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Femtosecond pulsed laser deposition of cobalt ferrite thin films

Georgiana Dascalu[a], Gloria Pompilian[b], Bertrand Chazallon[b], Ovidiu Florin Caltun[a,*], Silviu Gurlui[a], Cristian Focsa[b]

[a] Faculty of Physics, Alexandru Ioan Cuza University, 700506 Iasi, Romania
[b] Laboratoire de Physique des Lasers, Atomes et Molécules (UMR CNRS 8523), Université Lille 1 Sciences et Technologies, 59655 Villeneuve d'Ascq cedex, France

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ABSTRACT

The insertion of different elements in the cobalt ferrite spinel structure can drastically change the electric and magnetic characteristics of $CoFe_2O_4$ bulks and thin films. Pulsed Laser Deposition (PLD) is a widely used technique that allows the growth of thin films with complex chemical formula. We present the results obtained for stoichiometric and Gadolinium-doped cobalt ferrite thin films deposited by PLD using a femtosecond laser with 1 kHz repetition rate. The structural properties of the as obtained samples were compared with other thin films deposited by ns-PLD. The structural characteristics and chemical composition of the samples were investigated using profilometry, Raman spectroscopy, X-Ray diffraction measurements and ToF-SIMS analysis. Cobalt ferrite thin films with a single spinel structure and a preferential growth direction have been obtained. The structural analysis results indicated the presence of internal stress for all the studied samples. By fs-PLD, uniform thin films were obtained in a short deposition time.

1. Introduction

Cobalt ferrite is a ferrimagnetic material with an inverse spinel structure which presents the highest magnetocrystalline anisotropy and magnetostriction coefficient among ferrites [1,2]. These properties encourage their use as magnetic material in recording devices, sensors and actuators.

Cobalt ferrite thin films can be obtained by different methods [3–5] but the most promising technique to deposit epitaxial thin films with a preferential crystallographic direction and perpendicular magnetic anisotropy was found to be Pulsed Laser Deposition (PLD) [6,7]. So far, lasers with nanosecond pulse duration (e.g.: excimer and Nd-YAG lasers) have been used for film growth. In this temporal regime the thermal conductivity mechanisms control the ablation threshold fluence and the pulse duration is sufficiently long so that it interacts with the formed plume [8–10]. These ablation processes could explain the presence (in some cases) of large droplets on the surface of thin films obtained by ns-PLD. The presence of these micro-sized particles limits their use in industrial applications or in magnetoelectric multilayer systems where a low roughness is necessary to ensure good mechanical coupling between different phases. A possible solution to this problem can be ensured by ultrafast laser ablation. The femtosecond pulse duration is smaller than the time needed for the thermalization processes to evolve and the short laser pulse does not interact with the plume.The absence of liquid phase transformation at laser-target interaction can ensure stoichiometric and nano-sized particle ejection. Moreover, it was reported that plasma induced by femtosecond pulsed lasers has a shorter lifetime than the one generated by nanosecond ablation [11]. Another advantage of the ultrafast laser systems is the high repetition rate. Reilly et al. [12] deposited a 140 nm thick film in 20 min using the 74.8 MHz repetition rate of an amplified Ti:sapphire system.

This study was focused on the structural characterization of ferrite thin films obtained by femtosecond PLD with 1 kHz repetition rate. To our knowledge, results on cobalt ferrite thin films deposited by femtosecond PLD were not reported until now. Another aim of this work was to investigate the influence of Gadolinium oxide addition in the target preparation on the structural properties of cobalt ferrite thin films. Due to its large ionic radii, the inclusion of the rare earth element (Gd) into the spinel structure could determine an increase in lattice parameter and an internal stress is induced [13]. Also the high magnetic moment of Gadolinium ions as compared to the iron cations can produce significant changes in magnetic properties.

2. Experimental details

$CoFe_2O_4$ and $CoFe_{1.8}Gd_{0.2}O_4$ thin films were deposited by fs-PLD using 1.5 cm diameter, 5 mm thick disk targets synthesized by

* Corresponding author. Tel.: +40 232 20 11 74; fax: +40 232 20 11 74.
E-mail addresses: caltun@uaic.ro, ovidiu_caltun@yahoo.com (O.F. Caltun).

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solid state chemistry. For the stoichiometric cobalt ferrite target, the powder was obtained by co-precipitation method, pressed and sintered at 1150 °C for 5 h in air atmosphere as described in [14]. For the Gd-doped cobalt ferrite target the powder was obtained by solid state reaction in which the oxides of the constituent elements were mixed in adequate proportions. The resulting powder was calcined at 950 °C for 5 h in air atmosphere and then ball milled. In the sintering stage we used a higher temperature of 1250 °C (5 h, air atmosphere) to facilitate the crystallization process which can be restrained due to the large ionic radius of the rare earth cation.

An experimental set-up originally developed for the study of laser ablation plasma dynamics [8–10,15] has been exploited for fs-PLD of the cobalt ferrite thin films. The targets were placed on a multi-axis manipulator under vacuum (3×10^{-2} Torr) and a 40 fs Ti:Sa laser (Spectra Physics, λ = 800 nm, repetition rate = 1 kHz, fluence = 0.6 J/cm^2) employed as ablation source was focused at quasi-normal incidence on the target surface. The substrate ((1 0 0) monocrystalline silicon) was resistively heated at a temperature of 300 °C and positioned at 16 mm in front of the target. The deposition time was varied between 10 and 20 min. The microstructure characteristics of the thin films synthesized here were compared with the ones observed for other samples previously deposited by nanosecond PLD (λ = 532 nm, repetition rate = 10 Hz) [13] using the same two targets described above.

The structural characteristics of these thin films were investigated by Raman spectroscopy using an InVia Reflex spectroscope (Renishaw) coupled to an Olympus BXFM free-space microscope. The experiments were carried out at room temperature with an excitation radiation of λ = 514.5 nm produced by an air-cooled Ar^+ Laser source (Modu-Laser, Stellar-pro). The Raman analyses were complemented by X-Ray Diffraction (XRD) measurements with a Shimadzu LabX XRD-6000 diffractometer using Cu Kα radiation (λ = 1.54059 Å). In depth profiles of the constituent elements and of their oxides were obtained by Time of Flight–Secondary Ion Mass Spectrometry (ToF-SIMS) using an IonTof V SIMS instrument. A surface of $300 \times 300\ \mu m^2$ was sputtered using a beam of Cs^+ ions and the secondary ions generated by a beam of 25 keV $Bi_3{}^+$ from a central $100 \times 100\ \mu m^2$ area were analyzed. The thickness of the films was measured using a mechanical contact Veeco Dektak profilometer.

3. Results and discussions

The bulk materials used as targets in the deposition process (undoped and Gd-doped cobalt ferrite) were firstly analyzed by X-ray diffraction. For the undoped cobalt ferrite disk, the XRD pattern indicated the formation of a single spinel structure whereas for the Gd-doped sample, the presence of a second phase of $GdFeO_3$ was observed in 12% concentration [14]. These results were confirmed by the Raman spectroscopy analysis [13]. Cobalt ferrite has 5 Raman active modes where the peak at 465 cm^{-1} can be assigned to vibrations of the octahedral sublattice and the high-frequency mode at 684 cm^{-1} is determined by the vibrations of the tetrahedral sublattice [16]. For Gd-doped target additional vibrational modes were detected at 139 cm^{-1}, 155 cm^{-1}, 322 cm^{-1}, 477 cm^{-1} and 615 cm^{-1} which can be assigned to the second phase of Gd orthoferrite.

Using these bulk materials thin films of $CoFe_{2-x}Gd_xO_4$ (x = 0, 0.2) were deposited by PLD in various conditions. Their thicknesses were obtained by contact profilometry measurements, leading to the values listed in Table 1. Mechanical profilometers usually present a detection limit of 10 nm. These results are to be compared with the ones reported in [13] for the thin films deposited by nanosecond PLD. Using a high repetition rate of 1 kHz (and a lower fluence), in 20 min we obtained a thin film with the same thickness as the one deposited in 90 min with a 10 Hz repetition rate ns Nd-YAG laser. Using the Olympus microscope of the Raman spectroscopy set-up the surface morphology of the thin films was analyzed. The as-obtained images are revealed in Fig. 1, both for fs- and ns-PLD films. For this representation we used the cobalt ferrite films deposited in 10 min and 45 min respectively. As one can easily note, the surface of the ns-PLD film (NF) is affected by the presence of large (micrometer-sized) droplets, while the fs-PLD grown films (FF) present a very smooth surface. This is due to the much lower fluence used in the femtosecond regime (0.6 J/cm^2, compared to 10 J/cm^2 used in ns-PLD [13]), and also to the intrinsic lower thermal effects induced by the fs-laser ablation, which avoids (or at least greatly reduces) the formation of intermediary liquid-phase droplets during the process. The increased uniformity of the FF sample is confirmed by profilometry measurements. Thickness profiles of the considered thin films are presented in the inset of Fig. 1a and b.

By ToF-SIMS measurements, the distribution of the constituent elements on a 500/500 μm^2 area was analyzed in positive and

Table 1
Thin film thickness values obtained by profilometry analysis.

Sample	Repetition rate	Time of deposition (min)	Thickness (nm)
$CoFe_2O_4$	1 kHz	10	200
$CoFe_2O_4$		20	320
$CoFe_{1.8}Gd_{0.2}O_4$		10	140
$CoFe_{1.8}Gd_{0.2}O_4$		20	340
$CoFe_{1.8}Gd_{0.2}O_4$	10 Hz	90	350

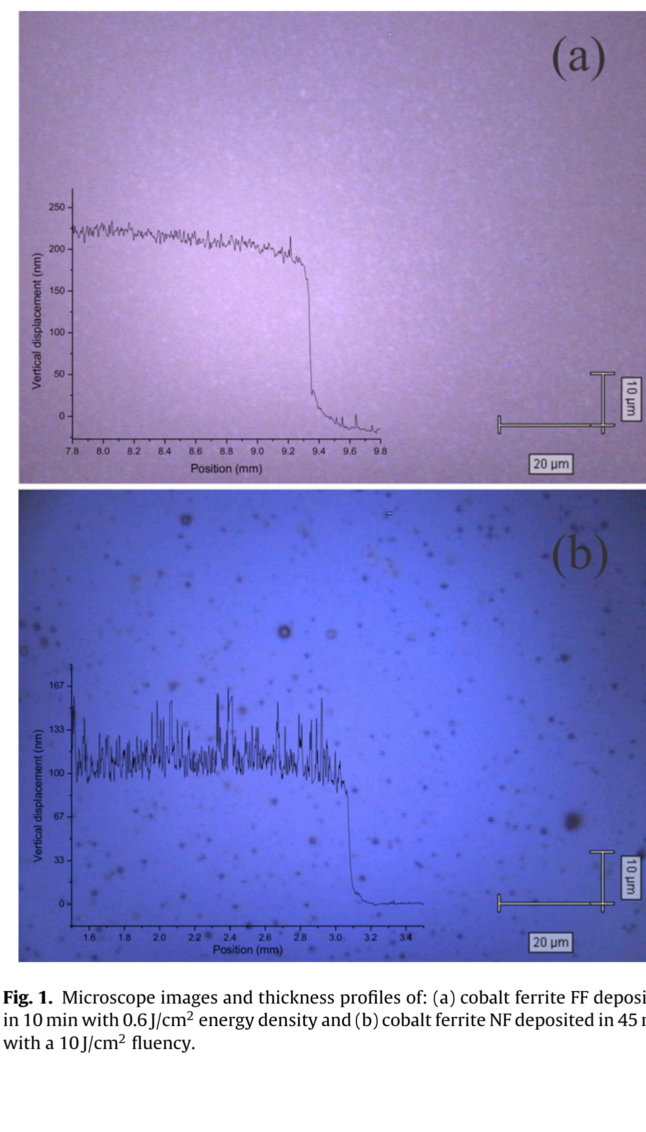

Fig. 1. Microscope images and thickness profiles of: (a) cobalt ferrite FF deposited in 10 min with 0.6 J/cm^2 energy density and (b) cobalt ferrite NF deposited in 45 min with a 10 J/cm^2 fluency.