The Growth and Magneto-optical Properties of Large Size Single-crystal Thick TmBiIG Films from Lead-free Flux by LPE Technology

Bing Mei, Huai-Wu Zhang, Qing-Hui Yang,
Shu-Chen Jin, Xiao-Jie Tian, and Ying-Heng Rao
State Key Laboratory of Electronic Films and Integrated Devices
University of Electronic Science and Technology, Chengdu 610054, China

(*Invited Paper*)

Abstract— In this paper, we prepared the 3-inch magneto-optical (MO) single crystal garnet film with the composition of $(TmBi)_3(FeGa)_5O_{12}$ by Liquid phase epitaxy (LPE) from lead-free flux. The MOgarnet films are grown on $Gd_3Ga_5O_{12}$ (GGG (111)) substrate because of the good lattice match between the film and the substrate. In our experiment, we choose the Bi_2O_3 as the fluxing agent not frequently-used PbO because the latter is poisonous and brings negative impact to the growth film. The good films with low defects, mirror surface, high Faraday Rotation angle(FR) and big thickness have been obtained by optimizing the flux ratio and LPE technological parameters. The thickness of the film can reach about 50–60 micrometers in 3-inch GGG substrate. The optimal growth rate is 0.85 ... 0.95 μm/min, and mismatch between TmBiIG film and GGG substrate gets its smallest and good magnetic and MO properties have been obtained with this growth rated. The biggest FR is 0.54 degree/ μm as the external magnetic field is as small as 25 Oe. The Ms and Hc of TmBiIG film reaches its biggest and smallest value as the growth rate is 0.92 μm/min, respectively, and the value is 50 emu/cm^3 and 5 Oe.

1. INTRODUCTION

Garnet films have been shown to be good material for MO application in high performance optical communication devices due to their high FR and low propagation loss [1–4]. A wide range of techniques have been applied to fabricate MO garnet films including liquid phase epitaxy (LPE), pulsed laser deposition (PLD) and radio frequency (RF) magnetron sputtering. In order to obtain the 45°FR in optical communication device, the thickness of single-crystal garnet film should be more than dozens of micrometers. However, it is very difficult to grow so thick film with PLD or RF sputtering because of the non-equilibrium growth mode, so the LPE is the only feasible method to grow the thick film. Generally, the pure $Y_3Fe_5O_{12}$ (YIG) film is not desirable for MO devices because of its small FR and the bismuth (Bi^{3+}) substitute garnet film (Bi: YIG) is the best choice. In Bi: YIG film, Bi^{3+} ions substituted the part of Y^{3+} ions on dodecahedron sites, and FR increases with the increase of bismuth content, since Bi^{3+} can increase the multiple split of energy level that excited by Fe^{3+} sub-lattice. However, the diameter of Bi^{3+} is bigger than Y^{3+} and leading to the lattice expound of the film and mismatch between the film and GGG substrate, and results in the failure epitaxy. There are two ways to solve this problem, one is growing the film on substitute GGG substrate which with the bigger lattice constant; This has been investigated by some groups, G. Y. Kima [5] and the researchers of Korean [6] Ceramic Society have reduced the mismatch of the film and the substrate by changing the characteristics of the substrate and grown MO garnet film on SGGG substrate; Another way is introducing the ions with small diameter to compensate the lattice expound because of Bi^{3+} ions, Lu^{3+}, Ga^{3+}, Yb^{3+}, Ho^{3+} et al., are the normal choice. LuBiIG [7–11], Bi: YIG [12], Bi: YbIG [13] and $(HoYb)_{3-x-y}CexBiyFe_5O_{12}$ [14] have been prepared by LPE on GGG substrate. But both of them can't epitaxial thick film more than tens of micrometers, and the maximum FR is corresponding to a huge magnetic field.

The main work of this paper is finding the best technology of preparing the $(TmBi)_3(FeGa)_5O_{12}$ more than 50 μm with big FR with the external magnetic field less than 75 Oe. Non-magnetic Bi^{3+}, Tm^{3+}, Ga^{3+} and Fe^{3+} ions were incorporated into the garnet matrix for the purposes of improving the lattice match between the film and the GGG substrate to guarantee the single crystal garnet film can be prepared by liquid phase epitaxy (LPE) method, and lead-free flux has been applied in order to decrease the absorption and increase the FR. Finally, high quality garnet films were successfully fabricated on GGG (111) substrate by LPE method with Bi_2O_3 as the melting agent by optimizing the growth conditions. The crystal structure, microstructure, magnetic and MO

properties were investigated in detail. Our results indicate that the thick garnet film has a perfect micro-structure,mirror surface and good MO and magnetic properties.

2. EXPERIMENT

In our experiment, the non-magnetic GGG (111) single crystal substrate was applied due to its good match to the garnet film in both lattice constant (12.383 Å) and thermal expansion coefficient (9.2×10^{-6}/°C). The oxides of Bi_2O_3, Ga_2O_3, Tm_2O_3 and Fe_2O_3 with high purity (99.999%) were mixed completely and then melted in a platinum crucible at 1000 ... 1050°C for 24 h. The solution was homogenized by stirring with a platinum paddle for another 12 h at 1000°C, and then cooled to the growth temperature. The substrate was mounted on a platinum holder with a small slant angle to the liquid surface. During the growth, the substrate was rotated at a rate of 60 ... 100 rpm/min, and the rotation direction was reversed with a fixed period. The growth rate of the film can be controlled by the growth temperature and the rotation speed. When the film growth was finished, the substrate was lifted from the flux, and hovered above the flux surface for 10 ... 60 min to drop out the appendiculate flux. Finally, the film/substrate was withdrawn from the furnace slowly to avoid the formation of micro-cracks due to surface shrinking (thermal expansion), and then cleaned in a hot nitric acid to eliminate the residual flux. By this method, three-inch $Tm_{2.28}Bi_{0.72}Fe_{4.3}Ga_{0.7}O_{12}$(TmBiIG) films were successfully fabricated on GGG substrates.

Table 1: Parameters for growing TmBiIG film by LPE method from lead-free flux (T_s is saturation temperature, T_g is growth temperature, V_R is rotation speed in growth process.

Flux Composition	T_s	T_g	V_R	Interval of rotation reversion
$Tm_{2.28}Bi_{0.72}Fe_{4.3}Ga_{0.7}O_{12}$	928°C	880 ... 920°C	60 rpm/min	5 s

A typical growth condition applied in our experiments is listed in Table 1. It is noted that the furnace temperature profile in the grown zone is strictly controlled with a variation less than 0.1°C, and a rotation that changes direction every 5 s during the growth is used to obtain a uniform film. The growth rate of the film is calculated from growth temperature and rotation speed to be 0.45 ... 1.45 μm/min. The growth time is about 40 ... 130 min, thus a thickness of about 50 ... 60 μm on each side of GGG substrate is expected for our epitaxial TmBiIG thick film.

The crystal graphic and surface morphology of the film were examined by a Bede D1 x-ray diffractometer (XRD) with Cu Kα radiation, a SEIKO SPA-300HV atomic force microscope (AFM) respectively. The magnetic characteristics were measured using VSMVT-800 vibrating sample magnetometer (VSM), and the MO characteristic was determined with Faraday loop tracer.

3. RESULTS AND DISCUSSION

The growth temperature of $(TmBi)_3(FeGa)_5O_{12}$ film is broad which is about 880 ... 920°C. Growth rate of the film decreases with the increasing growth temperature and can be changed from 1.45 ... 0.45 μm/min. As shown in Fig. 1, the growth rate decrease of 0.035 μm/min when the growth temperature increase of 1°C from point A to point B, and that value increases as the increasing temperature, it is 0.0468 μm/min from point B to C. In our experiment, the very thick film were grown and the garnet content in flux is decreasing distinctly during the growing process and leading

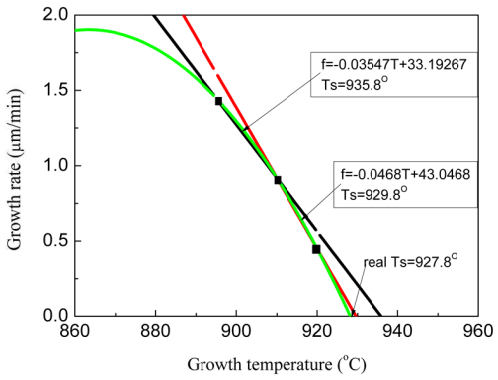

Figure 1: The growth rate depends on growth temperature.

to decreasing growth rate, so we should decreasing the growth temperature to compensate that. For example, it is about 3.2 g garnet is extracted from the flux for growing 3-inch 50 μm thick film, the growth temperature is decreased from 926 ... 922°C during the growth process.

In our experiment, the Bi_2O_3 replaced the PbO as the flux agent, and it acts as both the flux agent and composition of the film and does not bring other impurities to the film. But the flux is with high viscosity and can't be removed from the substrate after growth. The traditional method of removing the flux is rotating the film with high speed, but it not suitable for $(TmBi)_3(FeGa)_5O_{12}$, because its growth mechanism is different with the pure YIG. So we have to find another way to solve this problem. The "buffer method" is applied in our experiment which hovering the film just above the melt at the growth temperature for a long time to wait the flux flow along the declining substrate, and the time is decided by the thickness and the size of the film, it is usually from 10 ... 60 min.

Figure 2(a) shows 3-inch thick TmBiIG film sample, the thickness of film is 60.04 μm, and it is obvious that the sample surface is mirror, the film is clean and flat, and no micro-cracks and residual flux droplets are observed. The RMS surface roughness, estimated from the AFM image shown in Fig. 2(b), is as small as about 2 nm.

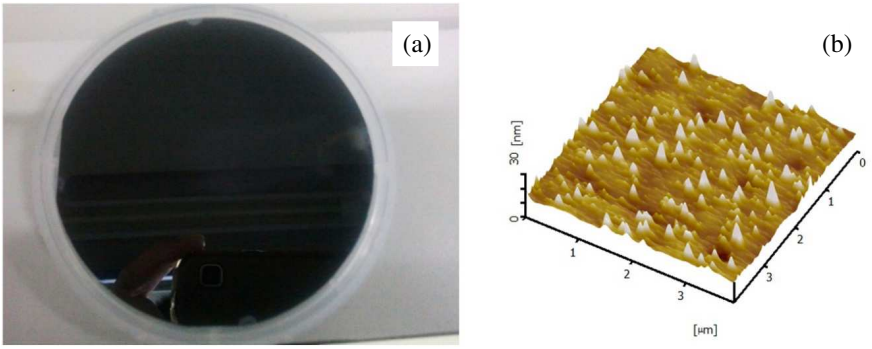

Figure 2: (a) The 3-inch thick TmBiIG film sample, (b) AFM picture of the TmBiIG film. Thickness of sample is 60.04 μm. Growth rate is 0.71 μm/min. Growth temperature is 905 ... 900°C.

The lattice constant match between the film and substrate is very important to grow the large size thick film, because the stress will increase obviously with increasing of film thickness and size and leading to the crack of the film. The composition of garnet film is $Tm_{2.28}Bi_{0.72}Fe_{4.3}Ga_{0.7}O_{12}$, only the lattice constant of garnet film with this composition will matched the lattice constant of GGG substrate and the film can be grown by LPE method. Fig. 3 shows the XRD patterns of $(TmBi)_3(FeGa)_5O_{12}$ film on GGG (111) substrate. It can be seen that the TmBiIG film exhibits a perfect crystalline structure with (444) diffraction peak, indicating that the film is a single garnet phase. The lattice constant of the film is 12.445 Å, and the lattice mismatch between the film and the substrate is as small as 0.05%. Such a small mismatch is due to the ionic radius compensation of Bi^{3+} and Tm^{3+} ions in the film. As we know, Bi^{3+} has a larger ionic diameter than Y^{3+} and

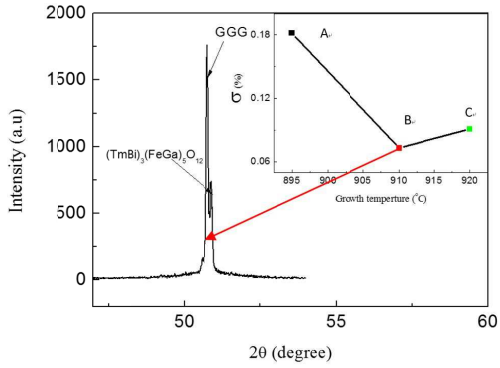

Figure 3: Figure 3 shows the XRD patterns of $(TmBi)_3(FeGa)_5O_{12}$ film on GGG (111) substrate. Thickness of sample A is 14.53 μm. Growth rate is 1.45 μm/min. Growth temperature is 895°C. Thickness of sample B is 9.18 μm. Growth rate is 0.92 μm/min. Growth temperature is 910°C. Thickness of sample C is 9.02 μm. Growth rate is 0.45 μm/min. Growth temperature is 920°C.

Fe^{3+} ions. Therefore, for the Bi^{3+}-doped garnet film the lattice constant solely increases with the Bi^{3+} concentration. Tm^{3+} ions, with smaller ion diameter, can balance out the lattice mismatch that occurs with Bi^{3+}-doped garnet film.

The Mismatch between the film and substrate can be expressed by,

$$\sigma = \frac{d_e - d_s}{d_s}$$

d_e is the spacing (444) of epitaxial films, d_s for substrate, σ is the mismatch. The lattice constant of epitaxial film can be modified by growth temperature and growth rate, so the mismatch σ can be adjusted to near zero to grow thick film. It is impossible to grow thick film when the lattice mismatch is bigger than 0.05%, just like point A and point C in the top right corner of Fig. 3, the films cracked when the thickness were more than 10 μm.

Figure 4(a) shows the magnetic hysteresis loop of $(TmBi)_3(FeGa)_5O_{12}$ film were measured under the condition of room temperature along in-plane and perpendicular-plane. The saturation magnetization (Ms) and coercive force (Hc) depends on growth rate is shown in Fig. 4(b) it can be seen that the easy axis of TmBiIG film is along the perpendicular because of the growth anisotropy by Bi^{3+} [15].

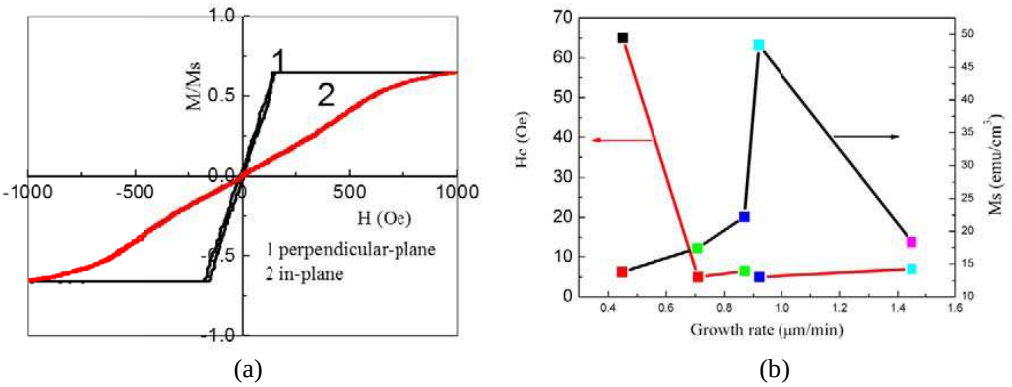

Figure 4: (a) The magnetic hysteresis loop of $(TmBi)_3(FeGa)_5O_{12}$ film were measured under the condition of room temperature along in-plane and perpendicular-plane directions. (b) The Ms and Hc depend on growth rate.

Figure 4(b) shows the Ms and Hc of the TmBiIG films depends on the growth rate. In general, Ms is determined bythe Fe^{3+} magnetic ion content in the tetrahedral and octahedral sites. Ga^{3+} is non-magnetic ions, when it is incorporated into the garnet crystal lattice, it will substitute the Fe^{3+} ion in tetrahedron and octahedral sites, and result the decreasing of Ms of the film. The content of Ga^{3+} ions which incorporate into the garnet film is various slightly as the growth rate is different, so the Ms of the film changes with the growth rate slightly. In YIG crystal, a unit of each formula have $2Fe^{3+}$ (a) and $3Fe^{3+}$(d), their magnetic moment against each other in parallel, the total magnetic moment is equal to the net magnetic moment of $1Fe^{3+}$. The total magnetic moment of the lattice for Fe^{3+} will be reduced due to the non-magnetic Ga^{3+} ions occupy the position of Fe^{3+} (d). So Ms is much lower than YIG garnet material. The Ms and Hc of TmBiIG film reaches its biggest and smallest value as the growth rate is 0.92 μm/min, respectively, and the value is 50 emu/cm^3 and 5 Oe.

The FR of $(TmBi)_3(FeGa)_5O_{12}$ film were measured at the wavelength of 633 nm along the perpendicular-plane. The Fig. 5 shows the relationship between FR of TmBiIG film at different growth rate and external magnetic field. We can see that the FR all reach their maximum value as the external magnetic field is smaller than 75 Oe, it is a desirable value for the MO film applied in devices, means that the MO component can be driven by flat magnetic field, it is beneficial to reduce the volume and weight of the devices. Additionally, the Faraday loop traces are different as the growth rate because the composition of the film changed slightly with the growth rate. We can see that the FR reaches 0.54 degree/μm when the growth rate is 0.87 μm/min. It is because that the film has more Bi^{3+} in the composition of the film.

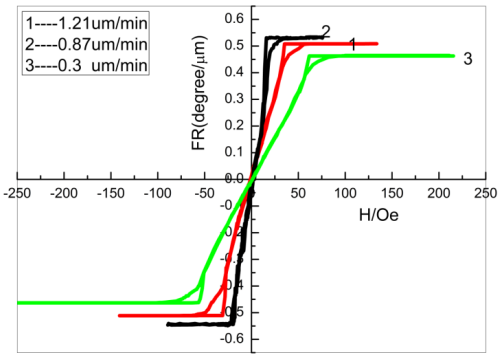

Figure 5: The relationship between FR and external magnetic field.

4. CONCLUSION

In this paper, 3-inch MOTmBiIGthick film was synthesized by LPE method. The Bi_2O_3 was applied as flux agent replaces the normal PbO flux. The effects of the growth rate on the structure, magnetic and MO properties were studied experimentally. Results show that the MO and magnetic properties of the TmBiIG film can be modified by growth rate. We can grow the TmBiIG film with thickness of 50–60 μm as the growth rate between 0.8 to 0.9 μm/min, the mismatch between the film and substrate can be near zero. The FR reach its biggest value 0.54 μm/min, this is due to the slightly increase of Bi^{3+} in the film composition and leading to the splitting of excited energy lever caused by bismuth ion substitution.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (NSFC) under Grants 61021061, 51272036 and 51002021, 61131005, International cooperation project 2012DFR 10730, 2013HH0003 and 2012CB933104, 111project No. B13042.

REFERENCES

1. Pritchard, J., M. Mina, R. J. Weber, and S. Kemmet, "Low power field generation for magneto-optic fiber-based interferometric switches," *J. Appl. Phys.*, Vol. 111, No. 7, 07A941-1–07A941-3, 2012.
2. Xu, Q., B. Schmidt, S. Pradhan, and M. Lipson, "Micrometre-scale silicon electro-optic modulator," *Nature*, Vol. 435, No. 7040, 325–327, 2005.
3. Vlasov, Y., W. M. J. Green, and F. Xia, "High-throughput silicon Nan photonic wavelength-insensitive switch for on-chip optical networks," *Nat. Photon.*, Vol. 2, No. 4, 242–246, 2008.
4. Ghosh, S., S. Keyvaninia, W. Van Roy, T. Mizumoto, G. Roelkens, and R. Baets, "Ce: YIG/SOI optical isolator realized by BCB bonding," *Proc. 8th IEEE Int. Conf. GFP*, 196–198, 2011.
5. The Korean Ceramic Society, "Growth of Bi: YIG thick films by change of PO/Bi_2O_3 molar ratio," *Journal of the Korean Ceramic Society*, Vol. 39, No. 6, 589–593, 2002.
6. Kima, G. Y., S. G. Yoona, I. S. Chungb, S. B. Parkb, S. J. Suha, and D. H. Yoona, "Growth and magnetic properties of LPE-grown $(EuTbBi)_3(FeAlGa)_5O_{12}$ garnet films," *Thin Solid Films*, Vol. 475, Nos. 1–2, 246–250, Mar. 22, 2005.
7. Syvorotka, I. I., I. M. Syvorotka, and S. B. Ubizskii, "Growth peculiarities and magnetic properties of $(LuBi)_3Fe_5O_{12}$ films by LPE method," *Solid State Phenomena*, I. I. Syvorotka et al., Vol. 200, 256, 2013.
8. Keszei, B., Z. Vértesy, and G. Vértesy, "Growth of Bi and Ga substituted YIG and LuIG layers by LPE method," *Crystal Research and Technology*, Vol. 36, Nos. 8–10, 953–959, Oct. 2001.
9. Kono, T., T. Machi, N. Chikumoto, K. Nakao, N. Koshizuka, N. Adachi, and T. Okuda, "LPE growth of bismuth substituted iron garnet films with in-plane magnetization," *Journal of the Magnetics Society of Japan*, Vol. 30, No. 6_2, 600–603, 2006.
10. Görnert, P., T. Aichele, A. Lorenz, R. Hergt, and J. Taubert, "Liquid phase epitaxy (LPE) grown Bi, Ga, Al substituted iron garnets with huge Faraday rotation for magneto-optic applications," *Physical Status Solidi (A)*, Vol. 201, No. 7, 1398–1402, May 2004.

11. Huang, M. and Z.-C. Xub, "Liquid phase epitaxy growth of bismuth-substituted yttrium iron garnet thin films for magneto-optical applications," *Thin Solid Films*, Vol. 450, No. 2, 324–328, Mar. 1, 2004.
12. Xu, W., X. W. Xu, T. C. Chong, Y. S. Tay, G. Y. Zhang, M. H. Li, and B. Freeman, "Magneto-optical properties of Ce and Bi co-substituted iron garnets grown by the Bi_2O_3 self-flux technique," *Applied Physics A*, Vol. 81, No. 3, 565–568, Aug. 2005.
13. Kim, T., S. Nasu, and M. Shima, "Growth and magnetic behavior of bismuth substituted yttrium iron garnet nanoparticles," *Journal of Nanoparticle Research*, Vol. 9, No. 5, 737–743, Oct. 2007.
14. Zhuang, N., W. Chen, L. Shi, J. Nie, X. Hu, B. Zhao, S. Lin, and J. Chen, "A new technique to grow incongruent melting Ga:YIG crystals: The edge-defined film-fed growth method," *Journal of Applied Crystallography*, Vol. 46, No. 3, 746–751, Jun. 2013.
15. Kahl, S., V. Popov, and A. M. Grishin, "Optical transmission and Faraday rotation spectra of a bismuth iron garnet film," *J. Appl. Phys.*, Vol. 94, 5688, 2003.