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Structure and properties of Zn-doped $CoFe_2O_4$ thin films via a sol–gel method

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Abstract Zn-doped cobalt ferrite $Co_{0.9}Zn_{0.1}Fe_2O_4$ (CZFO) films with the spinel structure were fabricated on Pt(111)/Ti/SiO_2/Si(100) using a sol-gel method, and the effect of annealing temperature and time on structure and magnetic properties of the CZFO thin films were investigated. The coercivity and saturation magnetization of the films are not sensitive to annealing time, and increase with a rise in the annealing temperature below 800 °C. The CZFO thin films annealed at 800 °C show the best crystallization and the highest coercivity (3.5 kOe), and above 800 °C, the coercivities of the films decrease as a result of formation of multi-domains, while the saturation magnetization comes to stable.

Keywords Cobalt ferrite · Thin films · Sol–gel · Magnetization · Coercivity

1 Introduction

Ferrite thin films with the spinel structure are of increasing scientific interest and of importance in microwave industry because of their low cost, easily manufacturing and remarkable electric and magnetic properties. Among various ferrite materials, a spinel type of cobalt ferrite, $CoFe_2O_4$, is a well-known hard magnetic material which has been studied in details due to its high coercivity, moderate saturation magnetization, remarkable chemical stability and mechanical hardness [1, 2], as well as the largest magnetostriction in the spinel ferrites, by which was used in combination with ferroelectrics to produce magnetoelectric effect [3]. The magnetic and electric properties of cobalt ferrites can be modified by adding small amount of foreign ions, such as Li^+ [4], Al^{3+} [5] and lanthanide ions [6].

Thin films of cobalt ferrite have been prepared by several techniques such as sol–gel method [7, 8], pulsed laser deposition [9], magnetron sputtering [10] and ion-beam deposition [11]. Recently, among these various preparation methods of the ferrite thin films, the sol–gel processing has gained much interest, because of its many advantages for preparing thin films. For example, the sol–gel method is a simple process with excellent control of the stoichiometry, and a homogeneous film with small grain size of ferrite can be formed over a large area via the sol-gel method at a relatively low processing temperature, which is required for high-density magnetic recording media [12].

In this study, we report the growth of Zn-doping Co ferrite thin films on silicon substrates by a sol–gel method. The films are characterized by using an X-ray diffractometer (XRD), a vibrating sample magnetometer (VSM), scanning electron microscopy (SEM) as a function of the annealing temperature and the time. Magnetic and structural properties of $Co_{0.9}Zn_{0.1}Fe_2O_4$ thin films prepared by the sol–gel method will be presented.

2 Experiment

Zn-doped cobalt ferrite $Co_{0.9}Zn_{0.1}Fe_2O_4$ (CZFO) films with a thickness of about 240 nm were deposited on conventional Si(100) substrates by a sol–gel method, whose details were described below.

$Co(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were used as the starting materials, which were dissolved in

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2-methaoxyethanol with a molar ratio of Co/Zn/Fe= 0.9:0.1:2. The solution was mixed and stirred for 3 h. The concentration of the final solution was adjusted to 0.2 M. After aging the hydrolyzed solution for 24 h, thin-film deposition was carried out on Si(100) substrates by spin coating each layer at 3,000 rpm for 30 s. The coating was dried at 200 °C for 300 s, and preannealed at 400 °C for 300 s to prepare the precursor films. The desired film thickness (about 240 nm) was achieved by repeating the spin-coating–drying–annealing process. Then the precursor films were annealed at 600~900 °C for 150~1,200 s by rapid thermal processing. No magnetic field was applied while annealing, so the magnetic grains were randomly orientated.

The crystalline phase of the thin films was identified by X-ray diffraction. To observe the morphology of films, scanning electron microscopy (SEM) investigation was carried out. Vibrating sample magnetometer (VSM) was used to measure the magnetic properties of the films.

3 Results and discussion

XRD patterns of CZFO thin films after annealed at different temperatures for 600 s are shown in Fig. 1. XRD measurements show that the Co ferrite films annealed at and above 600 °C is polycrystalline with a single phase of the spinel structure and that the films exhibits no preferred crystallite orientation. All peaks correspond to a cubic spinel-type lattice without any secondary or impurity phases. It is shown in the XRD patterns that the increase in the annealing temperature yields the sharpness of the major peaks (311) owing to the increase of the grain sizes of Co–Zn ferrite films. With increasing the annealing temperature from 600 to 900 °C, the CZFO peak intensity increase. But above 800 °C, the increase in the peak intensities is very little due to well-crystallization at temperature over 800 °C for the CZFO films. Figure 2 shows the XRD patterns of the films annealed at 700 °C for different time. The results indicate that the results are not sensitive to annealing time, and that there is no obvious difference between the films annealed for 60 and 1,200 s, which suggests that 60 s is enough for crystallization of the CZFO thin films by rapid thermal processing.

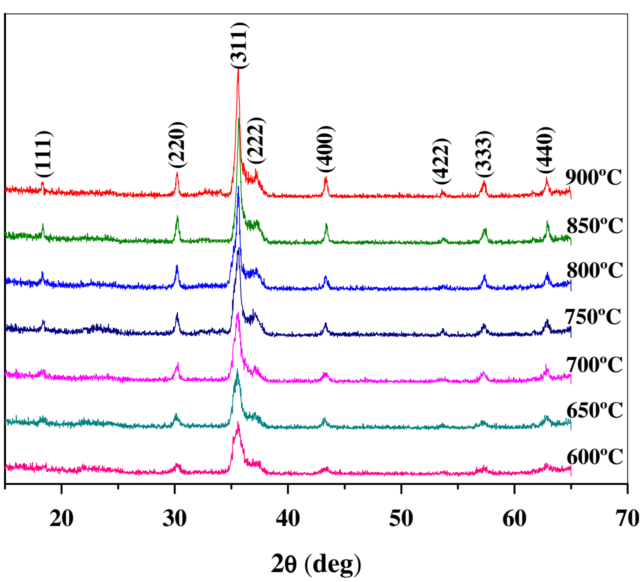

Fig. 1 X-ray diffraction patterns of the thin films prepared by a sol–gel method and annealed at different temperature for 600 s

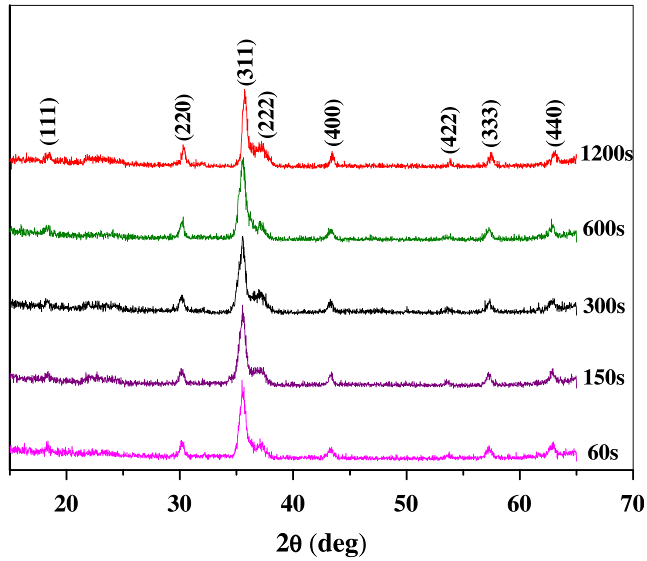

Fig. 2 X-ray diffraction patterns of the thin films prepared by a sol–gel method and annealed at 700 °C for different time

The surfaces of the CZFO thin films on Si(100) substrate annealed at different temperatures for 600 s were observed by SEM. As shown in Fig. 3, the films have a dense and uniform microstructure without any cracks at different temperatures. With the temperature rising from 600 °C [Fig. 3(a)] to 900 °C [Fig. 3(d)], the sizes of grains increase clearly, from about 20 nm at about 600 °C to 122 nm at 900 °C. By comparing Fig. 3(b),(e) and (f), the grain sizes, which have no obvious change as increasing annealing time, are not sensitive to annealing time. It is in agreement with the above measurement results. Figure 4 shows the SEM cross-sectional microstructure of the CZFO thin film annealed at 600 °C for 600 s. The films were prepared by repeating spin-coating for two times, each for about 120 nm, possessing a total thickness of about 240 nm.

The magnetic properties of the films have been determined at room temperature by applying magnetic fields parallel and perpendicular to the film plane with a vibrating sample magnetometer. Figure 5 shows the typical hysteresis loops of the CZFO films annealed at 600 °C which were measured with the fields up to 10 kOe. The two loops are almost the same in shape, while the out-of-plane loop has a

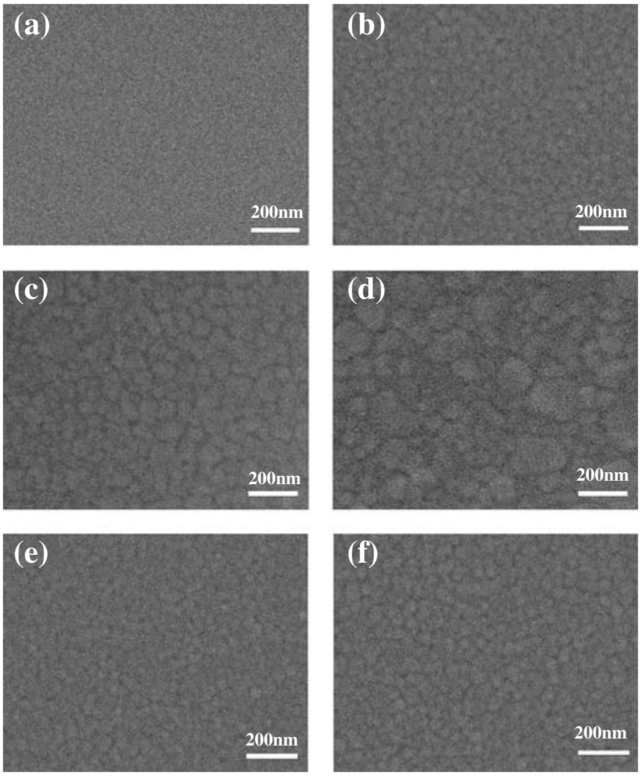

Fig. 3 SEM micrographs of the CZFO thin films annealed at (**a**) 600 °C, (**b**) 700 °C, (**c**) 800 °C, and (**d**) 900 °C for 600s; and at 700 °C for (**e**) 60s and (**f**) 300s

little larger coercive force than the in-plane loop. This is because the easy axes of the grown ferrite films are randomly oriented. As indicated in the XRD measurement, the films show no structurally preferred orientation, and thus the easy axes, i.e., (100) planes, are randomly located. It can therefore be concluded that the magnetic properties of the magnetic thin films are almost independent of the direction of the applied external field. This means that the film is suitable for isotropic recording application.

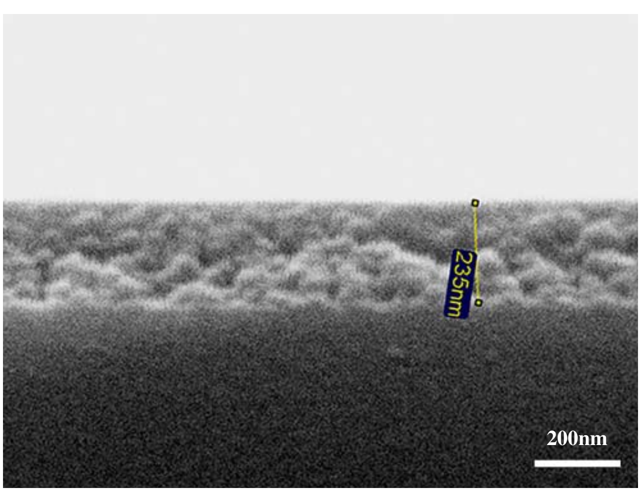

Fig. 4 SEM micrograph of the cross-section of the CZFO thin films

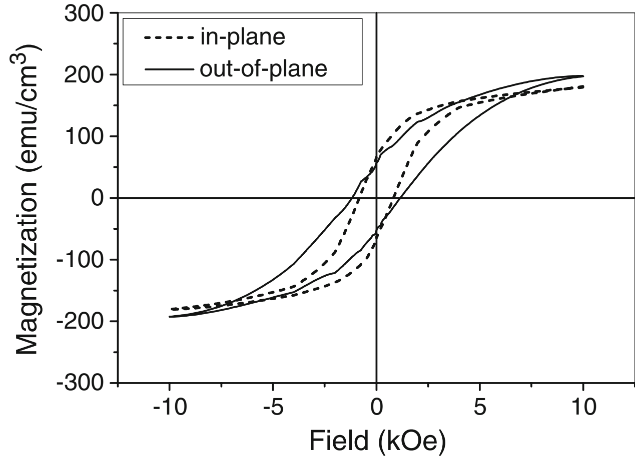

Fig. 5 In-plane and out-of plane hysteresis loops of the thin film fired at 600 °C

Figure 6 shows that the coercivity (H_c) and saturation magnetization (M_s) of the films change with the annealing time and temperature. As the annealing time is prolonged, the coercivity and the saturation magnetization of the films increase a little [Fig. 6(a)], indicating that the crystallization of the films becomes a little better when annealed for a bit longer time. But the change is not obvious from XRD

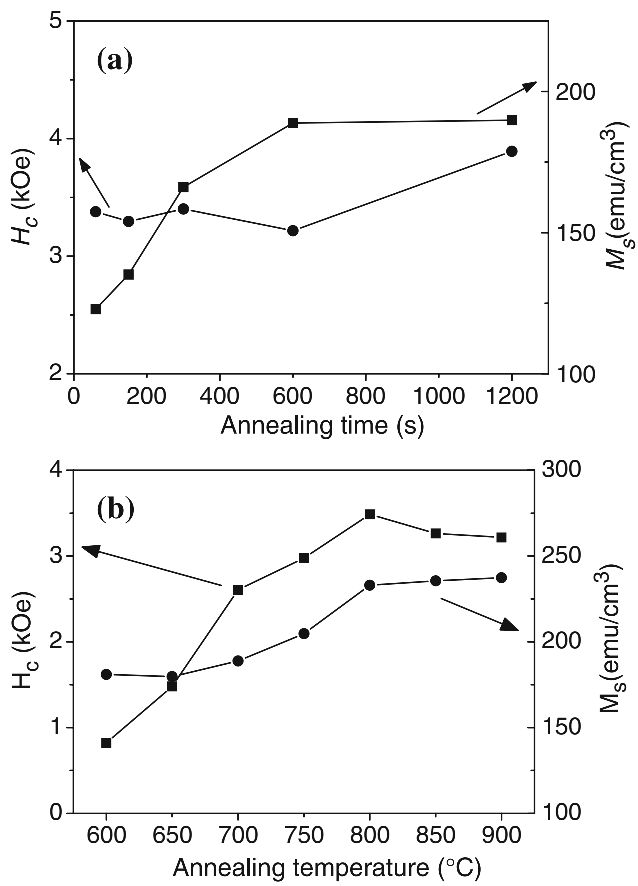

Fig. 6 (**a**) Annealing time and (**b**) temperature dependence of coercivity H_c and saturation magnetization M_s for the CZFO thin films

patterns and SEM micrographs of the thin films. The coercivity H_c and the saturation magnetization M_s increase with the rise in the annealing temperature when the films are annealed below 800 °C for 600 s [Fig. 6(b)], since the higher the annealing temperature, the better the crystallization. According to Luborsky [13], the reduction in grain size results in the increase in the coercivity of the cobalt ferrite powder initially and then the coercivity becomes decreased. It is believed that the films have grain sizes small enough to make their coercivities increase as the annealing temperature rises higher. When the grain sizes increase to a critical size, in the films, single-domains, which possesses high coercivities, begin to transform into multi-domains, leading to the reduction in the coercivities. For the cobalt ferrite $CoFe_2O_4$, the critical single-domain size is about 70 nm [14]. SEM micrographs indicate the grain sizes in the films are about 70 nm annealed at 800 °C, which is pretty much the same thing with the critical single-domain size, resulting in the highest coercivity (3.5 kOe) at this annealing temperature. Above 800 °C, the coercivities of the films decrease as a result of the formation of multi-domains.

4 Conclusion

In conclusion, Zn-doped Co-ferrite thin films has been deposited on Si(100) single-crystal substrates by using the sol–gel method. The films are polycrystalline with a single phase of the spinel structure. The influence of annealing temperature and time on the magnetic characteristics of the films has been investigated. The coercivity and saturation magnetization are not sensitive to annealing time, and increase with a rise in the annealing temperature below 800 °C, and above 800 °C, the coercivities of the films decrease as a result of the formation of multi-domains while the saturation magnetization come to stable.

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