Applied Surface Science 283 (2013) 283–289

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Patterned ferrimagnetic thin films of spinel ferrites obtained directly by laser irradiation

I. Pasquet[a,b], L. Presmanes[a,b], C. Bonningue[a,b], Ph. Tailhades[a,b,*]

[a] Université de Toulouse, UPS, INPT, Institut Carnot CIRIMAT, 118, route de Narbonne, F-31062 Toulouse Cedex 9, France
[b] CNRS, Institut Carnot Cirimat, F-31062 Toulouse, France

ARTICLE INFO

Article history:
Received 5 February 2013
Received in revised form 24 April 2013
Accepted 31 May 2013
Available online 26 June 2013

Keywords:
Laser patterning
Laser irradiation
Spinel ferrite
Iron oxide
Magnonic crystals
Magneto-photonic crystals

ABSTRACT

Some spinel ferrites can be oxidized or transformed at moderate temperatures. Such modifications were carried out on thin films of mixed cobalt copper ferrites and maghemite, by heating small regions with a low-power laser spot applied for about 100 ns. The very simple laser heating process, which can be done directly with a conventional photolithographic machine, made it possible to generate two-dimensional magnetization heterogeneities in ferrimagnetic films. Such periodic structures could display the specific properties of magneto-photonic or magnonic crystals.

1. Introduction

From the pioneering works of Yablonovitchh [1] and John [2] optical periodic structures, called photonic crystals, have attracted much attention, not only because of their fundamental interest, but also because of their potential technological applications due to their original collective properties [3]. Making such periodic structures with ferro or ferrimagnetic materials, is also very attractive for several reasons. Firstly, optical indices can be tailored by an external magnetic field in such structures, due to the magnetic birefringence and dichroic properties of the core material. Tunable optical devices, which can be called "magneto-photonic crystals", can thus be imagined [4,5]. The second reason is that two-dimensional magnetization heterogeneities in a ferro or ferrimagnetic material, can lead to a structure able to manage spin wave propagation. These magnetic counterparts of photonic crystals are generally called "magnonic crystals"[6–8]. The two-dimensional magnetization heterogeneities can be holes or a second material, having different magnetic properties than the matrix inside which it is inserted. Such magnonic devices could find technological applications in narrow-band optical or microwave filters or high speed switches [9].

2D periodic structuration of magnetic films, has already been performed to make magnonic crystals. However, the materials used were single garnet films or magnetic alloys and the method carried out resorted to quite heavy optical or electron lithography processing [9–12]. This paper proposes a very simple laser processing of spinel ferrite films, with the aim to fabricate new magnetic devices, for instance magneto-photonic or magnonic crystals. Laser beams or spots have already been used to anneal [13–16], sinter [17] or pattern [18–24] a lot of oxides, notably spinel oxides [25,26]. Of course, spinel ferrites were chosen for this work, because of their ferrimagnetic properties, which can be easily adjusted by proper cationic substitutions. But the other reason, which is the key to successful patterning with low-power laser spots, is that spinel ferrite thin films can often display a real "thermal reactivity" at moderate temperatures. "Thermal reactivity" means reactivity towards oxygen for spinel containing cations capable of higher valence states [27], or metastability for strongly non-stoichiometric ferrites [28,29] or quite low sintering temperatures, mainly for copper substituted ferrites [30,31]. Such thermal sensitivities are already used for optical data storage [32–34].

This paper will mainly focus on thin films of mixed cobalt copper ferrites, because of their high sensitivity to laser irradiation. It will also give another example with laser patterned γ-Fe_2O_3 thin films.

* Corresponding author at: Université de Toulouse, UPS, INPT, Institut Carnot CIRIMAT, 118, route de Narbonne, F-31062 Toulouse Cedex 9, France.
Tel.: +33 05 61 55 61 74; fax: +33 05 61 55 61 63.
E-mail address: tailhade@chimie.ups-tlse.fr (Ph. Tailhades).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.05.160

2. Experimental

2.1. Sample preparation

Thin films of spinel ferrites were prepared by radio-frequency sputtering of 10 cm diameter oxide targets. For mixed cobalt copper ferrites, an oxide target having Co:Cu:Fe cations in the proportions 0.15:0.85:2 was used. The second target was made of magnetite Fe_3O_4. The sputtering machine was an Alcatel A450 equipped with a radio-frequency-generator (13.56 MHz) device as well as a pumping system (a mechanical pump coupled with a turbo molecular pump) which reaches residual pressures down to 10^{-5} Pa, a gas flow controller, a water cooled target holder and two water cooled sample holders. The films were deposited on glass substrates with an average arithmetic roughness lower than 0.5 nm.

Conventionally, a residual vacuum of 5×10^{-5} Pa was reached in the sputtering chamber before introducing the argon deposition gas. In order to obtain various microstructures for $Co_{0.15}Cu_{0.85}Fe_2O_4$, target-substrate distances of 5 and 8 cm and argon pressures of 0.5 and 2 Pa, were used. Moreover, for each experimental condition, the targets were sputtered for 20 min before starting film deposition on the glass substrate. The sputtering power was maintained at about 3 W cm^{-2} for each of the sputtering conditions used.

Below, the mixed cobalt copper ferrite samples are named "P**x**d**y**" with **x** the value of argon pressure in Pascal, and **y** the sample target distance in centimetres.

Magnetite films were obtained by magnetite target sputtering P0.5d5 conditions. These samples were oxidized at 300 °C for 2 h in order to form γ-Fe_2O_3 metastable phase.

2.2. Laser patterning

Most of the patterning experiments were done using a DWL 200 machine from Heidelberg Instruments MikroTechnik. This machine is generally dedicated to mask manufacture for optical lithography. It is a high precision tool using pixel generation technology by He–Cd laser scanning (λ = 442 nm, maximal power 125 mW). The writing speed was about 1 mm^2/s or 10 M pixels/s. The average duration of laser insolation for each pixel, is close to 100 ns and the maximal light energy is 7.8 J/cm^2. The optical system is made of an Autofocus, which has a pneumatic servo-control to correct the flatness defects. The tuning range of the Autofocus is 70 μm and its *z* resolution is 100 nm. The working distance between the sample and the objective lens was 100 μm.

Other experiments were carried out with a machine designed for the production of masters for optical disc manufacturing. The 476 nm wavelength of an Ar laser was focused by an objective lens with a numerical aperture of 0.8, flying over the sample at a distance close to 1 mm. The writing time for each pixel was close to 100 ns and the maximal light power at the sample surface was about 20 mW.

2.3. Characterization techniques

2.3.1. X-ray diffraction

Structural characterizations of films were performed by grazing angle X-ray diffraction ($\alpha = 1°$) on a Siemens D 5000 diffractometer equipped with a Brucker sol-X detector. The X-ray wavelength was that of the copper Kα ray ($K\alpha_1$ = 0.15405 nm and $K\alpha_2$ = 0.15443 nm).

2.3.2. Raman spectroscopy

Raman spectra were collected under ambient conditions using a Horiba Scientific Raman microscope fitted with a laser wavelength of 532 nm and a 100× objective lens. During the measurement, the resulting laser power at the surface of the sample was adjusted to 1.1 mW. The final spectrum is the average of three 300 s accumulations. Examination of multiple spots showed that the samples were homogeneous.

2.3.3. Magnetic measurement

The magnetic properties were measured in the plane of the films, with a SQUID magnetometer MPMSXL 7 from Quantum design. The maximal applied field for the measurements was 70 k Oe. The magnetizations of the samples were corrected for substrate contribution.

2.3.4. Thickness measurement and microscopy

Film thicknesses were measured using a Dektak 3030ST profilometer. Atomic force microscopy (AFM) was carried out with a Veeco Dimension 3000 atomic force microscope, equipped with a super sharp TESP-SS AppNano© tip (nominal resonance frequency 320 kHz, nominal radius of curvature 2 nm). Magnetic Force Microscopy (MFM) observations were also performed with the same apparatus using magnetized tips (Co/Cr coating, nominal resonance frequency 70 kHz). AFM was used to reveal the heated areas of the films, where changes in volume occurred due to stress relaxation, oxidation or crystallization. MFM is not really appropriated to study such strong topographic deformations in ferrimagnetic films. Indeed, the magnetic contrast is generally low and the topographic signal due to a high bump or a deep hollow, is difficult to remove totally from the magnetic signal. However, MFM is very powerful to reveal changes in local magnetic properties when there is no topographical modification. MFM was then used only to reveal local maghemite–hematite transformations, which can occur without topographical change and which involve the formation of antiferromagnetic zones in ferrimagnetic ferrite films.

The microstructure of the samples was also investigated by scanning electron microscopy with a JEOL JSM 6700F apparatus. The proportion of cations was determined by EDX (Princeton Gamma Tech). Some patterns were also observed with a Keyence VHX-600 digital optical microscope using a VH-Z100R or VH-Z500R objective system, having both a high resolution and a large depth of field.

3. Results and discussion

3.1. Mixed cobalt copper spinel ferrites

The ferrite thin films prepared were poorly crystallized but they displayed the main X-ray diffraction (Fig. 1) and Raman peaks (Fig. 2) of the spinel structure. Moreover they were ferromagnetic at room temperature as revealed by their M = *f*(H) hysteresis curves (Fig. 3). EDX analyses also showed that the metal chemical composition was 0.15Co:0.85Cu:2Fe, the same as that of the target. The thin films were then made of a $Co_{0.15}Cu_{0.85}Fe_2O_4$ spinel ferrite. The samples prepared at 0.5 Pa argon pressure and 5 cm from the target (samples P0.5d5), had X-ray diffraction peaks shifted towards the small angles compared to the peak positions for a powder having the same composition. An in-plane compressive stress, making the reticular distances larger in a direction close to the perpendicular of the film surface, was assumed to be responsible for this shift. By contrast, the P2d8 samples were submitted to a slight tensile stress (Fig. 1 and Table 1). Atomic force microscopy clearly shows the polycrystalline structure of the films (Fig. 4), which were made of small crystallites of about 25 nm and 40 nm for 100 nm and 1 μm thick samples respectively. The samples prepared at a high argon pressure (P2d8) displayed crystallites aggregated in larger grains separated by porosity. This porosity clearly appeared for P2d8, mainly for 1 μm thick films (Fig. 4).