Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

MAGNETITE AND MAGHEMITE THIN FILMS FOR MAGNETIC RECORDING

T.S. Chin and W.D. Chang
Department of Materials Science and Engineering, Tsing Hua University,
Hsinchu, 30043, Taiwan, Republic of China

Abstract — High coercivity thin Fe_3O_4 and γ-Fe_2O_3 films were deposited on Si substrate under well controlled O_2 partial pressure by dc-reactive magnetron sputtering. The coercivity of as-deposited magnetite films is below 640 Oe. After oxidizing at 360°C for 10 minutes, the films transform to maghemite γ-Fe_2O_3 completely, and the coercivity increases greatly to 2100 ~ 4120 Oe, depending on modification or not with minor addition of Co or/and Mn. The origin of coercivity enhancement is attributed mainly to magnetic anisotropy arisen from interfacial stress. The addition of 5 at% Co and 5 at% Mn greatly enhances coercivity and squareness ratio. These films are potential for ultra-high density recording applications.

I. INTRODUCTION

Due to the benefits such as large recording volume, high read-write stability, rapid access time, strong resistance to damage and comparatively low price, magnetic recording remains governing information storage technology nowadays. Though thin film media with coercivity in the range of 1200 to 1800 Oe are currently used in high density rigid disks, the competetion in consumer market pushes the development towards higher coercivity to meet increasingly higher recording capacity [1]. Besides, in order to lower the production cost, the deletion of underlayers and texturing before medium deposition has been under rigorous study.

Sputtered γ-Fe_2O_3 thin films have been very attractive magnetic recording media due to their excellent corrosion and wear resistance. The reported coercivity of pure γ-Fe_2O_3 thin films is only 200 to 800 Oe, which seems too low to match the demand of high density recording in the future [2]. Furthermore, the coercivity of films can be increased from 1000 to 2100 Oe by doping some modifiers like Co,Ti, Os with long period annealing to enhance their magnetocrystalline anisotropy [3]. In advance, according to a prior report by the present authors, Co-Mn modified γ-Fe_2O_3 thin films prepared by the above method were found to obtain coercivity of up to 3000 Oe without annealing [4]. The films serve with much higher coercivity, much stronger corrosion and wear resistance, and lower media noise than Co-based thin films at once. Such excellent properties match the necessity for high density recording in the future. However, even without further annealing process, these films still require long term heat-treatment process to achieve higher coercivity. Moreover, the atmosphere and temperature control during reduction process were found to be very crucial. Such a complex process does increase not only the difficulty in manufacture, but also the cost of final products. Besides, the reason why the coercivity is enhanced is still not clear.

In this study, high coercivity γ-$(Fe,Co,Mn)_2O_3$ thin films were prepared by post annealing $(Fe,Co,Mn)_3O_4$ film in-situ deposited by dc-reactive magnetron sputtering. Hence the process is much clarified and denote great potintial in true application. In addition, the origin of such a high coercivity was prospected since pure and doped γ-Fe_2O_3 thin films provide a vivid comparison to study the relationship between physical properties, synthesis processes, and composition of the films.

II. EXPERIMENTAL

Thin $(Fe,Co,Mn)_3O_4$ films of 240 nm were in-situ deposited on Si substrates of 380μm thickness at 25°C by dc-reactive magnetron sputtering in an $Ar+O_2$ atmosphere. The sputtering system was pumped to a base pressure of $5x10^{-6}$ Torr. Total gas pressure during sputtering were fixed at 2 mTorr. The partial pressure ratio of O_2/Ar (P_{Oxy}) was varied within the range of 0.4% to 0.75%, which was regulated by a set of mass flow controller and monitored by a residual gas analyzer (RGA). The rotating speed of the substrate during deposition was 20 rpm. The substrate temperature was set at 25°C. The working dc-power was set at 6 W/cm², leading to a deposition rate of 48 nm/min. Oxidation of the deposited films was carried out at 280 to 360°C for 10 minutes in air.

Magnetic properties of the films were measured by a vibrating sample magnetometer (VSM) with a maximum applied field of 2 T. The phase identification and lattice constant were determined by x-ray diffraction (XRD) using Cu-kα radiation at a scanning speed of 1°/min. In-situ stress-temperature curves of the films during oxidation were recorded by a bending beam apparatus at a heating-rate of 5°C/min from room temperature to 360°C in air, soaking for up to 90 minutes, and then furnace-cooled to room temperature.

III. RESULTS AND DISCUSSION

Typical magnetic properties of as-deposited films are shown in Table I. In comparison to pure Fe_3O_4 films, those films doped with Co or (Co,Mn) always show higher coercivity.

Table 1 Magnetic properties of as-deposited films

Composition Fe/Co/Mn in at%	Film	P_{Oxy} %	Hc	Ms	Mr
100/0/0	A	0.5	400	280	120
95.2/4.8/0	B	0.6	600	260	105
90.2/4.7/5.1	C	0.6	570	315	150

*Hc in Oe, Ms and Mr in emu/cc

P_{Oxy} during deposition affects final stable phase and magnetic properties of the films to some extent. According to XRD patterns of resultant films, FeO phase appears when P_{Oxy} is lower than a critical value, say 0.5%. Yhe available P_{Oxy} range to form pure Fe_3O_4 phase varies with different target compositions. In addition, it was found that P_{Oxy} is slowly decreasing during deposition, as observed by RGA. Although it is not clear the reason why the P_{Oxy} in the vacuum chamber is decaying during sputtering, but such a disturbance on oxygen results in lower saturation magnetization of the films due to non-stoichiometry, as comparing to pure Fe_3O_4 having a saturation magnetization of 420 emu/cc.

In due oxidation, saturation magnetization of films is reduced by 4 ~ 10%, but coercivity of films is increased to 4 ~ 7 times higher, especially in the case of 5 at% Co or/and 5 at% Mn doped films which have a coercivity of 2400 to 4120 Oe and squareness of 0.82 to 0.84. The squareness of films can be further enhanced to 0.9 when using glass substrate instead of Si. Such films are promising for high density recording purpose, particularly for MR heads which call for media with high coercivity but lower saturation magnetization. This obvious increment in coercivity may be attributed to, as a rule of thumb, the enhancement of magnetocrystalline anisotropy arisen from Co and Mn. We had studied maghemite particles with the same Co, Mn, Fe composition, which had coercivity within the range of 400 to 1800 Oe [6]. Obviously, the coercivity of the films is much higher. As exploited by Mössbauer spectroscopy and high resolution transmission electron microscope (HRTEM), the coercivity of maghemite particles is found to be totally contributed from magnetocrystalline anisotropy brought by Co and Mn ions [6], this implies that the directional order mechanism is not enough to justify such a huge coercivity enhancement.

It is well known that residual stress can influence the magnetic properties due to magnetoelastic effect. In this studied system, phase transformation from magnetite to maghemite results in a decrease in lattice constant, it is evidenced by the lessening

in film thickness and induces huge in-plane tensile stress. Difference of thermal expansion between the film and the substrate also leads to unavoidable misfit stress in the film. Thus, the induced anisotropies, especially the stress-induced anisotropy, is worthy of discussion [7].

Table 2 Magnetic properties of the films after oxidation at T°C for 10 minutes.

Film	T, °C	Hc	Ms	S	d(313)
A1	360	2100	230	0.59	2.501Å
A2	320	720	280	0.64	2.519Å
B1	360	4120	275	0.82	2.503Å
B2	320	3760	230	0.46	2.507Å
B3	280	1360	280	0.54	2.524Å
C1	360	2400	285	0.84	2.516Å

*Hc in Oe; Ms in emu/cc; S = Mr/Ms, the squareness ratio

Generally speaking, x-ray diffraction is a faithful semiquantitative device to resolve the stress state of films. Based on measured (313) d-spacing of these maghemite films shown in Table II, coercivity almost increases linearly with decreasing (313) d-spacing. This represents that films under larger in-plane tensile stress own higher coercivity. Furthermore, bending beam measurement, as shown in Fig.1, gives us more direct information to verify stress effect on coercivity. In-situ stress-temperature curve confirms that all films have an initial residual in-plane tensile stress, and doped films show higher value. On the other hands, this tensile stress of films increases through the oxidation process, but the behavior during isothermal period of pure and doped films is different. For the pure γ-Fe_2O_3 films, the tensile stress increases during the first 20 minutes of soaking, holds for a while, and then decreases to the end of soaking process, meaning that thermal relaxition begins. For (Co,Mn) doped films, it almost increases during the whole soaking period, keeps constant in the last 10 minutes. Though the stress of these films varies in different ways, it reveals that oxidation is completed in the constant stress region. Moreover, films with Co and Mn doping have much higher final residual stress and show much higher coercivity. The drop in stress during final cooling denotes film crack due to too large in interfacial stress. By doping Co or/and Mn, the extent in stress-drop is much less, denoting higher film strength.

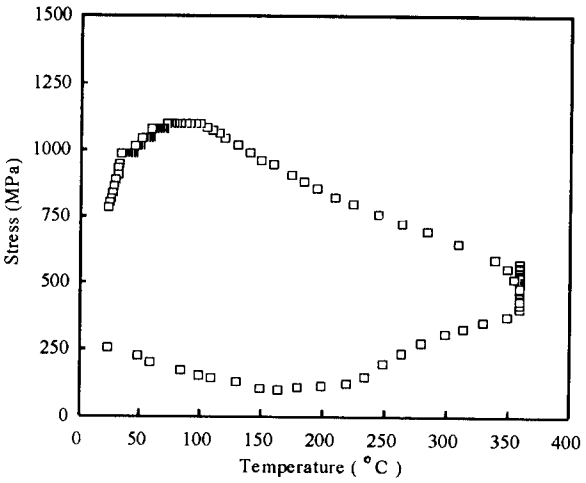

Fig. 1. In-situ stress-temperature curve of the A2 film during oxidation

According to stress-induced magnetoanisotropy, coercivity increment arise from magnetoelastic effect can be calculated as :

$$\Delta Hc = 3|\lambda\Delta\sigma|/M_S \quad (1)$$

Though the magnetostriction λ of these films is unknown, such a big discrepancy beyond coercivity originated from directional order adequately means that stress plays much more important role in the mechanism of enhancing coercivity. Thus it is concluded that stress-induced magnetoanisotropy is the major contribution. in addition to directional order mechanism, to the enormous enhancement in coercivity of the films.

Since in the studied films, only single magnetite or maghemite phase exists, the mixed-phase theory of coercivity enhancement [8], usually up to only 1000 Oe, does not prevail.

IV. CONCLUDING REMARKS

Magnetite thin films can be prepared by in-situ DC reactive magnetron sputtering. High coercivity maghemite films with coercivity up to 2100 ~ 4120 Oe can be obtained with a short time oxidation at 360°C for only 10 minutes. The saturation magnetization of the films is 230 to 285 emu/cc while the squareness ratio can be higher than 0.82, or up to 0.9 by using glass substrate. These films thus show great potential for use in ultra-high density magnetic recording using MR heads in the near future.

ACKNOWLEDGMENTS

The authors are grateful for the sponsor of this work by the National Science Council of the Republic of China under grant NSC84-2216-E-007-028.

REFERENCES

[1] E.S. Murdock, R.F. Simmons and R. Davidson, "Roadmap for 10 Gbit/in^2 media: Challenges", *IEEE Trans. Mang.*, vol. 28, pp.3078-3083, Sep. 1992.

[2] T.C. Arnoldussen, "Thin-film recording media", *Proc. of IEEE*, vol. 74, pp.1526-1539, Nov. 1986.

[3] O. Ishii, F. Yoshimura and S. Ohara, "High coercivity sputter-deposited maghemite thin-film disk", *IEEE Trans. Magn.*, vol. 23, pp.1985-1994, July 1987.

[4] W.D. Chang, T.S. Chin and M.C. Deng, "High coercivity Co-Mn modified γ-Fe_2O_3 thin films for high density recording", *IEEE Trans. Mang.*, vol. 29, pp. 3682-3684, Nov. 1993

[5] S. Chikazumi, *Physics of Magnetism*, , New York: John-Wiley and Sons, 1964, Ch. 17.

[6] M.C. Deng and T.S. Chin, "Fine structure and magnetic properties of Mn and Co doped nanocrystalline γ-Fe_2O_3", *J. Appl. Phys.*,.vol. 73, pp. 5888-5890, 1994.

[7] W.D. Chang and T.S. Chin, H.S. Wu, S.W. Jou and J.H. Jou, "Stress effect on coercivity of γ-Fe_2O_3 thin films", ***J. Appl. Phys.*** 77(3), pp.1184-1188, Feb. 1995.

[8] Y. Yamazaki, K. Okuda, N. Komachi, M.Sato and T. Namikawa, "TEM observation of Fe_3O_4-γ-Fe_2O_3 intermediate thin films", ***Proc. ICF6***, pp. 401-404 1992.