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Field Emission Performance of Nitrogen-doped Carbon Nanotubes

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Field emission can be used for various applications such as field emission displays and other devices. Our experiments show that nitrogen-doped carbon-based nanotubes can provide different properties for field emission according to the different geometries of nitrogen doping, which can be the origin of difference in field emission performances due to different nitrogen doping levels.

Key words: field emitter, nitrgen doping, carbon nitride nanotubes, turn on & threshold voltages, raman spectroscopy

Field emission, the phenomenon that electrons are extracted from the surface of materials by quantum tunneling[1], has recently attracted considerable attention owing to its numerous applications, including vacuum microwave telecommunications[2], electron microscopes[3], luminescent tubes[4], gas discharge tubes[5], X-ray tubes[6], back light units[7], and other vacuum electronic devices. Field emission displays (FEDs) are a particularly notable application. Utilizing as a type of flat panel display technique, the FED has many unique advantages compared to the cathode ray tube (CRT) and liquid crystal display (LCD). These include the following: 1) FED is as energy efficient as LCD while CRT requires more power consumption; 2) FED can emit sufficient light intensity comparable to that of CRT whereas LCD is deficient in this regard: 3) FED and CRT can respond to signal alteration quickly whereas LCD is characterized by some delay. (Note that (2) and (3) are the main reasons that CRT, instead of LCD, is still widely used in professional video game competitions); 4) FED and CRT offer much wider viewing angles than LCD; 5) FED based on field emission does not require time for warming up, which is necessary for CRT based on the principle of thermionic emission; 6) Unlike CRT, which works under ultrahigh voltage, FED can work under relatively low voltage; and 7) In principle, FED devices can be made with thickness as small as that of paper whereas CRT requires a large-sized vacuum tube.

A key aspect in developing FEDs and other field emission-based devices is the fabrication of "cold cathodes", which are distinguished from hot cathodes based on thermionic emission[8]. According to previous studies[8-10]: 1) an emitter with higher aspect ratio has a higher field enhancement factor, whose definition is the ratio of local field to the applied electric field. The higher the local field, the easier the emission of electrons; 2) Low work function materials have lower potential barrier for electron emission; and 3) Localized states near the Fermi level of the materials supply electrons for emission. As the carrier density is increased, the emission current also becomes greater. Carbon nanotubes (CNTs), one-dimensional hollow cylindrical structures formed from rolled graphite sheet(s)[11], have been shown to be good candidates for field emission applications[12] owing to their innate high aspect ratio, excellent electrical and mechanical properties, and chemical inertness. De Heer *et al*. proposed a field emission display prototype based on aligned carbon nanotubes for the first time in 1995[13]. Choi *et al*. reported the successful fabrication of a 4.5 inch fully sealed FED device that is considered as a milestone in this field[14]. Teo *et al*. showed that arrays of individual vertically aligned carbon nanotubes with uniformities in height and diameter could be made by plasma enhanced chemical vapor deposition (PECVD)[15]. These results point toward the possibility of making a reliable large area display panel with uniform properties over the whole area. To further improve the field emission performance, nitrogen was introduced as an n-type dopant to raise the donor level in a carbon nanotube[10]. Although some useful experimental[16] and theoretical investigations[17] on this topic were reported, a sound understanding of the nitrogen doping effect on field emission properties has yet to be reached.

Herein, we report the fabrication of a FED device of 25×25 pixels, where the size of each pixel is 0.2 mm ×0.2 mm and the dot pitch is 0.2 mm. These pixels are

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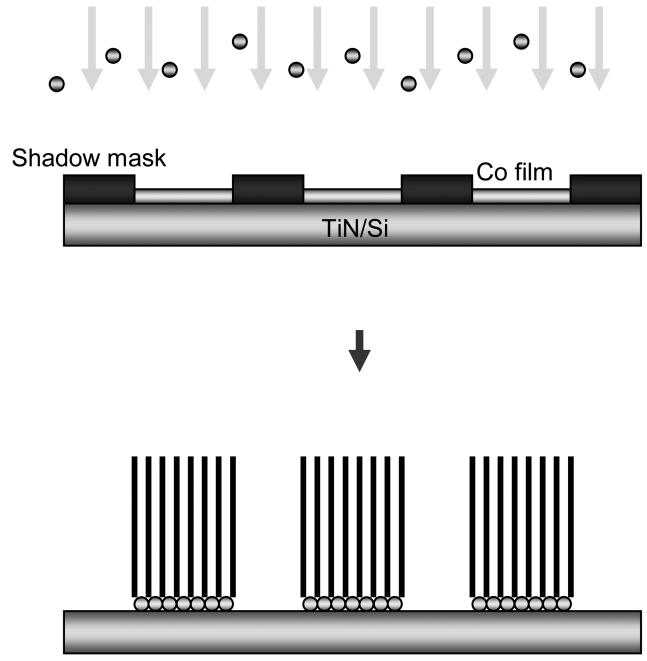
composed of carbon nanotubes. By varying the nitrogen doping level of nanotubes comprising the FED devices, the field emission performance of the devices will change accordingly. Therefore, we found that there exists an optimal nitrogen doping level that can maximize the field emission ability while both excessively high and exceedingly low doping levels show worse field emission performances.

The carbon nanotubes for the FED were synthesized by PECVD on TiN coated Si substrates using Co thin film as a catalyst and CH_4 and H_2 or/and N_2 as flowing gases. A shadow mask of 25×25 square holes was used to realize the patterned growth of nanotubes (Scheme 1). Here, TiN served as a diffusion barrier to maintain the activity of the catalyst. Moreover, titanium carbide formed at a high temperature can decrease the contact resistance between nanotube emitters and the substrate[15]. To control the nitrogen doping level, we varied the N_2 concentration of the flowing gases[18] from 0 to 85%, as summarized in Table 1. Accordingly, the samples were named 1 N, 20 N, 55 N, and 85 N. In this manner, CN_xNT featuring bamboo-liked structures were synthesized[19, 20].

Two major parameters are employed here to examine the field emission performance of different samples: (1) the turn-on field, defined as the applied field to achieve a current density of 10 μA/cm^2; and (2) the threshold field, defined as the applied field to achieve a current density of 1 mA/cm^2. Table 2 lists these two parameters for all samples studied.

Table 1. Growth conditions of nanotubes studied in present work

Samples	Plasma pre-treatment	N_2/H_2 (sccm/sccm)	N %	CH_4 flowing rate (sccm)
1N	N_2+H_2 6 min	1/84	1	15
20N	N_2+H_2 6 min	20/65	20	15
55N	N_2+H_2 6 min	55/30	55	15
85N	N_2+H_2 6 min	85/0	85	15



Scheme 1. Fabrication of patterned nanotube array field emitters.

The field emission performances of these samples can be divided into three groups: sample 20N shows the best field emission performance, specifically, the lowest turn-on and threshold fields of 1.6 and 2.3 V/μm, respectively; the samples with 1N show intermediate turn-on and threshold fields of ~2.1 and 3.3 V/μm, respectively. On the other hand, the samples larger than 55N show the highest turn-on and threshold fields of ~3.0 and 4.8 V/μm, respectively. These results indicate that there is an optimal nitrogen concentration between the lowest and highest nitrogen doping level to achieve the best field emission performance. The Fowler-Nordheim model, which describe the relation between emission current and applied field, can be used to explore the field emission data here:

$$J = 1.42\times10^{-6}\phi^{-1}(\beta V/d)^2\exp(10.4\phi^{-1/2}) \exp[-6.44\times10^{9}\phi^{1/5}d/(\beta V) \quad (1)$$

In equation (1), J (A/m^2) is the emission current density, ϕ (eV) is the work function of cold cathode materials, β is the field enhancement factor, and V (V) and d (m) are the applied voltage and separation between cathode and anode, respectively. If we substitute F with (V/d) in equation (1), we can deduce:

$$\ln(J/F^2) = [1.42\times10^{-6}\phi^{-1}\beta^2+10.4\phi^{-1/2}] - [6.44\times10^{9}\phi^{1.5}\beta^{-1}](1/F) \quad (2)$$

Therefore, $\ln(J/F^2)$ and $1/F$ have a linear relation. When the applied field is low, only the nanotubes with ultrahigh field enhancement factors emit electrons. As the applied

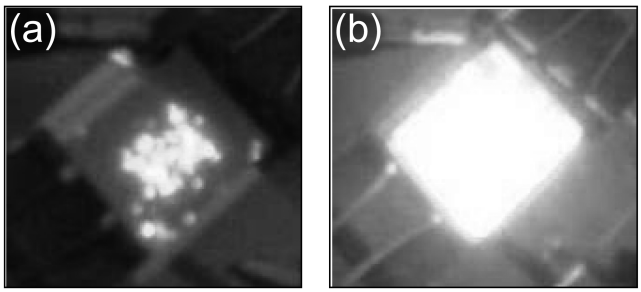


Fig. 1. Field emission pattern at a) low applied field and b) high applied field.

Table 2. Field emission properties of the samples of the present study

Samples	1N	20N	55N	85N
Turn-on	2.1	1.6	2.9	3.0
Threshold	3.3	2.3	4.8	4.8

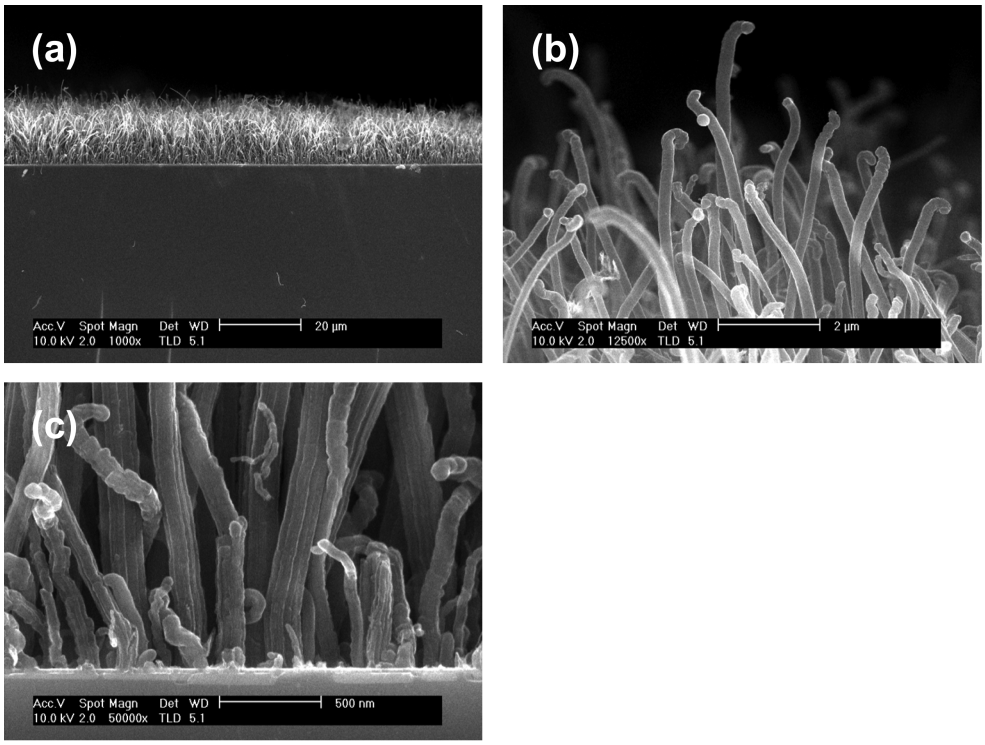
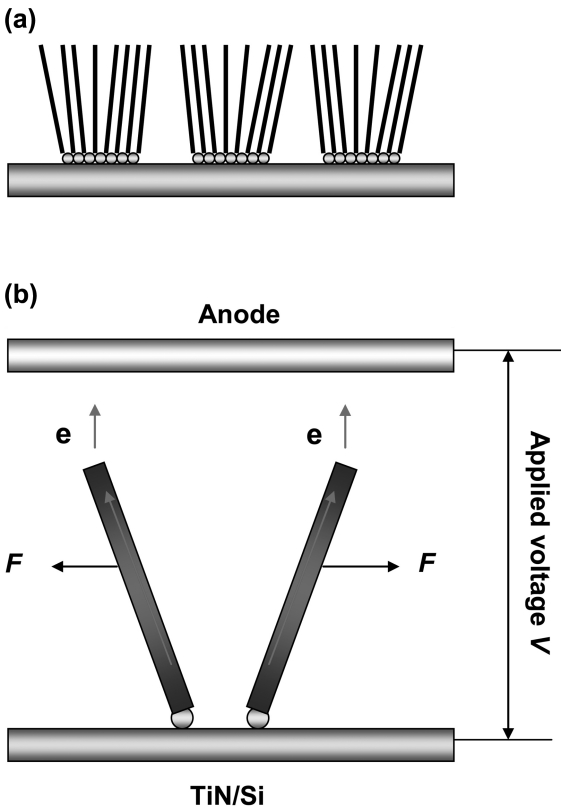


Fig. 2. SEM images of nanotubes (55N) after field emission measurement: a) cross-sectional view, b) tip part and c) bottom part.

field becomes increasingly higher, a greater number of nanotubes are activated and finally they all emit electrons at a certain field (Fig. 1). Thereafter, an increase in the applied field no longer changes the emission area and the thin film emitters show a different field emission from that in the lower applied field.

After the FE measurement, the morphologies of the nanotube samples were examined by SEM again. Individual nanotube tips are separated and exposed (Figs. 2a-b and Scheme 2a) from the closed-packed tangled state. This phenomenon could be explained as the result of repulsion between electrons as shown in Scheme 2b. As a result, the nanotubes will repulse each other. Thus, the emission current will increase owning to a reduction of the screening effect.

In addition, we performed a Raman spectroscopy analysis to examine the structural differences between different nanotubes having different vibration modes. Similar to graphite, the D mode peak around 1290 cm^{-1} is attributed to defects and the high energy mode (HEM) around 1600 cm^{-1} is independent of defects. Thus, the intensity ratio I_D/I_{HEM} can be used to relate the defect concentration. On the other hand, Thomsen *et al*. indicated that D and HEM are the result of double-resonance. Maultzsch *et al* also showed that both are proportional to the defect concentration by a boron-doping experiment. and Maultzsch *et al* found that the D* mode of ~2580 cm^{-1}, twice for D mode, is independent of the defect concentration. In this respect, the ratio intensity I_D/I_{D*} is considered to be proportional to the defect concentration. The



Scheme 2. a) Geometries of nanotubes after field emission measurement. b) Emitting nanotubes subjected to repulsion between electrons.

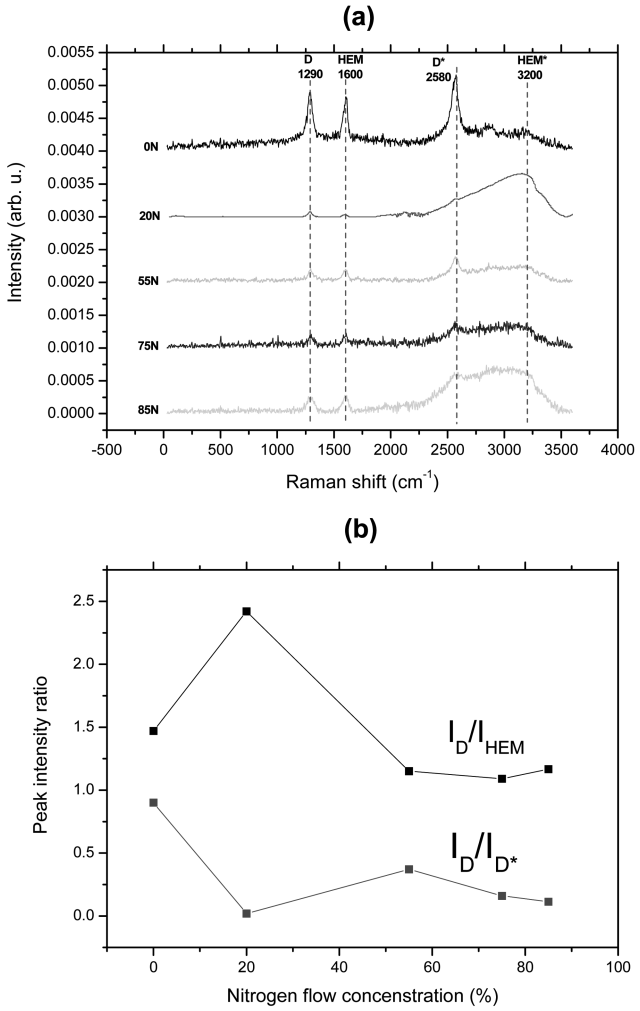


Fig. 2. a) Raman spectrums of 5 samples: 0N, 20N, 55N, 75N, and 85N. The wavelength of the laser for excitation is 1064 nm. b) Relation between nitrogen concentration and the intensity ratios (I_D/I_{HEM} and I_D/I_{D^*}). I_D/I_{HEM} might be related to the field emission performance in the present study.

Raman spectra of the present samples (Fig. 2a) show that the peak intensities of D* mode and HEM* mode (~3200 cm^{-1} being twice the frequency of HEM) are very strong. The sample 20N, which shows the best FE performance, has an extraordinarily strong HEM* peak in the spectra. The values of I_D/I_{D^*} and I_D/I_{HEM} are shown in Fig. 2b. When I_D/I_{HEM} of the present samples is higher, better FE properties are observed. Nevertheless, the mechanism underlying the Raman spectra of nitrogen doped carbon nanotubes is still unclear at present and further study is required.

In conclusion, field emission properties of nitrogen-doped carbon nanotubes with different nitrogen concentration were studied by experiments. Nitrogen doping level in nanotubes was controlled by the nitrogen concentration in flowing gases. Experimental results indicate that an optimal amount of nitrogen doped into the nanotube structure can improve the field emission performance. On the other hand, the field emission current can be reduced by heavy doping. The finding of an optimal nitrogen concentration may indicate a direction to improve the field emission properties of large area nanotube array emitters.

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