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## Magnetite $\text{Fe}_{3-\delta}\text{O}_4$ : a Stoichiometry and Structure Analysis of MBE Grown Thin Films Using $\text{NO}_2$ as the Oxidising Source

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**Abstract.** Epitaxial single crystalline films of iron oxides have been grown on  $\text{MgO}(100)$  substrates by means of MBE. Natural Fe or  $^{57}\text{Fe}$  was evaporated from alumina crucibles, and oxidised simultaneously with a dosed flux of  $\text{NO}_2$ . The resulting oxide layers have been characterised in situ with RHEED, LEED, XPS, and AES. RHEED intensity oscillations, observed during deposition of the oxides, indicate a layer-by-layer growth for all substrate temperatures between 373 and 673 K. A stoichiometry analysis with CEMS, performed ex situ, shows that it is straightforward to prepare both the stable magnetite  $\text{Fe}_3\text{O}_4$  and the metastable maghemite  $\gamma\text{-Fe}_2\text{O}_3$  phases. Moreover, also all solid solutions in between these two extreme phases, i.e.  $\text{Fe}_{3-\delta}\text{O}_4$  with  $0 < \delta < 1/3$ , could be formed. Ion beam channelling has been used to examine the epitaxy of the films. It was found that the films grow coherent on  $\text{MgO}(100)$ .

### 1. Introduction

With the recent developments in Molecular Beam Epitaxy (MBE) growth techniques, it has become possible to prepare magnetite  $\text{Fe}_{3-\delta}\text{O}_4$  thin films on a routine basis. The ability to manufacture thin films offers many advantages, since it allows the formation of artificial structures with properties that can be tailored to the desired application. Moreover, thin films often exhibit properties that deviate from bulk behaviour. Especially multilayers or superlattices, composed of alternating layers of different oxides, have shown many new interesting phenomena. Iron oxide films are usually prepared as epitaxial layers on single crystalline substrates, by evaporating Fe in an  $\text{O}_2$  ambient [1,2]. In this paper, we report on a study of  $\text{Fe}_{3-\delta}\text{O}_4$  thin films prepared with directed fluxes of  $\text{NO}_2$  as the source of oxygen. The main advantage of this technique is that it allows the preparation of magnetite films with every desired composition, ranging from almost perfect stoichiometric  $\text{Fe}_3\text{O}_4$  (vacancy parameter  $\delta = 0$ ) to very heavily oxidised phases. Even the maghemite phase  $\gamma\text{-Fe}_2\text{O}_3$  with  $\delta = 1/3$  can be formed in a single step process, without subsequent annealing treatments. With conventional  $\text{O}_2$ -assisted MBE methods only partially oxidised magnetite films ( $\delta \leq 0.06$ ) can be obtained [2]. Another advantage is that, since we use a small directed beam of  $\text{NO}_2$ , the deposition of the oxide can be stopped abruptly by simultaneously shuttering the Fe and  $\text{NO}_2$  fluxes. This allows a very accurate stoichiometry control. Using a background pressure of  $\text{O}_2$ , the oxide layer will inevitably be suspended for some time under an oxidising atmosphere after closing the Fe source. This can lead to post-oxidation of the magnetite. Finally, with  $\text{NO}_2$  the oxide can be deposited under near-UHV conditions ( $p \leq 1 \cdot 10^{-5}$  Pa). This opens up the possibility to perform systematic studies on freshly prepared, clean surfaces with STM, XPS and other surface sensitive techniques.

### 2. Experimental

$\text{MgO}(100)$  substrates were cleaved ex situ, and cleaned prior to deposition by annealing for 12 hrs. at 900 K under an  $\text{O}_2$  pressure of  $1 \cdot 10^{-4}$  Pa. Cleanliness and crystal quality were checked with XPS, AES, RHEED and LEED. The annealing procedure invariably lead to atomically clean and well-ordered surfaces. Oxide layers were grown by evaporating Fe from alumina crucibles, with the simultaneous oxidation of the metal deposit with a beam of  $\text{NO}_2$  particles. This  $\text{NO}_2$  was fed through a needle valve into a buffer volume, and from here it was free to flow through a stainless steel pipe directed at the substrate surface. By adjusting the buffer volume pressure, the flux at the substrate and therewith the degree of oxidation could be varied. To facilitate Mössbauer studies, 200 Å thick  $\text{Fe}_{3-\delta}\text{O}_4$  layers were grown with the isotope  $^{57}\text{Fe}$ , sandwiched between 50 Å thick buffer- and capping layers grown with natural Fe. The Mössbauer spectra were recorded ex situ at room

temperature, using the conversion electron (CEMS) technique. RBS/channelling spectra were obtained using 1 MeV He<sup>+</sup> ions from a Van de Graaff accelerator.

### 3. Results and Discussion

RHEED intensity oscillations of the specularly reflected beam were observed during deposition for all substrate temperatures between 373 and 673 K. This indicates that in this regime the oxide has a Frank-van der Merwe (layer-by-layer) growth mode, which will result in thin films with relatively smooth surfaces. From the LEED and RHEED patterns, and from XRD measurements, it is derived that the Fe<sub>3- $\delta$ O<sub>4</sub> films grow (100) oriented on MgO(100), with the <100> axes aligned parallel to those of the substrate. One striking feature of the RHEED and LEED patterns is that the (100) surface of Fe<sub>3- $\delta$ O<sub>4</sub> is p(1 $\times$ 1) reconstructed with respect to the spinel unit cell, which has a fcc symmetry [3].</sub></sub>

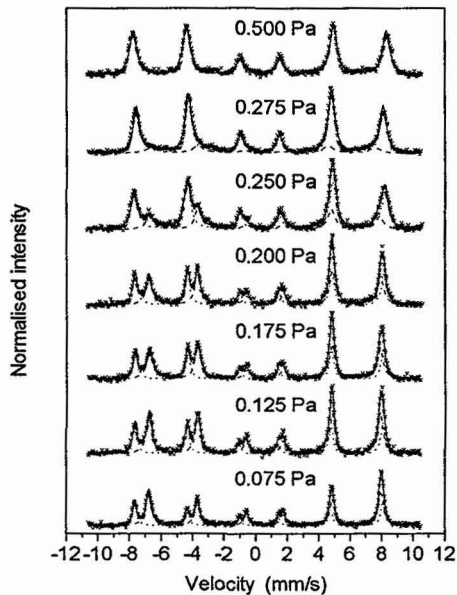


Figure 1 CEMS spectra of 300 Å thick Fe<sub>3- $\delta$ O<sub>4</sub> layers on MgO(100) substrates, deposited at 523 K, as a function of the NO<sub>2</sub> buffer volume pressure (indicted above each spectrum).</sub>

tilt can be explained by assuming a coherent interface between the substrate and the thin film crystal structures at the interface, accompanied by a small tetragonal distortion due to the lattice mismatch. From the Poisson ratio of Fe<sub>3</sub>O<sub>4</sub>, it can be calculated that the observed tetragonal distortion corresponds with unrelaxed, completely coherent films.

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### References

- [1] D.M. Lind, S.D. Berry, G. Chern, H. Mathias and L.R. Testardi, Phys. Rev. B **45** (1992) 1838.
- [2] T. Fujii, M. Takano, R. Katano, Y. Bando and Y. Isozumi, J. Appl. Phys **66** (1989) 3168.
- [3] F.C. Voogt, T. Hibma, G.L. Zhang, M. Hoefman and L. Niesen, Surf. Sci. **331-333** (1995) 1508.
- [4] J.M. Daniels and A. Rosenswaig, J. Phys. Chem. Solids **30** (1969) 1561.
- [5] F.C. Voogt, T. Fujii, T. Hibma, M. Hoefman, P.J.M. Smulders, G.H. Wijnja, G.L. Zhang and L. Niesen, Hyperfine Interactions **97/98** (1996) 99.

Figure 1 shows a selection of CEMS spectra of Fe<sub>3- $\delta$ O<sub>4</sub> layers, as a function of NO<sub>2</sub> buffer volume pressure during deposition (indicated above each spectrum). The spectra have been fitted with two components, ascribed to Fe<sup>3+</sup> and Fe<sup>2.5+</sup> ions. The latter ions are actually Fe<sup>2+</sup> and Fe<sup>3+</sup> ions on octahedral sites that participate in an electron hopping process. From the ratio of the two components, the number of vacancies  $\delta$  per formula unit Fe<sub>3- $\delta$ O<sub>4</sub> can be derived [4,5]. It is found that, by varying the NO<sub>2</sub> pressure, magnetite layers with all possible stoichiometries can be obtained. As can be seen in the figure, the compositions range continuously from nearly perfectly stoichiometric Fe<sub>3</sub>O<sub>4</sub> (bottom spectrum;  $\delta = 0$ ) to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (top spectrum;  $\delta \approx 1/3$ ). The relative intensities of the lines of each sextet is a measure of the average orientation of the spins, with respect to the gamma ray beam. This can be expressed in the quantity  $\chi = (A_2 + A_5)/(A_1 + A_3 + A_4 + A_6)$ , where  $A_i$  is the area of line  $i$  in the sextet. For  $\chi = 1$  all spins are in the surface plane, while  $\chi = 0.5$  corresponds to either a random orientation or to spins aligned parallel to the <111> easy axes. In case of pure magnetite, we are close to the latter situation, but with increasing oxidation the spins gradually turn to the surface plane.</sub></sub>

RBS spectra were recorded both with a random orientation of the ion beam, and with the beam channelled along the [100] and [110] crystal axes. The minimum yield in the channelled direction was reasonably low ( $\leq 10\%$ ) for all films, indicating a good crystal structure with few defects. It is found that the [110] crystal axes of the films are slightly tilted towards a more in-plane direction. For the MgO substrate, we find an angle between the [100] and [110] axes of exactly 45°, but for the Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> films these angles deviate from 45° by 0.16 and 0.47°, respectively. This