Journal of Magnetism and Magnetic Materials 394 (2015) 287–291

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Magnetism of $CoFe_2O_4$ thin films annealed under the magnetic field

Y.Q. Dai [a], J.M. Dai [a,*], X.W. Tang [a], Z.F. Zi [a], K.J. Zhang [a], X.B. Zhu [a], J. Yang [a], Y.P. Sun [a,b]

[a] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China
[b] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, PR China

ARTICLE INFO

Article history:
Received 16 July 2013
Received in revised form
16 January 2014
Accepted 30 June 2015
Available online 4 July 2015

Keywords:
Magnetic annealing
$CoFe_2O_4$ thin films
Magnetic anisotropy
Chemical solution deposition

ABSTRACT

Polycrystalline $CoFe_2O_4$ thin films were deposited on Si (100) substrates by chemical solution deposition with and without magnetic annealing. Magnetic field directions were applied parallel and perpendicular to the film surface during the magnetic annealing process. The variations of strain, microstructure and magnetic anisotropy of the films caused by the magnetic annealing are investigated. The results show that the film densification is promoted and grain morphology is changed by the magnetic annealing, which can be attributed to the promoting effect of magnetization force on the grain growing and grain boundary diffusing. Magnetic measurements indicate the enhancement of anisotropy and saturation magnetizations of the polycrystalline $CoFe_2O_4$ after magnetic annealing. Furthermore, the rotation of easy axis along the field direction, the increased occupation of Co^{2+} ions at B sites and the additional strain induced by the magnetic field are considered as the main reasons of the increased magnetic anisotropy.

1. Introduction

Cobalt ferrite $CoFe_2O_4$ (CFO), due to the large coercivity (H_c) and magnetization, strong magnetocrystalline anisotropy, high resistivity and good chemical stability, has been widely studied and regarded as an ideal candidate for several technologically important applications [1–4]. It is also considered as one of the best magnetic components of multiferroic composite materials because of its excellent magnetic and electronic behaviors [5,6]. In recent years, as the unique superiorities of thin films compared with ceramics and the trend of electronic devices miniaturization, more attention has been paid to the CFO thin films and a wide range of applications have been developed, such as magneto-optic media, hybrid data storage, microwave applications, magnetostrictive actuator and torque sensor [7–12].

The properties of CFO thin films can be affected by many factors, such as microstructure, chemical composition and processing method etc. Magnetic annealing, applying an external magnetic field (H_a) during the heating process, has a significant impact on the microstructure, grain morphology, defects as well as magnetic properties of the final materials. A lot of studies about the magnetic annealing effect on the polycrystalline CFO have been reported [13–16]. The uniaxial behavior was observed in the magnetic hysteresis loops and magnetostrictive measurement for the low-field-annealed polycrystalline CFO ceramics, which showed a significantly enhanced magnetostriction of −273 PPM when the measuring magnetic field was applied perpendicular to the annealing field direction [15]. A reduction of the coercivity (in the easy axis) as well as a dramatic increase in the magnitude of the magnetostriction along the hard axis were also observed in the polycrystalline CFO annealed in an external field [16]. However, few works about CFO thin films performed by the magnetic field annealing are reported. Considering the great effect of magnetic annealing on the CFO as mentioned above, the research of CFO thin films annealed with magnetic field is very necessary. Chemical solution deposition (CSD) method as an alternative approach for film preparation caused widespread concern due to several advantages, such as low cost, strict control of stoichiometry and easy to operate for large area films even on complex-shaped substrates.

In this paper, the CFO thin films are fabricated on Si (100) substrate by CSD method with and without magnetic annealing processes. Parallel and perpendicular directions of the external magnetic fields are applied during the annealing process. The effects of magnetic annealing on the grain morphology, residual strain and magnetic properties of the thin films are investigated.

2. Experimental procedure

The CFO films were deposited on Si (100) substrates via the CSD

* Corresponding author.
E-mail address: jmdai@issp.ac.cn (J.M. Dai).

http://dx.doi.org/10.1016/j.jmmm.2015.06.089
0304-8853/

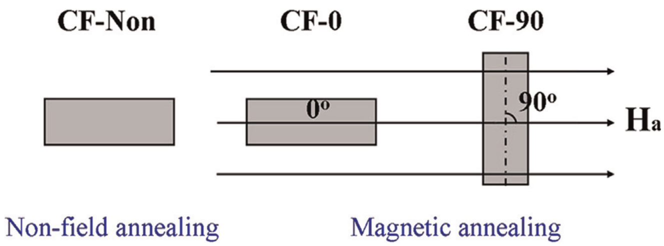

Fig. 1. Schematic illustration of the magnetic annealing process of CFO thin films.

method. Iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$, 99.99% in purity] and cobaltous acetate [$C_4H_6CoO_4 \cdot 4H_2O$, 99.5% in purity] were used as the raw materials to prepare the CFO precursor solution. 2-Methoxyethanol and acetic acid were used as the solvents with a ratio of 3:2 in volume. The final concentration of the precursor solution was 0.3 M, and ethanolamine was added to adjust the viscosity of the final solution.

The precursor solution was spin-coated on Si substrates with rotation speed 6000 rpm for 10 s, and then baked at 350 °C for 10 min in a preheated tube furnace in air. To get the desired thickness, the coating and pyrolysis processes were alternately repeated 6 times. Finally, the CFO precursor films were annealed in a tube furnace at 750 °C for 2 h with and without external magnetic field of H_a=5 kOe produced by water-cooled magnet. The films surfaces were set parallel and vertical to the external magnetic annealing field (H_a), as shown in Fig. 1. According to the angles between H_a and films surface, the samples with magnetic annealing were defined as CF-0 and CF-90, respectively. And the non-field annealing (annealed without magnetic field) sample was defined as CF-Non.

The crystallization quality and out-of-plane orientation of the films are analyzed with a Philips X'pert PRO X-ray diffractometer (Cu Kα). The surface morphologies and thickness are checked up with the field-emission scanning electronic microscopy (FE-SEM, FEI Sirion 200 type). The magnetic properties are studied by a quantum design superconducting quantum interference device (SQUID, MPMS XL5 type).

3. Results and discussion

X-ray Diffraction patterns of the CFO thin films with and without magnetic annealing process are shown in Fig. 2(a). It is observed that all the samples are single-phase without any undesirable phases, and all the diffraction peaks can be indexed with a spinel structure (Fd3m space group). The compositions obtained from the EDX spectrum, which is not shown here, indicate that Co: Fe with a ratio of 1:2.02. No apparent differences can be observed between the magnetic annealing and non-field annealing samples except the relative intensity of several peaks. But the enlarged part around the diffraction peak (311) shows a peaks shift toward the higher angle, as shown in inset of Fig. 2(a).

Because of the large misfit in thermal expansion coefficient [17,18] and lattice constant between CFO and Si as well as the different promoting effects imposed by the applied magnetic field with different directions, the residual strains in the samples must be different. Thus, based on the XRD patterns, the lattice constant a and the strain defined as $\varepsilon = \Delta a/a_0 \times 100\%$ are calculated and plotted in Fig. 2(b), where $\Delta a = a - a_0 , a_0$ is taken as the lattice constant of CF-Non. It is observed that the films lattice constant decreased and compressive strain increased. Compared with the CF-Non, both CF-0 and CF-90 have larger compressive strain. The magnetic domain wall motion of the films would be changed by the different strains and the magnetization behaviors are greatly affected, which will be discussed in the magnetic part.

Surface and cross-section FE-SEM images of the CFO thin films with and without magnetic annealing are shown in Fig. 3. The films total thickness is about 300 nm deduced from the cross-section FE-SEM image. As shown in Fig. 3, the surface morphologies of the films exhibit some apparent changes under the magnetic annealing and non-field annealing films. Especially, compared with the non-field annealing films, more densification and different grain morphologies can be observed in magnetic annealing samples. It clearly illustrates that the densification and grain connectivity of the thin films are improved by magnetic annealing. Densification and grain connectivity are important factors to the magnetic properties of the thin films. The changes lead to some different magnetic properties for the magnetic annealing films compared with the non-field annealing samples, which will be discussed in the magnetic part.

The magnetic materials can be affected by magnetization forces produced by the magnetic field, and the nature of magnetization force depends on the magnetic properties of the materials. The CFO is one of the typical ferrimagnetic materials at room temperature and paramagnetic during the annealing process, the magnetization force is a pulling one. The magnetization force, as a driving force, drives the grain boundary diffusing and grain growing along the field direction in order to decrease the free energy. In this condition, the driving force acting on the boundary of two grains that have different susceptibilities is given by$p_m = \frac{\mu_0 H^2}{2}(\chi_1 - \chi_2)$, where μ_0 is the vacuum permeability, H is the magnetic field strength, $\chi_1$and χ_2 are the magnetic susceptibilities of the adjacent grains to the boundary, respectively [19,20]. The properties of magnetic materials could be improved due to the magnetic force, which can change the densification and grain

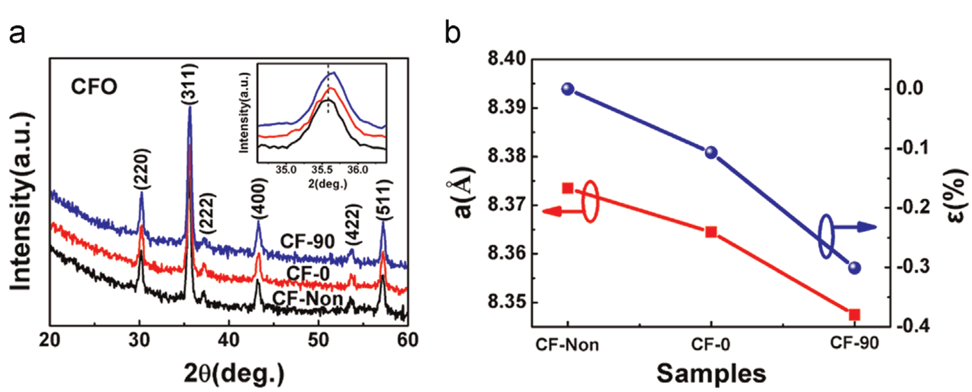

Fig. 2. (a) XRD patterns of the CFO films with and without magnetic annealing prepared by chemical solution deposition. (b) Variation of lattice constants and strains for the different samples.