Crystallinity and magnetic properties of $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ thick film prepared by MOD technique

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In order to apply for magneto-optical (MO) devices, the thermally non-equilibrium $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ (BIG) films have been investigated. The films were prepared by metal organic decomposition (MOD) technique. The BIG thick film prepared in our previous processing showed the low Faraday rotation which was the same performance of the film with 300 nm. According to our previous preparation process, the crystallization from the amorphous phase to the garnet phase by post annealing was achieved after final spin-coating. We modified the process and repeated the post annealing process after every 5 times coating, then we obtained the thick film with high MO performance. The XRD analysis showed cube on cube crystal growth of the film on the substrate. The Faraday rotation of the film increased in proportion to the thickness of the film. The saturation magnetization was approximately 150 mT. The ferromagnetic resonance indicated the in-plane magnetic anisotropy. The microstructure of the cross section of the film revealed some damage at the interface area between the film and the substrate, which suggests more improvement of the annealing process. However, the BIG thick film prepared by MOD technique has high MO performance for the application for the optical devices.

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1. Introduction

The bismuth iron garnet ($\text{Bi}_3\text{Fe}_5\text{O}_{12}$: BIG) has the largest magneto-optical (MO) effect in infrared and visible light region among the garnet materials, however, that material is thermally non-equilibrium system. Since the first successful synthesis of BIG,¹⁾ much attention of this material has been attracted for the application in nonreciprocal waveguide devices, waveguide optical isolators, MO imaging of superconducting materials^{2),3)} and recently, MO imaging of high frequency electromagnetic field or MO spatial modulator for 3D display.^{4)–6)} The growth techniques of BIG films have been mainly studied by vapor phase depositions such as a reactive ion beam sputtering (RIBS) technique and a pulsed laser deposition (PLD),^{1),7)} whereas, the films prepared by those techniques often appeared misfit dislocations and voids which prevent optically smooth surface. In order to realize a flat surface of the film, the growth from the liquid phase has a great advantage. Recently, the highly Bi substituted garnet films have been possible to prepare by liquid phase such as metal–organic decomposition (MOD) techniques.⁸⁾ The surface morphology of the film prepared by MOD technique is inferior to the film prepared by liquid phase epitaxi-technique (LPE), however, the MOD film superiors to the film prepared by RIBS or PLD technique from the point of view of optically smooth surface. We applied the MOD technique for the synthesis of BIG film and successfully obtained the film with large Faraday rotation of approximately 6°/micrometer at 630 nm.⁹⁾ These characterizations were performed by using the thin film where metal–organic solution was spin-coated only 5 times on the substrate. For the practical application, thicker films are necessary. Unfortunately, we found that the film with the thickness of more than 1 microm-

eter indicated a poor MO effect which was almost the same performance of the film with 300 nm thickness. In this paper, we report the improvement of the preparation process for the thick BIG films by MOD technique. Also, we show the crystallinity and magnetic properties of the BIG thick films.

2. Experimental

The precursor of BIG films were prepared by spin-coating of a metal–organic solution (molar ratio Bi:Fe = 3:5, Kojundo Chemical Lab. Co.) The total concentration of Bi and Fe carboxylate in the metal–organic solution was fixed to 4%. The metal–organic solution was spin-coated on $\text{Gd}_3(\text{ScGa})_5\text{O}_{12}$ (100) (GSGG) single crystal substrate (lattice parameter $a_s = 12.373 \text{ \AA}$) at 3000 rpm for 30 s. The substrates were 1 inch diameter and 0.5 mm thick. After drying at 100°C for 30 min, the films were pre-annealed at 400°C for 30 min in order to decompose the metal–organic solution. In our previous preparation, these processes were repeated up to the designed thickness. Then, the film was finally crystallized in a furnace for 3 h at 480°C. We changed the annealing process as follows; the crystallization annealing at 480°C was repeated after every 5 times coating. Total coating times was 50 times. The crystalline analysis of the annealed films was performed by X-ray diffraction (XRD) technique (Rigaku RINT1000 and Rigaku ATX-E). The thicknesses of the films were estimated by the cross section observations by the scanning electron microscopy (JEOL: JSM-7000FO). The magnetic properties were measured by SQUID magnetometer (Quantum Design MPMS 7). The ferromagnetic resonance (FMR) was measured by the ESR spectrometer (Bruker E500). Faraday rotation was measured by using the MO spectrometer (JASCO K-250).

3. Results and discussions

The XRD spectra of the film with 50 times coating on GSGG substrate are shown in Fig. 1(a). The film (1) is the specimen

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Fig. 1. (a) The XRD spectrum of the BIG(100) thick film with 50 times coating. The diffraction peaks denoted ▼ indicate the 100 diffraction peaks from the film and the peaks denoted □ indicate the diffraction peaks from the substrate due to the $\text{Cu-K}\beta$ radiation which is not completely cut off. The film (1) is the specimen annealed at 480°C after every 5 times coating and the (2) is the specimen annealed at 480°C only after 50 times coating. (b) The 800 diffraction peaks of the film (1) after 5, 10, 20, 40 and 50 times coating, respectively.

annealed at 480°C after every 5 times coating and the (2) is the specimen annealed at 480°C only after 50 times coating. For the both films, only the (100) diffraction peaks of the garnet phase appeared. The diffraction peaks from the film (symbols ▼) appeared at lower angle than the peaks from the substrate. The small diffraction peaks (symbols □) of $k\beta$ line from the substrate passed through the Ni cut filter were also observed. The lattice parameter a_0 of the films was deduced by plotting a_0 against the Nelson-Riley function;

$$\frac{a_{\cos\theta} - a_0}{a_0} = K \cdot \cos^2\theta \cdot \left(\frac{1}{\sin\theta} + \frac{1}{\theta} \right), \quad (1)$$

where $a_{\cos\theta}$ is an interplane distance calculated from the apparent Bragg peak position at 2θ and K is a fitting coefficient. The lattice parameters $a_{\cos\theta}$ calculated from (400) , (800) , (1200) Bragg reflections for the films. The a_0 , obtained as an extrapolation of $\cos^2\theta$ to 0, were found to be $12.63 \text{ \AA}$, which is the same with the films prepared by vapor phase depositions.⁷⁾ Although the specimen's size of film (1) and (2) is not the same, the diffraction peaks of the film (1) seem larger than those of film (2). Figure 1(b) shows the 800 diffraction peaks of the film (1) after 5, 10, 20, 40 and 50 coating. The intensity of the peak tends to increase up to 20 times coating, whereas no remarkable differences are observed above 20 times coating.

The rocking curves of (400) reflections of the film in comparison with the GSGG substrate is shown in Fig. 2. The full

Fig. 2. The Rocking curves of (400) peaks from the film and the substrate, respectively. The scale of the substrate was reduced to be half due to strong intensity.

Fig. 3. The φ -scans of off-normal (1040) plane in BIG film and GSGG substrate. The $k\alpha_1$ and $k\alpha_2$ diffraction peaks from the substrate are observed due to sharpness.

width at half maximum (FWHM) is approximately 3° for the film and 0.03° for the substrate, respectively. Bragg reflections from off-normal $\{1040\}$ planes of the film and substrate are shown in Fig. 3 as φ scans. Although the broadened rocking curve of the film indicates the formation of the mosaic structure, the fourfold symmetry observed φ scans and the correspondence between diffractions peaks from the film and substrate prove cube on cube crystal growth of the film on the substrate to a certain extent.

The Faraday rotations spectra of the film annealed after every 5 times coating increased in proportion to the film thickness (shown in Fig. 4) up to 50 times coating. Whereas, the film annealed only after 50 times coating showed small Faraday rotation which corresponds to the value of the film with 10 times coating. This result suggests that there is a critical thickness for the crystallization of garnet phase from the amorphous phase for the case of MOD technique. The BIG garnet cannot be crystallized from the amorphous phase on the glass substrate without inserting some garnet buffer layer.¹⁰⁾ Even for the case of the crystallization on the single crystal substrate, small Faraday rotation of the film annealed only after 50 times coating indicates that the amorphous phase was not partially changed into garnet phase. The crystallization process from the amorphous phase is not realized at the present stage. However, it is clear crystal growth on the garnet structure has an important role for the crystallization from amorphous phase to the garnet phase. The experimental results suggest that such critical thickness lies between 100 nm and 300 nm. The preparing of thick BIG film is possible by repeating the post-annealing process within the

Fig. 4. The Faraday rotations spectra of the film annealed after every 5 times coating depending on the coating times up to 50 times. Note that the symbol ** is the data of the film annealed only after 50 times coating.

Fig. 5. The Faraday hysteresis curves of the film annealed after every 5 times coating depending on the coating times up to 50 times. The MO image of magnetic barcode on a credit card using the film with 50 times coating is shown in the insert.

critical thickness.

The Faraday hysteresis curves measured at 630 nm are the same tendency as shown in Fig. 5. The Faraday rotation of the film annealed after every 5 times coating increase almost in proportion to the coating time up to 50 times coating and the film with 50 times coating showed large Faraday rotation over 10° . This value corresponds to be $6^\circ/\mu\text{m}$. The film thickness was estimated to be $1.7\mu\text{m}$ from the cross section SEM micrograph shown later. The reported value of the PLD and RIBS film are approximately $8^\circ/\mu\text{m}$.⁷⁾ The magnetic field to saturate the rotation was approximately 1.5 kOe (119 kA/m), which is a little smaller than the values [2 kOe (159 kA/m)] of the films prepared by the vapor deposition technique. Magnetic anisotropy energy seems to become smaller for the MOD film. By using the film with 50 times coating, the MO image of the magnetic barcode on a credit card could be clearly observed (shown in the inset Fig. 5) The FMR spectra of the film in the magnetic field parallel to the plane and perpendicular to the plane are shown in Fig. 6(a), respectively. Figure 6(b) shows the angular dependence of the resonance fields to the out of plane. The resonance fields changed as a sine function and the resonance field in the magnetic fields parallel to the film plane [$H_{\text{res}} = 2.9$ kOe (230 kA/m)] is much smaller than the resonance field in the field to the normal to the film plane [$H_{\text{res}} = 4.7$ kOe (373 kA/m)]. These results suggest that the film has in-plane magnetic anisotropy.

The saturation magnetizations of the film with 50 times coating are plotted in Fig. 7 as a function of temperatures. The extrapolation of T to 0 K indicates approximately 150 and 130 mT at

Fig. 6. The FMR spectra of the film with 50 times coating (a) and the resonance fields vs. rotation angle to the out of the film plane (b). The solid line is plotted by the sine curve.

Fig. 7. Temperature dependence of the saturation magnetization of the film with 50 times coating.

room temperature, respectively. Note that the measurements were achieved above 50 K because the paramagnetic magnetization of the substrate containing Germanium was enhanced in the low temperature. The experimental error becomes large below 50 K although the magnetization of the substrate is subtracted from the raw data (film+substrate). Even as the error is concerned, the saturation magnetization of the BIG with 50 times coating seems to be smaller than the value of the $\text{Y}_3\text{Fe}_5\text{O}_{12}$. Yttrium and Bismuth are non-magnetic, thus the net magnetic moment of YIG and BIG come from the $5\mu_B$ of Fe^{3+} per formula unit. According to magnetization measurements of pure YIG, the results are approximately $M_s = 250$ mT at 4.2 K and $M_s = 180$ mT at room temperature, respectively.¹¹⁾ The small value of the MOD BIG film may come from the crystallinity or the density of the film. Figure 8 shows the cross section TEM micrograph of the film with 50 times coating. According to the diffraction images, both diffraction spots and ring pattern appeared in the film. The number of spots and rings decreased in the interface area between

Fig. 8. The cross section TEM micrograph of the film with 50 times coating annealed at 480°C after every 5 times coating. The diffraction patterns of top, middle and interface area are also shown.

the film and the substrate and the halo pattern appeared. The crystallinity of the film is different as a function of the depth. This result suggests that many times or long time annealing process may give some damage of the film. Strictly speaking, it is not clear at the present stage which annealing effect at 400 or 480°C affect the crystallized film. It is also unclear why the Faraday rotation continues to increase up to 50 times coating if the crystallinity of the film begins poor from the interface. At least, we think the annealing process at 480°C should be more investigated because the crystallized annealing process determined the quality of MO performance in our past experiments. The more optimum growth condition for the thick film may be necessary in the future, however, the film with 50 times coating can give clear MO images such as the magnetic bar code images and these high performance of the MO effect of the MOD thick film must be attractive for the application of the MO devices.

4. Conclusion

The $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ thick film was prepared by MOD technique and the modified coating process realized high performance of the

MO effect for the case of the 50 times coating film. The crystallinity of the film should be more optimized, however, the high ability as magnetic image sensor can be expected for the application of the MO devices in the near future.

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