

Columnar co-ferrite films with high coercivity on glass and silica substrate by sol-gel method

Y. OKAZAKI*, H. OHASHI, Y. OHYA, S. YANASE, S. HASHI

Department of Materials Science, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu, 501-1192, Japan

Magnetic properties related to nano-structure have been investigated for sol-gel grown Co-ferrite thin films on the substrates of glass and SiO₂(100). The magnetic properties depended on the annealing temperature and the coercivity of 7.7 kOe was obtained at 923 K on the SiO₂(100) substrate. The microstructure transformed into columnar from granular at the annealing temperature of 923 K.

(Received March 13, 2008; accepted May 5, 2008)

Keywords: Co-ferrite, Thin film, Coercivity, So-gel method, Microstructure, Crystallization

1. Introduction

Co-ferrite (CoFe₂O₄) has the highest value of magneto-crystalline anisotropy and magnetostriction among ferrite materials and has been researched as a candidate for high density magnetic recording media. For the applications of Co-ferrite, high coercivity of the Co-ferrite thin films is necessary. However, relatively low coercivity always limits the potential applications of Co-ferrite. Many intensive researches have been conducted in the world to obtain higher coersivity of Co-ferrite films by controlling the microstructure or doping with different element. A coercivity as high as 5.4 kOe was obtained in Co-ferrite powder prepared by chemical method[1] and a coercivity as high as 9.3 kOe was reported by sputtering method and subsequent annealing of 1173K[2].

On the other hand, coercivity in Co-ferrite films made by sol-gel method had been reported as low as 2.5 kOe [3-5]. We have reported a high coercivity of 6.3 kOe of Co-ferrite films prepared by sol-gel process obtained in the film annealed over 923K where the microstructure of the films changed from granular to columnar [6]. Here, we examined a mechanism to obtain high coercivity of Co-ferrite films by sol-gel method considering crystallization procedure and microstructure of the films. A coercivity of 7.7 kOe was achieved on SiO₂ substrate which is three times higher than that ever reported in Co ferrite thin films by sol-gel method.

2. Experiments

Co-ferrite thin films were prepared by a sol-gel method. Weighed amount of Fe(NO₃)₃·9H₂O, and Co(NO₃)₂·6H₂O were dissolved in 2-methoxyethanol and refluxed for 24 hours. Films were deposited by a spin coating method on Corning#1737 glass and a thermally oxidized SiO₂ (100) substrate with 3000rpm for 25 seconds. The films obtained were dried at 383K for 10 minutes and annealed at various temperatures from 773K to 1073K for 30 minutes in atmosphere. These serial procedures were repeated two to twelve times and two to twelve layers of Co-ferrite were obtained. Most of the films were deposited six times and the thickness was 200-250 nm. The deposited films were characterized by

X-ray diffraction (XRD) and examined microstructure on the surface and in the cross section by scanning electron microscopy (SEM). Magnetic properties, coercivity and magnetization, were measured in parallel (in-plane) and perpendicular (out-of-plane) directions to the films by a vibrating sample magnetometer (VSM) magnetized up to 20 kOe.

3. Results and discussion

Fig.1-a, b show the XRD patterns of the films annealed at various temperatures a) from 773K to 973K for the glass and b) from 893K to 1073K for SiO₂ substrates, respectively. All films consist of a single-phase spinel structure consistent with a typical spinel structure of Co-ferrite powder prepared by a conventional solid state reaction method of which peaks are indicated by Joint Committee on Powder Diffraction Standards (JCPDS) in Fig.1. The increase of annealing temperature advanced the degree of crystallization. The films on the glass substrate annealed over 923K exhibited (400) peak. The films on the SiO₂ substrate showed the sharp (400) peak from low temperature of 873K and the peak enlarged at higher temperature that indicated a texture along <100> axis was developed perpendicularly to the film plane. Fig. 2 shows the intensity ratio of I(400)/I(311) vs. the annealing temperature. The relative peak intensity of (400) increased more on the SiO₂ substrate than the glass with the increase of annealing temperature.

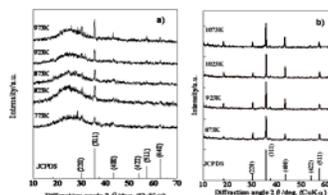


Fig. 1. XRD patterns of Co-ferrite films annealed at various temperature on glass (a) and SiO₂ (b) substrate.

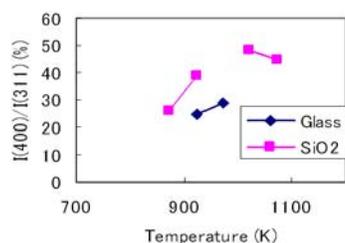


Fig. 2. Intensity ratio of (400)/(311) vs. annealing temperature.

The microstructure observation by SEM revealed that the columnar microstructure was obtained in the films annealed over 923 K on the both substrates, while the microstructure in the films annealed at 773-873 K remained granular. Fig. 3 shows the microstructure of the films annealed at a) 873 K, b) 923 K on the glass substrate and c) 923 K on the SiO₂ substrate. The microstructure on the SiO₂ substrate at 923 K showed few granular grains adjacent to the substrate and the columnar grains grew straight from the substrate as shown in Fig. 3c. On the other hand, for the glass substrate the columnar grains grew slantingly to the substrate and more granular grains remained in the neighbor of the substrate that reflected the intensity ratio of (400)/(311) in Fig. 2.

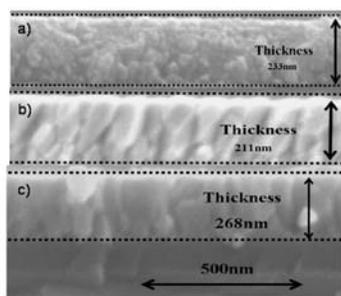


Fig. 3. Microstructure of the cross section of the films by SEM, annealed at a) 873K, b) 923K on the glass and c) 923K on the SiO₂ substrate.

Fig. 4 shows the grains on the top surface of the films annealed at (a) 823K and (b) 923K observed by SEM. The grain size, averaged in 500 nm square, increased from 20nm to 130nm with the increase of annealing temperature and the grain size dispersed widely over 973K due to abnormal grain growth as shown in Fig.5.

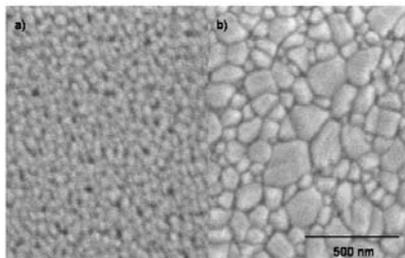


Fig. 4. Microstructure of the top surface of the films annealed at a) 823 K and b) 923 K.

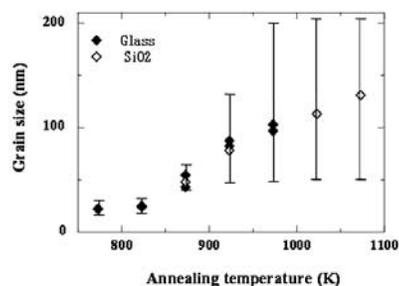


Fig. 5. The average grain size vs. annealing temperature.

Magnetic properties of the films on the glass and SiO₂ substrate at different annealing temperature were measured. Fig. 6 and Fig. 7 show the coercivity (H_c) and saturation magnetization (M_s), respectively. The in-plane and the out-of plane coercivity of the films increased with increasing annealing temperature up to 923 K and then decreased at higher than 923 K. The coercivity of the films on the SiO₂ substrate, both in-plane and out-of-plane, was relatively higher than that on the glass substrate, as shown in Fig. 6. The coercivity both in-plane and out-of-plane was about 2 kOe annealed at 773-823 K.

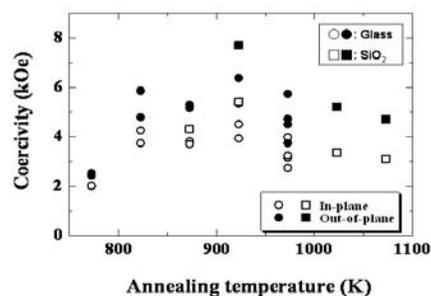


Fig. 6. Annealing temperature dependent coercivity measured in-plane and out-of-plane.

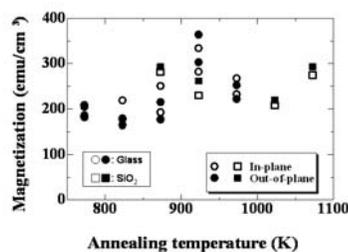


Fig. 7. Annealing temperature dependent magnetization measured in-plane and out-of-plane.

The 7.7 kOe is the highest coercivity ever reported in Co-ferrite films by sol-gel methods. The coercivity of the films on the glass substrates showed the maximum of 6.4 kOe in the out-of-plane, which was the same value as reported [6]. The coercivity in-plane on the glass and SiO₂ substrate showed 4.5 kOe and 5.4 kOe, respectively, at 923K. The saturation magnetization (M_s) was the highest

of 364 emu/cm³ for out-of-plane annealed at 923 K on the glass substrate, while Ms on the SiO₂ substrate was relatively high from 873 K to 1073 K.

The maximum coercivity of 7.7 kOe was obtained at 923K in out-of-plane of the film on the SiO₂ substrate.

Fig. 8a and Fig. 8b show the hysteresis loops of the films in-plane and out-of-plane on the glass and SiO₂ substrates, respectively. No anisotropy was seen in the film

annealed at 773 K. The coercivity in out-of-plane increased as the annealing temperature increased up to 923 K on both the glass and the SiO₂ substrats, which was quite contrary to the Co-ferrite films by sputtering [2]. The magnetization also increased with the increase of annealing temperature up to 923 K and decreased at 973 K.

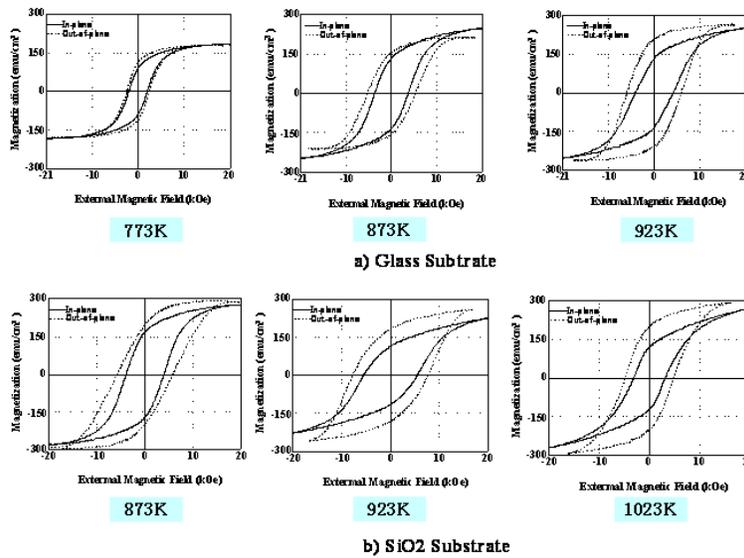


Fig. 8 Hysteresis loops of the films on a) glass substrate and b) SiO₂ substrate, annealed at various temperatures (Solid line: in-plane, dotted line: out-of-plane).

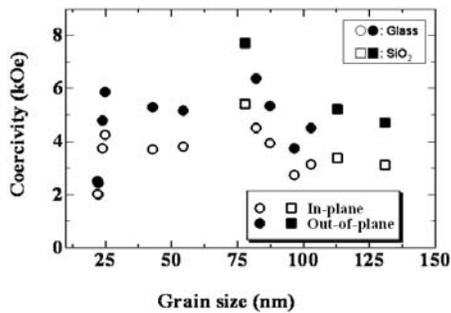


Fig. 9. The average grain size dependent coercivity.

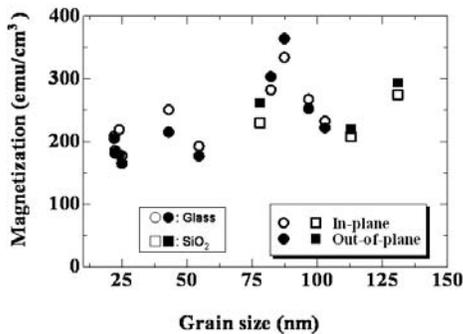


Fig. 10. The average grain size dependent magnetization.

Fig. 9 and 10 show the grain size dependence on coercivity and saturation magnetization. The optimum averaged grain size for both coercivity (Hc) and saturation magnetization (Ms) was found to be 80-85 nm.

The results of XRD analysis and the microstructure observation made it clear that the columnar grain was essential in order to obtain high coercivity in any Co-ferrite films prepared by sol-gel or sputtering methods. On the other hand, the low coercivity of Co-ferrite films by the conventional sol-gel methods would come from granular grains. The new method we found to obtain the columnar microstructure was to crystallize each coating layer after drying each spin coating. The crystallized grains in the first layer grew to the next coating layer one by one. Therefore, it may be important for the crystallographic axis of the grains in the first layer adjacent to the substrate. More grains with (100) parallel to the substrate were produced on the SiO₂ substrate than on the glass substrate due to the affinity between SiO₂ (100) and these (100) grains grew predominantly, as shown in Fig. 2c. On the other hand, the grains in the first layer on the glass substrate were relatively random oriented and some grains with disadvantage orientation could grow to the next layer and remained in the first layer as shown in Fig. 8b.

The new sol-gel method of crystallizing each coating layer just after each spin coating would be able to grow the (100) grains preferably and grows the columnar grains step by step. To verify our new method, an experiment was performed. Co-ferrite films were prepared by sol-gel method with six layers by using the same solutions. However, in this case, each coating layer was not annealed just after spin coating for crystallization but only dried at 383 K. After depositing six coating layers in this way, the films with six layers were finally annealed at 923 K for 3 hours. Fig. 11 shows the microstructure of the film with granular grains. The coercivity was as low as 2 kOe and the hysteresis loops indicated magnetic isotropy as shown in Fig. 12. Thus, the films by the conventional sol-gel method showed low coercivity and remained granular grains. As the result, the columnar grains were found to be inevitable to obtain high coercivity for Co-ferrite films.

The columnar grains could be identified with the aspect ratio which was measured by the averaged ratio of length to width of the grains in cross section observed by SEM. Fig. 13 shows that the coercivity depended on the aspect ratio of the columnar grains on both the glass and SiO₂ substrates. High aspect ratio of more than 2.5 would be preferable for higher coercivity.

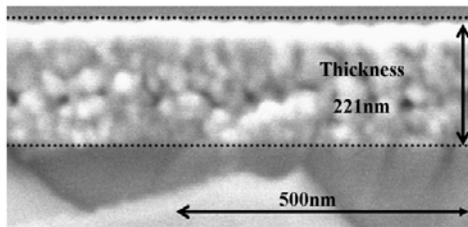


Fig. 11. Microstructure of the film crystallized at a time after six depositions.

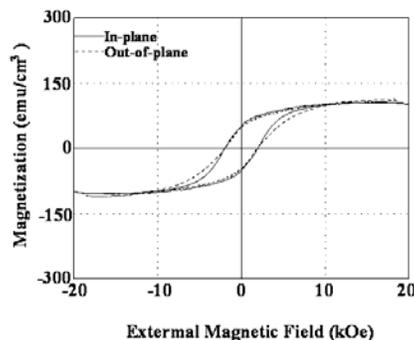


Fig. 12. The hysteresis loop of the film crystallized at a time after six depositions.

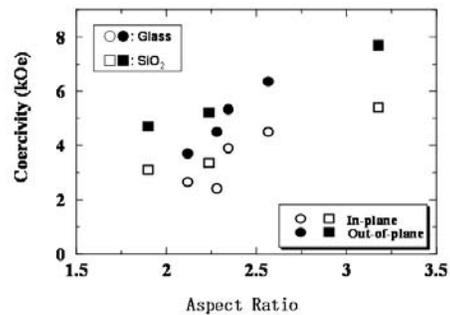


Fig. 13. Coercivity dependence on the aspect ratio of the columnar grains.

4. Conclusions

Co-ferrite thin films prepared by sol-gel method showed the highest coercivity of 7.7 Oe on the SiO₂ (100) substrate. We found the columnar grain structure is essential to obtain higher coercivity in Co-ferrite which could be obtained by annealing and crystallizing each deposited layer just after spin coating process. The crystalline structure has changed from the granular to columnar between 873 K and 923 K of annealing temperature. The SiO₂ (100) substrate advanced the columnar grain growth and higher coercivity.

References

- [1] G. Pourroy, S. Lakamp, M. Multigner, A. Hernando, J. L. Dormann, R. Vanluzuela-Monjaras, *J. Phys. IV* **7**, 327 (1997).
- [2] Y. C. Wang, J. Ding, J. B. Yi, B. H. Lie, T. Yu, Z. X. Shen, *J. Mag. Mag. Mater.* **282**, 211 (2004).
- [3] J. G. Lee, H. M. Lee, C. S. Kim, Y. J. Oh, *J. Mag. Mag. Mater.* **177-181**, 900 (1998).
- [4] J. Vejpravová, J. Plocek, D. Ninansky, A. Hutlová, *IEEE Trans Mag.* **41**(10), 3469 (2005).
- [5] K.P. Chae, J. G. Lee, W. K. Kim, Y. B. Lee. *Journal of Mag. and Mag. Mater.* **248**, 236 (2001).
- [6] H. Ohashi, Y. Okazaki, Y. Ohya, S. Yanase, S. Hashi, *IEEE Trans Mag.* vol.42, No.10, 2891 (2006).

*Corresponding author: okazaki@gifu-u.ac.jp