

Pulsed Laser Deposition as a Novel Growth Technique of Multiferroic LuFe₂O₄ Thin Films

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ABSTRACT

Growth of polycrystalline Lutetium Iron Oxide via pulsed laser deposition in thin film form is reported for the first time herein, and the multiferroic LuFe₂O₄ phase is stabilized. Fluence and pressure dependent phase growth is demonstrated, along with crystalline structure in vacuum ($\sim 10^{-5}$ torr) conditions. Thermodynamic considerations at the laser-target interaction were investigated, as well as at the plume-substrate interface, which reveal that the necessary Gibbs free energy is available in the optimized growth environment to allow formation of the LuFe₂O₄ polycrystalline phase. The resulting growth rate is found to be related to the Gibbs free energy and concentration of nucleation sites on the substrate. Characterization of the multiferroic aspect of LuFe₂O₄ entailed direct measurement of the ferroelectricity in the thin film, as well as magnetic behavior, both at various temperatures. In particular, the ferroelectric polarization vs. voltage data yield values of 0.61 $\mu\text{C}/\text{cm}^2$ at 300 K to 3.29 $\mu\text{C}/\text{cm}^2$ at 183 K; moreover, these data are in agreement with those reported in the literature. Magnetization vs. applied field data shows the magnetization at 300 K to be 180 emu/cm^3 and increasing to 200 emu/cm^3 at 10 K.

INTRODUCTION

Pulsed laser deposition (PLD) was used as a novel approach to deposit thin films of the target material on heated substrates in order to realize the hexagonal LuFe₂O₄ phase. Thin films of LFO have not heretofore been reported or characterized, nor does the literature contain information regarding the use of PLD for LFO thin film deposition. For the purposes of this work thin films will be defined as in ^[1], i.e. the thin film regime begins at $t_{film} < 500$ nm. PLD is superior to other conventional thin film deposition techniques such as ion beam sputtering, magnetron sputtering, and molecular beam epitaxy due to having several orders of magnitude ^[2] larger affinity towards producing stable nucleation sites.

EXPERIMENT

§1. Laser-target interaction

A LuFeO₃ target was used in the PLD process to make thin films of LuFe₂O₄. Scanning electron microscopy (SEM) images of the target show the surface features at the Excimer laser-target surface interaction regions (figure 1). The number of pulses per track is on the order of 20,000 shots, the repetition rate = 10 Hz, the rate of rotation is 23 rpm, and the difference between the outer and inner diameter of each track is 3 mm. Utilizing multiple tracks on the target allows for a uniform surface deformation on the target, which ultimately admits higher

quality thin films. Figure 1a reveals the surface features and grain sizes for the non-ablated central region of the target, and 1b an ablated region with an inset at 1000 times magnification to show the target surface morphology. The directional cones form as a result of repeated track use; the aggregate effect is the plasma velocity vector increasingly aligns with the incident Excimer pulse due to the increased electric field formed at a sharp corner^[4]; i.e. $E(d) \sim \sqrt{d}$ where d is the sheet thickness around the smooth conical edge.

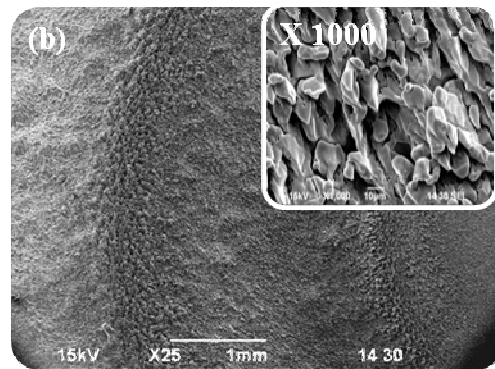
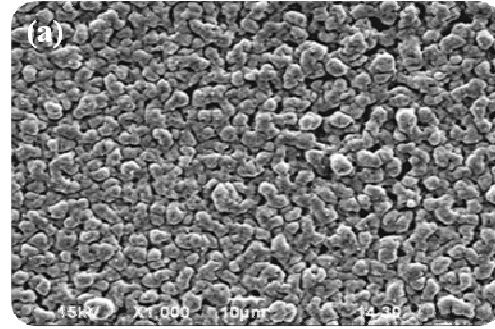
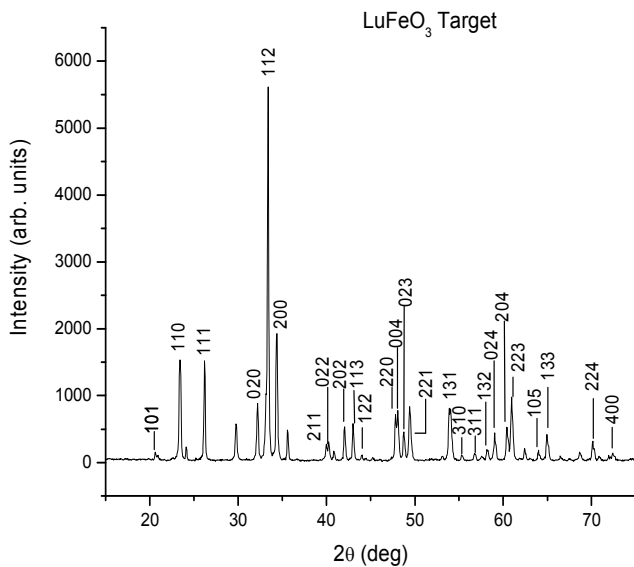


Figure 1: XRD analysis of the target shows the stoichiometric phase^[3] LuFeO₃. (a) The central unablated region of the target. (b) An ablation track with the conical structures inset.

§2. Crystalline growth of lutetium iron oxide

Crystalline growth of LFO on a Si substrate via PLD depends on many parameters including energy, the degree to which the target material is ionized, temperature at the substrate, and the ambient O₂ pressure in the growth chamber. Through a series of fluence, temperature, and pressure studies the optimal growth conditions for the formation of the LuFe₂O₄ phase were found to be a minimum O₂ ambient and a large amount of ionization energy. The XRD for P = 10⁻⁵ torr over several high fluences is shown in figure 2.

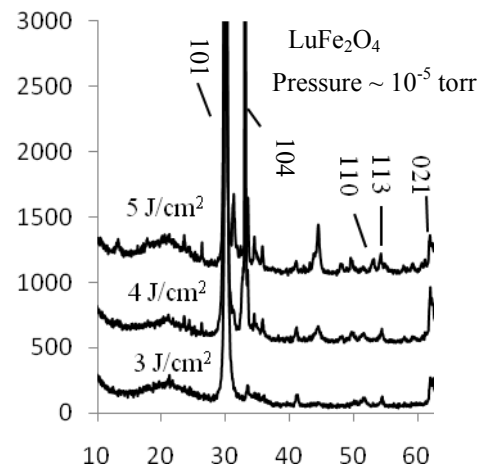


Figure 2: XRD of LuFe₂O₄ deposited via PLD.

§2.1 LuFe₂O₄ growth related to thermodynamics

The Gibbs free energy at the plasma-substrate interface dictates the formation (or lack thereof) of nucleation sites and hence phase growth; in turn the partial oxygen pressure influences the ability for such sites to form and accumulate. The relationship between the changing O₂ pressure and the standard molar Gibbs free energy^[7, 16] is governed by the relation

$$\Delta G^0 \propto RT \ln P(\text{O}_2). \quad (1)$$

Refer to Table 1 for the tabulated free energies for three phases of LFO. Thermodynamic considerations follow which focus on the plasma with high kinetic energy (v_{plasma} is on the order of 10^4 m/s^[8, 9]) at the heated (650 °C) silicon substrate.

Table 1: Gibbs free energy for three phases of LFO.

Tabulated ^[14] Gibbs Free Energy ΔG^0 (kJ)		
LuFeO ₃ perovskite phase	LuFe ₂ O ₄ hexagonal phase	Lu ₃ Fe ₅ O ₁₂ garnet phase
-130.30	-44.64	-8.07

Noting that for $\Delta G^0 < 0$ a reaction is favorable by the second law of thermodynamics, the LuFeO₃ phase will tend to form before the LuFe₂O₄ phase since $\Delta G^0_{\text{LuFeO}_3} < \Delta G^0_{\text{LuFe}_2\text{O}_4}$ ^[Table 1]. According to Eq. 1 in order for the LuFeO₃ phase to form at a partial pressure $P(\text{O}_2) = 10$ mtorr the required free energy is $\Delta G^0 = -64.68$ kJ/mol, while for the LuFe₂O₄ phase $\Delta G^0 = -21.56$ kJ/mol. The trend in the free energies ($\Delta G^0_{\text{LuFeO}_3} < \Delta G^0_{\text{LuFe}_2\text{O}_4}$) continues for each increase in ambient oxygen pressure.

§ 2.2 LuFe₂O₄ growth and thermodynamics

The LuFe₂O₄ phase has well coordinated growth in multiple planes over the entire range of fluences investigated; however the O₂ pressure dependence is distinct from the LuFeO₃ phase. Interestingly, for relatively high fluences $F = 4$ J/cm² to $F = 5$ J/cm² with chamber pressure on the order of low 10^{-5} torr (vacuum) multiple XRD peaks are exhibited, from which one may conclude that the ablated material contains enough volatile oxygen to facilitate the LuFe₂O₄ phase growth. Conversely, for every order of magnitude of 1 – 1000 mtorr, all peaks of this phase are suppressed, pointing to the sensitivity of this phase's growth in an O₂ environment. Thus, the oxide LuFe₂O₄ thrives in an energy rich, O₂ deprived environment in the PLD process. This result has tremendous up-scaling potential for industrial application as single phase LuFe₂O₄ has multiple proven electronic^[17] and magnetic^[18] properties.

§3. Growth rate

Using LFO in future device construction requires an investigation of the growth rate with respect to the various parameters explored. To that end an initial study of the growth rate as a function of the fluence is plotted for various pressures (see figure 3). The curves are each fitted and truncated to include only the two highest dominant terms. For pressure in the range 1 mtorr to 100 mtorr the growth rates follow a cubic relation at high fluence, with no sign of saturation; the implication being for those pressures additional energy will improve film growth rate. One must consider an opposing effect: there exists a threshold in escalating energy

at the laser-target interaction area which will effectively decrease film quality. Essentially, large amounts of ablated material will eject from the target which are either not fully ionized [6]; or in the case of a metallic material the highly energized electrons will effectively reflect the incoming high energy laser pulse, versus a ceramic type material which would require fluences which are beyond the experimentally operational conditions of the PLD process used in this study. Therefore, even the relatively low 1 mtorr to 100 mtorr range the optimum laser fluence is not tractable for the PLD chamber used in this study. However, in vacuum especially, in the experimentally realizable fluence region of 4 J/cm² to 5 J/cm² there is saturation of 0.8 Å/pulse in the growth rate.

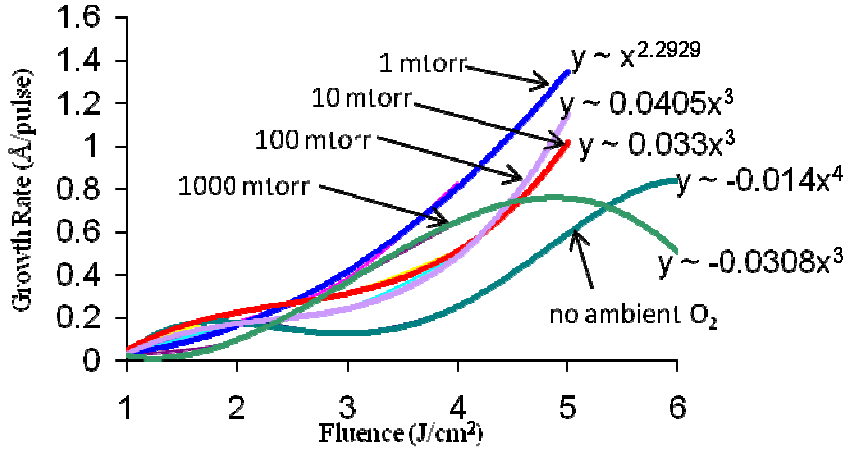


Figure 3: Growth rates as a function of energy density at the target. Various ambient O₂ environments were studied, as well as vacuum.

§3.1 Theoretical growth rate considerations

As an approximation the growth rate can be defined as the product [6]

$$R_{\text{growth}} = R_{\text{arrival}} \cdot C_{\text{nuclei}}$$

where R_{arrival} is the arrival rate of critical sized nuclei, and C_{nuclei} is the concentration of critical nuclei. C_{nuclei} relates to the Gibbs free energy $\Delta G^0 \propto RT \ln P(\text{O}_2)$ through [6]

$$C_{\text{nuclei}} \propto e^{\frac{-\Delta G^0}{kT}} \quad (2)$$

with the partial pressure $P(\text{O}_2)$ evaluated in atm. Noting that all O₂ pressures under consideration are in the millitorr range, and hence all $P(\text{O}_2)$ in atm are between zero and unity, the mathematical trend is for increasing ambient O₂ pressures to yield strictly increasing ΔG^0 whose values are negative due to the range of the natural logarithm function. The growth rate is inversely proportional to the ambient O₂ pressures as revealed by

$$R_{\text{growth}} \propto C_{\text{nuclei}} \propto e^{\frac{-\Delta G^0}{kT}} \propto e^{\frac{-RT \ln P(\text{O}_2)}{kT}} \approx \frac{1}{P(\text{O}_2)}. \quad (3)$$

R_{growth} also depends on [10] $R_{\text{arrival}} \propto P(\text{O}_2)^{-1/3} \ll P(\text{O}_2)^{-1}$ in the millitorr range, hence, the dominant consideration is in the C_{nuclei} term. Therefore, the growth rate is inversely proportional to the partial oxygen pressure, which indicates that additional levels of O₂ hinder the growth rate. These analyses elucidate the fact the LuFe₂O₄ phase is realized as opposed to the perovskite

LuFeO₃ phase in the low pressure regime. However, increasing levels of O₂ correspond to depreciating R_{growth} for fluences above 2.5 J/cm² (see figure 3). In the range of fluence below 2.5 J/cm² reported growth rates are on the order of 1 Å/pulse^[11, 12, 13], which again coincide with all of the experimental pressures (including vacuum) included in this study.

§4. Magnetic and electric polarization

Bulk material of LuFe₂O₄ (LFO) is known to exhibit multiferroic character; as such an investigation of the magnetic and electric polarization in thin films of LFO began as an effort to search for device applicable properties. Room temperature magnetic hysteresis was found with a saturation magnetization of 180 emu/cm³. The 10 K magnetic hysteresis follows. A room temperature electric polarization was found to be 0.61 μC/cm² (see fig. 4). The low temperature (183 K) polarization was found to be near 3.29 μC/cm². The increased polarization may be due to the reduced leakage current as the film became more resistive at low temperature.

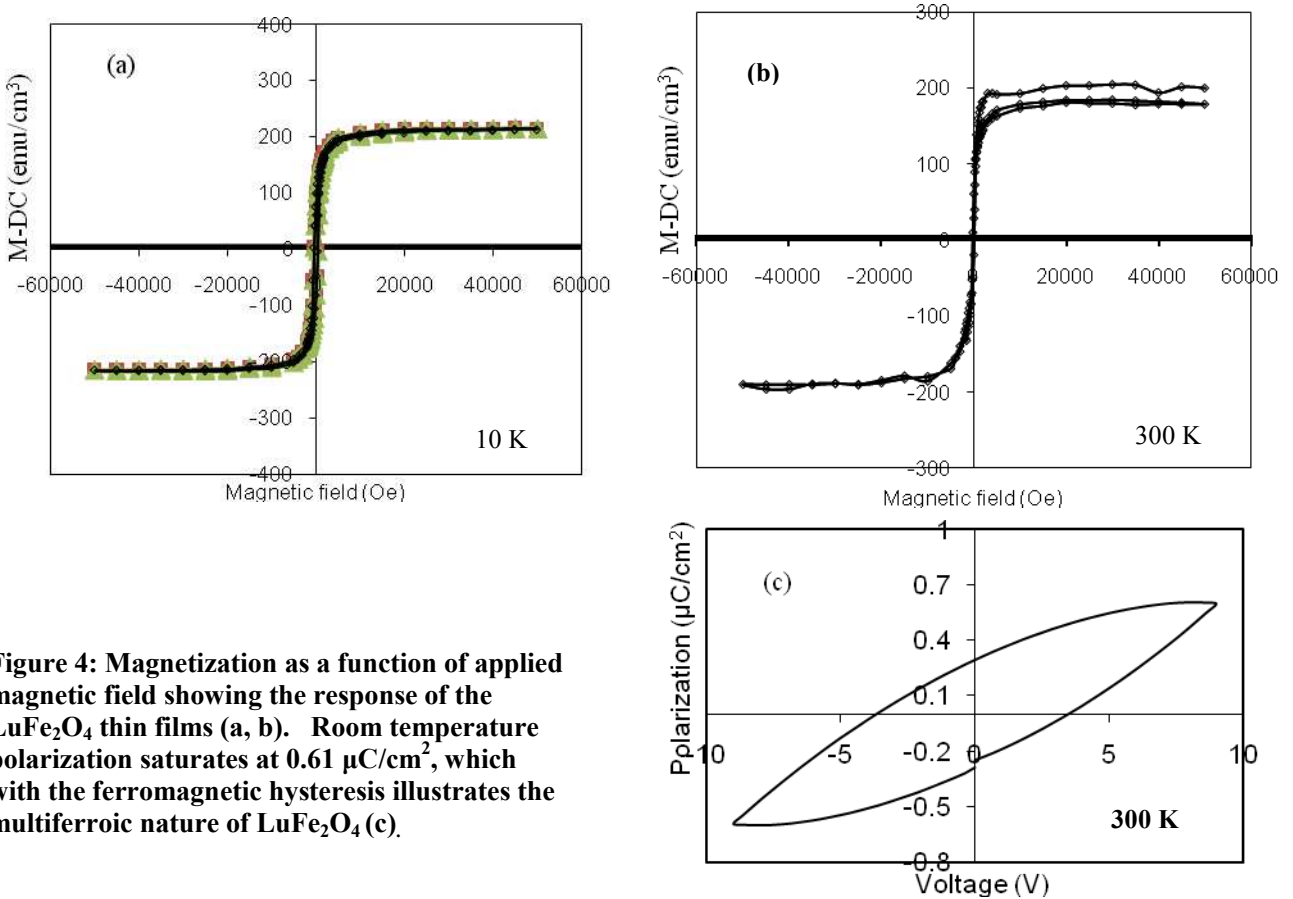


Figure 4: Magnetization as a function of applied magnetic field showing the response of the LuFe₂O₄ thin films (a, b). Room temperature polarization saturates at 0.61 μC/cm², which with the ferromagnetic hysteresis illustrates the multiferroic nature of LuFe₂O₄ (c).

CONCLUSIONS

In conclusion, the parameters for growth of polycrystalline LuFe₂O₄ have been explored in a novel manner using pulsed laser deposition. Thermodynamic analyses in the pertinent regimes of experimental capability indicate the availability of adequate Gibbs free energy for the growth process to occur in a pulsed laser technique; moreover, the transition from one chemical

composition to another (LuFeO_3 to LuFe_2O_4) can be accomplished. The growth rate dependence on Gibbs free energy and ambient O_2 pressure are then explored, and an inverse proportionality is established with respect to the latter. Most importantly, the fascinating rare Earth oxide LuFe_2O_4 is now realizable in the thin film form, and the multiferroic character has been elucidated, allowing the potential device applications to be explored.

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