Synthesis of Completely Substituted $Bi_3Fe_5O_{12}$ Garnet Films by Metal Organic Deposition Technique

(New Preparation Technique of Completely Substituted Bismuth Garnet Films)

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Thermally non equilibrium garnet $Bi_3Fe_5O_{12}$ was prepared by metal organic decomposition (MOD) technique and the magneto-optical properties were investigated for the magneto-optical (MO) imaging. The spin-coating process on the $Gd_3Ga_5O_{12}$ (100) substrate was repeated 5 times and the thickness was approximately 150 nm. The garnet phase was epitaxially crystallized on the single crystal substrate at the annealing temperatures of 500 and 550℃ and the lattice constant of the garnet film was estimated to be 12.64 Å. The saturation magnetization was estimated to be 1.67 kgauss and the maximum Faraday rotation at the wavelength of 635 nm showed 6.7 degree/μm. High performance of the MO properties can be expected to be the probe sensor of high frequency electromagnetic field with high spatial resolution.

Keywords: completely substituted bismuth iron garnet, MOD technique, magneto-optics, in-plane anisotropy

1. Introduction

Completely substituted bismuth iron garnet film ($Bi_3Fe_5O_{12}$: 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 by the reactive ion beam sputtering (RIBS) technique[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),4)] and recently, MO imagings of high frequency electromagnetic field[5),6)]. The growth techniques of BIG films have been mainly studied by vapor phase depositions such as electron cyclotron resonance (ECR) sputtering, RF sputtering and pulsed laser deposition (PLD)[7)-9)], whereas, those techniques often induced 3-dimensional (3D) island growth or misfit dislocations which prevents optically smooth surface of the films. In order to realize the flat surface of the film, the growth from the liquid phase has a great advantage. The liquid phase epitaxy technique is practically used as a commercial technique for optical isolators of the Bi substituted garnet materials; however, there is no flux with low melting point below 600 ℃ at the present stage. Recently, the highly Bi substituted garnet films prepared by liquid phase such as metal-organic decomposition (MOD) techniques have been studied and the real time observations of the magnetic flux distribution in superconducting materials have already been achieved[4),10),11)]. In this paper, we report the synthesis of thermally non equilibrium materials from the liquid phase using MOD technique and show the high performance of MO effect of the film with the thickness of nanometer order.

2. Experiments

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 3 %. The metal-organic solution was spin-coated on $Gd_3Ga_5O_{12}$ (100) single crystal substrate (lattice parameter a_s = 12.373 Å) at 3000 rpm for 30 seconds. In comparison with (111) substrate, (100) substrate is easier to grow the film with magnetic easy axis parallel to the film plane because

<111> axis is the magnetic easy axis of the garnet crystal. The film with magnetic easy axis parallel to the film plane is necessary for the high resolution MO imaging [3]. The substrates were 1 inch diameter and 0.5 mm thick. After drying at 100℃ for 30 minutes in an oven, the films were pre-annealed at 400 ℃ for 30 minutes in order to decompose the metal-organic solution. These processes were repeated 5 times. Then, the substrate was cut into approximately 5 × 5 mm^2 and the amorphous films placed on Pt plate were annealed in infrared furnace for 3 hours at 450 500, 550 600 and 650 ℃, respectively. All annealing treatments were achieved in an air atmosphere. The crystalline analysis of annealed films was performed by X-ray diffraction (XRD) technique (Rigaku RINT1000). 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 Faraday rotation was measured by using the MO spectrometer (JASCO K-250). The measurements of magnetizations and MO properties were performed at room temperature.

3. Results and Discussions

Differential thermal analysis showed that the metal-organic solution was decomposed through 2 steps as shown in Fig. 1. The organic solvent was evaporated near the temperature of 100 ℃ and the exothermic DTA peaks appeared around 290 ℃ and 400 ℃ indicates the decompositions of metal organic compounds through 2 steps. The temperature of the pre-annealing of the films was adjusted to the upper reaction temperature of 400 ℃. Since the bismuth is volatile, the change of the composition ratio of Bi: Fe was checked before and after annealing process. A few milliliters of MOD liquids were placed in an alumina crucible and they were annealed at 400, 550, and 700 ℃, respectively. The precipitate was dissolved in heated nitric acid. As a result of the Inductively Coupled Plasma (ICP) analysis shown in Table I, no change of the composition ratio was confirmed before and after annealing the MOD liquids. The composition ratio of Bi: Fe of the annealed spin-coated films are also considered to be 3 : 5.

Table I. ICP analysis of the annealed MOD liquid

400 ℃	atomic %	molar ratio
Bi	0. 373	2.983
Fe	0. 627	5.000

550 ℃	atomic %	molar ratio
Bi	0.386	3.145
Fe	0.616	5.000

750℃	atomic %	molar ratio
Bi	0.369	2.920
Fe	0.631	5.000

The XRD spectra of the film annealed between 400 and 650 ℃ are shown in Fig.2. At the annealing temperatures below 450 ℃, no diffraction peaks from the films were observed. The (00*l*) diffraction peaks of the garnet phase appeared for the film annealed at 500 and 550 ℃. This indicates that the garnet phase was epitaxially crystallized from the amorphous phase in the temperature range between 500 and 550 ℃. Those (00*l*) peaks disappear for the films annealed above 600 ℃.

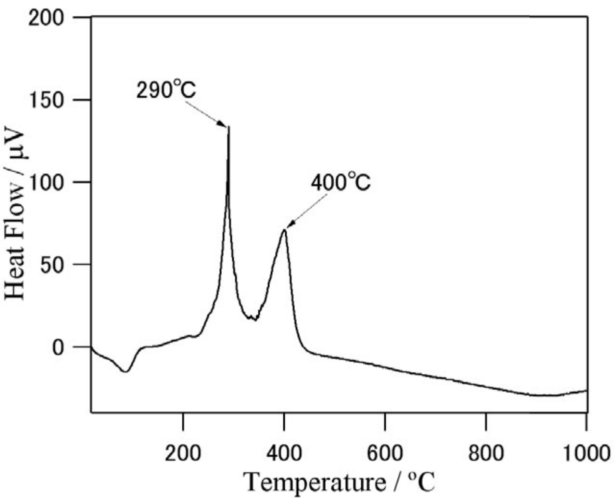

Fig. 1. DTA curve of MO solution (molar ration of Bi : Fe = 3 : 5).

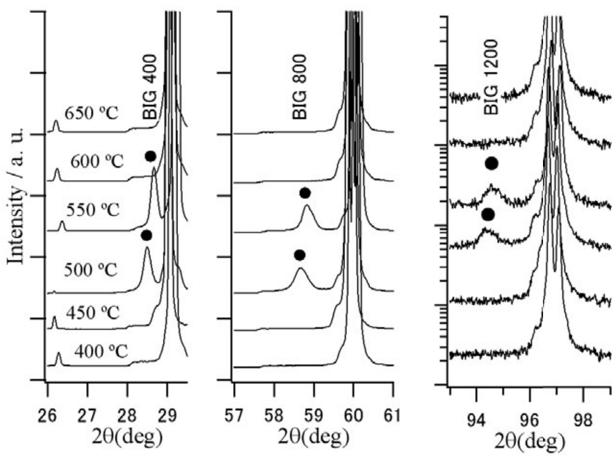

Fig.2. XRD θ-2θ scans in CuK_α radiation for pre-annealed and annealed films on GGG (100) substrates grown by MOD technique.

Since BIG phase is thermally non-equilibrium, the garnet phase of the film was considered to be decomposed due to the high temperature.

The lattice parameter a_0 of the films was deduced by plotting a_0 against the Nelson-Riley function[12]:

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

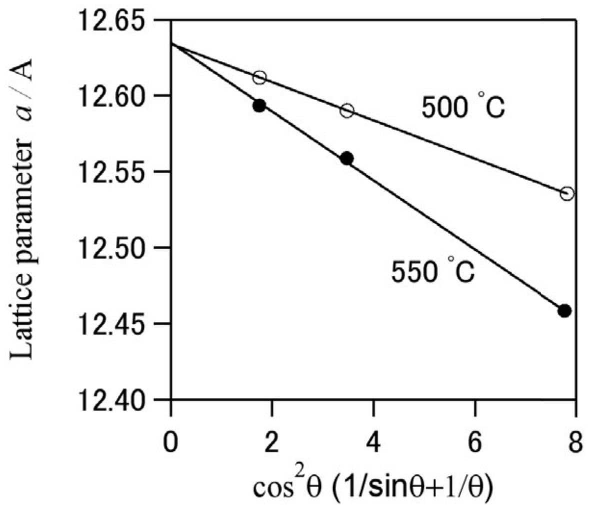

Fig.3. Lattice parameters for films annealed at 500 ℃ (symbols ○) and 550 ℃ (symbols ●) techniques. Lattice parameter $a_{cos\theta}$ was calculated from (004), (008), (0012), and (0016) Bragg reflections position. Experimental $a_{cos\theta}$ vs. θ dependence has been fitted to Nelson-Riley equation (1) to extrapolate at cosθ → 0.

where $a_{cos\theta}$ is an interplane distance calculated from the apparent Bragg peak position at 2θ and K is a fitting coefficient. Fig. 3 presents the lattice parameters $a_{cos\theta}$ calculated from (004), (008), (0012) Bragg reflections for the films. The "true" lattice parameters a_0, obtained as an extrapolation of $\cos^2\theta$ to 0, were found to be 12.635 Å for the film annealed at 550 ℃, 12.634 Å for the film annealed at 500℃, respectively. Taking into account the experimental errors, the lattice parameters of the films prepared by the MOD technique can be regarded to be the same with the films prepared by vapor phase depositions[5].

The optimum annealing temperature has been concluded to be around 550 ℃ by Faraday rotation measurements. The film annealed at 550 ℃ indicates a larger MO effect than the film annealed at 500 ℃. The Faraday hysteresis loops at 635 nm are shown in Fig.4. The maximum Faraday rotation of the film annealed at 550 ℃ reached approximately 1°. The annealing temperature of 550 ℃ is the same as the optimum deposition temperature of the BIG films prepared by the PLD technique[9]. The magnetizations per unit volume and the Faraday rotations per unit length are calculated by using the thickness value of 150 nm estimated from the scanning electron microprobe (SEM) observations. Strictly speaking, the raw data of the magnetization and the Faraday rotation include the components of the paramagnetic GGG substrate. The paramagnetism of the substrate dominates the raw magnetization data. For the MO effect, the Faraday rotation due to the magnetic garnet dominates the raw data, however, those values are not negligible for the case of the very thin films with nanometer thickness. As both the magnetization and the Faraday rotation of the substrate increase linearly with increasing the magnetic field, it is possible to separate the component of the film from the draw data by subtractive calculations of the substrate components. The calculated magnetic hysteresis loop per unit volume and the Faraday rotation hysteresis per unit length are

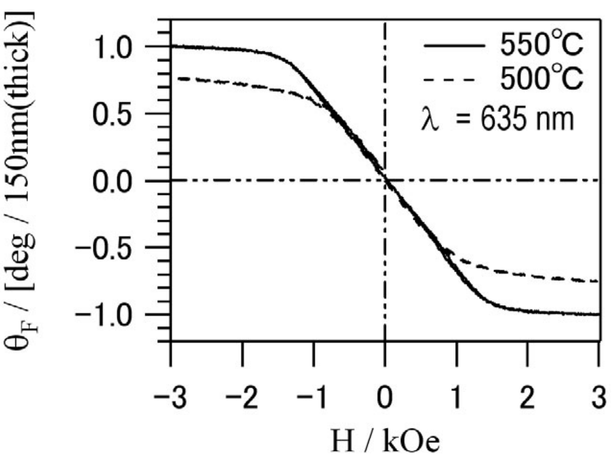

Fig.4. Faraday rotation θ_F vs. $H_\perp$ at 635 nm of the film plus the GGG substrate.

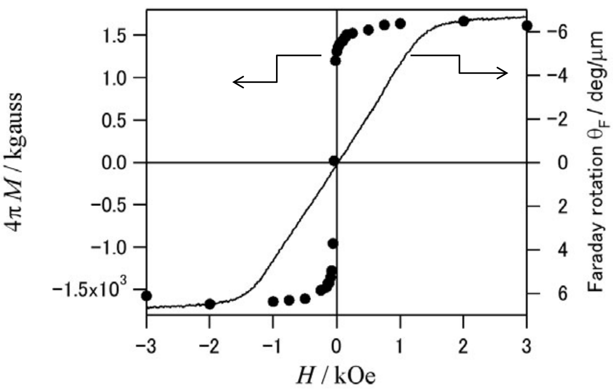

Fig.5. Magnetizations of the film per unit volume in the magnetic field parallel to the film plane (solid line) and the Faraday rotation θ_F vs. $H_\perp$ at 635 nm per unit length (symbols ●). Paramagnetic contribution from GGG substrate has been subtracted.

shown in Fig.5. The magnetization easily saturates for the case of the applied magnetic field parallel to the film plane, which indicates the in-plane magnetic anisotropy. The Faraday rotation saturate at approximately 2 kOe. The saturation magnetization of the film was deduced to be approximately 1.7 kgauss and the maximum Faraday rotation shows a large performance of 6.7°/μm at 635 nm. In order to visualize a distribution of high frequency electromagnetic field on integrated circuits, a high spatial resolution is necessary for the MOI probe. The high performance of MO effect of BIG film may enable high resolution observations of the order of 1 micrometer. Enough Faraday rotation can be expected for the BIG thin film of the thickness less than 1 micrometer and the spatial resolution can be reduced to the order of the visible light wavelength. In addition, simple spin coating method will be also expected for the application of magnetophotonic crystal with multilayered structure[13),14)] because a spin coating process is possible to control the nanometer thickness of the film and easy to change the composition of the layer at each coating.

4. Conclusions

Single crystal $Bi_3Fe_5O_{12}$ (100) films have been successfully synthesized on GGG (100) substrates by MOD technique. The amorphous phase of the spin-coated film was crystallized to the garnet phase at the annealing temperature of 500 ℃ and 550 ℃. For the film annealed at 550 ℃, the saturation magnetization and the maximum Faraday rotation at 635 nm are 1.7 kgauss and 6.7°/μm, respectively. These results are characteristic of a completely substituted bismuth iron garnet. The preparation of BIG films from the liquid phase will give good advantages to the application of the MO imaging.

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