VERTICALLY ALIGNED NANOSTRUCTURES FOR ELECTROCHEMICAL SENSORS

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Abstract

The creation of an indented surface is essential for an effective enlargement of the active area of microsensors. The enlargement of electrodes leads to a significant increase in the microsensor sensitivity and signal response. The enlargement can be accomplished in a number of ways but the most simple and low-cost technology is the template-based electrodeposition method. The method consists of two phases. At first, the Al₂O₃ template is made by anodic oxidation, which the nanostructures are formed through and then the nanostructure formation by galvanic and chemical deposition.

Electrodeposition repose on the metal deposition on the conductive substrate (representing cathode) leaving the insulant Al₂O₃ template. After that the template dissolved in a suitable dissolvent (e.g. NaOH) the nanostructured surface is obtained.

1. INTRODUCTION

Nanostructures have attracted increasing attention because of their potential use in a wide range of technological applications, and also because of their novel properties. Fabrication of aligned arrays of nanostructures can be advantageous in any application in which the surface area is considered to be a crucial parameter. Microsensors, especially electrochemical, are expected to achieve higher sensitivity if their sensing electrodes are enlarged. Thus, fabrication of nanostructures on a surface results in enlarging the surface area and improving some qualitative properties of various devices. Besides, nanostructures are also considered promising because of their unique properties [1-2].

Nanotubes or nanowires can be created in various ways such as electrochemical step edge decoration at graphite surfaces, lithography, etc. One of the generally inexpensive methods is the template-based method which enables to achieve smaller dimensions of nanostructures and deposition of various materials. The template-based method consists of two steps. At first, a non-conductive porous alumina template has to be created and then a metal is deposited into the porous template which is coated by a metal layer on one of its sides or placed on a conductive substrate. After dissolving the template, nanostructures are obtained [2-3]. The process is illustrated in Fig. 1.

Either nanotubes or nanowires (nanorods) can be produced by this method. The type of the structure can be influenced mainly by ultrasound waves, the nanopores diameter, and the pH. The width and the density of created nanostructures are given by the template. The length of nanostructures depends on amount of deposited metal, thus the required length of nanostructures can be achieved if the current density and the time of electrodeposition are adequate [3].
The alumina templates are created by anodic oxidation (anodization) of aluminium under specific conditions, such as anodizing voltage, temperature, composition and concentration of used electrolyte, etc., which favour the self-organization ability of the growing alumina. Aluminium, which is used for anodization, can be either in the form of an aluminium foil or a thin film deposited on a conductive substrate. In order for the surface of the aluminium foil to be smooth enough, the aluminium foil has to be annealed and electrochemically polished prior to the anodization process. Anodization of the aluminium foil takes longer time than anodization of a thin aluminium film and remaining aluminium needs to be etched away. In order for the nanopores to be hexagonally arrayed, two-step anodization should be applied.

![Nanostructures fabrication process](image)

**Fig. 1:** Nanostructures fabrication process

The two-step anodization consists of short anodization, followed by etching of the produced Al₂O₃ structure, and another anodization during which the ordered structure is formed. The resulting alumina layer is comprised of hexagonally ordered nanopore arrays, perpendicular to the surface. The diameters of the nanopores and their distribution are proportional to the anodizing voltage. There is an alumina barrier layer at the bottom of the nanopores which can be selectively etched, although the nanopores are enlarged too. Not only straight nanopores can be prepared by described method. Nanoporous structures with other shapes may be prepared as well by adjusting certain anodization conditions, such as electrolyte composition, using various anodizing voltages and repeating the anodization processes. The created nanopores can be tortuous, conical, joined into larger nanopores, and they can have different nanopore diameters alongside the nanopore length [1], [4-6].
Metal nanostructures are fabricated by electrodeposition of the required metal into the nanopores of the template. Metal ions are attracted to the cathode (conductive substrate of the template) leaving the insulant alumina template. After dissolution of the template in a suitable solvent, metal nanostructures are obtained.

Diameters of the pores of the template and their distribution determine the width and the density of created nanostructures. The length of nanostructures is given by amount of metal deposited into the nanopores which is dependent on the time of the deposition, the current density (with a certain limitation of the diffusion, electron transfer, electrical potential, chemical potential, the processing temperature which can influence the mobility of ions, crystal growth, etc.). Creation and growth of metal crystals can be influenced by various parameters such as the current density, the electrolyte concentration, the temperature, the crystal structure of the substrate, the free surface energy, adhesion energy, lattice orientation of the electrode surface, kinetics of the nucleation, etc. [6].

2. EXPERIMENTS

The templates used for experiments on the nanostructure growth were obtained from Whatman. The thickness of Whatman templates was approx. 60 µm and nominal nanopore diameters were 20 and 100 nm. The templates were sputtered on one side (either the side with the nanopores of nominal diameters or the side with larger nanopores) with gold which represented the working electrode during electrodeposition. During electrodeposition, the sputtered template was attached to a Cu adhesive tape because of its fragility [7].

A metal (usually nickel, gold, palladium or tin – the composition of plating solutions is listed in the Table 1) was deposited by electroplating and under various electroplating conditions (e.g. various pH and concentration, the use of the ultrasound waves, etc.). The templates were usually dissolved in NaOH or low concentrated H₃PO₄. The nanostructures were examined by scanning electron microscopy (SEM) and the electroplating conditions which can affect the growth of nanostructures have been investigated [1], [7-8].

Table 1: Aqueous solution used for electrodeposition

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Component</th>
<th>Qty in Solution</th>
</tr>
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<tbody>
<tr>
<td>Ni electroplating bath</td>
<td>Nickel Sulfate NiSO₄ x 6H₂O</td>
<td>250 g/l</td>
</tr>
<tr>
<td>(Watts bath)</td>
<td>Nickel Chloride NiCl₂ x 6H₂O</td>
<td>50 g/l</td>
</tr>
<tr>
<td></td>
<td>Boric Acid H₃BO₃</td>
<td>35 g/l</td>
</tr>
<tr>
<td>Au electroplating bath</td>
<td>Potassium Cyanide K[Au(CN)₂]</td>
<td>6 g/l</td>
</tr>
<tr>
<td>(cyanide bath)</td>
<td>Boric Acid H₃BO₃</td>
<td>2,32 g/l</td>
</tr>
<tr>
<td>Pd electroplating bath</td>
<td>Palladium(II)Chloride PdCl₂</td>
<td>0,4 g/l</td>
</tr>
<tr>
<td></td>
<td>Hydrochloric acid HCl 37%</td>
<td>2,5 ml/l</td>
</tr>
<tr>
<td>Sn electroplating bath</td>
<td>Commercial solution Sn5500</td>
<td></td>
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</table>

The current density over the total area of nanopores was usually 15 mA/cm² for Ni nanostructures, 0.25 mA/cm² for Au nanostructures, 1 mA/cm² for Pd and 20 mA/cm² for Sn nanostructures. The values of nanopore sizes were considered average for both sides of the template. The duration of electrodeposition was adjusted according to the current density so that nanorods of approx. 1 µm tall should be created.
The temperatures of plating baths were approx. 55°C for Ni nanostructures, 50°C for Au nanostructures and 25°C for Pd and Sn nanostructures. The growth of nanostructures has been examined on both sides of templates. The templates filled with metal were dissolved in 5 M NaOH and 5% H₃PO₄ for fine treatment [1], [8].

3. RESULTS AND DISCUSSIONS

The SEM analyses revealed that both nanotubes (Fig. 2) and nanorods (Fig. 4), have been fabricated. There is a top view of nanorods in Fig. 3c, and side views in Fig. 3b. In some cases the nanorods may grow in clusters (Fig. 3a). It has been found, that the nanorods are usually formed in the nanopores of nominal sizes while the nanotubes are often created when metal is deposited into the template region which contain wider nanopores. Therefore, the size of nanopores in the template is a crucial parameter in fabricating certain types of nanostructures. In the case of nickel nanostructures, the type of structure can be also influenced by electroplating parameters like the concentration and the pH of the electrolyte. An example of palladium long nanowires is in Fig. 2.

Fig. 2: Metal nanotubes

Fig. 3: Pd long nanowires
4. CONCLUSIONS

The template-based electrodeposition method proved to be suitable for fabricating arrays of vertically aligned nanorods, nanowires and diverse kinds of nanotubes from Ni, Au, Sn and Pd to the working electrode. We suppose to obtain the same results with others metals.

The developing technique of creation of nanostructured surface is expected to be applicable everywhere, when it is essential to enlarge an active area, e.g. solar panels, gas sensors, sensors of detection of heavy metals, sensors for solution conductivity measurement etc. The nanostructures also exhibit changed physical properties due to their small dimensions and react with surrounding matter differently in comparison to macrostructures. This is why the nanostructures are considered as promising in the various fields of thin-film technology.

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REFERENCES


