CEMS AND FARADAY ROTATION STUDY OF γ-Fe_2O_3 – Fe_3O_4 FILMS OBTAINED BY A NEW PYROLISIS TECHNIQUE

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ABSTRACT

Thin film iron oxides prepared by a new pyrolisis technique are studied by means of CEM spectroscopy and Faraday rotation measurements. It is shown that Fe_3O_4 spinel oxides are obtained when the deposition is performed under Ar atmosphere. These spinel-ferrite films present an important magnetization component perpendicular to the film plane. It is also shown that the Fe_3O_4 films are converted to γ-Fe_2O_3 by oxidation in air while retaining a uniaxial magnetic anisotropy. We interpret this induced magnetic anisotropy as arising from a magnetoelastic coupling with the substrate. Faraday rotation hysteresis loops confirm the existence of a strong induced uniaxial magnetic anisotropy in these films.

INTRODUCTION

Spinel ferrite thin films are very attractive materials for high density magnetic recording because of their superior resistance to wear and corrosion over metallic thin films /1/. Several preparation methods for obtaining γ-Fe_2O_3 thin films have been used in the past : oxidation of vacuum evaporated Fe films /2/, reduction and oxidation of α-Fe_2O_3 films obtained by a reactive sputtering /3/, reduction of Fe_3O_4 films sputtered from Fe_3O_4 samples /4/ and direct γ-Fe_2O_3 rf sputtering under controlled O_2 atmosphere /5,6/.

A new method is now proposed for preparing thin film oxides with the advantage of a simple and economic procedure while retaining a good quality: The spray pyrolisis of organometallic solutions by means of an ultrasonic pump /7/. Using this method, and depending on the atmosphere and substrate temperature, spinel ferrites Fe_3O_4 and γ-Fe_2O_3 and the β-Fe_2O_3 phase /8/ could be obtained.

We report in this work a conversion electron Mössbauer spectroscopy (CEMS) study of spinel ferrite films obtained by this method with a view to characterizing the chemical and magnetic properties of thin films so prepared. We report as well a Faraday rotation study of these samples.

EXPERIMENTAL PROCEDURE

The magnetic thin films studied in this work were prepared by the pyrolisis method reported in /7/. Essentially it involves the pyrolisis of an iron acetylacetonate solution, which is sprayed by an ultrasonic pump and transported to the furnace where the glass substrate is located, by means of a carrier gas flow. In order to obtain crystalline spinel ferrite films the substrate temperature was kept between 420º and 540ºC, and the flowing gas was Ar. When deposition is performed at temperatures higher than 420ºC under air atmosphere the phase β-Fe_2O_3 is obtained. If the synthesis is carried out at lower temperatures, an amorphous phase is obtained.

In this work we investigated the as-prepared spinel oxide samples (Ar atmosphere, different substrate temperatures T_S) and the effect of air oxydation on these films (annealing temperature T_a=400ºC). they had thickneses ranging from 1000 Å to 5000 Å and X-ray diffraction measurements /7/ did not show any crystallographic texture. The mean grain sizes ranged from 300 to 1500 Å, depending on the deposition temperature T_s.

The room-temperature CEM spectra were recorded with a conventional Mössbauer spectrometer using a home-made proportional gas electron detector. A 10 mCi ^{57}Co:Rh source was employed, and the γ-rays were in all cases perpendicular to the surface of the films. The velocity calibrations were made with an α-Fe foil and the analysis of the spectra were performed with a least-squares fitting program.

Faraday rotation hysteresis loops were measured with a He-Ne laser (λ =632 nm) under magnetic fields up to 5 Tesla perpendicular to the film plane.

RESULTS AND DISCUSSION

The strategy of this work is as follows: a) We report first several CEM spectra corresponding to thin film samples which do not display a spinel-like crystal structure. Then we concentrate on spinel thin films and investigate : b) The dependence of CEM spectra on the substrate temperature T_S during the deposition under Ar atmosphere. c) For a given temperature T_S, we analyze the effect of film thickness on their magnetic characteristics; d) Finally, the influence of an air-annealing thermal treatment at T_a= 400ºC on the composition and on the magnetic moment orientation is discussed.

In figure 1 we show the CEM spectra of a β-Fe_2O_3 sample prepared at 450ºC in air atmosphere and a spectra corresponding to an amorphous thin film deposited at $T_S < 400$ºC in the same atmosphere. The paramagnetic character of the β-Fe_2O_3 spectra together with the sharpness of the Lorentzian lines is consistent with the magnetic properties of β-Fe_2O_3 (T_N=170 K) /8/, and with the good crystallinity observed by X-ray diffraction /7/. Concerning the spectrum corresponding to the amorphous thin film, the coexistence of a quadrupole doublet with an enlarged sextet may be interpreted as arising from superparamagnetic small particles of α-Fe_2O_3 with a broad distribution of grain sizes and hence of relaxation times. The inner quadrupole doublet (ε_Q =0.73 mm/s), corresponding to a well crystallized phase, can be attributed to β-Fe_2O_3.

In Table I we summarize the relevant Mössbauer parameters obtained from the fit of the CEM spectra of samples prepared under Ar atmosphere at deposition temperatures $420 \leq T_S \leq 540$ºC. The inspection of this table reveals some important features that should be emphasized. First, the isomer shift (IS) values in both sextets are in a very close agreement with those observed for polycrystalline Fe_3O_4 /9/, and their area

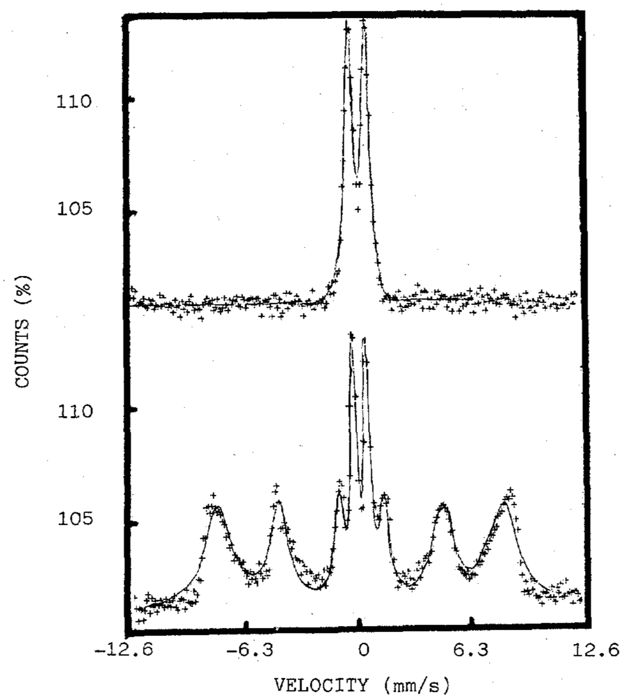

Fig.1.- CEM spectra of the β-Fe_2O_3 and amorphous thin film.

ratio is essentially 1:2. However, at low deposition temperatures T_s the hyperfine fields, see fig. 2, are relatively lower than those corresponding to Fe_3O_4. This fact must be correlated with the decrease of crystallite size on decreasing T_s, as observed by SEM and XRD /7/, and with the corrresponding decrease in saturation magnetization M_s /7/. In general, thin films must be considered as a set of strongly interacting particles, so that a collective superparamagnetism or superferromagnetism /10/ behaviour may be anticipated. A decrease of the particle size leads to an enhancement of collective magnetic excitations which in turn decrease the mean hyperfine field.

From the area ratio $A_{2,5}/A_{1,6}$ of the Lorentzian lines corresponding to $\Delta m=0$ and $\Delta m=1$ transitions we have determined the orientation (θ) of the hyperfine field with respect to the perpendicular to the film plane. It is found (see table I) that in the films with $T_s > 510$ºC, the hyperfine field evolves towards the film surface (greater θ value). This fact must be correlated with a corresponding decrease of the coercive field at the same T_s values, observed by Langlet et al. /7/ in the same films. As a matter of fact, the appearance of a spontaneous magnetization component perpendicular to the film plane in a sample with no crystallographic texture and no crystallite shape anisotropy (spherical grains, /7/) must be interpreted on the basis of a stress-induced magnetic anisotropy. Because of the difference between the thermal expansion of the films and the substrate a residual stress (σ) would appear within the film. This, in turn, thorough the magnetoelastic coupling, would lead to a stress-induced uniaxial anisotropy with $K_u=-(3\lambda_s\sigma/2)$, where λ_s is the magnetostriction coefficient. In this way, when $K_u > \frac{\mu_0}{2}M_s^2$ the magnetic easy axis is perpendicular to the film plane. Thus, our experimental observation of a reduced θ value at T_s=510ºC, together with a higher coercive field arises from a higher internal film compression ($\sigma < 0$, because $\lambda_s(Fe_3O_4) > 0$), which has been independently shown by means of θ- θ scanning X-ray diffraction measurements /11/.

In figure 3 we show the CEM spectra corresponding

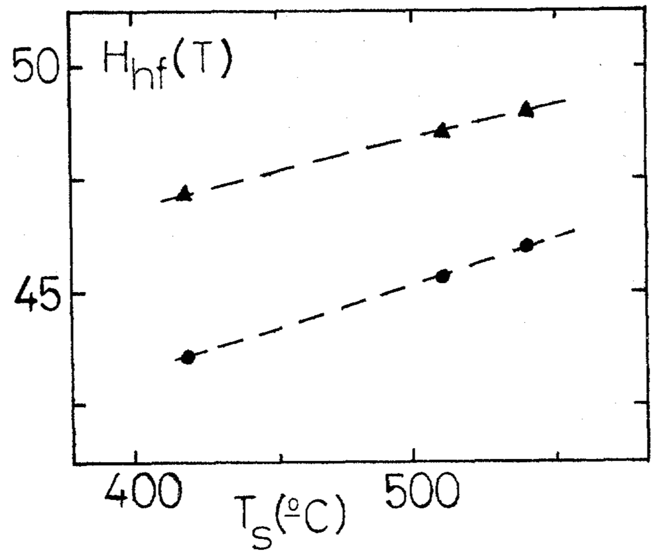

Fig.2.- Magnetic hyperfine field dependence on substrate temperature, Ts.

to samples prepared under Ar atmosphere at T_s=510ºC with different thicknesses (1000 and 5000 Å). The similarity of the hyperfine parameters of the spectra means that effects associated with the substrate-film interface do not persist at thicknesses greater than about 1000 Å. The only noteworthy difference between the spectra is the slight modification of the mean angle θ of the magnetic moment (see table I). The enhanced uniaxial anisotropy of the thinner film is consistent with a substrate-induced stress relaxing across the film.

We have finally studied the effect of annealing in air at T_a= 400°C on Fe_3O_4 samples obtained under Ar. The Mössbauer parameters obtained from the spectrum reveal

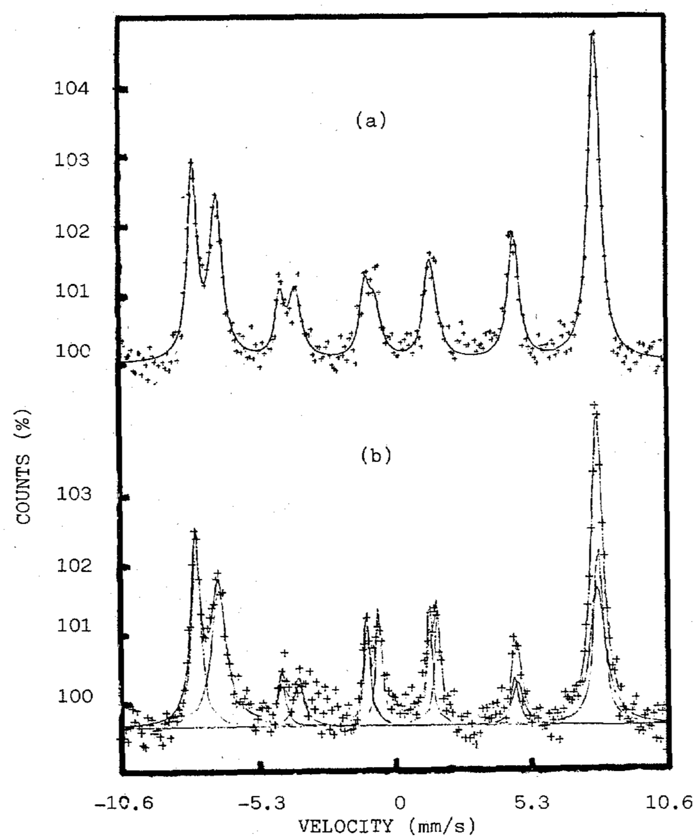

Fig.3.- CEM spectra for samples with different thicknesses. (a) 5000 Å, (b) 1000 Å.

Table I.- Relevant Mössbauer parameters from CEM spectra.

T_s (ºC)	T_a (ºC)	IS1 (mm/s)	IS2 (mm/s)	H_{hf1} (T)	H_{hf2} (T)	A(1) (%)	A(2) (%)	$\bar{\theta}$ (º)
450(+)	–	0.23	–	–	–	100%	–	–
350(+)	–	0.24	0.26	48.2	–	80%	20%	–
420	–	0.17	0.48	47.0	43.4	33%	67%	35
510*	–	0.15	0.55	48.4	45.5	44%	56%	32
510**	–	0.18	0.53	48.5	45.3	34%	66%	41
450	400	0.26	0.10	52.6	48.8	63%	37%	50
540	–	0.15	0.55	49.0	46.0	23%	77%	54
540	400	0.21	–	49.6	–	100%	–	43

IS values respect to Co:Rh source.
(*) Thickness 1000 Å; (**) Thickness 5000 Å. (+) Air atmosphere.

that the sample has been completely oxidised leading to a γ-Fe_2O_3 phase, in accordance with the X-ray diffraction and magnetic measurements /7,11/. Similarly the sample prepared at T_s=450ºC has also been completely oxidised (see table I). However, in that case the transformation to γ-Fe_2O_3 appears to be partially supressed and a small fraction of an extra sextet remains in the spectrum. The existence of some impurities in the low-temperature substrate synthesis appears to play an important role in the phase transformation.

It is to be remarked that the results of the annealing treatment show the evolution of the equilibrium angle of the magnetization θ; while an increase of θ is observed for the sample prepared at 540°C, the contrary occurs for the T_s= 450ºC sample. This striking behaviour may be associated to a difference in the initial film-stress /11/: while samples prepared at T_s< 510ºC are in a compressed state (σ<0) at tempeartures T_s> 520ºC they are in a tensile state (σ> 0). Hence, because of the γ-Fe_2O_3 smaller lattice parameter, in the first case the annealing relaxes the stress, while in the second case an enhancement of the stress is obtained.

Summarizing the results we may state that our Mössbauer study confirms that Fe_3O_4 films are obtained when the pyrolisis is performed in Ar atmosphere at temperatures 420ºC$\leq T_s \leq$ 540ºC. These samples display a stress-induced anisotropy which depends on the deposition temperature T_s and when they are annealed in air they oxydize to γ-Fe_2O_3 and the uniaxial stress induced anisotropy may be enhanced or decreased depending on the initial deposition temperatures. Hence, we may conclude that the present method allows γ-Fe_2O_3 thin films to be made with greater uniaxial magnetic anisotropy than that observed in sputtered γ-Fe_2O_3 films /12/.

A typical hysteresis loop after subtracting the contribution of the support, is shown in Fig.4. It corresponds to a 2500 Å sample prepared at T_s=510°C under Ar. The more relevant features of this figure are :
(a) Saturation is not reached even at 5 T showing the strong influence of the stress-induced magnetic anisotropy. (b) The coercivity is remarkably higher (0.12 T) than that observed from magnetization measurements /11/ but in this case, the applied magnetic field was only of 2 T. In addition, the longer time scale of the magnetization measurements with respect to the Mössbauer and Faraday rotation characteristic times may enable to observe some superparamagnetic relaxation phenomena, and

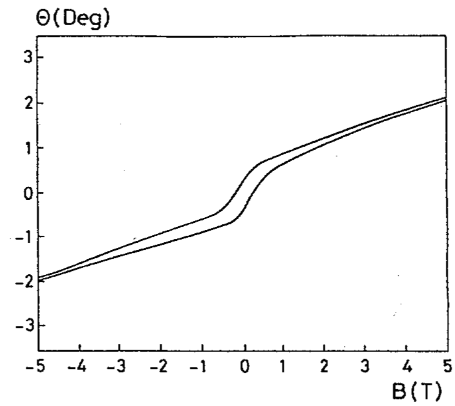

Fig.4.- Typical Faraday rotation hysteresis loop for a 2500 Å sample.

consequently, a lowering of the coercive field and magnetization /11/. (c) The observed Faraday rotation (~1·10^4 º/cm) at λ=632 nm is comparable with the results obtained for Bi-substituted garnets /13/.

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