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Thermal and irradiation induced interdiffusion in magnetite thin films grown on magnesium oxide (001) substrates

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ABSTRACT

Epitaxial Fe_3O_4(001) thin films (with a thickness in the range of 10–20 nm) grown on MgO substrates were characterized using low-energy electron diffraction (LEED), conversion electron Mössbauer spectroscopy (CEMS) and investigated using Rutherford backscattering spectrometry (RBS), channeling (RBS-C) experiments and X-ray reflectometry (XRR). The Mg out-diffusion from the MgO substrate into the film was observed for the directly-deposited Fe_3O_4/MgO(001) films. For the Fe_3O_4/Fe/MgO(001) films, the Mg diffusion was prevented by the Fe layer and the surface layer is always a pure Fe_3O_4 layer. Annealing and ion beam mixing induced a very large interface zone having a spinel and/or wustite formula in the Fe_3O_4-on-Fe film system.

1. Introduction

Magnetite (Fe_3O_4) – the first known magnetic material has been investigated extensively due to its high technological applications in high-density recording media, corrosion and catalysis [1,2]. More recently, a large interest has been focused again on magnetite, since it is viewed as a promising candidate for use as pure spin sources in spintronic devices at room temperature, such as spin valve, sensitive magneto-resistive devices [3,4]. It has been theoretically predicted to be half-metallic having a 100% spin polarization at the Fermi level E_F [5]. However, the experimental results from spin-resolved photoelectron spectroscopy have pointed out that the maximal polarization value can be obtained is only 80% [6,7]. At room temperature Fe_3O_4 crystallizes in the cubic inverse spinel structure with a lattice constant of $a = 8.396$ Å, in which 32 O^{-2} ions form a close-packed cubic *fcc* structure, while Fe ions occupy two distinct interstitial sites denoted as A and B. Eight Fe^{3+} ions locate in the tetrahedrally coordinated A-sites, while 8 Fe^{2+} and 8 Fe^{3+} ions occupy randomly the octahedrally coordinated B-sites. Below the Néel temperature of 858 K, magnetite is ferrimagnetic with a net magnetic moment of 4.1 μ_B per formula unit. A specific feature of magnetite is the Verwey transition around 125 K characterized by an abrupt drop in conductivity by two orders of magnitude upon cooling through the transition and a pronounced anomaly in many physical properties [8]. Despite of extensive studies, the nature of this transition remains still puzzling. For reviews of structure and magnetism of Fe_3O_4 and the debate about the nature of the Verwey transition see Refs. [8–11].

Recently, an increasing interest is focused on the growth, characterization and investigation of the thermodynamic properties of magnetite thin films. The MgO(001) substrate has been frequently used due to the fact that in the (001)-plane the very small lattice mismatch (0.31%) between the Fe_3O_4 film and the MgO substrate provides favorable conditions for the molecular beam epitaxial (MBE) growth. However, many features of structural, electronic and magnetic properties of these thin film materials are still not fully understood, such as the surface termination and the driving force for the $(\sqrt{2} \times \sqrt{2})R45°$ surface reconstruction commonly observed for the Fe_3O_4(001) surface. For reviews see Refs. [12–14]. In addition, a large reduction of the Verwey temperature and a strong deviation from the bulk properties were observed in magnetite thin films due to the size-effects (reduction of the film thickness) and the formation of a magnesium rich phase at the Fe_3O_4/MgO interface [15,16]. Moreover, antiphase boundaries were observed in Fe_3O_4 films grown on MgO as an intrinsic consequence of the nucleation and growth mechanism in films [17].

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In order to prepare the high-quality films, in addition to their structural, chemical, and electromagnetic properties, it is important to obtain the stabilised and optimal parameters of the material. The $Fe_3O_4(001)$ films prepared in a standard reactive deposition directly on MgO substrates possess a good crystalline quality [18,19]. However, for these films, as the result of surface oxidation when exposed to a clean air at the atmospheric pressure, the surface layer is the oxidized phase γ-Fe_2O_3 (maghemite) with a thickness of a few nanometers [15]. The surface stoichiometry can be restored by annealing the sample at 600 K for 1 h in UHV. However, annealing promotes Mg diffusion from MgO substrate into the Fe_3O_4 film inducing a large change of the surface structure. The alternative preparation method is to deposit an Fe_3O_4 layer on an epitaxial Fe(001) buffer layer grown epitaxially on the MgO substrate [14]. For such films, the magnetite surface was found to remain stable upon thermal annealing as well as in exposing to clean air. Moreover, the Fe(001) layer acts as an effective layer barrier against Mg diffusion into the Fe_3O_4 film [16].

The goal of the present work is to investigate the surface and interface stoichiometry and crystalline quality of epitaxially-grown magnetite films using Rutherford backscattering spectrometry (RBS), channeling experiments (RBS-C) and X-ray reflectometry (XRR) measurements. We focus our attention on the solid state reaction at the Fe_3O_4/MgO interface of the directly-deposited magnetite films (Fe_3O_4/MgO(001) films) and the Fe_3O_4/Fe and Fe/MgO surface of the magnetite-deposited-on-Fe films (Fe_3O_4/Fe/MgO(001) films). The results obtained for the Fe_3O_4/MgO(001) films were published recently [18,19]. In this work we present and analyse the different features of two different types of magnetite films in three different states: as-grown, under thermal annealing and ion irradiation.

2. MBE growth and characterization of magnetite films

The film growth and characterization by low-energy electron diffraction (LEED) and conversion electron Mössbauer spectroscopy (CEMS) have been carried out in a multi-chamber UHV system consisted of a miniature MBE system, a four-grid LEED/AES spectrometer and the CEMS chamber. Details of film growths and characterization by LEED and CEMS have been reported elsewhere [14–16]. In the present work we have studied the Fe_3O_4 films with nominal thicknesses of 10 and 20 nm grown on (commercially purchased) polished MgO(001) substrates. Sample S1 – the 10 nm Fe_3O_4/MgO(001) film and sample S2 – the 20 nm Fe_3O_4/MgO(001) film were prepared by the standard reactive deposition method [18]. Sample S3 – the 10 nm Fe_3O_4/10 nm Fe/MgO(001) film was prepared by deposition of Fe_3O_4 layer on an epitaxial Fe(001) film (the so-called magnetite-on-Fe film/buffer) [16]. The Fe film was first grown on MgO(001) substrate by iron evaporation from thermal sources on MgO(001) substrate. Then a magnetite film was prepared on the Fe(001) film by a reactive deposition of Fe-vapor deposition under a partial oxygen pressure of about 1×10^{-6} mbar. We also investigated sample S4 – the 10 nm Fe_3O_4/10 nm Fe(o)/MgO(001) film obtained as a result of annealing a 15 nm-thick Fe film grown on MgO for 50 min at 550 K under a partial oxygen pressure of 5×10^{-6} mbar (i.e. magnetite film formed by oxidation of an Fe film). The CEMS and RBS spectra of the two samples S3 and S4 in the as-grown state were identical. Thus for further considerations concerned magnetite-on-Fe film system we have used only the sample S3.

After preparation and in situ characterization by LEED, the samples were characterized ex situ by CEMS technique using a proportional He/CH_4 flow detector and 200 mCi ^{57}Co (Rh) source. The sample size was 10 mm × 10 mm × 1 mm. After the CEMS experiments, each (as-grown) film was cleaved into two pieces. One piece was used for Rutherford backscattering (RBS) and channeling measurements (performed one week after the CEMS measurements). Then the CEMS were performed on these pieces again (i.e. samples after one-month-exposure to air and after (He) ion irradiations). The results were compared to those from the second pieces (i.e. samples after one-month-exposure to air only).

The sample characterizations by LEED and CEMS measurements have revealed the good quality of the films. The CEMS results of numerical least-square analysis for four films in the as-grown state are given in Table 1. The results indicated that:

(1) The in situ LEED patterns of the Fe_3O_4/MgO and Fe_3O_4/Fe/MgO films have displayed clearly a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction typically observed for magnetite (001) surfaces (see e.g. Fig. 1 [16], Fig. 9 [16], respectively).
(2) The CEMS analysis of the directly-deposited Fe_3O_4/MgO film in as-grown state [18] suggested that the interface region is the spinel phase $Mg_xFe_{3-x}O_4$ with $x = 0.10$–0.15 and a thickness of 2 nm, as a result of Mg diffusion into the magnetite film.
(3) CEMS analysis of the sample S1 in three experimental states (i.e. as-grown, non-irradiated and after one-month-exposure to air, and irradiated plus after one-month-air-exposure one) (see Table 1 and Fig. 1 Ref. [18]) suggested that an oxidized phase γ-Fe_2O_3 with a thickness of 1.5 nm was formed on the surface of magnetite films and that 2 MeV He^+ ion irradiation did not cause any significant changes in the film structure.
(4) The CEMS spectrum of 10 nm Fe_3O_4/10 nm Fe/MgO(001) film could be fitted by four components. The A and B components represents Fe ions in tetra- and octahedral sites, respectively. The third component corresponds to the pure metallic iron (α-ion). The fourth component (interface (D)) is coming from the interfacial layer formed between Fe_3O_4 and metallic iron. The CEMS data analysis suggested that there was no diffusion at the Fe/MgO interface and that the remaining Fe layer serves as an effective barrier for Mg diffusion into the Fe_3O_4 film. Moreover, no visible change in the CEMS spectrum for the exposed-to-air Fe_3O_4/Fe/MgO(001) film in comparison to that for the as-grown one [16] indicating that the magnetite films prepared on Fe buffer layers are remain stable under exposure to air.

3. Rutherford backscattering and channeling experiments

The RBS and RBS-C experiments were performed at the Institute of Nuclear Physics of the University Frankfurt/Main. RBS measurements were carried out using a 2 MeV He^+ ion beam at a backscattering angle of 171°. The incident ion beam was directed along the normal to the sample surface. 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 the data evaluation the computer code SIMNRA [20] was used taking into account the electronic stopping power data by Ziegler and Biersack, Chu + Yang's theory for electronic energy-loss straggling and Andersen's screening function to Rutherford cross-section. The layer thickness values (in nm) were estimated from the simulated RBS areal density values (in at/cm^2) using the bulk density of magnetite (and iron) taking into account the small density change related to Mg diffusion into the films (forming the spinel and wustite layers) and/or the density values determined from XRR measurements. In order to improve the depth resolution for such very thin films the RBS spectra were collected and evaluated at different tilt angles (φ) up to 45°. A strong channeling effect was observed when the beam was exactly parallel to the main crystallographic (001) direction, i.e. $\varphi = 0^\circ$ (indicating the good crystallin-