Stable and high emission current from carbon nanotube paste with spin on glass

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A carbon nanotube (CNT) paste was synthesized by mixing multiwalled CNTs (MWNTs), organic vehicles, and inorganic binder. The paste with spin on glass (SOG) showed improved uniformity, dispersion, and adhesion characteristics of the CNT paste layer. The emission characteristics of CNT paste with SOG were improved, and compared to those of a CNT paste with a glass frit. When the organic vehicle was changed from ethyl cellulose to acryl solution, current density of CNT paste increased. The firing condition for CNT pastes was investigated and optimized. It was found that firing at 450 °C under N2 was the most suitable condition for pastes with MWNTs. We obtained stable and high emission current of 100 mA at an electric field of 8.35 V/μm from CNT paste with SOG printed on a Ni plate. © 2005 American Vacuum Society.

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I. INTRODUCTION

Carbon nanotubes (CNT) exhibit excellent field emission characteristics and are one of the most actively studied materials for cold cathode field emitters due to CNTs’ high aspect ratios, small tip radii of curvature, mechanical strength, and good chemical and thermal stability.1,2 Field emitter arrays have been regarded as attractive electron sources in various applications such as field emission displays,3–5 x-ray tubes,6 lighting devices,7 microwave power amplifiers, and electron microscopy. Recently, both the direct growth method, such as chemical vapor deposition (CVD), and the screen-printing method using CNT paste have been recognized as two promising techniques for the fabrication of the field emission array. However, the CVD method has several problems such as low throughput, high cost, and high growth temperature in large area cold cathode fabrication. However, the screen-printing process using CNT paste has been adopted as an effective method for fabricating the large area cold cathode because of low cost, simple process, uniform emission site, and mass production advantages.3,5 CNT paste was synthesized by mixing CNT powders, organic vehicles, and inorganic binder. For the stable, uniform, and high emission current of the screen-printed cold cathode field emitter, uniformity and adhesion of CNT films to the substrate is necessary. In order to improve the adhesion between CNT paste film and the substrate after the firing process, a glass frit was conventionally used as an inorganic binder. However, CNT paste with a glass frit has shown poor uniformity in cathode film formation and emission characteristics. In this work, through the optimization of paste composition and firing condition, we studied the formation of the CNT paste layer for high field emission current. CNT pastes with different inorganic binders and organic vehicles were prepared and tested. The field emission characteristics were investigated for CNT pastes with different compositions after firing under various conditions.

II. EXPERIMENT

CNT paste was synthesized by mixing CNT powders, organic vehicles, and inorganic binder. Multiwalled carbon nanotubes (MWNTs) powders grown by CVD and ethyl cellulose (EC) solution (or acryl solution) were used as an electron emission source and organic vehicle, respectively. We prepared CNT pastes with different inorganic binders such as glass frit and spin on glass (SOG). Figure 1 shows the schematic diagram of the CNT paste formation process. The mixture of CNT powders, organic vehicles, and inorganic binder was premixed through the solder paste softener for 15 min. Then the three-roll mill process was carried out for mixing and dispersion of CNT powders in the organic vehicle used as a polymer matrix. Mechanically well-dispersed CNT paste was printed onto 2 × 2 cm2 of the indium tin oxide (ITO) coated soda lime glass. In order to remove the solvents in the CNT paste, heat treatment was performed in a forced convection oven for 15 min at 90 °C in an air atmosphere. An organic vehicle plays an important role for the rheological properties of CNT paste such as viscosity, thixotropy, and printability. However, residue of the organic vehicle causes problems such as outgassing and arcing during the field emission. Therefore, the organic vehicles in CNT paste must be removed in order to obtain stable emission current. The CNT paste film was fired in air or nitrogen (N2) at temperatures ranging from 400 to 450 °C.
Field emission scanning electron microscopy (FESEM) was employed for the characterization of CNT paste morphology. The emission characteristics of CNT paste were measured in a vacuum chamber with a parallel diode-type configuration at pressure of $5 \times 10^{-6}$ Torr after surface activation treatment with adhesive tape. The distance between the cathode and the anode was 200 $\mu$m. For the measurement of the emission current, we used both a direct current (dc) power supply and a pulsed voltage power supply with a duty cycle of 1/500.

### III. RESULTS AND DISCUSSION

Two types of CNT paste were synthesized. One type was composed of CNT powder, EC solution, and a glass frit. The other type was prepared by using SOG instead of a glass frit.

Figure 2 shows FESEM images of CNT pastes with different inorganic binders. When we changed an inorganic binder from a glass frit to SOG, the morphology of the cathode layer significantly changed after firing at 450 °C under an air atmosphere. Figures 2(a) and 2(b) are cross sectional and top views of CNT paste with a glass frit, respectively. In the case of CNT paste with a glass frit, we observed a small amount of CNTs and partially melted glass frits. The low density and poor uniformity of CNT emitters were due to the fact that both organic materials and MWNTs were exposed to air during firing at 450 °C. Therefore, in the case of CNT paste with a glass frit, the optimization of firing conditions such as the gas ambient and firing temperature, was required to obtain the uniform cathode layer with a reasonable density of CNT emitters. Figures 2(c) and 2(d) are cross sectional and top views of CNT paste with SOG, respectively. As shown in Figs. 2(c) and 2(d), uniform and thick cathode layers with a reasonable CNT emitter were obtained after the same firing process as that used in the CNT paste with a glass frit. The film thickness was about 7.1 $\mu$m.

The emission characteristics of these CNT pastes were measured in a vacuum chamber with a parallel diode-type configuration at a pressure of $5 \times 10^{-6}$ torr. We used a pulsed voltage power supply with a duty cycle of 1/500. To obtain high emission current density and uniform emission site from the screen-printed CNT emitters, special activation treatments such as laser irradiation, ion irradiation, and adhesive tape method were reported. Before current-voltage ($I-V$) measurement, we carried out the activation treatment by using adhesive tape. Figure 3 shows the current density-electric field ($J-E$) curve and the Fowler–Nordheim (F-N) plot of the activated CNT paste films with a glass frit and SOG. The F-N plot confirmed the electron emission from the quantum mechanical tunneling. The emission current density at an applied field of 7.95 V/$\mu$m increased from 133 to 265 $\mu$A/cm$^2$ when the inorganic binder changed from a glass frit to SOG.

The organic vehicle makes a significant effect on the emission characteristics and rheological properties of CNT paste.
paste. CNT paste was synthesized by using the acryl solution as an organic vehicle instead of the EC solution to study the effects of the organic vehicle on the properties of CNT paste. A glass frit and SOG were used as inorganic binders. Figures 4(a) and 4(b) show SEM images of acryl based CNT paste with different inorganic binders. When acryl solution was used as organic vehicle, the thickness of CNT pastes was increased. Figure 4(c) shows the J–E curve of the paste with different inorganic binders. The inset of Fig. 4(c) shows the F-N plot. When the organic vehicle changed from the EC solution to the acryl solution, the emission current density at an applied electric field of 5 V/μm increased from 54 to 228.5 μA/cm² in the paste with a glass frit, and from 61 to 302.5 μA/cm² in the paste with SOG. The current density increased by five times in magnitude after the organic vehicle changed from the EC solution to the acryl solution irrespective of the type of an inorganic binder. However, the film uniformity and emission current density of the CNT paste with SOG was better than that of the CNT paste with a glass frit when the acryl solution was used as the organic vehicle. These results suggest that the acryl solution is more suitable and is a better organic vehicle than the EC solution for field emission applications.

To obtain high emission current from printed CNT emitters, the effect of firing condition was investigated. CNT paste films using the acryl solution were prepared and fired at temperature ranging from 400 to 450 °C in air or N₂. Figure 5 shows the effects of the firing condition on the emission properties of acryl based CNT paste with SOG. The best emission properties of CNT paste were obtained when the CNT paste was fired at 450 °C in an N₂ ambient. The current density at an applied electric field of 5 V/μm was 302 μA/cm². The electric field at the current density of 300 μA/cm² was 4.4 V/μm.

For high electron emission applications ITO-coated soda lime glass as a cathode electrode is not suitable because of low electrical conductivity. Therefore, CNT paste was printed onto a Ni plate. Figure 6 shows scanning electron microscopy (SEM) images of the acryl based CNT paste with SOG printed onto a Ni plate. As shown in the inset of
Fig. 5. The emission characteristics of acryl-based CNT paste with SOG depending on different firing conditions.

Fig. 6(a), uniform CNT paste film was formed with a thickness of about 20 µm. Figure 6(b) shows CNTs protruded from the CNT paste surface by surface treatment using adhesive tape.

J–E measurement was carried out using dc voltage in a high vacuum chamber. For the emission current measurement, a stainless steel plate was used, as an anode instead of ITO coated glass, because ITO coated glass is not strong enough to endure a high density of electron bombardment at a high electric field. The emission area was 1 x 1 cm². The distance between anode and cathode was 170 µm. Figure 7 shows the cycled J–E plot from acryl-based CNT paste with SOG printed onto a Ni plate. The CNT paste shows stable emission current after the third measurement. The F-N plot is shown in the inset of Fig. 7, indicating that the electron emission comes from the quantum mechanical tunneling. We obtained a very high emission current of about 100 mA at the electric field of 8.35 V/µm from CNT paste film printed on the Ni plate.

IV. CONCLUSION

CNT paste was synthesized by using SOG as an inorganic binder instead of a glass frit. We improved the emission properties of CNT paste through optimization of the paste composition and the firing condition. CNT paste with SOG showed enhanced emission characteristics compared to CNT paste with a glass frit. When the organic vehicle changed from the EC solution to the acryl solution, the current density of CNT paste increases by about five times in magnitude. Firing at 450 °C under N₂ is the most suitable condition for CNT paste. From CNT paste with SOG, we obtained stable and high emission current of 100 mA at an electric field of 8.35 V/µm. Our experiments have shown that CNT paste with SOG can be used as an efficient electron emitter in vacuum nanoelectronics applications.

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