Structure, composition and crystallinity of epitaxial magnetite thin films

N.-T.H. Kim-Ngan [a,*], A.G. Balogh [b], J.D. Meyer [c], J. Brötz [b], S. Hummelt [b], M. Zając [d], T. Ślęzak [d], J. Korecki [d,e]

[a] *Institute of Physics, Pedagogical University, 30 084 Kraków, Poland*
[b] *Institute of Materials Science, Darmstadt University of Technology, Petersstrasse 23, 64287 Darmstadt, Germany*
[c] *Institute for Nuclear Physics, J.W. Goethe-University, Max-von-Laue-Str. 1, 60438 Frankfurt/Main, Germany*
[d] *Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland*
[e] *Institute of Catalysis & Surface Chemistry, Polish Academy of Sciences, 30-239 Kraków, Poland*

ABSTRACT

Epitaxially-grown $Fe_3O_4(001)$ thin films by reactive deposition on MgO(100) substrates were studied using low-energy electron diffraction (LEED), conversion electron Mössbauer spectroscopy (CEMS), Rutherford backscattering spectrometry (RBS), channeling (RBS-C) experiments and X-ray reflectometry (XRR). No visible influence from the ion irradiation of the samples on the CEMS spectra was found, while surface oxidation of the samples was observed after exposure to the atmospheric pressure. RBS analysis indicated the presence of magnesium with an average amount of 3% in the films. RBS-C experiments yielded a value of 22% for the minimum yield of Fe and a value of 0.62° for the half-angle for Fe in the film indicating a good crystal quality of the films. The value for film-thickness obtained from XRR is in a good agreement with that from RBS and the nominal value.

1. Introduction

Magnetite (Fe_3O_4), a ferrimagnet with a net magnetic moment of $4.1\mu_B$ and a Néel temperature of 858 K, is the oldest known magnetic material and has been investigated extensively due to its high technological applications in recording media, corrosion and catalysis [1–3]. In recent years, magnetite has attracted again theoretical, experimental and technological interest. It is referred as one of the semi-metallic materials having a full spin polarization on the Fermi level E_F [4]. Thus it is viewed as an ideal candidate for room temperature spintronic applications [5]. Recently, studies of high-quality Fe_3O_4 thin films using spin-resolved photoelectron spectroscopy have indicated that it was not possible to obtained the desired value of −100% polarization at E_F and thus Fe_3O_4 is not a true half-metallicity ferromagnet [6].

Magnetite crystallizes in the inverse spinel cubic structure (space group $Fd\bar{3}m$. In an unit cell with a lattice constant of $a = 8.396$ Å, 32 oxygen anions O^{-2} form a close-packed face-centered-cubic *fcc* lattice, 8 Fe^{3+} cations locate in the tetrahedrally coordinated A-sites, while 16 octahedrally coordinated B-sites are occupied randomly by 8 Fe^{3+} and 8 Fe^{2+} cations. The bulk crystallographic structure of magnetite parallely to the (001) plane can be represented as a stacking sequence of two alternative layers; the A-layer contains only tetrahedral Fe ions while the B-layer con-

sists of oxygen and octahedral Fe ions. The smallest interlayer spacing of the A–B layer is of 0.105 nm, while that of the A–A layer and B–B layer is of 0.21 nm. In the B-layers, only half of the octahedral sites are occupied and Fe ions form rows along the [110] directions which are rotated by 90° with respect to one another in successive octahedral planes. A well-known feature of magnetite is the so-called Verwey transition (T_V) around 125 K reflected by distinguished anomalies in many physical properties. Despite of extensive studies, the nature of the Verwey transition remains still puzzling [7]. For over 60 years it has been described as a metal–insulator transition or a charge order–disorder transition related to the electrons resonating between Fe^{3+}–Fe^{2+} adjacent octahedral sites [8]. Recent studies demonstrating an absence of charge ordering at low temperatures suggest that the Verwey transition is caused by strong electron–phonon interaction [9]. LDA band structure calculations have proved that the combination of the on-site Coulomb interaction between 3d electrons and the electron–phonon coupling implied an opening of a gap (∼0.2 eV) at the Fermi energy is the key feature responsible for the Verwey transition [10].

Recently an increasing interest is focused on the growth of iron oxide thin films on various oxide and metal substrates due to their importance in the model catalyst studies, magnetic thin films, surface geochemistry and corrosion. The growth of magnetite thin films with a high crystalline quality is especially important for spin dependent transport devices, as the mobile electrons may be 100% polarized. The very small lattice mismatch (0.31%) between the Fe_3O_4 film and the MgO substrate in the (001)-plane provides

* Corresponding author. Tel.: +48 12 6626314; fax: +48 12 6372243.
E-mail address: tarnawsk@ap.krakow.pl (N.-T.H. Kim-Ngan).

favorable conditions for the molecular beam epitaxial (MBE) growth. However, many features of structural, electronic and magnetic properties of thin films are still under debate. For instance a $(\sqrt{2} \times \sqrt{2})R45°$ surface reconstruction was commonly observed for the (001) surface. The charge neutrality condition of the polar $Fe_3O_4(001)$ as a driving force for such a reconstruction, however, is still not fully understood and explained. Many different reconstruction models based on A- or B-type layer termination were proposed and discussed [11,12]. The first combined study of in situ LEED, STM and CEMS suggested that a mixed A- and B-type termination exists on one surface [13].

In magnetite, the electronic transport is determined by the short-range interactions between the nearest neighbors (i.e. the Fe ions in the octahedral sites). ^{57}Fe Mössbauer spectroscopy is an extremely efficient tool for local composition and stoichiometry analysis. The room temperature Mössbauer spectrum of magnetite consists of two sextet components corresponding, respectively, to Fe_A^{3+} ions at the tetrahedral A-sites and the $Fe_B^{2.5+}$–like average signal from the cations at the octahedral B-sites. The intensity ratio $\beta = I(B)/I(A)$ of the two spectral components is a sensitive measure of the stoichiometry ($\beta = 1.88$ for the perfect stoichiometric magnetite) [14]. It has been proved that for the systems with reduced dimensionality e.g. MBE thin films, the conversion electron Mössbauer spectroscopy (CEMS; in particular for the films prepared with a pure Mössbauer isotope) provides a possibility to characterizing simultaneously chemical, structural and magnetic properties with monoatomic-layer sensitivity [13,14]. The combined in situ LEED, CEMS and STM studies of epitaxial magnetite thin films have indicated large size-effects reflected by a reduction of the Verwey temperature (T_V; for film-thicknesses less than 50 nm) and a strong deviation from the bulk properties due to formation of a magnesium rich phase near the MgO/Fe_3O_4 interface (for film-thickness down to 10 nm range) [13,15]. Moreover, it was found that the magnetite surface oxidizes when exposed to a clean air at the atmospheric pressure and the oxidized phase was identified as a few nanometers thick surface layer of γ-Fe_2O_3 (maghemite) formed on Fe_3O_4 (both have the same spinel structure). Annealing the sample at 600 K for 1 h at UHV can restore the surface magnetite stoichiometry but it promotes cation diffusion at the Fe_3O_4/MgO interface forming a Mg rich phase ($Fe_{3-x}Mg_xO_4$) at the Fe_3O_4/MgO interface and/or an iron oxide ($Fe_{1-y}O$-wustite type) in the MgO substrate. This phenomenon sets a temperature limit for the growth of $Fe_3O_4(001)$ on $MgO(001)$ by the standard reactive deposition. An alternative preparation method consisted of depositing an oxide layer on an epitaxial $Fe(001)$ deposited on the $MgO(001)$ substrate [16].

Important physical properties like stoichiometry, crystalline quality or the atomic transport processes at the interfaces can be studied in more details using Rutherford backscattering spectrometry (RBS) and channeling experiments (RBS-C) [17]. Interface reactions between epitaxially-grown ion–oxide films on MgO substrates have been investigated by using RBS [18,19]. Annealing the films in a partial oxygen atmosphere up to 970 K enhances largely Mg out-diffusion into the films and results a film with composition close to magnesioferrite ($MgFe_2O_4$) formed at the interfaces.

The goal of the present work is to investigate the surface and interface stoichiometry of epitaxially-grown $Fe_3O_4(001)$ thin films on MgO substrates prepared by reactive deposition using RBS and channeling techniques. The film-characterization by LEED and CEMS has been carried out prior to the RBS and channeling experiments. The influence from ion bombardments on the film-quality have been checked by comparison the CEMS spectra of the non-irradiated and irradiated samples. Additionally, X-ray reflectometry measurements were also performed on these films.

2. Experimental details

The magnetite film preparation and characterization by LEED and CEMS have been carried out using a multi-chamber UHV system (base pressure 10^{-10} mbar) consisted of a miniature MBE system, a four-grid LEED/AES spectrometer and the CEMS chamber described previously [20]. Magnetite films have been grown on (commercially purchased) polished MgO(001) substrates. LEED patterns at different electron energies were taken several times during the film growth. Prior to the film growth the substrates were annealed for 1 h at 870 K in UHV. After this treatment the MgO(001) surface showed an atomic cleanness and perfect structural order checked with AES and LEED. Two films with thicknesses of 10 nm and 20 nm (sample S1 (10 nm Fe_3O_4/MgO) and S2 (20 nm Fe_3O_4/MgO), respectively) were produced by a standard reactive deposition directly on MgO substrates. They were grown by the Fe-vapor deposition at the rate of approximately 1 nm/min, in the presence of oxygen (with the partial pressure of about 1×10^{-6} mbar). The MgO (100) substrate temperature was held at 520 K. Oxygen was provided, using a precision leak valve, from a nozzle placed 1 cm from the substrate to achieve a relatively high local O_2 pressure avoiding contamination of the chamber. For the Mössbauer measurements ^{57}Fe isotope was used. After the deposition the films were annealed for 0.5 h at 570 K. Details of the sample growth have been reported elsewhere [15,20]. After preparation and in situ characterization by LEED, the samples were characterized by CEMS technique using a proportional He/Ch4 flow detector and 200 mCi ^{57}Co (Rh) source. The sample dimensions were 10 mm × 10 mm × 1 mm. After the CEMS experiments each sample was cleaved into two pieces (10 mm × 5 mm × 1 mm). One piece of the samples was taken for Rutherford backscattering (RBS) and channeling measurements (performed one week after the CEMS measurements). After the ion beam analysis samples were measured again by CEMS and then compared with those without ion-irradiation.

The RBS and RBS-C experiments were performed at the Institute of Nuclear Physics of the University Frankfurt/Main. The 2 MeV He$^+$ ion beam at a backscattering angle of 176° was used for RBS. The incident ion beam was directed along the normal to the sample surface. The pressure in the target chamber during the analysis was $3–5 \times 10^{-6}$ mbar. The beam current was about 20 nA. The beam spot on the target had a square shape of 1.0×1.0 mm^2. For a chosen sample the RBS spectra were taken at room temperature and at liquid nitrogen temperature. RBS-C experiments were performed using 1.5 MeV He$^+$ ions at a backscattering angle of 160° and a beam spot of 0.5×0.5 mm^2. The aligned and random spectra were taken, respectively, between 0° and 1.2–1.5° with an angle step of 0.04–0.08°.

X-ray reflectometry (XRR) measurements were performed at a Seifert two-circle diffractometer using a rotating anode with 40 kV and 120 mA. Primer to the sample, a LiF monocromator and a slit system was used to separate the Cu K Alpha 1 line. The beam width was 0.1 mm and on the secondary side we used a 0.05 mm slit. For a quantitative analysis of the XRR data the Seifert Reflectivity software was used.

3. Sample characterization by LEED and CEMS

The in situ LEED patterns taken at electron energy of 92 eV of the deposited Fe_3O_4/MgO films have displayed clearly a $(\sqrt{2} \times \sqrt{2})R45°$ reconstruction (see e.g. Fig. 1a; [13]). Annealing (for 0.5 h at 570 K) improves the LEED patterns.

After preparation samples were characterized ex situ by CEMS at room temperature. The CEMS spectra for 10 nm-thick magnetite film obtained in three experimental states are shown in Fig. 1: for