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Surface Science 575 (2005) 35–50

SURFACE SCIENCE

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Epitaxial growth of iron oxide films on Ag(1 1 1)

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Received 18 April 2004; accepted for publication 27 October 2004
Available online 28 December 2004

Abstract

Epitaxial iron oxide films are grown on Ag(1 1 1) by two methods. The oxide films are characterized using low-energy electron diffraction, X-ray photoelectron spectroscopy, and X-ray photoelectron diffraction. The first growth method is deposition of Fe films with thickness ranging from 1–10 monolayers on Ag(1 1 1) and oxidizing these films. The Fe film structure prior to oxidation is identified as poorly ordered bcc-Fe(1 1 0), and oxidation leads to the growth of poorly ordered FeO(1 1 1) films. The second method is sequential deposition of sub-monolayer Fe films (typically $\leqslant$0.5 ML) followed by oxidation. This procedure is repeated until the desired oxide film thickness is achieved. Iron oxide films grown by sequential deposition are identified as FeO(1 1 1) for oxide film thickness below ~10 Å with growth of Fe_3O_4(1 1 1) for thicker films. Iron oxide films grown by the sequential deposition method have much better crystallographic order than those grown by oxidizing thicker iron films. Finally, the surface termination of the Fe_3O_4(1 1 1) films is investigated using X-ray photoelectron diffraction.

Keywords: Electron–solid diffraction; Low energy electron diffraction (LEED); Photoelectron diffraction; Growth; Oxidation; Iron oxide; Interfaces; Single crystal epitaxy

1. Introduction

Iron oxides and their surfaces are important in a variety of technical areas including magnetic recording, corrosion, and catalysis. Consequently many recent studies of the surface science of these materials have been made. A central issue in these studies is the preparation of well-defined stable surfaces. This is a difficult endeavor for iron oxide because of the similarity in the structures of the different iron phases, the complexity of the surfaces involved, and the interconversion of different phases under different oxidizing or reducing conditions. As a result of these initial investigations, a number of different strategies for the growth of well-defined stable surfaces have been adopted. These include, but are not limited to, oxidation

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doi:10.1016/j.susc.2004.10.050

of bulk single crystals [1–4], oxygen assisted molecular beam epitaxy (MBE) onto oxide substrates [5–9], and sequential iron deposition/oxidation cycles on metallic substrates [10–17].

The most straightforward method for preparing iron oxide surfaces is oxidation of bulk iron surfaces. This method is somewhat limited because of the mismatch in lattice parameters between the oxide and the bulk iron. This approach was adopted by Kim et al. [4]. They grew iron oxide films by oxidizing the Fe(1 1 0) surface. Different iron oxide phases were reported for different oxidation conditions. Based on low-energy electron diffraction (LEED) and X-ray absorption spectroscopy (XAS) results they conclude that, for oxygen exposures below 300 L, a thin film of FeO(1 1 1) is formed. For higher oxygen doses (beginning at about 600 L) they observe additional LEED beams consistent with either a (2 × 2) reconstructed FeO(1 1 1) surface or with a Fe_3O_4(1 1 1) surface. On the basis of XAS results they conclude that the higher exposure oxide films are Fe_3O_4(1 1 1). The magnetic properties of these films, however, are quite different from the bulk magnetic properties of magnetite. This difference is attributed to oxygen deficiencies at the surface of the oxide film, but the structure, and particularly the surface termination of these films, is poorly characterized.

A successful method for growing iron oxide films on metallic substrates was pioneered by Weiss et al. [10–17]. They grew ordered films of FeO and Fe_3O_4 on a Pt(1 1 1) substrate by depositing single monolayer (ML) iron films, oxidizing them, and finally annealing them. This process was repeated until the desired oxide film thickness was achieved. For growth temperatures of ∼600 °C and oxidizing pressures of $\sim 10^{-6}$ Torr, 2–3 ML of FeO(1 1 1) are formed. Subsequent growth under the same conditions results in cluster formation of Fe_3O_4(1 1 1) on the FeO layers. When the growth takes place at ∼730 °C, only a single ML of FeO is formed before the formation of Fe_3O_4 clusters. Subsequent detailed LEED I–V analysis of the thicker films was interpreted in terms of a complex highly relaxed surface terminated by 1/4 ML Fe ions. The driving force for the relaxation is the minimization of the number of surface dangling bonds as well as the electrostatic surface energy. Subsequent studies by the same group [10] showed that high pressure oxidation ($\sim 10^{-1}$ Torr) of the Fe_3O_4 clusters produced well ordered α-Fe_2O_3(0 0 0 1) films.

The surface termination of Fe_3O_4(1 1 1) was also investigated using STM [18]. A natural magnetite crystal that was prepared by in situ Ar^+ sputtering followed by annealing at ∼730 °C in an oxygen partial pressure of $\sim 10^{-6}$ Torr was used. This study identified the coexistence of two surface terminations believed to be an unreconstructed Fe_3O_4(1 1 1) termination that exposes 3/4 ML Fe ions and 1/4 ML O ions on a close-packed oxygen layer, and another unreconstructed Fe_3O_4(1 1 1) layer that exposes 1/2 ML Fe ions over a close-packed oxygen layer. Subsequent studies by the same group [19] show that annealing in more reducing conditions (without oxygen) produced ordered superstructures of coexisting FeO(1 1 1) and Fe_3O_4(1 1 1). Finally, an STM study by Shaikhutdinov et al. [16] on Fe_3O_4 films grown by the sequential deposition method on Pt(1 1 1) have different surface structures depending on growth temperature. For growth at ∼730 °C, the surface termination is consistent with their previous LEED I–V study that suggested a single 1/4 ML Fe terminated surface. For growth at ∼600 °C they identified coexisting surface structures interpreted as FeO and Fe_3O_4 in nature that cover only about 5% of the surface with the remainder composed of the "regular" Fe_3O_4(1 1 1) surface that is found at ∼730 °C. It is clear that the surface structure of iron oxide films is complex and highly dependent upon growth conditions.

In this study we have attempted to extend the examination of surface structures for Fe_3O_4 films by use of element specific X-ray photoelectron diffraction (XPD) complemented by LEED and X-ray photoelectron spectroscopy (XPS) measurements. Our approach was to grow ordered oxide films on a Ag(1 1 1) substrate. Fe(1 1 0) is reported to grow epitaxially on the Ag(1 1 1) so this substrate allowed us to investigate the oxidation of the Fe(1 1 0) surface [20]. In addition, the Ag(1 1 1) substrate is well matched to the various iron oxides. For example, the Ag–Ag distance is 2.89 Å. The different iron oxides can be constructed from