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Formation of Cu and Ni Nanowires by Electrodeposition

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Abstract

In this work, the formation of Cu and Ni nanowires by electrodeposition inside alumina templates was analyzed. The deposits were performed from $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ and $\text{NiSO}_4 + \text{NiCl}_2 + \text{H}_3\text{BO}_3 + \text{H}_2\text{SO}_4$ solutions for the electrodeposition of Cu and Ni, respectively. To allow the cations deposition, sufficiently negative potentials were used. The experience time was ranged between 500s and 1h. After the metal electrodeposition, the sample was immersed in NaOH to dissolve the alumina membrane and to expose the generated deposit. The obtained nanostructures were characterized by SEM (scanning electron microscopy). Deposits were corresponded with nanowires having an average diameter of 300 nm. The length of the nanostructures was about 10 microns.

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Keywords: Nanowires; Electrodeposition; Aluminium oxide template; Copper; Nickel.

1. Introduction

Currently, the fabrication of nanostructured materials and the study of their properties have attracted considerable scientific and technological interest because the chemical, catalytic, mechanical, electrical, optical and magnetic properties of these materials can be very different from those at higher scales, depending strongly on the particle size. From the electrochemical standpoint, interest in nanostructured materials lies in the potential applications that such structures have for developing electrocatalyst materials, coatings, sensors, etc.

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A way to generate metal nanowires is based on the use of restrictive masks or templates, which have pores or cylindrical nano-voids, and can be obtained on different substrates. In these cases, the metal of interest is deposited into these pores by the use of different techniques, among them electrodeposition has attracted much interest (Bhushan, 2007; Cao and Liu 2008). Electrochemical techniques include deposition by direct and alternating current, cyclic voltammetry and potentiostatic pulse mode. Electrochemical growth is controllable in the direction perpendicular to the substrate surface and the length of the nanowire can be varied by controlling the electrodeposition time.

For assisted deposition in masks, the chemical stability and mechanical properties of the used mask, the diameter uniformity and density of the pores are very important. The aluminium oxide membrane is one of the materials that can be used for this purpose because it possesses many desirable characteristics, consisting of a film with uniform thickness, which has a regular hexagonal arrangement of parallel channels. These membranes have high mechanical and corrosion resistance, good chemical stability, low thermal and electrical conductivity, but high ionic conductivity (Masuda et al, 1997; Li et al, 1998; Hurtado et al, 2007).

Ni and its alloys are recognized as potential electrode materials to reduce the overpotential of the hydrogen evolution reaction (HER) at the industrial level (Chen et al, 2009) and by its magnetic properties, which are strongly influenced by the dimensions of the crystal (Rahman et al, 2003). On the other hand, Cu is known for its potential application in devices such as electrostatic dissipative and current collectors for batteries of Li (Inguanta et al, 2009).

The present work constitutes a first step, in which the synthesis of Cu and Ni uni-metal nanowires is studied, and then it continues with the formation of bimetallic nanostructures of the above metals. Specifically, in this paper the electrodeposition by potentiostatic pulse of uni-metal nanowires of Cu and Ni using alumina templates is analyzed.

2. Experimental

Commercial aluminium membranes were used as templates (WhatmanAnodisc 25). These membranes were glued with silver paint on a conductive substrate, so as to seal the base of the pores and enable the subsequent electrodeposition of the metals. After achieving the metal deposit, the membrane was dissolved using 5% NaOH solution.

Solutions used throughout the study were prepared from suprapure chemicals (Merck, Darmstadt) and fourfold distilled water. In the case of Cu nanowires, 0.6 M CuSO_4 + 5 mM H_2SO_4 solution was used. For deposition of Ni nanostructures, an electrolyte composed of 165 g/L NiSO_4 + 22.5 g/L NiCl_2 + 37 g/L H_3BO_3 , adjusted to pH = 4 with H_2SO_4 , was used.

Conventional electrochemical studies were performed in a standard three-electrode electrochemical cells. The counter electrode was a platinum sheet (1 cm^2) and the reference electrode was a $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ saturated electrode (SSE). All potentials in this study are referred to the SSE. The measurements were carried out with an EG&G Princeton Applied Research Model 273A potentiostat-galvanostat. SEM studies were carried out using an EVO 40 XVP (LEO) microscope, with an accelerating voltage of 20 or 30 KeV.

3. Results and Discussion

3.1 Characterization of the alumina membrane

Fig. 1 shows SEM images of the structure of the aluminium oxide membrane used as template. The mask consists of an array of highly ordered hexagonal of parallel channels (Fig. 1a). The pore diameter is between 60 and 75 nm, while the wall thickness is on the order of 30 - 40 nm. It can be seen in the typical side-view micrograph (Fig. 1b), that the membrane consists of a film of uniform thickness of about 60 μm . Subsequent use of this membrane as a template for the growth of nanowires allow to expect that the length of these nanostructures is proportional, not higher than the aforementioned thickness.

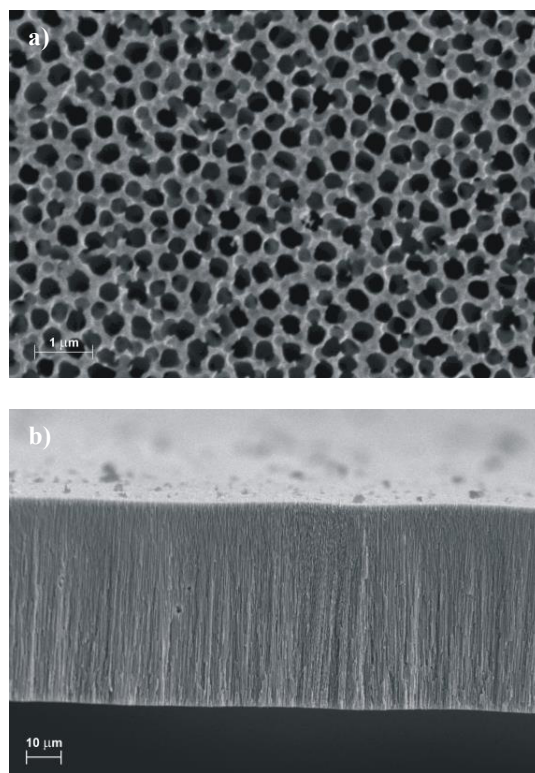


Fig. 1. Characterization of the alumina membrane: a) top view, b) lateral view.

3.2 Cu nanowire formation

The formation of Cu nanowires by electrodeposition was performed by applying a potentiostatic step at $E = -0.5$ V during 500 s. Afterwards, the electrode was immersed in the 5% NaOH solution for 10 min in order to partially remove the membrane and to expose the metal deposit.

Fig. 2 shows different magnification SEM images of the generated Cu deposit. At low magnification (Fig. 2.a) dense clusters of nanostructures (bundles) with a regular distribution are seen, indicating the difficulty for long Cu nanowires to be self-standing. These clusters are formed due to electrostatic attractions that minimize the free energy of the system (Chen et al, 2009; Xu et al, 2006). At higher magnification (Fig. 2.b and c), it is possible to see that the deposit perfectly corresponds to nanowires which have variable lengths, being the highest in the order of 10 μm. Moreover, it can be seen that there is uniformity in diameter with a typical thickness of 300 nm.

3.3 Ni nanowire formation

Following a procedure analogous to that reported in the previous section, Ni deposit into the pores of alumina membranes was performed. In this case, the potentiostatic step was applied at $E = -0.9$ V for 1 h. Afterwards, the electrode was immersed in the NaOH solution to remove part of the membrane and to expose the Ni deposit. As can be seen in Fig. 3, Ni nanowires are distributed across the surface, have random orientations and collapse. Again it is clear that the deposit corresponds with nanowires, which have variable lengths, being the largest in the order of 10 μm. The diameter is similar for all nanostructures being 300 nm.

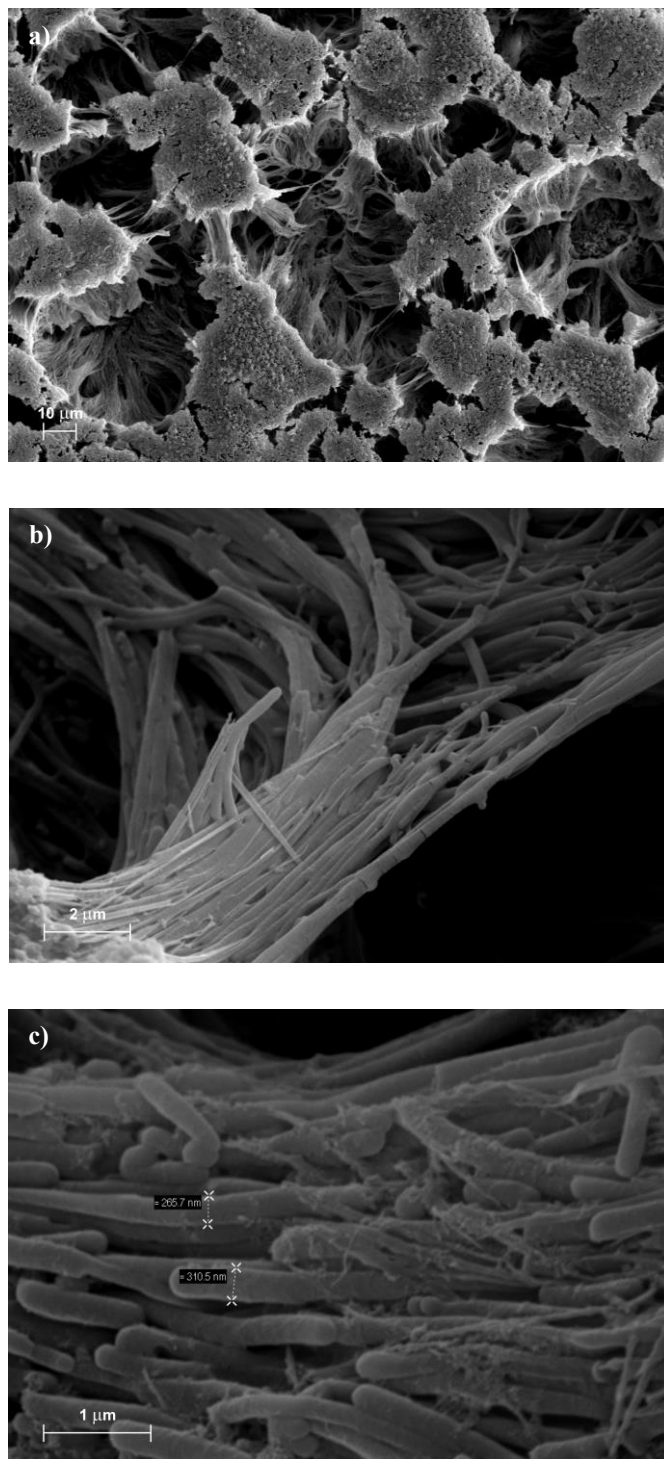


Fig. 2. SEM images of the Cu deposit obtained at: a) 15000x, b) 20000x, c) 50000x.

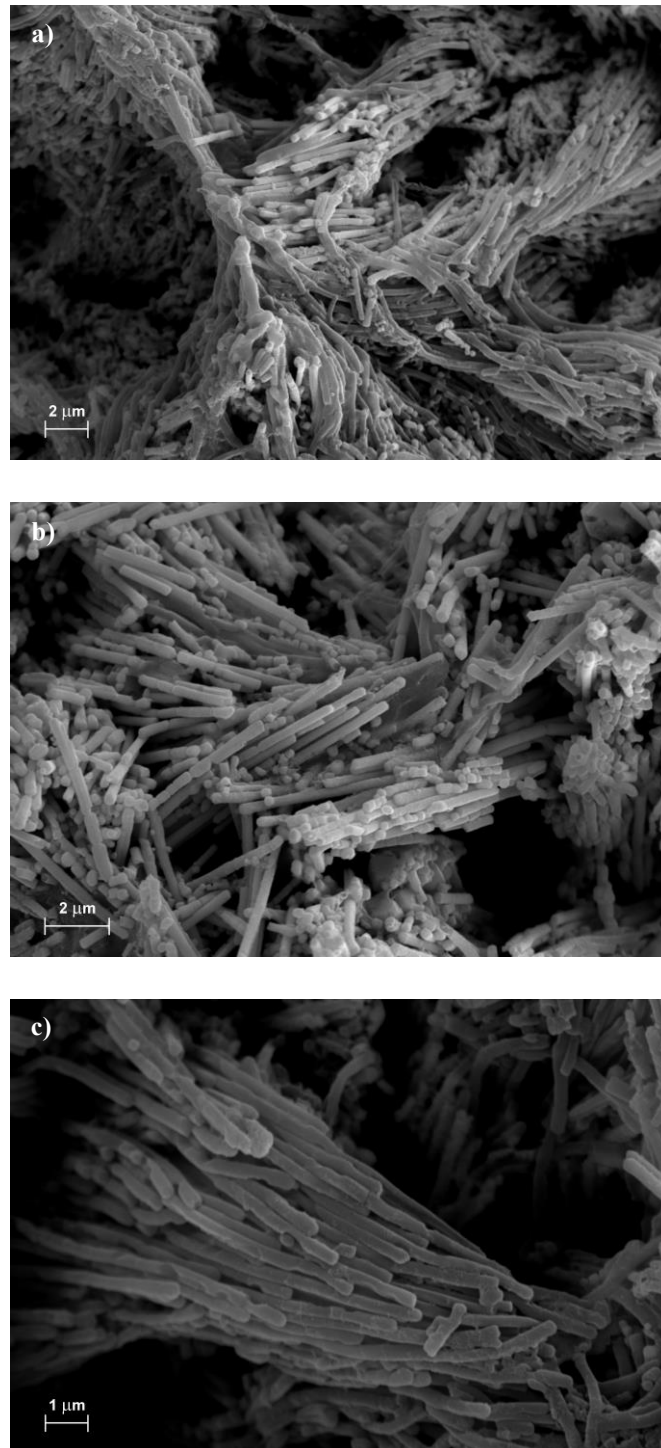


Fig. 3. SEM images of the Ni deposit obtained at: a) 15000x, b) 20000x, c) 50000x.

4. Conclusions

In this work, the electrodeposition of Cu and Ni, inside the pores present in alumina commercial membranes has been obtained by potentiostatic pulse mode. These masks were previously characterized by SEM, showing the typical arrangement of pores, quasi-hexagonal and relatively uniform, which is necessary for the subsequent filling of the pores by electrodeposition.

The SEM images revealed that the obtained nanostructures correspond with nanowires, which have an average diameter of 300 nm for both metals. Nanostructures length is variable, being up to 10 μm , not exceeding the thickness of the alumina membrane.

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