Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 253 (2007) 5980–5984
applied surface science
www.elsevier.com/locate/apsusc

Field emitters with low turn on electric field based on carbon fibers

Qilong Wang [a,b], Hui Mu [b], Xiaobing Zhang [b], Wei Lei [b,*], Jinchan Wang [b], Hongping Zhao [b]

[a] School of Biomedical Engineering, Southeast University, Nanjing 210096, China
[b] School of Electronic Engineering, Southeast University, Nanjing 210096, China

Received 9 October 2006; received in revised form 20 December 2006; accepted 22 December 2006
Available online 7 January 2007

Abstract

Field emitters of vertical carbon fibers on a silicon substrate are fabricated by catalytic chemical vapor deposition. After an ageing process of 150 min, field emission measurement of the fibers is carried out in a vacuum chamber with a base pressure of 5.0×10^{-4} Pa. The experimental results display that field emission performance of the carbon fibers depends strongly on the vacuum level during the experiments. After the field emission measurement, damage to the carbon fiber field emitters is observed from the scanning electron microscopic images.

PACS : 81.05.Uw; 81.15.Gh; 79.70.+q

Keywords: Carbon fibers; Chemical vapor deposition; Field emission

1. Introduction

People have known that filamentous carbon can be fabricated by the catalytic decomposition of carbon-containing gas on a hot metal surface [1]. In the 1950s, lots of reports established that carbon filaments could be fabricated by the interaction of a wide range of hydrocarbons with metal catalysts, the most effective of which were iron, cobalt, and nickel [2,3]. In 1991, Iijima discovered that carbon nanotubes are formed during arc-discharge synthesis of C60 and other fullerenes. Following this discovery, catalytic plasma-enhanced chemical vapor deposition (CPECVD) was introduced to provide additional control mechanisms over the growth of carbon nano-structures [4–6].

In the early 1960s, Charbonnier et al. had begun to work on field emission cathodes (cold cathodes) to replace thermionic emitters in high-frequency or RF vacuum electronic devices [7]. At the present time, the field emission properties of various carbon materials including carbon nanotubes and carbon fibers are being widely investigated [8]. They are applied for different electronic devices such as field emission displays and electron guns. Past publications have reported that carbon fibers have excellent field emission properties [9,10].

Using a typical catalytic thermal chemical vapor deposition (CTCVD) method, the authors have formed vertical carbon fibers on a doped p-type silicon substrate. The field emission behavior of the carbon fibers has been studied. The field emission characteristic is optimized after an ageing process. Experimental results show the turn on electric field that is applied on the electrode of the silicon substrate is quite low. The field emission performance of the carbon fibers depends strongly on the vacuum level during the experiments. Damage to the field emitters based on the carbon fibers is observed from the SEM images.

2. Experiment

The carbon fibers on the silicon substrate are fabricated in a furnace with a pressure-regulated quartz tube. The silicon substrates are coated with Cu film. The catalyst that is nickel is deposited on the substrates. The typical catalytic thermal chemical vapor deposition method is applied under a flowing mixture of acetylene and hydrogen.

The silicon substrates have been cleaned with ethanol and acetone in the ultrasonic chamber for 60–70 min. Using physical thermal vapor deposition, one Cu layer is fabricated on the silicon substrate as the electrode. The thickness of the Cu film is about

* Corresponding author. Tel.: +86 25 83794756x8181; fax: +86 25 83363222.
E-mail addresses: northrockwql@seu.edu.cn (Q. Wang), lw@seu.edu.cn (W. Lei).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2006.12.115

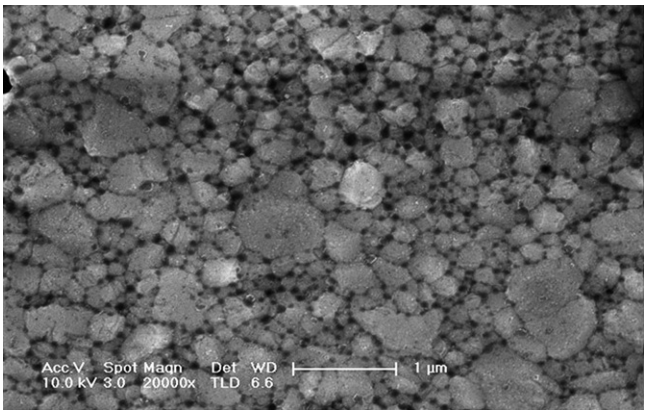

Fig. 1. SEM image of Ni films with thickness of 100 nm after annealing at 700 °C.

500 nm. A thin film of catalyst, Ni, is deposited on the substrate by the RF sputtering and the thickness is about 100 nm after annealing at 700 °C in the quartz tube (see Fig. 1). During the annealing process, the temperature rises to 700 °C at a rate of 150 °C/h, keeps at 700 °C for 1.5 h, and is cooled naturally (room temperature). The substrate is placed into one metal boat made of Aluminum in the pressure-regulated quartz tube.

The growth process of the carbon fibers is: during the first 60 min, the temperature rises to 500 °C and keeps at 500 °C through the following 60 min; the hydrogen flow is introduced into the quartz tube all the time; when the temperature rises to 700 °C, the reacting gas (acetylene flow) is introduced and the hydrogen flow is cut off; the reacting process lasts 60 min and the reacting gas is cut off; the heating set of the furnace is shut down and the hydrogen flow is introduced again as the protecting gas when the temperature decreases gradually. The total air pressure of the CVD system keeps at 0.8 MPa all the time by using a mechanical pump.

The field emission measurement is carried out in a vacuum chamber with a base pressure of 5×10^{-4} Pa. The substrate with the carbon fiber field emitters is placed on a sample holder with a stainless-steel anode for measurement. The carbon fibers formed are very high (>1 mm, see Fig. 2(a)) and the distance between the electrodes is set to 1.1 mm. A carbon layer is found to exit on the tips of the carbon fibers from the scanning electron microscopic images and energy distribution spectrum (see Fig. 3). In order to remove the carbon layer from the tips of the carbon fibers and enhance the local electric field, the field emitters need to have an ageing process. The anode–cathode bias is set up at 2.1 V/μm and the ageing process lasts nearly 150 min. During the ageing process and the field emission measurement, the anode is biased by using a DC high voltage supply (Fug 14500) and the emission current is automatically measured by a multimeter (Keithley Model 2001, controlled by the computer through the GPIB cable).

3. Results and discussion

The scanning electron microscopic (SEM) images show the surface morphology of the vertical carbon fibers fabricated in the CVD system in this study. The carbon fibers tend to be coiled and quite entangled (see Fig. 2). From Figs. 2 and 3, a carbon layer can be seen on the tips of the carbon fibers. The SEM images also display that most of the carbon fibers stand close together on the silicon substrate. The energy distribution spectrum (Fig. 3) displays the material on the tips of the fibers is

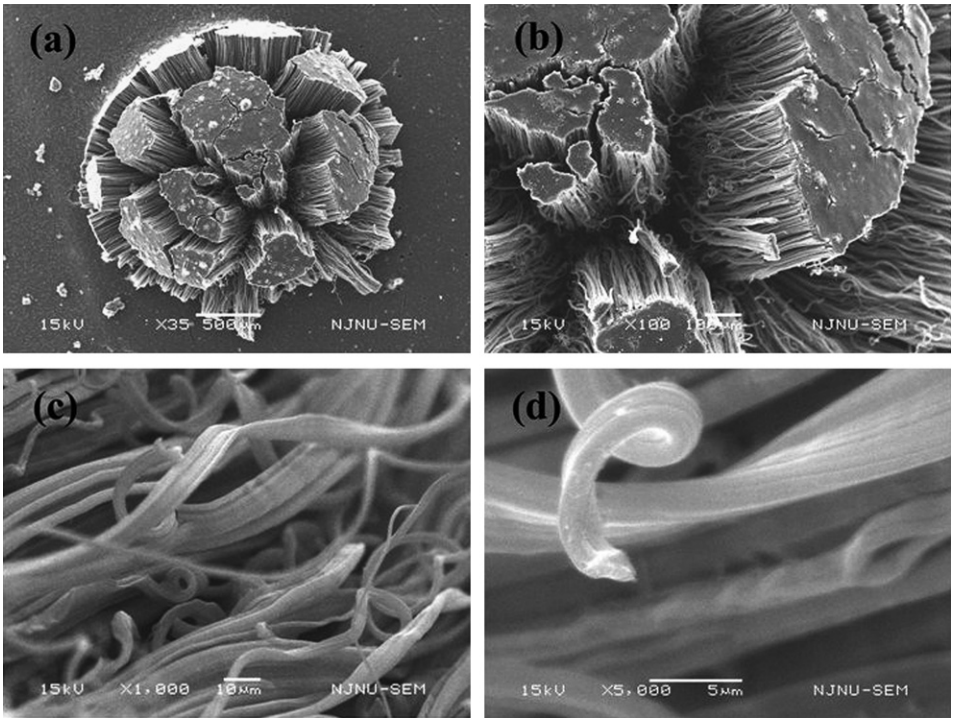

Fig. 2. SEM micrographs of carbon fibers (before measurement) (a) top view of carbon fibers, (b) magnified top view of carbon fibers, (c) magnified cross section view of carbon fibers and (d) micrograph of single carbon fiber.

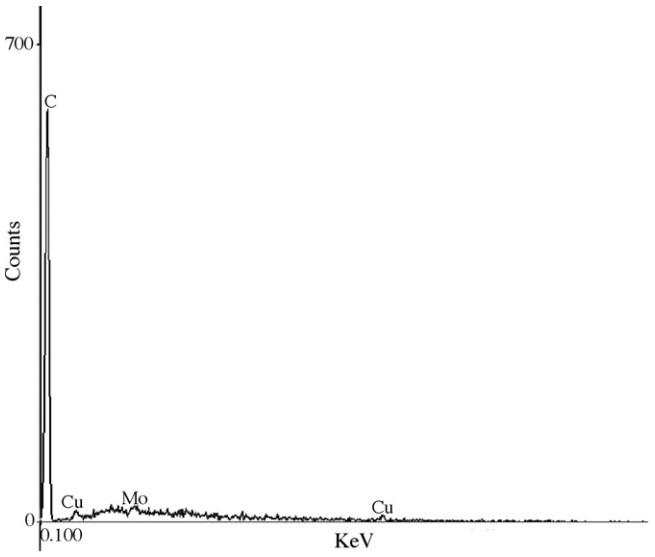

Fig. 3. Energy distribution spectrum of the materials on the tips of the carbon fibers.

almost carbon. Fig. 2(c and d) are magnified cross section images of carbon fibers. The diameter of a single carbon fiber is about 0.5 μm with a length of 1.5 mm, and the aspect ratio is calculated to be 3000 (see Fig. 4).

The emission current depends on the local electric field at the emitting surface, E, and on the work function of the materials, ϕ. Fowler and Nordheim offered one model based on the early experimental evidence to describe the dependence of emitted current on E and ϕ. The field emission performance is generally expressed as the Fowler–Nordheim equation,

$$J = \frac{1.56 \times 10^{-6} E^2}{\phi} \exp\left[-\frac{6.83 \times 10^{7} \phi^{3/2}}{E} \right] \quad (1)$$

Here, ϕ is the work function in eV, and the local electric field E can be expressed by $E = \beta V/d$. β, V and d are the enhancement factor, the applied voltage and the distance between the anode and the cathode [11]. The local electric field strongly depends on the shape of a surface and can be significantly enhanced at the apex of sharp features. Such influence can be expressed as a geometric field-enhancement factor, β. For a thin cylinder, β is roughly proportional to the height-to-diameter ratio, or aspect ratio [12,13]. From Eq. (1), a linear relation of $\ln(I/V^2)$ and (I/V) can be obtained as (2),

$$\ln\left(\frac{I}{V^2}\right) = \ln\left(\frac{1.56 \times 10^{-6} A\beta^2}{\mathrm{d}^2\phi}\right) - \frac{6.83 \times 10^{7}\, \mathrm{d}\phi^{3/2}}{\beta} \frac{1}{V} \quad (2)$$

Here, A is the emission area in cm^2.

Because of the carbon film on the tips of the carbon fibers formed on the substrate, the emission area is very small. That means field emitters based on carbon fibers are shielded from the local electric field and the onset voltage is so high. So the ageing processing is necessary to remove the carbon layer. Fig. 5 shows the ageing process of carbon fibers (electric field, ~2.1 V/μm; vacuum level, 9.0×10^{-3} Pa; time, 150 min; room temperature). Due to the poor vacuum level, flash arc generates between the electrodes when the electric field is ~2.1 V/μm. The carbon layer is burned and gases (CO, CO_2) generate. Fig. 6 displays the mass spectrum graph of the gases generated during the ageing process. The gases are expelled from the vacuum chamber by a molecular pump and a mechanical pump. With the removal of the carbon layer and the improvement of the vacuum level, more field emitters are exposited and emit electrons at the electric field. The emission current increases steadily from 250 to 350 μA at the electric field of 2.1 V/μm, as shown in Fig. 5.

Fig. 7(a) displays the I–E curves and F–N plots based on the Fowler–Nordheim equation are shown in Fig. 7(b). Before the

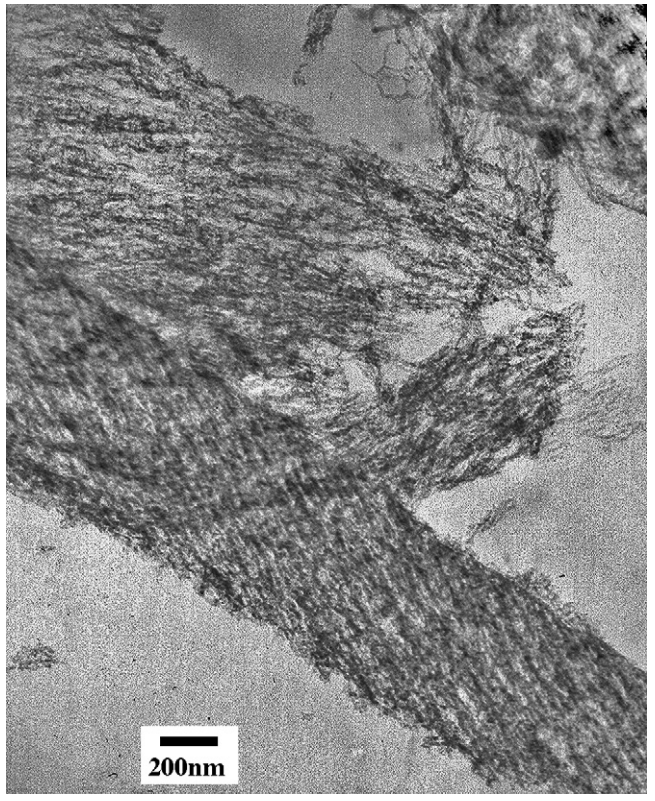

Fig. 4. TEM image of the carbon fiber fabricated.

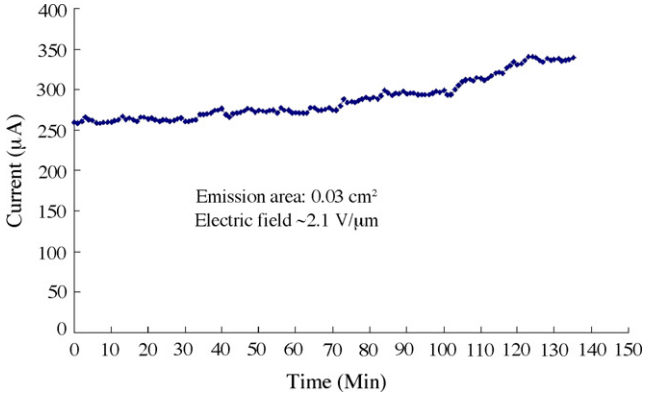

Fig. 5. Ageing of carbon fibers (electric field: 2.1 V/μm; vacuum level: 9×10^{-3} Pa).

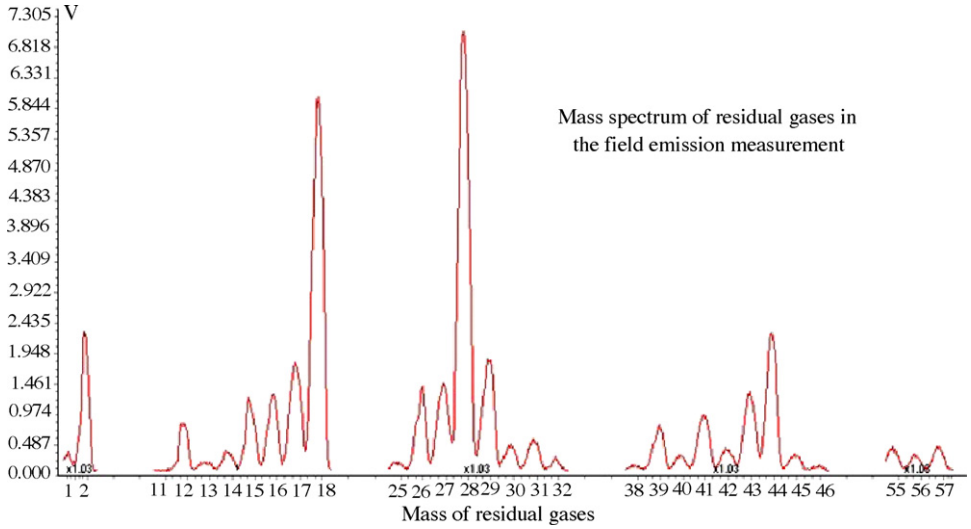

Fig. 6. Mass spectrum graph of the residual gas generated in the ageing process.

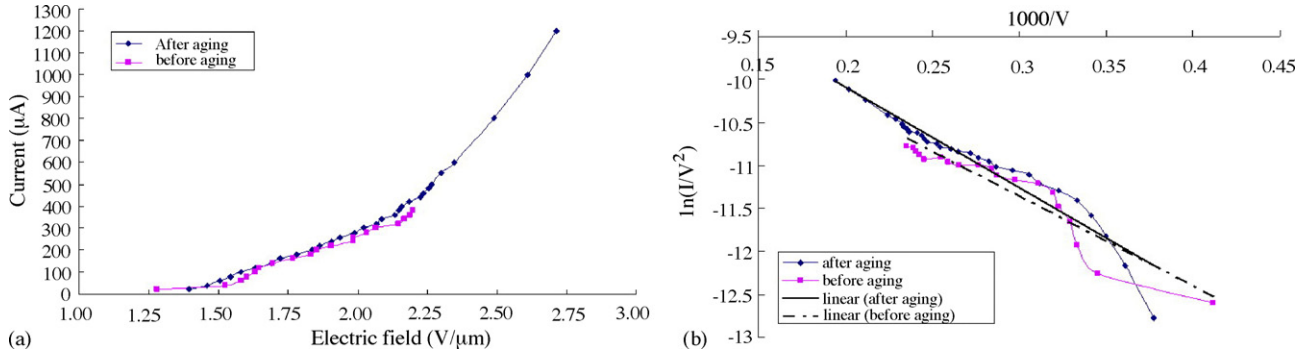

Fig. 7. Field emission properties of the carbon fibers fabricated on the silicon substrate (onset electric field after ageing: ~1.35 V/μm). (a) *I–E* curves (*I*: field emission current and *E*: electric field). (b) F–N plots for the *I–E* curves.

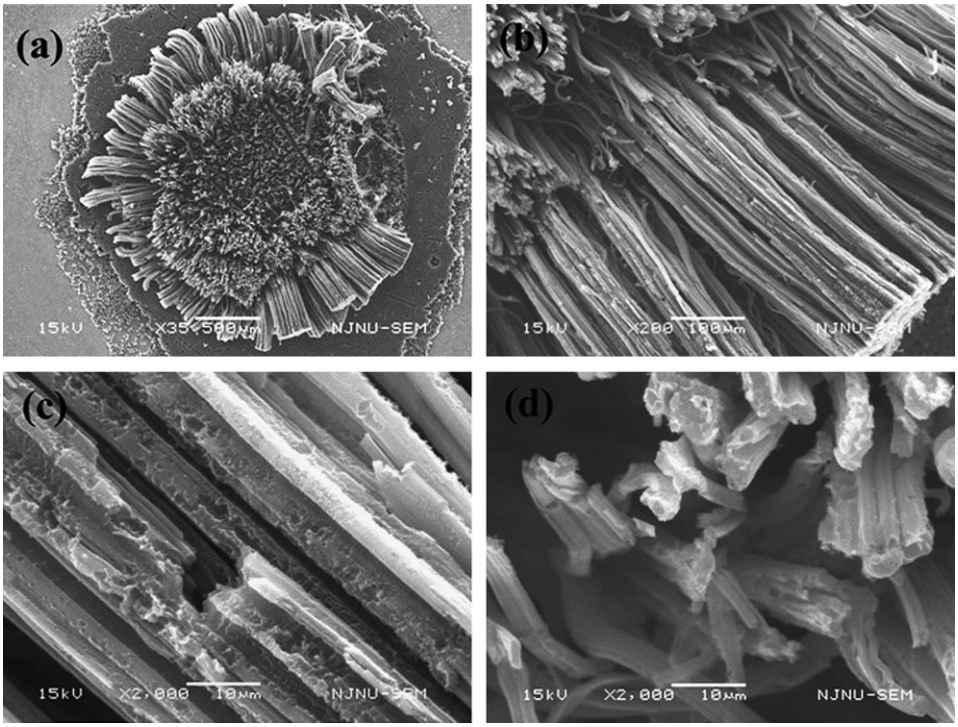

Fig. 8. SEM images of the carbon fibers fabricated by using catalytic thermal CVD method (after measurement) (a) top view of carbon fibers, (b) magnified top view of carbon fibers, (c) magnified cross section view of carbon fibers and (d) micrograph of top of carbon fibers.

ageing process, the emission current is not stable and is limited to 450 μA. Field emission is stable and the *I–E* curve goes exponentially after ageing. The onset electric field (when the emission current is 20 μA) decreases to 1.35 V/μm. The emission current is fairly stable at 1.4 mA (emission current density: >46.7 mA/cm^2) at the electric field of 2.8 V/μm, and it rises to 2 mA or higher when the electric field is tuned to 3 V/μm. Based on the experimental results, the emission area is assumed to be enlarged. F–N plots shown in Fig. 7(b) display the field enhancement factor, β, also increases after the ageing process. The onset electric field decreases and the emission current becomes stable.

From Fig. 8, the carbon fibers are found to be damaged after the field emission measurement. Most of the carbon fibers in the center are found to be destroyed (see Fig. 8(a and b)). The tips and the bodies of the fibers are also defaced (see Fig. 8(c and d)). In our last paper, we suggested that the cathode is bombarded and damaged by the ion bombardment in the field emission device while at work [14]. Using the Monte-Carlo method, we have simulated the generation process of the ions when the high-energy electrons collide with the molecules of residual gas. At the electric field, the ions are accelerated and bombard the surface of the cathode. The simulation result given in our last paper [14] shows that the damage in the center is the most serious.

4. Conclusions

Using the typical catalytic thermal chemical vapor deposition (CT-CVD), vertically aligned carbon fibers are fabricated on a silicon substrate. The fibers are seen to be entangled and coiled, standing on the substrate vertically. A carbon layer exists on the tips of the carbon fibers. After the ageing process and the removal of the carbon layer, the onset electric field of carbon fibers is 1.35 V/μm. The emission current density increases to 46.7 mA/cm^2 at an electric field of 2.8 V/μm. The emitters perform dramatically well like some other carbon field emitters. The field emitters based on the carbon fibers are found to be destroyed from the scanning electron microscopic images. The experimental results and images also display the field emission performance of the emitters depends strongly on the vacuum level.

Acknowledgements

The authors are thankful for the support from the Science & Technology Ministry and the Education Ministry, China (973 Project 2003CB314706 & 2003CB314702). Some work done in the paper is supported by the Program of New Century Excellent Talents in University, China (NCET-04-0473). PHILIPS Display Company supplied the simulation platform, some materials and experimental equipments in our research. We show a special appreciation to our guest professors Daniel den Engelsen and W.M. Alphen for their help and direction. The authors are also grateful for the writing direction given by Mr. George Culler.

References

[1] T.V. Hughes, C.R. Chambers, US Patent 405480 (1889).
[2] R.T.K. Baker, Carbon 27 (1989) 315.
[3] R.T.K. Baker, P.S. Harris, The formation of filamentous carbon, in: P.L. Walker, Jr., P.A. Thrower (Eds.), Chemistry and Physics of Carbon, vol. 14, Dekker, New York, 1978, p. 83.
[4] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science 282 (1998) 1105.
[5] V.I. Merkulov, D.H. Lowndes, Y.Y. Wei, G. Eres, E. Voekl, Appl. Phys. Lett. 76 (2000) 3555.
[6] Z.F. Ren, Z.P. Huang, D.Z. Wang, J.G. Wen, J.W. Xu, J.H. Wang, L.E. Calvet, J. Chen, J.F. Klemic, M.A. Reed, Appl. Phys. Lett. 75 (1999) 1086.
[7] F.M. Charbonnier, J. Barbour, L.F. Garrett, W.P. Dyke, Proc. IEEE 51 (1963) 991.
[8] N.S. Xu, Ultramicroscopy 79 (1999) 59.
[9] E.P. Sheshin, Ultramicroscopy 79 (1999) 101.
[10] A.S. Baturin, J. Vac. Sci. Technol. B 21 (2003) 354.
[11] R.H. Fowler, L. Nordheim, Proc. R. Soc. Lond. A 119 (1928) 173.
[12] T. Utsumi, IEEE Trans. Electron Dev. 38 (1991) 2276.
[13] V. Filip, D. Nicolaescu, D. Tanemura, F. Okuyama, Ultramicroscopy 89 (2001) 39.
[14] H.P. Zhao, W. Lei, X.B. Zhang, X.H. Li, Q.L. Wang, J. Vac. Sci. Technol. B 23 (6) (2005) 3148–3152.