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High-coercivity Co-ferrite thin films on (100)-SiO_2 substrate

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Co-ferrite films were deposited on SiO_2 single-crystal substrates. The as-deposited films were amorphous. The crystallization required an annealing at 700 °C or higher. Magnetic properties were found to be strongly dependent on annealing temperature, annealing duration, and film thickness. A small film thickness can restrict the formation of large particles. A coercivity as high as 9.3 kOe was achieved in the 50 nm film after annealing at 900 °C for 15 min deposited on (100)-SiO_2 substrate. The high coercivity was associated with a nanostructure, lattice strain, and larger Raman shift with a relatively sharp peak. [DOI: 10.1063/1.1695438]

Co-ferrite has been a very interesting subject for both research and application for many decades, because of its unique properties, such as high Curie temperature, relatively high saturation magnetization, diffusion anisotropy, and good chemical stability.[1–5] Recently, Co-ferrite has shown high coercivity and high remanence in thin films and nanopowders.[6,7] Large Kerr and Faraday rotations have been reported in Co-ferrite-based materials.[8,9] Co-ferrite thin films with high coercivity possess a significant potential in many applications including magnetic recording, magneto-optical recording, and microelectromechanical system devices.[9–12]

In this work, we have deposited Co-ferrite films on SiO_2 single-crystal substrates. Coercivity as high as 9.3 kOe was achieved in 50 nm Co-ferrite film on (100)-SiO_2 substrate. This value is a high room temperature coercivity for Co-ferrite. We have found that magnetic properties are strongly dependent on heat treatment condition and film thickness. An increase in lattice strain and larger Raman shift were found in thin films with high coercivity.

A sputtering target with a stoichiometric composition of $CoFe_2O_4$ was prepared by sintering at 1300 °C. Films were prepared by rf sputtering with a deposition rate of 0.2 Å per second. The film thickness was estimated using a profiler. Films were annealed in an air atmosphere at a temperature between 500 and 1200 °C for between 5 and 120 min. The structure was characterized by Cu $K\alpha$ x-ray diffraction (XRD), atomic force microscopy (AFM), high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy. Magnetic properties were measured using a vibrating sample magnetometer.

Figure 1 shows the XRD patterns of 100 nm films after annealing at different temperatures for 2 h. No crystalline peaks were found in the XRD pattern of the as-deposited film, indicating an amorphous structure. The formation of the spinel Co-ferrite phase required an annealing at 900 °C or higher. In the XRD pattern of the film annealed at 900 °C, a small peak at 33.2° indicated the presence of a small amount of hematite (Fe_2O_3).

Table I gives magnetic properties (saturation magnetization, coercivity, and remanence measured in the two directions—in plane and out of plane) of 100 nm films before and after annealing at different temperatures for 2 h. It can be seen that the film after annealing at 500 °C still possessed low magnetization, confirming the amorphous structure which is expected to be paramagnetic.[13] A significant increase in magnetization was found after annealing at 700 °C, showing the formation of the ferrimagnetic Co-ferrite phase. Coercivity reaches a maximum of 7.5 kOe after annealing at 900 °C and then decreases with increasing annealing temperature. Our XRD and AFM studies showed that the decrease in coercivity was associated with the growth of grain size. The calculated grain size from XRD is shown in Table I. The sample annealed at 900 °C possessed an average grain size of 70–80 nm, while the average grain size increased to 120–130 nm after annealing at 1200 °C.

In this work, we have studied the effect of film thickness on magnetic properties (as shown in Table II), when films were annealed at the optimized temperature for 2 h (900 °C). When the film was very thin (20 nm), coercivity was low (3.5 kOe). The 50 nm film possessed a very high value of coercivity (8.4 kOe). An increase in film thickness resulted in a reduction of coercivity.

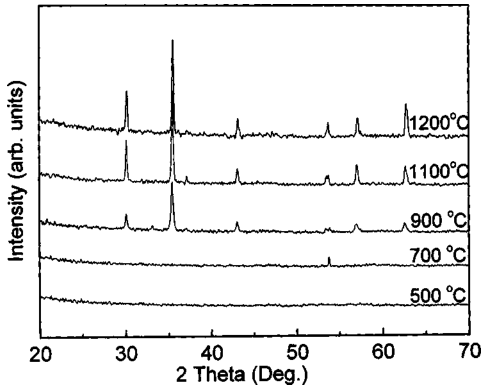

FIG. 1. XRD patterns of Co-ferrite films with a thickness of 100 nm after annealing at different temperatures for 2 h.

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TABLE I. Magnetic properties of 100 nm films in the as-deposited state and after annealing at different temperatures for 2 h. (Coercivity $H_{c\parallel}$ measured in the film plane—in plane; the remanence ratio $(M_r/M_s)_\parallel$ in plane; coercivity $H_{c\perp}$ measured perpendicular to the plane—out of plane; remanence ratio $(M_r/M_s)_\perp$ out of plane; saturation magnetization M_s; grain size determined from Scherrer's formula.)

	$H_{c\parallel}$ (kOe)	$(M_r/M_s)_\parallel$	$H_{c\perp}$ (kOe)	$(M_r/M_s)_\perp$	M_s (emu/cm^3)	Grain size (nm)
As-deposited	0.01	⋯	0.01	⋯	10	⋯
500 °C	0.05	⋯	0.025	⋯	48	⋯
700 °C	2.6	57%	2.2	45%	195	⋯
900 °C	7.5	75%	6.1	65%	303	75.1
1100 °C	5.7	76%	5.1	72%	341	99.2
1200 °C	2.0	70.8%	1.3	50%	350	126.1

Our AFM study revealed a clear relationship between microstructure and coercivity. As shown in Fig. 2, the 20 nm film was not continuous and the microstructure was not uniform (since a few relatively large particles were visible). The 50 nm film possessed a uniform microstructure, as all particles were found in the range of 40–50 nm. Figure 3 gives HRTEM images of the 50 nm film after annealing at 900 °C for 2 h. Grains of 30–50 nm were observed under HRTEM. The grain size was in the same order of the particle size under AFM. In the 100 nm film, the average particle size under AFM was bigger (70–80 nm) and a few large particles were observed. The presence of the larger particles indicated the possibility of abnormal grain growth. When the film thickness was grown to 450 nm, the surface was fully covered with large particles and the microstructure was not uniform. This work showed that the microstructure is strongly dependent on the film thickness. When the film was too thick, large particles were formed immediately after crystallization. These results indicated that a thin film can restrict the formation of large particles. The decrease in coercivity with increasing film thickness was certainly associated with the formation of large particles.

In this work, we have studied magnetic properties as a function of annealing time at the optimized temperature (900 °C). A reduction in annealing time resulted in a further increase of coercivity. The high value of coercivity (9.3 kOe) was obtained after annealing for 15 min. This value is much higher than the coercivity of bulk Co-ferrite (below 1 kOe). This film possessed an in-plane anisotropy, as high coercivity and remanence were measured in plane, as shown in Fig. 4.

It is very interesting to investigate the coercivity mechanism. Except for a nanograined structure, the fitting of XRD peaks for thin films indicated the presence of strain. Strain in Co-ferrite thin films has been reported previously, and it may contribute to high coercivity.[7,12] Raman spectroscopy is a powerful tool for the examination of strain.[14]

TABLE II. Magnetic properties of Co-ferrite films with different thicknesses. All samples with different thicknesses were annealed at 900 °C for 2 h. (Coercivity $H_{c\parallel}$ measured in the film plane—in plane; the remanence ratio $(M_r/M_s)_\parallel$ in plane; coercivity $H_{c\perp}$ measured perpendicular to the plane—out of plane; remanence ratio $(M_r/M_s)_\perp$ out of plane; saturation magnetization M_s; grain size determined from Scherrer's formula.)

Thickness (nm)	$H_{c\parallel}$ (kOe)	$(M_r/M_s)_\parallel$	$H_{c\perp}$ (kOe)	$(M_r/M_s)_\perp$	M_s (emu/cm^3)	Grain size (nm)
20	3.5	80.6%	1.8	61%	220	28.9
50	8.4	85%	2.0	60%	250	55.6
100	7.5	75%	6.1	65%	303	75.1
150	3.2	78%	3.1	66%	291	168.5
450	2.7	81.6%	2.4	69%	345	259.2

Figure 5 shows the Raman spectra of the tetrahedral site for Co-ferrite powder and the Co-ferrite films (50 nm and 450 nm, respectively, after annealing at 900 °C) together with the reference sample (Co-ferrite powder).[15] There are two sites (octahedral and tetrahedral, as denoted as O and T sites) for $3d$ ions in the spinel structure. Because of a strong overlapping of the O-site peak with the peaks of SiO_2, only the peak of the T site is shown in Fig. 5. It can be seen that the T-site peak of the reference sample is broadened. The 450 nm Co-ferrite appeared sharper and a small blueshift was visible. For the 50 nm Co-ferrite, the sharper peak had a more obvious blueshift. As reported previously,[14] lattice strain may result in a shift of the Raman peak. A blueshift in Co-ferrite films in this work was associated with the lattice strain observed in our XRD examinations.

As reported,[16] diffusion anisotropy can be achieved in Co-ferrite, because spinel Co-ferrite may contain a relatively high density of vacancies and possess a relatively high diffusion rate of ions.[7] In this work, we have performed magnetic annealing on a powder reference sample and Co-ferrite films. The reference powder sample possessed a relatively large diffusion anisotropy after a magnetic annealing at 300 °C. On the other hand, the 450 nm film only had a small magnetic anisotropy after magnetic annealing, while no sig-

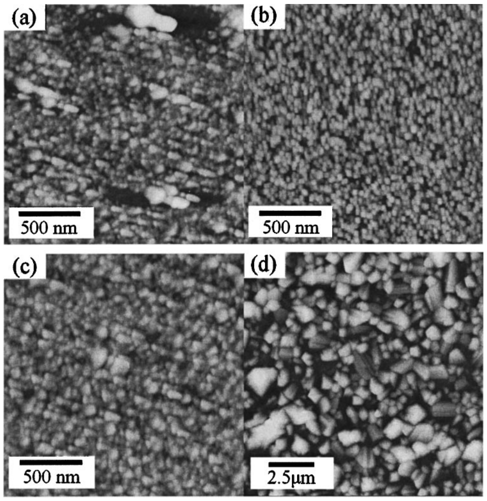

FIG. 2. AFM images of Co-ferrite films after annealing at 900 °C for 2 h with different thicknesses: 20 nm (a), 50 nm (b), 100 nm (c), and 450 nm (d).

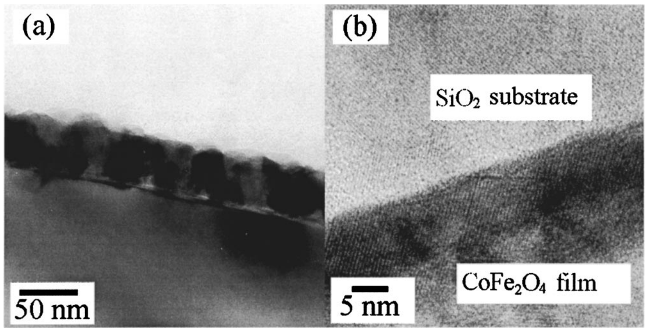

FIG. 3. HRTEM images of the 50 nm Co-ferrite after annealing at 900 °C for 2 h: Grain structure (a) and cross section (b).

nificant magnetic anisotropy was observed in the 50 nm film after magnetic annealing. This result indicated that the ionic diffusion is strongly restricted in Co-ferrite films, particularly in thin films (50 nm). These could be related with the sharpness of Raman peak[15] and high coercivity in Co-ferrite thin films. The investigation will be continued in our future study.

As found in this work, thin Co-ferrite films deposited on a (100)-SiO_2 substrate possessed high values of coercivity accompanied by the presence of a relatively large lattice strain. Co-ferrite and SiO_2 have a relatively large difference in thermal coefficient.[17] The relatively large lattice strain in Co-ferrite thin films was probably due to the difference in thermal coefficient, because the Co-ferrite phase was formed at a relatively high temperature (900 °C). The presence of lattice strain may induce a large magnetic anisotropy and therefore lead to high coercivity.[12,18] The lattice strain is expected to be reduced with increasing film thickness, while coercivity decreased with film thickness. The coercivity mechanism and the relationship with lattice strain need to be investigated further.

In conclusion, Co-ferrite thin films were deposited on SiO_2 single-crystal substrates. The influence of annealing temperature and film thickness on magnetic properties has been investigated. A coercivity of as high as 9.3 kOe was achieved in the 50 nm Co-ferrite film on a (100)-SiO_2 substrate after annealing at 900 °C for 15 min. This coercivity value is very high for Co-ferrite. The high coercivity is associated with nanograined structure and lattice strain, accompanied by a blueshift and sharper peak in the Raman spectrum.

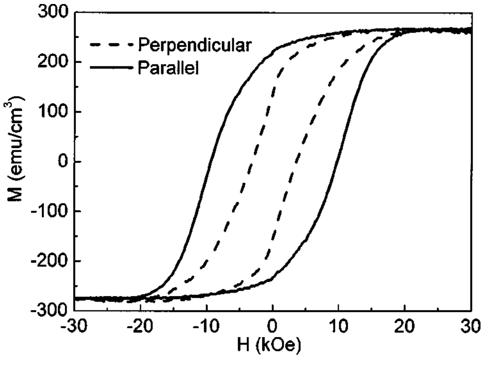

FIG. 4. Hysteresis loops of the 50 nm $CoFe_2O_4$ film after annealing at 900 °C for 15 min in the two directions, perpendicular and parallel to the film plane.

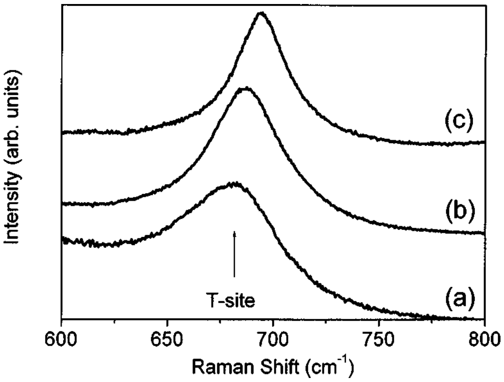

FIG. 5. Raman spectra of the $CoFe_2O_4$ reference sample (compacted powder pellet) (a), 450 nm $CoFe_2O_4$ film (b), and 50 nm film (c).

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