



# Growth and characterization of epitaxial magnesium ferrite thin films



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## ABSTRACT

Epitaxial magnesium ferrite thin films have been grown by molecular beam epitaxy (MBE) on MgO(100). Growth conditions such as substrate temperature and growth rates were optimized. By using different characterization techniques, structural, electrical and optical properties of the films were studied as a function of Mg content. In particular, we highlight the importance of the growth rate on the actual Mg/Fe ratio in the film.

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## 1. Introduction

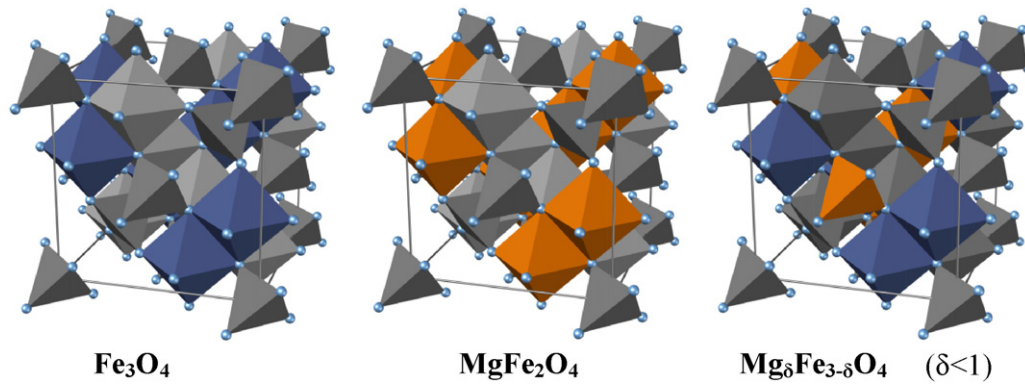
Spinel ferrites are a class of compounds with the general formula of MFe<sub>2</sub>O<sub>4</sub> (where M = Mn, Co, Ni, Zn, Mg etc.). There is a near infinite pool of options for partially substituting cations into this spinel structure (see Fig. 1). This can be represented by the chemical formula M<sub>δ</sub>Fe<sub>3-δ</sub>O<sub>4</sub> where δ can range from 0 to 3, and even multiple alternate cations can be simultaneously inserted, e.g., Mn<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>. Spinel ferrite materials have already been widely used in devices such as transformer cores and microwave magnetic devices for more than fifty years [1,2]. Much research and development in the field of spinel ferrites is still on-going, ranging from studying the basic properties of these materials to their applications. From a more fundamental perspective, epitaxial ferrite films have provided a model system to study the effect of modified super-exchange interaction and cation redistribution [3]. Among the investigated ferrites, magnesium ferrite (MgFe<sub>2</sub>O<sub>4</sub>, MFO) is a soft magnetic n-type semiconductor with a partially inverse spinel structure. The typical degree of inversion is 0.9 but can vary depending on the preparation conditions [4,5]. MFO possesses good chemical stability, and its band gap of ~2.0 eV makes it a suitable candidate for a wide range of applications in heterogeneous catalysis, adsorption, sensors, lithium-ion batteries, and photo electrochemical water splitting [6–10]. Moreover, it has a high Curie temperature, making it interesting for spintronic applications. To date, most studies on MgFe<sub>2</sub>O<sub>4</sub> have focused on its different morphological varieties, such as nanoparticles [6–10] or nanopillars [11]. However, less attention has been paid to epitaxial MgFe<sub>2</sub>O<sub>4</sub> thin films even though they are of great interest from both fundamental and practical perspectives. These thin films, when

fabricated with high epitaxial quality and synthesized at lower temperatures than bulk ceramics, often show significantly different physical properties compared to bulk material [12,13]. The physical properties of magnesium ferrite strongly depend on the site location of the Mg<sup>2+</sup> ions, while the growth techniques as well as processing conditions also play an important role [14–19]. Among the various thin film growth techniques, molecular beam epitaxy (MBE) is very attractive for deposition of high crystalline quality thin film oxides. By varying the individual evaporator temperatures the molecular flux of different species can be accurately controlled, providing a way to alter the composition and doping profile in thin spinel ferrite films. MBE grown magnetite and cobalt ferrite thin films have previously been shown to have excellent magnetic properties [20–23]. In contrast there have been few attempts to grow magnesium ferrite thin films using MBE [5,19,24]. None of these reports have studied the magnesium ferrite thin film physical properties as a function of deposition conditions in detail. In a previous study carried out by some of us, certain properties of epitaxial MgFe<sub>2</sub>O<sub>4</sub> films using the same growth technique and substrate have already been studied [19]. Newly available data, in particular on the stoichiometry of films at reduced growth rate and the optical properties of the films, led to this more comprehensive study, where we will demonstrate that a reduced growth rate primarily alters the film composition rather than solely the thin film strain as previously assumed. Here we will discuss this behavior in terms of the growth process and growth temperature.

## 2. Experimental details

A series of MgFe<sub>2</sub>O<sub>4</sub> films with a thickness of 95 nm were grown on MgO(100) oriented single-crystal substrates with a size of 1 cm<sup>2</sup>.

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**Fig. 1.** Crystal structure of magnetite ( $\text{Fe}_3\text{O}_4$ ), magnesium ferrite  $\text{MgFe}_2\text{O}_4$  and non-stoichiometric  $\text{Mg}_\delta\text{Fe}_{3-\delta}\text{O}_4$ . The spinel tetrahedral A-sites are occupied by  $\text{Fe}^{3+}$  while the octahedral B-sites are occupied by  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  (dark blue). In ideal  $\text{MgFe}_2\text{O}_4$  the  $\text{Mg}^{2+}$  replaces all  $\text{Fe}^{2+}$  octahedral sites (orange). Which B-site is occupied by  $\text{Mg}^{2+}$  and which with  $\text{Fe}^{3+}$  can either be random as illustrated or show a long range order. Additional site disorder can also lead to  $\text{Mg}^{2+}$  occupying the tetrahedral A-sites as illustrated for the non-stoichiometric  $\text{Mg}_\delta\text{Fe}_{3-\delta}\text{O}_4$ .

Substrates were first cleaned in an ultrasonic bath for 15 min in methanol, isopropanol and acetone subsequently. Prior to deposition they were annealed in-situ at 600 °C in an oxygen partial pressure of  $1.7 \times 10^{-3}$  Pa in the molecular beam epitaxy chamber (DCA MBE M600). This system uses e-beam evaporators, where the source material (Kurt. J. Lesker, Iron pellets (EVMFE35QXQ) 99.95% purity; MgO pieces (EVMMGO3-6MMB) 99.95% purity) is locally heated by high energy electrons. The flux of the molecular beam was controlled by varying the power applied to the e-beam evaporators, while the growth rate was measured by a calibrated quartz crystal oscillator for each source. The individual quartz crystal oscillators have been calibrated at our reference rate of 0.6 and 0.3 Å/s by growing  $\text{Fe}_3\text{O}_4$  and MgO reference samples respectively. The resulting thickness was measured by X-ray reflection and the difference between nominal and real thickness is used to adjust the tooling factor of the quartz crystal balance. This calibration procedure is repeated after each vent and/or refill of the e-beam pockets. Metallic Fe and ceramic MgO were evaporated from separate e-beam evaporators in order to grow  $\text{MgFe}_2\text{O}_4$  films. Each source (Fe and MgO) has a dedicated port to house a quartz crystal balance, positioned in such a way that it's shielded from the other sources. To grow stoichiometric oxides from metal sources the growth is assisted by an oxygen plasma from an OSPrey ECR-plasma source operated in an oxygen partial pressure of  $2.6 \times 10^{-4}$  Pa with a current of 30 mA.

To investigate the influence of growth conditions on film properties, the growth rate and substrate temperature were systematically varied (see Table 1). The ratio between the Fe and MgO flux rate was kept at a constant value (of Fe:Mg = 2:1), in order to preserve the nominal cation stoichiometry in the deposited films. Post growth each sample thickness was measured by X-ray reflection and observed deviations from the nominally expected thickness were in the range of 3–10%, with the larger deviations occurring for smaller growth rates.

Despite the similar thickness of all films as confirmed by X-ray reflection (XRR), the films are optically different and show a systematic variation in electrical and magnetic properties upon variation of the

growth rate. To understand the  $\text{MgFe}_2\text{O}_4$  growth a comprehensive characterization of crystalline quality, chemical composition, optical, and electrical properties was performed. This included high resolution X-ray diffraction (HRXRD), UV-Vis Spectroscopy, X-ray photoelectron spectroscopy (XPS) and resistance-temperature measurements (RT).

Crystallographic characterization was performed with a Bruker D8 Advance X-ray diffractometer equipped with a Cu  $K_\alpha$  source and a double bounce Ge crystal monochromator.  $\theta/2\theta$  scans were taken after aligning to the MgO (200) substrate reflex. To assess the in-plane epitaxial strain reciprocal space maps around the MgO (113) reflex were taken. The resistivity of each film was measured as a function of temperature (100 – 300 K) in linear four point probe geometry using gold contact patches deposited in-situ (after film growth) via a shadow mask. The magnetic hysteresis loops of the films were measured using a Quantum Design physical properties measurements system (PPMS) with a vibrating sample magnetometer (VSM) at room temperature with fields up to 2 T. The actual Mg/Fe ratio of the  $\text{MgFe}_2\text{O}_4$  films was determined by quantitative XPS in an Omicron Multiprobe XPS system using Al  $K\alpha$  X-rays ( $h\nu = 1486.7$  eV) with an EA125 U5 analyzer. For ex-situ XPS measurements, all samples were chemically cleaned in acetone and isopropanol with an ultrasonic bath and sputter-cleaned using an Ar ion gun operated at 500 eV for 10 min with a sputter current of 2–3  $\mu\text{A}$  to remove surface carbon and hydroxides formed after exposure to air. Optical properties, in particular the fundamental optical gap were measured by UV-VIS spectrophotometry in a Perkin Elmer Lambda 650S using an integrating sphere in transmission with air as reference.

### 3. Results

#### 3.1. Crystallographic properties

Fig. 2 shows the  $\theta/2\theta$  diffraction pattern for the (200) Bragg reflections of the MgO substrate and the (400) thin film reflection for films grown with a substrate temperature of (a) 300 °C and (b) 350 °C. Patterns for all evaporation rates (R1–R6) are shown stacked for clarity.

**Table 1**

Lists the different substrate growth temperatures and nominal individual source evaporation rates used for growth of the films. The nominal rates refer to the readings of the quartz oscillators for each source. Each was calibrated at R6, by growing individual binary  $\text{Fe}_3\text{O}_4$  and MgO test samples using a single source only. Their thickness was measured post growth by XRR and appropriate tooling factors for the quartz balance have been calculated. The indicated errors for the iron growth rate are based on the measured deviations of measured individual film thickness (XRR) from the nominal thickness based on the quartz balance reading.

$T_s$ (°C)	Growth rate (Å/s) R6	Growth rate (Å/s) R4	Growth rate (Å/s) R2	Growth rate (Å/s) R1
300	$R_{\text{Fe}} = 0.6 \pm 0.02$ $R_{\text{MgO}} = 0.3$	$R_{\text{Fe}} = 0.4 \pm 0.015$ $R_{\text{MgO}} = 0.2$	$R_{\text{Fe}} = 0.2 \pm 0.012$ $R_{\text{MgO}} = 0.1$	$R_{\text{Fe}} = 0.08 \pm 0.01$ $R_{\text{MgO}} = 0.04$
350	$R_{\text{Fe}} = 0.6 \pm 0.02$ $R_{\text{MgO}} = 0.3$	$R_{\text{Fe}} = 0.4 \pm 0.015$ $R_{\text{MgO}} = 0.2$	$R_{\text{Fe}} = 0.2 \pm 0.012$ $R_{\text{MgO}} = 0.1$	$R_{\text{Fe}} = 0.1 \pm 0.01$ $R_{\text{MgO}} = 0.05$

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