Effect of PbO on the Field Emission Characteristics of Carbon Nanotube Paste

Junseop Kim[A], Jeung Choon Goak[A], Han Sung Lee[A], Ji Hyun Jeon[A], Jin Hee Kim[A], Yeon Ju Lee[A], Jin Pyo Hong[B], Naesung Lee**[A]*

[A]Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747

[B]New Functional Material and Device Laboratory, Department of Physics, Hanyang University, Seoul 133-791

Phone: +82-2-3408-3786, Fax : +82-2-3408-3664

E-mail: nslee@sejong.ac.kr

Abstract

In the CNT paste for field emission, PbO frit had a fatal influence on CNTs by accelerating a decomposition of CNTs during firing. In the thermogravimetric analysis on the mixtures of CNTs and other ingredients, it was evident that CNTs began to burn out at ~350℃ by reacting with PbO. This problem was overcome by replacing the PbO frit by the Pb-free frit such that most of CNTs could survive during firing. Consequently, the emission current of the CNT paste prepared using the lead-free frit was improved as much as 250 %, compared to the PbO-containing one. The CNT paste was further optimized by adding a dispersant, whose dispersibility was assessed by measuring the resistance of the paste. With 10% dispersant added, the emission properties of the paste was greatly enhanced as 50 times higher as those of the paste without a dispersant.

1. Introduction

Carbon nanotubes (CNTs) currently belong to the most promising electron emitter materials studied ever for field emission displays (FEDs), which has been attracted as a state-of-art display, due to their excellent chemical and mechanical stability as well as their high aspect ratios [1]~[4]. The CNT emitters have been fabricated in most cases either by directly growing CNTs or printing a CNT paste. Since display manufacturers are now keenly competing in the panel size and cost, the screen-printing method seems to be more promising than the direct growth one in these respects. In the screen-printing method, the CNT paste, which has a great effect upon the field emission characteristics, has to be designed mainly in consideration of dispersion, printability, adhesion, conductivity, a population density of CNT emitters, etc. [5]. The CNT paste thus consists of, in most cases, organic binder, dispersant, inorganic and conductive fillers, CNTs, and solvent, each of which plays its own unique role in the paste. Among them, PbO frit has been usually used to bring a strong adhesion between CNT paste and a substrate. The paste printed on glass has been fired at a suitable temperature, i.e. 420℃, to remove an organic binder and sometimes to consolidate the fillers. This study showed that PbO reacted with CNTs during firing, causing a drastic decrease of the population density of CNTs. The PbO-based frit, therefore, was replaced with the Pb-free frit such that most of CNTs could survive during firing [6]. The CNT paste was also investigated by adding different amounts of dispersant, which resulted in a drastic improvement of field emission properties upon optimization.

2. Experimental and Results

2.1 Effect of PbO frit on the CNT paste

The CNT paste was prepared by using 3-roll-mill to uniformly blend the mixture of multi-walled CNT (MWCNT, ILJIN) powder, organic binder, inorganic frit, and solvent. The CNT emitters were fabricated by the following processes; printing the CNT paste on an Ag-printed glass substrate, drying at 60℃ for 10 min, firing at 420℃ in air, and finally treating the surface by using an adhesive tape. The optimum firing temperature of the paste was decided using thermogravimetric analysis (TGA) to minimize a residual organic binder after firing. We also investigated the reaction of CNTs with other ingredients of the paste by using TGA. Field

emission characteristics were evaluated in a diode-type configuration with the CNT cathode and the phosphor-coated glass anode which were separated apart by 1 mm glass spacers. High voltages with a square pulse shape (duty ratio of 1/50) were applied to the anode while the cathode was grounded. Fig. 1

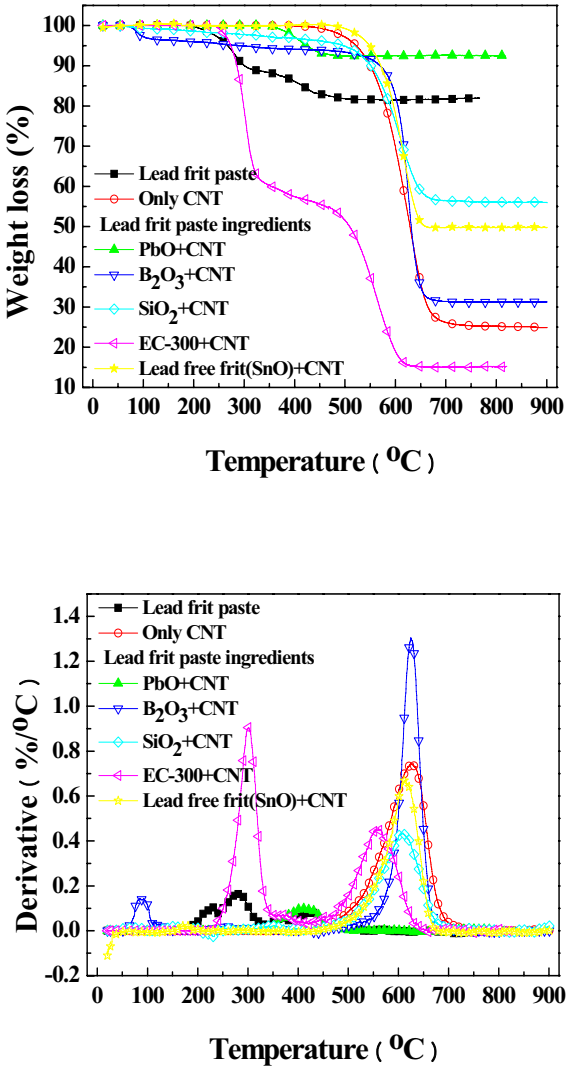

Fig. 1 TGA and derivative weight curves of the PbO frit-containing and the Pb-free CNT pastes, the pristine CNTs, and the mixture of CNTs and the other ingredients of pastes.

shows TGA and derivative weight curves of the PbO frit-containing and the Pb-free CNT pastes, the pristine CNTs, and the mixture of CNTs and each paste ingredient. Their thermal properties are expected to provide the optimal composition of the paste and its optimal firing temperature. The MWCNTs are burned out at 500~700℃ in a pristine state, but at 350~470℃ upon their residence inside the PbO frit-containing paste. The decomposition temperature of the CNTs is lowered by ~200℃ by reacting with other materials in the paste. Thus the TGA experiments were carried out for the mixtures of the CNTs with other ingredients of the paste, PbO, B_2O_3, SiO_2, and ethyl cellulose-300. Only PbO and ethyl cellulose-300 reduce the burning temperatures of CNTs by ~200 and ~50℃, respectively, while the others exert no influence. The PbO frit and the CNT paste containing PbO were analyzed by XRD after firing to verify the formation of any new products, as shown in Fig. 2. In the CNT paste, new peaks, designated by triangles (▲), occur to be assigned to $PbCO_3$. It seems that PbO decomposes CNTs by an oxidizing reaction, $PbO + C \rightarrow PbCO_3$ [7]. In many cases, metallic oxides can serve as a catalyst to oxidize the CNTs. For survival of more CNTs during firing, therefore, we replaced the PbO frit with the Pb-free frit (so-called, SnO frit) in the CNT paste. As intended, in Fig. 1, there is no decrease of the burning temperature of CNTs in the paste containing the SnO frit.

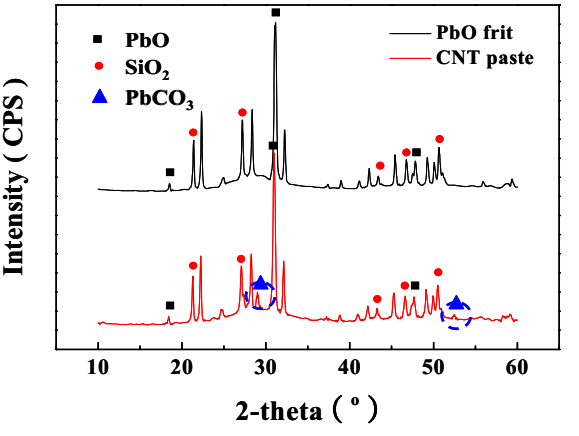

Fig. 2 XRD spectra of the PbO frit and the CNT paste containing PbO frit.

Fig. 3 is SEM images of CNTs prepared from the PbO frit- and the SnO frit-containing CNT pastes. They were fabricated by printing the CNT paste on glass substrates, firing, and tape-activating. Although the same amount of CNTs is engaged in preparing

both pastes, much less CNTs are observed in the PbO frit-containing paste than in the SnO frit-containing one. It is concluded that most CNTs survive in the SnO frit paste. Fig. 4 shows field emission characteristics of CNT emitters prepared from the CNT pastes containing different amounts of PbO frit

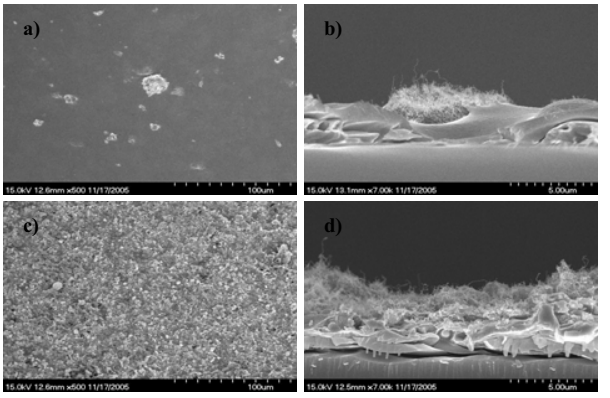

Fig. 3 SEM images of screen-printed CNT emitters after firing and treating with an adhesive tape, prepared from the CNT pastes based upon (a), (b) the PbO frit and (c), (d) the SnO frit. (a), (c) plan views and (b), (d) cross-sectional views

and SnO frit. Even if there is no dependence upon the adding amount of frits, the Pb-free CNT paste shows a considerable improvement of field emission properties than the PbO frit-based paste. At the applied field of 3.5 V/㎛, for example, the current densities are ~0.6 and ~1.5 mA/cm^2 for the PbO frit-based and the Pb-free CNT pastes, respectively. It is considered that the improvement of field emission properties in the SnO frit-containing CNT paste is due to a higher density of CNTs survived during firing.

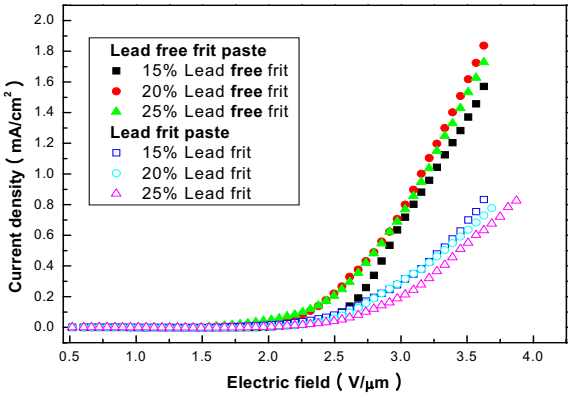

Fig. 4 Field emission characteristics of the CNT pastes containing different amounts of PbO and SnO frits.

2.2 Effect of dispersant in the using SnO-paste

CNTs are usually agglomerated each other due to their hydrophobic nature. Even though CNTs survive during firing, they have to be evenly distributed on the emitter surface. One of the ways to reach this purpose is to add dispersant to the CNT paste for good dispersion of CNTs in the paste [8]. This study attempted several different dispersants, BCA (Diethylene glycol monobutyl ether acetate, JUNSEI), Aquet (Bel-Art products), Tergitol NP-9 (Nonyl phenol polyethylene glycol ether, ALDRICH), and Triton X-100 (Polyoxyethylene(10) isocthlcyclohexyl ether, ALDRICH), to find the optimal one for CNTs. CNTs 0.006g were mixed in each dispersant 10g for 30 min by ultra-sonication. For the prepared solutions, the degree of dispersion of CNTs was monitored for 7 days by observing the precipitation at the bottom. As a result, Triton X-100 turned out to have the best dispersibility among them. We prepared the CNT paste samples by fixing the amounts of organic binder, SnO frit, and CNTs, while changing the relative amounts of a vehicle and a dispersant, as showed in Table 1. The dispersion of CNTs was analyzed by measuring the electric resistance of the pastes, which were printed between two ITO electrodes line-patterned on glass. As shown in Fig. 5, the resistance, measured 10 times each, considerably decreases by adding 5% of the dispersant, but is saturated above 5%. We measured the field emission characteristics of two samples, 0 and 10% dispersants, having the highest and lowest resistances of 1684 and 764 Ω, respectively. As presented in Fig. 6, field emission characteristics are greatly improved for the well dispersed sample. The emission current is saturated at ~0.8 mA/cm^2 for the no-dispersant sample, but at ~35 mA/cm^2 for the 10%-dispersant sample in the high electric field region, probably due to the current-limiting effect of their resistances [9,10]. Although the SnO frit contributes to an improvement of field emission properties of the CNT paste, its low fluidity at a firing temperature causes a rough emitter surface, which may be overcome by decreasing a particle size of the SnO frit powder.

Sample	1	2	3	4	5	6	7
Vehicle (%)	30	25	20	15	10	5	0
Dispersant (%)	0	5	10	15	20	25	30

Table 1. Amounts of a vehicle and a dispersant added in percentages to the CNT paste.

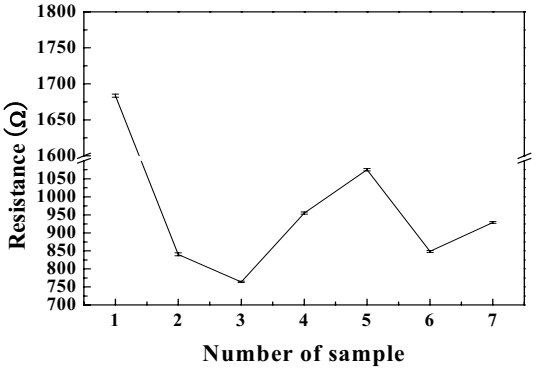

Fig. 5 Resistances of the CNT pastes with different amounts of dispersant.

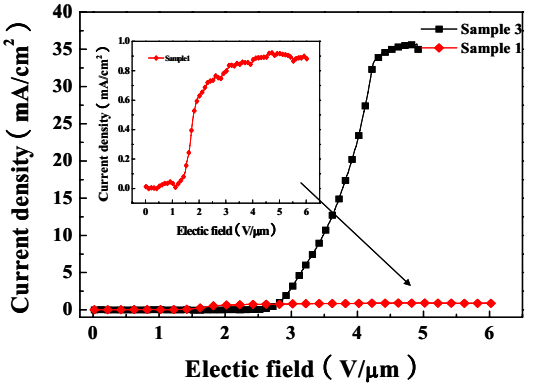

Fig. 6 Field emission characteristics of two samples, 0 and 10% dispersants, having the highest and lowest resistances of 1684 and 764 Ω, respectively, which were measured at 100 Hz and 1% duty for the gap of 500 ㎛.

3. Conclusion

In the PbO-containing paste, CNTs were decomposed by an oxidizing reaction with PbO during firing. A substitution of the PbO frit by the SnO (Pb-free) frit gave rise to a survival of most CNTs during firing and resultantly a considerable improvement of field emission characteristics of the CNT paste. The CNT paste was further optimized by adding a dispersant, whose dispersibility was assessed by measuring the resistance of the paste. With 10% dispersant added, the emission properties of the paste was drastically enhanced as 50 times higher as those of the paste without a dispersant.

4. References

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