Effects of Stoichiometry on the Magnetic and Structural Properties of Perpendicular Barium Ferrite Thin Film Media

Zailong Zhuang, Bo Bian, Maithri Rao, Robert M. White, *Fellow, IEEE*, and David E. Laughlin

***Abstract*—The effects of stoichiometry factor n on the magnetic and structural properties of perpendicular barium ferrite thin films with composition of $BaO \bullet n(Fe_2O_3)$ were systematically investigated. Within the range $2.2 < n < 6$, the c-axis for barium ferrite thin films can be oriented perpendicularly by the use of Pt underlayer and with optimized processing conditions. Perpendicular c-axis orientation becomes worse as n decreases from 6 to 2.2. The average grain size was greatly reduced from about 2000 Å to 300 Å with the decrease of n. The decrease of the grain size can be related to the existence of nonmagnetic phase $BaFe_2O_4$, which was observed by X-ray diffraction.**

***Index Terms*—Barium ferrite, perpendicular c-axis orientation, stoichiometry factor, thin film media.**

I. Introduction

BARIUM ferrite thin film media are attractive candidates for high density overcoat free magnetic recording due to their large uniaxial anisotropy, high chemical stability, and corrosion resistance [1]–[3]. To utilize such materials, grains as small as 100 Å are desired to obtain a reasonable signal to noise ratio in recording at high areal density. Barium ferrite with small grain size and random c-axis orientation was reported by increasing barium content [4]. It was also found that barium ferrite with small grain size and perpendicular c-axis orientation was achieved by enriching effective barium content and optimizing the oxygen partial pressure [5]. In this study, we systematically investigate the effects of stoichiometry on the magnetic and structural properties of perpendicular barium ferrite thin films with composition of $BaO \bullet n(Fe_2O_3)$. We define n as the stoichiometry factor. The stoichiometric composition occurs when n is equal to 6. The value of n was decreased gradually to 1.5 to increase the effective barium content in the films.

II. Experimental

Barium ferrite thin films and Pt films were deposited by rf diode sputtering in a Leybold Z-400 sputtering system. Barium ferrite targets with different stoichiometry factor n were used to make barium ferrite films with different composition. A base pressure of less than 1×10^{-6} Torr was achieved before deposition. For all the films, a 500Å-thick Pt underlayer was first deposited onto a thermally oxidized silicon substrate. The Pt underlayer was deposited in pure Ar gas, with a pressure of 5.0 mTorr and a deposition rate of about 100 Å/min. The purpose of Pt underlayer is to promote the perpendicular orientation [3]. Barium ferrite thin films were then deposited in a mixture of Ar and O_2 on the Pt underlayer with a target power of 100 W. The partial pressure ratio of Ar gas with respect to O_2 gas was changed for barium ferrite films with different stoichiometry factors, while the total pressure is fixed at 5.7 mTorr. The as-deposited barium ferrite films are amorphous, and were annealed in a Rapid Thermal Annealing (RTA) furnace at a temperature of 800°C for about 60 s to fully crystallize the films.

The magnetic properties of the films were studied using either an alternating gradient magnetometer or a vibrating sample magnetometer (VSM). The crystal structures and textures of the films were characterized by X-ray diffraction (XRD) using Cu K_α radiation. A Philip EM420T transmission electron microscope (TEM) was used to characterize the grain size and grain orientation. The composition of the sputtered barium ferrite films was determined by a energy dispersive X-ray fluorescence (EDXRF) system (Tracor Spectrace 5000)

III. Results and Discussion

To optimize the perpendicular c-axis orientation, stoichiometric films with $n = 6$ and nonstoichiometric films with $n < 6$ were made with different oxygen partial pressures. The partial pressure ratio of Ar to O_2 for stoichiometric films is 5.0/0.7, while no oxygen gas was used for all the nonstoichiometric films. The total pressure is fixed at 5.7 mTorr. For stoichiometric films, oxygen partial pressure is essential to grow the barium ferrite with perpendicular c-axis orientation. Without reactive sputtering with oxygen gas, the single spinel phase will be developed instead of hexagonal barium ferrite phase [2]. For nonstoichiometric films, the hexagonal barium ferrite phase will be developed with and without reactive sputtering with oxygen gas. The choice of zero oxygen partial pressure is to optimize the perpendicular c-axis orientation [5]. Within the range from 6 to 2.2 for n, barium ferrite films show strong perpendicular c-axis orientation with the use of Pt underlayer and careful control of oxygen partial pressure. The films with $n = 1.5$ show very weak perpendicular c-axis orientation. Fig. 1 shows the dependence of Ms on the stoichiometry factor n for barium ferrite films. There is a gradual decrease of Ms from 280 emu/cc to 160 emu/cc,

Manuscript received February 14, 2000. This work was supported by the National Science Foundation under Grant ECD-8907068. The United States government has certain rights in this material.

The authors are with the Data Storage Systems Center and the Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, PA 15213 USA (e-mail: zhuang@ece.cmu.edu).

Publisher Item Identifier S 0018-9464(00)09041-5.

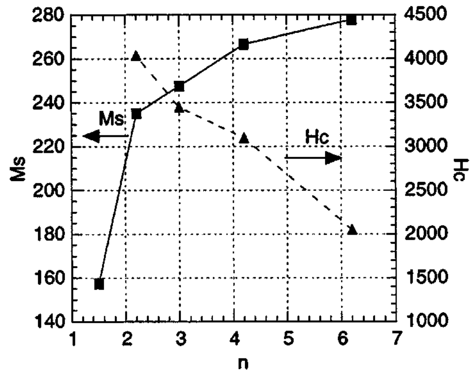

Fig. 1. Dependence of Ms and perpendicular coercivity Hc on stoichiometry factor n for 600 Å-thick barium ferrite films on 500 Å-thick Pt underlayer.

TABLE I
MAGNETIC PROPERTIES OF BARIUM FERRITE THIN FILMS WITH DIFFERENT STOICHIOMETRY FACTOR n. S_out AND S_in STANDS FOR PERPENDICULAR SQUARENESS AND IN-PLANE SQUARENESS. Hc_{out} STANDS FOR PERPENDICULAR COERCIVITY

Factor n	S_out	S_in	δM/Mr	Ms emu/cc	Hc_out Oe
6	0.85	0.16	-0.55	279	2000
4.2	0.92	0.25	-0.4	264	3200
3	0.9	0.3	-0.3	244	3400
2.2	0.87	0.35	-0.3	235	4000

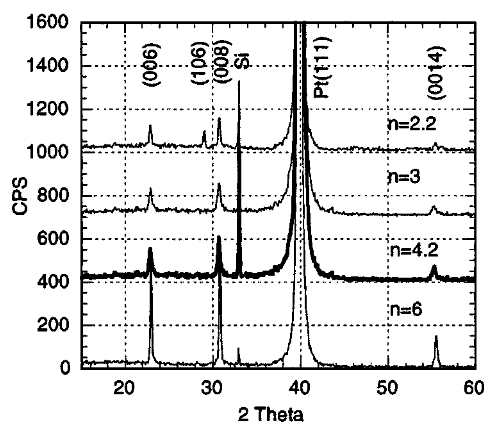

Fig. 2. XRD curves for barium ferrite films with different n on a 500 Å-thick Pt underlayer. The thickness is 600 Å for all the films.

as stoichiometry factor n decreases from 6 to 1.5. Within the range from 6 to 2.2 for n, Ms only shows a modest decrease of about 50 emu/cc from 280 emu/cc. The perpendicular coercivity (Hc) increases from 2000 Oe to 4000 Oe with the decrease of n from 6 to 2.2, as shown in Fig. 1. The magnetic properties of the films with n from 2.2 to 6 are shown in Table I. In-plane squareness increases from 0.16 to 0.35 as stoichiometry factor decreases from 6 to 2.2, which indicates more in-plane oriented grains in the films as n decreases. δM has a value of -0.55 for stoichiometric films, while δM is in the range of -0.3 to -0.4 for all the nonstoichiometric films. The negative value of δM indicates that magnetostatic interaction among grains dominates in the perpendicular direction for all the films. The smaller absolute value of δM for nonstoichiometric films suggests less magnetostatic interactions among the grains.

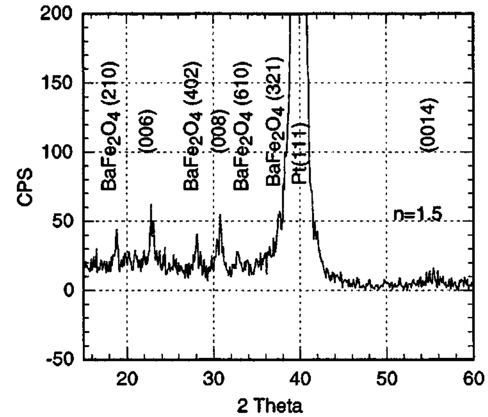

Fig. 3. XRD curves for 2000Å-thick barium ferrite films with $n = 1.5$ on a 500 Å-thick Pt underlayer.

XRD results for films with different n are shown in Fig. 2. The dominant texture for all the films is (00l) for n between 2–6. The strongest (00l) peaks are for films with n equal to 6. With the decrease of n from 6 to 2.2, there is a gradual decrease in the intensity and broadening of (00l) peaks. From the phase diagram of barium ferrite, we know that there are two possible solid phases with n from 1 to 6, namely the hexagonal $BaFe_{12}O_{19}$ phase and orthorhomic $BaFe_2O_4$ phase. The $BaFe_2O_4$ phase should exist for the barium rich films with n between 2.2–6. The $BaFe_2O_4$ phase was not observed in the XRD results due to the small amount for the films with n between 2.2–6. To show the existence of $BaFe_2O_4$ phase for barium rich films, a 2000 Å-thick film with n equal to 1.5 was made and characterized by XRD. $BaFe_2O_4$ phase was clearly observed in addition to $BaFe_{12}O_{19}$ phase for the film, as indicated by the (210), (321) and (610) reflections for the $BaFe_2O_4$ phase shown in Fig. 3. The existence of the nonmagnetic phase is consistent with the gradual decrease of Ms with the decrease of n shown in Fig. 1.

Transmission electron microscope (TEM) was used to characterize the grain size for barium ferrite with n values between 2.2–6. The average grain size is about 2000 Å for films with n equal to 6, as shown in Fig. 4(a). The average grain size was reduced to about 800–1000 Å for films, as n is decreased to 4.2, as shown in Fig. 4(b). The grain size was further reduced to about 300–500 Å for the films with n equal to 3 and 2.2, as shown in Fig. 4(c). These results show that the grain size can be greatly reduced with the increase in the effective barium content by decreasing stoichiometry factor n from 6 to 3. The grain size doesn't show a significant change when n is further reduced from 3 to 2.2, as shown in Fig. 4(d). Most of the grains are plate-like. Electron diffraction results show the six fold symmetry for the plate-like grains for all the films with n from 2 to 6, which indicates that the c-axis is perpendicular to the plane for the films. One electron diffraction pattern from a plate-like grain from the film with $n = 4.2$ is shown in Fig. 5,

The gradual decrease of grain size is consistent with the gradual increase of the Hc observed in Fig. 1, since the incoherent rotation of magnetization is more pronounced in larger grains. It is believed that the decrease of the grain size for barium rich films can be related to the existence of nonmagnetic

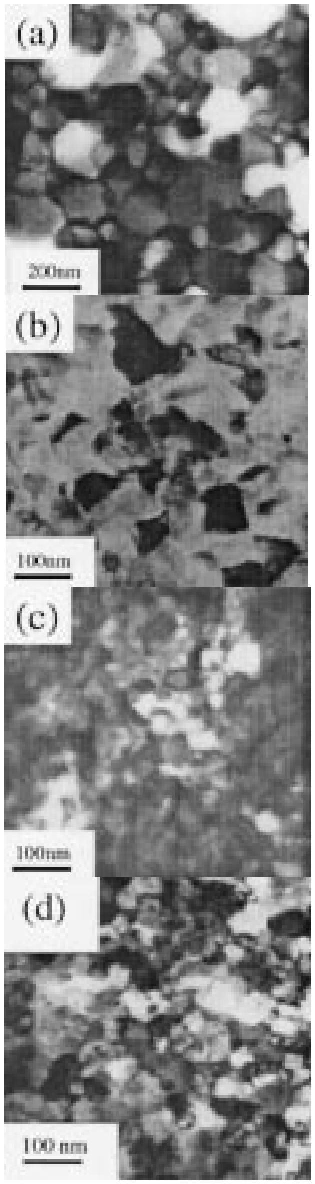

Fig. 4. TEM BF images for 600 Å-thick barium ferrite with different n on a 500 Å-thick Pt underlayer:(a) $n = 6$; (b) $n = 4.2$; (c) $n = 3$ (d) $n = 2.2$.

phase $BaFe_2O_4$, as shown by the XRD data in Fig. 3. The nonmagnetic phase is likely to grow along the grain boundary of the hexagonal $BaFe_{12}O_{19}$ phase. The $BaFe_2O_4$ phase, whose crystalline structure is different from the crystalline

Fig. 5. An electron diffraction pattern for 600 Å-thick barium ferrite thin films taken from a plate-like grain from the film with $n = 4.2$, showing sixfold symmetry.

structure of $BaFe_{12}O_{19}$, may exert a force against the boundary movement due to the interaction between the $BaFe_2O_4$ phase and the grain boundary. This will inhibit the motion of the grain boundary, thereby decreasing their rate of growth and their ultimate size. This explains why smaller grain sizes were obtained for off-stoichiometric barium rich films.

IV. Conclusion

We have investigated the effects of stoichiometry on the magnetic and structural properties of perpendicular barium ferrite thin films with composition of $BaO \bullet n(Fe_2O_3)$. Barium ferrite thin films with perpendicular axis orientation can be made with the range of 2–6 for stoichiometry factor n. The grain size can be greatly reduced from about 2000 Å to 300 Å by enriching the effective barium content.

References

[1] T. L. Hylton, M. A. Parker, M. Ullah, K. R. Coffey, R. Umphress, and J. K. Howard, "Ba-ferrite thin film media for high-density longitudinal recording," *J. Appl. Phys.*, vol. 75, no. 10, pp. 5960–5865, 1994.

[2] A. Morisako, M. Matsumoto, and M. Naoe, "The effect of oxygen gas pressure on Ba-ferrite sputtered films for perpendicular magnetic recording media," *IEEE Trans. Magn.*, vol. 24, pp. 3024–3026, 1988.

[3] X. Sui, M. Scherge, M. H. Kryder, J. E. Snyder, V. G. Harris, and N. C. Koon, "Barium ferrite thin-film recording media," *J. Magn. Magn. Mater.*, vol. 155, pp. 132–139, 1996.

[4] Y. Chen, D. E. Laughlin, X. Ma, and M. H. Kryder, "Influence of Ba content on the grain size and dynamics of crystallization in barium ferrite thin films," *J. Appl. Phys.*, vol. 81, no. 8, pp. 4380–4382, 1997.

[5] Z. Zhuang, M. Rao, R. M. White, D. E. Laughlin, and M. H. Kryder, "Barium ferrite thin film media with perpendicular c-axis orientation and small grain size," in *MMM 99*, San Jose, CA.

[6] J. Smit and H. P. J. Wijin, *Ferrites*, New York: Wiley, 1959, ch. 11.