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## The enhanced field-emission properties of screen-printed single-wall carbon-nanotube film by electrostatic field

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#### ABSTRACT

In this work, we improved the field-emission properties of a screen-printed single-wall carbon-nanotube (SWCNT) film by applying a strong electrostatic field during the drying process after the printing. By applying the strong field, more tips of SWCNTs could emerge from the screen-printed film and turn somewhat toward the erecting direction because of the repulsive force among the SWCNTs. The fieldemission properties of the film were thus improved obviously. The improved field emitters sample has low electron emission turn-on field ( $E_{to} = 1.22 V/\mu m$ ), low electron emission threshold field  $(E_{\rm th} = 2.32 \text{ V}/\mu\text{m})$  and high brightness with good uniformity and stability. The lowest operating field of the improved sample is below 1.0 V/ $\mu$ m and its optimum current density exceeds 3.5 mA/cm<sup>2</sup>.

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#### 1. Introduction

Since the initial reports in 1995 [1,2], electron emission of carbon nanotubes has been drawing the attention of scientists from different fields, such as field emission displays (FED) [3], cathode ray lamps [4], X-ray sources [5], and electron sources for electron microscopes [6]. The carbon nanotube field emitter has large aspect ratio, so the field enhancement factor ( $\beta$ ) of the carbon nanotube field emitter can reach high value [7,8]. By using carbon nanotube field emitter, field emission voltage of the FED device can be lowered in addition to the stability of emission current due to its strong physical properties.

The present work is mainly focused on the improvement of field-emission properties of screen-printed single-wall carbonnanotube (SWCNT) film by applying a strong electrostatic field in the fabrication process. In general, three known methods can be adopted to make field emitters with CNTs: screen-printing [9–12]. spray deposition [13] and chemical vapor deposition (CVD) [14-16]. Among them, the screen-printing method is highly efficient, and can produce low-voltage field electron emitters with large emitting (working) area. Moreover, it has become a more mature

Corresponding author. E-mail address: miaowang@css.zju.edu.cn (M. Wang). technology in other display manufacturing areas. The direct chemical vapor deposition method encounters problems in the fabrication of CNT emitters, such as high growth temperature, complicated process, etc.

However, the screen-printing method still needs to be improved due to its poor electron emission characteristics. In the electrostatic field, the erecting tips have large field enhancement factor. The current existing difficulty with the traditional screen-printing method is that, most of the tips of CNTs are buried in the surface film, leading to a disadvantage for the field emission. However, if the sample is placed in a strong electrostatic field during the drying process, the CNTs at the surface will repel each other because of the electrostatic force and more tips will be exposed and turn somewhat toward the normal direction. Thus, they become competent for field emission. According to the authors' knowledge, the use of electrostatic field during the fabrication process to improve the field-emission properties has not been reported by other researchers.

#### 2. Experiment

#### 2.1. Fabrication of the SWCNTs

In this study, SWCNTs were synthesized by arc-discharging method for screen-printing. Firstly, the arc-discharge chamber was

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Fig. 1. The fabricating process of cathode and anode plate (a and b); (c) is the structure of FED.

pumped and when the gas pressure reached 0.5 Pa, 0.010 MPa  $H_2$  and 0.016 MPa Ar were loaded. In the course of arc-discharge, the interval spacing was always 2 mm between an extensible cylindrical 8 mm-diameter graphite-rod anode (which contains the catalyzers, i.e., 0.1% Fe and 0.3% Mo) and a fixed 5 cm-diameter graphite-sphere cathode. The arc current was 70 A. After a 3-min arc-discharge process, much elastic web-like material containing SWCNTs was formed on the walls of the chamber around the electrodes.

#### 2.2. Purification of the SWCNTs

To scatter the SWCNTs, firstly the raw material sample (0.827 g) was put in alcohol and ultrasonic dispersion was executed on them for 30 min. The solution was filtered and dried. The sample was dissolved in toluene by magnetic stirrer in order to remove the fullerene. After the solution was precipitated and swilled out of the upper solution, the rest of the solution was dried. Afterwards the sample was put in 100 mL concentrated nitric acid (63 vol.%) with a regular monofrequency ultrasonic bath (maximum power) for a few minutes. The suspension was then refluxed under magnetic stirring at 80 °C for 8 h in order to remove the metal oxide. It was precipitated and swilled and dried again. Finally the sample was treated with 37% hydrochloric acid for 48 h. After each procedure above the wet powder was washed with distilled water and dried in an oven at 120 °C. About 0.26 g of the purified SWCNTs was obtained finally.

#### 2.3. The fabrication of the cathode and anode

The SWCNTs were printed on the conductive glass coated with indium tin oxide (ITO) film as shown in Fig. 1a. Before being printed, the SWCNTs were mixed with organic carriers (ethyl cellulose and terpineol). Then SWCNTs paste was printed through a fine net-screen on an indium–tin-oxide (ITO) glass substrate as the cathode of FED. After screen-printing, the ITO glass with the SWCNTs film coated was kept in an electrostatic field (about 6 kV/ cm) for 5 min as shown in Fig. 1b until the film became dry. At the same time, one sample without being treated by the electrostatic field was prepared for comparison. Finally the printed cathode was

sintered at temperature of 400  $^\circ$ C for 2.5 h to remove the organic carriers and some amorphous carbon.

Similar to the above process, the anode was prepared only using the green phosphor instead of the SWCNTs paste.

#### 2.4. The measurements of the SWCNTs cathode

The samples were measured under the same conditions. The field-emission measurements of the SWCNTs film printed cathode were made in a vacuum chamber of pressure  $3 \times 10^{-5}$  Torr and with spacer of thickness 150  $\mu$ m between the anode and cathode plates as shown in Fig. 1c. After being aged for a period of time in the high field, relation between the current density  $J(\mu A/cm^2)$  and the electric field strength  $E(V/\mu m)$  was measured systematically.

#### 3. Results and conclusion

In this study some raw sample of SWCNTs were characterized using Philips CM200 ultratwin HRTEM as shown in Fig. 2, and by Raman spectrum at room temperature as shown in Fig. 3. In Fig. 2, it can be found the raw SWCNTs are usually assembled in ropes. The Raman spectrum of the sample, which was obtained at the room temperature with the laser wavelength of 514.5 nm, shows the characteristic breath and tangential band at 190–275 cm<sup>-1</sup> (inset of Fig. 3) and 1567 cm<sup>-1</sup>, respectively, while the characteristic peak of amorphous carbon is at 1346 cm<sup>-1</sup>. The ratio of the intensity between SWCNTs and amorphous carbon is 18:1. It is obvious that the sample is highly pure with little amorphous carbon. The diameter of SWCNTs is calculated by the formula  $d = 237.5/\omega$  ( $\omega$  is the character peak in low-frequency zone). The diameter of SWCNTs in the sample is 0.86-1.22 nm. The results show that the Raman analysis is in agreement with the observation of HRTEM.

Field-emission properties of the prepared SWCNTs film as a cathode were studied. Due to the application of the electrostatic field during the drying process of sample preparation, the tips of SWCNTs emerged from the screen-printed film. It is found that the FED with the SWCNTs cathode treated by electrostatic field had low turn-on field, low threshold field and high brightness. The macroscopic fields needed to produce current densities of 100  $\mu$ A/cm<sup>2</sup> and 1 mA/cm<sup>2</sup>

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