Effects of constituents in CNT pastes on the field emission characteristics of carbon nanotubes

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Abstract

Carbon nanotubes (CNTs) have been significantly used for the field emitters for display applications. However, the lifetime of CNT emitters which are formed by screen printing technique is not guaranteed yet, because the constituents in CNT paste affect the lifetime of CNTs. The CNT pastes for screen printing are normally composed of organic vehicles (nitro cellulose, ethyl cellulose, etc) and additives (glass frits, ITO, etc) with CNTs.

In this study, the effects of constituents in CNT pastes on the lifetime and emission characteristics of CNTs were investigated by thermal and electrical analysis. Use of glass frits worsened the lifetime and electron emission of CNTs. However, an addition of ITO to CNT paste rather improved the lifetime of CNTs. Degradation of CNTs was small when nitro cellulose was used in CNT paste as an organic vehicle.

1. Introduction

Carbon nanotubes, which have a nano-scale sharpness, high chemical stability, thermal conductivity, and mechanical strength, have been widely applied to field emission display (FED) as a field emitter [1,2]. Field emitters using CNTs have been mainly fabricated by chemical vapor deposition (CVD) [3,4] and screen printing method [5,6]. However, CVD techniques have some disadvantages such as complicated vacuum process, high cost, and high growth temperature, especially for large area FED. Therefore, the screen printing method using CNT paste has been more adopted because of its large scalability at low cost and through a simple process.

In spite of the economy of screen printing process, CNT emitters still have problem in lifetime because the constituents in CNT paste affect the thermal, electrical, and crystalline properties of CNTs during thermal process such as removal of organic vehicles, panel sealing, etc. The CNT pastes for screen printing are normally composed of organic vehicles (nitro cellulose, ethyl cellulose, etc in terpineol or butyl carbitol acetate) and additives (glass frits, ITO, etc) with CNTs. These CNT pastes should be burned-out after printing to remove organic vehicles because organic residues are the source of contamination during electrical emissions, degrading the emission characteristics of CNTs.

In this study, the effects of constituents in CNT pastes for screen printing on the emission characteristics of CNT field emitters were investigated for the improvement of lifetime and stability of CNT emitters. CNT field emitters were prepared from screen printing using the mixture of organic vehicles and additives with CNT powders and its thermal/emission properties were characterized.

2. Experiments

CNT paste for screen printing was formulated with multi-walled carbon nanotubes (MWNTs), additives (glass frits and ITO powders), organic vehicles such as ethyl cellulose (E.C) in terpineol or nitro cellulose (N.C) in butyl carbitol acetate (BCA). CNT paste was prepared by mixing 2 wt% of CNTs and 6 wt% of additives in organic vehicles. The CNT paste was then milled by 3-roll mill for better dispersion of CNTs. Here, the CNT paste having two different kinds of additives were printed on a patterned-Ag electrode (10×10 mm^2). The printed-patterns of CNT paste were kept at 150 ℃ for 30 minute for drying and 400 ℃ for 1 hour for removing organic binders. The taping method was used for post-treatment.

The thermal and field emission properties of CNTs were characterized by FE-SEM, TG-DTA, emission measurement, and I-V measurement with variation of organic binders and additives

3. Results and Discussion

To improve emission current of CNT emitters, the post-treatment method using an adhesive tape is well known [7]. Figure 1 shows the cross-sectional images of CNTs which were printed with some additives, burned-out, and taped as a post-treatment. The vertical standing of CNTs was evidently shown after post-treatment irrespective of kinds of additives. The height deviation of the printed-CNTs was small in case of no additive in CNT paste (Fig. 1(b)) compared to non-uniform dispersion of additive particles (Fig. 1(c)-1(e)). However it is necessary to perform post-treatment for vertical standing and better emission of CNTs. Additives are required to get good adhesion of CNTs to substrate during post-treatment process.

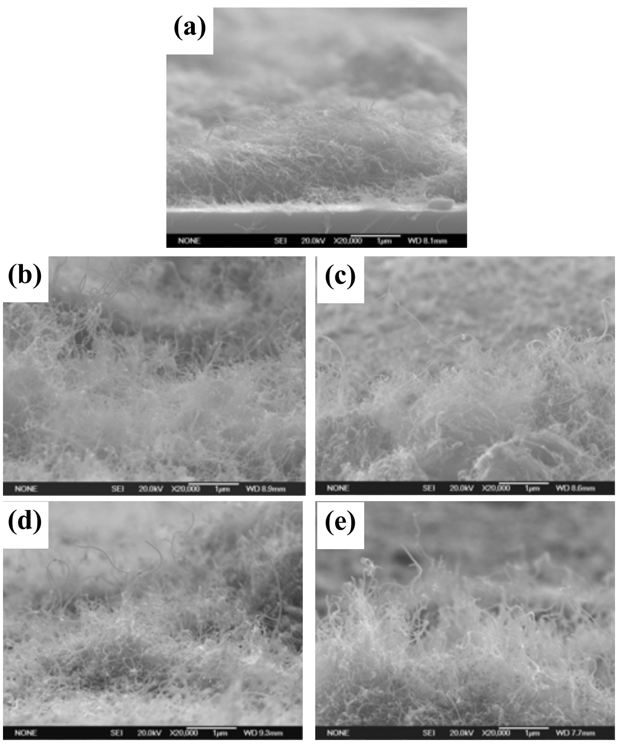
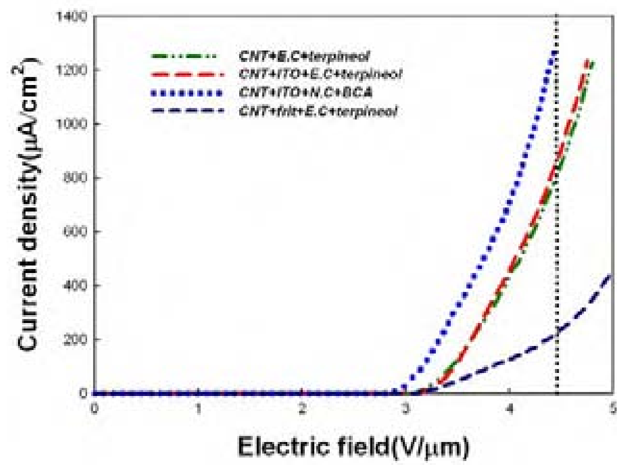


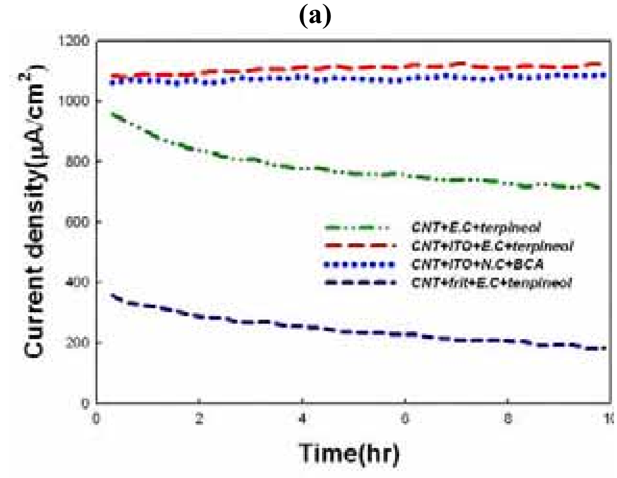
Fig. 1. SEM images of CNTs with (a) no additive + no treatment, (b) no additive + taping, (c) an additive (frits in ethyl cellulose) + taping, (d) an additive (ITO in ethyl cellulose) + taping, and (e) additive (ITO in nitro cellulose) + taping.

Figure 2(a) shows I-V curves of CNTs with organic binders (ethyl cellulose and nitro cellulose) and additives (glass frits and ITO powders). Addition of frits or ITO to CNTs increased turn-on field and decreased emission current density from I-V curves as shown in Fig. 2(a). Use of nitro cellulose instead of ethyl cellulose as an organic binder in CNT-ITO paste improved the emission characteristics of CNTs, i.e. decrease in turn-on field from 3.2 V/μm to 2.9 V/μm and increase in emission current density from 907 μA/cm^2 to 1291 μA/cm^2. Here, the turn-on field for the electron emission from CNTs is defined as the electric field (V/μm) acquiring the current density of 10 μA/cm^2. The I-V measurement data of CNTs were tabulated in Table 1.

Figure 2(b) shows lifetime of CNTs with variation of organic binders and additives. In case of no additives in CNT emitters, the electron emission of CNTs decreased to 30% after 10 hr operation. Addition of frits to CNT emitters much decreased electron emission to 50%. However, it is interestingly noted that addition of ITO to CNT emitters rather improved the electron emission of CNTs by about 2.5%.



(a)



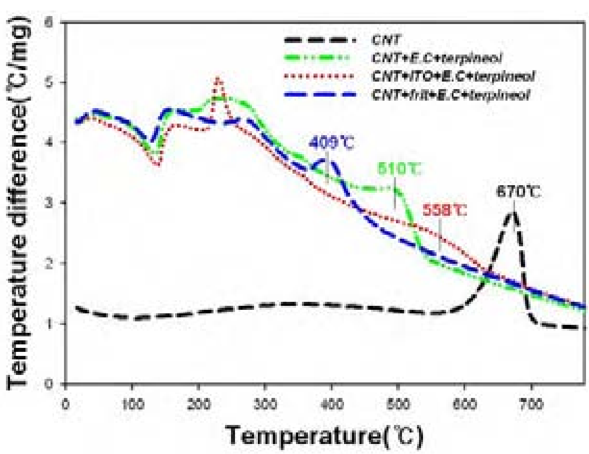
(b)

Fig. 2. (a) I-V curve and (b) degradation of emission of CNT emitters with different organic binders and additives at an applied voltage of 1.0 kV (DC).

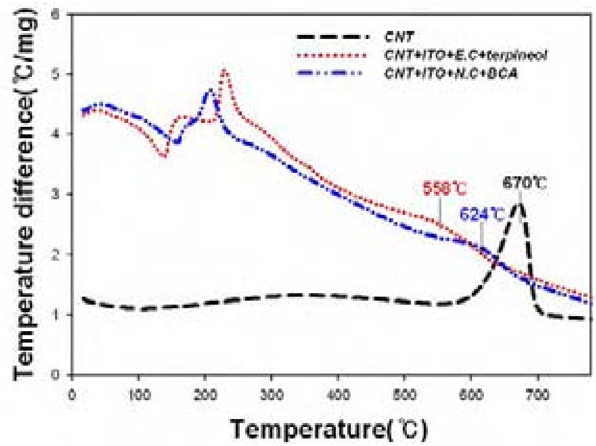
Table 1. Comparison of paste contents in I-V curves and lifetime.

Paste Contents \ Property	(a) I-V curves		(b) lifetimes	
	turn-on field (V/μm)	current density at 4.5 V/μm (μA/cm^2)	current density at initial (μA/cm^2)	current density after 10 hr (μA/cm^2)
CNT + E.C + terpineol	3.15	855	1000	709
CNT + Frit+ E.C + terpineol	3.25	221	367	182
CNT + ITO + E.C + terpineol	3.20	907	1099	1130
CNT + ITO + N.C + BCA	2.90	1291	1062	1086

Figure 3 shows DTA curves of CNT paste including organic binders and additives. The thermal oxidation of pure CNTs peaked at 670°C. Addition of organic binders and additives into CNTs shifted the oxidation temperature of CNTs to lower temperature, which means that CNTs are chemically reacted and degraded during thermal process. Conventional CNT paste of ethyl cellulose in terpineol with no additive worsened the oxidation of CNTs from 670°C to 510°C. Whereas addition of frits worsened more CNTs to 409°C, addition of ITO enhanced CNTs to 558°C (Fig. 3(a)). Use of nitro cellulose is better in thermal property of CNTs compared to use of ethyl cellulose (Fig. 3(b)).



(a)



(b)

Fig. 3. Thermal analysis (DTA) of CNT pastes with (a) additives and (b) organic binders.

Figure 4 shows the emission images of CNT patterns with post-treatment and additive materials in a vacuum of 10^{-7} Torr. Emission images were performed at the anode voltage 1.8kV with gap distance of 400 ㎛. When ITO powders and nitro cellulose were used in CNT paste, the emission characteristics of CNTs were found to be improved (Fig. 4(d)).

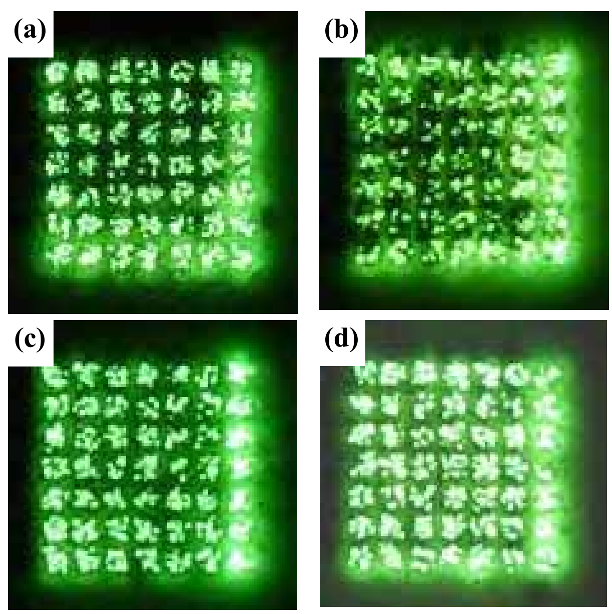


Fig. 4. Emission images of CNT emitters at 1.8kV using CNT paste of (a) CNT + ethyl cellulose + terpineol, (b) CNT + Frit + ethyl cellulose + terpineol, (c) CNT + ITO + ethyl cellulose + terpineol, and (d) CNT + ITO + nitro cellulose + butyl carbitol acetate

4. Conclusion

From thermal and electrical analysis of CNT pastes, it was found out that the thermal oxidation of CNTs was quite affected by the constituents in CNT paste such as organic binder and additives. Among those constituents, addition of ITO powders helped lifetime and emission characteristics of CNTs. Use of nitro cellulose as an organic binder in CNT paste is better for thermal property of CNTs compared to ethyl cellulose.

5. Acknowledgements

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6. References

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