Effect of post deposition reduction treatment of YIG thin films on stabilizing cubic garnet phase[†]

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Abstract. Yttrium iron garnet thin films have been prepared by low pressure metallo-organic chemical vapour deposition method (MOCVD). Dipivaloyl methanates of yttrium and iron have been used as the precursors in the MOCVD growth of the garnet films. Post deposition O_2 annealing at 900°C is required to form a garnet phase which also shows orthoferrite and component Y_2O_3 and α-Fe_2O_3 phases. We show that a partial H_2 reduction treatment minimizes secondary phases and stabilizes the garnet phase. These treatments also enhance the magnetic properties considerably.

Keywords. Yttrium iron garnet; thin films; MOCVD; LPCVD; dipivaloyl methanates; inplane magnetization; orthoferrite; yttrium oxide.

1. Introduction

Garnet thin films are important due to their several applications in magnetic recording (Abe and Gomi 1987), microwave (Han and Li 1992), and optical (Mizumoto et al 1992) devices. These films have been grown by various techniques like r.f. sputtering, chemical pyrolysis, pyrosol and MOCVD. R.F. sputtering using a YIG ceramic target in Ar or Ar/O_2 atmosphere has been extensively studied (Gomi et al 1986; Kano et al 1989). Pyrolysis of chemically casted films have been reported by Cho et al (1989) for the growth of garnet films with uniaxial perpendicular magnetization. Deschanvres et al (1989) described the growth of YIG films by pyrosol (pyrolysis of an aerosol produced by ultrasonic spraying) process using the metallo-organic precursors of yttrium and iron acetyl acetonates [$Y(acac)_3$ and $Fe(acac)_3$] dissolved in butanol. YIG films deposited by the pyrosol technique showed an in-plane magnetization. Chemical vapour deposition (CVD) of garnet films have been reported by Taylor and Sadogopan (1971) using pure metal with HCl transport and by Heinz et al (1971) using metal halide precursors vapourized at very high temperatures of about 1000°C. All these methods have advantages as well as disadvantages. Films grown by r.f. sputtering technique show poor signal to noise (S/N) ratio due to grain boundary scattering whereas the films grown by CVD technique show minimum grain boundary effects, thereby improving the S/N ratio. MOCVD offers better deposition control because it uses metallo-organic precursors as source material which have low vapourization temperatures and can be dissociated at comparatively lower ($\sim 600°C$) temperatures.

To observe optimum magnetic and magneto-optic (MO) effects, the garnet film must be highly crystalline, preferably oriented and stoichiometric. As-deposited films made by most of the above deposition techniques show poor structural quality and even an

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amorphous character. Both *in situ* high substrate temperature (Gomi *et al* 1987; Kano *et al* 1989), and post-deposition high temperature O_2 annealing (Krumme *et al* 1984; Shono *et al* 1987) methods are often used to crystallize the garnet phase in sputtered films. The main problem often faced in garnet film preparation is the inclusion of secondary phases, obtained from non-stoichiometric Y to Fe (3:5) ratio in the vapour phase during sputtering and due to differential oxidation kinetics of Y and Fe in the chemical processing techniques of CVD and pyrolysis. These secondary phases are typically orthoferrite $YFeO_3$, Fe_2YO_4, α-Fe_2O_3 or Y_2O_3 etc. Low values of saturation magnetization ($M_s < 95\,kA/m$) and magnetic coercivity ($H_c < 8\,kA/m$) in garnet films are attributed to their presence (Taylor and Sadogopan 1971; Krumme *et al* 1984; Deschanvres *et al* 1989).

In this paper, we describe a post deposition treatment procedure to eliminate secondary phases and stabilize the garnet phase in the films. The films were prepared by MOCVD technique using volatile metallo-organic dipivaloylmethanates (DPM) of yttrium ($Y(DPM)_3$) and iron ($Fe(DPM)_3$) precursors. Starting with requisite ratios of Y and Fe complexes as the source material, high degree of stoichiometry can be easily maintained in the films. Magnetic and structural studies are also presented.

2. Experimental

Polycrystalline YIG films were deposited in a low pressure chemical vapour deposition (LPCVD) reactor onto quartz substrates at a temperature of 590°C. The LPCVD reactor consisted of a quartz tube with three distinct heating zones and was operated at low pressure (~ 0.5 Torr). The source heating zone had four different source chambers to deposit multi-component films which were resistively-heated individually to produce precursor vapours. Source temperature of 165 and 170°C were used for $Fe(DPM)_3$ and $Y(DPM)_3$ respectively, which produced enough precursor vapours without causing any dissociation. In the mixture heating zone, precursor vapours were mixed at temperatures slightly above the maximum vapourization temperature. Substrates were heated in reaction zone by resistive heating and were mounted on an inclined (45°) susceptor made of stainless steel (Dhara *et al* 1994a). Metallo-organic dipivaloylmethanate (HDPM) complexes of iron [$Fe(DPM)_3$] and yttrium [$Y(DPM)_3$] were used as source materials for the deposition of YIG films. These precursors were synthesized in our laboratory by reacting metal chelates with HDPM in the presence of KOH. These were crystallized and purified by partial sublimation before using for the garnet film deposition. Mixed $Fe(DPM)_3$ and $Y(DPM)_3$ vapours were transported by O_2 gas into the reaction zone where they were pyrolyzed at the heated substrate kept at 590°C which is much above the pyrolysis threshold of the precursors. Ensuing free radical formation and their concurrent oxidation reaction led to the formation of YIG garnet films. As-deposited films were later annealed in flowing O_2 at 900°C for 5 h (hereafter referred to as 'directly oxidized' films) to crystallize the garnet phase. Directly oxidized films were later subjected to a partial reduction process in H_2 atmosphere at 350°C for 3 h as an intermediate step. A second stage reoxidation step on post-reduced film under the conditions similar to direct oxidation enhanced the process of crystallization. The process conditions are summarized in table 1.

Table 1. Garnet film growth and treatment conditions.

	Pressure	0·5 Torr
	Precursors	Fe(DPM)$_3$, Y(DPM)$_3$
	Evaporation temp.	165 C, 120 C
Growth	Carrier gas	Ar
	Reactant gas	O$_2$
	Substrate temp.	590 C
Garnet phase	Oxidation temp.	900 C/5 h
stabilization	Reduction temp.	350 C/3 h
	Reducing atm.	H$_2$

3. Results and discussion

3.1 *Crystallographic studies*

X-ray diffraction pattern of the as-deposited film is characteristic of the polycrystalline and multi-phased material (figure 1). The structure shows garnet phase as well as yttrium orthoferrite (YFeO$_3$) and unreacted component oxides Y$_2$O$_3$ and α-Fe$_2$O$_3$ along with several unknown phases. Indexing of XRD pattern shows garnet Y$_3$Fe$_5$O$_{12}$ (fcc) as a minor phase, indicated by (400), (330) and (440) diffraction planes. In addition, characteristic diffraction lines from (012), (104) and (122) planes of α-Fe$_2$O$_3$ phase, (211) and (440) planes of Y$_2$O$_3$ phase and diffraction line (310) of YFeO$_3$ phase are also observed. A number of diffraction lines at low 2θ are unknown to this system and may be due to intermediate unreacted or mixed secondary phases in the films.

It may be noted that post-deposition high temperature annealing of the as-deposited film in O$_2$ ambient is a necessary step to crystallize the Y$_3$Fe$_5$O$_{12}$ (fcc) garnet phase. High temperature studies on MOCVD formed films reveal that crystallization threshold is above 850°C. Optimized annealing conditions are at 900°C for 5 h (Dhara *et al* 1994a). Diffraction pattern from crystallized films is shown in figure 2. A higher degree of crystallization of the film is revealed by a large number of additional diffraction lines. New and distinct diffraction lines corresponding to the cubic garnet phase from planes (420), (332), (442), (440), (721), (642) and (732) in the annealed films are observed. The analysis was made by comparison with the ASTM card (No. 27–977). Based on fcc crystallographic lattice, the lattice parameter is calculated to be 12·358 Å which is lower than the lattice parameter (12·3774 Å) of the stoichiometric bulk garnet. This deviation in the lattice parameter for the thin film indicates the presence of excess O$_2$ in the annealed films (Dhara *et al* 1994b). Although, a dominant fcc garnet crystallite phase is obtained after the annealing step, diffraction lines (112), (220), (304), (114), (312) of YFeO$_3$ are also present. Lines (012), (024), (214) and (300) of α-Fe$_2$O$_3$ and (440) of Y$_2$O$_3$ are observed, which indicate that some secondary phases are still present, although in lesser ratio than that of the as-deposited films. There are several other diffraction lines, particularly at low 2θ values which could not be identified and may arise from mixed secondary phases as observed in the as-deposited films. The existence of unknown phases is quite common for polycrystalline thin film growth.

Unlike sputter deposition, the MOCVD process involves large concentration of O$_2$, in excess of that required for Y$_3$Fe$_5$O$_{12}$ garnet growth. In fact, both as-deposited and O$_2$ annealed films show excess O$_2$. Partial reduction of the directly oxidized YIG films
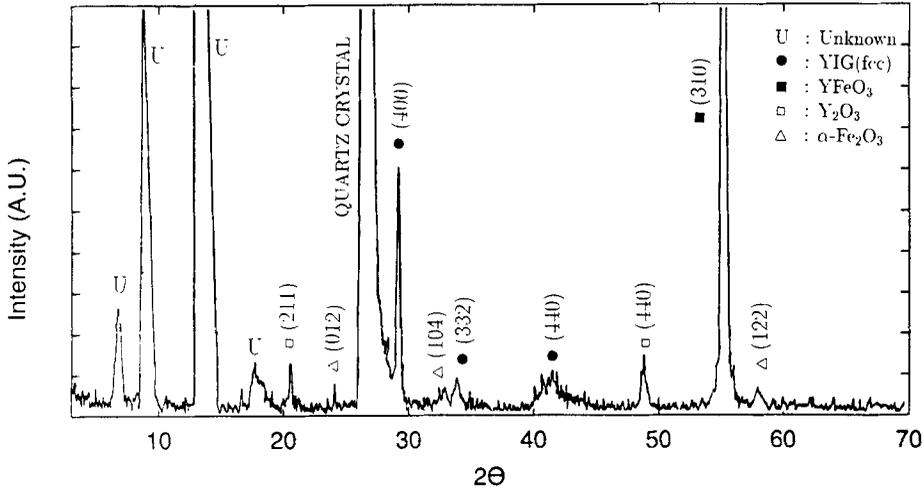
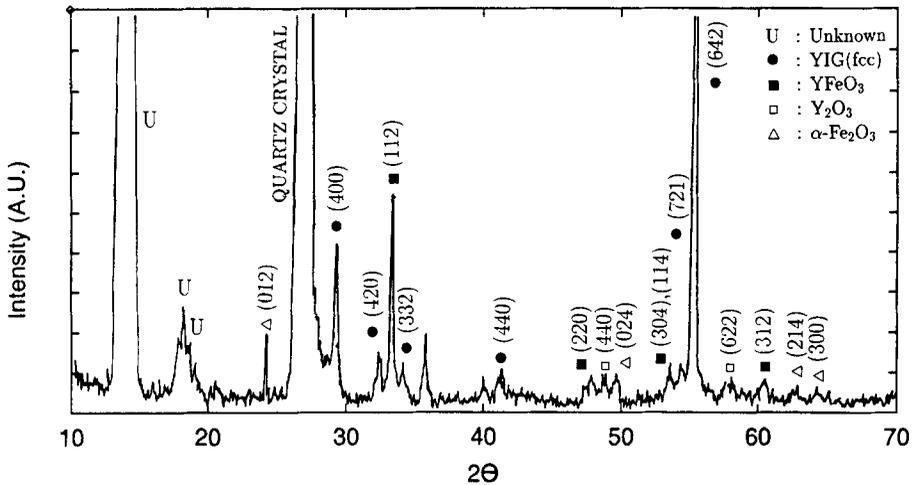**Figure 1.** X-ray diffraction pattern of as-deposited film.

Figure 2. X-ray diffraction pattern of directly oxidized film.

was carried out in hydrogen ambient at a temperature of 350°C for 3 h. Following this treatment, the number of diffraction lines corresponding to the different phases including the lines belonging to the garnet phase are reduced. An important consequence of the hydrogen reduction is that the unknown secondary phases which exhibit diffraction lines at low 2θ values disappear completely (figure 3). The unknown secondary phases as inferred from the XRD patterns of as-deposited and oxygen annealed films thus may have originated from the oxygen excess phases of yttrium and/or iron oxides. On reduction in the H_2 atmosphere, as the excess oxygen is removed from the garnet thin film, the yttrium and iron oxides transform into a metastable lower oxidation state. This has been shown by our earlier studies on α-Fe_2O_3 (Dhara *et al* 1994b). These phases could rapidly re-react at 350°C and crystallize as a garnet phase.
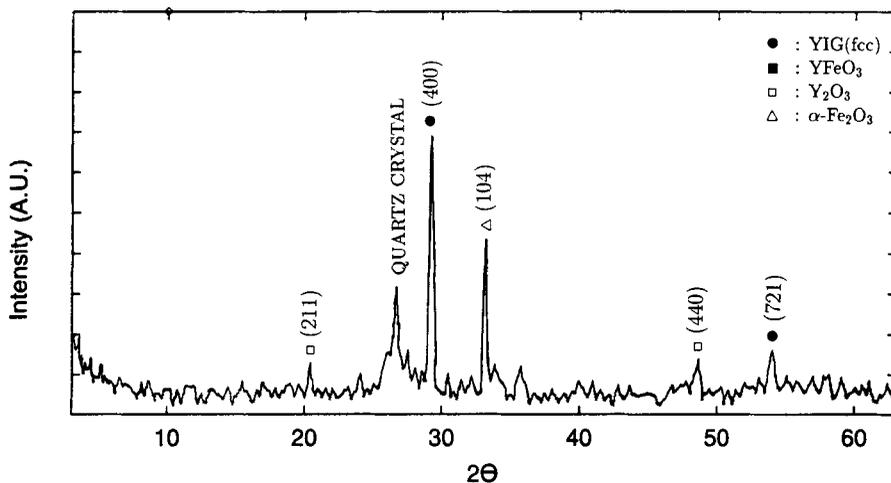
Figure 3. X-ray diffraction pattern of partially hydrogen reduced film.

It is further seen that the characteristic perovskite $YFeO_3$ diffraction lines and lines at higher 2θ values have disappeared in the partially H_2 reduced film. However, small peaks corresponding to the diffraction planes (211) and (440) of Y_2O_3 phase along with the newly appeared (104) peak of α-Fe_2O_3 phase remained. Absence of (420), (332), (422), (440) and (642) diffraction lines of garnet phase and increase in the intensity of (400) and (721) lines suggest that on H_2 reduction, removal of excess O_2 has resulted in the rearrangement of the garnet lattice. A significant change in the phase behaviour of H_2-reduced garnet film is the exclusion of non-magnetic orthoferrite phase. Higher reactivity of lower oxidation state of Y_2O_3 and α-Fe_2O_3 would also promote formation of garnet phase and minimization of secondary phases. Detailed microstructural studies (Moorthy *et al* 1995) have shown the substantial reduction in grain size on H_2 treatment.

The result that the unknown peaks are completely eliminated as well as the secondary phases are substantially reduced in intensity and number is important from the view point of application of garnet films in magnetic recording. It is worth noting that sputter deposited YIG films in the reducing atmosphere (H_2 or Ar) show lower noise levels in the MO recording as reported by Gomi *et al* (1986). It is apparent that the removal of secondary phases and partial amorphous nature of garnet structure particularly at the grain boundary region could have been responsible for the behaviour.

3.2 *Magnetic properties*

The as-deposited films show in-plane magnetization with poor magnetic properties due to the presence of mixed secondary phases of $YFeO_3$, Y_2O_3 and α-Fe_2O_3. The directly oxidized films, however, show a significant increase in the M_s, M_r, H_c and SQ values in comparison to the as-deposited films. Characteristic M–H loop for direct oxidized films is shown in figure 4a. The saturation magnetization M_s value of 142 kA/m observed for these films was similar to that reported for the r.f. sputtered films. The magnetic coercivity, H_c value (8·7 kA/m) is higher and the squareness value (0·55) is
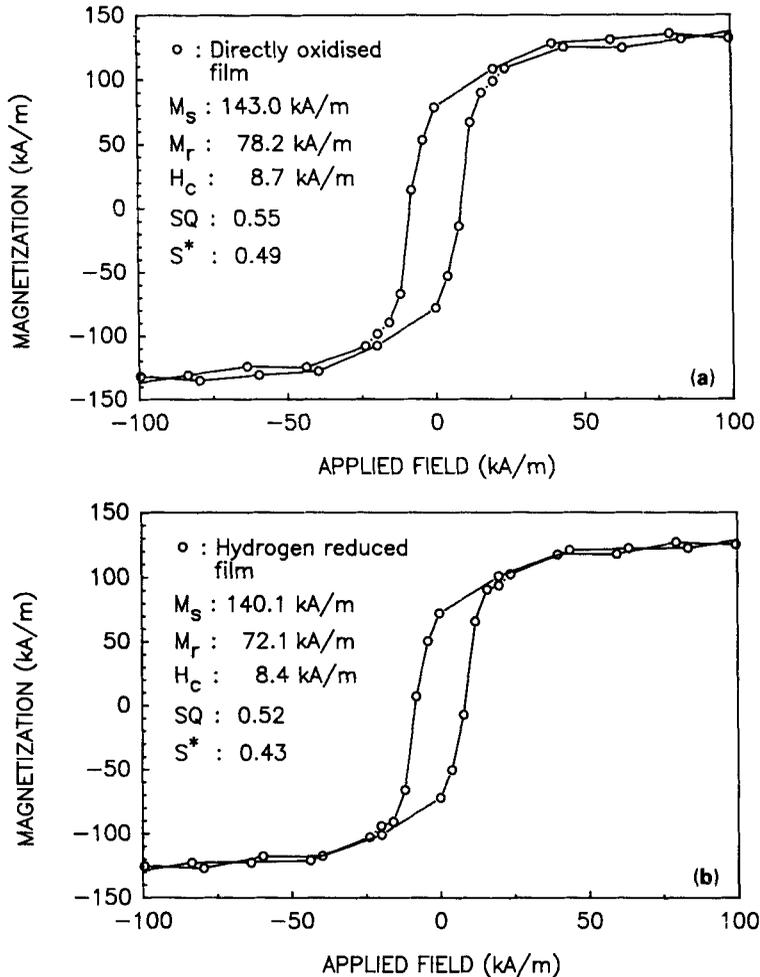
Figure 4. M–H loop characteristics of (a) directly oxidized and (b) partially hydrogen reduced.

lower than H_c (6·4 kA/m) and squareness (0·80) reported for the r.f. sputtered films. Slope value (dH/dM) of 0·49 at H_c (expressed as S^*) was obtained for the oxidized films. YIG films deposited by the MOCVD technique always showed easy axis of magnetization lying in the plane of the film irrespective of the post deposition heat treatment as also reported by Deschanvres *et al* (1989).

On H_2 reduction the direct oxidized films show only a slight deterioration in the magnetic properties with M_s, M_r, H_c, SQ and S^* values of 140 kA/m, 72 kA/m, 8·4 kA/m, 0·52 and 0·43, respectively. This is shown by $M–H$ loop in figure 4b. Although, secondary phases of α-Fe_2O_3, Y_2O_3 and $YFeO_3$ are largely removed, the loss of crystallinity for fcc garnet phase due to oxygen vacancy related defects (as shown by XRD studies), could be responsible for marginal deterioration in the magnetic behaviour.

This small reduction in magnetic parameters is not significant considering the fact that uncrystallized garnet film gives much lower H_c values, typically about 8 kA/m (Gomi *et al* 1987).

4. Conclusions

The as-deposited films of YIG by MOCVD technique are polycrystalline in nature and contain secondary phases of orthoferrite $YFeO_3$, Y_2O_3 and α-Fe_2O_3 along with unknown mixed oxygen excess phases of yttrium and/or iron oxides. Direct oxidation of these films leads to the formation of crystalline fcc YIG phase containing excess oxygen. Secondary phases as nucleated during the initial MOCVD deposition continued to persist in the directly oxidized films. Partial hydrogen reduction of directly oxidized films cause substantial reduction of secondary phases and stabilization of garnet phase without affecting its magnetic properties rendering them more suitable for use in the recording media.

Acknowledgements

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