CHARACTERIZATION OF ORDERED METAL GOLD NANOWIRES FABRICATION PROPERTY VIA HEXAGOAN ORDERED NANOPOROUS ALUMINA

Radim HRDY, Hana KYNCLLOVA, Jana DRBOHLAVOVA, Jana CHOMOUCKA, Jan PRASEK, Dmitry SOLOVEI, Petra BUSINOVA, Jan PEKAREK, Jaromír HUBALEK

Brno University of Technology, Brno, Czech Republic, EU, hrdy@fee.vutbr.cz

Abstract
The purpose of this work is to characterize the nanostructured electrochemical sensors composed of ordered gold nanowires array. Noble metals, especially, gold, are very suitable for biological applications in the field of fragment DNA detection. In this case, the EIS (electrochemical impedance spectroscopy) is usually used for surface characterization and following DNA detection. Moreover, the EIS has showed the high dependence between the rate of nanomachining and active electrochemical surface area, which is directly related to the level of sensitivity. The present paper also deals with the fabrication of nanoporous anodic aluminium oxide (AAO) for thin film applications. Namely, AAO has been used as a template for the growth of various functional nanomaterials and as a scaffold for nanodevices and systems. A new electrochemical approach of pore opening from AAO bottom, i.e. selective perforation of oxide barrier on AAO bottom using re-anodization technique was developed. The skip phasing of oxide barriers wet etching is the significant advantage of re-anodization compared to other techniques for AAO, since it does not cause the widening of the naturally grown pore size. The dissolution of oxide barrier is carried out in the same acid as the anodization process and the perforation is controlled only by current density and applied voltage.

Keywords: nanoporous anodic alumina, electro deposition, oxide barrier, metal nanowires

1. INTRODUCTION
Recently, porous AAO membranes have attracted significant interest due to the simple synthesis and broad exploitation in nanoscience studies. Namely, the nanoporous AAO has been the most often used template for electrodeposition of metallic conductive or semiconductive nanowires and nanotubes or as scaffold for nanoelectronical applications such as electrochemical or gas sensors [1, 2]. AAO thin films on metal substrates (see Fig.1 a-d) have monodisperse pores with diameters of a few tens of nanometers and with lengths of micrometers. The pores are formed at specific anodization conditions in hexagonal close-packed arrays with interpore spacing from 10 nm to 400 nm [3]. The pores in AAO bottom are isolated by oxide barrier (Fig. 1.c). In order to incorporate nanoparticles into the pores of AAO template, this oxide barrier must be removed to reach the electrical conductive layer (metallic or polymer), which is deposited below the template [4, 5].

The recent works reported on several methods for oxide barrier removal, but many of them were based on wet etching, which causes enlargement of nanopores or collapse of template structures [6]. In some cases, the intermetallic layer, such as a thin film of Ti, Ta, W and Nb, between electric metal contact (metallic underlayer) and aluminium layer have been deposited. These metals have higher ionic conductivity than aluminum and therefore, they are able to perforate the barrier during the anodization process [7-9]. When all aluminum is consumed, the intermetallic layer starts to oxidize. In consequence, small nanodots of TiO₂, Ta₂O₅, WO₃ or Nb₂O₅ can penetrate oxide barrier and grow through the pores (Fig 1.e, f). These nanodots can be eventually used further as base for various nanowires growth.
Fig 1 - Schematic diagram of porous alumina growth. The porous alumina starts to grow on thin electrode and the pores are spontaneously formed to a hexagonal structure (a). The aluminum layer is gradually consumed and the pores grow (b) to the point, where the oxide barrier on aluminum/aluminum oxide interface on bottom of alumina template touch based metal electrodes (c). At this moment, the down step voltage is applied; the barrier is thinned and subsequently dissolved after the complete aluminum consumption (d). The next steps are following: electrodeposition of metal through the pores (e), aluminum template dissolution and exposure of nanowires (nanocolumns) (f).

If the creation of nanostructures directly on metallic underlayer is required (i.e., the direct ohmic contact between metal underlayer and final nanowires), these nanodots have to be selectively removed by chemical etching in order to open the nanopores without etching of porous AAO. However, this process of penetrating oxides removal (e.g., TiO₂, Ta₂O₅, WO₃ and Nb₂O₅) has not been reported in earlier studies, because the mentioned oxide nanoparticles are very stable in aqueous solutions. Another frequent difficulty during penetrating oxides removal is the delaminating of porous AAO on etched metal/metal oxide interface due to the decrease of physical contact.

Electrochemical high resolutions detection of heavy metals ions or DNA fragments can be improved by nanomechanized surface of electrochemical sensors [10]. The main idea of using nanoparticles is enlarging the active surface of working electrodes and gaining some special new abilities such as higher selectivity and signal stability. However, the simply growing metal nanowires on electrodes are not always the right way to obtain the improved system. According to previous papers, it is known the long nanowires covered surface has not as improved parameter of detection as flat electrodes without nanoparticles. The responses of nanomachined sensors to analyst are usually worse which is caused by the interactions with ions only with the top part of nanowires. One of the solutions is the change of nanowires geometry and concurrently the parameters and form of diffusion layer.

This work describes the simple use of technique for preparation of straight through thin film template with strong adhesion on electrodes. In particular, improvement of in situ electrochemical method of AAO barrier dissolution is discussed. Subsequently, AAO template was used for gold nanowires fabrication in order to increase the active surface of thin film electrochemical microsensors on silicon wafer.

2. EXPERIMENTAL

2.1 Materials
Titanium (purity 99.999%), aluminium (purity 99.999%, Goodfellow, GB), oxalic acid (C₂H₂O₄, 99.5%, p.Penta, Czech Republic), potassium sulphate (K₂SO₄, p.Lachema, Neratovice, Czech Republic), potassium dicyanoaurate (K[Au(CN)₂], 68%, Safina, Czech Republic), boric acid (H₃BO₃, p.Penta, Czech Republic), phosphoric acid (H₃PO₄, 98%, p.a., Penta, Czech Republic), potassium ferricyanide (K₃[Fe(CN)₆], 99%, asc, Sigma Aldrich, USA), potassium chloride (KCl, 99.95%, p.a., Penta, Czech Republic), were used as
purchased without any purification. Deionised water was obtained from Millipore RG system MiliQ (Millipore Corp., USA, 18.2 MΩ).

2.2 Fabrication of Nanostructures

The micro system, which represents a small comb-like electrochemical sensor was prepared by the deposition of gold microstructures on n-type silicon wafer coated with silicon oxide and finally with titanium buffer layer. Subsequently, a thin aluminum film (1 µm) was deposited on electrode surface using thermal evaporation. The thin porous AAO template was obtained by one-step anodization process under constant voltage of 40 V in 0.3 M oxalic acid at 17 °C [11]. For successful management of the process, an asymmetrical anodization current signal with amplitudes of $I_{\text{min}} = 2 \text{ mA.cm}^{-2}$ was applied with the counter electrode gold electrode (see Fig.2) [12]. The electrolyte was intensively stirred in a pumping system (80 mL.min$^{-1}$).

![Fig 2 - Typical current versus time course during templates formation. The detail shows the down step phase of bottom oxide barrier thinning.](image)

The anodization process ran to the point, where the current density started to decrease. At this moment, the equilibrium process of aluminum ions exchange through the barrier, was slow down, which indicated that the oxide barrier touched the underlaying electrode. Consequently, a down step voltage (0.5 V.s$^{-1}$) was applied and the oxide barrier was thinned. At this time, a major part of remaining aluminium between barriers was consumed and the oxide barrier started to dissolve. The continuous application of voltage caused the complete dissolution of the oxide barrier, which lasted approx.15 sec.

Concerning the next application of the open AAO, the template was used for the electrodeposition of nanowires. The electrolyte used for gold nanostructure growth was composed of 6 g.L$^{-1}$ of K[Au(CN)$_2$] and 2.32 g.L$^{-1}$ of H$_3$BO$_3$. The current density for Au nanostructures deposition related to the total area of nanopores was usually 0.25 mA.cm$^{-2}$. The optimal deposition time was 10 seconds. The temperature of plating bath was approx. 50 °C. In the next phase, the filled AAO template was dissolved in 5% H$_3$PO$_4$. The surface morphology and homogeneity of the fabricated samples were investigated with MIRA II Tescan field scanning electronic microscope operated at 1–30 keV in high vacuum mode.

2.3 Sensors measurement

Measuring system Metrohm µAutolab III with FRA2 module was used for the EIS characterizations of sensors. Samples were measured in 10 ml of potassic sulfate of various concentrations (0.1 µM – 10 mM).
The frequency range was set on 1 Hz – 1 MHz and the amplitude was 60 mV. A three electrodes cell with Pt auxiliary electrode and Ag/AgCl/3M KCl the reference electrode were used for the measurements.

3. RESULTS AND DISCUSSIONS

The method of AAO thinning was firstly reported by Santos et al. [13] in the form of thick alumina foil, nevertheless, no papers on alumina thinning in the form of thin films have been presented yet. Therefore we developed a new simple method for thinning of AAO directly on silicon wafers, based on voltage control repulsive dissolution of oxide barrier. The following method combines the aforesaid procedure and the fact that the bubbles of gaseous oxygen are evolved during anodization at the point when the underlaying metal electrode is reached. Usually, the nanoporous AAO is delaminated from the electrode when the cracks appear on its surface which results in the electrode exposure to the electrolyte. Hence, the formed bubbles can violate the adhesion on metal/oxide interface due to strong electrolysis. Therefore, the process must be controlled in order to avoid complete dissolution of alumina template on metal/oxide interface and its delamination from underlaying electrode.

In our case, the oxide barrier was thinned to the point where it touched the electrode and the thickness of oxide was so small that electrolysis of water was unavoidable. The gaseous oxygen catalyzed the dissolution of alumina on the interface and consequently caused the pores opening. The template was prepared without delaminating effect and widening of pore diameters. The gold nanowires array deposited through this alumina template on an electro-conducting metal layer had the same geometrical parameters as its pores. Figure 3.a, b show a typical example of fabricated porous structure. The final diameter of pores was in the range of 30–80 nm with an interpore distance of 40–80 nm. As can be seen in Fig. 3. b, the top part of nanoporous structure is not homogenous, especially in the right top side. This inhomogeneity generally appears when one step anodization process is used. Since the homogeneity ratio grows towards the bottom side of template, this upper inhomogeneity has no effect on final of nanowires, because their deposition start at the bottom side of template, where the homogeneity is nearly perfect (close to hexagonal ordering). The obtained nanowires have usually, shorter length than that of nanopores. The original porous structure can be seen in Fig. 3. a, b. and gold nanowires in Fig. 3. c, d with high resolution detail of base of nanowires, as well. These cross sections show the gold nanowires after nanoporous template dissolution, especially Fig. 3.c., where connections between metal base and nanowires are more evident. The array of nanowires is integrated on gold electrode surface and can be used for further modification or application in microsystems.

![Fig 3 - Nanoporous structures (top view) (a), cross section of nanoporous templates with dissolved oxide barrier (b), cross section of template with deposited Au nanowires (c) and detail of deposited structures (d).](image-url)
importance. Both of nanomachined samples have a similar diffusion part, which means the same angle in comparison with surface without nanoparticles. The angle close to 90° indicates the added capacitance of a nanolayer. However, the remaining part of the long deposited nanowires surface is very similar as the flat surface. The value of double layer capacity and charge transfer resistance are equal. On the other hand, the short nanorods have ten times less impedance than the rest of them that has shown the fact that the real electrochemical surface area has increased.

4. CONCLUSION
We believe that the reported method of thin nanoporous alumina template synthesis brings several benefits. The first one is a very simple preparation of nanowire-based vertically aligned structures directly on conductive electrode. The second is the elimination of intermetallic layers deposition for oxide barrier perforation or additional wet etching with ineligible template geometrical changes. And the last one is the suitable usage of the method for thin film applications such as sensors and microchips for subsequent development of lab on chip equipment. The important fact of the sensors area increasing has been shown. The direct proportion of nanowire length and area enlarging has limits. The simple deposition of nanowires on electrodes does not cause in ceasing the active electrochemical area

ACKNOWLEDGEMENTS:
This research was supported by the Grand Agency of Czech Republic GACR P102/09/1601 (IMINAS), GACR P102/11/1068 (NanoBioTeCell), SIX CZ.1.05/2.1.00/03.0072 and CEITEC CZ.1.05/1.1.00/02.0068

LITERATURE