Vacuum 85 (2011) 827–832

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Room temperature mass production of carbon nanotube field emission micro-cathode arrays using electroplating of a CNT/Ni composite followed by micro-machining

Min Deng, Guifu Ding, Yan Wang*, Xuemei Cui, Hong Wang, Faheng Zang, Huiqing Wu

National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Institute of Micro and Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200240, PR China

ARTICLE INFO

Article history:
Received 14 October 2010
Received in revised form
14 December 2010
Accepted 16 December 2010

Keywords:
Carbon nanotube
Electroplating
Micro-machining
Micro-cathode
Field emission

ABSTRACT

A room temperature fabrication method for the mass production of carbon nanotube (CNT) field emission micro-cathode arrays is reported. The technique combines electroplating of a CNT/Ni composite and micro-machining. This method combines the advantages of direct growth and screen printing conventionally used to fabricate such structures and avoids their disadvantages. Due to its integration and room temperature processing, the technique is proven to be advantageous in mass production and low cost. Results of field emission testing show that the CNT micro-cathodes have excellent field-emission properties, such as high current density (15.7 mA/cm^2), field enhancement factor (2.4 × 10^6/cm), and good stability (109 h for 10% degradation of current density from 400 μA/cm^2).

1. Introduction

Electron field emitters based on carbon nanotubes (CNTs) are currently being investigated as next-generation materials for cold cathodes [1–6]. Compared to other field emitters such as Spindt-type and silicon field emitter arrays, CNTs possess the advantages of very high aspect ratio, small radius of curvature, lack of vacuum-arcing, low sputter yield, chemical inertness, thermal stability and low work function of electron tunneling [7]. CNT field emission cold cathodes have a potential to be applied to emission devices which include flat panel display, cathode ray tubes, backlights for liquid crystal displays, outdoor displays and traffic signals [8–13]. In the realization of CNT field emission micro-cathodes, two approaches have been basically used in the application of CNTs. One involves printing a paste of CNT/epoxy composites [14–18]. This method has been commonly used in the economic fabrication of diode-type emitters for large area field emission displays which employ pixels of relatively large areas. It uses the CNTs distributed and exposed out of the paste in a random manner; thus, the fluctuation in the height of the CNT tips requires a relatively large cathode-to-anode distance to ensure the stability and reliability of the emission. The triode structure made of an extension of the same technology also requires a relatively large cathode-to-gate distance as shown in the literature. The other method, meanwhile, directly deposits CNTs on a pre-patterned selective area of the pixels which are coated with catalyst metal films through the chemical vapor deposition [19–29]. The method is of high efficiency for controlling the CNT alignment, density, and length. However, the preparation method has the following three disadvantages: (1) the adhesion of the CNTs which are catalytically grown on the substrates is often not strong enough to survive the mechanical shaking involved in the fabrication processes; (2) the high temperature condition (800–1000 °C) which may damage some glass substrates is obligatory for this method. In addition, direct growth and screen printing may cause the tubes be contaminated with some impurities, like metallic catalyst particles, amorphous carbon or organic residues which can introduce further defects into the CNTs during their removal [30–32]. If all these advantages in both methods are combined and all disadvantages are eliminated, a CNT field emission micro-cathode with good properties can be fabricated.

In this study, we demonstrate an effective approach to fabricate CNT field emission micro-cathode arrays at room temperature. Initially, pretreated multi-walled CNTs and Ni are deposited onto an Au bottom electrode layer by composite electroplating; subsequently, protruding tips of CNTs are obtained by etching away a layer of Ni as emitters, followed by emitter pixels and triode-typestructure layer being formed by electroplating and micro machining.

* Corresponding author. Tel.: +86 21 34206687; fax: +86 21 34206686.
E-mail addresses: dengmin265719@yahoo.cn (M. Deng), wyyw@sjtu.edu.cn (Y. Wang).

0042-207X/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2010.12.005

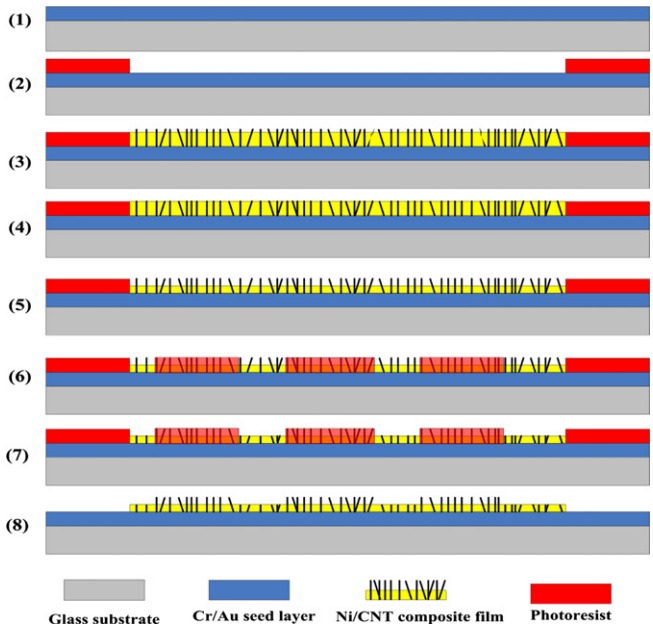

Fig. 1. Fabrication process for the CNT emitters:(1) sputtering a Cr/Cu (30/50 nm) conducting layer on a glass substrate, (2) photolithography of CNT emitter pixels, (3) composite electroplating of the CNT/Ni composite film, (4) polishing of the surface of CNT/Ni composite film, (5) wet chemical etching of Ni layer, (6) photolithography of CNT emitter arrays, (7) and (8) removing the photoresist after RIE of CNTs not used as the field emitters.

2. Experimental details

Referring to Fig. 1, the fabrication process of CNT emitters is described as follows: [32]

(1) Cr/Cu (30/50 nm) is deposited on a glass substrate as the conducting layer by sputtering.
(2) Photoresist spin coating and photolithography are performed to form emitter pixels.
(3) The CNT/Ni composite film is deposited on Cr/Cu conducting layer by composite electroplating (the reason for choosing Ni as the basement is its good resistance to corrosion). Initially, multi-walled CNTs with tube diameters ranging from 20 to 40 nm are boiled in potassium hydroxide molten for 5 h and concentrated sulfuric acid for 21 h in order to obtain pure and dispersed emitting materials. Then, the pretreated CNTs are added into Ni electroplating solution, and the solution is sonicated at 21 kHz for 3 h to produce a homogeneous suspension. Finally, the CNT/Ni composite film are deposited on the Cr/Cu conducting layer by composite electroplating using the CNT suspension.
(4) The CNT/Ni composite film is polished by polisher to form a flat surface (roughness Ra <0.2 μm).
(5) A layer of Ni is etched away from the CNT/Ni composite film with a flat surface to obtain protruding tips of CNTs as emitters by wet chemical etching, the etching depth is carefully controlled by etching time in order to keep the roots of CNTs still remain in the metal matrix.
(6) Photoresist spin coating and photolithography are performed to protect those CNT arrays used as field emitters in the process of reactive ion etching (RIE).
(7) Removing the photoresist after RIE of CNTs not used as field emitters.

All experimental steps stated above in (1)–(7) are executed at room temperature [32].

On the basis of preparing the CNT emitters above, we propose a novel design of CNT field emission micro-cathode arrays. The 3D structure drawing is shown in Fig. 2, compared with previously

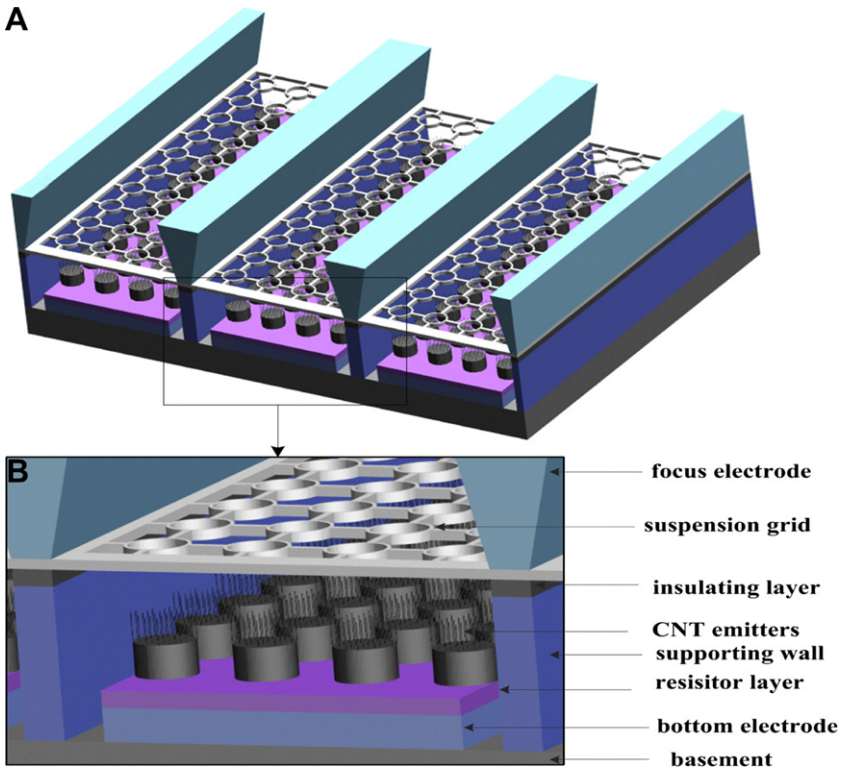

Fig. 2. The 3D structure drawing of the CNT field emission micro-cathode arrays (A) and its local enlarged view (B).

reported CNT field emission micro-cathode [33–36], this structure has relatively complete functional units, including bottom electrode, down-lead, current-limiting resistance, CNT emitters, supporting wall, insulator layer, suspension grid and focusing electrode. In this design, each structure layer is fabricated by using layer by layer lithography alignment process at room temperature.

The flow of the fabrication process for the CNT field emission micro-cathode arrays is shown in Fig. 3 and the detail process is described as follows:

(1) First, a patterned Au layer (~1 μm) is deposited on the Cr/Cu (10/40 nm) seed layer as bottom electrode by photolithography and electroplating (Fig. 3A).
(2) Then, a polysilicon film (~50 nm) is sputtered on the Au electrodes as resistor layer (Fig. 3B), and the fabrication of patterned CNT emitters is performed (Fig. 3C).
(3) Afterward, a patterned Ni supporting wall (~5 μm) is prepared by photolithography and electroplating (Fig. 3D).
(4) Then, an Al_2O_3 insulator layer (~80 nm) is deposited on the supporting wall to suppress the leakage current by sputtering (Fig. 3E).
(5) Subsequently, patterned Ni gate electrode (~1 μm) is performed by electroplating (Fig. 3F,G)
(6) Finally, patterned focus electrode (~3 μm) is formed by photolithography and electroplating (Fig. 3H).

3. Results and discussion

The optical images of the integrated devices are shown in Fig. 4 (A and B) and their higher magnifications are shown in Fig. 4(C–E). It can be seen that the integrated CNT field emission micro-cathode arrays have uniform structure and good repeatability. The gate pores' diameter is ~1 μm and the height between the Ni metal gate and the CNT pattern edge is ~5 μm (Fig. 4D). The pore density is about $1.2 \times 10^5/cm^2$. The inset map in Fig. 4E is a magnified view of

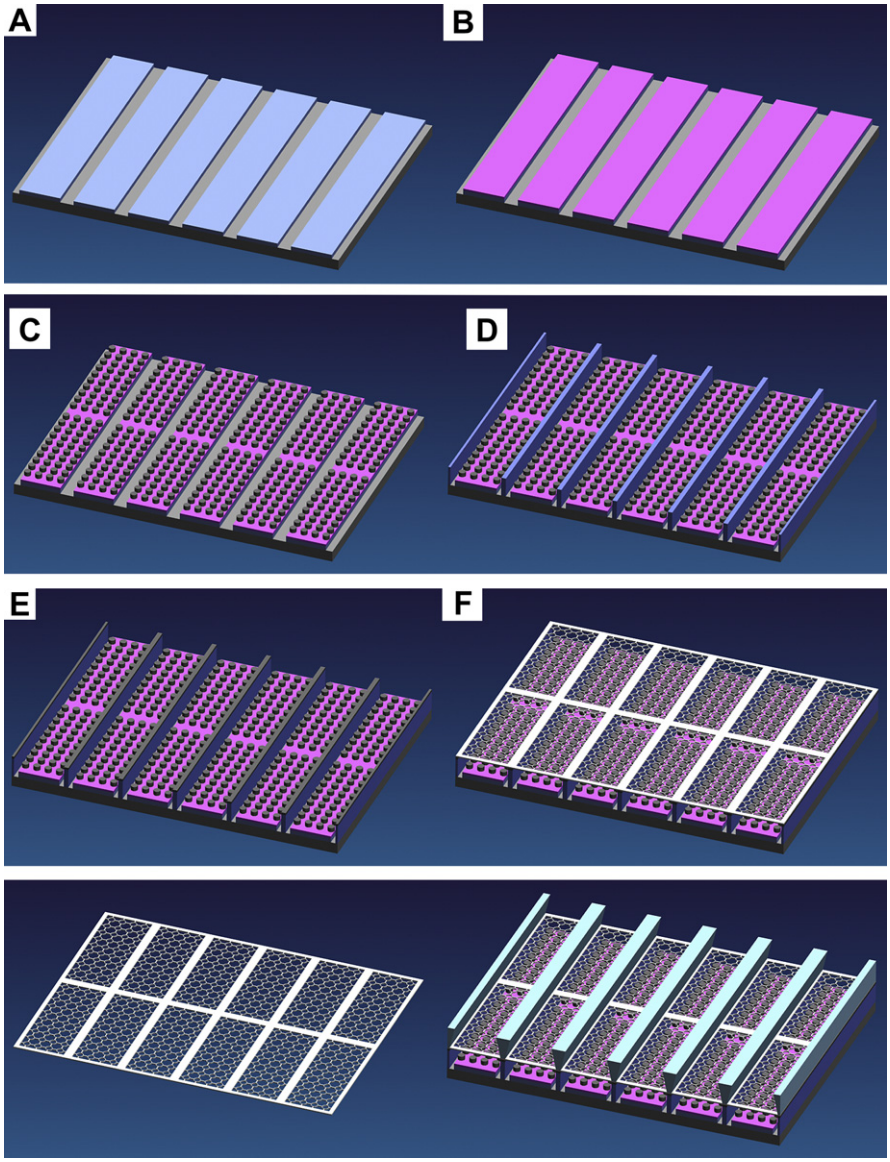

Fig. 3. Schematics of the fabrication process for the CNT field emission micro-cathode arrays: (A) patterned bottom electrode (Au) is deposited on the Cr/Cu seed layer by electroplating, (B) resistor layer (ploysilicon) is deposited on the bottom electrode by sputtering, (C) patterned CNT emitters are fabricated by photolithography and composite electroplating, (D) patterned Ni supporting wall is prepared by electroplating, (E) patterned Al_2O_3 insulator layer is deposited on the supporting wall by sputtering, (F)(G) patterned Ni gate electrode is performed by electroplating, (H) patterned Ni focus electrode is performed by electroplating.

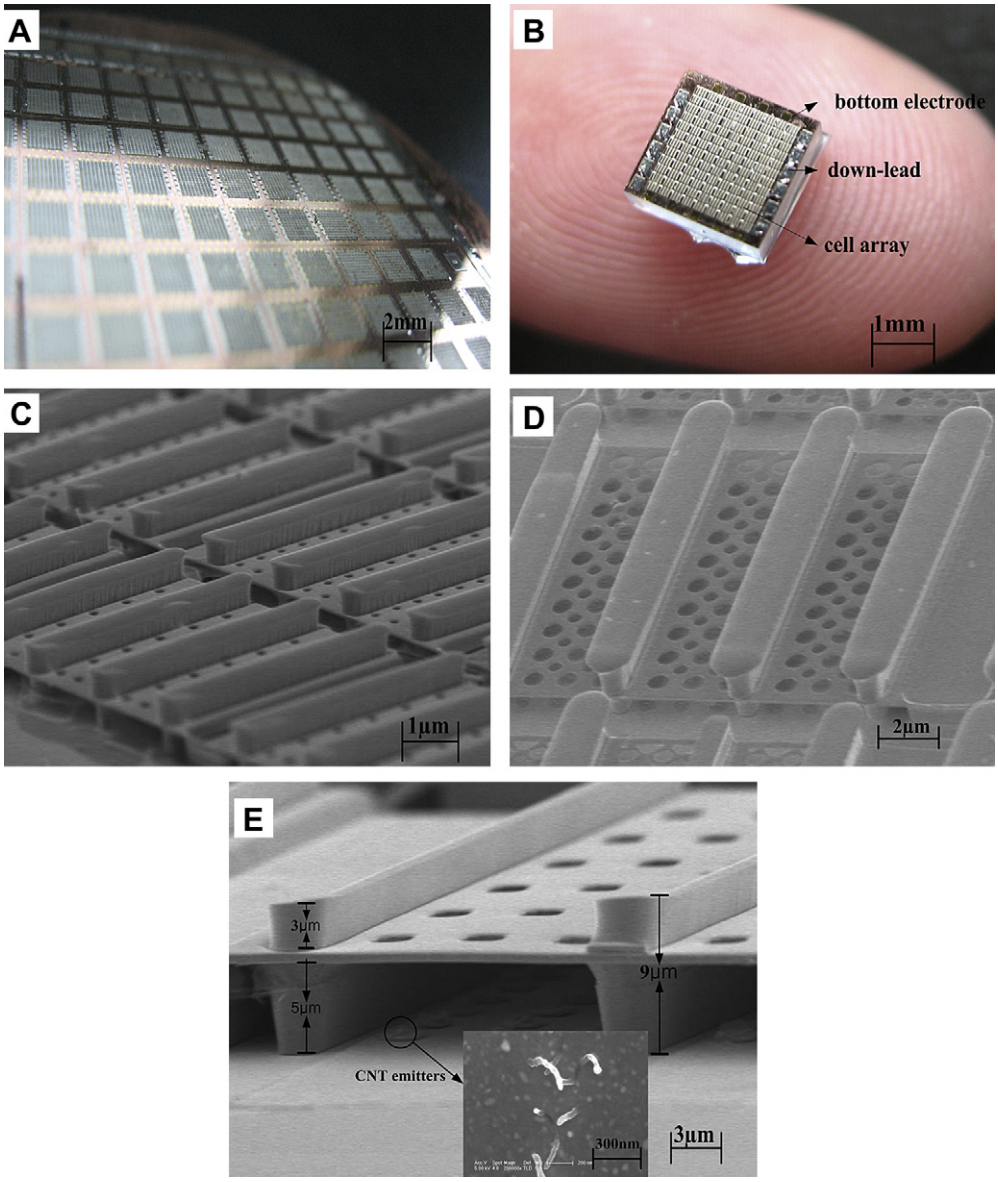

Fig. 4. The optical images of integrated devices (A, B) and their higher magnifications (C, D and E). The inset map in Fig. 4E is a magnified view of a CNT emitter pixel and the active CNTs.

a CNT emitter pixel; the CNTs are uniformly embedded in the pixel and the active CNT density is 5–8/μm^2 in the CNT emitters as shown in the inset map. The emitter pixel spacing shouldn't be too small, small emitter pixel spacing would induce the field-screening effect between adjacent emitters. However, big emitter pixel spacing would decrease the display effect of field emitters. In the fabrication process of the integrated devices, it is convenient to adjust the size of emitter pixels by masking and photolithography. The optimized distance between CNT emitter pixels is 2.5 μm and the area of emitter pixel is 9 μm^2 in the present study.

The dc electron field-emission properties of the device are measured in a vacuum chamber at a pressure of 1.7×10^{-5} Pa. The gate voltage is varied up to 60 V. The gap between the gate and the cathode is 5 μm, and the electric field referring to the value of the applied voltage mentioned in the following descriptions is divided by the electrode distance. Fig. 5 shows a plot of the field-emission current density (ECD) versus the applied electric field, and the corresponding field emission curve is shown in the inset. It is easy to find that all dots on the field emission curve fit a single straight line well, which indicates the Fower-Nordheim-type field-emission behavior. Obviously, the ECD of the emitters increases monotonically with the applied field. When the applied electric field is high, the gate current gets saturated and remains constant. The highest gate current density is about 15.7 mA/cm^2 at an applied electric field of 12 V/μm and the measured turn-on field to extract a current density of 10 μA/cm^2 is 2.4 V/μm.

The device characteristics are compared with those in other CNT emitter structures, although they are all fabricated by different structures and processes [36]. Pirio et al. [37] observed turn-on voltages of 9–15 V, defined at 0.1 nA/cm^2. The low turn-on voltage was obtained with a sub-micrometer gate-to-tip distance realized using a self alignment process. However, the turn-on field remained at relatively high values of 18–30 V/cm. In Hu et al. [38], a structure fabricated by screen-printed CNTs with a turn-on voltage of 40–45 V was obtained with ~5 μm gate-to-tip distance. Jang et al. [39] obtained a turn-on voltage of 20 V (turn-on field ~1 V/μm) at ~10 nA/cm^2 with pasted CNTs. They all report, at most, mA/cm^2 range values for the maximum current density. On the other hand,

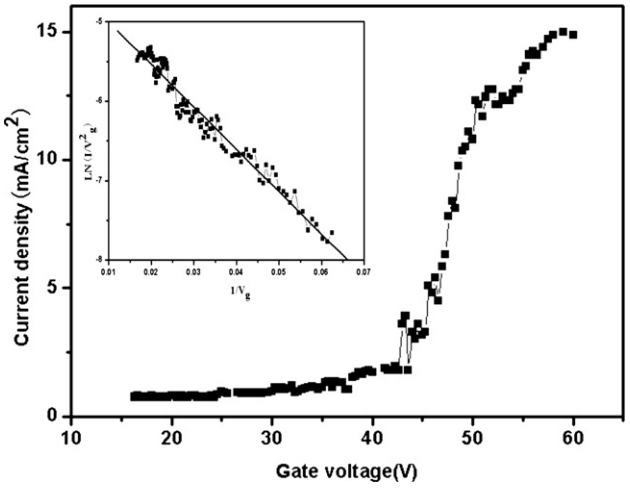

Fig. 5. The ECD versus the applied electric field for the CNT field emission micro-cathodes. Inset shows the Fowler–Nordheim plot.

Uh [40] obtained an exceptionally high current density of 275 mA/cm^2 with a turn-on voltage of 38 V using catalytically grown CNTs. In summary, the triode emitter structure fabricated on a glass template using composite electroplating and micro machining shows a very low turn-on voltage and a high current density, which are better than or, at least, compatible with those of other triode structures. The field enhancement factor (β) for the CNT emitters is derived from the slope of the graph by assuming that the work function of CNTs is found to be 2.4×10^6/cm under the assumption of the work function to be the same as that of graphite (4.5 eV), which is calculated from the following equation: $\beta = 2.84 \times 10^7 \cdot \text{Ø}^{3/2}/\text{S}$, where Ø and S represent the work function of CNTs and the absolute value of the slope of the F–N plot. The field enhancement factor extracted from triode-type configuration is approximately two orders of magnitude higher than that of diode-type configuration fabricated by using the same method and also much higher than typical values reported for CNT cathodes, such as 400–1200 for CNTs on silicon and glass substrates, and 2600–3500 for highly ordered CNT arrays on porous aluminum oxide [41,42]. The very high field enhancement factor confirms the high efficiency of the triode structure in electron extraction. The structure shows good field-emission properties, but the challenge of fabricating an applied device still remains including the further optimization of integral construction and preparation technology.

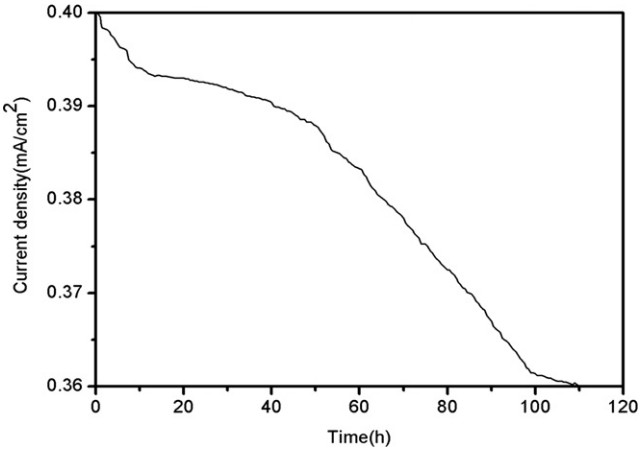

Fig. 6. Emission stability of the CNT field emission micro-cathodes, operated in continuous dc mode.

The result of lifetime tests is shown in Fig. 6. The time required for 10% degradation of current density from 400 μA/cm^2 is approximately 109 h for the sample. The electric field applied to measure the emission stability is approximately 5.7 V/μm. The lifetime values for the field emitters are favorably, compared with those of previous reports, which are in the range of 6–98 h [27,32]. The reasons leading to the stable field emission performance might be concluded as the uniformity in distribution of the emitters and the firm combination between CNTs and Ni substrates. The result is also consistent with what we forecast in this paper.

4. Conclusions

A new CNT field emission micro-cathode array structure fabricated by composite electroplating and micro machining is achieved. The relevant processing technology is also developed. Integrated CNT field emission micro-cathodes have intact structure and good repeatability. The structure revealed a very efficient performance as indicated by the high field enhancement factor and current density, low turn-on voltage and good emission stability. The micro-cathodes can obtain practical applications such as backlight units of liquid crystal displays and cathode ray tubes. This study laid a foundation on the device integration and cost-effective mass production, but it requires further optimization in the device configuration and processing.

Acknowledgements

The works was supported by the high-tech research and development program of China (grant No. 2006AA04Z308), the Important Projects in the Scientific Innovation of Colleges and Universities (708037) and the Chinese National Natural Science Foundation (50775148, 50675139).

References

[1] Jung MS, Jung HY, Suh JS. Horizontally aligned carbon nanotube field emitters having a long term stability. Carbon 2007;45(15):2917–21.
[2] Saito Y, Uemura S. Field emission from carbon nanotubes and its application to electron sources. Carbon 2000;38(2):169–82.
[3] Suh JS, Jeong KS, Lee JS, Han I. Study of the field-screening effect of highly ordered carbon nanotube arrays. Appl Phys Lett 2002;80(13):2392–4.
[4] Wang QH, Setlur AA, Laurehaas JM, Dai JY, Seeling EW, Chang RPH. A nanotube-based field-emission flat panel display. Appl Phys Lett 1998;72(22):2912–3.
[5] Zhu L, Sun Y, Hess DW, Wong CP. Well-aligned open-ended carbon nanotube architectures: an approach for device assembly. Nano Lett 2006;6(2):243–7.
[6] Klinke C, Delvigne E, Barth JV, Kern K. Enhanced field emission from multiwall carbon nanotube films by secondary growth. J Phys Chem B 2005;109(46):21677–80.
[7] Wong YM, Kang WP, Davidson JL, Choi BK, Hofmeister W, Huang JH. Fabrication of aligned convex CNT field emission triode by MPCVD. Diam Relat Mater 2005;14(11):2069–73.
[8] Lee NS, Chung DS, Han IT, Kang JH, Choi YS, Kim HY, et al. Application of carbon nanotubes to field emission displays. Diam Relat Mater 2001;10(2):265–70.
[9] Uemura S, Nagasako T, Yotani J, Shimojo T, Saito Y. Carbon Nanotube FED Elements. JSID 1998;29(1):1052–5.
[10] de Heer WA, Châtelain A, Ugarte D. A Carbon Nanotube Field-Emission Electron Source. Science 1995;270(5239):1179–80.
[11] Rinzler AG, Hafner JH, Nikolaev P, Lou L, Kim SG, Tománek D, et al. Unraveling Nanotubes: Field Emission from an Atomic Wire. Science 1995;269(5230):1550–3.
[12] Fan S, Chapline MG, Franklin NR, Tombler TW, Cassell AM, Dai H. Self-oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties. Science 1999;283(5401):512–4.
[13] Normile D. Nanotubes generate Full-Color Displays. Science 1999;286(5447):2056–7.
[14] Lee HJ, Lee YD, Cho WS, Ju BK, Lee YH, Han JH, et al. Field-emission enhancement from change of printed carbon nanotube morphology by an elastomer. Appl Phys Lett 2005;14(3):850–4.
[15] Collins PG, Zettl A. A simple and robust electron beam source from carbon nanotubes. Appl Phys Lett 1996;9(13):1969–71.

[16] Li WZ, Xie SS, Qian LX, Chang BH, Zou BS, Zhou WY, et al. Large-scale synthesis of aligned carbon nanotubes. Science 1996;274(5293):1701–3.
[17] Milnoux E, Groening O, Teo KBK, Dalal S, Ganggloff L, Schnell JP, et al. Achieving high-current carbon nanotube emitters. Nano Lett 2005;5(11):2135–8.
[18] Zhao X, Ohkohchi M, Wang M, Iijima S, Ichihashi T, Ando Y, et al. Preparation of high-grade carbon nanotubes by hydrogen arc discharge. Carbon 1997;35 (6):775–81.
[19] Davydov DN, Sattari PA, AlMawlawi D, Osika A, Haslett TL, Moskovits M. Field emitters based on porous aluminum oxide templates. J Appl Phys 1999;86 (7):3983–7.
[20] Kang DW, Suh JS. Fabrication temperature effect of the field emission from closed and open tip carbon nanotube arrays fabricated on anodic aluminum oxide films. J Appl Phys 2004;96(9):5234–8.
[21] Han IT, Kim HJ, Park YJ, Lee N, Jang JE, Kim JW, et al. Fabrication and characterization of gated field emitter arrays with self aligned carbon nanotubes grown by chemical vapor deposition. Appl Phys Lett 2002;81 (11):2070–2.
[22] Dean KA, Chalamala BR. The environmental stability of field emission from single-walled carbon nanotubes. Appl Phys Lett 1999;75(19):3017–9.
[23] Kim JM, Choi WB, Lee NS, Jung JE. Field emission from carbon nanotubes for displays. Diam Relat Mater 2000;9(3–6):1184–9.
[24] Gao B, Yue GZ, Qiu Q, Cheng Y, Shimoda H, Fleming L, et al. Fabrication and electron field emission properties of carbon nanotube films by electrophoretic deposition. Adv Mater 2001;13(23):1770–3.
[25] Kurnosov DA, Baturin AS, Bugaev AS, Nikolski KN, Tchesov RG, Sheshin EP. Influence of the interelectrode distance in electrophoretic cold cathode fabrication on the emission uniformity. Appl Surf Sci 2003;215:232–6.
[26] Oh SJ, Zhang J, Cheng Y, Shimoda H, Zhou O. Liquid-phase fabrication of patterned carbon nanotube field emission cathodes. Appl Phys Lett 2004;84 (19):3738–40.
[27] Choi WB, Jin YW, Kim HY, Lee SJ, Yun MJ, Kang JH, et al. Electrophoresis deposition of carbon nanotubes for triode type field emission display. Appl Phys Lett 2001;78(11):1547–9.
[28] Bae JC, Yoon YJ, Lee SJ, Baik HK. Field emission properties of carbon nanotubes deposited by electrophoresis. Physica B 2002;323(1–4):168–70.
[29] Wang SC, Huang BC. Field emission properties of Ag/SiO_2/carbon nanotube films by pulsed voltage co-electrophoretic deposition. Thin Solid Films 2008;26(11):436–9.
[30] Choi WB, Chung DS, Kang JH, Kim HY, Jin YW, Han IT, et al. Fully sealed, high-brightness carbon-nanotube field-emission display. Appl Phys Lett 1999;75 (20):3129–36.
[31] Bonard JM, Salvetat JP, Stockli T, de Heer WA, Fotrro L, Chatelain A. Field emission from single-wall carbon nanotube films. Appl Phys Lett 1998;73 (7):918–25.
[32] Deng M, Ding GF, Yan W, Wu HQ, Yao YJ, Zhu LD. Fabrication of Ni-matrix carbon nanotube field emitters using composite electroplating and micro-machining. Carbon 2009;47(15):3466–71.
[33] Wu JF, Wyse M, McClain D, Thomas N, Jun J. Fabrication and Field Emission Properties of Triode-Type Carbon Nanotube Emitter Arrays. Nano Lett 2009;9 (2):595–600.
[34] Nguyen VQ, Nguyen DH, Wan JY, Cho YS, Gyu SC, Kim DJ. The use of anodic aluminium oxide templates for triode-type carbon nanotube field emission structures toward mass-production technology. Nanotechnology 2006;17 (5):2156–60.
[35] Hahn J, Jung SM, Jung HY, Heo SB, Shin JH, Suh JS. Fabrication of clean carbon nanotube field emitters. Appl Phys Lett 2006;88(11):3101–76.
[36] Nguyen VQ, Nguyen DH, An MC, Cho YS, Kim DJ. A high-performance triode-type carbon nanotube field emitter for mass production. Nanotechnology 2007;18(6):345–51.
[37] Pirio G, Legagneux P, Pribat D, Teo BK, Chhowalla M, Amaratunga GAJ, et al. Fabrication and electrical characteristics of carbon nanotube field emission microcathodes with an integrated gate electrode. Nanotechnology 2002;13 (4):143–7.
[38] Hu WC, Yuan LM, Chen Z, Gong DW, Saito K. Fabrication and Characterization of Vertically Aligned Carbon Nanotubes on Silicon Substrates Using Porous Alumina Nanotemplates. J Nanosci. Nanotechnol 2002;2(7):203–7.
[39] Jang YT, Choi CH, Ju BK, Ahn JH, Lee YH. Suppression of leakage current via formation of a sidewall protector in the microgated carbon nanotube emitter. Nanotechnology 2003;14(5):497–500.
[40] Uh HS. Low Turn-On Voltage Field Emission Triodes with Selectively Grown Carbon Nanotube Emitters. J Kor Phys Soc 2004;45(5):516–8.
[41] Xu X, Brandes GR. A method for fabricating large-area, patterned, carbon nanotube field emitters. Appl Phys Lett 1999;74(17):2529–32.
[42] Wan JY, Cho YS, Choi GS, Do J. Patterned carbon nanotube field emitter using the regular array of an anodic aluminum oxide template. Nanotechnology 2005;16(5):291–5.