Available online at www.sciencedirect.com
ScienceDirect
Physica B 403 (2008) 2662–2665
PHYSICA B
www.elsevier.com/locate/physb

High-field electron emission of carbon nanotubes grown on carbon fibers

Leyong Zeng[a,b], Weibiao Wang[a,*], Da Lei[a,b], Jingqiu Liang[c], Haifeng Zhao[a], Jialong Zhao[a], Xianggui Kong[a]

[a]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China*
[b]*Graduate School of Chinese Academy of Sciences, Beijing 100049, PR China*
[c]*State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China*

Received 18 October 2007; received in revised form 22 January 2008; accepted 26 January 2008

Abstract

Carbon nanotubes with uniform density were synthesized on carbon fiber substrate by the floating catalyst method. The morphology and microstructure were characterized by scanning electron microscopy and Raman spectroscopy. The results of field emission showed that the emission current density of carbon nanotubes/carbon fibers was 10 μA/cm^2 and 1 mA/cm^2 at the field of 1.25 and 2.25 V/μm, respectively, and the emission current density could be 10 and 81.2 mA/cm^2 with the field of 4.5 and 7 V/μm, respectively. Using uniform and sparse density distribution of carbon nanotubes on carbon fiber substrate, the tip predominance of carbon nanotubes can be exerted, and simultaneously the effect of screening between adjacent carbon nanotubes on field emission performance can also be effectively decreased. Therefore, the carbon nanotubes/carbon fibers composite should be a good candidate for a cold cathode material.

PACS: 61.48.+c; 79.70.+q

Keywords: Carbon fibers; Carbon nanotubes; Floating catalyst; Field emission

1. Introduction

Carbon nanotubes (CNTs) have many exceptional physical and chemical properties. It has important application in field emission displays because of the large aspect ratio, the small tip radii of curvature, the high chemical stability, and so on. In comparison with other cold cathode materials (metals, silicon micro-tips, diamonds films, etc.), CNTs have much predominance in field emission: the low threshold field, the large emission current, the long emitter lifetime, and the low fabrication cost. Therefore, CNTs have become one of the most promising field emission electron source materials [1–5]. To date, CNT films have been typically prepared by the screen-printing method and the electrophoretic deposition method [6,7]. However, organic impurity was easily brought about by the process of screen printing, which may lead to the instability of the emission current and the invalidation of the emitters. Electrophoretic deposition can lead to the unevenness of CNT films, which can easily burn the cathode because of the large local current. Moreover, in CNT films prepared by screen printing and electrophoretic deposition, most of the CNTs were flatly placed, and the tip predominance of the CNTs could not emerge. When aligned CNT films grown directly on the substrate were used as an emission cathode, the tip structure of the CNTs played in important role in field emission. However, most of the aligned CNT films have a very large density. The field emission performance of the aligned CNT films may have similar results as that of the flat panel cathode because of the large screening effects between adjacent CNTs. Some reports

*Corresponding author. Tel./fax: +86 431 86176339.
E-mail address: wangwbt@126.com (W. Wang).

0921-4526/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2008.01.032

showed that less-dense "short and stubby" aligned CNT films have good electron field emission characteristics [8]. In order to sufficiently exert the superior field emission properties of CNTs, preparation of the CNT cathode should assure that the tip predominance of CNTs must be revealed and the screening effects between adjacent CNTs must be decreased (properly controlling the density and height of the CNTs). Using electrically conductive and chemically stable carbon fibers as substrate, the synthesized short and sparse CNTs should have good field emission performance.

In the previous work, we have synthesized CNTs on carbon fiber substrate by the floating catalyst method with the pretreatment of carbon fibers [9], and the density of CNTs on the carbon fiber surface is uniform and sparse. The method used in the experiment solved the growth difficulty of CNTs on the carbon fiber substrate [10,11], and simultaneously overcame the bad effect of screening effects on the field emission of CNTs. In this paper, we report the electron field emission properties of CNTs on carbon fibers. We characterize the morphology and microstructure of CNTs/carbon fibers by scanning electron microscope (SEM) and Raman spectroscopy. Finally, under the environment of ultra-high vacuum, we test the field emission performance of the CNTs/carbon fibers composite.

2. Experimental details

Before the growth of CNTs, the carbon fiber substrate needs to be cleaned and activated. The growth of CNTs was carried out in a tubular furnace by the floating catalyst method. The detailed experimental process was introduced in the previous report [9].

The morphology and Raman spectroscopy of CNTs/carbon fibers were characterized by a SEM (Hitachi S-4800) operated with an accelerating voltage of 15 kV and by a Raman spectrometer (Jobin Yvon HR800) with a laser wavelength of 488.0 nm by an Ar^+ laser, respectively. Under the condition of high vacuum, the field emission performance of CNTs/carbon fibers was tested by a diode assembly.

3. Results and discussion

Fig. 1 shows the morphology of CNTs on a carbon fiber substrate. As seen in Fig. 1(a), the surface of carbon fibers was entirely covered by CNTs. The root of CNTs forms a netty structure and its top is basically perpendicular to the surface of the carbon fibers, as shown in Fig. 1(b). The diameters of the CNTs range from 40 to 60 nm, and the length of the emerging part is about 500 nm. Compared with the aligned CNTs films, the density of CNTs grown on carbon fiber substrate is lower, in which the average spacing between adjacent CNTs is estimated to be about 300 nm.

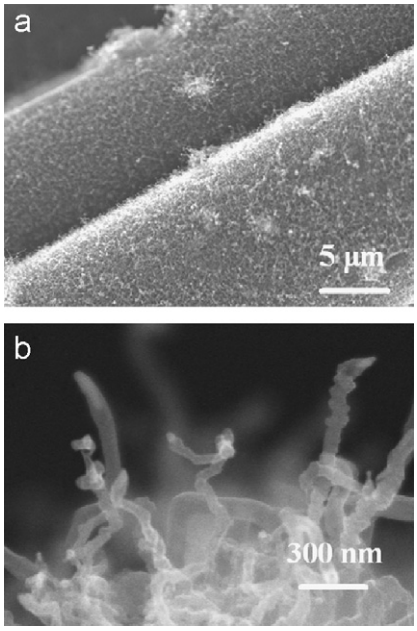

Fig. 1. The low-resolution (a) and high-resolution (b) SEM images of CNTs on carbon fiber substrate.

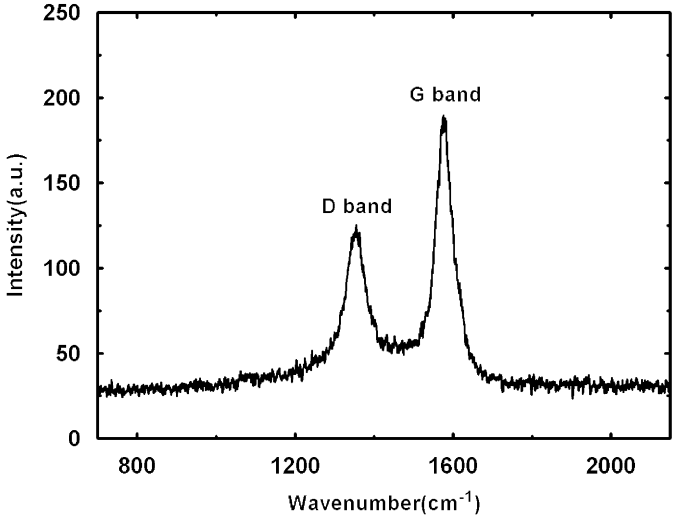

Fig. 2. Raman spectrum of CNTs on carbon fiber substrate.

Fig. 2 shows the Raman spectrum of CNTs grown on carbon fibers. Two bands can be observed: the D band at about 1352 cm^{-1} and the G band at about 1578 cm^{-1}. The stronger G peak shows the high crystal quality and graphitization degree of CNTs. Furthermore, the ratio of I_D/I_G is also related to the quality of CNTs. Based on the Raman spectrum in Fig. 2, the ratio of I_D/I_G can be estimated to be about 0.632. The lower ratio of I_D/I_G indicates the high graphitization degree of CNTs.

The measurement of the field emission performance of CNTs/carbon fibers was carried out in a diode assembly with the vacuum pressure of 2.5×10^{-4} Pa. The circuit diagram of the field emission test is shown in Fig. 3. First,

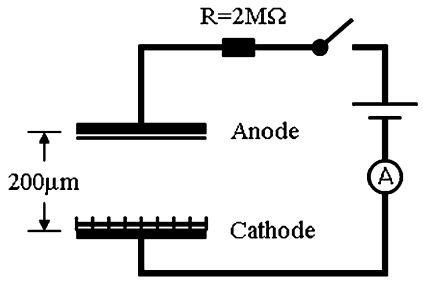

Fig. 3. The circuit diagram of field emission test.

the specimen was attached to a copper pedestal, which was used as a cathode. Glass with indium-tin-oxide (ITO) coating was used as an anode. The space between the cathode and the anode was about 200 μm. The *J–E* plot of the CNT carbon fibers is shown in Fig. 4(a). It can be clearly seen that the emission current densities of the CNTs/carbon fibers are 10 μA/cm^2 and 1 mA/cm^2 at the applied field of 1.25 and 2.25 V/μm, respectively. With an increase of the applied field, the emission current density can be up to 10 and 81.2 mA/cm^2, when the applied field is 4.5 and 7 V/μm, respectively. The corresponding Fowler–Nordheim (F–N) plot is shown in Fig. 4(b). The tiny vibration of the F–N plot can be attributed to the error of measurement and to the difference of electron emission at different applied fields. On the one hand, at the low field, the electrons first escaped from the surface of the longer CNTs into vacuum because of the larger field enhancement factor. When the applied field wassufficiently high, the electrons were also excited via tunneling the surface barrier of the shorter CNTs. Because of Joule heating, the surface temperature of CNTs increases up to at least 2000 K with the current density in the order of 10 mA/cm^2. The adsorbate on the surface of CNTs was desorbed and the resistance of CNTs decreased with an increase of temperature, which could change the electron work function of CNTs [12–15]. On the other hand, several emitters were disabled at high field because of structural defect. Although the emission ability between the CNT emitters is different, the current of the CNT films on carbon fibers is high, compared with that of the screen-printed or electrophoretic-deposited CNT films [6,7].

From the F–N theory, the emission current density J can be written as [16]

$$J = 1.54 \times 10^{-6} \frac{\beta^2 E^2}{\Phi} \exp\left[-6.83 \times 10^7 \frac{\Phi^{3/2}}{\beta E}\right], \quad (1)$$

where J is in A/cm^2, the applied field E is in V/cm, β is the field enhancement factor and the work function Φ is in eV. Eq. (1) can be rewritten and simplified as

$$\ln(J/E^2) = -6.83 \times 10^7 \frac{\Phi^{3/2}}{\beta E} + ln\left(1.54 \times 10^{-6} \times \frac{\beta^2}{\Phi}\right) \quad (2)$$

$$\frac{\mathrm{d}\ln(J/E^2)}{\mathrm{d}(1/E)} = -6.83 \times 10^7 \frac{\Phi^{3/2}}{\beta}. \quad (3)$$

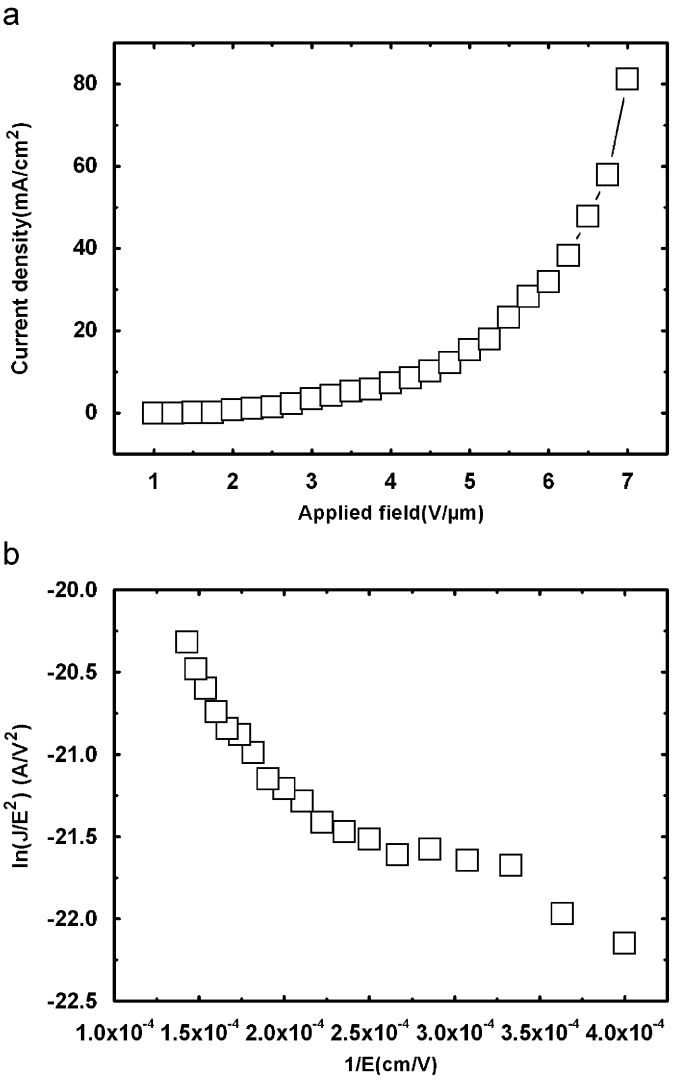

Fig. 4. The *J–E* curve (a) and F–N plot (b) of CNTs grown on carbon fiber substrate.

Eq. (3) indicates that the slope of the F–N plot is proportional to $-\Phi^{3/2}/\beta$. We define $\Phi'^{3/2} = \Phi^{3/2}/\beta$ as the effective work function of emitters. Based on the slope of the F–N plot in Fig. 4(b), the effective work function of CNTs could be calculated to be $\Phi' = 0.002216$ eV. We assume that the work function of CNT emitters is equal to that of graphite (about 5 eV) [17,18]. Therefore, the field enhancement factor β of the CNTs tip can be estimated to be about 5000.

CNTs grown on the carbon fiber surface show good field emission performance. On the one hand, the density sites played a key role in electron emission. On the other hand, the interface between the carbon fiber and the CNTs formed conductor–semiconductor or conductor–conductor behavior in view of the semiconductive and metallic CNTs. Some reports have investigated the relation between the inter-tube distance and the field enhancement factor by theoretical calculation and experimental investigation [3,19–22]. Their conclusions were that the intermediary density of CNTs emitters had an important effect on field

emission. However, the quantitative relation is hard to be concluded because of the difference between the quality, morphology, and structure of CNTs.

4. Conclusion

In summary, using the floating catalyst method, CNTs were synthesized on carbon fiber substrate, and the electron field emission of CNTs/carbon fibers was tested by a diode assembly. The results showed that the emission current density of CNTs/carbon fibers was $10\,\mu A/cm^2$ and $1\,mA/cm^2$ at the applied field of 1.25 and $2.5\,V/\mu m$, respectively, and could achieve 10 and $81.2\,mA/cm^2$ at the applied field of 4.5 and $7\,V/\mu m$, respectively. Because of the sparse density and uniform distribution of the CNTs on the carbon fiber surface, the tip predominance of CNTs can be exerted; simultaneously, the screening effect between adjacent CNTs can also be effectively decreased. Moreover, carbon fibers/CNTs can be fabricated at low cost and in large size. Therefore, CNTs/carbon fibers can be a good candidate for a cold cathode material.

Acknowledgment

This research work was supported by the National Natural Science Foundation of China (NSFC, Grants nos. 50072029 and 50572101).

References

[1] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Science 297 (2002) 787.
[2] J.M. Bonard, J.P. Salvetat, T. Stockli, L. Forro, A. Chatelain, Appl. Phys. A 69 (1999) 245.
[3] J.M. Bonard, M. Croci, C. Klinke, R. Kurt, O. Noury, N. Weiss, Carbon 40 (2002) 1715.
[4] P. Groning, P. Ruffieux, L. Schlapbach, O. Groning, Adv. Eng. Mater. 5 (2003) 541.
[5] Y. Saito, J. Nanosci, Nanotechnology 3 (2003) 39.
[6] Y.K. Li, C.C. Zhu, X.H. Liu, Diam. Relat. Mater. 11 (2002) 1845.
[7] A.R. Boccaccini, J. Cho, J.A. Roether, B.J.C. Thomas, E.J. Minay, M.S.P. Shaffer, Carbon 44 (2006) 3149.
[8] M. Chhowalla, C. Ducati, N.L. Rupesinghe, K.B.K. Teo, G.A.J. Amaratunga, Appl. Phys. Lett. 79 (2001) 2079.
[9] Y.X. Xia, L.Y. Zeng, W.B. Wang, J.Q. Liang, D. Lei, S. Chen, H.F. Zhao, Appl. Surf. Sci. 253 (2007) 6807.
[10] P.S. Weiser, S. Prawer, A. Hoffman, R. Manory, J.K. Paterson, S. Stuart, J. Appl. Phys. 72 (1992) 4643.
[11] S. Zhu, F. Shahedipourand, H.W. White, J. Am. Cerem. Soc. 81 (1998) 1041.
[12] M. Sveningsson, M. Jonsson, O.V. Nerushev, F. Rohmund, E.E.B. Campbell, Appl. Phys. Lett. 81 (2002) 1095.
[13] K.A. Dean, B.R. Chalamala, Appl. Phys. Lett. 76 (2000) 375.
[14] P. Li, K. Jiang, M. Liu, Q. Li, S. Fan, Appl. Phys. Lett. 82 (2003) 1763.
[15] S.T. Purcell, C. Journet, V.T. Binh, Phys. Rev. Lett. 88 (2002) 105502.
[16] S.T. Purcell, V.T. Binh, R.J. Baptist, J. Vac. Sci. Technol. B 15 (1997) 1666.
[17] D.W. Kang, J.S. Suh, J. Appl. Phys. 96 (2004) 5324.
[18] J.P. Sun, Z.X. Zhang, S.M. Hou, G.M. Zhang, Z.N. Gu, X.Y. Zhao, W.M. Liu, Z.Q. Xue, Appl. Phys. A 75 (2002) 479.
[19] Y.B. Zhu, W.L. Wang, K.J. Liao, Acta Phys. Sin. 51 (2002) 2335.
[20] L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J. Bonard, K. Kern, Appl. Phys. Lett. 76 (15) (2000) 2071.
[21] A.N. Obraztsov, I. Paviovsky, A.P. Volkov, E.D. Obraztsova, A.L. Chuvilin, V.L. Kuznetsov, J. Vac. Sci. Technol. B 18 (2) (2000) 1059.
[22] V. Semet, V.T. Binh, P. Vincent, D. Guillot, K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W. Milne, P. Legagneux, D. Pribat, Appl. Phys. Lett. 81 (2) (2002) 343.