Field-emission enhancement from change of printed carbon nanotube morphology by an elastomer

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The surface morphology of screen-printed carbon nanotube films was modified by using the poly-dimethylsiloxane (PDMS) elastomer. 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. In addition, the cathode film morphology of top-gated triode structures can be treated by using the proposed surface treatment technique, which is a low-cost process. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2179114]

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 (FEDs).[8] In particular, screen-printing is a commonly used industrial technique for fast, inexpensive deposition. The screen-printing technique for obtaining the carbon nanotube (CNT) film consists of the following three steps: (i) preparation of a 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 caused by the 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 polydimethylsiloxane (PDMS) elastomer (Sylgard™ 184, Dow Corning), which can be easily processed by molding, instead of the known surface treatment techniques such as laser irradiation,[11] soft rubber roller,[12] and adhesive taping.[13] The adhesive taping or soft rubber roller cannot entirely touch the all printed CNT paste due to the inhomogeneous surface morphology of the film, as schematically shown in Fig. 1(a). Virtually, most of the noncontact nanotubes at the interface between the film surface and adherent face cannot contribute to field-emission, resulting in possible 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(c).[14,15] Until now, several surface treatment techniques to modify the CNT film morphology of the triode-type have been considered, such as laser irradiation and focused ion beam. From a practical viewpoint, however, the former is more expensive compared to our technique. Before curing, the PDMS 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(c)].

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

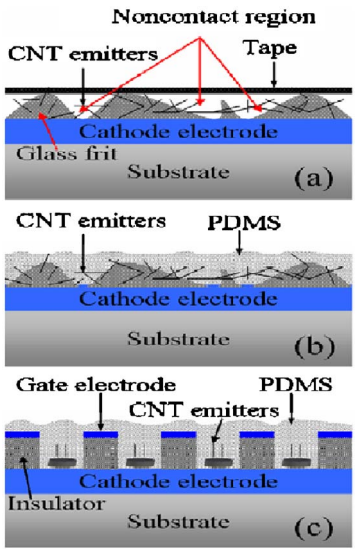

FIG. 1. (Color online) Schematic diagrams showing the surface treatment method of screen-printed CNT films by (a) adhesive taping, (b) PDMS elastomer, and (c) PDMS elastomer of the triode-type structure with a top gate.

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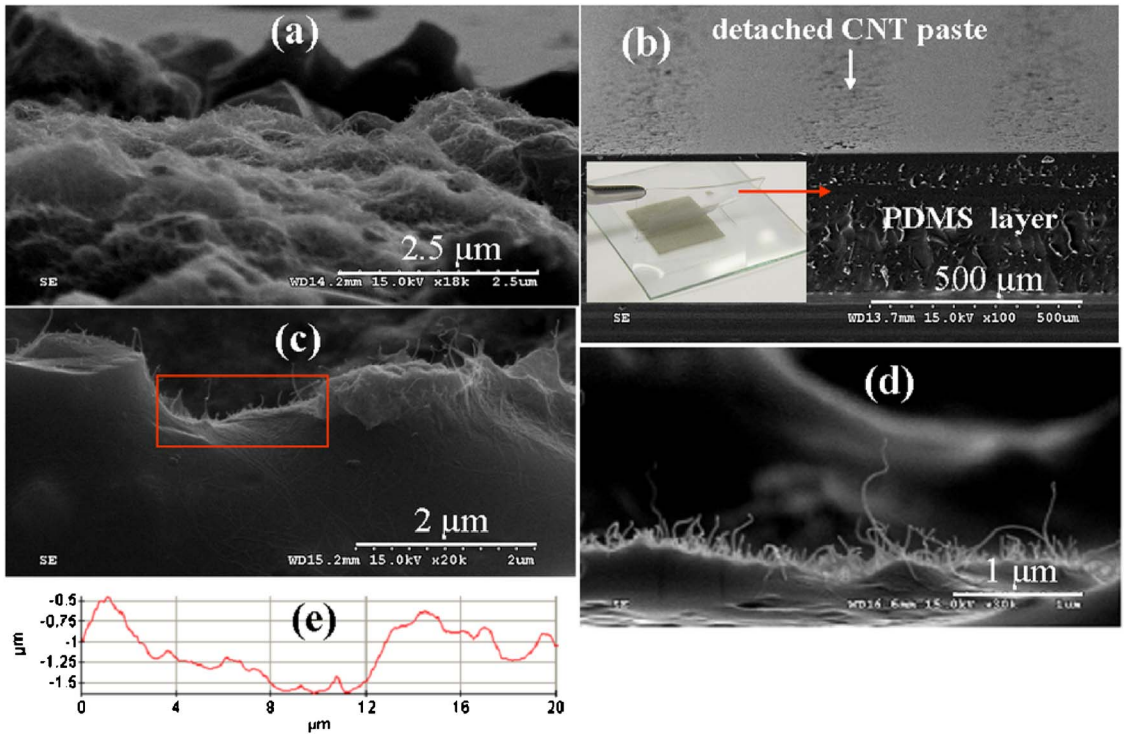

FIG. 2. (Color online) SEM images of the printed CNT film and a line profile of the AFM image: (a) as-deposited CNT film and (b) PDMS layer detached from the cathode. The inset shows a process of the PDMS layer detachment from the cathode surface, (c) inhomogeneous surface of the CNT film treated by the PDMS elastomer, (d) cross-sectional SEM image showing the optimal surface morphology after PDMS elastomer treatment, (e) AFM image of the surface of the screen-printed CNT film.

30 min at 300 °C and 400 °C, respectively, in nitrogen atmosphere to remove the organic binder. Surface treatment was performed on the cathode film by using PDMS to modify the surface morphology. A mixture of PDMS prepolymer 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, as shown in the inset of Fig. 2(b). The scanning electron microscope (SEM) image depicted in Fig. 2(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 after heat treatment. Obviously, field-emission was critically affected by the lack of vertically aligned CNTs and the CNT bundles with high density. Nilsson *et al.*[16] reported that high-density CNTs show very poor electron emission characteristics due to electrostatic screening effect[17] 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 line profile of the atomic force microscope (AFM) [Fig. 2(e)]. The CNT film with highdensity and an uneven surface morphology was optimized by using PDMS. Figure 2(b) shows the nanotubes and matrix materials such as organic binders, inorganic frits, and contaminants that adhered to the PDMS layer during the detaching step. 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. As shown in the rectangular solid line of Fig. 2(c), rough surface morphology of several microscales ($\sim\mu$m) could be easily treated by using PDMS. Figure 2(d) shows the marked changes in surface morphology after surface treatment. The nanotubes with relative optimal density were well distributed and vertically aligned to the cathode substrate.

Figure 3(a) shows the current-voltage (I-V) characteristics 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 had higher field-emission currents than that before PDMS treatment. Very uniform emission sites achieved by PDMS treatment are also shown in Figs. 3(b) and 3(c). These results clearly show that CNTs are protruded on the surface and aligned mostly perpendicularly to the substrate. Also, the densely packed nanotubes seen in Fig. 2(a) markedly distributed, as shown in the SEM image of Fig. 2(d). On the other hand, the inset of Fig. 3(a) 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 experienced several times repeatedly by the field-emission cycles, electron emission did not improve. This result implies that although the emitter density on the surface of as-deposited film was high, as shown in Fig. 2(a), if entangled CNT bundles were not broken up into individual free standing CNTs, the field-emission characteristics would be very poor.

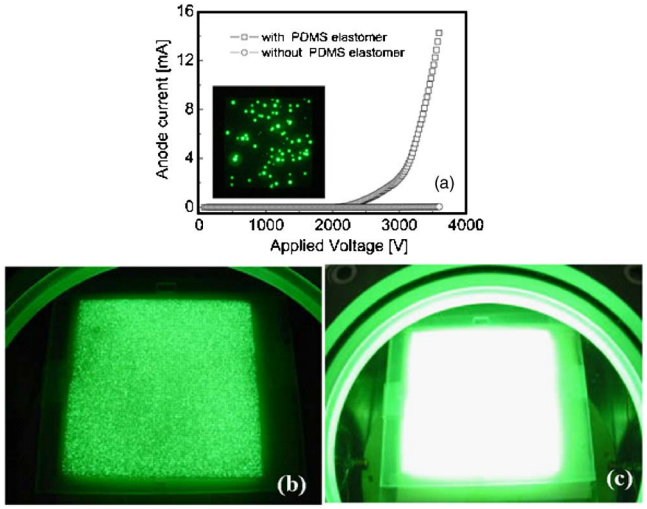

FIG. 3. (Color online) Curves of the current versus voltage (*I-V*) and the corresponding emission images (active area of 8×8 cm^2) from the screen-printed CNT film after and before surface treatment: (a) measured *I-V* curves. The inset in (a) shows that few pixels emit electrons in the as-deposited CNT film, (b) and (c) phosphor screen images after the surface treatment (at the anode voltage of 3 kV and 3.7 kV).

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. 4(a). Figure 4(b) shows the PDMS layer after its detachment from the CNT film. As shown in the SEM image, the treatment process was completed. For a given PDMS layer, we 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 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. As shown in Fig. 4(d), the emission currents of the gate and anode were achieved 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 emission image of the 4.5 in. top-gated type lamp (active area of 8×8 cm^2) is presented in Fig. 4(c). The relative optimal emission image shows 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.

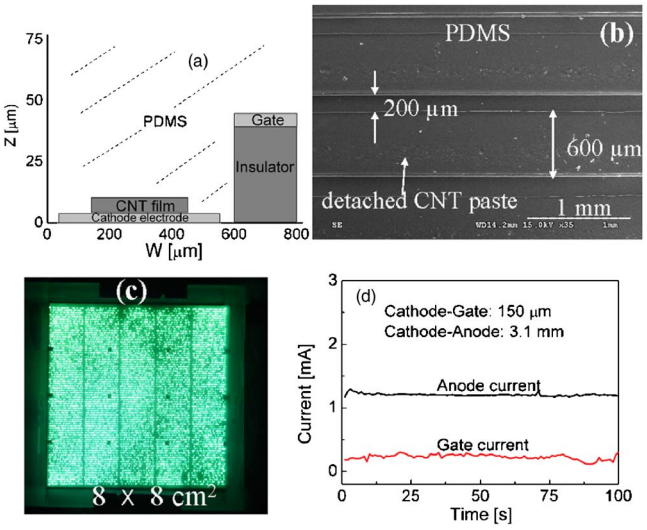

FIG. 4. (Color online) (a) Schematic diagram of the triode-type structure prepared for PDMS treatment, (b) PDMS layer detached from the cathode, (c) emission image of a 4.5 in. triode structure panel using the green phosphor anode plate, (d) *I-V* curves of the gate current vs the anode current with time at a fixed voltage.

In conclusion, the screen-printed CNT film was post-treated with an optimized polydimethylsiloxane (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 patterned triode-type with a top gate. This surface treatment method for triode structures gave very promising results including superior electron emission.

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