The Study of Optimizing Growth Conditions for Improving Field Emission Property of W$_{18}$O$_{49}$ Nanorod Arrays

L. F. Chi$^{1,2}$, S. Z. Deng$^1$, N. S. Xu$^{1,a}$, J. Chen$^1$, J. C. She$^1$, X. H. Liang$^1$

$^1$ State Key Lab of Optoelectronic Materials and Technologies, Guangdong Province Key Laboratory of Display Material and Technology, Sun Yat-Sen (Zhongshan) University, Guangzhou 510275, People’s Republic of China

$^2$ Department of Physics, Shantou University, Shantou, 515063, People’s Republic of China

a) The corresponding author’s E-mail address: stsxns@mail.sysu.edu.cn

Abstract Large-area tungsten oxide nanorod arrays were synthesized by the catalyst-free tungsten hot-filament thermal vapor method. The diameter, height, interval and alignment of the nanorods were all found to be sensitive to the distance between hot filament and substrates. And the field emission property of the nanorod arrays prepared at various distances was shown to be significantly different. This demonstrates that optimal conditions can be found for preparing W$_{18}$O$_{49}$ nanorod arrays of better field emission property.

1. Introduction

Lately, one-dimensional (1D) nanostructure materials were found to be the potential candidate as the cold cathode in field-emission devices [1] and vacuum nanoelectronics [2]. Tungsten oxide (WO$_x$) is an important functional material, its nanowires, nanorods and nanotips can be synthesized by thermal vapor deposition method [3-8], and were shown to have excellent field emission property [3, 4]. But it is still a challenge to control the field emission performance of WO$_x$ nanorod array. It was reported that the field emission of WO$_x$ nanostructures is related to their phase structure, and can be adjusted by changing the vapor source temperature [7]. In this paper, we used tungsten hot-filament array as vapor source for preparation of large-area tungsten oxide nanorod arrays. Then the W$_{18}$O$_{49}$ nanorods array growth condition, i.e. the gap between hot filament array and substrates, was researched to tune their field emission properties. Since this growth technique can be scaled up, the results reported here may be important to the development of large-area cold cathode field electron sources.

2. Experimental and Discuss

2.1 The synthesis of samples and characterization

The synthesis approach is similar to that described in our previous report elsewhere [8]. Briefly, an array of clean tungsten filaments was installed in the center of a vacuum chamber as the heating vapor source. The clean silicon substrates were placed beneath the tungsten filament array. In a series of experiments, the distance (d) between filament array and substrates was set at 2, 3, 4 and 5 mm respectively, for studying the effect of the d value. Base pressure and reactive pressure were $4.0 \times 10^{-5}$
Torr and 0.8 Torr, respectively. A tunable AC current was allowed to pass the filaments and heat them. The high purity argon (99.99%) with 200 standard cubic centimeters per minute (sccm) was introduced to the vacuum chamber during the synthesis process, which lasted for 30 minutes.

Figure 1(a)-(d) show the cross-section views of nanorod arrays synthesized at d = 2, 3, 4 and 5 mm, respectively. The typical height of nanorods prepared at d = 2 mm is about 4.5 μm, which is longer than that of the nanorods grown at d = 3 (~3 μm), 4 (~3 μm) and 5 mm (~1 μm). The typical diameters of the nanorods synthesized at different d values are diverse. The nanorods prepared at d = 2 mm is the largest, with a diameter of about 150 nm. The typical diameter of the nanorods changes with increasing d, with diameter of about 100, 80 and 100 nm, corresponding to the d = 3, 4 and 5 mm, respectively. The nanorod arrays prepared at d = 4 mm have the largest aspect ratio value (~38). In addition, the nanorod arrays synthesized at d = 3 mm is seen to have best alignment, while the alignment of the nanorod arrays grown at d = 5 mm is the worst.

Figure 2(a)-(c) show the typical high resolution TEM (HRTEM) image of a single nanorod, the corresponding selected area electron diffraction (SAED) pattern and the EDS result of the nanorods, respectively. Figure 2 (c) indicates that the nanorods consist of W and O elements, while the C and Cu signals were from the TEM copper grid. From Figure 2(a), the crystallographic planes with interplanar spacing of 0.38 and 0.46 nm can be observed, which correspond to the (010) and (103) planes of monoclinic W18O49 (JCPDS 05-0392). The SAED pattern shown in Figure 2(b), indicates that the nanorod is a single crystal with monoclinic structure and that the growth direction is [010]. For there was not any catalyst used in the whole synthesis process, the purity of W18O49 nanorods is high. The growth mechanism of W18O49 nanorods might be attributed to the vapor-solid (V-S) process [8].

2.2 The field emission property and discussion
The field emission characteristics of the W18O49 nanorod arrays were measured in an ultrahigh vacuum system at room temperature. The transparent-anode and a Mo anode were applied to obtain the emission site distributions and measure turn-on / threshold fields, respectively. The vacuum gap between the anode and the surface of sample was set to 200 μm.

The characteristics of emission current density versus applied electric field (J-E curves) of the W18O49 nanorod arrays are shown in Figure 3(a). The sample of d = 3 mm has the lowest turn-on field ($E_{on}$) and threshold field ($E_{th}$), which are defined as the macroscopic fields required to produce
current density of 10 μA/cm² and 10 mA/cm² respectively. The typical $E_{fo}$ and $E_{th}$ values were 2.5 and 5.5 MV/m respectively for the W_{18}O_{49} nanorod array prepared at d = 3 mm, which are compatible to the best of those of tungsten oxide nanotips [9] and nanowires [10]. For the sample synthesized at d = 5 mm, its typical $E_{fo}$ (8.3 MV/m) and $E_{th}$ (12.2 MV/m) were the highest among the four different arrays. The $E_{fo}$ of nanorod array prepared at d = 2 and 4 mm were 3.8 and 8.3 MV/m, respectively, and $E_{th}$ of them were 6.6 and 8.9 MV/m in sequence. The difference in the field emission characteristics among the four samples is significant. The results indicated that the nanorod array should have a combination of both good alignment and medium interval (see figure 1) to give rise to better field emission property. This is similar to the findings from the early studies of the field emission property of the carbon nanotubes film [9, 10].

Figure 3. (a) shows the J-E curves of the four type tungsten oxide nanorod arrays, and (b) the corresponding F-N plots. The symbols ●, ■, □ and ○ denote the field emission property of tungsten oxide nanorods array prepared at d = 2, 3, 4 and 5 mm, respectively.

Figure 3(b) shows the corresponding Flower-Nordheim (F-N) plots of four typical nanorod arrays of different d values, which exhibited distinctly different features from each other. For the nanorods of the d values of 2 and 3 mm, the F-N curves exhibits approximately linearity; however, for those nanorods of the d values of 4 and 5 mm, their F-N curves showed a significantly non-linear behavior, and can be approximately divided into several nearly-straight lines. This was similar to the results reported in the study of non-metal nanostructures field emission property [11-13].

Figure 4. (a), (b), (c) and (d) show the emission site distributions of nanorods array prepared at d = 2, 3, 4 and 5 mm, respectively. The white dashed rims enclose the areas of the samples.

The variation of another important field emission property, i.e. the field emission site distribution is shown in Figure 4. The emission site distributions were recorded at the emission current of 1 mA/cm². It is noticed that the field emission site distributions of the nanorod arrays prepared at d = 2 and 3 mm were quiet uniform, as compared to those samples prepared at d = 4 and 5 mm. The effective emission site density of four typical nanorod arrays prepared at d = 2, 3, 4 and 5 mm was calculated to be $3.0 \times 10^3$ cm⁻², $4.2 \times 10^3$ cm⁻², $6.5 \times 10^2$ cm⁻² and $4.1 \times 10^2$ cm⁻², respectively. So the emission uniformity of sample of d = 3 mm is the best, this may be attributed to the good alignment and medium interval of the nanorods array.
From the above experiment results, one can see that the W$_{18}$O$_{49}$ nanorod array synthesized at d = 3 mm had the best field emission properties. The explanation to why its corresponding turn-on and threshold fields are lower may be given: a typical single nanorod of the array of d = 3 mm has larger aspect ratio, i.e. 30. However, it is smaller than the value of nanorod prepared at d = 4 mm (~38). So the relative high aspect ratio is not a key factor for the observed low turn-on and threshold fields. The values of field enhancement factor ($\beta$-value) were calculated based on the low field section of the F-N curves with the assumption of the value of work function of 5.27 eV. The four $\beta$-values of the samples prepared at four d values (d = 2, 3, 4 and 5 mm) are calculated to be 1620, 5700, 560 and 270 respectively, which are a lot larger than their corresponding aspect ratios, i.e. 30, 30, 38 and 10. Thus, the field emission characteristics of W$_{18}$O$_{49}$ nanorod arrays are not determined only by the aspect ratio of nanorods, and the other factors should also be considered. We believe that the large low field $\beta$-values are due to the fact that the semiconducting nature of W$_{18}$O$_{49}$ nanorods is not properly included into our calculation. The F-N theory assumes that the nanorods are metallic; however, W$_{18}$O$_{49}$ is an n-type semiconductor that may have poor conductivity. So the following two facts should be considered: field penetration into the tip end of the nanorod and the band bending at large emission current. If these happen, the surface barrier height may not be much smaller. This may lead to low field $\beta$-values, and it needs a lot more theoretical study.

2.3 Conclusion
The tungsten oxide nanorods arrays were synthesized by the catalyst-free hot-filament thermal vapor approach. The aspect ratio, interval and alignment of nanorods can be tuned by changing the distance between hot-filament and substrate set for a growth experiment. The field emission property of tungsten oxide nanorod arrays is strongly dependent on the aspect ratio, the interval of nanorods and the alignment of nanorods, so by optimizing the distance between hot-filament and substrate and nanorod arrays with better field emission property can be obtained.

Acknowledgements
N S Xu, S Z Deng and Jun Chen gratefully acknowledge the financial support of the project from the National Natural Science Foundation of China (Grant No. U0634002, 50725206, 60571035, 50672135, 50021202), Science and Technology Ministry of China (Grant No. 2003CB314701, 2007CB935501), Education Ministry of China, the Science and Technology Department of Guangdong Province, the Education Department of Guangdong Province, and the Science and Technology Department of Guangzhou City.

References
[1] Xu N S and Huq S E 2005 Mat. Sci. Eng. R. R48 47
[2] Huang X M H, Zorman C A, Mehregany M and Roukes M L 2003 Nature 421 496
[3] Zhou J, Gong L, Deng S Z, Chen Jun, She J. C, Xu N S, Yang R S and Wang Z L 2005 Appl. Phys. Lett. 87 223108.
[4] Li Y B, Bando Y and Golberg D 2003 Adv. Mater. (Weinheim, Ger.) 15 1294
[5] Liu Z W, Bando Y and Tang C C 2003 Chem. Phys. Lett. 372 179
[6] Mahan A H, Parilla P A, Jones K M and Dillon A C 2005 Chem. Phys. Lett. 413 88
[7] Liu J G, Zhang Z J, Zhao Y, Su X, Liu S, Wang E G and Wang E G 2005 Small 1 310
[8] Chi L F, Xu N S, Deng S Z, Chen Jun and She J C 2006 Nanotechnology 17 5590
[9] Nilsson L, Groening O, Emmenegger C, Kuettel O, Schaller E, Schlapbach L, Kind H, Bonard J-M, 2000 Appl. Phys. Lett. 76 2071
[10] Suh J S, Jeong K S, Lee J S and Han I T 2002 Appl. Phys. Lett. 80 2392
[11] Chen Jun, Deng S Z, Xu N S, Wang S H, Wen X G, Yang S H, Yang C L, Wang J N and Ge W K 2002 Appl. Phys. Lett. 80 3620
[12] Chen Y, Deng S Z, Xu N S, Chen J, Ma X C and Wang E G. 2002 Mat. Sci. Eng. A327 16
[13] Li S Q, Liang Y X and Wang T H 2006 Appl. Phys. Lett. 88 053107.