doi:10.3788/gzxb20144304.0423001

增强碳纳米管场发射性能的沟槽形冷阴极制作

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摘　要:基于烧结工艺和丝网印刷技术,研发了一种新的沟槽形冷阴极.底部绝缘层由黑色绝缘浆料被烧结后制成,且在底部绝缘层中存在倾斜面.将银浆丝网印刷在条形电极上,依次经烘烤和烧结工艺后形成银电极.利用细砂纸,对银电极进行适当的抛光工艺,以便获得光滑的电极表面.由于特有的银电极形状,从而易于获得更大的场增强因子.将碳纳米管制备在银电极上,形成场发射极.致密的碳纳米管层完全覆盖银电极表面,特有的边缘场增强效应能够使得碳纳米管发射出更多的电子.顶部绝缘层则用于抑制碳纳米管的横向电子发射.结合沟槽形冷阴极,制作了三极结构的场致发射显示器,该显示器具有良好的场致发射特性及优良的发光图像均匀性.与普通冷阴极场致发射显示器相比,沟槽形冷阴极场致发射显示器能够将开启电场从 1.86 V/μm 降低到 1.78 V/μm,将最大场致发射电流从 1 537 μA 增加到 2 863 μA,且将最大发光图像亮度从 1 386 cd/m^2 提高到 1 865 cd/m^2.该制作技术在场致发射显示器中具有较强的实际应用性.

关键词:银电极;烧结;丝网印刷;场致发射;增强;条形电极;阴极面板
中图分类号:TB383;O462　　**文献标识码**:A　　**文章编号**:1004-4213(2014)04-0423001-7

Fabrication of Groove Shape Cold Cathode for Enhancing Field Emission Properties of Carbon Nanotube

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Abstract: Based on sintering process and screen printing technique, a novel groove shape cold cathode was developed. The black insulation slurry was sintered to fabricate the bottom insulation layer, in which a gradient surface existed. The silver slurry was screen-printed on the bar electrode. With the baking and sintering process in proper sequence, the silver electrode was formed. Using fine sandpaper, a proper polishing process for silver electrode was conducted, so a smooth electrode surface was obtained. Due to the special silver electrode shape, a larger field enhancement factor was achieved easily. Carbon nanotubes were prepared on the silver electrode to form the field emitters. The dense carbon nanotube layer would cover the silver electrode surface completely. Owing to the special edge field enhancing effect, lots of electrons would be emitted from the carbon nanotube. The top insulation layer was used to restrain the side electron emission of carbon nanotube. With the groove shape cold cathode, a triode field emission display was fabricated, which exhibited good field emission properties and better luminescence image uniformity. Comparing with the common cold cathode field emission display, the turn-on electric field could be reduced from 1.86 V/μm to

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Foundation item: The National Natural Science Foundation of China (Nos. 60976058, 61274078)

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Received: Aug. 5, 2013; **Accepted**: Aug. 15, 2013

1.78 V/μm, the maximum field emission current had been increased from 1 537 μA to 2 863 μA, and the maximum luminescence image brightness would be enhanced from 1 386 cd/m^2 to 1 865 cd/m^2. The developed fabrication technology had a potential practical application in field emission display.

Key words: Silver electrode; Sintering; Screen-printing; Field emission; Enhancement; Bar electrode; Cathode faceplate

OCIS Codes: 230.2090; 230.4685; 350.5730; 230.4320

0 Introduction

Carbon nanotube (CNT) had attracted considerable interest due to their small radii of curvature at tip and superior mechanical strength. With the applied external electric field, CNT could supply lots of electrons in the "field emission" form on sealed vacuum environment. So CNT was excellent field emission material, and had been used as an promising cold cathode in field emission display (FED)[1-5]. In FED cathode, the CNT layer was prepared on the substrate electrode. On the one hand, with the substrate electrode the cathode potential could be conducted to the CNT layer; on the other hand, only depending on the formed electric field with fabricated substrate electrode, the electrons could be emitted from the CNT layer. Thus the field emission capability of CNT was closely related to the substrate electrode[6-11]. However, the substrate electrode with undesirable shape would reduce the surface electric field of CNT layer, so the visible light might not be formed normally in FED due to the decreasing of emitted electrons from CNT layer. The substrate electrode with poor conducting performance would lower the cathode potential, so the non-uniform electron emission of different CNT layer would exist and the driving circuit cost must also be increased. These problem should be solved if the development of FED was expected to proceed smoothly. The substrate electrode formed with chromium-copper layer had good electrode surface. Although the uniform field emission characteristics had been confirmed, the poor CNT adhesion performance might be its disadvantage. The substrate electrode fabricated with silicon wafer possessed better electric conduction capacity. But the patterned fabrication of CNT cathode which was necessary in FED was impossible. The substrate electrode formed with dielectric layer had superior adhesion property, and the good cathode patterned fabrication was easy. But the manufacture process was too complex and the fabrication cost was also high. Therefore, the research on the fabrication of CNT cathode which could meet the requirement of triode FED had been intensively conducted in recent years[12-18].

In this paper, a novel groove shape cold cathode was developed, and the fabrication process was also presented in detail. The sintered silver electrode fabricated on bar electrode possessed smooth electrode surface because of the proper polishing process. The larger field enhancement factor was obtained because of the special silver electrode shape. The triode FED porotype with groove shape cold cathode was fabricated, which possessed better luminescence image uniformity, larger field emission current and good field emission properties.

1 Experimental details

1.1 Structure of groove shape cold cathode

The soda-lime flat glass was used to form the cathode faceplate with rectangular shape, which the thickness of cathode faceplate was 3 mm. The groove shape cold cathode was fabricated on the cathode faceplate surface. A structural schematic diagram of groove shape cold cathode was shown in Fig. 1. For one groove shape cold cathode, five parts were included, namely, the top insulation layer, the bottom insulation layer, the bar electrode, the silver electrode and the CNT layer. The CNTs were prepared on the silver electrode surface, which were used to form the field emitters. Electric connection was performed between the silver electrode and the bar electrode, which served as the substrate electrode together in triode FED. The top insulation layer fabricated on the bottom insulation layer was adopted to restrain the side emission of field emitters.

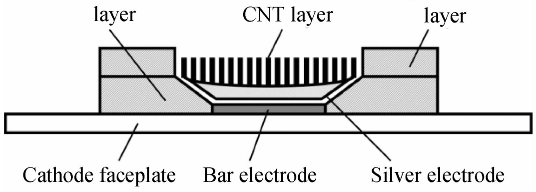


Fig. 1 Structural schematic diagram of groove shape cold cathode on cathode faceplate

1.2 Fabrication of groove shape cold cathode

Firstly, the indium tin oxide film covering on cathode faceplate was etched to form the bar electrodes. The developing solution was NaOH (the concentration was 0.4%) and the developing temperature was approximate 28℃. The corrosive solution was a mixed liquid with HCl + HNO_3, in which the etching temperature was about 58℃ and the etching time did not exceed 5 min. Many bar electrodes were arranged on cathode faceplate surface to form a bar electrode matrix. The width of one bar electrode was 300 μm and the distance between the adjacent bar electrode was 700 μm. Secondly, the insulation slurry was fabricated on the cathode faceplate with high effective screen printing technique. For the printed insulation slurry, the baking and sintering processes were conducted in proper sequence. The constant baking temperature was 185℃ and the baking time was 35 min; the maximum sintering temperature was 535℃ and the maintaining time was 8 min. The whole course sintering time was approximate 75 min. So the bottom insulation layer was formed. Thirdly, the silver electrode was fabricated with the screen-printed silver slurry. In the fabrication course, the baking process was performed in the automatic electric oven, which the baking temperature was 235℃ and the baking time was 30 min. The sintering process was finished in the chain sintering furnace, in which the maximum sintering temperature was 512℃ and the holding time was 10 min. The whole sintering time was about 65 min. A proper polishing process with fine sandpaper was performed for the sintered silver slurry in order to obtain a smooth electrode surface. Fourthly, the insulation slurry was again printed on the bottom insulation layer to form the top insulation layer. The baking and sintering processes parameters for the top insulation layer were identical with the ones of the bottom insulation layer. Finally, the CNT paste was prepared, which was mixed with the double-walled CNT, the terpineol and the ethyl cellulose. The CNT paste was printed on the silver electrode surface to form the CNT layer. After proper post-treatment process, the field emitters were formed. So the fabrication of groove shape cold cathode was completed.

1.3 Full-sealing of triode FED

On anode faceplate, the phosphor paste was printed onto the patterned anode electrode to form the luminous layer. The silver slurry was screen-printed on the grid substrate, and the solidified silver slurry was utilized to form the grid electrode. The cathode electrode and the grid electrode were arranged in orthogonal directions, which the electron emission of CNT layer in groove shape cold cathode at the intersection could be effective controlled. As shown in Fig. 2, a vacuum chamber was sealed with the sintered glass frit, and the getters resided on the cathode faceplate were activated, which would lead to the completion of triode groove shape cold cathode FED prototype. For comparison, the other kind of triode FED prototype using the common CNT cathode was also fabricated with a similar fabrication process.

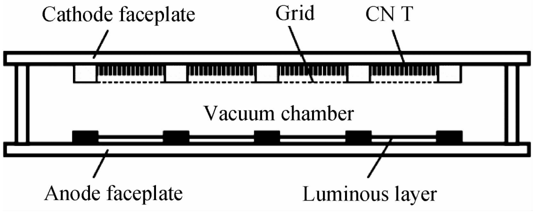
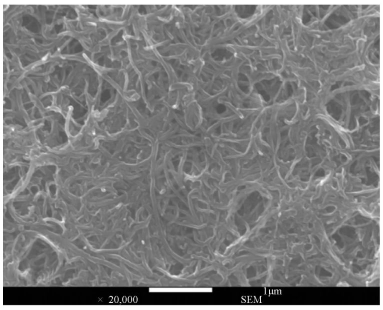


Fig. 2 Structural schematic diagram of groove shape cold cathode FED

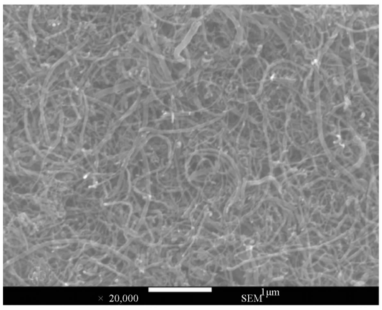
2 Results and discussions

2.1 Surface morphology of CNT

The SEM photos of surface morphology for CNT in groove shape cold cathode were given in Fig. 3. Thereinto, Fig. 3(a) was the SEM photo of baked CNT. Seen from the photo, on the groove shape cold cathode surface, organic slurry was mixed with the CNT together. Due to the absence of necessary sintering process and proper post-treatment process, massive organic slurry existed. As we know, without the organic slurry, the CNT could not be prepared with the screen printing technique at all. However, lots of ogranic slurry was included in the CNT paste, and the viscous organic slurry would hinder the CNT to emit electrons because many CNTs were buried in the CNT paste. So, once the CNT was transplanted appropriately to the silver electrode surface in groove shape cold cathode on cathode faceplate, the residual organic slurry must be removed. Fig. 3(b) exhibited the SEM photo of post-treated CNT. Seem from the photo, several achieved results were as follows.



(a) Backed CNT



(b) Post-treated CNT

Fig. 3 SEM photos of the surface morphology

1) A large number of CNTs existed on the groove shape cold cathode surface, and a dense CNT layer

could be formed easily. These experimental outcomes were completely in agreement with our desired results. In FED cathode, the CNT was mainly used to emit lots of electrons. There was no doubt that the field emission current would be enhanced in groove shape cold cathode FED with a dense black CNT layer.

2) The silver electrode under the CNT layer would become invisible. In groove shape cold cathode, the silver electrode could not, and was also not allowed to, emit electrons directly. As previously mentioned, the silver electrode could conduct cathode potential for the CNT layer. And the silver electrode would also partake in the formation of electric field on CNT layer surface, which would enforce the CNT to emit lots of electrons. However, the silver electrode would not emit electrons, so there was no any sense for the exposed silver electrode to form the high-velocity electron beam.

3) More CNTs were distributed evenly on the groove shape cold cathode surface, and other impurities was not observed. It would indicate that the cathode electrons would derive from the CNT entirely in the FED operation course. If other impurity existed on the groove shape cold cathode surface, the CNT layer with better uniformity would be damaged. In addition, after the proper polishing process, the even silver electrode surface had been formed, which was also beneficial to make a uniform distributed CNT layer. The even silver electrode surface was covered completely by the dense CNT layer, so the parasitic electron emission from the fine silver particle could also not generated. The parasitic electron emission from the fine silver particle would seriously distrub the normal field emission course of CNT.

4) These CNTs adhered each other, and tightly attached to the surface of silver electrode. Many CNT ends were also exposed on the CNT layer. It would imply that the fabricated of silver electrode and bar electrode were suitable to support the CNT layer. Otherwise, if the silver electrode in groove shape cold cathode had a bad influence on the prepared CNT layer, the phenomenon including the large-area CNT block abscission and a rough CNT layer surface would appear. For the much exposed CNT ends, more electrons could be emitted, which was advantageous to enhance the luminescence image brightness of triode groove shape cold cathode FED prototype.

2.2 Real photograph of groove shape cold cathode FED prototype

The real photograph of groove shape cold cathode FED prototype was presented in Fig. 4. The anode pixels were arranged on the anode faceplate inner surface, which was formed with a 8 × 16 matrix. So there were 128 anode pixels for the fabricated groove shape cold cathode FED in total. The one anode pixel was square form, which the fabrication area was $550\times 550\ \mu m^2$. And the size of all the 8 × 16 pixels was identical. After bombarding by the high speed electrons emitted from the groove shape cold cathode in a vacuum environment, the anode pixels would generate visible light. And the luminescence image would be formed after the visible light penetrated the transparent anode faceplate.

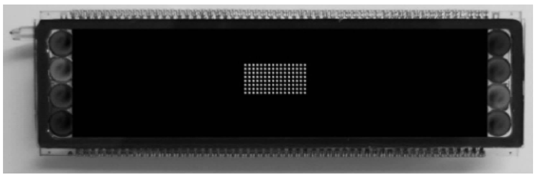


Fig. 4 Real photograph of groove shape cold cathode FED prototype

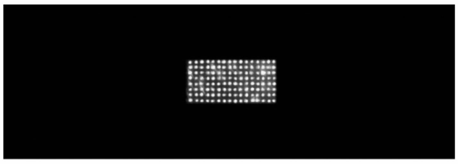
The anode faceplate, the cathode faceplate and the glass frame would combine to make a vacuum chamber. For avoiding the cracking of whole triode groove shape cold cathode FED prototype in the sintering course, the fabrication material for the two flat glass and the glass frame was identical, which was the cut soda-lime glass. Furthermore, the sintered low-melting glass frit in good condition could also be observed (seen the edge part of FED prototype), which would indicate that the full-sealed groove shape cold cathode FED could normal operate for a long time.

In Fig. 4, the groove shape cold cathode fabricated on the cathode faceplate was invisible because it had been encapsulated in FED inner. When the measured vacuum level of vacuum system was on the order of 2.6×10^{-4} Pa, the sealing-off process was performed for the groove shape cold cathode FED prototype. In one FED there were 8 getters, which would reside on the sides of cathode faceplate. The activated getters were used to maintain the high vacuum state of vacuum chamber in groove shape cold cathode FED prototype.

2.3 Green luminescence image

The typical luminescence images of triode FED prototype were presented in Fig. 5. Thereinto , Fig. 5

(a) Common cold cathode FED



(b) Groove shape cold cathode FED

Fig. 5 The green luminescence image

(a) showed the luminescence image of common cold cathode FED, while the one of groove shape cold cathode FED was illustrated in Fig. 5(b). The applied anode voltage of 1. 75 kV was same, and the luminescence images were took with digital camera. As could be seen from the given luminescence image, several results would be gained.

1) Whether for the common cold cathode FED or the groove shape cold cathode FED, the luminescence image could be normal displayed. Because only the green phosphor was adopted for the luminous layer on anode faceplate in the fabrication course, the green luminescence image could be observed, and other color luminescence image such as the red color and yellow color would not occur.

2) Due to the higher electric field, more electrons were emitted from the CNT layer. So some bright white light had appeared on the middle position of single anode pixel. The groove shape cold cathode FED could operate, which would mean that not only the groove shape cold cathode was a qualified FED cathode since the electron emission of CNT had been conducted successfully, but also the fabrication process of groove shape cold cathode was feasible. The developed manufacture method possessed considerable potential for practical applications owing to its simplicity and low fabrication cost.

3) Comparing with the two different luminescence images, there were obvious differences in both luminescence image brightness and luminescence image uniformity. In Fig. 5(a), only part of anode pixels had been lighted, and other part of anode on anode faceplate could not generate the visible light at all with the same electric field. For the lighted anode pixels, some anode pixels were dark, and some other anode pixels were brighter. Even the luminescence image brightness for several anode pixels had been higher than the one of anode pixels in groove shape cold cathode FED. So for the common cold cathode FED, it was obvious that the luminescence image uniformity was poor and the total luminescence image brightness was low. However, in Fig. 5(b), all the anode pixels on anode faceplate could be lighted, which would imply that the cathode potential had been conducted to the CNT layer in groove shape cold cathode. Of course, the total luminescence image brightness was high. On the whole, the luminescence image brightness difference of different anode pixels was not distinct, which would also indicate that the uniform electron emission capability of CNT layer in groove shape cold cathode had been effective enhanced.

2.4 Field emission curves

The field emission characteristic curves of two kinds of triode FEDs were plotted in Fig. 6. Thereinto, the curve a exhibited the field emission property of groove shape cold cathode FED, while the curve b revealed the characteristics of common cold cathode FED. In the measuring course, the external test conditions were same. The anode voltage was fixed with 1. 68 kV; by appling different grid operation voltage, the electric field between grid and cathode was varied. And the field emission current was monitored with the ammeter.

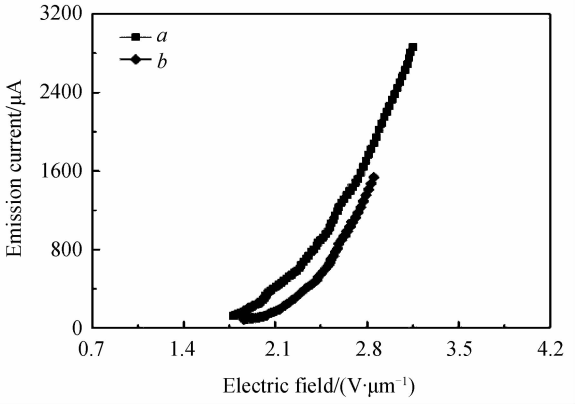


Fig. 6 Typical field emission curve

Comparing with the given curves, some results were achieved.

1) Seen from the curvilinear trend, all the two types of FEDs possessed typical field emission property, and the groove shape cold cathode FED seemed to have lower turn-on electric field. This showed that the CNT layer in groove shape cold cathode had already emitted lots of electrons normally. Not only the cathode potential could be conducted to the CNT layer through the silver electrode and the bar electrode in groove shape cold cathode, but also the electric field would also be formed easily on the CNT layer surface. Obviously, the field emission current could not be formed owing to the insufficiency of enough electrons in FED if the groove shape cold cathode did not possessed above-mentioned functions. The turn-on electric field of groove shape cold cathode FED was approximate 1. 78 V/μm, while the one of common cold cathode FED was about 1. 86 V/μm.

2) The groove shape cold cathode FED possessed superior field emission characteristic. With the same electric field of 2. 19 V/μm, the field emission current of groove shape cold cathode FED was 507 μA, which was larger than that of the common cold cathode FED (was about 243 μA). On the contrary, for the same field emission current of 406 μA, the needed electric field for groove shape cold cathode FED was about 2. 09 V/μm, which would less than the one for common cold cathode FED (was approximate 2. 34 V/μm). The maximum field emission current for groove

shape cold cathode FED had reached 2 863 μA，while that for common cold cathode FED was only 1 537 μA. We think that the groove shape cold cathode would play an important role in FED.

In groove shape cold cathode，the etched bar electrode and the sintered silver electrode were utilized，which all possessed good conducting capability. Not only the invalid voltage drop could be reduced effectively，but also the wiring flexibility on cathode faceplate was also confirmed. The silver electrode and the bar electrode were separate. For making full use of the cathode faceplate area，the arranging of bar electrode could be adjusted. But，because the silver electrode under CNT layer was not changed，the "matrix addressing" mode in FED would not be effected. Due to the proper polishing process，the formed burrs on silver electrode surface would be eliminated in the fabrication course. Otherwise，the short circuit between the grid and cathode would occur usually owing to the too long and too many tiny burrs. Using the fine sandpaper，the rubing process was performed on silver electrode surface. Of course，the smooth silver electrode was also advisable for improving the field emission uniformity of different CNT layers. However，it was more important that the triode FED would possessed larger field enhancement factor due to the special silver electrode shape in groove shape cold cathode. The electrode surface was usually flat for the common cold cathode.

As we know，the electric field on the edge of common cold cathode would be enhanced remarkablely owing to the edge effect. For the groove shape cold cathode，the silver electrode was fabricated on the gradient bottom insulation layer surface. In the sintering course for the printed silver slurry，the center section of silver electrode would be contracted due to large thickness. So the slightly upturned form of silver electrode edges appeared. On the silver electrode edges the radius of curvature would become smaller. It was natural that the more larger field enhancement factor could be obtained. The CNT preparig on the silver electrode surface in groove shape cold cathode，especially on the silver electrode edge，would emit more electrons. Comparing with the common cold cathode FED，the inevitable results was the groove shape cold cathode FED possessed more larger field emission current.

2.5 Luminescence brightness curves

The typcial luminescence brightness curves of triode FED were plotted in Fig. 7. Thereinto，the curve a showed the function relation of luminescence brightness vs. electric field for the groove shape cold cathode FED，while the curve b demonstrated the one for the common cold cathode FED.

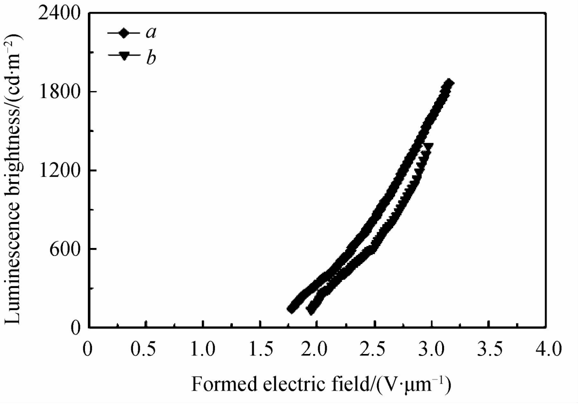


Fig. 7 Luminescence brightness curves

Seen from the given curves，for obtaining the same luminescence brightness of 586 cd/m^2，the required electric field of groove shape cold cathode FED was about 2.29 V/μm，which was less than the one of 2.45 V/μm for common cold cathode FED. The maximum luminescence brightness of groove shape cold cathode FED had reached 1 865 cd/m^2，and the one of common cold cathode FED was only approximate 1 386 cd/m^2. As previously mentioned，with the groove shape cold cathode，the field emission current of triode FED had been enhanced. So it was natural that the groove shape cold cathode FED would possess higher luminescence image brightness. The comparision result would also indicate that the luminescence image quality was also be improved for triode FED.

3 Conclusions

1) A new groove shape cold cathode was proposed firstly with sintering process and screen-printing technique. The silver electrode formed with the sintered silver slurry and the bar electrode were utilized，which both possessed good conducting capability. A polishing process was performed for the silver electrode to obtain a smooth electrode surface，which could improve the electron emission uniformity of CNT layer. Due to the special silver electrode shape，a larger field enhancement factor was achieved，which could further increase the field emission current. The developed fabrication process possessed considerable potential for practical applications due to its better process repeatability and large-area production feasibility.

2) An groove shape cold cathode FED prototype had been fabricated，which possessed good field emission properties and better luminescence image brightness uniformity. Comparing with the common cold cathode FED，the maximum field emission current had been increased from 1 537 μA to 2 863 μA，and the

maximum luminescence image brightness would be enhanced from 1 386 cd/m^2 to 1 865 cd/m^2. The luminescence image quality of triode FED was also improved effectively.

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