ELECTRODEPOSITION OF METALLIC MULTILAYERS BY A PULSE METHOD

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ABSTRACT

Metallic magnetic and non-magnetic thin films have been produced by the pulse potential method using a single bath. Electrodeposition conditions were studied in order to produce Ni₈₀-Fe₂₀/Cu multilayers. It was found that the addition of a surfactant – Sodium Dedocyl Sulfate – prevents the formation of pinholes in the deposit and reduces its roughness.

INTRODUCTION

The discovery of the giant magnetoresistance (GMR) effect in Fe/Cr /1/ superlattices has stimulated much research into magnetic and non-magnetic multilayers. The electrodeposition method, which was developed by Yahalom and Zadok /2/ is a more straightforward method of obtaining multilayers than physical techniques, such as sputtering.

For electrodeposited Ni-Co-Cu/Cu multilayers a GMR of up to 20% in 8K_{Oe} was observed /3/, but the required fields are too large for most technical applications. It is therefore considered that electrodeposition of multilayer systems consisting of a soft ferromagnetic material with Cu spacer layers is of interest. Permalloy (Ni₈₀-Fe₂₀) is an obvious choice as it is already used in magnetic recording applications due to its zero magnetostriction and near-zero magnetocrystalline anisotropy.

The object of the present study is to produce Ni₈₀-Fe₂₀/Cu multilayers by electrodeposition.

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EXPERIMENTAL

The electrochemical apparatus used for the deposition included an EG&G (PARC) model 273 potentiostat-galvanostat with an EG&G (PARC) model 616 RDE Electrode Rotator. A Pyrex glass cell with a standard three electrode configuration was used: a platinum wire as a counter electrode and a saturated calomel reference electrode, which was positioned as close as possible to the working-rotating electrode. The electrodeposition experiments were conducted on the polished end of copper rods with an exposed surface area of 0.3 cm².

RESULTS

Preliminary experiments were conducted to find a suitable solution for the deposition of Ni and Fe. According to Horkans /4/, the Ni-Fe system exhibits a phenomenon of anomalous codeposition. It was found that in most electrodeposition conditions the Fe⁺² ions, which are the less noble component, inhibit the reduction of the Ni⁺² ions. Thus, the concentration ratio of Ni⁺² to Fe⁺² ions in the electrolyte has to be much higher than the ratio required in the multilayered system. Different baths solutions of Ni-Fe electrolytes were tested (Table 1).

Table 1

A list of tested bath compositions for the electrodeposition of Ni-Fe

Solution	A [M]	B [M]	C [M]	D [M]	E [M]
FeSO ₄ ·7H ₂ O	1.75	1.08	0.06	0.17	---
NiSO ₄ ·6H ₂ O	0.38	0.38	0.81	2.3	0.81
FeCl ₂ ·4H ₂ O	0.21	0.21	---	---	---
(NH ₄) ₂ FeSO ₄ ·6H ₂ O	---	---	---	---	0.06
H ₃ BO ₃	0.49	0.49	0.24	0.5	0.24
(NH ₄) ₂ SO ₄	0.45	0.45	---	---	---
C ₆ H ₈ O ₆	---	---	0.05	0.16	0.05

In all solutions the pH was set between 2-3.

The solution that produced the best results was solution C, which is a sulfate electrolyte, based on the electrolyte used by Chassaing *et al.* /5/

The composition ratio in the Ni-Fe film was checked at several potentials from -1 to -1.8V (SCE), and a Ni-Fe film with a composition ratio of 4:1 was obtained at -1.7V (SCE).

Keeping the concentration of copper ions at the lowest possible level is required to limit the amount of copper in the Fe-Ni alloy. A good deposit of copper was achieved with a minimum concentration of 0.007M of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The pulse potential for copper was determined from the potentiodynamic curve (Fig. 1) and was chosen to be -500mV (SCE), while the optimum rotation speed of working electrode was set at 500 rpm .

Multilayers of Cu/ Ni80-Fe20 were prepared with the addition of several surfactants in order to minimize the co-discharge of hydrogen with the transition metals Fe-Ni and to cause detachment of the hydrogen bubbles from the deposit. The discharge of hydrogen bubbles may cause pinholes in the deposit, which can, in turn, reduce the GMR effect. The surfactants used were formic acid, cumarin, Triton X-100, saccharine, glucose, glycerol and sodium dedocyl sulfate (SDS).

The electrodeposition conditions are presented in Fig. 2.

The composition ratio of the deposited Fe-Ni alloy was determined by Energy Dispersive X-ray Spectroscopy (EDS), conducted on a JEOL scanning electron microscope (SEM). The ratio of Ni to Fe in the deposit was 4:1.

Fig. 1: Potentiodynamic curves of Solution C with and without stirring

Fig. 2: Schematic representation of the square-wave pulse for the electrodeposition of Cu/Ni-Fe multilayers

The influence of the surfactants on the deposit was checked using a Leo 982 high-resolution scanning electron microscope (HRSEM). Without the addition of surfactant the copper layer was almost hole-free, the size of the grains was about 50 nm, and the surface was rough. The layer of Fe-Ni alloy was similar in its morphology to the copper layer, but it contained 50-100 nm holes (Fig. 3a). The addition of 1g/l formic acid or 1.3 g/l Triton X-100 or 0.3 g/l saccharine did not help in avoiding the holes formation, but worsened the quality of the deposit.

a) Without surfactant

b) With the addition of:
Sodium Dodecyl Sulfate.

Fig. 3: HRSEM micrograph of electrodeposited Ni-Fe layer (top view)

The addition of 1g/l glucose resulted in less rough deposit, which contained however many more holes. With the addition of 1g/l glycerol the surface was smoother with smaller holes. The addition of 0.7g/l cumarin worsened the deposit, causing it to be less uniform, with many non-plated islands, although it was less rough.

The addition of sodium dedocyl sulfate (Fig.3b) produced the best results. The deposit was fine-grained, with no holes, although it was still somewhat rough. Thus, the addition of SDS seems desirable, but the interface of the layers and the magnetic properties are yet to be examined.

Samples of cross-section layers [Ni80-Fe20/Cu] were examined by HRSEM. The structure of layers as seen in the cross-section sample is presented in Fig. 4.

Fig. 4: HRSEM micrograph electrodeposited Cu/Ni-Fe multilayer (cross section specimen-showing the layering)

CONCLUSIONS

A modulated structure of Cu/Ni-Fe can be achieved by using the pulse potential method. The addition of Sodium Dedocyl Sulfate (SDS) prevents the formation of holes within the layers and reduces roughness of the deposit. An additional examination is underway on the influence of the surfactant on the magnitude of the magnetoresistance, as well as on the relative influence of pinholes in the deposit and the presence of a surfactant on the magnetic properties. These will be reported separately.

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