Journal of Magnetism and Magnetic Materials 460 (2018) 361–367

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Research articles

Influence of oxygen vacancies and $La_{0.7}Sr_{0.3}MnO_3$ layer on the structure and magnetic properties of cobalt ferrite thin films

G.Q. Gao, C. Jin *, P. Wang, X. Pang, D.X. Zheng, H.L. Bai

Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, Faculty of Science, Tianjin University, Tianjin 300350, People's Republic of China

ARTICLE INFO

Article history:
Received 26 December 2017
Received in revised form 10 March 2018
Accepted 5 April 2018
Available online 6 April 2018

Keywords:
Cobalt ferrite film
Ferrimagnetism
Oxygen vacancies
Magnetic properties

ABSTRACT

$CoFe_2O_4$ thin film is expected to be used as the spin filter in spintronics. In order to prepare high-quality $CoFe_2O_4$ thin films for spin filtering, we studied the influence of oxygen vacancies on the structure and magnetic properties of cobalt ferrite ($Co_{1-x}Fe_{2+x}O_4$, CFO) films prepared in different atmosphere, and obtained the CFO films without significant soft magnetic phase under optimum Ar and O_2 atmosphere condition. We further investigated the magnetic properties of the CFO/$La_{0.7}Sr_{0.3}MnO_3$ (CFO/LSMO) bilayers containing various thicknesses of CFO films, and found that the CFO/LSMO bilayers with the ultrathin CFO films primarily display the soft magnetic properties.

1. Introduction

Spinel ferrites are promising alternatives for spintronics, due to their rich electric and magnetic properties with high Curie temperatures (T_C) [1–5]. Among spinel ferrites, $CoFe_2O_4$ is a hard magnetic insulator with stable chemistry property. Ideal $CoFe_2O_4$ belongs to the inverse spinel ferrite, with half of Fe^{3+} cations occupying the tetrahedral sites (A) made up by O atoms and all of Co^{2+} cations and the remaining Fe^{3+} cations occupying the octahedral sites (B) [6]. Due to the unquenched orbital momentum of Co^{2+} in the low symmetrical crystal field, $CoFe_2O_4$ has the unique magnetic properties with the large magnetostriction (8×10^{-4}), first magnetic crystal anisotropy constant (4×10^6 ergs/cm^3) [7] and coercivity ($H_C = 12.5$ kOe) [8] at room temperature. These unique properties and high Curie temperature ($T_C = 793$ K) make it as a candidate for ferroelectromagnet [9,10] and spin filtering [11].

Due to its complex and susceptible structure, the properties of $CoFe_2O_4$ films were tailored by the strain which can change the density of antiphase boundaries [12], cation redistribution [13] and spin canting state [14]. Beside the cations doping [14,15] from the stoichiometry standpoint, the magnetic and electric properties of spinel ferrites were systematically studied by the oxygen and cation vacancies which can be simply introduced by varying deposition [16–18] or annealing [19] atmosphere. And it was reported that the magnetization may be determined by the valences of cations, for the $CoFe_2O_4$ thin films grown at various oxygen flow rates [20].

Moreover, the $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) shows the novel magnetic and electronic properties determined by the competition between the charge, spin, orbit and lattice degrees of freedom [21], and is very promising for the application in full oxide spintronics [22] with its colossal magnetoresistance [23] and half-metallic properties at room temperature [24]. The magnetotransport properties of LSMO/$CoFe_2O_4$/Nb(0.5%):$SrTiO_3$ junctions were investigated and the spin-filter efficiency of the $CoFe_2O_4$ layer is estimated to be 20% [25]. However, the ideal $CoFe_2O_4$ tunnel barrier is expected to present the high spin-filter efficiency even at room temperature [26]. Recently, the partially ferromagnetic properties were revealed at the interface of the ultrathin $CoFe_2O_4$ films [27]. Thus, the magnetic properties of the $CoFe_2O_4$/LSMO bilayers with the various thicknesses of the $CoFe_2O_4$ films are interesting.

In this work, we investigated the structure and magnetic properties of the cobalt ferrite ($Co_{1-x}Fe_{2+x}O_4$, CFO) films prepared in various atmospheres, and the CFO/LSMO bilayers with various thicknesses of CFO films deposited and annealed in the optimum atmosphere.

2. Experimental

The CFO films were deposited on $SrTiO_3$ (STO) (1 0 0) substrates by DC magnetron reactive co-sputtering at O_2 flow rate (φ_{O2}) ranging from 3.0 sccm to 10.2 sccm, and then annealed in vacuum and deposition ($O_2 + Ar$) atmosphere, respectively. The depositing equipment has been fully detailed elsewhere [28]. The Fe (99.99%

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* Corresponding author.
E-mail address: chaojin@tju.edu.cn (C. Jin).

https://doi.org/10.1016/j.jmmm.2018.04.008
0304-8853/

purity) and Co (99.9% purity) targets were sputtered at the DC power of 64–72 W and 36–28 W, respectively. During the deposition, the Ar (99.999% purity) flow rate (φ_{Ar}) was kept at 100 sccm with the φ_{O2} (99.999% purity) at 3.0, 5.4, 7.8 and 10.2 sccm, respectively. The sputtering pressure was maintained at 2.0 Pa with substrate temperature at 550 °C for 20 min. After the deposition, the films were annealed at 550 °C for 1 h, and then cooled to room temperature at 5 °C/min in vacuum and O_2 + Ar atmosphere, respectively. The film thickness is about 280, 240, 200 and 160 nm and the x is estimated to be about 0.06, 0.19, 0.25 and 0.32, for the $Co_{1-x}Fe_{2+x}O_4$ films with the φ_{O2} increasing. For the CFO/LSMO bilayers, the LSMO (≈30 nm) layers were grown on STO (1 0 0) substrates under the 1 Pa atmosphere of φ_{O2}=30 sccm and φ_{Ar} = 50 sccm, and then the CFO films with the different thicknesses (5, 10, 20, 30 and 60 nm) were subsequently deposited on the LSMO/STO layers at the atmosphere of φ_{O2} = 7.8 sccm and φ_{Ar} = 100 sccm and annealed under the O_2 + Ar atmosphere, mentioned above.

The film thicknesses were revealed by Dektak 6M surface profiler. The structure properties were analyzed by X-rays diffraction (XRD, Cu K_α source), and the surface morphologies were characterized by atomic force microscope (AFM). The chemical compositions were determined by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS) attached on a scanning electron microscopy (SEM). The magnetic properties were measured by Quantum Design magnetic property measurement system (SQUID–VSM).

3. Results and discussion

3.1. Structure properties of the CFO films

Figs. 1 and 2 show the typical XRD patterns of the CFO films deposited at φ_{O2} = 3.0, 5.4, 7.8 and 10.2 sccm, and then annealed in vacuum and O_2 + Ar atmosphere, respectively. The XRD pattern of a bare STO substrate from the same batch is used to identify the peaks of substrate in Figs. 1(e) and 2(e), respectively. The peaks can be divided into two sets: one from the spinel CFO films, and another from the STO substrate. Besides the strong (4 0 0) and (8 0 0) diffraction peaks, the weak (2 2 0), (3 1 1) and (4 4 0) diffraction peaks of CFO films appear. These weak peaks are mainly ascribed to the large deposition rates (8–14 nm/min) and the large lattice mismatch (7.4%) between the films and substrates. The large deposition rate cannot allow for the full mobility of ions, which results in the decreasing of oriented growth [29]. Moreover, the large interface strain, caused by the large lattice mismatch, can be released by different oriented nucleation [30].

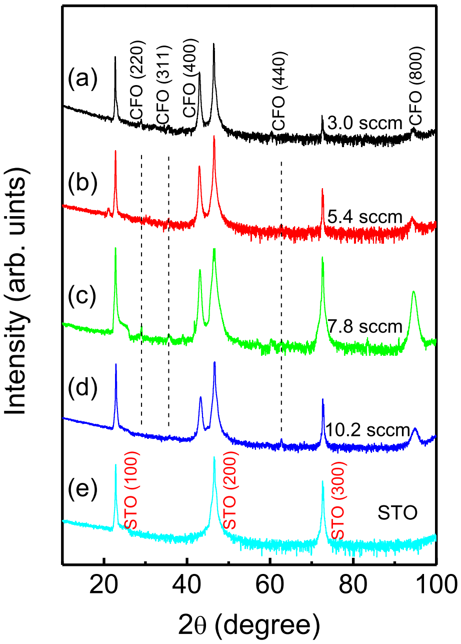

Fig. 1. XRD of the STO substrate and the CFO films deposited at different O_2 flow rates and annealed in vacuum.

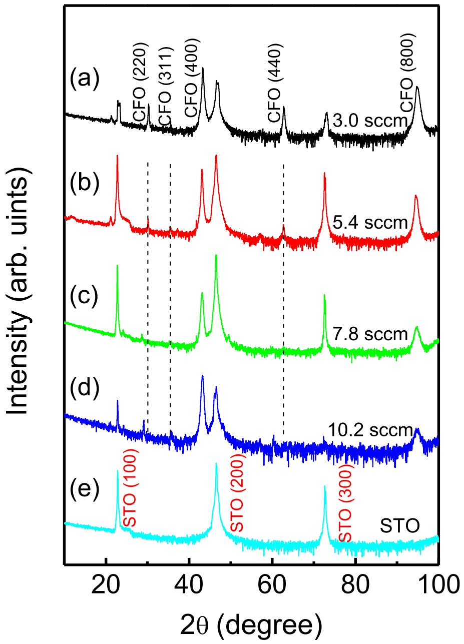

Fig. 2. XRD of the STO substrate and the CFO films deposited at different O_2 flow rates and annealed in O_2 + Ar atmosphere.

Fig. 3(a)–(d) and (f)–(g) present the surface morphologies of CFO films annealed in different atmosphere, respectively. As shown in Fig. 4, the average grain size on the surface of the film annealed in O_2 + Ar atmosphere is larger than that of the one annealed in vacuum and deposited at the same φ_{O2}, except for the films deposited at φ_{O2} = 7.8 sccm. The morphologies of CFO films are mainly attributed to the misfit dislocations on the island growth mode which is resulted by the large lattice mismatch (7.4%) between the films and the substrates [31,32]. Moreover, the CFO films are not easy oxidized [33] and oxygen vacancies on the surface are formed at vacuum annealing [34], which may reduce their surface crystal quality.

For the films deposited at the high φ_{O2} (7.8 sccm and 10.2 sccm), the cracks are observed, which are more obvious for films deposited at φ_{O2} = 7.8 sccm, shown in Fig. 3. For the film deposited at φ_{O2} = 7.8 sccm and annealed in O_2 + Ar atmosphere, the density and average size of grains are smallest among all the films, shown in Figs. 3 and 4. These observations suggest that the film deposited at φ_{O2} = 7.8 sccm and annealed in O_2 + Ar atmosphere has the optimum surface property. The island growth mode relates to the O_2 flow rate and growth rate [33,29]. As the O_2 flow rate increases, the growth rate reduces. At the optimal O_2 flow rate (7.8 sccm), the adequate mobility of the ions significantly reduces the misfit dislocations and surface roughness. The reduction of the misfit dislocation decreases the strain relief. The cracks are the results of the strain relief for the films deposited at low growth rates. The thicker cracks significantly increase the roughness for the film deposited at φ_{O2} = 7.8 sccm and annealed in vacuum. At higher O_2 flow rate (10.2 sccm), the ejected metal species may be oxidized by excess oxygen before the adequate mobility [35], which increases the surface roughness.