Characterization of epitaxial $(Y,Bi)_3(Fe,Ga)_5O_{12}$ thin films grown by metal-organic decomposition method

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Epitaxial $(Y,Bi)_3(Fe,Ga)_5O_{12}$ garnet thin films have been prepared on $Gd_3Ga_5O_{12}$ (111) substrates by a metal-organic decomposition (MOD) method using carboxylic acids. The chemical compositions of the films prepared in this study are $Y_2BiFe_5O_{12}$ (YBFO), $Y_3Fe_4GaO_{12}$ (YFGO), and $Y_2BiFe_4GaO_{12}$ (YBFGO). Epitaxy of these films was confirmed by x-ray diffraction and Rutherford backscattering (RBS) measurements. Full width of half maximum values of the 444 diffraction peaks of YFGO and YBFGO were 0.4° and 0.04°, respectively. RBS channeling was clearly observed for the YFGO film with a minimum yield χ_{min} along the [111] direction of ~7.5%. These garnet films could also be reproducibly obtained by the MOD method without any deterioration in the MOD solutions over two years. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1827339]

I. INTRODUCTION

Bi-substituted rare earth iron garnet (RIG; R=Y, Gd, Nd, etc.) films have been attracting great attention as materials for magneto-optical (MO) applications due to their huge Faraday rotation in the visible to infrared range and controllable magnetic properties.[1,2] Recently, BI:RIG thin films have been used as magneto-optical indicators to visualize magnetic vortices in superconductors.[3] In order to achieve resolution that is high enough to be within the optical limit in MO microscopy, high-quality single crystalline garnet films with a thickness less than 1 μm are required, since the magnetic flux generated by the samples rapidly diminishes with distance from the samples.

Garnet films have been prepared by several techniques: liquid phase epitaxy,[4] rf magnetron sputtering,[5] a pyrolysis method,[6,7] a sol-gel method,[8,9] and a metal-organic decomposition (MOD) method.[10] Azevedo *et al.* used the MOD method utilizing metal-organic carboxylates, which have good stability, instead of nitrate acids. They succeeded in preparing polycrystalline $Gd_2BiFe_5O_{12}$ and $(DyBi)_3(Fe,Ga)_5O_{12}$ thin films on glass substrates.[10] In the techniques mentioned above, the sol-gel and MOD methods are advantageous not only for the homogeneity of the thin film, the controllability of composition, and the formation over a large area, but also for the good productivity, since the methods involve simple processes, those of spin coating a solution containing the constituent elements, and annealing. For the sol-gel method, however, a problem exists in that nitrate acids dissolved in the solution are chemically unstable. Considering stability in addition to the advantages mentioned above, we consider that the MOD method is the most promising technique for producing single crystalline thin films of magnetic garnet.

In this paper, we report on single crystalline $(Y,Bi)_3(Fe,Ga)_5O_{12}$ thin films prepared on $Gd_3Ga_5O_{12}$ (GGG) substrates by the MOD method.

II. EXPERIMENT

The starting materials for the MOD solutions were Bi, Y,Fe and Ga carboxylates. The coating reagents were prepared by dissolving the organometallic complexes, synthesized from carboxylic acids with carbon numbers from 3 to 20 by a reaction with rosin, in organic solvents such as esters. This procedure is important especially for Y, because Y carboxylate cannot be dissolved in the solvents by the process described in Ref. 10. MOD liquids for garnet films were prepared by mixing each solutions with desired chemical compositions; $Y_2BiFe_5O_{12}$ (YBFO), $Y_3Fe_4GaO_{12}$ (YFGO), and $Y_2BiFe_4GaO_{12}$ (YBFGO). The total concentration of carboxylates in those MOD liquids was fixed at 3%. This MOD solution is quite stable and precipitation or other changes have not been observed over two years.

Thin film preparation for this process is similar to the sol-gel process, although the chemical reactions are quite different. GGG (111), corning 7059 glass, and Si (001) were used as substrates. GGG was used to obtain epitaxial thin films, and the glass and Si were used to investigate the optimal conditions for the process. The solution was spin-coated on the substrates in a two step process: 500 rpm for 5 s and

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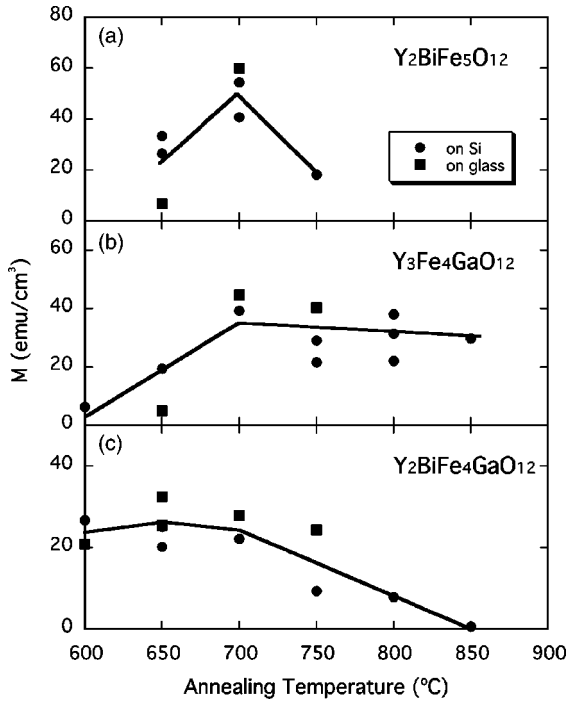

FIG. 1. Ms vs the annealing temperature for (a) YBFO, (b) YFGO, and (c) YBFGO thin films prepared on Corning 7059 glass and Si (001) substrates.

3000 rpm for 30 s, followed by drying at 150 °C for 2 min using a hot-plate. In order to decompose organic materials and to obtain amorphous oxide films, samples were preannealed at 550 °C for 5 min. These processes, i.e., spin coating, drying, and preannealing, were repeated to obtain an appropriate thickness. The typical thicknesses of the films obtained in the present study were 200–500 nm. Finally, samples were annealed for crystallization in a furnace at 600–850 °C for 1 h. All thermal treatments were performed in air.

The magnetic properties of these films were analyzed by a Toei VSM-5 vibrating sample magnetometer (VSM). x-ray diffraction patterns and x-ray reflectivity spectra were measured using a Philips type X'pert with a double Ge (220) crystal monochromator that reduces the intensity of the $K\alpha_2$ line to less than 3% compared to that of $K\alpha_1$. To analyze the crystallinity of these films, Rutherford backscattering (RBS) analysis was carried out with a 1.5 MeV $^4He^+$ beam using a Van der Graff accelerator. Backscattered particles were detected at a scattering angle of $\theta = 150°$ with a silicon surface barrier detector. The experimental setup has been described elsewhere.[11]

III. RESULTS AND DISCUSSION

In order to find the optimal annealing conditions for crystallization, the saturation magnetization Ms was measured with various annealing temperatures. Figure 1 shows the Ms vs the annealing temperature for (a) YBFO, (b) YFGO, and (c) YBFGO thin films prepared on Corning 7059 glass and Si (001) substrates. The Ms of the Bi-substituted films, YBFO and YBFGO, shows a maximum at 650–700 °C and decreases above 700 °C, whereas that of the YFGO film decreases gradually up to 800 °C.

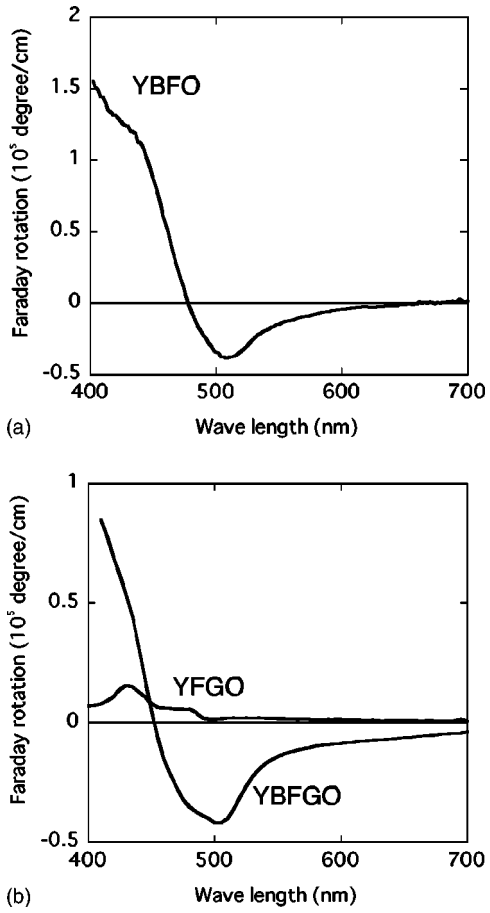

FIG. 2. Faraday spectra of thin films prepared on GGG substrate. (a) YBFO and (b) YFGO and YBFGO thin films.

Figure 2 shows Faraday rotation spectra of thin films prepared on a GGG substrate. For the YBFO thin film, which has an easy axis of magnetization parallel to the surface, a magnetic field of 1.7 T was applied to measure the magneto-optical spectra. Note that, in this case, magneto-optical signals suffer from the paramagnetic effect of the GGG substrate. On the other hand, the YFGO and YBFGO spectra were measured for remanence states ($H = 0$), since these films contain Ga and exhibit perpendicular magnetization. The spectral features in Fig. 2 are in good agreement with those reported for single crystals.[12]

The thickness and flatness of the films were evaluated by x-ray reflectivity measurement. Figure 3 shows x-ray reflectivity spectra of (a) YFGO and (b) YBFGO thin films prepared with a single coating process on Si substrates. Oscillations caused by interference of the x rays in the films are clearly observed, and from these the thickness of the YFGO and YBFGO thin films was determined to be 44 and 37 nm, respectively, with a surface roughness of less than 2 nm.

Figure 4 shows XRD patterns of YFGO and YBFGO thin films prepared on GGG substrates after repeating the MOD processes ten times. The 444 diffraction peaks of YFGO and YBFGO are observed close to the 444 peak of the GGG substrate. The asterisk indicates a satellite peak, which will be discussed later. No other phases could be observed in the XRD patterns. However, small peaks can be observed for polycrystalline YBFGO [marked with + in Fig. 4(b)], al-

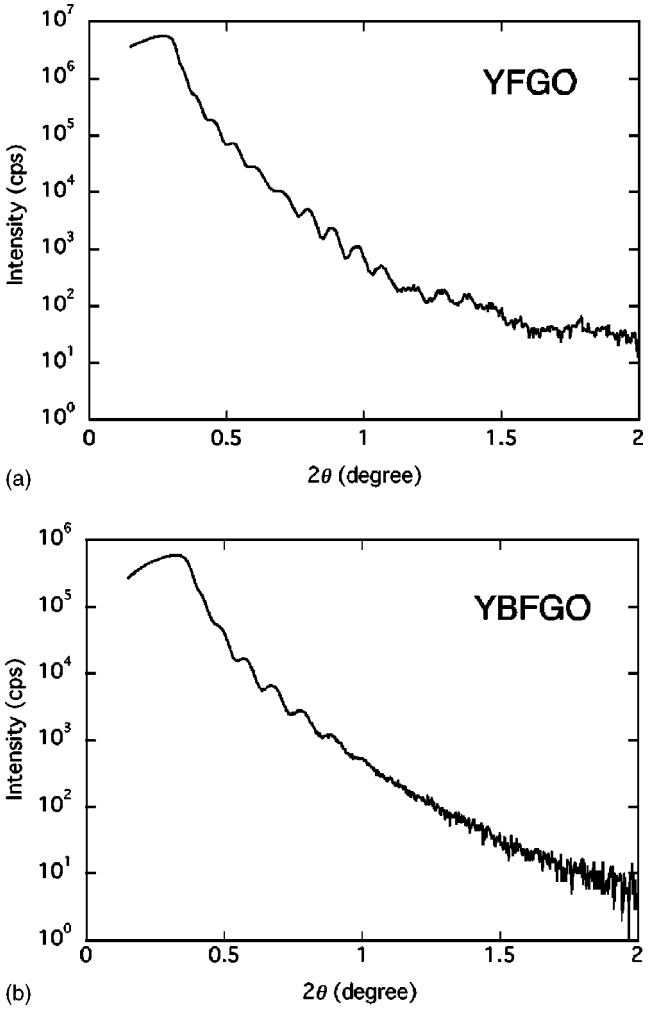

FIG. 3. X-ray reflectivity spectra of a single-coated YFGO and YBFGO thin films prepared on Si substrate.

though their intensity is less than 1% of the 444 diffraction intensity. The lattice constants obtained from lattice spacing of the (444) planes are 1.234 and 1.248 nm for YFGO and YBFGO, respectively. These values are reasonable taking into account the concentration of substituted Bi and Ga.[12,13] The full width at half maximum (FWHM) values of the 444 diffraction peaks from the YFGO and YBFGO films are 0.04° and 0.4°, respectively, indicating that the crystallinity of the YFGO film is better than that of the YBFGO film. One possible cause for the variation may be the difference in annealing temperatures. Therefore, we consider that optimization of the annealing conditions is required to improve the crystallinity of Bi-substituted yttrium iron garnet films.

For the YFGO film, the FWHM is sufficiently narrow to observe satellite peaks caused by interference in the thin film itself or by the layered structure existing after the multicoating process. Figure 5 shows the x-ray diffraction (XRD) pattern around the 444 reflection of the YFGO thin film. Many satellite peaks can be observed, from which two different periods were deduced. The marks Δ and | indicate the positions for interference calculated using thicknesses of 45.9 and 459 nm, respectively. These correspond to the thicknesses of the film prepared by a single MOD process and the total thickness of the film after ten repeated processes. These

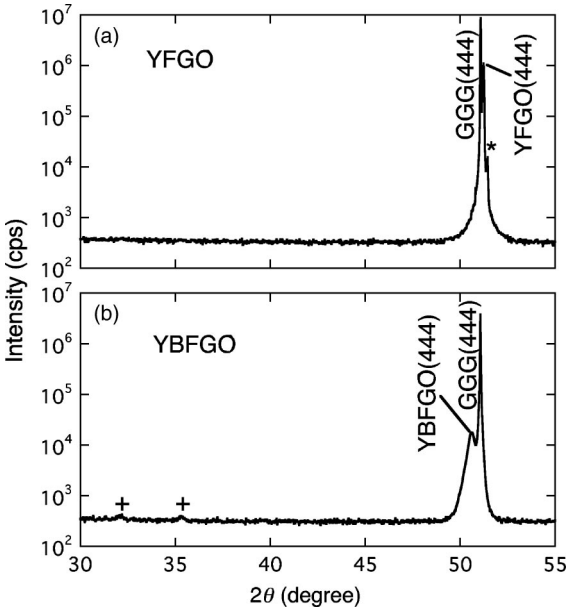

FIG. 4. XRD patterns of YFGO and YBFGO thin films prepared on GGG substrates.

results indicate that the YFGO thin film is sufficiently crystalline and flat to observe interferences of x rays in the thin film, although a periodic variation corresponding to the one coating of MOD liquid exists. However, a question arises as to the origin of the interference in the single layer. We consider that this interference is due to modulation of the chemical composition in each prepared layer or defects at the interfaces between layers.

In order to confirm the crystallinity, RBS measurement was carried out. Figure 6(a) shows RBS spectra of the YFGO film grown on the GGG (111) substrate. The dashed line indicates an aligned RBS signal measured with the $^4He^+$ ion incident along the [111] direction of GGG, and the solid line shows a random signal. Signals of the constituent atoms Y, Fe, and Ga are clearly observed in the film at a higher channel number (190–430), and signals of Gd and Ga in the GGG substrate are observed at channel numbers lower than 320 and 280, respectively, as shown in the decomposed spectra [Fig. 6(b)]. This result indicates that the film is homogeneous and there is no change in the composition along the [111]

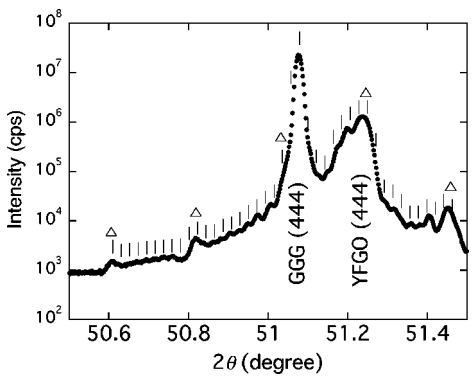

FIG. 5. XRD pattern around the (444) reflection of the YFGO thin film. "Δ" and "|" show calculated satellite peak positions for the thickness of 45.9 and 459 nm, respectively.

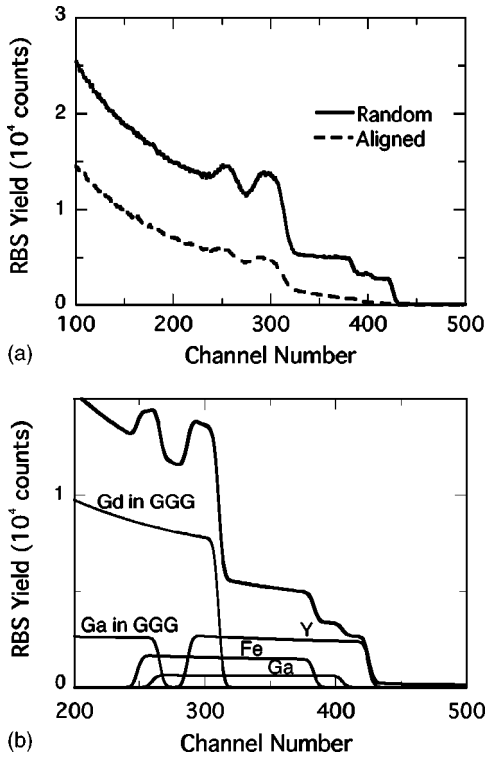

FIG. 6. RBS spectrum of the YFGO film grown on GGG (111) substrate. (a) Random and align spectra, (b) decomposed spectra.

direction. The chemical composition of this film is determined from Fig. 6(b) to be Y:Fe:Ga=2.84:4:1.16, which agrees with the composition of the initial MOD liquid within experimental error. Moreover, the backscattering yield of the aligned spectrum is extremely low in comparison with that of the random spectrum, which indicates that the crystallinity of this film is good. The minimum yield $\chi_{\min}$ was determined by channeling analysis to be ~7.5% along the [111] direction as shown in Fig. 7. As far as we know, we believe this value to be the best achieved on garnet films. Taking into account the good value of $\chi_{\min}$ it is considered that the interference corresponding to the single-coated layer thickness in Fig. 5 is caused by a slight deviation in Ga composition within each layer.

IV. CONCLUSIONS

Epitaxial $(Y,Bi)_3$ $(Fe,Ga)_5$ O_{12} garnet thin films were prepared on $Gd_3Ga_5O_{12}$ (111) substrates by the MOD method using carboxylic acids. The data, including Faraday

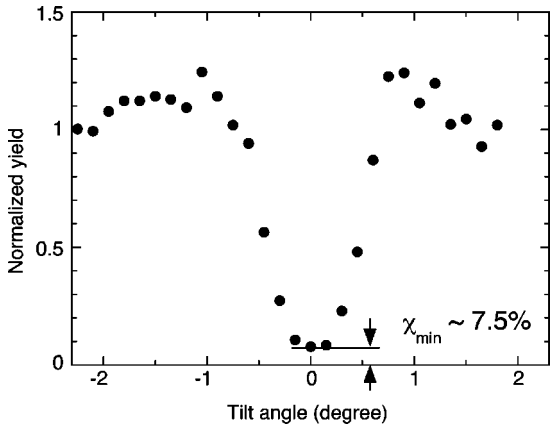

FIG. 7. Channeling spectrum of the YFGO film grown on GGG (111).

spectra, XRD patterns, and x-ray reflectivity spectra, all indicated that $(Y,Bi)_3(Fe,Ga)_5O_{12}$ thin films of high quality were successfully prepared. The YFGO thin film, especially, is of quite good quality, exhibiting a $\chi_{\min}$ of 7.5% in RBS measurement. We believe that MOD has promise as a technique to prepare epitaxial oxide thin films.

ACKNOWLEDGMENTS

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