$CoFe_2O_4$ thin films deposited by PLD with in situ heating and post annealing

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Cobalt ferrite thin films are receiving increasing interest due to their high coercive field, high Curie temperature and chemical stability. Different values of the coercive field can be obtained by modifying the temperature of the substrate and the pressure of the O_2 gas introduced in the chamber. For target ablation we used an excimer laser with a pulse energy of 60mJ, at a repetition rate of 10Hz. Structural, chemical and magnetic properties were investigated through XRD, XPS, AFM, SEM and VSM analysis. For the spinel phase formation a thermal treatment in air atmosphere at 900^{o}C for 2 hours was applied.

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1. Introduction

Due to their high coercive field, high magnetocrystaline anisotropy and moderate saturation magnetization cobalt ferrite thin films present an increasing interest in applications like magneto-optical devices, high-density recording media or magnetostrictive material for sensor application [1-5]. Also their use as a magnetic phase in magnetoelectric composites is justified by their large magnetostriction coefficient relative to the other ferrites.

Various sample preparation methods like sol-gel, sputtering, spin spray, chemical vapor deposition and molecular beam epitaxy were used to obtain cobalt ferrite films [6]. The goal is to obtain high textured thin films through methods that don't imply high temperatures and low pressures and are easy to implement [7]. However this priority is not always achieved. In this article we investigate the structural and magnetic properties of cobalt ferrite thin films deposited on (100) Si single crystal substrate through pulsed laser deposition technique. Two different heat treatments were used. The first one was the in situ heating of the substrate up to a temperature of 600^{o}C and the second one was the thermal treatment applied after the deposition process. Other parameters like pressure, time of deposition and target-substrate distance were varied

2. Experimental set-up

Cobalt ferrite thin films were deposited through PLD technique using an excimer XeCl laser with a wavelength of 308 nm (UV) and a fluence of approximately 6 J/cm^2. A high vacuum pumping system ensured the "depollution" of the deposition chamber, target and substrate. To achieve the desired thickness the target substrate distance as well as the time of deposition were modified. The films were grown on silicon substrate in oxygen pressures that ranged from 10^{-5} torr to 7.3 10^{-5} torr. The substrate was heated at a temperature of 600^{o}C. The structural properties were investigated using X-ray Diffraction (XRD) with a CuKα radiation, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). The hysteresis loops were obtained using a Vibrating Sample Magnetometer (VSM). Magnetic measurements were conducted for in plane and out of plane configurations of the films in magnetic fields up to 20 kOe.

The target was prepared by standard ceramic technique, using high purity Fe_2O_3 and Co_3O_4 as starting materials. The oxides were mixed in the required proportions and were pre sintered at 900^{o}C for 2 h in air atmosphere. In the final sintering process, the materials were heated up to 1250 ^{o}C for 2 h in air atmosphere. This process was followed by a natural cooling of the sample to room temperature.

3. Results and discussions

The XRD measurements of the as deposited films revealed the presence of a mixture between an amorphous phase and a crystalline phase. In order to obtain the spinel structure a thermal treatment at a temperature of 900^{o}C for two hours in air atmosphere was applied on the thin films. In fig.1 are represented the XRD patterns of two thin films deposited at different pressures after the thermal treatment.

The P2 sample was deposited at a pressure of 7.3 10^{-5} torr and the P4 at a pressure of 0.75 torr. For these two samples the target substrate distance (3 cm), the time of deposition (30 min) and the temperature of the substrate (600^{O}C) were kept constant.

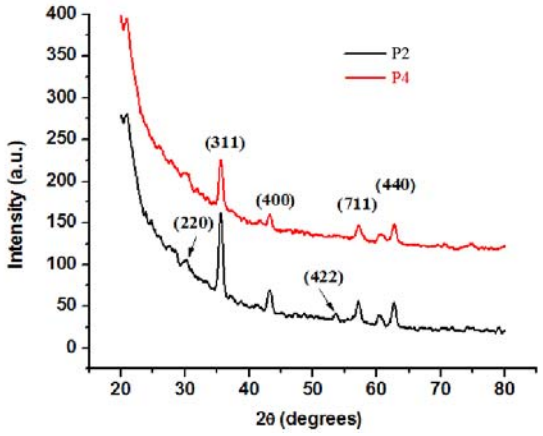

Fig. 1. XRD patterns of the P2 and P4 thin films

The X-ray diffraction spectrum showed that the films are polycrystalline with a cubic, spinel type, structure. The crystallite sizes were determined using Scherrer's formula:

$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the used radiation, β represents the full width at half maximum of the (311) peak and θ the Bragg angle. Thus for both samples it was calculated a crystallite size of approximately 13 nm. The SEM images for P2 and P4 are revealed in fig. 2. It was determined an average grain size of 70 nm for the first film and 40 nm for the second film. The SEM image of the P4 sample revealed a uniform distribution of the grains but in the case of the P2 sample large particles are present due to the use of a lower pressure. These results are confirmed by the AFM analysis that was detailed in [8].

The chemical analysis of the as deposited thin films was investigated using X-ray Photoelectron Spectroscopy. The binding energy observed for Co $2p_{3/2}$ corresponds to the chemical bond of cobalt to oxygen in Co_3O_4 [9]. The presence of the cobalt oxide could be explained by the thermal treatment that determined a surface oxidation of the thin films. This oxidation was also confirmed by the XRD analysis which revealed the existence of a secondary phase. The in plane and out of plane hysteresis loops are represented in fig. 3 after the subtraction of the diamagnetic component. For the P4 sample it can be observed a narrowing of the hysteresis loops at low fields. This shape could be explained by the presence of two phases, one ferrimagnetic given by the cobalt ferrite and one antiferromagnetic given by the cobalt oxide present at the surface of the film. This narrowing is observed only for the P4 sample which has the smallest thickness of approximately 170 nm. The presence of the cobalt oxide at the surface of the films was confirmed for the P2 and P7 samples as well, but in their case the antiferromagnetic contribution is smaller than the magnetic one given by the $CoFe_2O_4$. The P7 sample was deposited at the same pressure of 7.3 10^{-5} as P2 but the time of deposition was 60 min. The other parameters were kept constant.

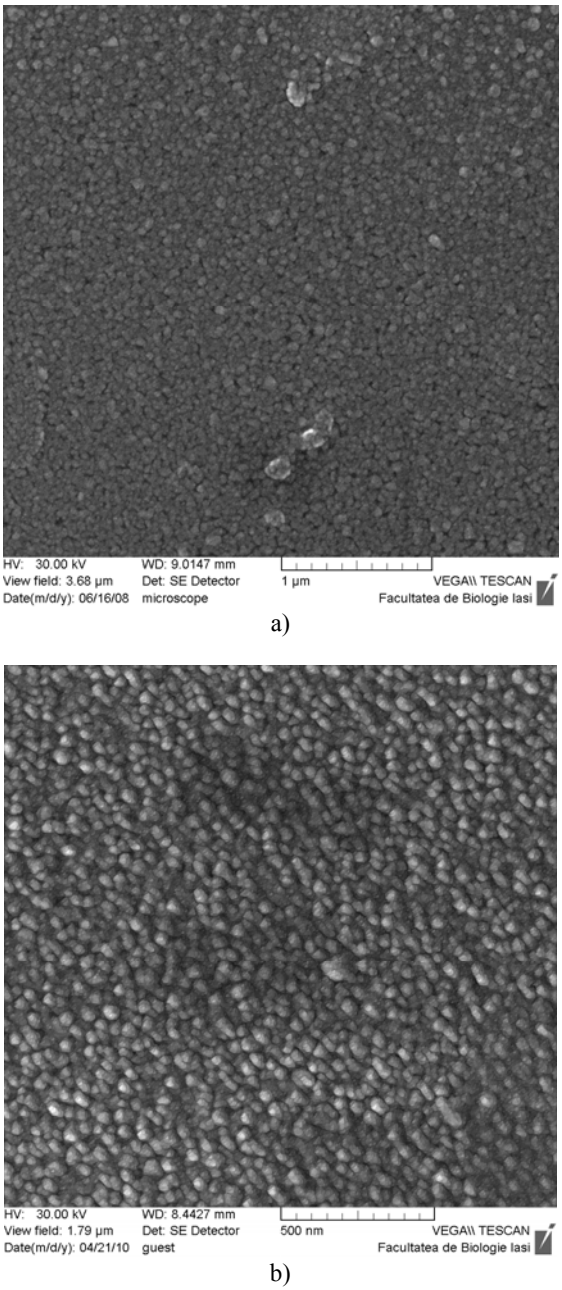

Fig. 2. SEM images of the a) P2 and b) P4 samples

The values of the coercive fields and of the ratios between the remanence magnetization and the saturation magnetization are given in Table 1. The hysteresis loop of the target is represented in the insertion in Fig 3(c). The coercive field of the target (600 Oe) is smaller than the one observed at the films, the crystallite size of the target being

smaller than the one calculated for the thin films as the XRD patterns revealed as well.

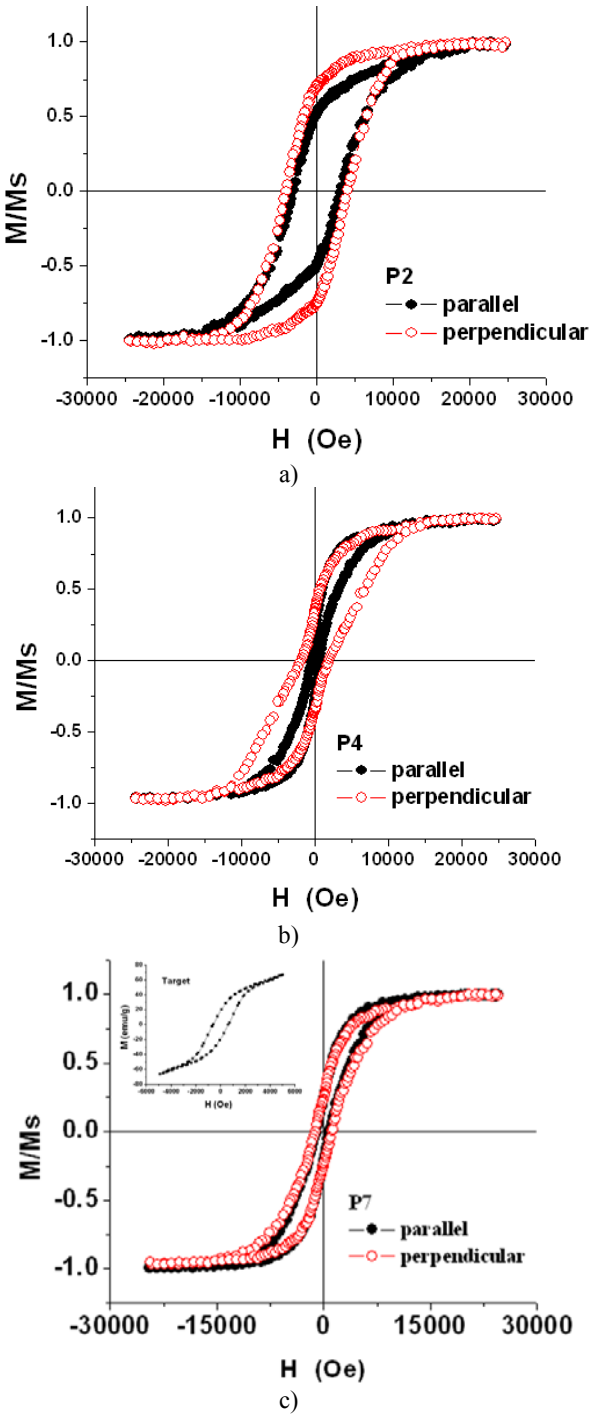

Fig. 3. The histeresis loops measured at 300K of the P2, P4 and P7 samples for in plane (solid points) and out of plane (open points) configurations

For the P2 and P4 samples there are slight differences between the coercive fields obtained from the parallel and perpendicular hysteresis loops indicating the presence of a preference of the particles for perpendicular orientation and perpendicular anisotropy. From the X-ray diffraction patterns it was determined a lattice parameter of 8.36 Å which is smaller than the one for the bulk cobalt ferrite (8.39 Å) due to the mismatch between the lattice parameter of $CoFe_2O_4$ and the silicon substrate.

Table 1. The values of the coercive fields and remanence ratios for the in plane and out of plane configurations.

Sample	S_T	$S_\parallel$	$H_{c\parallel}$ (Oe)	H_{c_T} (Oe)
P2	0.7	0.52	3146	4038
P4	0.35	0.20	603	1921
P7	0.25	0.25	1158	1160

The magnetoelastic stress anisotropy constant was calculated using the equation $K_a = (3/2)\lambda_{100}\sigma$ where λ_{100} is $-590 \cdot 10^{-6}$ and $\sigma = Y \cdot \varepsilon$ [10]. The value of this constant is $4.64 \cdot 10^6 erg/cm^3$ which is higher than the intrinsic magnetocrystaline anisotropy of bulk cobalt ferrite $3 \cdot 10^6 erg/cm^3$. The shape of the hysteresis loops in the out of plane and in plane configurations are almost the same, with a slight increase of the H_{c_T}. This indicated that the easy axes of the grains are randomly oriented.

4. Conclusions

Thin films of cobalt ferrite were deposited using PLD technique at various pressures and times of deposition. Polycrystalline thin films were obtained after a thermal treatment at 900°C. The XPS measurements revealed the presence of an antiferromagnetic phase at the surface of the as deposited thin films. The cobalt oxide phase determined a narrowing of the hysteresis loops observed only at the P4 sample. From the VSM measurements it was observed a slight perpendicular anisotropy for P2 and P4 samples. In the case of the P7 sample the values of the coercive fields obtained from the hysteresis loops in the in plane and out of plane configurations were approximately the same. As the thickness of the films increases the stress is released and the induced anisotropy constant decreases. The XRD analysis didn't reveal any structural preferred orientation. We can conclude that the magnetic properties of the samples are almost independent of the direction on which the external field is applied. Thus the thin films are suitable for isotropic recording media.

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