

FABRICATION OF ALUMINUM OXIDE TEMPLATES AND SYNTHESIS OF Ni NANOWIRES WITHIN PORES

A.Kh. KARIMOVA

Institute of Physics, National Academy of Sciences of Azerbaijan

AZ -1143 , H. Javid, 131, Baku, Azerbaijan

e-mail: ayselkerimova00@mail.ru

The aim of the paper is to describe the applications of AAO as a template in metal nanostructures formation and to present the experimental results obtained by us in this field. The basic mechanism of the processes of both anodic oxidation of aluminum as well as electrochemical metal (Ni) deposition in AAO were described. The influence of oxidation parameters on the AAO structure was discussed as well.

Keywords: anodic oxidation of aluminum (AAO), metal nanostructures, Nickel.

PACS: 81.15Cd, 61.05.fg

INTRODUCTION

Metals in a state of high dispersion currently play an important role in technology. Their chemical and physical macroscopic properties, such as the rate of their reaction with other substances, colours and mechanical properties are significantly different from the bulk metals. Fundamental research and technology development over the last decade have resulted in wider use and implementation of metal-containing materials in a state of high dispersion into the industrial practice.

The fabrication of nanoscale structures has attracted much interest recently owing to their potential use in highdensity magnetic memories,[1,2] single-electron devices,[3] nanoelectrodes for the direct deposition of nanoparticles from the gas phase,[4] and optical media [5]. The production of nanostructures based on hexagonally arranged porous alumina as a mask or matrix structure is cheaper than that based on traditional methods like nanoscaling using electron beam lithography.[7] To use such an alumina template for new applications of nanostructures, the pores have to be filled with a

conducting or semiconducting material, for example via electrochemical deposition. In contrast to other deposition methods like chemical vapor deposition (CVD), during electrochemical deposition the growth of nanowires starts at the pore tips and continues in the pore direction from the pore bottom to the pore opening.

EXPERIMENTAL AND RESULTS

1. Fabrication of aluminum oxide templates

The hexagonally ordered porous alumina membranes have been prepared via a two-step anodization process, which is described in detail elsewhere [8,9].

The electrochemical anodization of the Al was conducted in a simple homemade two-electrode cell which was provided with electrical motor for intensive stirring of the solution. For fabrication of AAO templates we used 0.4 M oxalic acid solution. The process was conducted under constant cell potential of 40 V at 3–5°C under intensive stirring of solution for 30 min – 2 hour depending on thickness of Al layer.

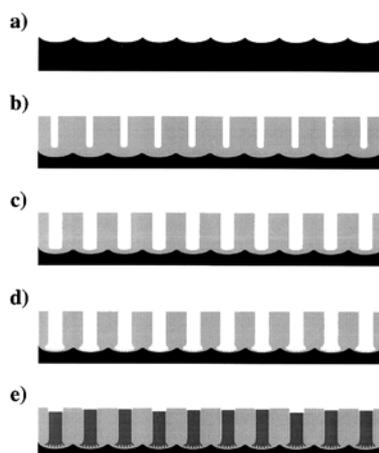


Fig. 1. Schematic diagram describing the fabrication of a highly ordered porous alumina matrix and the preparative steps necessary for the subsequent filling of the structure. a) The Al substrate was pre-structured by anodizing for a long period of time and removing the oxide. b) A highly ordered alumina pore structure was obtained in a second anodization step. c),d) pore widening and the barrier layer etching process. e) Electrodeposition of nickel in the pores.

A first longduration anodization causes the formation of channel-arrays with a high aspect ratio and a regular pore arrangements via self-organization [9]. After complete dissolution of the oxide structure (Fig. 1a), the surface of the aluminum substrate keeps the regular hexagonal texture of the self-organized pore tips, which act as a self-assembled mask for a second anodization process. After a second anodization for 2 h, an ordered nanopore array (Fig. 1b) is obtained with straight pores from top to bottom and a thickness of typically 1 mm. The parameters are 0.4 M oxalic acid, $U = 40$ V, and $T = 2^{\circ}\text{C}$. During the course of anodization, the oxide dissolution and formation rate are in equilibrium at the barrier layer, thus the anode current and thickness of the barrier layer remains stable. The measured current is approximately proportional to the anodization voltage under these equilibrium conditions. The interpore distance (110nm) and the thickness of the barrier layer (1mm) are proportional to the applied cell potential.

The barrier layer is thinned by chemical pore widening and by current limited anodization steps.

The pore widening and the barrierlayer etching were performed in a 5% orthophosphoric acid solution at 60°C (Fig. 1c,d).

The composite systems AAO–metal can be formed by inexpensive and simple method of electrochemical metal deposition. The first attempts of metals electrodeposition inside the pores of the anodic oxide layer on aluminum AAO were associated with the development of electrochemical technology. Metal nanoparticles can be deposited into the pores of Al_2O_3 layer by transferring a freshly prepared sample to the solution of the salt of easily reducible metal and then use of cathodic polarization.

The electrodeposition of nickel was performed in temperature 25°C in the following solutions: 300 g/L $\text{NiSO}_4 \times 6\text{H}_2\text{O}$, 45 g/L $\text{NiCl}_2 \times 6\text{H}_2\text{O}$, 45 g/L H_3BO_3 , pH 4.5 (Fig. 1e).

SEM images of AAO (Fig.2) confirmed the creation of an array of highly ordered hexagonal cell structures with pores about 40-60 nm in diameter.

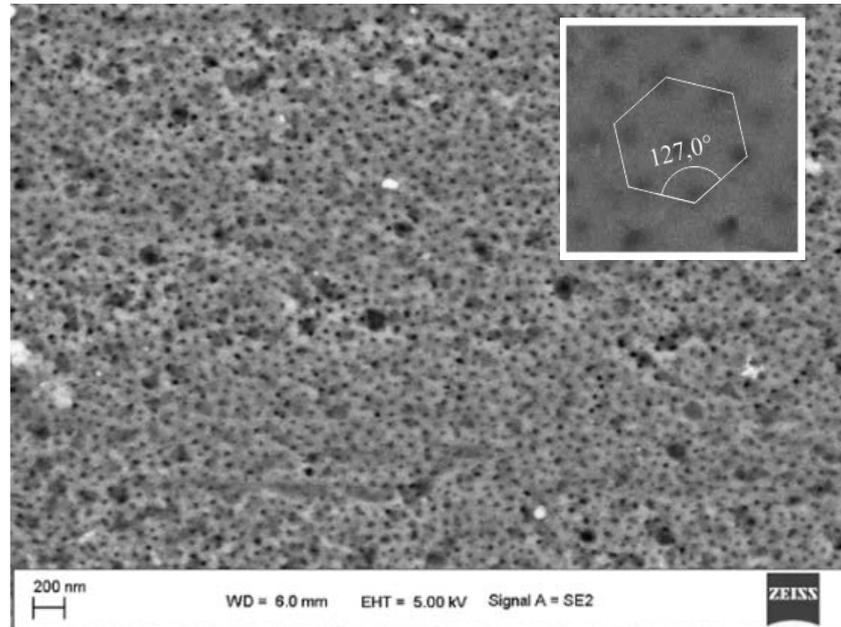


Fig.2. The SEM image of the AAO film (left) and its an enlarged fragment (right).

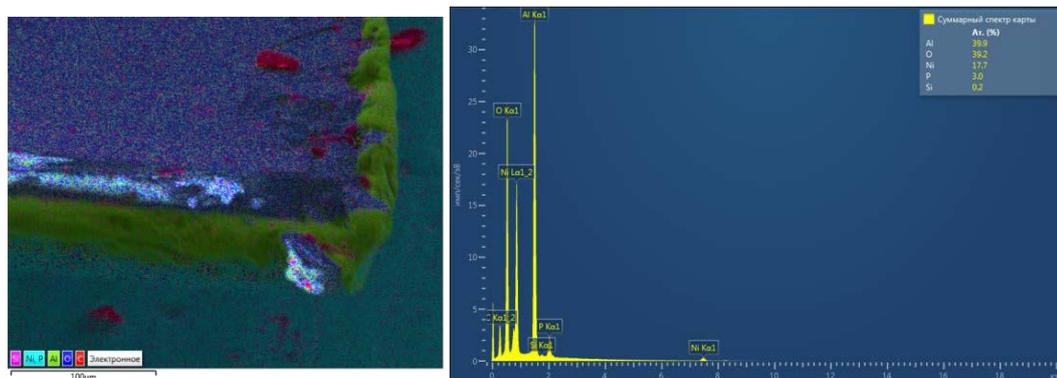


Fig.3. EDX Image of Multi-layer and spectrum data of the AAO thin film.

Figure 3 displays a EDX spectrum (with a 5% accuracy of the entire structure) of Multi-layer and spectrum data of the AAO thin film. The values of the measured atom composition of Al, O, and certain impurities including Ni, P and Si are shown inset table in the figure. As can be seen from both the EDX spectrum and the inset table, the atomic ratio of aluminium to oxygen in the film is typically 1:1 (Al = 39.9%, O = 39.2 at%).

2. Synthesis of Ni nanowires within pores

In figure 4 shown digital photographs of the electrochemical deposited Ni into AAO sample and experimental process of electrodeposition of Ni. The mixture is very similar to the less concentrated electrolytes that were used earlier for the metal electrodeposition into porous alumina at room temperature.



Fig. 4. View of electrochemical cell taken during deposition of Ni (left) and sample upon deposition (right).

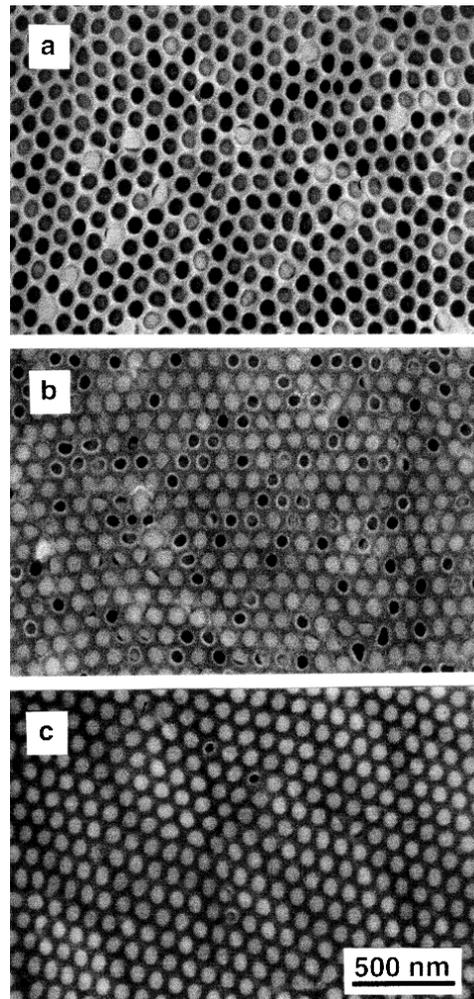


Fig. 5. Top view SEM micrographs of a nickel-filled alumina membrane.

The filled alumina samples were examined by scanning electron microscopy (SEM) to determine the degree of pore filling and the extension of the nickel nanowires. By thinning the filled porous alumina from the top, nanowires ending below the matrix surface became observable for SEM investigation. Thinning the sample by a focused ion beam yielded a 100 nm deep and funnel-shaped excavation in the structure. The depth of the hole is calculated from the thinning time. As micrographs of the filled pores are taken at different depths beneath the initial membrane surface, an overview was obtained about the extent of nanowires along the pore axis and the length distribution of the nanowires was evaluated. Before the SEM investigations, a thin silver film of a few nanometers thickness was sputtered onto the filled structure to enhance the surface conductivity for the SEM observations. Figure 5 shows top view SEM micrographs of a highly ordered alumina pore structure filled with nickel. For electrodeposition in the pores of this sample, a delay time $t_{\text{off}} = 60\text{sec}$ was chosen. The measured pore diameter is between 45 and 55 nm and the pore distance is 110 nm. Figure 5a shows a region outside the thinned area and in some pores the nickel nanowires have grown up to the pore opening. Figure 5b shows a micrograph of an area

about 50 nm below the initial surface. Finally, the lowest point of the excavation is shown (Fig. 5c), where a layer of 100 nm has been removed from the 1 mm thick membrane.

RESULT AND CONCLUSION

As a result, we obtained the best nickel filling in the AAO membranes for t of about 5 min. In summary, a highly efficient method for deposition of nickel into ordered nanochannels of porous alumina has been presented. By thinning the barrier layer homogeneously, the porous structure could be kept on the aluminum substrate for the whole process. Our approach to the fabrication of a highly ordered metal nanowire array is inexpensive and very flexible with respect to the size and thickness of the pore structure. In addition, the thickness of the barrier layer and the pore diameter could in principle be varied independently of each other. The use of electrodeposition is well-suited for a uniform deposition in the pores of porous alumina structures, as demonstrated for nickel electrodeposition. Nearly 100% of the pores were filled with nanocrystalline nickel and only a very small fluctuation in growth rate of these nanowires was observed.

-
- [1] *D. Al Mawlawi, N. Coombs, M. Moskovits. J. Appl. Phys.* 1991, 70, 4421.
 - [2] *F. Li, R. M. Metzger, W. D. Doyle. IEEE Trans. Magn.* 1997, 33, 3715.
 - [3] *A.A. Tager, J.M. Xu, M. Moskovits. Phys. Rev. B* 1997, 55, 4530.
 - [4] *F.E. Kruis, K. Nielsch, H. Fissan, B. Rellinghaus, E. F. Wasserman. Appl. Phys. Lett.* 1998, 73, 547.
 - [5] *E. Wäckelgård. J. Phys.: Cond. Matter* 1996, 8, 5125.
 - [6] *H. Masuda, K. Fukuda. Science* 1995, 268, 1466.
 - [7] *D. Routkevitch, A. A. Tager, J. Haruyama, D. Al Mawlawi, M. Moskovits, J. M. Xu. IEEE Trans. Electron Devices* 1996, 43, 1646.
 - [8] *H. Masuda, K. Yada, A. Osaka. Jpn. J. Appl. Phys.* 1998, 37, L 1340.
 - [9] *A.P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele. Adv. Mater.* 1999, 11, 483.

Received: 01.11.2022