



# Electrophoretic deposition and field emission properties of patterned carbon nanotubes

Haifeng Zhao<sup>a</sup>, Hang Song<sup>a,\*</sup>, Zhiming Li<sup>a</sup>, Guang Yuan<sup>b</sup>, Yixin Jin<sup>a</sup>

<sup>a</sup>Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 Dongnanhu Avenue, Changchun 130033, PR China

<sup>b</sup>Physics Department, Information Science and Engineering College, Ocean University of China, 5 Yushan Road, Qingdao 266003, PR China

Available online 25 May 2005

## Abstract

Patterned carbon nanotubes on silicon substrates were obtained using electrophoretic method. The carbon nanotubes migrated towards the patterned silicon electrode in the electrophoresis suspension under the applied voltage. The carbon nanotubes arrays adhered well on the silicon substrates. The surface images of carbon nanotubes were observed by scanning electron microscopy. The field emission properties of the patterned carbon nanotubes were tested in a diode structure under a vacuum pressure below  $5 \times 10^{-4}$  Pa. The measured emission area was about  $1.0 \text{ mm}^2$ . The emission current density up to  $30 \text{ mA/cm}^2$  at an electric field of  $8 \text{ V}/\mu\text{m}$  has been obtained. The deposition of patterned carbon nanotubes by electrophoresis is an alternative method to prepare field emission arrays.

© 2005 Elsevier B.V. All rights reserved.

PACS: 61.46.+w; 82.45.-h; 79.70.+q

Keywords: Carbon nanotubes; Electrophoresis; Field emission; Field emission arrays

## 1. Introduction

Carbon nanotubes (CNTs) are very attractive as electron field emitters for their nanometer scale, high aspect ratio [1,2], superior mechanical strength [3], good conductance and high chemical stability. Several groups have reported electron field emission from

CNTs [4–6]. Many efforts have been made to develop differing methods for making patterned CNTs [7,8]. Patterned CNTs could be grown on some substrates with catalyst by chemical vapor deposition (CVD) method [9,10], while it always required relatively high growth temperatures ( $\geq 600^\circ\text{C}$ ), which limited us to use some substrates with low melting temperatures. Also, the patterned CNTs could be fabricated by a screen printing method [11]. Patterned deposition of dispersed CNTs on silicon wafers or conducting layer-coated glass substrates would be useful to fabricating

\* Corresponding author. Tel.: +86 431 4627073; fax: +86 431 4627073.

E-mail address: [songhang@public.cc.jl.cn](mailto:songhang@public.cc.jl.cn) (H. Song).

the carbon nanotube field emission arrays (FEAs) or carbon nanotube based field emission displays (FEDs) devices. In this paper, the patterned CNTs on silicon substrates formed by electrophoretic method, and the field emission properties of it were reported.

## 2. Experiments

In this study, the substrates were p-type silicon (1 0 0) wafers with resistivity of 5–8  $\Omega\text{cm}$ . First, a silicon dioxide layer on silicon substrates with the thickness of about 300 nm was prepared by wet oxidation method. Then, the silicon dioxide layer was patterned by the photolithography and chemical etching treatment to form some apertures with the diameter of about 25  $\mu\text{m}$  at the space of 25  $\mu\text{m}$ . The patterned silicon dioxide layer was used as a mask to perform a selected deposition of carbon nanotubes.

The multiwall nanotubes (MWNTs) were synthesized by CVD method, and purified by ultrasonic agitation in solution with 1:1 ratio of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . The MWNTs were dispersed in isopropyl alcohol solution that contained little dissolved  $\text{Mg}(\text{NO}_3)_2$ . A little amount of dissolved ethyl cellulose was added to the suspension to disperse the CNTs. The CNTs electrophoresis suspension was ultrasonically dispersed for about 5 h, and then stably placed over night for depositing the large sized CNTs conglomerations. The top fraction of the suspension was used in electrophoresis procedures.

The patterned silicon wafer as a cathode and a stainless steel mesh as an anode were immersed into the CNTs electrophoresis suspension at room temperature. An adjustable direct voltage was applied to the electrodes. In this study, the electrodes kept at a constant gap of 2 cm, the applied voltage was varied from 30 to 600 V, and the deposition time was varied from 2 to 10 min. Lastly, the patterned CNTs were deposited on silicon wafers by electrophoresis, and carbon nanotube FEAs were obtained.

## 3. Results and discussion

The electrophoretic rate of CNTs depended on some experimental factors that included the concentrations of the CNTs, the electrolyte in the suspension,

as well as the current density on the electrode surfaces. The CNTs migrated towards the negative electrode instead of the positive one under the applied voltage. This is because the  $\text{Mg}^{2+}$  ions were absorbable by suspending CNTs, and then formed the double electron layers around the CNTs in the suspension. The patterned CNTs arrays adhered well on the conducting silicon substrates. The good adhesion might be due to the formation of metal hydroxide derived from the metal ions reaction on the substrate electrode surface as proposed elsewhere [12].

The morphology of the CNTs arrays was observed by scanning electron microscopy (SEM). Fig. 1 depicts a typical SEM image of patterned CNTs arrays deposited on a silicon substrate. The CNTs deposited preferably on the patterned conducting silicon surface rather than on the insulated silicon dioxide mask layer. From the cross-section SEM images, the average thickness of the patterned CNTs layer was about 3  $\mu\text{m}$ . The thickness was controllable by adjusting the deposition time.

The measurement of field emission properties was carried out in a diode structure under a vacuum pressure below  $5 \times 10^{-4}$  Pa. The specimen was attached to a copper pedestal using conducting glue, which was used as a cathode. While a stainless steel plate was used as an anode. The gap between the electrodes was 260  $\mu\text{m}$ . The measured field electron emission area was about 1.0  $\text{mm}^2$ . The area summed up the circle areas of the carbon nanotube arrays, excluded the area of silicon dioxide layer. The curve of current density versus electric field of the CNTs arrays

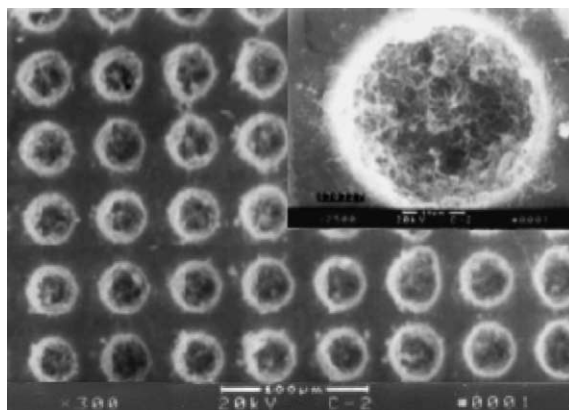


Fig. 1. SEM image of the patterned CNTs on a silicon substrate.

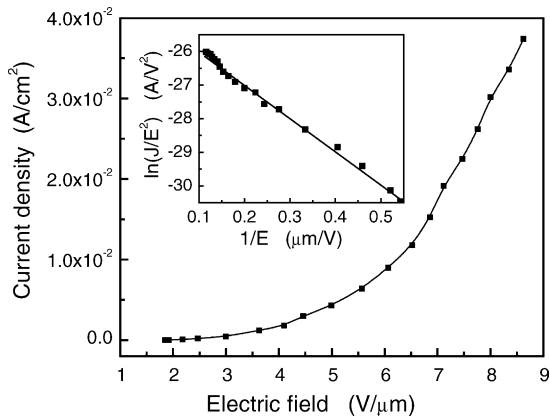


Fig. 2. The curves of current density vs. electric field.

is shown in Fig. 2. The emission current density was up to  $30 \text{ mA/cm}^2$  at an applied electric field of  $8 \text{ V}/\mu\text{m}$ . The Fowler–Nordheim (FN) plot of the data is also shown in the inset of Fig. 2. The plot of  $\ln(J/E^2)$  versus  $1/E$  yielded a straight line in agreement with the FN equation, confirmed the current resulted from electron field emission. The carbon nanotube FEAs deposited on silicon substrates by electrophoretic method presented good dispersing and fine electrical contact, which would be helpful to attain a high emission current density at a low electric field.

#### 4. Summary

Patterned carbon nanotube FEAs on silicon substrates were achieved by electrophoresis. In this study, the carbon nanotube arrays showed excellent electron field emission properties, and an emission

current density up to  $30 \text{ mA/cm}^2$  at an electric field of  $8 \text{ V}/\mu\text{m}$  has been obtained.

#### Acknowledgments

This work was supported by the “973” National Key Basic Research Development Program in China, under Grant Nos. 2003CB314701 and 2003CB-314702, and the Innovation Project of Chinese Academy of Sciences.

#### References

- [1] S. Iijima, *Nature* 354 (1991) 56–58.
- [2] A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tomanek, P. Norlander, D.T. Colbert, R.E. Smalley, *Science* 269 (1995) 1550–1553.
- [3] M.R. Falvo, G.J. Clary, R.M. Taylor II, V. Chi Jr., F.P. Brooks, S. Washburn, R. Superfine, *Nature* 389 (1997) 582–583.
- [4] J.M. Bonard, J.P. Salvetat, T. Stöckli, L. Forro, A. Chatelain, *Appl. Phys. A* 69 (1999) 245–254.
- [5] W. Zhu, C. Bower, O. Zhou, G. Kochanski, S. Jin, *Appl. Phys. Lett.* 75 (6) (1999) 873–875.
- [6] J.I. Sohn, S.H. Lee, Y.H. Song, S.Y. Choi, K.I. Cho, K.S. Nam, *Appl. Phys. Lett.* 78 (7) (2001) 901–903.
- [7] J. Li, C. Papadopoulos, J.-M. Xu, M. Moskovits, *Appl. Phys. Lett.* 75 (3) (1999) 367–369.
- [8] S. Huang, A.W.H. Mau, T.W. Turney, P.A. White, L. Dai, *J. Phys. Chem. B* 104 (10) (2000) 2193–2196.
- [9] H. Kind, J.M. Bonard, C. Emmenegger, L.O. Nilsson, K. Hernadi, E. Maillard-Schaller, L. Schlapbach, L. Forró, K. Kern, *Adv. Mater.* 11 (15) (1999) 1285–1289.
- [10] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tomblor, A.M. Cassell, H. Dai, *Science* 283 (1999) 512–514.
- [11] N.S. Lee, D.S. Chung, J.H. Kang, H.Y. Kim, S.H. Park, Y.W. Jin, Y.S. Choi, I.T. Han, N.S. Park, M.J. Yun, J.E. Jung, C.J. Lee, J.H. You, S.H. Jo, C.G. Lee, J.M. Kim, *Jpn. J. Appl. Phys.* 39 (2000) 7154–7158.
- [12] B.E. Russ, J.B. Talbot, E. Sluzky, *J. SID* 4 (3) (1996) 207–211.