Fine Grain Barium Ferrite Thin Films With Perpendicular C-axis Orientation

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Abstract— Perpendicular barium hexaferrite thin films were fabricated using ex-situ and in-situ annealing. Our experimental results suggest that there are two different types of nucleation processes during the ex-situ annealing of the amorphous barium ferrite thin films. The nucleation within the film “bulk” tends to form crystallites with random c-axis orientations, whereas the nucleation at the interface(s) with the substrates or underlayers forms crystallites with the c-axis predominantly perpendicularly oriented. A Pt underlayer was shown to promote the interface nucleation which results in better perpendicular orientation. The barium ferrite films with Ba content higher than stoichiometry which were previously shown to have finer grain size, however, tend to grow grains of random orientation even on Pt underlayers due to the much enhanced “bulk” nucleation. Nearly perfect perpendicular orientation can be achieved in the high Ba content films if the films are made to be thin $< 300 \text{ \AA}$, and a two-step annealing is used. The films using in-situ annealing showed self-epitaxial growth of grains with perpendicular orientation, which can also be improved by using a Pt underlayer.

Key words: barium hexaferrite, Pt underlayer, perpendicular recording, grain size

I. INTRODUCTION

Barium ferrite thin films are promising candidates for both longitudinal and perpendicular recording applications. They can be fabricated by sputter deposition with either in-situ or ex-situ annealing [1, 2]. Barium ferrite films deposited with in-situ annealing often exhibit perpendicular orientation even when oxidized silicon substrates are used without an underlayer [1]. Various underlayers, such as ZnO, were used in order to enhance the perpendicular orientation [3]. Barium ferrite films fabricated using ex-situ annealing generally exhibit random c-axis orientation when deposited on SiO_2 substrates [2]. A Pt underlayer was shown to be effective in promoting perpendicular orientation [4]. The films previously studied had nearly stoichiometric composition. These films, despite their excellent c-axis perpendicular orientation, exhibit low coercivity ($\sim 1500 \text{ Oe}$) and large grain size ($\sim 2000 \text{ \AA}$), which would not meet the needs for high density recording applications.

It has been shown that barium ferrite films with Ba content higher than stoichiometry have high nucleation rates and lower growth rates during the post-deposition crystallization process [5]. As a result, much finer grain size was achieved in the high Ba content films. The films which are 10 wt% rich in BaO have a grain size of about $300 \text{ \AA}$ and a coercivity of about $4500\text{--}5000 \text{ Oe}$, which appear promising for future high density recording applications.

In this study, effects of a Pt underlayer on the barium ferrite thin films of nearly stoichiometric composition and 10 wt% BaO rich were investigated. It is shown that fine grain and high coercivity barium ferrite films with nearly perfect perpendicular c-axis orientation can be achieved.

II. EXPERIMENTAL PROCEDURES

Barium ferrite thin films were deposited from two targets of different BaO contents by rf diode sputtering in a Leybold Z-400 sputtering system. The BaO contents in the films are 12 wt% and 23 wt%. A sputtering power of 30 W at a rate of about $7.5 \text{ \AA/min}$, and Ar/O_2 gas with flow ratio of 67/12 sccm were used for films with ex-situ or in-situ annealing. Pt underlayers were deposited using a sputtering power of 100 W at a rate of $130 \text{ \AA/min}$ with 75 sccm Ar flow. The Pt underlayers were $2000 \text{ \AA}$ thick except when the effect of Pt thickness was being studied and varied from 200 to $2000 \text{ \AA}$.

When in-situ heating was used, SiO_2 substrates with or without $2000 \text{ \AA}$ Pt underlayers were silver pasted and dried on a heater stage in the sputtering chamber in order to ensure good thermal contact. The heater stage was then heated to 800°C in vacuum and this temperature was maintained during the sputtering process.

The ex-situ annealed films were deposited at room temperature and annealed after deposition using a rapid thermal annealing (RTA) furnace. Since the high Ba content films are easier to crystallize, they were annealed at 790°C for 60 s. The low Ba content films were annealed at 810°C for 60 s. Such annealing conditions were sufficient to fully crystallize these films and the saturation magnetization M_s showed no increase upon further annealing. Some as-deposited films were annealed using a two-step annealing process [6]. They were homogenized at 600°C in a tube furnace for 10 hours before RTA.

The magnetic properties of the films were studied using an alternating gradient magnetometer (AGM). The out-of-plane torque curves were measured using a torque magnetometer at a field of 12000 Oe . The perpendicular anisotropy field H_k was calculated from the peak-to-peak torque values and saturation magnetization M_s using $H_k = 2K_u/M_s$.

The crystalline structures of the films were characterized using X-ray diffraction.

An atomic force microscope was used to study the surface morphology of the barium ferrite films and the Pt underlayers.

III. RESULTS

A. Ex-situ annealing

The low Ba content barium ferrite films deposited directly onto SiO_2 substrates are not ferromagnetic at thickness less than $500 \text{ \AA}$. At $800 \text{ \AA}$ or more, the films have similar in-plane and perpendicular magnetic properties, and the asymptotic values of $0.55\text{--}0.6$ and 2500 Oe were reached for squareness (S_q) and coercivity (H_c), respectively. The values of S_q and H_c were slightly higher in the perpendicular direction for the $500 \text{ \AA}$ thick film. The films with the two-step annealing have slightly lower M_t , S_q and H_c values.

The films deposited on 2000 Å Pt underlayers became ferromagnetic even at 200 Å. At the thickness of 300 Å, M_t is about 0.6 memu/cm² in the perpendicular direction. It is about 2 memu/cm² for the 1250 Å thick film, which is about 25% higher than the film of the same thickness deposited on the SiO₂ substrate. The values of M_t are much greater in the perpendicular than in-plane direction, especially for thinner films. The values of S_q are over 0.9 in the perpendicular direction for the films of 300 Å ~ 800 Å as shown in Fig. 1. They are less than 0.25 in-plane. Even higher perpendicular S_q values than in-plane were found in the films using the two-step annealing. The 500 Å film (A) using the two-step annealing, whose hysteresis loops are shown in Fig. 2a, has S_q of nearly 1 in the perpendicular direction, but only 0.05 in-plane. For the films which were 500 Å or less in thickness, the two-step annealing also resulted in much reduced in-plane coercivity as seen in Fig. 3. The 1250 Å thick films have less different in-plane and perpendicular S_q and similar H_c values as shown in Figs. 1 and 3. The values of H_c also increase to over 2500 Oe for the 1250 Å film using RTA only. Such an increase was not observed for the film of the same thickness, but which underwent the two-step annealing.

The high Ba content films deposited on SiO₂ become ferromagnetic at the film thickness of 300 Å or more. Similar in-plane and perpendicular magnetic properties were observed except in the 300 Å films. In fact, in the 300 Å film using the two-step annealing, the perpendicular and in-plane S_q are 0.84 and 0.1, and H_c are 1800 Oe and 450 Oe, respectively. For the films which were 500 Å or thicker, S_q is in the range 0.5 ~ 0.6 and H_c is in the range 4000 ~ 4500 Oe.

The films with high Ba content deposited on 2000 Å Pt underlayers were weakly magnetic even at 200 Å thickness. The films of 500 Å or larger thickness have similar in-plane and perpendicular M_t , S_q and H_c values as shown in Figs. 4 and 5, which show the thickness dependence of S_q and H_c , respectively. S_q is about 0.6 ~ 0.65, and H_c is about 4500 Oe for films of 500 Å or more thickness. Much higher S_q and H_c were, however, observed in the perpendicular direction in the 300 Å thick film (B) with the two-step annealing. This film, whose hysteresis loop is shown in Fig. 2b, has S_q of 0.9, H_c of 4000 Oe and M_t of 0.4 memu/cm² in the perpendicular

Fig. 1. Thickness dependence of the in-plane and perpendicular squareness of the low Ba content films deposited on Pt underlayers.

Fig. 2. The in-plane and perpendicular hysteresis loops of film A, a 500 Å low Ba content film (a), and of film B, a 300 Å high Ba content film (b). Both were deposited on Pt underlayer and ex-situ annealed using the two-step annealing.

Fig. 3. Thickness dependence of the in-plane and perpendicular coercivity of the low Ba content films deposited on Pt underlayers.

direction; while the same quantities are almost zero in the in-plane direction, indicating nearly perfect perpendicular orientation.

The values of H_k measured from the torque are about 13000 Oe and 12000 Oe for films A and B, respectively. The values of H_k may also be taken as the field where the hard axis and easy axis loops intersect with each other as shown in Fig. 2. They are consistent with the torque measurements.

The X-ray diffraction patterns of films A and B are shown in Fig. 6. The predominant (00l) diffraction peaks indicate perpendicular c-axis orientation of in both films. Much weaker peaks were observed in film B with high Ba content, which is consistent with its reduced grain size.

The Pt underlayer thickness was also varied from 200 Å to 2000 Å, while keeping the barium ferrite layer at the thickness of 500 Å. For the low Ba content films, the values of perpendicular H_c , which are in the range of 1200~1400 Oe, are relatively independent of the Pt thickness. A gradual increase of the perpendicular S_q from 0.9 to about 0.99 was observed as the Pt thickness was increased from 200 Å to 2000 Å in the films using the two-step annealing. The in-plane S_q decreased from 0.25 to 0.05 for the same films. The in-plane H_c also decreased from 1200 Oe to 200 Oe, and showed a broad maximum when the Pt underlayer was 500 Å thick. The in-plane H_c showed a sharp maximum of 2000 Oe at the Pt thickness of 300 Å in the films using RTA only. The magnetic properties of the 500 Å high Ba content films were

Fig. 4. Thickness dependence of the in-plane and perpendicular squareness of the high Ba content films deposited on Pt underlayers.

Fig. 5. Thickness dependence of the in-plane and perpendicular coercivities of the high Ba content films deposited on Pt underlayers.

found to be independent of the Pt underlayer thickness. Larger surface morphological features were observed by using an AFM in the thicker Pt underlayers which may be related to the larger Pt grain size.

B. In-situ annealing

Under in-situ annealing, the low Ba content films deposited on SiO_2 substrates even without Pt underlayers have moderately higher perpendicular S_q than in-plane S_q , as shown in Fig. 7. By using a Pt underlayer the S_q in the

perpendicular direction was enhanced. The magnetic properties of high Ba content films with in-situ annealing are quite similar to the low Ba content films as shown in Table I. The perpendicular H_c of the thicker high Ba content films is about 3000 Oe, which is higher than the low Ba content films, but lower than the ex-situ annealed films.

The X-ray diffraction patterns as shown in Fig. 8 indicate much stronger (00 l) peaks in the film on a Pt underlayer than on SiO_2 , both of which were 800 Å thick, and in-situ annealed with low Ba content. Weaker (00 l) peaks were found in thinner films. No other barium ferrite peaks were found. The XRD patterns of the in-situ annealed high Ba content films are quite similar to the low Ba content films.

Fig. 7. In-plane and perpendicular squareness of the in-situ annealed low Ba content films having the thickness of 300 Å, 500 Å, 800 Å.

TABLE I
MAGNETIC PROPERTIES OF IN-SITU ANNEALED FILMS ON Pt UNDERLAYERS

Ba content/ Thickness	In-plane			Perpendicular		
	M_s/area (memu/cm ²)	S_q	H_c (Oe)	M_s/area (memu/cm ²)	S_q	H_c (Oe)
low, 300 Å	0.53	0.078	418	0.50	0.539	2390
low, 500 Å	0.61	0.127	491	0.59	0.558	2520
low, 800 Å	0.94	0.221	763	0.94	0.779	2040
high, 300 Å	0.60	0.136	423	0.55	0.154	1270
high, 500 Å	0.71	0.143	537	0.69	0.552	2920
high, 800 Å	0.90	0.222	1070	0.94	0.848	2900

Fig. 6. X-ray diffraction patterns of film A and film B.

Fig. 8. X-ray diffraction patterns of two in-situ annealed films on 2000 Å Pt underlayer, and on SiO_2 substrate. The thickness of both films are 800 Å.

IV. DISCUSSION AND CONCLUSION

The experimental results suggest that there are two different types of nucleation during the ex-situ annealing process. The nucleation within the film "bulk" tends to form crystallites with random c-axis orientations, whereas the nucleation at the interface(s) with the substrates or underlayers forms crystallites with the c-axis predominantly perpendicularly oriented. The atoms deposited on the Pt underlayer may be arranged more easily into their lowest surface energy state. As a result, more sites with higher in-plane short-range atomic order are formed at the Pt interface. The amorphous films which have in-plane short-range order were shown to become films with perpendicular c-axis orientation after annealing [7]. These sites are nucleation centers for grains with perpendicular c-axis orientation. The layers which are at a distance from the interface (or in the "bulk") may not have the in-plane short-range order and only have random short-range order. These sites are the nucleation centers for randomly oriented grains. The pre-anneal at 600 °C before crystallization at 790 °C or 810 °C appears to promote the surface nuclei more than the "bulk" nuclei, and change the distribution of nuclei in favor of perpendicular c-axis orientation.

The barium ferrite films with low Ba content were shown to have low nucleation in the "bulk" [5]. It is, therefore, easier to obtain perpendicular orientation in these films when Pt underlayers are used. The low Ba content films which are 800 Å thick or even 1250 Å with the two-step annealing are still perpendicularly oriented as indicated by the higher S_q in the perpendicular direction. In contrast, the high Ba content films became almost randomly oriented at 500 Å, as suggested by the similar M_t , H_c and S_q values in perpendicular and in-plane directions. In fact, S_q values of 0.5~0.6 as found in these films also indicated nearly 3-D random c-axis orientation [8]. The "bulk" nucleation can be dominant in high Ba content films due to the greatly enhanced nucleation rate and reduced growth rate, which, however, results in random c-axis orientation. In order to enhance surface nucleation in high Ba content films relative to the "bulk" nucleation, thus producing films with small grains and stronger perpendicular orientation, very thin film thickness and the two-step annealing process are required. Since the number of "bulk" nucleation sites decreases linearly with the film thickness, while the number of nucleation sites at the interface is relatively independent of the film thickness, nearly perfectly perpendicular orientation can be achieved in high Ba content films at the film thickness of 300 Å using the two-step annealing.

Better perpendicular orientation can be obtained in 500 Å thick low Ba content films on a 2000 Å thick Pt underlayer than on thinner Pt underlayers. This is possibly due to the larger Pt grain size which may be more suitable for the surface nuclei of barium ferrite to form. The 500 Å high Ba content films were not affected by the Pt underlayer thickness due to the predominant "bulk" nucleations in these films.

It was shown that incoherent rotation, which causes lower H_c values than the anisotropy field H_k , is more dominant in the films with larger grain size [9]. In fact, the Stoner-Wohlfarth coherent rotation model predicts that H_c becomes equal to H_k in a system with aligned easy axes [8]. Due to incoherent rotation, however, neither the 500 Å low Ba content film A, nor the 300 Å high Ba content film B, despite their excellent perpendicular orientations, have H_c values nearly as high as H_k .

The grains whose c-axes are perpendicularly oriented are generally larger than those with random orientation. The grains with random c-axis orientation have one of the two fast grain growth directions in the ab plane restrained by the film thickness [10, 11]. The grains with c-axis perpendicular to the film plane have both of their fast growth axes in-plane, and their growth will continue until the crystallites have completely encroached on one another. The average growth rate is, therefore, higher in the films with perpendicular c-axis orientation, and the grain size is larger. As a result, the change of film orientation from random to perpendicular usually causes a decrease in H_c due to increased incoherent rotation and as seen in Fig. 3.

The films deposited on SiO₂ suffer from interdiffusion with Si, which may suppress nucleation in the diffused layer [12]. As compared to the films deposited on Pt underlayers, the films on SiO₂ have lower M_s , and thicker films are required for crystallization under the same annealing conditions.

Self-epitaxial growth may occur in films with in-situ annealing due to higher atom mobility [1]. The perpendicular surface film texture is maintained upon further film growth. Perpendicular orientations were thus observed in the in-situ annealed films even when SiO₂ substrates were used without Pt underlayers. The lower value of H_c in the high Ba content films under in-situ annealing than in those under ex-situ annealing could be related to the larger grain size [9], which may be due to higher atom mobility under in-situ annealing.

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