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The effect of underlayers on grain orientation and magnetic properties of barium-ferrite thin film

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The effect of employing various sputtered underlayers has been studied in order to optimize the characteristics of barium ferrite (BaM) thin films for magnetic recording media. BaM thin films and underlayers (Fe, Cr, Al_2O_3, Fe_2O_3, $ZnFe_2O_4$, TiO_2) were prepared by rf/dc magnetron sputtering on (100) oriented bare Si substrate, and were crystallized by post-annealing. All the BaM films, except the BaM/Fe/Si film, attained nearly the same perpendicular and in-plane coercivities. Perpendicular anisotropy was observed in BaM/Fe/Si film. The BaM/TiO_2/Si exhibits the highest coercivity. However, regardless of the underlayer, BaM grains are oriented at random. By adopting $ZnFe_2O_4$ as an underlayer, the interdiffusion of Si from substrate was prohibited to some degree. The microstructure of BaM in BaM/TiO_2/Si was strongly dependent on both the microstructure of TiO_2 underlayer and the total sputtering gas pressure. The control of an underlayer microstructure is one of the important factors to control grain size and shape of the BaM layer.

Key words: *BaM film; underlayer; anisotropy; coercivity; microstructure*

1. Introduction

Hexagonal barium ferrite (BaM) thin film is considered to be an attractive magnetic recording medium because of its large coercivity, corrosion resistance, high -anisotropy field, mechanical hardness, and chemical stability. The mechanical hardness and stability of BaM film may make it possible to achieve a low flying height without an overcoat [1]. The preparation of BaM films with a uniaxial magnetic anisotropy in the out-of-plane direction is problematic when BaM is deposited directly onto amorphous substrates such as Si wafers with a thermally oxidized surface layer (SiO_2 /Si) or a fused quartz slide [2]. It has been shown that the microstructure and magnetic properties of BaM thin film can be improved using an underlayer [3]. Hyl-

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ton, Parker, and Howard [4] have reported that interdiffusion between the BaM film and the substrate strongly affects the magnetic properties. They suggests the need for applying a buffer layer between the film and substrate. In-plane magnetocrystalline anisotropy, high coercivity, and remanence have been reported in BaM films deposited on sapphire [5] and other buffer layers [6]. The anisotropy was raised because the *c*-axis of BaM crystallites was dominantly oriented in the film plane. This is attributed to the uniaxial magnetic anisotropy with easy axis in the plane of the film. General criteria for selection of substrate and appropriate underlayer materials are low cost, mechanical hardness coupled with the ability to withstand high-temperature annealing, chemical stability, and limited interdiffusion while providing good adhesion with the BaM film [4]. Wee et al. [6] employed various underlayers such as Al_2O_3, Cr_2O_3, SiO_2, CuO, and TiO_2 to optimize the characteristics of BaM thin films for magnetic recording applications. Both high coercivity (400 kA/m) and squareness (about 0.92) were achieved using Al_2O_3 as an underlayer, while the TiO_2 underlayer exhibited the lowest coercivity (28 kA/m) of all underlayers studied. In contrast to earlier work [6], we report in this article the dependence of microtexture, microstructure, and magnetic properties of barium-ferrite thin films on the kind of the underlayer.

2. Experimental

BaM thin films were prepared using an rf/dc magnetron-sputtering system onto the (100) oriented bare silicon substrates. All films were deposited in-situ. The targets for the deposition of the BaM and $ZnFe_2O_4$ underlayers were sintered ferrite disks with

Table 1. Sputter deposition conditions for underlayer and barium-ferrite thin films

Thin film		Method	Sputtering gas	Substrate temp.	Total gas pressure (mm Hg)	Thickness (nm)
Underlayer	Fe	DC	Ar	room temp.	10,000	100
	Cr	DC	Ar	room temp.	10,000	100
	Fe_2O_3	RF	Ar + 10% O_2	room temp.	10,000	50
	Al_2O_3	RF	Ar + 10% O_2	room temp.	10,000	100
	$ZnFe_2O_4$	RF	Ar + 10% O_2	room temp.	5,000	50
	TiO_2	DC	Ar + 30% O_2	room temp.	5,000 10,000	70
Magnetic layer	BaM	RF	Ar + 10% O_2	room temp.	5,000 10,000	60

the stoichiometric composition of $BaFe_{12}O_{19}$ and $ZnFe_2O_4$. The Fe_2O_3 and TiO_2 underlayers were reactively sputtered with oxygen gas. All other underlayers were deposited using Cr, Fe and Al_2O_3 targets. After having evacuated the sputter chamber to a pressure below 2×10^{-6} mm Hg (TiO_2 – below 3×10^{-7} mm Hg), argon and oxygen gases were introduced into the chamber. The total gas pressure was maintained at either 5,000 mm Hg or 10,000 mm Hg. The deposition conditions for the underlayers and the BaM layer are given in Table 1. All as-deposited films were annealed in the range of 700–850 °C for 10 min using a rapid thermal annealing furnace oven to achieve a magnetic crystallization BaM phase. The crystallographic structure and microstructure of the annealed films were characterized by means of X-ray diffraction (XRD) and field-emission scanning electron microscope (FESEM), respectively. The magnetic properties of the films were measured by a vibrating sample magnetometer.

3. Results and discussion

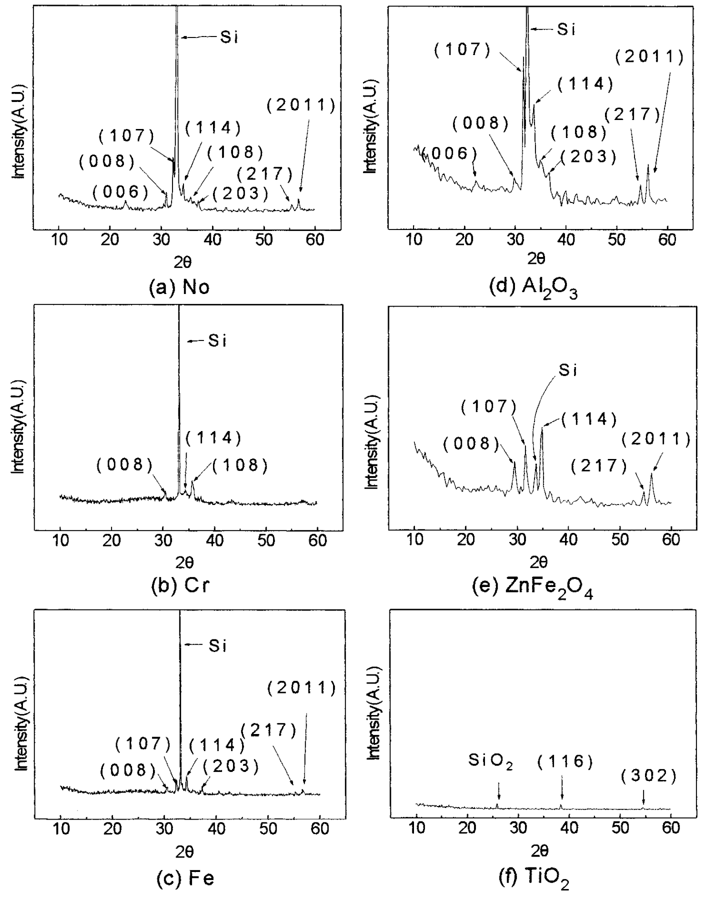
Figure 1 shows XRD patterns of BaM films with various underlayers. The basal planes, which are (006) and (008) peaks, as well as other planes such as (107) and (114) peaks were observed. The relative intensities of (107) and (114) peaks, which correspond to the inclined *c*-axis orientation, are higher than those of (006) and (008) peaks. These results indicate that the grains of all the BaM films are favourably crystallized and developed the random orientation of crystal structure. On the other hand, all major peaks for the BaM crystalline phase disappeared for the BaM/TiO_2/Si film except for the (116) and (302) peaks. In the case of BaM/$ZnFe_2O_4$/Si film, the intensity of Si peak, originating from Si substrate, was extremely weak compared to those of BaM films with other underlayers. This result supports the conclusion that the $ZnFe_2O_4$ underlayer prevented, to some degree, the interdiffusion of Si from the substrate to the BaM film.

Table 2. Coercivity values of barium-ferrite thin films with various underlayers

Underlayer	Coercivity (kA/m)	
	Longitudinal	Perpendicular
Fe	16	88
Cr	350	366
Fe_2O_3	263	247
Al_2O_3	287	287
$ZnFe_2O_4$	183	151
TiO_2	374	350

The coercivity values of BaM films with various underlayers are summarized in Table 2. All films revealed nearly the same coercivity in both in-plane and out-of

-plane directions except for BaM/Fe/Si film, indicating that all the films do not possess crystalline magnetic anisotropy. This is consistent with the results of XRD. With regard to the effect of underlayer thickness on coercivity, the Fe_2O_3 underlayer, thinner than all other underlayers, exhibits almost the same coercivity as those of the films with other underlayers. This suggested that about 26 kA/m of coercivity is achievable with the 50 nm thick Fe_2O_3 underlayer compared to the other underlayers 100 nm thick. It was suggested that Fe_2O_3 underlayer was effective in reducing thickness for obtaining desirable coercivity of BaM film. In contrast to Wee's results [6], BaM/TiO_2/Si films exhibit the highest coercivity of all films with underlayers.



(a) No

(b) Cr

(c) Fe

(d) Al_2O_3

(e) $ZnFe_2O_4$

(f) TiO_2

Fig. 1. X-ray diffraction patterns of barium-ferrite thin films with various underlayers

The BaM/Fe/Si film shows the hard magnetic property (88 A/m) for the out-of-plane direction compared to the soft magnetic behaviour (16 A/m) for the in-plane direction (Fig. 2). The saturation magnetization (225 emu/cm^3) for the in-plane direction is about three times larger than that for the out-of-plane direction. The high perpendicular coercivity is not attributed to the magnetic crystalline anisotropy of the BaM layer because BaM grains are randomly oriented, which is evidently shown by X-ray diffraction pattern. Morisako et al. [3] have reported that during a post-annealing process, both Ba and Fe diffused into the substrate, and the Fe atoms diffused deeper into the substrate than Ba atoms, consequently changing the Ba/Fe ratio in the BaM film. This change may cause a large increase in both the in-plane saturation magnetization and the perpendicular coercivity of the BaM film.

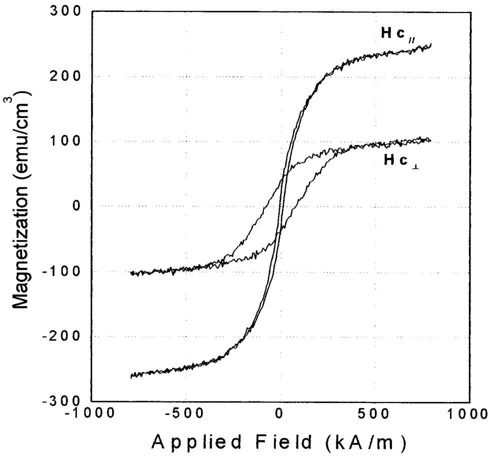


Fig. 2. Magnetization hysteresis of barium-ferrite thin films with Fe underlayer, post-annealed at 850 °C for 10 min

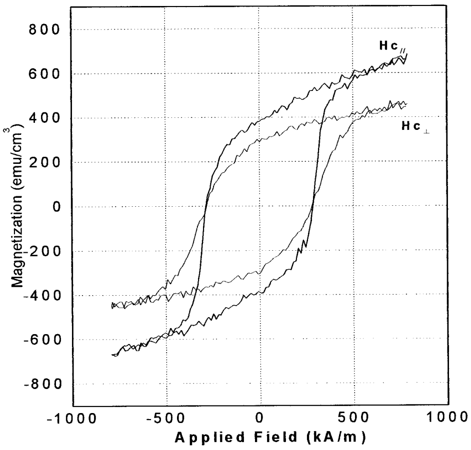


Fig. 3. Hysteresis loops of the BaM/Al_2O_3/Si thin films post-annealed for 10 min at 850 °C

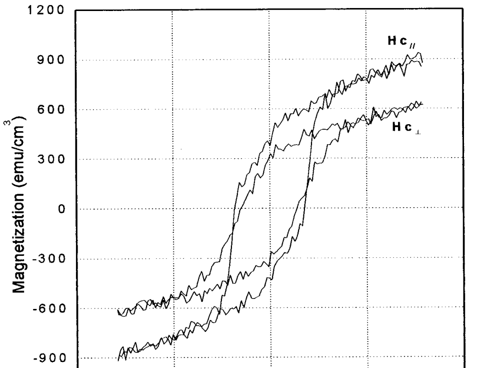


Fig. 4. Hysteresis loops of the BaM/$ZnFe_2O_4$/Si thin films post-annealed for 10 min at 850 °C

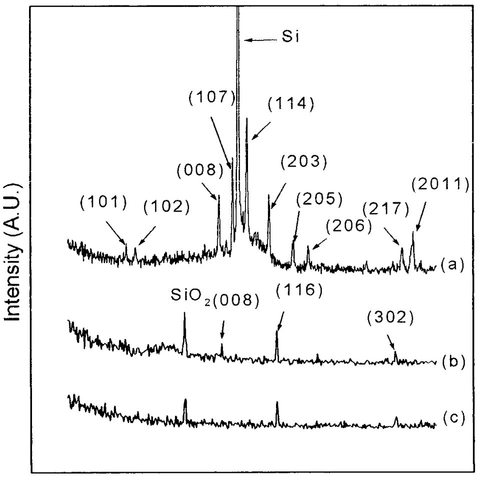


Fig. 5. XRD patterns for BaM thin films without or with TiO_2 underlayer: a) no underlayer, 850 °C, b) TiO_2 underlayer, 800 °C, c) TiO_2 underlayer, 750 °C

The hysteresis loops of the BaM/Al_2O_3/Si and BaM/$ZnFe_2O_4$/Si thin films are shown in Figs. 3 and 4. Longitudinal recording media have been successfully achieved by deposition on sapphire substrate [5]. However, the high cost of sapphire limits the commercial application of these films. Therefore, we investigated the effect of polycrystalline Al_2O_3 underlayer on the BaM thin film. As shown in Fig. 4, BaM/Al_2O_3/Si thin films reveal that the coercivities in perpendicular and in-plane direction are the same and equal to 287 A/m. It was reported that when BaM film was deposited onto the sputtered ZnO underlayer, $ZnFe_2O_4$ was formed between BaM and ZnO layers. $ZnFe_2O_4$ is the product of the reaction of BaM with ZnO, which reduces the lattice mismatch between these layers [7]. It is expected that $ZnFe_2O_4$ underlayer can improve perpendicular *c*-axis orientation of BaM film deposited onto it. However, the hysteresis loops shown in Fig. 5 have similar shapes and reduced coercivities in both in-plane and out-of-plane directions.

Figure 5 shows X-ray diffraction diagrams of BaM films with or without TiO_2 underlayer. BaM/TiO_2/Si thin film deposited on the Si substrate at a room temperature was amorphous. In the BaM/Si thin film of Fig. 5a, the basal planes, which are (008), as well as other planes such as (107) and (114) reflections were observed after annealing. The relative intensities of (107) and (114) peaks, which correspond to the inclined *c*-axis orientation out of the film plane, were higher than those of the (008) peak. These results indicate that the BaM films were favourably crystallized and developed the random orientation of crystal structure. In addition, the absence of those peaks in Fig. 5b, c associated with the underlayers confirms the amorphous state of the underlayer film. For the BaM/TiO_2/Si film, the diffraction of merely (116) and (302) peaks was observed when BaM/TiO_2/Si thin film was crystallized at 750 °C by post-annealing. On the other hand, BaM/Si films with no underlayer were well crystallized at 850 °C. There was no significant increase in the peak intensity as the annealing temperature increased to 800 °C. This result suggests that TiO_2 underlayer is effective in lowering the annealing temperature of as-deposited BaM film.

Figure 6 shows micrographs of post-annealed BaM/Si, TiO_2/Si and BaM/TiO_2/Si films. The grain shapes of BaM/Si film are indicative of epitaxial growth of the film. The grains of a small size (about 20 nm) with elongated shape are present, in which BaM grows with the *c*-axis parallel to the film plane. However, as shown in Fig. 6c, the platelet and elongated grains were observed in BaM/TiO_2/Si film. The growth of BaM films was significantly influenced by a TiO_2 underlayer. As shown in Fig. 7, BaM/TiO_2/Si thin film was crystallized at 750 °C by post-annealing. For most of BaM/TiO_2/Si thin films, the coercivity values of the films prepared at 750 °C were higher than those of the films prepared at 800 °C. The microstructure of BaM in BaM/TiO_2/Si films was strongly dependent on the total Ar/O_2 gas pressure. Although acicular grains are usually grown in BaM film without underlayer [8], pop-corn type grains were observed at 10,000 mm Hg, and elongated grains at 5,000 mm Hg. It was evident that the BaM reproduces the microstructure of the TiO_2 underlayer (Fig. 6).

The selection of underlayer should be considered to optimize magnetic properties and microstructure of BaM films.

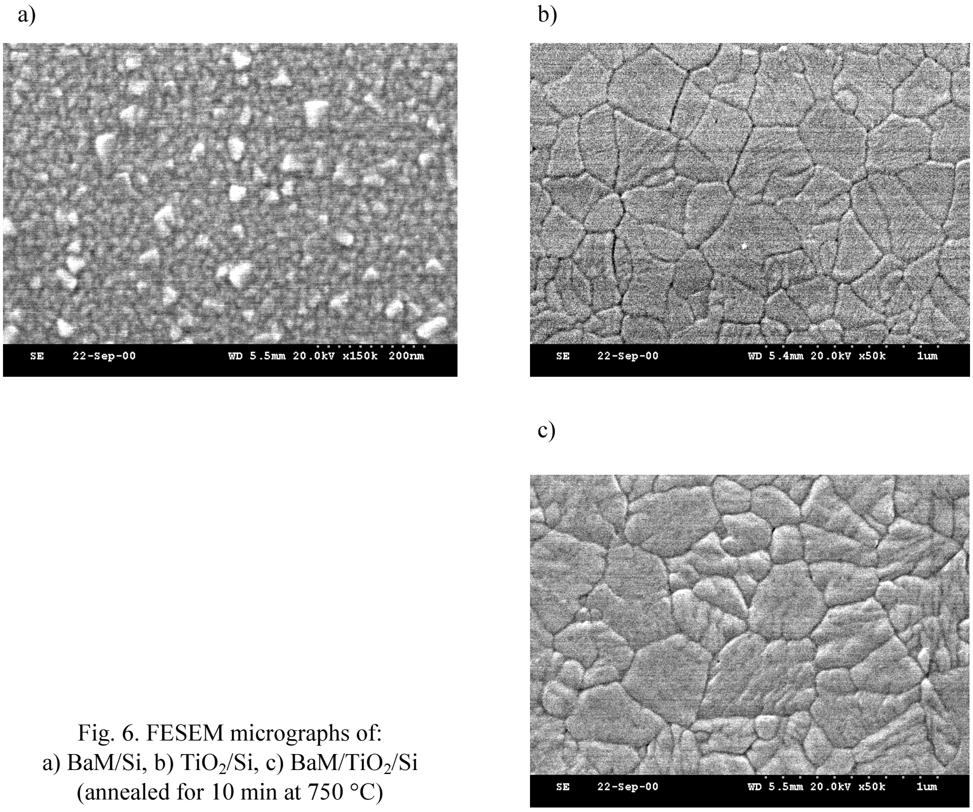


Fig. 6. FESEM micrographs of:
a) BaM/Si, b) TiO_2/Si, c) BaM/TiO_2/Si
(annealed for 10 min at 750 °C)

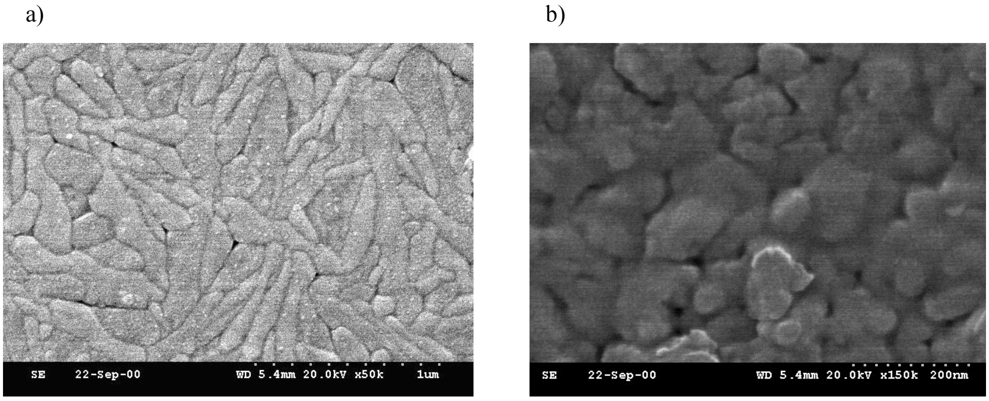


Fig. 7. FESEM micrographs of BaM/TiO_2/Si thin films deposited at: a) 5,000 mm Hg, b) 10,000 mm Hg

4. Conclusions

All the films with various underlayers, except for BaM/Fe/Si film, showed nearly the same out-of-plane and in-plane coercivities, indicating random orientation of BaM grains. BaM/Fe/Si thin film exhibited a strong out-of-plane magnetic anisotropy. Comparing with underlayer thickness, the coercivity of BaM/Fe_2O_3/Si film was almost the same as those of BaM films with other underlayers. By adopting $ZnFe_2O_4$ as an underlayer, the interdiffusion of Si from substrate was prohibited to some degree. The microstructure of BaM/TiO_2/Si film was strongly dependent on both the microstructure of the TiO_2 underlayer and the total gas pressure. The control of the underlayer microstructure is one of the important factors to control the grain size and shape of the BaM layer.

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