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Synthetic study of Bi–YIG sputtered films

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Synthetic process of Bi–YIG films has been studied in terms of Fe concentration. The garnet films were prepared by rf–sputtering using targets which had various Fe contents. In the wide range of Fe content from about 3.9 to 5.4, garnet phases were obtained at an annealing temperature of 650°C. For the Fe contents from 1.9 to 5.1, M_s increased linearly, and for more Fe content, it dropped sharply. By considering the θ_F/M_s values and Curie temperature, it is expected that the Y concentration in the garnet phase crystallites in the prepared films is higher for small Fe content of 3.9, than that for larger Fe contents of 4.4, 5.1 and 5.4. The lack of Bi in the garnet phase for the Fe content of 3.9 weakened the Faraday rotation of the film. It was observed that the excess Bi ions in low Fe content films concentrated in the surface and edge of the films by EDX and SIMS analyses.

1. INTRODUCTION

Bismuth substituted iron garnet films are very attractive material for magneto-optical applications. Sputtering method has been applied to the preparation of the garnet films because some remarkable progresses were made by substitution of Bi^{3+}, Ce^{3+} etc. to the garnet structure. It was reported that in spite of the considerable deviation from the stoichiometric composition of garnet, a single phase of garnet structure could be obtained by sputtering method[1, 2]. It is worthwhile to determine the composition range in which the garnet structure can be obtained, and to clarify the film structure in order to make clear the synthetic process of Bi substituted garnet films by sputtering method.

In this paper, we prepare Bi–YIG sputtered films using targets which have various Fe contents, and analyze the structural, magnetic and magneto-optical properties of the films.

2. EXPERIMENTAL

The films were prepared on vitreous SiO_2 and Corning 0317 glass substrates by rf–sputtering under the conditions given in Table 1. The targets were prepared first by mixing oxide powders, then it was fired at 800°C for 4h and ground with a mill. Then it was pressed at 200kg/cm^2 to form a disk. The as-deposited amorphous films were annealed in air at 650°C for 4h to crystallize the films.

Table 1 Sputtering conditions

Target	$Bi_2YFe_xO_{4.5+1.5x}$ (x=1, 2, 3, 4, 5, 6)
Sputter gas	Ar, 6.7 Pa
Substrate	Corning 0317, SiO_2(Vitreous)
Substrate temperature	400°C
rf power density	2.5W/cm^2
Deposition rate	4.3nm/min

3. RESULTS AND DISCUSSION

3.1. Film composition

Film compositions are given in Table 2. The chemical compositions of the as-deposited films were determined by inductively coupled plasma spectroscopy. We show two kinds of film composition in Table 2. We presume, for the first indication, the sum of cation in films is equal to the sum of cation in targets(a). Comparing the film composition (a) with target composition, content of the Y in the films is more than that of the targets, while the Bi content is less than that of the targets. But the contents of Bi and Y in the films are almost constant, and the Fe content in the films is a little more than the Fe content of targets. For the second indication, we assume the ratio of cation to anion as 8/12 (b), because the ratio taken is for garnet structure. We will use (b) to indicate the film composition in this

Table 2 Film compositions

Sample No.	Target			Film						
				(a)			(b)			(Bi+Y)/Fe
	Bi	Y	Fe	Bi	Y	Fe	Bi	Y	Fe	
1	2	1	1	1.7	1.3	1.0	3.4	2.7	1.9	3.21
2	2	1	2	1.4	1.2	2.4	2.2	1.9	3.9	1.05
3	2	1	3	1.7	1.0	3.3	2.2	1.4	4.4	0.82
4	2	1	4	1.5	1.1	4.4	1.7	1.2	5.1	0.57
5	2	1	5	1.5	1.1	5.4	1.6	1.0	5.4	0.48
6	2	1	6	1.5	1.0	6.5	1.3	0.9	5.8	0.38

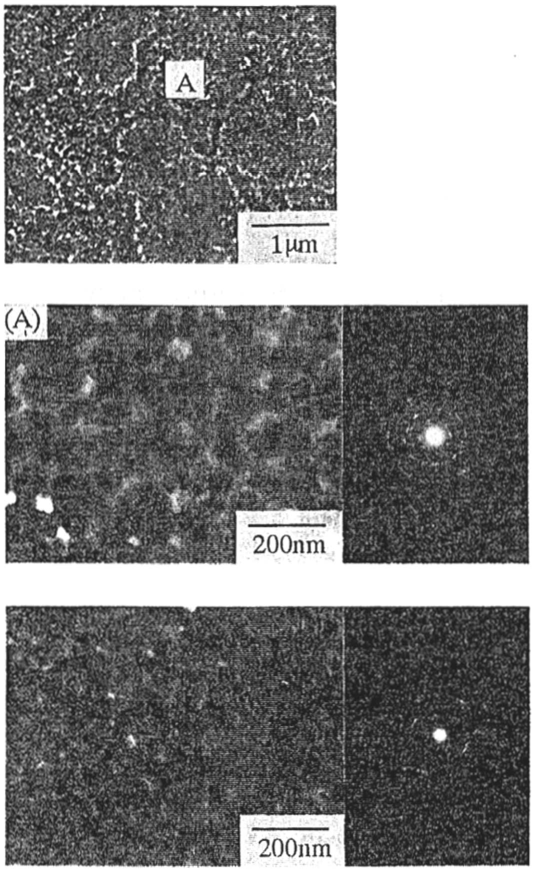

Fig. 1 TEM images and THEED patterns of $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film.

paper. The values of 0.38–3.21 for (Bi+Y)/Fe listed in Table 2 are indicating considerable deviation from the stoichiometric garnet value of 0.6.

3.2. Film structure

From the X-ray diffraction patterns of the samples (shown in Ref. [3]), following results are obtained. For Sample 1, garnet peaks are scarcely observed. For Sample 2, while a impurity phase appears a little, almost all peaks are assigned to garnet. All peaks of Sample 3, 4 and 5 are assigned to garnet. Then, for Sample 6, the intensity of garnet peaks becomes weak and a impurity phase appears. In the wide range of Fe content from about 3.9 to 5.4, the garnet structure can be obtained at the an-nealing temperature of 650°C.

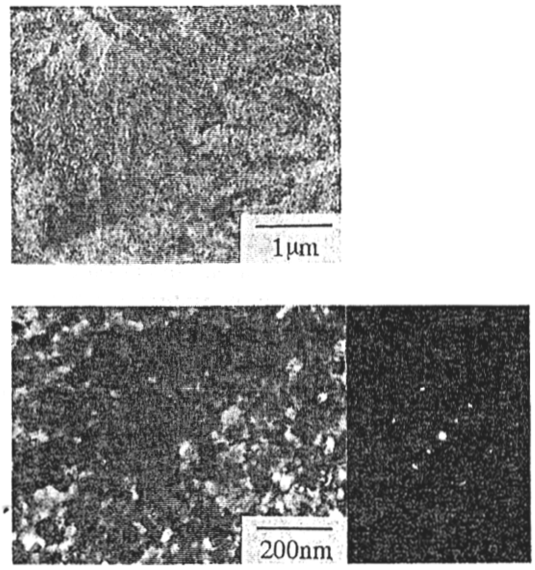

Fig. 2 TEM images and THEED pattern of $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film.

Figure 1 and 2 show TEM images and THEED patterns of Sample 4 and 2. Films are prepared on NaCl substrates by 20 minutes sputtering in order to obtain the TEM samples. In Fig. 1 of Sample 4 ($Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film), there are two areas shown as A and B in the figure. In Area A, grains which are about 100nm, are confirmed clearly. The THEED

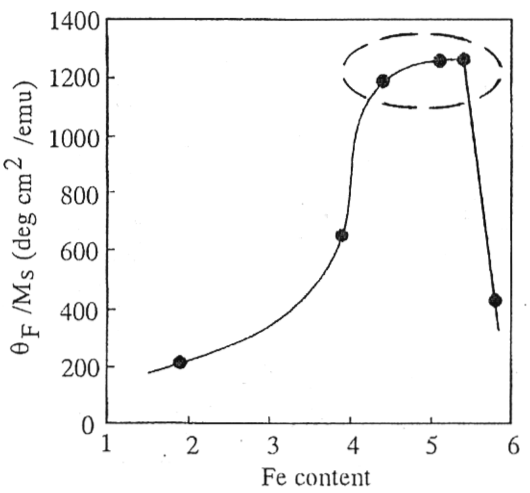

Fig.3 θ_F /M_S vs. Fe content for the films annealed at 650°C.

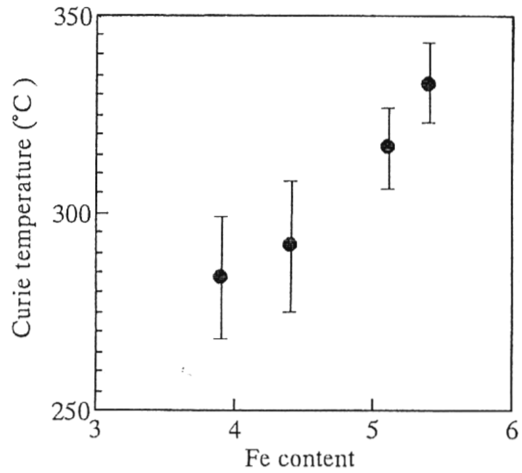

Fig. 4 Curie temperature of the films for various content.

pattern of Area A is assigned to garnet. On the other hand, grain boundary is not clear at Area B. From the THEED pattern of Area B, there are unknown phases except the garnet phase. In Fig. 2, $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film is homogeneous, however, from the THEED pattern, this film also contains unknown phase in Area B of Sample 4.

3.3. Magnetic and magneto-optical properties

The M_s and Faraday rotations of the films were measured as a function of Fe content. These data were shown in Ref. [3]. The M_s increased linearly for the Fe content less than 5 and dropped sharply for the Fe content over 5. It is presumed that M_s increases in proportion to garnet volume until Fe content 5, and garnet structure decomposes suddenly over Fe content 5. The Faraday rotation of the films was measured at 520nm. The curve of the Faraday rotation as a function of Fe content was similar to that of M_s. By comparing the film of Fe content 3.9 and the film of Fe content 5.4, M_s is almost the same, however, the value of Faraday rotation for 5.4 Fe content is about twice that for 3.9 Fe content.

Figure 3 shows θ_F/M_s as a function of Fe content. It can be assumed that there were no other magnetic phases except garnet phase in the films. Therefore, the value of θ_F/M_s represents the magnitude of Faraday rotation of the garnet phase formed in the films. In the region of Fe content 4.4 to 5.4, the values of θ_F/M_s increases gradually but they are almost constant. At 3.9 Fe content, the θ_F/M_s is half of the constant value in the region of Fe content 4.4 to 5.4. It is considered that in the film of Fe content 3.9, Bi and Y are contained in amorphous phase in the films. Y is incorporated more stably in the garnet structure than Bi because a special technique must be used to prepare highly Bi substituted YIG[4]. Considering that Faraday rotation is much enhanced by Bi[5, 6], this result suggests that the garnet phase formed in the films of 3.9 Fe content, contains less Bi ions than the garnet phase formed in the films having the Fe content around 5.

Figure 4 shows the Curie temperature of the films for various Fe contents. It is reported that the Curie temperature increases linearly with Bi content in the system of $Bi_xY_{3-x}Fe_5O_{12}$ [7]. In this case, since the Curie temperature increases as Fe content increases, it is considered the Bi content of the garnet structure increases with Fe content. This result is consistent with the consideration on Fig. 3.

3.4. Distribution of Bi

Though $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film has more Bi ions in the film than $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film, θ_F/M_s of $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ is much smaller than that of $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$. Considering large amount of Bi remains without constituting the garnet structure in the film, it is needed to clarify the area where Bi ions concentrated in the films.

Figure 5 shows a SEM image near the edge of

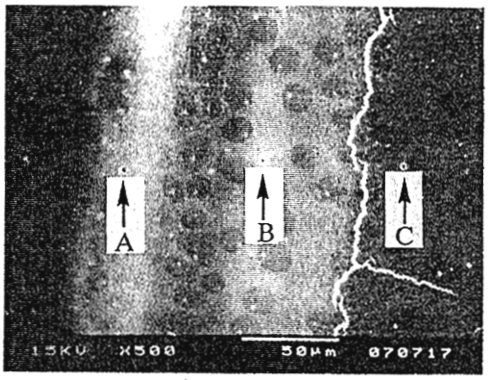

Fig. 5 SEM image of $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film annealed at 650°C.

$Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film annealed at 650°C. Compositions are measured with EDX at A, B and C points. The results are indicated in Table 3. The proportion of Bi increases as approaching the edge of the film. This result is also confirmed in as-deposited $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film. But in $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film, this tendency is not observed.

Table 3 Compositions at A, B and C areas in Fig. 6

Area	Bi	Y	Fe (at. %)
A	54.92	13.45	31.63
B	36.43	19.95	43.62
C	23.48	23.92	52.59

Depth profiles of as-deposited $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film is shown in Fig. 6. This profile was obtained with a secondary ion mass spectrometer (SIMS). It is found that certain amount of Bi exists in the surface of the film. It is homogeneous under the surface of the film.

From these results, it is considered that excess Bi ions exist in the surface and edge of the films.

4. CONCLUSIONS

To make clear the synthetic process of garnet films by sputtering method, we prepared the films which have nonstoichiometric composition of the garnet by rf-sputtering using $Bi_2YFe_xO_{4.5+1.5x}$ targets. Through the magnetic and magneto-optical measurements on the various Bi-YIG sputtered films, the following results were obtained. In the wide range of Fe content from about 3.9 to 5.4, the garnet structure could be obtained at the annealing temperature of 650°C. It is presumed that M_s increases in proportion to the volume of the crystallites having garnet structure until Fe content of 5, and garnet structure decomposes for the Fe content over 5. All Bi were not incorporated in garnet phase in the film having Fe content of 3.9, therefore, the film showed a small value of θ_F/M_s.

This result was supported by Curie temperature data of the films. From the results of EDX and SIMS analyses, it is considered that the excess Bi ions exist in the surface and edge of the film.

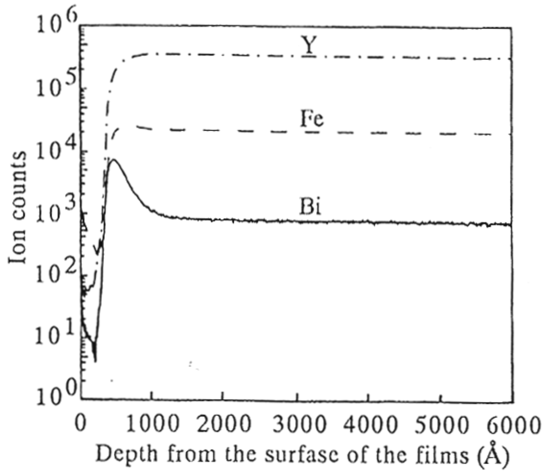

Fig. 6 Depth profile of $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film, 500Å of Au was coated on the surface of the film.

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