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Electrodeposition Efficiency of Co and Cu in the Fabrication of Multilayer Nanowires by Polymeric Track-Etched Templates

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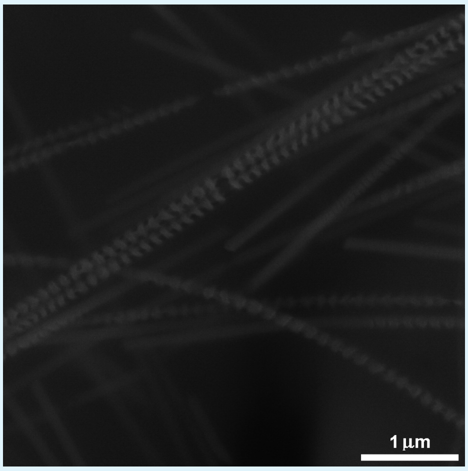
ABSTRACT: Co/Cu-multilayer nanowires can be exploited to develop magnetoresistive sensors. One of the easiest methods for their production is filling nanoporous templates by pulsed-electrodeposition (PED) from a single bath. Multiple parameters effecting the growth of these nano-objects must be controlled to tailor their properties. In this study, the deposition efficiency of Co/Cu-multilayer nanowires produced in nanoporous-polymeric membranes is assessed, and the influence of the space confinement produced by the nanopores themselves on the continuous and pulsed-electrodeposition is evaluated. The growth dependence on some of the most significant process parameters has been investigated. It is shown here that, for each species, when depositing Co and Cu separately, a decrease of current efficiency is observed when the charge density is increased and the pore diameter is reduced; on the contrary, in the Co/Cu-PED, changing the degree of polarization for each deposition step of the different metals results in a sensible reduction of this effect.

KEYWORDS: electroplating, multilayered nanowires, magnetoresistance, nanodevices



1. INTRODUCTION

One-dimensional (1D) nanostructures have been a matter of interest in the past decade. To have this type of system fabricated, many approaches have been followed; among them, the chemical vapor deposition (CVD) is typically used to grow nanowires on nanocatalysts. Top-down lithography and ion milling are exploited to prefabricate nanoporous membranes and lift-off masks to be filled, at a second stage, with a desired material to form nanowires and nanobelts, respectively. In this context, electrodeposition has been widely utilized to fill nanoporous templates. In particular, this technique, referred to here as template electrodeposition (TED) when used to fabricate single-element nanowires or template pulsed electrodeposition (TPED) when used to fabricate multilayer nanowires, has met outstanding consideration;[1−6] in fact, it is a simple method to manufacture nanomaterials on large areas both for fundamental studies and for the production of nanodevices in high volumes. Among the plethora of applications investigated, the aforementioned technique is acknowledged as being promising to mass produce magnetic-field sensors and magnetic based microsystems.[7−9] The present work refers specifically to the use of the TPED for the fabrication of Co/Cu-multilayer-nanowire arrays exhibiting giant magnetoresistance (GMR). The conventional GMR systems are developed by physical deposition techniques which require sophisticated and expensive equipments to be adopted; on the contrary, the TPED simply requires a galvanic cell controlled by a low-cost potentiostat. The simplicity of this technology is considered a great advantage for industrialization; therefore, for this reason, the main objective of the present work was to master the TPED process to pave the way for the mass production of multilayer-nanowire-array based current perpendicular to plane (CPP) GMR sensors for automotive contactless positioning systems, as for example, variable valve lift monitoring.

TPED can be carried out in different manners, among them, one of the most promising methods is to employ a single electrolytic solution.[1−5] Two different types of templates are commonly used in the art, namely, the ion-track etched (TE) polymers and the anodic porous alumina membranes. Although both membrane types can provide nanochannels tailored to a given diameter, their nature and morphology present some important differences influencing the filling process and, therefore, they must be considered with particular attention.[5,10,11]

Even though it is commonly acknowledged from an industrialization standpoint that TPED is a cost-effective technique and easily scalable, mainly due to a wide plurality of factors affecting the nanowire growth,[12] there are still contradicting process details in the published literature which make the technology not ready yet to be scaled up. In fact, there are a great deal of process variables which influence the electrodeposition to a higher or lesser degree: concentration of species, pH, presence of complexants and/or, brighteners, temperature,

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voltage and current cycling, and the membrane used (material, pore diameter, and length). Today, a systemic analysis of TPED taking into account these variables is still missing. In principle, all the mentioned variables might affect the current efficiency of the overall process, i.e., the amount of charge transferred that effectively turns into the actual mass of deposited material. In the present study, the influence of some of the aforementioned aspects on the current efficiency when Co/Cu-nanowire arrays are grown by TPED into polycarbonate TE templates has been evaluated.

2. EXPERIMENTAL PROCEDURE

To gain a deep insight into the influence of a space confinement on the electrodeposition (within nanopores) of Co and Cu, three different series of experiments were set up in the present study. A first series of experiments was carried out by the potentiostatic deposition of single-metal thin films of Cu and Co on a flat substrate (gold sputtered Si wafer) without using template membranes to exclude possible space confinement effects. In a second series of experiments, the same identical deposition conditions were used to fill TE polycarbonate membranes to fabricate single-element nanowires of Cu and Co. These experiments were intended to gauge the influence of a space confinement on the ion mobilities during deposition. Finally, as always by the use of identical deposition potentials and the same electrolytic solution, the fabrication of Co/Cu-multilayer-nanowire arrays was carried out in a third series of experiments. This latter was intended to quantify the effect of potentials' alternation and its temporization on the TPED deposition efficiency in the confined space. As described below in detail, to find the most profitable conditions of fabrication, the experiments described above were repeated for different sets of deposition potentials. It is important to mention here that, in order to obtain a direct comparison between PED in confined and not-confined environments, preliminary experiments intended to measure the current efficiency of multilayered structures deposited on flat substrate were performed. Unfortunately, under the deposition conditions used, the thickness of the single layers was not homogeneous over large areas to be measured accurately by the approach followed in the present research.

Therefore, in the present work, the influence of the space confinement on the TED and TPED was investigated by the use of 12 μm thick TE polycarbonate film with different nanopore diameters, namely 30, 50, and 100 nm. High quality templates were provided by the Université catholique de Louvain which pioneered the development of these membranes for industrial use. In particular, templates of 4×10^9 cm^{-1} pore densities were used for 30 and 50 nm pore diameters, while for the larger size ones (100 nm), the pore density was equal to 4×10^7 cm^{-1}. It is important to notice here that membranes of different porosities exhibit different surface areas exposed to the galvanic bath (namely, effective deposition area) during deposition. Therefore, in the analytical part of the work for all the experiments carried out, the effective deposition areas were considered to calculate the current efficiency. For all cases, a layer of gold of about 200 nm thickness was sputtered on one side of the membrane to close up all nanopores in order to have the all-around electrical continuity of the electrodeposition setup. The gold layer at the bottom of nanopores, granting the electrical continuity, was operated as working electrode of a three-electrode electrodeposition cell used in this work.

The three-electrode cell, properly designed to host flexible polycarbonate TE-templates, was made of PTFE. A Pt grid was employed as a counter electrode, and a saturated calomel electrode (SCE) was employed as the reference one. The open end of nanopores was arranged to face upward, i.e., anode over cathode configuration,[13] and the deposition area was of 2 cm^2. Prior to deposition, when the nanoporous membranes were arranged properly, the cell was always placed in an ultrasonic agitation bath for 5 min to allow the complete wetting of the membranes' nanopores. As published elsewhere,[10] it was corroborated here that said sonication time is sufficient to have the complete filling of the nanopores, allowing a homogeneous growth of nanowires over the whole exposed area. The deposition was carried out at room temperature without stirring. As a result, the complete filling of the nanopores, resulting in the maximum fabrication rate of nanowires, could be achieved with success by both TED and TPED.

The TPED of Co/Cu-multilayer nanowires is carried out by the alternative deposition of Co and Cu metal ions from a single bath solution.[1−5] Each of these materials can be deposited by applying the proper voltage to the cell (voltage cycling). The single bath technique consists of the use of a sole electrolytic bath made with salts of both the metal ions to be deposited, where the ion−concentration ratio is highly unbalanced toward the less noble metal. As Cu deposits at a lower negative potential than Co, the former is the nobler element; therefore, its concentration in the deposition solution has to be smaller. As a consequence of that, 100% purity copper can be deposited, but traces of Cu are also deposited within the Co deposition step. According to the Co purity desired, one can tailor the ratio of the species present in the galvanic bath. In this specific context, the Cu impurity contents in the Co layers badly affect the magnetic properties of Co; therefore, from the application standpoint, the Cu precursor in the bath has to be lowered to the minimum. On the contrary, the smaller the Cu concentration is, the slower is the growth of the Cu layers. As a matter of fact, the optimal Cu concentration was chosen from a trade off between a cost-effective fabrication throughput and the GMR performance of the multilayer stack.[14] In this work, the electrolyte used was a sulfate bath prepared by dissolving 520 g/L (1.85 mol/L) $CoSO_4 \cdot 7H_2O$, 5.2 g/L (0.021 mol/L) $CuSO_4 \cdot 5H_2O$, and 52 g/L (0.84 mol/L) H_3BO_3. The latter compound was added to buffer the pH of the electrolytic solution to an approximate constant value of 4.5 throughout the deposition duration. These values result in a ion concentration ratio $[Co^{2+}]/[Cu^{2+}]$ of about 90 to 1. Analytical grade chemicals and purified water with a resistivity higher than 16.8 MΩ cm were used throughout.

Multilayer nanowires were then fabricated, alternating square-pulse potentials by the computer controlled potentiostat AMEL 500. The deposition potentials used were chosen between −0.3 and −0.6 V for Cu deposition and between −0.8 and −1.0 V for Co. Both potentials were referred to the SCE. In all the TPED experiments, the potentials were constantly switched from the Co deposition potential to the Cu one at defined time pairs: a first time defining the Co deposition duration and a second time defining the Cu one. Duration of each single deposition step was chosen in the ranges from 1 to 32 s for Cu and from 0.1 to 3.2 s for Co. The deposition time pairs were chosen to have both layers of the same nominal thickness. Direct electron-microscopy measurements of the layer thickness allowed choosing the proper values of the time pairs by the use of the Faraday's law. During deposition, the complete filling of the nanopore membrane could be detected by a sudden increase of the current density, corresponding to a three-dimensional extra-growth of nanowires when starting to come out from the membrane nanopores. The formation of hemispherical caps at the end of all the nanowires could be depicted by electron microscopy for all the extra-growth cases. For all the deposition employing nanoporous templates, the extra growth of nanowires was then minimized.

The deposition current efficiency was calculated for the first and second series of experiments (i.e., on a flat substrate and infiltrated into the nanoporous membranes, respectively) by the gravimetric method.[15] In all these cases, the current efficiency was calculated, from the experimental value of the charge transferred by the potentiostat, as the ratio between the measured deposited mass, and its theoretical value was given by the Faraday's Law. For the third series of experiments, the current efficiencies of Co and Cu were determined by following a different method. The single layer volumes, which, at constant charge load, have to be theoretically invariant along the nanowire length, were determined by microscopy direct measurements of the layer diameters, tilt angle, and thicknesses. For each sample, a large number of layers belonging to central portions of nanowires were considered and the mean value of the volumes deposited at each metal layer were calculated. The average layer masses of Cu and Co were obtained and compared with those calculated theoretically by the Faraday's law after integrating the current recorded over the time interval of the corresponding deposition steps. The Co anodic peaks taking place at the beginning of the following Cu deposition cycles were not taken into account. In doing so, the theoretical to real deposition value could be directly compared. Finally, the current efficiencies of Cu and Co were calculated as the ratio between the measured values of layer mass and the theoretical ones. As they presented the narrowest distribution of layer diameters and thicknesses, for the analysis, only the central part of the nanowires was considered.[16] Following the chemical dissolution of the polycarbonate membranes, the morphology analysis of the nanowires was performed by transmission electron microscopy and complemented in some cases with scanning electron microscopy. As explained elsewhere, different methods to enhance the contrast between layers for a more accurate measurement were used.[12]

GMR measurements were carried out by a four-contact method on each sample fabricated. A thin layer of gold was sputtered on the top side of the template membrane to ensure the electrical continuity. A magnetic field was applied orthogonally to the wire axes according to a conventional CPP whereas current flows along the wire axes. Saturation was always reached. GMR was calculated according to ref 4 as $\Delta R/R_{\max}$. A typical magnetoresistance to field curve had been previously presented by the same authors in ref 12.

3. RESULTS AND DISCUSSION

In the present section, the results obtained, and a discussion of the possible phenomena which might be at their basis, are presented. In Figure 1, the current efficiency of Cu and Co deposited on a flat substrate and through nanoporous membranes of different pore diameters are reported. These graphs display the current efficiency of the addressed materials as a function of the measured potential. The graph encompasses the whole set of cell potentials tested out. As all tests are carried out under potentiostatic control, the current density is calculated by integrating the current directly measured during deposition to obtain the whole charge transferred. This point forced a careful monitoring of the current evolution when filling the nanoporous membranes; in fact, since the deposition current increases fast when the nanowire tips approach the free surface of the membrane and, therefore, the bulk solution,[17] a prompt stop of growth is mandatory to avoid altering the current efficiency calculation due to the nanowires' extra growth.

From Figure 1, it is apparent that the Cu current efficiency measured here is very close to the 100%, value assumed in other works with similar electrolytes.[1−5] Instead, the Co one can be larger, under specific process conditions, than the values typically considered, i.e., about 70%.[4] In this latter case, it is proven here that the current efficiency depends on the potential applied, and it varies as a function of the pore diameter. Specifically, the current efficiency decreases approximately linearly with lower potential, and the smaller the pore diameter, the larger is its dependence rate. This tendency could be explained, to a certain extent, as a reduction, for larger currents, of the nanopore's effective diameter due to the "double-layer" formation at the pore walls produced by the ions present in the electrolyte. In fact, in the case of polymeric templates, one can expect the presence of functional groups on the nanopore's wall which contributes to a distributed surface charge to the formation of the double layer in question. The double-layer thickness can be estimated by the Debye−Hückel screening length (κ^{-1}). For concentrated electrolytes, the Debye−Hückel coefficient can be very small; for the experimental parameters used here, it results in being about 0.3 nm, as this value is 2 orders of magnitude lower than the smallest channel diameter experimented. The double layer formed in this way can play a role at reducing the effective channel size, although it is not of prime importance.[18] As the Debye−Hückel theory is only valid for dilute solutions, this analysis must be considered cautiously here.

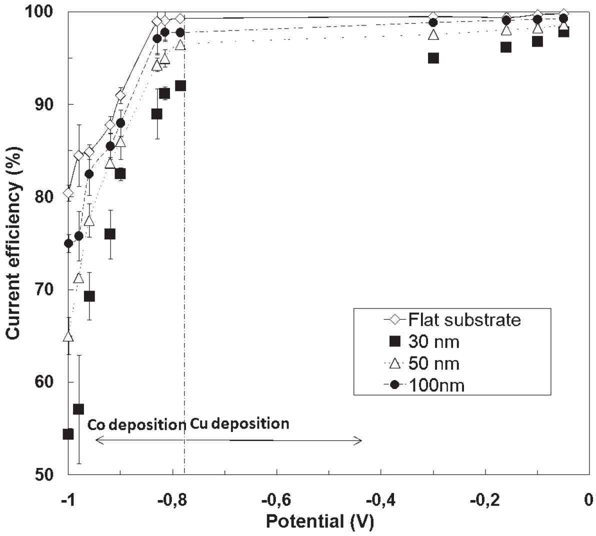

Figure 1. Current efficiency as a function of the applied potential for planar substrates and PC membranes of different pore size-Cu deposition potential range on the graph (right side), Co deposition potential range on the graph (left side).

Another possible effect, which might explain the reduction of current efficiency when larger current densities are used, can lead one back to ion−ion interaction phenomena. In fact, the mobilities of cations and anions cannot be considered unaffected by the presence of other charged carriers in their vicinity and by their relative motion. In fact, ions in water solutions cannot be considered as isolated units; instead, they can be modeled as charged particles surrounded by clouds of ionic species of contrary sign, water molecules (solvation).[19] To estimate the size of these clouds, the Debye−Hückel theory can be used, as above, in a similar fashion. For the electrolytic solution used in this work, the effective diameter of the metal ions deposited was calculated, and its value resulted in a value a little larger than 2 Å. Since the effective distance among ions results to be about 1.1 nm in a homogeneous solution, the ion−ion interaction is expected to play a role in the observed behavior.

On the other hand, another fact to be considered is related to the diffusion of ions (by concentration gradient) and their migration due to the electrostatic field applied during deposition. In the case of single cation electrolytes, both these aspects contribute to the mobility of ions, but with the presence of a second cationic species in a much larger amount, this latter practically takes on the whole conduction current and, hence, the total flux by migration. This is the case of the Co ions which, although indifferent to the electrochemical reaction taking place at the electrode in the Cu deposition cycle, do mainly contribute

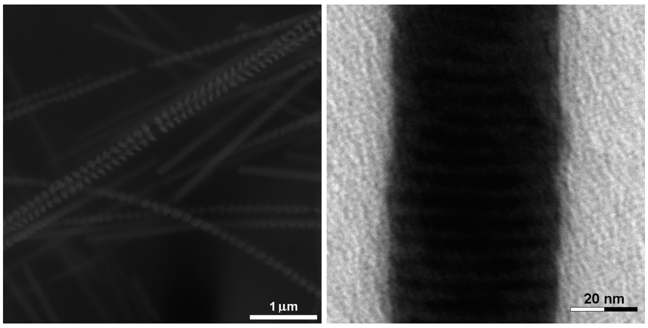

Figure 2. SEM (left) and TEM (right) images of different multilayer nanowires fabricated for this study. A selective chemical etching step was performed to increase the tone contrast between layers.[12]

to build up the conduction current.[19] Specifically, the migration under the electric field of Cu ions is hindered by the presence of the much larger concentration of Co ions and only the diffusional force moves the Cu ions toward the electrode. As a result, during the Cu deposition cycle, although only the chemical reduction of Cu at the metal—electrolyte interface takes place, there is a migration competition of both the metal ions due to the electrostatic field. The motion of both the species together with their respective ionic clouds (hydration shell) can cause adverse interactions in the net movement of the electroactive species to be chemically reduced at the electrode. Therefore, it is reasonable to expect that all the effects described here may influence the deposition efficiency of the metal ions addressed in this work, as the larger is the space confinement produced by the nanopores. In fact, with a similar electrolyte, Schönenberger et al.[10] encountered a reduction of about 3 times of the diffusion coefficient of copper ions in 15 nm nanopores of even shorter length with respect to the bulk diffusion of the same metal ions deposited onto a flat nonporous electrode.

Also, the deposition potential plays an important role on the final current efficiency. In fact, in both metal depositions investigated, there is another important phenomenon contributing very likely to the overall efficiency decrease, which consists of the reduction at the electrode of some protons to yield molecular hydrogen. This effect is more pronounced when more negative deposition potentials are used.[20]

As for the production of single element nanowire arrays, knowing the respective current efficiencies of Co and Cu as a function of the deposition potentials in the TPED regime, when Co and Cu are deposited in an alternate fashion to form bilayer stratification, was a main goal of this work. In particular, the third series of experiments carried out here was intended to measure the TPED efficiency in the fabrication of the Co/Cu multilayer nanowires previously reported in ref 12. As an example, Figure 2 reports two electron microscopy images of Co/Cu multilayer nanowires fabricated having Co and Cu layers of similar thicknesses along the whole nanowire length. The picture on the left side is a low magnification scanning electron microscopy (SEM) image clearly showing identical nanowires of 100 nm diameter whose stratification period is equal to 120 nm, whereas the picture on the figure's right side is a transmission electron microscopy (TEM) image of a 50 nm nanowire of about 6 nm period of stratification. A discussion on the layer local tilt, which is apparent in the SEM image, as well as the method used to calculate the mass forming the tilted layers has been already presented elsewhere.[12]

To corroborate the conclusions of this work on the TPED efficiency measurements, the systems of literature characterized by very similar morphology (diameter and layers thicknesses) and fabricated with similar process parameters (membrane material and morphology, deposition temporization, deposition potentials, electrolytic solution, deposition temperature, etc.) were carefully analyzed. Specifically, the comparison has been made between literature systems made up of Co/Cu multilayer nanowires of 30 and 100 nm diameter with those ones made by the authors in the present work. The Figure 3 shows the thickness of both the Cu and Co layers deposited here by TPED when the most commonly reported deposition potentials and temporization are used. For both cases, a satisfactory correlation with a linear dependence between the layers thickness (and, therefore, the stratification periodicity) and the charge transferred (per net unit area and cycle, i.e., each single metal deposition step) was found to be in agreement with the results published by other authoritative authors.[21−23] In all cases of

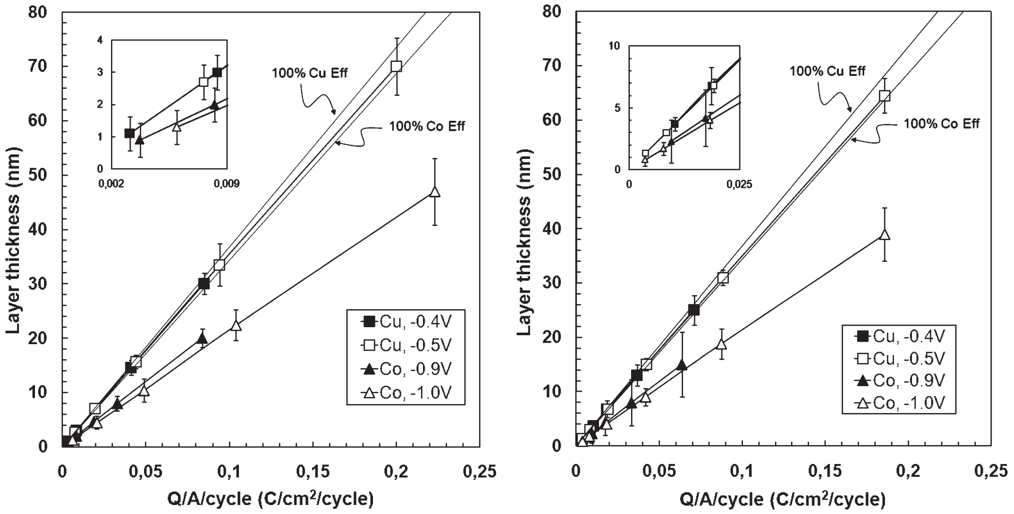

Figure 3. Co/Cu layer thickness as a function of pore size, deposition potential, and charge transferred per cycle and per unit area. Left, 100 nm pore membranes, and right, 30 nm pore membranes. 100% efficiency curves are displayed for each element. Insets display in detail data near the origin.

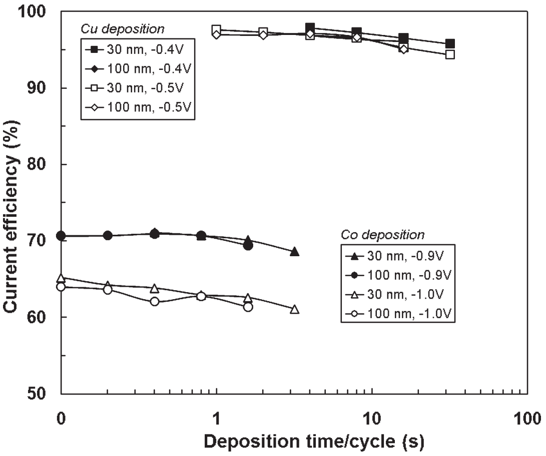

Figure 4. Current efficiency of TPED of Co/Cu multilayer nanowires as a function of the deposition time per cycle.

Figure 3, the copper current efficiency results are very close to 100% as commonly assumed, whereas the cobalt one ranges between 60 and 70% (see Figure 4). As a conclusion, consideration of the efficiency values measured for the fabrication of Co/Cu nanowire array with the parameters of the present study is a realistic assumption.

The time evolution of the current efficiencies of Co and Cu in the TPED is shown by Figure 4, which shows their correlation with the deposition time needed to build a layer. In particular, in this figure, multilayer nanowire arrays of 30 and 100 nm diameters fabricated with the most significant potential pairs are reported. Both for Co and Cu cases, one can observe a slight reduction of the current efficiency when longer deposition duration is experienced. The more in depth, during short deposition cycles, cations are abundant in solution, the TPED is charge controlled and the growth rate is only limited by the rapidity which ions can be chemically reduced at the interface. For the shortest deposition cycles, in fact, the process only depends on the applied potential irrespectively of the diameter of pores to be filled. For longer cycles, due to a limited ions' diffusion speed, a gradient of species concentration is created inside the nanopore and the overall current efficiency depends on the ions' diffusion velocity. Therefore, it should not astonish one that, the longer the deposition cycles, the smaller is the current efficiency. Furthermore, contributing to the Cu current efficiency reduction in the TPED mode is the fact that Cu ions are deposited during the Co cycle as well, and when the Cu cycle starts, the electrochemical bath is more depleted of Cu ions, as the longer Co cycle previously concluded. For what was said previously on TED, it is reasonable to expect a dependence of current efficiency on the pore diameter also in the TPED case. However, in this work, the authors proved that the pore diameter does not play a significant role on the current efficiency in the TPED mode. A possible explanation of this fact can be explained considering that, after a deposition cycle is concluded, the change in potential intended to deposit the new species the degree of polarization is changed. By doing this, the conditions of the bath are changed, involving the modification of the double-layer and ion migration and diffusion, somehow resulting close to those of a space-unconfined deposition.

By comparing Figures 1 and 4, the current efficiency of Cu measured for all the potentials experimented here in the TPED mode is very close to 100%; instead, it is apparent for Co that a consistent reduction has been observed; the Co TPED efficiency ranges between 60% to nearly 71%. In a first instance, the significant reduction of Co current efficiency can be accounted as a redissolution of Co during the Cu deposition cycle.[23] This hypothesis is corroborated by the presence of a high anodic peak observed at the beginning of each Cu deposition cycle; the peak shows itself in the first instants after the potential switches. Due to this fact, Co dissolution can drastically change the actual layer thicknesses with respect to the nominal values deduced from Faraday's law,[24,25] and therefore, the direct measurement method presented in this manuscript, although difficult and time-consuming, is fairly suited to ascertain the real deposition efficiencies in multilayered nanowires. This peak can be reduced by the adequate selection of the Cu deposition potential as showed by Liu et al.[26] and Peter et al.[27] to higher absolute values (i.e., −0.6 V). Finally, Figure 4 also shows that the current efficiency of Co drastically decreases, the larger is the absolute value of the potential used. As for TED, this effect is very likely linked to the chemical reduction of hydrogen at the electrode as noted by Péter et al.,[27] at expenses of the Co one, and becomes more important the larger is the absolute potential applied. Hydrogen evolution is likely the main factor causing the efficiency drop of Cu/Co TPED when the −0.5 V/−1.0 V potential pair was used.

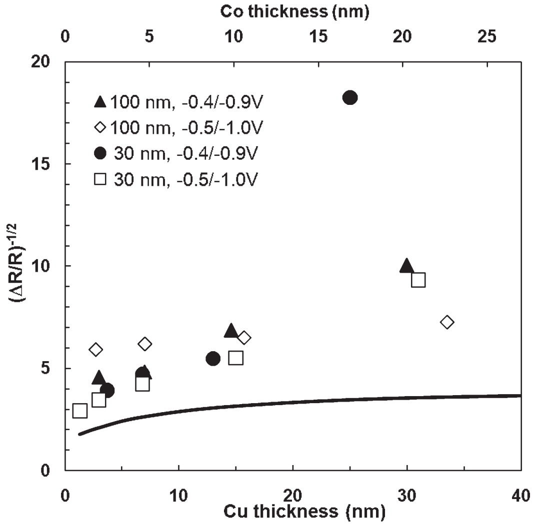

Figure 5. GMR values (as inverse square root) as a function of Cu thickness. The solid line represents the theoretical values calculated by the Valet and Fert model.

The Figure 5 reports, for all the systems fabricated, the magnetoresistance measured by the four-probe technique. The GMR response was observed to vary as a function of Cu thickness, as predicted by the Valet and Fert model in the long spin diffusion length limit which is about 120 nm for Cu.[4] Figure 5 also plots the reference theoretical results of the model. Although the present investigation yielded lower values of GMR than the theoretical ones, the trend is apparent. The discrepancy observed for thicker layers could be reasonably attributed to material defects. The best magnetoresistance values experienced in this work are for nanowires 30 nm in diameter; the slight differences measured are linked to the different potential pairs experimented.

4. CONCLUSIONS

Many parameters are to be considered in the fabrication of multilayer nanowires by pulsed electrodepositon into nanoporous polymeric templates. The presence of different species, the interaction with the same membrane, the space-confinement effect of nanochannels onto the filling process, and other side effects as hydrogen evolution, as well as the recharge or depletion of species by a potential alternation, play an important role on the infiltration current efficiency. During continuous deposition of single species, both over a flat substrate and inside the membrane's nanochannels, a decrease of current efficiency has been observed as the charge density per cycle is increased and the pore diameter is reduced. Unexpectedly, in the case of pulsed electrodeposition of multilayer nanowires, the potential switching changes the degree of polarization of the deposition, each cycle resulting in a lower influence of a space confinement on the growth process, and the rising of other side effects are mainly dependent on the deposition potential and duration of pulses.

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