CHANGES OF ABSORPTION IN LPE GROWN (GdBiCa)₃Fe₅O₁₂ FILMS BY Ar SPUTTER-ETCHING

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ABSTRACT

Change of optical absorption after etching was experimentally studied on Ca and Bi doped GdIG films. When argon sputter-etching was performed on as-grown films for a period of time, absorption decreased to the same level as when reduction treatment was performed in Fe(OH)₂ solution. Measurement of lattice constant showed that it increased up to a certain value in both cases of sputter-etching and reducing treatment. Further sputter-etching resulted in the increase of loss, while lattice constant remained unchanged. Change of absorption can be explained by changes in valency of ferric ions, whereas change of lattice constant is mainly attributed to reduction of Pb⁴⁺ to Pb²⁺.

1. INTRODUCTION

Rare earth iron garnets known to be transparent in near infrared region are promising materials for the optical nonreciprocal devices, such as optical isolators and circulators. For the purpose of realizing these devices, low loss and large magneto-optical effect are desired.

In the case of rare earth iron garnet films which are prepared by LPE technique, optical absorption becomes large depending on the growth conditions. The absorption in the near infrared region is thought to originate in Fe⁴⁺ and/or Fe²⁺ ions which are produced in order to compensate for charge unbalance due to impurity ions such as Pb²⁺, Pb⁴⁺ and Pt⁴⁺ and/or imperfections incorporated during the crystal growth. Therefore, absorption can be reduced if the occurrence of Fe²⁺ and Fe⁴⁺ ions is prevented. Reducing treatment to the Ca-doped films is known to be effective for this purpose.[1] The mechanism of absorption reduction is explained in Ref.[2].

Considering the garnet films applied to the magneto-optical devices of waveguide-form[3]-[8], etching of garnet films will be required. However, etching of Ca-doped LPE-grown iron garnet films results in great change of absorption, especially when sputter-etching is performed in argon atmosphere. In this paper, we present experimental results on absorption changes of Ca-doped gadolinium bismuth iron garnet films (abbreviated as Ca:GdBiIG) due to etching.

2. EXPERIMENT

Ca:GdBiIG films were prepared using a conventional LPE technique of isothermal dipping with horizontal rotation with a rotation rate of 70 rpm. A PbO-B₂O₃ system was used as a solvent. The melt composition is as follows: Fe₂O₃/Gd₂O₃=25.3, PbO/B₂O₃=7.25, PbO/Bi₂O₃=6.16, CaCO₃/Gd₂O₃=0.2, and (Fe₂O₃+Gd₂O₃+CaCO₃)/(Fe₂O₃+Gd₂O₃+PbO+B₂O₃+Bi₂O₃+CaCO₃)=0.094. Nd₃Ga₅O₁₂ (NGG) was used as a substrate. The saturation temperature of the melt was 792°C and the growth temperature ranged between 710 and 740°C. The film composition was determined by electron probe microanalysis (EPMA). Results are presented in Table 1. Films grown at 710°C showed 2800 deg/cm of Faraday rotation at wavelength of 1.152μm.

Changes of both absorption loss and lattice constant of film due to several treatments were measured. In the Ar Sputter-etching, Ar gas and background pressure were 2X10⁻³ and 1X10⁻⁴ Torr, respectively. Etching rate of 50 Å/min was obtained with Rf plate voltage of 2000 V. Etching was also carried out in diluted nitric acid (HNO₃ : H₂O =1:4 volume ratio) at 95°C with the rate of 50 Å/min. Reducing and oxidation treatments were performed in Fe(OH)₂ solution flowing with N₂ gas and in 0.4 mole/l of KMnO₄ solution both at 80°C, respectively.

Table 1. Composition of films vs. growth temperature T_g.

T _g (°C)	Gd	Bi	Ca	Pb	Fe	Pt
710	2.040	0.853	0.022	0.084	4.950	0.050
730	2.132	0.773	0.020	0.075	4.959	0.041

The absorption loss was measured by the guided-wave optics technique using rutile prism coupler and 1.152 μm He-Ne Laser as light source. In the experiment, absorption more than 70 dB/cm was impossible to be measured. A conventional X-ray diffraction method was used to determine the lattice constants. The unstrained lattice constants of the films were calculated by using 0.30 for Poisson ratio and 12.509 $\text{\AA}$ for lattice constant of NGG.

3. RESULTS

In this chapter, we summarize the experimental results on changes of absorption loss and lattice constant after treatments.

3.1 Ar sputter-etching

Ca:GdBiIG film grown at the temperature of 710 $^{\circ}\text{C}$ was cut into two pieces immediately after LPE growth. Film thickness was 0.9 μm . One was Ar sputter-etched. The changes of absorption loss and lattice constant are shown in Fig.1(a) versus etching time. As sputter-etching proceeds, the lattice constant increases and the absorption loss decreases monotonically until 19 min of etching. However, when etching was further carried out, the absorption loss turned to increase, while the lattice constant remained unchanged.

Fig.2(a) shows the changes in the X-ray diffraction pattern during the sputter-etching. There are four peaks in each pattern because X-rays with two different wavelengths were incident onto the sample. The two of them appearing at lower angle indicated by F correspond to the film and the other two correspond to the substrate, indicated by S. The diffraction pattern remains sharp and only the diffraction angle changes with the progress of etching until 19 min. (A-type changes) This indicates the film layer remains homogeneous during the etching.

3.2 Reducing treatment

When reducing treatment was performed on the other piece of the sample cut in the preceding experiment, its absorption loss and lattice constant changed as shown in Fig.1(b). The lattice constant increased with decreasing absorption loss as the treatment proceeded. However, after 5.5 hours of treatment, absorption loss remained unchanged with a minimum value of about 9 dB/cm, which was almost same as the minimum absorption loss obtained in the sputter-etching.

As shown in Fig.2(b), the changes of X-ray diffraction pattern in reducing treatment of the sample are different from those of sputter-etched sample. That is, as the reducing treatment proceeds, the reflection patterns corresponding to the film spread and/or the original film reflections decrease with appearance of new reflections at lower angles. (B-type changes) These indicate the film is inhomogeneous

Fig1. Changes of absorption loss and lattice constant due to (a) sputter-etching and (b) reducing treatment.

Fig.2 Changes of X-ray diffraction patterns; (a) sputter-etching, (b) reducing treatment.

during the treatment.

The fact that the absorption of the film decreased as the reduction proceeded indicates that Fe^{4+} ions produced by divalent ions were reduced to Fe^{3+} . The increase of lattice constant is thought to be mainly due to the reduction of Pb^{4+} to Pb^{2+} ions in Ca-doped YIG.[9] At this moment, it is not clear whether contribution of ferric ions to the increase of lattice constant is negligible.

3.3 Reducing treatment after sputter-etching

Another Ca:GdBiIG film grown at 710°C whose thickness was about $1\mu\text{m}$ was sputter-etched for 10 min and reduced successively in $\text{Fe}(\text{OH})_2$ solution. Changes of absorption loss and lattice constant are shown in Fig.3 with symbols Δ and $\blacktriangle$, respectively. After 10 min of sputter-etching, lattice constant increased from $12.532\text{\AA}$ to $12.535\text{\AA}$. By successive reducing treatment, it increased up to $12.540\text{\AA}$ and became constant with 22 dB/cm loss after 7 hours of treatment. The absorption of the sample immediately after sputter-etching was too large to be measured. Though the sample was grown at the same temperature as that used in the preceding experiment, 22 dB/cm of loss obtained after reducing treatment is significantly larger than minimum value shown in Fig.1(b). This is mainly attributed to optical scattering of the sample used in this experiment.

In addition, when reducing treatment was carried out to the same sample immediately after crystal growth without sputter-etching, lattice constant changed as shown in Fig.3 with symbol $\bullet$. After about 5 hours of treatment, it became almost constant. The same applies to loss. Nevertheless, as compared to the case when reducing treatment was performed after sputter-etching, the increase of lattice constant is more rapid as shown in Fig. 3.

3.4 Sputter-etching after reducing treatment

Sputter-etching was performed for 12 min to the film grown at 740°C after reducing in $\text{Fe}(\text{OH})_2$ solution for 24 hours. Film thickness of as-grown sample was $0.4\mu\text{m}$. After the sputter etching, lattice constant remained unchanged within experimental errors. However, loss increased from 5 dB/cm before etching to above measuring limits (approx. 70dB/cm). Similar results were obtained for several samples with film thickness ranging between 0.35 and $0.8\mu\text{m}$.

Furthermore, sample whose loss was remarkably increased by sputter-etching was oxidized in 80°C KMnO_4 solution. Changes of loss and lattice constant are shown in Fig.4. Loss increased due to sputter-etching was again reduced by appropriate oxidizing treatment and was restored to the same level as when reducing treatment was sufficiently performed after crystal growth. Within this period of time, lattice constant hardly changed. When oxidation was further performed, loss increased again and lattice constant decreased distinctly. This is considered to indicate the oxidation of Fe^{3+} and Pb^{2+} ions to Fe^{4+} and Pb^{4+} ions, respectively.

3.5 HNO_3 etching

After reducing treatment for 24 hours etching was performed in HNO_3 on Ca:GdBiIG film grown at 730°C . The film thickness was $0.4\mu\text{m}$ in the as-grown state. Changes of loss and lattice constant versus etching time are shown in

Fig.3 Changes of absorption loss and lattice constant in the case of reducing treatment after sputter etching for 10 min (Δ $\blacktriangle$) and without sputter-etching ($\circ$ $\bullet$)

Fig.4 Changes of absorption loss and lattice constant in the case of oxidation after reducing treatment and sputter-etching.

Fig.5 Changes of absorption loss and lattice constant due to HNO_3 etching after reducing treatment.

Fig.5. As the etching proceeded, loss increased while the lattice constant decreased. These can be explained with assumption of oxidation by HNO_3 .

As support for this assumption, when reducing treatment was performed in $\text{Fe}(\text{OH})_2$ solution after the etching, loss and lattice constant returned to the initial values observed before etching.

4.DISCUSSION

As is shown in sections 3.1 and 3.3, the lattice constant of as-grown film increased as Ar sputter-etching proceeded to a certain value. This is considered to indicate that Pb^{4+} and/or Fe^{4+} were reduced to Pb^{2+} and/or Fe^{3+} , respectively. Absorption loss decreased until this point, since Fe^{4+} was reduced to Fe^{3+} . This might be explained by assuming oxygen ions are sputtered out from Ca:GdBiIG by argon collision.

When sputter-etching was further performed after loss took the minimum, loss changed as shown in Fig.1(a). Loss increased remarkably when sputter-etching was performed on the film which had been sufficiently reduction-treated after growth until minimum loss. It can be explained by assuming Fe^{3+} ions were partly reduced to Fe^{2+} . The fact that lattice constant remained unchanged suggests that contribution of reduction from Fe^{3+} to Fe^{2+} to lattice constant is negligible.

As mentioned in sections 3.1 and 3.2, film was homogeneous during sputter-etching but was inhomogeneous during reducing treatment. In the process of treatment, reducing reaction from Fe^{4+} and Pb^{4+} to Fe^{3+} and Pb^{2+} actually occurred in the film surface. This surface reactions can be expressed by the following equations.

The diffusion process from the bulk to the surface of the film can be described by

where $\square$ indicates oxygen vacancy and suffices S,B are surface and bulk, respectively. Here, the reaction rate is dependent on the diffusion rate of the oxygen ions, since the transport of lead and ferric ions from the bulk to the surface is a charge transport, which can be assumed to be much faster than the displacement of oxygen.[10] Considering the above two factors, the film's reaction rate as a whole is not determined only by surface reaction rate but it also depends on the diffusion rate.

A-type changes observed in sputter-etching occur when diffusion rate is faster as compared to surface reaction rate. Such a high diffusion rate can be attributed to high temperature of the sample[11] during sputter-etching. Contrary to this, B-type changes observed in reducing treatment occur when diffusion rate is slower than surface reaction rate.

5.CONCLUSION

It was shown that the absorption loss of Ca-doped rare earth iron garnet film was affected due to etching. Loss of as-grown film after sputter-etching decreased to the same level as that reduction-treated. Further sputter-etching resulted in the increase of loss. These results can be explained by assuming that Fe^{4+} are reduced to Fe^{3+} ions in the first stage and Fe^{3+} partly to Fe^{2+} . Care must be taken in the case of making waveguide-type magneto-optical devices using these materials.

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REFERENCES

1. B.Antonini, S.L.Blank, S.Lagomarsino, A.Paoletti, P.Paroli, F.Scarinci and A.Tucciarone : J.Magnetism and Magnetic Mat. 20 (1980) 216
2. Y.Yokoyama, N.Koshizuka and N.Takeda : IEEE Trans.MAG. MAG-21 (1985) 1666
3. S.Wang, M.Shah and J.D.Crow : J.Appl.Phys. 43 (1972) 1861
4. J.P.Castera and G.Hepner : IEEE Trans.MAG. MAG-13 (1977) 1583
5. Y.Miyazaki : J.Magnetic Soc. Japan 6 (1982) 254
6. K.Ando, N.Takeda, T.Okuda and N.Koshizuka : J.Appl.Phys. 57 (1985) 718
7. T.Mizumoto, K.Oochi, T.Harada and Y.Naito : J.Lightwave Tech. LT-4 (1986) 347
8. Y.Okamura, H.Inuzuka, T.Kikuchi and S.Yamamoto:J.Lightwave Tech.LT-4(1986) 711
9. Y.Yokoyama, T.Takahashi and N.Koshizuka : IEEE Trans.MAG. MAG-22 (1986) 1245
10. W.H.de Rooode and C.A.P.W.van de Pavert : J.Appl.Phys. 55 (1984) 3115
11. R.C.LeCraw, E.M.Gyorgy, R.D.Pierce, J.W.Nielsen, S.L.Blank, D.C.Miller and R.Wolfe : Appl.Phys.Lett. 31 (1977) 243