Preparation and Characterization of Bi substituted gadolinium iron garnet Films by Metal Organic Decomposition and their Dependence on Annealing Gases

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We report the preparation and characterization of bismuth substituted gadolinium iron garnet thin films on (111) gadolinium gallium garnet (GGG) substrates prepared by metal organic decomposition (MOD). Magnetization, Faraday rotation and X-ray diffraction (XRD) were used to examine their dependence on annealing temperatures and different annealing gas mixture (with and without O\textsubscript{2}). Our results from measurements revealed that Bi substituted gadolinium iron garnet samples annealed without O\textsubscript{2} (100% N\textsubscript{2}) crystallized at lower annealing temperatures. The magnetic fields to saturate the Faraday rotation were larger for the samples annealed without O\textsubscript{2} than those of samples annealed with 20% O\textsubscript{2}. The possible mechanisms responsible for these phenomena are discussed.

Key words: magnetic garnet, metal organic decomposition, Faraday effect, magnetic anisotropy

1. Introduction

Bi-substituted rare-earth iron garnets have long been known and received much attention because of their high magneto optical effects (high transparency and large Faraday rotation in near infrared region\textsuperscript{1}) which made these materials very attractive among all semi-transparent dielectrics for various fundamental investigations as well as practically usable materials for magneto-optical device elements such as optical isolators\textsuperscript{2}, circulators\textsuperscript{3,4}, printers\textsuperscript{5} and MPC which is used in magneto-optic spatial light modulators (MOSLM)\textsuperscript{6,7,8,9}. A single crystal garnet with perpendicular magnetic anisotropy and two polarizers have been used as a pixel element to switch the optical output depending on the up and down magnetization owing to Faraday effect in MOSLMs. Application of MOSLMs is highly expected because of their extremely fast pixel switching speed and non-volatile property. Bismuth substituted gadolinium iron garnet (Bi:GdIG) is an important ferrimagnetic material, and exhibits a large Faraday rotation which increases with increasing bismuth concentration in the visible to near infrared region, perpendicular magnetic anisotropy, and has high frequency applications\textsuperscript{10}.

There are several methods to prepare the bismuth substituted rare-earth iron garnet thin films such as a laser ablation\textsuperscript{11}, a liquid phase epitaxy\textsuperscript{12}, RF magnetron sputtering\textsuperscript{13}, etc. Among them, MOD is a promising method to prepare magnetic garnet film, because it is a simple fabrication method, and guarantees high  uniformity in chemical composition and purity combined with chemical stability\textsuperscript{1,14,15,16,17}.

In this paper, we report preparation and characterization bismuth substituted gadolinium iron garnet (Bi:GdIG) thin films on gadolinium gallium garnet (GGG) substrates prepared by metal organic decomposition (MOD) method in order to obtain high-quality garnet crystal with a large Faraday rotation and control the magnetic anisotropy of magnetic garnet by changing the fabrication condition, annealing temperature and annealing gas. So far, there have been no reports to investigate the presence of O\textsubscript{2} gas in the annealing process of MOD method and its influence on the magneto-optical property, and magnetic anisotropy of Bi:GdIG films. We used two kinds of annealing gas of 0% O\textsubscript{2} and 20% O\textsubscript{2} and annealed the samples at annealing temperatures of 620, 650, 700, 750, and 800°C. We measured the magnetization, X-ray diffraction, Faraday effect, and optical transmittance of the fabricated samples.

2. Experiments

We have fabricated bismuth substituted gadolinium iron garnet (Bi:GdIG) thin films by metal organic decomposition method on (111) GGG substrates with different annealing temperature and annealing gas. The area of the GGG substrate is 12 mm x 12 mm. A MOD liquid used in this experiment consists of solutions made from Bi, Gd and Fe carboxylates with chemical composition ratio of Bi:Gd:Fe = 1:2:5 by Kojundo.
Fig. 1 X-ray diffractions of Bi:GdIG samples annealed at 620°C–800°C with annealing gas of 20% O2 and 0% O2.

Chemical Laboratory Ltd. The total concentration of carboxylates in these MOD solutions was fixed at 3%. After spin coating in 2 steps process of 500 rpm for 10 s and 3000 rpm for 20 s, followed by drying on a hot plate at 120°C for 10 min. In order to decompose organic materials and obtain amorphous oxide films, the samples were pre-annealed at 550°C for 10 min. and annealed at 620°C–800°C for 2 hours (final annealing) for crystallization. Spin coating, drying and pre-annealing, were repeated for 6 times to obtain an appropriate thickness. The thickness of all samples obtained in the present study is approximately 300 nm. In order to investigate the presence of O2 gas in annealing process of MOD method and its influence on the magneto-optical property of Bi:GdIG, the pre annealing and final annealing were performed with two kinds of annealing gas of 20% O2 and 0% O2. The pressure during the annealing was atmospheric pressure. Bi:GdIG thin films prepared in this study were investigated by X-ray diffraction (XRD), optical transmittance spectra, Faraday effect with its spectra and magnetic field dependence and magnetization measurements. All the measurement was done at room temperature. We measured the XRD from the central part of the samples. The diameter \( d \) of the X-ray beam is about 0.4 mm. Therefore, the measurement results of the XRD show average crystallinity of the samples over \( d = 0.4 \) mm. Also, the film thickness is thin at the center of the
samples, and thicker at the edge of the samples, owing to the influence of the viscosity of the MOD source, and the spin coating process. Because of the limited sample area, we could not fully discuss the in-plane uniformity of crystallinity of all over the samples.

### 3. Results and Discussion

Figure 1 shows the X-ray diffraction pattern of Bi:GdIG on GGG substrate crystallized at 620 – 800°C for 2 hours with 20% O2 and 0% O2. 444 and 888 diffractions peaks of Bi:GdIG are clearly observed and other peaks associated with polycrystalline or impurity phases were not observed. The diffraction peaks indicating that single crystal garnet structures are observed for all samples.

**Figures 2 and 3 show the diffraction intensities and lattice constants of 444 peak for Bi:GdIG crystallized at different annealing temperature of 620 – 700°C with different annealing gas of 20% O2 and 0% O2, respectively. The X-ray diffraction intensities of Bi:GdIG films annealed with 0% O2 were stronger than those annealed in 20% O2, indicating good crystallinity of the samples annealed with 0% O2. The lattice constants were smaller for the samples annealed at 620 – 700°C.**

**Fig. 3** Annealing temperature dependences of the lattice constant of Bi:GdIG samples annealed with 20% O2 and 0% O2.

**Fig. 4** Faraday rotation spectra of Bi:GdIG samples with different annealing temperatures. (a) Annealed with 20% O2 and (b) 0% O2.

**Fig. 5** Maximum Faraday rotation of Bi:GdIG samples around wavelength of 510 nm annealed with 20% O2 and 0% O2.

Figures 2 and 3 show the diffraction intensities and lattice constants of 444 peak for Bi:GdIG crystallized at different annealing temperature of 620 – 800°C with different annealing gas of 20% O2 and 0% O2, respectively. The X-ray diffraction intensities of Bi:GdIG films annealed with 0% O2 were stronger than those annealed in 20% O2, indicating good crystallinity of the samples annealed with 0% O2. The lattice constants were smaller for the samples annealed at 620 – 700°C.
These experimental results indicate that the crystals grow pseudomorphically at lower annealing temperature of 620 – 700°C with 20% O₂, and the strain relaxed for the samples annealed at higher temperature of 750 – 800°C with 20% O₂, and the samples annealed with 0% O₂. The amount of the compressive strain and the dislocation defects at the interface between the Bi:GdIG film and GGG substrate are smaller for the samples annealed at higher temperature of 750 – 800°C with 20% O₂ and the samples annealed with 0% O₂. This situation is similar to superconducting YBa₂Cu₃O₇-δ thin films grown by an electrochemical method, where YBa₂Cu₃O₇-δ thin film was grown at lower temperature with lower O₂ pressure. The authors discussed that equilibrium decomposition line could be favorable in the growth process of YBa₂Cu₃O₇-δ thin films. The equilibrium decomposition process is one of the key to explain the reason why Bi:GdIG samples annealed with 0% O₂ crystallized better at lower annealing temperature compared with those annealed with 20% O₂.

The magnetic field of 1T was applied perpendicular to the samples. The Faraday rotation of Bi:GdIG increases with increasing the annealing temperature. Faraday rotation showed maxima at the wavelength of about 510 nm for all the samples. In order to find the influence of annealing temperature and annealing gas on Faraday rotations, the Faraday rotation at the wavelength of 510 nm were summarized in Figure 5. It was found that the sample with annealing temperature of 800°C and annealing gas of 20% O₂ shows the largest Faraday rotation among all the samples. Furthermore the maximum Faraday rotation is almost the same between the samples with two kinds of annealing gas for all the annealing temperature.

Figure 6 shows the optical transmission spectra of the samples. With increasing the annealing temperature, the transparency decreased in the wavelength range between 430 nm (2.88 eV) and 900 nm (1.38 eV), and almost the same in the wavelength longer than 900 nm. It was reported that the energy gap between the valence band of O²⁻ and Fe²⁺oct (t₂g) was 2.9 eV. The reason for the drop of the optical transmission at the wavelength of 430 nm can be the roughness, pinning sites or domain size, etc. One of the possible reasons is energy gap between the valence band of O²⁻ and Fe²⁺oct (t₂g). There are donor levels by the O₂ vacancy (defect) with the activation energy of ~1eV below the Fe²⁺oct (t₂g) state. The samples annealed at higher temperature showed lower optical transmittance in the wavelength range of 430 nm and 900 nm, suggesting that concentration of the O₂ vacancy (defect) states increased and the transition between the Fe²⁺oct (t₂g) and the O₂ vacancy (defect) states increased in the samples annealed at higher temperature. The bumps at the wavelengths of 900, and 1350 nm are observed, which was generated by changing optical filters during the spectral measurements.

Figure 7 and figure 8 show the magnetic field dependence of the Faraday rotation (normalized) of Bi:GdIG samples at the wavelength of 600 nm. The wavelength of 600 nm was selected, because the samples have high transparency (>40%) at the wavelength of 600 nm. With increasing the annealing temperature, the magnetic field to fully magnetize the sample became lower. The coercive forces (Hc) of the samples are slightly higher in the samples annealed with 0% O₂ compared with samples annealed with 20% O₂. The magnetic field dependence of the Faraday rotation of the
sample annealed with 0% O$_2$ at 620°C is similar to that annealed with 20% O$_2$ at 800°C.

![Graph showing magnetic field dependence of Faraday rotation](image)

**Fig. 7** Magnetic field dependence of Faraday rotation of Bi:GdIG samples annealed with (a) 20% O$_2$ and (b) 0% O$_2$.

Figure 9 shows the magnetization characteristics of the samples measured by an alternating gradient field magnetometer (AGFM). The magnetic field of +/- 0.1T was applied in plane and perpendicular to the sample. The measurement was done at room temperature. Larger perpendicular magnetic anisotropy was observed for the samples annealed at 620 – 650°C with 0% O$_2$, compared with the samples annealed at 620 – 650°C with 20% O$_2$. Also, with increasing the final-annealing temperature with both annealing gases, perpendicular magnetic anisotropy became higher. This tendency is consistent with the measurement results from Faraday effect. Since Bi substituted gadolinium iron garnets show perpendicular magnetic anisotropy owing to its small saturation magnetization and diamagnetic field, one of the possible reasons for lower perpendicular magnetic anisotropy of samples annealed at 620 – 650°C with 20% O$_2$ compared with other samples, is that crystal growth is not completed with annealing temperature of 620 – 650°C with 20% O$_2$, showing smaller XRD diffraction intensity, and smaller Faraday rotation. Another possible reason is that the amount of O$_2$ deficiency and Fe$^{2+}$ increased in the samples annealed with 0% O$_2$, leading to larger perpendicular magnetic anisotropy. It was reported that the modulation of the number of 3d electrons caused the change of the magnetic anisotropy in ferromagnetic metal Fe$_{50}$Co$_{50}$ ultrathin films$^{20}$. It was also reported that the incorporation of O$_2$ defect in magnetic garnet brings the magnetic anisotropy$^{21}$.

![Graph showing magnetic field dependence of the Faraday rotation of Bi:GdIG samples](image)

**Fig. 8** Magnetic field dependence of the Faraday rotation of Bi:GdIG samples annealed at 620, 650, 700, 750, and 800°C, with 20% O$_2$ and 0% O$_2$.

### 4. Conclusion

We have prepared bismuth substituted gadolinium iron garnet (Bi:GdIG) thin films on (111) GGG substrates by metal organic decomposition (MOD)
method at different annealing temperature (620 – 800°C) and with different annealing gases (20% O₂ and 0% O₂). We characterized the X-ray diffraction (XRD), Faraday effect, optical transmittance and magnetization of the samples. The XRD pattern shows that Bi:GdIG thin films with high crystalline quality were successfully fabricated.

The lattice constant decreased with increasing the final annealing temperature and by changing the annealing gas from 20% O₂ to 0% O₂. The optical transmittance is decreased in the wavelength range of 430 nm and 900 nm, with increasing the final annealing temperature. Faraday rotation increased with increasing final annealing temperature. Magnetization measurements revealed larger perpendicular magnetic anisotropy for the samples annealed at 620 – 650°C with 0% O₂ and at higher annealing temperature for the samples annealed with 0% O₂ and 20% O₂. The possible reasons of the influence of annealing conditions on the perpendicular magnetic anisotropy were discussed, including the crystal growth process, and O₂ vacancy defect.

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