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Enhanced surface morphologies of screen-printed carbon nanotube films by heat treatment and their field-emission properties

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Abstract

A heating process for obtaining free-standing carbon nanotube emitters is presented with the aim of improving field-emission properties from the screen-printed multiwalled carbon nanotube (MWCNT) films. Using an atmosphere with an 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 a 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 a high reproducibility in emission current density which makes the films suitable for practical applications.
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1. Introduction

Recently, a CNT paste mixture has been screen-printed as arrays of field emitters on a metallic electrode [1–9]. The CNT film made by screen-printing has advantages such as low costs and simplicity when used for large displays. 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 focused ion beam [5] or laser irradiation [5–9] have been carried out 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 also are not useful to the triode-type structure with top-gates located highly to the cathode. For the top-gated triode structure, the laser or plasma exposure seems to be effective to modify surface morphologies of the CNT film. Disadvantages in their use are more expensive and slow compared to our proposed method. In this study, we report that field-emission (FE) properties without above-mentioned special surface treatment, 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

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reports that showed low electron emission properties from as-deposited CNT film without surface treatments [2–11]. Therefore, an additional processing step, such as surface treatment to expose CNT emitters, was not necessary in our study. Furthermore, our method can be applied to the cathode used in field-emission displays (FEDs) with the top-gated triode structure [12–14].

2. Experimental

The CNT paste was prepared by mixing ethylcellulose (binder polymer), MWNTs, fillers, and inorganic frits in terpineol (solvent). CNT samples used in this study were MWNTs obtained from Iljin nanotech, Inc. (Korea), which were synthesized by chemical vapor deposition (CVD). Fig. 1 shows high-resolution transmission electron microscopy (HRTEM) images of purified MWCNTs. The premixed CNT paste was better dispersed by the 3-roll milling process. The CNT films with an active area of $1 \times 1\ cm^2$ (Dot type) were deposited onto indium tin oxide (ITO)-coated sodalime glass and then dried at 120 °C for 1 h. In 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 be only processed under either air or N_2 atmosphere [15]. Air is necessary to burn out completely 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 Fig. 2b. Fig. 2a shows top view of a conventional oven with a nitrogen atmosphere for heat treatment of CNT films.

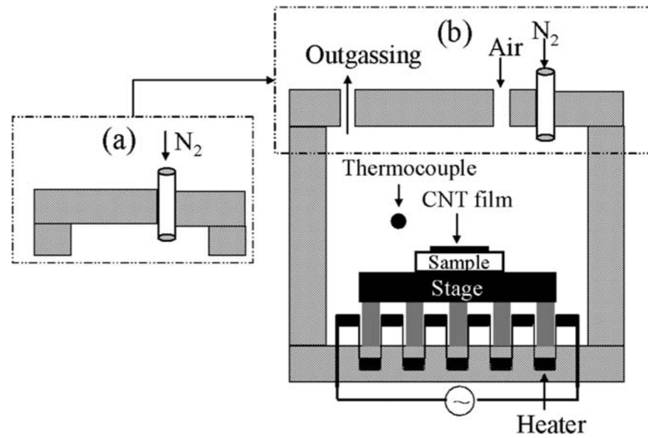

Fig. 2. Schematic diagrams of the furnace for heat treatment of the CNT films: (a) a conventional N_2 atmosphere oven and (b) a combination atmosphere oven of N_2 and air.

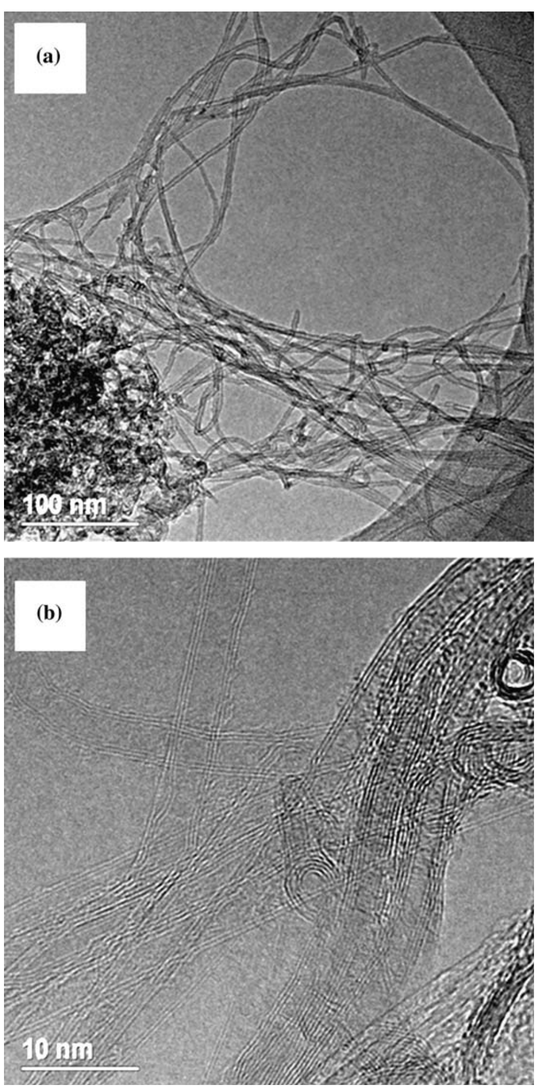

Fig. 1. TEM images of carbon nanotubes. (a) Low-resolution TEM micrograph and (b) high-resolution TEM micrograph of purified multi-walled carbon nanotubes.

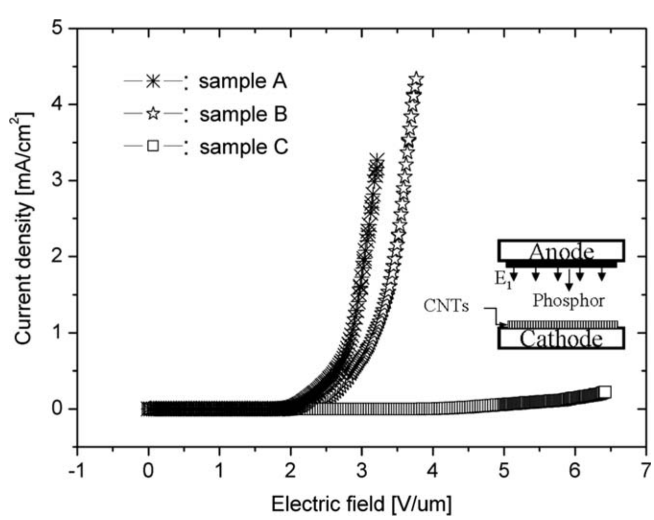

Fig. 3. The current–voltage (I–V) curves of the CNT films (for sample A) with and (for samples B and C) without surface treatment. The inset shows the schematic of the field-emission measurement.

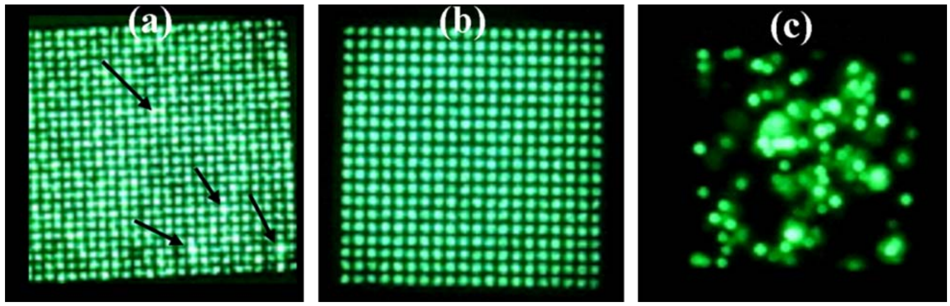

Fig. 4. The corresponding emission patterns from CNT films (a) by adhesive taping using N_2 atmosphere in the conventional furnace (for sample A at 3.2 V/μm), (b) without special surface treatment using a combination of nitrogen and air (for sample B at 3.2 V/μm), and (c) without special surface treatment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

3. Results and discussion

3.1. 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 centered 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. Other samples were fired by the same processes in a conventional N_2 ambient furnace as depicted in Fig. 2a. 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 5×10^{-6} Torr using a direct current (DC) mode. The gap between the cathode and anode was 0.28 mm.

3.2. FE characteristics with and without special surface treatment

Fig. 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 Fig. 3 shows the schematic of the FE measurement. The 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–voltage (*I–V*) properties as a function of voltage (*V*) and current (*I*). The sample B indicated the better FE property than that of the sample C. In sample B, the turn-on field was about 1.95 V/μm and current density is high as same as that of sample A with turn-on field of 1.8 V/μm 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 Fig. 4a and b. In sample C, the measurements were characterized by the same procedures. The *I–V* curve of the sample C in Fig. 3 shows that the current density was quite different than that of the sample A and B, and the turn-on field was about 4 V/μm. As the previous reports [2–11], only few emission sites are presented. Although multiple field-emission cycles were repeatedly applied, actual emission sites were not improved. The result of the sample A suggests that a extremely high current can be extracted from such "activated" (at least or several) pixels, more completely contacted by an adhesive tape, and such extraction has caused emission uniformity problems, called "*hot spots*", as shown in at arrow points of Fig. 4a. Sample A also showed no emission sites from a few pixels in noncontact (not activated) with the adhesive

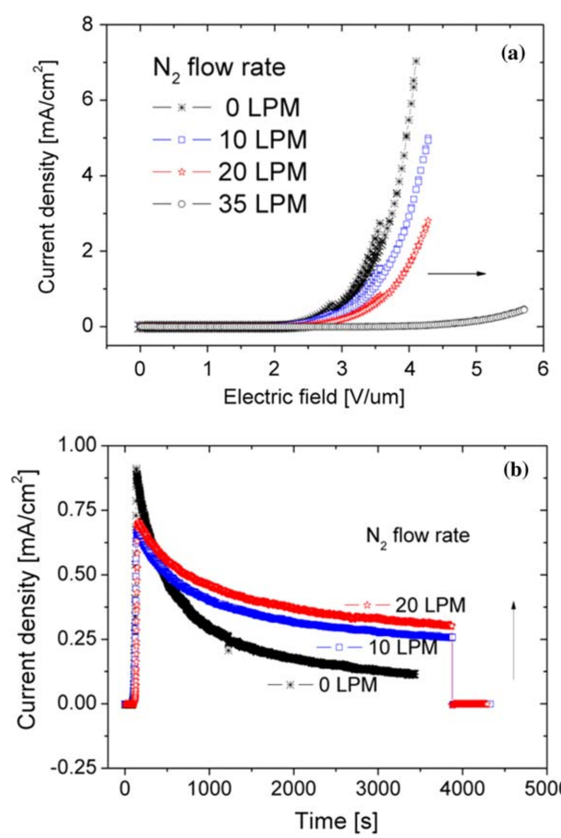

Fig. 5. (a) *I–V* characteristic curves and (b) emission current stability plots from CNT films with different nitrogen flow rates in an air oven.

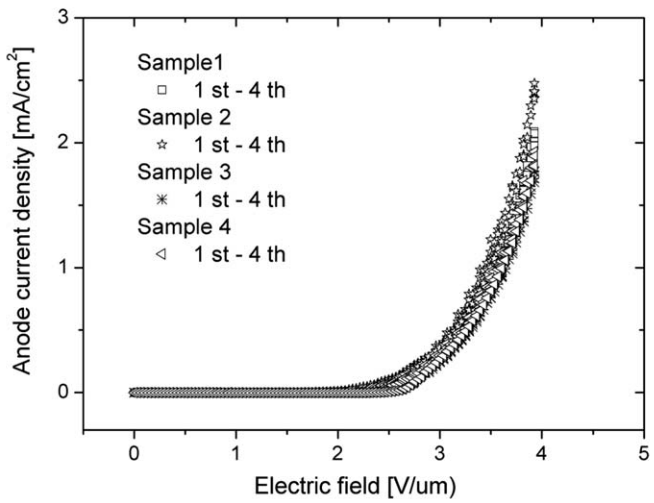

Fig. 6. The *I–V* characteristic curves showing a high reproducibility in emission current density from the printed CNT films after +3 field-emission cycles, respectively.

tape, and hence, needed to be heat-treated under an atmosphere with a combination of air and N_2 to improve its FE properties in terms of relatively low turn-on field and homogenous emission sites. Fig. 5a shows changes of current densities according to nitrogen flow rates under an air atmosphere for samples. When the nitrogen flow rate in an air ambient oven is gradually increased such as 0, 10, 20, and 30 LPM, the turn-on field was right shifted and the current density was lower. In the case of the sample with the nitrogen flow rate with 30 LPM, the turn-on field was very high and just 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 the improvement of field-emission properties. Consequently, current densities of the CNT films were governed by the residue of the organic binder in CNT paste, leading to problems such as poor electron emission properties from buried CNTs, out-gassing and arcing during field-emission driving. The continuous emission current of CNT films with different nitrogen flow rates was shown in Fig. 5b as

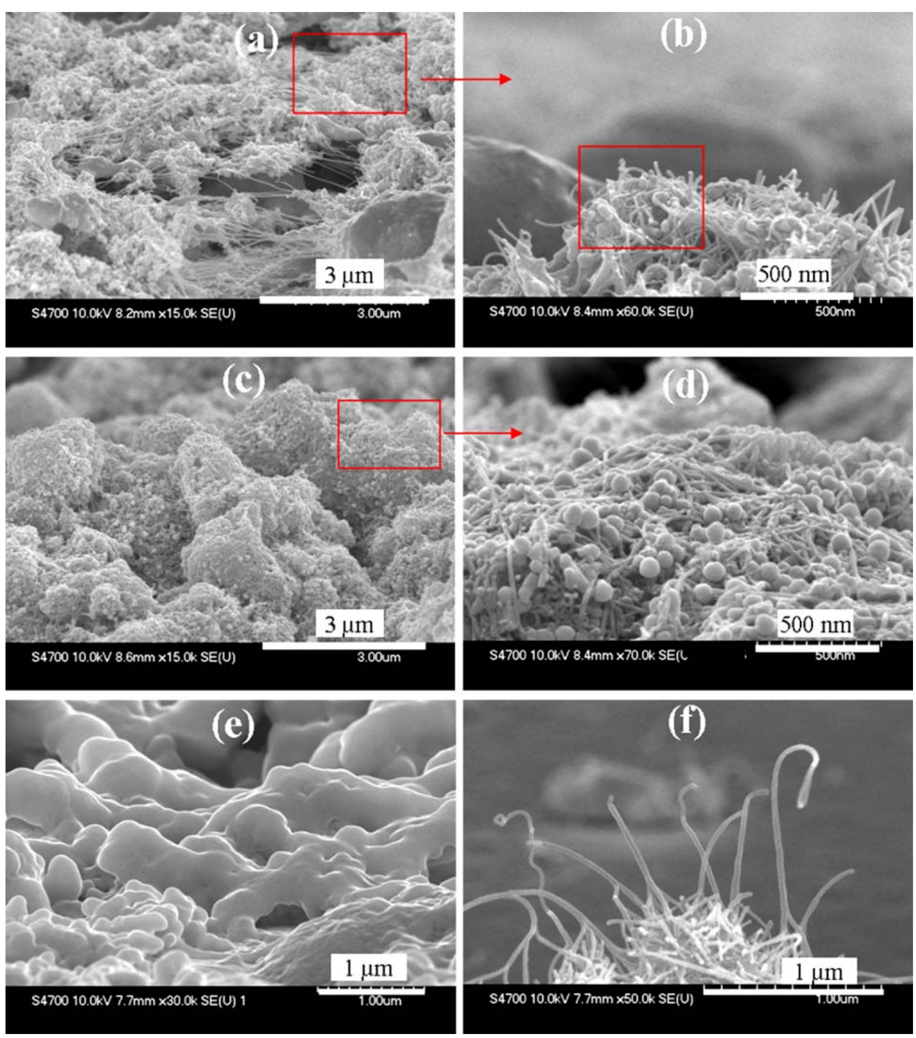

Fig. 7. SEM images showing the morphological difference between the samples heated by [(a) and (b)] N_2 and air, [(c) and (d)] N_2, (e) N_2 environment at high temperature (430 °C) and (f) high-resolution SEM image of the rectangular solid line of (b).

a function of time at the applied electric field of 3.5 V/μm (dc mode). The CNT emitters under N_2 flow rate with 10 and 20 LPM exhibited a small fluctuation than current density under an air atmosphere. Because the heat treatment of CNT paste was performed in air atmosphere, the CNTs may be oxidized by thermal effect. Although the heat-treated sample in air exhibited early good current–voltage (*I–V*) characteristics, as shown in Fig. 5a, oxidation of the CNTs affected seriously field-emission stability. Fig. 6 shows the *I–V* characteristics of CNT films after heating of four samples under the proposed atmosphere. The *I–V* curves of samples are almost identical. The repeated *I–V* measurement results confirm that the CNT films by a heating process shows a good possibility with reproducibility in emission current density for practical application, as shown in Fig. 6.

3.3. Comparison of SEM images by heat treatment

Enhancement of the FE property of the sample B was also confirmed from FESEM images, as shown in Fig. 7. Using FESEM, we observed morphological changes from two kinds of samples – sample B showing good FE characteristics and sample C showing 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 Fig. 7a and b. This suggests that the organic binders surrounding CNT emitters were almost removed by using the air and N_2 atmosphere. As a result, the CNT emitters could be made to protrude from the surface. Therefore, FE properties were considerably improved without additional surface treatment 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. In Fig. 7a and b, these morphological changes were very similar in appearance to those previously reported by adhesive taping or soft rubbing roller method which exposed and vertically aligned CNTs on the surface because the loosely packed organic binder residues have been removed from the film (here not shown) [3,4]. Fig. 7c and d shows 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 completely remove organic binders under N_2 atmosphere, one sample was sintered at high temperature. After sintering for 20 min at 430 °C in N_2 atmosphere, the SEM image of Fig. 7e showed that the CNT emitters were completely covered with the melted glass frits. This morphology is not advantageous for electron emission since the CNTs do not protrude from the film surface. Fig. 7f shows high resolution SEM image of the rectangular solid line of Fig. 7b. As shown in figure, the screen-printed CNTs with random bent complex structures were straightened permanently after heat treatment.

4. Conclusions

In summary, a high current density and number of emission sites were achieved from the screen-printed CNT film without surface treatment by using a combination of N_2 and air for heat treatment of CNT films. The change of surface morphology of the CNT films has eliminated additional processing steps which may result 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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