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Crystallographic and Magnetic Properties of Polycrystalline $BaFe_{12}O_{19}$ Films Grown by Pulsed Laser Ablation Technique

논문
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Abstract

Oriented barium hexaferrite thin films were grown on (110)Al_2O_3, (001)Al_2O_3, and (012)Al_2O_3 substrates by laser ablation technique utilizing a KrF excimer laser. For (100) on (110)Al_2O_3 and $BaFe_{12}O_{19}$ (001) on (001)Al_2O_3 planes, the degree of alignment of more than 93 % were accomplished with a laser beam energy density of 6.65 J/㎠. The growth of heteroepitaxial films of (114) $BaFe_{12}O_{19}$ on (012)Al_2O_3 was possible to be grown under the oxygen partial pressure P(O2) of 900 mTorr.

The optimized magnetic properties ($4\pi M_s$ is 3823 G, iH_c 3083 Oe, and squareness 0.72) were obtained from the as deposited films at the substrate temperature of 700 ℃ and post annealing treatment was not needed to enhance the magnetic properties. The saturated magnetization ($4\pi M_s$) of 3610~3820 G and the coercivities (iH_c) of 3060~3090 Oe which approach 85 % of those of bulk barium ferrite composed of single domain particles were obtained successfully.

Key Words(중요용어) : Pulsed Laser Ablation technique, Polycrystalline $BaFe_{12}O_{19}$ films, Oxygen partial pressure, Magnetic properties

I. Introduction

Barium ferrite($BaFe_{12}O_9$) is an important material with many technological applications.

Its strong magneto-crystalline anisotropy and high coercivity, along with chemical and mechanical stability make it a very attractive material for magnetic recording.

It also finds many applications in microwave devices due to its high resistivity and permeability at high frequencies. Different applications require optimization of different film properties such as coercivity, anisotropy and grain size which is usually realized through different film preparation techniques and processing conditions. Much work has been done to study barium ferrite films fabricated by techniques such as sputtering[1~4], metal-organic chemical vapor deposition[5] and liquid phase epitaxy[6]. Recently, barium ferrite films prepared by pulsed laser ablation technique(PLA) have received much attention[7~8].

PLA is a relatively new deposition technique with many unique advantages over other techniques in the growth of complex multicomponent materials. PLA has become the established technique for producing high quality high critical temperature superconducting thin films. Because of the similar chemical properties of the two ceramic oxide compounds yttrium barium copper oxide and barium ferrite, and our interest in the microwave propertes of both, we investigated the possibility of film growth of the latter. A pulsed laser ablation technique for the growing of barium ferrite films were

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firstly applied by Vittoria et al.[9-10].

The purpose of this study is to evaluate the applicability of the laser ablation technique for producing the barium ferrite films of perpendicular anisotropy reproducibly. Many parameters such as oxygen partial pressure, substrate species, and temperature influencing the characteristics of the films were systematically investigated.

Ⅱ. Experiment

A commercial polycrystalline barium ferrite target with purity of 99.9 wt.% was mounted on a rotating axle turning at a rate of 3~5 revolutions per minute. The target discs were 0.5 ㎝ thick × 5.0 ㎝ diameter. Films were deposited by focusing 200~500 mJ, 20 ns pulses to give a fluence of 4.5~6.65 J/㎠/pulse at 10 Hz. The laser beam was incident on the target at the angle of 45° from the normal and the substrate holder (heater) was set 5 ㎝ away from the target. The substrates were $(001)Al_2O_3$, $(110) Al_2O_3$ and $(012)Al_2O_3$. After the vacuum chamber was evacuated to the base pressure less than 4×10^{-6} Torr, the substrate temperature and oxygen pressure were raised to the desired deposition settings and held constant during film growth. The ranges of substrate temperature and oxygen partial pressure were 650~850 ℃ and 20~900 mTorr, respectively. The lasing density mentioned above gave a deposition rate of 0.5~2.0 Å/sec. Once the deposition was completed, the substrate heater was cooled to 300 ℃ at a rate of 3~5 ℃/min, and then vented to room temperature.

By using both the scanning electron microscope (SEM) and "alpha step", the film thickness was measured. Structural charaterization was performed using X-ray diffraction as well as SEM, and the compositions of the films were confirmed using an energy dispersive spectroscopy (EDS) and an inductively coupled plasma (ICP) analyzer as well. The magnetic properties of the films were mearured using a vibrating sample magnetometer (VSM).

Ⅲ. Results and Discussion

We found that barium ferrite films start to crystallize at 700℃ when the $(001)Al_2O_3$ substrate was used. Therefore, all the films in this work were grown at the substrate temperature of 700℃. The lasing energy density was fixed with 6.65 J/㎠.

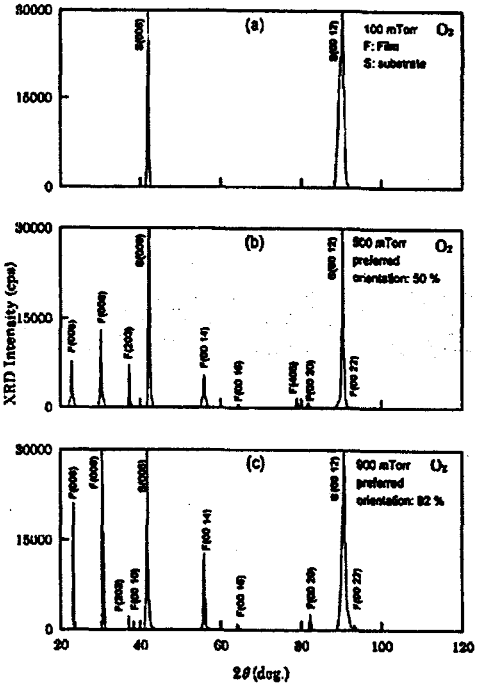

Fig. 1. X-ray diffraction patterns for the films grown on (001) Al_2O_3 substrate at the oxygen partial pressure of (a) 100, (b) 500, and (c) 900 mTorr, respectively.

$P(O_2)$ was very important to control the microstructure, magnetic properties and compositions of films as well.

Fig. 1 shows the dependence of X-ray diffraction results for the film growth upon oxygen pressure during deposition. The degree of epitaxial formation was found to be higher at a high $P(O_2)$, while the deposition rate decresed from 2 Å/sec to 1Å/sec with increasing the oxygen partial pressure up to 900 mTorr. The same results were obtained for all the substrates used in this study.

X-ray diffraction patterns clearly show the trend that as $P(O_2)$ increases from 100 to 900 mTorr for the films grown on $(001)Al_2O_3$, the degree of texture formation increased gradually. The degree of textured structure indicated in (b) and (c) was estimated by the Harris method[10]. The texture coefficient is given by the expression

$$TC = \frac{I_{hkl}/I_{o,hkl}}{\left(\frac{1}{n}\right)\Sigma I_{hkl}/I_{o,hkl}} \qquad (1),$$

where n is the number of considered peaks, I_0 the calculated intensity, and I the observed intensity.

Fig. 1 (c) indicates a near-epitaxial (001)planes on $(001)Al_2O_3$ substrate. The effect of $P(O_2)$ on the formation of barium ferrite films was quite different from the results obtained from yttrium iron garnet (YIG) via the same laser ablation technique[11-12]. The influence of $P(O_2)$ on the microstructure of YIG films, which is in the same oxygen stoichiometry, is generally known that depositing with increasing $P(O_2)$ causes ejection and splash of submicron particles from porous target body due to the expansion of oxygen in the pores. Accordingly, it was believed that the formation of epitaxial films deteriorated as $P(O_2)$ increased. However, the barium ferrite films ivestigated in this study showed the opposite results while as-deposited films of barium ferrite at the high $P(O_2)$ of 900 mTorr exhibited a textured structure, that of YIG formed a textured structure at the low $P(O_2)$ of 20 mTorr.

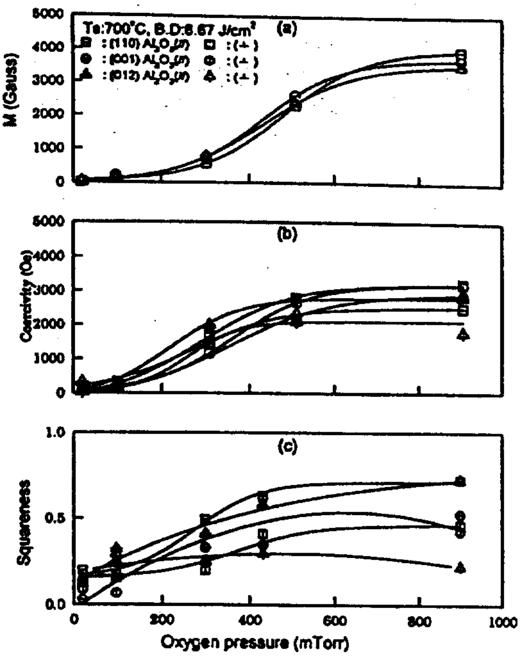

Fig. 2. The variation of magnetic properties against oxygen partial pressure for the films grown on three different sapphire substrates at 700 ℃ with the laser beam energy density 6.65 J/㎠.

It is noted that the barium ferrite films grown on $(012)Al_2O_3$ gave a perfect epitaxial character and showed better magnetic properties as shown in Fig. 2. The variation of $4\pi M_s$, iH_c, and the squareness of hysteresis curves measured from the films grown on (110), (001) and $(012)Al_2O_3$ substrates is plotted against the variation of $P(O_2)$ as shown in Fig. 2. The rightly dashed open symbols denote the data measured along the perpendicular direction to the film plane, and the horizontally dashed open symbols are of in-plane direction. The measurement along the plane direction was made by such a way that a squared sample of 5×5 ㎟ was rotated 90° with respect to the axis perpendicular to the film surface after each measurement. However, no difference was found in hysteresis loops. In Fig. 2(a). $4\pi M_s$ values measured normal to the film plane are not plotted due to their insignificance. However. $4\pi M_s$ measured normal to the film on (001) Al_2O_3 was always higher ($4\pi M_s$ = 3678 Gauss at 900 mTorr) than that measured at in-plane direction ($4\pi M_s$ = 3620 Gauss). This is because easy magnetization axis(c-axis) lies normal to the plane. The other two (110) and (012)Al_2O_3 substrates seem to induce the c-axis to lie in the film plane. But it is not obvious if the c-axis is inclined more or less. Both the $4\pi M_s$ and H_c values increased prominently as $P(O_2)$ increases from 500 up to 900 mTorr as shown in Fig. 2 (a) and (b). This seems to be resulted from the fact that the stoichiometry of $BaFe_{12}O_{19}$ could be achieved as $P(O_2)$ approached 900 mTorr. When one considers the squareness of hysteresis curves measured at in-plane and normal to the film grown on (110) Al_2O_3. the c-axis seems to lie in the film plane. The hyteresis curves of the films on (012)Al_2O_3 also show a similar behavior. However. taking into account the recent report regarding the anisotropic properties of Ba-ferrite films grown by a sputtering method[13]. it is strongly possible for the c-axis to be inclined about 24°(measured)~26.9° (calculated angle) with respect to film surface. Fig. 3 (a). (b) and (c) are SEM micrographs showing the grain aspect at film surface for (110). (001). and (012)Al_2O_3 substrate. respectively. The deposition was performed at $P(O_2)$ of 900 mTorr for 1 hour to have the films of 6000~7000 A thick using the energy density of 6.65 J/㎠. However, since the preferred orientation is different from each substrate the grains at the surface appear quite different in shape and size.

However. it was noted that higher oxygen pressure enhanced the growth of in-plane c-axis oriented grains and the tuning of film properties such as crystalline orientation and grain size was possible by careful control of the oxygen pressure during film growth.

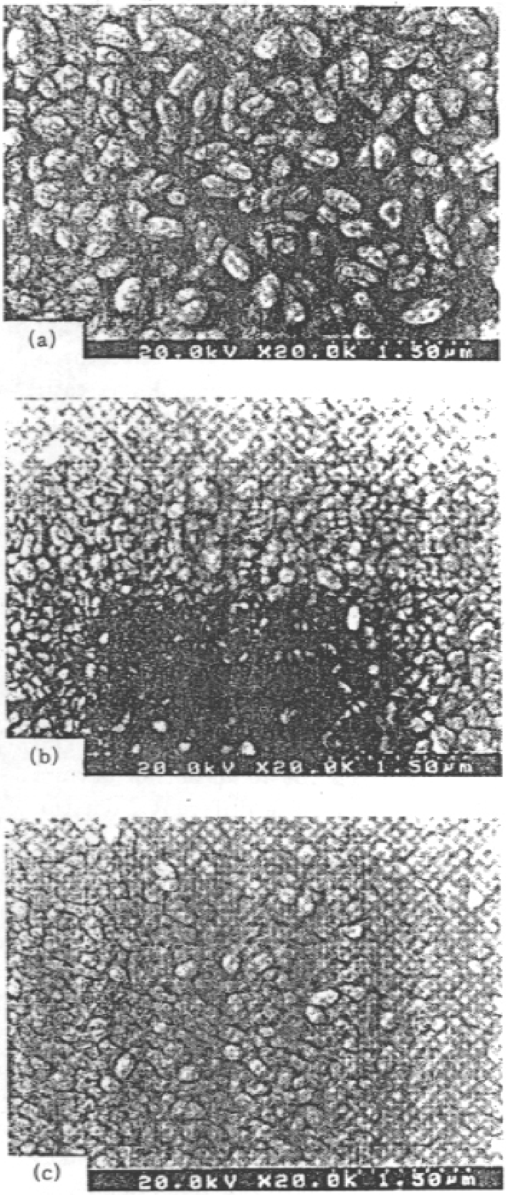

Fig. 3. SEM micrographs showing the grain aspect at the surface of the $BaFe_{12}O_{19}$ films grown on (a) (110). (b) (001). and (c) (012) Al_2O_3 substrates at $P(O_2)$ of 900 mTorr.

Typical magnetic hysteresis curves which correspond to the films with (100)$BaFe_{12}O_{19}$/(110)Al_2O_3, (001)$BaFe_{12}O_{19}$/(001)Al_2O_3 and (114)$BaFe_{12}O_{19}$/(012)Al_2O_3 are shown in Fig. 4. The curves of solid line are for the measurements in the film plane and the curves of dashed lines are for normal to the plane.

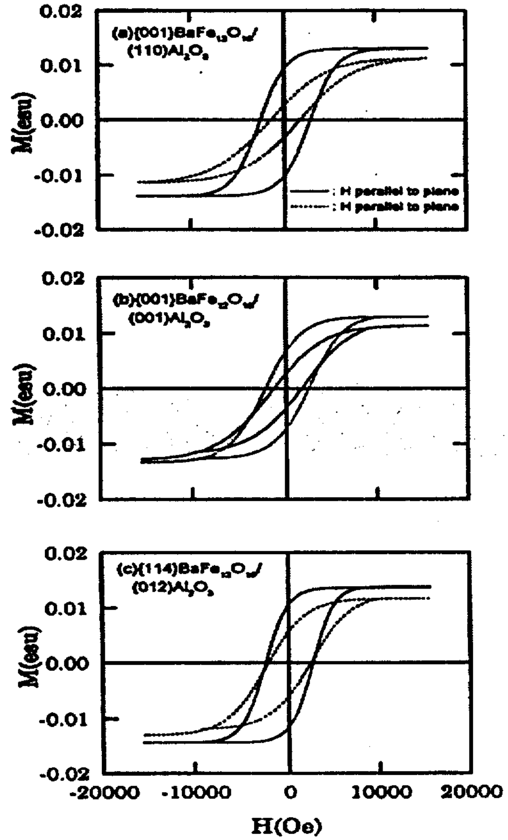

Fig. 4. Typical magnetic hysteresis curves of the films grown with (a) (100) $BaFe_{12}O_{19}$/(110) Al_2O_3, (b) (001) $BaFe_{12}O_{19}$/(001) Al_2O_3, and (c) (114) $BaFe_{12}O_{19}$/(012) Al_2O_3 relationships.

Fig. 4 (a) and (c) indicate the easy magnetization axis of $BaFe_{12}O_{19}$ crystals lying in the plane, and Fig. 4 (b) indicates the easy axis lying normal to the film surface. The heteroepitaxial relationships are summarized in Table I. It can be mentioned from the result that the availability of epitaxial films is mainly dependent upon the mismatch of interfacial planes between the substrate and the barium ferrite film on it. A slight mismatch in (114)$BaFe_{12}O_{19}$/(012) Al_2O_3 relationship exhibited a perfect epitaxial structure.

Table I. The crystallographic relationship between barium ferrite films and sapphire substrates.

epitaxial relationship	lattice mismatch (%)	c-axis of $BaFe_{12}O_{19}$	degree of texture (%)
(100)$BaFe_{12}O_{19}$/ (110)Al_2O_3	4.9~10.7	in-plane	95
(001)$BaFe_{12}O_{19}$/ (001)Al_2O_3	1.3~10.7	perpendicular	93
(114)$BaFe_{12}O_{19}$/ (012)Al_2O_3	1.3~2.4	24°~26.9° inclined	100

Some optimum processes where the post annealing treatment is not needed to obtain a perfect epitaxial relationship such as (114) $BaFe_{12}O_{19}$/(012)Al_2O_3 were formed during the course of evaluating the effect of substrate species and oxygen partial pressure for producing epitaxial $BaFe_{12}O_{19}$ films on sapphire. The typical magnetic properties obtained from barium ferrite films grown on (012)Al_2O_3 exhibited the maximum $4\pi M_s$ of 3828 Gauss which is more than 85 % of that of a bulk, and Hc of 3076 Oe. The easy magnetization (c-axis) direction was found to lie in the plane when a (110)Al_2O_3 substrate was used while a perpendicular anisotropy was obtained when the (001)$BaFe_{12}O_{19}$/(001)Al_2O_3 relationship was established.

Ⅳ. Conclusions

Oriented barium hexaferrite thin films were grown on $(110)Al_2O_3$, $(001)Al_2O_3$, and $(012)Al_2O_3$ substrates by laser ablation technique utilizing a KrF excimer laser. For (100) on $(110)Al_2O_3$ and $BaFe_{12}O_{19}$ (001) on $(001)Al_2O_3$ planes, the degree of alignment of more than 93 % was accomplished with a laser beam energy density of 6.65J/㎠. The growth of heteroepitaxial films of (114) $BaFe_{12}O_{19}$ on $(012)Al_2O_3$ was possible under the oxygen partial pressure $P(O_2)$ of 900 mTorr.

The optimized magnetic properties ($4\pi M_s$ is 3823 G, iH_c 3083 Oe, and squareness 0.72) were obtained from the as-deposited films at the subs-trate temperature of 700 ℃. Thus, post annealing treatment was not needed to enhance the magnetic properties. The saturated magnetization ($4\pi M_s$) of 3610~3820 G and the coercivities (iH_c) of 3060~3090 Oe which approach 85 % of those of barium ferrite bulk composed of single domain particles were obtained successfully.

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