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Synthesis of Copper Nanowires in Highly Ordered Nanoporous Anodic Alumina Template

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

In this paper, the fabrication of nanoporous anodic alumina template from aluminum foil has been demonstrated using hard anodization process. Copper nanowires arrays were fabricated using continuous and pulse electrodeposition technique into the porous alumina template. Copper nanowires are grown successfully in anodic alumina nano-template. The pulse deposition technique using 50 ms off-time showed better quality samples than those made with continuous deposition technique due to cooling of barrier layer during the off-time.

Keywords: Copper nanowire; nanoporous template; electrodeposition.

1. INTRODUCTION

Nanoporous anodic alumina template have attracted considerable attention due to their potential technological applications as a template for the fabrication of various functional nanostructures, such as nanowires [1], nanotubes [2], which have versatile applications in many fields [3]. The formation and dissolution of aluminum oxide during the electrochemical reaction can be expressed by Eq. (1) and Eq. (2), respectively.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 6H^+ + 6e^- \quad (1)$$

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$$Al_2O_3 + 6H^+ \longrightarrow 2Al^{3+} + 3H_2O \quad (2)$$

This dissolution mechanism is due to a weakening of the Al-O bonds in the oxide lattice occurring at the film-electrolyte interface. The electrical field is the main reason for the possibility of the ions to move through the barrier layer at all [4]. In recent years, there has been increasing interest in the fabrication of one-dimensional nanostructures because of their potential utilization in electronic, magnetic, optical, and micromechanical devices. Metallic nanowires are of great interest from a fundamental point of view as well as for future applications [5]. Metallic nanowires, rods, and dots can be used in a number of applications in micro and nanosystems, such as nanowire-interconnects (wires) [6], magnetic nanowire [7], on-chip magnetic storage devices (rods), on-chip Peltier cooling devices (wires and rods), and plasmonic waveguides (dots), SERS biosensors [8] and pore loading for drug delivery [9]. The ability to precisely prepare such structures on a large scale is an important goal of materials science. Many studies have focused on the fabrication of copper nanowires [10] because of their potential applications in the micro/nanoelectronics industry and, in particular, for interconnection in electronic circuits. Copper is one of the best metals in modern electronic technology. Template synthesis is considered to be most suitable and useful for growth of nanowires. Electrochemical deposition route is easy, low-cost as well as less cumbersome compared to other fabrication techniques, namely, pulsed laser deposition (PLD), vapour-liquid-solid (VLS) and chemical vapor deposition (CVD) [11-13]. Electrochemical cell used in electrodeposition of copper in pores of anodic alumina template was fabricated in our laboratory. Morphology of electrodeposited copper nanowires has been studied using scanning electron microscopy (SEM). The influence of the preparation conditions on the structure of the Cu nanowires is also discussed. The diameter of nanowires depends upon the pore size of template. Anodic alumina discs of 60 nm pore diameter were selected for this purpose [14].

2. EXPERIMENTAL DETAILS

Nanoporous alumina films are obtained by electrochemical oxidation of high-purity (>99.998%) aluminum foils. Prior to anodization, several cleaning treatments are employed. The substrate is first degreased in ethanol, followed by soft chemical polishing in acetone (CH_3COCH_3) and inside the ultrasonic bath for 10 minute, which removes the native oxide layer, being then rinsed in deionized water. In the work here presented, in the first step, the anodization voltage is 40 V during 30 min time, and then a hard anodization procedure is used in order to achieve the desired organization of pore structure. The hard anodization were performed at constant voltage of 109 V during 1 hr time. As electrolyte 0.05 M oxalic acid aqueous solution was used and the temperature was kept constant at 0ºC. Fig. 1 shows the SEM (XL30 / TMP, PHILIPS) image of nanoporous anodic alumina template with 60 nm in diameter. Also, an applied potential of 109 V gives the best conditions for the appearance of organized patterns, as it is clearly seen in the SEM micrograph.

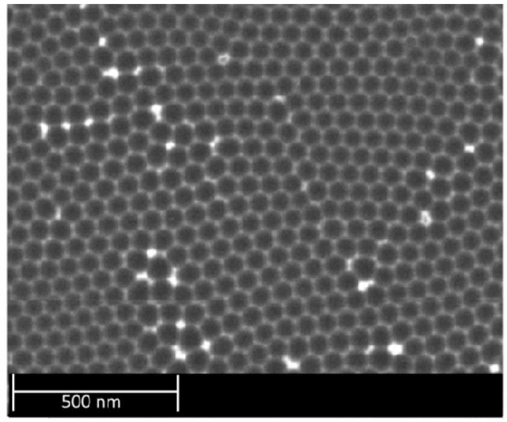

Fig. 1. SEM image of the nanoporous anodic alumina template

The electrodeposition was carried out in an organic bath that contains about 0.3 M of $CuSO_4.5H_2O$ and 40 g boric acid aqueous solution as the electrolyte and bath temperature is 30ºC. The nanoporous template was used as the cathode, and a platinum bar as the anode. Fig. 2 shows the sinusoidal voltage varied between 6 V(oxidation voltage) and 12 V (reduction voltage) with 50 ms time-off using programmable voltage source (R&S NGP 32).By the current curve and amount of the exchanged charges, we can control the deposition process. The maximum of reduction current is 35 mA and oxidation current is 21 mA. Hence, the average current of deposition in each pulse is 14 mA. The sample was kept immersed in 1 M NaOH for 3 hr time in a beaker to dissolve nanoporous alumina template. Copper nanowires were liberated from the host matrix so we washed in distilled water and dried in an oven at 500ºC for 30 min time. We can see the typical cross-sectional view of copper nanowires grown in alumina template (Fig. 4).Obviously the nano-scale template plays a critical role in the fabrication of Copper nanowires.

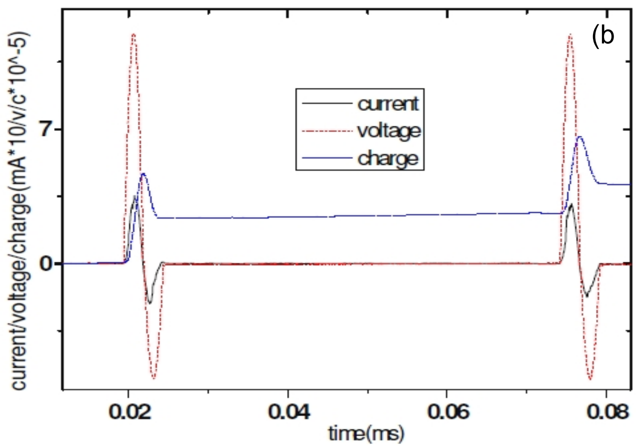

Fig. 2. a) View of the anodization and electrodeposition setup implemented in this work.b) Current/Voltage/Charge-time curves for electrodeposition process

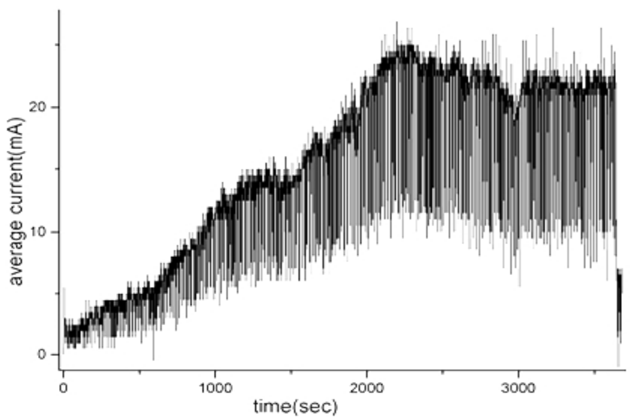

Fig. 3. The average current-time curve

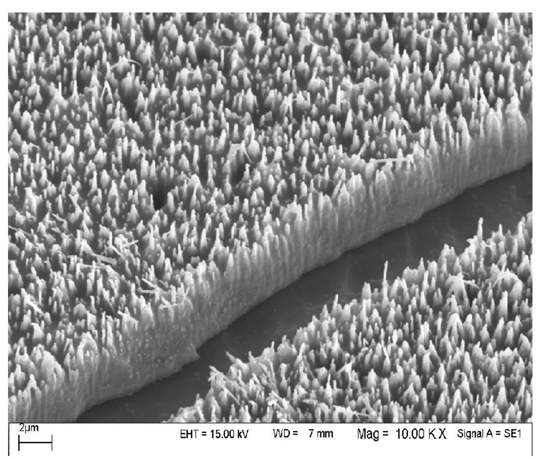

Fig. 4. The SEM images of copper nanowires in anodic alumina template

3. RESULTS AND DISCUSSION

The fabrication of nanoporous anodic alumina template from aluminum foil has been successfully demonstrated using hard anodization process. The structure and morphology of anodic films were greatly influenced by the anodization voltage and duration. In the modified anodization process, the best result was obtained using 40 V for the first anodization step, and then using 109 V for the second anodization step (Fig. 1).

Fig. 3 illustrates the average current-time curve. First, we see an initial increase of current is observed, with some fluctuations and a final levelling off at a plateau. This process takes two hours and the surface of sample changes to red color totally. When the oxidation and reduction current are equal, the net current is zero.

We reviewed other alternating voltages with 20, 50 and 100 mS time-off. The best deposition was obtained with a voltage pulse6-12 V with 50mS time-off. It means that the deposition performed uniformly while showing no damage in barrier layer. As regards this voltage, the net current is shown in Fig. 2b. As we investigated other voltages, intensive oscillations were see in the net current curve (Fig. 5a), which caused damage in the barrier layer. Because of the high current passing through the barrier layer, the layer was burned. The average current–time and current–voltage- charge curves shown in the Fig. 5. According to the Fig. 5b, although the applied voltage is high, the difference between reduction and oxidation current is very low and the amount of exchanged charges too low, which did not result in formation of extended and homogeneous Copper nanowires.

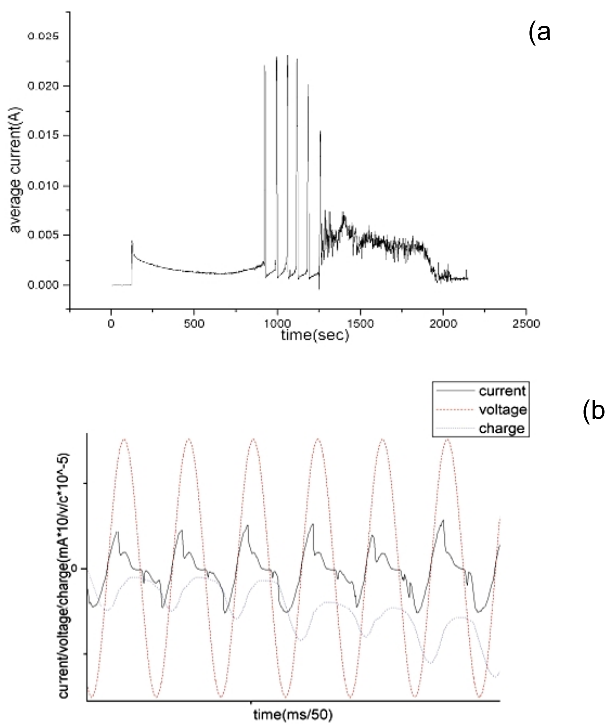

Fig. 5. a) The average current-time curve using continius sinusoidal voltage 15-15 V.b) The Current–voltage-Charge versus with time for this sample

4. CONCLUSION

Our investigations confirm that electrodeposition of copper nanowires in anodic alumina is possible. In this work we have identified the best operating conditions to perform this process. This is a comparatively inexpensive fabrication route that is promising for large scale industrial production

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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