The role of nucleation in the evolution of giant magnetoresistance with layer thicknesses in electrodeposited Co–Cu/Cu multilayers

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Abstract

Electrodeposited Co–Cu/Cu multilayers were prepared by a galvanostatic/potentiostatic (G/P) pulse sequence in which the Co-rich magnetic Co–Cu layer was deposited by current control and the non-magnetic Cu layer by potential control. The Cu deposition potential has been chosen so as to exclude the occurrence of a Co dissolution during the Cu deposition cycle. This ensured that the actual amounts of metals deposited were equal to the nominal ones. The multilayers with a total thickness of about 1.7\,\mu m were mechanically peeled off from their Ti substrate. Detailed room-temperature studies of the dependence of the magnetoresistance (MR) and the magnetic properties on Co and Cu layer thicknesses were performed with particular attention to analysing the field evolution of the MR. A giant magnetoresistance (GMR) effect was observed in most samples and a maximum GMR of 10\% measured at 1\,kOe could be achieved. No oscillatory GMR behaviour with increasing Cu layer thickness could be observed but rather a continuous evolution of the MR characteristics from anisotropic magnetoresistance (AMR) to GMR. This could be explained by the gradual increase of the Cu coverage on the Co-rich magnetic layer during each Cu pulse with increasing average Cu layer thickness. It was concluded that the Cu layer becomes continuous above about 2\,nm thickness only. For 2.5\,nm Cu layer thickness, the Co layer remained continuous down to 1.1\,nm thickness. However, for 1.1\,nm Cu layer thickness, the 1.1\,nm thick Co layer was broken up into superparamagnetic islands. The evolution of the coercive force with layer thicknesses well corroborated the above picture. From these results, an asymmetry in the nucleation of Cu on Co and Co on Cu could be deduced in agreement with some previous reports on evaporated multilayers.

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1. Introduction

Developments in the electrodeposition technology reached a level more than a decade ago that enabled the preparation of a variety of
high-quality nanoscale metallic multilayers [1]. Such systems can exhibit new phenomena with promising potential for applications, among them the giant magnetoresistance (GMR) effect of magnetic/non-magnetic multilayers [2] that is already used in magnetic field sensors of hard disk drives. Due to its cost-effectiveness and simplicity, electrodeposition has long been considered as a viable alternative to vacuum methods of multilayer preparation. This motivated an extensive research activity for studying GMR in electrodeposited multilayers [3]. However, these systems still usually show a lower GMR than multilayers prepared by sputtering or evaporation and this necessitates further investigations.

There has recently been some progress in exploring the importance of the metal exchange in multilayer formation by electrodeposition. For a GMR behaviour, an alternating sequence of magnetic and non-magnetic layers should be deposited. For electrodeposition, a typical system is the combination of Co and Cu layers [4] which are deposited from a single bath containing Co\(^{2+}\) ions and, in usually much lower concentration, Cu\(^{2+}\) ions. Either galvanostatic (current-controlled) or potentiostatic (potential-controlled) deposition can be applied for the multilayer preparation. During a high-current (high-potential) pulse, a magnetic Co layer (typically with a few percent of Cu incorporated) is deposited and during a low-current (low-potential) pulse a pure Cu layer is deposited. Due to the significantly different electrochemical potentials at which the less-noble (magnetic) Co layer and the more noble (non-magnetic) Cu layer is deposited, the dissolution of Co can take place during the Cu deposition pulse [5–7]. When Cu is deposited by current control at a lower current density than the mass transport limited current, Co atoms of the previously deposited magnetic layer are dissolved and Cu atoms are randomly deposited in equal amount, besides the normal Cu deposition via Faradaic current. When Cu is deposited at a fixed potential, a Co dissolution is superimposed on the Cu deposition at the mass transport limited rate; hence, an excess amount of Cu deposited has to compensate the missing Co. It has been demonstrated in several cases that these processes can highly influence the GMR behaviour of electrodeposited multilayers [8–15].

Among the consequences of the metal exchange, we can mention that the actual Co layer thickness will be smaller and the Cu layer thickness will be larger than the nominal ones derived from Faraday’s law. These changes could be clearly demonstrated by direct chemical analysis of Co–Cu/Cu multilayer deposits [12] and similar changes were found for Ni–Cu/Cu multilayers as well [7]. Another effect is a broadening of the width of the transition between the magnetic and non-magnetic layers, causing an interfacial intermixing.

It should be noted that in spite of the relatively strong metal exchange causing certainly a high degree of interfacial intermixing, the GMR could still remain substantial [12]. The most probable explanation for this can be derived from the results of a study on sputtered Co/Cu multilayers [16] in which the authors have concluded that the spin-dependent scattering into the split d-band of the ferromagnetic (FM) layer (Co) is the sole mechanism responsible for the GMR in Co/Cu multilayers (in contrast to, e.g., the Fe/Cr system with dominant spin-dependent scattering at the interfaces). The small amount of Cu in the magnetic layer of electrodeposited Co–Cu/Cu multilayers does not modify the picture. On the other hand, due to an interfacial intermixing, the antiferromagnetic (AF) coupling between neighbouring FM layers is certainly weakened and, as a consequence, a smaller degree of antiparallel alignment of the magnetization leads finally to a reduction of GMR.

Since the Co dissolution and the parallel Cu deposition processes take place randomly over the cathode area, the exchange reaction can also result in a fluctuation of the layer thickness and a roughening of both the interfaces and the multilayer surface with increasing bilayer number. Due to the layer thickness fluctuation, a change from AF to FM coupling may occur at many places. Such a situation was suggested [17] to result in a 90° coupling and, thus, in a decrease of GMR due to the reduced antiparallel alignment of layer magnetizations. The layer thickness fluctuations can also lead to the occurrence of an “orange-peel” coupling [18], favouring FM alignment due
to magnetostatic effects, again being deleterious for GMR. In extreme cases, the magnetic layer fluctuation may lead to the formation of “magnetic islands” decoupled from the rest of the magnetic layer. These nanosized islands are embedded in the non-magnetic (Cu) metal and can exhibit a superparamagnetic (SPM) behavior. The occurrence of such SPM regions has been invoked to explain the non-saturating behavior of the magnetoresistance (MR) in Ni–Cu/Cu [15], Ni–Co–Cu/Cu [19] and Co–Cu/Cu [20] multilayers, whereby the results of magnetic measurements have provided clear evidences for a SPM magnetization contribution in these multilayers [15,20].

Besides these achievements in understanding the GMR behavior of electrodeposited multilayers, some refinements have been made in the preparation technology as well. Namely, in a recent study [12], a new electrochemical cell construction has been elaborated that enables the preparation of electrodeposited multilayers with negligible lateral variation of composition and GMR. A new deposition pulse combination has also been introduced [12]. Conventionally, either galvanostatic (G) or potentiostatic (P) control is used for depositing both the magnetic and the non-magnetic layer (G/G and P/P deposition mode, respectively). In Ref. [12], the magnetic Co layer was deposited by galvanostatic, the non-magnetic Cu layer by potentiostatic control. This multilayer deposition sequence is called G/P mode.

During a detailed study of Co–Cu/Cu multilayers prepared by the G/P mode [12], we have revealed that via the control of the actual Co and Cu layer thicknesses, the metal exchange can drastically influence the GMR. Although a significant GMR could be observed even in the presence of metal exchange [12], its elimination would still be desirable according to the foregoing discussion. In Ref. [12], by measuring the charge and current evolution during the Cu deposition cycle, an attempt has been made to establish the degree of the metal exchange at a given Cu deposition potential. It has been shown in a subsequent work [21] that by this method an appropriate Cu deposition potential can be determined for any specific electrolyte composition at which the multilayer formation proceeds without a noticeable Co dissolution.

Based on these previous works [12,21], it was decided to perform a systematic study of the thickness dependence of the GMR of electrodeposited Co(Cu)/Cu multilayers under conditions where no exchange reaction is expected to occur. The basic importance of this circumstance is that the established nominal layer thicknesses are those actually formed in the multilayers (apart from a constant surface roughness factor, see Section 2.1). Further beneficial effects include a lesser degree of interfacial intermixing and interface/surface roughening. It was expected that in this way we can study finer details of the layer formation process which have remained unrevealed in previous investigations due to the uncontrolled degree of the metal exchange and we can establish the true evolution of GMR with layer thickness.

2. Experimental

2.1. Sample preparation

In preparing the Co–Cu/Cu multilayer films, we have mainly followed the procedure described in Ref. [12]. According to results of chemical analyses performed on deposits obtained under similar conditions in our previous studies [9], the magnetic layer contained about 5 at% Cu. Since this small amount of Cu does not influence significantly the magnetic and electrical transport properties of the magnetic layer, for simplicity we shall often refer to it as a Co layer.

Analytical grade CoSO$_4 \cdot 7$H$_2$O and CuSO$_4 \cdot 5$H$_2$O were employed to prepare the electrolyte for multilayer electrodeposition. The bath contained 1 M CoSO$_4$ and 0.025 M CuSO$_4$ without any buffering agents or additives (as it was shown previously [4,22], most additives are deleterious for GMR). The deposition was performed at room temperature and no stirring was applied. The multilayers were deposited in a three-electrode configuration cell with a saturated calomel electrode (SCE) as reference and with a Cu foil acting as a counterelectrode. A computer-controlled Electroflex EF453-type potentiostat was used to
monitor the entire electrochemical process. A G/P pulse combination [12] was used by which Co was grown under galvanostatic condition and Cu by potentiostatic control to obtain the Co–Cu/Cu multilayers. The magnetic layer (Co–Cu) was prepared at a cathodic current density of $-70.5 \text{ mA/cm}^2$ whereas a non-magnetic Cu layer was electrodeposited at $-0.62 \text{ V}$ deposition potential vs. SCE.

Fig. 1 shows the cyclic voltammogram of the current experimental bath according to which, at a potential of $-0.62 \text{ V}$, the deposition of Cu only is expected. It was proved in a detailed comparative study of pulse-plating and cyclic voltammetry [21] that for the particular electrolytic bath employed here at a Cu deposition potential of $-0.62 \text{ V}$ no cobalt dissolution occurs during the Cu deposition period in a G/P pulse sequence mode. Fig. 2 shows the time evolution of the current and the total charge at the cathode during the Cu deposition pulse. According to Fig. 2b, at this particular potential there is no initial anodic charge, i.e., no exchange reaction at the cathode when switching from the Co deposition pulse to the Cu deposition pulse. The change of the Cu current density with cycle number was caused by the increase of the $\text{Cu}^{2+}$ concentration in the bath due to the dissolution of the sacrificial anode.

The individual thickness for the Co–Cu and the Cu layers was controlled through the variation of the deposition parameters: the deposition time for the Co–Cu layer (galvanostatic control) and the total charge deposited for the Cu layer (potentiostatic control). The layer thicknesses were estimated from Faraday’s law under the assumption of 100% current efficiency for Cu deposition and 94% for Co–Cu deposition [9]. Based on our previous experiments for the same electrochemical system [12], $-3.1 \text{ mC/cm}^2$ charge corresponds to $1 \text{ nm}$ thickness for the Co–Cu layer and $-2.8 \text{ mC/cm}^2$ charge to $1 \text{ nm}$ thickness for the Cu layer. Owing to the lack of metal exchange under our deposition conditions, the actual layer thickness is linearly proportional to the nominal one where the proportionality factor scales with the surface roughness. For Co–Cu/Cu multilayers deposited under similar conditions, this factor was found to be 1.9 [9] and did not vary with deposition.

![Cyclic voltammetric curve of the electrolyte used for multilayer preparation.](image1)

![Fig. 2. (a) Evolution of the cathodic current recorded during the potential-controlled Cu deposition. Curves with increasing cathodic currents belong to every 50th cycle from 50 to 300. (b) Evolution of charge passed through the cathode with deposition time during Cu deposition. Curves with increasing negative slopes belong to every 50th cycle from 50 to 300.](image2)
conditions. As described below, in the present study, the total multilayer thickness was by about a factor of 5–10 smaller than in Ref. [9]. Therefore, the surface roughness factor can be expected to be much closer to unity here than in Ref. [9] and, thus, we shall indicate the nominal layer thicknesses throughout this paper.

A polycrystalline Ti sheet acted as substrate with a surface area of $8.5 \times 20 \text{ mm}^2$. The pretreatment procedure was performed by manual polishing with emery paper, degreasing with ethanol and rinsing with deionized water. After the pretreatments carried out in this order, the substrate was left drying in the air. Immediately prior to the deposition, the Ti sheet was immersed into 1M H$_2$SO$_4$ for about 1 min in order to activate the substrate surface. After deposition, the multilayers were peeled off mechanically from their substrates and attached to a Scotch tape for further studies.

The individual layer thicknesses were varied in a wide range: from 1.1 to 5.7 nm for Co and from 0.35 to 2.5 nm for Cu. The total bilayer number ($N$) was chosen for each multilayer such as to have roughly the same total thickness (about 1.7 μm). Three multilayer series were prepared. In two series, the Co layer thickness varied from 1.1 to 5.7 nm while keeping the Cu layer thickness constant at either 1.1 nm or 2.5 nm. In a third series, the Co layer thickness was chosen to be 3.4 nm and the Cu layer thickness ranged from 0.35 to 2.5 nm. Fig. 3 shows a schematic view of the layer thickness combinations and the applied bilayer numbers.

### 2.2. Structural characterization

Four samples with low and/or high layer thicknesses (samples in boxes with thick borders in Fig. 3) were selected for structural studies by X-ray diffraction (XRD) on a Philips X’pert diffractometer. The XRD patterns revealed a face-centred cubic (fcc) structure with a strong (111) texture for all these multilayers; the amount of a hexagonal close-packed phase remained below 1% in each case. The Bragg reflections of the fcc phase did not exhibit any splitting into separate fcc-Co(Cu) and fcc-Cu peaks, indicating a good coherency between the subsequent magnetic and non-magnetic layers. No discernible satellite reflections due to multilayer periodicity could be identified in any of these four multilayers including the one with the largest GMR reported in this work.

Fig. 3. Thicknesses of the magnetic Co(Cu) and the non-magnetic Cu layers for all multilayer samples prepared in the present experiments.
2.3. Magnetoresistance and magnetic measurements

The room-temperature MR curves and hysteresis loops were measured for all multilayers listed in Fig. 3.

The MR measurements were performed at room temperature in the current-in-plane/field-in-plane (CIP/FIP) geometry up to $H = 8\, \text{kOe}$ magnetic fields. The MR ratio was defined as $\text{MR} = [(R_H - R_0)/R_0] \times 100\%$ where $R_H$ and $R_0$ are the resistances measured in a magnetic field $H$ and in zero field, respectively. The resistance measurements were performed on typically 1–2 mm wide strips cut parallel to the long edge of the deposit. Both the longitudinal (LRM, magnetic field parallel to the current) and transverse (TMR, magnetic field perpendicular to the current) MR curves were measured for each multilayer sample. The MR results were very similar for each strip of the multilayer deposit.

The magnetic properties were investigated either on a strip used for the MR measurements or on another equivalent strip. A vibrating sample magnetometer (VSM) was applied to carry out the magnetization measurements.

3. Results

3.1. Multilayers with thick (2.5 nm) Cu layers

First, the MR results for the Co ($d_{\text{Co}}$)/Cu ($d_{\text{Cu}} = 2.5\, \text{nm}$) series will be presented for which the Co layer thickness varied between 1.1 and 5.7 nm. The LMR and TMR curves for the Co (5.7 nm)/Cu (2.5 nm) and Co (1.1 nm)/Cu (2.5 nm) multilayers are shown in Fig. 4 up to $H = 2\, \text{kOe}$. In both cases, we can observe a clear GMR behaviour in that both the LMR and the TMR components are negative for all fields, with the magnitude of the LMR component being slightly smaller. A clear splitting of the MR curves can be observed for both multilayers (Figs. 4a and b). The MR peak position values correlate well with the coercive fields ($H_c$) deduced from the corresponding hysteresis loops of these samples (Fig. 4c). For the multilayer Co (5.7 nm)/Cu (2.5 nm), the MR peaks are relatively narrow and the MR value reached at around 1 kOe changed very little only...
up to 8 kOe. According to Fig. 4c, the magnetization certainly also reaches technical saturation by around 1 kOe for this sample. Furthermore, there is about 1% difference between the LMR and TMR values that can be ascribed to an anisotropic magnetoresistance (AMR) contribution to the observed MR due to the relatively large Co layer thickness (5.7 nm) in this multilayer.

From the above-described magnetic and MR characteristics, one can conclude that the Co (5.7 nm)/Cu (2.5 nm) multilayer consists of (i) thick, continuous Co layers with a clear FM behaviour and (ii) paramagnetic Cu layers forming a continuous spacer between the FM Co layers. The clear MR peak splitting and the shape of the magnetization curve are indicative of weak or no interlayer AF coupling characteristic of thick Cu spacers [23]. The presence of the relatively large GMR indicates that an FM coupling cannot be present either, i.e., the Cu layers are continuous. In the absence of a significant interlayer coupling, the in-plane mutual alignment of the FM layer magnetizations is random. This results in some degree of partial antiparallel alignment of the magnetization of neighbouring Co layers [23,24] which then leads to spin-dependent scattering events. In such systems, the split MR peaks are usually around the coercive field values [24] although there may be some differences between $H_c$ and $H_p$ [19].

When decreasing the Co layer thickness, one can expect that, as long as both the magnetic and the non-magnetic layers remain continuous, the GMR increases due to the increasing number of magnetic/non-magnetic bilayers per unit thickness. This has indeed been observed here down to $d_{Co} = 1.1$ nm (Fig. 4b). Concomitantly with the increased GMR, the difference between the LMR and TMR components almost completely disappeared due to the strongly reduced AMR contribution by the very thin Co layers here. Although the main MR change is still within 1 kOe, the MR curves have slightly broadened and exhibit a larger splitting in comparison with Fig. 4a ($d_{Co} = 5.7$ nm). It can also be observed that at 2 kOe there is a finite slope of the MR curves. Actually, a nearly linear small MR decrease persisted up to 8 kOe (not shown here). The increased MR peak separation is well reflected also in the increased coercive force as shown by the changes of the magnetic hysteresis loop (Fig. 4c). All this points towards the fact that the 1.1 nm Co layer is still mainly continuous with a clear FM behaviour although there are some indications for the appearance of a very small SPM contribution to be discussed later.

The significant difference between the coercive fields of the two multilayers (Fig. 4c) is also consistent with the well-known behaviour of magnetic thin films in that the coercive field strongly increases with decreasing film thickness [25].

### 3.2. Multilayers with thin (1.1 nm) Cu layers

The situation changes drastically when we consider the results on the Co ($d_{Co}$)/Cu ($d_{Cu} = 1.1$ nm) series in the same Co thickness range as before (between 1.1 and 5.7 nm). For the Co (5.7 nm)/Cu (1.1 nm) multilayer, the MR curves (Fig. 5a) indicate a dominant AMR behaviour (LMR positive, TMR negative), whereas a clear GMR behaviour can be observed for the Co (1.1 nm)/Cu (1.1 nm) multilayer (Fig. 5b) although this is quite different from that of the Co (1.1 nm)/Cu (2.5 nm) multilayer (Fig. 4b). The hysteresis loops (Fig. 5c) show also qualitative differences between the magnetic behaviours of these samples with large and small Co layer thicknesses.

Comparing Figs. 4a and 5a, it can be established that the magnetic layers of the Co (5.7 nm)/Cu (1.1 nm) multilayer are mostly ferromagnetically coupled, giving rise to a pronounced AMR. This AMR is about half of the value observed in the bulk material of the magnetic layer [12], obtained by DC plating. This indicates that there are some areas in the multilayer structure where the magnetizations of neighbouring layers are not completely correlated (not completely ferromagnetically aligned) and these areas produce a GMR contribution. The magnetic hysteresis loop of this multilayer (Fig. 5c) indicates a very small coercive field in agreement with the unresolvable peak splitting of the MR curves (Fig. 5a). All this means that the 1.1 nm thick Cu layer in this multilayer...
can be assumed to be not continuous but it rather contains many pinholes or large discontinuities enabling a direct FM coupling at many places between the thick, continuous Co layers. The comparison of the coercive field values of the Co (5.7 nm)/Cu (2.5 nm) multilayer (about 130 Oe) and the Co (5.7 nm)/Cu (1.1 nm) multilayer (less than 30 Oe) also indicates that the effective equivalent thickness of the Co layers in the latter multilayer is actually much higher, at least in many places, than the nominal 5.7 nm thickness, i.e., the coercive field approaches the bulk alloy behaviour for $d_{Cu} = 1.1$ nm.

We can observe differences also when comparing the MR curves in Figs. 4b and 5b where $d_{Cu} = 1.1$ nm for both multilayers. Although in both cases a GMR effect is evident, the field dependence of the MR suggests two different types of behaviour. Whereas for $d_{Cu} = 2.5$ nm the MR curves saturate at around 2 kOe, for $d_{Cu} = 1.1$ nm no tendency for saturation can be seen at this magnetic field and this non-saturating behaviour persists up to 8 kOe. As discussed previously [14,15,19,20], this feature can be ascribed to the dominant MR contribution of SPM entities. This implies at the same time that with a discontinuous Cu layer of 1.1 nm thickness, the Co layer with the same thickness must also be discontinuous as discussed later (Section 4). Due to the randomness in the spatial occurrence of a discontinuity of both the Co and Cu layers, Co regions of different sizes can occur. This may be the reason for the appearance of two, more or less well-defined coercive forces in the hysteresis loop of the Co (1.1 nm)/Cu (1.1 nm) multilayer (Fig. 5c).

3.3. Dependence of MR and coercivity on Co layer thickness

As indicated in Fig. 3, for both $d_{Cu} = 1.1$ and 2.5 nm, several multilayers with $d_{Co}$ values between 1.1 and 5.7 nm were prepared and investigated. For these intermediate Co layer thicknesses, the MR characteristics and the magnetic properties varied systematically from the small to the large Co layer thickness. The evolution of the GMR with $d_{Co}$ for both Cu layer thicknesses is shown in Fig. 6a, indicating a continuous evolution with Co layer thickness. The evolution of the coercive field for the same multilayers is displayed in Fig. 6b which shows a continuous decrease of $H_c$ for both

![Fig. 5.](image-url)
Cu layer thicknesses. The coercive field range is rather large: the smallest value (below 30 Oe) being indicative of the nearly bulk behaviour of Co due to the discontinuous Cu layer whereas the largest value (over 230 Oe) being due to a very thin continuous Co layer.

The recent results of Cerisier et al. [26] for electrodeposited Co films support well our above findings. Namely, these authors have reported a linear decrease of $H_c$ and MR peak position $H_p$ of electrodeposited Co(Cu)/Cu multilayers with magnetic layer thickness for both thin and thick non-magnetic layers. The triangle ($\triangle$) indicates the coercive field of a single Co thin film electrodeposited on Cu [26].

According to Fig. 6b, the MR peak position ($H_p$) decreases similarly as the coercive field with Co layer thickness for both Cu layer thicknesses. However, in most cases the $H_p$ values lie systematically higher than the $H_c$ data. A similar behaviour was observed also for some electrodeposited Ni–Co–Cu/Cu multilayers [19]. The reason for a difference in the $H_c$ and $H_p$ values is that the condition for vanishing bulk magnetization ($H_c$) and for maximum antiparallel alignment of the magnetizations of neighbouring layers ($H_p$) are not necessarily exactly the same.

3.4. Dependence of MR and coercivity on Cu layer thickness

It turned out from the above results that the MR behaviour is quite different for small and large Cu spacer layer thicknesses. Therefore, in the next series [Co (3.4 nm)/Cu ($d_{Cu}$)], the Cu layer thickness was varied from 0.35 to 2.5 nm while keeping the Co layer thickness at an intermediate value of 3.4 nm (see Fig. 3). With increasing Cu layer thickness, the MR characteristics changed continuously from an AMR behaviour to a GMR behaviour. This is demonstrated in Fig. 7 where the results for the Co (3.4 nm)/Cu (0.7 nm) and Co (3.4 nm)/Cu (1.1 nm) multilayers are shown. For $d_{Cu} = 0.35$ nm (not shown) and $d_{Cu} = 0.7$ nm (Fig. 7a), the LMR component is positive and the TMR component is negative, indicating that the dominant contribution to the observed MR is due to AMR. This is because the very thin nominal Cu layers do not ensure a continuous separation between the Co layers (e.g., $d_{Cu} = 0.35$ nm layer thickness corresponds to one elementary cell height of the fcc-Cu lattice only). Therefore, there is a percolation of the Co layers via the discontinuities in the Cu layer and we get an AMR...
behaviour similar to that of a bulk ferromagnet. This shows up also in the very small value (again around 30 Oe) of the coercive field of the multilayers with $d_{Cu} = 0.35$ and 0.7 nm (Fig. 7c). When increasing the Cu layer thickness, the separation between the Co layers becomes more and more complete and, therefore, larger and larger areas will give rise to a GMR effect. For this reason, the LMR component becomes negative and the TMR component becomes more negative as we can see in Fig. 7b for the Co (3.4 nm)/Cu (1.1 nm) multilayer. This tendency continues with increasing Cu layer thickness and finally, for $d_{Cu} = 2.5$ nm the MR curves become intermediate between those shown in Figs. 4a and b for the same Cu layer thickness.

Similarly, to the case of the Co (1.1 nm)/Cu (1.1 nm) multilayer (Fig. 5c), the hysteresis loop of the Co (3.4 nm)/Cu (1.1 nm) multilayer (Fig. 7c) also indicates the presence of FM areas with two different coercive fields, corresponding to Co regions with different sizes. There are apparently percolated Co-regions with a bulk-like magnetic behaviour (low $H_c$) and extended layer-like Co-regions with higher $H_c$ values which are typical for thin films.

As Fig. 8 reveals, the MR and magnetic parameters show a continuous, monotonic evolution with increasing Cu layer thickness and no signs of an oscillating behaviour of the GMR can be observed. This agrees with many previous observations on electrodeposited multilayers and partly the very weak or even vanishing magnetic coupling of the neighbouring magnetic layers can be made responsible for it. Here we can ascertain another reason for the lack of GMR oscillation even in the presence of an AF coupling. Namely, according to the above considerations, below a certain thickness value the Cu layer does not form a continuous spacer between the FM Co layers. From Fig. 8a, we cannot ascertain this critical Cu thickness value but we can get some estimate from Fig. 8b where for $d_{Co} = 3.4$ nm (and probably also for $d_{Co} = 5.7$ nm) a sudden increase of the coercive field occurs from $d_{Cu} = 2.1$ to 2.5 nm that can be interpreted by the formation of a continuous separation between the Co layers beyond $d_{Cu} = 2.1$ nm.

Fig. 7. (a) Longitudinal and transverse MR curves of an electrodeposited Co(Cu)/Cu multilayer with a magnetic layer of intermediate thickness ($d_{Co} = 3.4$ nm) and with a very thin non-magnetic layer ($d_{Cu} = 0.7$ nm). (b) Longitudinal and transverse MR curves of an electrodeposited Co(Cu)/Cu multilayer with a magnetic layer of intermediate thickness ($d_{Co} = 3.4$ nm) and with a thin non-magnetic layer ($d_{Cu} = 0.7$ nm). (c) Magnetic hysteresis loops of electrodeposited Co(Cu)/Cu multilayers with two different Cu layer thicknesses at the same Co layer thickness ($d_{Co} = 3.4$ nm).
4. Discussion

It may now be appropriate to summarize some basic features of the results obtained in the present study. By excluding the metal exchange during the multilayer deposition process when choosing $-0.62\,\text{V}$ as the Cu deposition potential for our particular deposition conditions, it could be achieved that the actual layer thicknesses are equal to the nominal ones (apart from a small constant surface roughness factor). The observed evolution of the magnitude of the MR with Cu layer thickness was quite different than in our previous study where a substantial Co dissolution occurred at the selected $-0.25\,\text{V}$ Cu deposition potential [12].

A second feature of the present study is that for sufficiently thick (i.e., continuous) Cu layers, the Co layers can be continuous down to nearly 1 nm thickness. This state is characterized by sharp MR curves, saturation fields around 1 kOe and high coercivity typical for thin continuous films. By contrast, for insufficiently thick (i.e., discontinuous) Cu layers, the Co layer with a 1 nm nominal layer thickness can also become discontinuous and the observed MR is dominated by the contribution of SPM entities as observed for granular magnetic metals as well. In order to be able to discuss these latter features more properly, we should first recall our recent considerations about the different magnetic and MR components in electrodeposited magnetic/non-magnetic multilayers [15,20].

It has been pointed out by detailed measurements of the field and temperature dependence of the magnetization of electrodeposited Ni–Cu/Cu [15] and Co–Cu/Cu [20] multilayers that in these systems the magnetic layers can be considered as consisting of two different kinds of region which exhibit either FM or SPM behaviour. The relative fraction of the two components may vary with deposition conditions. (The occurrence of SPM regions in magnetic/non-magnetic multilayers has been evidenced also for samples produced by vacuum techniques with various element combinations [27–30].)

Concerning magnetotransport properties of these multilayers, conduction electrons travelling in the Cu spacer material between two FM regions which have some partial antiparallel alignment of their magnetization orientations were assigned [15,20] to contribute to a usual GMR effect as observed in conventional FM/PM-type multilayers (denoted as GMR$_{\text{FM}}$). On the other hand, conduction electrons of the multilayer structure also travel between a FM region and a SPM region or between two SPM regions. In such cases, owing to the rapid temporal fluctuation due to thermal agitation of the magnetization orientation of the SPM regions, a spin-dependent scattering event always occurs when the electron reaches the second magnetic region after travelling in the Cu spacer. As in granular metals, this gives rise to a strong GMR effect termed as GMR$_{\text{SPM}}$. 

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Fig. 8. (a) Evolution of the MR of electrodeposited Co(Cu)/Cu multilayers with non-magnetic layer thickness for several thicknesses of the magnetic layer. (b) Evolution of the coercive field $H_c$ and MR peak position $H_p$ of electrodeposited Co(Cu)/Cu multilayers with non-magnetic layer thickness for several thicknesses of the magnetic layer.
The approach to saturation of the GMRFM and GMR_{SPM} contributions follows the saturation behaviour of the corresponding magnetization components. If both before and after the spacer material the electron travelled in FM regions only, the magnetization saturates in a magnetic field of typically 1 kOe and the GMRFM component should also reach saturation at around this field. On the other hand, if a SPM region is also involved in the spin-dependent scattering process, since the SPM magnetization usually saturates in high magnetic fields only, the GMR_{SPM} contribution will also show a non-saturating behaviour for most typical field ranges investigated (SPM saturation is typically above 10 kOe at room temperature).

We can apply now this picture to describe the evolution of MR characteristics with layer thicknesses in the present Co–Cu/Cu multilayers. Fig. 9 displays a schematic view of the microstructure and the decomposition of the MR contributions for the four extreme Co–Cu/Cu multilayers for which the most detailed data have been presented above.

For thick Co and thin Cu layers [Co (5.7 nm)/Cu (1.1 nm)], the observed MR indicates a predominantly AMR behaviour (LMR > 0, TMR < 0, both components becoming linear with a common negative slope beyond technical saturation), typical for bulk ferromagnets. This could be interpreted as being the result of the presence of pinholes in the Cu layer at this small average thickness. This implies that at this thickness the Cu layer is unable to form a continuous deposit on top of a thick, continuous Co layer. The percolation of the Co layers through pinholes in the Cu layer is indicated also by the very low coercive field (30 Oe), again typical for a bulk metal. By contrast, for thin Co and thick Cu layers [Co (1.1 nm)/Cu (2.5 nm)], the MR behaviour is dominated by a GMRFM contribution besides the presence of a small GMR_{SPM} term. This can be assigned to thin FM Co layers well separated from each other by continuous thick Cu layers. The high observed coercive field (276 Oe) of this multilayer is in concord with the assumption of well-separated, continuous thin magnetic layers and at most a small fraction of the magnetic layer can exhibit SPM character.

Comparing now the results for the Co (5.7 nm)/Cu (1.1 nm) and Co (1.1 nm)/Cu (2.5 nm) multilayers, it seems that there is an asymmetry in the nucleation behaviour of Co on Cu and Cu on Co. Whereas Co even at an average thickness of 1.1 nm can cover continuously a Cu surface, the coverage by Cu at the same average thickness proceeds on a Co surface in a discontinuous manner. This conclusion is in good agreement with the study of Eckl et al. [31] on evaporated Co/Cu multilayers. These authors suggested that the nucleation of Cu on a Co surface preferentially starts at grain boundaries and then further growth is preferred on these existing Cu crystallites. Therefore, below a certain average Cu thickness, the deposited Cu atoms form islands only on the Co surface. A coalescence of the islands, i.e., the formation of a continuous Cu layer requires higher average Cu layer thickness. On the other hand, they have also concluded that a very thin Co layer is able to cover continuously the Cu surface, forming a uniform deposit on top of it, thereby retaining also the surface topography.

Egelhoff et al. [32] discussed the formation of Co/Cu multilayers by vacuum techniques and the influence of oxygen impurities, by emphasizing the importance of the fact that Co has a high surface free energy whereas Cu has a low one. It requires further studies as to what extent similar considerations can be applied to layer growth by electrodeposition.

With reference to Fig. 9, it can be seen that when increasing the Co layer thickness from 1.1 to 5.7 nm for $d_{Cu} = 2.5$ nm, the basic character of the MR behaviour is retained, indicating that all these multilayers consist of continuous Co and Cu layers. On the other hand, when decreasing the Cu layer thickness from 2.5 to 1.1 nm for $d_{Co} = 1.1$ nm, the character of the GMR behaviour changes. Specifically, for the Co (1.1 nm)/Cu (1.1 nm) multilayer the GMR_{SPM} contribution already dominates the observed MR characteristics. This feature is typical for granular metals and implies that the magnetic layer also breaks up into small regions most of which exhibit SPM behaviour. This can be explained as follows. Due to the discontinuous Cu layer when the growth of the next Co layer is started, the top of the surface
Fig. 9. Schematic view of the microstructural features and MR contributions for the four selected Co–Cu/Cu multilayers.
consists of both Cu and Co areas. Under such circumstances, the Co atoms are not able to provide a complete coverage of the surface at this small average Co layer thickness, probably because nucleation and growth preferentially takes place at the Co areas. Since the latter can then be covered by Cu randomly in the next step, this leads to the formation of Co islands of different sizes. These islands can eventually extend over several average nominal Co layer thickness along the growth direction. The close values of the coercive fields for the Co (5.7 nm)/Cu (2.5 nm) and Co (1.1 nm)/Cu (1.1 nm) multilayers (130 and 140 Oe, respectively) also indicate that in the latter one there may be Co regions which are similar in size to the Co layer thickness of the former multilayer structure.

5. Conclusions

Unwanted deviation from the nominal composition and layer thicknesses of electrodeposited Co–Cu/Cu multilayers could be suppressed by applying an appropriate Cu deposition potential determined by careful electrochemical measurements. As a result, the nominal thickness of constituent layers can be thought of as the real thickness (apart from a constant proportionality factor that scales with surface roughness and is somewhat higher than unity). We have prepared several series of Co–Cu/Cu multilayers under these conditions.

Room-temperature MR and magnetic measurements were performed to analyse the evolution of MR characteristics and magnetic properties with Co and Cu layer thicknesses. A fairly consistent picture emerged from this study according to which an average Cu layer thickness of at least 2–2.5 nm is required for the formation of a continuous Cu coverage on a Co surface. On the other hand, an average Co layer thickness of as small as 1.1 nm is already sufficient to cover completely a Cu surface. This asymmetry in the mutual nucleation behaviour of Co and Cu on each other is well in accord with the conclusions from Co/Cu multilayers prepared by vacuum technique. The reason for this nucleation asymmetry may lie in the surface energy differences of the two metals although this point needs further investigations.

Split MR curves were obtained for multilayers with GMR characteristics, with the peak positions roughly corresponding to the measured coercive fields. The MR splitting is indicative of the lack of a significant (either AF or FM) exchange coupling between the magnetization of neighbouring layers. The GMR effect observed can be ascribed to the random mutual alignment of the neighbouring layer magnetizations. A GMR in excess of 10% in magnetic fields around 1 kOe was achieved for multilayers with thin Co and thick Cu layers. For low Cu layer thickness, either AMR (thick Co layers) or granular type GMR (thin Co layers) behaviour was observed. The latter effect is caused by SPM islands which form during the magnetic layer deposition with low Cu layer thicknesses.

An oscillation of the GMR with increasing Cu layer thickness could not be obtained. This was explained, besides the weak or vanishing AF coupling, by the fact that under the current deposition conditions a complete separation of the magnetic layers by the Cu spacer materials is achieved beyond 2 nm average Cu layer thicknesses only.

The evolution of the coercive fields with layer thicknesses strongly supported the conclusions derived from the MR characteristics.

From an XRD study, a (111)-textured fcc structure was found for four selected multilayers with high and/or low Co–Cu and Cu layer thicknesses. No satellite reflections due to the multilayer periodicity were observed. In spite of this, the multilayer structure was of sufficiently high quality for yielding a significant GMR effect. This is in agreement with the results of Kubota et al. [33] who reported the usual high (over 50%) GMR magnitude for sputtered Co/Cu multilayers which also did not exhibit any sign of satellite reflections in the XRD pattern. In order to get further structural information on our multilayers and to verify the conclusions derived here about the microstructure evolution with layer thicknesses, transmission electron microscopic studies are planned to be performed.
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