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Materials Science and Engineering B 144 (2007) 19–22

MATERIALS SCIENCE & ENGINEERING B

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Dislocation network driven structural relaxation in hematite thin films

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Abstract

Using surface X-ray diffraction, we investigated 20 nm thick α-Fe_2O_3(0 0 0 1) thin films deposited on α-Al_2O_3(0 0 0 1) and Pt(1 1 1) single crystals. The films were grown in identical conditions by atomic oxygen assisted molecular beam epitaxy techniques. Both substrates offer close lattice parameter misfits. On sapphire an isostructural epitaxial relationship is observed and a 30° in plane rotation of the lattice for Pt(1 1 1). The crystalline quality of the film deposited on Pt(1 1 1) is much better and contained less parasitic contributions. The improved crystalline quality of α-Fe_2O_3(0 0 0 1) layers on Pt(1 1 1) is attributed to the presence of a very well ordered interfacial dislocation network which is missing when α-Al_2O_3 is used as substrate.

Keywords: Surface X-ray diffraction; Hematite; Relaxation; Dislocation network

1. Introduction

Many efforts are devoted nowadays in order to control the growth conditions of well defined oxide thin films. Obtaining well ordered single crystalline films of high structural quality remains a very challenging task for numerous compounds. These films may offer new properties because of reduced dimensions as well as an original way to produce surfaces that cannot be obtained from bulk crystals. Oxide surfaces are often used as catalysts or catalysts supports [1,2] and adsorbents in environmental remediation [3]. For example, hematite (α-Fe_2O_3) clusters have been proposed to suppress undesirable greenhouse gases [4]. Hematite is also a canted antiferromagnet [5] with high Néel temperature and may thus be used in magnetic data storage technologies. Within this framework, an improved understanding of the parameters influencing the crystalline quality α-Fe_2O_3 layers is very important.

In previous studies, using atomic oxygen assisted molecular beam epitaxy techniques, hematite films were grown on sapphire [6,8], platinum buffer layers deposited on sapphire [7] and Pt(1 1 1) single crystals [9]. Alternatively, magnetite layers deposited on Pt surfaces can be transformed into hematite after an anneal at 1000 K under high oxygen partial pressures [10,11]. It has been shown, qualitatively that the hematite layers deposited on Pt buffers are of better crystalline quality as compared to the ones deposited directly on sapphire [7]. In the present work we quantitative analyze, by X-ray diffraction, hematite layers on both substrates and determine the origin of the different crystalline qualities. In order to avoid elastic relaxation effects that are known to occur in the early stages of growth [8,9] we have investigated 20 nm thick layers for which residual strain is negligible. After providing the experimental conditions and the background necessary to describe the X-ray diffraction data, we will present and discuss the results.

2. Experimental

The sapphire substrates are single crystals (12 mm × 8 mm × 0.25 mm) with one face polished up to epitaxial quality and oriented perpendicular to the [0 0 0 1] axis within an error of ±0.5°. Before introduction in the UHV system, the sample is chemically cleaned in a solution of NH_4OH (28%):H_2O_2 (30%):H_2O—proportions 1:1:100) during 2 min [12]. The Pt(1 1 1) samples (Ø 10 mm, thickness 1 mm, aligned and polished perpendicular to the [1 1 1] axis within ±0.1°)) were prepared by two *in situ* cycles of ∼4 h annealing at 750 K. Both substrates were cleaned using a 5 min exposure to a high

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doi:10.1016/j.mseb.2007.07.083

brilliance oxygen plasma (power 300 W), leading to reflection high energy electron diffraction (RHEED) patterns typical for well ordered and clean surfaces as checked by auger electron spectroscopy (AES) [8,9,13].

The iron oxide growth, at a rate of 1 Å/min, was performed at ∼750 K in a dedicated setup described elsewhere [8,13]. A continuous sample rotation around the surface normal ensures a homogeneous deposit. The stoichiometry of the layers was checked in situ by X-ray photoelectron spectroscopy (XPS). Hematite is the most oxidized form of iron oxides and air-exposure of the samples does not produce phase changes. The layers can conveniently be regenerated after air exposure by outgassing during ∼30 min at 600 K under a 10^{-5} mbar oxygen partial pressure.

The surface X-ray diffraction experiments were all performed at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The α-Fe_2O_3(0 0 0 1)/α-Al_2O_3(0 0 0 1) (resp. Pt(1 1 1)) interface was investigated on beamline ID03 (resp. ID01) using a photon energy of 17 keV (resp. 18 keV). An horizontal sample geometry was used in both cases and, if not otherwise specified, the measurements were made at an incidence angle close to the critical angle (0.28° and 0.2°, resp.) for total external reflection in order to maximize the surface signal.

3. Background

Two crystals of different lattice parameters (a_s for the substrate and a_d for the deposit) with the same crystallographic structure, which are not deformed, and in epitaxy, show a coincidence site lattice at the interface. It corresponds to the smallest lattice that is common to the two primitive ones. The period Λ is given by $\Lambda = a_d/|f|$ (Fig. 1 (a)) where f is the lattice parameter misfit defined as $f = (a_d - a_s)/a_s$. In the mismatched regions, the atoms are subject to coherency forces that tend to reorganize the structure to form a network of misfit dislocations at the interface of period Λ. Semicoherent interfaces, for which the parameter misfit is accommodated by a localized and ordered misfit dislocation network, are often observed for small values of f ($\lesssim$10%) [14].

From the point of view of X-ray diffraction the resulting displacement field is periodic and can be expressed in the form of a Fourier series: $u(x) = \sum_n \Psi_n \sin(2\pi n(x/\Lambda))$. The resulting structure factor can be written, at first order, as: $F(q) = \sum_m \exp(iq(ma)) + i\Psi q \sum_m \sin(2\pi ma/\Lambda)\exp(iqma)$. The first term corresponds to the Bragg peak of the non-deformed film whereas the second term yield extra-peaks centered on the Bragg peak with a periodicity given by $\Delta q = 2\pi/\Lambda$. One should note that the expected extra-peaks arise from the displacement modulations and not from the periodicity of the dislocation network itself. X-ray diffraction is thus a well suited method to investigate dislocation networks as far as they are well ordered and/or that a periodic displacement field exists in the mismatched regions. In the case of incoherent interfaces, for which localized dislocations still may exist in order to relax the local strain, diffraction satellites will not be observed.

Bulk sapphire and hematite have rhombohedral symmetry, which is usually treated as hexagonal (space group $R\bar{3}c$ (D^6_{3d}, no. 167)), with 30 atoms (six M_2O_3 units, where M=Al or Fe) per primitive unit cell, and lattice parameters ($a = b = 4.7570$ Å, $c = 12.9877$ Å [15]) and ($a = b = 5.038$ Å, $c = 13.772$ Å [16]), respectively. Platinum has a cubic symmetry (space group $Fm\bar{3}m$, (O^5_h, no. 225)) with 3.92 Å the length of the side of the cubic unit cell. It is convenient, when considering surface X-ray diffraction [17], to describe the Pt(1 1 1) surface using a hexagonal mesh with $a = b = 2.772$ Å and $c = 6.789$ Å. By convention we use the hematite hexagonal lattice as the reference for the reciprocal space where the (h, k) indexes span the in-surface-plane space and L describes the perpendicular momentum transfer. For in-surface-plane scans L is close to 0, for simplicity the real value will not be reported.

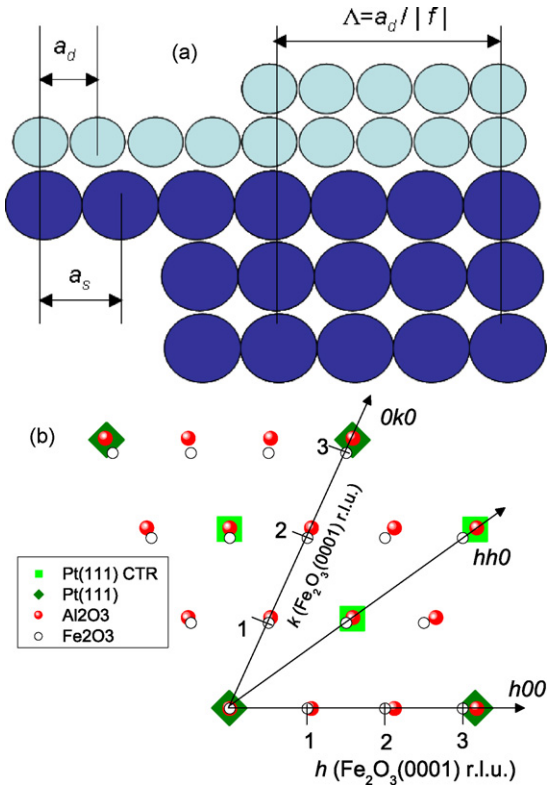

Fig. 1. (a) Schematic representation of a coincidence lattice network extending in one direction for a parameter misfit $f = 20\%$. (b) Reciprocal space for the isostructural epitaxy of α-Fe_2O_3(0 0 0 1)/α-Al_2O_3(0 0 0 1) and for the ($\sqrt{3}\times\sqrt{3}$)R30 epitaxy of α-Fe_2O_3(0 0 0 1)/Pt(1 1 1). The reciprocal space is indexed in units of the reciprocal lattice units (r.l.u.) of α-Fe_2O_3(0 0 0 1). The positions of the Pt(1 1 1) crystal truncation rods (CTR), which are expected to be of much smaller intensity, are indicated by a different symbol.

The oxide-on-oxide epitaxy is guided by the symmetry of the oxygen sublattices and it has been shown that α-Fe_2O_3(0 0 0 1)/α-Al_2O_3(0 0 0 1) [8] adopts an isostructural epitaxial relationship. Without the presence of an oxygen sublattice in the substrate and dealing with different lattice symmetries, an additional lattice rotation may provide extra relaxation and better lattice parameter match. The α-Fe_2O_3(0 0 0 1)/Pt(1 1 1) interface adopts a ($\sqrt{3} \times \sqrt{3}$)R30 [7,9] epitaxial relationship. The expected locations of the in-surface-plane diffraction peaks is pictured, for both situations in Fig. 1(b). The parameter misfit can be established from the oxygen atom sublattice which