Deposition of Lu-Fe-O thin films on silica glass substrates by MOCVD

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Abstract. Thin films of the Lu-Fe-O system were deposited by aerosol assisted MOCVD on silica glass substrates. Hexagonal $h$-LuFeO₃, garnet Lu₃Fe₅O₁₂, perovskite $o$-LuFeO₃ or hematite Fe₂O₃ phases were obtained, depending on the thermodynamic deposition conditions or post annealing temperature. Magnetic measurements confirm the ferromagnetic behaviour at room temperature of the thin films with garnet phase. An indirect bandgap of 1.78 eV was measured.

1 Introduction

Recently, the Lu-Fe-O system has received a great deal of attention due to the multiferroic properties of several phases of the system [1, 2]. The garnet phase, Lu₃Fe₅O₁₂, besides being ferromagnetic at room temperature, presented magnetodielectric effect [3]. The hexagonal LuFeO₃ phase shows multiferroic properties at room-temperature [4].

The $\frac{1}{2}$Lu₂O₃-$\frac{1}{2}$Fe₂O₃-FeO phase diagram is presented in figure 1a), following the sketches by Sekine [5], Kumar [6] and Wang [7]. According to this diagram it is important to consider the mixed valence states Fe(II)/Fe(III), adjustable by oxygen partial pressures during sample preparation. With higher oxygen partial pressures there are the Fe₂O₃ (hematite) and Lu₂O₃ terminal phases, plus the intermediate Lu₃Fe₅O₁₂ (garnet), $o$-LuFeO₃ (orthorhombic perovskite) and $h$-LuFeO₃ (hexagonal). The LuFeO₃ structure exhibits distortion from ideal perovskite due to the small ionic rare earth radius. This compound has two different structures: a stable Pnma orthorhombic perovskite ($o$-LuFeO₃) and a metastable hexagonal phase $P6_{3}cm$ ($h$-LuFeO₃). Decreasing the oxygen partial pressure, the phases Fe₃O₄ (magnetite), LuFe₂O₄ and Lu₂Fe₃O₇ appear. The other terminal phase of this diagram is FeO. The LuFe₂O₄ and Lu₂Fe₃O₇ phases are also metastable [7]. Peritetic decompositions of these phases give rise to $o$-LuFeO₃ and Lu₃Fe₅O₁₂ [8].

Wang suggests a Van't Hoff diagram for this system, as a result of his studies during PLD deposition of thin films on MgO (111) substrates [7]. According to this diagram it would be possible to obtain a mixture between the $h$-LuFeO₃ and LuFe₂O₄ phases by controlling the oxygen partial pressure around 2.7×10⁻⁵ mbar at 900°C.

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In the present study, we have deposited thin films of the Lu-Fe-O system, with different compositions and at different temperatures, by MOCVD, on silica glass substrates. These substrates are much less expensive than the traditional monocrystalline ones, like sapphire, YSZ, MgO, SrTiO$_3$ or LaAlO$_3$, among others. However, no epitaxy effects, enhancing the growing of a specific phase, are expected. The films were post annealed in air at increasing temperatures to investigate the thermodynamic stability of the phases. Structural characterizations were performed by X-ray diffraction. Further characterizations were performed by magnetic and optical measurements.

2 Experimental procedures

In the deposition of thin films by MOCVD[9], metalorganic precursors, Lu(tmhd)$_3$ and Fe(tmhd)$_3$, were synthesized from tmhd (2,2,6,6-tetramethyl-3,5-heptanediione) using the method described by Eisentraut and Severs [10] and purified by sublimation. These precursors were dissolved in bis-2-methoxyethylether (concentration from 2.5 up to 8.5 µM) and ultrasonic nebulized at 810 kHz to produce an aerosol with 3 µm mean-particle diameter. Argon was used as a carrier gas (40 mL/min) and heated at 260 °C to volatilize both solvent and metalorganics. Preheated oxygen (160 mL/min) was also mixed. The substrates were glued to the stainless-steel susceptor using silver paste and induction heated between 500°C and 850°C. Total pressure was 9 mbar (1.8 mbar of argon and 7.2 mbar of oxygen). The deposition time was 1 hour to produce a film thickness around 250 nm.

X-ray diffraction patterns were acquired on a Panalytical X’Pert Pro MPD equipped with a X’Celerator detector and secondary monochromator, in Bragg-Bentano geometry. A CuKα wavelength, with $\lambda=1.5418\text{Å}$, a step size of 0.017° with 100s/step was used. Rietveld refinement of the diffractograms was performed using PowderCell software [11], allowing phase quantification.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) were performed using a FEI Quanta 400 with W filament and EDAX system respectively.

Thermal treatments of the films were conducted on a tubular oven with a calibrated K thermocouple located just above the thin film.

The UV/Vis transmission spectra of the thin films were acquired using LLG UNISpec 2, from 200 up to 1100 nm. Direct and indirect bandgaps were calculated through Tauc plots [12, 13].

The UV/Vis spectra were simulated using the Swanepoel model [14] to obtain the film thickness, refractive index and absorption coefficient. According to this model, the experimental $T(\lambda)$ transmittance spectrum obtained for a thin film depends on the optical properties of the film and substrate.

Magnetic measurements were conducted using a SQUID Magnetometer from Quantum Design MPMS3, with a superconductor coil of up to 7 Tesla and temperatures from 1.8K up to 400K.

3 Results and discussion

In this work we selected four compositions of the Fe(III) part of phase diagram of fig. 1a), to perform depositions by MOCVD. These compositions are marked as A, B, C and D in fig. 1b). Composition A corresponds to Fe$_2$O$_3$, composition B to a region between Fe$_2$O$_3$ and Lu$_3$Fe$_5$O$_{12}$, region C to Lu$_3$Fe$_5$O$_{12}$ and composition D to a region between Lu$_3$Fe$_5$O$_{12}$ and LuFeO$_3$. 
Fig. 1 – a) Phase diagram of the ½ Fe₂O₃-½ Lu₂O₃-FeO system [5-7]; b) Fe(III) region of the Lu-Fe-O phase diagram representing the composition of the deposited films.

3.1 Films with composition A

The composition A corresponds to films deposited by MOCVD using only Fe(tmhd)₃ as metalorganic precursor. In fig. 2 a) we present the X-ray diffraction patterns of the films as deposited at temperatures from 500 up to 750°C together with expected diffraction pattern of Fe₂O₃ hematite [15]. The wide peak around 22° is due to the silica glass substrate. The (104) peak of hematite, the most intense one, appears as early as 500°C indicating that phase formation starts at this temperature. The (110) peak, the second most intense, appears at 650°C indicating a well crystallized phase. As expected from a deposition on an amorphous substrate, no preferable orientation is observed. At higher deposition temperatures no substantial changes in the diffraction patterns can be seen.

3.2 Films with composition B

The composition of these films is in the Lu/(Lu+Fe)=0.2-0.3 (atomic) range, below the garnet composition of Lu/(Lu+Fe)=0.375. In fig. 2 b) we see that a thin film deposited at 700°C is amorphous. Ex-situ thermal treatment at 850°C during 1 hour, promotes the crystallization of the film yielding mainly hexagonal h-LuFeO₃ phase and traces of garnet and hematite phases. At 900°C the h-LuFeO₃ phase starts to decompose and no traces of this phase is found at 950°C. In the opposite way, the garnet and hematite phases dominate at these temperatures, according to what is expected from the analysis of the phase diagram of fig. 1. However, some peaks of perovskite phase can also be detected, probably due to the peritectic decomposition of the hexagonal phase, indicating that the film is not in thermodynamic equilibrium. A small peak at 21.8° is due to the crystallization of the silica glass substrate into cristobalite phase [16].

3.3 Films with composition C

The composition of this film match the Lu/(Lu+Fe)=0.375 atomic ratio and was deposited by MOCVD at 800°C and consecutively thermal treated ex-situ at 825°C and 850°C during 1 hour. The corresponding diffraction patterns are displayed in fig. 2 c). At 800°C the film is mainly amorphous, with a trace of a broad (004) peak of h-LuFeO₃ phase at 30.9° and a narrow garnet Lu₁₁Fe₅O₁₂ phase (420) peak at 32.7°. The thermal treatment at 825°C promotes the crystallization of the garnet phase, which is well crystallized at 850°C.

3.4 Films with composition D

A film with Lu/(Lu+Fe)=0.4 atomic ratio was deposited at 700°C and consecutively thermal treated with 50°C steps, during 1 hour, up to 1000°C (fig. 2d). The as-deposited film was mainly amorphous with an incipient (004) peak of the hexagonal phase at 30.8°. The crystallization of this phase occurs at 800°C with the appearance of the (002) peak at 15.2°. At 900°C the hexagonal phases decomposes and the garnet and perovskite phases
crystallized. At 1000°C a new phase appears, monoclinic Lu₄Si₄O₁₄ [17], resulting from the interdiffusion of the lutetium to the substrate.

The X-ray diffraction patterns were deeply analysed by Rietveld refinement, allowing phase quantification. The silica glass structure was simulated by Le Bail method [18]. The results are displayed in fig. 3 a). To go deeper into the phase formation, the results of the Lu-Fe-O phases (hexagonal, garnet and perovskite) were normalized to 100% and plotted in fig. 3b). In this figure, we observed the decomposition of the hexagonal phase between 900 and 950°C and at the same time the increase of the garnet and perovskite phases.

![Figure 2](image2.png)

**Figure 2** – Temperature effects on the X-ray diffraction patterns of thin films deposited by MOCVD with different compositions: a) Composition A; b) Composition B; c) Composition c); Composition d).

![Figure 3](image3.png)

**Figure 3** – Phase quantification results from Rietveld refinement of film with D composition; a) results with all identified phases including silica glass amorphous substrate; b) normalized results with only the Lu-Fe-O phases.

### 3.5 Magnetic measurements

For the film with composition B, thermal treated at 900°C, presenting the garnet phase, we have measured the temperature dependence of magnetization M(T) at 100Ωe magnetic field, with increasing temperature up to 400 K, after a zero field cool down to 3.6 K (fig.
For this measurement we have considered a film thickness of 283 nm, determined by the Swanepoel model (fig. 5a), a substrate dimension of 5.9x5.9 mm², therefore a volume of 9.85x10⁶ cm³. An average density of 6.122 g/cm³ was estimated, resulting in a 6.0x10⁻⁷ g film mass. The film presents a magnetization of 3.4 emu/g at 4K and 2.5 emu/g at room temperature. The Curie temperature is clearly well above 400K. Previous published results of the Lu₃Fe₂O₁₂ phase indicate that Curie temperature is around 550 K [19].

\[
M(H) = M_s - M_s \frac{H}{H_c} \left(1 + \frac{H}{H_c} \right)
\]

for the ferromagnetic loop, made at room temperature, is presented in fig. 4b). A typical soft ferromagnetic loop is observed, with a small contribution from a diamagnetic phase due to the silica glass substrate. No exchange bias is detected. The coercive field is \(H_c=85\,\text{Oe}\). A saturation magnetization of \(M_s=4.2\,\text{emu/g}\) was measured, which is 30% of the reported value of 14 emu/g for a pure phase ceramic sample [20]. The amount of the garnet phase calculated by Rietveld refinement from the X-ray diffraction pattern is 29 wt%. We can consider that the hexagonal and the perovskite phases do not contribute to the magnetic moment.

\[
M_0 = M_{sat} = 4.2\,\text{emu/g}
\]

at 300K. a) \(M(T)\) at 100\,\text{Oe}; b) \(M(H)\) at 300K.

3.6 Optical measurements

The UV/Vis spectra of the films were simulated by the Swanepoel model. As a representative case, in fig. 5a) we present the results obtained with film of B composition. The estimated film thickness is 283±1 nm.

To our knowledge, the band structure is not published for these materials, so we do not know if the transition is direct or indirect. Direct and indirect bandgaps are calculated from Tauc plots in fig. 5b) and 5c) respectively. Heat treatment at 950°C decreases the direct band gap from 2.43 eV (for films deposited at 700°C) to 2.13 eV. These values, for a direct transition, agree with those published for hematite films, around 2.2 eV [21].

In the case of indirect transitions, there are two energies, as indicated by Misho, the highest (1.78 eV) being attributed to the band gap and the lowest (0.95 eV) to the energy required for the phonon. [22].

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4 Conclusions

Thin films of the Lu-Fe-O were successfully deposited by aerosol assisted MOCVD from β-diketones Lu(tmhd)$_3$ and Fe(tmhd)$_3$ on silica glass substrates. Depending on the composition and on the deposition or thermal treatment temperatures, hematite, Lu$_3$Fe$_5$O$_{12}$ garnet, hexagonal LuFeO$_3$ or orthorrombic LuFeO$_3$ perovskite phases are detected on the films by X-ray diffraction. A film with garnet phase presented ferromagnetic behaviour with $M_s$ of 4.2 emu/g and $H_c=85$Oe at room temperature. Optical measurements indicate a direct bandgap transition with 2.13 eV or an indirect bandgap of 1.78 eV.

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