



# Study on target–film structural correlation in thin cobalt ferrite films grown by pulsed laser deposition technique



V. Bilovol\*, L.G. Pampillo, F.D. Saccone

Laboratorio de Sólidos Amorfos, INTECIN-CONICET, Facultad de Ingeniería, Universidad de Buenos Aires, Buenos Aires C1063ACV, Argentina

## ARTICLE INFO

### Article history:

Received 1 August 2013

Received in revised form 14 April 2014

Accepted 15 April 2014

Available online 24 April 2014

### Keywords:

Cobalt ferrite

Thin films

Pulsed laser deposition

Structural properties

X-ray absorption near edge structure

## ABSTRACT

We prepared three films of crystalline cobalt ferrite under identical deposition conditions (time, temperature, pressure) using three different targets consolidated from  $\text{CoFe}_2\text{O}_4$  (CFO) crystalline nanoparticles (NPs). The NPs were previously prepared by a chemical route varying their synthesis conditions in order to promote different variations in the degree of structural distortions. The purpose of this work is to study how the degree of crystal distortion of the precursor material (target) influences the structural properties of the films when they are grown by pulsed laser deposition (PLD).  $^{57}\text{Fe}$  Mössbauer spectroscopy was used to study the local environment of iron atoms in the powders (targets for PLD). The Williamson–Hall plots were used to show the degree of the strain present in the films. X-ray absorption near edge structure spectra of the films, taken in grazing incidence geometry, were also carried out. The results explicitly demonstrate that the film with the largest strain was deposited using structurally more imperfect CFO powders whereas the film with the smallest strain was grown using the best powder from the structural point of view. These results were reinforced indirectly by magnetic measurements (exchange bias effect) in Fe/CFO bilayers (thin iron film was deposited additionally for this purpose) when hysteresis loops were analyzed after field cooling at a 3 T magnetic field. We show that the quality of thin cobalt ferrite films depends on the quality of the precursor material when the PLD technique is involved.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

It is known that the quality of the target strongly influences the film properties. Studies on structural relation between the target and the grown films are very important to fabricate controllable-properties of thin films. Cobalt ferrite (CFO) films have attracted considerable scientific interest because of their exceptional properties such as high coercivity and permeability at high frequencies, high chemical and mechanical stability for industrial purposes and also relatively low conductivity [1,2]. Pulsed laser deposition (PLD) growth is one of the widely used methods for CFO films' deposition because, as it is well known, this technique has the capacity to reproduce the target composition with relative facility and precise control of stoichiometry [3,4].

While a large number of reported works on CFO films are devoted to study the relationship between the deposition conditions (temperature, time, atmosphere, substrate and so on) [5–9] and film properties, little attention has been paid to the study of the structural relationship between the target and the film. In some previous works the authors analyzed the cation distribution on the magnetic properties of  $\text{ZnFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  magnetic thin films grown by PLD [10,11].

In this work, we focused our attention on the pair target–film and their structural correlation. Knowing well this relationship, it could help tuning the magnetic properties of films when particular features are required. Such may be the case, for instance, of the exchange bias (EB) effect that has become an integral part of spintronics with implications for basic research and for numerous device applications like random access magnetic storage units and spin valves.  $^{57}\text{Fe}$  Mössbauer effect spectroscopy (ME), X-ray diffraction (XRD), X-ray absorption near edge structure (XANES) technique and magnetic measurements were involved to demonstrate the relationship between the target quality and the fabricated films. Particularly, the XANES technique, a powerful synchrotron radiation tool, was applied in the grazing incidence geometry near the critical angle for total reflection where the X-ray beam is confined within a few nanometers of the surface, for studying the local distortions of probe atom.

## 2. Experimental details

Iron(III) nitride nanohydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , 99%, Anedra) and cobalt(II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 98%, Cicarelli) were used to synthesize  $\text{CoFe}_2\text{O}_4$  nanoparticles by co-precipitation method in a NaOH medium, keeping the molar ratio of Co/Fe = 0.5. Each ingredient was dissolved in a NaOH solution and then the solutions were mixed. The digestion was performed at 80 °C for 120 min. After the digestion,

\* Corresponding author.

E-mail address: [vbilovol@fi.uba.ar](mailto:vbilovol@fi.uba.ar) (V. Bilovol).

the gelatinous precipitate was filtered and washed several times using deionized water until the pH value of the solution became neutral. Finally, the gelatinous precipitate was dried at room temperature in air to obtain a powder sample.

The nanoparticles of  $\text{CoFe}_2\text{O}_4$ , with mean crystallite size  $d \approx 5$  nm, from the same batch were divided into three portions to be annealed at different conditions to promote variations on the structural features. One third was thermally annealed (TA) at  $700^\circ\text{C}$  for 5 h. After standard pressing (1.4 GPa), the corresponding target was labeled as *cf01*. A second portion was thermally treated at  $1000^\circ\text{C}$  for 5 h, with the target label being *cf02*. For the *cf01* target, using the XRD technique and grain size refinement by the Debye–Scherrer formulae,  $d$  was determined as 36 nm, while for the *cf02* target,  $d \approx 49$  nm. In order to elucidate any dependence of the crystallite size on the results, we worked with a third target, *cf03*, that was obtained by the following steps: i) TA at  $1000^\circ\text{C} \times 5$  h ( $d \approx 49$  nm), ii) ball milling (2 h), and iii) TA at  $1050^\circ\text{C} \times 5$  h ( $d \approx 36$  nm). The density of the targets is approximately  $3400\text{ kg/m}^3$ .

Films of  $\text{CoFe}_2\text{O}_4$  were deposited on Si (111) substrates by PLD using a Nd:YAG (Quanta Ray) laser at a wavelength of 355 nm, a repetition rate of 10 Hz and a fluence of  $2\text{ J/cm}^2$ . The pressure in the chamber during the deposition was 4 Pa with a substrate temperature of  $600^\circ\text{C}$ . Deposition time was 10 min with an average deposition rate of about  $4\text{ nm min}^{-1}$ . Structural properties were analyzed by XRD in a  $\theta$ – $2\theta$  diffractometer (Rigaku D/max equipped with a vertical goniometer) using  $\text{Cu-K}\alpha$  radiation and by ME under transmission geometry at room temperature (RT) with a standard constant acceleration spectrometer using a  $10\text{ mCi } ^{57}\text{CoRh}$  radioactive source. The isomer shifts ( $\delta$ ) were referred to  $\alpha$ -Fe. The magnetic properties were investigated (at RT and 20 K) in a Quantum Design PPMS vibrating sample magnetometer. Grazing incidence X-ray fluorescence (GIXRF) measurements were carried out at the XRF Fluorescence beamline of the LNLS (Campinas, Brazil), using a monochromatic X-ray beam of 9.7 keV. The setup includes  $150\text{-}\mu\text{m}$ -vertical and 4-mm slits limiting the beam size on the sample mounted on a high-precision goniometer. Angular scans around the critical angle of total (external) reflection were performed (between  $0$  and  $2^\circ$ ). The fluorescence emissions were collected using a 15-element Ge detector. After the angular scan, XANES Fe K edge (7112 eV) spectra in fluorescence mode were collected at different grazing angles using a Si (111) channel-cut monochromator. The incident beam intensity and the energy calibration were monitored using an ion-chamber and a Fe metal standard.

For the films' labels, we adopted capital letters coinciding with the corresponding targets (for instance, the CFO1 film was deposited using the *cf01* target).

### 3. Results and discussion

XRD data of the cobalt ferrite films are shown in Fig. 1. At low angles, the amorphous signal of the sample-holder contributes to the diffraction pattern together with the peak of the Si substrate. As it can be seen, all films have a preferential  $\langle 111 \rangle$  orientation. It was found that the value of the lattice constant  $a$  of the cobalt ferrite deviates from its bulk value

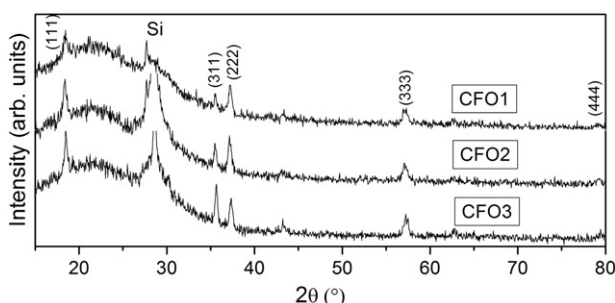


Fig. 1. XRD patterns of the films.

$8.38\text{ \AA}$  [12]. In all three samples using the position of (222) Bragg peak, the obtained  $a$  value is lower (in the range of 8.33 to  $8.37\text{ \AA}$ ). This indicates that the crystallites of the films are under some strain. Fingerprints of the (311) peak, the most intense in polycrystalline cobalt ferrite, are also present, indicating that the films are not epitaxial.

Short range order in the iron probes of the powder employed for target consolidation was analyzed by  $^{57}\text{Fe}$  ME. As this technique is sensitive to the iron environment, its spectral hyperfine parameters can give us valuable information about distortion of the crystalline lattice and bond properties. Bulk cobalt ferrite has an inverse spinel structure with one half of  $\text{Fe}^{3+}$  ions on tetrahedral (A) sites and the other half together with  $\text{Co}^{2+}$  ions on octahedral (B) sites [13].

We used two subspectra (sextets, corresponding to the Zeeman magnetic splitting of energy levels of the nucleus) for fitting procedures using Lorentzian shape lines. By similarity, only one fitted spectrum is shown (Fig. 2). The fitting parameters are collected in Table 1. One sextet corresponds to  $\text{Fe}^{3+}$  on the A sites, the other to  $\text{Fe}^{3+}$  on the B sites. The values of hyperfine magnetic fields as well as the values of the isomer shifts for both sites are very similar to those reported for partially inverted cobalt ferrite [12]. In the case of the *cf02* target, the value of the quadrupole shift,  $2\epsilon$ , is zero for both sites, indicating that iron ions have a cubic symmetry.

For the *cf03* target ( $d \approx 36$  nm)  $\delta$ , corresponding to Fe in the octahedral geometry, is a little higher ( $0.39\text{ mm/s}$ ) than the observed for the *cf02* target. Isomer shift brings out information about charge density (at nuclear sites), which can be modified by varying Fe–O bond length. The increase of  $\delta$  is attributed to the change in the  $\text{Fe}^{3+} - \text{O}^{2-}$  distance at the octahedral sites due to crystal distortion. When the distance of the ligand oxygen to iron is larger in the oxygen polyhedral, the lower is the  $s$ -electron density (at the Fe-nucleus), which results in increasing of the isomer shift. On the other hand, it was found that the quadrupole shift is distinct from zero, which indicates a deviation of iron's environment from cubic symmetry. This fact is related to synthesis conditions of the target powder. Since for the *cf01* target ( $d \approx 36$  nm), the  $\delta$  value is even higher ( $0.41\text{ mm/s}$ ), the deviation from cubic symmetry is more significant ( $2\epsilon = -0.07\text{ mm/s}$ ) suggesting even higher distortion of oxygen polyhedral.

Taking into account the sextet areas, proportional to the iron population in each site, we estimated that the concentration of  $\text{Co}^{2+}$  ions on the B-sites is the lowest in the *cf01* target (about 46%). This means that  $\text{Fe}^{3+}$  ions occupying the B-sites (octahedral) are surrounded not only by  $\text{Fe}^{3+}$  ions on the A-sites, but also by some  $\text{Co}^{2+}$  ions on the A-sites (neither  $\delta$  nor  $2\epsilon$ , for Fe in this latter position varies significantly for all powders, indicating that octahedral sites are more sensitive to structural distortion). Then, by this way it can be explained the existence of more distorted environments for Fe ions on the B-sites for the *cf01* powder

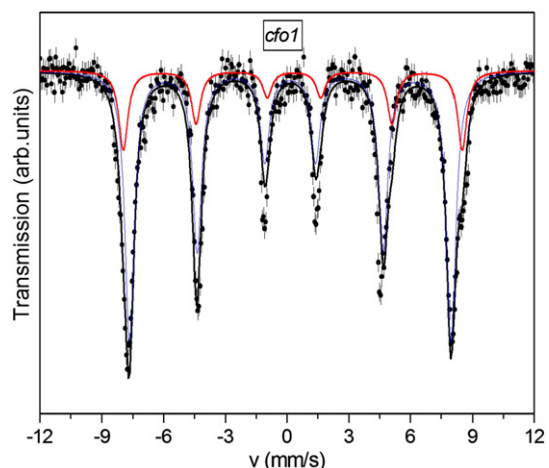


Fig. 2. Mössbauer spectrum of the target *cf01*.

Download English Version:

<https://daneshyari.com/en/article/1665179>

Download Persian Version:

<https://daneshyari.com/article/1665179>

[Daneshyari.com](https://daneshyari.com)