ELECTRODEPOSITION OF NiFe/Cu MULTILAYERS FROM A SINGLE BATH

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Introduction

There are mainly two techniques used for electrodeposition of multilayers involving dual bath (DBT) and single bath (SBT). In the former technique, the substrate is successively transferred between separate plating baths and each layer is deposited alternately to laminate the sublayer from the relevant bath. This technique has been exploited by many researchers for deposition of various multilayers such as Co/Cu [1], Cu/Ni [2], Ni/Sn [3], Co/Pt [4, 5], and Co-Ni/Pt [4]. However, DBT has a disadvantage because it is susceptible to the formation of an oxide layer on the substrate during the transfer between baths. Such an oxide layer can deteriorate the quality of multilayers. In SBT, an electrolyte containing two or more metal ions may be used. A deposition of multilayers from a single bath is normally carried out by periodically varying the current density or the potential owing to the difference in reduction potential for metals in electrolyte. When using an electrolyte with optimum concentrations of metal ions, where the concentration of a noble metal ion in the electrolyte is much lower than that of a less noble one (e.g. noble metal ion/less noble metal ions=1:100), only the noble metal is deposited at a lower current density, while the less noble metal is deposited at a higher current density. It is possible to limit the amount of the noble metal in the electrodeposited film by mass transfer. The thickness of each layer is proportional to the current density and deposition time [6]. This technique has gained more popularity because it uses a simpler apparatus, lowers the possibility of contamination or oxidation, and is more efficient for plating layers of nanometric thickness where enhanced physical properties are often observed. The major disadvantage of this technique is that some more noble metal is co-deposited during the deposition of a less noble component and it is not possible to deposit a pure ferromagnetic layer from a single electrolyte [7]. However, if the concentration of the more noble metal in the electrolyte is very low and it is plated at the diffusion limiting current, an alloy layer rich in a less noble component is plated at high pulse. This technique has been effectively used to produce Cu/Ni [8], Cu/Co [9], Cu/Co–P [10], Cu/Ag [11] and Cr/Ni [12] multilayers. However, there is little information on electrodeposition of NiFe/Cu multilayers from a single bath. In 1990, Romankiw and Olsen electroplated laminated NiFe/Cu films from a single plating bath for inductive recording heads and magnetic shields[13]. Four years later, Chang and Romankiw electrodeposited superlattices of CoFe/Cu and NiFe/Cu on n-type (111) Si single crystal wafers [14]. In 1995, Attenborough et al. presented the results of the investigation of the GMR of electrodeposited FeNiCu/Cu multilayers prepared onto textured polycrystalline Cu (100) and single-crystalline Cu (100) substrates in the potentiostatic mode from a sulfate-based electrolyte composition [15] that was taken from Romankiw and Olsen [13], the outcome of the GMR in electrodeposited $[(FeNiCu)_{2nm}/Cu_{2.5nm}]_{200}$ multilayers being 1.4%. In 1996, a French group, Chassaing et al. [16] also investigated the GMR of electrodeposited FeNiCu/Cu multilayers prepared in the potentiostatic mode [16]. The ionic concentration ratios of the solution used were Fe^{2+}:Ni^{2+}:Cu^{2+} = 60:810:7. The MR(H) curves measured for $[(FeNiCu)_{3\ nm}/Cu_{1.5\ nm}]_{30}$ multilayers at 77 K were nearly linear for the LMR and the TMR components, both being negative, and did not show a sign of saturation up to the maximum magnetic field applied (2 kOe) where the GMR was about 1% [17].

In the present paper the authors discuss the method for the preparation of NiFe/Cu multilayer system deposited from a single bath using modulating potentials. Two solutions were made based on the early works of Chang [14] and Romankiw [13]. Those two solutions were compared and deposited multilayers were characterized. The advantages and disadvantages of each are presented below.

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Experimental

Electrodeposition was performed using an 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. Solutions ***A*** and ***B*** were prepared based on Chang [14] and Romankiw's [13] compositions, respectively (Table 1), with analytical-grade (Merck) reagents and distilled water. Electropolished copper foil substrates, (200) oriented, were used as cathodes, each with 2 cm^2 area. Electrodeposition was carried out in a standard three-electrode cell with a saturated calomel electrode (SCE) as the standard electrode. 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 saturated calomel electrode (SCE) placed as close as possible to the cathode surface so as to minimize the ohmic potential drop in the electrolyte. The computer controlled potentiostat switched between these two potentials. A Pt foil counter electrode was placed directly opposite the working electrode substrate.

Table 1. Electrolytes compositions (g/l)

Electrolyte	$NiSO_4$	$FeSO_4$	$CuSO_4$	Saccharin	Sodium potassium tartrate	Sodium Dodecyl Sulphate (SDS)
A	15	2.25	2.5	1	1	–
B	30.8	0.3	0.3	2	–	0.02

Sodium Dodecyl Sulfate (SDS) was used in electrolyte ***B***. It is an ionic surfactant and acts as a wetting agent. Saccharin was used in both electrolytes but in different amounts. It is reported to enhance deposit adhesion, reduce film stress, and to decrease grain size [18]. A magnetic stirrer of 250 rpm was used to agitate the plating baths and the effect of stirring was investigated.

Table 2 presents the electrodeposition (ED) time as well as the characterization methods used for each sample. In order to investigate the fluctuations in the thickness of the layers, thick multilayers were deposited from both solutions initially (referred to as specimens 1 and 4 in Table 2). These specimens were then studied and compared by SEM. Then, the time for electrodeposition was reduced and XRD patterns were taken and interpreted (specimens 2 and 5). Finally, the time suggested by other authors was taken into account and samples were thoroughly observed by XRD, atomic force microscopy (AFM) and additional high resolution transmission electron microscopy (HRTEM) micrographs (specimens 3 and 6).

Table 2. Characterization of specimens

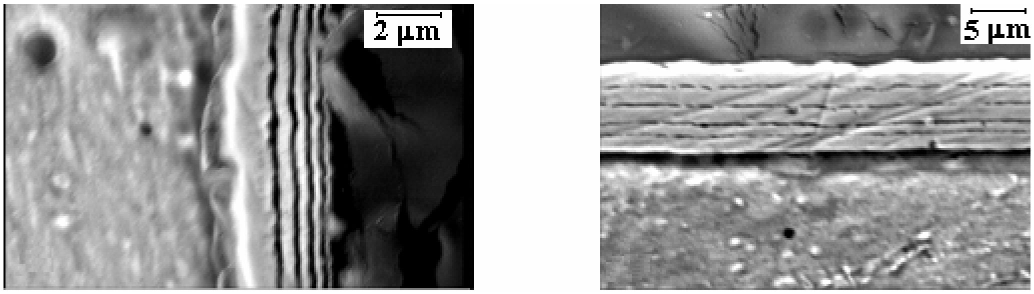
Specimen No.	Electrolyte	ED time for Cu	ED time for NiFe	No. of bilayers	Characterization techniques
1	***A***	200s	60s	5	SEM
2	***A***	30s	5s	30	XRD
3	***A***	0.2s	0.4s	300	XRD, TEM
4	***B***	200s	60s	5	SEM
5	***B***	90s	5s	5	XRD
6	***B***	150s	100s	5	AFM, TEM

XRD was carried out by means of the D8 Bruker instrument with a scan rate of 0.02 $°s^{-1}$ (Cu $K_{\alpha1}$ radiation, λ = 0.15405 nm). Morphological studies were carried out using an Oxford Instrument Stereoscan 120, SEM and HRTEM operating at the voltage of 200KeV (0.23resolution). Surface topology was taken with DME DS 95-50E AFM.

Results and discussion

SEM micrographs of specimens 1 and 4 are shown in Fig. 1. In each SEM image the brighter regions are Cu while the darker ones NiFe layers. Fig. 1,*a* shows the 5 bilayers electrodeposited from solution ***A*** vividly;

some roughness is seen, whereas the layers electrodeposited from solution ***B*** seem to be rather single-level and uniform. The thickness of the NiFe/Cu multilayers as estimated from the SEM observations was found to be approximately 840 nm/220 nm for specimen 1 and 1.54 μm/260 nm for specimen 4. This shows that using the same period of time, solution ***B*** results in thicker Cu layers.



a *b*

Fig. 1. SEM micrographs of (a) specimen 1 (b) specimen 4

The XRD patterns of samples 2, 3 and 5 are shown in Fig. 2. Small peaks are detected showing the existence of the NiFe layer grown with (111) and (200) texture for samples 2 and 5. In sample 5 the predominant texture of NiFe is (200) depicting a larger intensity.

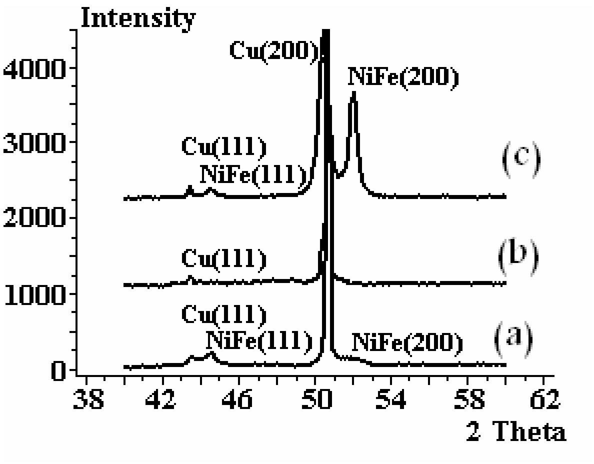


Fig. 2. XRD pattern of (a) specimen 2, (b) specimen 3, where no traces of NiFe are detected, and (c) specimen 5.

Decreasing deposition time to as low as 0.2s for the Cu layer and 0.4 s for the NiFe layer was supposed to yield layers of 2 nm thickness. However, as can be seen in Fig. 2,*b*, no NiFe layer was deposited. Although the substrate was covered with a silver-colored layer at the end of the electrodeposition, it seems that the underlayers either dissolved at each pulse or were not formed at all. This idea was confirmed by taking a TEM micrograph as shown in Fig. 3. The micrograph shows no deposited layers whatsoever. Only large grains of the copper foil substrate are seen. One problem with SBT is that the less noble component may dissolve when deposition of the more noble component starts, and this is one of the factors restricting the combinations of metals that can be electrodeposited as superlattices by this method.

Attenborough et al. calculated the nominal thickness of the layers using Faraday's equation assuming 100% efficiency [15]. After the experiment, they reported the efficiency of 50%, which demonstrates that the relationship is not reliable in this case.

Fig. 4 shows a typical cross-sectional TEM image obtained from specimen 6 comprising 10 repeats of alternating approximately 3 nm copper-rich layers (bright contrast bands) and 30 nm NiFe-rich (dark-contrast bands) $[Cu_{3nm}/NiFe_{30nm}]_{10}$ grown on a Cu(200) substrate under potentiostatic control. As seen from the image, a compositionally modulated Cu/NiFe multilayered structure was prepared. The growth and microstructure of the multilayers were dependent upon the deposition overpotential.

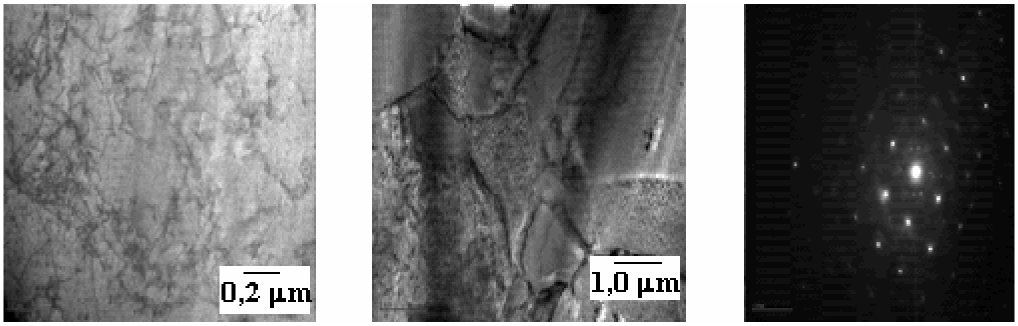


Fig. 3. TEM micrograph of specimen 3 showing no evidence of multilayers. Only the grains of the copper substrate are seen. The selected area diffraction (SAED) pattern shows the crystalline structure of copper

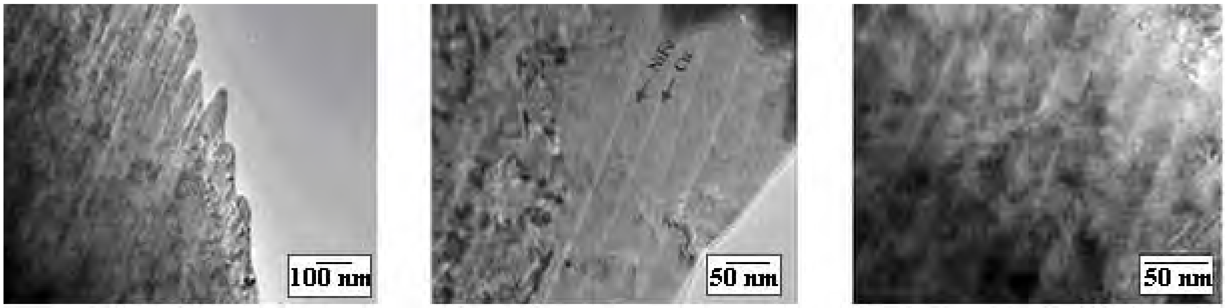


Fig. 4. TEM micrographs of specimen 6. Copper layers with approximately 3 nm and NiFe layers with 30 nm thicknesses are seen

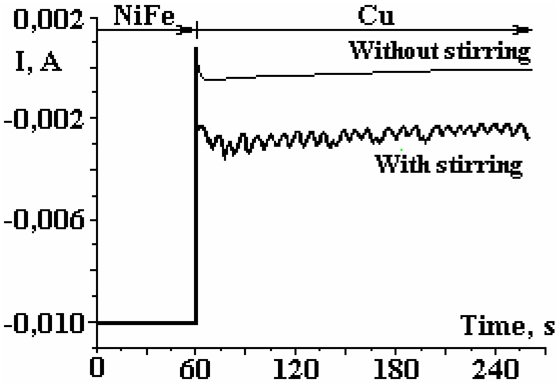


Fig. 5. Typical current-time response during the pulse potential deposition of sample 4 showing the effect of stirring during one cycle

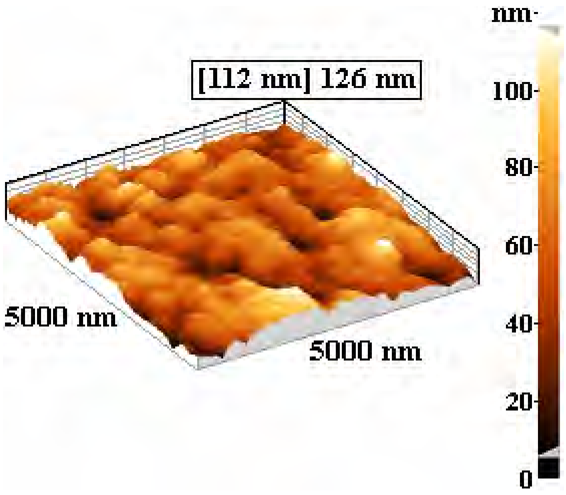


Fig. 6. The AFM micrograph of specimen 6

Fig. 5 shows the effect of stirring on sample 4 (refer to Table 2). Interestingly, stirring had no effect on NiFe deposition, but it increased the thickness of the copper layer, the latter proving to be diffusion controlled. In SBT, alternate layers of two metals are obtained by depositing the noble component, normally the nonmagnetic metal (Cu), at the diffusion limiting current and then plating the less noble component, normally the ferromagnetic metal (NiFe), under kinetic control. The current remained steady during NiFe deposition, while very small fluctuations occurred during copper deposition. The fluctuations were larger when stirring was applied.

The AFM micrograph of sample 6 is shown in Fig. 6, last layer being NiFe. A surface roughness rms (root mean square) of 18 nm is the major feature of this specimen, which indicates the existence of roughness in it. Much experimental work has been done to explain the role of interface roughness in GMR [19], but it is still not clear whether bulk or interface scattering process give the dominant contribution to the observed GMR. Apparently, both contributions are important but their relative role depends on such factors as quality of interfaces, amount of bulk scattering centers, compositions of multilayers and thickness of layers.

Conclusions

Thin multilayers of NiFe and Cu were successfully electrodeposited using a SBT in the potentiostatic mode. Electrodeposition from two different baths, ***A***, with ionic concentrations of Fe^{2+}:Ni^{2+}:Cu^{2+} 9:60:10, and ***B***, with ionic concentrations of 1:103:1, was compared and characterized. Results show that solution ***B*** is more promising, giving more uniform layers. TEM results confirmed that layers as thin as NiFe/Cu 3nm/30nm could be deposited by this solution, while XRD patterns pointed towards a predominant (200) texture for the NiFe layer and a (111) texture for the Cu layer. AFM micrographs displayed a roughness of 18 nm for this sample.

Applying stirring proved to aid the non-magnetic layer deposition making thicker layers, at the same time causing fluctuations in the applied current.

Measurement of the GMR of such layers by this method is a subject to be studied in future.

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REFERENCES

1. Jyoko Y., Kashiwabara S. and Hayashi Y., Characterization of electrodeposited Co/Cu ultrathin films and multilayers. *J. Magn. Magn. Mater*. 1997, **165**, 280–283.
2. Haseeb A.S.M.A, Celis J.P. and Roos J.R. Dual-Bath Electrodeposition of Cu/Ni Compositionally Modulated Multilayers. *J. Electrochem. Soc*. 1994, **141**, 230–237.
3. Wang W. and Singh R.N. Fatigue crack growth in Ni-Sn multilayered composite. *Mater. Sci. Eng*. 1998, **A251**, 184–191.
4. Jyoko Y., Kashiwabara S. and Hayashi Y. Preparation and characterization of electrodeposited Pt/Co Multilayers. *J. Magn. Magn. Mater*. 1996, **156**, 35–37.
5. Hayashi Y., Kashiwabara S. and Jyoko Y. Preparation and characterization of electrodeposited metallic multilayers. *Physica B*, 1997, **239**, 35–40.
6. Miyake T., Kume M. and Yamaguchi K. et. al. Electrodeposition of Cu/Ni–P multilayers by a single bath technique. *Thin Solid Films*. 2001, **397**, 83–89.
7. Dulal S. M. S. I., Charles E. A. and Roy S. Characterization of Co-Ni(Cu)/Cu multilayers deposited from a citrate electrolyte in a flow channel cell. *Electrochim. Acta*. 2004, **49**, 2041–049.
8. Lashmore D. S. and Dariel M. P., Electrodeposited Cu-Ni textured superlattices. *J. Electrochem. Soc*. 1988, **135**, 1218–1221.
9. Kasyutich O. I., Tochitskii T. A. and Fedosyuk V. M. Mechanism of structure formation of lowdimensional systems on the basis of electrodeposited Co-Cu films on Cu and Si substrates. *Phys. Stat. Sol. (a)*, 1997, **162**, 631–642.
10. Rivero G., Multigner M., Fraga E. et. al. Control of magnetic anisotropy in electrodeposited CoP/Cu multilayers. *IEEE Trans. Mag*. 1995, **31**, 4097–4099.
11. Tench D. and White J. New periodic displacement method applied to electrodeposition of Cu-Ag alloys. *J. Electrochem. Soc*. 1992, **139**, 443–446.
12. Rousseau A. and Benaben P. Single-bath electrodeposition of chromium-nickel compositionally modulated multilayers (CMM) from a trivalent chromium bath. *Plat. Surf. Fin*. 1999, **86**(9), 106–110.
13. Romankiw L. T. and Olsen J. D. Electroplated laminated Cu-NiFe films from a single plating bath for inductive recording heads and magnetic shield. *Proc. Symp. Magnetic Materials, Processes and Devices, Eds. L.T. Romankiw and D.A. Herman Jr*. 1990, **PV 90–8,** 339–345.

14. Chang J. W. and Romankiw L. T. Electrodeposited superlattices for CoFe/Cu and NiFe/Cu on n-type (111) Si single crystal wafers. *Elec. Soc. Proc. Ser*. 1994, **PV 94–6**, 223–232.
15. Attenborough K., Hart R., Lane S. J. et. al. Magnetoresistance in electrodeposited Ni-Fe-Cu/Cu multilayers. J. Magn. Magn. Mater. 1995, **148**, 335–336.
16. Chaissaing E., Nallet P.and Trichet M. F., Electrodeposition of Cu/Fe20Ni80 magnetic multilayers. *J. Elec. Soc.* 1996, **143**, L98–L100.
17. Bakonyi I. and Peter L. Electrodeposited multilayer films with giant magnetoresistance (GMR): Progress and problems. *Prog. in Mater. Sci*. 2010, **55–3**, 107–245.
18. Sam S.et al. Electrodeposition of NiFe films on Si(100) substrate. *Surf. Sci*. 2007, **601**, 4270–4273.
19. Neamtu J., Volmer M. and Coraci A. Magnetoresistive properties and microstructure of NiFe thin films and NiFe(t)/Cu(s)/NiFe(t) multilayer films. *Thin Solid Films*. 1999, **343–344**, 218–221.

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Summary

NiFe/Cu multilayers were deposited from a single bath in the potentiostatic mode using two different solutions. In solution ***A***, the ionic concentration ratios were Fe^{2+}:Ni^{2+}:Cu^{2+} 9:60:10 and in solution ***B*** they were 1:103:1. To characterize the layers, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and atomic force microscopy (AFM) were used. SEM results revealed the layered structure of the deposits for relatively thick bilayers. While HRTEM provided direct evidence for the composition modulation across successive layers in the NiFe/Cu nanometer-multilayered structure prepared from solution ***B***. Therefore, the layers prepared from solution ***B*** seemed to be more appropriate for giant magnetoresistance (GMR) applications. The effect of stirring during the electrodeposition process of the multilayers was also investigated.