Influence of organic additives on the interface width of electrodeposited cu-co multilayers

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Cu-Co nanometric multilayers are one of the most promising giant magnetoresistive systems [1]. In this work, their electrodeposition was investigated in the presence of two additives: sodium dodecyl sulfate (SDS), a surfactant often used as an anti-pitting agent and saccharin, a first class brightener, which also decreases the internal stress. The influence of additives on the properties of the multilayers remains unclear [2, 3]. They have been shown to improve the morphology of the layers. However, they have a marked effect on cobalt discharge and they markedly decrease the giant magnetoresistance (GMR) of these multilayers [4, 5].

Aiming at a better understanding of the effects of the additives and of the electrolyte pH, cross sections of the multilayers were examined by TEM and the interface properties were characterized using Fresnel fringe techniques.

EXPERIMENTAL

Cu-Co multilayers were electrodeposited on electropolished copper plates by means of potential pulse technique using a single electrolyte. The experimental conditions have already been described [6]. Table 1 summarizes the electrolyte compositions. The electrolytes contain 0.71M CoSO₄, 0.19M CoCl₂, 6.4 10^{-3} M CuSO₄, 0.65M H₃BO₃, 0.34M NaCl. 2g/L saccharin was added in electrolytes 3 and 5 and 0.2 g/L of SDS in electrolytes 4 and 5.

Defocussed TEM images display Fresnel fringes when there is an abrupt change of local electric potential, e.g. at an interface. The interface widths are determined by comparing the Fresnel fringe profiles obtained from images at various defocus values between \pm 1500nm with simulations of the same fringes in which the width is a parameter [6,7] The separate contributions of roughness and chemical interdiffusion to this width can also be estimated by analysing the waviness of the fringes [8].

RESULTS AND DISCUSSION

The cross section of multilayers deposited from solution 1 (without additive) exemplifies the regularity of the layers (Figure 1). The results of the Fresnel fringe analysis are included in the table.

The interface width is smaller for layers deposited at pH 3 than at pH 1.6; it is also smaller for layers deposited in the presence of saccharin than in additive-free solutions. In contrast, the roughness is increased in the presence of saccharin. SDS does not have a marked effect on the interface width or roughness.

The TEM data are compared with previous GMR results obtained for multilayers deposited on ITO glass (Table 1). It is usually expected that the GMR ratio is the highest for the sharpest interface. In the present work, we observed the opposite tendency. Two parasitic features may have a negative influence on the multilayer qualities: hydrogen evolution and the chemical displacement of cobalt by cupric ions during the potential reversal [3,4]. It has been shown that saccharin improves the planarity of

the layers at the micrometer scale and leads to less displacement of cobalt by copper [3,4]. This feature might explain the decrease in the interface width in the presence of saccharin. However the increased roughness may be detrimental for the GMR. The effect of SDS is mainly microscopic, though it may promote chemical displacement [2, 3]. An increase in pH improves the interface quality, though it is known that it reduces the GMR [9]. However, a low pH favors an fcc structure and hence enhances pseudo-epitaxial growth.

This work underlines the complex relationship between the interface structure and the GMR properties of electrodeposited multilayers.

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<u>Table 1</u>: Electrolytes, interface width, roughness and interdiffusion (nm), parallel magnetoresistance ratio at 77 and 4.2K for $[Cu(4.5nm) / Co(1nm)]_{20}$ deposited on ITO glass

	0.1.1	0.10	0.10	0.14	0.17
	Sol 1	Sol 2	Sol 3	Sol 4	Sol 5
Electro-	No add	No add	Sacch.	SDS	Sacch+SDS
lyte	pH 1.6	pH 3.0	pH 1.6	pH 1.6	pH 1.6
Width	1.00	$0.50 \pm$	0.70 \pm	$1.00 \pm$	$0.57 \pm$
	±0.10	0.15	0.20	0.20	0.20
Rough-	0.45 ± 0.18	0.46±0.19	0.75±0.3	0.52 ± 0.21	0.64 ± 0.20
ness					
Interdif-	0.90 ± 0.10	0.20±0.19	0.36±0.31	0.85±0.21	0.31±0.28
fusion					
GMR (%)	15	3	5	4	6
77 K					
GMR (%)	25	6			9
4.2 K					

Figure 1: Cross sction of multilayers deposited without additive at pH 1.6 with an overfocus of 1500 nm. The white and dark fringes correspond to the Co and Cu layers respectively. In insert: shape of a Fresnel fringe.

