GIANT MAGNETORESISTANCE AND SUPER-PARAMAGNETISM IN ELECTRODEPOSITED NiFe/Cu MULTILAYERS

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1. Introduction

A possible application of nanoscale multilayers exhibiting giant magnetoresistance (GMR) as magnetic field sensors has been the main driving force for the worldwide research into them. The first observation of GMR on sputtered magnetic/nonmagnetic multilayers [1; 2] was followed by the detection of the same effect in several electrodeposited multilayers such as CoCu/Cu [3], NiCu/Cu [4], CoNiCu/Cu [5; 6], NiFeCu/Cu [7; 8], CoFeCu/Cu [9] and quaternary CoFeNiCu/Cu [10].

It has been reported for several magnetic/nonmagnetic multilayer systems prepared by a variety of techniques such as sputtering [11; 12], MBE [13; 14] or electrodeposition [15; 16; 17; 18] that the magnetization may contain both ferromagnetic (FM) and superparamagnetic (SPM) contributions. One can visualize the magnetic layers in such multilayers as consisting of both FM and SPM regions whereby the SPM regions are magnetically decoupled from the FM regions. A pictorial representation of such SPM regions can be in the form of small magnetic islands [17] within the magnetic layers surrounded by some magnetically diluted or completely nonmagnetic (NM) regions, ensuring magnetic decoupling from the FM regions. It has also been reported for the same systems that the magnetoresistance (MR) can exhibit a strongly nonsaturating behavior, sometimes up to magnetic fields of several tens of kOe. Since the saturation against an antiferromagnetic (AF) coupling in multilayers can be usually achieved in a few kOe, this nonsaturating MR component should have a different origin. Magnetic measurements have revealed that in multilayers, in addition to the ferromagnetic (FM) term, the magnetization also has a superparamagnetic (SPM) term, the latter one sometimes even dominating over the FM contribution. The phenomenon of nonsaturating magnetoresistance and the occurrence of a SPM magnetization contribution are not restricted to any specific deposition technique or element combination. It is because, depending on layer's thicknesses and specific deposition conditions, they have been observed in multilayers of the Co/Au, Co/Cu, Ni/Cu, Ni-Fe/Cu, and Ni-Co/Cu systems grown by various methods such as molecular-beam epitaxy (MBE), sputtering, or electrodeposition [16].

According to Bakonyi and Peter [19], the actual physical appearance and location of these SPM regions in the multilayer structure has not yet been revealed. Nevertheless, evidence from the magnetic data clearly supports their possible presence in magnetic/nonmagnetic multilayers. Therefore, the aim of this paper is, firstly, to investigate the giant magnetoresistance of electrodeposited NiFe/Cu multilayers grown from a tailored single electrolyte. Secondly, to discuss the possibility of the existence of super-paramagnetic regions and to prove this idea with the aid of high-resolution transmission electron microscopy (HRTEM). The HRTEM studies do provide direct evidence for the actual physical appearance of these regions.

2. Experimental

2.1. Sample preparation

The composition of the single electrolyte used was a modified version of an early work of Chang et al. [20], i.e 0.4 M $NiSO_4$, 0.004 M $FeSO_4$, 0.01 M $CuSO_4$, and 0.2 M boric acid. A computer-controlled potentiostat was used to monitor the entire electrochemical process. The process was carried out at room temperature. 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 saturated calomel electrode (SCE) that was placed in the cell. The computer controlled potentiostat switched between these two potentials. A Pt foil counter electrode was placed directly opposite the working electrode substrate. The layer thicknesses were controlled via the pulse lengths and from the charge deposited during the pulse, the nominal layer thicknesses were determined by Faraday's law. The thickness of the NiFe layer was estimated to be 3 nm, while the Cu layer thickness 1.2 nm. Electrodeposited were150 repeats.

2.2. Morphological investigations

A high-resolution transmission electron microscope operating at the voltage of 200 keV (0.23 resolution) was used for morphological studies. Cu foils, (200) oriented, 1 cm^2 in area, were used as substrates. In order to perform the HRTEM 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.

2.3. Giant magnetoresistance measurements (GMR)

The multilayers prepared for magnetotransport measurements were deposited onto Si(100)/Cr(5 nm)/Cu(20 nm). 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 (LMR) and the transverse magnetoresistance (TMR) (field parallel to current and field perpendicular to current, respectively) components were recorded for each sample. 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.

3. Results and discussion

The result of magnetoresistance measurements is shown in Fig. 1. A slow saturation is seen, which is an indication of a superparamagnetic (SPM) character. 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.

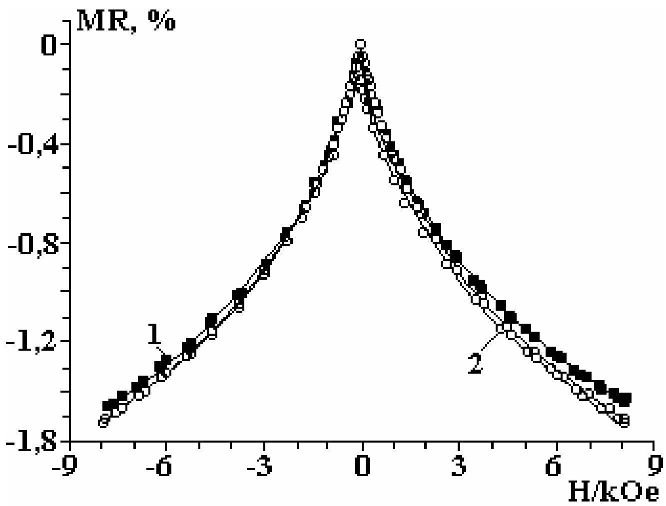


Fig. 1. Magnetoresistance measured at room temperature for electrodeposited $[NiFe_{(3nm)}/Cu_{(1.2nm)}]_{150}$ multilayers. 1 – LMR; 2 – TMR

In order to investigate and ensure the presence of these super-paramagnetic regions, a HRTEM image was taken. Fig. 2 shows the general view after sample preparation. Figs. 3 and 4 show the HRTEM images of the electrodeposited $[NiFe_{(3nm)}/Cu_{(1.2nm)}]_{150}$ multilayers. It is evident that there was no layered structure detected. In many cases, only Cu was detectable. In some areas, however, Ni and Fe were also found. In those areas, the distribution of some nanoparticles is seen. Fig. 5 shows the energy dispersive spectra (EDS) microanalysis corresponding to the area indicated shown in Fig. 4. Peaks of Fe and Ni are clearly seen. Large peaks correspond to Cu.

The first attempt to ascribe the nonsaturating magnetoresistance behavior to the presence of SPM regions was performed for MBE grown Co/Cu multilayers [21; 22]. Beyond technical saturation of the magnetization at about H_s=1.7 kOe, the field dependence of both the magnetization M(H) and the magnetoresistance MR(H) has been described by the Langevin function $L(x)$ where $L(x)=\mu H/kT$, with µ constituting the average magnetic moment of an SPM region. The magnitude of µ is typically in the range of 100–1000μ_B, where μ_B is the Bohr magneton. In the simultaneous presence of both FM and SPM regions, the GMR can contain three contributions [16]: (i) $GMR_{SPM\text{-}SPM}$, (ii) $GMR_{FM\text{-}FM}$ and (iii) $GMR_{SPM\text{-}FM}$, where by a term $GMR_{A\text{-}B}$ means a spin dependent scattering event for an electron path “magnetic region A nonmagnetic region magnetic region B. Each of these three cases makes a completely different contribution to the field dependence of the magnetoresistance MR(H) since for an SPM particle, a large magnetic field (typically well in excess of 10 kOe) is needed to align its magnetic moment whereas the moment of a FM particle is aligned in a much smaller magnetic field, typically in a few kOe.

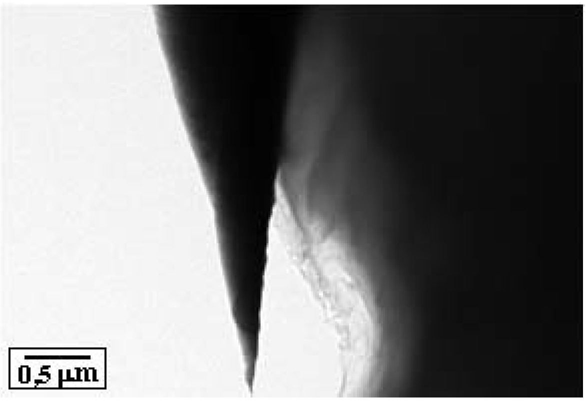


Fig. 2. General view of the sample after preparation by PIPS

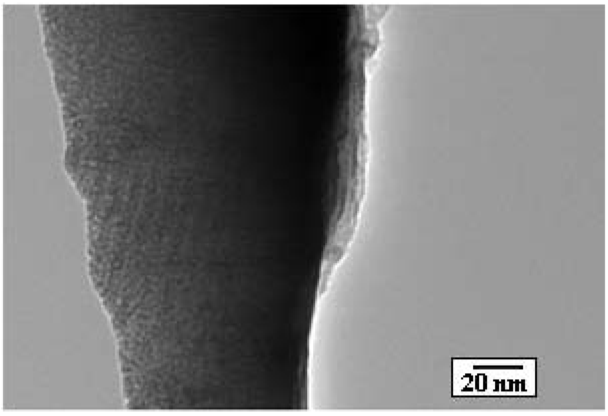
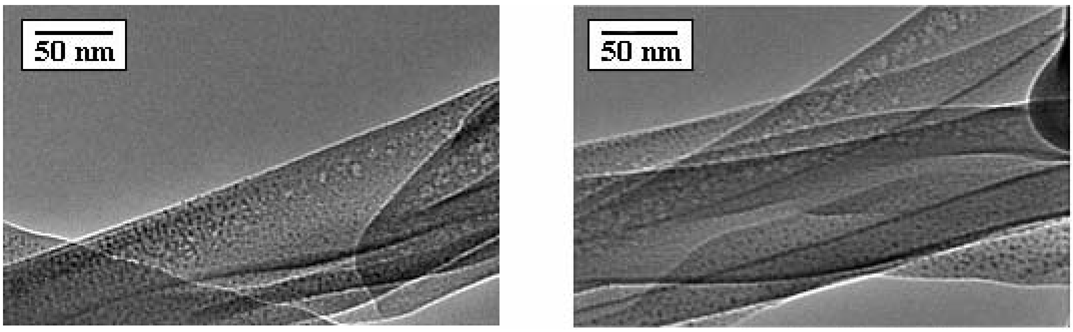


Fig. 3. The magnified area of the sample



a *b*

Fig. 4. Super-paramagetic (SPM) regions including the small islands of NiFe electrodeposited in the matrix of Cu

As seen in Fig. 4, an assembly of SPM particles is embedded in the copper matrix in a manner that there is a sufficient separation distance between the particles so that there in no magnetic interaction between their magnetic moments. A conduction electron just leaving a SPM entity is polarized by the magnetic moment of the particle. If this electron travels in the copper matrix and arrives at a neighboring SPM particle in a time shorter than its spin-memory time (i.e., it arrives with its original spin orientation), then at the second SPM particle it will undergo a spin-dependent scattering event since the orientations of the two SPM moments are uncorrelated. This spin-dependent scattering gives rise to a GMR contribution just as in the case of ferromagnetic/nonmagnetic multilayers when electrons travel via the nonmagnetic spacer between the two ferromagnetic layers of different magnetization orientations [19].

The three governing factors controlling the appearance of the SPM regions have been identified. These factors are discussed as follows. The improper choice of the deposition potential of the nonmagnetic metal, which can result in a significant increase of the GMR_{SPM} fraction [19]. In the case of immiscible elements such as Co and Cu, the tendency for the formation of SPM regions was found to be larger when the content of Cu in the magnetic layer increases [23].

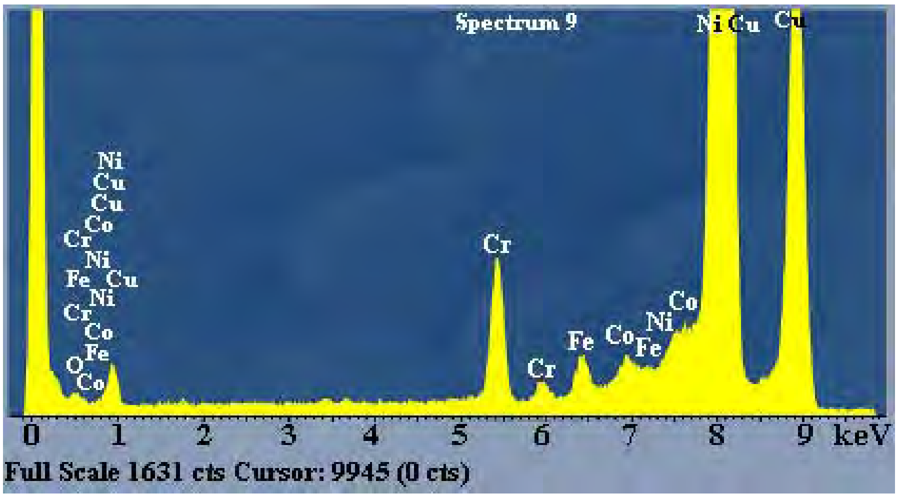


Fig. 5. A microanalysis (EDS spectra) corresponding to the area indicated in above image. Peaks of Fe and Ni are clearly seen. Large peaks correspond to Cu

A large GMR_{SPM} term may develop also for the sputtered Co/Cu multilayers deposited on rough Ta substrates (mechanically polished Ti foil) with respect to identical conditions on a smooth substrate (Si wafer with evaporated Ta or Cr adhesive and Cu seed layers) [24; 25].

The reason of the SPM character found in our samples could also be explained in Fig. 6 that 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 Cu 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 either the Cu deposition potential should be chosen to be more negative or the pulse length should be increased.

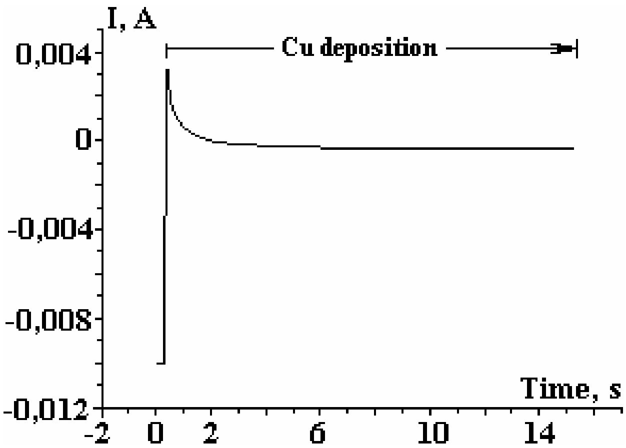


Fig. 6. Typical current-time response of one cycle during the pulse potential deposition.

4. Conclusions

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. In this research, for the first time, the presence of SPM regions in the electrodeposited NiFe/Cu multilayers was proved with the aid of high resolution transmission electron microscopy. The reason for that behavior was found to be the improper choice of the deposition potential. It is possible to improve the quality of layers and increase the thickness of magnetic layers in order to obtain higher magnetoresistances and eliminate the SPM regions.

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REFERENCES

1. Baibich M.N., Broto J.M., Fert A., Van Dau F.N., Petroff F., Etienne P. Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices. *Phys. Rev. Lett*. 1988, **61**, 2472–75.

2. Binasch G., Grunberg P., Saurenbach F., Zinn W. Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange. *Phys. Rev. B.* 1989, **39**, 4828–4830.

3. Liu Q.X., Péter L., Toth J., Kiss, L.F., Cziraki A., Bakonyi I. The role of nucleation in the evolution of giant magnetoresistance with layer thicknesses in electrodeposited Co-Cu/Cu multilayers. *J. Magn. Magn. Mater.* 2004, **280**, 60–74.

4. Toth J., Kiss L.F., Toth-Kadar E., Dinia A., Pierron-Bohnes V., Bakonyi I. Giant magnetoresistance and magnetic properties of electrodeposited $Ni_{81}Cu_{19}$/Cu multilayers. *J. Magn. Magn. Mater.* 1999, **198-199**, 243–245.

5. Alper M., Attenborough K., Hart R., Lane S.J., Younes C. Giant magnetoresistance in electrodeposited superlattices. *Appl. Phys. Lett.* 1993, **63,** 2144–6.

6. Nabiyouni G., Schwarzacher W., Rolik Z., Bakonyi I. Giant magnetoresistance in Ni-Co-Cu/Cu multilayers. *J.Magn. Magn. Mater.* 2002, **253**, 77–85.

7. Attenborough K., Hart R., Lane S.J., Alper M., Schwarzacher. W. Magnetoresistance n electrodeposited Ni-Fe-Cu/Cu multilayers. *J. Magn. Magn. Mater.*1995, **148**, 335–336.

8. Chassaing E., Nallet P., Trichet M.F. Electrodeposition of Cu/$Fe_{20}Ni_{80}$ multilayers. *J. Electrochem. Soc.* 1996, **143**, L 98–100.

9. Kakuno E.M., Da Silva R.C., Mattoso N., Schreiner W.H., Mosca D.H., Teixeira S.R. Giant magnetoresistance in electrodeposited $Co_{87}Fe_{13}$/Cu compositionally modulated alloys. *J Phys D: Appl. Phys.* 1999, **32**, 1209–13.

10. Huang Q., Young D.P., Chan J.Y., Jiang J., Podlaha Ej. Electrodeposition of FeCoNiCu/Cu compositionally modulated multilayers. *J. Electrochem. Soc.* 2002, **149**, C349–54.

11. Wu M., Abdul–Razzaq W. Spin-glass-like behavior in Cu/Ni multilayered films. *Phys. Rev. B.* 1990, **42**, 4590–3.

12. Vavassori P., Spizzo, F., Angeli E., Bisero D., Ronconi F. Evolution from multilayer to granular behavior via cobalt layers fragmentation in Co/Cu multilayers. *J. Magn. Magn. Mater.* 2003, **262**, 120–3.

13. Xu J., Howson M.A., Hickey B.J., Greig D., Veillet P., Kolb E. Giant magnetoresistance and superparamagnetism in Co/Au multilayers. *J. Magn. Magn. Mater.* 1996, **156**, 379–80.

14. Xu J., Howson M.A., Hickey Bj., Greig D., Kolb E., Veillet P. et al. Superparamagnetism and different growth mechanisms of Co/Au(1 1 1) and Co/Cu(1 1 1) multilayers grown by molecular-beam epitaxy. *Phys. Rev. B.* 1997, **55**, 416–22.

15. Tokarz A., Wolkenberg A., Przeslawski T. Magnetic properties of electrochemically deposited Ni/Cu superlattices. *J. Electrochem. Soc.* 2002, **149**, C607–9.

16. Bakonyi I., Péter L., Rolik Z., Kiss-Szab´ K., Kupay Z., Toth J. et al. Decomposition of the giant magnetoresistance of multilayers into ferromagnetic and superparamagnetic contributions. *Phys. Rev. B.* 2004, **70**, 054427/1–10.

17. Bakonyi I., Toth J., Kiss L.F., Toth-Kadar E., Péter L., Dinia A. Origin of GMR contributions in electrodeposited Ni–Cu/Cu multilayers. *J. Magn. Magn. Mater.* 2004, **269**, 156–67.

18. Péter L., Rolik Z., Kiss L.F., Toth J., Weihnacht V., Schneider C.M. et al. Temperature dependence of the giant magnetoresistance and magnetic properties in electrodeposited Co–Cu/Cu multilayers: the role of superparamagnetic regions. *Phys. Rev. B.* 2006, **73**, 174410/1–10.

19. Bakonyi I., Péter L. Electrodeposited multilayer films with giant magnetoresistance (GMR): Progress and problems, *Prog. in Mater. Sci.* 2010, **55-3**, 107–245.

20. Chang J.W., Romankiw L.T. Electrodeposited superlattices of CoFe/Cu and NiFe/Cu on n-type (111) Si single crystal wafers. *In: Romankiw LT, Herman Jr DA, editors. Magnetic materials, processes, and devices III. Pennington (NJ): The Electrochemical Society Proceedings Series **[PV 94-6]***. 1994, 223–32.

21. Barlett D., Tsui F., Glick D., Lauhon L., Mandrekar T., Uher C. et al. Langevin-like giant magnetoresistance in Co–Cu superlattices. *Phys. Rev. B.* 1994, **49**, 1521–4.

22. Clarke R., Barlett D., Tsui F., Chen Bx., Uher C. An alternate route to giant magnetoresistance in MBE-grown Co–Cu superlattices. *J. Appl. Phys.* 1994, **75**, 6174–7.

23. Liu Qx, Péter L, Padar J, Bakonyi I. Ferromagnetic and superparamagnetic contributions in the magnetoresistance of electrodeposited Co–Cu/Cu multilayers. *J. Electrochem. Soc.* 2005, **152**, C316–23.

24. Cziraki A, Péter L, Weihnacht V, Toth J, Simon E, Padar J., et al. Structure and giant magnetoresistance behaviour of Co–Cu/Cu multilayers electrodeposited under various deposition conditions. *J. Nanosc. Nanotechnol.* 2006, **6**, 2000–12.

25. Péter L, Weihnacht V, Tóth J, Padar J, Pogany L, Schneider C.M., et al. Influence of superparamagnetic regions on the giant magnetoresistance of electrodeposited Co–Cu/Cu multilayers. *J. Magn. Magn. Mater.* 2007, **312**, 258–65.

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Summary

The giant magnetoresistance of electrodeposited NiFe/Cu multilayers from a single bath under potentiostatic control is studied. The observed nonsaturating behavior urged us to investigate the probability of the occurrence of superparamagnetic regions in these multilayers. In this research, for the first time, the presence of super-paramagnetic regions in electrodeposited NiFe/Cu multilayers is shown and proved via high resolution transmission electron microscopy. The reason was found to be the existence of a very large anodic transient at the beginning of the copper deposition pulse, which could be eliminated by choosing a more negative potential.