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# Clean Carbon Nanotube Field Emitters Aligned Horizontally

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## ABSTRACT

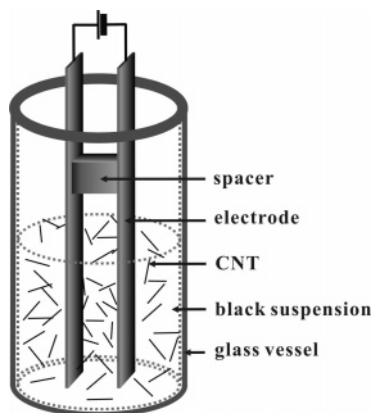
Horizontally aligned carbon nanotube (CNT) field emitters, which strongly adhere to the substrate and show good field emission properties, were fabricated by electrophoresis deposition and fissure formation techniques. A thin film of CNTs was deposited on a substrate, by electrophoresis, from an aqueous mixture of CNT and detergent, and then the detergent was deposited also by electrophoresis. CNTs with a clean surface were exposed in the fissures produced by firing. The field emission was increased significantly due to the additional deposition of the detergent. When the CNTs were cut by increasing the firing time, the field emission increased significantly, while their stability decreased considerably. Our method does not require any further treatment for field emission.

Electron field emitters based on carbon nanotubes (CNTs) are currently being investigated as the next-generation cold cathode materials, particularly for flat-panel field-emission displays (FEDs).<sup>1–6</sup> CNTs possess several favorable properties as field emitters, such as a high aspect ratio, high chemical stability, high thermal conductivity, and high mechanical strength.<sup>1,7</sup> Much effort has been made to develop various methods for fabricating CNT field emitters.<sup>8–17</sup> These methods can be categorized into two fundamental types—a direct growth method of CNTs on substrates and a screen-printing method. The former has several disadvantages such as difficulties in controlling each CNT, complexity of the fabrication process, and high growth temperature. The latter is a relatively simple process and can be used for mass production. However, it has many technical limitations that include the nonuniform dispersion of CNT powders, poor adhesion between the substrate and the CNT layer, low reproducibility due to numerous steps in the manufacturing process, and short lifetime.<sup>17</sup> The relatively uniform dispersion of CNT powders has been achieved by electrophoresis.<sup>18–22</sup> The main problem with this method is the weak adhesion of CNTs to the substrate. To produce a surface charge on the CNT powder, a charger or detergent or both are added to the powder suspension. The detergent may perform two important roles simultaneously: it can serve as a charge supplier and dispersion medium to create the CNT suspension. The hydrophobic tail of the detergent is adsorbed on the surface of CNTs by hydrophobic interaction. Consequently, CNTs covered with the detergent will have some surface charge due to the hydrophilic tail of the

detergent, and they will be attracted by an electric field. Thus far, the utility of the detergent coated on CNTs after electrophoresis has not attracted any attention. Generally, the focus has only been on removing the detergent because it could decrease the field emission due to its insulating property. The detergent coated on CNTs could be used as an organic binder to increase the adhesion between the CNTs and substrate. Further, it could perform an important role in the formation of CNT emitters with a clean surface. In this paper, we report a method to fabricate clean horizontally aligned CNT field emitters, which adhere strongly to the substrate and show good field emission properties, by electrophoresis deposition and fissure formation techniques.

Single-walled carbon nanotubes (SWNTs) synthesized by chemical vapor deposition were used as an emitting material. The diameter was approximately 1 nm, and the tubes were very long (at least 20  $\mu\text{m}$ ). As an initial step, 0.05 g of SWNTs and 0.2 g of sodium dodecyl sulfate (SDS, Aldrich) were added to 100 mL of deionized water and then sonicated at 200 kHz for 20 min to produce a black suspension. SDS was used as the dispersion medium to produce a CNT sol and as an organic binder after electrophoresis deposition. After sonication, the solution was centrifuged at 3400 rpm for approximately 10 min. The supernatant liquid containing unbound SDS was discarded. To obtain a uniform dispersion of CNTs, sonication and centrifugation were repeated several times. The final centrifugate was dissolved in 100 mL of water and then sonicated for 20 min. Therefore, the black suspension exhibited fine and homogeneously dispersed CNTs. The CNTs were deposited onto the substrate by the electrophoresis of the black suspension. Figure 1 shows a schematic diagram of the electrophoresis process for the

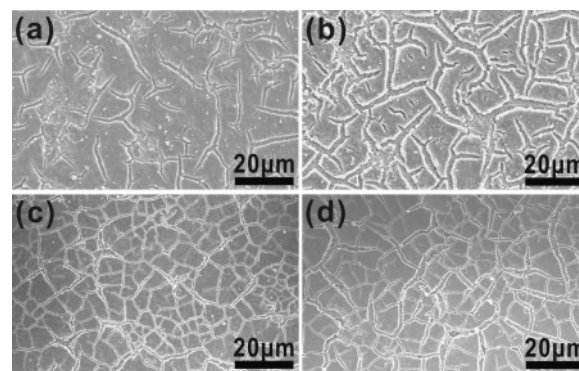
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**Figure 1.** Schematic diagram of the electrophoresis process for the selective deposition of CNTs.

selective deposition of the CNTs. Ti plates ( $3 \times 5 \text{ cm}^2$ ) were used as working and counter electrodes. Two electrodes were maintained at a distance of 1 cm by introducing a Teflon spacer between them. A constant potential of 50 V dc was initially applied for 1 min; this resulted in a thin deposit of the CNTs on the surface of the positively biased electrode. For some samples, SDS was deposited on the CNT films in 0.1 wt % SDS aqueous solution for 1 min by the second electrophoresis, under the same conditions as the first. The thickness of the naturally dried SDS was approximately 700 nm. The CNT films were dried naturally for 24 h at room temperature; therefore, they resembled gelatinized thin films. To increase the uniformity of the deposited materials, the surface of the films was compressed with a covering glass slide, which was cleaned by sonication in acetone and then washed with deionized water. The sample plate coated with a gelatinized thin film was then fired for 5–20 min by placing it in a quartz tube furnace, whose temperature was  $350^\circ\text{C}$ , under a natural air environment. The electron field emission properties of the CNT thin films were measured using parallel-plate geometry in a vacuum chamber under a pressure of  $2 \times 10^{-6}$  Torr. The aperture size for field emission measurements was  $20 \text{ mm}^2$ . A variable dc voltage was applied between the CNT cathode and anode separated by  $150 \mu\text{m}$ . The anode was a glass substrate with an indium tin oxide (ITO) coating covered by a phosphor layer. Although field emission began from the first run, data were collected after the initial burn-in (by applying  $4 \text{ V}/\mu\text{m}$  for a few minutes). The emission current was monitored with a Keithley 6517 electrometer and recorded at 1.0 s intervals. A field-emission scanning electron microscope (FESEM, JSM-6700F) was also used to analyze the surface morphology. The emission current image was taken using a digital camera.

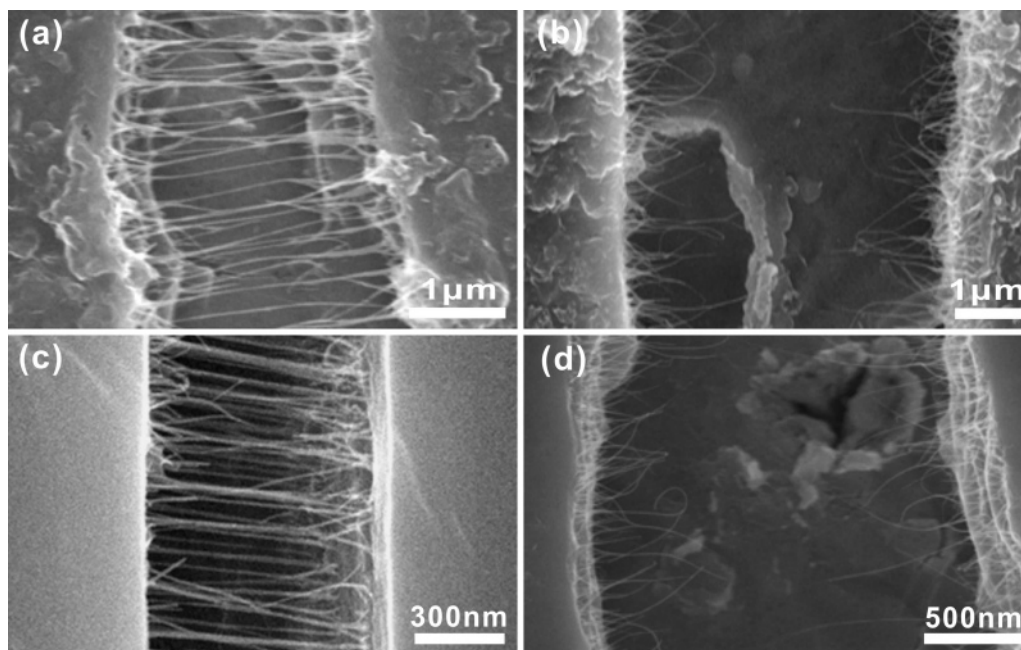
FESEM images of the CNT films deposited on Ti substrates by electrophoresis after the firing process are shown in Figure 2. Four different samples were prepared by varying the conditions. The samples in parts a and b of Figure 2 were prepared without the additional deposition of SDS, while those in parts c and d of Figure 2 were prepared by SDS deposition. The samples in parts a and b of Figure 2 were fired for 5 and 10 min, respectively, while those in



**Figure 2.** SEM images of the CNT films deposited on Ti substrates after the firing process: without deposition of SDS and fired for (a) 5 and (b) 10 min; with deposition of SDS and fired for (c) 10 and (d) 20 min.

parts c and d of Figure 2 were fired for 10 and 20 min, respectively. The figures reveal fissures produced by firing. The fissures were probably produced by the shrinkage and movement of the film due to firing. The number density of the fissures shown in parts c and d of Figure 2 was greater than that of the fissures in parts a and b of Figure 2. This implies that more fissures were produced by the additional deposition of SDS on the CNT films. The average size of the fissures increased with the firing time; however, the number density, particularly for the films deposited SDS additionally, was almost constant. For the same firing time, the average size of the fissures in the CNT film produced by additional SDS deposition was considerably less than that of those in the film produced without additional SDS deposition (compare parts b and c of Figure 2). From these observations, it is concluded that more densely arranged and smaller fissures are produced by the additional deposition of SDS on the CNT films.

The typical fissure images in Figure 2 are magnified in Figure 3. It is observed that the CNTs protrude from the fissures. These may be bundles of SWNTs. The surface of the exposed CNTs is devoid of SDS and very clean. Devoid of SDS on the surface of the exposed CNTs may mean that the attraction force between SDS is stronger than that between the CNT and SDS. The surface cleanliness of CNTs is very important for efficient field emission. The CNTs in parts a and c of Figure 3 are uncut. The CNTs, which were very long and had a strong mechanical strength, could exist between two islands like tightened strings. On the other hand, those in parts b and d of Figure 3 are cut. Their firing time was not the same; it was 5, 10, 10, and 20 min for the CNTs in Figure 3a–d, respectively. The CNTs in the film produced without additional SDS deposition were cut by firing for 10 min (see Figure 3b); however, the CNTs in the film produced by additional SDS deposition were uncut for the same firing time (see Figure 3c). This implies that a relatively longer firing time is required to cut the CNTs in the film produced by additional SDS deposition. Although the fissure size in Figure 3d is slightly less than that in Figure 3a, the CNTs in the former are cut while those in the latter are uncut. This means that the CNTs in the film produced by additional SDS deposition are cut in a relatively smaller fissure than those

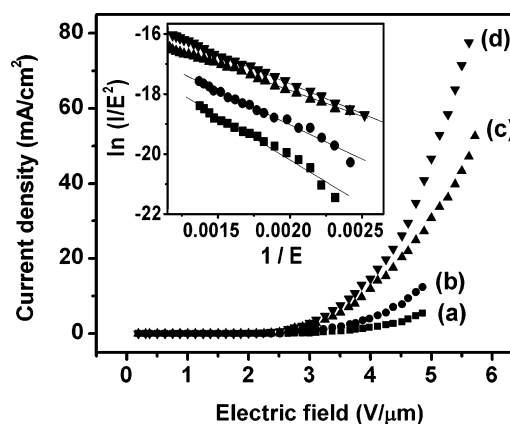


**Figure 3.** High-magnification SEM images of the CNT films shown in Figure 2 but focused on fissures: without deposition of SDS and fired for (a) 5 and (b) 10 min; with deposition of SDS and fired for (c) 10 and (d) 20 min. The thickness of the CNT films is approximately  $1.2 \mu\text{m}$  and that of SDS layer deposited additionally is approximately  $200 \text{ nm}$ .

without SDS deposition. To be cut in a smaller size fissure, a stronger force must be applied to the CNTs. To apply a stronger force to the CNTs, they should be more tightly gripped. Therefore, it can be concluded that the adhesion between the CNTs and SDS would be increased by the deposition of SDS on the CNT films. It is evident that the additional SDS deposition on the CNT films plays an important role in the formation of fissures and cutting of CNTs. A smooth top layer can be observed in parts c and d of Figure 3. This corresponds to the SDS layer that was additionally deposited on the CNT films. In parts a and c of Figure 3, it appears that at least some of the CNTs are suspended between SDS islands. In fact, they were electrically connected to the substrate and other CNTs. The CNTs that were very long (at least  $20 \mu\text{m}$ ) were randomly deposited on the surface of the substrate by electrophoresis. At least some parts of the CNTs deposited in an early stage would be physically in contact with the substrate, and more CNTs would be deposited on them. Therefore, they came into contact with each other, became entangled, and were electrically connected.

Another important effect of the firing process was that the adhesion of the CNT thin film to the substrate improved significantly. The CNT island films formed by firing were very strongly adsorbed onto the substrate. It was difficult to remove them with a spatula. Strong substrate adhesion is very important for the fabrication of a stable field emitter. Further, the firing process removes some volatile materials, which could contaminate the CNT emitters under vacuum conditions.

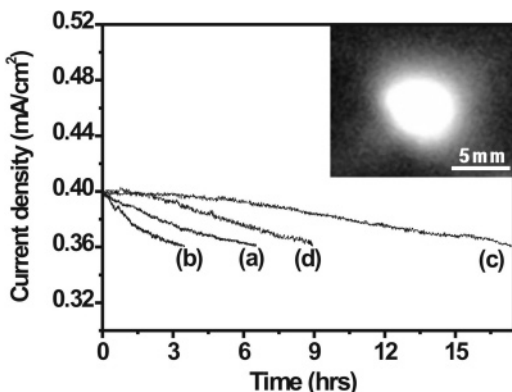
The measured field emission currents are shown in Figure 4 as a function of the applied field for each CNT film shown in Figure 2. The current density was calculated simply by dividing the measured current by the area of the aperture,



**Figure 4.** Field-emission current density vs the applied electric field for the CNT films shown in Figure 2: without deposition of SDS and whose CNTs were (a) not cut and (b) cut; with deposition of SDS and whose CNTs were (c) not cut and (d) cut. Inset shows the Fowler–Nordheim plots.

which was  $20 \text{ mm}^2$ . The current–applied field ( $I$ – $E$ ) curves are relatively smooth and reproducible. When the applied field was somewhat excessive, the current saturated and stopped increasing, and arc discharging occurred. Current fluctuations were observed in high field regimes. The highest current density was approximately  $77 \text{ mA/cm}^2$  at an applied field of  $5.7 \text{ V}/\mu\text{m}$ , while a current density of  $1 \text{ mA/cm}^2$ , which is required particularly for a flat panel display,<sup>23</sup> was obtained at  $2.2 \text{ V}/\mu\text{m}$ . Although the current density exhibited a large variation, the turn-on field, at which the emission current density reaches approximately  $100 \mu\text{A/cm}^2$ , was almost the same at approximately  $1.8 \text{ V}/\mu\text{m}$  for all four samples. The current densities shown in parts c and d of Figure 4 are considerably higher than those in parts a and b of Figure 4. The CNT films in the case of parts c and d of





**Figure 5.** Emission stability of the CNT films, continuously operated in a dc mode: without deposition of SDS and whose CNTs were (a) not cut and (b) cut; with deposition of SDS and whose CNTs were (c) not cut and (d) cut. Inset is the field emission image of the CNT film (c) by applying a field of 5.4 V/ $\mu$ m.

Figure 4 were produced by additional SDS deposition, while those in parts a and b of Figure 4 were not. Therefore, it is concluded that the current density increases significantly due to additional SDS deposition. This is possibly because the CNT films produced by additional SDS deposition have more fissures than those produced without SDS deposition and they will have more CNT emitters. Moreover, the additional SDS deposition on the CNT films could reduce the contact resistance between the CNTs and the substrate, and such CNT films might show higher field emission. This effect should be studied in detail. It is certain that the current density is proportional to the number of CNT emitters. The field emissions of the CNT films in parts b and d of Figure 4 were higher than those in parts a and c of Figure 4, respectively. The CNTs in the case of the former were cut, while those in the latter case were not. Therefore, it is concluded that CNTs that are cut show a higher field emission current than those that are uncut.

The field emission data were analyzed using the Fowler–Nordheim model<sup>24</sup> ( $\ln I/V^2 \sim 1/V$ ). The data were replotted as  $\ln(I/E^2)$  versus  $1/E$ , as shown in Figure 4; this revealed the Fowler–Nordheim-type field-emission behavior. The enhancement factor  $\beta$  was derived from the slope of the graph by assuming that the work function of the CNTs was the same as that of graphite ( $\sim 5$  eV). The enhancement factors for the CNT films corresponding to parts a–d of Figure 2 were 3954, 5050, 6701, and 5809, respectively. The highest enhancement factor was obtained for the CNT films produced by additional SDS deposition and for the CNTs that were uncut by firing for a relatively short time. This value can be favorably compared with the reported values, which are in the range of 2000–5000.<sup>25–27</sup>

The result of lifetime tests is shown in Figure 5. Approximately 7 and 3 h are required for 10% degradation of the CNT films produced without deposition of SDS and whose CNTs were (a) not cut and (b) cut, respectively. On the other hand, approximately 18 and 9 h were required for 10% degradation of the CNT films produced with deposition of SDS and whose CNTs were (c) not cut and (d) cut, respectively. The CNT film on which SDS was deposited

and whose CNTs were uncut exhibited significantly higher stability than the others; it barely reduced for several hours. By considering the long time for 10% degradation with the application of a dc voltage, it can be concluded that the CNT film has long-term stability. From the results of the current density measurement and lifetime tests, it is concluded that the field emission current increases, while stability decreases when the CNTs are cut. This is reasonable since the broken tip of CNTs is chemically more active than their sides; therefore, they degrade relatively easily. From our observations, it is concluded that the CNT films on which SDS is deposited and whose CNTs are not cut by a relatively short firing time have the optimum field emission properties such as high field emission, low turn-on voltage, uniform emission, and long-term emission stability. For films, on which SDS is deposited and whose CNTs are uncut, the CNTs are aligned horizontally and parallel to the surface of the plate. Therefore, the distance between the CNTs and anode will become almost equal for all the CNTs exposed in the fissures. A uniform distance is essential for homogeneous field emission in all areas since the field emission is critically affected by the distance between the tip of CNT emitters and the anode. The image shown in the inset of Figure 5 is uniform across the entire area observed through an aperture.

In summary, we developed a method to fabricate horizontally aligned CNT field emitters by electrophoresis deposition and fissure formation techniques. We deposited a thin film of CNTs on a Ti substrate from an aqueous mixture of CNTs and SDS by electrophoresis; we then deposited a thin layer of SDS from an aqueous SDS solution by electrophoresis. We dried the layer naturally and then compressed the surface to smoothen it. Due to firing at an appropriate temperature, the thin film changed into numerous micro-sized islands of films and consequently CNTs with a clean surface were exposed in the fissures formed. The field emission properties of the CNT filter improved significantly due to the additional deposition of SDS on the CNT film. When the CNTs were cut, the field emission current density increased to some extent; however, their stability decreased considerably. The CNT film on which SDS was deposited and whose CNTs were not cut and aligned horizontally showed good field emission properties such as high current density, low turn-on voltage, and long-term stability. Our method has the following advantages: the process is relatively simple and the raw CNT soot can be used without any purification, the CNT tips are very clean and no further treatment is needed to augment field emission, and there is no intrinsic limit on the device size because it depends on the size of the electrodes, which is not restricted.

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