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$(Re,Bi)_3(Fe,Ga)_5O_{12}$ (Re=Y, Gd and Nd) thin films grown by MOD method

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Abstract

Bi- and Ga-substituted rare-earth iron garnet $(Re,Bi)_3(Fe,Ga)_5O_{12}$ (Re=Y, Gd and Nd) thin films were fabricated on glass, Si(1 0 0) and GGG(1 1 1) substrates using the metal organic decomposition (MOD) method, in which the metal-organic solution is spin-coated, dried, and sintered. Thin films with a garnet single phase were successfully obtained for sintering temperatures less than 750 °C. Thin films prepared on GGG were single crystalline, while those prepared on glass and Si were polycrystalline. The thickness and surface roughness of the polycrystalline film are estimated to be 40 and 0.8 nm, respectively, for a single coating in the MOD process. The magnetic and magneto-optical properties of the films are comparable to those of films prepared by other methods.

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1. Introduction

It is well known that Bi-substituted rare-earth iron garnet films (Bi:ReIG) are suitable for magneto-optical devices because of the large Faraday rotation in the visible IR light. For example, a Faraday rotation of 45° is utilized for an optical isolator. On the other hand, the thin film less than 1 μm is required for a magneto-optical indicator to visualize the magnetic flux penetrating into the superconductors, because, for high-T_c superconductors, an observation of single vortices is necessary for the determination of the magnetic phase diagram. Recently, Goa et al. succeeded to visualize a single vortex in $NbSe_2$ superconductors using a Bi:ReIG film with a thickness of less than 1 μm [1]. In order to obtain higher resolution and high magnetic sensitivity, thinner films are required, because the magnetic

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flux through vortices is rapidly smeared out with the distance from the surface of the superconductors.

Garnet films have been prepared by several techniques, liquid-phase epitaxy (LPE) [2], RF magnetron sputtering [3], pyrolysis method [4,5], a sol–gel method [6,7] and a metal-organic decomposition (MOD) method [8]. In these techniques, the sol–gel method utilizing nitric acids and the MOD method utilizing metal-organic solutions have advantages of homogeneity and controllability. In order to obtain thin magnetic garnet films of a good quality, we carried out the MOD method. In this paper, we report on Bi:ReIG thin films (Re = Y, Nd and Gd) prepared by the MOD technique.

2. Experiment

Starting materials for MOD solutions are Bi, Y, Nd, Gd, Fe and Ga carboxylates. The coating reagents were prepared by dissolving the organometallic complexes, synthesized from carboxylic acid having a carbon number from 3 to 20, in organic solvents such as ester. This reaction allows us to prepare a complete solution of metal carboxylates. MOD liquids for garnet films were prepared by mixing each carboxylate solution with desired chemical compositions; $Y_2BiFe_5O_{12}$ (YBiFeO), $Y_2BiFe_4GaO_{12}$ (YBiFeGaO), $Nd_2BiFe_4GaO_{12}$ (NdBiFeGaO) and $Gd_2BiFe_4GaO_{12}$ (GdBiFeGaO). A total concentration of carboxylates in those MOD liquids was fixed to 3%. This MOD solution was quite stable and any change or precipitation has not been observed over 2 years.

Thin film preparation process is quite similar to the sol–gel process although the chemical reaction process is quite different. $Gd_3Ga_5O_{12}$ (1 1 1) (GGG), corning 7059 glass and Si(0 0 1) were used as substrates. The solution was spin-coated on the substrates with a two-step process; 500 rpm for 5 s and 3000 rpm for 30 s, followed by drying process at 150 °C for 2 min using a hot plate. In order to decompose organic materials and to obtain amorphous oxides films, samples were pre-annealed at 550 °C for 5 min. These processes, spin-coating, drying and pre-annealing, were repeated to obtain an appropriate thickness. Typical thickness of the films obtained in the present study is approximately 200 nm.

Magnetic properties of these films were analyzed by Toei-type VSM-5 vibrating sample magnetometer (VSM). X-ray diffraction patterns and X-ray reflectivity spectra were measured by using Rigaku-type RADII-C and Phillips-type X'pert-MRD. Surface morphology was analyzed by atomic force microscope using Seiko Inst., type SPI3800N. Chemical compositions were measured by energy dispersive X-ray micro-analyzer (EDX). Magneto-optical spectra in the wavelength between 400 and 700 nm were measured by a magneto-optical spectrometer utilizing an optically modulation technique [9].

3. Results and discussion

Chemical compositions of these thin films were measured by EDX, and are consistent with the composition in the MOD liquid within an experimental error of less than 10%. This is an advantage of the MOD method that it is easy to control the chemical compositions, compared with other techniques such as sputtering technique.

Fig. 1 shows XRD patterns of YBiFeO, YBiFeGaO, NdBiFeGaO and GdBiFeGaO thin films prepared on Si(0 0 1) substrates. In all the

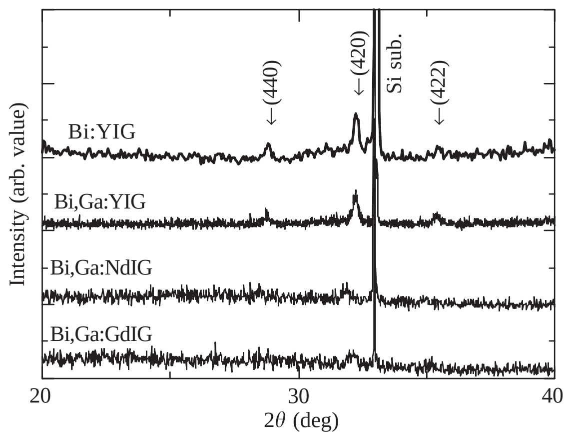

Fig. 1. XRD patterns of films fabricated on Si substrates.

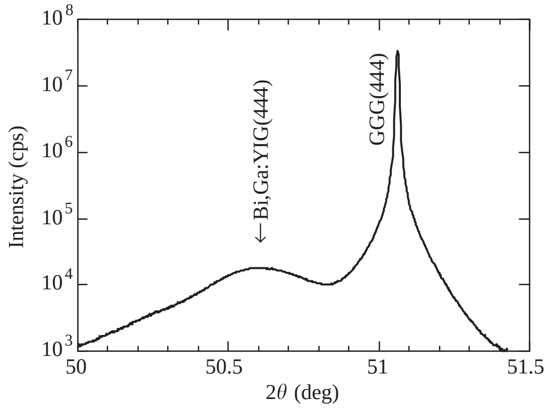

Fig. 2. XRD pattern of a film fabricated on GGG(1 1 1) substrate.

cases, (4 2 0), (4 4 0), (4 2 2) and small lines associated with polycrystalline garnet structures are observed. Polycrystalline films were obtained for both Si substrate and glass substrate for all garnet films prepared in this experiment. On the other hand, single-crystalline thin films were grown on GGG(1 1 1) substrates with quite good quality as shown in Fig. 2. An RBS channeling was observed in a $Y_3Fe_4GaO_{12}$ thin film prepared on GGG substrate, and will be reported elsewhere.

The thickness of these films was measured by X-ray reflectivity measurements. Oscillations due to interference of X-ray in thin films were clearly observed, and the thickness was determined to be 40 nm for a single garnet layer prepared by a single coating of the MOD liquid and to be 80 nm for double layers as shown in Fig. 3. The thickness of the films mainly depends on the rotation speed and time of the spin-coating. The roughness of the film surface can be also determined by the reflectivity measurement, and it was less than 1 nm for single and double layers. Since the X-ray reflectivity measurement is not possible to be used for the films with a thickness of more than 100 nm, the roughness of thick films was analyzed by AFM. An RMS was measured to be 2 nm for the polycrystalline YBFGO thin films with a thickness of 200 nm prepared on the Si substrate. These results indicate that the roughness does not become worse by the repetition of the coating process.

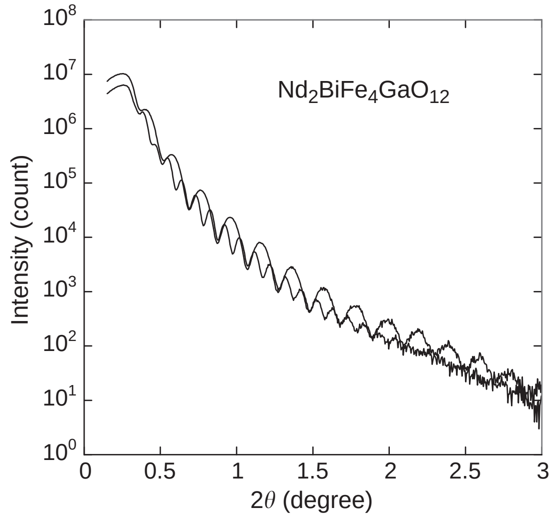

Fig. 3. X-ray reflectivity spectra of NdBiFeGaO single and double layers.

Fig. 4 shows M–H curves at room temperature of a YBiFeGaO thin film on GGG substrate, NdBiFeGaO and GdBiFeGaO thin films prepared on Si substrates. The annealing temperature was 700 °C for YBFGO and 650 °C for NdBiFeGaO and GdBiFeGaO. All samples with the Ga-substitution show that an easy axis of magnetization is perpendicular to the surface, while in-plane magnetization is observed in YBFO thin films. The magnetization of GdBiFeGaO thin film is comparatively small, because the compensation temperature for the magnetization is near room temperature. On the other hand, YBiFeO thin films showed an in-plane magnetization. These magnetic characteristics are consistent with other reports [3–8]. In case of YBFGO, the coercivity is 200 Oe for on Si substrates, and 50 Oe on GGG substrates.

Fig. 5 shows a saturation magnetization M_s of YBFGO depending on annealing temperatures. Open circles are samples prepared on Si substrates, and closed circles are those on glass substrates. It is found that there is a maximum of M_s between 650 and 700 °C. A sample annealed at 800 °C loses transparency indicating that other phases are formed.

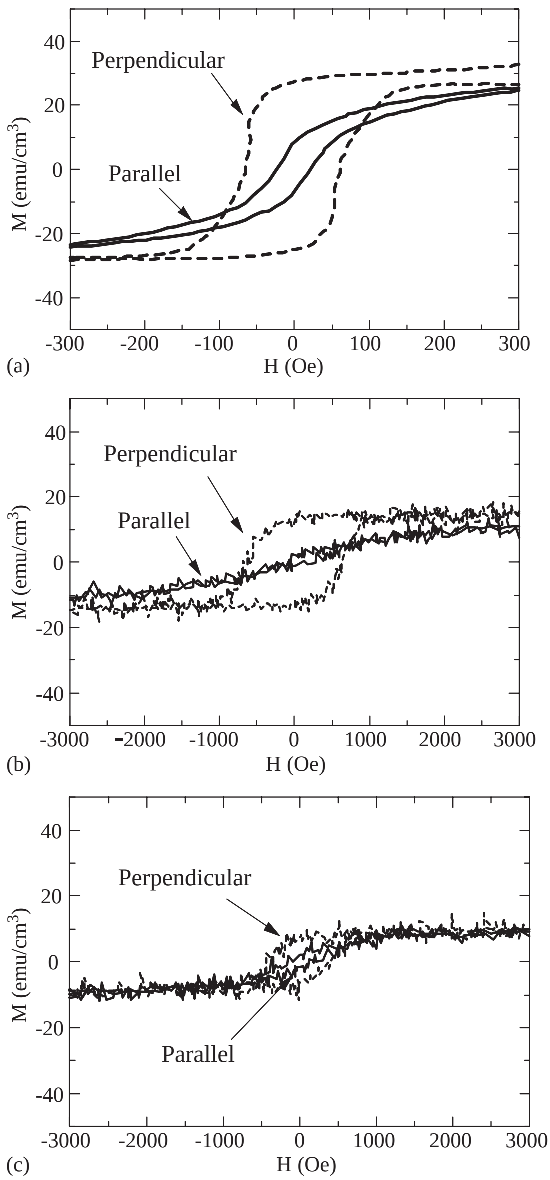

Fig. 4. *M–H* curves of (a) YBiFeGaO on GGG substrate, (b) NdBiFeGaO and (c) GdBiFeGaO on Si substrates.

Finally, Faraday rotation spectra of those thin films are shown in Fig. 6. All the spectra were measured at the remanence states (H=0), in order to prevent a signal of GGG substrates. Spectral features in Fig. 6 show a good agreement with other reports [10], although some differences in the structures are considered to be due to interference effects.

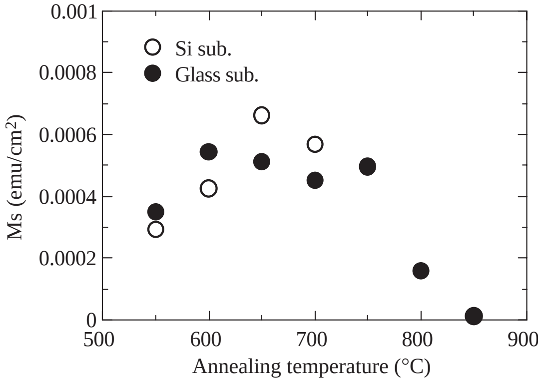

Fig. 5. Dependence of the saturation magnetization M_s in YBiFeGaO thin films on the annealing temperatures.

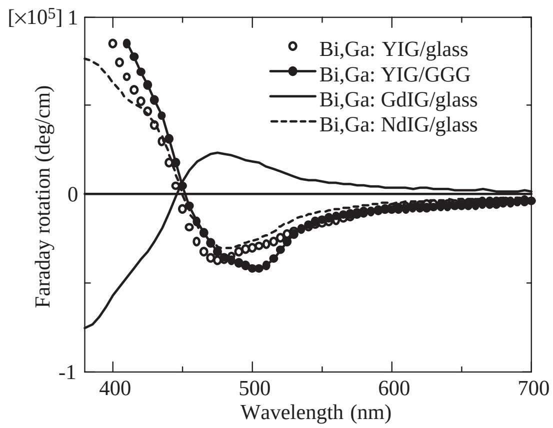

Fig. 6. Faraday rotation spectra of Bi, Ga substituted ReIG films.

4. Conclusions

Bi, Ga-substituted ReIG (Re=Y, Gd and Nd) thin films were prepared on Si(0 0 1), glass and GGG(1 1 1) substrates. Polycrystalline thin films were obtained on the glass and Si substrates, and epitaxial thin films were obtained on the GGG substrates.

The thickness of the film with a single coat was also determined to be 40 nm, and the roughness of surface was also determined to be less than 1 nm by measuring an oscillation appeared on the X-ray reflectivity spectrum. The optimal annealing condition was between 650 and 700 °C. Magnetic and magneto-optical properties showed a good agreement with other reports. Magneto-optical spectra of these films measured between 400 and 700 nm demonstrate the same spectra as those in the literatures suggesting the good quality of these films. Faraday rotation was as large as 1×10^5 deg/cm at 400 nm in all the samples prepared. It is found that this technique is useful for the preparation of thinner films of 40–400 nm, which is suited for the magneto-optical indicator as mentioned above. Finally, we should note that this technique had a quite good reproducibility, and the MOD liquid was very stable for at least 2 years.

Acknowledgements

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References

[1] P.E. Goa, et al., Rev. Sci. Instrum. 74 (2003) 141.
[2] P. Hansen, C.-P. Klages, K. Witter, J. Appl. Phys. 60 (1986) 721.
[3] M. Gomi, T. Tanida, M. Abe, J. Appl. Phys. 57 (1985) 3888.
[4] M. Gomi, M. Asogawa, M. Abe, J. Magn. Soc. Jpn. 10 (1986) 217.
[5] K. Matsumoto, K. Yamaguchi, A. Ueno, T. Fujii, J. Magn. Soc. Jpn. 14 (1990) 247.
[6] K. Matsumoto, S. Yamamoto, Y. Yamanobe, A. Ueno, K. Yamaguchi, T. Fujii, Jpn. J. Appl. Phys. 30 (1991) 1696.
[7] K. Matsumoto, S. Sasaki, K. Haraga, K. Yamaguchi, T. Fujii, J. Appl. Phys. 71 (1992) 2467.
[8] A. Azevedo, S. Bharthulwar, W.R. Eppler, M.H. Kryder, IEEE Trans. Magn. 30 (1994) 4416.
[9] K. Sato, H. Hongu, H. Ikekame, Y. Tosaka, M. Watanabe, K. Takanashi, H. Fujimori, Jpn. J. Appl. Phys. 32 (1993) 989.
[10] S. Wittekoek, T.J.A. Popma, J.M. Robartson, P.F. Bongers, Phys. Rev. B 12 (1975) 2777.