Review

Structural and magnetic properties of electrodeposited (Co/Co_{1-x}Zn_{1-x})_n thin films

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Abstract

We present the experimental results of (Co/Co_{1-x}Zn_{1-x})_n (with x<6.5%) films grown from electrochemical dual bath based on (CoSO_4·7H_2O) and (ZnSO_4·7H_2O). X-ray diffraction patterns have shown the polycrystalline structure of CoZn layers with the structural lattice parameters close to those of the monoclinic CoZn_{13} compound. With the interfacial effects we have explained the magnetization behaviour for the (Co/Co_{1-x}Zn_{1-x})_n multilayers. The atypical profile of the magnetic hysteresis curves indicates that our samples present two magnetic components with different anisotropy.

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1. Introduction

In a previous study [1], we have shown that it is possible to grow well-defined electrodeposited multilayers consisting of ferromagnetic Co_{x}Zn_{1−x} alloys separated by non-magnetic Cu layer. We have also shown the existence of a large mixing at the interfaces that gives rise to a ternary phase. In this phase, the influence of Cu is to increase magnetic isolation of magnetic particles, which can be responsible for a reduction of a transport process and for a presence of superparamagnetism. Otherwise, in the multilayers composed of magnetic and non-magnetic layers, the anisotropy of interface is envisaged, moreover when the direction of easy magnetization becomes perpendicular to the plane of the layer, this could be technologically important in magnetic applications [2]. The CoZn alloy presents, in general, two main crystalline phases: CoZn_{13} (monoclinic) and Co_{2}Zn_{21} (cubic) and their structural parameters are well known. Recently, a new CoZn phase has been determined and corresponds to the Co_{2}Zn_{13} alloy with a complex structure that is described as built from isocahedra [3].

Literature data concerning the deposition and magnetic properties of multilayers consisting of pure Zn and Co metals or their alloys are quasi-absent. In the case of the deposition of multilayer system in which a (magnetic or non-magnetic) layer is binary or ternary, Zn alloys new question arise as compared to sublayers of different metals. These effects may be especially important on the magnetic and magnetoresistive properties [4]. The Zn atom has a larger atomic volume than that of Co, molar volume of the Zn element is 9.15 and 6.62 cm^3/mol for Co element.

The aim in this work was to produce electrodeposited Co_{x}Zn_{1−x} film, (Co/Co_{x}Zn_{1−x}/Co) sandwiches and (Co/Co_{x}Zn_{1−x})_n multilayers and to investigate the structural properties, the magnetic feature and to determine the anisotropy contributions for the multilayers. The fact of...
considering a separating layer of CoZn rather than Zn is to reduce the lattice mismatch. The decrease in the stress and the change in electronic structure may influence the interface phenomena as the grain size, and influence the transport properties; measurements of magnetoresistance are envisaged on these samples.

2. Experimental details

The films have been grown using the electrodeposition technique. The \((\text{Co}/\text{Co}_x\text{Zn}_{1-x}/\text{Co})_n\) sandwich and the \((\text{Co}_x\text{Zn}_{1-x}/\text{Co})_n\) multilayers were electrodeposited by the dual-bath technique [5]. The two baths are listed in Tables 1 and 2. For the two baths, the pH is 2.5. The temperature of the electrolytes was 25\(^\circ\)C.

The electrolyte A is a modification of one that has been used for the electrodeposition of Co\(_{x}\)Zn\(_{1-x}\) multilayers by Kirilova et al. [6]. The different currents used for Co\(_{x}\)Zn\(_{1-x}\) electrodeposited were varied between 2 and 25 mA/cm\(^2\) and the deposition time is between 15 and 2 s. The Co layer is deposited during 2 s at 2 A/cm\(^2\).

The electrodeposition of multilayer is carried out in a current standard three-electrode electrochemical cell at room temperature. The samples have been deposited on glass or SiO\(_2\) substrates covered by a 240 nm thick Cu buffer layer sputter-deposited at room temperature. The auxiliary electrode was Pt plate.

The SEM observation shows homogenous surface morphology. From the energy dispersive X-ray analyses (EDAX), the percentages in weight of the deposit elements were found.

The X-ray diffraction measurements were performed at room temperature with monochromatic Co K\(_\alpha\) radiation (\(\lambda = 1.789\) Å). Magnetization measurements were performed using an alternating gradient force magnetometer (AGFM) at room temperature with the magnetic field applied parallel and perpendicular to the film plane.

3. Results and discussion

The (Co/Co\(_y\)Zn\(_{0.99}\))\(_{12}\) multilayer spectrum (Fig. 1, inset) exhibits a main peak labelled SR\(_1\), at 2\(\theta = 50.68^\circ\), close to the Cu (1 1 1) buffer Bragg peak (2\(\theta = 50.73^\circ\)), which corresponds to the (2 2 1) reflection of the CoZn\(_{13}\) monoclinic structure. Around this main peak SR\(_{i}\), there are two weak peaks at, respectively, 2\(\theta_{i-1} = 49.18^\circ\) and 2\(\theta_{i+1} = 52.38^\circ\), whereas there is no existence of these peaks neither in the Co\(_{0.6}\)Zn\(_{0.35}\) single film nor in the (Co/Co\(_y\)Zn\(_{0.99}\)/Co) sandwich. These SR\(_{i-1}\) and SR\(_{i+1}\) peaks correspond to the first order superlattice satellites and allow to determine the superlattice period \(\lambda_{\text{exp}} = 67\) Å from the formula [8]:

\[
A = \frac{\lambda_{\text{Co}}}{\sin \theta_{i+1} - \sin \theta_{i-1}}.
\]

This value agrees with the nominal thicknesses \(l_{\text{Co}} = 40\) Å and \(l_{\text{CoZn}} = 30\) Å, estimated from Faraday’s formula in which the density of deposit was determined separately for both Co and CoZn layers. The comparison between the obtained values gives us an indication concerning the approximation on the nominal values of thicknesses.

Figs. 2a and 2b show the magnetization hysteresis loops respectively for the (Co/Co\(_y\)Zn\(_{1-x}\))\(_n\) (\(x = 1; \ 6.5\) at% Co) multilayers with the field applied parallel \(H_{\parallel}\) and perpendicular \(H_{\perp}\) to the film plane. These \(M(H)\) curves for \(H_{\parallel}\) and \(H_{\perp}\) field give the saturation magnetization values (530 emu/cm\(^3\) \(\leq M_s \leq 545\) emu/cm\(^3\)) and evidence a clear magnetic anisotropy. This reduced saturation magnetization \(M_s\) value in comparison with the expected saturation magnetization of pure cobalt (1422 emu/cm\(^3\)) can be explained by several origins: (i) the first possibility is an overestimation
of the magnetic thickness layer due to the difficulty to determine separately the thicknesses of the magnetic and the non-magnetic layers; (ii) the second one, transferring the multilayer deposit from bath to the other to change layer composition may cause surface oxidation and gives rise to a magnetic oxide over few monolayers, which is antiferromagnetic and consequently reduces the magnetization value; and (iii) the last possible origin is an interdiffusion at the Co–CoZn interfaces, which is likely to occur in electrodeposition process. In this interfacial mixing, the influence of Zn causes a reduction in \( M_s \) and can even lead to the formation of a dead layer. The magnetization decreases with the decrease in Co layer thickness. This could be explained also in terms of a magnetically dead layer of Co at each interface due to structural effects as interfacial mixing or roughness. It is known from the dead layer model that the magnetization of multilayer can be expressed by:

\[
M_s = M_0 \left( 1 - \frac{2d}{t_{Co}} \right),
\]

where \( M_0 \) is the bulk Co value and \( d \) is the dead layer thickness at each interface. The thickness of such a dead layer can be estimated as shown in Fig. 3, where we have plotted the product \( M_s t_{Co} \) as a function of \( t_{Co} \). The slope which corresponds to the saturation magnetization yields to the value of 602 emu/cm\(^3\). This value is much smaller than the value of pure Co. This is not surprising if we take into account the deposition conditions of the layers by dual bath electrodeposition method which may cause some oxidation at the interface, and thickness overestimation and other surface effects as previously explained. The intercept on the abscissa gives the value of \( d \) equal to 13.5 Å at 300 K. This value is indeed high compared to our previous values obtained on electrodeposited Ni/Cu multilayers [9]. This support the ideas developed above to explain the small saturation magnetization value.

We have studied the anisotropy parameters from the effective magnetic anisotropy \( K_{eff} \) whose value was deduced from AGFM measurements as the area between the perpendicular and parallel magnetization curves. The layer thickness dependence of the effective anisotropy in the multilayers can be described also by the phenomenological model as follows:

\[
K_{eff} = K_V + \frac{2K_s}{t_{Co}},
\]

where \( K_V \) is the sum of the shape anisotropy \( K_D \), magnetostrictive \( K_{MC} \) and magnetoeelastic anisotropy \( K_{ME} \), while \( K_s \) is the interface anisotropy. From the linear variation of \( K_{eff} t_{Co} \) as function of \( t_{Co} \) (Fig. 4), we deduce \( 2K_s = 0.12 \text{ erg/cm}^2 \) and \( K_V = -1.5 \times 10^6 \text{ erg/cm}^3 \).

The value of shape anisotropy is \( K_D = -2\pi M_s^2 = -1.86 \times 10^6 \text{ erg/cm}^3 \), where \( M_s \) is the average value of the saturation magnetization for various thicknesses, and then \( K_{MC} + K_{ME} = 0.4 \times 10^6 \text{ erg/cm}^3 \); the magnetostrictive anisotropy \( K_{MC} \) is much lower than that of the pure hexagonal cobalt (\( K_{MC} = 5.56 \times 10^6 \text{ erg/cm}^3 \)) [10] and than
that of (Co/CoPt) multilayer ($K_{MC} = 5 \times 10^6 \text{erg/cm}^3$) [11]. This results is a good indication of a great roughness at the Co/CoZn interfaces as well as the low value of surface anisotropy ($K_s = 0.06 \text{erg/cm}^2$) compared to that of Co HCP ($K_s = 0.84 \text{erg/cm}^2$) [12].

For the multilayers (Co/Co$_x$Zn$_{1-x}$)$_n$, Figs. 5a and 5b show a deformation on the hysteresis loops. This profile can be explained by the presence of two different components in magnetization from Co to CoZn through the interface, with different anisotropies, magnetic saturation fields, and different saturation magnetizations. The reversal of the weak anisotropy component and the strong one is realized independently, and depends on the layer thicknesses as it is shown in Figs. 5a and 5b. The similar atypical behaviour was already observed in (Cu/Co/Cu/NiFe)$_n$ [13] and explained by the presence of soft and hard magnetic components; the magnetizations of the two components are oriented perpendicular with each other and gives rise to the curvature of $M(H)$ loop when the external field is applied to align all the components along its direction.

4. Conclusion

Using electrodeposition, we have produced multilayers of Co separated with Co$_x$Zn$_{1-x}$ alloys not studied until now. We established the importance of the interface between Co and CoZn layers in the strong reduction of the saturation magnetization and on the anisotropy components. From the relationship between $K_s$ and $K_V$, we found a great variation in surface anisotropy reported for nominally equivalent systems and we deduced the presence of a great roughness at the interface. The existence of interfacial effects as a large mixing at interfaces gives rise to an atypical profile of magnetic hysteresis loops and a small saturation magnetization.

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References


