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High density copper nanowire arrays deposition inside ordered titania pores by electrodeposition

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ABSTRACT

Large area and free-standing TiO_2 films was prepared by ultrasonic splitting and a chemical etching step was used to open the closed bottom end of TiO_2 films and yields a high aspect-ratio anodic titanium oxide membrane open at both ends. Ordered Cu nanowire structures were fabricated by a simple electroplating method inside high aspect-ratio anodic titanium oxide membrane. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and the X-ray diffraction (XRD) were employed to characterize the resulting samples. Detailed results and the possible mechanism are presented.

1. Introduction

Nanostructured titanium dioxide (TiO_2) crystalline material is widely studied due to its potential technological applications as solar cells, rechargeable lithium batteries, gas sensors [1–3]. One-dimensional TiO_2 nanostructures have attracted significant scientific interests in the aspect of nanotubular synthesis. Self-organized electrochemical growth of TiO_2 nanotube on Ti has been given particular interest. In 2001, Gong et al. [4] reported the fabrication of vertically oriented, high ordered TiO_2 nanotube arrays by potentiostatic anodization of titanium in a HF aqueous electrolyte. Later, TiO_2 nanotube arrays with the length of 134 μm were successfully produced in a non-aqueous electrolyte [5]. Recently, free-standing TiO_2 nanotube membrane was fabricated by dissolving the titanium in CH_3OH/Br_2 solution, and the bottom of the wet TiO_2 nanotube membrane can be opened by exposing in HF vapors [6], which can also be obtained by using solvent-evaporation-induced delamination [7] and ultrasonic splitting [8].

Self-organized TiO_2 nanotubes can be used as channels to vertically grow nano-crystallites and which may have new potential applications. Macak et al. [9] reported that Pt/Ru nanoparticles were on the top of the nanotubular TiO_2 by electrodepositing. Fe_2O_3 nanorods were synthesized inside a TiO_2 nanotubular array template by pulsed electrochemical deposition [10], while the Fe_2O_3 nanorods were also found on the surface of the membrane from their scanning electron micrograph (SEM) and transmission electron microscopy (TEM) images. CdTe can be electrodeposited into the TiO_2 nanotube [11], whereas a high quality of CdTe/TiO_2 junction was difficultly achieved due to the equal conductivity of the TiO_2 tubes in the surface and the bottom [11–13]. Therefore, Macak et al. [14] switched the pore bottoms to a higher conductivity by electrochemical self-doping and then the pore was filled by electrodeposition.

In the present study, a free-standing TiO_2 nanotube arrays are firstly attained by using ultrasonication, after that, two-end-opened TiO_2 membranes are achieved by chemical etching, and at last Cu nanowire arrays are electrodeposited into the channels of the self-organized TiO_2 nanotubes.

2. Experimental

2.1. Materials preparation

The anodic titania templates with pore size of about 120 nm were grown on high purity titanium plates (0.30 mm thick, 99.5% purity) by potentiostatic anodization with the voltage of 60 V in glycol at 20 °C for about 48 h. After that, the whole sample was transferred into 95% of ethanol solution and ultrasonic agitation was applied at room temperature for several minutes. During the ultrasonication, the titania membrane will be detached from the Ti substrate, then the titania membrane was taken out from the solution and rinsed with anhydrous ethanol for three times. The barrier layer of the titania membrane was hereafter dissolved by using a 5 wt% NH_4F–1 M H_2SO_4 solution. Finally, an Ag sol was

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coated onto one of the surfaces of the membrane and dried at 100 °C for 12 h.

Cu was deposited using a constant current (−1 mA) in 0.5 M $CuSO_4$ solution at room temperature with magnetic stirring at 500 rpm, and Pt gauze was used as the counter electrode.

2.2. Materials characterization

The morphological characterization of the samples was carried out by scanning electron microscopy (JSM 6700F; JESL, Tokyo, Japan). For transmission electron microscopy, the template with Cu nanowire was separated by ultrasonically dispersion in 1 ml of water, then a drop of the solution was placed on a Cu grid covered with carbon film. A transmission electron microscope (JEM-3010; JESL, Tokyo, Japan) was employed to study the morphology of the array structure. X-ray diffraction measurement was carried out on a MXPAHF X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å).

3. Results and discussion

A schematic method employed to fabricate Cu nanowire arrays inside the nanoporous titania template is shown in Fig. 1. Ti is firstly anodized and ultrasonic agitated, the free-standing nanoporous titania membrane will be gained. The nanoporous titania membrane is thereafter soaked in 0.5 wt% NH_4F–1 M H_2SO_4 solution and then two-end-opened TiO_2 membranes are achieved. After drying, one side of the membrane is daubed by Ag sol and the nanoporous titania template is achieved. The template is transferred into 0.5 M of $CuSO_4$ aqueous solution and the Cu nanowire is grown inside the template.

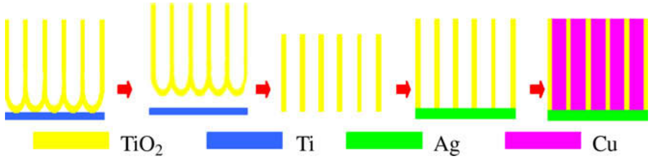

Fig. 1. Schematic of the process employed to produce the Cu nanowire arrays into the porous anodic titania template.

Fig. 2a shows the digital image of the free-standing TiO_2 nanotube membrane and it is displayed that the dimension of the membrane is about 2.5 × 2.0 cm^2. The top surface of the membrane by SEM is shown in Fig. 2b and it is evident that the array is consisted from very regular tubes with a diameter of about 120 nm and a wall thickness of about 10 nm. The layer (in Fig. 2c) is about 115.9 μm and has very smooth walls typical of nanotubes grown in organic electrolytes [5]. Fig. 2d shows the back layer side and the bottom of the nanotube is closed.

Fig. 3a and b present the SEM of the free-standing TiO_2 nanotube membrane after soaking in 5 wt% NH_4F–1 M H_2SO_4 solution for 5 and 15 min, respectively, it can be seen that the pores are partly opened after 5 min soaking and completely opened after 15 min. Fig. 3c is SEM of the top side of the membrane after 15 min soaking and it shows the nanotube becomes nanowire. To overcome this problem, we have designed a new device (a home-made box), which can prohibit the top side of TiO_2 membrane immerging the NH_4F–H_2SO_4 solution (in Fig. 3d). The bottom side and four walls of the box are composed of organic glass, the top side of the box is composed of steel nets, and TiO_2 membrane is laid on steel nets. During the experiment, the box is filled with 5 wt% NH_4F–1 M H_2SO_4 solution. The result is similar with Fig. 2b.

The images of a highly ordered free-standing TiO_2 nanotube filled with Cu are shown in Fig. 4a, b by SEM and Fig. 4c by TEM, and it is seen that the TiO_2 nanotube is filled with Cu. The array/template composite is also assessed by X-ray diffraction (XRD), as seen in Fig. 4d. The arrays are dominated by the 1 1 1 Cu peak,

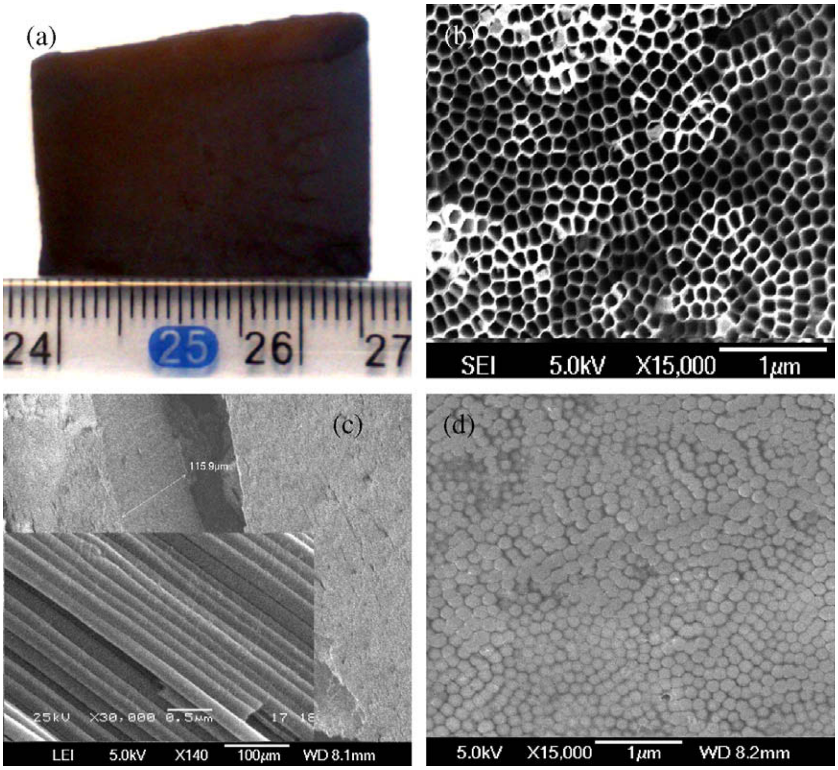

Fig. 2. The digital image (a) of the titania membrane after anodization at 60 V for 48 h, and the SEM image of the titania membrane after anodization: top view (b), cross-sectional view (c), bottom view (d).