Electrochemical behaviour and physical properties of Cu/Co multilayers

E. Gómez a,1, A. Labarta b, A. Llorente a, E. Vallés a,2,*

a Laboratori de Ciència i Tecnologia Electroquímica dels Materials (LCTEM), Departament Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain
b Departament Física Fonamental, Facultat de Física, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

Received 17 September 2002; received in revised form 2 December 2002

Abstract

Cobalt/copper multilayer formation was analysed over different substrates in order to control the bilayer thickness and quality of coatings. Using a sulphate–citrate bath, at pH 4.7, electrodeposition conditions were optimised to prepare good alternate Cu/Co layers with high efficiency, by minimising the oxidation of cobalt layers during copper deposition. For multilayers with cobalt and copper layers of several nanometers, direct observation by scanning electron microscopy (SEM) or tapping mode-atomic force microscopy (TMAFM) gives layer thickness in agreement with the value calculated from deposition charges. Therefore, this calculation has been used to estimate the thickness of the thinner layers for which direct observation was difficult or impossible. A relation between the response of different characterisation methods was found. When the thickness of each layer in Cu/Co multilayers is >1.8–2 nm, potentiodynamic stripping experiments show separate peaks related to cobalt and copper oxidation. In these conditions, magnetoresistance of the coating is low. For thinner layers, the stripping response shows overlapping peaks or even a single oxidation peak. In these conditions the magnetoresistance begin to increase.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cobalt–copper; Multilayers; Electrodeposition; Stripping

1. Introduction

Multilayer materials have received increasing attention in recent years because of their special properties (mechanical, optical, electrical, magnetic) with respect to traditional alloys. In recent years electrodeposition has proved to be an alternative technique for preparing alternate micrometric [1–4] or nanometric layers [5–9]. In this line, Cu/Co multilayers present a great interest because of their possible transport properties [10–17] and several authors report their preparation from different baths [10,11,14,16,18,19]. A serious difficulty in electrodeposition multilayer preparation is to test when experimental deposition conditions lead to good alternate layers, especially when thin layers are desired. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques have been used to characterise some electrodeposited multilayers [19–22] although a hard sample preparation is necessary in successful multilayer observation. However, the direct observation of bilayers of few nanometers is very difficult or not feasible by means SEM and TEM and, most of studies take the presence of well-ordered multilayers for granted.

The properties of multilayered systems depend on bilayer thickness, global thickness and good multilayer formation. Therefore, it is important to control the electrodeposition conditions that lead to good deposit formation and to measure the response of the multilayered system to different characterisation methods depending on the bilayer thickness of the coatings.

Our final interest will be the preparation of Cu/Co multilayers for their potential applicability in microsystems (MST). As different materials might be used as

* Corresponding author. Tel.: +34-93-402-1234; fax: +34-93-402-1231.
1 ISE member.
2 ISE member.
E-mail address: e.valles@qf.ub.es (E. Vallés).
components of the devices, several substrates were investigated. The first goal of the present work is to monitor, on different substrates, the conditions of electrodeposition that lead to the formation of good alternate Cu/Co layers with high efficiency, avoiding, the oxidation of the less noble metal (cobalt) during the deposition of the more noble metal (copper).

The second objective proposed was to relate the information provided by means of electrochemical methods (stripping analysis) with that obtained from physical characterisation techniques as SEM, TEM, X-ray diffraction (XRD), TMAFM and magnetoresistance measurements (MR) of the prepared coatings. In this way, the electrochemical analysis can be useful to predict the goodness of the multilayer formation and also useful to inform about the magnetoresistive behaviour.

2. Experimental

Chemicals used were CuSO4·5H2O, CoSO4·7H2O and sodium citrate (Na3C6H5O7·2H2O), all of analytical grade. All solutions were freshly prepared with water first doubly distilled and then treated with a Millipore Milli Q system. The bath contained 0.7 mol dm−3 CuSO4 and CuSO4 ranging between 0.004 and 0.008 mol dm−3. Citrate medium 0.25 mol dm−3 was added to each solution, maintaining the pH close to 4.7. Before and during the experiments, solutions were de-aerated with argon. Deposition was performed at 25 °C with stirring at 60 rpm.

Electrochemical experiments were carried out in a conventional three-electrode cell using both an EG&G 273 potentiostat/galvanostat controlled by a microcomputer and an Autolab with PGSTAT30 equipment and GPES software. Multilayers were prepared using an analitical system Belport 105 potentiostat together with an EG&G 175 signal generator and the Autolab PGSTAT30 equipment.

Different electrodes were used depending on the preparation or characterisation experiments: vitreous carbon rod (Metrohm), copper and nickel rods (John Matthey 99.99%), indium tin oxide (ITO) thin films sputtered on glass plates (thickness of ITO layer = 25 nm) and silicon wafers with titanium/nickel (100/50 nm) seed layers. Vitreous carbon electrode was polished to a mirror finish using alumina of different grades (3.75 and 1.87 μm) and cleaned ultrasonically for 2 min in water. Copper and nickel electrodes were polished to a mirror finish before each experiment using paper of 4000 grade and alumina (0.3 and 0.05 μm) suspended in distilled water and cleaned ultrasonically for 2 min in water. Glass/ITO and Si/seed layer electrodes were first cleaned with acetone and later with water. The counter electrode was a platinum spiral. The reference electrode was an Ag | AgCl | NaCl 1mol dm−3 mounted in a Luggin capillary containing 0.5 mol dm−3 Na2SO4 solution. All potentials refer to this electrode.

Voltammetric experiments were carried out at 10 mV s−1, scanning at first to negative potentials. Only one cycle was run in each voltammetric experiment. Stripping analysis was always performed immediately after deposition. All potentiodynamic-stripping experiments were made at a scan rate of 10 mV s−1 and an initial potential at which deposition did not occur was chosen. Multilayers were attempted by potentiostatic pulse electrolysis.

SEM examined multilayers morphology with a Leica Cambridge Stereoscan S-360 scanning electron microscope. For a successful SEM observation it was necessary to follow an accurate sample preparation. The sample was cut slowly in order to avoid damage of multilayers and then was resin-encased in a mould. Polishing was initiated with papers of coarse grain (1000 and 2400 grade) until the multilayers cross-section appeared. At this point accurate manual polishing was necessary. Fine paper of 4000 grade was used prior to using alumina of 0.3 and 0.05 μm suspended in distilled water. The samples were washed in distilled water between each polishing step.

TMAFM studies were performed with a Multimode microscope stand controlled by Nanoscope III electronics, both from Digital Instruments. The cantilever probes were made on silicon and microfabricated by Nanosensors. For TMAFM observation of the multilayers, it was necessary, after performing the same sample preparation procedure of SEM characterisation, to attack one kind of layers selectively, in order to create a relief of the surface that allowed us to distinguish the individual layers. Selective chemical etching of copper was performed for 5 s in a Nital solution (HNO3 65 wt.% solution in ethanol). The samples were washed in distilled water before TMAFM observation.

Microstructure was examined using a transmission electron microscope Philips CM-30. TEM-selected area diffraction was used.

Electron probe microanalysis (EPMA) was performed on a Cameca SX-50 electron microprobe. X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5600 multitechnique system and Auger spectroscopy measurements were done with a PHI 670 scanning Auger nanoprobe system.

XRD analysis was performed on a Siemens D-500 diffractometer. The Cu-Kα radiation (λ = 1.5406 Å) monochromatiser was selected by means of a diffracted beam flat graphite crystal. 2θ/θ diffractograms were obtained in the range of 2θ = 10 or 30–100° with a step range of 2θ = 0.05° and a measuring time of 3 or 6 s per set.

Magnetoresistance was measured by an alternating current four-point probe technique at 27 and 300 K in
magnetic fields up to 11 kOe, applied parallel to the current.

3. Results and discussion

3.1. Voltammetric study

In order to select the deposition potentials adequate to prepare good alternate layers of cobalt and copper, a previous voltammetric study was made. For each selected electrode, a starting potential at which no current is detected was used. On all electrodes tested, similar behaviour was observed; For low cathodic limits, only copper was deposited and a single oxidation peak was detected (Fig. 1, curve a). It was necessary to decrease the negative limit to induce the start of the cobalt deposition process. The peak which appeared during the positive scan previous to copper oxidation corresponded to cobalt oxidation (Fig. 1, curve b).

Although the qualitative behaviour of the deposition process was similar on the different substrates, different deposition rates were attained from the different analysed electrodes. Both metallic substrates and vitreous carbon were more active than Si/seed-layer, glass/ITO being the less active substrate (Fig. 2).

3.2. Multilayers formation and stripping experiments

Multilayer preparation was performed using potentiostatic pulses ranging from a potential at which only copper deposited ($E_{Cu}$) to a potential at which mainly cobalt deposited ($E_{Co}$). A time $t_{Cu}$ was applied to deposit the Cu layer followed by a much shorter period $t_{Co}$ at potential $E_{Co}$ to grow the Co layer. This Cu/Co cycle was repeated for some minutes to allow the desired multilayer growth.

Related to the voltammetric results, appropriate $E_{Cu}$ and $E_{Co}$ values for each substrate were selected as the manner that: At $E_{Cu}$ the deposition rate was low enough to favour the formation of non-dendritic deposits thus ensuring the formation of the continuous copper layer, but not too positive that the oxidation of the cobalt layers occurred at the start of the deposition of each copper layer. At $E_{Co}$, cobalt was predominantly deposited and low simultaneous hydrogen co-evolution took place. EPMA analysis showed that a small percentage of copper ($\leq 2\%$) was always detected in deposits obtained at $E_{Co}$ potential. By controlling the deposition parameters: (copper concentration, applied potential and step deposition time) multilayers of variable thickness were prepared.

Potentiodynamic stripping was tested as an electrochemical method able to allow information about the electrodeposited multilayers formation. In order to avoid interferences in the response due to the possible substrate oxidation, a vitreous carbon electrode was selected to perform these experiments. The oxidation of deposits had been made, both in the deposition solution itself and in a blank solution ($0.7 \text{ mol dm}^{-3} \text{ Na}_{2}\text{SO}_{4} + 0.008 \text{ mol dm}^{-3} \text{ CuSO}_{4} + 0.25 \text{ mol dm}^{-3} \text{ Na}_{3}\text{C}_{6}\text{H}_{5}\text{O}_{7}$ solution, 10 mV s$^{-1}$). In all experiments, the oxidation scan was started at a potential value for which no deposition occurred. A similar response was obtained from both solutions.

Fig. 3A shows the oxidation of both Cu/Co and Co/Cu bilayers, next to the oxidation of copper and quasi-pure cobalt layers (curves b and a). When one bilayer was deposited, their oxidation showed different responses depending on whether copper or cobalt was the upper metal. The oxidation of the Cu/Co bilayer appeared in the form of two clear separate peaks (curve c), the more cathodic, corresponding to the oxidation of the cobalt (the upper metal), and the second one corresponding to the oxidation of the copper.
between different numbers of alternate layers.

When a Co/Cu bilayer was electrodeposited, when a Co/Cu bilayer was electrodeposited, the first layer of quasi-pure cobalt hindered, but did not prevent, the complete cobalt oxidation, which occurred at more positive potentials. An increase in the deposition charge of the upper copper layer makes the cobalt oxidation more difficult.

When samples of different number of layers were prepared, a generalised behaviour was observed in the stripping response (Fig. 3B). Cobalt oxidation occurred at two different potentials: When cobalt was the upper layer, the oxidation of this cobalt layer occurred at the same potential at which the oxidation of a single layer of cobalt occurred (curves a and b), revealing the goodness of the cobalt layer formation, even after a few number of cycles. The oxidation of the other cobalt layers took place at more positive potentials (curves c and d), since in this case cobalt oxidation was hindered by the presence of the copper layers. Copper was always oxidised at the same position, although at potentials slightly more negative than that corresponding to pure copper. This is probably because the copper remaining after cobalt oxidation had a more porous structure than a compact copper layer.

When a set of samples were prepared at fixed deposition potentials by gradually reducing the thickness of the layers, the stripping response tended towards the appearance of only one oxidation peak at an intermediate position between cobalt and copper oxidation (Fig. 3C). In these conditions, the stripping peak moved according to the relative proportions of cobalt and copper presence in the layered system. For example, maintaining the deposition charge of the copper layers and increasing the deposition charge for the cobalt layers, the position of the stripping peak moved to cobalt oxidation position, as a consequence of a presumed increase in the global content of cobalt in the layered system. In this case, a similar stripping response was observed to that obtained for the oxidation of a Co–Cu solid solution electrodeposited [23].

Therefore, the stripping of multilayer samples showed different kind of responses depending on the thickness of the layers prepared. Different oxidation peaks were recorded for the thicker layers, whereas only one oxidation peak was observed when reducing the thickness of the layers electrodeposited. Similar results were obtained in all tested substrates.

The stripping method also allowed us to check the optimality of the electrodeposition conditions selected. Only conditions that lead to high $Q_{ox}/Q_{red}$ ratio, higher than 0.9 were considered to prepare multilayers.

However, when a Co/Cu bilayer was electrodeposited, stripping response showed a small peak followed by a great oxidation peak at more positive potentials (curve d). The charge involved in this stripping curve ($Q_{ox} = 2.40 \times 10^{-4} \text{ C}$) was similar than the reduction charge measured during bilayer deposition ($Q_{red} = -2.52 \times 10^{-4} \text{ C}$). This result indicates that, practically all the Co/Cu bilayer was oxidised in the stripping experiment, although some of the cobalt was oxidised at potentials more positive than those corresponding to pure-cobalt oxidation. Then, the presence of the thin copper layer over the first layer of quasi-pure cobalt hindered, but did not prevent, the complete cobalt oxidation, which occurred at more positive potentials. An increase in the deposition charge of the upper copper layer makes the cobalt oxidation more difficult.

When samples of different number of layers were prepared, a generalised behaviour was observed in the stripping response (Fig. 3B). Cobalt oxidation occurred at two different potentials: When cobalt was the upper layer, the oxidation of this cobalt layer occurred at the same potential at which the oxidation of a single layer of cobalt occurred (curves a and b), revealing the goodness of the cobalt layer formation, even after a few number of cycles. The oxidation of the other cobalt layers took place at more positive potentials (curves c and d), since in this case cobalt oxidation was hindered by the presence of the copper layers. Copper was always oxidised at the same position, although at potentials slightly more negative than that corresponding to pure copper. This is probably because the copper remaining after cobalt oxidation had a more porous structure than a compact copper layer.

When a set of samples were prepared at fixed deposition potentials by gradually reducing the thickness of the layers, the stripping response tended towards the appearance of only one oxidation peak at an intermediate position between cobalt and copper oxidation (Fig. 3C). In these conditions, the stripping peak moved according to the relative proportions of cobalt and copper presence in the layered system. For example, maintaining the deposition charge of the copper layers and increasing the deposition charge for the cobalt layers, the position of the stripping peak moved to cobalt oxidation position, as a consequence of a presumed increase in the global content of cobalt in the layered system. In this case, a similar stripping response was observed to that obtained for the oxidation of a Co–Cu solid solution electrodeposited [23].

Therefore, the stripping of multilayer samples showed different kind of responses depending on the thickness of the layers prepared. Different oxidation peaks were recorded for the thicker layers, whereas only one oxidation peak was observed when reducing the thickness of the layers electrodeposited. Similar results were obtained in all tested substrates.

The stripping method also allowed us to check the optimality of the electrodeposition conditions selected. Only conditions that lead to high $Q_{ox}/Q_{red}$ ratio, higher than 0.9 were considered to prepare multilayers.
3.3. Morphological characterisation and analysis of the deposits

The checking of multilayer formation was firstly attempted by SEM. For this purpose, different Cu/Co multilayers had been grown over different electrodes. In all cases, after multilayer deposition pure-copper was electrodeposited to protect the multilayers between bulk copper. As multilayer observation requires cross-section imaging, better results were obtained when the mechanical properties of both the substrate and the multilayers were similar. For glass/ITO and Si/seed layer substrates, hard particles of substrate might scratch the multilayers during polishing. Copper substrate proved to be a good substrate for SEM observation, because it has similar hardness to the multilayers and improves its adherence to the substrate.

Observation of prepared samples by SEM revealed that metallic layers parallel to the substrate were obtained (Fig. 4), although the increase in the deposition time produced an increase in surface roughness. Co/Cu bilayer thickness measured from the images logically depended on the pulse duration, leading to 180 nm from Fig. 4A and 70 nm for Fig. 4B. The bilayer thickness observed was similar to that calculated from deposition charges of cobalt and copper accepting high efficiency (171 nm for conditions of Fig. 4A and 65 nm for conditions of Fig. 4B). The bilayer thickness \( h_b \) was calculated by means the equation (1) in which the small copper percentage in cobalt layer was not considered:

\[
h_b = \frac{(Q_{Cu} \cdot V_{Cu} + Q_{Co} \cdot V_{Co})}{2F} \cdot \frac{N_A}{A} \tag{1}
\]

where \( Q_{Cu} \) and \( Q_{Co} \) are the deposition charges corresponding to one layer of copper and cobalt, respectively, \( V_{Cu} \) and \( V_{Co} \) are the atomic volumes in the crystalline lattice, \( N_A \) is the Avogadro’s number, \( F \) is the Faraday constant and \( A \) is the electrode area. High current efficiency is a condition assessed by stripping results.

In a parallel way TMAFM was used to analyse the Cu/Co multilayer formation. TMAFM imaging of the prepared samples at different points of the section coating showed alternated multilayered structure (Fig. 5). The profile of the surface of the cross-section showed a periodic variation in the \( z \) direction due to the selective chemical etching, the copper layers being lower than the cobalt layers, revealing the good selectivity of the etching procedure. Individual layers were clearly distinguished, showing an average value of bilayer thickness (from the start of one cobalt layer to the end of next etched copper layer) of 140 nm. This value was similar to that calculated from deposition charges \( h_b = 136 \) nm. However, it was not possible to get evidence of multilayers of lower bilayer thickness by TMAFM, probably due to non-selective chemical etching of the copper layers when these were too thin.

Cu/Co multilayer deposition took place with low hydrogen evolution and avoiding cobalt dissolution during copper deposition. The estimation of the thickness from the deposited charge was possible. When the objective is to prepare multilayers of very thin layers, for which direct observation is not possible, it is fundamental to adjust the electrodeposition conditions to high current efficiency.

EPMA analysis allowed determining the global composition of the prepared multilayers. Measured values were compared with the calculated values obtained from Faraday’s law from the electrodeposited charge. The sufficient concordance between both results aided to use the theoretical spaced calculation. Then, a non-destructive method such as EPMA allowed us to contrast the
calculated thickness by means the electrodeposition charge involved in each of the layers.

The analysis of the multilayered coatings, obtained over Ni substrate, using XPS and Auger techniques showed that both experimental methods were unable to detect the cobalt and copper alternance in the deposits. From these techniques global composition was always obtained. The metal percentages obtained from these experiments were similar to those obtained by means of EPMA measurements and were also similar to values obtained by means of the theoretical calculations from the deposition charges of copper and cobalt.

3.4. Structural characterisation

Cu/Co multilayers of different layer thickness were also analysed using XRD. For this purpose, glass/ITO and Si/seed layer were mainly selected due to the absence of intensity at 2θ values next to copper or cobalt responses.

Fig. 6A shows a typical diffractogram on glass/ITO substrate. Next to the response of the substrate, four main peaks were detected corresponding to the coating response at around 44, 51, 75 and 91° 2θ. All indexed peaks correspond to a fcc structure and appeared at diffraction angles between the lines corresponding to electrodeposited fcc copper and fcc cobalt. Moreover, XRD showed that the deposited multilayers consist of a highly (111) textured structure.

Upon varying the \( \frac{Q_{Co}}{Q_{Cu}} \) ratio, i.e. the global coating composition, the position of the diffraction peaks moved clearly. Fig. 6B and C show the magnification of the peak (111) of coatings obtained both on glass/ITO and Si/seed layer substrates. The position of each diffraction peak shifted towards the position of the cobalt line as the \( \frac{Q_{Co}}{Q_{Cu}} \) ratio increased. This diffraction response was similar to that obtained when the formation of Co+Cu solid solution with variable cobalt percentage in the deposits took place [23,24]. The analysis of the global composition of the coatings studied by XRD allowed us to corroborate that the diffraction peak position from multilayers response varies as a function of Vegard’s law, in a similar way to that of Co+Cu solid solution formation. From these results, the relative position of the diffraction peaks with respect to pure-copper and pure-cobalt position was another way of estimating the cobalt content in the coatings.

For all diffraction experiments made, no clear satellite peaks were detected to calculate the superlattice period.

Similar results were found when TEM-selected area diffraction was used to study the Cu/Co multilayers. Deposits obtained on Si/seed layer substrates led to spotty diffraction rings (Fig. 7). The measurement of the ring diameter \( (2d_{hkl}) \) related to the \( (hkl) \) reflection in the
diffraction patterns allowed us to assess the mean lattice parameter of the Cu/Co multilayer. Next to the rings identified as those corresponding to silicon or titanium of the substrate, six rings were assigned to the coating. Rings corresponding to the nickel seed layer were not detected. The coating rings corresponded to a fcc structure and they appeared at an intermediate position between those of pure-cobalt or pure-copper for all the multilayers analysed, corroborating the results obtained by XRD. A lattice parameter of the fcc structure, intermediate between the parameter of fcc copper (0.361 nm) and fcc cobalt (0.354 nm), was obtained.

3.5. Magnetoresistance values

The resistance of some Cu/Co multilayers, obtained on glass/ITO substrate, with a fixed copper layer thickness of about 1.2–1.3 nm was measured as a function of the external magnetic field, \( H \), in samples with the thickness of the cobalt layer ranging from 0.7 to 3 nm. All thickness values were estimated from the deposition j-t transient obtained for each layer. As we have previously shown [25], a copper layer slightly greater than 1 nm thick is the optimum value, which ensures the continuity of the deposited layer, but it is not so large as to reduce the MR signal by decreasing the relative contribution to the total resistance of the Co–Cu interfaces with respect to that of the current flowing through the inner part of the Cu layers. The present work was aimed at elucidating the effect of the cobalt layer thickness on the MR response of these samples. Three sets of multilayers obtained after 5, 10 and 15 min of deposition time were prepared. These values of the deposition time, which lead to coatings ranging between 0.1 and 0.3 \( \mu \)m, guarantee that the obtained multilayers are free of internal stresses and have moderate surface roughness.

From the \( R(H) \) measurements, the MR ratio was calculated as \( \Delta R/R_0 \), where \( \Delta R = R(H) - R_0 \) is the change of the resistance due to the application of \( H \) and \( R_0 \) is the maximum value of \( R(H) \) at the coercive field. In Fig. 8, the value of the MR ratio at 27 K measured at a field of 11 kOe for the three sets of multilayers is depicted as a function of the thickness of the cobalt layer. The maximum MR for each curve is achieved for cobalt thickness in the range of 1–1.5 nm, irrespective of the deposition time (number of Cu/Co bilayers). In fact, the optimum value is in the middle point of this range, close to about 1.2 nm, which is the same value estimated for the optimum copper thickness [25].

Deeper insight into the morphology of the cobalt layer may be gained by analysing the MR curves in the vicinity of the coercive field. In Fig. 9, a detail of the MR curves for samples with cobalt thickness of 1 and 1.5 nm, both obtained after 15 min of deposition time, are compared. For a cobalt thickness of 1 nm (curve b) the MR curve shows rounded peaks centred at a
coercive field of about 200 Oe, indicating the existence of a distribution of Co isles of variable size (lost of continuity of the Co layer). In contrast, the MR curve for a cobalt thickness of 1.5 nm (curve a) shows sharper peaks located at about 300 Oe, which is in agreement with the values of the coercive field observed in other cobalt samples grown by electrodeposition [26,27]. This is consistent with the formation of a continuous Co-rich layer with magnetic response similar to that of the bulk material. Consequently, the maximum value of MR occurs at the minimum Co thickness (about 1.2 nm) for which a continuous Co-rich layer appears.

The MR curves measured at 27 and 300 K, respectively, in a multilayer with 1.2 nm of cobalt thickness obtained after 15 min of deposition are shown in Fig. 10. The MR at 27 K and with an applied field of 11 kOe is $-6.2\%$, the maximum value. MR at 11 kOe is reduced as the temperature increases, the value observed at room temperature being $-2.4\%$. This reduction is associated with the thermal demagnetisation of the cobalt present at the interfaces. Moreover, the electrodeposition method produces a high degree of dilution of the cobalt atoms at the interfaces with the copper layers, which is responsible for the moderate MR values observed, both at low and room temperatures, as compared with those corresponding to similar samples prepared, by another nonequilibrium techniques such as sputtering, especially over a buffer layer [28–30].

4. Conclusions

Electrodeposition was used to obtain Cu/Co multilayers on different substrates. Voltammetric and stripping studies were used to select deposition conditions that lead to a $Q_{ox}/Q_{red}$ ratio greater than 0.9 even on the low active substrates. Under these conditions, the recorded current response during layer deposition allowed us to estimate the layer thickness ($h_b$) because for the thickest bilayers prepared this theoretical calculation lead to similar values to those obtained from direct observation of multilayers from SEM or
TMAFM experiments. Therefore, it was demonstrated that when thin layers (of 0.5–3 nm) are prepared to measure magnetoresistance, the theoretical calculation can be used, with low error, to assess the bilayer thickness.

It has been found that stripping responses of multi-layered systems can inform us about the thickness of cobalt and copper layers able to show magnetoresistive response. For the Cu/Co multilayers prepared, when the layers were not so thin (greater than 1.8–2 nm) and different peaks were obtained in the stripping response, the measured values of magnetoresistance are low. In contrast, when stripping response evolved into overlapped peaks or only one peak, a clear increase in the magnetoresistance of the corresponding Cu/Co coating was observed. However, very thin layers, below 1 nm, lead, again, to a clear decrease in the magnetoresistance of the material, revealing that very short deposition times were not able to obtain well-formed alternate layers.

XRD, XPS and Auger experiments allowed us to detect the global composition in the multilayered system. XRD showed a similar response to that obtained for a solid solution formation. Cobalt percentages calculated from Vegard’s law agree with the theoretical values obtained from the deposition charges.

Magnetoresistance results of the Cu/Co samples analysed indicate that similar arguments used to justify the optimum value of the copper thickness [25] also might be applied to the cobalt layers, fact which demonstrates that MR in these multilayers is mainly associated with electron scattering at the Co–Cu interfaces. Consequently, the optimum cobalt thickness must be enough to ensure the formation of well-defined Co–Cu interfaces, but not as large as to produce an intermediate cobalt layer without copper intermixing which would act as a nonmagnetoresistive channel. Besides, for a fixed thickness of the copper layers, MR increases with the deposition time, accordingly with the increasing number of Co–Cu interfaces.

Acknowledgements

The authors thank the Serveis Científicotsènics (Universitat de Barcelona) for equipment availability. This research was supported financially by contract MAT 2000-0986 and MAT 2000-0858 of the Comisión Interministerial de Ciencia y Tecnología (CICYT) and by the Comissionat of the Generalitat de Catalunya under Research Project SGR 2000-017.

References