

## 具有一维梯度直径的金属银纳米线的制备与结构表征

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### Preparation and Characterization of Ag Nanowires with Gradient Sizes

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**Abstract:** A new one-dimensional gradient material with graded sizes was prepared. A two-step anodic oxidation of high purity aluminum was used to fabricate porous alumina templates with graded pore sizes. Based on the templates, metal silver graded nanowires were obtained by electrochemical deposition. SEM and TEM results show that the resulted metal silver nanowires have obvious graded diameters with gradient ranging from about 12 to 31 nm along the nanowire direction, and are single-crystalline with a preferential growth along  $\langle 100 \rangle$  direction.

**Key words:** silver graded nanowire; size gradient; anodic aluminum oxide template; electrochemical deposition

Since the concept of functionally graded materials (FGM) is proposed<sup>[1,2]</sup>, much attention has been paid to FGM studies. Generally, FGMs were designed with the gradient distribution of composition and structure, and the graded structure of FGM is achieved by a composition gradient from one side of materials to the other, resulting in gradient properties. It is well-known that properties of nanometer-sized materials strongly depend on their sizes. Such size effect offers a new concept for the design of FGM by size gradient. For example, as the diameter becomes smaller, some metal nanoparticles have a gradual increase in resistance<sup>[3]</sup>,

while nanosemiconductors have a size-controlled band-gap<sup>[4]</sup>, and thus possibly present some novel tunable electronic and optical properties. Furthermore, if one-dimensional nanomaterial (i.e. nanowire, nanotube) has a graded diameter in one-dimensional direction, its properties may also present graded change along the direction because of the size effect. Therefore, the one-dimensional graded nanowires may be a new promising FGM.

Recently, there has been an increasing interest in nanoscaled tips and conical nanostructures, which are similar to the above-mentioned graded nanowires, due

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to their potential applications in areas such as scanning probes<sup>[5]</sup>, field emitters<sup>[6]</sup>, as well as nanodrills and nanoidenters<sup>[7]</sup>. Several techniques, e.g. optical lithography<sup>[8~10]</sup>, electron-beam or focused-ion-beam lithography<sup>[11]</sup>, plasma etching<sup>[6,12,13]</sup>, chemical vapor deposition<sup>[14]</sup>, laser ablation<sup>[15]</sup>, have been employed to fabricate these nanoscaled tips and conical nanostructures,. However, the established techniques seem to have technologic and economic limits in the case of fabricating one-dimensional graded materials. Until now, there has been considerable interest in a so-called template-synthesis of one-dimensional structures including nanowires<sup>[16~18]</sup>, nanotubes<sup>[19]</sup>, nanorods<sup>[20]</sup>, and nanopillars<sup>[21]</sup> based on anodic aluminum oxide (AAO) template. The AAO template prepared by an anodic oxidation of aluminum under appropriate electrolyte solutions and anodizing voltages is with typical self-ordered nanoporous structures including straight, Y-shaped, dendriform and torous pores. These pores have been applied to fabricating Y-shaped, dendriform and torous nanowires or nanotubes<sup>[22~24]</sup>. Here, we report the fabrication of graded metal nanowires by a simple method based on the AAO templates with graded pore diameter prepared by an improved anodic oxidation.

## 1 Experimental

The preparation of the metal Ag graded nanowires mainly involves two steps: fabricating the

graded nanochannel, which is the key step, and depositing graded Ag nanowires in the nanochannel. The procedure is illustrated in Fig.1. Briefly, a high-purity aluminum sheet (99.999%) was first anodized in 0.3 mol·L<sup>-1</sup> sulfuric acid for 30 min to form porous alumina membrane on aluminum sheet<sup>[25,26]</sup>. Then the membrane was removed in a mixture of phosphoric acid (6wt%) and chromic acid (1.8wt%) at 40 °C, and the Al sheet was anodized again in 0.3 mol·L<sup>-1</sup> sulfuric acid under a starting voltage of 10 V for 1 min, and followed by gradually increasing the voltage to 25 V in 20 min. During the second-step anodization, the AAO template with graded pore diameter was formed because its pore diameter is proportional to the voltage. Subsequently, Ag was electrochemically deposited into the graded pores in a mixture solution of silver nitrate and sulfuric acid with a graphite as electrode under 10 V(AC) for 5 minutes. During this process, the transparent color of alumina was slowly turned into golden. Finally, the free-standing graded Ag nanowires were obtained by removing the AAO template in 10wt% NaOH solution. The obtained graded nanowires were characterized by scanning electron microscopy (SEM; JEM-6700F) and transmission electron microscopy (TEM; Tecnai F20). XRD measurement was performed using a D/MAX-2000PC X-ray diffractometer with Cu K $\alpha$  incident radiation.

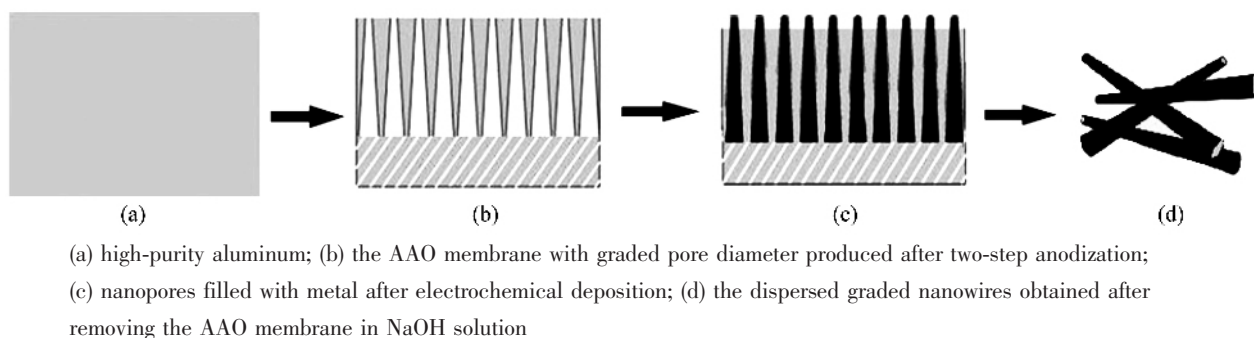
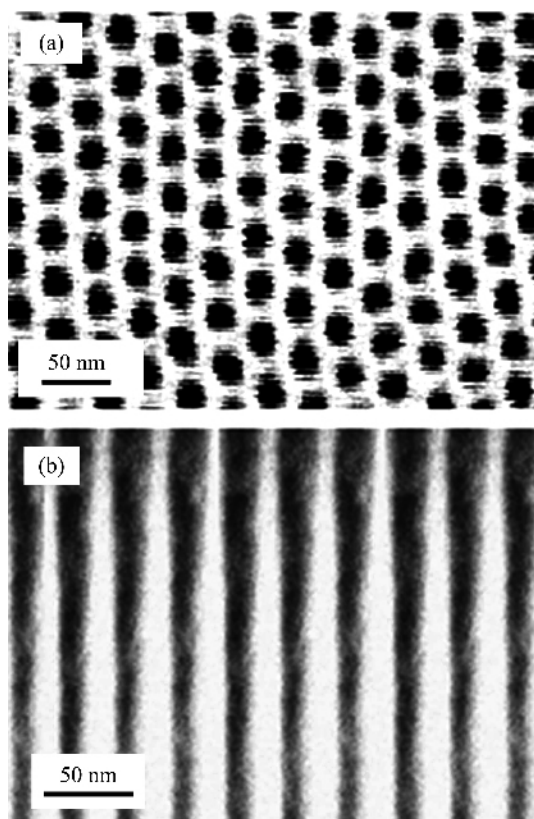


Fig.1 A schematic diagram for fabricating grade metal nanowires

## 2 Results and discussion

Fig.2 shows SEM images of typical AAO template obtained by gradually increasing the anodization voltage from 10 to 25 V in sulfuric acid.

The AAO template exhibits a hexagonal close-packed pore arrangement. From cross-section observation (see Fig.2b), it can be seen that pore diameter of the AAO template has an obvious graded change along pore depth direction.



(a) top view; (b) cross-section view

Fig.2 SEM images of the AAO template with graded pore sizes

Fig.3 gives XRD pattern of the graded Ag nanowires obtained by electrochemically depositing Ag into the above-described AAO template. XRD results show that the graded Ag nanowires are a face-centered cubic crystal structure. In the XRD pattern, the (111) peak, which is the most intense diffraction peak of Ag powders, become very weak, while the (200) diffraction peak become the most intense,

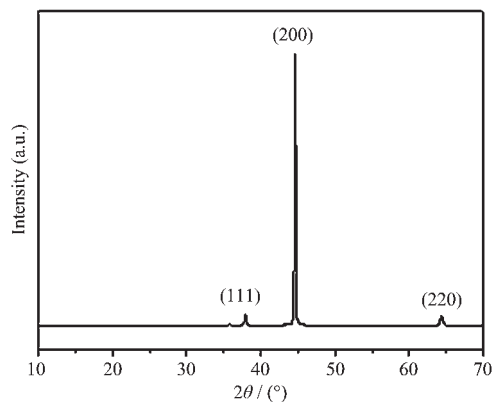


Fig.3 XRD pattern of graded Ag nanowires in the AAO template

indicating that the graded Ag nanowires have a preferential growth along  $\langle 100 \rangle$  direction.

Fig.4 gives SEM and TEM images of typical Ag nanowires obtained by the above-described procedure. It can be seen from the figure that the Ag nanowires have a gradient diameter along the nanowire direction, and two terminal diameters are about 12 and 31 nm,

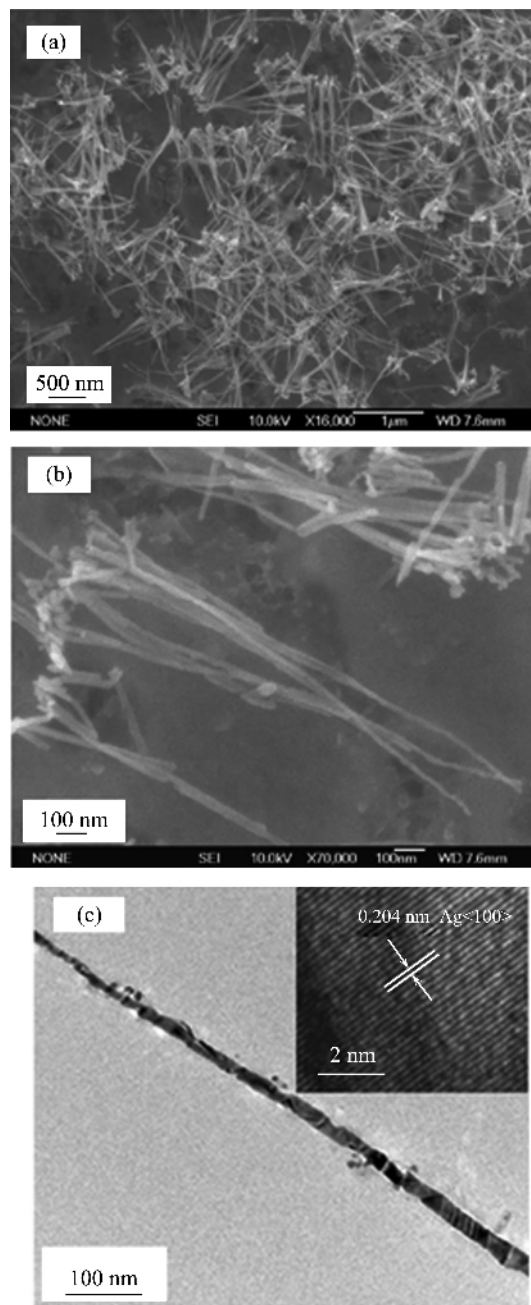


Fig.4 (a) SEM image of a bundle of graded Ag nanowires and (b) the corresponding high-magnification image; (c) TEM image of single graded Ag nanowire and the corresponding high-resolution TEM (inset)

respectively. According to the previous literatures<sup>[27~30]</sup>, the pore diameter of AAO template is proportional to the anodizing voltage with proportionality constant of  $1.29 \text{ nm} \cdot \text{V}^{-1}$ . It is reasonable to conclude that the pore diameter should have a graded change from 13 to 32 nm with increasing the anodization voltage from 10 to 25 V. This shows that the graded Ag nanowires perfectly copy the graded pores of the AAO template. From the high-resolution TEM image shown in the inset of Fig.4c, the deposited metal nanowire is a single-crystal structure with interplanar spacing of 0.204 nm, which corresponds to the  $\langle 100 \rangle$  plane of the face-centered cubic system of Ag, indicating  $\langle 100 \rangle$  as the growth direction for the graded Ag nanowires, which is in agreement with the XRD results.

The electrodeposition based on the AAO template is promising approach for the preparation of one-dimensional nanomaterials. A wide variety of metal and some semiconductor nanowires can be readily electrochemically produced within the pores<sup>[30,31]</sup>. And these nanowires faithfully reproduce the shape of the pores<sup>[32]</sup>. Thus, in principle, many metal and some semiconductor graded wires can be accomplished by the template-electrodeposition based on the template with graded pore diameter. In fact, we have applied this method to prepare other graded metal nanowires (e.g. Fe and Bi). Furthermore, many functionally graded nanowires (e.g. metal oxides, nitrides, sulfides, and phosphide) can be achieved by chemical conversion of the corresponding graded metal nanowires. This offers a simple but useful approach for fabricating one-dimensional graded materials.

In summary, we have demonstrated a template-electrodeposition method for fabricating the graded metal Ag nanowires based on the AAO template with the graded pore diameter. Such Ag nanowires may have a gradual increase in resistance, and even have a continuous transition from usual metallicity to semiconductivity or nonconductivity along one-dimensional direction.

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## References:

- [1] Niino M, Hirai T, Watanabe R. *Jpn. J. Soc. Comp. Mater.*, **1987**,**13**:257~261
- [2] Rabin B H, Shiota I. *MRS Bulletin*, **1995**,**20**:14~18
- [3] Qi W H. *Physica B(Amsterdam Neth.)*, **2005**,**368**:46~50
- [4] Bhattacharyya S S, Saha K, Chakravorty D. *Appl. Phys. Lett.*, **2000**,**77**:3770~3772
- [5] Eason D B, Yu Z, Hughes W C, et al. *Appl. Phys. Lett.*, **1995**, **66**:115~117
- [6] Hafner J H, Cheung C L, Lieber C M. *Nature*, **1999**,**398**:761~762
- [7] Lo H C, Das D, Hwang J S, et al. *Appl. Phys. Lett.*, **2003**,**83**: 1420~1422
- [8] Zhang G Y, Jiang X, Wang E G. *Science*, **2003**,**300**:472~474
- [9] Williams C C, Davis R C, Neuzil P U. *S. Patent 5*, **1999**,**969**: 345~345
- [10] Tarntair F G, Chen L C, Wei S L, et al. *J. Vac. Sci. Technol. B*, **2000**,**18**:1207~1211
- [11] Kichambare P D, Tarntair F G, Chen L C, et al. *J. Vac. Sci. Technol. B*, **2000**,**18**:2722~2729
- [12] Lowndes D H, Fowlkes J D, Pedraza A. *J. Appl. Surf. Sci.*, **2000**,**154~155**:647~658
- [13] Hsu C H, Lo H C, Chen C F, et al. *Nano. Lett.*, **2004**,**4**:471~475
- [14] Shang N G, Meng F Y, Au Frederick C K, et al. *Adv. Mater.*, **2002**,**14**:1308~1311
- [15] Mani R C, Li X, Sunkara M K, et al. *Nano Lett.*, **2003**,**3**:671~673
- [16] Jeong D H, Zhang Y X, Moskovits M. *J. Phys. Chem. B*, **2004**,**108**:12724~12728
- [17] Zhao W B, Zhu J J, Chen H Y. *J. Crystal Growth*, **2003**,**258** (1~2):176~180
- [18] Hulteen J C, Martin C R. *J. Mater. Chem.*, **1997**,**7**:1075~1087
- [19] Li J, Papadopoulos C, Xu J, et al. *Appl. Phys. Lett.*, **1999**,**75**: 367~369
- [20] Pacholski C, Kornowski A, Weller H. *Angew. Chem. Int. Ed.*, **2002**,**41**:1188~1191
- [21] Yuan Z H, Huang H, Fan S S. *Adv. Mater.*, **2002**,**14**:303~306
- [22] Li J, Papadopoulos C, Xu J. *Nature*, **1999**,**402**:253~254
- [23] Gao T, Meng G, Zhang J, et al. *Appl. Phys. A: Mater. Sci. Process.*, **2002**,**74**:403~406
- [24] Yuan Z H, Huang H, Liu L, et al. *Chem. Phys. Lett.*, **2001**, **345**:39~44

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- [25]Masuda H, Sotoh M. *Jpn. J. Appl. Part 2*, **1996**,**35**:L126~129
- [26]Li A P, Müller F, Birner A, et al. *J. Appl. Phys.*, **1998**,**84**: 6023~6026
- [27]O' Sullivan J P, Wood G C. *Proc. R. Soc. London A*, **1970**, **317**:511~543
- [28]Keller F, Hunter M S, Robinson D L. *J. Electrochem. Soc.*, **1953**,**100**:411~426
- [29]Thompson G E. *Thin Solid Films*, **1997**,**297**:192~201
- [30]Routkevitch D, Tager A A, Haruyama J, et al. *IEEE Trans. Electro. Devices*, **1996**,**43**:1646~1657
- [31]Klein J D, Herrick R D, Palmer D, et al. *Chem. Mater.*, **1993**, **5**:902~904
- [32]Pontifex G H, Zhang P, Wang Z, et al. *J. Phys. Chem.*, **1991**, **95**:9989~9993