Structure and magnetic properties of hexagonal barium ferrite films deposited by alternate layer deposition method

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Abstract — Deposition of *c*-axis perpendicularly oriented hexagonal barium ferrite thin films were formed by an alternate periodic deposition of *S* (Fe_6O_8) and *R* ($\text{BaFe}_6\text{O}_{11}$) layers. BaM film with excellent *c*-axis orientation and good crystallinity was obtained when *S* layers 4.7 Å thick and *R* layers 6.9 Å thick was deposited on a ZnO underlayer. To reduce the amount of the Zn ions diffusing from the ZnO underlayer to the BaM film, the thickness of the ZnO underlayer was reduced. An underlayer less than 10 nm thick, however, significantly degraded the *c*-axis orientation of the BaM films. We also tried to deposit BaM films on various kinds of underlayers such as α - Fe_2O_3 and amorphous barium ferrite (a-BaM). A BaM film with *c*-axis orientation was obtained only on a ZnO underlayer and an a-BaM/ZnO underlayer, although the *c*-axis of the BaM crystallites in the film deposited on a ZnO underlayer inclined about 2 degrees from the normal to the film surface.

Key words : hexagonal barium ferrite, *c*-axis orientation, alternate periodic deposition, underlayer

I. INTRODUCTION

A hexagonal barium ferrite thin film is promising candidate as a high-density magnetic recording medium because of its high anisotropy field, mechanical hardness, and chemical stability. In recent years, much effort has been concentrated on the *c*-axis textured growth of barium ferrite thin films. [1]-[4] In this study, a deposition of *c*-axis perpendicularly oriented hexagonal barium ferrite thin films was attempted by means of an alternate periodic deposition of *S* (Fe_3O_4) and *R* ($\text{BaO} \cdot 3\text{Fe}_2\text{O}_3$) layers, since the hexagonal barium ferrite (BaM : $\text{BaFe}_{12}\text{O}_{19}$) has a periodic layered structure composed of *S* blocks (Fe_6O_8) and *R* blocks ($\text{BaFe}_6\text{O}_{11}$) alternating in the *c*-axis direction. A BaM film with excellent *c*-axis orientation was obtained by alternately depositing *S* layers 4.7 Å thick and *R* layers 6.9 Å thick on a ZnO underlayer. We also attempted to reduced in the thickness of the ZnO underlayer and deposited

BaM films on various underlayers, such as α - Fe_2O_3 and amorphous barium ferrite, in order to prevent the diffusion of Zn ions from the ZnO underlayer to BaM film. This paper describes in detail the structure of the BaM films deposited on *c*-axis oriented ZnO underlayers of various thickness and of the BaM films deposited on the various underlayers.

II. EXPERIMENT

Hexagonal barium ferrite thin films were deposited using a DC facing targets sputtering apparatus with three sputtering sources (for the deposition of the ZnO underlayer, the *S* layer, and the *R* layer) shown in Fig. 1. The various underlayers — such as ZnO, α - Fe_2O_3 , amorphous $\text{BaFe}_6\text{O}_{10}$ (a- $\text{BaFe}_6\text{O}_{10}$) and amorphous barium ferrite (a-BaM) thin film — were first deposited on a thermally oxidized silicon wafer substrate. Then *S* layers 4.7 Å thick and *R* layers 6.9 Å thick were alternately deposited at 580°C under an ambient atmosphere consisting of 10% O_2 and 90% Ar. The deposited barium ferrite films were about 1150 Å thick, and a typical deposition condition for the underlayer and the BaM film are listed in Tables I and II.

The crystal structure of the films was investigated by x-ray diffraction, and the magnetic properties of the films were measured by using a vibrating sample magnetometer (VSM).

III. RESULTS AND DISCUSSION

Figure 2 shows a typical x-ray diffraction diagram for a film obtained by the alternate deposition of *S* layers 4.7 Å thick and *R* layers 6.9 Å thick on a *c*-axis-orientated ZnO underlayer 15 nm thick. It should be noted that the diffraction peaks from the BaM (004) and (0012) planes are clearly evident. This indicates that the BaM film

Fig. 1. Sputtering system used for film preparation.

Table I. Underlayer preparation conditions.

underlayer	Sputtering gas	Gas pressure	Substrate temperature	thickness
ZnO	20%O ₂ +Ar	5 mTorr	250°C	~15 nm
α-Fe ₂ O ₃	10%O ₂ +Ar	3 mTorr	200°C	16 nm
a-BaFe ₆ O ₁₀				15 nm
a-BaM				23 nm
a-BaM/	20%O ₂ +Ar	5 mTorr	250°C	23 nm
ZnO				15 nm

Table II. BaM film preparation condition.

	BaO·3Fe ₂ O ₃ <i>R</i> layer	Fe ₃ O ₄ <i>S</i> layer
Target	BaO·3Fe ₂ O ₃	Fe ₃ O ₄
Substrate	ZnO/SiO ₂ /Si	
Sputtering gas	10%O ₂ +90%Ar	
Gas pressure	3 mTorr	
Substrate temperature	580°C	
Target voltage	500-600 V	600-700 V
Discharge current	57 mA	50 mA
Deposition cycles	100	
Thickness of layer	6.9 Å	4.6 Å

has excellent *c*-axis orientation and good crystallinity. The saturation magnetization of this film, however, was only about 250 emu/cc, much smaller than that of bulk BaM. This small value of the saturation magnetization seemed to be caused by the formation of ZnFe₂O₄ in the film, since diffraction peaks from ZnFe₂O₄ (111) plane are

Fig. 2. X-ray diffraction diagram of a film with *S* layers 4.7 Å thick and *R* layers 6.9 Å thick, deposited on a *c*-axis-orientated ZnO underlayer of 15 nm thick.

Fig. 3. SEM surface micrographs of a ZnO underlayer 100 Å thick.

also clear in the diffraction diagram. This ZnFe₂O₄ is thought to be formed by the diffusion of Zn ions from the ZnO underlayer into the BaM film. [4], [5]

To reduce the amount of the ZnFe₂O₄ in the film, we tried using a thinner ZnO underlayer. Figure 3 shows SEM surface micrographs of a ZnO underlayer 100 Å thick. A continuous ZnO underlayer with *c*-axis orientation was also obtained at a thickness below 100 Å. BaM films were deposited on ZnO underlayers less than 150 Å thick, and Fig. 4 shows x-ray diffraction diagrams of those films. It is clear that when the thickness of the ZnO underlayer decreases below 100 Å, the diffraction peaks from the *c*-plane of the BaM become small and the diffraction peak from the BaM (107) plane become large. These results suggest that a decrease in the thickness of the ZnO underlayer below 100 Å leads to a significant degradation of the *c*-axis orientation of the film. To obtain a BaM film with *c*-axis orientation, we

should therefore use a ZnO underlayer more than 150 Å thick.

Figure 5 shows x-ray diffraction diagrams of BaM films deposited on various kinds of underlayers. A BaM film with (001) texture was obtained only on ZnO and a-BaM/ZnO underlayers. The BaM films deposited on the α -Fe₂O₃, a-BaFe₆O₁₀, and a-BaM underlayers have diffraction peak from the BaM (107) plane. X-ray diffraction diagrams of these underlayers are shown in Fig. 6. The α -Fe₂O₃ underlayer has a random orientation, which may result in the formation of a BaM film with random orientation. The a-BaFe₆O₁₀, a-BaM, and a-BaM/ZnO underlayers appear to have amorphous structure, since they have no clear diffraction peaks. Unlike the diffraction diagram of the BaM film deposited on a-BaM underlayer, the diffraction diagram of the BaM film deposited on a-BaM/ZnO underlayer did not have a diffraction peak from (107) peak. This result suggests that the surface structure of an a-BaM film deposited on a ZnO underlayer differs from that of an a-BaM film deposited on a SiO₂/Si substrate.

Figure 7 shows, for BaM films deposited on various underlayers, the rocking curves of the BaM (008) diffraction peak and the full width at half-maximum values of the rocking curve ($\Delta\theta_{50}$). The shape and width of rocking curve depend on the kind of underlayer. The rocking curve of the BaM film deposited on a ZnO underlayer has two peaks indicating that the *c*-axis of the BaM crystallites in the film tilts about 2° from normal to the substrate surface. The film deposited at a high temperature on a ZnO underlayer has a normal rocking curve with one peak. The mechanism of the growth of the tilted crystallites on the ZnO underlayer is still unclear.

The magnetic properties of the BaM films deposited on the various underlayers are listed in Table III. Since the amorphous BaM film is not crystallized at a temperature below 700 °C, diffusion of Zn ions from the ZnO underlayer to the BaM film is expected to be suppressed when the film is deposited on a-BaM/ZnO underlayer. The film deposited on α -Fe₂O₃ underlayer has a very small M_s (160 emu/cc) and very small $H_{c\parallel}$ (0.15 Oe), perhaps because of poor crystallinity of the BaM film. A clear increase in saturation magnetization, however, was not observed when the BaM film was deposited on a a-BaM or a-BaM/ZnO underlayer, although the coercivity in the perpendicular direction $H_{c\perp}$ increased considerably. This increase in $H_{c\perp}$ may be caused by the suppression of the diffusion of Zn ions.

Fig. 4. X-ray diffraction diagrams of the films deposited on ZnO underlayers less than 150 Å thick.

○ — *c*-plane of BaM ● — Other planes of BaM
△ — ZnFe₂O₄ * — Substrate

Fig. 5. X-ray diffraction diagrams of BaM films deposited on various underlayers : (a) on α -Fe₂O₃ (b) on a-BaM (c) on a-BaFe₆O₁₀ (d) on ZnO (e) on a-BaM/ZnO

Fig. 6. X-ray diffraction diagrams of α -Fe₂O₃, ZnO, and a-BaM/ZnO underlayers

Fig. 7. Rocking curves of the BaM (008) diffraction peak and the full widths at half-maximum values for these curves ($\Delta\theta_{50}$) when the BaM films were deposited on various underlayers : (b) on a-BaM (c) on a-BaFe₆O₁₀ (d) on ZnO (e) on a-BaM/ZnO

Table III. Magnetic properties of BaM films deposited on the various underlayers.

	M_s [emu/cc]	$H_{c\perp}$ [kOe]	$H_{c\parallel}$ [kOe]
Fe ₂ O ₃	160	1.86	0.15
a-BaM	215	4.50	3.55
a-BaFe ₆ O ₁₀	255	4.78	3.49
ZnO	238	1.60	0.24
a-BaM/ZnO	206	2.73	0.69

IV. CONCLUSIONS

A c -axis perpendicularly oriented hexagonal barium ferrite thin films were deposited on various underlayers by using an alternate periodic layer deposition technique, and the following results were obtained :

(1) A ZnO underlayer more than 150 Å should be used in order to obtain a BaM film with c -axis orientation.

(2) The c -axis of the crystallites in the BaM films deposited on a ZnO underlayer is tilted about 2° from the normal to the substrate surface.

(3) Suppressing of the diffusion of Zn ions from ZnO underlayer to BaM film by using an amorphous BaM intermediate layer leads to a considerable increase in coercivity of the film but does not increase the saturation magnetization.

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