Influence of field emission on agglomerated carbon nanotubes in pastes

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The authors have studied the modification of surface morphologies of screen-printed carbon nanotube (CNT) film by a liquid pretreatment and the agglomeration influence of CNT emitters. Liquid pretreatments before and after heat treatment are efficient as a removal process for organic binders for the improvement of field emission. In addition, this method enables to entangle an emitter to free individual standing CNTs.
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I. INTRODUCTION

Screen printing has many advantages in fabricating field emission devices. Some of these advantages are low cost and simple fabrication process in large area flat panel display.[1–3] The uniform surface treatment in field emission from the screen-printed carbon nanotube (CNT) film is very important to various applications. There have been many previous reports on the improvement of poor field emission from CNT films because CNT emitters are randomly distributed, easily entangled, and buried in matrix materials such as organic binders. These CNTs need surface treatments to change the surface morphology. Vink *et al.* have demonstrated excellent electron emission properties using an adhesive tape.[4] Kim *et al.* have improved electron emission with a good uniformity using a soft rubber roller and multiple field emission cycles.[5] Kim *et al.* have enhanced the surface morphology of CNT paste by ion irradiation.[6] Kanazawa *et al.* have used an Ar plasma treatment to improve field emission characteristics.[7] These methods have improved field emission characteristics through the surface morphological change of the CNT emitters covered with organic residues after heat treatment.

In this study, we describe our work in modifying surface morphologies of screen-printed CNT films by a liquid pretreatment before heat treatment. By performing this method, organic binders adhering to freestanding CNT emitters can be effectively removed because of a more direct exposure to a heat atmosphere during heat treatment.

II. EXPERIMENTS AND RESULTS

We first examined field emission characteristics of the entangled CNT bundles prepared by spray deposition, so the influence of the organic binders on field emission of the CNT film was eliminated. In our experiment, the prepared suspension of multiwalled carbon nanotubes (MWCNTs)/fillers [indium tin oxide (ITO) powder] dispersed in ethanol was sprayed onto the glass substrate coated with high purity (99.9999%) indium. It was then heated above the melting point of indium (about 160 °C) in air to improve the adhesion between the nanotubes and as the cathode electrode. The emission evaluations were conducted in a vacuum system of $\sim 10^{-6}$ Torr. The measured current density–voltage (*J-V*) curves and the corresponding Fowler-Nordheim (FN) plots for the samples before and after surface treatment are presented in Fig. 1. Turn-on fields, which correspond to the current density of 1 $\mu A/cm^2$, were measured as 1.7 and 1.85 $V/\mu m$ with and without surface treatment, respectively. After a mechanical surface treatment using an adhesive tape, the current density was considerably increased from about 0.1 to 2.5 mA/cm^2 at an electric field of 3 $V/\mu m$. Previously reported results have presented about an influence of organic residues after heat treatment.[8] Our results suggested that although the CNT film prepared by spray deposition did not contain organic materials such as binders, electron emission properties from as-deposited film were not improved as expected because entangled CNT bundles and dense CNTs were either already presented or formed in the CNT film (not shown here). Thus these morphologies played a dominant role in field emission. This was mainly because of the strong agglomeration of CNTs, indicating that the van der Waals forces between the CNTs caused them to mutually attract each other rather than homogeneously disperse. According to these results, although organic materials in the screen-printed CNT films were completely removed by proper heat treatment, the presence of entangled CNT bundles or agglomeration of CNTs also seemed to cause a poor electron emission

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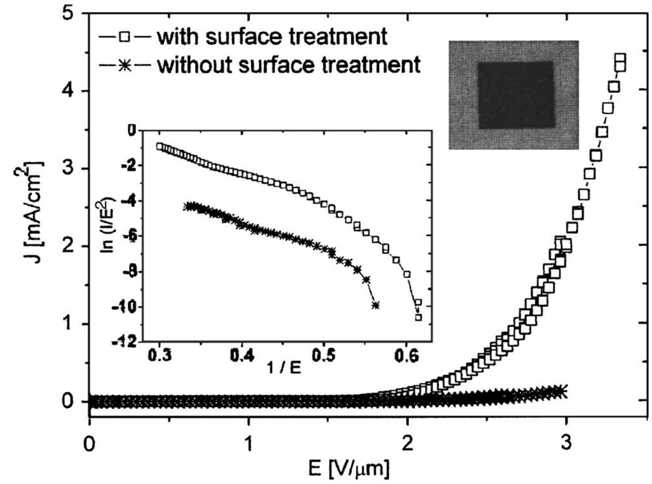

FIG. 1. Field emission characteristics of the CNT film by spray method on high purity (99.9999%) indium (In) substrate. *J-V* curves and FN plots (inset). The inset shows a photo image of sprayed CNTs on indium layer.

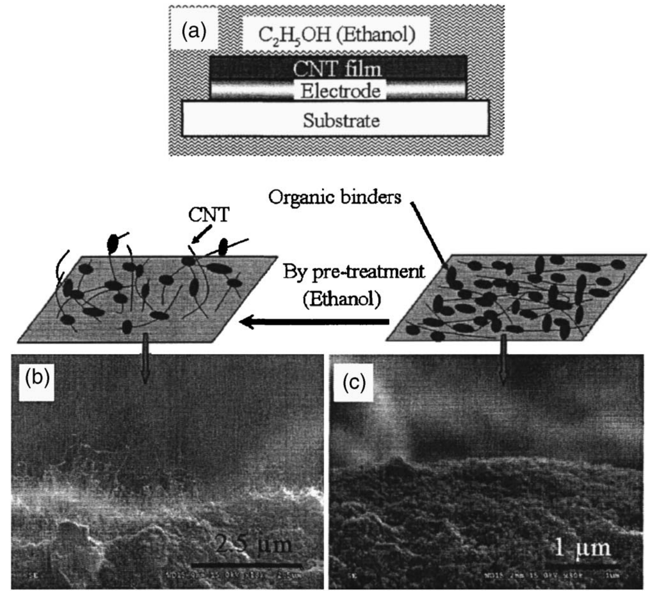

FIG. 2. (a) Schematic diagram of the CNT film treated by liquid pretreatment, (b) SEM image, and (c) schematic diagram and SEM images of screen-printed CNT films before liquid pretreatment.

as in the case of the sprayed CNT film. The inset of Fig. 1 shows a real image of the prepared sample with the CNT film on an indium electrode.

The CNT paste mixture which was composed of MWCNTs, an organic binder, a filler, and inorganic frit was prepared by using three-roll milling. The paste was screen printed with an active area of 2×2 cm^2 onto an ITO-coated glass substrate. The paste was then dried at 120 °C for 20 min. Pretreatment of the CNT film was carried out by the following processes. The prepared sample was immersed for several seconds in ethanol (C_2H_5OH). Figure 2(a) shows a schematic diagram of the organic binder adhered to the free-standing CNTs with removal of a small amount of organic binder and then after drying ethanol on the film surface, it was treated by using an adhesive tape to expose the CNTs and break up CNTs that were easy to agglomerate, bundled together, and entangled, leading to a poor electron emission in the film. This method presented optimum CNT emitters without destruction of the pattern shape. The final procedure was to fire the film at 380 °C in a nitrogen atmosphere to remove the organic binder. Ethanol may weaken the binding between entangled CNTs and the organic binder materials in the CNT film and was thus used as a liquid pretreatment. The surface treatment using a sticky tape with a low adhesive enabled the entangled CNTs to be broken up into individual freestanding CNTs. It was easier to remove the organic binders that adhered to individual distributed CNTs than the entangled CNT bundles with organic binders. Figure 2(b) shows a scanning electron microscope (SEM) image of the protruded CNTs after liquid pretreatment. On the other hand, as shown in Fig. 2(c), we show the as-deposited CNT film, packed as entangled CNT bundles with an organic binder and the cross sectional SEM image before liquid pretreatment. Differences in two morphological characteristics after and before pretreatment of CNT film are clearly shown in Figs. 2(b) and 2(c). As mentioned previously, the CNT film, obtained by the liquid pretreatment, was relatively well-aligned vertically out of the surface, whereas the as-deposited CNTs were densely packed or agglomerated with possible organic binders. When carrying out the mechanical surface treatment only without ethanol treatment, the morphological characteristics of the CNT film were not changed because of the strong binding between CNTs and organic binders. We believe that the organic binders, by using the liquid pretreatment, could be reduced enough compared to those of the as-deposited film. These morphologies can contribute to electron emission without heat treatment. The SEM results

TABLE I. Summary of field emission characteristics for each process treatments. Surface treatment (adhesive taping), liquid pretreatment (ethanol and adhesive taping), post-treatment (adhesive taping), and heat treatment (HT).

Sample	Turn-on field (V/μm)	*J* (applied electric field) (2.5 V/μm) (mA/cm^2)
Sprayed CNT film without surface treatment	1.85	0.03
Sprayed CNT film without surface treatment	1.70	0.54
Printed CNT film with liquid pretreatment before HT	1.47	2.87
Printed CNT film with liquid pretreatment after HT	1.76	1.13
Printed CNT film with post-treatment after HT	1.62	1.13

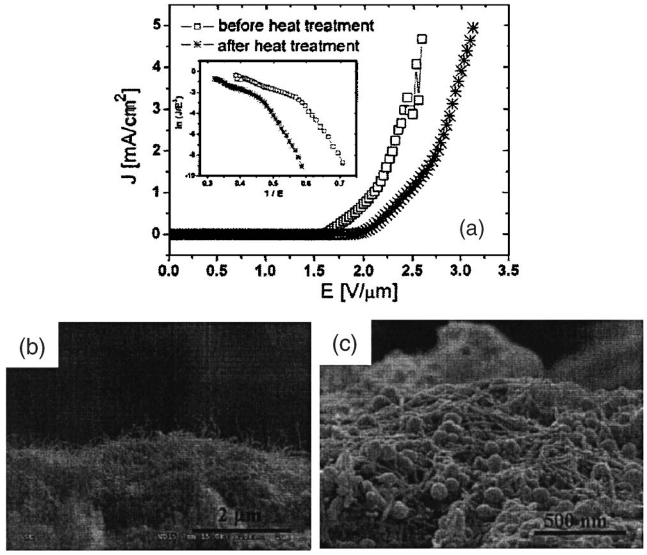

FIG. 3. (a) *J*-*V* curves of the CNT paste with liquid pretreatment after and before heat treatment. The inset curve is FN plots. [(b) and (c)] SEM images of CNT paste with and without liquid pretreatment after heat treatment, respectively.

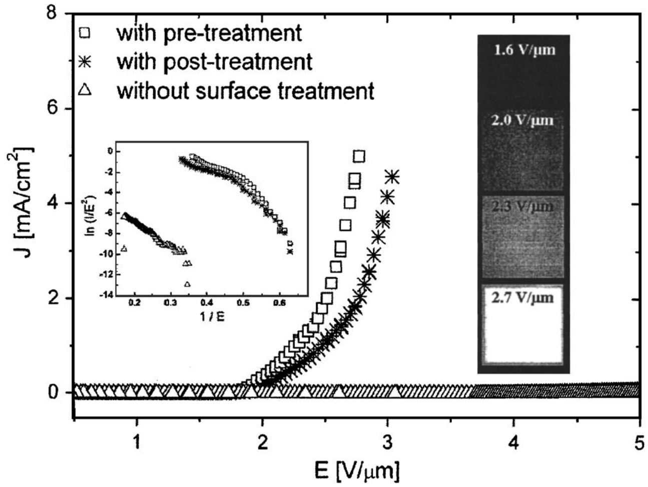

FIG. 4. *J*-*V* curves and FN plots (inset) of the CNT films treated with different methods: with a liquid pretreatment before heat treatment, with a post-treatment by adhesive taping after heat treatment, and with no surface treatment after heat treatment. The inset shows the corresponding emission images of the CNT film with liquid pretreatment before heat treatment.

also show that the organic binders binding to the surface of the vertically well-aligned CNT emitters can be effectively removed than those of the entangled CNT bundles during heat treatment process because of more exposure to the major part of the organic binders that adhered to the individual nanotubes. That is, since the surface area of the exposed organic binders was increased, the organic binders were well burned out during the heat process.

Figure 3(a) shows the *J*-*V* characteristics of the CNT paste depending on the liquid pretreatment after and before heat treatment and the corresponding FN plots. The turn-on electric fields were 1.47 and 1.76 V/μm with liquid pretreatment before and after heat treatment, respectively. The *J* also were obtained as 2.87 and 1.13 mA/cm^2 at 2.5 V/μm before and after heat treatment, respectively. The field enhancement factors (β) were calculated from slopes of the FN model[9] using ln (J/E^2) vs $1/E$ in low voltage assuming the work function of the CNT to be 4.5 eV, as shown in the inset of Fig. 3(a). The field enhancement factors were 3043 and 2708 without and with heat treatment, respectively. The sample with the applied liquid pretreatment before heat treatment showed better emission characteristics than the sample with the applied liquid treatment after heat treatment. Because a firing process to burn out the organic vehicle was applied to the CNT paste, the emission property of the CNT paste was enhanced because of a decrease in thermal damage and oxidation of the CNT, whereas the organic vehicle caused arcing under high voltages during measurement. In order to analyze the morphological change of the pretreated CNT film, a SEM examination was performed. Figures 3(b) and 3(c) show SEM images of the CNT paste with and without liquid pretreatment after the heat treatment. As shown in the SEM images, the sample with liquid pretreatment had better surface morphologies than the sample without liquid pretreatment.

Figure 4 shows the *J*-*V* curves and FN plots (inset) measured as a function of the voltage applied at the CNT films with three different methods: with liquid pretreatment before heat treatment, with post-treatment by adhesive taping after heat treatment, and without surface treatment after heat treatment with the same conditions. The different results seemed to originate from removing the top of the film using an adhesive tape to expose the vertically aligned emitters, whereas the pretreatment in other reports was intended to expose emitters from an entangled CNT film. The field emission characteristics of the samples were measured using a simple diode configuration. The gap between the cathode substrate with the CNT film and the anode was 270 μm. As a result, for the sample with the applied liquid pretreatment, the turn-on field was significantly decreased, and the emission current was somewhat increased compared to those samples of post-treated CNT film. The process treatments and the field emission results for each of the samples are summarized in Table I. The inset of Fig. 4 shows the corresponding emission patterns with electric fields of 1.6, 2.0, 2.3, and 2.7 V/μm, respectively, indicating very uniform emission sites after liquid pretreatment. The field emission patterns were observed on the anode screen, which was coated with phosphor.

III. CONCLUSIONS

Screen-printed CNT film underwent a pretreatment with ethanol to improve the surface morphology of the film and remove organic binders. The vertical alignment of the pasted CNTs and enhanced field emission were obtained by this method without surface treatment after firing.

ACKNOWLEDGMENTS

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