Effects of additives and post-treatments on emission characteristics of carbon nanotubes field emitters by screen printing method

Duck-Jin Lee, Sam-Soo Kim, Yang-Kyu Lee, Hyun-Tae Chun, and Dong-Gu Lee[1]
School of Advanced Materials & Systems Engineering, Kumoh National Institute of Technology
1, Yangho-Dong, Gumi-City 730-701, Gyungbuk, Korea

Abstract

Carbon nanotube field emission display devices were fabricated using screen printing techniques. The CNT pastes are composed of organic binder, CNT, and additive materials such as glass frit, silver or ITO powders. The change in mixing ratio of various organic binders in CNT paste varied the electron emission characteristics. With increasing the contents of additive materials in CNT paste, turn-on field were increased, leading to decrease in electron emission current. The post-treatment process in this study induced the vertical alignment of carbon nanotubes on glass, resulting in the improvement of electron emission uniformity.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Dr. Iijima in 1991[1], CNTs have drawn attention as a good field emitter material in FED (field emission display) owing to their small radius of curvature, high mechanical strength, and excellent thermal endurance.[2-4] Field emitters using CNTs have been fabricated mainly by screen printing[5-6] or chemical vapor deposition (CVD)[7-8] process. There have been still some problems for commercialization of CNT-FED such as lifetime, driving voltage, emission uniformity, etc.

In this study, CNT devices were fabricated by screen printing techniques and the electron emission properties of CNT emitters were observed as a function of post-treatment, additive materials, mixing ration of various organic binders.

2. Experiments

CNT pastes were formulated with organic binders (ethyl cellulose in terpineol or butyl carbitol acetate (bca)), multi-walled carbon nanotubes (MWNTs), and some additives. The CNT pastes were then milled by 3-roll mill for better dispersion of CNTs. Here The CNT pastes having three different kinds of additives (glass frit, silver, and ITO powders) were printed on a patterned-Ag electrode (10 x 10 mm^2). The printed-patterns of CNT pastes were kept at 150°C for 0.5 hour for drying and 400°C for 1 hour for removing organic binders.

The effect of additives in CNT pastes on emission characteristics was observed. The post-treatment was performed in two different methods such as taping and rubber rolling. The printed-CNT emitters were characterized with FE-SEM, optical microscope, I-V measurement, viscometer, etc.

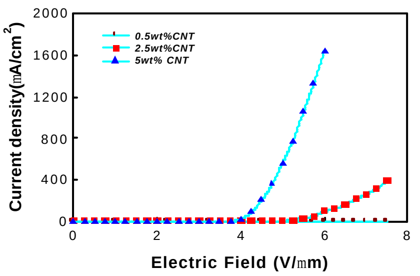
3. Result

Figure 1 shows the I-V curves of the printed CNTs with CNT contents and mixing ratio of different organic vehicles (terpineol and bca) in the CNT pastes. The CNT pastes were formulated with 0.5-5 wt% CNT and 8.5 wt% ethyl cellulose in only terpineol solvent or a mixed solvent (bca/terpineol =1). As shown in Fig. 1, an increase in the CNT contents from 0.5 to 5 wt% resulted in the decrease in the turn-on field of CNTs. The partial replacement of terpineol with bca in 50% in case of 5 wt% CNT paste improved the turn-on field from 5 V/μm only with terpineol to 4 V/μm as well as emission current density.

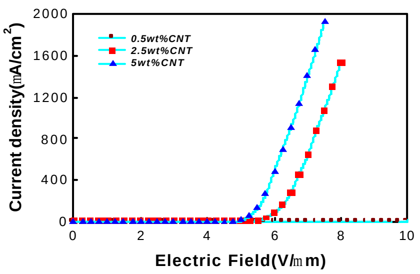
Figure 2 shows the cross-sectional images of CNTs after burning CNT pastes formulated with different organic solvents. The viscosity of bca is originally lower than that of terpineol. The higher viscosity (or stickiness) of terpineol in the pastes causes CNTs to be embedded or bent into the organic vehicle. Even after printing and burning out the paste, the shape of CNTs remained lied or bent. On the other hand, the lower viscosity of bca does not affect the original free-style of CNTs. Therefore the protrusion of a lot of CNTs can be observed. These protrusions

[1]Corresponding author: dglee@kumoh.ac.kr

(i.e. vertical standings) of CNTs helped the electric field enhancement and increased the electron emission of CNTs (Fig. 2(a)). The change in viscosity and printed-thickness of CNT pastes as a function of CNT contents are shown in Fig. 3. The more CNT is added, the viscosity and thickness are higher. Although there was a little difference in viscosity between only use of terpineol solvent and the use of terpineol-bca mixture at lower contents of CNTs, the thickness of printed-CNTs was not much changed. From these results, it is notable that the some addition of low viscous bca improved the emission characteristics of CNT emitters.

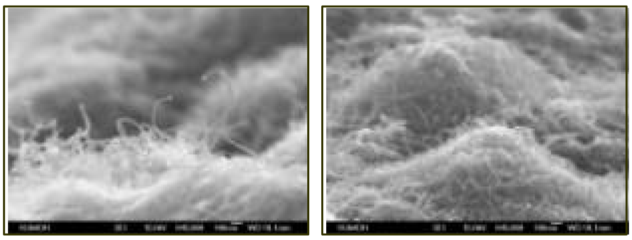


(a)



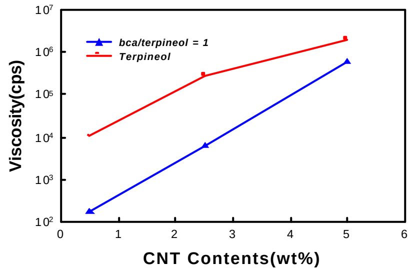
(b)

Figure 1. I-V curves of different contents of CNT emitters with use of (a) a mixed solvent (bca/terpineol=1) and (b) terpineol solvent only (5 wt% CNTs with 8.5 wt% E.C. in various solvents).

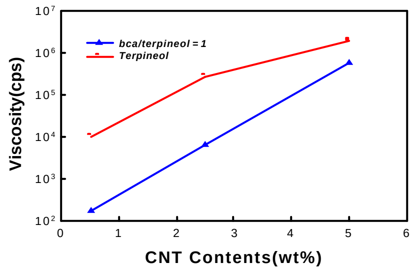


(a) **(b)**

Figure 2. SEM images of CNTs with use of (a) mixture solvent of bca/terpineol=1 and (b) terpineol only.



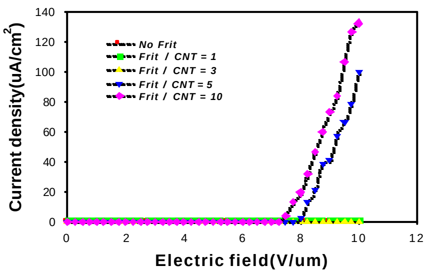
(a)



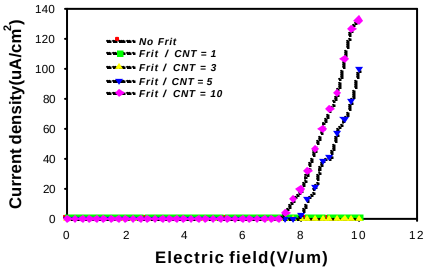
(b)

Figure 3. Change in (a) viscosity and (b) thickness of printed-CNTs as a function of CNT contents.

The I-V characteristics of CNT emitters with variation of mixing ratio of frits to CNTs in weight are shown in Fig. 4 with no post-treatment. While the addition of glass frits in low content (0.5 wt%) of CNT paste increased the emission current, the addition of frits in higher content (2.5 wt%) of CNT paste rather decreased the emission. There might be a possibility of binding effect of frits at low contents of CNTs (0.5 wt%). However in case of higher content (2.5 wt%) of CNTs, the total amount of frits in the paste is quite large compared to the 0.5wt% CNT paste. This excessive amount of frits might cover the CNT emitter surfaces (Fig. 5).

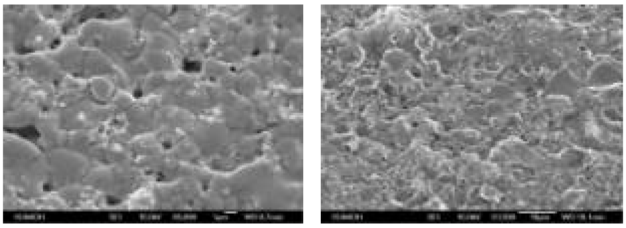


(a)



(b)

Figure 4. I-V curves of CNT emitters with variation of mixing ratio(frit/CNT in weight) on basis of (a) 0.5wt% CNT paste and (b) 2.5wt% CNT paste.



(a) (b)

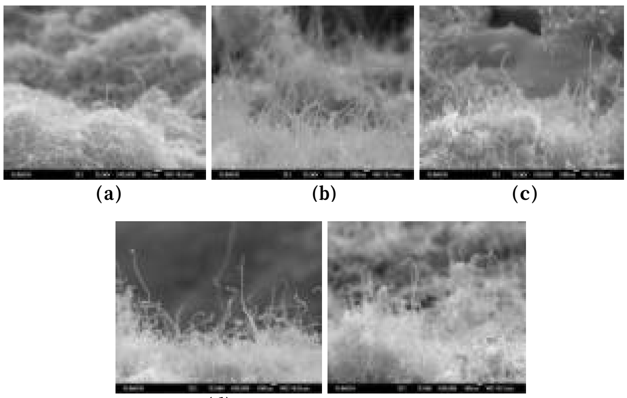
Figure 5. SEM images of screen-printed (a) 0.5 wt% CNT paste and (b) 2.5 wt% CNT paste with addition of glass frit (frit/CNT = 5).

For the improvement of emission current of CNT emitters, the post-treatment method using adhesive force such as taping or rubber-rolling is well known. Figure 6 shows the cross-sectional images of CNTs with some additives (additive/CNT=3 on basis of 4 wt% CNTs) after taping or rubber-rolling as a post-treatment. The vertical standings of CNTs were evidently shown after the both post-treatment methods irrespective of kinds of additives. Same as the result of Fig. 5, the emission of high contents (4 wt%) of CNTs was decreased with addition of high contents of additives (additive/CNT=3). No additives in CNT pastes gave the best emission characteristics after post-treatment as shown in Fig. 7(a). However the reproducibility of emission characteristics was bad in many samples because of the weak adhesion of CNTs to substrates with no additives. Therefore it may be necessary to include some additives into CNT pastes for better adhesion to substrates for the post-treatment process although the emission characteristics are slightly decreased.

Taping method as a post-treatment in this study gave better results in emission characteristics of CNTs than rubber-rolling due to higher adhesive force. However the stronger adhesives do not always give better results as in other report[9]. The stronger adhesives sometimes remove the whole CNT surface layer, worsening the emission of CNTs. Therefore the optimum adhesives enough to erect CNTs and not to harm CNT surface layer should chosen.

The emission current density was measured with different kinds of post-treatment and additive materials as shown in Fig 7. The printed emitters before post-treatment turned on at a field of 5.1 V/μm. After post-treatment, the emitters turned on at a field as low as around 3.0 V/μm and the emission uniformity was increased. The glass frit presented more efficient electron emission than ITO or silver powders.

Fig 8 shows the emission images of CNT patterns with different post-treatments and additive materials in a vacuum of 10^{-7} torr. Electrical testing were performed at the anode 1.5kV with gap distance of 350 μm. This demonstrated that the uniformity of electron emission and the emission current of treated-CNTs were increased remarkably compared to no treatment.



(a) (b) (c)

(d) (e)

Figure 6. SEM images of CNTs with different additive materials and post-treatment. (a) no additive with no treatment, (b) no additive with taping, (c) glass frit with taping, (d) no additive with rubber-rolling, and (e) ITO with rubber-rolling

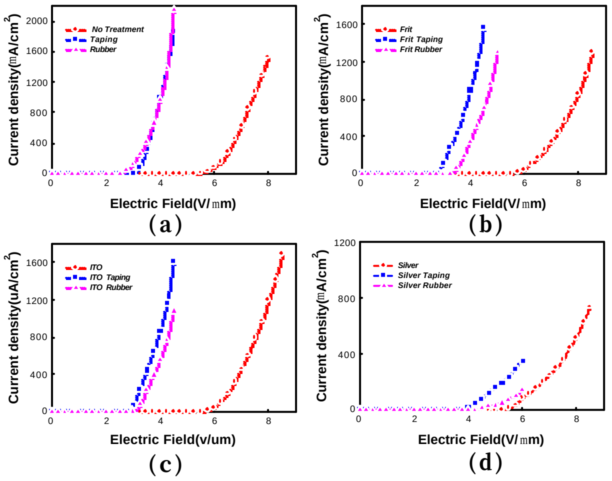


Figure 7. I-V curves of CNT emitters with (a) no additive, (b) glass frits, (c) ITO, and (d) Ag powders with different post-treatments.

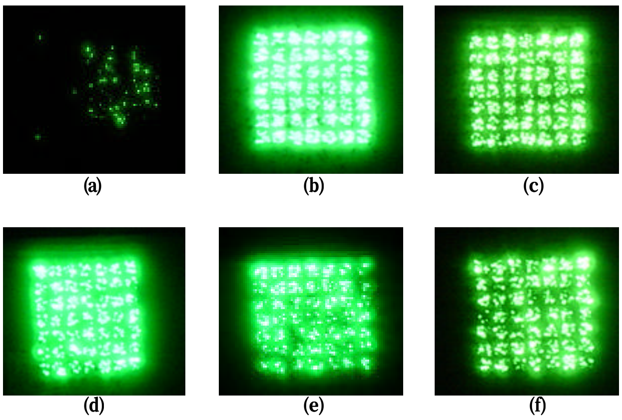


Figure 8. Emission images of CNT emitters with different additives and post-treatment at an applied voltage of 1.5kV. (a) no additive with no treatment (Ia=18 μA), (b) no additive with taping (Ia=930 μA), (c) no additive with rubber-rolling (Ia=530 μA), (d) frits with taping (Ia=520 μA), (e) frits with rubber-rolling (Ia=480 μA), and (f) ITO with rubber-rolling (Ia=320 μA)

4. Conclusions

Economic screen printing technique was applied and fundamental data were provided for the fabrication of CNT field emitters as follows.

The partial addition of bca into terpineol solvent improved the emission characteristics of CNT emitters. It is necessary to include some additives required for the good adhesion of CNTs to substrates for the vertical standings of CNTs (post-treatment) and the higher current density/uniformity. Among those additives, glass frits powder was best. Taping method in this study was better than rubber-rolling.

5. Acknowledgements

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6. References

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