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

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Highly oriented $BaFe_{12}O_{19}$ films were obtained by a KrF excimer laser ablation technique using $(110)Al_2O_3$, $(001)Al_2O_3$ and $(012)Al_2O_3$ substrates, respectively. The degree of alignment of more than 95 % were achieved for (100) on $(110)Al_2O_3$ and (001) on $(001)Al_2O_3$ planes, and heteroepitaxial films of (114) on $(012)Al_2O_3$ were possible to be grown with a lasing energy density of 6.67 J/cm^2 at an oxygen partial pressure (PO_2) of 900 mTorr. The best magnetic properties 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. Experimentally saturated magnetization ($4\pi M_s$) of 3600～3800 Gauss and coercivities (H_c) of 3050～3080 Oe, which approach 85 % of those of Ba-ferrite bulk composed of single domain particles, were obtained in this study.

1. Introduction

Ferrimagnetic films have many applications in microwave devices [1, 2] as well as information storage media [3-5]. First of all, yttrium iron garnet based films are used as magnetostatic wave components due to their low resonance linewidth. Barium hexaferrite also shows a potential use in milimeter wave devices, where use is made of mechanical strength and chemical stability as well as its high uniaxial anisotropy field [6]. However, thin films with perpendicular anisotropy are of great interest for high density magnetic recording media [7] and microwave monolithic substrate as well [4]. Thin films of barium ferrite used to be produced by dc sputtering [8] or rf sputtering to form a perpendicular anisotropy [4, 9]. Recently the use of metal organic chemical deposition was introduced in the formation of barium ferrite thin films [10]. A pulsed laser ablation technique for the growing of barium ferrite films were firstly applied by Vittoria et al. [11, 12].

The present work was carried out 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 clarified.

2. Experiment

Laser ablation targets of polycrystalline 99.9 % pure barium ferrite were commercially purchased. The target discs were 0.5 cm thick X 5.0 cm diameter. Films were deposited by focusing 200～500 mJ, 20 ns pulses to give a fluence of 4.4～6.67 J/cm^2/pulse at 10 Hz. The laser beam was incident on the target at angle of 45° from the normal and the substrate holder (heater) was set at a distance of 5 cm from the target. The substrates used were $(001)Al_2O_3$, $(110)Al_2O_3$ and $(012)Al_2O_3$. The target and substrate heater was programed to rotate respectively at a speed of 3～5 rpm during deposition. After the vacuum chamber was evacuated to the base pressure ($< 4 \times 10^{-6}$ 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 5～2.0 Å/sec. Once the deposition was complete, the substrate heater was cooled to 300 ℃ at a rate of 3～5 ℃/min, and then vented allowing to room temperature.

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

3. Results and Discussion

A. The Effect of Oxygen Partial Pressure on the Magnetic

Properties and Microstructure of the Films

To begin with determining the crystallization temperature of the as-deposited barium ferrite films, primary films on $(001)Al_2O_3$ substrates were obtained by heating from 600 to 750 ℃, respectively. The lasing energy was fixed with 6.67 J/cm^2 at the oxygen partial pressure, P (O_2), of 500 mTorr. It was found that the films grown at the temperature below 700 ℃ always gave amorphous films while the films grown above 700 ℃ resulted in highly textured grains in (001) orientation. Accordingly the substrate temperature was fixed at 700 ℃ thereafter. Again an optimized lasing energy density was chosen using the same $(001)Al_2O_3$ substrate at 700 ℃ with the oxygen partial pressure of 500 mTorr by varing the density from 4.4 to 6.67 J/cm^2. The magnetic properties and hysteresis behavior of the films were measured to be the same. However only the deposition rate increased with increasing the beam energy density. Therefore the energy density of 6.67 J/cm^2 giving the highest deposition rate was used. Film thickness obtained from the conditions mentioned above were 6000 ~ 7000 Å in general.

P (O_2) was very important to control the microstructure, magnetic properties and compositions of the films as well. As shown in Fig. 1, the deposition rate decreases from 2 Å/sec to 1 Å/sec with increasing the oxygen partial pressure up to 900 mTorr which was commonly true for all the substrates used. However, the degree of epitaxial formation was found to be higher at a high pressure. X-ray diffraction patterns in Fig. 2 clearly show the trend that as P (O_2) increases from 100, 500 to 900 mTorr for the films grown on $(001)Al_2O_3$, the degree of textured formation enhances gradually. The degree of textured structure indicated in (b) and (c) was defined by Harris method [13]. Fig. 2 (c) indicates a near-epitaxial (001) planes on $(001)Al_2O_3$ substrate. The effects 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 [14, 15]. The influence of P (O_2) on the microstructure of YIG films, which is in the same high 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. The formation of epitaxial films accordingly deteriorated with increasing P (O_2). The barium ferrite films, however, showed a reversed effect of P (O_2) in this study.

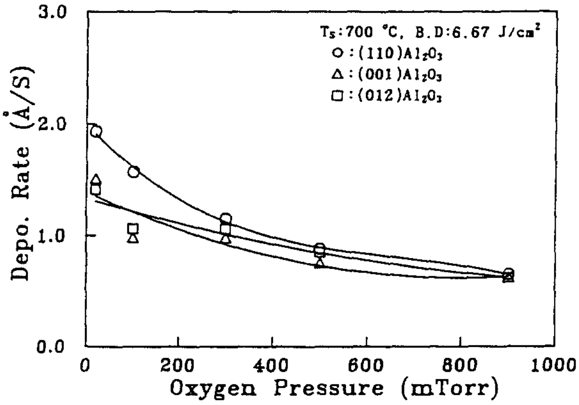

Fig. 1 The deposition rate as a function of oxygen partial pressure, P (O_2), with the lasing energy density of 6.67 J/cm^2 at the substrate temperature of 700 ℃.

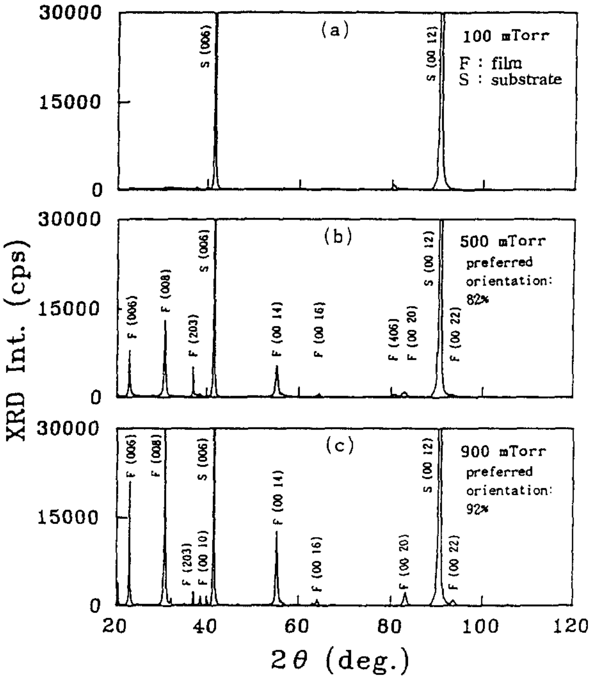

Fig. 2 X-ray diffraction patterns obtained from films grown on $(001)Al_2O_3$ substrate at the oxygen partial pressure of (a) 100, (b) 500, and (c) 900 mTorr, respectively.

A detailed composition analysis was done for the films grown at different P (O_2) and the results are shown in Fig. 3 (a) and (b). The dashed lines in the figure indicate the exact stoichiometric composition ratio. As P (O_2) increases the composition ratio of stoichiometric composition, especially for the films on $(012)Al_2O_3$ substrate. It must be mentioned that the barium ferrite films grown on $(012)Al_2O_3$ gave a perfect epitaxial character and showed the best magnetic properties which will be shown in Fig. 4. The variation of experimentally saturated magnetic moment ($4\pi M_s$) and coercivity (H_c) as well as the squareness of hysteresis curves are plotted against the P (O_2) used in Fig. 4 for the films on each (110), (001) and $(012)Al_2O_3$ substrates. The solid symbols denote the data measured along the perpendicular direction to the film plane, and the 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 mm^2 was rotated 90° with respect to the axis perpendicular to the film surface after one measure to another. However, no difference was found in hysteresis loops. In figure (a) $4\pi M_s$ values measured normal to the film plane are not plotted due to their meaninglessness. However $4\pi M_s$ measured to normal to the films on $(001)Al_2O_3$ were always higher ($4\pi M_s$ = 3684 Gauss at 900 mTorr) than those in-plane direction ($4\pi M_s$

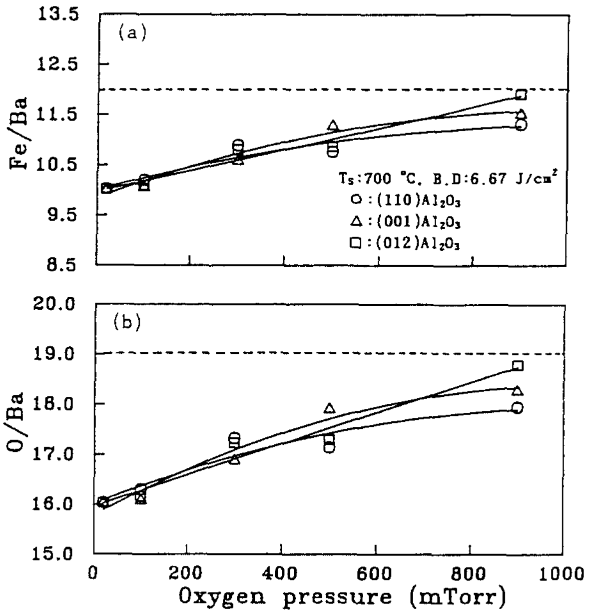

Fig. 3 The variation of (a) Fe/Ba and (b) O/Ba composition ratio as a function of oxygen partial pressure for the films grown on three different substrates at 700 ℃ with the lasing energy density of 6.67 J/cm^2.

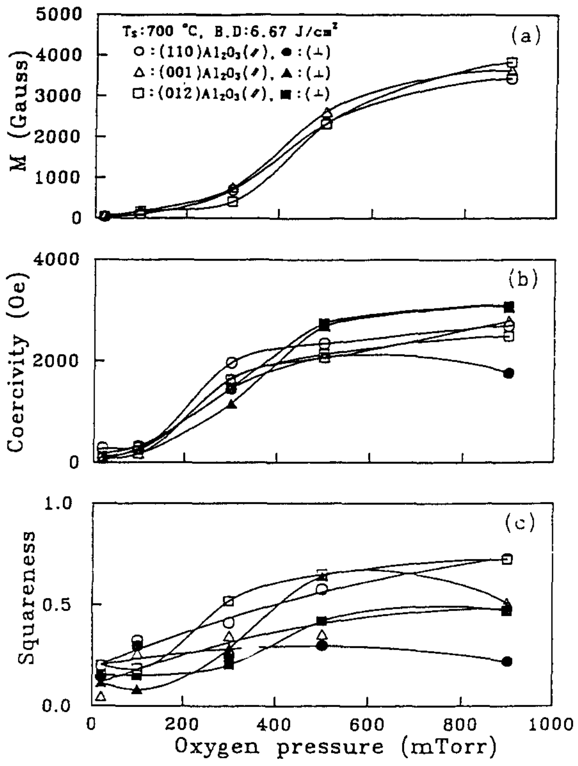

Fig. 4 The variation of magnetic properties against oxygen partial pressure for the films grown on three different sapphire substrates at 700 ℃ with the lasing energy density of 6.67 J. cm^{-2}.

= 3624 Gauss). This is because easy magnetization axis (c-axis) lies normal to the film plane. The other two (110) and (012)Al$_2$O$_3$ substrates seem to induce the c-axis to lie in 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 increase prominently as P (O$_2$) increases through 500 up to 900 mTorr as shown in figures (a) and (b). This seems to be resulted from the fact that the stoichiometry of BaFe$_{12}$O$_{19}$ can be achieved as P (O$_2$) approaches 900 mTorr as shown in Fig. 3. When one consider the squareness of hysteresis curves measured in-plane and normal to the film directions for each substrate, it is clearly shown that the films grown on (110) Al$_2$O$_3$ and have the c-axis lie in film plane. The hysteresis curves of the films on (012)Al$_2$O$_3$ 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 [16], it is very possible for the c-axis to be inclined about 24° (measured) ~ 26.9° (calculated angle) with respect to the film surface.

B. The Effect of Substrate on the Formation of Film Structure

Fig. 5 (a), (b) and (c) are SEM micrographs showing the grain aspect at film surface for each (110), (001) and (012)Al$_2$O$_3$ substrate. The deposition was performed at P (O$_2$) of 900 mTorr for 1 hr to have the films of 6000 ~ 7000 Å thick using the energy density of 6.67 J/cm^2. As mentioned previously, since the preferred orientation is different from each substrate the grains at the surface appear quite different in shape and size as well. In Fig. 6 x-ray diffraction patterns of the films grown on three different substrates at P (O$_2$) of 900 mTorr using the en-

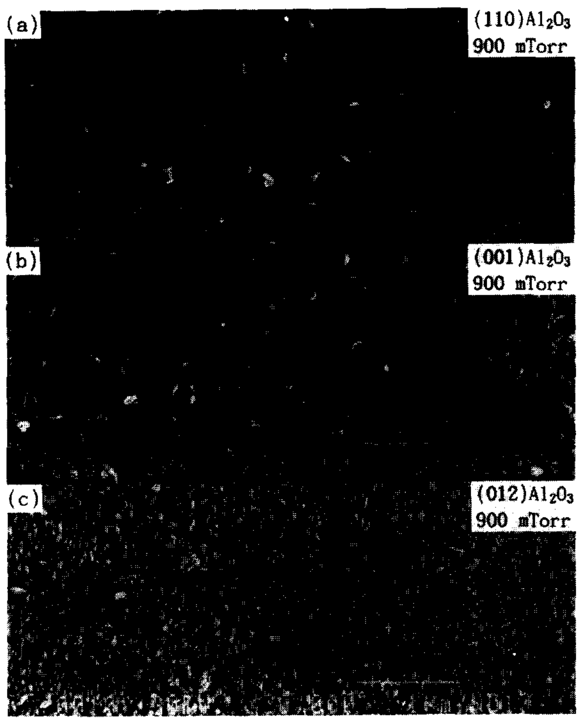

Fig. 5 SEM micrograrphs showing the grain aspect at the surface of the BaFe$_{12}$O$_{19}$ films grown on (a) (110), (b) (001), and (c) (012)Al$_2$O$_3$ substrates, respectively, at P (O$_2$) of 900 mTorr.

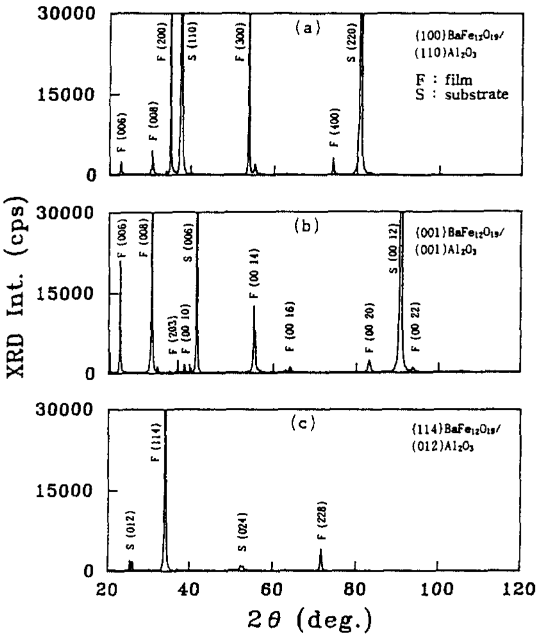

Fig. 6 X-ray diffraction patterns obtained from the films with (a) {100}/(110), (b) {001)/(001), and (c) {114} $BaFe_{12}O_{19}/(012)Al_2O_3$ relationships grown at 700 ℃ with the lasing energy density of 6.67 J/cm^2.

ergy density of 6.67 J/cm^2 are shown. Those films grown with the optimized lasing conditions exhibit $(100)BaFe_{12}O_{19}/(110)Al_2O_3$, $(001)BaFe_{12}O_{19}/(001)Al_2O_3$ and $(114)BaFe_{12}O_{19}/(012)Al_2O_3$ relationships, respectively. Particularly the perfect (114) heteroepitaxial films were obtained on $(012)Al_2O_3$ as shown in figure (c). The typical magnetic hysteresis curves, which corresponds to the films of Fig. 6, suggesting the anisotropy of the films are shown in Fig. 7. The curves of solid line are for the measurements in the film plane and curves of dashed lines are of normal to the plane. Figures (a) and (c) indicate the easy magnetization axis of $BaFe_{12}O_{19}$ crystals lying in the film plane, and figure (b) indicates the easy axis lying normal to the film surface. The heteroepitaxial relationships are analyzed in Table 1. It can be said from the resulatant data that the availability of epitaxial films is mainly dependent upon the mismatch of interfacial planes between substrate and barium ferrite film on it. A slight mismatch in $(114)BaFe_{12}O_{19}/(012)Al_2O_3$ relationship exhibited a perfect epitaxial structure.

4. Conclusion

During the course of evlauating the effect of substrate species and oxygen partial pressure for producing epitaxial $BaFe_{12}O_{19}$ films on sapphire, some optimization processes were found to be able to obtain a perfect epitaxial relationship such as (114) $BaFe_{12}O_{19}/(012)Al_2O_3$ where post annealing is not needed at all. The typical magnetic properties obtained from barium fer-

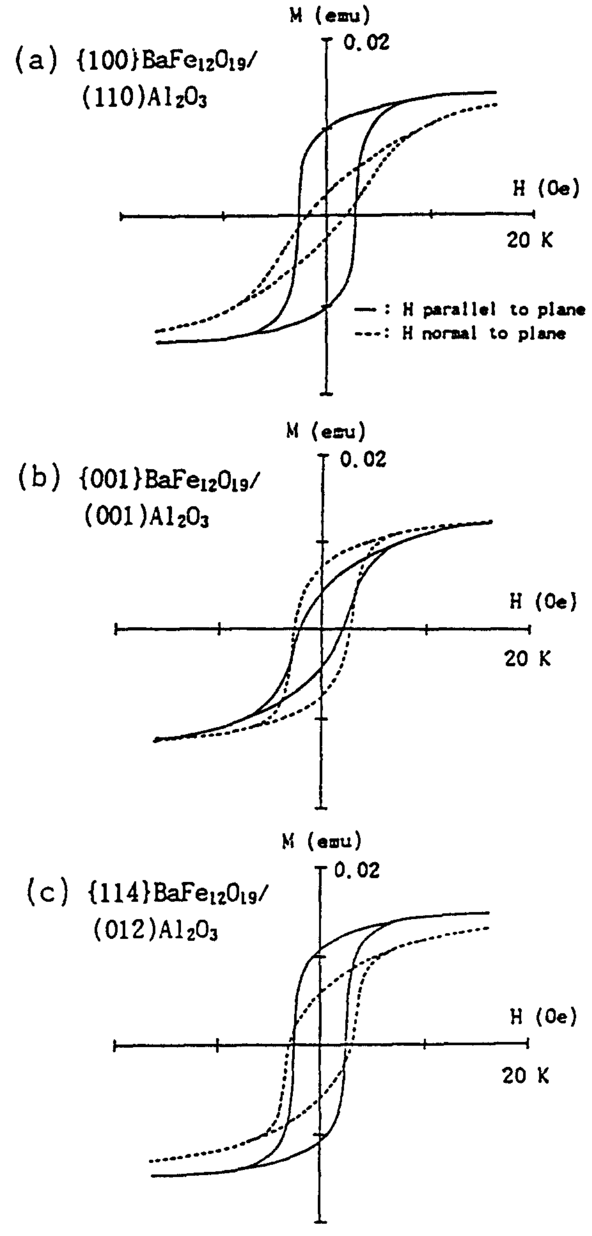

Fig. 7 The typical magnetic hysteresis curves of the films grown with (a) {100}/(110), (b) {001}/(001), and (c) $\{114\}/(012)Al_2O_3$ relationships, respectively.

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

epitaxial relationship	lattice mismatch (%)	c-axis of $BaFe_{12}O_{19}$	degree of texture (%)
$(100)BaFe_{12}O_{19}/$ $(110)Al_2O_3$	4.8～10.8	in plane	96
$(001)BaFe_{12}O_{19}/$ $(001)Al_2O_3$	1.2～10.8	perpendicular	92
$(114)BaFe_{12}O_{19}/$ $(012)Al_2O_3$	1.2～2.3	24°～26.9° inclined	100

rite films grown on (012)Al_2O_3 exhibited the maximum $4\pi M_s$ of 3832 Gauss which is more than 85 % of a bulk, and H_c of 3083 Oe. The easy magnetization (c-axis) direction was found to lie in the film 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.

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