

Preparation of metallic nanowires with magnetic properties using the template method

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Metallic nanowires with magnetic properties were prepared by electrochemical deposition in nanoporous ion track membranes. Thus, we prepared Co-Cu alloy and Co/Cu multilayered nanowires. The technique allows the preparation of uniform arrays of parallel nanowires with desired properties. The process of electrochemical deposition of metals in nanoporous membranes was studied by means of cyclic voltammetry and impedance spectroscopy. The influences of deposition conditions such as bath composition, temperature and deposition potential on the morphological, structural and compositional properties of the nanowires were systematically studied.

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1. Introduction

During the last decade the interest in the fabrication of low dimensional structures increased strongly. The attractiveness of the field for researchers all over the world was driven by the wide field of applications in various domains ranging from textiles to medicine and life sciences or electronics and communication industries. Moreover, the nanostructured materials promise not only an improvement of the domain of applications but a revolution in preparing smaller, cheaper and smarter devices.

The preparation of quasi- one dimensional structures such as nanowires or nanotubes represents one extremely interesting field out of this domain. A wide range of methods of preparing nanowires of metal, semiconductors or insulators were developed in the last few years. One extremely appealing method is the so-called template method [1-5]. It consists in filling the pores of a nanoporous membrane (the template) with the desired material. The methods used to fill the pores are usually electrochemical and chemical deposition. The membranes which are mostly used as templates are anodic alumina and ion track membranes. Anodic alumina is prepared by controlled anodization of aluminum. The membranes present a uniform regular distribution of nanopores, which form a two-dimensional hexagonal lattice (highly ordered when a 2 step anodization process is employed). Such a membrane is used typically when a dense array of nanowires is desired, taking into account that the close packing of the pores leads to pore densities of up to 10^{12} cm⁻² while diameters can be as low as 5 nm. The ion track membranes present a stochastic distribution of pores, with pore diameters down to 20 nm. In the case of ion track membranes the fact that for each ion passing through the material foil a pore is generated leads to the fact that

templates with pore densities ranging from 1 pore/sample to 10^9 pores/cm². Moreover when compared to anodic alumina another major advantage must be taken into account: it is possible to adjust independently the pore diameter and the pore density.

In the present report we present our results on deposition of metallic nanowires and nanotubes with magnetic properties using ion track membranes as templates.

2. Experimental

Polymer foils (polycarbonate) with thickness of 30 micrometers were irradiated with swift heavy ions (specific energy 11.4 MeV/nucleon) using the linear accelerator (UNILAC) at GSI Darmstadt. The fluences used were in the range 1 ion/sample to 10^8 ions/cm². The foils containing the ion tracks were subsequently etched in order to produce the nanopores. The etching was performed in baths containing NaOH and methanol at different temperatures and for different time in order to obtain pores with the desired shape and dimensions.

After etching on one side of the membrane a thin gold layer (thickness < 100 nm) was sputtered. This layer which will play during the electrochemical deposition the role of the anode was subsequently strengthened by electrochemical deposition of a layer of copper. This process is necessary in order to increase the mechanical stability of the system.

The deposition of nanowires was performed after clamping the sample in an electrochemical cell with the pores exposed to the growth solution. We used a two electrode set-up with a copper anode, the voltages presented in the paper meaning the potential difference

between the potential of the membrane working electrode and the copper anode.

The morphology of the wires was studied by means of electron microscopy while their composition was analyzed by means of energy dispersive X ray analysis. In order to be able to make such observations on nanowires the polycarbonate template was dissolved using dichloromethane.

3. Results and discussion

Ion track etching

As stated earlier in order to prepare the nanowires the first step is represented by the preparation of the nanoporous membrane. Etching of the ion track is an extremely important process taking into account that the etching parameters are the one which will determine the shape and dimensions of the wire. During this process a high selectivity bath is used to remove the ion track (the damaged cylindrical zone produced in the material by the swift heavy ion). Two parameters are important for the process and determine the final shape of the resulting pore: the track etch rate v_t and the bulk etch rate v_b . The resulting pore has a conical shape with the opening angle $\tan\alpha = v_t/v_b$. For high selectivity etching baths, i.e. $v_t \gg v_b$, the pore shape can be well approximated by a cylinder [6]. The ratio between the two rates can be easiest adjusted for polycarbonate. This is done by varying parameters such as concentration of etching bath and temperature. In our experiments we used for cylindrical wires a solution containing 5M NaOH and 10% methanol at 50°C while for conical wires we used a solution containing 50% 5 M NaOH and 50% methanol at room temperature.

Electrochemical deposition

The deposition of metals in porous membranes is a process which depends on a wide range of parameters: composition of the deposition bath, deposition temperature and overvoltage being the most important parameters. Also of high importance regarding the growth process was proved to be the agitation of the growth bath by ultrasonation.

In our case in order to prepare alloy nanowires or multilayered ones we employed a bath containing the two metals. In the case of the copper cobalt alloys and multilayeres the deposition bath contains copper and cobalt ions. Due to the fact that the reduction potential of copper ions is much more positive than the one for cobalt, it is relatively easy to design a bath which can be employed for depositing multilayers of copper and cobalt or alloys just by choosing the appropriate deposition potential. Thus if the bath contains both copper and cobalt ions at more positive potentials only copper will be deposited while at more negative potentials a copper cobalt alloy will be formed. If the concentration of copper in the deposition bath is small compared to the cobalt one, at higher potential the alloy will contain only a few percent cobalt. The method was employed for almost a decade for

the deposition of multilayered nanowires with giant magnetoresistive properties.

In our studies we tried to find the conditions in order to be able to grow high quality nanowires from the point of view of structural and morphological properties. For the copper component our results confirmed the ones obtained in baths containing only copper ions [7] namely a tendency to grow single crystals was observed for depositions at low overpotentials even if we employed low copper ion concentration (Fig. 1).

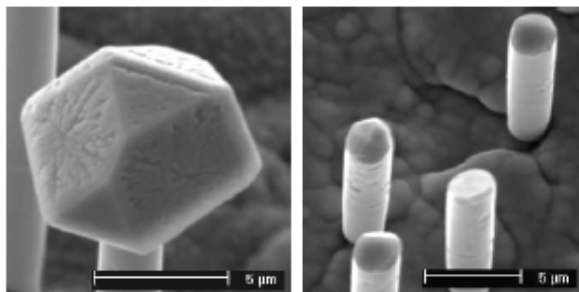


Fig. 1. Copper wires deposited from a bath containing 320g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}/\text{l}$, 3.2g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{l}$ and 32g $\text{H}_3\text{BO}_3/\text{l}$ at (a) 50 °C and (b) 55 °C at -40mV.

More negative potentials affect the morphology of the deposited wires, the process resulting in wires with diameters smaller than the one of the pores (Fig. 2).

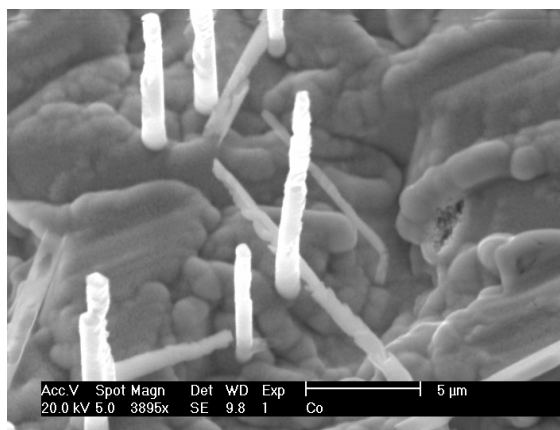


Fig. 2. Wires deposited from a bath containing copper and cobalt at -600 mV.

At potentials higher than -700 mV cobalt starts to deposit. We found for a bath where the ratio between the cobalt and the copper ions is 32:1 that we can obtain wires with cobalt content as high as 85%. This composition is reached for a deposition potential of -1V. Too high deposition potentials for cobalt rich alloy wires is also decreasing their morphological quality leading to hollow structures as can be seen in Fig. 3.

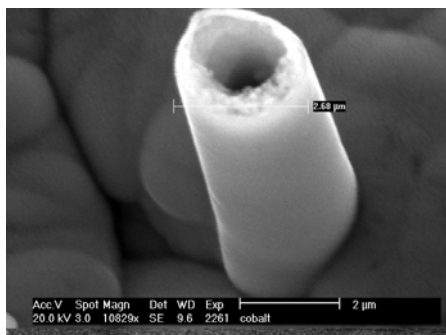
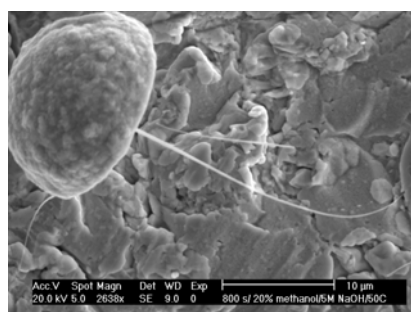
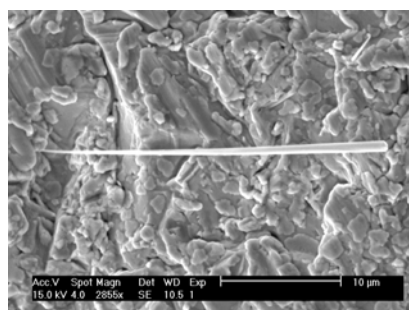


Fig. 3. Cobalt rich alloy hollow wire prepared at -1.1 V from a bath containing copper and cobalt ions in a ratio of 1:32.

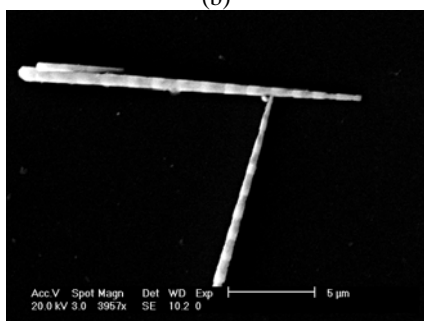
These observations allowed us to employ the best conditions in order to obtain cobalt copper alloy and multilayered wires with high morphological quality (Fig. 4).



(a)



(b)



(c)

Fig. 4. Copper (a), cobalt rich alloy (b) and copper/cobalt multilayered wires.

4. Conclusions

The template technique was employed to deposit cylindrical and conical nanowires with high morphological quality. Based on etching conditions wires with desired geometrical parameters can be obtained. By choosing the appropriate deposition conditions such as bath composition, temperature and overvoltage wires with the desired morphological and compositional characteristics can be prepared.

By using single pore templates [8, 9] one can use the technique for the fabrication of single nanowire sensors based on giant or anisotropic magnetoresistance effect.

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References

- [1] G. E. Possin, Forming very small diameter wires; *Rev. Sci. Instrum.* **41**, 772 (1970).
- [2] C. R. Martin, Nanomaterials, A Membrane – Based Synthetic Approach; *Science* **266**, 1961 (1994).
- [3] T. Ohgai, X. Hoffer, L. Gravier, J.-E. Wegrowe, Ansermet, J. Ph., Bridging the gap between template synthesis and microelectronics: spin-valves and multilayers in self-organized anodized aluminium nanopores; *Nanotechnology* **14**, 978 (2003).
- [4] L. Piraux, J. M. George, J. F. Despres, C. Leroy, E. Ferain, R. Legras, K. Ounadjela, A. Fert, *Appl. Phys. Lett.* **65**, 2484 (1994).
- [5] L. Gravier, J.-E. Wegrowe, T. Wade, A. Fabian, Ansermet, J.-Ph., Thermopower and GMR of a Single Co/Cu Multilayer Nanowire, *IEEE Trans. Mag.* **38**, 2700 (2002).
- [6] See Introduction to ion track etching by Pavel Apel and Reimar Spohr at <http://www.iontracktechnology.de>.
- [7] M. E. Toimil-Molares, V. Buschmann, D. Dobrev, R. Neumann, R. Scholz, I. U. Schuchert, Vetter, J., Single-Crystalline Copper Nanowires Produced by Electrochemical Deposition in Polymeric Ion Track membranes; *Adv. Mater.* **13**, 62 (2001).
- [8] I. Enculescu, Z. Siwy, D. Dobrev, C. Trautmann, Toimil M. E. Molares, R. Neumann, K. Hjort, L. Westerberg, R. Spohr, Copper nanowires electrodeposited in etched single-ion track templates; *Appl. Phys. A* **77**, 751 (2003).
- [9] M. E. Toimil-Molares, N. Chtanko, T. W. Cornelius, D. Dobrev, I. Enculescu, R. H. Blick, R. Neumann, Fabrication and contacting of single Bi nanowires, *Nanotechnology* **15**, 201 (2004).

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