

Improved Field Emission by Liquid Elastomer Modification of Screen-Printed CNT Film Morphology

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Abstract

The effect of improvement on the surface morphology of screen-printed carbon nanotube (CNT) films was studied by using the optically clear poly-dimethylsiloxane (PDMS) elastomer for surface treatment. After the PDMS activation treatment was applied to the diode-type CNT cathode, the entangled carbon nanotube (CNT) bundles were broken up into individual free standing nanotubes to remarkably improve the field-emission characteristics over the as-deposited CNT film. Also, the cathode film morphology of a top gated triode-type structure can be treated by using the proposed surface treatment technique, which is a low-cost process, simple process. The relative uniform emission image showed high brightness with a high anode current. This result shows the possibility of using this technique for surface treatment of large-size field emission displays (FEDs) in the future.

Keywords : field emission, carbon nanotube, surface treatment, FED, screen printing

1. Introduction

The variety of field-emission (FE) properties of carbon nanotubes make them promising candidates for field emission display (FED) applications. Carbon nanotubes (CNTs) as cold cathodes must meet specific requirements such as a high stability of emission current, high emission current, and high emission uniformity. Spray deposition, screen-printing [1], and electrophoresis deposition [2] as well as direct growth [3-7] by chemical vapor deposition (CVD) have been recently developed for field emission displays [8]. In particular, screen-printing is a commonly used industrial technique for fast, inexpensive deposition. The screen-printing technique for obtaining the CNT film consists of the following three steps: (i) preparation of

suitable paste dispersed in an organic binder; (ii) screen-printing of the paste on suitable substrates using a polyester or stainless steel mask; and (iii) heating of the screen-printed layer to remove the organic binder. However, poor field-emission property of screen-printed carbon nanotubes could be attributed to insufficient protrusions of nanotubes to the surface, random distribution of nanotubes, and organic residues. To alleviate these disadvantages, various surface treatments are required [9-13]. In this study, we modified the morphology of the screen-printed CNT film by using the low-cost poly-dimethylsiloxane (PDMS) elastomer (SylgardTM 184, Dow Corning), which can be easily processed by molding, instead of using the conventional surface treatment techniques such as laser irradiation [11], soft rubbing roller [12], and adhesive taping [13]. The adhesive tape or soft rubbing roller cannot entirely touch the all printed CNT paste due to the inhomogeneous surface morphology of the film. Virtually, most of the noncontact nanotubes at the interface between the film surface and adherent face should not contribute to field-emission, as it may possibly create problems in emission uniformity. Also, these surface treatment techniques are not useful to the cathode film of the triode-type structure with a top-gate located above the cathode, as shown in Fig. 1(b) [14,15]. Until now, several surface

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treatment techniques to modify the CNT film morphology of the triode-type have been considered, such as laser irradiation or focused ion-beam [16,17]. From a practical viewpoint, however, the former is more expensive compared to our technique. Before curing, the PDMS

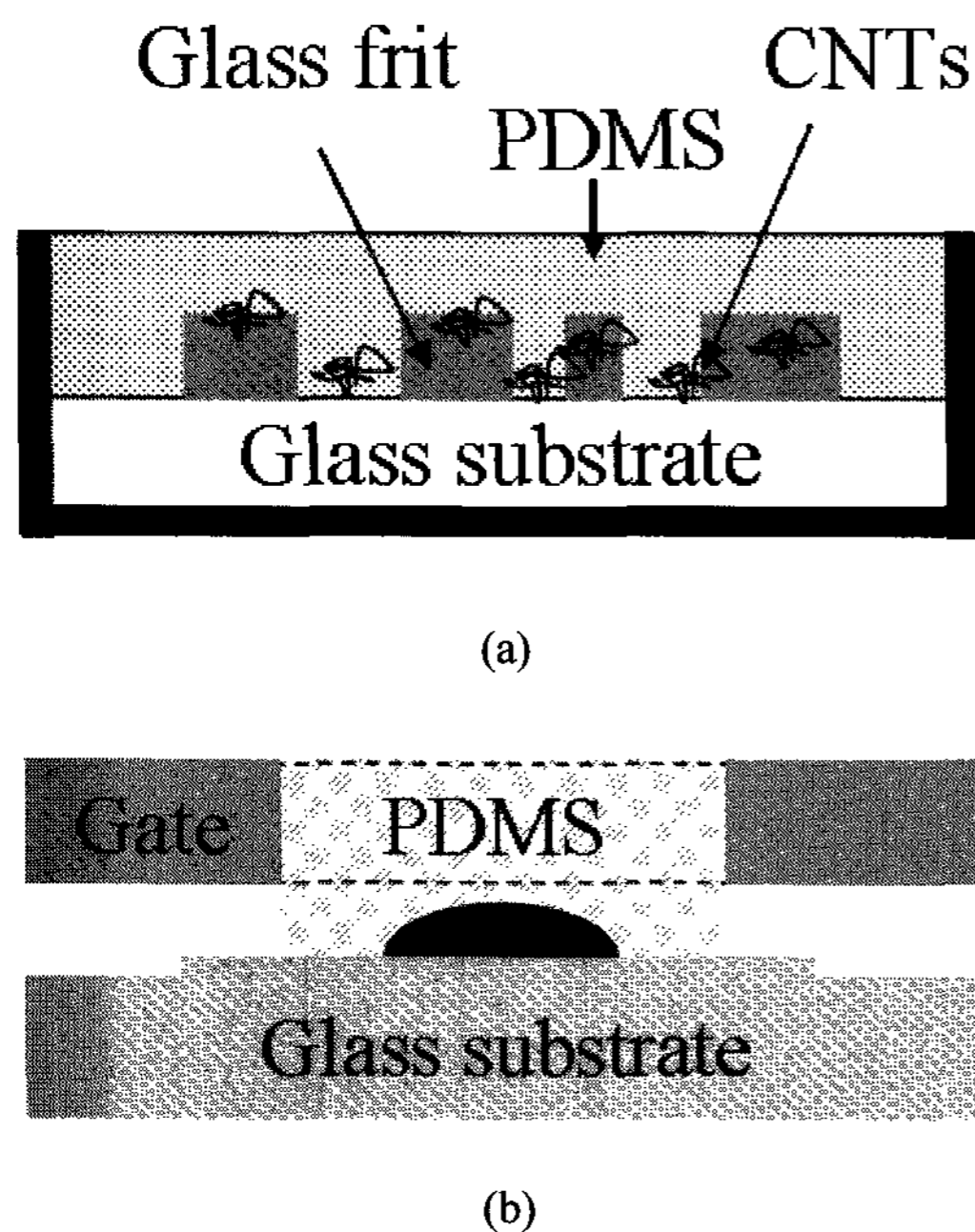


Fig. 1. Schematic diagram showing the surface treatment method of screen-printed CNT films by (a) PDMS elastomer and (b) PDMS elastomer of the top gated triode-type structure.

elastomer is initially a viscous gel, so that it can uniformly cover the entire screen-printed CNTs film, regardless of a pattern shape of the film or uniformity in surface morphology, and be easily applied to a triode-type structure [see Figs. 1 (a)-1(b)].

2. Experiments

In our experiment, the mixture of CNT paste, which consists of the multiwalled carbon nanotubes (MWNTs), glass frits, and organic binder materials, was screen-printed onto the indium tin oxide (ITO)-coated soda lime glass. The cathodes were maintained at room temperature for 10 min and dried at 150 °C for 1 h, both in air and finally heated for 30 min at 400 °C under nitrogen atmosphere to remove the organic binder. Surface treatment was performed on the cathode film by using PDMS to modify the surface

morphology. Fig. 2 shows a surface treatment process of CNT film by PDMS. A mixture of PDMS pre-polymer and a curing agent (10:1) was prepared, and the PDMS layer was fabricated by pouring the mixture solution onto the printed CNT film. After thermal curing at 150 °C for 10 min, the PDMS layer was separated from the CNT film.

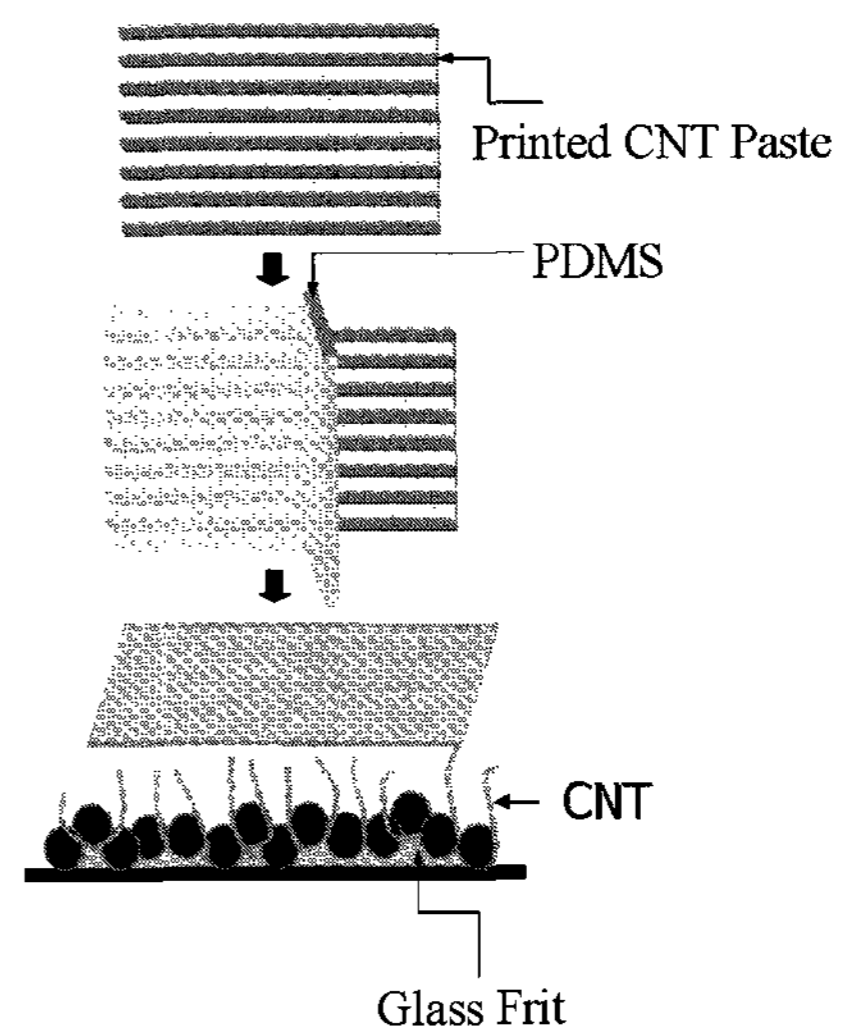


Fig. 2. Surface treatment process of the CNT film by PDMS.

3. Results and Discussion

The scanning electron microscope (SEM) image depicted in Fig. 3(a) shows the morphology of the as-deposited film and also the inhomogeneous surface morphology of the film with high density CNTs, which are in close contact with each other. Furthermore, we also observed that the majority of the emitters exist as bundles with possible residual organic materials on the film surface. Obviously, field-emission was critically affected by the lack of vertically aligned CNTs and the CNT bundles with high-density. Nilsson *et al.* [18] reported that high-density CNTs show very poor electron emission characteristics due to electrostatic screening effect [19] as well as charge by the presence of many nanotubes per unit area. These reasons contributed to problems related to the cohesion of melted glass frits, the particle size of glass frit materials, and the screen-printing technique as well as random distribution of the emitters. For the printed CNT film, nonuniformity of the morphology is confirmed by the atomic force microscope (AFM) image [Fig. 3(c)]. The CNT film with high-density and an uneven surface

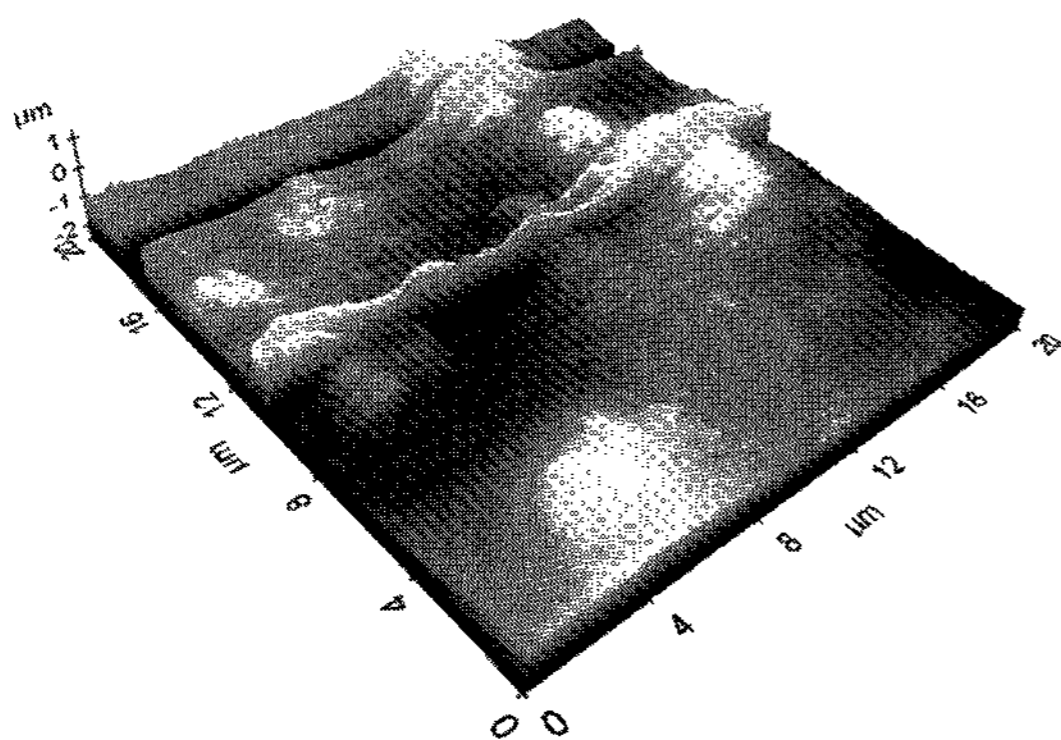
morphology was optimized by using PDMS. The PDMS layer with a low adhesive force could only remove the top of the screen printed CNT film. Therefore, the loosely adhesive CNTs and possible organic matrix materials on the top of the film surface were detached so that most of the bounded CNTs could remain on the cathode layer. Fig. 3(b) shows the marked changes in surface morphology after



(a)



(b)



(c)

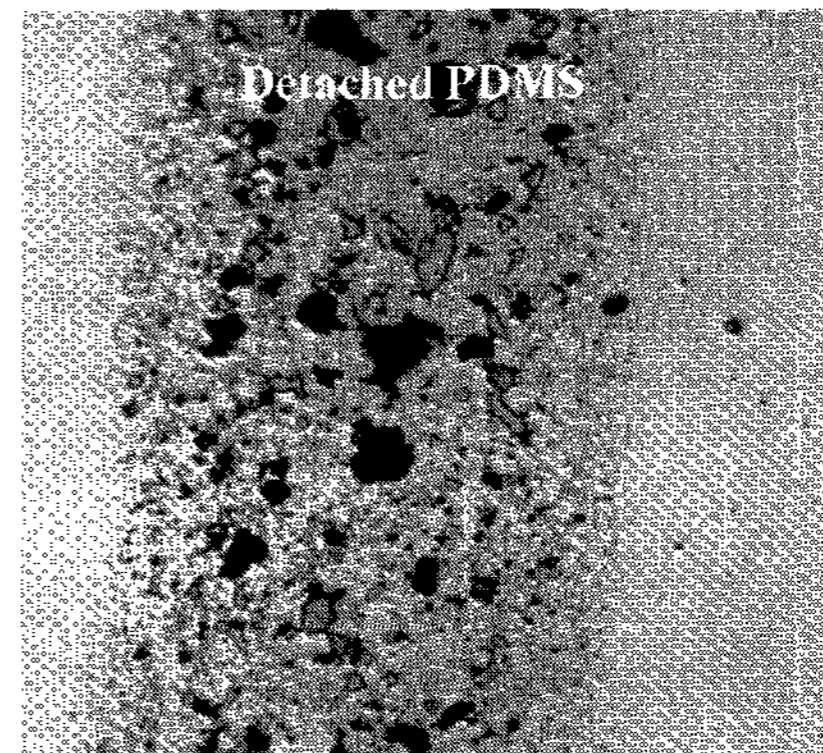
Fig. 3. SEM images of the screen-printed CNT films and the AFM image: (a) as-deposited CNT film, (b) cross-sectional SEM image showing the optimum surface morphology after PDMS elastomer treatment, and (c) AFM image of the screen-printed CNT film.

surface treatment. The nanotubes with relative optimal density were well distributed and vertically aligned to the

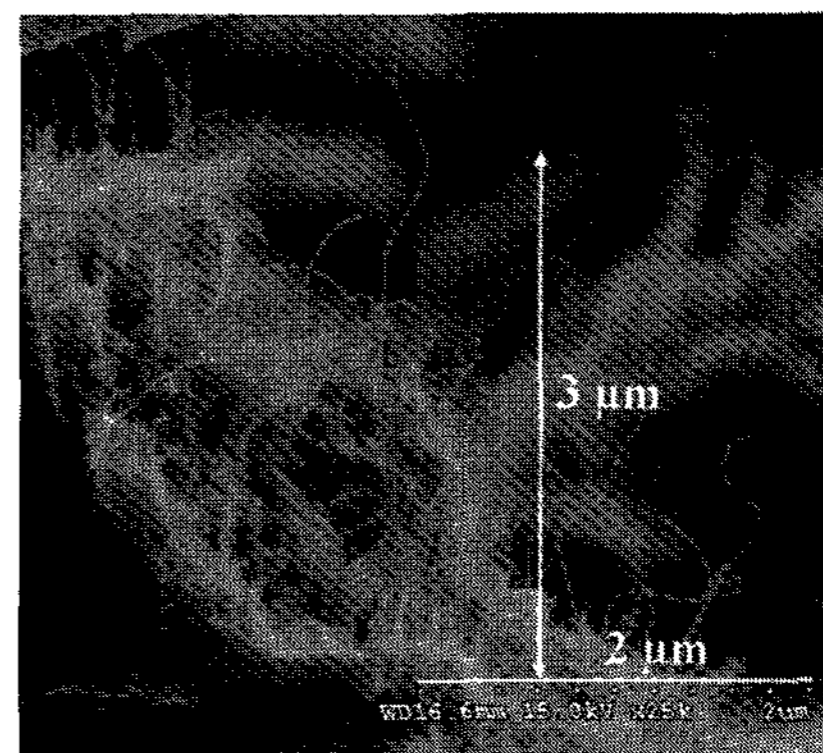
cathode substrate.

Fig. 4(a) shows the nanotubes and matrix materials such as organic binders, inorganic frits, and contaminants that adhered to the PDMS layer during the detaching step. This confirms that as shown in the arrow line of Fig. 4(b), rough surface morphology of several microscales ($\sim\mu\text{m}$) could be easily treated by using PDMS.

Fig. 5(a) shows the current-voltage (I - V) characteristics



(a)

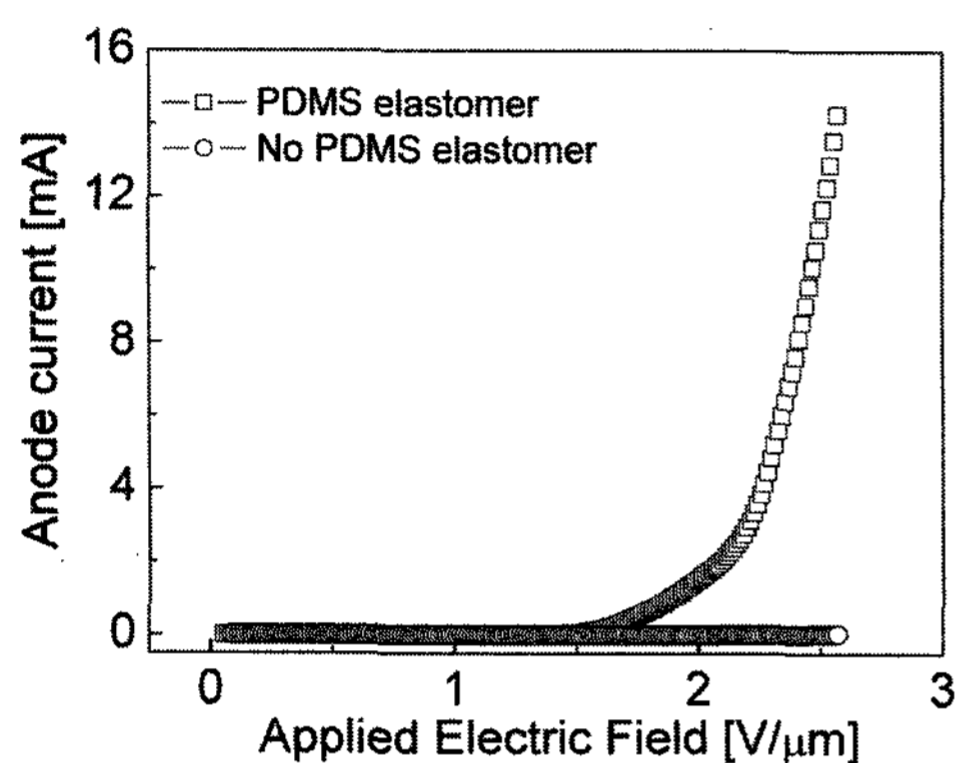


(b)

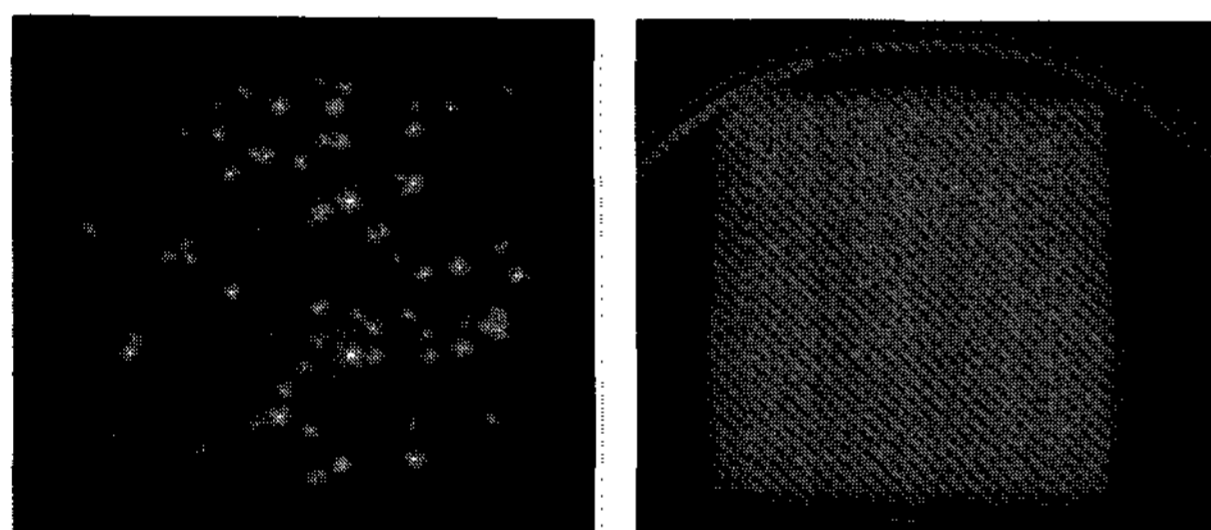
Fig. 4. (a) Microscope image of the PDMS layer detached from the cathode surface and (b) the inhomogeneous CNT film treated by the PDMS elastomer.

of two samples at dc mode before and after surface treatment by means of the PDMS elastomer. The field-emission properties were tested in a diode configuration under the vacuum system of 5×10^{-6} Torr. The distance between the anode and cathode was about 1.6 mm. At the same voltage, the sample after PDMS treatment has higher field-emission currents than that before PDMS treatment. Very uniform emission sites achieved by PDMS treatment are also shown in Fig. 5(c). These results clearly show that

CNTs are protruded on the surface and aligned mostly perpendicular to the substrate. Also, the densely packed nanotubes seen in Fig. 3(a) markedly distributed, as shown in the SEM image of Fig. 3(b). On the other hand, Fig. 5(b) shows the field-emission image from the as-deposited film before surface treatment. The image shows a rather inhomogeneous emission pattern. Although the sample was observed several times repeatedly by the field-emission cycles, improvement in electron emission was not.



(a)



(b)

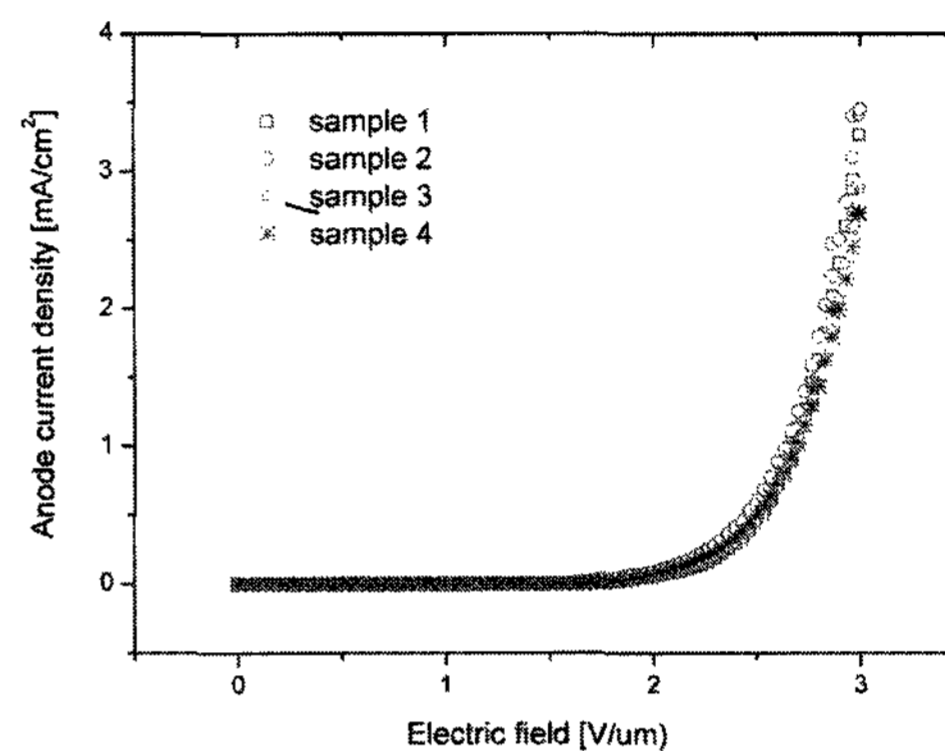
(c)

Fig. 5. Curves of the current versus voltage (I - V) and the corresponding emission images (active area of $8 \times 8 \text{ cm}^2$) from the screen-printed CNT film before and after surface treatment: (a) measured I - V curves, (b) phosphor screen image of the as-deposited CNT film before, and (c) phosphor screen image after the surface treatment (at the anode voltage of 3 kV).

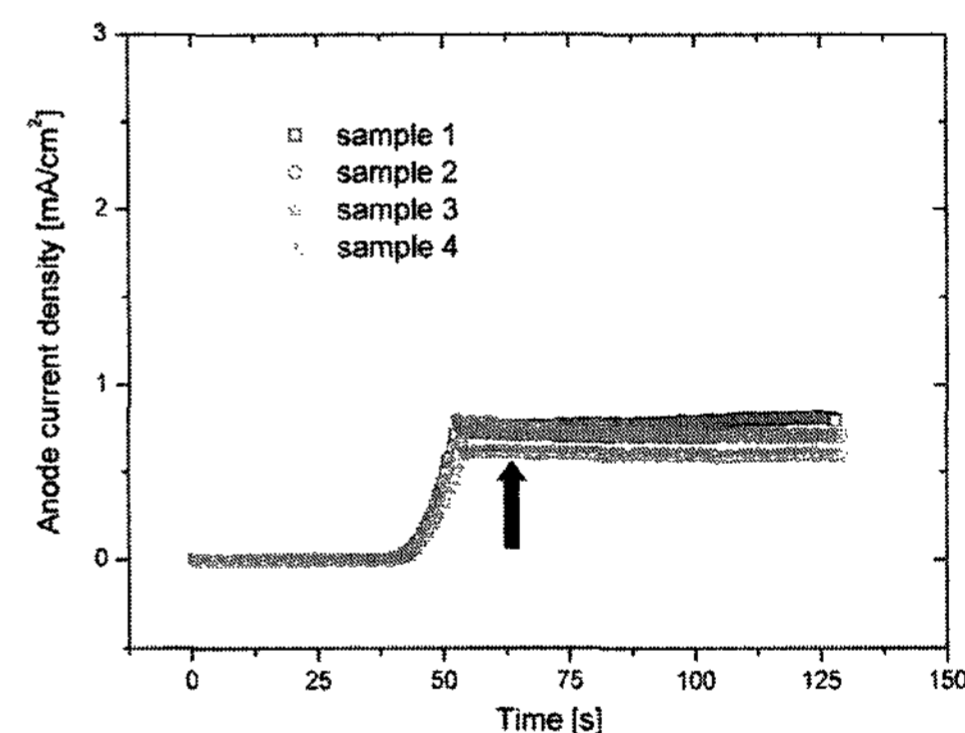
This result implies that although the emitter density on the surface of as-deposited film was high, as shown in Fig. 3(a), if entangled CNT bundles were not broken up into individual free standing CNTs, the field-emission characteristics would be very poor.

We also tested the reproducibility in current density of PDMS treated several samples as a function of an applied electric field and stability in emission as function of time

current obtained at $2.7 \text{ V}/\mu\text{m}$ after run. Samples with the emission site of $1 \times 1 \text{ cm}^2$ were prepared. The gap between the anode and cathode was about $300 \mu\text{m}$. In Fig. 6(a), according to increasing an electric field at the anode plate, I - V curves are almost identical for four samples. Then, it can be seen that emission become stable at the fixed voltage. The current stability is also very similar for the three samples except for one sample, as shown in Fig 6(b). The emission current densities of 0.76, 0.73, 0.64 and 0.76 mA/cm^2 at the applied electric field of $2.7 \text{ V}/\mu\text{m}$ were



(a)

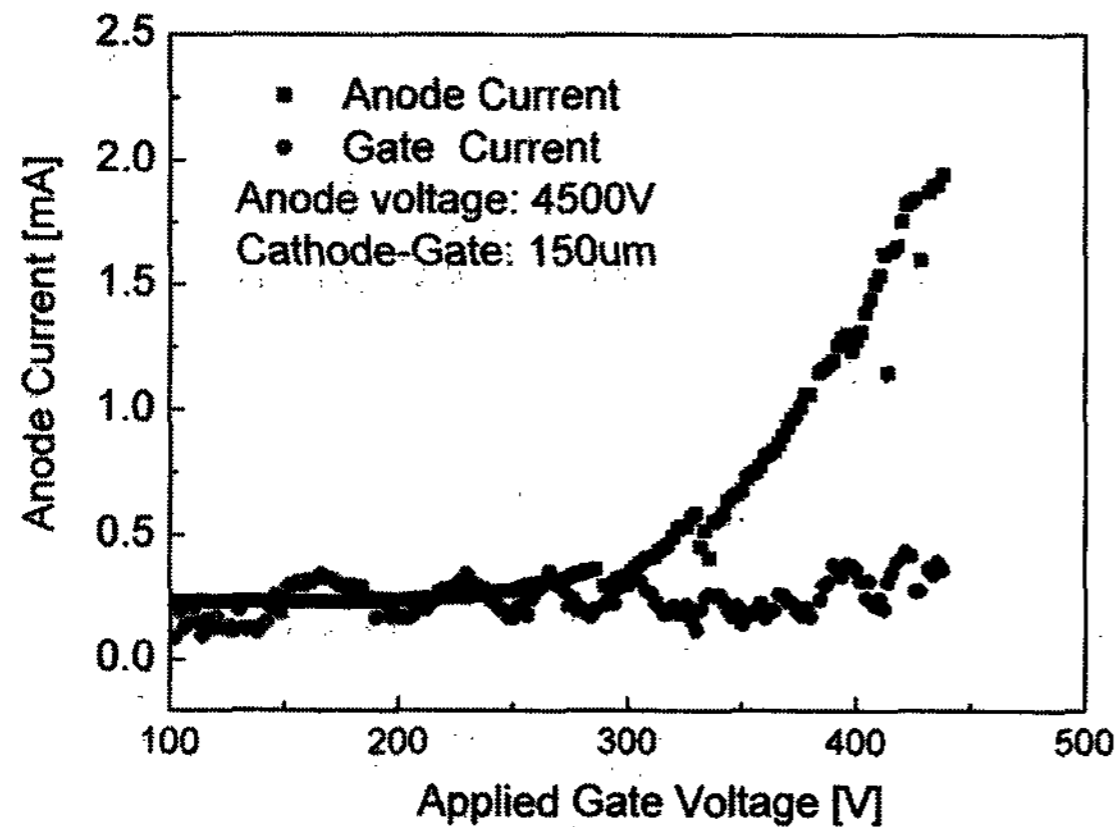


(b)

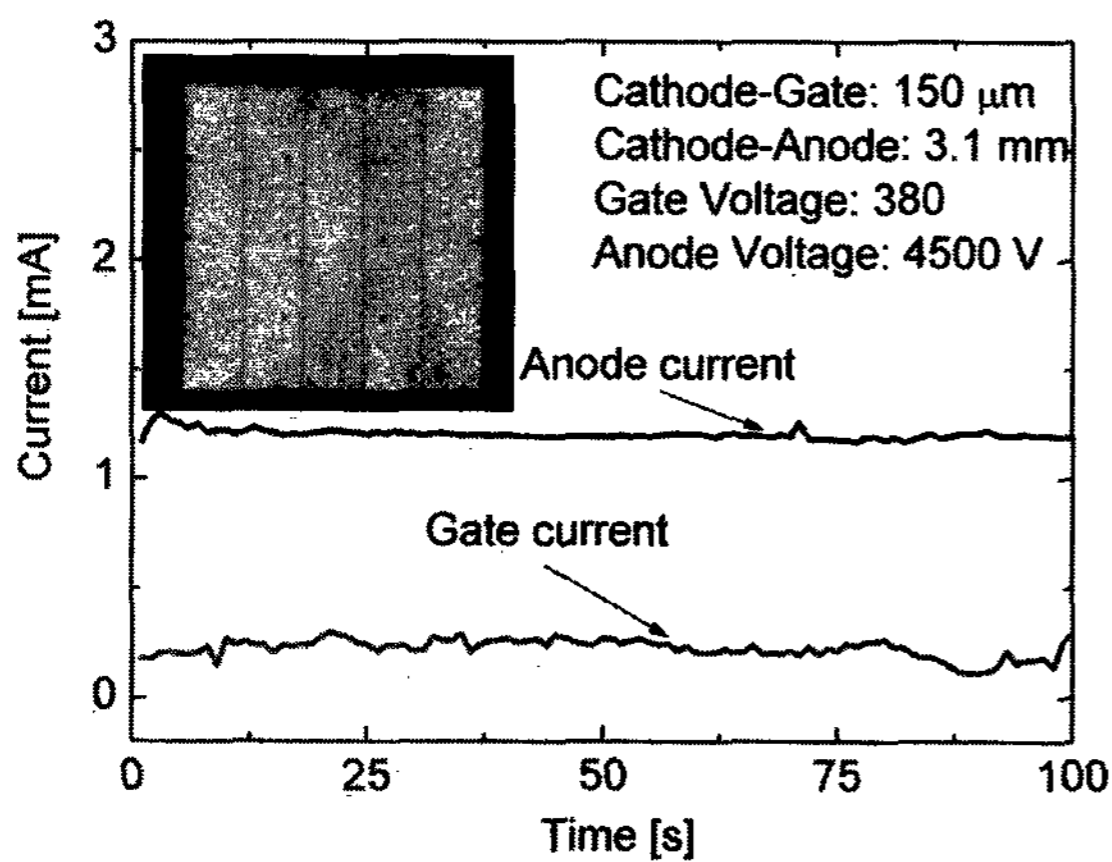
Fig. 6. (a) The reproducibility in current density of several samples as a function of an electric field (a) and (b) stability in emission as function of time current as obtained at $2.7 \text{ V}/\mu\text{m}$ after run.

obtained, respectively (at an arrow point). These observed differences in the current density between samples is associated with some kind of random distribution of CNTs in printed cathode layers and/or formation of paste and thus needs the further investigation for uniform dispersion of CNTs in paste. We confirm that if a dispersion problem of

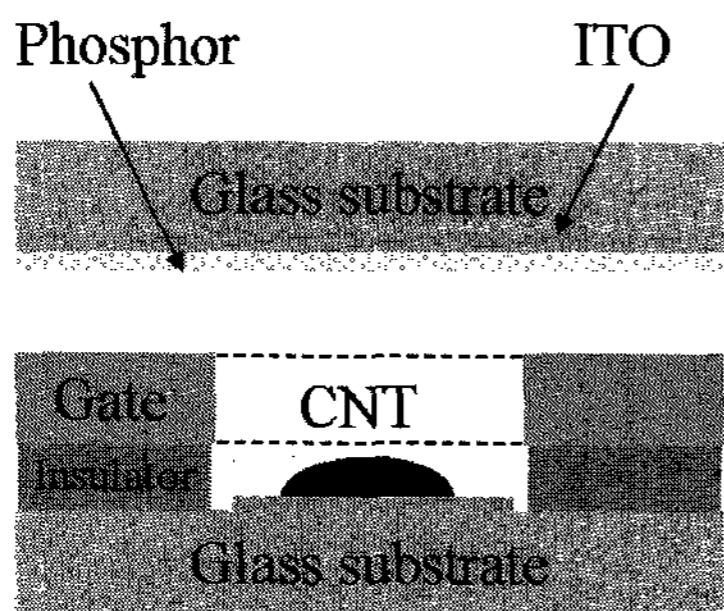
CNTs in printed paste can be solved, this process using an elastomer will show the good possibility of reproducing emission current density.



(a)



(b)



(c)

Fig. 7. (a) The I - V characteristics and (b) emission current stability plot (I - t) of the gated triode-type CNT emitters. The inset shows emission image of a 4.5-in. triode structure using the green phosphor anode plate after PDMS treatment. (c) Schematic diagram of the top gated triode-type structure.

The surface treatment by PDMS was applied to the cathode film of the patterned triode-type structure. The cathode film with a top-gated structure was prepared as schematically depicted in Fig. 7(c). In this structure, CNT emitters of 300 μ m width lines and a thickness of 10 μ m are defined on the Ag cathode electrode with a width of patterned 600 μ m. The insulator layer was deposited between the cathode substrate and thick Ag gate electrodes.

After detaching PDMS layer from the CNT film of a triode-type structure, the treatment process was completed. From an observed PDMS layer, we also confirmed that a low adhesive layer of about submicron scales can be removed from the top of the printed CNT film without damage of the film pattern. Field-emission characteristics of the top gated triode-type structure were investigated as a function of the applied gate voltage. The spacing between the cathode electrode and anode screen was fixed by 3.1 mm spacers. Figures 7(a) and (b) show the I - V characteristics and emission current stability plot (I - t) of the gated triode-type CNT emitters. The emission currents of the gate and anode reached 0.2 mA, and 1.3mA at the gate voltage of 380 V (duty 1/50, frequency 1 kHz) and the anode voltage of 4.5 kV (dc mode), respectively. The stable field-emission was continued with time at a fixed voltage. The inset showed emission image of a 4.5-in. triode structure using the green phosphor anode plate after PDMS treatment. The relative optimum emission image showed high brightness. As a result, the cathode surface morphology with a top-gated triode structure could be markedly changed by using surface treatment technique, the PDMS elastomer.

4. Conclusions

In this study, the screen-printed CNT film was post-treated with an optimized poly-dimethylsiloxane (PDMS) elastomer to improve the surface morphology of the film. Entangled carbon nanotube bundles were broken up into individual free standing CNTs to improve the field-emission characteristics beyond those of the as-deposited CNT film. To reduce the costs, PDMS surface treatment was also applied to the CNT film of the top gated triode-type structure. The relative uniform emission image with high brightness was obtained at the driving voltage of 380

V (Duty 1/50). This surface treatment method for triode structures gave very promising results as well as superior electron emission.

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