A NEW SINGLE BATH FOR THE ELECTRODEPOSITION OF NiFe/Cu MULTILAYERS EXHIBITING GIANT MAGNETORESISTANCE BEHAVIOR

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A new single bath for the electrodeposition of ultrathin NiFe/Cu multilayers was developed and magnetoresistance measurements were conducted. Complementary methods such as scanning electron microscopy (SEM), x-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the multilayers. Magnetoresistance measurements indicated that the multilayers grown from this new bath exhibited a giant magnetoresistance (GMR) behavior.

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INTRODUCTION

Since the discovery of giant magnetoresistance (GMR) in 1988 [1], multilayered structures consisting of ferromagnetic layers separated by a nonmagnetic spacer layer have been studied worldwide. Among different choices, the material combination of permalloy/copper (denoted by Py/Cu) has raised great interest regarding its application potential as magnetoresistance read heads in the new generation of magnetic recording storage devices [2]. Several papers have been published on the GMR effect of deposited NiFe/Cu multilayers grown by ion-beam [3], magnetron sputtering [4], face to face sputtering [5] and vacuum evaporation technique [6]. These techniques have the advantages of a high control of film growth and a pure material can be easily obtained but they inevitably require high vacuum and/or temperatures. However, electrodeposition exhibits advantages of low cost, simplicity and ease of production [7].

A great deal of research has been performed on the investigation of the magnetic behavior of Py/Cu multilayers deposited by physical methods after Parkin [8] found that saturation magnetoresistance values at 300K of these multilayers exceeds 16% for saturation fields of only 600 Oe. Nakatani et. al [3] observed oscillatory magnetoresistance changes with copper thickness for NiFe/Cu multilayers formed by ion beam sputtering and a GMR of 19% was reported. Urbaniak et. al [9] investigated the GMR effect and magnetization reversal processes of Py/Cu multilayer obtained by face-to-face sputtering. It was shown that for such multilayers a high field sensitivity of GMR effect and negligible hysteresis can be found for a low number of Py layers. Heitmann et. al [10] reported that the Py/Cu multilayers, grown by magnetron sputtering, consisting of alternating blocks of first and second anti-ferromagnetic coupling maximum can display a GMR ratio up to 20%. Fulthorpe [11] determined the structural changes that occur during the annealing of Py/Cu multilayers grown by the same method. Luo et. al [12] also grew Py/Cu multilayers by magnetron sputtering and applied reflection anomalous fine structure analysis to find a strained permalloy layer at the Py/Cu interface. In 2005, Ene et. al [13] analyzed the sputtered NiFe/Cu multilayer stacks by atom probe tomography and studied annealing effects which degrade the GMR ratio. Ai et. al [2] investigated the microstructure nanomechanical behavior of Py/Cu magnetic multilayers deposited by a DC magnetron sputtering system.

Research in this area is still in progress; however, few papers addressing the electrodeposition of NiFe/Cu multilayers have been published to the date. In 1994, Chang and Romankiw [14] demonstrated that it was possible to electroplate thin layers of NiFe/Cu onto an N-doped (111)-oriented Si wafer from a single solution, but GMR studies were not performed. To the best knowledge of the authors, so far two groups have reported the GMR of electrodeposited NiFe/Cu multilayers apart from studies on nanowires: The first results of GMR in electrodeposited NiFeCu/Cu multilayers was presented by Attenborough et. al [15] in 1995. This group used a single electrolyte based upon the electrolyte used by Romankiw and Olsen [14]. A GMR of 1.4% was reported for $[NiFeCu_{(2nm)}/Cu_{(2.5nm)}]_{200}$. The MR curves were quite sharply peaked but they did not saturate even with an applied field of 8 kOe which suggested that some regions of the film layers were

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antiferromagnetically coupled. The copper content within the magnetic layers was estimated to be 9%. One year later Chassaing et. al [16] reported a magnetoresistance value of 2% at 2 kOe for $[NiFe_{(3nm)}/Cu_{(1.5nm)}]_{30}$ at 77 K. Such magnetic couplings were observed for a copper layer thickness ranging between 1.5 nm and 3.5 nm. For thinner magnetic layers no coupling was observed. Tokarz et. al [17] have also electrodeposited NiFe/Cu multilayers by a single bath technique. A columnar structure deposit with column diameter in the range from 10 to 30 nm was observed. The line scans acquired using energy dispersive spectra confirmed the layered structure of the deposit, but pointed towards the possibility of intermixing of species from alternating sublayers. No magnetic and magnetotransport data were reported.

In the present research, the solution proposed by Chang and Romankiw [14] was used and multilayers were deposited, characterized and magnetoresistance (MR) measurements were taken and studied. Since the MR results were not satisfactory, the solution was modified and a new solution was introduced. The concentration of the metal salts was adjusted and additives which proved to be deleterious for the GMR of electrodeposited multilayers [18] were omitted so as to obtain a giant magnetoresistance behavior. Multilayers deposited from this new solution were characterized and GMR measurements were made. GMR behavior was observed from the NiFe/Cu multilayers deposited from this new solution.

EXPERIMENTALSAMPLE PREPARATION

Electrodeposition was performed using a potentiostat, model Auto Lab Equipment (PGSTATX, BSTR10A) equipped with a general purpose electrochemical system (GPES) software. The computer-controlled potentiostat was used to monitor the entire electrochemical process. Experiments were conducted in the potentiostatic mode for both layers. Two solutions were prepared which were based on the early work of Chang and Romankiw [14], although one of the solutions was used after some modifications. Compositions are given in table 1, respectively. Analytical-grade (Merck) reagents and distilled water was used. Electrodeposition was carried out in a standard three-electrode cell with a saturated calomel electrode (SCE) as the reference electrode. The counter electrode was a platinum wire. Since copper is one of the most noble metals, it requires only a small negative potential for reduction to occur, whereas nickel and iron (less noble metals) require a much higher potential [15]. Therefore, the deposition potentials were chosen to be –2.5 V for the NiFe layer and -0.4 V for the Cu layer, measured relative to a SCE as close as possible to the cathode surface, to minimize the ohmic potential drop in the electrolyte. The computer controlled potentiostat was adjusting these two potentials. A Pt foil counter electrode was placed directly opposite the working electrode substrate. Electrodeposition from Chang's solution was carried out at 40°C, whereas deposition from the new solution was performed at room temperature with no stirring.

Table 1. Electrolytes compositions

Electrolyte	$NiSO_4$	$FeSO_4$	$CuSO_4$	Saccharin	Sodium Dodecyl Sulphate (SDS)	Boric acid
Chang solution	0.2 M	0.002 M	0.002 M	2 (g/l)	0.02 (g/l)	–
New solution	0.4 M	0.004 M	0.01 M	–	–	0.2 M

MORPHOLOGICAL INVESTIGATIONS

An Oxford Instrument Stereoscan 120 scanning electron microscope (SEM) and a transmission electron microscope (TEM) operating at an accelerating voltage of 200 keV (0.23 nm resolution) were used for morphological studies. Cu foils, (200) oriented and 2 cm^2 in area, were used as substrates. Thick multilayers were electrodeposited from both solutions under the same conditions and compared. In order to perform the high resolution transmission electron microscopy study, the samples were polished mechanically and then thinned by means of Ar^+ bombardment to achieve the appropriate thickness, which allows electrons to pass through the sample (around 100 nm). The samples were then mounted on a copper holder.

LOW ANGLE X-RAY DIFFRACTION (LAXRD)

Low angle x-ray diffraction (LAXRD) was used to investigate the structure of the deposits using a Phillips X'pert Pro x-ray diffractometer (Cu $K_{\alpha 1}$ radiation, $\lambda = 0.15405$ nm) by scanning in the $2\theta = 40^\circ–60^\circ$

range with 0.01 steps at a grazing angle of 5°. Glasses sputtered with 100 nm gold, 2 cm^2 in area, were used as substrates for the LAXRD studies.

MAGNETORESISTANCE MEASUREMENTS (MR)

Multilayers prepared for magnetotransport measurements were deposited onto Si(100)/Cr(5nm)/Cu(20nm). The Cr adhesive layer and the Cu seed layer were prepared by evaporation on the Si wafer. The magnetoresistance was measured on 2 mm wide strips at room temperature with the four-point-in-line method in magnetic fields between -8 kOe and +8 kOe in the field-in-plane/current-in-plane geometry. Both the longitudinal magnetoresistance (LMR, field parallel to current) and the transverse magnetoresistance (TMR, field perpendicular to current) components were measured. The following formula was used for calculating the magnetoresistance ratio: $\Delta R/R_0=(R_H-R_0)/R_0$ where R_H is the resistance in a magnetic field H and R_0 is the resistance value of the magnetoresistance peak around zero field. The shunt effect of the substrate was not corrected. Table 2 presents the number of the prepared specimens along with the characterization techniques and experiments carried out on each specimen.

Table 2. Characterization of specimens

Specimen No.	Electrolyte	No. of bilayers	Characterization techniques
1	Chang	4	SEM, LAXRD
2	Chang	50	MR
3	Chang	100	MR, TEM
4	Chang	150	MR
5	New	5	SEM, LAXRD
6	New	50	MR
7	New	100	MR
8	New	150	MR

RESULTS AND DISCUSSION

Cross-sectional scanning electron microscopy (SEM) images of sample 1 are shown in fig. 1. In each SEM image the brighter regions are NiFe while the darker ones are Cu layers. A total of 4 periods (8 continuous layers, 4 of Cu and NiFe each) are visible. The Cu layers have an average thickness of 500 nm while that of NiFe, 1 μm. The SEM investigations confirm the periodical formation of the multilayers from Chang's solution deposited onto the copper substrate.

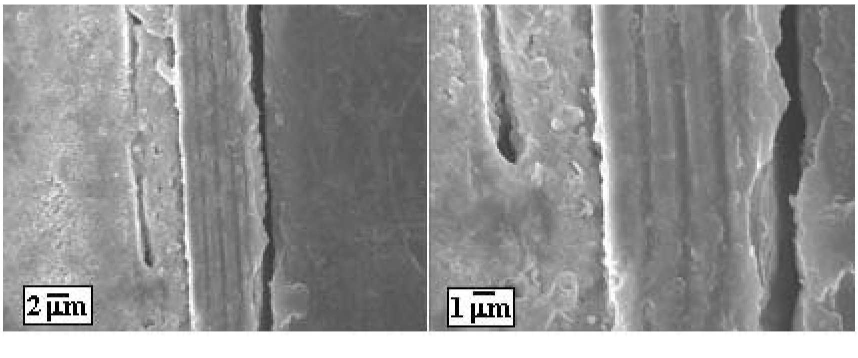
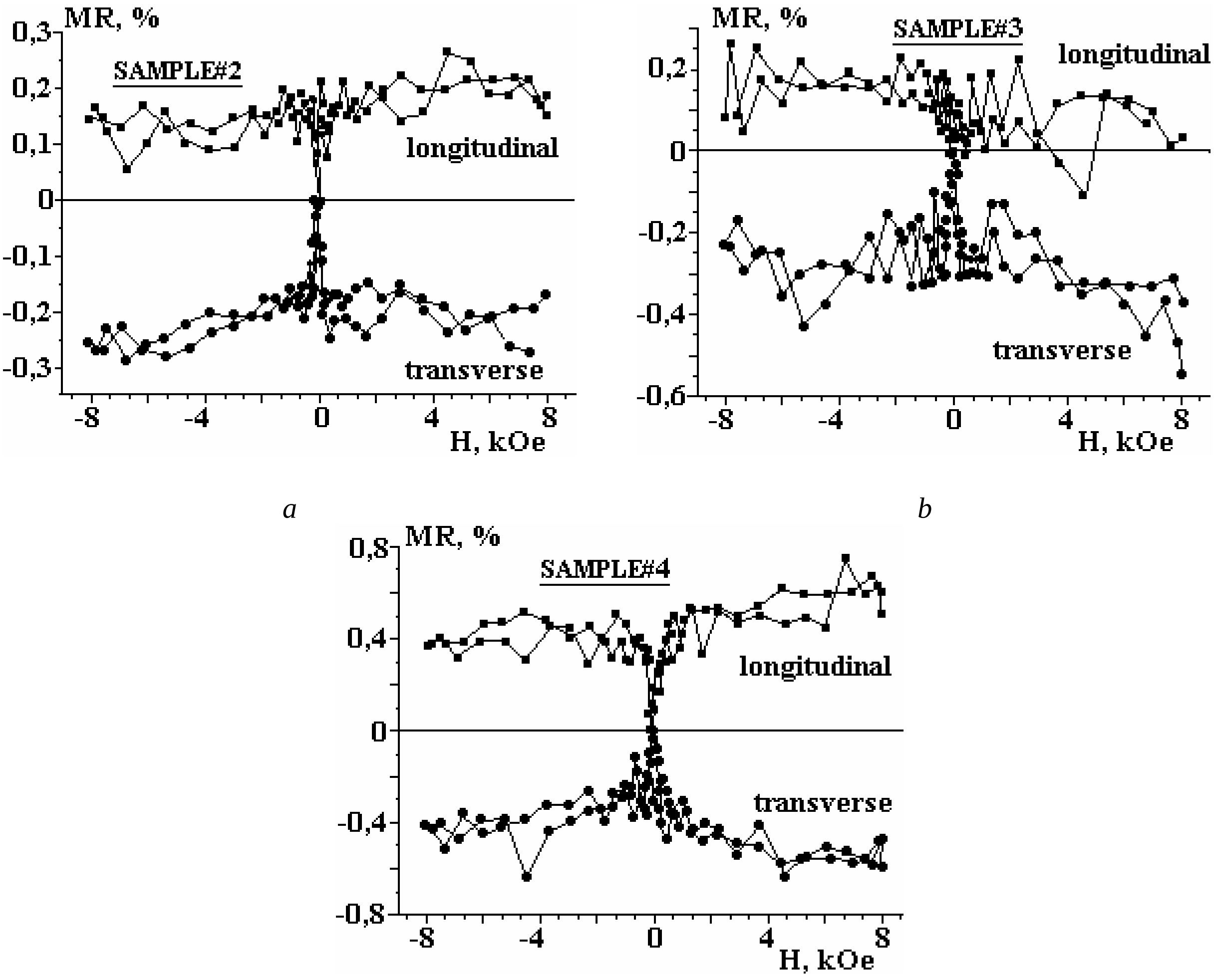


Fig. 1. SEM micrographs of sample 1 showing the 4 bilayers of [NiFe/Cu]$_4$ deposited from Chang's solution. NiFe layers are the brighter bands while Cu layers are the darker ones

Fig. 2 shows the room-temperature magnetoresistance curves for samples 2, 3 and 4 grown from Chang's solution. As seen, all samples show anisotropic magnetoresistance (AMR) instead of giant magnetoresistance (GMR) i.e. the deposit exhibits ferromagnetic behavior similar to that of bulk NiFe. Positive LMR and negative TMR components are obtained with an AMR=LMR-TMR value amounting to some 1%.

In order to investigate the reason of the absence of GMR behavior from these samples, cross sectional transmission electron microscopy images were taken. The modulated structure of NiFe/Cu multilayers with thin bilayer thickness prepared from Chang's solution is shown in fig. 3. Transmission electron microscopy (TEM) results show that there are some ordered regions which are very small. The bilayers thickness also seems to vary too much. Additionally, the orientation of the stripes is rather random, while in a real multilayer one should see a dominant layer plane which is roughly perpendicular to the growth direction. Therefore, these pictures are in accord with the MR properties, namely, the lack of the laminar structure and the occurrence of the AMR.



a *b*

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Fig. 2. Longitudinal (LMR) and transverse (TMR) components of the magnetoresistance saturation for samples deposited from Chang's solution: (a) sample 2, (b) sample 3, and (c) sample 4

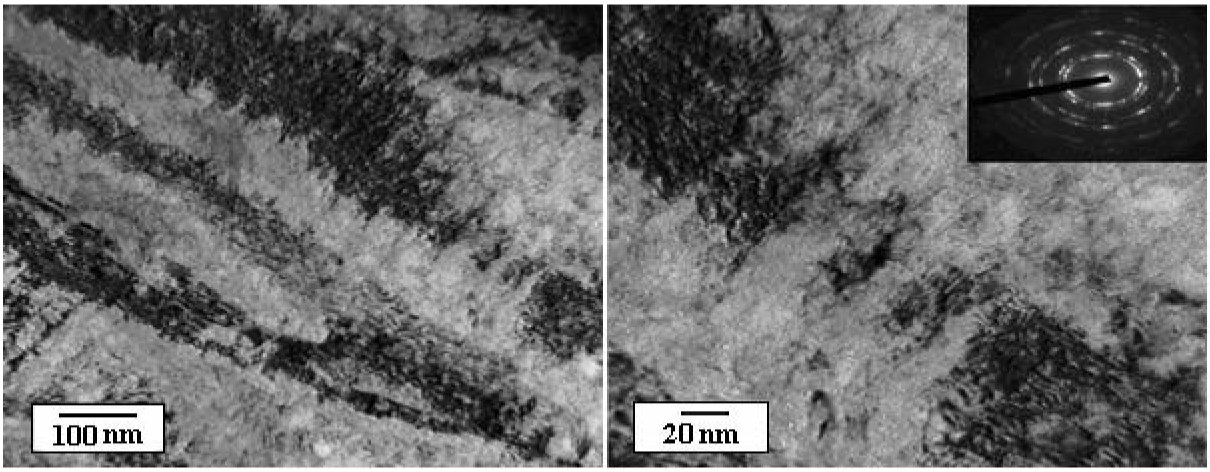


Fig. 3. Cross sectional transmission electron microscopy image of NiFe/Cu multilayers of sample 3 made from Chang's solution

To modify Chang's bath, all components that were taken from the classical experience of the plating industry, i.e. sodium saccharin and sodium dodecyl sulfate, were omitted. These components serve as stress relievers and brighteners for decorative plating but at the same time decrease the crystallite size drastically. As a result, the growth of continuous and even layers will become less and less likely. This could be one reason why samples 2, 3 and 4 did not show any GMR. The typical additives used as surfactants such as sodium dodecyl sulfate (SDS), sulfur organic compounds such as saccharin, both known as levelers, stress relievers and brighteners are harmful for the formation of the layer structure and result in the loss of GMR [18]. On the other hand, saccharin is known to decrease the crystallite size. The decrease in the crystallite size always leads to the increase in resistivity, simply because the electrons are frequently scattered at the grain boundaries where the atomic ordering is imperfect. Since the MR ratio is referred to the zero-field resistivity, a drastic increase in the latter quantity leads to a decrease in the MR ratio to the same extent. In addition, the concentrations of the metal salts were changed. The Ni^{2+} ion concentration was raised to 0.4 mol/l while the Fe^{2+} ion concentration was increased to 0.004 mol/l. The concentration of the Cu^{2+} ion was very small in Chang's bath, therefore it was increased to 0.01 mol/l. Apart from the metal salts, 0.2 mol/l boric acid was also used. Boric acid is known to buffer the pH, help prolong the plating bath life, and produce more uniform deposits [19]. The preliminary experiments showed that the rest potential of the magnetic layer is rather close to -0.65 V vs SCE. Nevertheless, the dissolution of the NiFe layer at -0.4 V is not very fast, so even at this potential the misestimation of the layer thicknesses due to the Fe to Cu exchange is negligible.

The SEM micrographs taken from thick deposits of multilayers electrodeposited from the new solution are shown in fig. 4. A thick NiFe layer was deposited first which indicates that the NiFe layers are the brighter bands with an average thickness of 450 nm and the darker bands are the Cu layers with a nominal thickness of 480 nm.

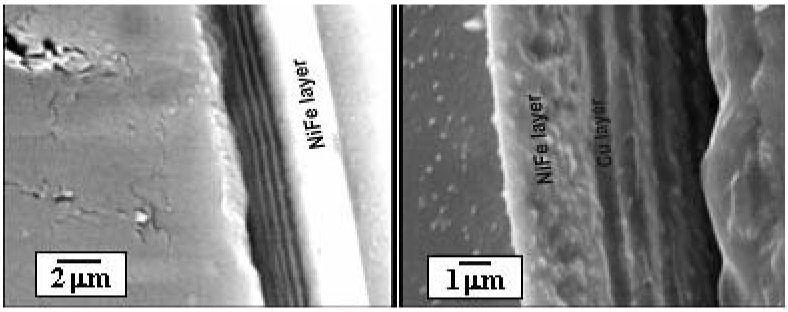
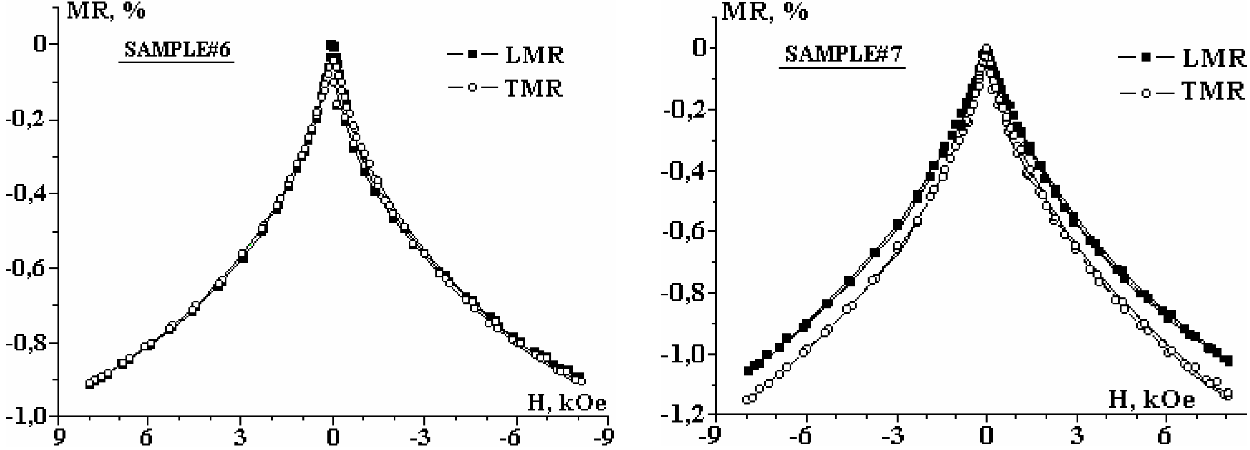


Fig. 4. SEM micrographs of sample 5 containing five bilayers of [NiFe/Cu]$_5$ *multilayers deposited from the modified solution. A thick NiFe layer separates the multilayer region from the substrate*

Fig. 5 shows the results of GMR measurements for samples 6, 7 and 8. The GMR effect is very evident. All samples exhibit a superparamagnetic (SPM) – the so-called magnetically isolated islands within the magnetic layers [18, 20] – character which is shown by the slow saturation. The effect is not very large. The SPM character of the GMR curves tells that the magnetic layer is either fragmented or quite rich in Cu and there is some element segregation.



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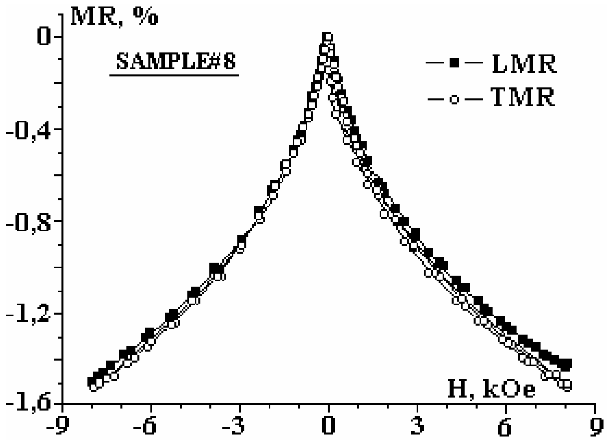

c

Fig. 5. Magnetoresistances measured at room temperature for samples 7, 8 and 9. (a)$[NiFe_{(3nm)}/Cu_{(1.2nm)}]_{50}$ (b) $[NiFe_{(3nm)}/Cu_{(1.2nm)}]_{100}$ (c) $[NiFe_{(3nm)}/Cu_{(1.2nm)}]_{150}$

The reason of the SPM character found in these samples could also be explained in fig. 6 which shows the typical current-time response during the pulse potential deposition of sample 8. A very large anodic transient at the beginning of the Cu pulse is depicted which means that there is a significant dissolution at the beginning of the pulse until the Cu layer fully covers the surface. The dissolution of the magnetic layer contributes to both the interface roughening and the fragmentation of the magnetic layer. To overcome this problem, the Cu deposition potential should be chosen more negative.

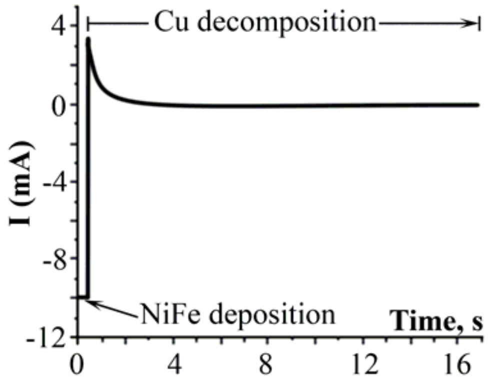

Fig. 6. Typical current-time response of one cycle during the pulse potential deposition of sample 8

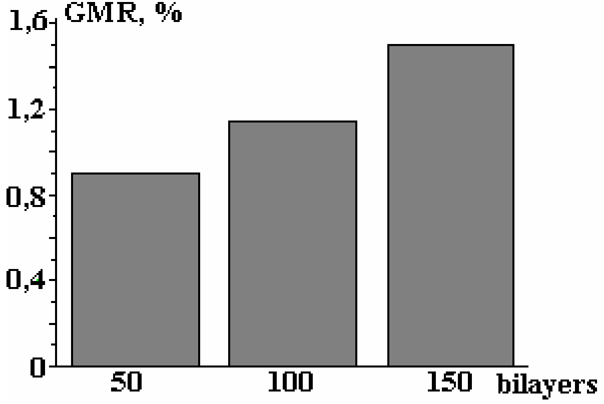

Fig. 7. Dependence of number of layers on GMR ratio

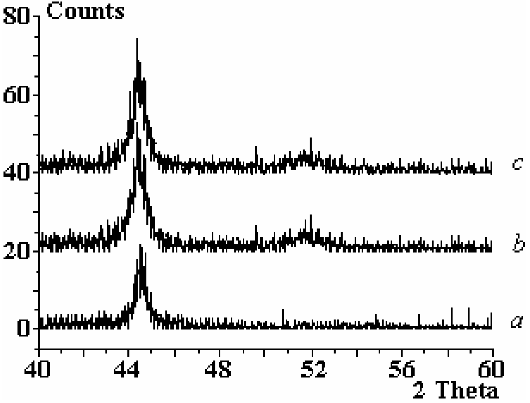

Fig. 8. LAXRD of (a) glass substrate sputtered with a 100 nm-Au layer, (b) sample 1, $[NiFe/Cu]_4$ multilayers deposited from Chang’s solution on the latter substrate (c) sample 5, $[NiFe/Cu]_5$ deposited from the modified solution on the latter substrate

Fig. 7 shows the effect of the number of layers on the GMR effect exhibited by this modified solution. As the number of layers increases, the system exhibits a larger amount of GMR. This effect is caused by a decreased contribution of the outer boundary scattering to conducting processes and a higher number of magnetic-nonmagnetic interfaces within the electron mean free path. In other words, increasing the amount of interfacial material increases the magnitude of the GMR.

The low angle x-ray diffraction (LAXRD) patterns of samples 1 and 5 (fig. 8) reveal the dominant orientations of the Cu and NiFe layers to be (111) and (200) respectively. No multilayer satellites were observed in the thick layers studied, which is either the indication of a non-coherent growth of the subsequent layers or that of the undulated interfaces. The occurrence of satellite peaks is expected around the main multilayer peak, if there exists any, but in the absence of such peaks the lack of the satellite is a very natural feature of the diffractograms [21].

Further studies on this electrolyte are currently taking place in order to optimize and increase the GMR effect achieved from this bath and to obtain further structural information on the multilayers, transmission electron microscopic studies are planned to be performed.

CONCLUSIONS

NiFe/Cu multilayers were electrodeposited by a single bath technique in the potentiostatic mode. No GMR behavior was observed using the electrolyte suggested by previous researchers, therefore the solution was modified by omitting harmful additives and changing the concentrations of the chemicals and a new electrolyte was introduced. The multilayers deposited from this electrolyte exhibited a GMR ratio up to 1.5%. GMR effect was more pronounced in samples containing higher number of bilayers. Structural studies pointed towards a (111) orientation in the copper layers and a dominant (200) orientation for the NiFe layers. The inferior GMR characteristics of electrodeposited multilayers as compared to physically deposited multilayers can be ascribed to microstructural features leading to the appearance of SPM regions, pinholes in the spacer layers and not sufficiently perfect interfaces.

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Реферат

Была разработана методика электролитического осаждения сверхтонких многослойных покрытий NiFe/Cu из одной ванны, и были проведены измерения магнитосопротивления. Для характеристики слоев применялась сканирующая электронная микроскопия (СЭМ), рентгеноструктурный анализ, электронная микроскопия высокого разрешения. Измерения магнитосопротивления показали, что для многослойных покрытий, осажденных из одной ванны, характерен эффект гигантского магнитосопротивления (ГМР).