Effect of electrical aging on emission stability of carbon nanotube paste

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Abstract

We report effects of electrical aging on the emission stability of carbon nanotube (CNT) paste for low cost and high low-cost and large area field emission devices or displays. Photosensitive carbon nanotube paste was formulated by using of spin on glass (SOG) as an inorganic binder and investigated emission properties and stability depending on electrical aging condition.

Introduction

Carbon nanotubes (CNTs) have been one of the most actively studied materials for cold cathode emitter [1,2]. Due to their geometrical properties (e.g. high aspect ratios and small tip radii of curvature) and good chemical and thermal stability, CNTs exhibit excellent field emission characteristics. Recently, the direct growth method such as chemical vapor deposition (CVD) and the screen-printing method using CNT powders were used for fabrication of field emission array (FEA). However, CVD techniques have problems in controlling each CNTs, complicated process, high cost and high growth temperature.

Carbon nanotube (CNT) paste has been proposed as a capable technology for large area field emission devices or displays (FED) due to excellent emission properties, low cost, simple process, and mass production [3,4].

For realization of high resolution FEDs, the emission characteristics of CNT emitter should be stable over very long periods of time. To obtain reasonable emission stability and lifetime of screen-printed CNT emitter, the electrical aging treatment is very important. In this study, we investigated effects of electrical aging on emission properties and stabilities of screen-printed CNT (sp-CNT) emitter.

Experiments

Photosensitive CNT paste was formulated by using of spin on glass (SOG) as an inorganic binder. Multi-walled CNTs (MWNTs) powders grown by CVD and acryl based organic solution were used as an electron emission source and organic vehicle, respectively. To form photosensitive organic vehicle, acryl was dissolved in terpineol and mixed with photosensitive additives such as photosensitive monomers, photosensitive oligomers and photo initiators. SOG is a type of glass that can be applied as a liquid and cured to form a layer of glass similar to SiO_2. SOG is originally employed in the planarization coating as smoothing layer, and dielectric materials for integrated circuit manufacturing.

The mixture of CNT powders, organic vehicles and inorganic binder was pre-mixed through solder paste softener for 15 min. Then the three-roll mill process was carried out for mixing and dispersion of

CNT powders in organic vehicle as polymer matrix. The mechanically well-dispersed CNT pastes were screen-printed onto an indium tin oxide (ITO) coated glass through a metal mesh and subsequently dried at 90 °C for 15 min in a forced convection oven. For uniform thickness and patterning of CNT emitter, backside ultraviolet (UV) exposure and organic solvent development techniques were applied. After the UV exposure process, CNT paste films were etched away by a spraying process (development) using organic solvents. The CNT paste was simply patterned because of the difference in solubility between UV exposed region and unexposed region. The residue of organic vehicle leads to problems such as out-gassing and arcing during a field emission measurement. Organic materials in paste have to be removed in order to obtain the stable emission characteristics. Therefore, CNT emitters were fired at 450 °C in nitrogen (N_2).

Field emission scanning electron microscopy (FESEM) was employed for the characterization of CNT paste and the emission characteristics of screen-printed CNT FEA were measured in a vacuum chamber with a parallel diode-type configuration at a base pressure of 5×10^{-6} Torr.

Results and discussion

Figure 1 shows FESEM images of screen-printed CNT emitter films after the backside exposure and firing. The CNT film easily formed a uniform thick film. The thickness of CNT paste films is under 2 μm.

For the emission stability measurement, screen-printed CNT emitters with SOG was prepared and fired at 450 °C in a N_2 ambient. After activation treatment, CNT emitter was transferred into a vacuum chamber at a working pressure below 5×10^{-6} Torr. In this case, we have adopted direct current (dc) voltage and a super used stainless steel (SUS) plate was used as the anode. The emission area was 1×1 cm^2 and the distance between cathode and SUS anode was maintained at 200 μm.

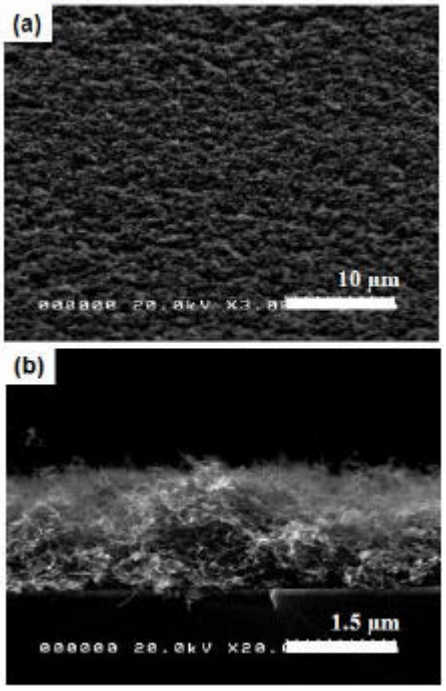

Figure 1. Top and cross-sectional SEM images of screen-printed CNT emitter

The I-V characteristics and the Fowler-Nordheim (F-N) plots [5] of CNT emitter before and after the electrical aging were shown in Figure 2. Stable and uniform emission currents from CNT emitter were obtained during the multiple field emission cycling. Before the lifetime measurement, we carried out the electrical aging by applying a constant voltage of 410 V (2.05 V/μm) for 72 h to CNT emitter. We can observe the emission current fluctuation at the initial stage of electrical aging. This current fluctuation was gradually reduced and electron emission stabilized as time passes.

The CNT emitter showed remarkable difference in the emission characteristics before and after the electrical aging as shown in Figure 2(a). The turn-on electric field, E_{to}, was defined as the electric field to obtain a current density of 10 μA/cm. The E_{to} of CNT emitter increased from 1.67 to 2.27 V/μm and then the total emission current was substantially decreased. From the F-N plots in Figure 2(b), we observed two characteristics regions. The I-V curve fits well to the F-N relation at the low field region. The I-V curve deviated from the linear F-N plot is due to current saturation of CNT emitters at the high field region. Although several mechanisms such as gas adsorbates and space charging effect have been proposed to explain current saturation phenomena, it is not clear yet [6-9]. According to the F-N model, the field-enhancement factor (b) and the emitting area (A) were calculated from the slope and the intercept of the F-N plot by assuming work function of the CNT emitters to be 5 eV, similar to graphite. The calculated β values of the CNT emitter before and after aging were 1727.5 and 1720, respectively. The corresponding A values were dramatically decreased from 1.77×10^{-8} to 1.23×10^{-11} after the electrical aging. It is suggested that the decrease in emitting area is attributed to the removal of relatively weak CNTs caused by resistive heating during the electrical aging at a high voltage, resulting in the suppressed emission current [7,10].

The long-term emission stability of CNT emitter was measured at constant voltage of 550 V (2.75 V/μm) after multi cycling and electrical aging. The current variation was represented in Figure 3 as a function of time. The electrical aged CNT emitter showed stable emission properties without degradation and arcing during operational time. The emission current fluctuation was less than 5 %. The emission current density of CNT emitter was approximately 387 μA/cm^2 after 19 h (not shown here). After the electrical aging treatment, emission properties of CNT emitter were suppressed but long-term emission stability was improved.

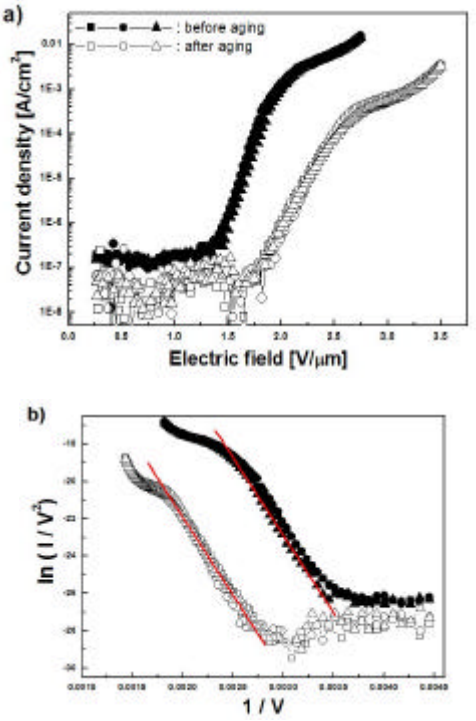

Figure 2. (a) The I-V characteristics and (b) the F-N plot of CNT emitter before and after the electrical aging.

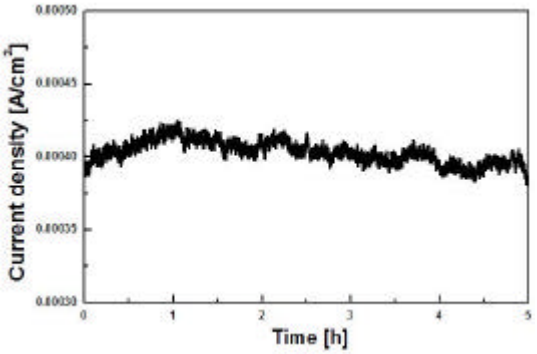

Figure 3. The long-term emission stability of CNT emitter after multi cycling and electrical aging.

Conclusions

Photosensitive CNT paste films with SOG were prepared and their emission properties were evaluated before and after electrical aging treatment. The emission properties of CNT emitter were decreased but long-term emission stability was improved after the electrical aging treatment.

Acknowledgment

This research was funded by the Ministry of Industry and Energy of Korea and Korea Science and Engineering Foundation (KOSEF) through the Center for Nanotubes and Nanostructured Composites (CNNC) at Sungkyunkwan University.

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