The effect of Ar neutral beam treatment of screen-printed carbon nanotubes for enhanced field emission

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This study examined the effectiveness of an Ar neutral beam as a surface treatment for improving the field emission properties of screen-printed carbon nanotubes (CNTs). A short period of the neutral beam treatment on tape-activated CNTs enhanced the emission properties of the CNTs, showing a decrease in the turn-on field and an increase in the number of emission sites. The neutral beam treatment appeared to render the CNT surfaces more actively by exposing more CNTs from the CNT paste without cutting or kinking the already exposed long CNT emitters. The treated CNTs emitted more electrons than the CNTs treated using other methods. When the field emission properties were measured after the neutral beam treatment, the turn-on field decreased from 1.65 to 0.60 V/μm and the emission field at 1 mA/cm^2 decreased from 3.10 to 2.41 V/μm. After the neutral beam treatment for 10 s, there was an improvement in the stability of the emission current at a constant electric field. It is expected that the neutral beam treatment introduced in this study will provide an easy way of improving the emission intensity and stability of screen-printed CNT emitters. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714648]

I. INTRODUCTION

Recently, the excellent material and electrical properties of carbon nanotubes (CNTs) have led to investigations into applications as field emission tips in a field emission display (FED).[1–4] CNT emission tips can have a field enhancement factor one hundred times larger than the Spindt-type emission tips due to their high aspect ratio (a few micrometers in length with a few tens of nanometers in diameter), which can reduce the field emission voltage.[5] In addition, a stable emission current can be expected due to the strong physical properties of CNTs.

In general, there are two different methods currently under development to apply CNTs as field emitters on FED. One is to grow the CNTs directly onto patterned catalyst layers at low pressure by chemical vapor deposition[6,7] (CVD), and the other is to screen print the CNTs mixed with organic vehicles.[8–10] There are problems associated with the direct growth of CNTs on a glass substrate for FED. These include the need for an expensive large area vacuum system for the substrate and the difficulty in generating a uniform plasma over a large area particularly for plasma enhanced CVD. Therefore, the screen printing of CNTs on FED glass substrates has attracted more attention for commercial applications. However, the screen printing of CNTs have problems such as the presence of a paste residue on the CNT surface, outgassing from the paste, nonuniform dispersion of CNTs during the mixing with the paste, etc. Therefore, special surface treatments are often needed to achieve the required low-voltage emission characteristics and high emission site density. Several methods for overcoming these problems have been suggested including adhesion tape activation, plasma exposure, and soft rubber rolling.[11–18] Among these methods, adhesive tape activation and soft rubber rolling are easy methods for removing the paste layer on the CNTs. However, these methods tend to leave some residues and destroy the CNT patterns, which can result in nonuniform emission sites. The remaining residue could be removed by the plasma treatment after the tape activation or soft rubber rolling. However, during the plasma treatment process, long CNT emitters are bombarded intensively and cut by the positive ions due to the high electric field at the long CNT tip, resulting in a short length and damaged CNTs.

In this study, screen-printed CNT pastes were treated using the adhesive tape activation method to remove a major part of the organic matrix material and to distribute the CNTs sparsely. Subsequently, the tape-activated CNT paste was further treated using an Ar neutral beam instead of an Ar plasma to decrease the intensive bombardment of the long CNT tips. In the case of the Ar neutral beam treatment, the neutral beam collides not only with the longer CNT emitters with a higher electric field but also with the inactivated CNT emitters on the paste sample surface. Therefore, a larger number of activated CNT emitters are possible without cutting the long CNT emitter tips, which could improve the emission uniformity.

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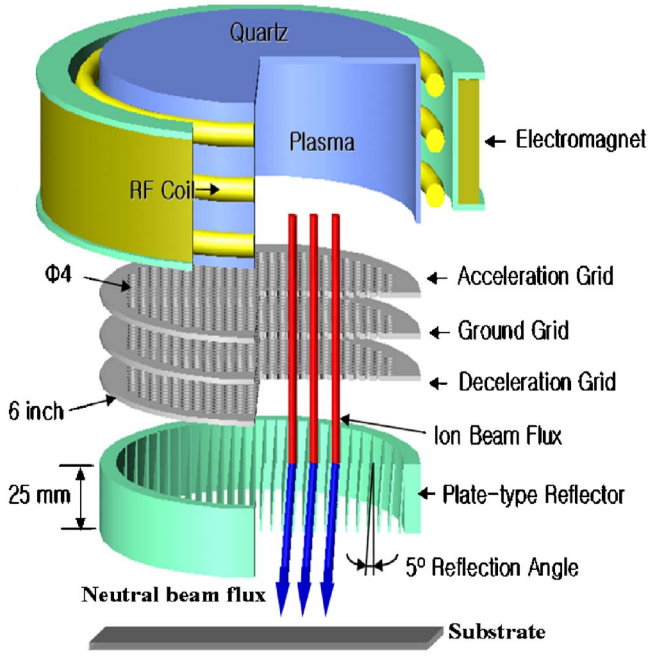

FIG. 1. (Color online) Schematic diagram of the neutral beam treatment system used in this study.

II. EXPERIMENTAL DETAILS

A CNT paste composed of multiwalled carbon nanotubes (MWNTs) synthesized by thermal CVD and printed on a 2 $\times 2$ cm^2 active area of an indium tin oxide (ITO) coated soda lime glass substrate was used as the sample. The samples were baked in an oven at 120 °C for 10 min and fired at approximately 380 °C under N_2 ambient in order to remove the organic binders, which was followed by natural cooling to room temperature. After a physical surface treatment using an adhesive tape to expose the vertically aligned emitters, a CNT paste on the glass substrate was treated with an Ar neutral beam to improve the emission stability, emission current, and uniformity.

The neutral-beam source used in this study consisted of a rf ion gun with a three-grid system and a planar reflector and the schematic diagram of the source is shown in Fig. 1. The diameter of the ion guns and hole size of the grid system was 6 in. and 2 mm, respectively. A 200 W rf power at a frequency of 13.56 MHz was applied to the ion gun. Ar was used to generate the plasma in the ion gun and the ions from the plasma were extracted using a grid assembly. The Ar gas flow to the ion gun was 5 SCCM (SCCM denotes cubic centimeter per minute at STP) and, at this flow rate, the chamber pressure was about 4 mTorr. In the three-grid system, a potential of +100 V (V_a) was applied to the first grid located close to the source (acceleration grid), a potential of −400 V (V_e) was applied to the second grid (extraction grid), and the third grid located outside of the ground was grounded to obtain a parallel ion beam with an energy of approximately 100 eV. The reflectors were made from a parallel stack of polished stainless steel supported by an Al block and were arranged to have a 5° angle to the ion beam direction. The plates of the reflector were matched to each hole of the grid of the ion gun. The depth of the reflector plate was optimized to reflect all the parallel ions extracted from the ion gun and to neutralize the ions.[19] The neutralization efficiency was >99%.

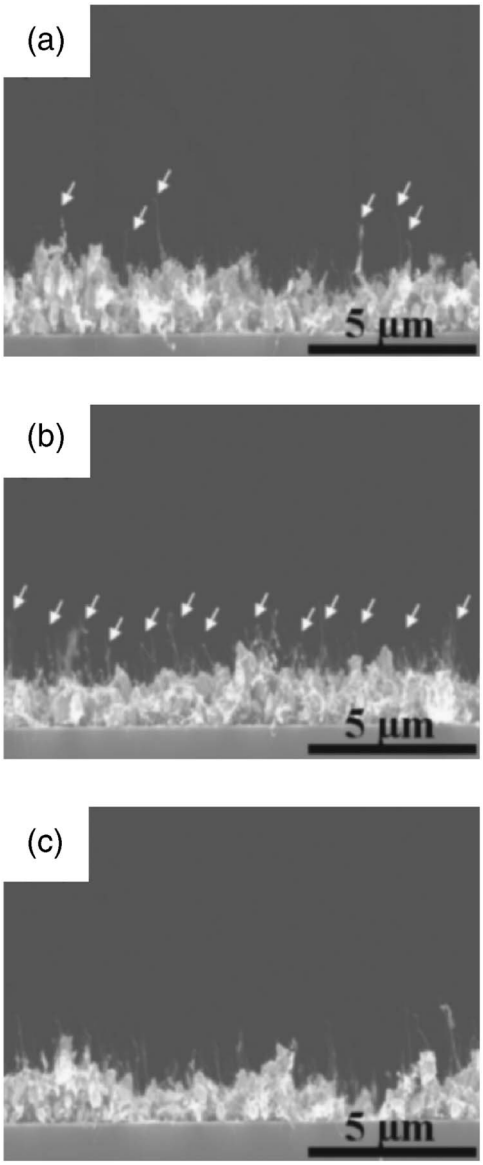

FIG. 2. SEM images of the screen-printed CNT samples (a) after removing the top part of the layer by adhesive tape (adhesive tape activation), followed by a neutral beam treatment of ~100 eV for (b) 10 s and (c) 60 s.

III. RESULTS AND DISCUSSION

Figure 2 shows the surface morphology of the screen-printed CNT samples before and after the neutral beam treatment. Figure 2(a) shows the scanning electron microscope (SEM) image of the printed CNT emitter on a glass substrate after the physical surface treatment using adhesive tape activation to expose the vertically aligned emitters. Tensile forces were applied to the CNT paste while removing the tape. These forces are directed perpendicular to the CNT paste, which induces the observed orientation of the CNTs. However, as shown in the figure, the CNT emitters fabricated by the taping method show a large distribution of CNT lengths, which produces nonuniformly distributed hot emission sites. Figure 2(b) shows a SEM image of the CNT paste

treated with the Ar neutral beam for 10 s after the adhesive tape activation. The Ar neutral beam was operated at a rf power of 200 W, an acceleration voltage of 100 V, and an extraction voltage of −400 V to obtain approximately 100 eV of a parallel Ar neutral beam. As shown in Fig. 2(b), the buried CNTs were exposed out of the binder paste, and the number of activated CNT emitters was higher after the neutral beam treatment.

In general, the enhancements in the field emission properties of the CNTs after the plasma treatment are due to an increase in the dispersion of CNTs and an increase in the number of activated CNT tips by ion bombardment. Zhi *et al.* reported an improvement in the emission characteristics after a hydrogen plasma treatment of CNTs grown by CVD and showed that this improvement was the result of an increase in the number of activated CNT tips and the removal of the catalyst particles remaining on the CNT tips.[20] Gohel *et al.* also reported an improvement in the field emission properties of CNTs grown by CVD after a N_2 plasma treatment and concluded that it was from the reduction in the nanotube density and nitrogen doping in the treated CNTs.[21] However, an increase in the electron emission stability and the improvement in the emission uniformity were not reported. On the other hand, Kim *et al.* reported an improvement in the emission stability of the screen-printed CNTs after a Xe/Ne plasma treatment by removing a small portion of the protruding emitters, which dominates the initial emission characteristics.[22] During the treatment process, CNT emitters with a long length appeared to be kinked or cut by the bombardment of positive ions in the plasma due to the high electric field that is concentrated on the long CNT tips, resulting in short emitters, which are believed to improve the emission stability. However, a higher turn-on field was observed after the plasma treatment as a result of the cutting of the long CNT tips and by damage to the CNTs. In the case of the neutral beam treatment carried out in our experiment, the Ar neutral beam collides not only with the longer CNT emitters protruding out of the paste but also with the inactivated CNT emitters on the paste sample surface due to a lack of an electric field during the neutral beam treatment, resulting in a higher number of activated CNT emitters without the removal of long CNT emitter tips. Figure 2(c) shows a SEM image of the paste CNTs after the neutral beam treatment for 60 s. It was found that the length and the number of the CNT emitters did not change significantly with increasing processing time.

The field-emission properties of the screen-printed CNTs were measured with a parallel diode-type configuration using a dc power supply in a vacuum chamber (2×10^{-6} Torr). The CNT emitter area was 2×2 cm^2 and the distance between the top anode electrode (glass coated with indium tin oxide) and the CNT layer was 400 μm. Figure 3(a) shows the electric field (E) versus current density (J) of the CNTs at different neutral beam treatment times after adhesive tape activation. The figure shows that the turn-on electric field (defined as the electric field at 1 μA/cm^2 of the emission current density) before the neutral beam treatment was 1.65 V/μm, and a current density of 1 mA/cm^2 was obtained at an electric field of 3.10 V/μm. As shown in the

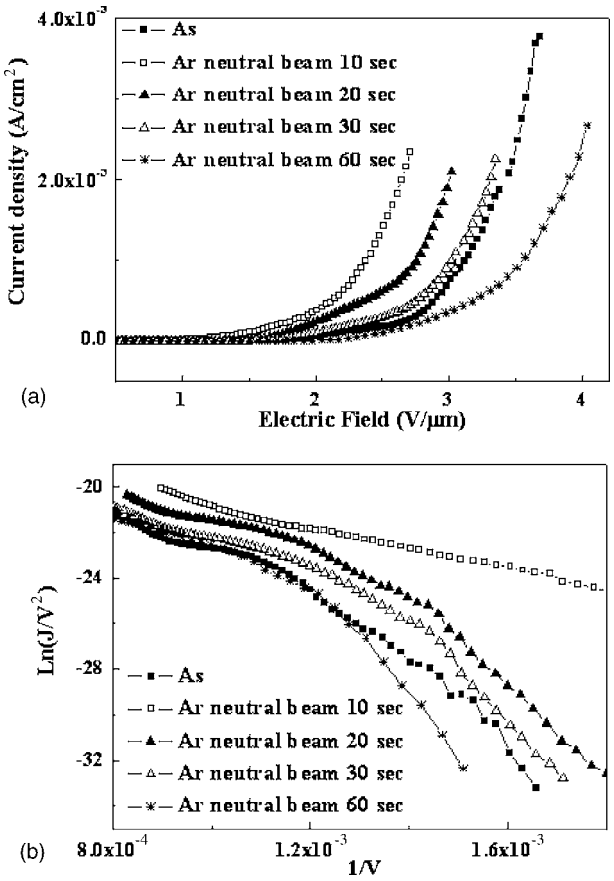

FIG. 3. (a) *I-V* characteristics and (b) Fowler-Nordheim plot of the CNTs as a function of the neutral beam treatment time after adhesive tape activation.

figure, after the Ar neutral beam treatment for 10 s, the turn-on electric field decreased from 1.65 to 0.60 V/μm. However, the turn on electric field of the CNT emitters increased from 0.60 to 1.83 V/μm with increasing treatment time from 10 to 60 s. A current density of 1 mA/cm^2, which is essential for flat panel displays, was obtained at 2.41, 2.70, 3.05, and 3.57 V/μm after the treatment for 10, 20, 30, and 60 s, respectively. It is believed that the decrease in the turn-on field after the Ar neutral beam treatment for 10 s is due to the increase in the number of activated CNT emitters by the neutral beam treatment. The increase in the turn-on voltage after the further increase in the Ar neutral beam treatment time appears to be related to the damage to the exposed CNT emitter tip due to heavy bombardment by the Ar neutral atoms with an energy of ~100 eV even though it is difficult to observe this in Fig. 2(c). However, as shown in the figure, until the neutral beam treatment time was increased to 30 s, the turn-on voltage and electric field at 1 mA/cm^2 were lower for the neutral beam treated CNTs than the nontreated CNTs. Even though the increase of the Ar neutral beam treatment time from 10 to 60 s increased the turn-on field for 100 eV of the Ar neutral beam energy, when the Ar neutral beam energy was lowered to 50 eV, the turn-on field was continuously decreased from 1.64 to 1.40 V/μm with increasing treatment time from 10 to 60 s showing the improvement of field emission characteristics by the neutral beam bombardment even though the optimum condition was not obtained even with the 60 s treatment (not shown). It is

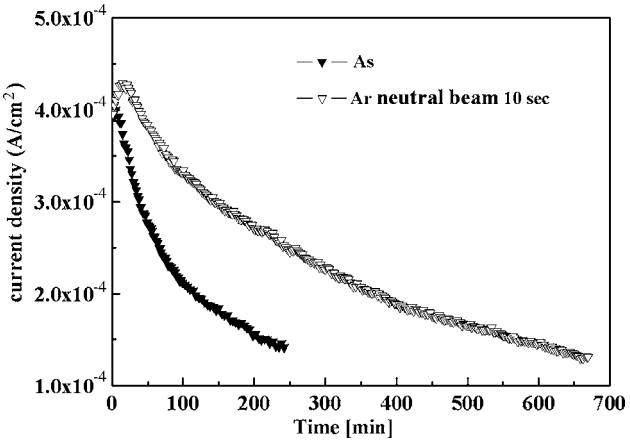

FIG. 4. Long-term emission stability of the CNT emitter before and after the neutral beam treatment for 10 s.

believed that an optimum CNT treatment condition can be achieved by using the treatment energy between 50 and 100 eV for a fixed treatment time such as 60 s.

Figure 3(b) shows the Fowler-Nordheim (F-N) plot of the field-emission curve. The emission current density (J) can be represented by the following F-N equation:[23–26]

$$J = (AE^2/\Phi)\exp(-B\Phi^{3/2}/E),$$

where $A = 1.54 \times 10^{-6}$ A eV V^{-2}, $B = 6.83 \times 10^9$ eV$^{-3/2}$ V m^{-1}, $\Phi = 5.0$ eV, and E is the local field at the emitting tip $[E = \beta E_0 = \beta(V/d)]$. β is the field enhancement factor. The field enhancement factor β for the CNT emitters was calculated from the above assumptions and the slopes were obtained from the F-N plots shown in Fig. 3(b). The field enhancement factors (β) calculated for the CNT emitters after the neutral beam treatment for 0, 10, 20, 30, and 60 s were 1975, 3123, 2489, 2102, and 1900, respectively. Therefore, the field enhancement factor of the CNT emitters after the Ar neutral beam treatment for up to 30 s was higher than that of the untreated sample. The differences in these β values can be explained by the increase in the number of nonseverely damaged activated CNT emitters caused by the surface treatment by the neutral beam.

The long term emission current stability of the CNT emitters was measured at a constant voltage of 1200 V before and after the neutral beam treatment for 10 s. Figure 4 shows the variation in current as a function of the operation time. As shown in the figure, significant degradation in the current density was observed over a 4 h period in the case of the untreated sample. However, the CNT emitters after the Ar neutral beam treatment for 10 s showed more stable emission properties than the untreated sample without any significant degradation or arcing during the operation time. The emission current density of the treated-CNT emitter was approximately 100 μA/cm^2 after 11 h of operation. Therefore, after the neutral beam treatment, both the emission properties of the CNT emitter and the emission stability were improved. At a current density of 150 μA/cm^2, the lifetime of the neutral beam treated-CNT emitters increased three times compared with the untreated-CNT emitters.

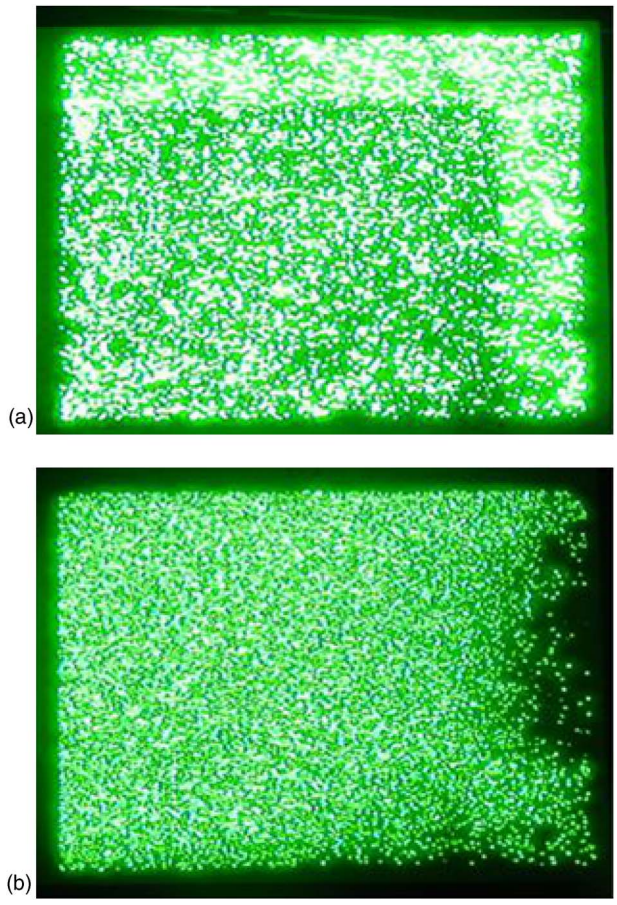

FIG. 5. (Color online) Field emission images of CNTs (a) after adhesive tape activation and (b) after the neutral beam treatment for 10 s for the CNT sample in (a).

Figure 5 shows the field emission image of the CNTs (a) after adhesive tape activation and (b) after the 10 s neutral beam treatment of the adhesive tape activated CNT sample in Fig. 2(a). The emission images shown in Fig. 5 were obtained at an anode voltage of 1500 V. As shown in the figure, the CNT emitters after the adhesive tape activation produced a good emission image over almost the entire emitter area except for a low density of CNT emitters with hot emitting sites. However, the CNT sample after a further treatment with the neutral beam for 10 s showed more uniform and homogeneous emission over the whole sample area without the presence of hot emitting sites. Therefore, the emission site density was increased after the neutral beam treatment.

IV. CONCLUSIONS

In this study, the effects of the Ar neutral beam treatment to the screen-printed CNTs after the adhesive tape activation on the morphology of CNTs and the electrical properties of CNT emitters were investigated. The results showed that after a neutral beam treatment with an energy of approximately 100 eV the buried CNTs protruded out of the binder paste to produce activated CNT emitters. The turn-on field decreased from 1.65 to 0.60 V/μm after the 10 s Ar neutral beam treatment. The lifetime of the 10 s neutral-beam-treated CNT emitters at a current density of 150 μA/cm^2 increased three times compared with the untreated-CNT emitters. However,

a further treatment by the neutral beam degraded the CNT field emission properties possibly due to the physical damage to the exposed CNT tips. It is believed that the neutral beam treatment introduced in this study improves the emission site density and emission stability of the CNTs emitters fabricated using various methods.

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