Fabrication of Vertically Aligned Arrays of Metal Nanorods and Nanotubes by Template-Based Electrodeposition Method

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Abstract. The template-based electrodeposition method consists of two main steps. At first, a non-conductive nanoporous template is created and then a metal is electroplated into the nanopores of the template. The template is created by anodic oxidation of aluminium, which can be in the form of an electropolished foil or vapour deposited or sputtered film on a conductive layer. If the anodic oxidation proceeds under very specific conditions (anodizing voltage, temperature, electrolyte composition, etc.) the resulting alumina layer is comprised of a hexagonal array of cells with cylindrical nanopores. The nanoporous alumina structure is then used as the template during the following electroplating process. The conductive layer on the bottom of the alumina template serves as the working electrode and metal ions are attracted to the conductive substrate through the nanopores and deposit in the form of solid metal. After filling the nanopores with the metal, the template is dissolved in a suitable solvent and metal nanostructures are obtained. The created nanostructures are then analysed by scanning electron microscopy (SEM). It has been found that both nanorods and nanotubes can be created by the single template-based method. The type of nanostructure is given by electroplating conditions and the size of the nanopores in the template.

Introduction

Nanostructures have gained increasing attention because of their novel properties and potential use in various technological applications. There is a large number of ways in which various nanostructures from a wide range of materials can be fabricated. One of the most effective methods for the production of an array of nanostructures, which can be applied in photonic band gaps, electrochemical sensors, etc. [1-2], is the template-based method. This method offers many advantages such as good control over the dimensions and distribution of nanostructures and low cost. Nanostructures can be also fabricated from a diverse range of materials.

The template-based method, which is illustrated in *Fig. 1*, consists of galvanostatic deposition into a template which contains an array of nanopores (*Fig. 1a*). After filling the template with desired material (*Fig. 1b*), the template is removed and only an array of nanostructures remains (*Fig. 1c*).

There is a variety of templates, such as polycarbonate membranes, alumina membranes, or mica crystals available [3-5]. Polycarbonate membranes are easy to handle (not brittle like alumina membranes) and can withstand high pH conditions for a longer time [6]. However, the alumina membranes (templates) have good characteristic for array fabrication because they are thermally and mechanically stable and can be produced with a high density of high-aspect-ratio, parallel, and nearly uniform nanopores. Moreover, the alumina nanopore diameter can be tuned by adjusting the fabrication conditions [3],[7].

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 growing alumina. Aluminium, which is used for anodization, can be either in the form of an aluminium foil [8-10] or a thin film deposited on a conductive substrate [7],[11-12]. 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.

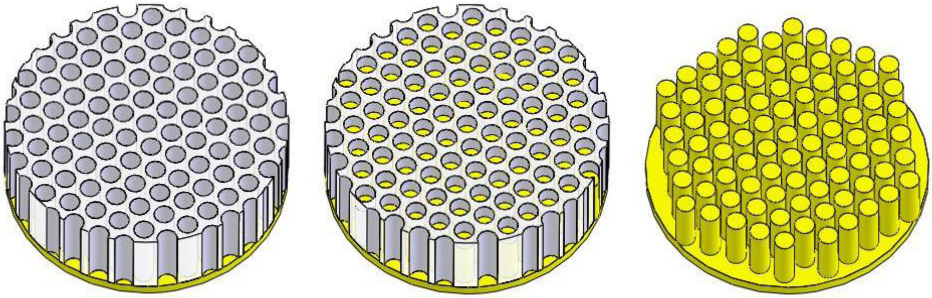

Fig. 1: Nanostructure fabrication process

a) nanoporous alumina template sputtered with gold on the bottom side

b) nanoporous alumina template filled with galvanic gold

c) gold nanorods (after dissolution of the template)

In order for the nanopores to be hexagonally arrayed, two-step anodization should be applied. The two-step anodization consists of short anodization, followed by etching of the produced Al_2O_3 structure, and another anodization during which the ordered structure is formed [13].

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 [14-16]. 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 [17].

Ultrafine membrane filters (such as Whatman Anodisc), with metal sputtered on one side of the membrane, have also been used for the creation of nanostructures [1],[3-4],[18-21]. These membranes are 60 μm thick and consist of non-uniform nanopores in the hexagonal configuration.

After the template preparation, metal is electroplated into the nanopores. Metal ions are attracted to the conductive layer/substrate at the bottom of the nanopores and deposit in the form of solid metal. After dissolution of the template in a suitable solvent, metal nanostructures are obtained. The spacing and diameters of nanostructures are determined by used template. The height of nanostructures depends on the amount of metal deposited into the template. Therefore, the height of nanostructures is proportional to the current density and the duration of electrodeposition. Since stirring of the electrolyte does not reach the volume in the nanopores, the exchange of species between the bulk electrolyte and the bottoms of the nanopores is a diffusion-controlled process [22].

Both DC and AC electrodeposition can be used to grow the nanostructures in the alumina template. AC electrodeposition can be used even if the barrier layer at the bottom of the nanopores is not removed while DC electrodeposition can be used for almost all kinds of metals and alloys and its deposition rate is much higher than that of the AC mode. [7],[23-24] .

An alternative process to electrodeposition is vapour deposition which can be used even if the barrier layer at the bottom of the nanopores is not dissolved. However, electrodeposition techniques are better for adjusting the material composition of nanostructures. Moreover, the growth of nanostructures starts at the nanopore bottoms and continues to the nanopore openings so the nanopores cannot get plugged [24-26].

Various nanostructures, such as nanorods, nanotubes, nanowells [19], etc., can be created by the template-based method. The nanostructures can be also multi-segmented, fabricated either by electrodeposition from a solution of two or more kinds of metal ions and by changing applied potential or by electrodeposition from different electrolyte solutions [20].

Experimental

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. However, SEM analyses and literature [3],[20] proved that the templates consist of an approx. 1 μm thick layer containing interconnected nanopores of diameters corresponding to the nominal value. The rest of the template consists of wider and non-connected nanopores. 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.

Metal used for the nanostructure fabrication was nickel, which has gained great interest in the field of nanotechnology because of its magnetic properties and potential applications e.g. in storage media [27-29], and gold for its electrochemical properties. The composition of plating solutions is listed in the *Table 1*:

Table 1: Aqueous solutions used for electrodeposition:

Electrolyte:	Component:		Qty in Solution [g/l]	pH
Ni electroplating bath (Watts bath)	*Nickel Sulfate*	$NiSO_4.6H_2O$	*250*	*approx: 3.5*
	Nickel Chloride	$NiCl_2.6H_2O$	*50*	
	Boric Acid	H_3BO_3	*35**	
Au electroplating bath (cyanide bath)	*Potassium Cyanide*	$K[Au(CN)_2]$	*6*	*approx: 6.7*
	Boric Acid	H_3BO_3	*2.32*	

*The quantity is stated for 100% Watts Bath without altered pH, although the value of the pH was adjusted in many experiments by an additional amount of H_3BO_3 or KOH.

The current density over the total area of nanopores was usually 15 mA/cm^2 for Ni nanostructures and 0.25 mA/cm^2 for Au 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. In the case of nickel plating solution, the volume concentration was ranging from 5 to 100 % and the pH was ranging from 3 to 6. The purpose of altering these parameters was to find their influence on the growth of nanostructures. In the case of gold plating, the concentration and the pH remained unchanged. The temperatures of plating baths were approx. 55°C for Ni nanostructures and 50°C for Au nanostructures. The growth of nanostructures has been examined on both sides of templates. The templates filled with metal were dissolved in 5 M NaOH.

Results and discussion

The SEM analyses revealed that both nanorods (*Fig. 2*) and nanotubes (*Fig. 3*), either from nickel or gold, have been fabricated. There is a top view of nanorods in *Fig. 2a*, and side views in *Fig. 2b* and *Fig. 2c*. In some cases the nanorods may grow in clusters (*Fig. 2b*). 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. If an experiment on the nanostructure growth is carried out under adjusted electroplating parameters, i.e. low volume concentration (approx. 10 %) and high pH (approx. 5), it usually results in the creation of thin-walled nanotubes (*Fig. 3a*), regardless of which side of the template was sputtered and used for the experiment. The nickel nanotubes fabricated by electrodeposition into the template with wide nanopores are usually thick-walled (*Fig. 3b*). An example of gold nanotubes is in *Fig. 3c*.

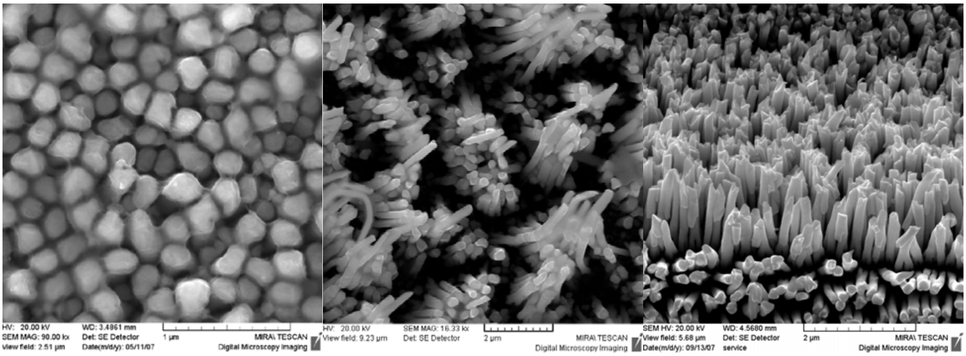

Fig. 2: metal nanorods

a) ordered nickel nanorods b) clustered nickel nanorods c) gold nanorods

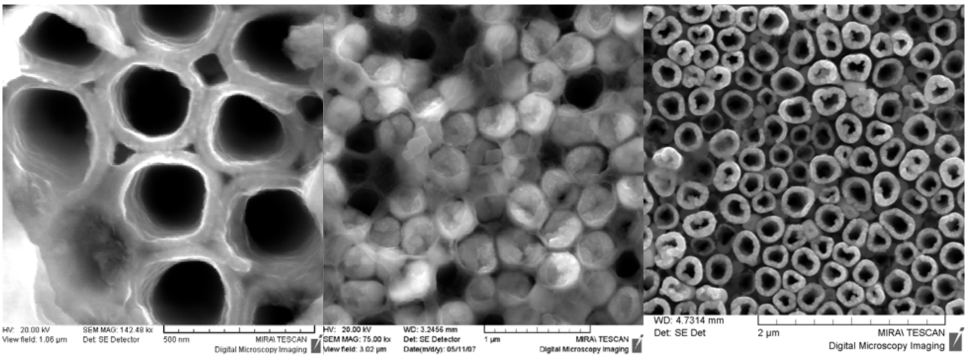

Fig. 3: metal nanotubes

a) thin-walled nickel nanotubes b) thick-walled nickel nanotubes c) gold nanotubes

Nanotubes can be also obtained using a double-templating approach, proposed by Sander et al. [30], or by chemical modification of the nanopore walls by surfactants and subsequent electroless deposition of desired metal [21],[31]. Nevertheless, the method which consists only of electrodeposition with some altered parameters seems to be simpler and less time consuming.

Some samples contained both nanorods and nanotubes. These mixed nanostructures were produced using 0.1 µm Whatman Anodiscs and the side of the template, where electrodeposition proceeded, contained the nanopores with wider diameters than was the nominal value. It is possible that during the initial stage of electrodeposition, nickel tends to deposit faster on the edges of the nanopores than in the centres, which causes the creation of cavities inside the nanotubes. The cavities are filled up when a sufficient amount of metal is deposited into the nanopores and when the non-uniform size of the nanopores is small enough. Apparently, the formation of nanotubes is only an initial stage of the growth of nanorods and if the duration of electrodeposition would be prolonged, the nanotubes would transform into nanorods. An example of these nanostructures is in *Fig. 4*.

If the duration of electrodeposition is long enough, metal can almost completely fill the template and the resulting nanostructure is comprised of nanowires (*Fig. 5*). The maximum height of nanowires is equal to the thickness of the template, which is approx. 60µm in the case of Whatman Anodiscs. If electrodeposition lasts too long, metal covers the surface of the template.

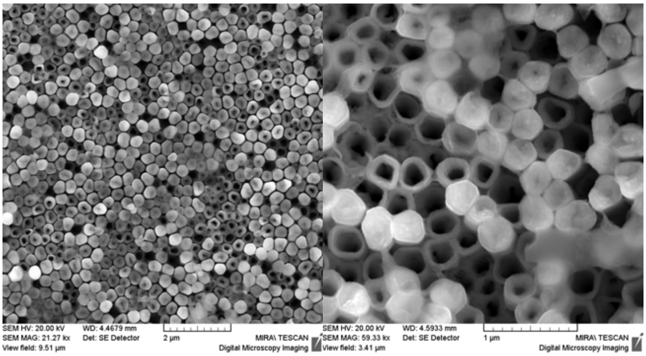

Fig. 4: mixed nanostructures
a) nanorods and nanotubes b) nanorods and nanotubes (detail)

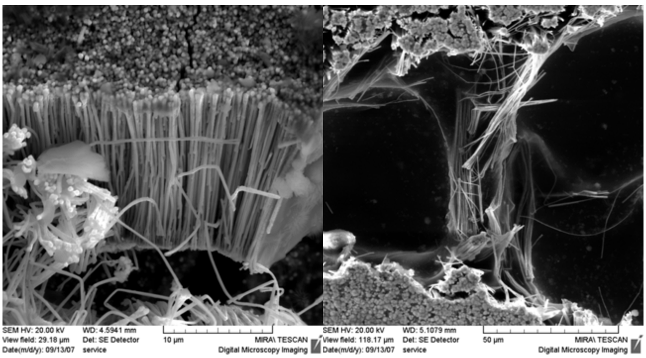

Fig. 5: nickel nanowires
a) clustered nanowires b) nanowires (detail)

The nanotubes and nanarods growing can be distinguished during the process by observing voltage polarization of the working electrode. There is a graph of the reference voltage against the duration of DC electrodeposition in *Fig. 6*. We have found that for many samples the polarization of the working electrode increases with time in the case of nanotubes growing. It may be caused by enlargement of the electrode surface by growing nanotubes.

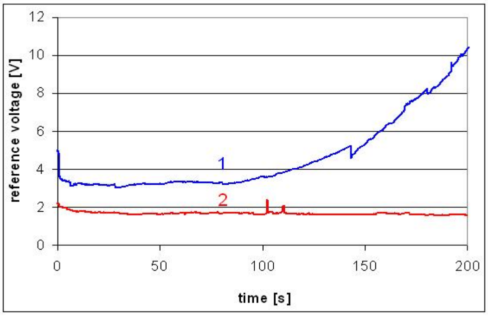

Fig. 6: Course of reference voltage, (1) nanotubes carried out at high pH (approx. 5.1) and low concentration (approx. 10%), (2) nanorods carried out at low pH (approx. 3.5) and high concentration (100%) of the Watt bath.

It is sometimes difficult to distinguish the metal nanotubes from insufficiently dissolved alumina templates because insufficiently dissolved alumina can take the form of nanotubes too (*Fig. 7*). Some of the recent literature [32],[33] is even dedicated to the formation of alumina nanotubes, nanorods, etc. These alumina structures are fabricated by the same dissolution process as is used in our case, i.e. by etching of the nanoporous alumina templates in dilute NaOH. Therefore, this feature of insufficient alumina dissolving might be useful in other applications.

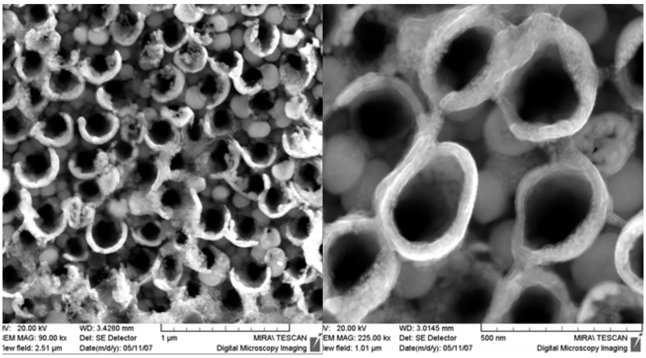

Fig. 7: alumina nanotubes
a) Al_2O_3 nanotubes b) Al_2O_3 nanotubes (detail)

Conclusion

The template-based electrodeposition method proved to be suitable for fabricating arrays of vertically aligned nanorods, nanowires and diverse kinds of nanotubes from nickel and gold to the working electrode. We suppose to obtain the same results with others metals. It is possible to fabricate a certain type of nanostructure on purpose by adjusting specific electroplating parameters (the pH and the concentration of the plating bath) and by choosing the template with certain pores diameter. The nanotubes or nanorods growing can be determined during process observing polarization of the working electrode.

The arrays of nanostructures offer many advantages such as high surface area to volume ratio. It can be utilized in all applications in which the large surface is an important parameter (e.g. electrochemical microsensors, capacitors, etc.).

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