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Effect of additives on nickel nanowires electrochemical deposition

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The paper presents the effect of additives on nickel nanowires preparation by employing a template approach. The nanostructures were obtained by electrochemical deposition in ion track nanoporous membranes. The main goal was to find a wetting agent which increases the pores filling efficiency. Due to the fact that the polycarbonate nanoporous membranes used as templates are strongly hydrophobic problems appear when filling the nanopores with the aqueous electrochemical baths. We found that polyvinylpyrrolidone (PVP) added in the bath improves membrane wetting, thus increasing the deposition efficiency up to 80%. Electrochemical polarization and chronoamperometry were employed for identifying and studying the processes which take place in the case of cathodic deposition of nickel nanowires. Scanning electron microscopy was employed for nanostructure morphology characterization.

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1. Introduction

The deposition of metallic nanowires with magnetic properties proved to be an attractive field in the last decade due to the wide field of potential applications. Thus, by this method, one can prepare nanowires with exotic properties, like anisotropic or giant magnetoresistance [1-3]. These quasi 1-dimensional nanostructures can be employed as building blocks in the development of devices such as magnetic field sensors or nonvolatile RAM memories.

The template approach represents one of the most important methods of preparation for this class of nanostructures [4-6]. Typically, the templates are either polymer nanoporous membranes, with parallel cylindrical pores obtained by swift heavy ions bombardment and subsequent etching, or nanoporous alumina obtained by electrochemical anodization.

The polymer ion track membranes are ideal from several points of view for being used as templates for magnetic nanowires growth. Thus, the pore morphology, dimensions and density can be independently controlled by controlling the etching conditions and the ion flux. One can obtain in this way membranes with a large number of pores (up to 10^{10} pores/cm^2) for measurements were a larger quantity of material, i.e. a larger amount of nanowires, is necessary (e.g. X ray diffraction or magnetization) while membranes with low pore density (down to 1 pore/sample) can be employed for transport measurements on individual nanowires [7,8].

In this report we present an improvement in the algorithm of nanowires preparation using polycarbonate ion track membranes as templates and electrochemical deposition. Thus, one important drawback of the approach is given by the fact that polycarbonate is hydrophilic. This characteristic makes difficult to wet the pores with the deposition solution and thus to grow nanowires with high pore filling efficiency. By adding additives in the deposition solution we succeeded in improving the template wetability and in this way to improve the efficiency of the nanostructures fabrication process.

2. Experimental

The nickel nanowires were prepared following four steps. In the first one the polymer foils were irradiated with swift heavy ions (e.g. Au^{28+}, U^{32+}, specific energy of 11.4 MeV/nucleon) with fluencies of 10^7ions/cm^2. Each ion produces in the target material a cylindrical track with a diameter of few nanometers. After irradiation, in order to obtain the nanopores, the ion tracks are selectively etched away, the polycarbonate foils being dipped in a solution of 5M NaOH at 50^{o}C.

The next step is the deposition of the work electrode which will be used for the electrochemical deposition. Thus, a gold thin film was deposited by dc-sputtering on one side of the nanoporous membrane. On the gold thin film a copper layer was electrochemically deposited, in order to increase the mechanical resistance of the membrane and to completely cover the nanopores opening.

The most important step is the nanowires electrochemical deposition. The nickel nanowires deposition was realized using a Watts bath containing nickel sulfate and nickel chloride as nickel ion sources. The bath pH was about 5 (by adding boric acid) and working temperature was about 60^{o}C. A three electrodes arrangement with a saturated calomel as reference electrode was employed. The bath was connected to the reference electrode by a salt bridge and a nickel wire was employed as counter-electrode.

3. Results and discussion

A comparison between the deposition of nanowires without additives and with polyvinylpyrrolidone and gelatin in the deposition bath was made.

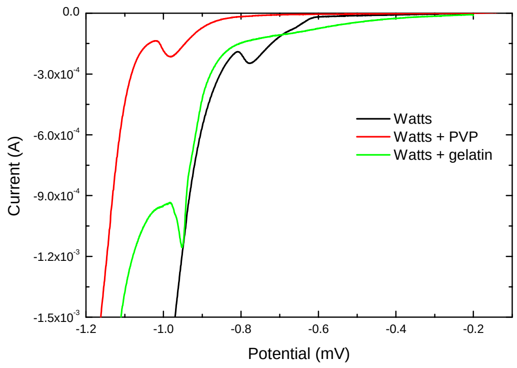

Fig. 1. The polarization curves for the three studied solutions (Watts bath without additives and with gelatin and PVP); the measured potential vs. SCE, scan rate 5 mV/s, pores density of 10^7/cm^2, samples 15 min etched in a solution contents 6 M NaOH at 50 °C i.e. 500 nm.

In Fig. 1 the polarization curves for the three solutions, the Watts bath without additives, a bath with gelatin and another one with PVP are comparatively presented. One can notice a strong correspondence between the three polarization curves, the main difference consisting in the shift to more electronegative potentials of the peak corresponding to nickel deposition for the baths with additives.

Based on the results obtained from the polarization curves the electrochemical deposition was performed.

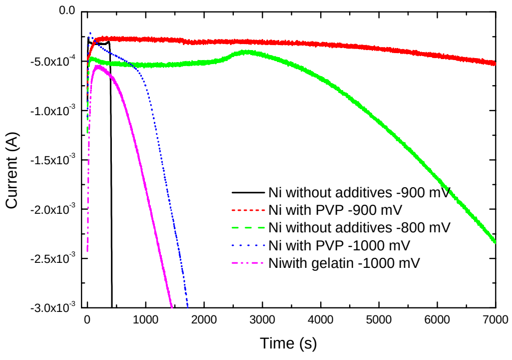

Fig. 2. The cronoampermetric curves for the three studied solutions: Watts without additives, with gelatin and with PVP, measured potential vs. SCE.

In Fig. 2 the cronoampermetric curves for deposition in different conditions of potential are presented. A deposition curve presents three phases: the first one is representative for solution polarization and double layer formation; the second is the nanowire growth and the third phase appears after the complete filling of the nanopores and is observed like a strong increase of the deposition current. It can be noticed that the adequate time for completely filling the pores is different according to experimental conditions, i.e. the nanowires growth rate strongly depends on the applied potential and bath composition. Moreover, the growth rate strongly influences the nanowires structure and morphology.

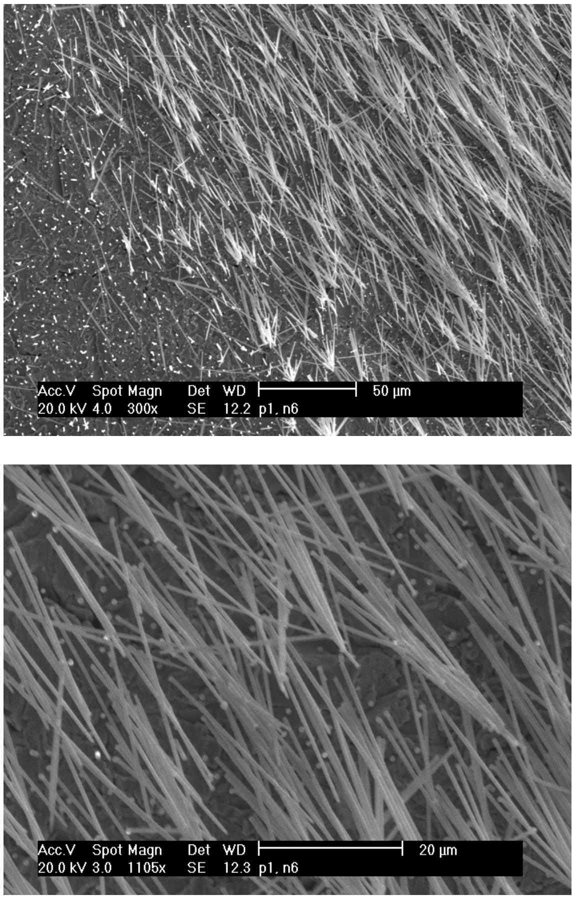

Fig. 3. SEM images of a nickel nanowire array obtained by electrochemical deposition from a Watts bath without additives at a deposition potential of -800 mV vs. SCE.

The scanning electron microscopy images of a nanowire arrays grown from a solution without additives at a deposition potential of -800 mV vs. SCE are presented in figure 3. The nanowires have a good morphological quality and smooth walls. There are regions on which the deposition is unequal, that means there are regions which probable weren't wetted by electrolyte and regions which were well wetted.

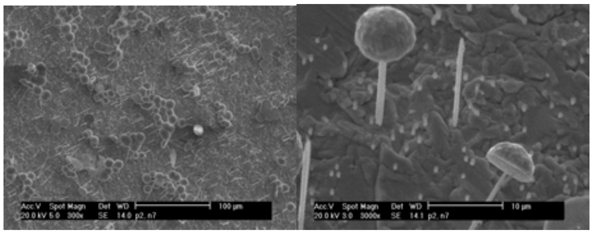

Fig. 4. SEM images of a nickel nanowire array electrochemical deposited from a Watts bath without additives at a potential of -900mV vs. SCE.

Scanning electron microscopy images for a nickel nanowire array obtained at a deposition potential of -900 mV vs. SCE are presented in figure 4. In this case the density of the pores filled with nickel is lower than in case of -800mV deposition potential. The pores were completely filled and on the surface of the membrane nickel caps were grown. Comparatively with the deposition performed at a lower potential, the nanowires surface seem to be rougher, because of the higher growth rate. By comparing the chronoampermetric curves for the two cases, one can notice that the nanowires growth rate is about four times higher while the current density is lower. This observation is in accordance with SEM images in which a lower nanowire density can be observed for the sample deposited at a more electronegative potential.

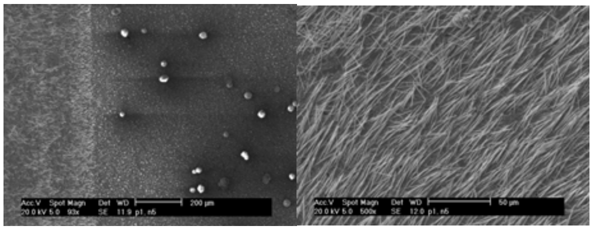

Fig. 5. SEM images of a nickel nanowire array electrochemical deposited from a Watts bath with gelatin as additive at a potential of -1000mV vs. SCE.

In Fig. 5 the SEM images of nanowire arrays grown at a potential of -1000 mV vs. SCE using an electrochemical bath with gelatin as additive are presented. For the deposition solution with gelatin the peak corresponding to nickel deposition is shifted with about 200 mV towards more electronegative potentials. From the data presented in the chronoampermetric curve it can be interfered that the growth rate is similar with the one obtained for the solution without additives at a potential of -900 mV.

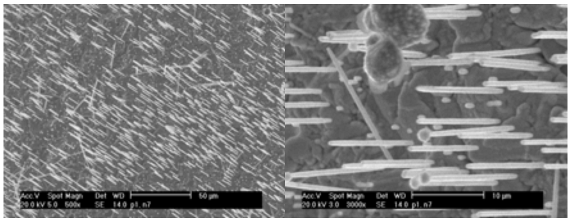

Fig. 6. SEM images of a nickel nanowire array deposited from a Watts bath with PVP as additive at a potential of -900mV vs. SCE.

The SEM images of nanowires arrays deposited at a potential of -900 mV from a bath containing polyvinylpyrrolidone as an additive are presented in figure 6. A quite increased density of nanowires was obtained. Also, from caps morphology results that the structures are polycrystalline. One can also notice that in this case there is a large number of wires which are not broken, proving a higher structural quality.

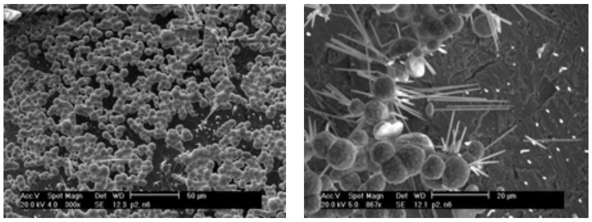

Fig. 7. SEM images of a nickel nanowire array electrochemical deposited from a Watts bath with PVP as additive at a potential of -1000mV vs. SCE.

In Fig. 7 the results obtained for the deposition performed at -1000 mV, using a deposition bath containing PVP as additive are presented. It is interesting that all nanowires have already caps grown which are obtained after pores filling. In this case, all the caps have almost the same dimensions, proving a high growth process uniformity.

Table 1. The efficiencyof pore filling with aqueous electrochemical liquid

Solution	Potential vs. SCE	Charge	Filling pores efficiency
Without additives	-800 mV	1.36666	48 %
Without additives	-900 mV	0.11473	4 %
With PVP	-900 mV	2.26	79%
With PVP	-1000 mV	0.47584	17%
With gelatin	-1000 mV	0.28219	10%

In Table 1 the results regarding the efficiency of pore filling for all the cases are summarized. The efficiency was calculated taking into account the pore diameter and the pore density and the charge transferred from the electrode during the second step, i.e. pore filling, of the process. The charge was calculated by integrating the curves from figure 1. As one can notice an efficiency of almost 80% was obtained for the deposition taking place at -900 mV from the bath containing PVP as an additive.

An explanation for the fact that for higher deposition potentials the efficiency decrease may be related to hydrogen development which results in the formation of gas bubbles which plugs the nanopores stopping in this way the growth process.

4. Conclusions

In this paper we reported our results regarding the effect of two different additives on Ni nanowires preparation by electrochemical deposition in ion track nanoporous membranes. The main parameter which was observed was the pore filling efficiency.

Due to the fact that the polymeric membranes used as templates are hydrophobic, not all the pores are filled with electrolyte during the growth process. Moreover, gas or vapor bubbles can be formed on the membrane or inside the pores, which leads to an interruption of the deposition process on certain areas of the membrane. As a consequence the deposition takes place inside a limited number of pores. It was found that for the bath without any wetting additives the deposition takes place with an efficiency of maximum 48%.

The PVP employment as an additive in the growth bath gives an increase of pores filling efficiency, up to 80%, allowing the preparation of high density nanowire arrays.

For higher deposition potentials the efficiency decreases for all the cases. An explanation may be given by the fact that at such potentials hydrogen is produced, enabling the production of bubbles and thus plugging the nanopores and stopping the deposition.

By employing PVP as a wetting agent the reproducibility of the experiments will increase also for the case of low pore density membranes. Such templates, with pore densities down to 1 pore per sample, are used mainly for transport measurements on nanowires, the approach overcoming the difficulties related to nanowire manipulation and contacting.

Acknowledgements

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