Static magnetic and microwave properties of Li-ferrite films prepared by pulsed laser deposition

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Highly textured Li-ferrite films have been synthesized by pulsed laser deposition from bulk targets onto *c*-plane sapphire substrates. For substrate temperatures approaching 1000 °C the growth mode was predominantly (333). A similar growth mode was recently reported for Ni-ferrite films grown onto *c*-plane sapphire substrates. The films were 4–8 μm thick and were grown at deposition rates of 3–5 Å/s at oxygen partial pressures of 200–400 mTorr. Magnetic measurements were made by SQUID and 9.5 GHz ferromagnetic resonance (FMR) on the as deposited films. Textured Li-ferrite films with x-ray diffractometer intensity ratios of $I(333)/I(311)=10.3$ for films made in 200 mTorr oxygen and 14.5 for films made in 400 mTorr oxygen exhibited room temperature in-plane intrinsic coercivities of <100 Oe for SQUID magnetometer measurements. Highly (333) textured Li-ferrite films made in 400 mTorr oxygen exhibited clean symmetric FMR absorption lines with a derivative peak-to-peak linewidth of 335 Oe for the in-plane static field configuration. The FMR profiles for the perpendicular-to-plane field configuration were highly distorted. The magnetization versus field measurements and the in-plane FMR field position yielded saturation flux density $4\pi M_s$ and effective saturation flux density $4\pi M_{\text{eff}}$ values of 3.6–4.0 kG and 3.56–3.70 kG, respectively. These values are in the same range as for bulk Li-ferrite. The in-plane FMR linewidths were significantly larger than expected for bulk single crystals or large grain size, dense polycrystals.
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INTRODUCTION

The development of ferrite films for use in monolithic microwave integrated circuits is an area of active research.[1] Generally most methods of ferrite film preparation require multiple step processing. Pulsed laser deposition (PLD) is an exception to this since deposition with flowing oxygen onto heated substrates can produce spinel ferrite films without any subsequent heat treatments as first shown for Zn ferrite.[2] Polycrystalline Ni–Zn–ferrite films were also deposited onto glass substrates by pulsed laser deposition at relatively low substrate temperatures.[3] Pulsed laser deposition oriented Ni ferrite films with certain orientations have been reported for some substrates.[4] The synthesis of certain ferrite films has been reviewed recently.[5] Sputtered film growth usually requires a post-deposition heat treatment to develop the spinel ferrite structure.[6] Preferential (*hhh*) textured spinel films were obtained following post-deposition annealing for ion beam sputtered films.[6]

In a recent article we reported the first synthesis of well defined (*hhh*) textured $NiFe_2O_4$ produced by PLD onto *c*-plane sapphire substrates.[7] In this article we report the synthesis of single step, single phase (*hhh*) textured $LiFe_5O_8$ ferrite films prepared by pulsed laser deposition from bulk lithium ferrite targets. Distinctly different crystal textured films were grown by using different substrates. No other reporting of such fully textured Li-ferrite films has been found in the literature. The microwave properties of the films were characterized by ferromagnetic resonance (FMR) measurements at 9.5 GHz. The in-plane linewidths were wider than values reported for bulk samples, but the saturation magnetizations were consistent with values reported for bulk samples which range from 3.2 to 3.9 kG.[8] Li-ferrite is of special interest because of the absence of ferrous ions in well defined $LiFe_5O_8$ samples.

EXPERIMENT

A Nd-YAG pulsed laser deposition system located at the Center for Materials Research and Technology, Florida State University, MARTECH, FSU, has been used to deposit lithium ferrite films onto various heated substrates. The laser wavelength was 1064 nm with 30 pulses per second, each 8 ns wide. The pulse energy was 700 mJ with a peak power of 85 MW. The laser beam was directed at 20° from the target normal with a target to substrate distance of 1.5 cm. The laser beam was rastered over the target surface by a computer controlled movable mirror. Different polished substrates were used, but this article concentrates on textured films made onto *c*-plane sapphire substrates. The substrate size was 5 mm $\times$ 5 mm. A flowing O_2 gas pressure of 200–400 mTorr was used during the deposition for the data presented here. The films were deposited at an average rate of 3–5 Å/s for 2 h. This allowed relatively thick films to be

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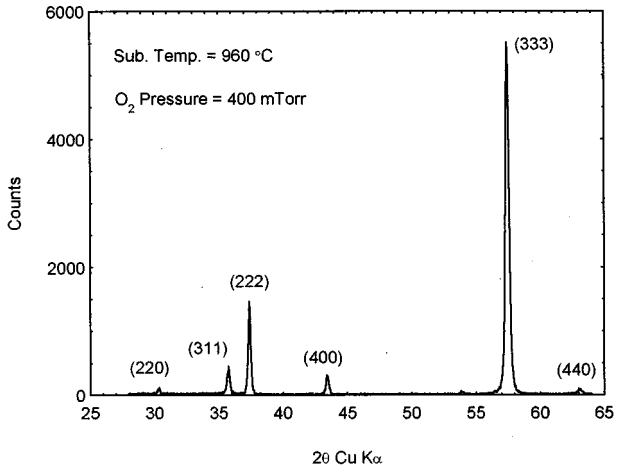

FIG. 1. X-ray diffractometer trace of intensity vs 2θ, taken with Cu $K\alpha$ radiation, for a $LiFe_5O_8$ film deposited on a c-plane sapphire substrate held at 960 °C. The oxygen pressure during deposition was 400 mTorr. The $LiFe_5O_8$ fitted film lattice parameter was $a=8.334\pm0.004$ Å.

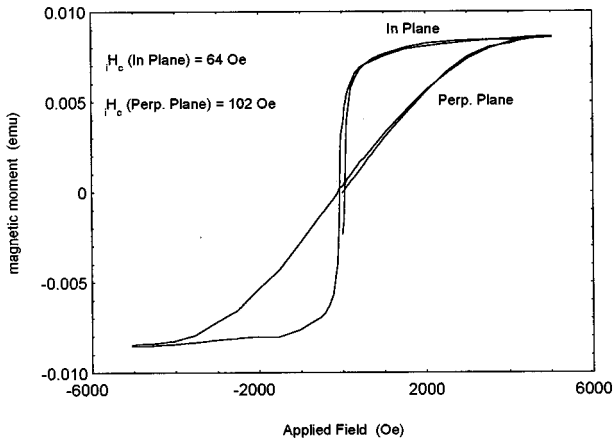

FIG. 2. Room temperature hysteresis loops of magnetic moment vs static applied field for the sample of Fig. 1. Data are shown for the in-plane and perpendicular-to-plane static field directions, as indicated. The perpendicular to the plane emu values for a linear extrapolation of the data saturate at an applied field value of 3.6–4.0 kOe.

produced and steady state deposition conditions to be established. The films on c-plane sapphire were 2–9 μm thick. Lower O_2 pressures resulted in films exhibiting α-Fe and impurity phases. Except as noted the samples have not been subjected to any post-deposition heat treatments.

X-ray diffraction data were collected using a diffractometer with Cu $K\alpha$ radiation. The film thicknesses were measured with a profilometer in some cases. Magnetic measurements were made using a SQUID magnetometer located at MARTECH, FSU. The FMR measurements were made at Colorado State University. Ferromagnetic resonance field modulation derivative absorption curves versus the applied static field were measured with a frequency stabilized low Q cavity at 9 GHz. These measurements were made for both the in-plane and perpendicular-to-plane static field configurations. A basic uniform mode analysis for isotropic films of infinite extent was then used to estimate the effective saturation flux density $4\pi M_{\text{eff}}$ from the in-plane field FMR position.

RESULTS AND DISCUSSION

Highly textured Li-ferrite films oriented to have the cubic cell diagonal perpendicular to the substrate plane were grown by using pulsed laser deposition to deposit the films at relatively high temperatures onto c-plane sapphire substrates. An x-ray diffraction trace of such a fully oriented film grown onto a c-plane sapphire substrate at 960 °C and oxygen gas pressure of 400 mTorr is shown in Fig. 1. Only the $LiFe_5O_8$ (333) and (222) reflections are dominant, with weak (220), (311), (400), and (440) reflections also noted in the figure. The (006) c-plane sapphire line at 41.68° is very weak so that there are no competing substrate lines. The intensity ratio of the (333) to the normally dominant (311) reflection was 14.5:1. The film Li-ferrite lattice parameter fitted from these six lines was 8.334 ± 0.004 Å. The bulk parameter listed in JCPDS is 8.337 Å.[9] For polycrystalline $LiFe_5O_8$ the (311) reflection is dominant with the relatively strong (511) $[I(511)/I(311)=0.45]$ reflection masking the weak (333). The (222) reflection of the powder is not masked by other lines and has a powder ratio $I(222)/I(311)=0.02$. For the textured film of Fig. 1 $I(222)/I(311)=2.5$, which helps to identify the film line at 57.46° as (333). Our experience with single crystal $NiFe_2O_4$ films also confirms this peak identification.[7] Films made at slightly lower substrate temperatures showed more random properties with a more pronounced (311) reflection. Relatively high oxygen pressures of at least 200 mTorr during deposition were also required to obtain clear ferrite diffraction patterns free of α-Fe.

Figure 2 shows room temperature hysteresis loops of the sample magnetic moment versus the static applied field for the sample of Fig. 1 in both the in-plane and perpendicular-to-plane static field configurations. The in-plane and perpendicular-to-plane intrinsic coercivities were 64 and 102 Oe, respectively. The saturation flux density $4\pi M_s$ of the film was obtained as the value of H applied required to saturate the sample in the perpendicular-to-plane configuration. This saturation field is 3.6–4.0 kOe. With the perpendicular-to-plane demagnetizing factor equal to 4π for a thin film, $4\pi M_s$ is 3.6–4.0 kG. Von Aulock[8] cites literature values of $4\pi M_s$ for Li-ferrite at room temperature in the 3.24–3.90 kG range. Note that this saturation field estimation of $4\pi M_s$ does not require the measurement of the film thickness. This determination of the saturation magnetization is consistent with that obtained from the FMR measurements to be presented shortly. For this film a sufficiently accurate thickness was not obtained to make the conversion to $4\pi M$ warranted.

Figure 3 shows typical FMR absorption derivative response versus static applied field curves for the sample of Fig. 1. Figure 3 data are for H applied in the plane of the film. The operating frequency was 9.5293 GHz for both cases. The data were obtained at room temperature. Figure 3 data for the in-plane static field show a symmetric response indicative of a near-Lorentzian FMR absorption curve. The FMR position at the zero crossing of the derivative response is at $H_{\text{appl}}=H_{\text{IN}}=1.84$ kOe and the peak-to-peak derivative linewidth is 335 Oe. Data for the perpendicular-to-plane field

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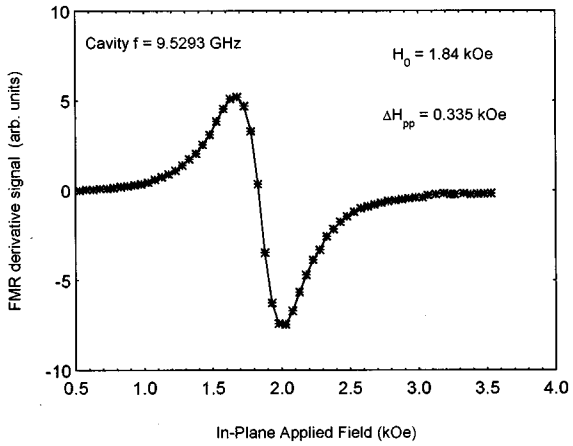

FIG. 3. FMR absorption derivative response vs static applied field for the sample of Fig. 1. The frequency was 9.5293 GHz and the static applied field was in-plane.

case showed a severely distorted line shape. The nominal FMR position in the perpendicular case was the 6.5–6.8 kOe range. The distorted line makes the perpendicular-to-plane FMR position and linewidth difficult to determine with any degree of accuracy.

The in-plane FMR field position of 1.84 kOe can be used to estimate the effective saturation flux density $4\pi M_{\text{eff}}$ from the FMR condition $f/|\gamma|=[H_{\text{IN}}(H_{\text{IN}}+4\pi M_{\text{eff}})]^{1/2}$, where f denotes the FMR frequency and γ is the gyromagnetic ratio. From von Aulock,[8] the Lande g factor for Li-ferrite at room temperature and 9.5 GHz is 2.158–2.139 and the corresponding $|\gamma|$ is 2.993–3.022 GHz/kOe. From these numbers, one obtains a $4\pi M_{\text{eff}}$ of 3.56–3.70 kG. These values overlap the hysteresis loop saturation field estimate given above and are in the middle of the range of literature values for bulk Li-ferrite cited in Ref. 8. Keep in mind that the FMR techniques can determine only an effective value of the saturation flux density which may include, among other things, contributions from anisotropy and magnetostriction.

The derivative in-plane FMR linewidth of 335 Oe for the present pulse laser deposited Li-ferrite film is large, relative to linewidths reported for bulk materials. The microwave linewidth situation for bulk Li-ferrite materials is summarized in Ref. 10. The bulk value indicated for the target material was ΔH at 3 db=346 Oe.[11] The room temperature, 10 GHz derivative linewidth in bulk single crystals of Li-ferrite are on the order of a few Oe at most. Corresponding FMR derivative linewidths and near resonance effective linewidths in bulk polycrystals are typically in the 100–200 Oe range. Note that the half power linewidths typically quoted in the literature are a factor of $3^{1/2}$ larger than derivative linewidths for a Lorentzian line shape. The present in-plane field FMR derivative linewidth converts to a half power linewidth of about 600 Oe. This large linewidth indicates the presence of significant inhomogeneities and/or impurities which typically broaden the FMR response. The distorted FMR line shape in the perpendicular-to-plane configuration is also consistent with this indication. The line shape in perpendicular FMR is typically much more sensitive to microstructural inhomogeneity influences than in the in-plane case. These qualitative conclusions are also consistent with the highly textured nature of the films.

CONCLUSIONS

The most important result of this article is that highly (333) textured $LiFe_5O_8$ films can be grown by pulsed laser deposition onto c-plane sapphire substrates. The crystallites of (333) oriented $LiFe_5O_8$ films exhibit threefold symmetry in the substrate plane and $d_{111}=4.812$ Å exceeds the a lattice parameter of Al_2O_3 ($a=4.758$ Å)[12] by only 1.13%. These conditions allow the growth of highly (333) textured $LiFe_5O_8$ films and with refinements should allow single crystal $LiFe_5O_8$ films to be grown as observed for $NiFe_2O_4$ grown onto c-plane sapphire substrates.[7] Relatively high substrate temperatures of $\geqslant$900 °C have been required to grow completely oriented and or textured films. The saturation flux densities of the films are in the same range as the comparable values for bulk Li-ferrite materials. The linewidths are large. The derivative linewidths of 335 Oe or so are well above the 1–2 Oe derivative linewidths expected for single crystals or the 100–200 Oe derivative linewidths found in dense polycrystals.

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