Insitu magnetization measurements of Cu/Co multilayers during the process of electrodeposition

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The electrocrystallization of Cu–Co multilayers has been investigated by means of *in situ* magnetization measurements, during the electrodeposition, using an electrochemical alternating gradient magnetometer. The hysteresis loops were also recorded *in situ*. This allowed us to measure a magnetization efficiency, ratio of the magnetization increase to the electrical charge used. This efficiency tends to decrease as the number of bilayers increases, probably as a result of the increase in the roughness of the surface. It exhibits the same dependency on cobalt plating time as the Faradaic efficiency, which confirms that at the beginning of cobalt deposition, hydrogen evolution is the main reaction. The multilayers exhibit a typical ferromagnetic behavior. The magnetization increases and the coercive field decreases when the number of bilayers and/or the thickness of the cobalt layer increase. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1413233]

I. INTRODUCTION

Cu–Co nanometric multilayers constitute one of the most promising giant magnetoresistive systems.[1] Using the single-electrolyte technique and the potential pulse method Cu–Co multilayers have been electrodeposited on indium–tin–oxide (ITO) glass.[2,3] High magnetization and large magnetoresistance ratio were obtained.[3] However, for low cobalt thickness, the Cu–Co multilayers seem to behave more like granular alloys than continuous layers. Some superparamagnetism always seems to be present, even for thick cobalt layers, which might indicate the presence of isolated cobalt particles.[4] The magnetization is usually smaller than expected with regard to the mass of deposited cobalt.

It is well known that electrodeposited layers are less perfect than layers grown by MBE or sputtering: the purity is inferior, especially because of the incorporation of hydrogen which is codeposited during cobalt discharge. The presence of pinholes may also decrease the continuity of the layers. In addition, layers grown on ITO glass have a (111) preferred orientation which is considered to induce stacking faults and reduce the magnetotransport.[5] Roughness may develop as a result of substrate roughness (especially on ITO) or as a result of electrocrystallization conditions.

The goal of the present work was a better understanding of the growth of the layers. The electrocrystallization was characterized using *in situ* magnetization measurements during the deposition.

II. EXPERIMENTAL PROCEDURE

We used a single electrolyte containing the salts of the two metals to be deposited. The working conditions have been already described elsewhere.[2,3] The electrolyte contains a low concentration of copper sulfate and large amounts of cobalt salts (0.71 M $CoSO_4$, $7H_2O$; 0.19 M $CoCl_2$, $6H_2O$; 6.410^{-3} M $CuSO_4$, $5H_2O$; 0.34 M NaCl; 0.65 M H_3BO_3). The *p*H was adjusted to 1.7 by adding dilute sulfuric acid. The solutions were deaerated prior to each experiment, the temperature was kept at 30 °C. A mercurous sulfate electrode (MSE) was used as a reference. The counter electrode was a platinum wire. The working electrodes were gold foils (100 μm thick). Some experiments were also carried out on ITO glass plates. We used the potential pulse technique monitored using a personal computer with the HPVEE package. The pulse potentials E_{Cu} and E_{Co} were chosen so as to achieve the usual current densities: $E_{Cu} = -800$ mV/MSE ($i_{Cu} = 200$ μA cm^{-2}), $E_{Co} = -1350$ mV/MSE ($i_{Co} = 20$ mA cm^{-2}).[3]

In situ magnetization measurements were performed during the electrodeposition and the hysteresis loops were recorded *in situ* after different deposition time intervals. The layers were dissolved and new samples were deposited several times. We used an electrochemical alternating gradient magnetometer developed at the LAM.[6] A small electrolytic cell was placed in the pole piece gap of the magnet and connected to the electrochemical setup and to the magnetic measurement sensor.[6] A field of 500 Oe, i.e., larger than the coercive field of the layers, can be applied during the deposition, either perpendicular or parallel to the layers. A small coil provides a weak alternating field for the measurement of the magnetization, which was recorded *in situ* during the

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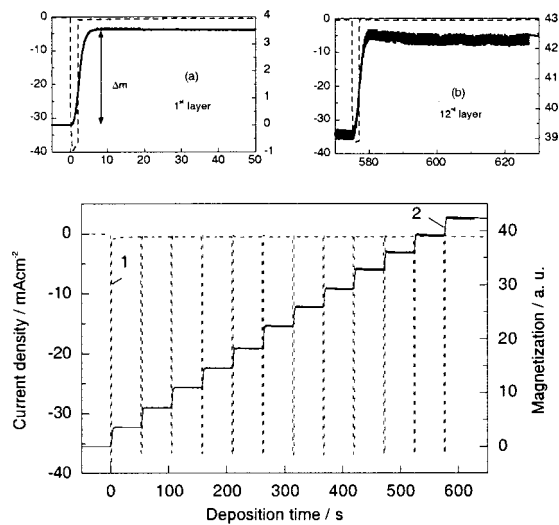
FIG. 1. Current density (curve 1) and magnetization responses (curve 2) during the potential pulse deposition of 12 [Co/Cu] bilayers, respectively, at $E_{Co} = -1.35$ V/MSE and $E_{Cu} = -0.80$ V/MSE. (Co thickness: 13 nm, copper thickness: 11 nm): (a) enhancement of the first cycle; and (b) enhancement of the 12th cycle.

deposition. The substrates were stuck on a glass support and connected to a potentiostat/wave generator and a piezoelectric sensor for the magnetic measurements.

We investigated the influence of the number of bilayers, the effect of the cobalt deposition time, starting either with cobalt or with copper, and the influence of the substrate type (either a gold foil or ITO glass).

III. RESULTS

Figure 1 shows an example of current density and magnetization responses recorded, with the magnetic field parallel to the layers, during the pulse deposition of a Co–Cu multilayer (12 bilayers) on a gold substrate. The individual thicknesses were 11 nm for copper and 13 nm for cobalt. The magnetization (curve 2) increases during cobalt deposition. Due to the integration time necessary for magnetization measurement, it is very difficult to observe whether any cobalt dissolution occurs when the potential is switched from E_{Co} to E_{Cu}. Such dissolution may result from the chemical displacement of cobalt by the cupric ions, according to the reaction: $Co + Cu^{2+} \rightarrow Co^{2+} + Cu$. This phenomenon has been shown to occur for Cu–Co and Cu–Ni layers pulse plated in galvanostatic conditions.[7,8] In our case we applied potential pulses, so the displacement is probably less important than in galvanostatic conditions. As shown in Fig. 1(a), no decrease in the magnetization is observed when the potential is reversed from E_{Co} to E_{Cu}, for the first few pulses. After deposition of a large number of layers, a decrease in the magnetization was sometimes observed during the pulse at E_{Cu} [Fig. 1(b)].

For each potential step we measured the relative increase Δm in the magnetization. It was labeled in arbitrary units since the magnetometer was not calibrated. To compare the different experiments, the increase Δm was divided by the electrical charge Q_{Co} used for the deposition of cobalt during the pulse at E_{Co}. This ratio can be considered as the

magnetization efficiency by analogy with the Faradaic efficiency, though it is not a dimensionless number. Figure 2 shows that, although some scatter exists in the data, this ratio $\Delta m/Q_{Co}$ increases from the first layer to the second and then it tends to decrease. The decrease is probably related to the enhancement in roughness, which is observed when the number of layers increases.[4]

Examples of hysteresis loops recorded *in situ* for various numbers of layers deposited on ITO glass are shown in Fig. 3. They exhibit a typical ferromagnetic behavior. The saturation magnetization M_s was measured at 3 kOe. The squareness of the hysteresis loops was estimated by the ratio of M_r, the remanent magnetization to M_s. The coercive field H_c was also measured. Figure 4 shows that, whatever the substrate, gold (curve 1) or ITO (curve 2), both the squareness of the loops [Fig. 4(a)] and the coercive field [Fig. 4(b)] decrease when the number of layers increases. This may be related to the increase in the grain size. The inferior square-
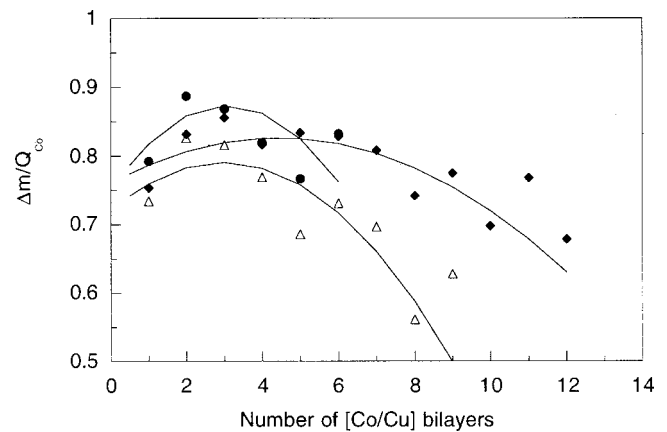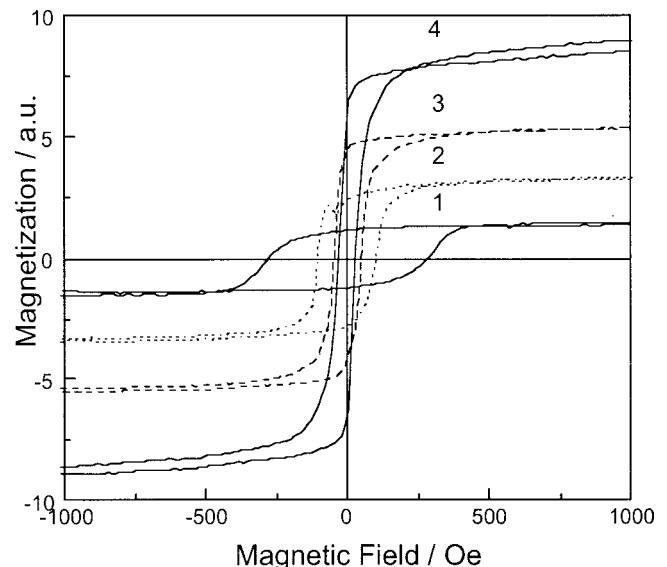

FIG. 2. Examples of the $\Delta m/Q_{Co}$, ratio of the magnetization increase divided by the electrical charge used, as a function of the number of [Co(13 nm)/Cu(11 nm)] bilayers.

FIG. 3. Hysteresis loops recorded *in situ* after the deposition of the [Co(13 nm)/Cu(11 nm)] for various numbers n of bilayers (substrate ITO glass). (1) $n=1$, (2) $n=2$, (3) $n=3$, and (4) $n=6$.
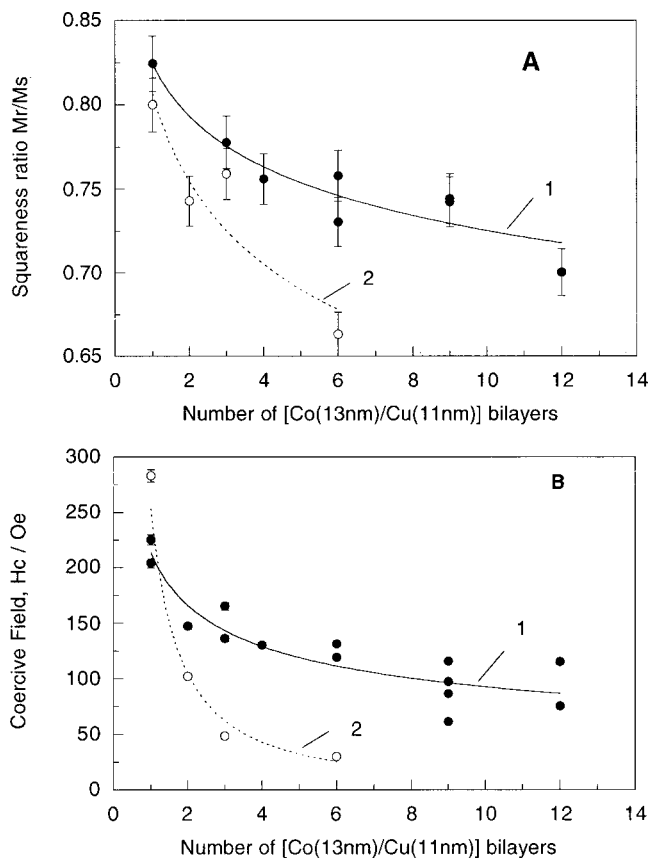
FIG. 4. Squareness ratio M_r/M_s (A) and coercive field, H_c (B) as a function of the number of [Co(13 nm)/Cu(11 nm)] bilayers: Curves (1) gold foil substrate; curves (2) ITO glass substrate.

ness observed when the layers are deposited on ITO glass may be due to the higher roughness of this substrate. Indeed ITO glass has a rather rough surface with some irregularities (1.5–3 nm Ra). When one bilayer is deposited, the roughness increases slightly (4 nm). For 20 bilayers the roughness increases markedly up to 10–20 nm.[4,9]

We also investigated the influence of the nature of the first layer, cobalt, or copper. The squareness M_r/M_s of the multilayers is larger when the first deposited layer is cobalt (Table I). The effect on the coercive field is less pronounced. According to AFM and SEM observations, the roughness of the films is larger when copper is the first layer; this is because copper is discharged under diffusion control which favors rough or dendritic growth, whereas cobalt is deposited under activation control which leads to smoother layers.[4,9]

TABLE I. Squareness ratio M_r/M_s and coercive field H_c for one and three bilayers of [Co(13 nm)/Cu(11 nm)] deposited on a gold foil or on ITO glass, starting either with cobalt or copper.

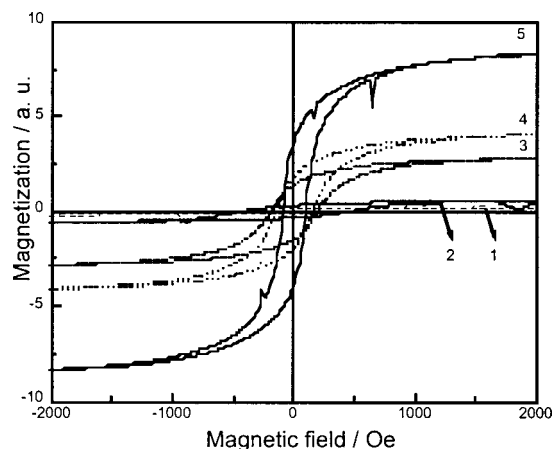|	M_r/M_s			H_c (Oe)		
	(Co 1st)	(Cu 1st)	(Co 1st)	(Co 1st)	(Cu 1st)	(Co 1st)
Number of bilayers	Au foil		ITO glass	Au foil		ITO glass
1	0.81	0.74	0.80	205	265	280
3	0.73	0.65	0.76	165	155	50

FIG. 5. Examples of hysteresis loops recorded *in situ* after the deposition of the [Cu(11 nm)/Co] bilayers with increasing cobalt plating times. (1) t_{Co} = 0.5 s, (0.6 nm), (2) t_{Co} = 1 s, (1.7 nm), (3) t_{Co} = 4 s, (10 nm), (4) t_{Co} = 6 s, (19 nm), (5) t_{Co} = 12 s (65 nm).

A. Influence of cobalt deposition time

Two series of [Co/Cu] bilayers were deposited on a gold foil with a constant deposition time of 50 s for copper (i.e., thickness of 11 nm) and variable cobalt deposition times from 0.5 to 15 s. In series (a), cobalt was the first deposited layer, whereas in series (b) copper was first. Figure 5 shows examples of hysteresis loops for series (b). The saturation magnetization M_s increases with plating time. For short durations, up to about 5 s, the magnetization efficiency M_s/Q_{Co} increases with the plating time and tends to stabilize for longer deposition times (Fig. 6, curve 1). Similar experiments have been carried out with an electrochemical quartz-crystal microbalance (EQCM), which allows measurement of the deposited mass, enabling calculation of the faradaic efficiency (Fig. 6, curve 2).[10] Both curves exhibit the same time dependency. These behaviors clearly confirm the fact that, at the beginning of cobalt deposition, hydrogen evolution is the predominant reaction.[10] The relative importance of this side reaction, controlled by the diffusion of protons, decreases with time. For long pulses at copper deposition (i.e., 50 s), proton concentration is restored, and the same evolution of the faradaic efficiency is observed for successive cobalt pulses.
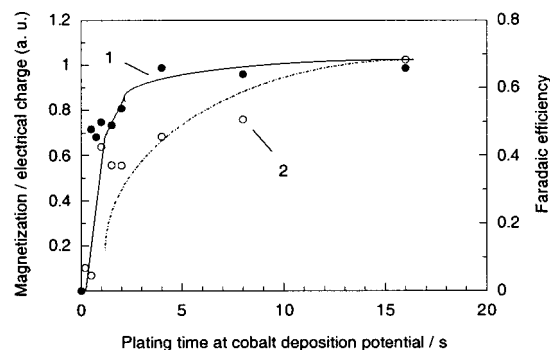

FIG. 6. Influence of the plating time at the cobalt deposition potential (−1.35 V/MSE) on the ratio of the magnetization efficiency (M_s/Q_{Co}) (curve 1) and on the faradic efficiency measured by the EQCM (curve 2).
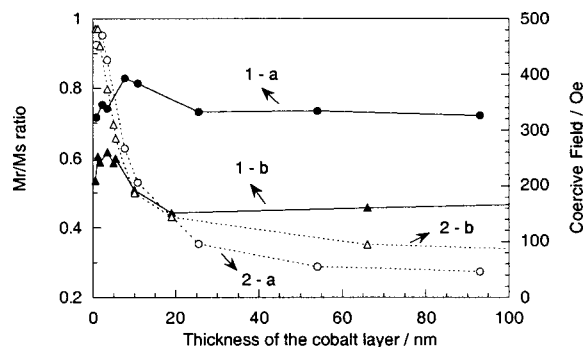
FIG. 7. M_r/M_s ratio (curves 1) and coercive field (curves 2) as a function of the thickness of the cobalt layer for a bilayer: series (a) cobalt is the first deposited layer on the gold substrate, and series (b) copper is the first deposited layer on the gold substrate.

The magnetization data are plotted in Fig. 7 as a function of the cobalt layer thickness. The coercive field is very large in the small thickness range, indicating that the samples are mostly particle-like, with a single domain structure. This probably results from the three-dimensional island growth of cobalt. In both series, the ratio M_r/M_s exhibits a maximum for a cobalt thickness of 5–10 nm. The squareness is again larger when the first deposited layer is cobalt, indicating more perfect layers [series (a)]. This ratio is close to 0.83, which is the value expected for randomly oriented single domain particles, having a face-centered cubic structure.[11] In series (b) where a copper layer (11 nm thick) is deposited first on the gold foil, the squareness is smaller and the maximum is close to 0.62, which might indicate a contribution from cobalt having the hexagonal compact structure. For greater cobalt thicknesses, both the coercive field and the M_r/M_s ratio decrease, indicating that the size of the particles grows and they become multidomained.

IV. CONCLUSION

The simultaneous *in situ* current density and magnetization measurements yield important information about the electrocrystallization of Cu/Co multilayers. They confirm that hydrogen evolution is the main reaction at the beginning of the cobalt deposition. The chemical displacement of cobalt by copper seems to occur only when a certain roughness of the layers develops: for higher numbers of layers or when the substrate is ITO glass.

The magnetization increase Δm and the magnetization efficiency, $\Delta m/Q_{Co}$ are influenced by the electrocrystallization process and especially by the roughness of the layers. They both tend to decrease when the number of bilayers increases. Their values depend on the nature of the substrate on which cobalt is deposited: they are smaller when copper is the first deposited layer or when the substrate is ITO glass instead of gold foil.

The coercive field H_c is mainly affected by the amount of magnetic material, i.e., by the grain size. It decreases rapidly when the thickness of the cobalt layer increases or when the number of bilayers increases.

ACKNOWLEDGMENT

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