CREATION OF ARRAYED NANOSTRUCTURED ELECTRODES BY TEMPLATE-BASED ELECTRODEPOSITION METHOD

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ABSTRACT

The procedure of template preparation and nanostructures fabrication is described. The nanoporous non-conductive template is created by anodization of aluminium under specific conditions. The nanostructures are produced by metal deposition into the pores of the template. After the template dissolving in a sufficient dissolvent, ordered nanostructures are obtained and then analysed by SEM. Both nanotubes and nanowires of various dimensions can be created by this method.

1. INTRODUCTION

The creation of an indented surface, i.e. nanostructures, can be used for an essential enlargement of the surface area. This enlargement can be employed in various fields of technology. For example, microsensors are expected to gain high sensitivity (in spite of their miniaturization) due to the modification of the electrode surface of their sensing elements. The surface modification 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 in two phases. At first, the Al_2O_3 template, which the nanostructures are formed through, has to be created and then is the nanostructure formation itself. The process of the nanostructures creation is illustrated in *Fig. 1* [1].

The Al_2O_3 template is produced by anodization of a thin (vapour deposited) aluminium film. Aluminium (as well as titanium) is well-known for its self-assembling ability which occurs during anodization under specific conditions as well as titan. This ability enables to create the template which contains hexagonally ordered nanopores. The anodization process can be either one-step or two-step. The two-step anodization which consists in the anodization itself (one-step), subsequent dissolving of the anodized layer, and another anodization, provides significantly more ordered structure then the one-step anodization [2]. The resulting Al_2O_3 porous layer with a conductive substrate on one of its sides (representing cathode during the following electrodeposition process) forms the template which is used for the nanostructures creation [3].

The 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 the process of metal deposition the template is dissolved (e.g. in NaOH) and the nanostructures are obtained.

Diameters of the pores and their distribution in the template 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 and 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.). The 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. [4], [5],[6].

Deposition of metal into the nanopores can be considered as electrodeposition on arrayed nanoelectrodes which differs from deposition on macroscopic substrates to a certain extend. These differences are mainly caused by dimensions of the nanopores. Because of high aspect ratio (lenght/width) only diffusion as a way of mass transport can be taken into account in a solution close to the nanoelectrode (diffusion layer). It has several impacts, such as an increased ohmic drop of potential caused by raise in an ohmic resistance represented by the electrolyte volume in the pores, a current increase due to enhanced mass transport at the nanoelectrode boundary, changes in current density distribution etc. In the case of macroscopic planar electrodes with the flux of a species perpendicular to the electrode plane, the flux is uniform over the surface of the electrode and the concentration reaches the bulk value at a far smaller distance from the surface than in high aspect ratio nanopores where edge effect has a significant impact, and the diffusional flux toward the nanoelectrode is inhomogeneous over the surface (a quasi spherical diffusion layer of the nanopore is added on the top of the linear diffusion layer); it increases with decreasing distance from the nanoelectrode edge. The difference between electroplating on macroscopic substrates and on nanoelectrodes also depends on time. After a sufficiently long time, a steady state is established for large planar (or spherical) electrodes. A steady state cannot be achieved on nanoelectrodes if the length of the nanopores tends to infinity [7], [8].

In the case of diffusion, another very important parameter is the distance between the nanopores. If the quasi spherical diffusion layer is smaller than a half of the distance between the nanopores the diffusion layers of single nanoelectrodes do not overlap, nanoelectrodes do not affect one another and the overall current measured is the sum of the currents passing through the individual nanoelectrodes. If it be on the contrary thus the diffusion layers partially overlap then the overall current is smaller than the sum of the currents passing through the nanoelectrodes when they operate independently. If the diffusion layers almost totally overlap, the array behaves as a continuous electrode having the surface area equal to that of the whole array. The extent of the diffusion layer overlap can be expressed in terms of the overlap factor derived from the ratio of the overall current to the sum of the currents at the independent individual nanoelectrodes. The value of the overlap factor depends on the nanoelectrode geometry and the time of electrolysis [7].

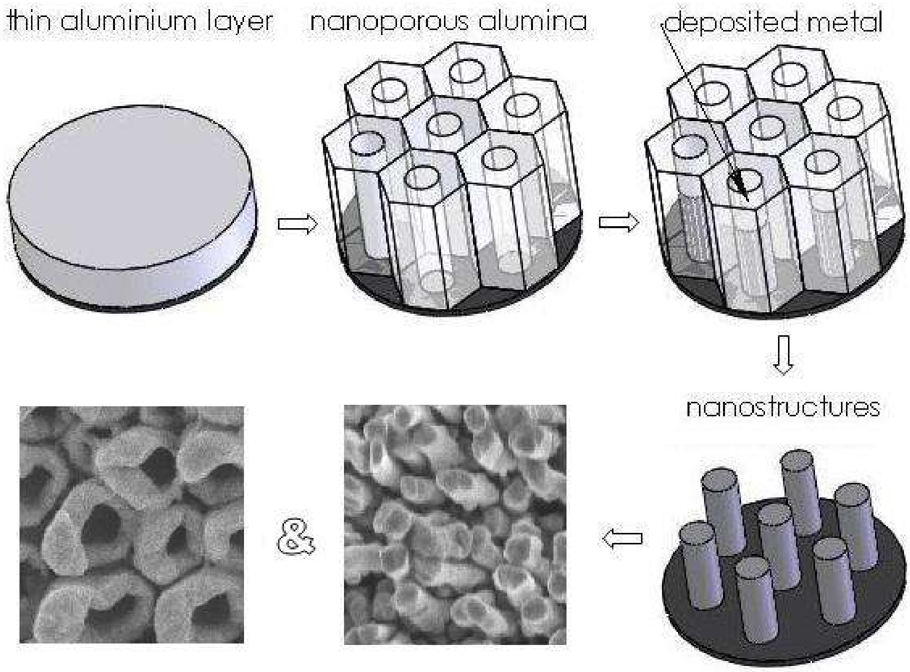

Fig. 1: Procedure of nanostructures creation

2. EXPERIMENTS

The metal used for the experiments on the nanostructure fabrication was mainly nickel. Watts Bath, containing 250g/l of $NiSO_4$, 50g/l of $NiCl_2$, and 34g/l of H_3BO_3, was used as an electrolyte. The nanostructures were created under various electroplating conditions such as the use of the ultrasound waves, a wide range of current densities, various concentrations, various diameters of the nanopores, etc. Dependence of the dimensions of the nanostructures on the time and the current density was experimentally and numerically determined. For the first experiments Whatman Anodiscs [9] were used as templates and then the Al_2O_3 templates which were created only for the purpose of nanostructure fabrication were employed. These templates differ from the Whatman Anodiscs, e.g. in the width and diameters of the pores. In the case of the latest experiments standard stirring of the solution has been replaced by forced circulation of the electrolyte (by a pump). The pump supplies the fresh electrolyte continuously to the area where electrodeposition (or anodization in the case of the template fabrication) should proceed. A stainless steel needle which injects the electrolyte to the metal deposition (or anodization) area serves also as the anode (cathode). After the electrodeposition process, when the pores of the template are filled by the metal, the used template is dissolved in either NaOH or H_3PO_3. The created nanostructures were examined by scanning electron microscopy (SEM).

3. RESULTS AND CONCLUSION

SEM analysis of the fabricated nanostructures revealed that both nanotubes (*Fig. 2 a; b*) and nanowires (*Fig. 2 c; d*) were created. The type of the structure is given by the specific conditions under which the nanostructures are being created. It has been found that the pH of the electrolyte, the concentration, the diameters of the pores of the template, and usage of the ultrasound waves can affect the structure. The nanostructures which were carried out at low values of the pH or deposited through the nanopores of very small diameters (approx. 20 nm) were usually nanowires while the nanostructures created at high values of the pH or deposited through the nanopores of wide diameters (approx. 200 nm) usually turned out to be nanotubes. The nanostructures fabricated at low concentration of the electrolyte tend to be nanotubes and nanowires were usually created at highly concentrated electrolytes. The usage of the ultrasound waves during electrodeposition causes that the probability of nanotubes creation is higher than when the ulrasound bath is not employed. The nanotubes which can be formed through the templates can vary in the wall thicknesses. An example of thin-walled nanotubes is in *Fig. 2 a* and thick-walled nanotubes are in *Fig. 2 b*. Unique phenomenon occurred on a few samples. The nanowires were created in clusters (*Fig. 2 d*) instead of uniform covering of the surface. The reason has not been made clear yet. The length of created nanowires is usually consistent with the length determined by calculations which were derived from electrodeposition on the macroscopic samples. However, in the case of some nanotubes and only few nanowires the length differed from the calculated. It is possible that the length differs due to the effect of diffusion. The material which was used for the nanostructures creation was mainly nickel (and copper in the case of a few samples) but other metals such as gold or platinum are considered for further experiments and practical applications.

The developing technique of creation of the 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.

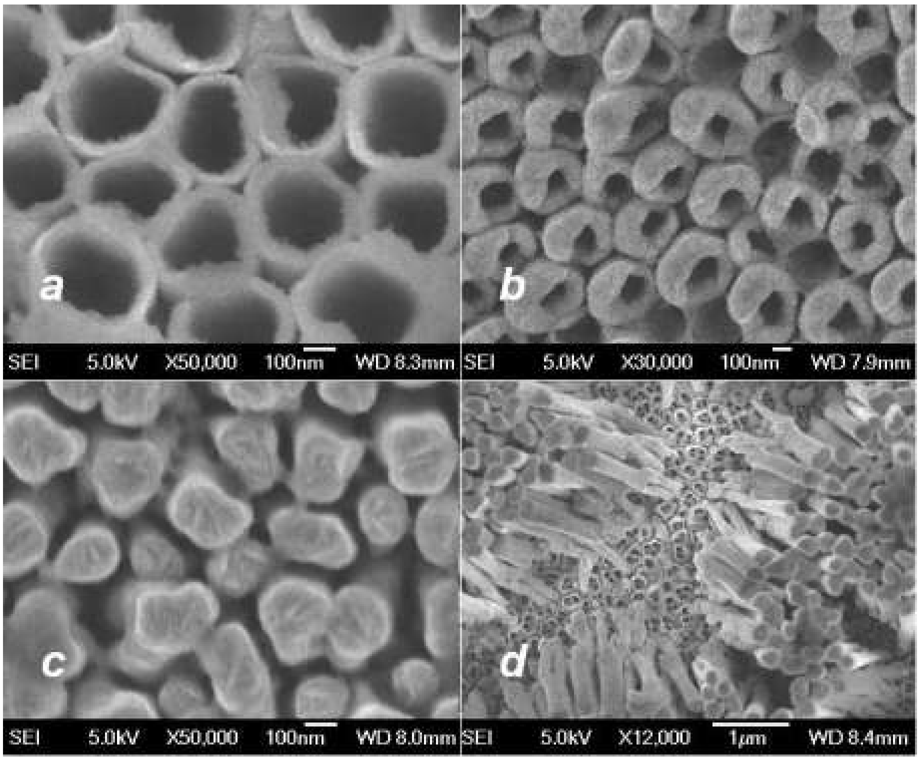

Fig. 2: SEM analysis of created nanostructures

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