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A well-ordered surface oxide on Fe(110)

Markus Soldemo [a], Yuran Niu [b], Alexei Zakharov [b], Edvin Lundgren [c], Jonas Weissenrieder [a],*

[a] KTH Royal Institute of Technology, Material Physics, 164 40 Kista, Sweden
[b] Max Lab, Lund University, Box 118, 221 00 Lund, Sweden
[c] Synchrotron Radiation Research, Lund University, Box 118, 221 00 Lund, Sweden

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ABSTRACT

A well-ordered surface oxide grown on Fe(110) has been studied using scanning tunneling microscopy (STM), low energy electron diffraction, low energy electron microscopy, and core level photoelectron spectroscopy. The iron oxide film exhibits wide terraces and is formed after exposure to 100–1000 L at 1×10^{-6} mbar O_2 and 400 °C. Two domains, mirror symmetric in the Fe(110)-lattice mirror symmetry planes but otherwise equal, are observed. The surface oxide forms a relatively large coincidence surface unit cell (16.1 Å × 26.5 Å). Imaging by STM reveals a strong bias dependence in the apparent height within the surface unit cell. The oxygen terminating atomic layer has a hexagonal atomic structure, FeO(111)-like, with the atomic spacing of 3.2 Å, that is expanded by ~6.3% relative to bulk FeO(111).

1. Introduction

Iron and its oxides are among our society's most important materials with applications in a wide range of areas, all from its use as a major alloying element in steel [1] to heterogeneous catalysis [2] and magnetic storage [3]. Because of its importance, much attention has been dedicated to iron and its oxidation or corrosion [4,5] throughout the last century. Several studies have investigated the properties of iron oxides through the growth of well-ordered thin films on substrates other than native iron, e.g. Pt(111) (e.g. [6,7]), Mo(100) [8], Ag(001) [9], and MgO(111) [10]. For native oxide formation, the Fe(100)-surface has been in focus for both experimental and theoretical studies, e.g. [11–14]. However, the oxidation of the (110)-surface, that is the most stable surface of iron, still remains largely uncharted. Iron has a lattice constant of 2.87 Å [15].

The few studies of the oxidation of Fe(110) single crystals include early studies using low energy electron diffraction (LEED) and Auger electron spectroscopy, e.g. Pignocco and Pellissier [16], Leygraf and Ekelund [17], and Langell and Somorjai [18]. Cappus et al. found that a FeO(111) film is grown on Fe(110) at temperatures of 600 K [19]. Xue et al. studied the influence of temperature on the oxide structure [20]. These studies provide an understanding that oxidation at different temperatures and pressures may lead to the formation of different oxide phases. Of interest for this study is a surface oxide phase originally presented with a LEED-pattern by Langell and Somorjai [18]. The phase has later also been observed by Weissenrieder et al. using scanning tunneling microscopy (STM) [21]. However, none of these studies provide a more detailed description of the surface oxide. Other large surface unit cells of iron oxides grown on Fe(110) have been reported by e.g. [22].

In this study, a thin film of iron oxide supported on Fe(110), that is well-ordered over large areas and easily reproduced, is studied. STM at atomic resolution is used to show that the iron oxide displays a termination similar to that of an oxygen terminated FeO(111) but with an expansion of the atomic distances within the surface plane. The oxide forms a relatively large surface coincidence unit cell (moiré-pattern), and the apparent height within the coincidence unit cell changes with applied bias (STM). Low energy electron microscopy (LEEM) and micro-low energy electron diffraction (μLEED) are used to study the periodicity of the structure. It is shown that two mirror domains coexist on the surface.

2. Experimental details

The Fe(110) sample used in this study is a commercially acquired single crystal that deviates less than 0.5° from the (110)-plane (Surface Preparation Laboratory, The Netherlands). The cleaning procedure consists of cycles of argon sputtering at 1 keV at room temperature followed by flash annealing to 540 °C, repeated until the sample exhibits a sharp (1 × 1) LEED-pattern. The iron oxide film was grown by exposing the sample to 1×10^{-6} mbar oxygen gas at 400 °C, which is within the parameter range used by Langell and Somorjai [18].

Scanning tunneling microscopy (STM)/spectroscopy (STS) characterization was performed using an Omicron VT-STM at room

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* Corresponding author.
E-mail address: jonas@kth.se (J. Weissenrieder).

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temperature and in ultra-high vacuum conditions. The imaging was performed in the constant current mode and the spectroscopy was performed in the current imaging tunneling spectroscopy (CITS) mode with one IV-curve recorded every fifth imaging pixel and every fifth imaging row. All STM-images and STS-data were recorded using electrochemically etched W-tips. The STM-chamber is attached to a preparation chamber, which is equipped with facilities for argon sputtering, sample annealing, leak-valves for introduction of gases and a LEED. The base pressures in both chambers are low 10^{-10} mbar [23].

Oxygen coverage measurements were carried out using X-ray photoelectron spectroscopy (XPS) at the high-resolution core level photoelectron spectroscopy endstation at beamline I311 at Maxlab, Sweden. The endstation is comprised of a Scienta SES-200 analyzer, LEED, and standard surface science sample preparation equipment [24]. The oxygen coverage of the iron oxide thin film was measured by integrating the O 1s-spectrum intensity. The integrated O 1s spectrum intensity from Pt(111)-p(2×2)O was used as a reference signal, see e.g. [25]. The O 1s-spectra were measured using a photon energy of 870 eV.

LEEM and μLEED measurements were carried out at the LEEM/PEEM endstation at beamline I311 at Maxlab, Sweden. The LEEM-setup is a SPELEEM III, Elmitec GmbH, and has a lateral resolution of 20 nm. The preparation chamber had facilities for sample cleaning and sample preparation; argon sputtering and annealing, leak-valve for introducing oxygen gas, and LEED [26]. The base pressures in both chambers are low 10^{-10} mbar.

3. Results

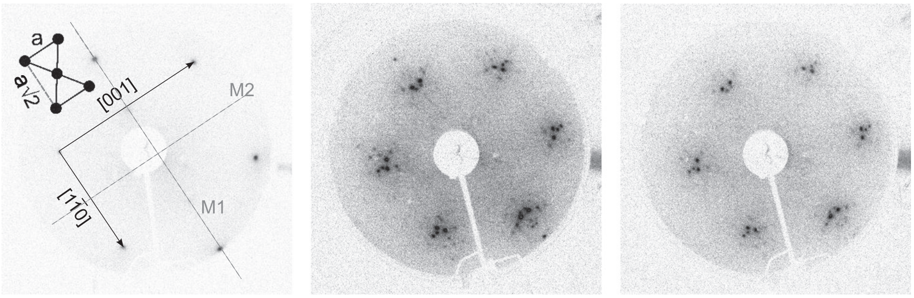
The iron oxide phase of interest in this study has the same LEED-pattern as Langell and Somorjai reported in [18, Fig. 6(b)]. That LEED-pattern is here shown in Fig. 1 together with the LEED-image of the clean Fe(110) surface. The mirror planes in the LEED-image for the clean Fe(110) surface (M1 and M2 in Fig. 1(a)) are also mirror planes in the LEED-pattern of the oxidized Fe(110) surface (Fig. 1(b) and (c)). A ball model of the real space Fe(110)-lattice is drawn in Fig. 1(a). It is orientated such that both the reciprocal space and real space lattice directions are aligned. Both in LEED and STM, the oxide phase is observed over a wide oxygen gas dose range. However, at 500 L of oxygen gas exposure the coverage of the structure is peaking and it is basically the only structure observed. The Fe(110)-spots are decreasing in intensity as the coverage of the oxide increases, however faint Fe(110)-spots can still be observed even at a dose of 500 L O_2. By XPS-measurements, the iron oxide film at this dose is found to contain an amount of oxygen corresponding to 3.2 oxygen FeO(111)-layers or 2.3 oxygen atoms per iron atom on the unreconstructed Fe(110) surface.

To disentangle the oxide structure's LEED-pattern into its components, LEEM- and μLEED-techniques were used. Bright-field LEEM and dark-field LEEM images with corresponding μLEED-patterns from a surface dosed with 100 L O_2 are shown in Fig. 2. The colored rings in the LEED-pattern around the (0,0)-spot in the upper left inset of the bright-field LEEM-image in Fig. 2(a) show the selected spots for the dark-field LEEM-images in Fig. 2(b) and (c). The dark-field LEEM-images in Fig. 2 clearly show that the black regions in one of the images match the non-black regions in the other. The imaged non-black regions (in slightly varying shades of gray) is dominated by one of the two mirror domains, but may also contain minor contributions from the opposite domain. The sizes of individual patches of the different domains may be too small to be resolved by the instrument since the lateral resolution is 20 nm at best. Thus, the non-black regions are interpreted as high density of patches of one of the domains and the black regions as low density of patches of that domain. The domains are observed to extend over micrometer ranges.

In the μLEED-patterns corresponding to the bright regions in the dark-field LEEM-images, geometrical figures are drawn to point out different features. The strongest spots form a slightly elongated hexagonal pattern that is associated with the atomic configuration on the surface, and the surface's superstructure form a parallelogram. The two μLEED-patterns are mirror symmetric to each other in the M1- and M2-planes of Fe(110), see Fig. 1(a). In the direction of the hexagon elongation, a 9 times periodicity is observed, which is rotated approximately 2°off the Fe(110) [$\bar{1}$11]- and [1$\bar{1}$1]-directions for the two different domains.

If the slightly elongated hexagons in the μLEED-images are approximated as hexagons, the superstructure is described by the matrix (9, 2; 0, 5). The [10]-direction within the hexagonal layer (corresponding to [10$\bar{1}$]-, [$\bar{1}$10]- or [0$\bar{1}$1]-direction on fcc(111)) is in real space rotated 33.3° off the Fe(110) [1$\bar{1}$0]-direction to fit the LEED-pattern. The atomic distance within of the hexagonal pattern is 3.2 Å and the superstructure consists of a parallelogram with sides 16.1 Å and with 26.5 Å with 72.2° as the smallest angle. A real space ball model comparison between the Fe(110)-pattern and the superstructure is shown in Fig. 3(a), where the gray balls represent the Fe(110) surface, the red balls represent the surface terminating oxygen atoms, the black balls represent the positions where the substrate Fe(110) iron atoms and the surface layer atoms are in registry, the blue balls indicate the corners of the experimentally determined surface superstructure and the blue parallelogram the experimentally determined surface superstructure unit cell. Since the black balls and blue balls do not superimpose, the superstructure cannot solely be explained by the mismatch between the surface structure and the Fe(110)-substrate. Using the configuration in Fig. 3(a), and the mirror symmetric structure, the corresponding patterns in the reciprocal space are shown in Fig. 3(b).

Scanning tunneling microscopy reveals that the surface oxide is well-ordered over wide areas and that there are two different mirror domains present. High resolution images of the oxide are shown in Fig. 4 for a wide range of different imaging parameters. These images



(a) (b) (c)

Fig. 1. LEED-images collected at an electron energy of 80 eV (in inverted gray scale). (a) Clean Fe(110) together with a ball-model of the surface, lattice directions and mirror symmetry lines (marked M1 and M2). The iron oxide is formed at 400 °C with oxygen gas doses of (b) 250 L and (c) 1000 L.