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FAST FABRICATION OF DIAMETER-MODULATED METALLIC NANOWIRES IN 3D ANODIC ALUMINUM OXIDE TEMPLATES

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ABSTRACT
Simple method to fabricate the diameter-modulated metallic nanowires was introduced with low cost and short processing time. The 3D nanostructure of anodic aluminum oxide film was produced based on sprinkling electrolyte method in hard anodization technique. The control of the duration of current pulse provides an interesting way to tune the shape of pores and the structure of anodic aluminum oxide film. Template was prepared to ac electrodeposition without removing the barrier layer, by thinning process from hard to mild anodization condition. The scanning and transmission electron microscopy investigation demonstrate the metals electrodeposition process transform the pore profiles into the metallic nanowires.

KEYWORDS: Nanostructure Anodic Aluminum Oxide; Metallic Nanowire; Electrodeposition

1. INTRODUCTION

Recently, fabrication of nanowire arrays, especially metallic nanowire arrays due to their potential applications in chemical and biological sensors, optical and electronic devices has become the subject of extensive researches (Tang *et al*, 2004; Shima *et al*, 2003; Liu *et al*, 2003; Bennett and Xu, 2003) Several methods such as lithographic techniques, deposition into ordered template, self-assembly and reactive ion etching have been used to fabricate the various types of nanowires (Kawakami *et al*, 2007; Chik and Xu, 2004; Hsu *et al*, 2004; Erlebacher *et al*, 2001; Prevo, 2005) Lithographic techniques allow controlling the size and shape of nanowire but these techniques could be expensive. Electrodepositing into nanoporous membrane has been the simple and inexpensive method for fabricating various metallic nanowires. Among templates, nonoporous anodic aluminum oxide (AAO) membranes have been one of the most popular templates for fabricating various nanostructure materials (Matsumoto *et al*, 2005). Aluminum anodization process leads to formation of cylindrical and vertically aligned arrays of nanometer pores. One of these techniques is mild anodization (MA) process (Masuda and Fukuda, 1995; Masuda et al, 1997; Li, 1998; Masuda et al, 1998). MA is a slow process to obtain AAO film and limited in three growth regimes. Recently, hard anodization (HA) technique has been developed to fabricate self-ordered AAO film at relatively high current density (Lee, 2006). HA is applied in wide range of pore size and interpore distance and that is able to fabricate ordered AAO film in short processing time. The HA or MA process only lead to fabricate two dimensional AAO film, therefore synthesized nanowires based on these templates are straight and smooth nanowires. Transport behavior of electrons and phonons along nanowire axes in diameter–modulated nanowire is different from straight and smooth nanowires (Datta, 1995). The transport phenomena effectively affected by different boundary condition of diameter–modulated nanowire. For fabrication of diameter–modulated nanowire we need to produce AAO films with periodically modulated diameter nonporous. These three dimensional nanostructures have been produced by several method such as combining MA and HA process, pulse anodization and electrolyte sprinkling (Lee *et al*, 2006. Lee *et al*, 2008; Losic and Losic, 2009; Moradi *et al*, 2011). Other problem in fabrication of diameter-modulated nonowires is in electrodeposition process. Most of dc electrodeposition processes which are reported to date are performed by removing the remaining aluminum substrate, opening the pore bottoms and sputtering a conducting layer such as gold on the back of the template (Yoo and Lee, 2004; Tian *et al*, 2006; Fu *et al*, 2008).

However, these films are very brittle and are not easily manipulated for applications where a rapid and simple method in template fabrication is required. Another possibility is barrier layer thinning through a gradual step down of the voltage after the diameter modulated nanopores are grown to the desired depth. The thinning process leads to a considerable reduction in the barrier layer electrical resistance, where the barrier layer is thin sufficient to enable ac electrodeposition through barrier layer without requirement of aforesaid complex and time consuming processing steps (Nielsch *et al*, 2000). In this work we produce a 3D nanostructure AAO film by sprinkling electrolyte method and without removing the barrier layer, by thinning process from HA to MA prepared the template for ac electrodeposition.

Finally, ac electrodeposition technique was employed to electrodeposit the metallic ions into porous aluminum oxide templates to fabricate the diameter-modulated nanowires.

2. EXPERIMENTAL SECTION

High purity (99.999%) aluminum foil with 0.25mm thickness and 1.2 cm diameter was degreased in acetone and washed with de-ionized water. The sample was electropolished at 5 ºC in 25:100 volume mixture of $HClO_4$ and ethanol at a constant voltage 20V, for 4 minutes to diminish the roughness of aluminum foil surface. Before the HA process, we need to create a protective layer against burning the sample at high voltage and current so the procedure was started by MA at 40V for 10 minutes. Then the anodization process was switched from MA to HA by increasing the anodization voltage slowly (Lee *et al*, 2006). The anodization voltage was increased to a final value and kept constant. When the current density reaches to the steady state, the anodization procedure was continued by pulse sprinkling of the pump (Moradi *et al*, 2011). Then the voltage was controllably decreased to promote thinning of the barrier layer. The anodization voltage was decreased exponentially to desired value according to an exponential equation as follows:

$$V_{thin}(t) = V_a \exp(-\eta t)$$

The time constant η which controls the rate of reduction voltage was 0.0015 s^{-1}, V_{thin} and V_a were thinning and anodization voltages, respectively. Electrolyte of electrodeposition contains 0.3M Co^{+2} and H_3PO_3 (40 gr/l) for formation Co nanowire and $AgNO_3$ (20 gr/l) and H_3PO_3 (40 gr/l) for formation Ag nanowire. The AC electrodeposition was done under reductive oxidative voltage of -18V and 18V using sine wave form (200 Hz). Figure 1 shows the schematic diagram, describing fabrication steps of diameter modulated metallic nanowires in 3D PAA film. Field Emission Scanning Electron Microscopy (FE SEM) was used to investigate the morphology of sample. TEM images of nanowires were collected on a Philips CM-10 transmission electron microscope. Finally, AAO films solved in 0.3M NaOH etching solution at room temperature for 1 h. The resulted nanowires were sonicated briefly in distilled water and deposited on to coated copper grids for TEM analyses. The nanowires crystal structure was examined by x- ray diffraction.

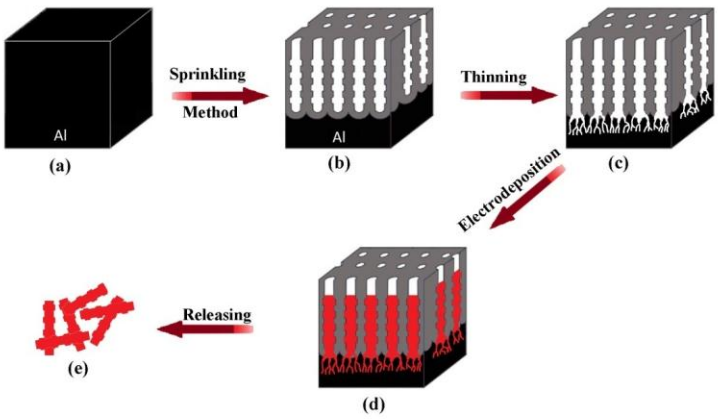

Figure 1. Schematic diagram describing the fabrication steps of diameter modulated metallic nanowire arrays based on porous anodic alumina template.

3. RESULTS AND DISCUSSION

Our Purpose here is to fabricate diameter-modulated metallic nanowire. For this purpose, 3D alumina nanostructure was fabricated by using controlled sprinkling of electrolyte on template during the anodization process. In Fig. 2 the effect of pump operation on current density behavior can be clearly seen. Moreover the effect of current peak on alumina pore structure is shown in this figure. According to Fig. 2, when the pump is turned off at point m, the current increases about 15 times and decreases sharply when the pump turn on at point n. It is clear from the SEM micrograph the dept of the pores is proportional to the transferred charge density, Q, during each time interval, $L_P = KQ$, where L_p is the length of pores and K is a constant. For the peak duration the proportional constant k is 0.51 nm/c and when the pump is turned on we have k=0.64μm/c. Therefore the required structure of AAO film is achieved by controlling the charge. During the current peak, the pore diameter increases but duration of peak is limited by heat that produced at very high current magnitude. The heat production is proportional to j^2, therefore during current peak high amount of

heat release in barrier layer (reaction zone). This amount of heat damages the barrier layer in long duration peak [26]. The interval between peaks is controllable through tuning the charge transferring between two peaks. After the pump operation, for AC electrodeposition it is needed to decrease the barrier layer thickness. According to linear relation between barrier layer thickness and anodization voltage, it is possible to decrees the barrier layer thickness by gradually decreasing the anodization voltage that is called thinning process (Nielsch, 2000). By decreasing voltage, the current density decreases as it is seen in Fig. 3. During the thinning process we increase the electrolyte temperature to prevent of rapid decreasing of anodization current. During the thinning, the anodization process changes from HA to MA process slowly.

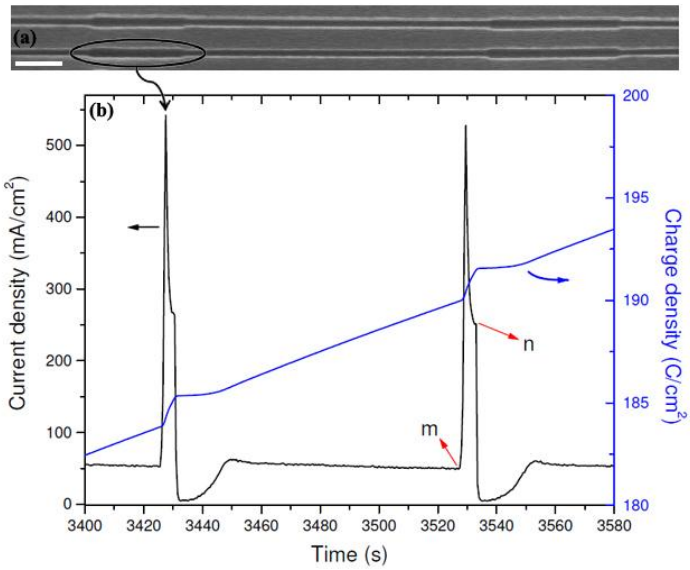

Figure 2. Current density and charge density–time curve of the sample made in the phosphoric/oxalic acid mixture containing 0.1M phosphoric acid at 170V and the corresponding cross-sectional SEM micrograph (The scale size is 300 nm).

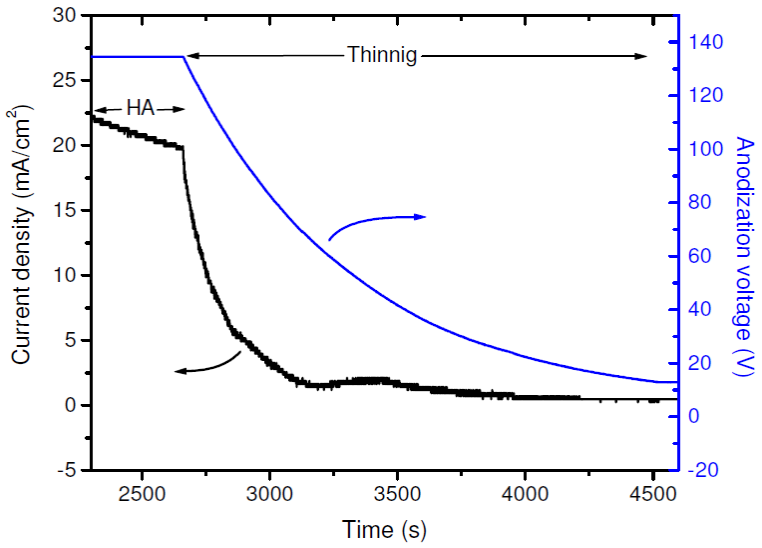

Figure 3. Current density, Voltage–time curve of sample during thinning process

The cross section SEM micrograph of sample in Fig. 4 shows a Cobalt nanowire inside the alumina pore. The 3D AAO film in this figure was fabricated in 170V anodization voltage. Pore diameter during the current peak reaches to 120nm while between peaks is about 80nm. This figure demonstrates the metals electrodeposition process transform the pore profiles into the Co nanowire. Therefore the shape of nanowire is exactly controllable by controlling the AAO film structure.

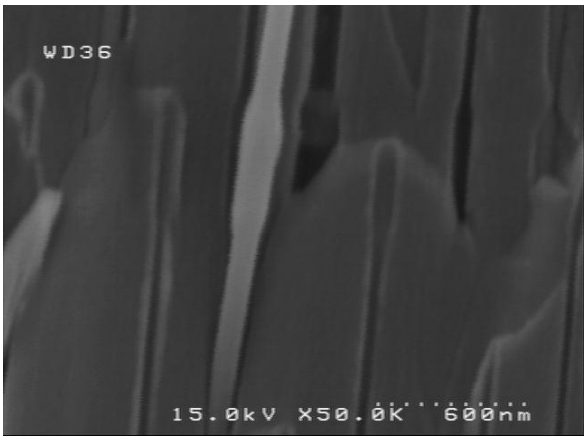

Figure 4. Cross section SEM micrograph of diameter–modulated Cobalt nanowire inside the alumina pore.

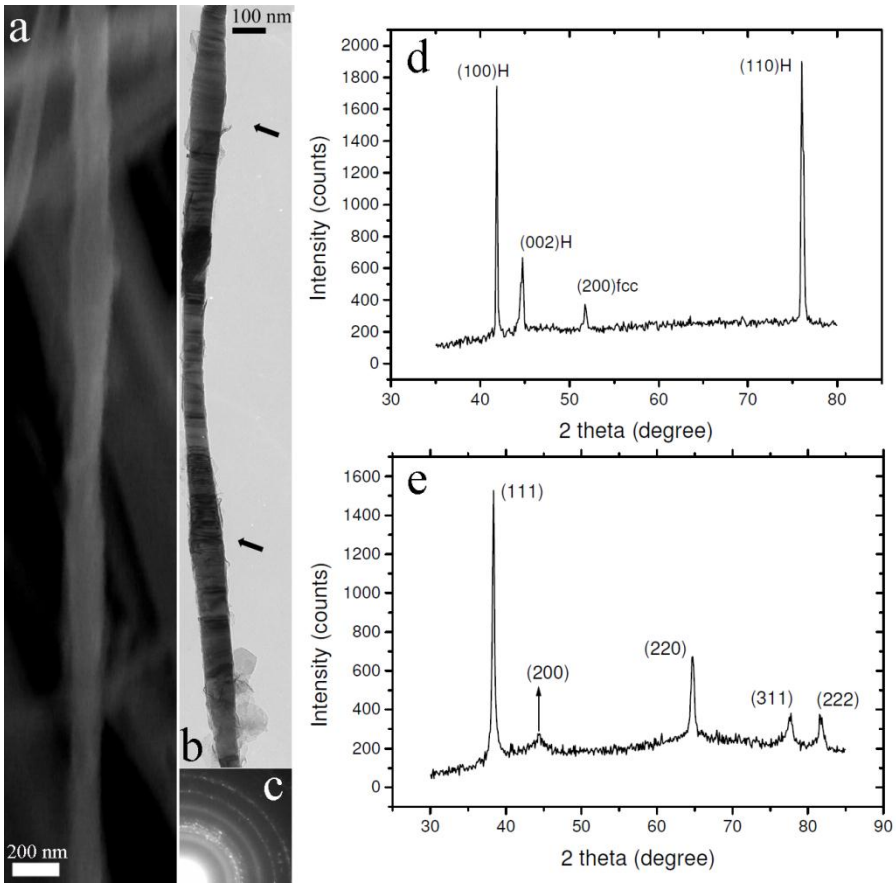

Figure 5. SEM image of diameter–modulated Ag nanowire after removal of AAO template. (b) TEM image of diameter–modulated Co nanowire and (c) corresponding ED pattern. (d) and (e) X-ray diffraction patterns of Co and Ag nanowires array respectively.

Fig. 5(b, c) shows the transmission electron microscopy (TEM) image of diameter–modulated Co nanowire and corresponding electron diffraction (ED) pattern. The 3D AAO film in this figure was fabricated in 140V anodization voltage. The periodic variation of the nanowire diameter is observed in this image. The arrays in Fig. 5(b) denote two sequent large part of Co nanowire. Between these two parts, a narrow region is corresponded to the interval between two peaks. The electron diffraction pattern was taken from the Co nanowire shows diffraction rings and it was found that the rings correspond to polycrystalline microstructure of Co nanowire. Furthermore, the crystal structure of nanowires was examined by X ray diffraction. Fig. 5(d) shows the corresponding X ray diffraction pattern of diameter–modulated Co nanowires in AAO template. This pattern confirms the ED pattern result.

Co namowires show the hcp and fcc phase but the hcp phase is dominate. Most of the Co particles are crystallized in the hcp structure with easy axis perpendicular to the nanowire axis while most of the Ag particles are crystallized in the fcc structure (Fig. 5(e)) with a preferential orientation in the direction of (1 1 1). Two dimensional nucleation growth mechanism is needed to achieved single crystalline metallic nanowires inside pores (Mingliang *et al*, 2003). The variation of pore diameter along the pore direction to render difficult the two dimensional nucleation growth and it was difficult to achieve the single crystalline metallic nanowire.

4. CONCLUSIONS

In summary, AAO film with periodic modulated pore diameter was fabricated by pulse sprinkling method in HA condition. In this method all parameter of current pulse is controllable. Then the barrier layer of AAO template was thinned by gradually decreasing the anodization voltage from HA to MA condition. After that metallic particle such as Co and Ag were filled in 3D AAO template by ac electrodeposion. The geometrical and microstructure properties of metallic nanowires were investigated and following conclusions have been achieved:

1. Metals electrodeposition process transforms the pore profiles into the metallic nanowire and nanowires shape exactly depends on the pore configuration.

2. The ED pattern and XRD measurement show that ac electrodeposition into 3D AAO film leads to polycrystalline growth of metallic nanowires.
3. It seems that two dimensional nucleation growth is difficult to achieve for fabrication of single crystalline metallic nanowire in diameter modulated alumina nanopores.

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