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Zaki, A.M., Blythe, H.J., Heald, S.M. et al. (2 more authors) (2018) Growth of high quality yttrium iron garnet films using standard pulsed laser deposition technique. Journal of Magnetism and Magnetic Materials, 453. pp. 254-257. ISSN 0304-8853

https://doi.org/10.1016/j.jmmm.2017.11.054

Growth of high quality yttrium iron garnet films using standard pulsed laser deposition technique.

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Abstract:

Thin films with properties comparable to bulk single crystals were grown by pulsed laser deposition using a substrate temperature of only 500 ^{0}C. This was achieved by a careful choice of both the oxygen pressure in the deposition chamber and the temperature of the air anneal. The best films were grown on gadolinium gallium garnet substrates but we also report data for films grown on the diamagnetic substrate yttrium aluminium garnet. The films were analysed using x-ray diffraction, near edge x-ray absorption and magnetometry. Our best films had a magnetisation of 143 emu/cm^3 and a coercive field of ~1 Oe.

Yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) is a very interesting material on account of its magnetic and magneto optical properties. [1] It is ferrimagnetic below its Curie temperature T_c=560 °C with a saturation magnetisation M_s= 143 emu/cm^3 and low coercive field Hc ~1 Oe at room temperature. [2] Pure YIG has long-lived spin wave with a low spin wave damping $\alpha \sim 10^{-5}$. [3] These properties mean that it is widely used in microwave devices such as resonators, isolators, circulators, capacitors etc. [1] YIG has a complex body centre cubic structure and a chemical structural formula $\{Y_3\}[Fe_2](Fe_3)O_{12}$ with eight formula units per unit cell and lattice constant a= 12.376 Å.[4][5]

There are a wide range of techniques used to grow YIG films. The most common techniques are: liquid phase epitaxy (LPE), sputtering and pulsed laser deposition

The films produced by LPE are high quality and single crystal but can only be grown on substrates that are unsuitable for microwave applications. [6] Also, it is hard to make films of less than few hundred nanometres thickness. [6]

Radio frequency (rf) magnetron sputtering is a convenient and economical low temperature technique compared with LPE. [7] It is easy to sputter dielectric materials. [8] However the films grown by this technique are usually off-stoichiometry because they have oxygen vacancies. [7]

Pulsed laser deposition (PLD) is good method to prepare high quality of films of oxides such as ferroelectrics and high temperature superconductors and so much effort has been expended to find the optimal conditions for preparing YIG films. The advantages of this method are that it is possible to control the oxygen stoichiometry by adjusting the oxygen pressure in the deposition chamber and also because there are usually very small differences in composition between the target and the film. [9-11] It was found that stoichiometric YIG could be grown by PLD provided that the substrate temperature was greater than ~800K. [11 -14] More recent work has obtained good films when they used a lower growth temperature of 650K with a high temperature anneal [9] or by cooling the film in the growth chamber in oxygen [15]. GGG is the substrate with the best lattice match but has the disadvantage, for some applications, of being paramagnetic. YAG is a possible replacement [10] but films have also been grown on other diamagnetic materials such as Si. [12]

In this work we describe fabrication of YIG films using a substrate temperature of only 500^0C. The process of optimisation of both the oxygen pressure in the PLD chamber and the temperature of the oven during the annealing process are given. The structures of the films were determined by using x-ray diffraction. Small concentrations of metallic iron, in sub-optimal films, were detected from magnetisation studies and also using x-ray absorption spectroscopy. Finally the quality of the films was checked by looking for films with the characteristic small coercive field. Films grown on GGG at the optimal oxygen pressure and correctly annealed had properties that were the were in the closest agreement with those of bulk YIG of any thin film [9,14]. Films grown on YAG, using the same optical conditions had a saturation magnetisation that also agreed with bulk but the anisotropy was higher due to strain. We also tried to grow polycrystalline films of pure YIG on sapphire, Al_2O_3, substrates but without success.

High quality YIG films grow best on gadolinium gallium garnet $Gd_3Ga_5O_{12}$ (GGG) substrates due to the excellent lattice-matching with lattice constant of GGG, a_{GGG}=12.38Å, compares with a= 12.376 Å for YIG. [10][11] In this work, yttrium aluminium garnet $Y_3Al_5O_{12}$ (YAG) substrate was also used, because it is non-magnetic. However, since it has a

smaller lattice constant than YIG, a_{YAG}= 12.013 Å, the resulting YIG films are strained [10]. The strain of the YIG film on GGG is very small = 0.06% comparing with the strain of the YIG film on YAG =3%.

Thin films of YIG with 120nm thickness were grown on 5x5x0.5 mm two side polished GGG (100) and YAG (100) substrates obtained from PI-KEM Ltd with the thicknesses which are given in table 1. The target was made by using a solid state reaction method, from yttrium oxide (Y_2O_3) powder (99.99% purity) mixed with iron oxide (α-Fe_2O_3) powder (99.98% purity). The powders were mixed in the required ratios and annealed at 1200 ºC for 10 hours. This step was repeated twice before the powder was pressed into discs of dimeter ~ 2.5 cm. Then, the target was sintered in the furnace at 1200 ºC for 15 hours before used it was used in the PLD chamber. A target made with annealing temperature less than 1200 ˚C was brittle and was destroyed during the ablation.

The films were ablated using a Lambda Physik LEXTRA 200 excimer laser (XeCl) with wavelength λ=308 nm and repetition rate 10 Hz with pulse length 28ns. The laser energy per pulse was 300 mJ. The distance between the substrate and the target was 3cm. The target was rotated. The substrate heater was set to T_{sub} of 500 ºC. The base pressure inside the chamber was $3x10^{-5}$ Torr and the pressure was increased by using pure oxygen to bring the pressure to 100, 400 or 500 mTorr. A substantial oxygen pressure was necessary to obtain good films. After the ablation, the film annealed at various temperatures up to 1200℃.

The structures of the films were analysed by using XRD Cu Kα (λ=1.5406 A) in θ-2θ geometry. The x-ray absorption near-edge structure (XANES) was measured at the Advanced Photon Source beamline 20-ID at Argonne National Laboratory in order to check the ionisation state of the Fe ions. All thicknesses of the films which are shown in table 1, were measured after the annealing by using a DEKTAK$^{(R)}$ profilometer.

The magnetic properties of the films were measured using a superconducting quantum interference device (SQUID). There was a large paramagnetic contribution from the GGG substrates; however, as this is well understood, it could be subtracted from the raw data at room temperature. However the use of GGG substrates prevented the measurement of magnetic properties at 5K because the substrate signal was just too big. The YAG substrates are diamagnetic and this signal was also subtracted from the raw data presented here.

X-ray diffraction, XRD, was used to measure the film quality. The films that had been annealed below 900 °C did not show the YIG lines or $YFeO_3$, only Y_2O_3 lines in the XRD. However, the whole film had sublimed after it was annealed at 1200 °C. The best magnetic properties were in the films annealed at 1000 °C so we only give data from the films annealed at 1000 °C in this letter.

The crystal structure and the lattice parameter, *a*, and the grain size, D, (calculated using Scherrer's formula) of the films was found from XRD analysis.

Figure (1) shows the XRD pattern of the films grown on GGG substrates at different oxygen pressures. It is clear all films have sharp diffraction peaks of YIG (400) and (800). The peak intensities of the films grown with P_{O2}=400 mTorr were higher than the others. The lattice constant of this film *a*=12.38Å is closer to the lattice constant of crystalline YIG *a*=12.376 Å. Figure 6 shows the XRD results for the film grow on YAG substrate. The peaks of YIG were shifted because of the lattice mismatch between YIG and YAG. The grain size was largest for the films grown on GGG. The results are summarised in table I.

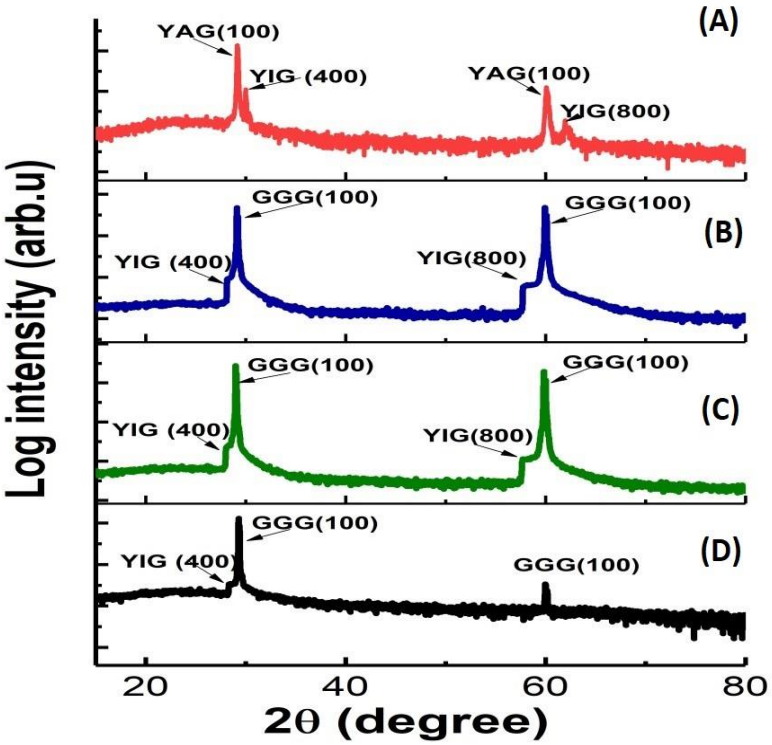

Figure (1): (color on line) the log intensity of the XRD of the films grown with P_{O2} (A) YIG/YAG, (B) 500 mTorr YIG/GGG, (C) 400 mTorr YIG/GGG and (D) 100 mTorr YIG/GGG.

The PLD has to be done in a high oxygen pressure so as to maintain the iron in the Fe^{3+} state. Normally 100mTorr would be considered a high oxygen pressure, P_{O2}, in the PLD chamber but the film grown at P_{O2}=100mTorr had a high value of the magnetisation indicating a substantial amount of metallic iron as may be seen from the magnetism data shown in Figure 2 (a). Figure (3) shows a comparison of the XANES signal of the YIG film grown at P_{O2} =100mTorr and pure YIG powder. The results show the film is close to the YIG but with possibly a small shift due to low valence Fe. If this is assumed to be due to metal it would imply 2±2% of the iron atoms as Fe^0. Assuming that the Fe ions are missing from the octahedral sites and Fe metal atoms carry the moment characteristic of bulk metal this would give a predicted magnetisation of 48±48emu/cm^3, much lower than that observed. This indicates that magnetic measurements may be a more accurate way to detect defect phases in this case.

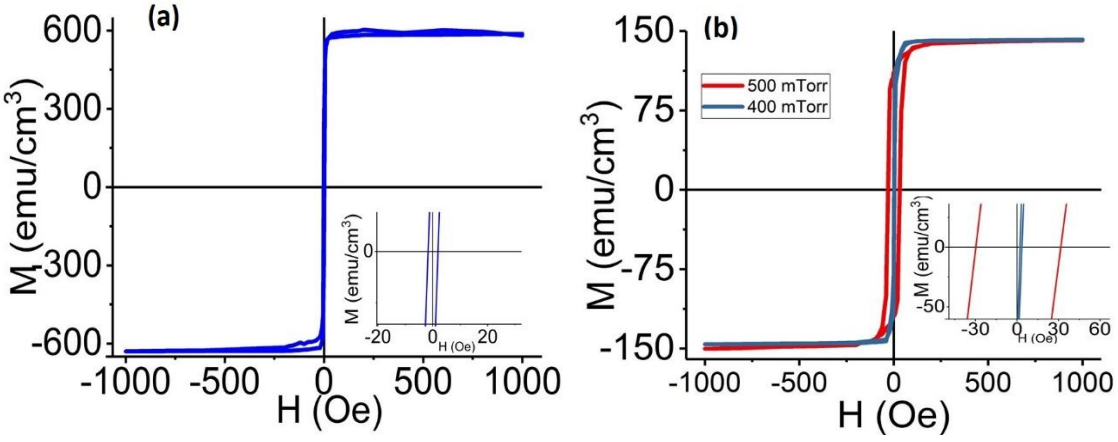

Figure (2): (color on line) The M-H loop at measured at room temperature for the films grown on GGG with (a) 100, (b) 400 and 500 mTorr oxygen in the PLD chamber. The insert shows the region around the origin (the signal paramagnetic from the GGG substrate has been subtracted from this data).

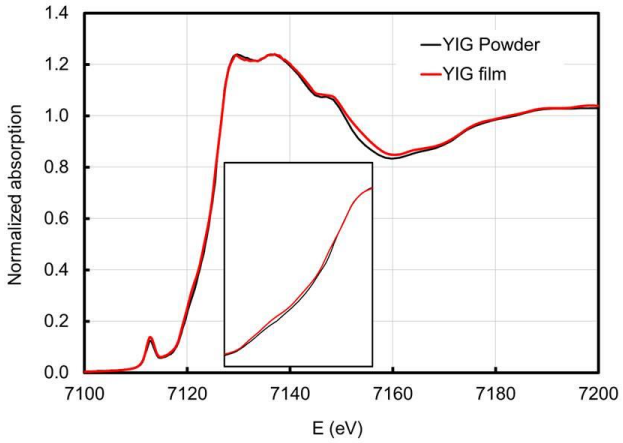

Figure (3) (color on line) XANES measurements for YIG/GGG grown with P_{O2}=100mTorr.

The magnetic loop obtained from the films grown at 400 mTorr and 500 mTorr are shown in Figure 1(b). The film grown on GGG with P_{O2}=400 mTorr O_2 pressure had the best magnetic properties close to these in pure YIG with *Ms*= 143 emu/cm^3 at 300K and a small coercive field of ~1 Oe. Increasing P_{O2} to 500mTorr produced no change in the saturation magnetisation but the coercive field had increased dramatically to 30 Oe. This means that a further increase the oxygen pressure had produced a strained film. The magnetic results for these three films are summarised in Table I.

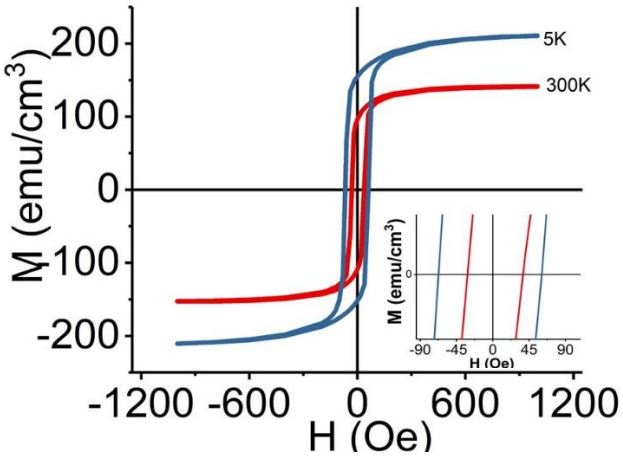

Figure (4): (color on line) The M-H loops for YIG/YAG films at a)5K and b) 300K (the diamagnetic signal from the YAG substrate has been subtracted from these measurements).

The GGG substrate is so strongly paramagnetic that it prevented magnetic data being taken at low temperatures. Films were grown on diamagnetic YAG in order to check the low temperature magnetic properties. A film of grown with P_{O2}=400 mTorr and annealed at 1000 °C was grown on YAG; the M-H loops for this film are shown in Figure 3. The saturation magnetization of the film was close to that of crystalline YIG however the coercive field was higher due to the strain caused by the lattice mismatch. The saturation magnetism increased as the temperature was lowered to a value of 200 emu/cm^3 at 5K which close to *Ms*=193 emu/cm^3 of bulk YIG at 5K [16][17]. However the coercive field was also increased dramatically from 34 Oe at 300 K to 63 Oe at 5K measured at 300 K as shown in table I compared with ≤1 Oe for a bulk crystal.

Table I : the structural and magnetic properties at 300K.

substrate	P_{O2} *mTorr*	*Thickness (nm)*	D (nm)	*a (Å)*	*Ms at 300K (emu/cm3)*	*Hc at 300K (Oe)*
GGG	100	110±3	22.4	12.345	588	1.7
GGG	400	120±2	23.4	12.38	143	0.7
GGG	500	120±3	28.5	12.4	142	30.6
YAG	400	120±2	18.2	12.0	142	34.2

In conclusion, we have prepared YIG films on YAG and GGG substrates at different oxygen pressures with a relatively cool substrate temperature of 500^{0}C. The films were subsequently annealed in air at 1000 ^{0}C. We found that this procedure using a substrate temperature of 500℃ gave films of comparable quality to single crystals and PLD films grown using a substrate temperature of 800 ^{0}C. This is significant because such high substrate temperatures are not available in many laboratories whereas a high temperature air anneal is more standard. We also found that the quality of the film depended crucially on the oxygen pressure in the PLD chamber and we found that the optimum value was 400 mTorr.

We found that epitaxial films could also be grown on YAG but that these suffered from more strain and hence had a larger coercive field due to the lattice mismatch. The temperature dependence of the saturation magnetisation was measured for the films on YAG and the

results shown increasing in the saturation magnetization about 29% when the temperature decreased to 5K.

We gratefully acknowledge the use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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