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Effect of Co^{2+} ions on the microstructure and magnetic properties of nanocrystalline $Co_xFe_{3-x}O_4$ films

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Abstract

$Co_xFe_{3-x}O_4$ nanocrystalline films ($x = 0.2 - 0.8$) on SiO_2 substrates were prepared by a sol–gel method. The microstructural and magnetic properties of samples were measured by an X-ray diffractometer (XRD) and a vibrating sample magnetometer (VSM), respectively. Atomic force microscopy (AFM) was used to investigate the surface image of the sample. The measurement results of XRD at room temperature show that the pure spinel structure of the film could be obtained at $x = 0.8$. The magnetic measurements reveal the magnetic properties of the samples depend strongly on Co^{2+} ions content, and the optimal parameters of the saturation magnetization and coercivity in $Co_xFe_{3-x}O_4$films are obtained at $x = 0.8$. Here the coercivity reaches 1.954 kOe. The average grain sizes of the film are less than 30 nm obtained from the microscopy images. The situ measurement at high temperatures of range from 293 to 773 K shows that the microstructures of $Co_{0.8}Fe_{2.2}O_4$ film have good thermal stabilization.

Keywords: Cobalt ferrite film; Magnetic property; Microstructure; Sol–gel technology

1. Introduction

Being high-density magnetic and magneto-optic recording materials, cobalt ferrite films have attracted considerable attention recently [1–5]. Cobalt ferrite is a spinel ferrimagnetic oxide which has shown high saturation magnetization, large magnetocrystalline anisotropy and large magneto-optical Faraday rotation, as well as excellent chemical stability and mechanical hardness. Especially cobalt ferrite films can be used for contact recording media that will be ultimately be required in the near future. At present, to be a good candidate magneto-optic recording media, with cobalt ferrite films two problems have to be solved. One is how to obtain appropriate coercivity and high saturation magnetization simultaneously, the other is how to improve film's quality and make a grain refinement which may enhance the signal-to-noise in magnetic recording process. Thus, it becomes worthy of being attended to reduce heat treatment temperature to make grain refined. Moreover, good thermal stabilization of structures is very much required, which can avoid a bad effect brought by disk reading and writing temperature on structure. Cobalt ferrite films can be prepared by sol–gel spin-coating technique, ion-beam deposition, RF sputtering, pulsed laser deposition and molecular-beam epitaxy (MBE). Films fabricated by a sol–gel spin-coating technique may possess some remarkable merits, such as low heat treatment temperature, homogeneous particles, small grain size, and low cost. Such films are favorable to commercial production. A series of $Co_xFe_{3-x}O_4$ ($x = 0.2-0.8$) films were synthesized by a sol–gel method with citric acid as complexing agent. The effect of Co^{2+} ions on the microstructure and magnetic properties is studied. The grain size of the samples is reduced effectively and the coercivity reaches 1954 Oe. Due to the research results on thermal stabilization reported above, that are very important to magneto-optic recording media a little heretofore, the thermal stabilization of microstructure and magnetic properties for $Co_{0.8}Fe_{2.2}O_4$ ferrite film were situ measured at high

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temperature. The experimental results show that the microstructures of $Co_{0.8}Fe_{2.2}O_4$ film have good thermal stabilization.

2. Experimental

With appropriate portions of Co $(NO_3)_2 \cdot 6H_2O$ and Fe $(NO_3)_3 \cdot 9H_2O$ as the former body, citric acid as the complexing agent and glycol as the thickener, the sol of Co-ferrite was prepared and its total concentration of the metal ions is 0.26 mol/L. Films were deposited on SiO_2 substrates by a spin-coating technique using 3500 rpm for 15 s. The coating was repeated seven times, and the deposited films were dried at 423 K for 15 min between coatings. $Co_xFe_{3-x}O_4$ films with approximately thickness of 2 μm were obtained by annealing the deposited films at 673–903 K for 1.5 h in air.

The structures of $Co_xFe_{3-x}O_4$ films were investigated by an X-ray diffraction (XRD) using CuKα radiation. The temperature dependence of the structure on $Co_{0.8}Fe_{2.2}O_4$ ferrite film was situ measured from room temperature to high temperature 773 K. The magnetic properties of the samples were obtained using a vibrating sample magnetometer (VSM) at an external field of 15 kOe at room temperature, while that of $Co_{0.8}Fe_{2.2}O_4$ ferrite film was measured with an external field of 2.5 kOe at high temperature. The external field was applied parallel to the film plane. To observe the surface morphology of the films and evaluate the grain size, atomic force microscopy (AFM) measurements were carried out at room temperature. The maximum scan size is 1.5 μm, and scan rate is 1 Hz.

3. Results and discussion

3.1. Microstructure of samples at room temperature

Fig. 1 shows the XRD patterns of $Co_{0.8}Fe_{2.2}O_4$ films annealed at 673–903 K. It indicates that the film annealed at 673 K has a spinel single phase and the spinel phase peaks increase as annealing temperature increases from 673 to 903 K. In Fig. 1, one can see the sharpness of the major peak (3 1 1) at 903 K, and this shows that the structure of film is a good crystal.

Crystallite sizes of all films were determined from the XRD patterns by using Debye–Scherrer equation. Table 1 gives the variation of crystallite sizes of $Co_xFe_{3-x}O_4$ films with annealing temperature. It is observed that the grain size varies between 14 and 81 nm. The grain size increases with annealing temperature when Co^{2+} content x is the same, and decreases basically with increasing Co^{2+} content x when annealing temperature is the same. Obviously, the grain size of the sample with high Co^{2+} content ($x \geqslant 0.6$) is small, which is advantageous to decrease the noise of grain boundary [6,7] and to enhance magnetic recording properties.

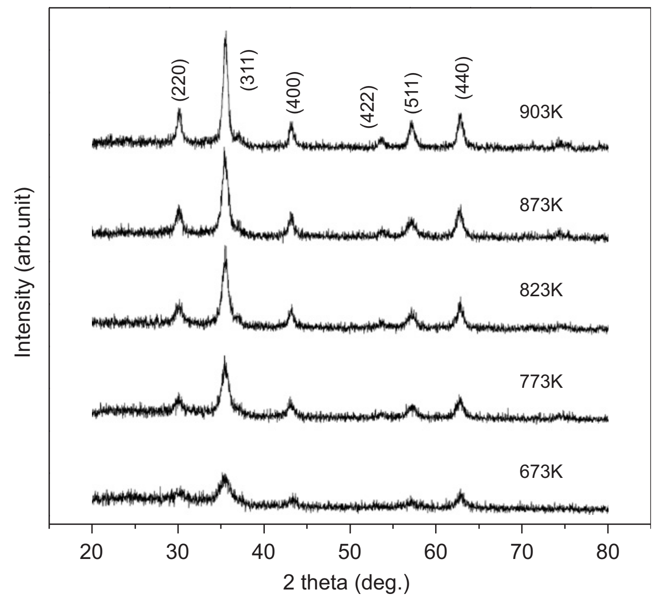

Fig. 1. XRD patterns of $Co_{0.8}Fe_{2.2}O_4$ film annealed at different temperatures.

Table 1
The variation of crystallite size of $Co_xFe_{3-x}O_4$ films with annealing temperatures

D (nm)					
T_a (K)	673 K	773 K	823 K	873 K	903 K
$x = 0.2$	18.4	33.2	47.5	63.1	81.3
$x = 0.4$	13.8	16.3	26.2	35.9	62.5
$x = 0.6$	14.7	17.4	26.0	28.4	31.2
$x = 0.7$	14.7	20.7	23.1	27.8	33.7
$x = 0.8$	14.2	16.9	23.1	26.5	29.6

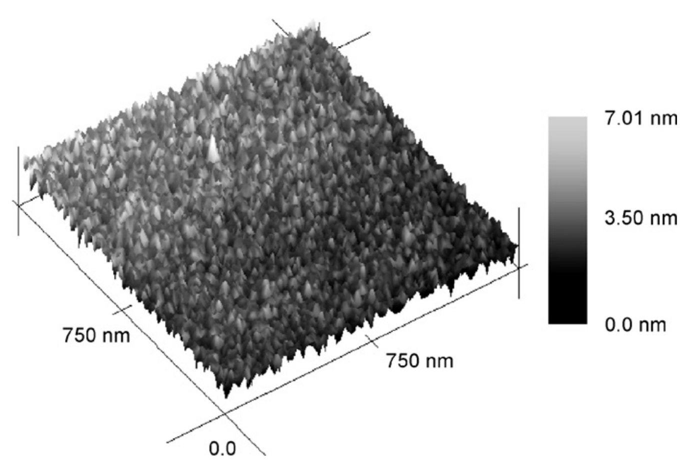

Fig. 2. AFM image of $Co_{0.8}Fe_{2.2}O_4$ film surface annealed at 823 K.

Fig. 2 shows the three-dimensional AFM image of $Co_{0.8}Fe_{2.2}O_4$ film annealed at 823 K. It is noted that the surface grain distribution of the film is uniform. AFM analysis indicated that the root mean square roughness of