Preparation of single crystal films of magnetic bubble materials— Rare earth yttrium iron gallium garnets by liquid phase epitaxy and their physical properties

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Abstract. The liquid phase epitaxial growth of rare earth-substituted magnetic garnet films suitable for magnetic bubble domain application by both vertical and horizontal dipping using PbO and B₂O₃ as flux is reported. The dependence of various parameters on lead incorporation in the films present as inhomogeneity has been studied.

Keywords. Liquid phase epitaxy; magnetic bubble materials; saturation temperature; growth temperature.

1. Introduction

To prepare magnetic bubble materials suitable for device application, thin layers of magnetic garnet films showing both high physical perfection and good reproducibility must be prepared. The physical parameters of these thin magnetic garnet layers are determined by their chemical composition which are governed by the growth parameters. In this paper, we report the successful preparation and some physical properties of thin single crystal films of rare earth substituted garnets of the type $Y_{3-x}R_xFe_{5-y}Ga_yO_{12}$ where R is Eu or Sm. The Pb incorporation is always found to be present as an impurity in the films grown at various temperature. These impurities in the film give rise to lattice mismatch and stresses which in turn change parameters like the anisotropy field H_A . The change in the anisotropy field H_A due to Pb impurity has been studied and reported in this paper.

2. Preparation of epitaxial layers

2.1 Epitaxial growth

Epitaxial growth of garnet films is achieved using the liquid phase epitaxy (LPE) method (Levenstein *et al* 1971; Giess *et al* 1972; Robertson *et al* 1974) by dipping a non-magnetic GGG (gadolinium gallium garnet) substrate into a supercooled melt containing PbO–B₂O₃ flux and garnet components. The ratio of PbO–B₂O₃ flux to garnet constituents is chosen such as to give a garnet phase only. Table 1 gives the melt-flux compositions for two different rare earth substituted garnet compositions attempted by us.

2.2 LPE furnace

The LPE furnace designed and fabricated is shown in figures 1 and 2. It is a three-zone kanthal wound vertical furnace giving a 8 cm constant temperature zone in the middle

Table 1. Melt-flux compositions (mole %)

Constituents	$Y_{3-x}Eu_xFe_{5-y}Ga_yO_{12}$	$Y_{3-x}Sm_xFe_{5-y}Ga_yO_{12}$
PbO	84.92	85.671
B ₂ O ₃	5.4	5.493
Y ₂ O ₃	0.55	0.25
Eu ₂ O ₃	0.17	—
Sm ₂ O ₃	—	0.047
Fe ₂ O ₃	7.83	7.423
Ga ₂ O ₃	1.13	1.116
T_s (°C)	992 ± 1	890 ± 1
(*) ΔT (°C)	12	15

(*) $\Delta T = T_s - T_g$

Figure 1. Scheme of liquid phase epitaxy apparatus.

with a temperature stability of $\pm 1^\circ\text{C}$. The furnace is incorporated with a substrate rotating/lowering unit, a temperature controller and a crucible rotating unit. The whole assembly is placed in a class 100 vertical laminar flow tent as shown in figure 2. This precaution is taken since dust free environment is one of the stringest requirements for growing bubble films.

Figure 2. LPE furnace inside a class 100 laminar flow tent.

2.3 Substrate cleaning

Substrate cleaning is an important and crucial factor before growing the films. Film perfection can be achieved mainly on the availability of a dust-free clean substrate. Hence cleaning of the substrate as well as the growth of the epitaxial layer must be done in dust free special clean rooms. Previous studies (Haisma *et al* 1974) have shown that imperfect and dirty GGG substrates can locally dissolve and defects such as small secondary garnet crystals come up. The substrates are cleaned by washing in warm

dilute detergent followed by thorough rinsing in deionized water using class 100 chemical benches. Final cleaning before loading the substrate into the furnace is done by treating it ultrasonically in trichloroethylene vapours under dust free condition.

3. Film growth

The garnet oxides and flux powders after mixing thoroughly are placed in the constant temperature zone of the furnace in a platinum crucible with a lid. This mixture is premelted at 1000°C and this process repeated twice since the volume of the unmelted powders is greater than that of the crucible. For homogenization and complete dissolution of garnet components into the melt, the melt is heated and stirred at 1100°C for about 8 hours. The substrate is then slowly lowered after decreasing the melt temperature to a fixed growth temperature T_g which is several degrees below the saturation temperature T_s . For horizontal dipping, the substrate is rotated at a constant speed for better uniformity of the layer whereas for the vertical dipping mode no rotation is necessary. In both cases, the substrate is held for a few minutes, prior to dipping, just above the supercooled melt to achieve temperature equilibration and then dipped for a known time. The substrate is removed and cleaned off the residual flux. Figure 3 represents the function and time schedule for our LPE growths. In case of vertical dipping the substrate rotation was zero RPM.

4. Results and discussions

The physical properties of the Eu and Sm substituted gallium garnets were studied by dipping smaller pieces of substrates prior to each run.

Figure 3. Function and time schedule for LPE film.

The film thickness (h) was measured by interface method by spherical contouring (Rosenbaum 1968), the room temperature saturation magnetisation ($4\pi M_s$) measured by using a vibrating sample magnetometer which was calibrated against YIG standard. The accuracy of the $4\pi M_s$ value is ± 50 Gauss. The film/substrate lattice mismatch Δa ($\Delta a = a_{\text{substrate}} - a_{\text{film}}$) was measured by x-ray diffraction method using $\text{CuK}\alpha$ radiation and the symmetric (888) reflection mode from which the film lattice parameter can be calculated (Besser *et al* 1971). The quantitative check on Pb content and the chemical analysis of the LPE films were done by electron microprobe analysis (Zimmer and Tolksdorf 1974) using a scanning electron microscope with an energy dispersive x-ray detector. The anisotropy field H_A was calculated from the ESR spectra.

The study of Pb content in various films showed that: (i) The transparency of the film rapidly diminished and had a brownish colouration for films having larger Pb-content. (ii) Lattice mismatch increases with the Pb-content. (iii) The anisotropy field H_A increased with the increase of Pb-content in the films.

The larger mismatch and higher anisotropy field values due to higher Pb content can be explained by the large stresses present in the film. These stresses are introduced by Pb impurities Pb^{2+} on C-site or Pb^{4+} on a -site.

Some of the stress anisotropy can be removed by annealing the films. The studies on the effect of annealing on anisotropy field are in progress and will be reported elsewhere. Some of the measured parameters and other results are summarized in table 2 and figure 4.

Table 2. Properties of rare earth yttrium iron gallium garnets.

Parameter	LPE composition			
	Eu, Ga: YIG	Sm, Ga: YIG		
h (μm)	10 ± 0.5	6 ± 0.5	4.5 ± 0.5	3 ± 0.5
a ($\text{\AA}$)	-0.015	-0.02	—	—
$4\pi M_s$ (G)	200 ± 50	100 ± 50	132 ± 50	150 ± 50
H_A (Oe)	1740	1790	1150	1049
γ ($\text{rad Sec}^{-1} \text{ Oe}^{-1}$)	1.71×10^7	1.7×10^7	1.7×10^7	1.7×10^7
Pb content (atoms per formula unit)	0.23	0.3	0.13	0.06
ΔT ($^{\circ}\text{C}$)	12	15	15	15
Rotation rate (RPM)	50	0	0	0
Melt Comp.	$\text{Eu}_x\text{Y}_{3-x}\text{Ga}_y\text{Fe}_{5-y}\text{O}_{12}$		$\text{Sm}_x\text{Y}_{3-x}\text{Ga}_y\text{Fe}_{5-y}\text{O}_{12}$	
x	0.6		0.38	
y	1.1		1.15	
Film Comp.				
x	0.53		0.2 to 0.25	
y	1.47		1.8 to 2

Figure 4. Changes in the anisotropy field with Pb-impurity in the film.

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