The Effects of Pb Addition on Crystal Structure and Magnetic Properties of Ba–Ferrite Sputtered Films

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Abstract—— Pb added Ba–ferrite films were prepared at the substrate temperature of 550 °C by dc magnetron sputtering and their crystallographic characteristics and magnetic properties were investigated. The addition of Pb facilitates the crystallization and improves the crystallinity for hexagonal M phase. The films prepared in this study exhibit a good c–axis orientation and the c–axis dispersion angle θ90 is as small as 1°. The coercivities Hc, and Hc⊥ and Ms of the films are 1.0 kOe, 0.2 kOe and 240 emu/cc, respectively.

Key words: Ba–ferrite, hexaferrite, hexagonal ferrite film, thin film, perpendicular recording media, sputtering

I. INTRODUCTION

Many researches have been focused on perpendicular magnetic recording since it was proposed by Prof. S. Iwasaki et al [1]. Perpendicular recording is substantially preferable for high density recording under the geometrical conditions of the head–medium configuration.

There are various candidates for the perpendicular recording materials such as Co–Cr thin films [2], Fe and Co plated films on aluminum oxide substrate [3], and Ba–ferrite particulates [4]. The Co–Cr thin films have been most intensively studied because of an excellent crystallographic characteristics and magnetic properties.

Good chemical stability and mechanical durability as well as excellent magnetic properties are essential for recording medium. The authors have been studying a magnetoplumbite type of hexagonal Ba–ferrite(BaM) thin films prepared by magnetron sputtering [5] and sol–gel method [6] and reported that BaM sputtered rigid disks with small c–axis dispersion angle θ90 possess an excellent recording characteristics [7]. According to their reports, the recording density D90 depends on θ90 and the smaller θ90 results in the higher D90. There are some problems to be solved in preparation of BaM films. The most important problem is that a high substrate temperature Ts is necessary to crystallize the hexagonal M phase. The Ts for preparing BaM films with c–axis dispersion angle θ90 as small as 2~3° is about 620°C [5] and such a high Ts limits the selection of substrate material. It is strongly recommended to reduce the Ts during deposition for the practical fabrication of the recording medium. Although the authors have already examined the low temperature deposition and successive heat treatment, BaM films with c–axis orientation could not be prepared [8].

It is known that there are some divalent ions such as Ba, Ca, Sr, and Pb, which have approximately the same ionic radii as that of oxygen divalent ion. These elements are the constituents of the hexagonal M–type ferrites. Among them, Pb is the easiest to obtain as a pure metal and the sintering temperature of PbM ferrite is lower than that of BaM. It is expected that crystallization temperature for M–type ferrite decreases by addition of Pb. In this study, Pb added BaM(Ba+Pb)M films were prepared by dc magnetron sputtering and the effects of Pb addition on the crystal structure and magnetic properties of the films were investigated.

II. EXPERIMENTALS

BaM films had been prepared by means of rf diode sputtering system in our previous study. In order to compensate the lack of Ba content in the films and to obtain the films with a stoichiometric composition of BaM(i.e. n=6 in BaO+nFe₂O₄), Ba content in the target was increased to 1.7 time(BaO⋅3.5Fe₂O₄) as much as that of stoichiometric composition of BaM. The decrease of Ba content in the films was considered to be mainly caused by the bombardment of high energetic ions from the plasma. The mobility of the electrons is much larger than that of the ions in an rf electric field. This results in a high plasma potential in the rf discharge. The authors have carried out the plasma diagnosis for their system by using a Langmuir probe [9]. The plasma potential Vp and the floating potentialVF, which is equivalent to the potential of
the substrate, at the pressure of 2 mTorr was 40 V and -15 V, respectively. The discharge ions bombard the film surface with the energy of $e \cdot V_d$, where $V_d$ is the difference of each potential ($V_p-V_f$) and $e$ is the electronic charge. The surface of the growing films is bombarded by discharge gas ions with the energy as high as 55 eV at 2 mTorr and this energy is high enough to re-sputter the weakly adsorbed atoms and to damage the crystallite. On the contrary, the potential difference $V_d$ in a dc magnetron sputtering system is less than 20 V at 2 mTorr. This implies that the difference in composition between the films and the target in the dc magnetron sputtering system is small as compared to that in the rf sputtering system.

In this study, the dc magnetron sputtering system was used to prepare Pb added BaM((Ba+Pb)M) films. The target is a sintered ferrite disk (8 cm diameter) with stoichiometric composition of BaM (i.e. n=6 in BaO$_n$Fe$_{12n}$O$_{3n}$) and Pb content was controlled by the numbers of Pb chip of 5 mm square on this disk. The substrate is a thermally oxidized silicon wafer and the substrate temperature $T_s$ is measured with a thermocouple in contact with the substrate surface. After evacuating a chamber to a pressure of below 1x10$^{-6}$ Torr, argon and oxygen gas were introduced into the chamber. The discharge gas pressure $P_{\text{Total}}$, which is a sum of each partial gas pressure, was set at 2 mTorr. The partial oxygen gas pressure $P_{\text{O2}}$ was 0.03 mTorr and an applied power was about 15 W. The thickness of (Ba+Pb)M films was about 1200 A.

\section{RESULTS AND DISCUSSION}

In this paper, the content of Pb is represented by the number of Pb chip on the target for convenience. With a target on which the numbers of Pb chip was 10, a deposit composition of Pb$_{0.35}$Ba$_{0.63}$Fe$_{12}$O$_x$ was obtained.

Figure 1 shows the x-ray diffraction diagrams for the films with various Pb content. The substrate temperature $T_s$ was set at 550°C. As shown in this figure, the diffraction lines are only from both c-plane of hexagonal M phase and (111) plane of spinel-like ferrite (represented as S). This spinel-like phase grows as an initial layer of BaM layer and is considered to be synthesized by the lack of Ba content in a very thin region of about 300Å[10].

Figure 2 shows the dependence of the normalized intensity of diffraction lines for (008) plane for M phase and (111) plane for spinel-like phase. The intensity of diffraction lines are normalized by the film thickness. The intensity for the pure BaM film, where Pb is not added, is very weak as compared to those for (Ba+Pb)M films. This implies that the $T_s$ is not high enough to crystallize for BaM crystallite. The intensity of the diffraction line for the M phase increases and that for the spinel-like phase is almost constant with the increase of Pb content. The intensity of diffraction line for M phase has a maximum at around 10 pieces of Pb chip on the target. This means that the addition of Pb facilitates the crystallization for M phase. The intensities of the diffraction line for M and spinel-like phase decrease and increase, respectively, with the further increase of Pb content above 15 pieces on the target. This may be caused by the deviation of the composition for M phase by the excessive addition of Pb. From these results, it is found that the
proper addition of Pb improves the crystallinity for M phase. Figure 3 shows the dependence of lattice constant \( c \) for the hexagonal M phase and \( a \) for the cubic spinel-like phase. The lattice constant \( a \) for the hexagonal M phase can not be evaluated because only the lines relating to c-plane for hexagonal M phase were observed, as shown in Fig.1. The lattice constant \( c \) once decreases slightly with the increase of Pb content up to 10

Fig.2 Dependence of normalized intensity of diffraction lines for (008) and (111) plane on Pb content.

![Fig.2 Dependence of normalized intensity of diffraction lines for (008) and (111) plane on Pb content.](image)

Fig.3 Dependence of lattice constant \( c \) for hexagonal M phase and \( a \) for spinel-like phase on Pb content.

![Fig.3 Dependence of lattice constant \( c \) for hexagonal M phase and \( a \) for spinel-like phase on Pb content.](image)

Fig.4 Dependence of c-axis dispersion angle \( \Delta \theta_{50} \) of films on Pb content.

![Fig.4 Dependence of c-axis dispersion angle \( \Delta \theta_{50} \) of films on Pb content.](image)

Fig.5 Dependence of saturation magnetization \( M_S \) on Pb content.

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Fig. 6 Dependence of coercivities $H_{c\perp}$ and $H_{c\|}$ on Pb content.

In addition to the previously extracted text, the image contains a graph illustrating the dependence of coercivities $H_{c\perp}$ and $H_{c\|}$ on the number of Pb chips. The coercivity $H_{c\perp}$ increases from 650 to 1000 Oe, while that in parallel to film plane $H_{c\|}$ is almost constant of 200 Oe with increase of Pb up to 10 pieces. $H_{c\perp}$ for the films with Pb addition above 12 pieces is almost constant of 1000 Oe with some scattering and $H_{c\|}$ for those films increases gradually to about 500 Oe.

IV. CONCLUSION

Crystallographic characteristics and magnetic properties of Pb added BaM films have been investigated.

The orientation of c-axis of hexagonal crystallite was improved by the addition of Pb and the c-axis dispersion angle $\Delta\theta_{50}$ was as small as 1°. The coercivities $H_{c\perp}$ and $H_{c\|}$ and saturation magnetization $M_s$ of (Ba+Pb)M films are 1.0 kOe, 0.2 kOe and 240 emu/cc, respectively. These values are suitable for high density magnetic recording medium.

REFERENCES