Magnetic Measurements of RE-Doped Cobalt Ferrite Thin Films

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Cobalt ferrite is a ferrimagnetic material with properties which support its use in different types of devices. In bulk form CoFe$_2$O$_4$ presents the highest magnetostriction coefficient relative to other ferrites making it a good candidate for sensors and actuators. Due to the industries miniaturization trend, several research groups focused their study on obtaining novel thin films with high magnetostriction coefficient. The aim of this work was to investigate the influence of the substrate temperature and rare earth addition on the properties of cobalt ferrite thin films deposited by pulsed laser deposition. CoFe$_2$O$_4$, CoFe$_{1.8}$Gd$_{0.2}$O$_4$ and CoFe$_{1.8}$La$_{0.2}$O$_4$ thin films were deposited using an Nd–YAG laser (532 nm) with a 10 Hz repetition rate and 10 ns pulse duration. The target-substrate distance of 2.5 cm and laser fluence of 10 J/cm$^2$ were kept constant. The substrate temperature was varied from 200 °C to 600 °C. The structural properties of the thin films obtained by Raman spectroscopy and scanning electron microscopy indicated the formation of a single cobalt ferrite structure. Hysteresis loops for both in-plane and out-of-plane configuration were obtained using a vibrating sample magnetometer. These results showed an increase in coercive field and maximum magnetization as the substrate temperature was raised from 200 °C to 400 °C. Vibrating sample magnetometer measurements of the cobalt ferrite thin film deposited at 400 °C revealed a tendency of the particles to a perpendicular magnetic arrangement.

Index Terms—Ferrite films, laser ablation, rare earth.

I. INTRODUCTION

In the last decade the interest of electronic industry was focused on obtaining bulk and thin film materials with remarkable properties for sensors and actuators. Interesting examples are the crystalline and amorphous magnetostriective materials with high magnetostriction coefficients [1]. The miniaturization of the sensors and their placement near the electronic circuit which processes the signal are two necessary requirements for obtaining advanced micro-systems. Thin films with magnetostriction coefficients hundred times bigger than bulk materials are widely studied due to their adjustment to integrated circuit fabrication with low cost.

An inexpensive and versatile candidate material is cobalt ferrite which in bulk form can present a magnetostriction coefficient up to $2 \times 10^{-6}$ [2] but in thin film configuration one can expect a much higher magnetostriction response. For sensors, thin films with in plane magnetic orientation (same as the driving magnetic field direction) can present a very important advantage.

In most cases the preferred applications are based on the in plane response where losses driven by demagnetizing fields are repressed. However the component of the magnetostriction coefficient parallel to the thin film surface $\lambda_{zz}$ is reduced due to the involved magnetization processes. Moreover the 180° domain wall motion does not contribute to the magnetostriction effect. The 90° walls which characterize the perpendicular magnetic anisotropy are the ones which employ magnetostriction through magnetization rotation processes [1].

An optimum example is the thin film in which the non-isotropic contribution of domain walls in demagnetizing state is taken into consideration. A preferred configuration would be an in plane orientation of the grain easy axis, perpendicular to the applied field direction [3]. For in-plane anisotropy, thin films with negative magnetostriction should be deposited with a constrained mechanical tension. The nature and magnitude of the induced mechanical tensions are influenced by the deposition conditions, thermal expansion mismatch between the substrate and the thin film and the subsequent applied thermal treatment so that an in-plane easy axis can be obtained.

A wide variety of cobalt ferrite thin films obtained by different methods were reported. Methods like sol-gel [4], sputtering [5], molecular beam epitaxy [6], spray pyrolysis [7] and electrochemical techniques were used to grow thin films with different characteristics.

The magnetic and magnetostriective properties of the thin films (e.g., anisotropy, Curie temperature, spontaneous magnetization, temperature dependence of magnetization, coercive field, magnetostriction coefficient, electrical resistivity etc.) are greatly influenced by the thickness of the sample but also by the growth method. Usually, the thin films obtained by sol-gel technique do not present a preferential crystallographic growth direction and the coercive field is influenced by the temperature of the thermal treatment.

Lee et al. [8] reported the deposition of cobalt ferrite thin films by RF sputtering with an in situ heating of the substrate. None of the as deposited thin films presented a preferential growth direction but a perpendicular coercive field of $H_{c,\perp} = 3.9$ kOe indicated the presence of a perpendicular anisotropy. Epitaxial cobalt ferrite thin films were obtained by pulsed laser deposition (PLD) [9], [10]. Yin et al. [11] obtained 100 nm thick CoFe$_2$O$_4$ thin films on quartz. For substrate temperatures that exceeded 300°C a perpendicular magnetic anisotropy was observed whereas an in plane easy axis was observed when lower temperatures were used. A 10.5 kOe coercive field was determined for the thin film grown at 550°C.

The aim of this study was to obtain cobalt ferrite thin films using a versatile deposition technique like PLD with different orientations of the particles easy axis related to the substrate.
Ferrite thin films were grown using targets with different chemical compositions and various deposition parameters (pressure, time of deposition, substrate temperature). The structural and magnetic properties of the samples were analyzed in order to interpret the hysteresis curves.

II. EXPERIMENTAL DETAILS AND DISCUSSIONS

A. Sample Preparation

CoFe$_2$O$_4$, CoGd$_{0.2}$Fe$_{1.8}$O$_4$, and CoLa$_{0.2}$Fe$_{1.8}$O$_4$ thin films were deposited by PLD with the experimental conditions detailed in [12] using a substrate holder which permitted a heating of the (100) silicon wafer ($10 \times 10 \times 0.4$ mm). For the plume formation, the targets obtained as described in [13] were irradiated using a Nd-YAG laser (wavelength = 532 nm, pulse duration = 10 ns, repetition rate = 10 Hz). The laser beam was focused on the target surface at a 45° incidence angle using an optic system which included mirrors, power attenuators, and a convergent lens.

The laser-target impact area was estimated at 300 $\mu$m$^2$. The laser energy was kept at 30 mJ and the target-substrate distance at 2.5 cm. The substrate temperature was varied from room temperature to 600 °C and a pressure of approximately 10$^{-2}$ torr was maintained during the deposition. The P1, P2, and P3 samples were deposited using the stoichiometric cobalt ferrite target as source material and a 45 min deposition time. For the P4, P5, and P6 samples, the laser beam was focused on the La doped cobalt ferrite bulk material and the deposition time was increased to 90 min. The same deposition time was used for the P7, P8, and P9 thin films of CoGd$_{0.2}$Fe$_{1.8}$O$_4$. The values of the substrate temperature used are listed in Table I.

B. Structural Characterization

The micro-Raman spectroscopy measurements on the target and thin films deposited on Si substrate were done using a InVia Reflex spectroscopy (Renishaw) coupled with an Olympus BXFM free-space microscope. The excitation radiation ($\lambda = 514.5$ nm) is produced by an air-cooled Ar$^+$ laser source (Modu-Laser, Stellar-pro). The Raman spectra of the CoFe$_2$O$_4$ target confirmed the spinel structure formation with the peak at 684 cm$^{-1}$ representing the vibrations of the tetrahedral sublattice and the other one at 465 cm$^{-1}$ the vibrational mode of the octahedral sublattice [14]. In the spectra of La and Gd doped cobalt ferrite bulk materials additional peaks were observed which indicated the formation of a second phase of LaFeO$_3$ and GdFeO$_3$ respectively [13]. Due to the large ionic radii of rare earth cations their insertions in the spinel structure can be rather difficult if no supplementary energy sources are used. For this reason a higher sintering temperature was applied in order to increase the La and Gd cations mobility but the presence of the second phase was still detected in 15% and 12% concentrations respectively.

The Raman spectra of the undoped and La doped cobalt ferrite thin films are represented in Fig. 1(a) and (b), respectively. All the thin films deposited at 200 °C and 400 °C present peaks corresponding to CoFe$_2$O$_4$. For the stoichiometric cobalt ferrite samples, the shift of the 684 cm$^{-1}$ peak to higher frequencies indicated the formation of a constrained spinel phase. These induced mechanical tensions can improve the magnetoelastic response. For La and Gd doped samples, the peak corresponding to the vibrations of the tetrahedral sublattice presented an approximately 12 cm$^{-1}$ shift to lower frequencies suggesting an increase in chemical bond. The shift variation of the same peak presented by the thin films of the same material is small for substrate temperatures between 200 °C–500 °C. The insertion of rare earth cations in the crystalline structure can induce a cell deformation due to their large ionic radii and thus an increase in lattice parameter. The thin films deposited at high temperatures (500 °C for CoFe$_2$O$_4$ sample and 600 °C for the doped ones) presented different Raman spectra. Two additional peak one at 275 cm$^{-1}$ and another one at 578 cm$^{-1}$ were observed which can correspond to iron oxide [15]. At these temperatures different growth processes and additional oxidation reactions can take place.

The microstructural characteristics of the samples were investigated using scanning electron microscopy (SEM) and several of obtained images are presented in Fig. 2. These did not indicate the existence of major differences between the surface morphologies of the analyzed thin films as the substrate temperature was increased. The presence of large droplets on the analyzed areas can be explained by the short target-substrate distance and by the high fluency used. For the La doped cobalt ferrite samples a decreased uniformity was observed which can be due to the influence of the large mass and radii of the La ions on the nucleation processes and particle migration on the substrate surface.

Neither an in-plane or perpendicular preferential growth direction were observed but a random distribution of the grains.

C. Hysteresis Curves Obtained Using a Vibrating Sample Magnetometer

The major hysteresis loops were recorded using a vibrating sample magnetometer Princeton 3900 Model at room temperature.

Fig. 3 presents the hysteresis curves of the thin films when the external magnetic field is applied parallel to the substrate surface. In the inset of the figures are presented the vibrating sample magnetometer (VSM) loops for the out-of-plane configuration. The values of coercive fields and maximum magnetization (at 10 kOe applied magnetic field) are mentioned in Table I.
Fig. 1. Raman spectra of (a) stoichiometric and (b) La doped cobalt ferrite thin films deposited at various substrate temperatures.

Fig. 2. SEM images of the cobalt ferrite and La doped cobalt ferrite thin films.

From the shape of the magnetic curves and from the values listed in Table I one can observe that there is no preferential magnetic orientation direction. For the P2 sample a slight tendency of the particles for an out-of-plane arrangement is observed. Even at low substrate temperatures, the cobalt ferrite thin films present high coercive fields which can be due to the fine particle dimensions and to the formation of a crystalline phase.

As the substrate temperature is increased from 200 °C to 400 °C the thin films present an enlarged hysteresis loop for both doped and undoped samples. The magnetic moment of cobalt ferrite is given by

\[ m = m_O - m_T \]

where \( m_O \) and \( m_T \) are the magnetic moments of the cations from the octahedral and tetrahedral sites respectively. A higher
value of the maximum magnetization was observed for the Gd doped samples. Knowing that the magnetic moment of Gd (8 \( \mu_B \)) is higher than the one of Fe (5 \( \mu_B \)), this increase can indicate an insertion of the rare earth element into the spinel structure in the octahedral sublattice. The decrease of the maximum magnetization for the La (0 \( \mu_B \)) doped samples supports this conclusion. Given their large ionic radii, the rare earth elements have the tendency to occupy the octahedral position due to the larger space of these sites. A weak magnetic moment was observed for the thin films of doped ferrites deposited at 600 °C confirming the formation of another phase indicated by Raman results.

For the rare earth doped samples, the values of the in plane and out of plane coercive fields are approximately the same indicating a random orientation of the particles easy axes. To confirm this arrangement, magnetic force microscopy measurements were carried out at room temperature and in zero external magnetic fields. Both in plane and out-of-plane directions were studied. The as obtained images did not indicate the presence of regions with a certain orientation of magnetic moments. The characteristics of the phase change images were correlated with the samples topography although a higher offset value was used to avoid the roughness contribution. The MFM results revealed a weak magnetic behavior of these thin films when no magnetic field is applied.

### III. Conclusion

Undoped and rare earth doped cobalt ferrite thin films were deposited by PLD. For the stoichiometric cobalt ferrite thin films, an out-of-plane magnetic orientation was observed when higher substrate temperatures were used. For the substituted samples, the structural characterization techniques indicated a crystalline phase formation with no preferential crystallo-graphic growth directions and a random distribution of the grains. Increasing the substrate temperature from 200 °C to 400 °C higher values of coercive fields and maximum magnetizations were obtained. The shift of the 684 cm\(^{-1}\) Raman peak to lower frequencies and the maximum magnetization changes with rare earth addition confirmed the substitution of Fe by Gd and La cations. The magnetic force microscopy results were influenced by the thin films’ roughness.

### Acknowledgment

This work was supported by the European Social Fund in Romania, under the responsibility of the Managing Authority for the Sectoral Operational Programme for Human Resources Development 2007–2013 under Grant POSDRU/88/1.5/S/47646. The authors would like to thank the research team from PhLAM Laboratory, Lille I University for the thin film deposition.

### References


