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# Improved Surface Morphologies of Printed Carbon Nanotubes by Heat Treatment and Their Field Emission Properties

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## Abstract

This paper presents heating process for obtaining standing carbon nanotube emitters to improve field-emission properties from the screen-printed multiwalled carbon nanotube (MWCNT) films. In an atmosphere with optimum combination of nitrogen and air for heat treatment of CNT films, the CNT emitters can be made to protrude from the surface. This allows for high emission current and the formation of very uniform emission sites without special surface treatment. The morphological change of the CNT film by this technique has eliminated additional processing steps, such as surface treatment which may result in secondary contamination and damage to the film. Despite its simplicity the process provides high reproducibility in emission current density which makes the films suitable for practical applications.

**Keywords** : Field emission, Carbon nanotube, Screen printing, Surface treatment, Paste

## 1. Introduction

Recently, a CNT paste mixture has been screen-printed as arrays of field emitters on a metallic electrode [1-9]. In screen-printed CNT films, poor electron emission due to entangled CNT bundles and the lack of CNTs protruding from the surface have become critical problems. Therefore, several surface treatment methods such as plasma treatment [2], mechanical surface rubbing [3, 4], and laser irradiation [5-9] have been used to improve the electron emission properties of screen-printed CNT films. The adhesive tape and soft rubber roller can bring secondary contamination on the due to leaving residual adhesive during surface treatment and damage by direct contact of the CNT film. They are also not useful to the triode-type structure with top-gates located highly to the cathode. In this study, we report that field-emission (FE) properties without surface treatment, so-called surface activation process, were remarkably improved from the screen-printed CNT films heated under an atmosphere with an optimum combination of air and nitrogen ($N_2$). By performing this heating process, the number of emission sites was considerably increased. The results are not consistent with other reports that showed low electron emission properties from as-deposited CNT film without surface treatments [2-11]. Therefore, we did not need an additional processing step, such as surface treatment to expose CNT emitters. Furthermore, our method can be applied to the cathode used in field-emission displays (FEDs) with the top gated triode structure [12-14].

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## 2. Experiments

The CNT paste was prepared by mixing ethylcellulose, MWNTs, fillers, and inorganic frits in terpineol. CNT samples used in this study were MWNTs obtained from Iljin nanotech, Inc. (Korea), which were synthesized by chemical vapor deposition (CVD). The high-resolution transmission electron microscopy (HRTEM) image showed that MWCNTs have the outer and inner diameter of the thin MWCNTs ranged from 1.7 to 5.2 nm and from 0.7 to 2.4 nm with from two to five walls as shown in Figure 1. The

pre-mixed CNT paste showed greater dispersion by the 3-roll milling process. The CNT films with an active area of 1 x 1 $cm^2$ (Dot type) were deposited onto indium tin oxide (ITO)-coated sodalime glass and then dried at 120 °C for 1h. During the preparation of the CNT film, heat treatment plays an important role in the removal of organic materials such as binders. Past conventional heat treatment could only be processed under either air or $N_2$ atmosphere [15]. Air is necessary to completely burn out the organic binder mixed into CNT paste and $N_2$ is used to avoid damage on CNTs at high temperature. Obviously, in either case, the heat treatment in any one environment is not advantageous with respect to CNT film morphology for field-emission. Also, the out-gassing by firing must be quickly exhausted to the air to prevent contamination of the CNT film. A schematic diagram of the proposed furnace is shown in Figure 2. Figure 2 shows the top view of a conventional oven with a $N_2$ atmosphere for heat treatment of CNT films. The oven was newly set up to keep an in situ suitable atmosphere of $N_2$ and air. The samples were placed on a quartz stage centred in a furnace and were fired for 20 min at 400 °C under a combination atmosphere of air and $N_2$ flow rate with 10 LPM , and then were naturally cooled to room temperature. The surface morphologies were evaluated by field-emission scanning electron microscopy (FESEM). The anode used to verify the uniformity of emission sites was prepared by depositing cathode-ray tube (CRT) phosphors onto the ITO electrode. FE characteristics of the CNT films were measured in a vacuum system with a diode configuration at 5 x $10^{-6}$ Torr using a direct current (DC) mode. The gap between the cathode and anode was 0.28 mm.

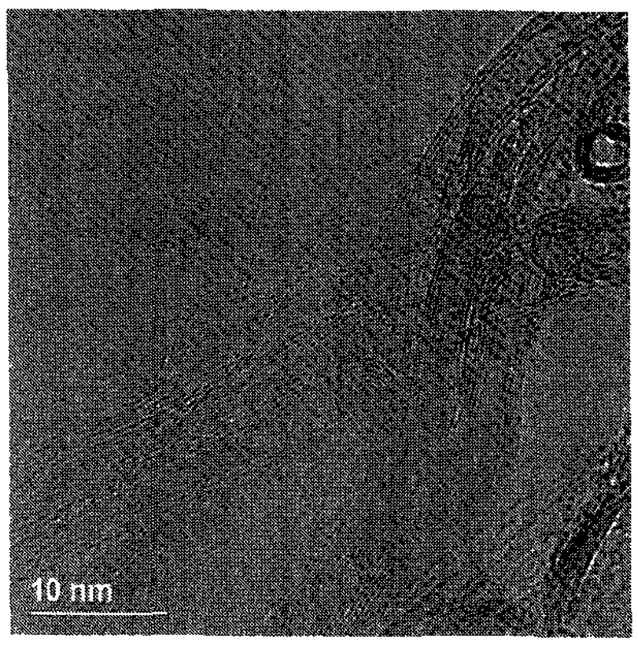


**Fig. 1.** High-resolution TEM micrograph of purified MWNTs.

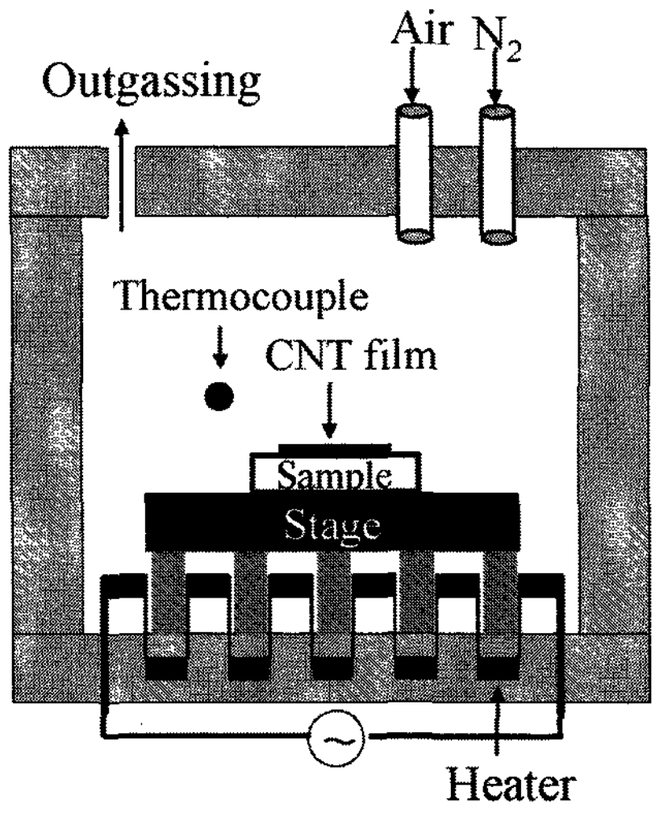


**Fig. 2.** Schematic diagrams of the furnace for heat treatment of the CNT films

## 3. Results and discussion

Figure 3 shows FE properties of the samples obtained by heat treatment in two different atmosphere ovens, the conventional $N_2$ atmosphere furnace (for sample A and C) and the furnace using an atmosphere with a combination of $N_2$ and air (for sample B). The inset of Figure 3 shows the schematic of the FE measurement. Sample A heated in the conventional $N_2$ atmosphere furnace was treated using an adhesive tape. Samples B and C were tested without special surface treatment. The curves show the current-

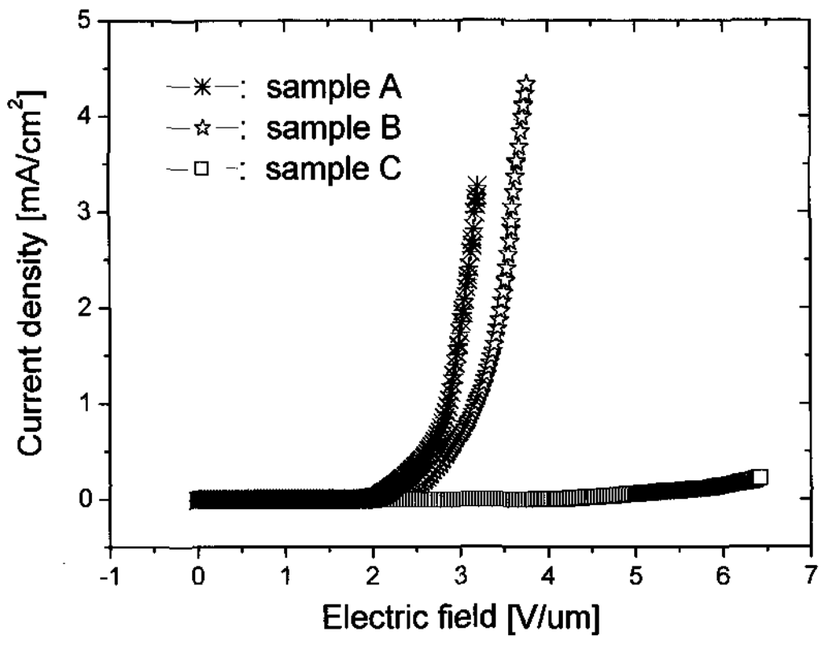


**Fig. 3.** The current-voltage (*I-V*) curves of the CNT films (for sample A) with and (for sample B and C) without surface treatment. The inset shows the schematic of the field-emission measurement.

voltage (*I-V*) properties as a function of voltage (V) and current (I). Sample B displayed better FE property than that of sample C. In sample B, the turn-on field was about 1.95 V/$\mu$m and current density was high as that of sample A with turn-on field of 1.7 V/$\mu$m after surface treatment by adhesive taping. Sample B also showed a more uniform emission image all over the dot pixels than sample A, as shown in the Figures 4a and b. In sample C, the measurements were characterized by the same procedures. The *I-V* curve of the sample C in Figure 3 shows that the current density was quite different than that of the samples A and B, and the turn-on field was about 4 V/$\mu$m. As previously reported [2-11], only few emission sites were presented. Although multiple field-emission cycles were repeatedly applied, the actual emission sites were not improved. The result of the sample A suggests that an extremely high current can be extracted from some pixels activated by an adhesive tape and such extraction causes emission uniformity problems, called "hot spots", as shown in Figure 4a.

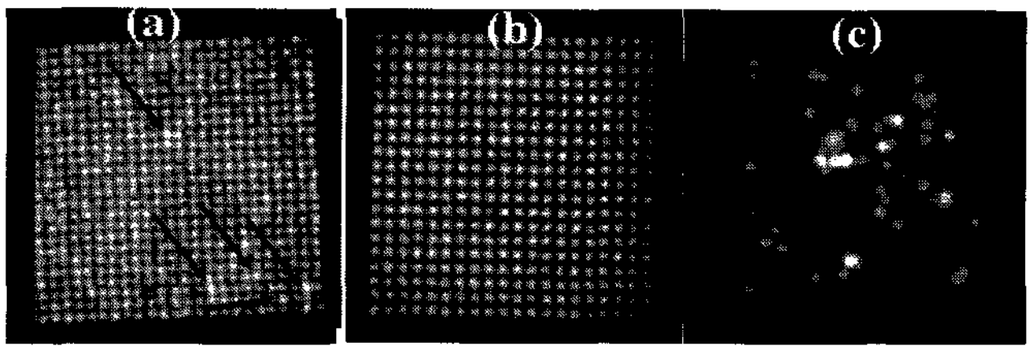


**Fig. 4.** The corresponding emission patterns from CNT films (a) by adhesive taping using $N_2$ atmosphere in the conventional furnace (for sample A at 3.2 V/$\mu$m), (b) without special surface treatment using a combination of nitrogen and air (for sample B at 3.2 V/$\mu$m), and (c) without special surface treatment using $N_2$ atmosphere in the conventional furnace (for sample C at 6.2 V/$\mu$m). The inset of Fig. 4a shows the inhomogeneous emission sites, called "*hot spots*".

In addition, smple A did not show any emission sites from a few pixels in noncontact (not activated) with the adhesive tape. Figure 5 shows changes in current densities according to $N_2$ flow rates under an air atmosphere for samples. When the $N_2$ flow rate in an air ambient oven was gradually increased such as 0, 10, 20, and 30 LPM, the turn-on field shifted to the right and the current density decreased. In the case of the sample with the $N_2$ flow rate with 30 LPM, the turn-on field was very high and just a few current densities were extracted as the sample heated under a conventional $N_2$ atmosphere. This result reveals that the air atmosphere for heat treatment of the CNT paste played an important role in improving field emission properties. Consequently, the current densities of the CNT films were influenced by the residue of the organic binder in CNT paste, causing problems such as poor electron emission properties from buried CNTs, out-gassing and arcing during field-emission driving to occur. Enhancement of the FE property of the sample B was also confirmed from FESEM images, as shown in Figure 6. Using FESEM, we observed morphological changes from two kinds of samples – sample B showed good FE characteristics while sample C showed poor FE characteristics. As expected, in sample B, most of the free-standing CNTs were highly aligned from the surface, although a few appeared to be slightly tangled and curved, as shown in Figures 6a-b. This suggests that the organic binders surrounding CNT emitters were almost entirely removed by using air and $N_2$ atmosphere. Through this, the CNT emitters could be made to protrude from the surface, consequently improving. the FE properties considerably without surface treatment. This was possible due to most of the exposed CNTs and the resulting CNTs oriented themselves normal to the surface (or parallel to the electric field direction) when the electric field was applied to the cathode during measurements. As shown in Figures 6a-b, these morphological changes were very similar in appearance to those previously reported by adhesive taping or soft rubbing roller (not shown here) [3,4]. In sample A, the printed CNT emitters were exposed and vertically aligned because the loosely packed organic binder materials had been removed from the film by an adhesive tape. Figures 6c and d show the SEM images of the sample C in as-deposited. The surface morphology is quite different from that of sample B. As shown in the SEM images, since the CNTs were densely packed and tangled with possible organic residues, there were no protruding CNTs that could improve the FE properties. In order to remove organic binders under a $N_2$ atmosphere, one sample was sintered at high temperature. After sintering for 20 min at 430 °C in $N_2$ atmosphere, the CNT emitters were completely covered with the melted glass frits as seen in the SEM image of Figure 6e This morphology is not advantageous for electron emission since the CNTs do not protrude from the film surface.

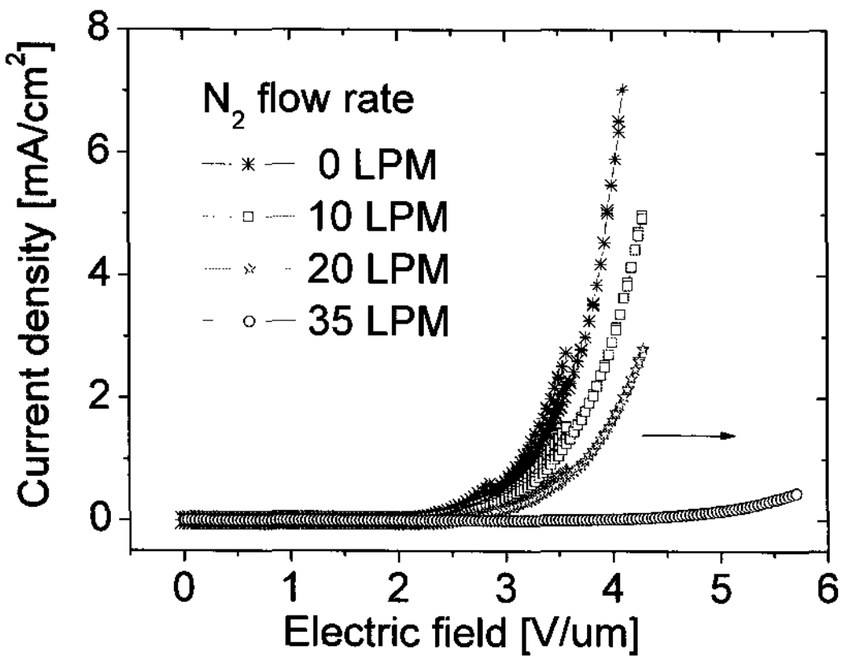


**Fig. 5.** *I-V* characteristic curves from CNT films with different $N_2$ flow rates in an air oven.

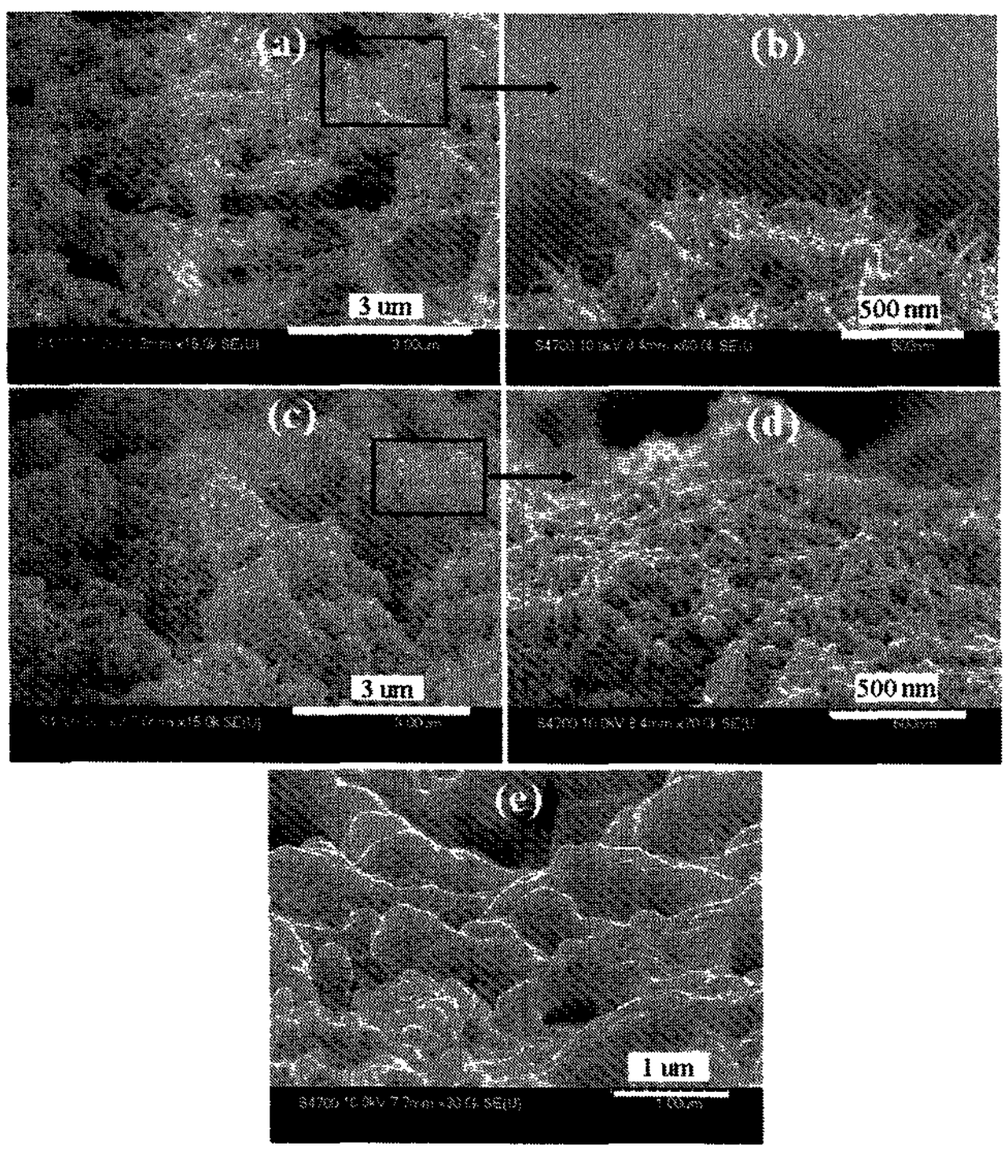


**Fig. 6.** SEM images showing the morphological difference between the samples heated by ((a)-(b)) N2 and air, ((c)-(d)) N2, and (e) $N_2$ environment at high temperature (430 °C).

## 4. Conclusions

In summary, a high current density and number of emission sites were achieved by using the screen-printed CNT film without surface treatment and simply using a combination of $N_2$ and air for heat treatment of CNT films. The change of surface morphology of the CNT films eliminated additional processing steps which would have resulted in secondary contamination and damage to the CNT film. A heating process could provide simple and efficient approaches to obtain the optimal emission surface of the CNT film for practical applications.

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