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Influence of electrodeposition techniques on Ni nanostructures

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1. Introduction

In recent years, nanostructured materials have attracted growing interest due to their specific properties, which allow application in several fields such as photonics, nanoelectronics, thermoelectronics. For example, nanostructured materials are employed for the fabrication of field emission devices, magnetic memories, nanoelectrodes, sensors, etc. The narrow size of nanostructured materials causes significant modifications of properties with respect to the bulk materials like thermodynamic stability, electrical conductivity, mechanical, magnetic features, etc. [1].

For these reasons, extensive investigations dealing with preparation and characterization of these materials have been carried out [2,3]. For the fabrication of nanostructures different methods, like lithography [4], chemical vapour deposition [5], sol–gel methods [6], elctrodeposition [7,8] and displacement deposition [9] were proposed. One of the most popular techniques for preparation of nanostructures is based on the use of a porous template, which can be either partially or completely removed after the synthesis [10,11]. Polycarbonate membrane and anodic alumina membrane (AAM) are usually used for this purpose. In particular, AAM is an almost ideal template, due to its morphology consisting in an ordered array of cylindrical pores perpendicular to the surface [12,13]. Another advantage of these membranes is the possibility to control their morphological features by adjusting the anodizing

ABSTRACT

Different Ni nanostructure arrays were fabricated by pulsed electrodeposition from a Watts bath inside the pores of anodic alumina membrane (AAM) templates. Under a trapezoidal waveform of potential, consisting of fast linear sweeps between 0 and -3 V (SCE) interleaved by delay times at 0 (10 s) and -3 V(0.1 s), Ni nanowires were grown. The rate of nanowires growth was constant up to 60 min of deposition. For longer times, the growth of nanowires was not uniform, and after about 180 min some nanowires reached the template surface exposed to the electrolyte. Under square potential pulses between the same potentials (pulse length 1 s), nanotubes of Ni are obtained. Morphological analysis of these nanostructures at different lengths revealed that the inner profile of nanotubes evolved from cylindrical to conical with increasing deposition time. The possibility to grow either nanowires or nanotubes in dependence of the potential waveform, as well as the growth rate of nanostructures were discussed taking into account the reaction of hydrogen evolution, occurring simultaneously with Ni electrodeposition.

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parameters, such as surface treatment of aluminium, potential and time of anodizing, nature and composition of electrolyte [14–24]. Besides, it is very easy and cheap to fabricate these membranes. In this work, we used AAM as template for producing Ni nanostructures which can be employed for fabrication of recording magnetic memory. The interest toward nanostructured magnetic materials is due to the fact that current carriers are confined in the radial direction; consequently, transport is possible only in the nanowire axial direction [25].

Vasquez and coworkers prepared Ni nanowires by electrodeposition inside AAM pores and found that the magnetic behaviour changes with the aspect ratio (length to width ratio) of nanowires [26-30]. Other authors reported that preferential plane of nanowires growth is dependent on AAM pore diameter; therefore, the magnetic behaviour can be controlled through this parameter [31,32]. The importance of fabricating regular arrays of magnetic elements, having sub-micron sizes, was emphasized by Prida et al. [25], who highlighted that each single-domain ferromagnetic nanowire represents one bit, depending on its magnetization state. In this way, data recording densities exceeding 150 Gbit cm⁻² can be achieved [33,34]. For these applications wire diameter and interwire spacing should be as small as possible in order to increase the recording density [35-37]. However, for other possible magnetic applications, such as those based on the magneto-optical [38] or microwave properties [39] of the arrays, larger wire diameters may be more useful.

Despite the large amount of data reported in the literature, at our knowledge no research has paid attention to the relation between waveform of applied potential and morphology of the nanostructures. Recently, the influence of electrodeposition condi-



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tions (direct and alternating) on the growth orientation of metallic gold and copper nanowires was investigated by Maurer et al. [40]. In this paper, we present results pertaining to the fabrication of Ni nanostructures by electrodeposition under unipolar pulsed potential. We found that either nanowires or nanotubes can be fabricated inside the channels of AAM, depending on the applied waveform. The nanostructures were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). The role of the hydrogen evolution process, occurring simultaneously with Ni deposition, is invoked in order to explain the different nanostructures.

2. Experimental

Ni nanostructures were deposited within commercial AAM (Whatman, Anodisc 47) having an average pore diameter of \sim 210 nm. The morphological characteristics of these membranes are presented elsewhere [41,42]. In particular, an AAM consists of a regular bi-dimensional array of pores uniformly distributed on the surface. Porosity of about 30% was evaluated by SEM analysis [43].

Prior to deposition, template pieces, having an overall area of the order of 1 cm^2 , were back sputtered with gold, mounted onto an electrode holder by means of a carbon conductive paste, and insulated laterally using an acrylic lacquer. The metallic Ni nanostructure arrays were grown in a Watts bath having the following composition: $300 \text{ gL}^{-1} \text{ NiSO}_4 \cdot 6 \text{H}_2 \text{O}$, $45 \text{ gL}^{-1} \text{ NiCl}_2 \cdot 6 \text{H}_2 \text{O}$, and $45 \text{ gL}^{-1} \text{ H}_3 \text{BO}_3$ [44]. Temperature and pH values were kept at $25 \,^{\circ}\text{C}$ and 4.5, respectively. The electrodeposition time was varied from 2 to 360 min. A typical three-electrode cell was used for the pulsed electrodeposition, with a platinum foil as counter-electrode and a standard calomel electrode (SCE) as reference. In the following all potentials are referred to SCE. Electrodeposition was performed in the potentiostatic mode, using an EG&G potentiostat/galvanostat (mod. 273A). Two different potential waveforms were applied between the same limits:

- (i) a trapezoidal wave, consisting of a linear ramp from 0 V to -3 V (SCE) at $1 V s^{-1}$, followed by a stop at -3 V for 0.1 s, a reverse ramp from -3 to 0 V at the same sweep rate, and an arrest at 0 V for 10 s;
- (ii) a square wave between 0 V and -3 V (SCE), with delay times of 10 and 1 s at the two limits, respectively.

XRD patterns were recorded soon after electrodeposition by using a Philips generator (mod. PW 1130) and a PW goniometry (mod. 1050). All diffractograms were obtained in the 2θ range from 10° to 100° with a step of 0.02° and a measuring time of 0.5 s for step, using the Cu K α radiation (λ = 1.54 Å). Peaks were identified according to ICDD database [45].

Morphology of electrodeposited nanostructures was observed, before and after dissolution of the AAM template in 1 M NaOH solution, by means of a SEM microscope (FEI ESEM, mod. XL30) equipped with an EDS probe for chemical composition analysis. Prior to SEM analysis, sample surface was coated with a sputtered layer of gold, to avoid electrostatic charging under the electron beam.

In order to ensure the reliability of the different characterizations, these were performed on different pieces of the same sample.

3. Results and discussion

3.1. Fabrication of nanowires

Ni nanowires were fabricated by electrodeposition applying a trapezoidal potential waveform. Fig. 1 shows two SEM images of these nanowires obtained after 60 min of deposition, corre-



Fig. 1. SEM images of Ni nanowires fabricated by electrodeposition under trapezoidal potential waveform for 60 min: (a) sectional-view and (b) top-view after partial dissolution of the template in 1 M NaOH for 1 h.

sponding to about 220 potential cycles. In Fig. 1a we report the sectional-view of the template with parallel Ni nanowires emerging from the channels. Fig. 1b shows the top-view of the nanowires after immersion of the membrane in 1M NaOH solution for 1 h, leading to partial dissolution of the template; this procedure was adopted in order to evidence the morphology of the nanowires. Specifically, a uniform diameter of the nanowires (about 210 nm) can be observed.

Fig. 2 reports the XRD patterns for the sample of Fig. 1. In agreement with the ICDD card 4-850 [45], Ni nanowires are polycrystalline with the most intense peak along the plane (111). By using the Scherrer formula [46], we calculated a grain size of about 95.4 nm. The inset of Fig. 2 shows a Ni EDS mapping of the same sample. Membrane is filled for a thickness of about 35 μ m with a quite uniform Ni distribution; however, the inner surface (that in contact with gold, where Ni nucleation occurs) appears perfectly flat while the outer surface (corresponding to the direction of nanowires growth) is slightly waved, indicating that length of the nanowires is not perfectly uniform.

Fig. 3 displays the potential waveform leading to the formation of Ni nanowires (curve a), and the current response after different



Fig. 2. XRD patterns for the nanowires of Fig. 1. Inset: Ni EDS mapping.

deposition times (curves b-g). The current transients during the potential scan change with the deposition time. After 2 min (curve b) a small cathodic wave with a peak current of about $20 \,\text{mA}\,\text{cm}^{-2}$ can be observed; the current wave became more pronounced with increasing the deposition time, and after 180 min its shape followed that of potential waveform (curve e). For longer deposition times the shape of current wave did not change anymore, with a cathodic peak of about 250 mA cm^{-2} after 360 min (curve g). This figure evidences some interesting issues. The progressive increase of the cathodic current is related to the growth of nanowires. In particular, the current response becomes similar to the potential waveform, as soon as nanowires reach the outer surface of the template, where a massive Ni layer was deposited (see below). Thus, the increase of current density with time seems due to the progressive decrease of the ohmic resistance, mostly due to the replacement of the electrolytic solution inside the channels of the template with metallic Ni. In fact, the proportionality between current density and potential for long deposition times (curves e-g) suggests that Ni deposition on the external surface occurs under ohmic control. This kind of control could be ascribed either to the ohmic drop through the nanowires connecting the outer surface of the template to the inner gold layer or to the hydrogen bubbles developing during Ni deposition. We underline that noticeable gas evolution was observed during electrodeposition since the initial pulses.

The progressive filling of the AAM channels is shown in Fig. 4. After 40 min of deposition the length of nanowires was about $19 \,\mu m$ (Fig. 4a), and after 60 min the length was increased to 35 μm (Fig. 4b). Micrographs 4c and d reveal that for longer deposition



Fig. 3. Applied potential waveform for the fabrication of Ni nanowires (curve a), and current transients at different deposition times (curves b–g).



Fig. 4. Sectional-view of Ni nanowires after different times of deposition under trapezoidal waveform of potential: (a) 40 min, (b) 60 min, (c) 180 and (d) 180 min (detail of (c) showing the edge between the section and the surface of the template).

times nanowires growth is not uniform. In particular, after 180 min some nanowires reached the outer surface, while other channels were only partially filled. Fig. 4c displays the whole thickness of the composite membrane, while the continuity between the nanowires and the hemispherical islands of Ni deposited on the external surface is evidenced in micrograph 4d. A careful control of nanowires length and its uniformity are of fundamental importance for applications. The present study shows that, in the chosen conditions, length is quite uniform up to 60 min of deposition (see inset of Fig. 2), while for longer deposition times significant differences in length are noticed between different channels (Fig. 4c and d). This is probably due to the parasitic hydrogen evolution reaction. which interferes with the reaction of Ni deposition. For deposition times less than 60 min, the cathodic current was rather low. Therefore, at the beginning of each negative potential sweep, membrane channels were practically free of hydrogen, because part of it was conveyed outside the channels and part was consumed during the long delay time at 0V, where the current was anodic. For longer deposition times as the cathodic current density increased, also the



Fig. 5. Morphology of the template external surface after different times of deposition: (a) and (b) 180 min, (c) 360 min.

rate of hydrogen production was higher. Consequently, some channels remained either partially or completely screened by hydrogen bubbles, because gas production rate was higher than that of consuming.

The progressive coverage of the AAM external surface with Ni is shown in Fig. 5. Fig. 5a shows some hemispherical metallic nuclei, some of which begin to coalesce, randomly distributed over the surface. The cause of the random distribution of these nuclei is elucidated in Fig. 5b, where it is possible to distinguish four white spots, which can be identified as sheaves of nanowires on the point of emerging to the surface. As one sheaf reaches the external surface of the membrane, deposition of massive Ni occurs over it, with the formation of metallic particles. In other words, after 180 min some nanowires have already reached the surface, and they generate the nuclei for the formation of Ni macro-particles on the external surface, while other nanowires were still growing inside the pores.



Fig. 6. Sectional-view of Ni nanowires grown by electrodeposition under trapezoidal potential waveform for 240 min. A copper tape was used to connect the gold layer of template to the electrode holder.

The progressive emersion of nanowires determines the formation of new Ni particles, so that the coverage of the external surface increases. After 360 min metallic coverage of the external surface was complete, as shown in Fig. 5c, where the coalescence of Ni nuclei is evident.

The rate of growth of nanowires was also investigated by changing some experimental condition, in order to explain some non-clarified issues of our previous work [24]. In that work, we observed a lower and poorly reproducible growth rate of Ni nanowires, with guite different values of nanowires length for apparently identical experiments. In this work, we have found that as the gold layer of the template is connected to the electrode holder through a copper tape rather than a carbon paste, the current density in otherwise identical conditions was lower, and consequently, shorter nanowires were formed. Fig. 6 shows Ni nanowires formed with a copper tape connection: in this case we obtained nanowires lengths equal to 4 and 14 µm after 240 min of deposition, in two apparently identical experiments, whereas with a carbon paste connection a length of about 50 µm was obtained after 180 min, with a satisfactory reproducibility. This finding suggests that the poor reproducibility of the experiments with copper tape is due probably to the poor quality of the electrical contact between electrode holder and gold.

3.2. Fabrication of nanotubes

Ni nanotubes were fabricated by pulsed electrodeposition applying a square potential waveform to the electrode. Fig. 7 reports two SEM images of these nanotubes obtained after 30 min of deposition (corresponding to 164 cycles) and etching of the template in 1 M NaOH solution for 1 h. This treatment was performed in order to dissolve the membrane and to evidence morphology of the nanostructures formed inside the AAM channels. EDS analysis confirmed that these nanotubes consisted of pure Ni (see below). Fig. 7a shows the top-view of the etched sample, with a quite uniform distribution of nanotubes. At higher magnification (Fig. 7b) it is possible to distinguish the almost perfect cylindrical shape of the nanotubes and their size. For this sample, the average internal diameter and the wall thickness are about 170 and 20 nm, respectively.

Composition of the deposited material was investigated, as shown in Fig. 8, where XRD patterns and EDS spectrum (inset) are reported. Like in the previous case, the deposit was polycrystalline, with a grain size (calculated from the main peak, by means of the Sherrer's equation [46]) of about 18 nm. The wave from $2\theta = 20^{\circ}$ to 30° in the XRD patterns is due to the amorphous nature of anodic alumina. The presence of Al₂O₃ in the XRD patterns is due to the



Fig. 7. SEM images with different magnifications of Ni nanotubes fabricated by electrodeposition for 60 min under square waveform of potential. Template was partially dissolved by immersion in 1 M NaOH for 60 min.



Fig. 8. XRD patterns of a membrane filled with Ni nanotubes fabricated by electrodeposition under square potential pulses for 60 min. Inset: EDS spectrum for the same specimen.



Fig. 9. Applied potential waveform for the fabrication of Ni nanotubes (curve a) and current response (curves b–g) at different electrodeposition times.

fact that this analysis was performed prior to dissolution of the template in NaOH. Also EDS spectrum show in the inset of the figure was taken before dissolution, as confirmed by the presence of O and Al peaks. EDS spectra were recorded also after template dissolution, and they are equal to that reported apart the absence of O peak and the low intensity of Al one. Au peaks, present in both spectra, are due to the gold sputtered on the back side of the template (XRD patterns) and on the AAM front surface before SEM analysis (EDS).

In Fig. 9, the potential waveform (curve a) and the current response after different times (curves b-g) are reported. The current transients show an initial spike of about $-170 \,\mathrm{mA\,cm^{-2}}$, independent of electrodeposition time, followed by a fast decay toward an almost constant value, dependent on the deposition time. After 2 min (curve b of Fig. 9), the value of current density at the end of the square wave is close to 0 mA cm^{-2} , while after 360 min it is about $130 \text{ mA} \text{ cm}^{-2}$ (curve g). This behaviour is typical of a potentistatic transient. The cathodic current spike is likely due to double layer charging following the potential sudden change. As the double layer is fully charged, current arises from the faradaic reactions and becomes almost constant. The current value at the end of transient increases with deposition time. This indicates a progressive decrease of the resistance inside the channels, analogous to the case of nanowires growth. Visual inspection of the electrode revealed hydrogen evolution during the electrodeposition process, even if outer gas bubbling was less intense than in the previous case in the presence of almost the same current density. This suggests a higher hydrogen trapping inside the AAM pores during the growth of nanotubes.

The length of nanotubes after different deposition times is shown in the sectional-views of Fig. 10. Fig. 10a is relative to nanotubes grown for 30 min, while Fig. 10b, which is relative to 360 min of electrodeposition, shows a detail of nanotubes close to the external surface of the membrane. From this last picture, a quite uniform length can be observed, indicating that nanotubes grow in each pore at about the same rate. Fig. 11 shows a linear dependence of the average length of nanotubes on deposition time. From this plot a growth rate equal to 0.164 μ m min⁻¹ can be inferred.

The shape of nanotubes is more evident after partial dissolution of AAM template in 1 M NaOH for 120 min. Following this treatment, the morphology of nanotubes grown after 360 min of deposition is shown in Fig. 12 at different magnifications. Fig. 12b (magnification of the squared area of Fig. 12a) shows that the inner diameter of the nanotubes, fractured at about half of their length, is about 60 nm, corresponding to a wall thickness of 75 nm, while after 30 min of deposition the wall thickness was 20 nm (see Fig. 7). Moreover, from Fig. 12a it can be seen that the wall thickness of the same nanotubes at the extremity close to the external surface



Fig. 10. Sectional-view of nanotubes after different times of electrodeposition: (a) 30 min and (b) 360 min.

of the template is about 100 nm (lower left part of the micro-graph).

This finding suggests that nanotubes are externally cylindrical but with an inner conical profile. Fig. 13 sketches a possible inner



Fig. 11. Average nanotube length vs. deposition time.



Fig. 12. (a) Micrograph of Ni nanotubes after 360 min of electrodeposition and partial dissolution of the template in 1M NaOH for 120 min and (b) magnification of nanotubes section at about half length.

shape of Ni nanotubes. The evolution of the inner shape from cylindrical to conical could be explained by assuming that the rate of growth along the axis of the channels is higher than the rate of growth in radial direction. Consequently, the basal plane is progressively occluded as deposition time increases. In order to obtain Ni nanotubes open on both sides (top and bottom), it is necessary to stop the electrodeposition prior to the closure of the bottom. Therefore, nanotubes length is limited by the occurrence of this



Fig. 13. Possible evolution of the inner profile of Ni nanotubes with time.

event. This means that it is possible to control the length and the inner diameter of the nanotubes by adjusting the deposition time and, probably, the potential limits of the square pulse.

The different rates of Ni deposition along the two channel directions (longitudinal and radial) could be due to the interference of hydrogen evolution, that probably influences also the shape of the nanostructures (either nanowires or nanotubes) associated to the potential pulse waveform.

Other authors invoked the occurrence of this parasitic reaction in order to explain the different shapes of nanostructures fabricated by using polycarbonate membrane as template [47]. In that work nanostructures were fabricated at constant current density, while our experiments were carried out imposing different potential pulse waveforms. When a trapezoidal potential pulse is applied, the increase of current during the cathodic potential scan, even if fast, is progressive, leading to the formation of small hydrogen bubbles that do not hinder the simultaneous deposition of Ni inside the channels. The surface of deposition is periodically renewed, because part of hydrogen is conveyed outside the channels and part is oxidized during the polarization at 0 V. Probably this mechanism leads to the formation of nanowires.

On the contrary, when a square potential pulse is applied, cathodic current increases abruptly when potential steps from 0 to -3 V, with the formation of bigger bubbles, easily detaching from the bottom than from the lateral walls, as evidenced by Fukunaka et al. [47], screening the lateral surface of the channels. In these conditions, Ni deposition can occur only in the gap between hydrogen bubbles and pore wall. By this way, nanotubes are formed. When gas bubbles detach from the deposition surface and evolve outside the pores, new deposition of Ni can occur on this surface, until new hydrogen bubbles are formed. Consequently, Ni is deposited adjacent to the pore wall and perpendicular to it at different rate because the time during which the surface at the bottom of the nanotubes is screened by hydrogen bubbles is higher than that one during which is electrochemically active. When hydrogen bubbles are evolved outside the channels, Ni can be deposited for the time during which the surface is free from gas bubbles. For long polarization times, the bottom of nanotubes is progressively occluded by the metal deposit, so that the inner shape of nanostructures evolves from cylindrical to conical.

4. Conclusions

In this work we investigated the fabrication of nanostructures by electrodeposition of Ni inside the channels of AAM under pulsed potential perturbations. It was found that the shape of nanostructures depends on the potential waveform. Under a trapezoidal wave, ranging between 0 and -3V (SCE), Ni nanowires were formed, whose length increased with deposition time. Their growth rate was constant up to 60 min of deposition, while for longer times non-uniform lengths were observed in different channels. After about 180 min, some nanowires reached the template external surface, over which deposition of massive Ni began. Hemispherical Ni particles were formed, that progressively coalesced leading to the formation of a compact metal layer. As the nanowires reached the external template surface, the shape of current transients modified, becoming equal to that of the potential pulse. This indicates an ohmic control of the deposition process.

Under a square potential waveform, nanotubes of Ni were fabricated inside the channels of AAM. Up to 30 min of deposition, nearly cylindrical nanotubes were formed. For longer times, the inner shape of nanotubes evolved from cylindrical to conical, due to the progressive shutting of the bottom. The formation of different nanostructures (either nanowires or nanotubes) and the modification of the inner shape of nanotubes with increasing the deposition time were explained both invoking the screening effect by hydrogen bubbles that are formed simultaneously to Ni deposition.

In the case of trapezoidal waveform, small bubbles of hydrogen are formed leaving sufficient free surface for deposition of Ni, which consequently, occurs over the entire inner surface of the channels. On the contrary, a square potential pulse leads to formation of bigger gas bubbles, that screen the bottom surface of pores; thus, the deposition of Ni is confined into the gap between bubbles and channel wall.

Further work is in progress in order to better controlling the growth rate of the nanostructures in dependence on potential waveform shape and limits, pH and composition of the deposition bath.

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