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Large induced magnetic anisotropy in manganese spinel ferrite films

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The oxygen pressure dependence of magnetic anisotropy in pulse laser deposited manganese ferrite (MnFe_2O_4) films was investigated. Magnetic anisotropy fields (H_a) are shown to exceed 5 kOe when films were processed at oxygen pressures below 5 mTorr. Further, it is shown that the magnetically preferred direction of H_a can be aligned either along the film plane ($p_{\text{O}_2} < 8$ mTorr) or perpendicular to it ($p_{\text{O}_2} > 8$ mTorr). The ability to induce large perpendicular magnetic anisotropy in spinel ferrites allows for new applications (i.e., phase shifters, filters, isolators, and circulators) near or above X-band frequencies to be considered. © 2005 American Institute of Physics.

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Manganese ferrite (MnFe_2O_4) is a well-studied spinel ferrite¹ that has low magnetic anisotropy at room temperature ($K_1 = -33 \times 10^3$ erg/cm³ or $H_a = 2|K_1|/M_S = 175$ Oe at 20 °C)² arising from the low magnetocrystalline anisotropy energy common to cubic magnetic structures. This low H_a limits the microwave applications of manganese ferrite, or more generally, most cubic spinel ferrites, to frequencies less than the X-band (8–12 GHz). To overcome this limitation, large magnetic fields are needed to achieve a high ferrimagnetic resonance (FMR) frequency. The current solution is to replace cubic ferrites with hexagonal ferrites (those having the magnetoplumbite structure) that have large magnetocrystalline anisotropy owing to their anisotropic crystal structure.³ Several reciprocal and nonreciprocal hexaferrite devices, including phase shifters, circulators, and isolators, operate at millimeter wavelengths.⁴ However, when considering film devices for monolithic microwave integrated circuits (MMICs), the high temperature (>900 °C) and high oxygen pressure required to grow hexaferrites degrade most semiconductor substrates. The spinel ferrite films are grown at comparatively lower temperatures and oxygen pressures making them potentially suitable for integration with semiconductor platforms. In this letter, we explore the ability to enhance magnetic anisotropy in MnFe_2O_4 films allowing them to be considered for MMIC applications at or beyond X-band frequencies.

The low magnetic anisotropy in bulk manganese ferrite can be attributed to the ⁶S ground state of manganous (Mn^{2+}) and ferric (Fe^{3+}) ions and the cubic crystalline symmetry. As $L=0$, the ⁶S state results in a small single ion anisotropy term in the spin Hamiltonian. For example, the cubic anisotropy coefficient of Fe^{3+} on the octahedral site [$a(\text{Fe}^{3+})$] was measured to range from 2.0 to 5.75×10^{-2} cm⁻¹, and its uniaxial anisotropy coefficient [$D(\text{Fe}^{3+})$] has values from

–0.2442 to –0.3402 cm⁻¹ (see Ref. 5). Further, the first order contribution of D to K_1 vanishes when summing over a unit cell with high crystalline symmetry (i.e., cubic).⁶

Here we report the processing, structure, and magnetic properties of MnFe_2O_4 films grown using a variant of the pulsed laser deposition (PLD) technique. In the processing scheme used here, MnFe_2O_4 films were grown by sequentially ablating (using a KrF excimer laser at a wavelength of 248 nm and an energy of 400 mJ per pulse) binary oxide targets (i.e., MnO and Fe_2O_3) at ratios that result in the control of local chemistry and structure. The thickness of each layer was controlled by adjusting the laser energy and the number of laser pulses incident upon the targets. The ratio of MnO to Fe_2O_3 laser shots was varied from 1:10 to 6:10, with a ratio of 4:10 resulting in magnetization values most closely matching the bulk value. The oxygen pressure was varied from 1 to 50 mTorr in depositions on (100) MgO single crystal substrates. Twice the lattice constant of MgO, $a_{\text{MgO}} = 4.216$ Å,⁷ nearly matched that of MnFe_2O_4 , $a_{\text{MnFe}_2\text{O}_4} = 8.511$ Å,¹ resulting in a lattice mismatch of 0.94%. The thermal expansion coefficients, $\delta_{\text{MgO}} = 1.26 \times 10^{-5}/\text{K}$ ⁷ and $\delta_{\text{MnFe}_2\text{O}_4} = 1.2 \times 10^{-5}/\text{K}$,¹ are within 5%, causing little strain in the resulting films. The temperature of the substrate during deposition was held fixed at 700 °C.

X-ray diffraction θ - 2θ scans, using Cu $K\alpha$ radiation, were performed to identify the phases in the films and to explore the degree of crystal texture. The results, illustrated in Fig. 1, show that the films have a high degree of crystal texture consistent with the epitaxial growth on MgO. In these films only the $\{0,0,4n\}$ peaks of the spinel phase are observed. Hexagonal phases that can provide high magnetic anisotropy have been ruled out.

In order to explore the short range order structure and cation distribution, select samples were subjected to extended x-ray absorption fine structure (EXAFS) measurements and modeling. Data collection was performed using beamline X23B at the National Synchrotron Light Source in fluorescence yield at room temperature as the storage ring

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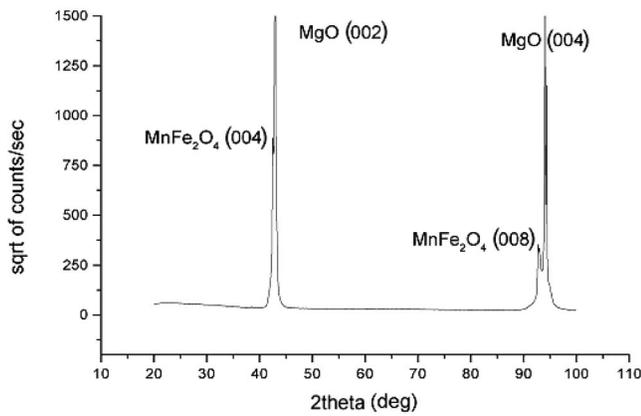


FIG. 1. X-ray diffraction θ - 2θ scans, using Cu $K\alpha$ radiation, acquired from a MnFe_2O_4 film deposited on a (100) MgO substrate at an oxygen pressure of 1 mTorr.

energy was 2.54 GeV and the ring current ranged from 180 to 250 mA. EXAFS determination of cation distribution in spinel ferrites was first performed by Harris *et al.* in 1996.⁸ This approach has been extended by Calvin, who in 2002 performed the first multi-edge corefinement of the spinel structure.⁹ Both Harris *et al.* and Calvin *et al.* made use of theoretical standards generated by FEFF codes of Rehr, Zabinsky, and Albers¹⁰ together with the well established EXAFS refinement procedures outlined by Sayers and Bunker in Ref. 11. Here the Mn and Fe K absorption edges were co-refined using the Athena and Artemis codes of Ravel¹² and Newville,¹³ respectively, to determine the cation distribution of samples produced under different oxygen pressures. Figure 2 is a plot of representative best fit data for both Mn and Fe EXAFS. The EXAFS-determined fitting parameters are listed in Table I. With increasing oxygen processing pressure, the octahedral site occupancy of manganese ions increases from 32% to greater than 50%. This is compared with the bulk equilibrium distribution of 20%.¹ Correspondingly, the Fe octahedral occupation reduces from 84% to 75%. We contend that cation disorder plays a significant role in determining the magnitude and alignment of the magnetic anisotropy field.

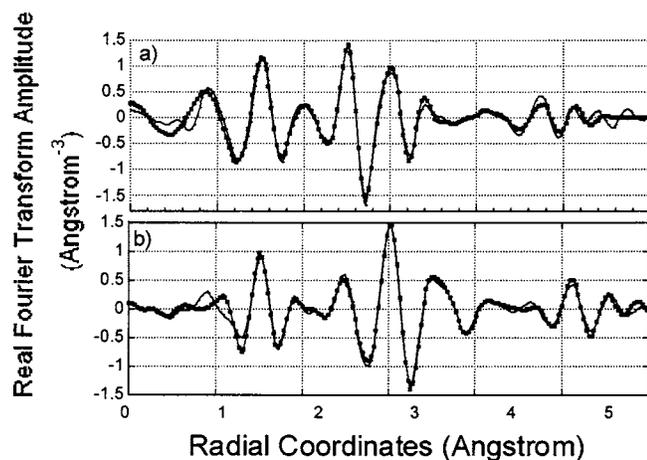


FIG. 2. EXAFS data as the real part of the Fourier transform from Mn (a) and Fe (b) K-edge absorption (solid curve) with best fit data (symbols) for a MnFe_2O_4 film deposited on a (100) MgO substrate at an oxygen pressure of 1 mTorr.

TABLE I. Results of fitting EXAFS data to a theoretical standard. Uncertainties in the least significant digit are given in parentheses.

	1 mTorr	5 mTorr	20 mTorr	Bulk
Lattice parameter (Å)	8.481(2)	8.526(2)	8.492(2)	8.511
Oxygen parameter	0.3913(8)	0.393(1)	0.3953(6)	0.3846
Octahedral (%)				
Manganese	31.9(3.3)	29.78(3.8)	48.82(2.8)	20
Iron (calculated)	84.0	84.8	75.6	90
R factor	0.04	0.05	0.02	—

The magnetic anisotropy field in the films was measured by perpendicular ferromagnetic resonance (FMR) using an X-band TE₁₀₂ rectangular cavity at room temperature. The FMR condition can be written as

$$\omega/\gamma = H - H_a - 4\pi M_S, \quad (1)$$

where ω is the radial frequency, γ is the gyromagnetic coefficient, H is the external magnetic field, H_a is the total magnetic anisotropy field, and M_S is the saturation magnetization. M_S was independently determined by vibrating sample magnetometry (Fig. 3). H_a in Eq. (1) is called the total magnetic anisotropy field since it includes both uniaxial (growth induced) and a small cubic contribution ($-2K_1/M_S = 180$ Oe at room temperature). To verify that the cubic contribution is small, we also measured the in-plane angular variation of FMR. We clearly observed large uniaxial anisotropy in the (100) films (Fig. 4). The cubic contribution deduced from in-plane FMR is on the order of 350 Oe, which is small compared to the measured anisotropy field except for films grown at $5 \text{ mTorr} < p_{\text{O}_2} < 15 \text{ mTorr}$ (i.e., in the region near the spin reorientation pressure). When the oxygen pressure used in PLD was 1 mTorr, the uniaxial anisotropy field was 5.4 kOe. Following the definition of H_a in Eq. (1), the positive sign of the uniaxial anisotropy field implies that the film plane is the preferential plane of the magnetization. When the oxygen pressure was increased, the uniaxial anisotropy field decreased and changed sign to negative values signaling a spin reorientation to perpendicular anisotropy (i.e., preferential direction of the easy axis of magnetization normal to

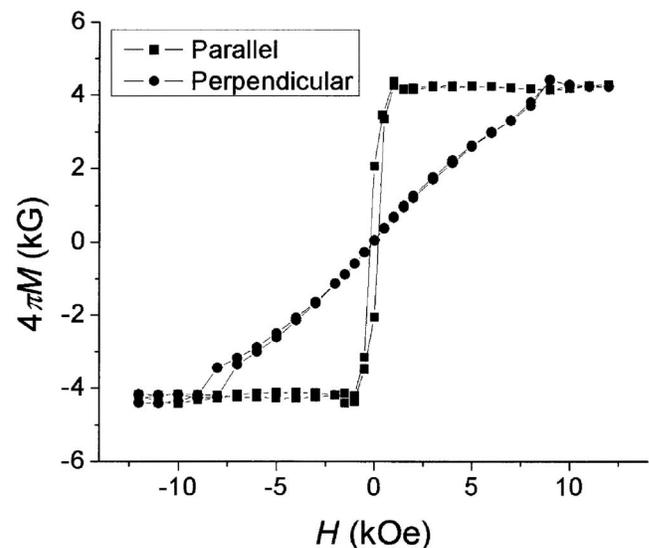


FIG. 3. Hysteresis loop (M vs H) acquired from a MnFe_2O_4 film deposited on a (100) MgO substrate at an oxygen pressure of 1 mTorr.

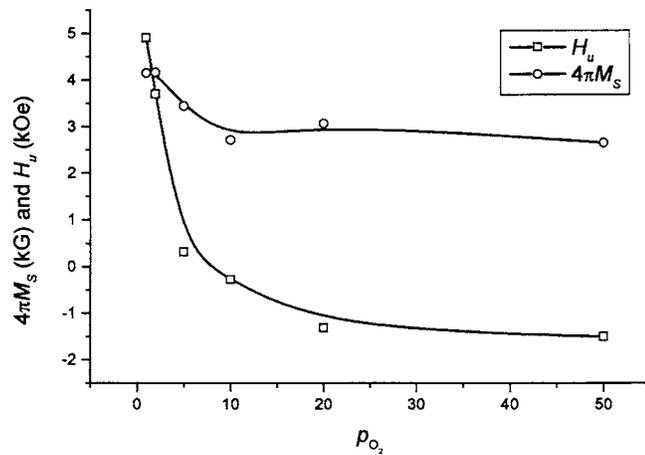


FIG. 4. Uniaxial magnetic anisotropy field (H_u) and saturation magnetization ($4\pi M_s$) as functions of oxygen pressure used in PLD growth.

the film plane). Uniaxial magnetic anisotropy fields with easy axes perpendicular to the film plane were measured to be as high as 1.5 kOe. The crossover point from in-plane to out-of-plane easy axis of magnetization occurred at an oxygen pressure near 8 mTorr.

As the oxygen pressure was increased from 1 to 50 mTorr there were significant changes in the physical state of the films that resulted in an enhancement of the amplitude and orientation of the magnetic anisotropy. We propose that at the low oxygen pressures ($p_{O_2} < 5$ mTorr), anion defects arise from the incomplete oxidation of cations on the surface of the growing film. These defects lead to a greater occupation of Fe^{2+} on the octahedral sites providing large contributions to anisotropy constant (K_u) from a single ion anisotropy mechanism. As oxygen pressure increases ($5 \text{ mTorr} < p_{O_2} < 15$ mTorr), anion defects are reduced and the measured magnetic anisotropy is comparable in magnitude to that arising from cubic magnetocrystalline and stress-induced mechanisms. At pressures ~ 8 mTorr, K_u changes sign and the easy axis of magnetization aligns perpendicular to the film plane (i.e., a spin reorientation transition). At higher pressures the ions in the ablated flux experience more collisions en route to the substrate reducing their kinetic energy and subsequently reducing their mobility on the surface of the growing film. This lack of mobility leads to the freezing in of cation disorder (in the case of $MnFe_2O_4$ this results in the inversion of Mn cations). As noted earlier, EXAFS measurements provide a direct measure of this effect. In Table I the Mn inversion coefficient, δ , [defined as $(Mn_{1-\delta}Fe_\delta)^{tet}[Mn_\delta Fe_{2-\delta}]^{oct}O_4$] increased from 0.30 at $p_{O_2} = 1$ mTorr to >0.50 at $p_{O_2} = 20$ mTorr. Another interesting trend seen in the EXAFS analysis is the increase in the oxygen displacement parameter (commonly denoted by u). An increase in u signals a local distortion of the tetrahedral sublattice.² This often leads to a reduction in space group symmetry of the unit cell. We speculate that this distortion is a consequence of the local strain caused by the cation disorder and is responsible for the induced uniaxial perpendicular

anisotropy and spin reorientation via magnetocrystalline anisotropy. (Jahn–Teller distortions from Mn^{3+} ions cannot be ruled out as a contributing mechanism.)

In summary, we have demonstrated that alternating target—PLD processing of $MnFe_2O_4$ films on (100) MgO substrates results in large growth induced uniaxial anisotropy fields either in the film plane or perpendicular to it depending upon the oxygen pressure used in processing. The spin reorientation is measured to occur at a processing pressure of 8 mTorr. We propose a phenomenological model that describes the physical and magnetic mechanisms that are responsible for the large induced uniaxial anisotropy. At low pressures (< 5 mTorr) anion defects lead to an increase of Fe^{2+} cations resulting in large single ion anisotropy contribution to the total anisotropy field. For $p_{O_2} > 15$ mTorr, cation disorder leads to a distortion from cubic symmetry. As the crystal symmetry is lowered from cubic, the contribution of the magnetocrystalline component to the uniaxial anisotropy is increased. The unique magnetic anisotropy in these spinel films makes them promising candidates for MMIC applications at or above X-band frequencies and may prove suitable for future semiconductor integration.

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