

Preparation of CoAg electrodeposited films

B. Dacuña^{a,*}, J. Mira^b, M.C. Blanco^a, M.A. López-Quintela^a, J. Rivas^b

^aDepto. Química-Física, Universidade de Santiago, 15706 Santiago de Compostela, Spain

^bDepto. Física Aplicada, Universidade de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Abstract

We have synthesized CoAg alloys using pulse electrodeposition. The effect of width and frequency of the pulse in the Co/Ag ratio has been studied. We find that a constant duty-cycle value leads to a fixed Co/Ag ratio of the films. We focus on Co₂₀Ag₈₀ samples obtained at different frequencies, maintaining a constant duty-cycle value, and observe that in spite of the unaltered stoichiometry, different pulse conditions alter significantly the magnetic properties of the annealed films. © 1999 Elsevier Science B.V. All rights reserved.

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Since the pioneering work of Baibich et al. [1], discovering a giant magnetoresistive effect (GMR) in anti-ferromagnetically coupled multilayers, many researchers focused their attention on the phenomenon. Subsequent advances covered many branches of the subject, from a theoretical to a synthesis point of view. In the latter case, one significative milestone is the obtaining of appreciable MR in sputtered heterogeneous Cu–Co and Ag–Co alloys [2,3]. More recently, electrodeposition has appeared as an alternative way for the fabrication of similar materials [4,5], due to the simplicity and low cost of the method. Many of the initial works dealt with the optimum proportions of the involved metals in order to obtain the maximum MR. Nevertheless, mass proportion between components does not play the only role in the resulting magnetic properties. In this paper we synthesize Co_xAg_{1-x} alloys (x = mass percentage) using pulse electrodeposition and study the effect of width and frequency of the voltage pulse on the structural and magnetic properties of the resulting films.

A scanning Potentiostat model 326 EG&G as the potential controller, connected to a Gould 20 MHz Digital Storage Type 1425 oscilloscope was used and the whole set was controlled by a computer. For pulse depos-

ition experiments a 20 Hz pulse generator HM 8035 and an Al rotating disk electrode (as working electrode) and an Ag/AgCl saturated electrode (as reference electrode) were employed. All pulsed experiments were carried out at 600 rpm to avoid the H₂ bubbles from being generated. For the measurement of the mass percentages a Perkin–Elmer 3110 atomic spectrophotometer was used. Magnetic measurements were taken with a DMS-1660 vibrating sample magnetometer. The electrolyte composition was as follows: 6, 40, 25, 0.0528 and 40 g/l of H₃BO₃, ammonium citrate (dibasic), magnesium sulfate, silver sulfate and cobalt sulfate, respectively. Also, 1 g/l of coumarine was added to the solution in order to avoid dendritic deposition [6].

By means of voltametric studies it was seen that the cobalt deposition process is irreversible, and quasiirreversible for silver [7]. The cobalt deposition does not appear to be controlled by diffusion, which could be expected because cobalt is in high concentrations and is not complexed. The silver tends to follow a dendritic growth, no nucleation occurs. In order to avoid the silver dendritic deposition we have employed pulsed current instead of DC deposition. Also, as commented before, organic molecules such as coumarine or complexant agents as citrate are introduced in order to hinder the reaction by molecules adsorbed on the electrode surface [8], in such a way smooth deposits are expected. We varied frequency and width of the pulse and observed

*Corresponding author. Fax: + 34-981-520676.

E-mail address: uscqfbdm@ds.cesga.es (B. Dacuña)

their effect on the mass ratio of the deposits. In Fig. 1a and Fig. 1b we observe how the increase of both pulse width and frequency increases the Co/Ag ratio. It is consistent because upon enlarging pulse width and frequency, the consumption of Ag ions (minority in the solution) at the interface is enhanced. Ag consumption is done by diffusion, therefore, by diminishing the diffusion layer width we will have an increase of the Ag/Co ratio. We have found that, if a constant duty-cycle value (product of width and frequency, i.e., the net ‘on’ time of applied voltage is the same) is fixed, we have a constant Co/Ag ratio (Fig. 1c). This implies that we have a tool to investigate if different atomic arrangements alter the magnetic properties of the materials at a given $\text{Co}_x\text{Ag}_{1-x}$ composition.

We have chosen $\text{Co}_{20}\text{Ag}_{80}$, which gives the maximum MR for this system [9,10], and synthesized samples at frequencies of 13.5, 135, 1350, 13 500 and 135 000 Hz, maintaining a fixed duty-cycle value of 27. These samples have been submitted to thermal annealings between 200 and 600°C. X-ray diffraction patterns correspond to Ag (Co is immersed in the Ag matrix and cannot be detected). We obtain Ag crystalline sizes applying Debye-Scherrer’s formula to peak widths. They are presented in

Fig. 2, where we see that, for low annealing temperatures, the size of Ag crystallites is larger for higher frequencies. For low-frequencies amorphicity persists until a certain activation temperature is reached, then an almost exponential thermal activated growth takes place. It indicates that a wider pulse (which means also a longer ‘off’ time between pulses) favors a deeper stabilization of the amorphous structure. The exploration of the Co structure can be made indirectly by magnetic measurements. From magnetic hysteresis loops between ± 10 kOe we see that coercive fields and quadrature (ratio of remanent magnetization, M_r , and maximum magnetization, M_s) reach a maximum for lower annealing temperatures for films synthesized under low pulse frequencies (Fig. 3). We interpret this result as a mark of the slower nucleation of Co cores for higher frequencies, that acts by dispersing more Co atoms within the Ag matrix (the ‘off’ time between pulses is reduced and cobalt ions have no time to

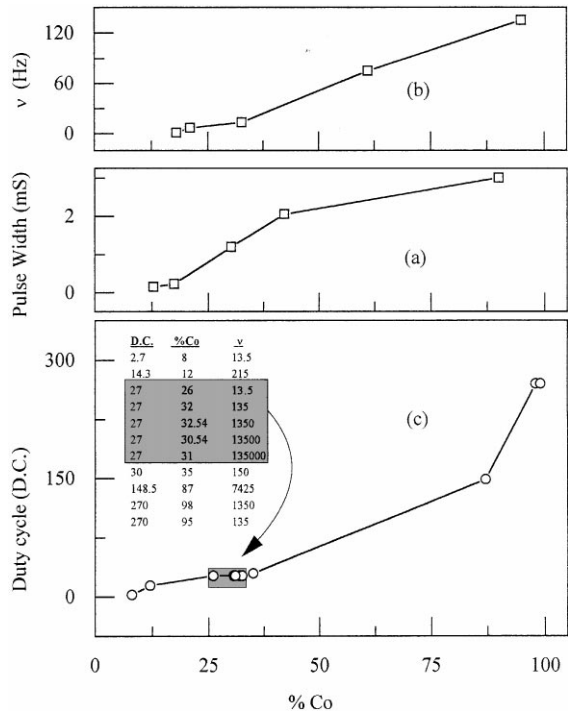


Fig. 1. Cobalt mass percentage of the deposits versus (a) pulse frequency, (b) pulse width and (c) duty-cycle value. The shadow marks the working zone, where it can be seen that, despite the important frequency variations, the Co percentage remains almost unaltered.

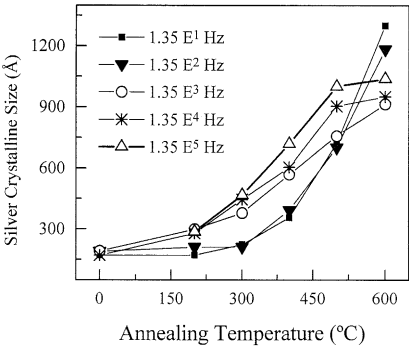


Fig. 2. Size of Ag crystallites in the studied films (duty-cycle value = 27).

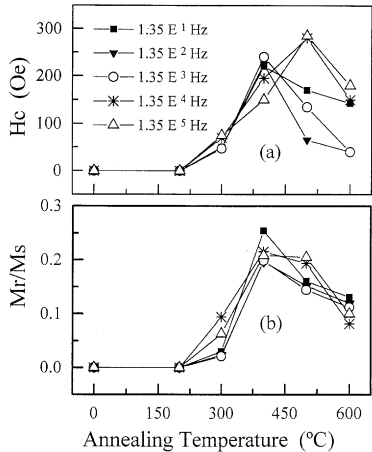


Fig. 3. (a) Coercive fields and (b) quadrature (M_r/M_s) versus annealing temperature for the synthesized films (duty-cycle value = 27).

accommodate in the structure, therefore migration of Co when annealing is more difficult). The growth of the Co cores continues until a point at which a magnetic single domain structure cannot be retained and a multidomain one sets up, reducing quadrature and coercivity; analogously to what happens in the same system synthesized by microemulsion routes [11].

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