



Layer-by-layer epitaxial growth of polar FeO(111) thin films on MgO(111)

Jacek Gurgul ^{a,*}, Ewa Młyńczak ^a, Nika Spiridis ^a, Józef Korecki ^{a,b}

^a Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

^b Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland

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ABSTRACT

We report on the structural properties of epitaxial FeO layers grown by molecular beam epitaxy on MgO(111). The successful stabilization of polar FeO films as thick as 16 monolayers (ML), obtained by deposition and subsequent oxidation of single Fe layers, is presented. FeO/MgO(111) thin films were chemically and structurally characterized using low-energy electron diffraction, Auger electron spectroscopy and conversion electron Mössbauer spectroscopy (CEMS). Detailed *in situ* CEMS measurements as a function of the film thickness demonstrated a size-effect-induced evolution of the hyperfine parameters, with the thickest film exhibiting the bulk-wüstite hyperfine pattern. *Ex situ* CEMS investigation confirmed existence of magnetic ordering of the wüstite thin film phase at liquid nitrogen temperature.

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1. Introduction

The latest advances in the description of polar oxide surfaces have shed light on the physical properties of the surfaces and interfaces of ionic materials [1]. However, our understanding of low-dimensionality effects in such materials is still very poor. Theoretical predictions and experimental results have shown that bulk-terminated polar surfaces are not stable because alternating layers of oppositely charged ions produce a large dipole moment perpendicular to the surface, which results in a diverging electrostatic potential. Two mechanisms provide solutions to this infinite energy problem: the surface could facet into neutral planes or it could reconstruct to balance its surface charge [1,2]. In contrast to the surfaces of single crystals, non-reconstructed polar surfaces can be produced in thin films below a critical thickness [1 and references therein]. From this perspective, the preparation and study of stable non-reconstructed polar surfaces are of great interest. On the other hand, the stabilization of orientations, which do not occur naturally when cleaving a bulk material, opens the way to the fabrication of artificial structures for controlled catalysis or nanostructures for electronic and magnetic applications.

The simple cubic rock-salt structure is one of the most stable structures for highly ionic solids, such as metal monoxides (*e.g.*, MgO, CoO, FeO, *etc.*). It consists of two interpenetrating fcc lattices

of anions and cations. While the {001} faces are neutral and can be easily stabilized by epitaxial growth [3], obtaining the polar plane orientation of the lowest index {111} is challenging. A crystal cut along (111) presents alternating layers of metal and oxygen ions. Because of charge compensation, the surface tends to reconstruct or facet. The most common stable surface configuration is found to be the octopolar (2×2) reconstruction [4 and references therein]. This reconstruction is obtained by removing 75% of the atoms in the outermost layer and 25% in the layer beneath, which produces {100} facets. Polar surface stabilization mechanisms may be altered in ultrathin polar films and nanostructures because of their reduced dimensionality [5]. Additionally, in these systems, surface relaxation, diffusion of atoms, filling of surface states or covalency modifications are possible stabilizing processes. However, these mechanisms have not yet been quantitatively assessed, and there is a need for experimental work in these fields.

We have chosen to study FeO because of its importance in basic research, as well as in technological applications. Iron monoxide (FeO) adopts the rock salt structure above its Néel temperature ($T_N \approx 198$ K). However, it is well known that FeO is nonstoichiometric, accommodating a cation deficiency by the formation of octahedral iron vacancies and a small number of tetrahedral iron(III) interstitials. These defects tend to aggregate and form tetrahedral units that have been identified by neutron diffraction and Mössbauer spectroscopy [6,7]. The bulk magnetic properties of wüstite Fe_yO are complex; it is an antiferromagnet with an exact Néel temperature that depends on the value of y [6,8]. Below the magnetic ordering temperature, it undergoes a rhombohedral distortion, and its iron spins align along the [111] direction of the unit cell, forming antiferromagnetically coupled alternate (111) iron ferromagnetic sheets [9].

* Corresponding author at: Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland. Tel.: +48 126395116; Fax: +48 124251923.

E-mail addresses: ncgurgul@cyf-kr.edu.pl (J. Gurgul), ncmlyncz@cyf-kr.edu.pl (E. Młyńczak), ncspirid@cyf-kr.edu.pl (N. Spiridis), korecki@agh.edu.pl (J. Korecki).

Although iron oxide thin films prepared by different methods, ranging from the direct oxidation of metallic Fe(110) and (001) surfaces to the deposition and oxidation of Fe layers on many substrates, are widely investigated (for a review, see [10]), the literature on polar FeO(111) films is scarce. Most studies consider ultrathin FeO(111) films prepared on Pt(111) [11]. There are several experiments showing that FeO(111) can be obtained by oxidation of the Fe(110) surface [12 and references therein], and to our knowledge, there has been only one example of the growth of FeO(111) monolayers on oxide surfaces [13]. In particular, there are no published papers related to FeO/MgO(111) systems.

In this paper, we report the successful preparation of polar FeO thin films on MgO(111). Because of the layer-by-layer technique, we were able to stabilize an epitaxial FeO film as thick as 16 ML. Every step of the preparation sequences was accompanied by detailed structural studies with low electron energy diffraction (LEED), Auger electron spectroscopy (AES) and conversion electron Mössbauer spectroscopy (CEMS). Compared to standard surface sensitive characterization methods, CEMS has the advantage of probing deeper layers (down to 100 nm) with a monolayer resolution, as well as their local structure and symmetry [3,14].

2. Material and methods

The experiments were performed in a multi-chamber ultrahigh vacuum (UHV) system (base pressure 2×10^{-10} mbar) equipped with facilities for the growth of epitaxial films, along with their structural and chemical characterizations and *in situ* CEMS measurements. The preparation chamber contains a molecular beam epitaxy (MBE) system, including an evaporator for iron that is 95% enriched with the ^{57}Fe isotope, a quartz monitor to control the deposition rate, a LEED/AES spectrometer for fast sample characterization and a MgO evaporator. A MgO(111) polished single crystal ($10 \times 10 \times 1 \text{ mm}^3$) was used as the substrate. The substrate was annealed at 903 K for 3 h at UHV, and a homoepitaxial 30 Å layer of MgO was deposited at 723 K in three steps (10 Å each) and annealed at 823 K (30 min) in oxygen atmosphere (5×10^{-9} mbar) to improve the quality of the surface. Single monolayers of FeO were grown by the deposition of an ^{57}Fe monolayer at normal incidence at RT and subsequent oxidation in O_2 (5×10^{-8} mbar, 10 L) at 543 K, followed by UHV annealing at 873 K for 30 min. The FeO monolayer deposition procedure was repeated 16 times, which resulted in the 16 ML FeO film. After every monolayer preparation cycle, the surface structure and composition of the thin films were monitored by LEED and AES.

The *in situ* CEMS measurements were performed at selected preparation stages at room temperature using an UHV spectrometer, similar to that described previously [15] and a standard 100 mCi Mössbauer $^{57}\text{Co}(\text{Rh})$ γ -ray source. The *in situ* spectra were taken at a fixed angle of 36° between the direction of the γ -ray propagation and the sample normal. For low temperature (LT) *ex situ* CEMS measurements, the sample was capped with a 50 Å protective MgO film. The LT CEMS experiments were performed at 80 K in a separate UHV system [16] equipped with a liquid nitrogen stationary cryostat.

The Mössbauer spectra were analyzed numerically by fitting a hyperfine parameter distribution (HPD) using the Voigt-line-based method of Rancourt and Ping [17]. In this method, the HPD for a given crystal site corresponding to similar structural, chemical and magnetic properties is constructed by a sum of Gaussian components for the quadrupole splitting (QS) distributions and, if necessary, the magnetic hyperfine field B_{hf} distributions. The isomer shift (IS) can be linearly coupled to the primary hyperfine parameters (QS, B_{hf}). The isomer shift values are quoted relative to α -Fe at room temperature.

3. Results and discussion

The Auger spectrum induced by 1.7 keV electrons showed small amounts of carbon (KE = 270 eV) and calcium (KE = 291 eV) at the

polished MgO(111) crystal surface (Fig. 1). To obtain a cleaner surface, homoepitaxial MgO buffer layers were deposited. The deposition of 30 Å of MgO clearly resulted in a calcium-free surface. However, small traces of carbon were still present at the surface. The oxygen KLL Auger electron peak at KE = 508 eV with respect to the Fermi level is characteristic for the uncharged surface of MgO [18].

Because of the insulating character of MgO, LEED patterns could be obtained only for high electron energies. Fig. 2 shows the LEED patterns recorded for a primary electron energy of 190 eV before and after the deposition of 30 Å of MgO. Both patterns exhibit a (1×1) hexagonal symmetry, confirming the homoepitaxial growth of MgO. The spots are less sharp in the case of the surface with an additional 30 Å of MgO, most likely because of stronger charging or slightly poorer structural long-range order.

The deposition of the thinnest FeO layers drastically changed the electrical state of the samples, making LEED observation possible down to the lowest energies, which demonstrates the much lower energy gap of FeO compared to MgO.

Fig. 3 compares the LEED patterns obtained from the FeO(111) films of different thicknesses. All patterns exhibit a (1×1) hexagonal symmetry that confirms epitaxial growth through the entire FeO film. The orientation of the FeO films is expected to be $(111)_{\text{FeO}} // (111)_{\text{MgO}}$ because of the small mismatch of the lattice parameters, and we can conclude that the FeO follows the orientation of the MgO substrate with high fidelity.

Remarkably, the metallic Fe monolayers produced very poor diffraction patterns with visible 3-fold symmetry (not shown here), and only the oxidation process caused meaningful improvement of the long range order of the surface. The brightness and sharpness of the spots are comparable for all cases, showing the good crystalline quality of the films and their uniform growth mode; however, the broadening of the diffraction spots is an indication of a grainy film structure. It is well known that the initial growth of iron on MgO is island-like [19], and this adsorbate morphology is transmitted to the oxide film. Under the above-mentioned conditions, there is no appearance of {100} facets, which can be easily understood in view of the low dimensionality of the oxide structure [5].

For discussion of the Mössbauer results that are presented below it is useful to recall the spectra for bulk compounds. Under ambient conditions, in the cubic rock-salt structure of FeO, the cations occupy octahedral positions, which have nominally perfect cubic symmetry O_h . In such a case, there are no lattice and valence electron contributions to the electric field gradient on the Fe^{2+} nuclei, and therefore quadrupole interaction should be negligible. Indeed, in stoichiometric

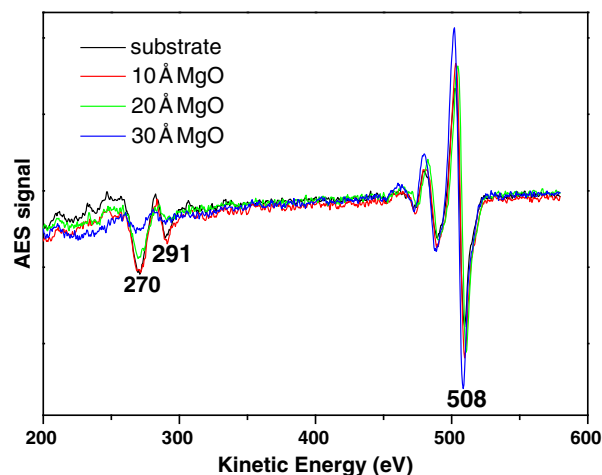


Fig. 1. The AES spectrum for annealed MgO(111) substrate before and after covering with homoepitaxial layers of varying thickness.

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