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# Nickel nanotubes prepared by electroless deposition in ion track templates

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Nickel nano- and micro- tubes were prepared by electroless deposition in ion track template membranes. By choosing the appropriate etching conditions membranes with cylindrical or conical pores were obtained allowing the preparation of cylindrical or conical tubules. The activation of the membranes was a two step process. The bath used for deposition was an acidic one. Typically for acidic bath deposition, by energy dispersive X ray analysis, a phosphorous content of up to 10 % was found in the deposit.

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## 1. Introduction

Synthesis of functional nanoscale materials and devices proves to be one of the most attractive fields in research nowadays, due mainly to the wide field of potential applications, ranging from electronics, computers and communications to life sciences and biotechnology. Nanoscale devices are important for such applications not only because they allow miniaturization but also because materials engineered at the nanoscale show properties which differ strongly from those of bulk materials.

A range of materials which shows great promise for future applications consists in high aspect ratio structures, namely nanowires or nanotubes. One method which allows the preparation of these quasi-one dimensional structures is the template technique [1]. By employing this approach one can obtain metallic [2-7] or semiconductor [8-11] nanowires or nanotubes with aspect ratios exceeding sometimes 1000. The method consists in filling the pores of a nanoporous membrane (the template) with the desired material. The templates usually employed are ion track or anodic alumina membranes. Both offer good quality parallel pores, and give the possibility of fabrication of nanowires and nanotubes with diameters as low as a few tens of nanometers. The ion track templates offer a few degrees of freedom which makes them very attractive for such applications namely: (a) the possibility of preparing nanopores with the desired shape (cylindrical, conical or double conical), (b) the possibility of choosing the desired pore density ranging from 1 pore/sample to $10^{10}$ pores/cm$^2$ by exposing the polymer foil to the desired ion fluence, (c) the possibility of choosing the most suited material for the membrane such as polymers (polycarbonate PC, polyethileneterephtalate PET, polyimide PI), glasses, quartz or mica.

A wide range of methods for filling the pores in order to obtain such nanostructures were reported in the last decade. Thus, the most widely employed method is electrochemical deposition but one should also mention electroless (autocatalytic) deposition [12], injection of molten substances [13] and so on. Electroless method proved itself an extremely versatile method in preparing hollow structures such as nanotubes, possible applications for the technique being already pursued [14].

In this report we present the particular case of the method applied for the preparation of nano and micro-tubes of nickel in polycarbonate ion track membranes, using the electroless deposition from an acidic bath.

## 2. Experimental

Polymer foils with thicknesses in the range 10 μm – 100 μm were the starting point in preparing the nanoporous templates for electrodeposition. Polycarbonate (Makrofol from Bayer) foils with thicknesses of 10, 30 and 100 μm and polyethylene terephtalate with the thickness of 19 μm were irradiated with swift heavy ions (e.g. Au with specific energy 11.4 MeV/nucleon) in the UNILAC accelerator at GSI Darmstadt with fluences in the range $10^5$-$10^8$ ions/cm$^2$.

After irradiation, in order to obtain the nanopores, the samples were etched in solutions with high selectivity, based on NaOH and methanol. In order to obtain pores with the desired shape and size the samples were etched either by completely dipping them in the etching solution for cylindrical or double conical pores or by exposing only one side of the membrane to the solution for conical pores [12].

A three step process was used for the deposition: (1) preactivation in a solution containing Sn ions, (2) activation in a solution containing Pd ions, and (3) deposition (figure 1). The deposition bath contains nickel chloride as a source of nickel ions, nickel citrate, sodium hypophosphite and sodium acetate. The pH of the solution

was of 4.5 and the deposition was performed at temperatures in the range 55-70°C.

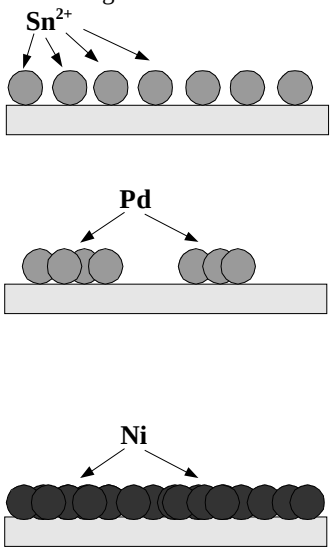


*Fig. 1. The three steps in electroless deposition: step (1) preactivation with $Sn^{2+}$ ions, (2) activation with palladium and (3) metal deposition either catalytic on palladium nuclei in the first step or autocatalytic.*

After the deposition scanning electron microscopy was employed to observe the nickel tubules arrays, either after dissolving the template in dichloromethane in the case of polycarbonate membranes or through a crossection in the case of PET membranes.

## 3. Results and discussions

a) Membrane preparation

Two parameters related to the etching process are most important for the preparation of nanoporous membranes with the desired pore shape and size namely track etch rate $v_t$ and bulk etch rate $v_b$. Usually the shape obtained when etching an ion track is a cone, the ratio $v_b/v_t$ determining the opening angle of the cone:

$$tg\alpha = v_b/v_t$$

In the case $v_t >> v_b$ (high etching selectivity) one obtains approximately cylindrical pores. The two etching rates can be adjusted by varying the parameters of the etching bath such as ingredients concentration or temperature. In order to obtain cylindrical pores we used an aqueous solution containing 5MNaOH and 10% vol. methanol. The etching temperature was 50°C. The bulk etch rate which determines the diameter of the pore was in this case 2 μm/hour. For conical pores we used a bath containing 50% vol. 9MNaOH and 50% vol. methanol and the etching was performed at room temperature. In order to obtain conical pores only one side of the membrane was exposed to the etching solution while by exposing both sides of the foil to the etching bath double conical pores were obtained.

b) Preactivation

The preactivation process is the most important one during the entire deposition. During this step the samples were immersed in a solution containing $Sn^{2+}$ ions which were adsorbed on the membranes' surface, including here the inner surface of the pore. In our previous experiments with copper tubules deposition we found that in order to achieve a large number of nuclei and thus thin, uniform nanotubes, the preactivation process should be carefully controlled [12]. We found out that the deposition takes place in very good conditions when the polymer surface which typically is hydrophobic becomes hydrophilic. So it is not necessary to carry out many microscopy observations, it is enough to observe when the membrane remains uniformly wet when pulled out from the pre-activation solution. This observation becomes extremely important when one deals with processes on an industrial scale, and when performing systematic microscopy measurements become difficult. The preactivation was performed at room temperature using a solution containing 40g/l $SnCl_2$ and 10 ml/l HCl (37% vol.). We noticed that variations as small as 2°C could mean variations in the time necessary to obtain a good wetability of the membrane and thus a high quality of the tubules of more than 50%. The average time we employed for preactivation at 20°C was of 10 minutes.

c) Activation

During the activation step of the procedure the template membranes were dipped in a solution containing $Pd^{2+}$ ions. The following reaction takes place:

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0$$

Thus palladium colloids are formed on the surface of the samples, this constituting the catalyst for the deposition reaction. Usually in commercial electroless metal deposition, a 2 step process is preferred. Such a process consists in the activation with palladium colloids which are stabilized by $Sn^{4+}$ ions and afterwards the deposition process. The reason for such an approach is given by the fact that the process is more stable and easier reproducible. However, for preparation of very small objects, the 3 steps algorithm presents a major advantage, namely the number of Pd nuclei which can be obtained on the surface is one order of magnitude higher than in the 2 steps procedure. This allows the deposition of thinner metal films with higher adhesion to the surface.

d) Deposition process

The deposition process is mainly a reduction of nickel ions from the solution in the presence of the catalyst. This can be either palladium in the first stages of the process or nickel itself after the palladium activated surfaces are covered with a first layer of nickel.

The main chemical reactions which take place in the deposition process are:

-the oxidation of the hypophosphite ions in the presence of catalytic surfaces into ortophosphite ions:

$$[H_2PO_2]^- + H_2O \rightarrow H^+[HPO_3]^{2-} + 2H\ [catalyst]$$

-the reduction of nickel ions:

$$Ni^{2+} + 2H[catalyst] \rightarrow Ni + 2H^+$$

So during the deposition process in the presence of catalytic surface the hypophosphite ions oxidize in ortophosphite ions. The hydrogen atoms which result in this reaction are partially adsorbed onto the catalytic activated surface, where the nickel reduction reaction takes place, metallic nickel being deposited onto the surface.

In electroless deposition of nickel from acidic baths, besides nickel, phosphor is also deposited, the reaction of phosphor formation being:

$$[H_2PO_2]^- + H \rightarrow H_2O + OH^- + P$$

In Fig. 2, SEM images of cylindrical nickel nanotubes are presented. The temperature of deposition was of about 70°C.

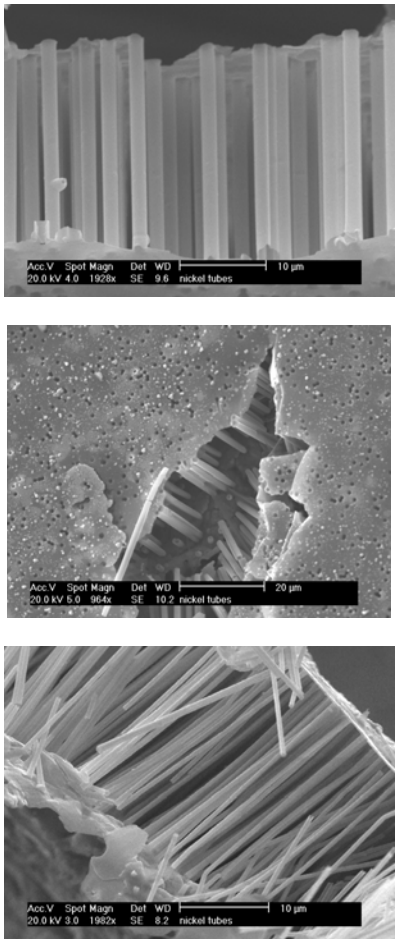


*Fig. 2. Nickel cylindrical tubules of different diameters prepared by electroless deposition.*

One can notice in Fig. 2 that arrays of uniform tubules can be prepared. Due to the method as can be observed the faces of the membrane are also covered with nickel. Taking into account that these thin nickel films are connected by the nickel tubes they are very difficult to remove in the case of high pore density membranes as the one presented in Fig. 2.

In Fig. 3, SEM pictures of conical and double-conical tubes are presented.

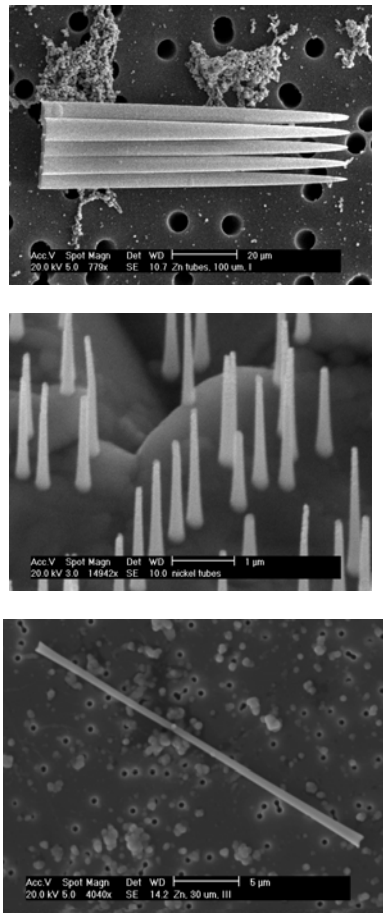


*Fig. 3. Nickel conical and double-conical tubes of various diameters prepared by electroless deposition.*

As we already mentioned the tubules were not purely nickel but they contain also phosphorous in various amounts. The composition of the tubules measured using energy dispersive X –ray analysis was found to vary between 89 – 91% Nickel and 9 – 11 % Phosphorous weight percent.

We performed the deposition at different temperatures varying from 55 to 70°C and we found that the speed of deposition is strongly influenced by this parameter. Thus if a complete coverage of the sample was obtained in a few minutes at 70° C at 55°C the time necessary for deposition was of several tens of minutes. No systematic dependence of the composition of the tubules as a function of temperature was observed, small variations of up to 1%

being even observed for different regions of the same sample.

It should be taken into account that the process of deposition inside the pores is determined by two parameters: the reaction rate and the diffusion rate. So the deposition takes place slower inside the pores than on the external surfaces of the membrane due to limitations in diffusion of reactants inside the pores. It is clear that a too high reaction rate can cause the closing of the pores at the surface and thus to completely stop the diffusion of reactants inside the nanopores which leads to incomplete grown tubules. As a consequence lower temperatures lead to better, complete tubes, in comparison to the growth at high deposition rates. However at temperatures lower than 55°C, even if the reaction rate decreases strongly the deposition does not take place uniformly on the surface of the sample. This limits somehow the maximum aspect ratio of the tubules, thus for 30 μm thick membranes we obtained the thinnest structures with an external diameter of about 400 nm while for 10 μm thick membranes we were able to deposit tubules with 200 nm external diameter.

## 4. Conclusions

The template method was employed in the preparation of nickel nanotubes using electroless deposition inside ion track membranes nanopores. The technique allows the fabrication of uniform nanotubes arrays with the desired morphology. Thus cylindrical, conical or double conical tubule arrays were deposited. It was found that besides nickel in the composition of the nanostructures about 10% is of phosphor.

Such hollow nanostructures can have a wide range of applications. Employing them as filtration membranes for magnetic nanostructures can be one of the most direct.

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