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Patterned procedure for template-synthesis and microstructural characterization of copper nanowires

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ABSTRACT

Highly ordered circular patterns of copper nanowire arrays were successfully deposited into designed anodic aluminum oxide templates. High-resolution transmission electron microscopy was used to study the microstructure of these Cu nanostructures. The results showed that the growth orientation of the copper nanowires was along [220] direction, and the broken orientation were along [202] and [022] directions, respectively. Regular cones were formed at the broken end of nanowires. Bent nanowires were also observed, this means that the copper nanowires have good mechanical properties when applied external force. Chemical analysis has been performed on Cu nanowires using electron energy-loss spectroscopy.

1. Introduction

Investigation of metal nanowires has attracted comprehensive attention owing to their potential applications. Among various synthetic processes, porous alumina template synthesis has been one of the most commonly used approaches, because it is easily fabricated and can be used to fabricate many types of nanostructures from polymer to metal [1–4]. Recently, a few previous works focused on the novel fabrication of copper nanowires [5–7]. Many groups fabricated copper nanowires by typical electrochemical synthesis method [8–10]. A great deal of effort has been devoted into studying the crystallization structure of copper nanowires [8,11,12]. These literatures reported that the copper nanowires were single crystal [8,11,12]. However, the electrical parameters influence the crystal size of the nanowires, and the Cu nanowires could be grown into polycrystalline structures [13]. To the best of our knowledge, the growth orientation and broken orientation has been unclear so far.

In this study, patterned copper nanowire arrays were fabricated by photolithography via electrodeposition within anodic aluminum oxide (AAO) pores. Photolithography is one of the most successful techniques in large-scale microfabrication [14], because it is a promising technique that has been employed to fabricate different designs and materials of nanopatterns [15–18]. Herein, we describe the effective method for preparing patterned nanowire arrays, and have been assembling gas ionization sensors and dye-sensitized solar cells with the patterned Cu nanowire arrays due to the Cu nanowire conducting.

The morphology of copper nanowire arrays was investigated by scanning electron microscopy (SEM). Single-crystalline nanostructure, growth orientation and broken orientation were investigated by high resolution transmission electron microscopy (HRTEM). The chemical composition of the nanowires was investigated using electron energy-loss spectroscopy (EELS).

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2. Experimental

2.1. Materials

Porous AAO template (purchased from Whatman International Ltd.) with an average pore diameter of about 200 nm (the depth is about 60 μm) was treated in alcohol in an ultrasonic bath to clean its surface before use. The photoresist is the type of BP-212 (Beijing Kehua Fengyuan Microelectronic Technology Co., Ltd.).

2.2. Preparation of Patterned AAO Membrane

The membrane was spin-coated with a layer of photoresist at 2700 rpm for 30 s to seal the pores of the AAO template, then "soft baked" at low temperature (313 K) for 20 min in order to remove the solvents from the photoresist and improve photoresist-AAO template adhesion. This composite was covered with a photolithographic mask and exposed to ultraviolet light (UV 365 nm) for 20 s, and then "hard baked" at higher temperature (363 K) for 20 min to further activate cross-linking processes and improve the mechanical stability of the pattern, and was subsequently developed in a developer, flushed with deionized water several times and dried in nitrogen. The pores of AAO were selectively opened only in area of exposure.

2.3. Electrodeposition of Cu Nanowires

The side of the AAO membrane with patterns was sputtered with a layer of Au as a work electrode. In a tri-electrode electrochemical system (SCE), the Cu nanostructure arrays were produced in the template pores from a solution of 0.5 mol/L $CuSO_4$ + 0.1 mol/L H_2SO_4 by direct current electrodeposition (applied voltage of −0.2 V and deposition time of 10 min). The electrodeposition was carried out using platinum as an anode and a calomel electrode as a reference electrode. AAO membrance with Cu nanowires was fixed on the glass slide with double-side adhesive, and then the patterned nanowire arrays were obtained after dissolution of AAO in a 3 mol/L sodium hydroxide solution.

2.4. Characterization of Cu Nanowires

The morphology of the Cu nanostructure arrays was investigated using a JEOL JSM-6390LV SEM. The structure and microstructure of the Cu nanowires were investigated using a JEOL JEM-2100 FEG TEM. The specimen for TEM observation was prepared by evaporating a drop (5 μL) of the nanostructure dispersion onto a carbon-film-coated copper grid.

3. Results and Discussions

Fig. 1 shows SEM images of patterned AAO templates and Cu nanowire arrays with circular patterns. Fig. 1(a) presents a typical SEM image of patterned AAO template formed by photolithography. The patterns were completely transferred onto the surface of AAO templates from mask. The distance between two adjacent patterns is 5 μm just like that of mask. As shown in Fig. 1(b), the pores are selectively opened in patterns, and are sealed by the photoresist around the pattern. It is clearly shown in Fig. 1(c) that the nanowire arrays are regular and the naked nanowires are ready to get together after removing AAO. It is believed that the nanowires incline to agglutinate together to minimize free energy of the system after the removal of the AAO template [19]. Some clusters are different in size, the reason for this is that a small amount of photoresist which remains at the edge of each circular pattern of AAO template, and stops Cu nanowires from depositing into the pores. So the diameters of some clusters are smaller, and the distance is larger than that of mask. An enlarged SEM image in Fig. 1d reveals that the length of the free-standing nanowires is 5–6 μm.

The length of the Cu nanowires increases with the electrodeposition time. It is clearly shown in Fig. 2 which presents three SEM cross-section images of un-patterned Cu nanowire arrays with different electrodeposition time (fabrication conditions of the three samples are the same as that of above patterned Cu nanowires). From Fig. 2, an array of perfectly aligned Cu nanowires can be observed. Fig. 2(a) shows a typical SEM image of Cu nanowires after deposition for 5 min, and the length of nanowires is about 3 μm. After 10 min, the length of nanowires is more than 5 μm, as shown in Fig. 2(b). The length continues to increase with the deposition time. From Fig. 2c, the length of the nanowires increases to about 12 μm after 20 min. As shown in Fig. 2, there is a distribution in the lengths of nanowires. This is due to the difference in the thickness of the barrier layer at each pore and due also to the difference in the appearance at each pore. Cu^{2+} ions are reduced during the electrodeposition by the electrons tunneled through the barrier layer. However the barrier layer at each pore could be branched differently during the barrier layer thinning process, resulting in different energy barriers for tunneling because of different barrier layer thickness [20]. Consequently, the rate of deposition becomes different at each pore, in fact the rate of deposition first decreased and then increased with time. Such phenomenon must be ascribed to an initial flash of H_2 evolution occurring on the sputtered gold film; this causes sudden gas bubbles formation into the alumina channels, with increase of solution resistance, followed by nucleation of metallic copper on gold. After the initial spike, the current gradually increases with the deposition time [13].

The structure and microstructure of an individual Cu nanowire were characterized by TEM after the AAO template had been thoroughly dissolved. TEM images in Fig. 3(a) and (b) show that the Cu nanowires are dense, continuous and uniform in diameter throughout the entire length of the wires. The results show that the diameters of the Cu nanowires are about 200 nm, in good agreement with those of the channels in the AAO template. From the selected-area electron diffraction (SAED) pattern shown in Fig. 3(c), we can tell that the growth orientation of the nanowires is along the [220] direction. The SAED pattern of the Cu nanowires does not change along the length of the wire. This indicates that the nanowire is single crystal. A HRTEM image (Fig. 3d) of a segment of the Cu nanowire shows that the longitudinal direction is [220]. The result is in good agreement with that of SAED pattern.

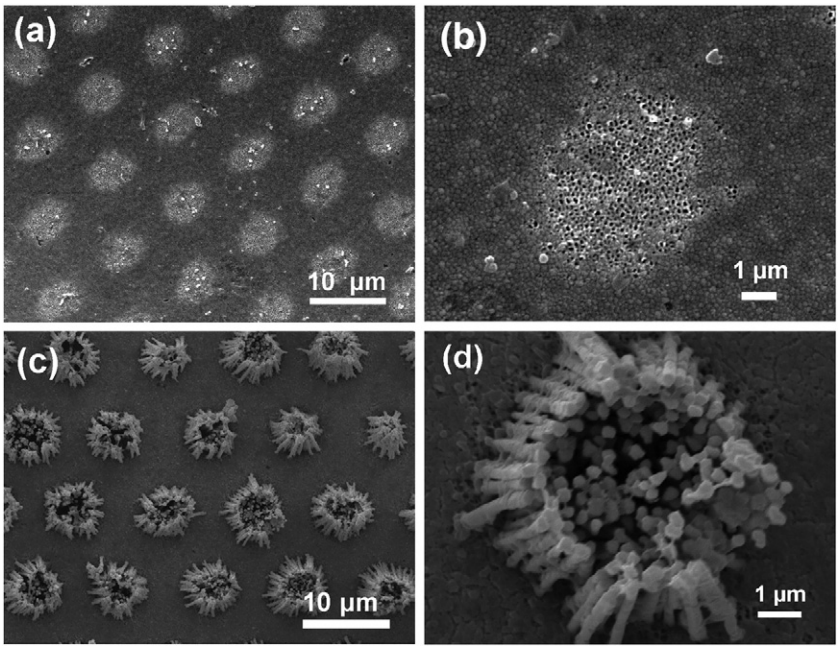

Fig. 1 – SEM images of patterned AAO templates and Cu nanowire arrays: (a) Patterned AAO template with circular patterns; (b) An enlarged pattern in panel (a); (c) SEM image of Cu nanowire arrays with circular patterns; and (d) An enlarged SEM image of the pattern in panel (c).

Many properties are dependent on the internal structure of Cu nanowires such as broken orientation. Cu nanowires are not broken along random surfaces when applied external force, but along some definite crystal faces. In our work, we found that Cu nanowires grow along the [220] direction, and broke along two facets of (202) and (022). From Fig. 3(b), it can be seen that both ends of the broken nanowires present regular cones. In addition, Cu nanowires present a good ductility when applied external force just like bulk metal. Bent Cu nanowire is shown in Fig. 3(e). From Fig. 3 (e), it can be seen that the bend perfectly keeps join, and is not broken.

The chemical composition of the nanowires was investigated using electron energy-loss spectroscopy (EELS). The typical EELS spectrum is shown in Fig. 4. The peaks around 930

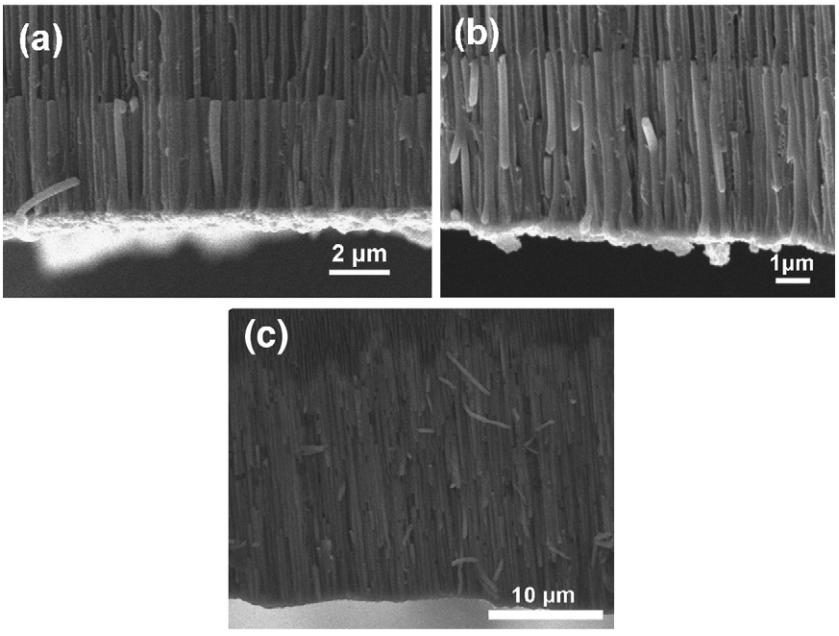

Fig. 2 – SEM images of the Cu nanowire with different deposition time: (a) 5 min; (b) 10 min; and (c) 20 min.

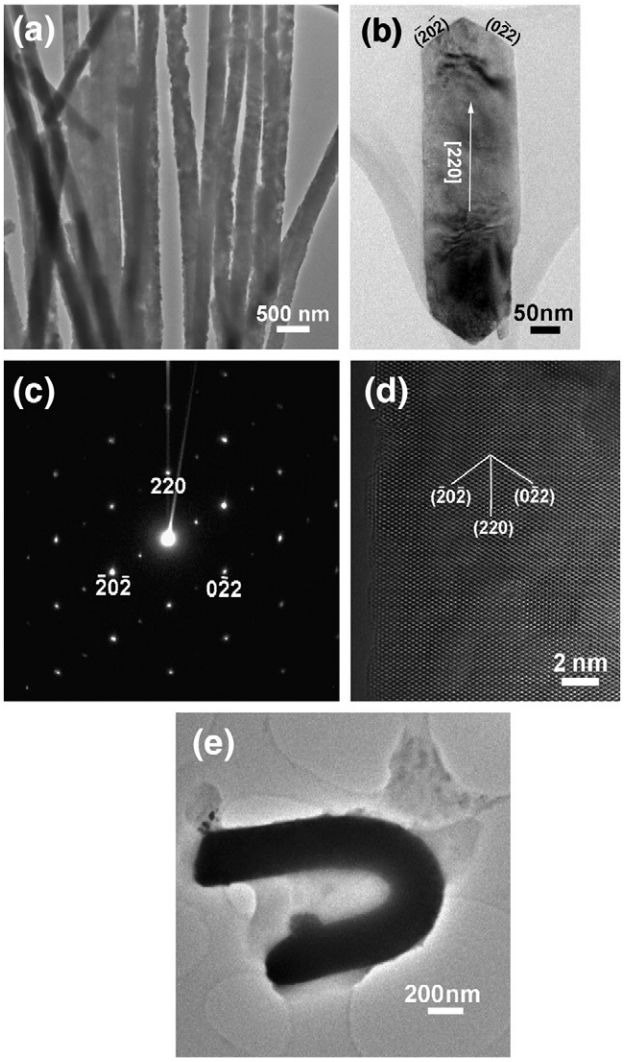

Fig. 3 – (a) TEM image of Cu nanowires; (b) TEM image of a randomly-selected Cu wire; (c) SAED pattern taken from (b); (d) HRTEM image of Cu nanowire shown in (b); and (e) TEM image of a bent nanowire.

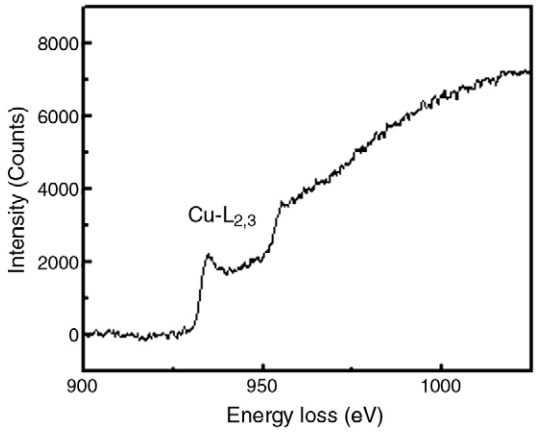

Fig. 4 – EELS spectrum of Cu nanowires.

and 950 eV correspond to Cu L_3 and L_2 edge. In addition, oxygen is not detected using EELS. This indicates that the nanowires are purely Cu.

4. Conclusions

In conclusion, we have fabricated regular and uniform patterned copper nanowire arrays into AAO using electrodeposition process by photolithography. The length of nanowires can be controlled by adjusting the deposition time. SEM images show the ordered Cu nanowire patterns. As single-crystal nanowires, the growth direction of nanowires is along [220]. Cu nanowires broke along surfaces of (202) and (022), and the regular cones were formed at the broken end of nanowires. The bent nanowires indicate that they have good mechanical properties when applied external forces. The EELS spectrum indicates that the nanowires are purely Cu.

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