Field-Emission Properties of Nanostructured WO₃ Arrays Fabricated Using Tungsten Hot-Filament Chemical Vapor Deposition

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Abstract

Nanostructured WO₃ arrays fabricated by tungsten hot-filament chemical vapor deposition in an oxygen/argon gas mixture were studied in order to develop field-emission materials. Nanostructured WO₃ arrays of different shapes were grown by controlling the substrate temperature and the distance from the hot filament. We observed that their field-emission properties strongly depended on their tip structure. Numerical calculations of field enhancement factors for different tip geometries were carried out to explain the experimental results. The numerical result reveals that the planar tip structure may help nanostructured WO₃ arrays exhibit better field-emission properties.

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A new research area of one-dimensional nanomaterials was opened with the discovery of carbon nanotubes (CNTs) by Iijima in the 1991.¹⁾ The field-emission (FE) property is one of the features of one-dimensional nanomaterials.²⁾ In 1999, a field-emission display based on CNT field emitters was first demonstrated by a Korean company, showing their great commercial potential.³⁾ In addition to work on the CNT field emitters, research studies on other one-dimensional semiconductor nanomaterials, such as ZnO ⁴⁾ and Si ⁵⁾, were also reported. Recently, tungsten oxide WO₃ has attracted attention as an interesting semiconductor material exhibiting the electrochromic (EC) effect. Numerous applications of the EC effect and related devices make WO₃ one of the most versatile materials.⁶⁾ The FE properties of a WO₃ nanowire array⁷⁻¹¹⁾ has also attracted much interest making WO₃ a potential material for FE application.¹²⁾ However, most of these works focused on the synthesis and structural characterization of WO₃, although the field-emission property was measured as well.⁷⁻¹⁰⁾ The effect of growth temperature on field-emission performance was studied by Liu et al.¹¹⁾ They studied the effect of coil temperature varying from 850 °C to 1300 °C on the structural and FE properties of tungsten oxide. The most ideal field emission property was obtained in the samples synthesized at 850 °C, as WO₂ was formed in the high-temperature region. However, the temperature of the substrate, which is very important for nanostructure growth, was not clearly determined, as substrate temperature depended on coil temperature. In this work, we studied the fabrication of nanostructured WO₃ arrays of different shapes using controlled tungsten hot-filament chemical vapor deposition (CVD) in an oxygen and argon gas mixture and their FE properties. By using an additional heating stage, the effect of substrate temperature on structure and FE property was studied. Moreover, different FE properties that depend on nanostructured WO₃ arrays synthesized at different substrate

temperatures were observed. We found that, even in the substrate temperature range of 700 °C - 850 °C, which was not a very broad range, the field-emission properties varied markedly depending on the morphology of the tip of the tungsten oxide array. Also, from a numerical calculation, we found that the planar tip structure of WO₃ nanorods is more suitable for FE application.

Tungsten hot-filament CVD was used to grow nanostructured WO₃ in an oxygen and argon gas mixture. A clean silicon substrate (p-type [100]) was placed on the heating stage and heated up to 700 - 850 °C in an Ar atmosphere (~53 Pa). Then a tungsten filament (0.6 mm) on which current was applied was heated to more than 1500 °C. It also served as the tungsten source to synthesize nanostructured WO₃ composites when oxygen was introduced in addition to Ar. Typically, the gas ratio of O₂/Ar was 5/95 sccm and the growth time was 2 - 5 min.

Figure 1 shows the morphology of three types of WO₃ nanostructures grown under different experimental conditions. Figure 1(a) shows an array of uniformly grown WO₃ nanorods each with widths about 40 - 50 nm, referred to as sample (a). Figure 1(b) shows another type of WO₃ nanorod with thinner nanowires with widths of 10 - 20 nm shown by arrows in the figure, which is referred to as sample (b). Figure 1(c) shows a microsized cone-shaped array, referred to as sample (c). The magnified image inserted in Fig. 1(c) shows that the tip of the cones had a straight nanorod with a width of about 40 nm and a length of about 100 nm. The substrate temperatures for (a) and (b) were kept at 700 and 750 °C, respectively. The structure of the extremely thin nanorods in sample (b) was very similar to that obtained by Zhou et al.¹⁰⁾ We think that the formation of this

structure was by secondary growth, as described by Chi et al.¹³⁾ When we prepared the samples shown in Fig. 1(c), where the distance of the filament from the substrate was reduced to half that for samples (a) and (b), the substrate temperature was roughly 850 °C. This experimental condition was set in order to demonstrate secondary growth. As a result, evident secondary growth of the sharp tips was observed. The secondary growth occurred while the chamber was cooling accompanied by a decrease in WO₃ partial pressure. In this work, however, we focus on the FE property rather than on the growth mechanism. Figure 2 shows a high-resolution transmission electron microscopy (HR-TEM) image and a selected-area electron diffraction (SAED) pattern of the WO₃ nanorods. The interplanar distance was about 0.380 nm and the SAED pattern confirmed the [010] growth direction, as previously reported.⁹⁻¹¹⁾ This growth mechanism made the tip of the nanorods rather flat, as the image shows.

Field-emission measurement was carried out under a pressure of 6.7×10^{-4} Pa. Figure 3 shows the field-emission plot of the three different types of WO₃ nanostructures. We found that the turn-on electric field of the WO₃ varied from less than 2 V/μm to more than 8 V/μm, depending on the type of structure. Furthermore, from the Fowler-Nordheim (FN) equation¹⁴⁾

$$J = \frac{A\beta E^2}{\phi} \exp\left(-\frac{B\phi^{3/2}}{\beta E}\right) \quad (1)$$

or

$$\ln(J/E^2) = \ln(A\beta/\phi) - B\phi^{3/2}/\beta E \quad (2)$$

where A and B are constants ($A = 1.546 \times 10^{-6} \text{ A} \cdot \text{eV} \cdot \text{V}^{-2}$, $B = 6.83 \times 10^3 \text{ eV}^{-3/2} \cdot \text{V} \cdot \mu\text{m}^{-1}$). We calculated the field enhancement factor β from the slope of the FN plot. Substituting $B = 6.83 \times 10^3 \text{ eV}^{-3/2} \cdot \text{V} \cdot \mu\text{m}^{-1}$ and $\phi = 5.7 \text{ eV}$ as the work function of WO₃, we calculated the values of β as tabulated in Table I.

Previous studies of the field-emission properties of WO₃ nanostructures showed a turn-on field range of 1.2 - 6.44 V/μm, as shown in Table II. In Chang et al.'s work,⁸⁾ the turn-on field and β of the N-doped WO₃ nanowires are 6.44 V/μm and 691, respectively, which are not very attractive. Liu et al.¹¹⁾ reported the lowest turn-on field of 1.2 V/μm and claimed that the WO₂ formed together with the WO₃ nanorods degrades FE performance. In our work, we found that the turn-on field also depends on the type of tip structure. Moreover, a very large β was also obtained. It is seen that sample (b) exhibits an excellent FE property, with a turn-on electric field lower than 2 V/μm and a β of more than 5000. We considered that this may be due to the small diameter and low density of the thin nanowires of sample (b). Note that sample (a) with a uniform nanorod array showed a larger β than sample (c) with a micro-sized cone tip array, but that its turn-on electric field was much higher than that of sample (c). The theory of the screening effect¹⁵⁾ of a high-density array, which produces lower emitting sites, may explain this phenomenon. Despite sample (c) having the lowest β among the three types of nanostructures, the micro-sized cone tip array exhibited the most stable field-emission current in the present work, which would be preferable for application.

From the planar tip structure shown in the HR-TEM image in Fig. 2, we discuss how the tip geometry affects the β . This geometry effect was discussed by Fang et al.¹⁶⁾ However, no clear conclusion has been drawn to the best of our knowledge. Here, we develop a simple model and perform a calculation to explain the present experimental results.

The model was constructed similarly to that in Zhu et al.'s work.¹⁷⁾ The β derived from the F-N equation can also be written as

$$\beta = \frac{E_m}{E_0} = \frac{E_m}{V/d} \quad , \quad (3)$$

where E_m is the maximum electrostatic field at the apex in the emission region and E_0 is the average applied field, which is simply defined by V/d with the applied voltage V and the spacing d between the cathode and the anode. In order to calculate β , we must solve the electric-field distribution near the tips. To simplify the model, we assume that the nanowires in the array are uniformly grown. Thus, each nanowire in the array is placed in an equal cylinder potential well. In every potential well, the potential distribution follows the Laplace equation

$$\frac{1}{r} \left(r \frac{\partial u}{\partial r} \right) + \frac{\partial^2 u}{\partial z^2} = 0 \quad . \quad (4)$$

This partial differential equation (PDE) can be solved using COMSOL Multiphysics, a type of finite element method software, depending on the boundary conditions. Using

$$E_m = |grad \ u|_{\max} \quad , \quad (5)$$

which is provided as a function in the software, combined with eq. (3), we can calculate β for different shapes of WO_3 nanorod arrays.

For simple computation and comparison, we use a nanorod tip diameter of 40 nm, a nanorod length of 10 μm , and a spacing between the cathode and the anode of 100 μm . The distance between the two nanorods equaled the length of the nanorods, in agreement with the optimized result from another group.¹⁸⁾ We modeled three different types of tip geometries, as shown in Fig. 4: type (a) a nanorod with a spherical tip, for comparison with our experimental result; type (b) a nanorod with a planar tip, corresponding to the structure showed in the Figs.1(a) and 1(b), and type (c), a nanorod with a planar tip on the cone, corresponding to the structure shown in Fig. 1(c). In the case of common multiwalled CNTs, tip structure should be of type (a), as the catalyst particles are generally present on the tip. In the present work, the WO_3 nanorods should be of type

(b), as seen from the HR-TEM image in Fig. 2. The micro-sized cone shape obtained in this work is of the type (c). Figure 4 shows the result of the numerical calculation of the contour of the normalized electric-field amplitude for different tip geometries. Even contour lines were on the spherical tip in Fig. 4(a), while most of the contour lines were centered in an extremely small area near the edge of the planar tip in Fig. 4(b). This calculation result strongly indicates the localized electric-field enhancement near the sharp edge. The numerically calculated values of β tabulated in Table III also support our expectation that the planar tip structure will have a higher β .

We clarified the diameter dependence of β from our simulation results, as shown in Fig. 5, and found that β approximately follows $\beta \approx (1/2)h/r$ ($h = L$, $r = d/2$) for the spherical tip [type (a)] case and $\beta \approx (3/2)h/r$ [type (b)] for the planar tip, where h is the height of the emitter and r is the radius of the emitter tip. The β approximately follows $\beta = h/r$ in the case of the cone and planar tip [type (c)], in agreement with the empirical formula.¹⁶⁾ In practical field-emission measurement, it is considered that the joule heating effect in tips pulls more electrons from the Femi level up to the vacuum level.¹⁹⁾ The β calculated from the F-N plot should be slightly higher than that calculated from this simulation result. The difference between the calculation and experimental results mainly originated from the different lengths of the nanorods, because $\beta = c \times h/r$ in the empirical equation, where the constant c is considered to usually be about 1. However, from our modeling computation work, the constant c is not equal to 1. Figure 5 shows the dependence of β on r assuming that the length of the nanorods is fixed to 10 μm , as it is difficult to directly measure the length of the nanorods. We obtain a c of about 1.5 for the planar tip and a c of about 0.5 for the spherical tip. Thus, if we assumed the length of the nano-rods to be 15 μm , there would be very small differences between the calculation and experimental results, which is shown in Table I.

Our numerical result also shows the great advantage of the planar tip over a spherical tip with the same tip diameter, for example, as a CNT emitter²⁰⁾. These interesting results may theoretically support the use of WO₃ as a potential field-emission material with a low turn-on voltage and a high field enhancement factor due to its advanced tip structure. Furthermore, the controlled secondary growth method will also help realize a stable electron emission by controlling the tip geometry. Lastly, it is emphasized that WO₃ has the great advantages of long lifetime of its FE property¹⁰⁾ and its low-temperature growth at ~200 °C.²¹⁾

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References

- 1) S. Iijima: *Nature* **354** (1991) 56.
- 2) R. Gomer: *Field Emission and Field Ionization* (Oxford University Press, Oxford, U.K., 1961).
- 3) W. B. Choi, D. S. Chung, J. H. Kang, H. Y. Kim, Y. W. Jin, I. T. Han, Y. H. Lee, J. E. Jung, N. S. Lee, G. S. Park, and J. M. Kim: *Appl. Phys. Lett.* **75** (1999) 3129.
- 4) C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh, and H. J. Lee: *Appl. Phys. Lett.* **81** (2002) 3648.
- 5) F. C. K. Au, K. W. Wong, Y. H. Tang, Y. F. Zhang, I. Bello, and S. T. Lee: *Appl. Phys. Lett.* **75** (1999) 1700.
- 6) S. K. Deb: *Sol. Energy Mater. Sol. Cells* **92** (2008) 245.
- 7) Y. Baek and K. Yong: *J. Phys. Chem. C* **111** (2007) 1213.
- 8) M. T. Chang, L. J. Chou, Y. L. Chueh, Y. C. Lee, C. H. Hsieh, C. D. Chen, Y. W. Lan, and L. J. Chen: *Small* **3** (2007) 658.
- 9) Y. B. Li, Y. Bando, and D. Golberg: *Adv. Mater.* **15** (2003) 1294.
- 10) J. Zhou, L. Gong, S. Z. Deng, J. Chen, J. C. She, N. S. Xu, R. Yang, and Z. L. Wang: *Appl. Phys. Lett.* **87** (2005) 223108.
- 11) J. G. Liu, Z. J. Zhang, Y. Zhao, X. Su, S. Liu, and E. G. Wang: *Small* **1** (2005) 310.
- 12) J. Chen, Y. Y. Dai, J. Luo, Z. L. Li, S. Z. Deng, J. C. She, and N. S. Xu: *Appl. Phys. Lett.* **90** (2007) 253105.
- 13) L. F. Chi, N. S. Xu, S. Z. Deng, J. Chen, and J. C. She: *Nanotechnology* **17** (2006) 5590.
- 14) R. H. Fowler and L. W. Nordheim: *Proc. R. Soc. London, Ser. A* **119** (1928) 173.
- 15) G. H. Chen, W. L. Wang, J. Peng, C. S. He, S. Z. Deng, N. S. Xu, and Z. B. Li: *Phys. Rev. B* **76** (2007) 195412.
- 16) X. S. Fang, Y. Bando, U. K. Gautam, C. H. Ye, and D. Golberg: *J. Mater. Chem.* **18** (2008) 509.
- 17) Y. B. Zhu, W. L. Wang, and C. G. Hu: *Acta Metal. Sin.* **16** (2003) 302.
- 18) L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J. M. Bonard, and K. Kern: *Appl. Phys. Lett.* **76** (2000) 2071.

- 19) S. T. Purcell, P. Vincent, C. Journet, and V. T. Binh: Phys. Rev. Lett. **88** (2002) 105502.
- 20) M. Chhowalla, C. Ducati, N. L. Rupesinghe, K. B. K. Teo, and G. A. J. Amaratunga: Appl. Phys. Lett. **79** (2001) 2079.
- 21) J. G. Liu, Y. Zhao, and Z. J. Zhang: J. Phys.: Condens. Matter **15** (2003) 453.

Table Captions

Table I Comparison of field enhancement factor β calculated from the slope of the F-N plot and the theoretical model for different array structures.

Structure	Nanorod array (uniform)	Nanorod array (thin wires)	Coneshaped array (sharp tips on cone)
Diameter (nm)	40-60	10-20	40-50
$V_{\text{turn on}}$ (V/ μm)	8	2	6
$\beta_{\text{FN-plot}}$	~ 1230	~ 5000	~ 750
β_{model}	1125	4500	750

Table II Comparison of the synthesis methods and turn-on fields reported previously and present results.

WO ₃ emitter	Synthesis method	Turn-on field (V/ μm)	Ref.
Nanowires	Thermal-evaporation process	4.8	7
	Thermal-evaporation process	6.44	8
Nanowires (W ₁₈ O ₄₉)	Infrared irradiation to heat W foils	2.6	9
Nanotips	Physical evaporation deposition process	2.0	10
Nanorod (WO _{2,9})	Thermal oxidization approach	1.2~6.6	11
Nanorod (WO ₃)	Hot filament evaporation process	1.5~2	present

Table III Field enhancement factor β numerically calculated for different tip geometries.

Structure	Type (a)	Type (b)	Type (c)
β	~ 240	~ 840	~ 525

Figure Captions

Fig. 1 FE-SEM images of nanostructured WO_3 : (a) uniform nanorod array, (b) nanorod array with thinner nanowires, and (c) micro-sized, cone-shaped array.

Fig. 2 HR-TEM image and SAED pattern of WO_3 nanorods.

Fig. 3 Field-emission plots of the three different types of WO_3 nanostructures.

Fig. 4 Modeling calculations of three different types of tip geometries: (a) spherical tip; (b) planar tip; (c) cone with a planar tip, using $r = 20 \text{ nm}$ and $L = 10 \text{ }\mu\text{m}$.

Fig. 5 Field enhancement factors calculated for the spherical and planar tip geometries as a function of rod diameter.

Fig. 1 Di Lu et al.

Fig. 2 Di Lu et al.

Fig. 3 Di Lu et al.

Fig. 4 Di Lu et al.

Fig. 5 Di Lu et al.