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NANOWIRES AND NANOTUBES PREPARED USING ION TRACK MEMBRANES AS TEMPLATES

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The template method proved itself to be an interesting approach for preparing structures with low dimensionality. The paper presents a review of our results using a particular case of the method namely the preparation of nanowires and nanotubes using ion track membranes as templates. Thus, metallic or semiconductor nanowires were prepared using electrochemical deposition in membranes with cylindrical or conical pores. Similar membranes were used to prepare tubules with different morphologies using electroless deposition. In the paper the main advantages of the method will be presented.

1. Introduction

In the last decade, the field of preparation of materials with low dimensionality and the investigation of their properties attracted more and more scientists. The reason for such an increase of the field was given by the wide field of applications, starting from electronics information and communications industry to medicine and biology or textiles industry. The key feature of nanostructures when compared with their bulk counterparts it is not given only by miniaturization of devices but consists in the strong change in properties induced by the low dimensionality and high surface to volume ratio.

The template approach represents an interesting path towards preparation of nanoobjects with controlled morphological properties mainly due to the fact that by appropriate choosing of host templates the shape and dimension of the prepared structures are precisely determined [1-3]. A type of templates which is widely used for such experiments is the nanoporous membranes. Most of the studies reported in literature are based on two types of such membranes: polymer ion track membranes and anodic alumina. Both present a number of advantages which makes them suitable for the fabrication of high aspect ratio nanostructures, namely nanowires and nanotubes.

The method of filling of the pores, thus of fabricating the nanostructures are various but by far the most employed one is electrochemical deposition [4-7]. Based on the knowledge gained in the case of thin films, electrodeposition was mainly employed for the preparation of metallic nanowires but also semiconductor nanowires are prepared using such an approach. Electrochemical deposition was used in filling pores in mica with metals by Possin, this being the first report describing a template preparation of nanowires and was written more than 30 years ago [8,9]. Electroless deposition was also used connected to nanoporous membranes allowing the preparation of hollow structures in contrast with electrochemical deposition which leads in most of the cases to rod-like deposits [10].

The reports in literature concerning preparation and properties of wires and tubes deposited in nanoporous membrane templates aim at studying various aspects of such structures including here magnetic behavior, transport phenomena or optical properties. The influence of the low dimensionality on different properties were from the beginning the main target of the investigators.

The purpose of this paper is to present a review of the results obtained in nanowires and nanotubes preparation and characterization using ion track polymer membranes as templates.

2. Template preparation

It is interesting and somewhat contradictory that for the preparation of ultra-small structures such as nanowires the first step involves the use of equipment which uses tremendous

amounts of energy and has a size of at least several tens of meters namely an ion accelerator. In order to produce etchable ion tracks the specific energy of the swift heavy ions should have specific energies higher than 1MeV/nucleon. Each ion passing through the polymer foil produces a track, a cylindrical zone of material with altered properties. The structure of the ion track corresponds to the energy deposited by the ion in the material, energy which leads to decomposition of the polymer material.

The fact that each ion passing through the material produces one ion track has a high importance, meaning that by choosing the appropriate ion fluences one can chose the number of pores desired for the porous membrane template. The extremes are 10^9 pores/cm^2 and 1 pore/sample. In the second case the method was developed by the Material Research group at GSI Darmstadt. In order to obtain a single pore is necessary that the sample is hit by only one ion. Thus it is necessary to reduce the flux of heavy ions to approximately 10^3 ions/cm^2·s. A metallic plate with thickness 0.2 mm with an aperture of 0.2 mm is inserted in front of the sample. A semiconductor detector is placed behind the sample with the purpose to detect each ion passing through the aperture and then through the sample. At such low fluxes the probability of an ion to pass through the aperture is of 1 event/s. This gives enough time to the automated system to switch of the beam using a fast chopper after an ion hit is detected by the detector.

The next step after irradiating the polymer is the chemical etching of the ion track with the aim to produce pores with the desired shape and size, according to the final purpose of the experiment. At this step one has to choose carefully the composition of the etching bath and the temperature at which the etching is performed.

There are two parameters which determine the shape and size of the pore: v_b the bulk etch rate (etching rate for non-irradiated material) and v_t the track etch rate (the etching rate along the ion track). Typically the etching results in a conical or double conical pore (depending if one or both faces of the foil respectively are exposed to the etching bath) with the opening angle α: $tg\alpha=v_b/v_t$. For the case of high selectivity etching conditions, i.e. $v_t>>v_b$ the shape of the pores can be approximated to a cylinder. Usually the polymer which is mostly employed for preparing nanoporous ion track membranes for both filtration purposes or as template is polycarbonate. Even if it has a lower chemical, mechanical and thermal stability when compared to polymers as polyethilenethereftalate or polyimide polycarbonate offers several big advantages: possibility to obtain easily both cylindrical or conical pores (the etching selectivity can be tuned on a wide range) and the ease to dissolve the template for direct nanostructures observation, polycarbonate dissolves easily in several organic solvents, e.g. dychlormethane.

Typical etching conditions we used are: - for cylindrical pores an aqueous solution containing 5MNaOH and 10% vol. methanol at 50°C and for conical pores aqueous solution containing 9M NaOH and 50% methanol at room temperature. The addition of methanol in the etching solution mainly improves the smoothness of the pore wall but also increases both track and bulk etch rates.

In Fig. 1 a typical aspect of a porous polycarbonate ion track membrane scanning electron microscope image can be observed.

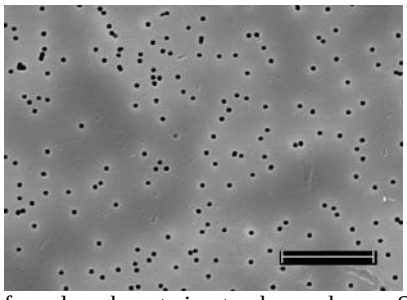

Fig. 1. Typical image of a polycarbonate ion track membrane. Size bar 2 micrometers; pore size 100 nm.

3. Nanowire preparation by electrochemical deposition

Using porous membranes as templates metal and semiconductor nanowires can be prepared. Electrochemical deposition is the most direct approach for this task and a wide range of materials can be deposited this way.

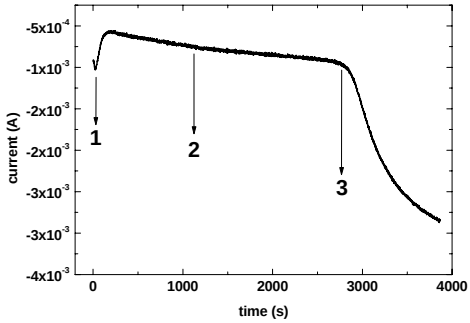

Fig. 2. Deposition current during nanowire preparation. The three steps correspond to 1- polarization, 2 – deposition inside the pores and 3 – complete filling of pores and deposition of caps on the surface.

The first step in preparing such nanowires is the deposition of a working electrode on one of the membrane surfaces by depositing a metallic thin film. In order to prepare an electrode with good adhesion to the membrane, a rough surface is preferred.

Sputtered deposition is performed, a gold thin film of approximately 50 nm thickness being obtained. In order to completely close the pores on the electrode side and to increase the mechanical stability of the system a copper layer is electrochemically deposited on top of the gold layer. The thickness of this copper layer is about 10 micrometers. The next step is to insert the sample in an electrochemical cell with the pores exposed to the deposition solution. The deposition of the wires can be performed using a potentiostat in a three electrode arrangement.

The deposition takes place in three steps which can be observed in Fig. 2. The first step (higher current in the beginning of the process) corresponds to the polarization phenomena taking place in the cell. The second step, where the current is relatively steady corresponds to the actually filling of the pores with the material. The beginning of the third step represents the moment when the pores are completely filled and a cap starts to grow on the surface of the membrane. The strong increase of the current during the third step is due to the increase in deposition surface when compared to phenomena taking place inside the pores.

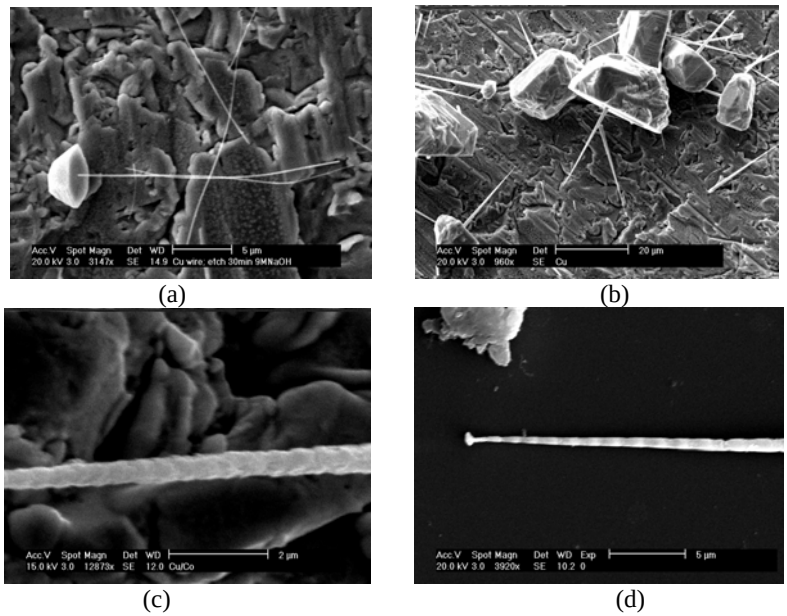

Fig. 3. Metallic nanowires prepared using the template method: (a) cylindrical copper wires (b) conical copper wires, (c) and (d) conical multilayered Cu/Co wires.

In Fig. 3 metallic nanowires deposited in ion track templates are presented. In order to image the wires using a scanning electron microscope the template polymer material is dissolved using dichlormethane.

In Fig. 3 (c) and (d) multilayered copper/cobalt wires are presented. Such wires are extremely useful for studying giant magnetoresistance behavior in a current perpendicular to plane approach, in contrast with the case for thin films where it is employed a current in plane geometry. The deposition of two metals in a layered arrangement is performed from a single electrolytical bath. The two metals are chosen in such a way that the difference between their deposition potential is high, thus when applying a lower overvoltage only the more noble metal is deposited. When a higher voltage is applied an alloy of the two metals is deposited. If the ratio between the ions of the two components is carefully chosen the alloy contains only spurious amounts of the nobler metal.

The template method allows relatively straightforward the measurement of transport properties in such nanowires. Usually for measurement of transport properties one has to employ a porous membrane containing a very small number of nanopores, ideally a single nanopore. After the wire is grown a second sputtering process provides the second electrical contact and current voltage characteristics or magnetoresistive behavior can be easily measured. For such samples encapsulation in acrylic resin strongly increases their life-time. It is very interesting that metallic nanowires electrochemically grown in ion track template membranes can withstand very high current densities (up to 10^9 A/cm^2 for copper).

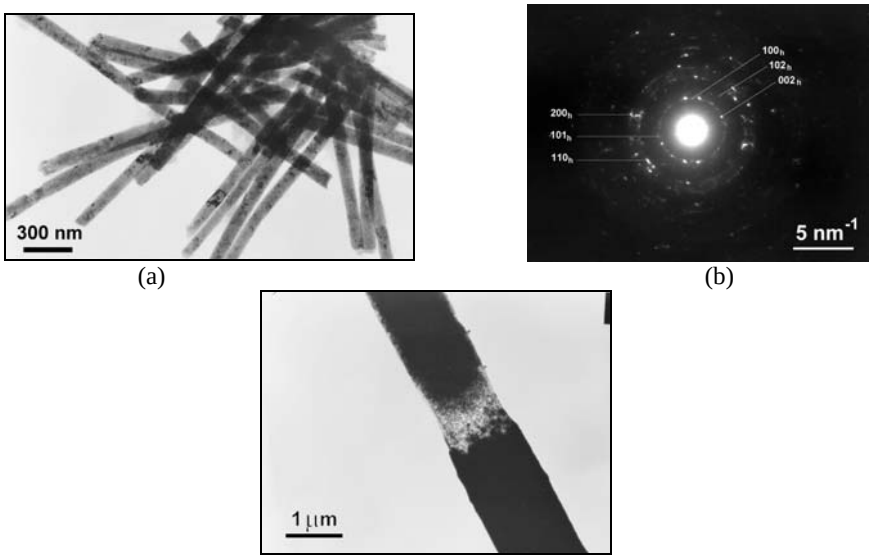

Fig. 4. CdTe wires obtained by electrochemical deposition in ion track templates: (a) CdTe 80 nm diameter wires, (b) corresponding electron diffraction image and (c) metal semiconductor junction Ni-CdTe.

Similar with metallic nanowires, semiconductor wires can be prepared. In order to perform transport measurements in semiconductors segmented wires (metal – semiconductor – metal) can be deposited. In Fig. 4 some example of semiconductor based wires are presented.

4. Nanotube preparation by electroless deposition

Electroless deposition can be employed as a tool in filling the pores of an ion track membrane with the aim to obtain hollow structures. The main feature of the process which allows one to obtain this result is that the deposition takes place only on the catalytic surface. Thus the pore walls can be covered with the desired material without completely filling. When compared to electroless deposition on macroscopic surfaces one needs to take into account the geometry of the pore. In order to achieve complete tubes is necessary to give time to the reactants to reach all over the pore, i.e. the reduction reaction should be slow in order to compensate for the diffusion.

In our opinion the best approach for electroless deposition is a three step process (-pre-activation with Sn^{2+} ions, activation with Pd and deposition) which allows the creation of a large

number of catalytic nuclei on the surface. In Fig. 5 some examples of hollow metallic structures prepared by electroless deposition are presented.

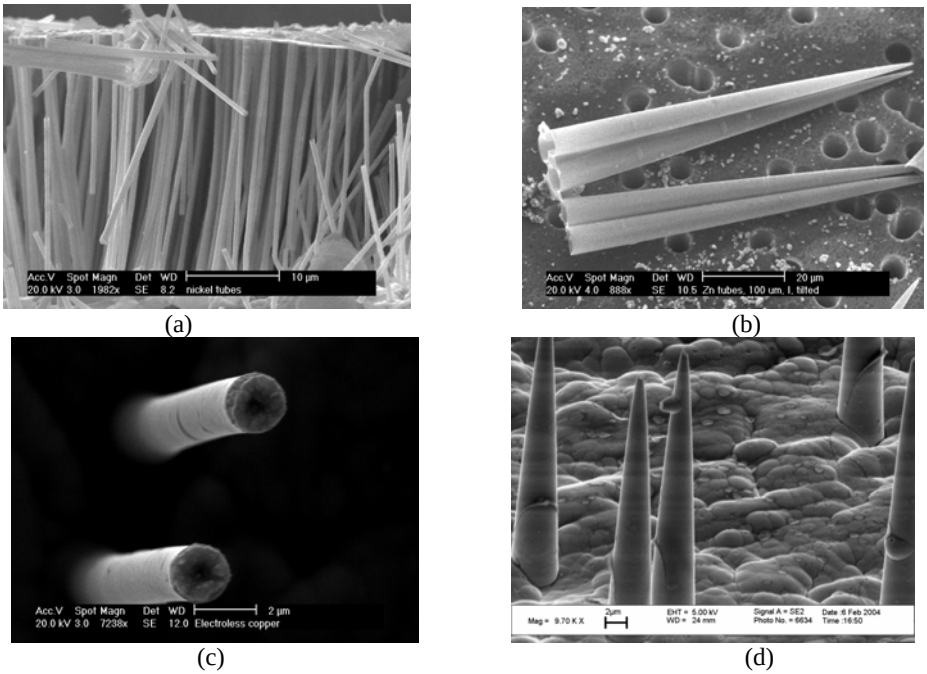

Fig. 5. (a) cylindrical nickel tubes; (b) conical nickel tubes; (c) cylindrical copper tubes and (d) conical copper tubes prepared by electroless deposition in ion track membranes.

5. Conclusions

The template method allows the preparation of nanostructures with high aspect ratio such as nanowires and nanotubes. The versatility of the process gives the opportunity to choose the shape and geometrical properties of the structures and the material either a semiconductor or a metal. Moreover, the approach opens the possibility to perform in a straightforward manner a wide range of measurements on the nanostructures starting with direct observations by electron microscopy to the investigation of optical or electrical characteristics.

From the point of view of applications as a function of the type of structures and their material the structures prepared using the template replication can be employed in a wide range of devices. The most appealing field for such structures it is at the moment related to sensors (e.g. magnetic field sensors based on GMR effect, photodetectors based on segmented nanowires and so on).

However, it should be emphasized that recent literature reports present an avalanche of possible application for nanostructures and it is only a matter of time until devices based on nanowires will enter the market. Here we find another huge advantage of the method, namely the ease in preparation of such structures and in scaling up the production to meet commercial demand.

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