Final report of the OTKA project No. K 75008

„Giant magnetoresistance (GMR) in electrodeposited multilayers (2009-2012)"

(Principal investigator: Imre BAKONYI)

INTRODUCTION

Project plan summary

Since its discovery in the late 1980s, the giant magnetoresistance (GMR) effect observed in various magnetic/non-magnetic multilayers has created large scientific interest and also found practical application in magnetic field sensing devices (e.g., in hard-disk drive read-out heads), in addition to boosting research into various fields of the so-called spintronics.

Magnetic/non-magnetic multilayers utilizing the GMR effect in practical applications are produced by various physical deposition (PD) processes. Electrodeposition (ED) has long been considered as a viable alternative to PD techniques to provide a simple and cheap technology for preparing high-quality spintronic materials. However, in spite of the progress achieved on ED multilayers, to a large extent by our group, since the first demonstration of GMR in ED multilayers in 1993, these materials have still proved to be inferior concerning the GMR parameters in comparison with PD multilayers.

The major goal of the current project was, based on the experience gained in the previous one and a half decade by our group in this field, to carry out further research into investigating how the GMR can be better controlled in ED multilayers via a more deeper understanding of the nucleation and growth processes of ED magnetic/non-magnetic multilayers since it has been revealed in former studies, both on PD and ED multilayers, that the multilayer microstructure is strongly interrelated with the GMR characteristics.

As a new approach, the application of surfactants which proved to be beneficial for PD multilayers was planned to be introduced also for the ED method in the case of the most-widely studied Co/Cu system. This implies the alloying of the Cu spacer layer with a small amount of Pb, Bi, Ag and/or Au since these elements are known from studies on PD layer formation to promote layer-by-layer growth instead of the island-like growth observed until now for ED multilayers.

The same perspective was kept in mind when planning investigations on ED Co/Cu multilyers to see if the deposition bath temperature can have an influence on the layer formation and, thus, on the GMR in this system. In order to reveal in more detail the multilayer formation, besides the application of direct structural studies by X-ray diffraction (XRD), surface studies were also planned by using atomic force microscopy (AFM) as well as an optical surface technique (ellipsometry).

In addition, an important objective of the project was to extend all these investigations beyond the Co/Cu system to other multilayers accessible to the ED technique. This was an important issue since although numerous studies have been carried out on the GMR of ED Ni-Co/Cu and Fe-Co/Cu systems, whereby the intention was to replace the magnetically hard Co layer by a magnetically softer alloy layer in order to reduce the GMR saturation field, all these previous works were performed without optimizing electrochemically the Cu layer deposition potential the method of which was established during our previous research activity. In the first approximation, the importance of the electrochemical optimization of the Cu deposition potential lies in the purpose of avoiding unwanted electrochemical reactions during the formation of the Cu spacer layer (dissolution of the previously deposited magnetic layer and incorporation of the magnetic elements in the spacer layer which latter is definitely deleterious on the GMR). At the same time, this electrochemically optimized potential ensures that the actual thicknesses of both the magnetic and the non-magnetic layers correspond to what is set during the ED experiment for multilayer preparation on the basis of Faraday's law (by accounting for an eventual deviation of the current efficiency from 100 % that can be properly assessed by independent experiments). Therefore, previous literature studies were unable to reveal the real layer thickness dependence of the GMR in ED Ni-Co/Cu and Fe-Co/Cu multilayers. We also planned a re-investigation of the Co/Ru system which can be used as an artificial antiferromagnet in spin-valve structures.

The problem of revealing the true layer thickness dependence of GMR in multilayers is further hampered by the fact that very often a superparamagnetic (SPM) contribution to the GMR also occurs pronouncedly in ED multilayers. Neglecting the separation of the ferromagnetic (FM) and SPM GMR contributions may hide the real dependence of GMR on layer thicknesses. Previously, we elaborated a method for separating the two contributions on the example of ED Co/Cu multilayers and the same has to be done also for the Ni-Co/Cu and Fe-Co/Cu multilayers. All these efforts should also contribute to settling the long-standing controversial issues concerning the presence or absence of an oscillatory GMR behavior in ED multilayers as a function of the spacer layer thickness which feature was well documented for most PD multilayers.

Summary of project achievements not containing original research results

Before describing the new research results achieved during the current project, it is noted that, upon instigation of the editors of the prestigious journal *Progress in Materials Science*, the two senior members of the project team wrote an extended review (140 printed pages) [1][*] which was published in the second year of the project. This comprehensive review provided, just in the initial stages of the project, a state-of-the-art report of the world-wide activity of GMR studies since the very beginning on ED magnetic/non-magnetic multilayer films. Since it covers all aspects of research subject of the current project, it was used as a starting point for carrying out our planned research. Therefore, also the above summary and the discussion of new results below is based on the knowledge described in this review paper and this is the reason that relatively few references to original research papers of the technical literature are included in the current project report. The review itself has been well received by the scientific community and by now it has already collected over 60 independent citations, surprisingly quite often even in papers not dealing with either GMR or ED multilayers.

Another project publication that does not contain original research was a comment [4] by one of the senior team members on the paper of a foreign research group which reported related results on GMR in ED multilayers. The comment pointed out some weaknesses in the paper as well as criticized the not sufficiently scientific approach to research in a topic strongly related to the field of the current OTKA project. By mistake, the OTKA project number is missing from the published version of the comment but herewith we certify that this publication is not used in supporting any other research project.

---

[*] These numbers in [] refer to the list of publications resulting from the present OTKA project which are given in Section A at the end of the report.

General overview of experimental techniques applied during the project

In the presentation of new experimental results achieved during the project, the organization will follow the above summarized workplan flow. However, in order to avoid any redundancy in describing the experimental circumstances for the various multilayer systems, it seems useful to summarize here those details which were common throughout the project work. More details on sample preparation and measurement techniques can be found in our review paper [1] as well as in the project papers listed at the end of the report.

The general approach during the project was to prepare magnetic/non-magnetic multilayers by electrodeposition and to investigate their composition, microstructure and magnetoresistance behavior. The multilayers were electrodeposited on Si wafers covered by an evaporated Cr layer (5 nm) and a Cu layer (20 nm). In these Si/Cr/Cu substrates, the Cr layer ensured adherence to the Si wafer and the Cu layer served as a conductive cathode surface for electrodeposition. For some preliminary experiments, a Cu foil substrate was also used. The upward facing substrate constituted the whole bottom of a tubular cell, ensuring a high degree of lateral homogeneity over the sample surface which enabled tracing out finer details than on multilayers commonly studied in the literature which were electrodeposited on vertical substrates in an open geometry. Electrodeposition was usually carried out in a typical three-electrode cell where an appropriate metal foil was used as counter electrode (anode) and a saturated calomel electrode (SCE) served as reference for regulating the cathode electrochemical potential. Electrodeposition was mostly performed at room temperature except in experiments where the influence of bath temperature was of interest. A galvanostatic/potentiostatic pulse combination (G/P mode) was applied to prepare the multilayers from a single bath the proper composition of which had to be established for each multilayer system separately. In the G/P deposition mode, during the G pulse a magnetic layer was deposited under current control and this was followed by the deposition of the more noble non-magnetic layer (Cu and some metallic additives) during the P pulse ensuring a potentiostatic control of deposition. Special care was taken to find the optimum value of the deposition potential applied during the P pulse the importance of which was already noticed above. Multilayer series with various thicknesses of the indivudual layers and with various total thicknesses were prepared. The layer thicknesses were set by using computer-controlled potentiostats monitoring the charge passing through the cell. For complementary studies, deposits under d.c. conditions were also prepared by either potentiostatic or galvanostatic control as well as by conventional pulse plating (a deposition pulse pulse is followed by a break with zero current). A scanning electron microscope (SEM) equipped with an analytical facility served for morphological studies and for establishing the deposit composition. The electrical resistivity and the magnetoresistance (magnetic field dependence of the electrical resistivity) were measured mostly at room temperature and, in some specific cases, even at low temperatures. Where it was necessary, the shunting effect of the Si/Cr/Cu substrate was taken into account to properly evaluate the electrical transport parameters of the multilayers. For the magnetoresistance, the ferromagnetic and superparamagnetic contributions to GMR were decomposed in cases when the latter one was not negligible. Atomic force microscopy (AFM) was used to investigate the surface of the deposits and the evolution of surface roughness with various deposition conditions. The starting surface roughness of the Si/Cr/Cu substrate was not larger than 3 nm. The microstructure and crystal structure of the deposits was investigated by wide-angle X-ray diffraction in collaboration with the Eötvös University. Some optical spectroscopic techniques were also applied (ellipsometry for estimating the nanoscale layer thicknesses and interferometry for measuring surface roughness).

REPORT ON NEW PROJECT RESULTS

I. Studies on the preparation of ED Co/Cu multilayers

Studies on the influence of surfactant element addition to the Co/Cu bath

(i) Codeposition experiments in the Co-Pb system and studies of Co-Pb electrodeposits [7]

As one of the main tasks, codeposition of Pb and Co was studied for both attempting to prepare Co/Pb multilayers and designing baths for examining the impact of Pb on the formation of Co/Cu multilayers since experience with physically deposited multilayers in the literature evidenced a beneficial effect of Pb for the layer-growth mode and the magnetoresistance (MR) properties.

It should be kept in mind that Co and Pb are immiscible metals with very dissimilar nearest neighbor distances in the stable crystalline forms. Pb has a face-centered cubic (fcc) structure at normal pressure and a hexagonal close-packed (hcp) structure at high pressure. Co has an hcp structure at room temperature that transforms to an fcc structure at 422 ^{o}C. Based on both the immiscibility and the large difference in the nearest neighbor distances of Co and Pb, it is expected that the production of either metastable Co–Pb alloys or Co/Pb multilayers requires highly non-equilibrium preparation techniques. Due to the lack of such previous studies, it was not known whether Co and Pb can form metastable alloys or whether a quasi-epitaxial growth is possible where one of the components stabilizes the metastable form of the other one via the interaction of interfaces.

Due to precipitate formation by Pb in sulfate type solutions commonly used for the electrodeposition of Co/Cu multilayers, new bath formulations had to be tested to make the codeposition experiments with Co and Pb possible. A detailed overview of previous literature results on the electrochemical codeposition experiments of Co and Pb was given in [7]. On the basis of this overview, preliminary experiments for the codeposition of Pb and Co were performed with three different baths. Two baths were based on good solubility of both Co^{2+} and Pb^{2+} ions in the presence of acetate and nitrate anions, while the chloride bath took the advantage of the $[PbCl3]^-$ complex formation at high Cl^- concentration. For the acetate bath, acetic acid was also added in order to suppress the hydrolysis of the acetate ions. The bath compositions are summarized in Table 1.

Source compound	Concentration / mol dm^{-3}		
	Acetate bath	Nitrate bath	Chloride bath
$Co(CH_3COO)_2 \cdot 4H_2O$	0.4	- - -	- - -
$Pb(CH_3COO)_2 \cdot 3H_2O$	0.013	- - -	0.006
CH_3COOH	0.1	- - -	- - -
$Co(NO_3)_2 \cdot 6H_2O$	- - -	0.4	- - -
$Pb(NO_3)_2 \cdot 3H_2O$	- - -	0.013	- - -
$CoCl_2 \cdot 6H_2O$	- - -	- - -	0.4
KCl	- - -	- - -	2.5
pH of the bath	5.15	4.55	4.55

Table 1 *Composition of the electrolytes used for Co-Pb codeposition experiments.*

Only the acetate bath yielded compact deposits that could be reliably contacted for electrical transport measurements, and the results described below will mainly refer to deposits obtained from this bath. (The reasons of the failure for the rest of the baths were discussed in [7]). In the case of the acetate bath, the deposition of Pb is a reversible process, while the deposition of Co is quasi-reversible. This is why the dissolution of Co is not a significant factor in the optimization of the experiments, unlike for Co/Cu multilayers produced in various other baths.

By using SEM images, it was revealed during the present studies that no compact Co-Pb alloy/mixture deposits can be obtained with a Co molar fraction below 0.8 in either current-controlled or potential-controlled mode because Pb is prone to develop dendrites. On the other hand, compact deposits have been obtained from the acetate bath by two-pulse electrodeposition using a G/P pulse combination (G: deposition of Co-rich deposit with constant current; P: deposition of pure Pb at constant potential) in the entire composition range. Composition analysis of the deposits combined with gravimetric measurements indicated that the G pulse results in the formation of a deposit with about 90 at.% Co and 10 at.% Pb in the optimum current density range of the G pulse. The dissolution of the deposits was also studied by an electrochemical quartz crystal microbalance. Two distinct dissolution peaks were found. One of them (observed at more negative potentials) corresponds to the dissolution of pure Pb, while the other is related to the dissolution of the Co-rich segments of the deposits. By observing both the oxidation charge and the weight change during the dissolution of the phases, their composition can be obtained. This analysis confirmed the formation of a metastable alloy. While the quartz microbalance analysis resulted in 7.5 at.% Pb in the Co-rich phase, the composition analysis yielded 10 at.% Pb in Co for a nominally identical sample, the two sets of data being in good agreement with each other.

XRD patterns recorded for two–pulse plated deposits revealed a nanocrystalline structure with grain sizes in the range 5 to 20 nm. The XRD peaks could be well indexed to pure face-centered cubic Co and Pb. This means that Pb atoms codeposited with Co during the G pulse are not dissolved in Co but are segregated in the form of a nanoscale mixture of the two constituent phases. This observation is in compliance with the immiscibility of Co and Pb and the large difference in the lattice distances of the stable crystalline forms of these elements. The formation of a multilayer structure could not be revealed from the XRD patterns.

Magnetotransport measurements revealed anisotropic magnetoresistance in both d.c.-plated and two-pulse plated Co–Pb deposits. This means that the observed magnetoresistance arises from spin-dependent electron scattering events dominantly within sufficiently large Co regions (comparable to or larger than the mean free path of electrons in bulk Co) and not along electron paths between two Co regions via Pb regions. No indication for a giant magnetoresistance effect due to either a ferromagnetic/non-magnetic layered structure or a granular magnetic structure could be observed.

Low-temperature resistivity measurements on the two-pulse plated Co-Pb deposits revealed a superconducting transition slightly below that of pure Pb. This could be ascribed to a proximity effect: the ferromagnetic Co grains suppress somewhat the superconductivity of the Pb phase due to the nanoscale phase mixture of the two constituents which was revealed by the XRD study. Some aging effects in the superconducting transition were also observed on a time scale of several months, indicating structural rearrangements in the two-phase mixture of Co and Pb which occur dominantly in the interfaces between the Co and Pb regions. A demonstration of low-temperature resistivity data for a Co-Pb deposit is given in Fig. 1. Such ferromagnetic/superconducting nanocomposites have been intensively investigated recently with various element combinations for a better understanding of the proximity effect.

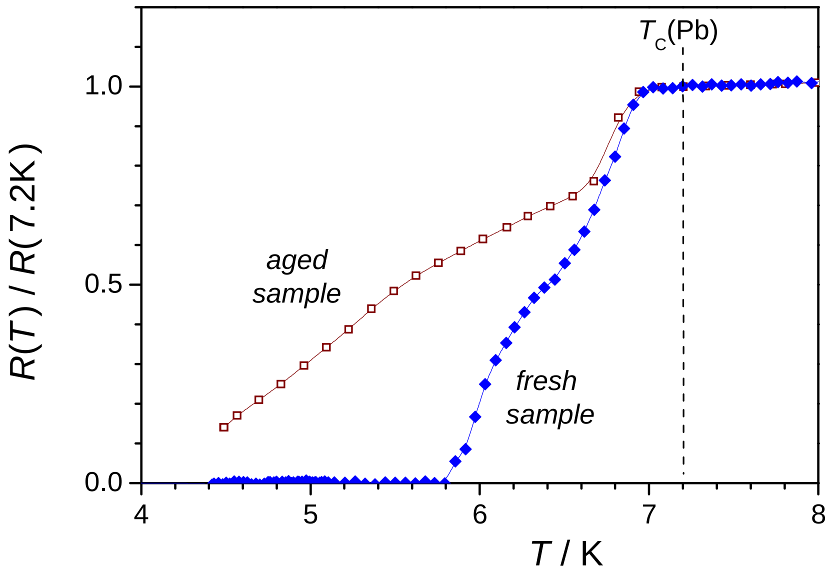

Fig. 1 *Low-temperature normalized resistance of a two-pulse plated Co-Pb sample for fresh and aged conditions. Note the fully superconducting state for the fresh sample below 5.8 K in spite of the presence of a significant amount of ferromagnetic Co grains in the sample.*

(ii) Studies on Co/Cu-Pb electrodeposits [14]

Samples containing Co and Cu only were also produced from an acetate-type bath. In this bath, the ion concentrations were identical to that of the Co-Pb bath with the exception that Pb^{2+} was replaced with Cu^{2+}. We first managed to deposit Co/Cu multilayers from this acetate-type bath. These samples showed a GMR effect. The Cu thickness was varied between 1 and 7 nm. As the Cu layer thickness increased, the saturation field of the MR(H) curves decreased. The decomposition of the GMR curves into FM and SPM contribution revealed that the decrease in the saturation field with increasing Cu layer thickness can be fully explained with the elimination of the GMR_{SPM} type contribution to the magnetoresistance. The Co layer thickness was typically 2.5 nm, and its thickness had a much smaller impact on the MR behavior of the deposits. The maximum GMR achieved was some 5%. In this respect, the acetate-type bath could yield Co/Cu multilayer samples comparable to those produced from the conventional sulfate- or sulfamate-type baths.

The Co/Cu-Pb samples were produced by using various electrolytes. These were mixed from the acetate-type Co/Cu and Co/Pb baths, and the Cu^{2+}:Pb^{2+} ratio was set by the mixing ratio of the electrolytes. Pulse-plated deposits were prepared with conditions that proved to be optimal in the sense of both the GMR achieved and the saturation field of the MR(H) curves for the Co/Cu multilayers obtained with the same type of bath.

The presence of Pb^{2+} led to the decrease in GMR. As the Pb^{2+} content of the bath increased, the saturation field of the MR(H) curves also increased, and finally the GMR character of the curves turned into the typical AMR behavior with positive LMR. A typical set of GMR curves is shown in Figure 2.

The codeposition of Pb was obvious from the composition analysis of the samples. Interestingly, the value of the AMR achieved approximately the same level as for pure Co/Pb deposits at a fairly low Pb concentration in the samples.

Another bath developed for the test of the Pb^{2+} ions was based on the perchlorate salt of each metal. The GMR achieved for the Co/Cu multilayers deposited from the perchlorate bath was even higher than for the acetate bath (8%). Hence, it was shown that the anions exhibiting at most a weak interaction with the metals being deposited (namely, sulfate, perchlorate or acetate) can all be used as an electrolyte component. It has been known from previous studies that strongly adsorbing anions like chloride or especially citrate, however, fundamentally alter the deposit character.

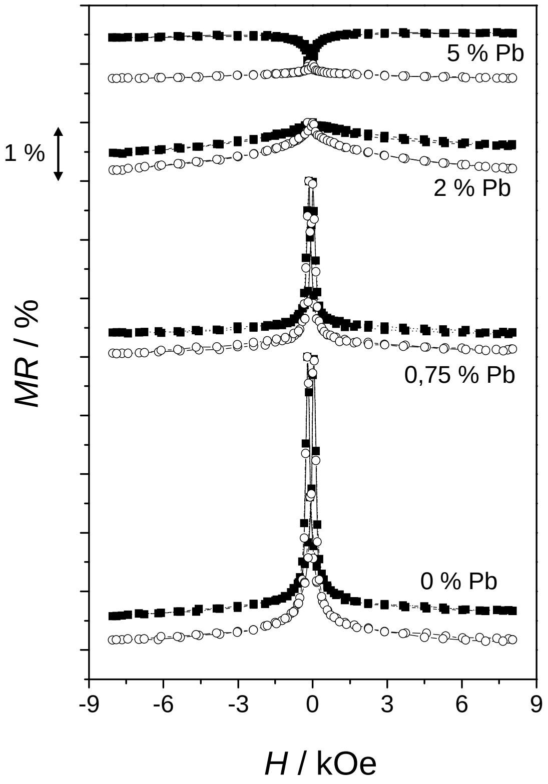

Fig. 2 *MR(H) curves of a few Co/Cu-Pb multilayers deposited from the acetate bath. The percentage next to the curves refer to the 100*c(Pb^{2+})/[c(Pb^{2+})+c(Cu^{2+})] ratio in the electrolyte. The curves are displaced along the ordinate in order to present them in a single figure.*

The way as the impact of the Pb^{2+} anions was studied in the perchlorate solutions was the same as for the acetate bath (i.e., using two baths of similar Cu^{2+} and Pb^{2+} concentrations). The magnetoresistance of the deposits as a function of the lead content of the bath is presented in Figure 3.

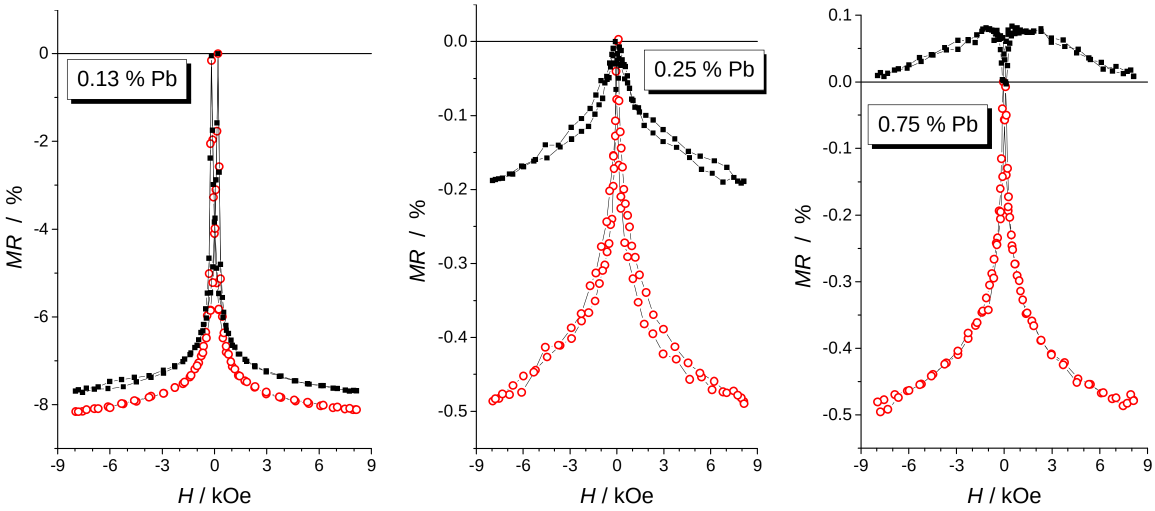

Fig. 3 *MR(H) curves of a few Co/Cu-Pb multilayers deposited from the perchlorate bath. The percentage next to the curves refer to the 100*c(Pb^{2+})/[c(Pb^{2+})+c(Cu^{2+})] ratio in the electrolyte.*

Although the GMR at zero lead content was higher for the perchlorate bath than for the acetate bath, the transition to the AMR happened at a lower relative Pb^{2+} concentration. The common conclusion of the experiments with Pb^{2+} was that no smoothening effect could be detected during the multilayer formation by using the magnetoresistance as the indicator of structural perfectness. Instead, the incorporation of the lead and its structure-breaking impact was dominant in each case studied.

It has to be noted that the codeposition of the three elements in the Co/Cu-Pb multilayers is not at all a trivial process. As the Pb^{2+} concentration increases in the bath, the Pb molar fraction in the deposit increases first, then it falls again. This behavior could not be elucidated on the basis of the known codeposition mechanisms.

(iii) Studies on Co/Cu-Ag electrodeposits [14]

The low solubility of most Ag salts imposes a strong limitation on the electrolyte solutions suitable for the study of the impact of Ag^+ ions. Although electrodeposition of silver from $AgNO_3$ solution is possible, the reduction of the nitrate ions makes it impossible to deposit a Co layer. Therefore, only perchlorate-type solutions could be used. The Co/Ag system did not need to be studied in detail since it was published prior to the start of the present project [J. García-Torres, L. Péter, Á. Révész, L. Pogány and I. Bakonyi, *Thin Solid Films* **517**, 6081-6090 (2009)].

The composition of the solution was optimized for the concentration of $Co(ClO_4)_2$ and H_3BO_3. It was found that boric acid is necessary to obtain a continuous and fairly smooth deposit that can be stably contacted for the magnetoresistance measurements. The following solution composition was found to be the most suitable for this series of experiments: $Co(ClO_4)_2$ (0.2 mol dm^{-3}), $Cu(ClO_4)_2$ (0.015 mol dm^{-3}), and H_3BO_3 (0.2 mol dm^{-3}). The deposition current density of Co was chosen to be -20 $mAcm^{-2}$. Lower current densities led to fragmented deposits, while at higher current densities the metallic shiny surface turned into a dull surface with many nonmetallic black spots. The impact of the Ag^+ ions was studied with a gradual replacement of the Cu^{2+} ions with Ag^+ ions, and the resulting properties were displayed as a function of the $100*c(Ag^+)/[c(Ag^+)+c(Cu^{2+})]$ ion ratio. The composition of the resulting multilayer deposits are presented in Figure 4.

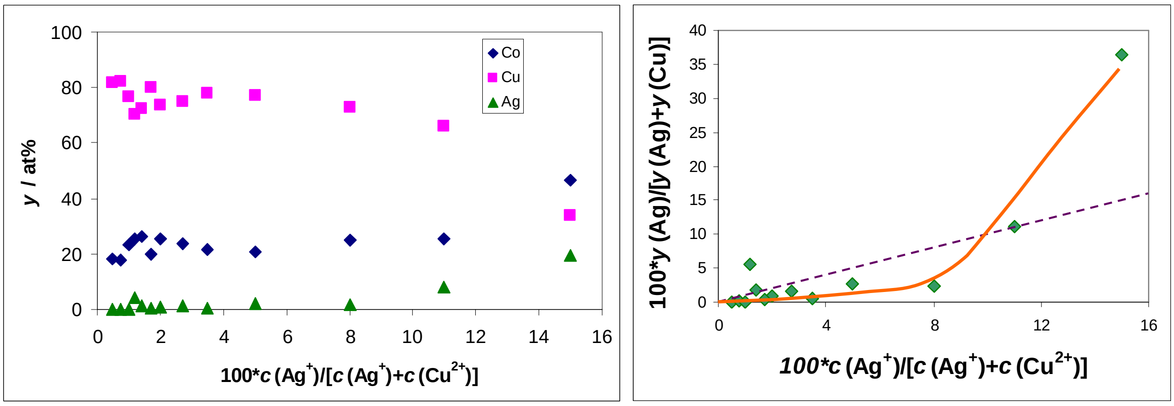

Fig. 4 *Composition of the Co/Cu-Ag mulatilayers. Left: all molar fractions as a function of the ionic ratio of the non-magnetic elements in the solution. Right: the relative molar fraction of Ag as a function of the ionic ratio of the non-magnetic elements in the solution. The dashed line is the reference line (where y=x) and the thick orange line is a guide for the eye.*

The total deposit composition indicates that the deposition of Ag leads to a decrease of the Co molar fraction in the deposit. The increase of the Cu molar fraction with the Ag^+ concentration does not mean that the partial current associated with Cu deposition could increase; instead, it is a result of the loss of the current efficiency at high Ag^+ concentrations.

The right-hand side chart of Figure 4 indicates that the deposition of silver is a hindered process at low Ag^+ concentration. For ionic ratios less than 8%, the relative Ag content of the deposit is smaller than what can be expected from the solution composition. Since Ag forms no equilibrium alloy with either Cu or Co, its deposition requires a high activation energy due to the nucleation of the Ag crystals. Therefore, the Ag^+ ions are fairly inactive in the deposition process itself, although the standard potential of the Ag^+/Ag system is by far more positive than that of the other metal ion/metal pairs present in the system. At high Ag^+ concentration, however, the trend is inverted, and Ag deposition becomes a relatively dominant process, which is indicated by the fact that the Ag molar fraction increases to a much higher value that the ionic ratio in the solution.

Figure 5 summarizes the magnetoresistance behavior of the Co/Cu-Ag multilayers. At low relative Ag^+ concentrations in the solution, the GMR increases, but this is not the result of a significant Ag incorporation into the samples, as shown by the composition data. The increase in the GMR can originate either from a beneficial effect of a small amount of Ag in the spacer layer or the impact of the Ag^+ on the deposition mode of the Cu layer independently of its codeposition. The increase in the GMR takes place with conserving the MR(H) curve shape.

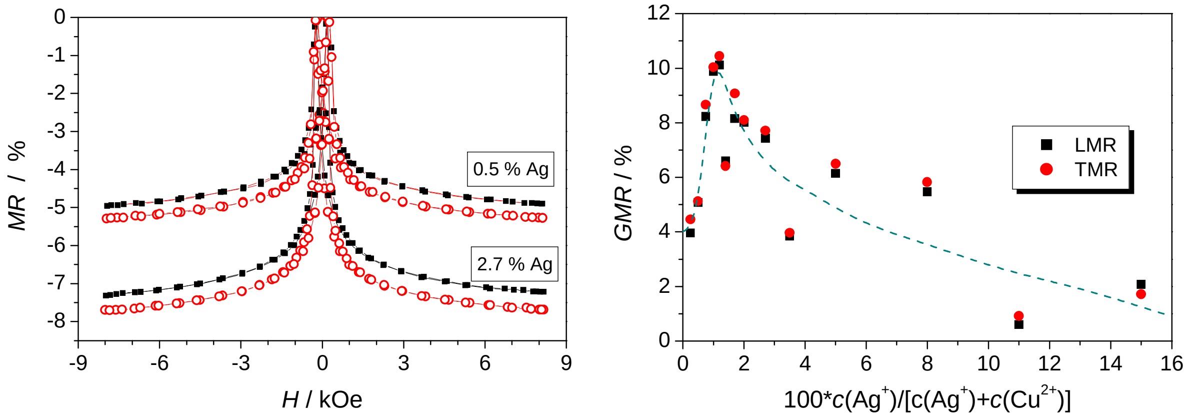

Fig. 5 *Magnetoresistance of Co/Cu-Ag multilayers. Left: two typical pairs of magnetoresistance curves for different* Ag^+ *concentrations. Right: GMR obtained as a function of the relative* Ag^+ *concentration in the solution. The dashed line is a guide for the eye.*

The magnetoresistance as a function of the relative Ag^+ concentration shows a maximum at about 1.5%. The GMR achieved at this relative Ag^+ concentration is about twice of the value achieved with an Ag-free solution. Since the GMR increment is obtained in the concentration range where the Ag incorporation in the deposit is still negligible, it is concluded that a similar effect was found as that obtained in the physical deposition methods.

(iv) Studies on Co/Bi and Co/Cu-Bi electrodeposits [14]

The solubility of bismuth(III)-oxide was studied in various electrolytes used for multilayer deposition experiments. It was found that no measurable Bi^{3+} concentration was found in any of the electrolytes used. The solutions tested ranged to sulfate, sulfamate, acetate, perchlorate and citrate type electrolytes.

Several experiments were also carried out with bismuth(III)-chloride. The solubility was too small in this case, too, if the pH was only moderately acidic. If the chloride ion concentration was at least 0.1 mol/liter and the pH was less than 1, the dissolution of a small amount of $BiCl_3$ could be achieved. Although all other components necessary for the multilayer deposition experiment were soluble in this solution, the low pH led to a loss in the current efficiency. No current density range could be established where deposits in the form of continuous films are obtained. Therefore, the impact of the Bi^{3+} ions on the multilayer deposition process could not be tested because of the above technical reasons.

(v) Studies on Co/Au, Co/Cu-Au and Co/Cu-Ag-Au electrodeposits [14]

Although we have already made efforts for studying the influence of Au in the spacer layer on the structure and GMR behavior of such multilayers, no reasonable results have been obtained until now. In the near future, we intend to continue these experiments which should then be incorporated into a project paper under preparation [14].

Studies on the influence of bath temperature on Co/Cu multilayer electrodeposition [13]

In order to obtain even deposits, a thermostated cell construction had to be designed. In such a case, two options can be considered: (i) A temperature-controlled bath with an immersion-type cathode holder; (ii) A cell optimally designed for obtaining an even deposit and applying external temperature control. Among these options, the latter was chosen. The resulting cell design is shown in Figure 6. The capillary ending of the reference electrode container vessel was placed on the plateau between the two plexiglass parts of the cell. The calomel reference electrode was not termostated but was situated outside of the cell. Therefore, this study was carried out with an anisothermic cell. The counter electrode was immersed into the solution from the top of the cell. The temperature of the bath was measured in the plating solution near the cathode.

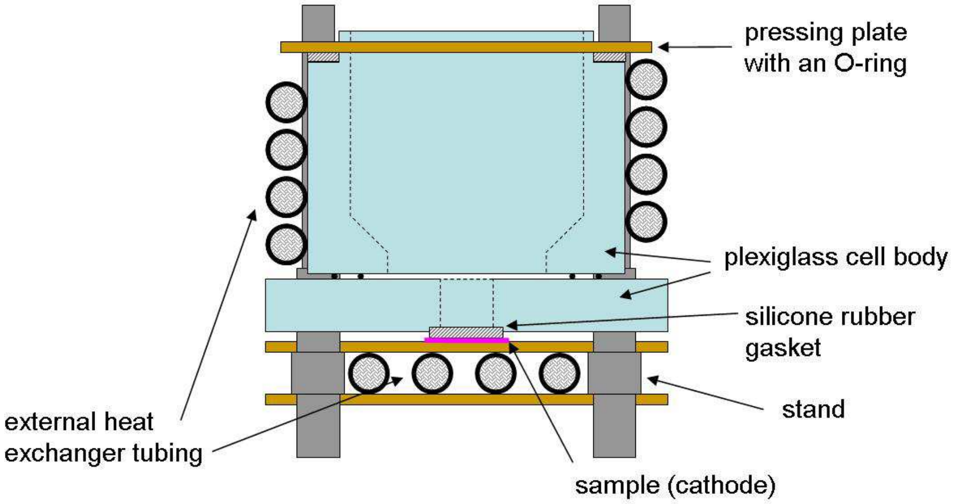

Fig. 6 *Schematic view of the cell used for multilayer deposition under temperature-controlled conditions.*

Electrodeposition was carried out with a bath of the following composition: $CoSO_4$ (0.8 mol dm^{-3}), $CuSO_4$ (0.015 mol dm^{-3}), H_3BO_3 (0.2 mol dm^{-3}) és $(NH_4)_2SO_4$ (0.2 mol dm^{-3}). This electrolyte formulation was used successfully in a previous study of ours [I. Bakonyi, L. Péter, Z.E. Horváth, J. Pádár, L. Pogány and G. Molnár, *J. Electrochem. Soc.* **155**, D688-D692 (2008)] . In contrast to the previous study, this cell design led to round-shaped samples.

The deposition potential of Cu had to be optimized for each temperature used in this study. This necessity originates from two reasons: (i) the anisotherm nature of the cell; (ii) the dependence of the equilibrium potential of the Co^{2+}/Co system with temperature. At each temperature, the optimum potential was used. At all temperatures, the nominal Cu layer thickness varied between 1 and 7 nm.

The Cu limiting current density increased with temperature as expected (see Figure 7). Therefore, the deposition time of the Cu layer decreased with temperature. Although the Cu content of the Co layer could also be a function of temperature due to the variation in the transport rate of the Cu^{2+} ions, this effect was taken of secondary importance and the Co deposition current density was fixed.

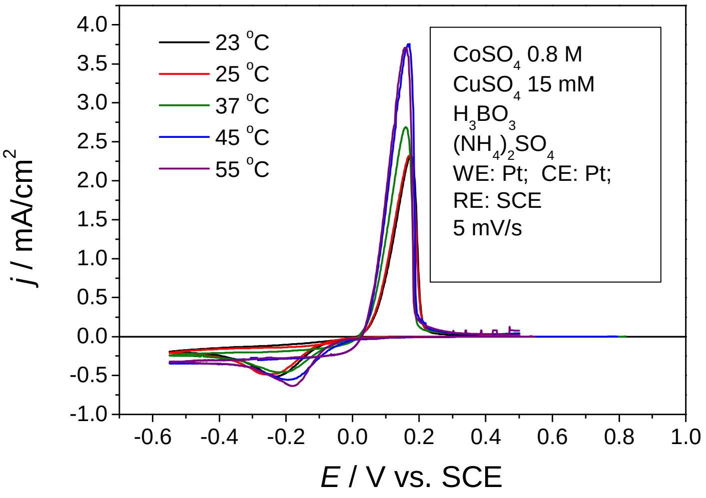

Fig. 7 *Temperature dependence of the Cu deposition and dissolution as investigated by the cyclic voltammograms by using the solution used for the deposition of the Co/Cu multilayers.*

The experience was that the GMR increased with Cu layer thickness in the range studied. At a fixed Cu layer thickness, the saturation field of the MR(H) curves decreased with increasing temperature. These effects are illustrated in Figure 8.

The impact of the change in temperature on the magnetoresistance behavior of the Co/Cu deposits is mostly manifested in a slight change in the ferromagnetic contribution of the GMR. This parameter is shown in Figure 9. As the temperature increased, the saturation field decreased somewhat and the saturation magnetoresistance increased. However, this trend was not fully uniform and there was a significant scattering in the data obtained. This scatering can be attributed to, e.g., the variation in the quality of the Si/Cr/Cu wafer susbtrates used for sample preparation.

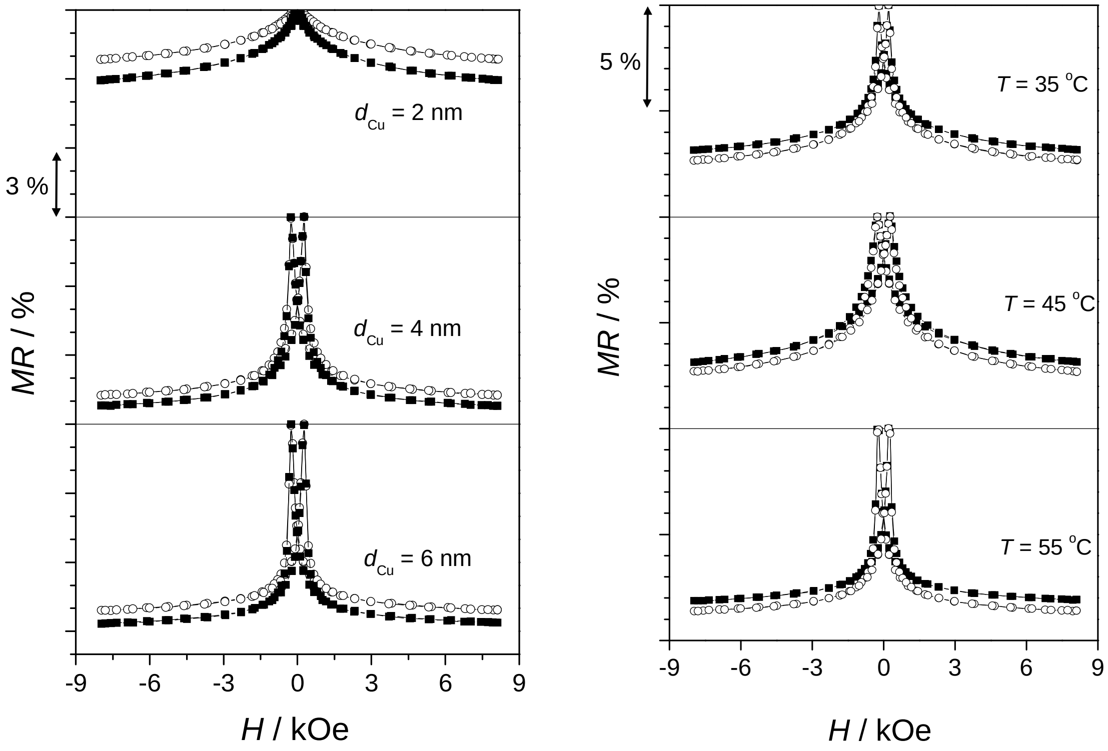

Fig. 8 *Typical magnetoresistance curves of Co/Cu multilayers produced at different temperatures. Left: dependence of the shape of the GMR curves at 35 °C. Right: Temperature dependence of the MR(H) functions at constant layer thicknesses;* d_{Cu}*= 5 nm.*

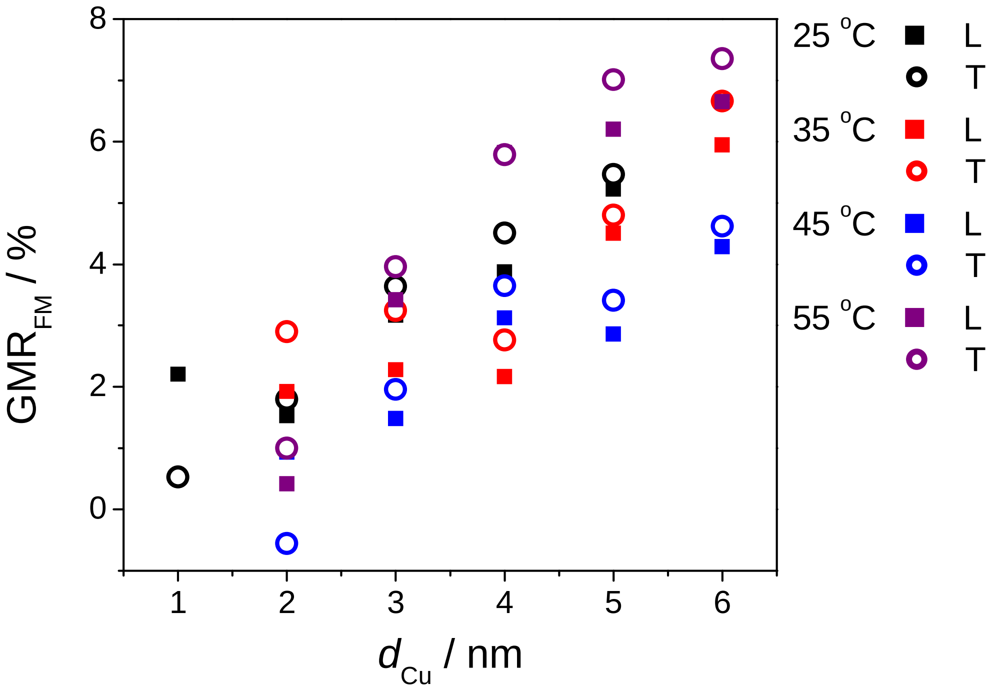

Fig. 9 *The ferromagnetic component of the total magnetoresistance as a function of the Cu layer thickness at different deposition temperatures. The Co layer thickness was constant for each sample.*

Surface studies of electrochemical growth by AFM on ultrathin Co/Cu multilayers [5]

Particular attention was paid to studying the nucleation and growth processes of electrodeposited multilayers by using AFM. Experiments were carried out on electrodeposited Co/Cu multilayers consisting of a few number (1 to 10) of bilayers only which was expected to yield important information on the initial nucleation steps during the deposit formation on the substrate.

The importance of this study was that whereas the GMR effect has been widely investigated on ED ferromagnetic/non-magnetic (FM/NM) multilayers generally containing *a large number of bilayers*, in most applications of the GMR effect layered structures consisting of a *relatively small number of consecutive FM and NM layers* are used. We have, therefore, extended our previous studies [1] on ED GMR multilayers to layered structures with a total thickness ranging from a few nanometers up to 70 nm. The evolution of the surface roughness and magnetoresistance of such ultrathin ED Co/Cu layered structures was investigated. Various layer combinations were produced including both Co and Cu either as starting or top layers in order (i) to see differences in the nucleation of the first layer and (ii) to trace out the effect of the so-called exchange reaction. For this purpose, two different Co/Cu multilayer series were prepared: one with alternating Co and Cu layers on the top (series 1) and another one made up of Cu/Co/Cu trilayers (series 2). A schematic view of these ED layered structures is depicted in Fig. 10.

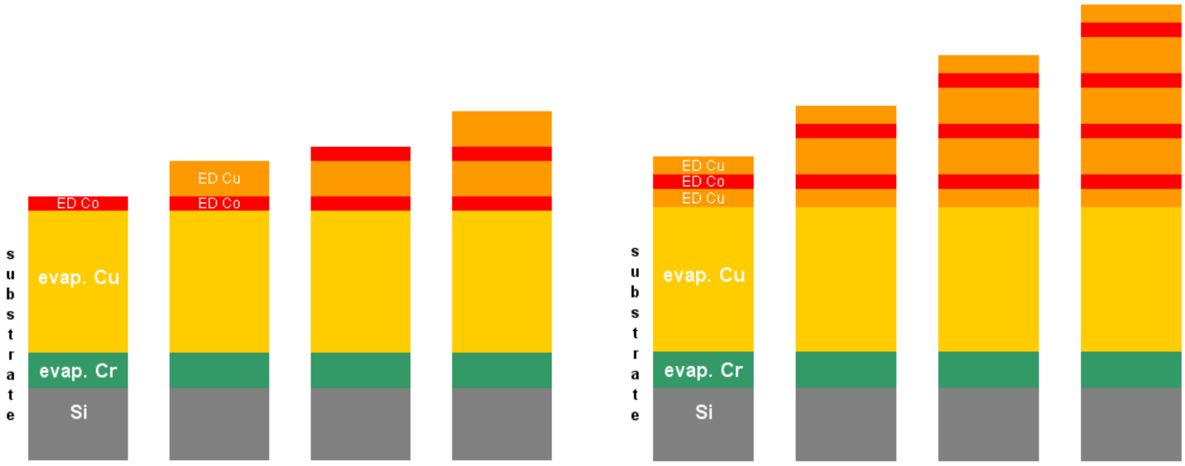

Fig. 10 *Schematic cross-sectional view of the investigated layer structures in series 1 (left panel) and series 2 (right panel).*

It was shown by AFM studies that although the exchange reaction between a topmost Co layer and the electrolyte deteriorates the continuity of the top Co layer (multilayers in series 1) and, thus, leads to the appearance of an SPM contribution to the magnetoresistance, it also makes the multilayer smoother. The root-mean-square surface roughness (R_q) for multilayer series 1 varied apparently randomly in a wide range with the addition of new layers to the stack (Fig. 11). The first Co layer subjected to the exchange reaction exhibited a large increase of the surface roughness with respect to the substrate roughness. This may be partly attributed to the hindered and, therefore, uneven nucleation of Co on the surface of the evaporated Cu underlayer from which the native oxide was not removed. Another possible reason of the surface roughness increment was the pronounced dissolution of the Co atoms and their random replacement by Cu atoms. The deposition of the next Cu layer leads to a smoothening. Since the second and subsequent Co layers are already deposited on a completely oxide-free surface, the nucleation of Co is much more homogeneous over the cathode area. Therefore, the top Co layers, in spite of the exchange reaction, lead to a smoothening, at least up to the fifth bilayer as indicated by the lines connecting the full circles (top Cu layer) with the subsequent open circles (top Co layer). On the contrary, the top Cu layers rather seem to cause a roughening in most cases. In summary, it seems that the dissolution makes the multilayer smoother: the samples with the partially dissolved Co covering layer are always smoother than the ones with a Cu layer on the top.

To prove this smoothening effect of the substitution of Co atoms by Cu atoms, an additional series of four samples was made. Each was made up by four bilayers of Cu(5.0 nm)/Co(2.0 nm) and, after finishing the deposition, the current was set to zero but the electrolyte was not removed from the sample for different waiting times (T_W). During this period, a replacement of the Co atoms with Cu atoms by the exchange reaction could occur. The root-mean-square surface roughness of the resulting sample was measured by AFM. According to Fig. 12, with increasing T_W the R_q values decrease exponentially. This is because both partial processes of the exchange reaction result in a roughness reduction. On the one hand, the dissolution of the Co atoms at the highest peaks has the largest probability because the binding energy of these atoms to the solid phase is the smallest. On the other hand, the deposition of the Cu atoms and their diffusion along the surface may lead to a filling-up of the cavities because the binding energy of the newly deposited atoms at these positions is the highest. The R_q values converge to a finite value (4.2 nm) which is somewhat higher than the initial substrate roughness. One should keep in mind that the lattice mismatch in a multilayer should unavoidably lead to a surface roughening because the layer with larger lattice constant can grow in island like form only at the beginning on the previous layer with smaller lattice constant.

In fact, the exponential decrease of the R_q values starts only after a certain waiting time (which is lower than the minimum 10 s we could reach), because the electrolyte near the surface is depleted for Cu^{2+} ions and thus the exchange reaction cannot start immediately after the deposition of the Co layer was finished. We can assume that the roughness starts to decrease at a very low rate, due to the lack of Cu^{2+} ions, and then, as the Cu^{2+}-content of the electrolyte near the sample surface reaches its bulk value, the smoothening rate increases. After a certain value of T_W, the amount of the Co atoms at the surface decreases to a low value as a result of which the R_q data converge to a finite value.

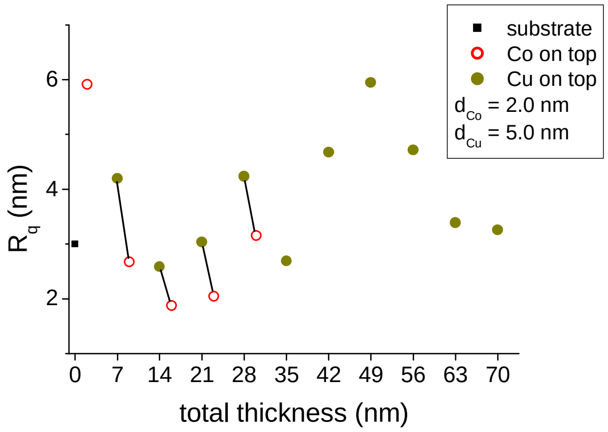

Fig. 11 *Evolution of the surface roughness parameter R_q with total deposit thickness for series 1. The lines connecting the full and open circles are just to indicate the sequence "top Cu layer" → "top Co layer".*

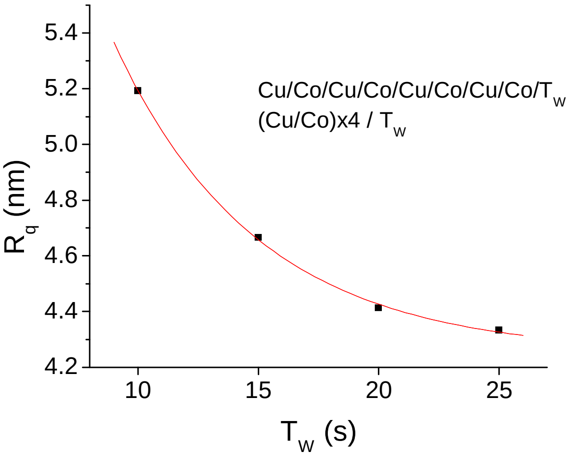

Fig. 12 *Evolution of the surface roughness parameter R_q with waiting time (T_W).*

It was also found that, in the multilayer thickness range investigated, the root-mean-square roughness of the multilayers made up by the trilayers develops linearly as the total multilayer thickness increases. Meanwhile, the GMR of the deposited multilayer saturates at six trilayers whereas the small SPM contribution to the MR increases in the whole investigated thickness range.

Special attention was paid to measure the field-dependence of the magnetoresistance, MR(H), in order to derive information for the appearance of superparamagnetic regions in the magnetic layers. This proved to be helpful for monitoring the evolution of the layer microstructure at each step of the deposition sequence. The importance of the present study is also emphasized by the fact that previously no report has been published on MR(H) mesurements obtained on such thin ED layered structures. On the basis of the measured MR(H) curves, a schematic picture could be sketched about the layer formation during the initial stages of deposition. This is demonstrated in Fig. 13 for the first four layers in series 1.

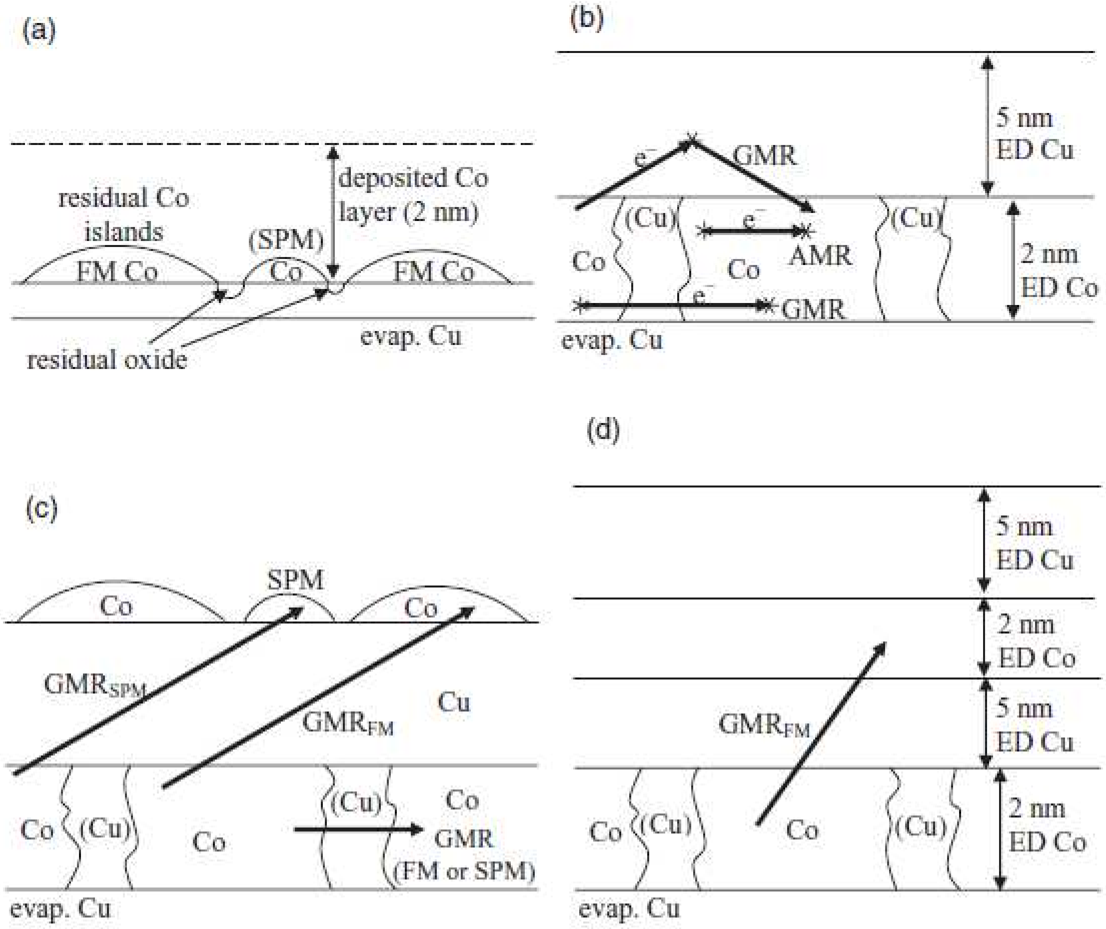

Fig. 13 *Sketches of the structure of the first four samples of series 1. The thicker arrows mark the electron pathways. Note that not all possible spin-dependent electron scattering paths are indicated in each sketch. The notation "(Cu)" indicates Cu-rich regions in the magnetic layer.*

Surface studies of electrochemical growth by ellipsometry on Co/Cu multilayers

The ellipsometric study was started with the characterization of the seed layers on the Si substrate. The Si/Cr/Cu substrate structure was essentially confirmed. The thickness of both evaporated layers (Cr and Cu) was in accordance with the nominal thickness. Ellipsometry detected SiO_2 at the Si/Cr interface and CuO at the substrate surface. These oxide layers can appear since the Si surface was not etched prior to the Cr seed layer evaporation and the Cu surface was examined in air. The thickness of the oxide layers was typically 3 nm, while the thickness of the metal layers was ±10% of the nominal value.

Ellipsometry data were also obtained for two sorts of specimens with electrodeposited layers, Si/Cr/Cu//Cu/Co/Cu and Si/Cr/Cu//Cu/Co/Cu/Co/Cu. In the latter sample structures, the double dash refers to the boundary of the evaporated and electrodeposited layers. The thickness of each electrodeposited layers was 5 nm. The ellipsometric data could also confirm these sample structures, and the layer thicknesses could be established with the same accuracy as the substrate layers. In the specimens coated with the electrodeposited layers, the copper oxide was detectable at the sample surface only.

For a deposit thickness of 35 nm or higher, the incidence depth of the electromagnetic radiation into the metallic layers did not make it possible the resolution of the layers underneath. Therefore, the ellipsometric study was not continued for higher deposit thicknesses.

The accuracy of the layer structure as obtained by the delineation of the ellipsometric data is highly model sensitive. The change in the layer structure causes a relatively little change in the ellipsometric spectrum. For instance, the smear-out of the layer boundaries leaves the spectra unchanged, although the sample structures cannot be taken identical. In this respect, ellipsometry fell behind the expectation. As compared to the direct destructive depth profiling methods (e.g., secondary neutral mass spectrometry), the sharpness of the layer boundaries was not detectable. Since the gradual change of the in-depth element concentrations can be modeled in ellipsometry as consecutive thin layers of constant metal ratios in each single layers, this method did not prove to be suitable to follow the sharpness of the layer boundaries. The ellipsometric spectra was also insensitive to pinholes in the electrodeposited layers caused by the hydrogen evolution.

Due to these experienced deficiencies of the method, the originnally planned development of an electrochemical cell for in-situ ellipsommetry studies was not pursued.

II. Studies on ED Ni-Co/Cu multilayers

Preparation and magnetoresistance study of ED Ni-Co bulk alloys [3]

As a preliminary step to the electrodeposition of Ni-Co/Cu multilayers, it was necessary to carry out investigations on the preparation and transport properties of the bulk alloys to be used as magnetic layers in these multilyers. Therefore, ED Ni-Co alloys in the form thick layers (about 2 μm) were prepared by d.c.plating under galvanostatic control over the whole composition range. For this purpose, an appropriate mixture of a Co-containing and a Ni-containig bath was prepared with each bath based on the electrolyte elaborated for the ED Co/Cu multilayer preparation as described above.

The electrical transport properties (zero-field room-temperature resistivity, temperature dependence of the resistivity, residual resistivity and the AMR) were investigated in detail for these Ni-Co alloys both in the as-deposited state and, in some cases, also after annealing.

It was established by XRD that the ED Ni-Co alloy deposits exhibited an fcc phase up to fairly high Co concentrations. A strongly textured fcc structure was found in the as-deposited state with an average grain size of about 10 nm. Upon annealing, whereas the crystal structure was retained, the grain size increased by a factor of 3 to 5, depending on alloy composition. The room-temperature zero-field resistivity was found to decrease strongly by annealing due to the increased grain size.

By measuring the temperature dependence of the resistivity down to 13 K, the residual resistivities of the annealed ED Ni-Co alloys were determined which were in good agreement with previously reported data on metallurgically processed Ni-Co alloys. The residual resistivity exhibits a maximum as a function of composition for the Ni-Co alloy system, corresponding to Nordheim's rule, although the maximum position is shifted from the expected equiatomic composition to about 20 to 30 at.% Co.

The anisotropic magnetoresistance (*AMR)* values were measured at room temperature and 13 K for the substrate-free ED Ni-Co alloys either in non-annealed or annealed states. The AMR values measured were in relatively good agreement with reported data on bulk Ni-Co alloys prepared by metallurgical means. The *AMR* also exhibits a maximum with a value of about 6 % in the same composition range as the residual resistivity in this alloy system.

Magnetoresistance and surface roughness study of ED Ni-Co/Cu multilayers [11]

Among multilayers prepared with physical methods, Ni-Co/Cu multilayers have simultaneously large GMR magnitudes and low GMR saturation fields which parameters are both very important from the viewpoint of sensor applications requiring high field sensitivity. Prior to the current project, no systematic studies have been carried out on ED Ni-Co/Cu multilayers in this system since the elaboration of a method for the optimization of the Cu layer deposition potential [1], which is a prerequisite for a quantitative control of the individual layer thicknesses in ED multilayers. Therefore, an extended study of ED Ni-Co/Cu multilayers prepared with optimized Cu deposition potential was performed by measuring the room-temperature transport properties (the zero-field resistivity, ρ_0, and the GMR) as a function of the individual layer thicknesses and total multilayer thickness. The surface roughness development was also studied by AFM.

(i) Composition control of the magnetic layers in ED Ni-Co/Cu multilayers

As a first step, a control of the composition of the magnetic layers had to be elaborated. In the multilayers over the entire composition range, there is a correlation between the relative ion concentration of cobalt in the electrolyte and the Co-content in the deposited Ni-Co alloy layers in the multilayer obtained with a constant current density of the G pulse. However, chemical analysis revealed that the steepness of the deposit composition evolution for small Co^{2+} concentrations in the bath is much higher for the magnetic layers in the multilayers [11] than obtained previously for d.c.-plated Ni-Co alloys [3]. This is due to the anomalous codeposition properties of Co with Ni owing to which at the beginning of the layer formation the electrolyte is depleted for Co^{2+}-ions. This makes the electrolyte near the sample surface to become more and more rich in Ni^{2+}-ions as the magnetic layer gets thicker. Thus the regions of the deposited alloy at larger distance from the substrate become richer in Ni until a steady state is reached with a certain Ni/Co ratio in the alloy. Because pulse plating (G/P pulse combination) is used for preparing the multilayers, after depositing a few nanometers of the magnetic alloy layer, the G pulse ends and during the subsequent Cu deposition pulse (P) which lasts for at least 10 seconds or, sometimes, even longer than one minute, the Co^{2+}-ion concentration of the bath at the cathode-electrolyte interface can recover to the bulk concentration of the electrolyte existing far from the sample surface. Therefore, the next layer will grow as a Co-rich alloy again and this explains the higher Co-content of the magnetic layer in the multilayers in comparison with the d.c.-plated Ni-Co alloy deposited under identical conditions (bath concentration and deposition current density).

Based on a preliminary study of the GMR in ED Ni-Co/Cu multilayers, the magnetic layer composition was chosen to be approximately equiatomic for the further studies since this yielded the largest GMR. This magnetic layer composition could be achieved with an ionic ratio $Co^{2+}/(Ni^{2+} + Co^{2+}) \sim 0.07$ on the basis of the deposit composition analysis data.

(ii) Surface roughness evolution with layer thicknesses in ED Ni-Co/Cu multilayers

The root-mean-square surface roughness (R_q) was found to show an exponential increase with total multilayer thickness as usually found for layers obtained via an atom-by-atom deposition process [W. Schwarzacher, J. Phys.: Cond. Matter 16, R859 (2004)]. This behavior can originate from two sources. The first is the cumulative surface roughening: the peaks at the top of the multilayer are more accessible to the ions in the solution and thus can grow faster than the valleys between them. The other is the misfit between the lattice parameters of the Ni-Co alloy and the Cu metal as a result of which a 3–D growth process tends to emerge. Once a small grain of the material of the subsequent layer can be deposited on the surface, it is energetically more favorable if the 3D-growth proceeds further instead of the formation of new “islands” of the same material (i.e., nucleation which is always hindered to some extent on the surface of a foreign metal or alloy). These grains occur at several surface sites and, after a certain time, they coalesce to form a continuous layer. By that time, at the connection points, there can only be a single atomic layer of the material deposited whereas at the point where the nucleation started, a high peak could already grow. The blocked nucleation and, thus, rather an island-like growth with coalescence is especially prone in the case of Cu layer growth on top of a Co layer as was concluded previously for ED Co/Cu multilayers [1].

The continuous multilayer roughening with increasing total multilayer thickness can be better assessed if samples are compared with different total thicknesses but with the same magnetic and non-magnetic layer thicknesses. If the topography of their surfaces is measured and the average height is set to the nominal thickness of the multilayer, the multilayer surface evolution along the thickness can be visualized as shown in Fig. 14. If we compare Figs. 14a and 14c, it can be seen that the 700-nm total thickness profile for a multilayer with 0.8-nm thick Cu layer is practically the same as that of the 300-nm total thickness profile of the multilayer having 6.0 nm Cu layer thickness. This clearly shows the roughening of the total multilayer due to the Cu layer thickness; however, this roughening effect cannot be recognized until a certain total multilayer thickness is achieved.

These surface roughness profiles show clearly that the nucleation is very uneven, high peaks and valleys develop as the total multilayer thickness increases.

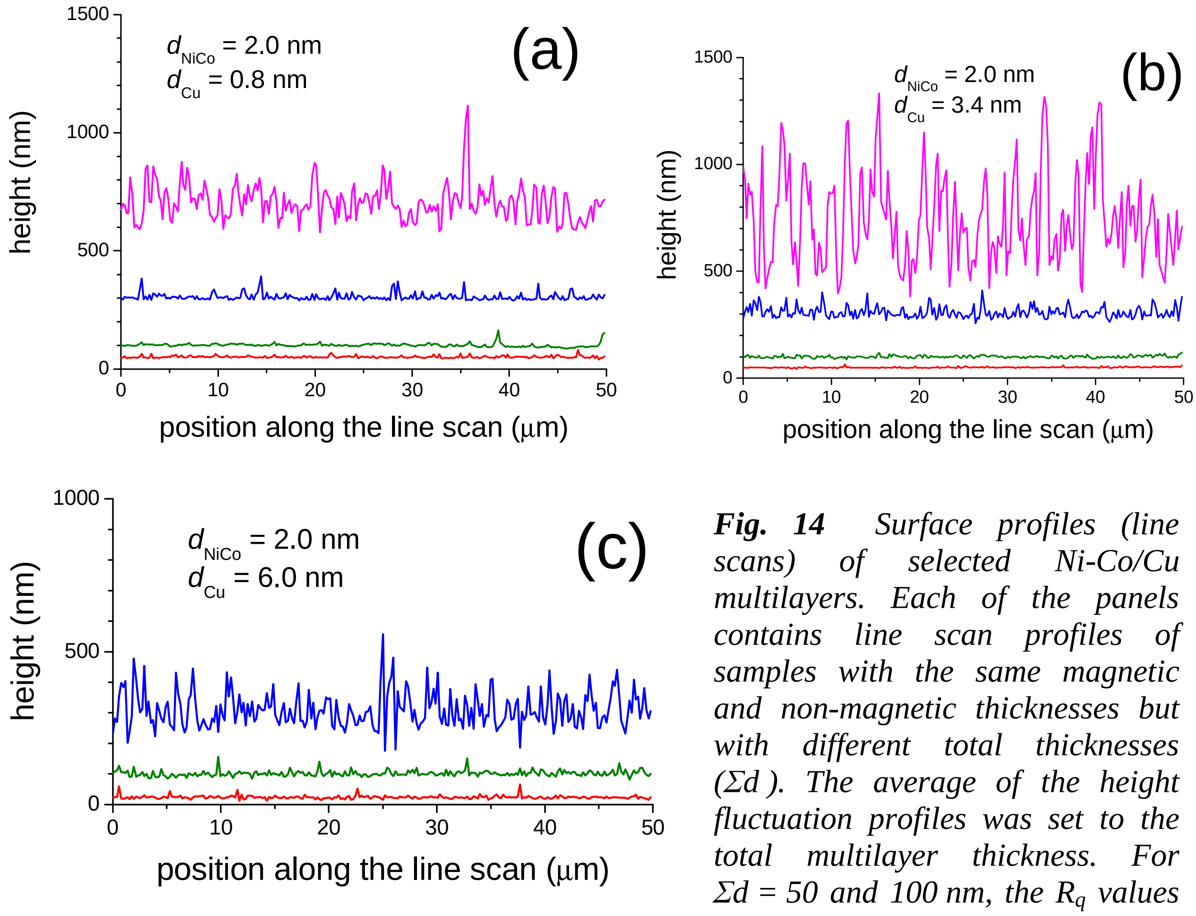

Fig. 14 *Surface profiles (line scans) of selected Ni-Co/Cu multilayers. Each of the panels contains line scan profiles of samples with the same magnetic and non-magnetic thicknesses but with different total thicknesses (Σd). The average of the height fluctuation profiles was set to the total multilayer thickness. For Σd = 50 and 100 nm, the* R_q *values are practically the same for all three Cu layer thicknesses.*

(iii) GMR evolution with layer thicknesses in ED Ni-Co/Cu multilayers

It was of particular interest to study the evolution of the GMR with Cu spacer layer thickness in order to see if there is any oscillatory GMR.

Figure 15a shows the GMR_{FM} data as a function of the Cu layer thickness for various total multilayer thicknesses. For each series, the *GMR* increases monotonically up to 5-6 nm Cu layer thickness where it reaches a maximum and then slightly reduces. Similarly to ED Co/Cu multilayers [1], the GMR does not show an oscillatory behavior also for ED Ni-Co/Cu multilayers if the SPM contribution to the GMR is properly separated from the experimental data.

The reduction of *GMR* for large spacer layer thicknesses may partly come from a simple dilution effect. Namely, with increasing d_{Cu} the bilayer repeat will be larger. In this manner, the number of FM/NM interfaces per unit thickness which are responsible for the spin-dependent scattering processes yielding the GMR effect is reduced.

It can also be inferred from Fig. 15a that the GMR_{FM} component increases with total multilayer thickness from 50 nm to 300 nm and then drops for 700 nm. In order to explain the observed evolution of the GMR with total multilayer thickness, we have to consider separately the variation of the zero-field resistivity ρ_0 and the field-induced change of the electrical resistivity $\Delta\rho_H$. We should keep in mind that the *MR* definition $MR(H) = [R(H) - R_0]/R_0$ is equivalent to $MR(H) = [\rho(H) - \rho_0]/\rho_0 = \Delta\rho_H/\rho_0$. In the following, $\Delta\rho_H$ will refer to the value calculated from the GMR_{FM} data (FM contribution to the GMR) by using these relations.

The evolution of $\Delta\rho_H$ with d_{Cu} and total multilayer thickness is presented in Fig. 15b. In agreement with the nearly same roughness for 50 nm and 100 nm total thickness (Fig. 14), the ρ_0 values were found also to be very similar. Thus, the definitely higher $\Delta\rho_H$ values for 100 nm (Fig. 15b) result in the clearly larger *GMR* values (Fig. 15a). Although the roughening is more pronounced for 300 nm total thickness and there is also a substantial increase in ρ_0 as well, the much larger $\Delta\rho_H$ values (Fig. 15b) still lead to a significant further increase of the GMR (Fig. 15a). On the other hand, the drastic roughening for 700 nm total thickness leads to a very large zero-field resistivity and even if $\Delta\rho_H$ further increases for 700 nm total thickness (Fig. 15b), the large ρ_o values suppress the resulting *GMR* (Fig. 15a).

Since each series can be taken as a slice from the bottom of the thicker series, if the multilayers were homogenous along their whole thickness, $\Delta\rho_H$ would be identical for all series. We should point out, on the other hand, that the continuous increase of $\Delta\rho_H$ with total multilayer thickness can be definitely related with the cumulative roughening. Namely, increasing roughening implies an enhanced undulation of the layer planes which, due to the applied current-in-plane geometry for measuring the magnetoresistance, enhances the probability of interface scattering (actually, many of the scattering events will be of the current-at-angle-to-plane type).

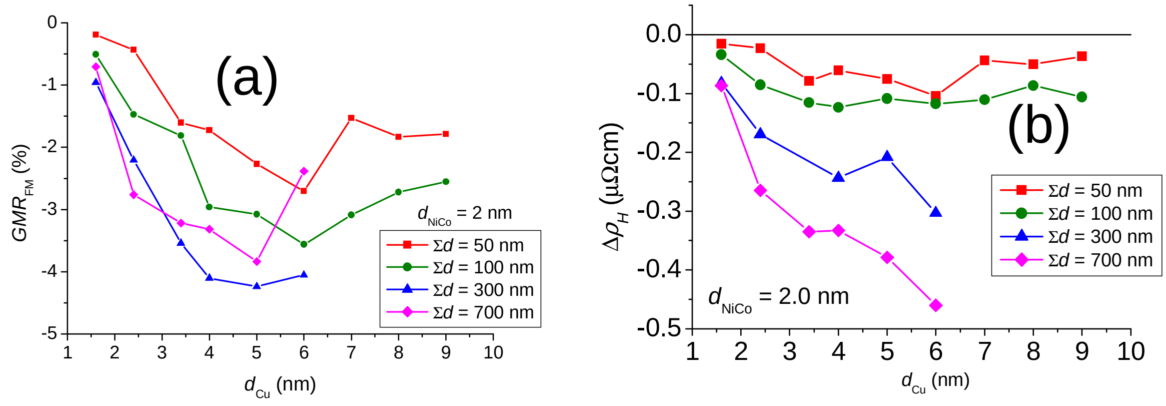

Fig. 15 *(a) Evolution of the (a) GMR_{FM} contribution and (b) the isotropic saturation resistivity change in a magnetic field with Cu layer thickness for various total multilayer thicknesses as indicated in the legend. The magnetic layer thickness was fixed at 2.0 nm.*

Influence of Cu deposition potential on GMR and surface roughness of ED Ni-Co/Cu multilayers [9]

It has been reported in our previous works [1] that the single-bath electrodeposition process used for the preparation of magnetic/non-magnetic multilayers with giant magnetoresistance (GMR) behavior can be optimized from an electrochemical point of view in order to avoid unwanted reactions taking place during the deposition of the more noble non-magnetic element. No systematic studies have been, however, carried out to establish to what extent this electrochemically optimized Cu deposition potential E_{Cu}^{EC} corresponds to the largest possible GMR that can be achieved for a given element combination by electrodeposition. In the present work, we have chosen the Co-Ni/Cu multilayer system with approximately equal concentrations of Co and Ni in the magnetic layer to explore this situation. In order to better understand the observed variation of the magnetoresistance with

Cu deposition potential, measurements of the overall chemical composition, X-ray diffraction patterns and surface roughness have also been performed on these multilayers.

(i) Surface roughness behavior

The cumulative roughening of electrodeposits gives rise to an ever increasing surface roughness. The root-mean-square surface roughnesses calculated from measurements by both AFM and white-light interferometry are presented in Figure 16 as a function of the preparation parameters.

As it can be seen in Fig. 16a, tuning the Cu deposition potential drastically changes the surface roughness (R_q) of the investigated Ni-Co/Cu multilayers. For Cu deposition potentials slightly more positive than E_{Cu}^{EC}, a significant smoothening of the surface sets in very abruptly and then the surface roughness remains practically constant. In this potential region, Co atoms are removed from the surface because of the Co dissolution. The interval of the Cu deposition potential where the surface remains fairly smooth is in good agreement with the occurrence of the dissolution process in the current transients. On the contrary, for Cu deposition potentials more negative than E_{Cu}^{EC}, a dissolution of the magnetic layer does not occur but magnetic atoms start to codeposit with Cu. Due to the high deposition preference of Co when codeposited with Ni, the actual surface will be rich in Co.

Figure 16a also indicates that, in contrast to the Ni-Co/Cu multilayers, the surface roughness of Ni/Cu and Co/Cu multilayers does not vary significantly with Cu deposition potential: the data are scattered more or less randomly. This suggests that the observed roughening of Ni-Co/Cu multilayers for more negative potentials with respect to E_{Cu}^{EC} is closely connected to the presence of both Ni and Co atoms at the deposit surface during the deposition period of the Cu layer.

To underpin the roughening effect due to the simultaneous presence of Ni^{2+} and Co^{2+} ions, seven further multilayers were prepared at the most negative potential used (-0.74 V). Each of them had different relative Co concentration in the magnetic layer as presented in Fig. 16b. The roughness values of the multilayers with either Ni or Co and the one with the $Ni_{50}Co_{50}$ alloy as magnetic layer coincide well with the values obtained on the previously discussed samples which were presented in Fig. 16a. According to Fig. 16b, the roughness values show a pronounced maximum with change in the composition of the magnetic layer. This means that this roughening does not come from the potential used but from the simultaneous codeposition of Ni and Co with Cu during the formation of the non-magnetic layer. The roughness reaches its maximum around a Co to Ni ratio of 1. Based on the composition of the sample prepared with the most negative potential in the P pulse (-0.74 V), the overall Ni and Co content of the Cu layer can be assessed as 13 at.%.

A possible explanation for this increased roughening for anomalously codepositing metals can be the model described in the literature [N. Zech, E.J. Podlaha and D. Landolt, *J. Electrochem. Soc.* **146** (1999) 2892] according to which the simultaneous deposition of Co and Ni may proceed not only in independent reaction routes as the case is for the deposition of Co or Ni alone in the absence of the other component. Instead, in the anomalous codeposition mechanism, the intermediates may contain the atoms of both metals, hence establishing a catalytic mechanism. The adsorbed reaction intermediates in the catalytic reaction may also contain several hydroxyl groups. Therefore, the adsorbed species, due to their large size, can effect the deposition of the majority component Cu as well. Due to the temporary blocking of some areas from growth by the intermediates, deposition will faster proceed at other places and this naturally leads to the observed surface roughening for the Ni-Co/Cu multilayers at large negative Cu deposition potentials. The locally and temporarily hindered simultaneous deposition of the three metals excludes the possibility of the formation of larger islands of the same element which can lead to the observed roughening of the surface.

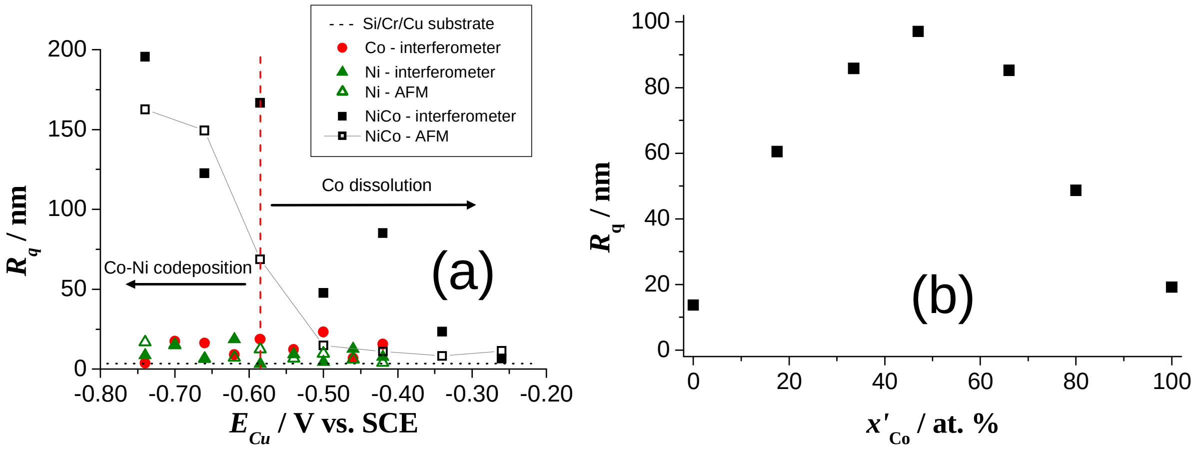

Fig. 16 *(a) Dependence of the root-mean-square roughness R_q of ED Ni/Cu, Co/Cu and Ni/Cu multilayers on the Cu-deposition potential. At the electrochemically optimized Cu deposition potential E_{Cu}^{EC} indicated by the dashed vertical line, neither Co and Ni dissolution, nor Co and Ni codeposition occurs. The full symbols represent the data measured with the white-light interferometer, the open symbols stand for the AFM data and the dotted line is the roughness of the substrate measured with both methods. (b) Dependence of the root-mean-square roughness R_q on the Ni/Co ratio of the magnetic layer in the case of E_{Cu} = -0.74 V.*

(ii) GMR evolution with Cu deposition potential

All the Ni-Co/Cu multilayers investigated exhibited GMR at room temperature. The *MR*(*H*) curves nearly reached complete saturation in magnetic fields around 2 kOe after which the resistivity change was already much smaller as shown for a typical multilayer in Fig. 17a. The saturating component is due to a ferromagnetic contribution to the GMR whereas the slowly saturating component is due to the presence of a small amount of superparamagnetic regions in the magnetic layers [1].

After separating the two contributions by a standard procedure [1] (as indicated for the TMR component in Fig. 17a), Fig. 17b shows the ferromagnetic contribution GMR_{FM} and the ratio of the superparamagnetic GMR contribution GMR (GMR_{SPM}) to the saturation value of the GMR (GMR_{S}) as a function of the Cu deposition potential. Since the difference between the LMR and the TMR values was small, an isotropic average of the GMR values was only displayed.

The GMR_{FM} contribution has a maximum at about -0.4 V which is the result of several different but not independent effects. The root-mean-square surface roughness has evidently a significant effect on the GMR_{FM} contribution (compare Fig. 16a and Fig. 17b): the smoother the multilayer surface, the larger the GMR_{FM} contribution. This should be connected with the improvement of the structural quality of the multilayers for E_{Cu} values more positive than E_{Cu}^{EC}. This was supported also by the XRD patterns measured on the same multilayers.

For very negative Cu deposition potentials, magnetic atoms are codeposited in the Cu layer. The presence of magnetic Co and/or Ni atoms in the Cu layer can effectively decrease the spin diffusion length of the electrons in the spacer layer even at moderate concentrations, which strongly diminishes the GMR effect. At large concentration of the magnetic atoms, especially when they are enriched locally, they can form a direct magnetic connection between adjacent magnetic layers and the resulting ferromagnetic coupling also reduces the GMR.

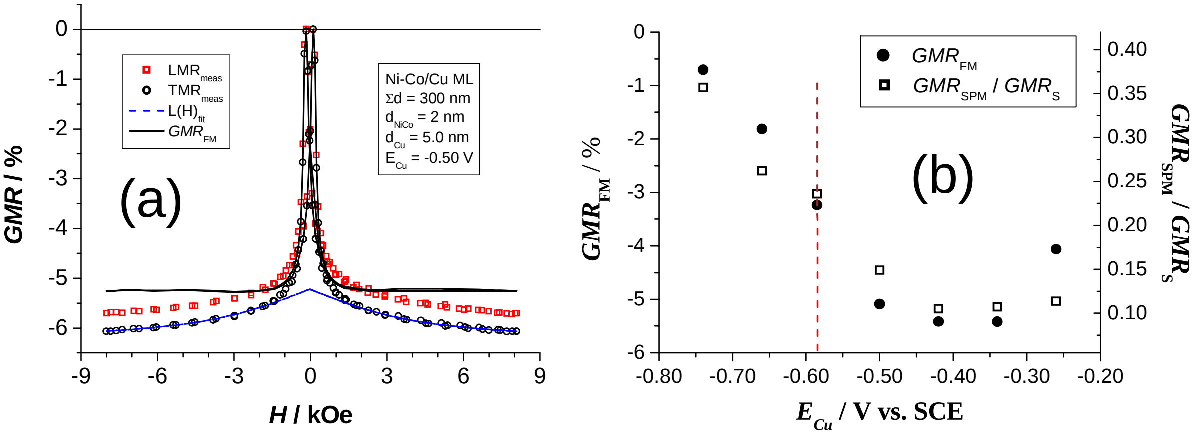

Fig. 17 *(a) A typical measured MR(H) curve. The open symbols represent the measured MR values (□: LMR, ○: TMR), the dashed line is the Langevin function fitted to the measured TMR data and the solid line is the FM contribution to the GMR which can be obtained by subtracting the fitted Langevin function from the measured values. The dashed line actually represents the field evolution of the SPM contribution to the GMR. (b) Dependence of the ferromagnetic contribution GMR_{FM} (solid symbols) and the ratio of the superparamagnetic contribution of the GMR to the saturation value of the GMR (open symbols) on the Cu deposition potential.*

Studies on the influence of bath temperature on Ni-Co/Cu multilayer electrodeposition [13]

The influence of the bath temperature on the resulting Ni-Co/Cu multilayers has been studied with the same methodology as described for the Co/Cu multilayers. The solution used was the same as that used for the study of the surface roughness of the Ni-Co/Cu multilayers.

First, the composition of the Ni-Co/Cu multilayers was established simultaneously as a function of the solution composition, the layer thickness of the Ni-Co layer and the temperature. Due to the large deposition preference of Co besides Ni, the solution concentrations were chosen in such a manner that the mean deposit composition varies in an approximately equidistant manner. The summary of this study is presented in Figure 18.

Fig. 18 indicates that the deposition preference decreases with the increase in temperature. Although the Co-Ni system shows anomalous codeposition (which means that $\gamma >> \sigma$), the relative abundance of Co in the deposit decreases with temperature. This trend was obtained for all solution compositions; however, the uncertainty in the deposit compositions was larger in some cases than the impact of the temperature.

Magnetoresistance of each specimen was measured and the Langevin fit was performed. The total magnetoresistance varied between 2 and 9 %, and the fraction of the FM contribution to the total magnetoresistance was between 0.1 and 0.4. However, no trend could be established as a function of either the solution composition or bath temperature. This behavior is not understood since the sample preparation in case of Co/Cu multilayers proved to be successful with the same thermostated cell, and the Ni-Co/Cu multilayers could be prepared with good magnetoresistance properties in a similar cell if the samples were square-shaped. Nevertheless, it is possible that the magnetoresistance measurement with the four-point in-line geometry was less suitable for the round-shaped samples than for the square-shaped samples, and a relatively little difference in the distribution of the magnetic elements over the sample surface may cause rather significant impact on the magnetoresistance.

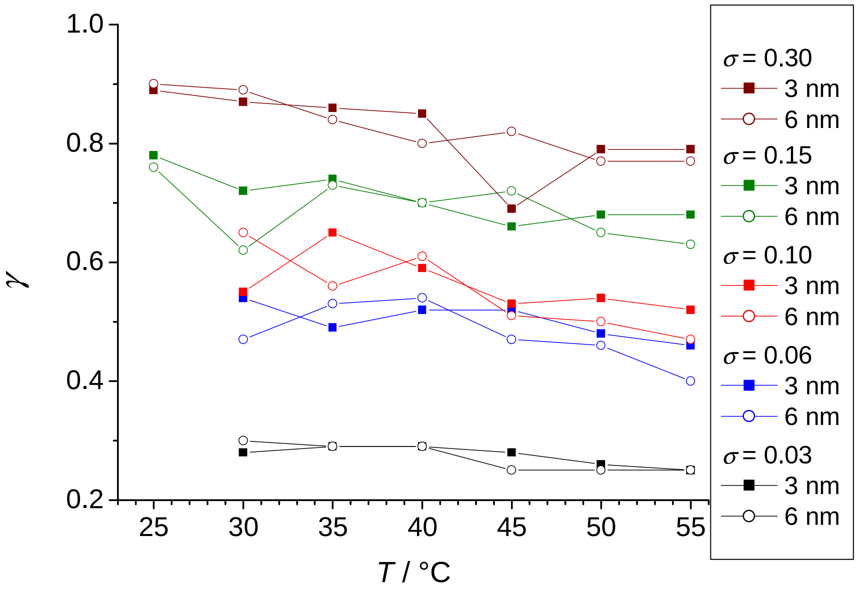

Fig. 18 *The composition of the magnetic layers as a function of the deposition temperature for various solution compositions and two different Ni-Co layer thicknesses. The ordinate shows the relative Co concentration of the magnetic layers as described with the expression* $\gamma = y(Co) / [y(Co)+y(Ni)]$*. The parameter* σ *refers to the* Co^{2+} *ionic ratio with respect to the* Ni^{2+} *ions in the solution and is defeined as* $\sigma = c(Co^{2+}) / [c(Co^{2+})+c(Ni^{2+})]$*.*

III. Studies on ED Fe-Co/Cu multilayers and ED Fe-based alloy layers

Preparation and GMR study of ED Fe-Co/Cu multilayers [12]

Iron and its alloys with Ni and Co, being good soft magnetic materials, have various applications nowadays. But while metallurgical preparation is quite easy, electrochemical deposition raises up several difficulties. It is hard to electrodeposit pure iron because of its sensitivity to water and oxygen and its high corrosivity compared to nickel and cobalt and because of the instability of electrolytes containing Fe^{2+} ions. This instability originates from the oxidization of Fe^{2+} ions to Fe^{3+} ions and the resulting formation of different precipitates (mostly $Fe(OH)_3$) in the electrolyte. Thus, besides a reduction of the concentration of Fe^{2+} ions which are appropriate for electrodeposition, some other components appear in the solution which may incorporate in the deposit during the deposition. The progress of this process is indicated by the opalescence of the solution, visible even by naked eye. As a result, contrary to electrolytes containing only salts of nickel, cobalt and copper ions, solutions containing iron can only be used for a short time.

Thus, because of the instability of the electrolyte, the electrodeposition of Fe-Co/Cu multilayers was a non-trivial problem to solve, especially at high Fe^{2+} ion concntrations.

In the only published paper reporting the GMR in ED Fe-Co/Cu multilayers [E.M. Kakuno, R.C. da Silva, N. Mattoso, W.H. Schreiner, D.H. Mosca and S.R. Teixeira, *J. Phys. D: Appl. Phys.* **32**, 1209 (1999)], the P/P deposition mode was applied but the authors have not established the electrochemically optimized Cu depositon potential (E_{Cu}^{EC}). The use of the optimized E_{Cu}^{EC} value is a prerequisite for a proper control of the individual layer thicknesses and for avoiding the incorporation of magnetic atoms in the non-magnetic spacer layer (Cu). An important task in the present study was, therefore, to establish E_{Cu}^{EC} for the electrolytes employed. Preparing ED Fe-Co/Cu multilayers with the optimized Cu deposition potential enables then a study of the evolution of the GMR magnitude on true layer thicknesses.

(i) Optimization of the preparation of ED Fe-Co/Cu multilayers

To get rid of the effect of the precipitates appearing in the solution with time, two basic electrolytes were prepared. The first one (Co-solution) was prepared on the basis of the previously used solutions designed to deposit pure Co. The second one (Fe-solution) was prepared with the required composition of the other components but the Fe(II)-sulfate was only added immediately before the electrodeposition experiments. The pH of the Fe-solution was set to 3.25, equal to the pH of the Co-solution. After this, the electrolytes for the deposition of the Fe-Co/Cu multilayers were mixed from these two stock solutions. The concentrations of the two stock solutions were as follows:

$CoSO_4 .7H_2O$	0.74 mol/ℓ	$FeSO_4 .7H_2O$	*0.74 mol/ℓ*
$CuSO_4 .5\ H_2O$	0.010 mol/ℓ	$CuSO_4 .5\ H_2O$	0.010 mol/ℓ
Na_2SO_4	0.10 mol/ℓ	Na_2SO_4	0.10 mol/ℓ
H_3BO_3	0.25 mol/ℓ	H_3BO_3	0.25 mol/ℓ
H_2NSO_3H	0.25 mol/ℓ	H_2NSO_3H	0.25 mol/ℓ

Iron and cobalt, like the Ni-Co system, show anomalous codeposition but, in this case, Fe is the metal with preferred deposition and this fact has to be taken into account during the preparation of the electrolytes.

For the optimization of the Cu deposition potential, first the polarization curves of the solutions with two different Fe^{2+} concentrations were measured (see Fig. 19).

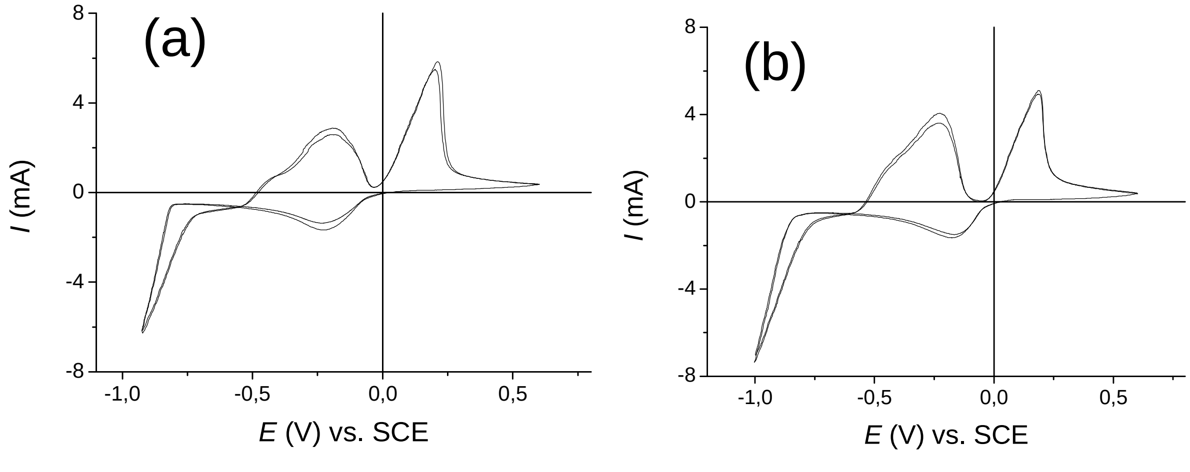

Fig. 19 *Cyclic voltammograms for two Fe-Co-Cu solutions with different* Fe^{2+}*-concentrations:: (a)* $c_{ion,Fe} = 5$ *%; (b)* $c_{ion,Fe} = 40$ *%.*

For the solutions containing Fe, because of the extended plateau, a potential range could only be selected where apparently neither the dissolution of the magnetic material, nor the codeposition of the magnetic material with Cu can occur. This is the potential range where the current transients are reasonable to be measured. The potential ranges determined from the polarization curves were as follows: -0.760 V to -0.520 V for the solution with $c_{\text{ion,Fe}} = 5$ % and -0.700 V to -0.600 V for $c_{\text{ion,Fe}} = 40$ % [here, $c_{\text{ion,Fe}}$ refers to the ionic ratio $Fe^{2+}/(Fe^{2+} + Co^{2+})$].

Contrary to the Ni-Co system, it was found for the Fe-Co system that the value of E_{Cu}^{EC} depends on the concentration of Fe^{2+} ions in the solution. This comes from the circumstance that Fe starts to dissolve from the cathode surface at a more negative potential than Co. Because of this difference, if both Fe and Co metals are simultaneously present on the surface with different ratio, the potential value at which the given alloy is neither deposited nor dissolved back into the electrolyte will also depend on the ratio of Fe and Co in the alloy. A further technical problem arises because only the total current flowing through the surface can be measured. Even if the total current is zero, it is possible that Fe is dissolved selectively and, in parallel, Co is deposited at the same rate.

In the next step, in the potential ranges selected on the basis of cyclic voltammograms, the current transients (Fig. 20) were measured during the Cu deposition cycle.

The potential value at which the transient curve decays the fastest without the appearance of a current more negative than the current value specific for the Cu deposition with constant rate (limiting current) corresponds to the optimum E_{Cu}^{EC} value. It could be derived from Fig. 19 that its value is -0.620 V in the case of $c_{\text{ion,Fe}} = 5\%$ and -0.660 V in the case of $c_{\text{ion,Fe}} = 40$ % (for $c_{\text{ion,Fe}} = 0\%$, E_{Cu}^{EC} is -585 mV [5]). Plotting these three potential values as a function of the ion concentration of the solution, the E_{Cu}^{EC} potential values can be determined for all Fe^{2+} ion concentrations by interpolation.

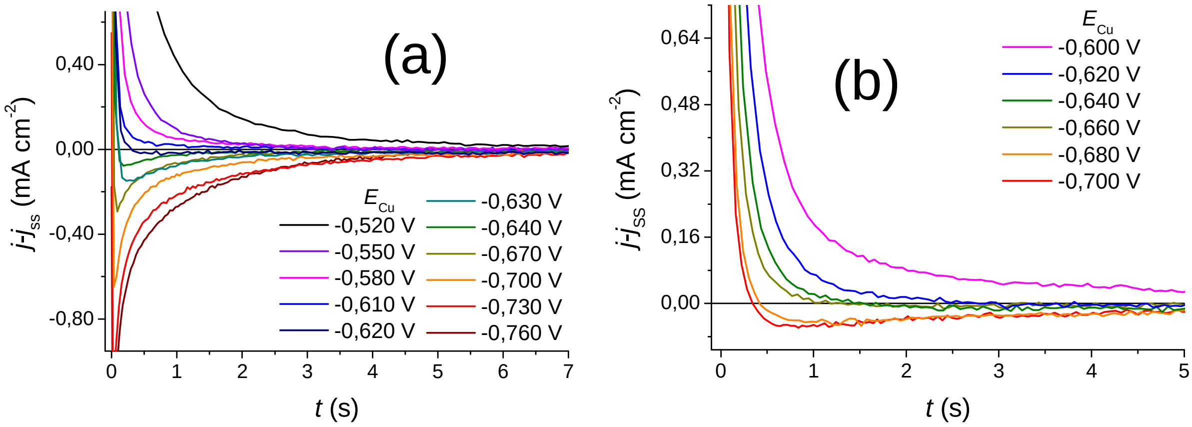

Fig. 20 *Current transients for the two Fe-Co-Cu electrolytes with different* Fe^{2+} *ion concentrations in the selected potential range to find the optimal Cu deposition potential* E_{Cu}^{EC}. *The transients were measured in the 20th cycle which can be considered as steady-state.* $j\text{-}j_{ss}$: *the difference between the measured and the steady-state current densities, t: time elapsed from the beginning of the pulse,* $d_{FeCo} = 2.5$ *nm,* $d_{Cu} = 3.0$ *nm. (a)* $c_{ion,Fe} = 5$ *% (b)* $c_{ion,Fe} = 40$ *%.*

By using the E_{Cu}^{EC} potential values determined from the current transients, a sample series was prepared with the help of which the dependence of the Fe concentration in the magnetic layer of the multilayers on the Fe^{2+} ion concentration in the electrolyte could be determined. The total thicknesses of the multilayers were 100 nm and the individual layer thicknesses were d_{Cu} = 3 nm and d_{FeCo} = 2,5 nm. The current density applied in the G pulse to deposit the magnetic layer was -31.25 mA/cm^2.

(ii) GMR study of ED Fe-Co/Cu multilayers

For multilayers with d_{Cu} = 3 nm és d_{FeCo} = 2.5 nm, it was found that the higher the Fe concentration of the magnetic layer, the smaller the GMR. Therefore, two Fe^{2+} ion concentration values were chosen, namely 2.3 % and 27.1 %, which resulted in 5 % and 44 % Fe in the magnetic layer, respectively, and the multilayers for the subsequent GMR studies were prepared with these two solutions.

Since there are no reliable data in the literature on the dependence of the GMR on the individual layer thicknesses, a set of multilayers was prepared with which the dependence on both the magnetic and non-magnetic layer thicknesses could be established. Therefore, the thickness of the magnetic layer was set to 1.0, 1.5 és 2.0 nm with a proper choice of the length of the G pulse. For all three d_{FeCo} values, several multilayers were prepared with different d_{Cu} values, namely 0.8, 2.4, 4.0, 6.0, 8.0, 10.0 and 12.0 nm. This means 21 multilayers for each of the two selected Fe concentrations.

By measuring the GMR on these series of ED Fe-Co/Cu multilayers and plotting the TMR_{FM} component, the results shown in Fig. 21 were obtained.

The values of the data points marked with full black circles (●) in Fig. 21(b) are all zero, indicating that these samples show AMR instead of GMR. This is also indicated by the coloring of the fitted surface.

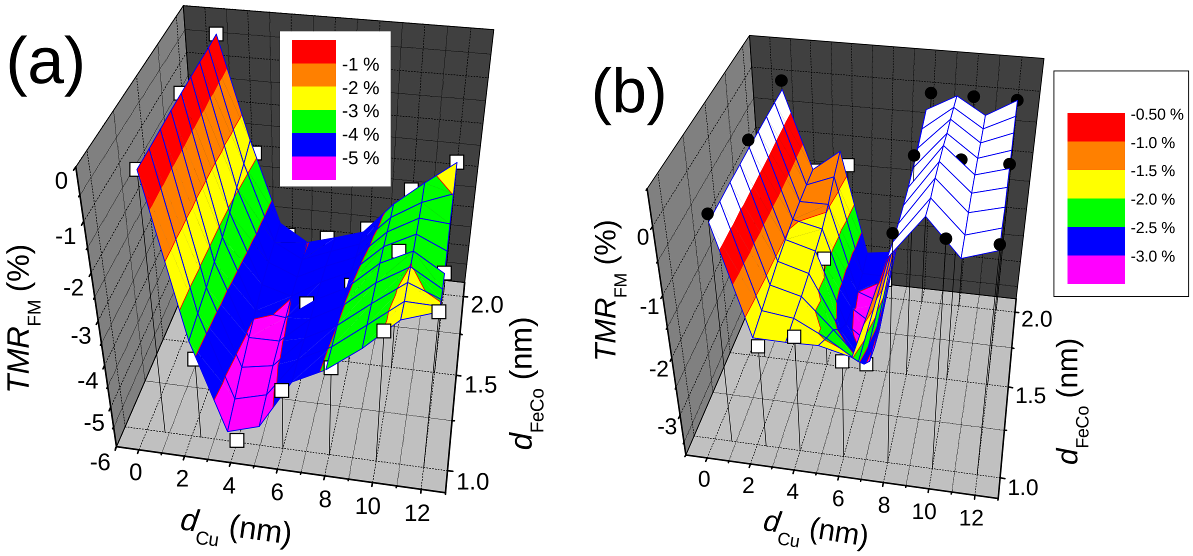

Fig. 21 *Dependence of the FM component of the TMR (TMR_{FM}) on the thickness of the magnetic layer (d_{FeCo}) and the Cu layer (d_{Cu}) in our ED Fe-Co/Cu multilayers. The Fe-content in the magnetic layers were z_{Fe} = 5 % (a) and z_{Fe} = 44 % (b). Empty squares (□) mark the TMR_{FM} component of samples showing GMR and black full circles (●) with 0 value represent the samples showing AMR. The surface was fitted to these points only to show the behavior of the MR.*

The GMR values obtained indicate that the thickness of the magnetic layer has no significant effect on the magnetoresistance in the thickness range explored.

On the contrary, there is a significant variation in the GMR with Cu layer thickness. But as was the case for electrodeposited Co/Cu and Ni-Co/Cu multilayers, no oscillatory GMR could be observed, only a monotonous increase up to a certain d_{Cu} value and a decrease for thicker non-magnetic layers. The decrease of the GMR with increasing Fe content can also be seen here.

These results seriously question the results of the single report on the GMR of ED Fe-Co/Cu multilayers [see above cited paper by Kakuno et al.]. Because the Cu deposition potential used in that work is much more positive (namely by 0.2 V) than the optimal value established in the present study, during the preparation of the samples by Kakuno et al., magnetic material from the previously deposited magnetic layer was certainly dissolved back into the electrolyte. Therefore the thicknesses of the magnetic layers were reduced and the thicknesses of the Cu layers increased with respect to the specified nominal values in that paper.

Furthermore, these authors reported only the TMR component which is negative for samples showing either AMR or GMR. For samples with Cu layer thicknesses smaller than 3 nm, the observed MR value is so small that it can originate also from AMR. The $MR(H)$ curves presented by Kakuno et al., in particular for d_{FeCo} values at and below 1 nm, are mostly of the SPM-type. Furthermore, every GMR „peak” in their GMR vs d_{Cu} curve corresponds to only one data point and has about 0.1 nm FWHM, which is much smaller than the usual results presented in the publications on oscillatory GMR, where one peak corresponds to several data points and has about 0.3 nm FWHM. Therefore, the most we can assess from the published data of Kakuno et al. is that the GMR increases in average with increasing Cu layer thickness.

Composition depth profile studies of ED magnetic alloy layers of Fe, Co and Ni

Due to the complex behavior of Fe ions during electrodeposition, in view of the planned studies on ED Fe-Co-Ni/Cu multilayers, it seemed worthwhile to carry out investigations on the electrodeposition of ternary Fe-Co-Ni and binary Fe-Ni alloys.

(i) Composition depth profile studies of ED Fe-Co-Ni alloys [2]

The composition depth profile of ED Fe-Co-Ni alloys was investigated by means of the so-called reverse depth profile analysis, a new method developed in our laboratory and successfully applied previously to study both homogeneous deposits and multilayers [K. Neuróhr, A. Csik, K. Vad, A. Bartók, G. Molnár, L. Péter: *J. Solid State Electrochem.* **15**, 2523-2544 (2011)]. This was a joint work with a team of ATOMKI (Nuclear Research Institute of HAS, Debrecen). It was found that the deposition of the Fe-Co-Ni alloys starts with a zone that is rich in Fe, whose deposition preference is the strongest among the metals forming the alloy. The fast depletion of the electrolyte for Fe^{2+} leads to a decrease in the molar fraction of Fe in the alloy and to an increase in the deposition rate of Co and Ni. The molar fraction of Co (i.e., the next metal in the row of deposition preference) increases first but starts to decrease after about 40 nm deposit thickness. The molar fraction of both Fe and Co achieves a minimum after 90-150 nm deposit thickness, depending on the deposition conditions. Typically, the Fe molar fraction decreases by about 0.5 for the alloys studied. This initial zone with drastic changes of the molar fractions is followed by the deposit regions where no systematic changes in the molar fractions occur. It was also detected that the occasional fluctuations can be described with a correlated increase/decrease of the molar fractions of Fe and Co. All these deposit features can be explained by the diffusion-controlled Fe deposition and the anomalous nature of Fe-Co-Ni codeposition.

(ii) Composition depth profile studies of ED Fe-Co-Ni alloys to establish the transport coefficient of Fe^{2+} ions in the electrolyte [15]

In connection with the planned studies of the Fe-Co/Cu and Fe-Co-Ni/Cu multilayers as well as previous work on ED Fe-Co-Ni layers [2], experiments were started to evaluate the transport coefficient of Fe^{2+} ions in the corresponding electrolytic baths. For this purpose, secondary neutral mass spectrometry was used to obtain the composition depth profile function of electrodeposited Fe-Co-Ni alloys. It was shown that the iron deposition is a mass transport limited process during the electrolytic alloy formation. The depth profiling method applied in the reverse sputtering mode was sensitive enough for calculating the transport coefficient of Fe^{2+} ions in the electrolyte. Clear Cottrell sections were obtained in the chronoamperometric functions derived from the composition depth profile functions for the Fe deposition. By comparing the transport coefficients obtained from the depth profile functions with those obtained from conventional electrochemical methods, it was found that the effective transport coefficient can sometimes be by an order of magnitude higher during the electrodeposition. The values obtained for the diffusivity, however, were in good agreement with those found in earlier nucleation studies. The diffusion coefficient obtained was a function of the Fe^{2+} concentration, but it proved to be independent of the current density. The possible origin of the abnormally large transport rate obtained could be discussed in detail.

(iii) Composition depth profile studies of ED Fe-Ni alloys [10]

Composition depth profiles of d.c.-plated and pulse-plated Fe-Ni alloys have been investigated with the reverse depth profile analysis method. When d.c. plating is applied, the molar fraction of iron near the substrate is higher than during steady-state deposition since iron is preferentially deposited beside nickel and the achievement of the steady-state deposition condition takes time. The steady-state composition was achieved typically after depositing a 90-nm-thick alloy layer. In the pulse-plating mode, samples with nearly uniform composition could be obtained at a duty cycle of 0.2 or smaller, and a continuous change in the composition profile could be seen as a function of the duty cycle above this value. A constant sample composition was achieved with pulse-plating in a wide peak current density interval. The composition depth profile was also measured for a wide range of Fe^{2+} concentration. The different characteristics of the composition depth profile as a function of the deposition mode can be explained mostly in terms of mass transport effects. The elucidation of the results is fully in accord with the kinetic models of anomalous codeposition and with the assumption of the superposition of a stationary and a pulsating diffusion layer. The results achieved help to identify the conditions for the deposition of ultrathin magnetic samples with uniform composition along the growth direction.

IV. Studies on ED Co-Ru deposits [6]

Based on the early work published in 2002 by the team on ED Co/Ru multilayers produced under non-optimized conditions, it was planned to reinvestigate this system on the basis of the knowledge acquired in the meantime on the electrodeposition process of mulitlayer formation. A study of ED Co/Ru multilayers constituted part of both the current project and another OTKA project of the team (OTKA NN79846, 2010-2011, in collaboration with TU Freiberg, Germany) but from different aspect of research. In the current OTKA project, emphasis was put on optimizing the GMR in ED Co/Ru multilayer whereas in the NN79846 project, by utilizing the special structural facilities of the German partner, the major interest was in defect formation during multilayer growth in a system with two components both having a hexagonal close packed stable structure as opposed to most of other multilayers with a face-centered cubic structure.

Unfortunately, every efforts to prepare ED Co/Ru multilayers with a reasonable well-defined layered structure remained unsuccessful during the project as it was indicated, among others, by the absence of any tendency of GMR behavior in the electrodeposits prepared. A possible reason for the lack of success for multilayer preparation may have been the use of new chemicals with respect to the previous study. Unfortunately, such kind of irreproducibility sometimes occurs in electrochemical experiments possibly due to various levels of uncontrolled impurities in various batches of chemicals as we also reported in another paper of the NN 79846 project [M. Jafari Fesharaki, L. Péter, T. Schucknecht, D. Rafaja, J. Dégi, L. Pogány, K. Neuróhr, É. Széles, G. Nabiyouni, I. Bakonyi: Magnetoresistance and structural study of electrodeposited Ni-Cu/Cu multilayers. *J. Electrochem. Soc.* **159**, D162-D171 (2012)].

Nevertheless, a paper [6] was published on the anomalous codeposition in the Co-Ru system on the basis of electrochemical investigations of the deposition process as well as compositional analysis, structural studies and magnetoresistance measurements of the resulting nanocrystalline two-phase electrodeposits. A summary of these results was included in the final report of the project OTKA NN 79846 and, therefore, no further details are given here repeatedly.

In the project workplan, it was also planned to extend the studies to Co-Ni-Ru multilayers. However, due to the failure in producing good Co/Ru multilayers with GMR, it did not seem reasonable to attempt the preparation of Co-Ni/Ru multilayers.

V. Modelling the magnetoresistance curves of multilayers [8]

In order to better understand the role of possible couplings in determining the GMR behavior of multilayers, a knowledge of the dependence of the GMR on magnetic field H appears to be useful. Since a few specific cases have only been treated theoretically in the literature, it was decided to carry out a modeling of the $GMR(H)$ curves of FM/NM) multilayers with various interlayer couplings. For simplicity, we focused on a trilayer structure (FM_1/NM/FM_2) corresponding fairly well to the case of a large number of FM/NM bilayers. To carry out the calculations, some fundamental assumptions were made: (i) each FM layer consists of a single domain and the magnetizations are in the layer planes; (ii) the magnetization of each layer is the same; (iii) the magnetization vectors rotate in the plane of the layers in an external magnetic field. In order to calculate the $GMR(H)$ function, we need to know the magnetization process in the trilayer, i.e., the $M(H)$ function. Therefore, first we calculate the equilibrium angle $\varphi(H)$ between the two magnetization vectors as a function of the field by minimizing the total energy of the multilayer. According to most previous theoretical and experimental works, the angular dependence of the *GMR* is fairly well described by the relation $GMR(\varphi) \propto (1 - \cos\varphi)$ and we used this relation to derive the *GMR*(*H*) function. Along this line, the *M*(*H*) and *GMR*(*H*) curves were calculated for the following cases: (i) pure AF coupling; (ii) pure orthogonal coupling; (iii) AF coupling and orthogonal coupling simultaneously present. As to the calculation of the *GMR*(*H*) curves, some of these configurations have not yet been treated formerly or for some specific parameter values only. For those cases for which calculations of *M*(*H*) and *GMR*(*H*) curves were reported in the literature our results agree with previous reports. Our result in Fig. 22 reproduces well the usual bell-shaped GMR(H) curve previously calculated and experimentally observed for the case of dominating AF coupling.

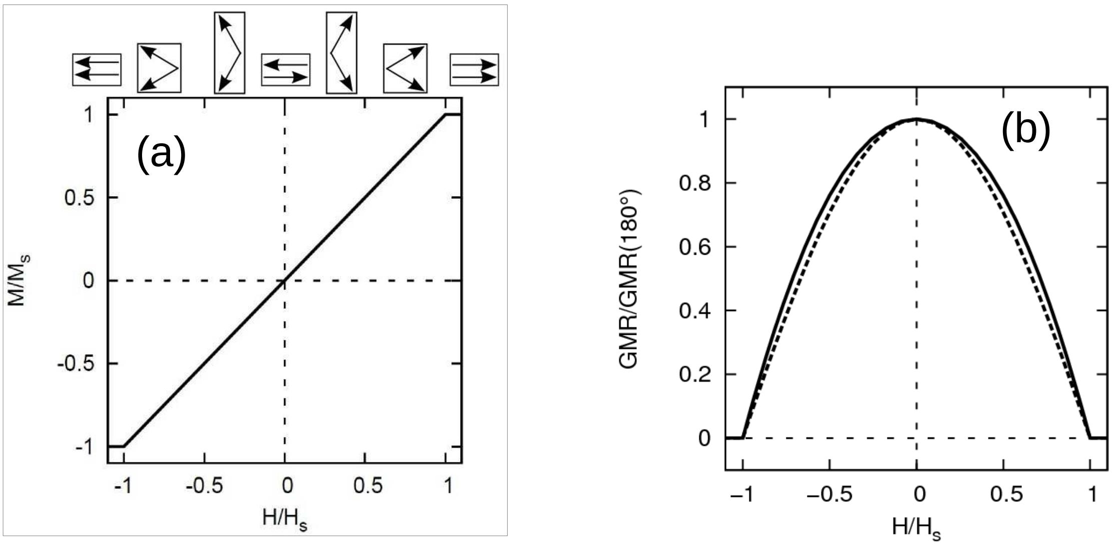

Fig. 22 *The normalized M(H) curve (a) and the GMR(H) curve (b) for a FM/NM/FM* ***trilayer with pure AF coupling*** *as a function of the magnetic field in units of the saturation field* H_S*. In (a), the arrows in the small boxes show the alignment of the magnetization vectors. In (b), the dashed line shows the field dependence of the GMR by assuming the relation* $GMR(\varphi) \propto (1 - \cos\varphi)$ *for the angular dependence of the GMR whereas the solid line is for the case when a quadratic correction to* $GMR(\varphi)$ *is also taken into account.*

On the other hand, our result calculated for the case of pure orthogonal coupling (Fig. 23) shows that this coupling results in a downward curvature of the GMR(H) function. Such a sharp-peaked curve shape is frequently observed in multilayers where a dominating AF coupling could not be demonstrated. According to our calculations, in the mixed case comprising the presence of both AF and orthogonal couplings, there is a continuous transition in the shape of both the M(H) and GMR(H) curves as the ratio of the two coupling constants is varied.

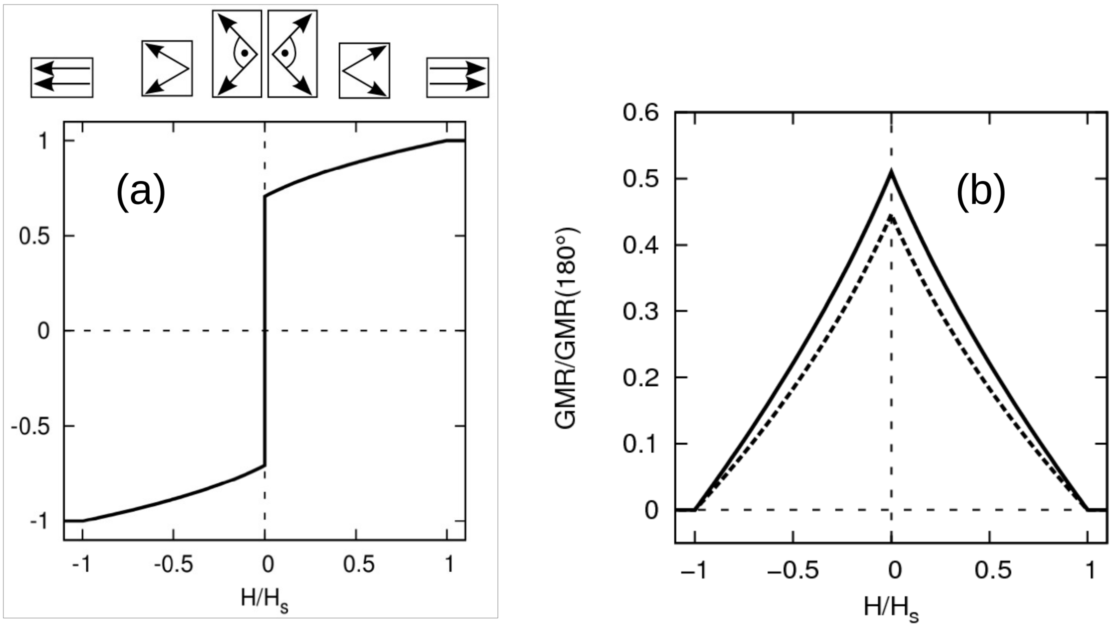

Fig. 23 *The M(H) curve (a) and the GMR(H) curve (b) for an FM/NM/FM **trilayer with pure orthogonal coupling**. (a) For the magnetization, there is an irreversible jump at H = 0. The arrows show the direction of the magnetic field changes; (b) For the GMR, starting from saturation (parallel alignment), the resistivity increases until H = 0 where the angle between the two magnetizations is maximum (90 degree); upon reversing the magnetic field, the angle between the magnetizations decreases which results in a decrease of the resistivity. The dashed and solid lines show the results calculated similarly as explained at Fig. 21.*

SUMMARY OF THE PROJECT RESULTS

It can be established that the project resulted in many important results concerning the preparation and GMR of ED mulitlayers of various compositions and provided a detailed description of the layer thickness dependence of the GMR in ED multilayers. It could be shown that in addition to the previously demonstrated absence of an oscillatory behavior of the ferromagnetic GMR contribution in ED Co/Cu mulilayers by our group, the situation is the same also for ED Ni-Co/Cu and Fe-Co/Cu multilayers if the magnetoresistance contributions are properly analyzed by accounting for the SPM contribution to the GMR. The surface roughness evolution with individual layer thicknesses as well as total multilayer thickness was established, by pointing out that the increase of the surface roughness beyond a certain level is definitely deleterious for the GMR magnitude. In the range 20 to 50 °C, the deposition bath temperature was found to exert no discernible influence on the GMR in ED Co/Cu and Co-Ni/Cu multilayers.

The present studies established the possible maximum GMR magnitude that can be achieved currently with reasonably small saturation fields in ED multilayer films. To go beyond these limits would certainly require in-situ scanning-probe microscopy studies during electrodeposition in order to reveal still unhidden fine details of multilayer formation the knowledge of which would be necessary for a more proper control of the atomistic steps of nucleation and growth.

SUMMARY OF SCIENTIFIC ACTIVITIES OF THE PROJECT PARTICIPANTS IN RELATION TO THE PROJECT TOPIC

At the end of the project report, a list of paper published on the results of the project is given as well other scientific activities of the project participants during the project duration are summarized. These include 9 papers in published in international journals with one extended review in *Progress in Materials Science* and further 6 papers already submitted or in preparation for submission to international journals, 10 invited lectures as well as 9 oral and 7 poster presentations at international conferences and workshops, 17 seminar presentations in foreign universities and research institutions and 6 presentations at domestic scientific meetings in Hungary. Both senior team members supervised a project participant Ph.D. student (one in physics, the other one in chemistry) who are expected to get their Ph.D. degree in 2013. An M.Sc. degree was also acquired by an undergradute project member during the project duration. An M.Eng. degree was acquired by an undergradute student at TU Freiberg, Germany on the basis of measurements on multilayer samples produced by the team members. In addition, a Ph.D. student from Iran also joined temporarily the project team and work carried out here became part of the succesfully completed Ph.D. thesis. Each of the two senior team members was invited to a Ph.D. thesis evaluation committee abroad in the field of the project. A student working on his Ph.D. in India was attracted to join the project team recently to carry out part of his research work here on GMR in ED multilayers.

Budapest, March 27, 2013.

Imre Bakonyi

Dr. Imre Bakonyi
principal investigator, senior team member

Project participants:

Dr. László Péter, senior team member
Dr. Ádám Révész
Dr. Áron Pekker
Dr. Tivadar Lohner
Dr. György Molnár
Dr. Lajos Pogány (part-time employed on the project’s budget)
Bence Tóth, Ph.D. student
Katalin Neuróhr, Ph.D. student (full-time employed on the project’s budget)
Krisztián Szász, undergraduate student

Scientific activities of the project participants in relation to the project topic

A. List of publications resulting from the present OTKA project in peer-reviewed international journals (cumulative impact factor of published papers: 35.23)
([I.F.] = journal impact factor; {I.C.} = independent citations to paper)

1. I. Bakonyi, L. Péter: Electrodeposited multilayer films with giant magnetoresistance (GMR): progress and problems. *Progr. Mater. Sci.* **55**, 107-245 (2010) [I.F.] = 16.579 {I.C.} = 64
2. Péter L, Csik A, Vad K, Tóth-Kádár E, Pekker Á, Molnár G; On the composition depth profile of electrodeposited Fe-Co-Ni alloys; *Electrochim. Acta* **55**, 4734-4741 (2010) [I.F.] = 3.642 {I.C.} = 4
3. B.G. Tóth, L. Péter, Á. Révész, J. Pádár, I. Bakonyi: Temperature dependence of the electrical resistivity and the anisotropic magnetoresistance (AMR) of electrodeposited Ni-Co alloys. *Eur. Phys. J. B* **75**, 167-177 (2010) [I.F.] = 1.575 {I.C.} = 9
4. Péter L; Comment on "Magnetoresistance of CoNiCu/Cu Multilayers Electrodeposited from Electrolytes with Different Ni ion concentrations" (J. Electrochem. Soc. **157**(10) D538-D545 (2010).); *J. Electrochem. Soc.* **158**, S1-S2 (2011) [I.F.] = 2.590 {I.C.} = 0
5. B.G. Tóth, L. Péter, I. Bakonyi: Magnetoresistance and surface roughness study of the initial growth of electrodeposited Co/Cu multilayers. *J. Electrochem. Soc.* **158**, D671-D680 (2011) [I.F.] = 2.590 {I.C.} = 1
6. M. Jafari Fesharaki, G.R. Nabiyouni, J. Dégi, L. Pogány, Á. Révész, I. Bakonyi, L. Péter: Anomalous codeposition of cobalt and ruthenium from chloride-sulfate baths. *J. Solid State Electrochem.* **16**, 715-722 (2012) [I.F.(2011)] = 2.131 {I.C.} = 0
7. Neuróhr K; Dégi J; Pogány L; Bakonyi I; Ungvári D; Vad K; Hakl J; Révész Á; Péter L: Composition, morphology and electrical transport properties of Co-Pb electrodeposits. *J. All. Comp.* **545**, 111-121 (2012) [I.F.(2011)] = 2.289 {I.C.} = 0
8. Szász K, Bakonyi I: Modeling the magnetoresistance vs. field curves of GMR multilayers with antiferromagnetic and/or orthogonal coupling by assuming single-domain state and coherent rotations. *J. Spintron. Magn. Nanomater.* **1**, 157-167 (2012) [I.F.] = – (new journal) {I.C.} = 0
9. Tóth BG; Péter L; Dégi J; Révész Á; Oszetzky D; Molnár G; Bakonyi I: Influence of Cu deposition potential on the giant magnetoresistance and surface roughness of electrodeposited Ni-Co/Cu multilayers. *Electrochimica Acta* **91**, 122-129 (2013) [I.F.(2011)] = 3.832 {I.C.} = 0
10. Neuróhr K; Csik A; Vad K; Molnár G; Bakonyi I; Péter L: Near-substrate composition depth profile of d.c.-plated and pulse-plated Fe-Ni alloys. Submitted to *Electrochimica Acta* (under review) [I.F.(2011)] = 3.832 {I.C.} = 0
11. B.G. Tóth, L. Péter, J. Dégi and I. Bakonyi: Magnetoresistance and surface roughness study of electrodeposited $Ni_{50}Co_{50}$/Cu multilayers. (manuscript in preparation)
12. B.G. Tóth, L. Péter and I. Bakonyi: Preparation and magnetoresistance study of electrodeposited Fe-Co/Cu multilayers. (manuscript in preparation)
13. Neuróhr K; Bakonyi I; Péter L: Dependence of GMR on deposition bath temperature. (manuscript in preparation)

14. Neuróhr K; Bakonyi I; Péter L: Influence of Pb, Bi, Au, Ag additives on GMR of ED Co/Cu multilayers. (manuscript in preparation)
15. Péter L, Csik A, Vad K, Molnár G; Transport coefficient of Fe^{2+} ions in the electrolyte during the deposition of Fe-Co-Ni alloys as determined from the composition depth profile of the deposits. (manuscript in preparation)

B. Invited talks at international conferences by the project participants:

L. Péter, A. Csik, K. Vad, A. Bartók, E. Tóth-Kádár and G. Molnár: Reverse Depth Profile Analysis of Electrodeposited Fe-Co-Ni Alloys and Co/Cu Multilayers. *206th Annual Meeting of the Electrochemical Society* (Vienna, Austria, 2009)

I. Bakonyi, L. Péter: Giant magnetoresistance in electrodeposited multilayer films: progress and problems (keynote lecture). *2nd Int. Conf. on Functional Nanocoatings* (Dresden, Germany, 2010)

I. Bakonyi, L. Péter: Giant magnetoresistance in (electrodeposited) magnetic nanostructures. *Int. Conf. on Superconductivity and Magnetism ICSM2010* (Antalya, Turkey, 2010)

L. Péter: Application of pulse plating for codeposition of immiscible metals: Deposit properties and trends of the structure formation. *European Pulse Plating Seminar* (Vienna, Austria, 2010)

I. Bakonyi: Atomistic aspects of nucleation and layer growth: deposition from liquid and gaseous phases. *1st European Workshop on Electrochemical Deposition of Thermoelectric Materials* (Kaub, Germany, 2011)

I. Bakonyi, L. Péter: Electrodeposition of multilayered film coatings. *1st SURFACE TREATMENT SYMPOSIUM* (Istanbul Technical University, Turkey, 2011)

I. Bakonyi, L. Péter: Giant magnetoresistance in electrodeposited multilayers in view on sensor applications (plenary talk). *Workshop on Electrochemical Techniques for Nano-Scale Surface Engineering - ECTNSE-2012* (Bhabha Atomic Research Centre, Trombay, Mumbai, India, Jan. 2012)

L. Péter: Comparison of the in-depth component distribution of pulse-plated and d.c.-plated alloys. *European Pulse Plating Seminar* (Vienna, Austria, 2012)

I. Bakonyi: Electrodeposition of multilayered film coatings. *The XVIIIth World Interfinish Congress & Exhibition - INTERFINISH2012* (Politecnico di Milano, Italy, 2012)

L. Péter, K. Neuróhr, A. Csik, K. Vad, G. Molnár: Composition depth profile of the near-substrate zone of electrodeposited alloys: One step towards interface engineering. *The XVIIIth World Interfinish Congress & Exhibition - INTERFINISH2012* (Politecnico di Milano, Italy, 2012)

C. Contributed talks at international conferences by the project participants:

B.G. Tóth, L. Péter, J. Dégi, I. Bakonyi: Giant Magnetoresistance Study of Electrodeposited Co-Ni/Cu Multilayers. *EAST FORUM - MINDE WORKSHOP* (Schwäbisch Gmünd, Germany, 2010)

K. Neuróhr, J. Dégi, L. Pogány, I. Bakonyi, L. Péter: Co-deposition of Co and Pb by D.C. and Pulse-Plating and Magnetoresistance Properties of the Deposits. *EAST FORUM - MINDE WORKSHOP* (Schwäbisch Gmünd, Germany, 2010)

K. Neuróhr, J. Dégi, L. Pogány, I. Bakonyi, L. Péter: Co-deposition of Co and Pb by D.C. and Pulse-Plating and Magnetoresistance Properties of the Deposits. *2nd Regional Conference on Electrochemistry – South-Eastern Europe* (Belgrade, Serbia, 2010)

L. Péter, A. Csik, K. Vad, E. Tóth-Kádár, G. Molnár: Composition depth profile of electrodeposited Fe-Co-Ni alloys. *2nd Regional Conference on Electrochemistry – South-Eastern Europe* (Belgrade, Serbia, 2010)

B. G. Tóth, L. Péter and I. Bakonyi: ELECTRODEPOSITION OF BULK Ni Co ALLOYS AND Ni Co/Cu MULTILAYERS AND THEIR MAGNETORESISTANCE BEHAVIOR. *1st European Workshop on Electrochemical Deposition of Thermoelectric Materials* (Kaub, Germany, 2011)

B.G. Tóth, L. Péter, I. Bakonyi: Surface roughness and magnetoresistance study of ultrathin electrodeposited Co/Cu multilayers. *8th Int. Workshop on Electrodeposited Nanostructures EDNANO-8* (Politecnico di Milano, Italy, 2011)

L. Péter, K. Neuróhr, A. Csik, K. Vad, G. Molnár: Measurement of near-substrate composition changes of electrodeposited alloys at the nanometer scale. *8th Int. Workshop on Electrodeposited Nanostructures EDNANO-8* (Politecnico di Milano, Italy, 2011)

L. Péter: Reverse composition depth profile analysis of electrodeposited alloys. *Annual Meeting of the International Society of Electrochemistry* (Prague, Czech Republic, 2012)

László Péter, Katalin Neuróhr, Attila Csik, Kálmán Vad and Imre Bakonyi: Near-substrate composition depth profile of d.c.-plated and pulse-plated Fe-Ni alloys. *9th Int. Workshop on Electrodeposited Nanostructures EDNANO-9* (University of Porto, Portugal, 2012)

D. Poster presentations at international conferences by the project participants:

B.G. Tóth, L. Péter, Á. Révész, J. Pádár and I. Bakonyi: Room-temperature magnetoresistance characteristics of electrodeposited Ni-Co alloys. *European School on Magnetism* (Timisoara, Romania, 2009)

Szász K, Bakonyi I: Modeling the magnetoresistance vs. field curves of GMR multilayers with various coupling and anisotropies by assuming single-domain state and coherent rotation. *European School on Magnetism* (Timisoara, Romania, 2009)

A. Bartók, A. Csik, K. Vad, G. Molnár, E. Tóth-Kádár, I. Bakonyi, L. Péter: Calculation of reverse depth profile analysis results from surface roughness data of electrodeposited multilayers. *2nd Int. Conf. on Functional Nanocoatings* (Dresden, Germany, 2010)

L. Péter, A. Csik, K. Vad, G. Molnár: Calculation of the transport coefficient of Fe2+ in the electrolyte from the composition depth profile of electrodeposited Fe-Co-Ni alloys. *Annual Meeting of the International Society of Electrochemistry* (Nice, France, 2010)

L. Péter, B..G. Tóth, I. Bakonyi: Electrodeposition of Ni-Co/Cu Multilayers and Their Magnetoresistance Study. *Annual Meeting of the International Society of Electrochemistry* (Niigata, Japan, 2011)

L. Péter, K. Neuróhr, A. Csik, K. Vad, G. Molnár: Reverse composition depth profile analysis of various electrodeposited alloys. *Annual Meeting of the International Society of Electrochemistry* (Niigata, Japan, 2011)

K. Neuróhr, J. Dégi, L. Pogány, I. Bakonyi, L. Péter: Codeposition of Co and Pb by d.c. and pulse plating and magnetoresistance properties of the deposits. *8th Int. Workshop on Electrodeposited Nanostructures EDNANO-8* (Politecnico di Milano, Italy, 2011)

E. Seminar talks abroad by the project participants:

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *Walther-Meißner-Institut, BAdW, München/Garching, Dec. 2009*

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *Physics Department, Uludag University, Bursa, Turkey, May 2010*

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *Department of Metallurgical and Materials Engineering, Istanbul Technical University, Isatnbul, Turkey, May 2010*

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *Physics Department, Universitat Autonoma de Barcelona, Spain, May 2010*

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *Department of Physical Chemistry, Universitat de Barcelona, Spain, June 2010*

L. Péter: Electrodeposition of compositionally modulated and nanostructured metals. *TU – Bergakademie Freiberg, Freiberg, Germany, July 2010.*

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *Institut für Angewandte Physik, Universität Hamburg, Germany, April 2011*

L. Péter: Electrodeposition research activity at the Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences. *Hitachi Research Laboratory, Hitachi City, Japan, September 2011.*

L. Péter: Electrodeposition research activity at the Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences. *Waseda University, Tokyo, Japan, September 2011.*

L. Péter: Composition depth profile analysis of electrodeposited metals. *Leibnitz Institute for Materials Research (IFW-Dresed), Dresden, Germany, November 2011.*

L. Péter: Magnetic Nanostructures through the Eyes of an Electrochemist. *University of Hamburg, Germany, 18th November 2011.*

L. Péter: Magnetic Nanostructures through the Eyes of an Electrochemist. *Christian-Albrecht-Universitat, Dept. of Physics, Kiel, Germany, 25th November 2011.*

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *Department of Physics, Indian Institute of Technology Delhi, India, Jan 2012*

L. Péter: Magnetic Nanostructures through the Eyes of an Electrochemist. *University of Porto, Portugal, 6th December 2011.*

I. Bakonyi: Giant magnetoresistance (GMR) in (electrodeposited) magnetic nanostructures. *National Institute for Research and Development in Technical Physics, Iasi, Romania, Sep. 2012*

K. Neuróhr: Codeposition of Co and Pb by d.c. and pulse plating and magnetoresistance properties of the deposits. *University of Hamburg, Physics Department, Hamburg, Germany (Nielsch Group Meeting in Roskilde, Denmark, 2012)*

L. Péter: Magnetic Nanostructures through the Eyes of an Electrochemist. *Laboratoire de Génie Electrique de Paris, France, 20th September 2012.*

F. Presentations at domestic scientific meetings by the project participants:

L. Péter: New results in the composition depth profile analysis of electrodeposited metals. *Meeting of the Electrochemistry Committee of the Hungarian Academy of Sciences, Budapest, Hungary, June 2009.*

K. Neuróhr, J. Dégi, L. Pogány, I. Bakonyi, L. Péter: Study of electrodeposited Co/Pb and Co/Cu mutilayers. *Poster presented at the Reporting Meeting of Ph.D. Students of the Chemistry Doctoral School of Eötvös University, Budapest, 2010.*

L. Péter: Reverse composition depth profile analysis in the nanoscale characterization of electrodeposited metals. *Joint Meeting of the Surface Chemistry and the Nanotechnology Committees of the Hungarian Academy of Sciences, Budapest, Hungary, October 2010.*

I. Bakonyi: Giant magnetoresistance (GMR) in magnetic nanostructures with particular attention to electrodeposited multilayers. *Autumn School on Materials Science and Diffraction* (Eötvös Physical Society of Hungary, Visegrád, Oct. 2011)

B. Tóth: Magnetotransport properties of electrodpeosited metallic alloys and multilayers. *Meeting of the Electrochemistry Committee of the Hungarian Academy of Sciences, Budapest, Hungary, 2011*

K. Neuróhr: Some special magnetic nanostructure prepared by electrodeposition. *Meeting of the Electrochemistry Committee of the Hungarian Academy of Sciences, Budapest, Hungary, 2011*

Contribution to the education of young scientists in relation to the project topic

Project participant Bence Tóth (M.Sc. in Physics) carried out his Ph.D. studies in the years 2008-2012 at Eötvös University Budapest, i.e., mainly during the project period and his work was supported by the Wigner Research Center for Physics and by the HAS. He submitted a Ph.D. thesis entitled *Giant magnetoresistance (GMR) in multilayers* (supervisor: principal investigator I. Bakonyi) to the Eötvös University in Jan. 2013 and the defence is expected to be in the spring of 2013. Bence Tóth was coauthor of project publications [3], [5], [9], [11] and [12].

Project participant Katalin Neuróhr (M.Sc. in Chemistry) carried out her Ph.D. studies in the years 2009-2012 at Eötvös University, Budapest, and she was fully employed from the project budget in this period. She is now supported by the Wigner Research Center for Physics to complete her Ph.D thesis entitled *Electrochemical preparation and investigation of metallic nanostructures* (supervisor: senior project participant L. Péter). The thesis is expected to be submitted to the Eötvös University mid 2013. Katalin Neuróhr was coauthor of project publications [7], [10], [13] and [14].

Undergraduate physics student Krisztián Szász (Eötvös University, Budapest) completed his M.Sc. thesis in 2009-2010 in the framework of the project and he was partially supported by the project budget. The title of the M.Sc. thesis was *Modeling the magnetoresistance vs. field curves of GMR multilayers with various coupling and anisotropies by assuming single-domain state and coherent rotation* (supervisor: principal investigator I. Bakonyi) and was the basis for project publication [8].

In the year 2010, Ph.D. student Marjan Jafary Fesharaki (Arak University, Iran) spent 7 months in our laboratory with a support from the Iranian government. She contributed to project publication [6] and these results were also part of her Ph.D. thesis which she defended in the meantime in Iran.

Undergradute student S. Sharafiev completed an M.Eng. thesis at the Technical University Freiberg, Germany in 2012. The experimental work of the thesis entitled *Early stages of the microstructure formation in electrodeposited Ni-Co/Cu multilayers* was carried out on samples prepared by the project team for the student.

Since October 2012, Ph.D. student N. Rajasekaran (Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India) joined the project team for 7 months to work on electrodeposited multilayers and nanowires with the support of the Hungarian Scholarship Board.

During the project period, two project participants were invited to the evaluation committee of a Ph.D. thesis abroad in the field of electrodeposited nanostructures:

In 2010, I. Bakonyi participated in the evaluation of the Ph.D. thesis submitted by José Manuel García Torres to the University of Barcelona (Spain).

In 2011, L. Péter participated in the evaluation of the Ph.D. thesis submitted by Celia T. Sousa to the University of Porto (Portugal).