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Pulsed laser deposition and optical characterizations of the magnetic samarium orthoferrite

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ABSTRACT

Pulsed Laser Deposition of magnetically ordered polycrystalline $SmFeO_3$ films has been optimized onto SiO_2 glass substrates as function of substrate temperature, oxygen pressure and pulsed laser fluency. Using a KrF excimer laser, crystallization temperature is found to be about 1048 K for a weak fluency of only 1.7 J cm^{-2}. We show that this growth temperature can be reduced using higher fluency and that it is possible to obtain a film texturation along the c axis by reducing the oxygen pressure at given temperature and fluency. In a second part, we focus on the $SmFeO_3$ optical constants determined by in situ ellipsometry using a stacking model and the Cauchy dispersion relation for $SmFeO_3$ layer. We show a good correlation between the transmission and reflection calculated from these data and measured by ex situ spectrophotometry in the visible range.

1. Introduction

Rare-earth orthoferrites with general formula *RE*FeO_3 (*RE* being the rare-earth element) have attracted significant interest in the 1950s and 1960s due to their interesting magnetic and magneto-optic properties with relatively high Faraday rotation [1–3].

X-ray diffraction (XRD) structural studies of *RE*FeO_3 compounds have revealed a weakly distorted perovskite structure. The orthorhombic distortion in orthoferrites increases with the size of the rare-earth ion and influences magnetic properties, essentially due to the superexchange via Fe–O–Fe bonds. Samarium orthoferrite has orthorhombic structure (Pbnm ($D2h^{16}$) space group) [4] with lattice parameters: a = 0.5394 nm, b = 0.5592 nm and c = 0.7711 nm. The iron cations with the electronic configuration $3d^5$ occupy octahedral sites whereas the rare-earth ions with an electronic configuration $4f^5$ are localized at the centre of void space formed by 8 iron–oxygen octahedra [5] (cf. Fig. 1). Historically, a fundamental research interest was developed for the canted antiferromagnetic compounds such as $SmFeO_3$ (SFO). More recently, this type of material has shown the spin dynamics one order of magnitude faster than ferromagnets, making them promising for applications [6]. Indeed, SFO presents a slight canting of the magnetic moments of Fe^{3+} ions due to Dzyaloshinsky–Moriya anisotropic exchange interaction. Therefore the SFO magnetization is relatively weak and this material was assigned to so called ‘weak ferromagnets’. Among possible magnetic configurations reported for the orthoferrites according to White [1], two are found in SFO. At low temperatures, the weak net magnetic moments are aligned along the *a* direction-magnetic configuration $\Gamma_2(F_x)$. In the temperature range between 450 K and 475 K an interesting spin reorientation occurs , as a continuous rotation of the magnetic moments leading to magnetic configuration $\Gamma_4(F_z)$, where the weak ferromagnetic moments are aligned along the crystallographic *c* axis. Above the Curie temperature 674 K [7], the magnetic ordering is lost due to the thermal disorder.

Considering the electrical properties, SFO shows a semiconducting behavior with an optical gap around 2–3 eV [8]. Current researches aim at introducing orthoferrite oxides in magnetic multilayers as a pinning layer for spintronic structures [9]. Therefore, it's important to control the strong uniaxial anisotropy of this material.

The development of the pulsed laser deposition (PLD) has recently facilitated thin film deposition even of orthoferrites [10], and our group has actively participated in tuning PLD deposition parameters particularly for $YFeO_3$ and SFO [11–13]. Different ways have already been followed to synthesize SFO films. Initially, the polycrystalline films were fabricated in two steps: first, the polycrystalline SFO target was ablated by Nd:YAG laser on the glass substrate at room temperature with subsequent sample annealing under oxygen atmosphere [10]. Later, Keller et al. [12] has managed to obtain good quality SFO films on SiO_2 glass in single step deposition by *in situ* substrate heating during the growth. Finally, Mistrik [14] studied interrelation between the laser fluency, substrate temperature and laser spot size diameter

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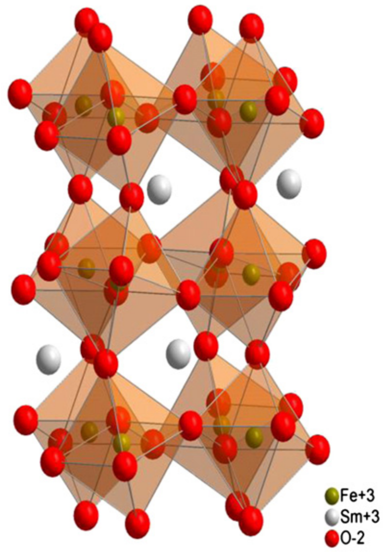

Fig. 1. Schematic representation of the $SmFeO_3$ P_{bnm} orthorhombic unit cell. Oxygen atoms are located at the tops of FeO_6 octahedra, Fe atoms at the center. Samarium atoms are placed at the center formed by 8 iron–oxygen octahedra.

for the SFO film formation. In this case, Nd:YAG laser (t = 9 ns, f = 10 Hz, λ = 355 nm) was associated with a scanner in order to homogenize the erosion of the target surface. The laser beam was focused to reach a spot size of 1 or 2 mm^2 on the target surface. For the lowest fluency (6 J cm^{-2}), SFO crystallized at temperatures above 1103 K, whereas for a higher fluency (20 J cm^{-2}), it was possible to decrease the SFO crystallization temperature down to 973 K. On the contrary, in this study, we have decreased the deposition rate by decreasing the laser fluency and obtain a better control of the quality of the films. For this, we have used a KrF laser with a 248 nm wavelength and 15–20 ns pulse duration. The beam focalization is carried out by displacement of the lens and the laser power can be tuned from 200 to 600 mJ to obtain a weak fluency ranging from 0.9 to 2.7 J cm^{-2} that is to say twice or six times less than the lowest fluency in the former study. Homogeneous target erosion is obtained by a simultaneous rotation and translation of the target. Rotation and translation speed have been optimized by simulation as a function of the target diameter and the laser repetition rate.

Influence of deposition conditions such as the substrate temperature, the oxygen pressure and the pulsed laser fluency has been investigated. Amorphous substrate, such as the SiO_2 glass, imposes no crystallographic constrains on deposited films, therefore films are relaxed and preferential crystallographic orientations (texture) can be evidenced with respect to deposition parameters. Other interest of SiO_2 glass substrate is given by the great optical contrast between the SFO film and the SiO_2 glass, in comparison with the generally used Strontium–Titanate ($SrTiO_3$) substrate. This increases the sensibility of the optical characterization, such as optical spectrophotometry and spectroscopic ellipsometry that have been used in our study.

2. Experiment

Three series of polycrystalline SFO films have been deposited by PLD onto SiO_2 glass substrate. A KrF laser (COMPEX 201-COHERENT) with a 248 nm wavelength, 15–20 ns pulse duration and 5 Hz repetition rate was used. The sample temperature was controlled using a thermocouple mounted in contact with the heater. The oxygen pressure (high purity 5 N) was regulated by a mass flowmeter, which allowed maintaining a stable oxygen pressure in the deposition chamber. The distance between substrate and the polycrystalline SFO target was 5 cm.

We investigated the influences of substrate temperature, oxygen pressure and laser fluency in three distinct series of samples (Table 1). In series I (effect of temperature), four samples were grown at oxygen pressure of 4 Pa with substrate temperature varying from 1023 K to 1098 K by steps of 25 K. The fluency was kept constant to 1.7 J cm^{-2}. In series II (effect of oxygen pressure), the oxygen pressure was 1.5, 4 and 6.5 Pa, whereas the substrate temperature and fluency were kept constant at 1098 K and 0.9 J cm^{-2}, respectively. Finally, in series III (effect of laser fluency), the substrate temperature and the oxygen pressure were fixed at 1098 K and 4 Pa, respectively. The fluency was set to following values: 0.9, 1.35, 2 and 2.7 J cm^{-2}. Deposition time was 3 h for series I and II and 1 h for series III.

The film growth was studied *in situ* by spectroscopic ellipsometer (Sentech-SE850) in the spectral range 350–850 nm operating in the rotating analyzer mode. The SFO film thicknesses and the complex refractive index ñ were determined numerically using the commercial Spectraray software, based on a Simplex algorithm in the spectral region of weak SFO absorption (500 to 850 nm). Sample reflectance and transmittance were recorded ex situ by a spectrophotometer (PERKIN ELMER—lambda 950). Surface topography was observed by atomic force microscopy (AFM) (VEECO—Dimension 3100) in contact mode with commercial DNP probes (VEECO). The crystallinity of the films was investigated by X-ray diffraction (XRD) using a θ–2θ diffractometer (SIEMENS—D5000) with the Cu K_α radiation. Peaks were indexed with ICSD 74-1474. Magnetic ordering and Curie temperature of SFO films has been determined from magneto-optic hysteresis loops recorded in Faraday configuration and at different temperatures. These measurements were carried out by custom made magneto-optic setup, which employs a photo-elastic modulator (sensitivity of around 0.5 mdeg), a xenon lamp, and monochromatic filters in the wavelength range 359–700 nm. Samples were mounted in a cryostat placed between poles of electromagnet with the maximum magnetic field of 1.2 T.

3. Results and discussion

Fig. 2(upper graph) shows the XRD scans and peaks indexation [15] of samples from the series I where the substrate temperature was varied in the range from 1023 K to 1098 K. The crystallization is obtained for substrate temperatures above 1048 K. Above 1073 K, no significant changes are observed. This is in perfect agreement with our previous study using the Nd:YAG laser. In the series II, the oxygen pressure was changed keeping constant other parameters as the temperature and the fluency at 1098 K and 0.9 J cm^{-2}, respectively. Fig. 2(middle graph) reports recorded XRD patterns. It is important to point out the appearance of a strong texture along the *c* axis, e.g. corresponding to the (001) family planes, as the oxygen pressure is decreased. For the film prepared at 1.5 Pa, from Bragg peak intensity ratio, we estimate that this film contains around 40 times more grains oriented in the (001) direction than in a randomly

Table 1
Summary of deposition parameters for SFO three series.

Series	Temperature (K)	Oxygen pressure (Pa)	Fluency (J cm^{-2})	Deposition time (h)
I	1023	**4**	**1.7**	**3**
	1048			
	1073			
	1098			
II	**1098**	1.5	**0.9**	**1**
		4		
		6.5		
III	**1098**	**4**	0.9	**1**
			1.35	
			2	
			2.7	

In bold are represented the fixed values in the series.