., Chung, W. S., Kim, K. H., Cho, Y. R., and Shin, B. C., “Effects of bonding materials in screen-printing paste on the field-emission properties of carbon nanotube cathodes,” *Journal of vacuum science & technology*, Vol. 23, no. 6, pp. 2369-2372, 2005.
2. Lee, C. C., Lin, B. N., Hsiao, M. C., Chang, Y. Y., Lin, W. Y., and Jiang, L. Y., “Development of CNT-FED by Printing Method,” *SID International Symposium Digest of Technical Papers*, Vol. 36, no. 2, pp. 1716-1719, 2005.
3. Kang, N. S., Kown, G. J., Shon, K. H., Jeon, K. S., Shin, E. J., Lee, S. E., and Choi, Y. H., “Effects of Surface Treatments on the emission properties of Screen Printed Carbon Nanotubes”, *FEW’05*, pp. 217-223, 2005.
4. Lee, H. J., Lee, Y. D., Cho, W. S., and Ju, B. K., “Field Emission Improvement by Liquid Elastomer Modification of Screen-Printed CNT Film Morphlogy,” *SID International Symposium Digest of Technical Papers*, Vol. 37, pp. 638-640, 2006.
5. Seong, M. S., Oh, J. S., Lee, J. E., Jung, S. J., Kim T. S., and Cho, Y. R., “Effects of Surface Treatment on Field Emission Properties for Carbon Nanotube Cathodes,” *Korean Journal of Materials Research*, Vol. 16, no. 1, pp. 37-43, 2006.
6. Li, J., Lei, W., Zhang, X., Zhou, X., Wang, Q., Zhang, Y., and Wang, B., “Field emission characteristic of screen-printed carbon nanotube cathode,” *Applied surface science*, Vol. 220, no. 1/4, pp. 96-104, 2003.
7. Shi, Y. S., Zhu, C. C., Qikun, W., and Xin, L., “Large area screen-printing cathode of CNT for FED,” *Diamond and related materials*, Vol. 12, no. 9, pp. 1449-1452, 2003.
8. Vink, T. J., Gillies, M., Kriege, J. C., van de Laar, and H. W. J. J., “Enhanced field emission from printed carbon nanotubes by mechanical surface modification,” *Applied physics letters*, Vol. 83, no. 17, pp. 3552-3554, 2003.
9. Kim, Y. C., Sohn, K. H., Cho, Y. M., and Yoo, E. H., “Vertical alignment of printed carbon nanotubes by multiple field emission cycles.” *Applied physics letters*, Vol. 84, no. 26, pp. 5350-5352, 2004.