Identification of O-rich Structures on Platinum(111)-Supported Ultrathin Iron Oxide Films

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Abstract:

Using high-resolution scanning tunneling microscopy (STM) we have studied the oxidation of ultrathin FeO films grown on Pt(111), which was accomplished by atomic oxygen exposure. At the initial stage of the FeO film oxidation, we identified three distinct types of line defects, all of which form boundaries between FeO domains of opposite orientation. Two types of line defects appearing bright (*type-i*) and dark (*type-ii*) in the STM images at typical scanning parameters are “metallic”, whereas the third line defect exhibits nonmetallic behavior (*type-iii*). Atomic-scale structure models of these line defects are proposed, with *type-i* defects exhibiting 4-fold coordinated Fe atoms, *type-ii* exhibiting 2-fold coordinated O atoms, and *type-iii* exhibiting tetrahedrally-coordinated Fe atoms. In addition, FeO₂ trilayer islands are formed upon oxidation, which appear at FCC-type domains of the moiré structure. At high scanning bias, distinct protrusions on the trilayer islands are observed over surface O ions, which are assigned to H adatoms. The experimental data are supported by density functional theory (DFT) calculations, in which bare and hydroxylated FeO₂ trilayer islands are compared. Finally, we compare the formation of O-rich features on continuous FeO films using atomic oxygen with the oxidation of Pt(111)-supported FeO islands accomplished by O₂ exposure.

Keywords: iron oxide, O adatom dislocations, FeO_{2-x} islands, catalysis, scanning tunneling microscopy (STM), density functional theory (DFT).

1. Introduction

Transition metal oxides are important in catalysis, where, among others, they are used as support materials for the actual active material – usually precious metal nanoparticles (Pt, Pd, Rh, Ru, Au) [1–4]. This simplified picture of a catalyst implies that the oxide supports would not be important for the catalytic reactivity. However, it has long been known that the supporting oxide material does influence the catalytic reactivity, especially if reducible oxides are used such as TiO_2 , CeO_2 or iron oxides [5–8]. One important reason for a promotional impact of reducible oxide supports on catalysis is that O ions of the support can participate in the chemical reactions. In the so-called “Mars-Van Krevelen mechanism”, O ions of the support are consumed within the surface reactions (reduction of the oxide support), and gas phase oxygen re-oxidizes the oxide support at the end of a catalytic cycle [9].

The removal of O ions from the oxide surface lattice in its stoichiometric form is energetically often very costly and cannot occur at low reaction temperatures [10]. In oxidation reactions at O_2 -rich conditions, an alternative is that O-rich surface structures or chemisorbed oxygen species at the oxide-metal interface are involved in the surface chemistry rather than O ions from the oxide lattice [11]. Accordingly, the structural and chemical assessment of O-rich structures on oxide surfaces is essential for an improved understanding of catalytic processes occurring at O_2 -rich conditions.

One of the best studied model catalyst systems that couples a reducible oxide phase to a noble metal surface is the polar $\text{FeO}(111)$ bilayer film grown on $\text{Pt}(111)$ [2,4,12]. This model system is of high relevance since Pt is one of the most common catalysts, for example, in three-way catalytic converters, and since iron oxide is used in a number of catalytic processes, including methanol oxidation to formaldehyde, the water-gas shift reaction, and styrene production [12]. In surface science, the study of thin films is often preferred over the study of single crystalline

bulk-oxides, because the preparation of metal-oxide surfaces with defined structures and stoichiometries can be very difficult [1,2].

The FeO(111) bilayer consists of hexagonal closed packed O- and Fe-layers with the O-layer at the surface and the Fe-layer sandwiched between the surface O-layer and the Pt(111) support. Because of a misfit angle of $\sim 0.6^\circ$ between the FeO(111) film and the Pt(111) support and the lattice mismatch between the FeO lattice (~ 3.1 Å) and the Pt(111) substrate (2.77 Å) the FeO(111) bilayer on Pt(111) is characterized by a moiré pattern, which shows a ~ 25 Å periodicity (see Fig. 1a). The FeO(111) bilayer film on Pt(111) has been studied in great detail by means of scanning tunneling microscopy (STM) [13–20], X-ray photoelectron diffraction [20,21], density functional theory (DFT) [15–17,19,20], and a number of other surface science techniques [12].

A related system has been derived from the FeO bilayer films, which consists of Pt(111)-supported FeO bilayer islands [22–24]. This is a so-called “inverse catalytic model system” [4,7,25], where the precious metals are covered by ultrathin oxide patches. In contrast to continuous FeO bilayer films on Pt(111), the FeO–Pt(111) interface in these model systems is accessible, rendering them catalytically very active, for example, in low temperature CO oxidation [22]. This interesting catalytic model system allows for detailed studies of the FeO–Pt(111) interface [26], so that structure-activity relationships can be established [22,24,27].

Another very interesting model system derived from FeO bilayer films is FeO₂/Pt(111). This system, also denoted as O–Fe–O (FeO₂) trilayer structure, was first proposed by Sun *et al.* who exposed a FeO(111) bilayer film to O₂ pressures in the mbar regime at elevated temperatures [6]. The observed enhanced CO oxidation activity [compared to clean Pt(111) and nm-thick Fe₃O₄(111)] following this preparation was linked to the formation of FeO₂ islands, which are characterized by an O–Fe–O–Pt stacking [6,28,29]. Thus, in contrast to the FeO(111) bilayer film, the FeO₂ trilayer islands contain O atoms at the interface between the oxide film and the Pt(111) substrate. Although the “FeO₂ trilayer structure” is catalytically very active, Fu *et al.*

reported that this system is less active in low-temperature CO oxidation than Pt-supported FeO bilayer islands [30].

We have previously studied the evolution of O-rich structures on FeO / Pd(111) by STM and DFT [31]. Upon exposure to atomic O, the formation of ordered, triangular O adatom dislocation loops was observed on the Pd(111)-supported FeO bilayer [31]. We found that the sides of these triangular structures are composed of 4-fold O-coordinated Fe atoms as opposed to the original 3-fold O-coordinated Fe atoms in the stoichiometric FeO film. The identification of the O adatom dislocation loops on FeO / Pd(111) was crucial for the assignments of the edge-terminations on Pt(111)-supported FeO nanoislands (see ref. [26] & [27]). Upon further O exposure the O dislocation loops on FeO / Pd(111) spread in a disordered manner, before the formation of FeO₂ trilayer islands set in. However, no systematic study on the evolution of O-rich structures on FeO / Pt(111) exists yet.

In the present work, we study the oxidation of FeO / Pt(111) by atomic O exposures at temperatures between 300 and 500 K in a stepwise fashion. Three distinct types of line defects are identified, all of which form boundaries between FeO domains of opposite orientation. Atomic-scale structure models of all these line defects are proposed on the basis of STM images. At high O exposures, FeO₂ trilayer islands are formed, which were found preferentially at FCC-type domains of the moiré structure. Distinct protrusions on the trilayer islands are observed over surface O ions, which we assign to H adatoms. This assignment and the structural details of the FeO₂ trilayer islands are further addressed in our DFT modeling.

2. Methods

2.1 Experimental methods

STM measurements were performed at room temperature using a home-built Aarhus STM, in an ultra-high vacuum system with a base pressure of 1×10^{-10} mbar [18,31]. The sample was imaged in constant current mode using a mechanically cut Pt/Ir tip. The Pt(111) crystal was cleaned by cycles of Ar⁺ sputtering and annealing at 1100 K, as well as by heating in 1×10^{-8}

mbar O₂ to remove carbon when necessary. The FeO film was grown [32,33] by deposition of Fe, supplied by an electron-beam evaporator, onto the clean Pt(111) surface at room temperature followed by oxidation in O₂ at 1000 K for a few minutes. Atomic oxygen was produced, as described previously [31], from molecular O₂ using a thermal cracker (Oxford Applied Research, TC-50). For these exposures the O₂ gas was flowed through the cracker at a background pressure of 1×10^{-8} mbar, while operating the cracker at a fixed power of 54 W. The actual exposure of atomic oxygen on the samples is unknown, but it is proportional to the O₂ pressure and the exposure time. Throughout, O exposures are given as exposure times (in sec) which all refer to a background pressure of 1×10^{-8} mbar. Atomic O exposures were performed with the sample at room temperature, after which the sample was briefly annealed at 500 K. The sample temperature was measured by a K-type thermocouple spot-welded to the edge of the crystal.

2.2 Computational methods

Spin-polarized DFT calculations were performed using the Dudarev's DFT+U approach [34], as implemented in the Vienna Ab Initio Simulation Package (VASP) code [35,36]. The projector augmented wave (PAW) potentials [37,38] were used for describing the electron-ion interactions, and the generalized gradient approximation (GGA-PW91) [39] was used to describe the exchange-correlation functional. The electron wave function was expanded using plane waves with a kinetic energy cutoff of 400 eV. The parameters describing the on-site Coulomb interaction between Fe 3d orbitals were chosen to be $U = 4$ eV and $J = 1$ eV ($U_{\text{eff}} = U - J = 3$ eV), which is precisely what we used in previous studies of the FeO / Pd(111) [31] and FeO / Pt(111) [1–19,27,40–42] systems. To model the FeO₂ trilayer islands, we used the experimentally observed ($\sqrt{91} \times \sqrt{91}$)R5.2° FeO / Pt(111) unit cell and inserted O atoms between the Pt(111) substrate and the Fe layer at the FCC domain. The substrate is a three-layer Pt(111) slab. All the Fe and O atoms, and the top Pt layer in the slab were allowed to relax, while the bottom two Pt layers were fixed at their bulk-truncated positions using the experimental value for the Pt–Pt spacing in the (111) plane of 2.77 Å [43]. The periodically repeated slabs were separated in the

z-direction by a vacuum region of ~ 14 Å. The first Brillouin zone was sampled at the Gamma point only. The initial guess for the magnetic structure is based on a row-wise anti-ferromagnetic (RW-AFM) structure, with a magnetic defect, due to the odd number of Fe atoms at the TOP domain [19,41,42]. All structures were optimized until the Hellmann-Feynman forces on relaxed atoms were smaller than 0.02 eV / Å.

3. Results and Discussion

3.1 Overview

An STM image of the pristine FeO film is given in Fig. 1a, showing the characteristic features of the moiré structure observed at low bias voltages. Detailed studies of the STM contrast of the FeO film at various bias conditions and with different tip states have made it possible to identify the different high-symmetry domains in the moiré pattern and the types of atoms imaged [17,19,41]. The three high-symmetry domains of the FeO monolayer are denoted according to the stacking of the Fe and O layers relative to the Pt surface: At face-centered cubic (FCC) domains, both Fe and O atoms sit above hollow sites, at hexagonal close-packed (HCP) domains, Fe atoms sit above hollow sites and O atoms above Pt atoms, and at TOP domains, Fe atoms sit atop Pt atoms while O atoms sit above hollow sites. At low bias, in the imaging mode shown here (which most closely reflects the film's local density of states [41]), the darkest regions correspond to FCC domains and the protrusions in these domains correspond to O ions. The bright regions exhibiting distinct protrusions correspond to TOP domains, and the protrusions to Fe ions. These features serve as reference points in the STM images of the oxidized film. In the high-resolution STM images we use the symbols $\square$, $\circ$, and $\triangle$ to designate the FCC, TOP and HCP domains, respectively. At large positive and negative bias (> 1 V or < -1 V), the contrast changes such that the FCC domains become bright.

Under UHV conditions the FeO monolayer film is effectively inert to O_2 . Thus, to oxidize the FeO film we have used atomic oxygen. Directly following atomic O exposure at room temperature, we found it impossible to establish stable tunneling conditions, presumably due to

the presence of weakly-bound oxygen species on the surface. However, stable imaging could be established after heating to 500 K, which probably caused desorption of the weakly-bound species, incorporation into more stable ordered structures, or both. An overview of the features observed with increasing O exposures is shown in Fig. 1b–d. The predominant features are bright islands, each occupying a single domain of the moiré structure and increasing in density with increasing O exposure. These islands show strong similarity to features observed previously following oxidation of FeO / Pt(111) with O₂ in the mbar range [6,28,29] and of FeO / Pd(111) with atomic oxygen [31], and are assigned to patches of trilayer FeO₂. Simultaneously, line defects are observed, commonly forming the boundaries of triangular domains, assigned to O-rich edges between regions of opposite rotational orientation. In the following, we look in detail at the structures formed on FeO / Pt(111) upon O exposure.

3.2 Line defects

Pristine monolayer FeO(111) films grown on Pt(111) and Pd(111) are found to grow in only one of two possible orientations, differing in the stacking arrangement of the Fe and O layers in relation to the stacking sequence of the close-packed substrate layers. Previous studies have shown that these films can accommodate slight O excesses and deficiencies by forming domains of the opposite FeO orientation by shifting the O layer, the excess or deficient O being determined by the structures of the domain boundaries [17,18,31]. Regarding the two possible FeO orientations we distinguish between favored and unfavored FeO [19,26]. FeO films on Pd(111) were observed to form only a single type of domain boundary, where Fe ions occurring in 4-fold O coordination appear bright in STM images [31].

In the case of FeO / Pt(111), we observe three distinct types of domain boundaries, examples of which are shown in Fig. 2a. The FeO film in this image is divided by these boundaries into three regions. At the left and upper right, the film exhibits the same orientation as that shown in Fig. 1a, i.e. the favored orientation of the pristine FeO film. In the large middle region, the orientation is reversed, as can be seen by observing the orientation of the bright,

triangularly-shaped domains. Separating this central region from the outer ones results into three types of domain boundaries which differ in their appearance, in their orientation relative to that of the FeO, and in the arrangement of the moiré domains in their vicinity. Two of the edges, denoted (i) and (ii), shown in greater detail in Fig. 2b,c, are oriented in the same directions and exhibit little variation in apparent height with bias voltage; *type-i* boundaries are imaged bright and *type-ii* boundaries are imaged dark relative to the surrounding FeO. These “metallic” line defects differ, however, in the arrangement of moiré domains on either side. Both *type-i* and *type-ii* line defects are bordered by FCC domains, but across the *type-i* line defects, the moiré domains are mirrored, while across *type-ii* lines they are mirrored and shifted by half the moiré periodicity, i.e. these act as glide lines.

Considering these symmetry properties as well as the placement of the nearby moiré domains, we construct models for the boundaries by joining two oppositely oriented FeO sheets such that the experimentally observed moiré structure is reproduced, and eliminating overlapping atoms or those with nearest-neighbors with the same type. The fact that these structures are so narrow –restricted essentially to a single atomic row – restricts the possibilities to the simplest structures, and we consider as plausible models exhibiting bond distances similar to those found in the pristine FeO film. This results in the structures shown in Fig. 3a,b. The *type-i* structure consists of a chain of 4-fold coordinated Fe atoms identical to the structure previously observed in oxidized FeO / Pd(111) [31], which appear as bright protrusions in the STM images. The *type-ii* structure, in contrast, appears to consist of a row of 2-fold-coordinated O atoms, as shown in Fig. 3b. This type of structure was not observed in the case of oxidized FeO / Pd(111). These 2-fold-coordinated O atoms are presumably pulled closer to the Pt substrate due to the missing Fe bond, possibly explaining the dark appearance of the domain boundary. As has been discussed previously [18,31], the amount of excess O or Fe incorporated by these types of line defects can be determined by considering the formation of closed triangular loops whose edges comprise the structures. A triangular dislocation loop bounded by *type-i* edges requires addition of a single row of O atoms the length of the triangle’s side, such that the edges themselves effectively

incorporate an oxygen excess of $1/3$ their length in atoms [31]. *Type-ii* edges, which are similar to O vacancy dislocation loops formed upon reduction of monolayer FeO but with O and Fe atoms exchanged, incorporate the same amount of excess oxygen ($1/3$ their length in atoms) as *type-i* edges, though in this case accomplished by reduced density of Fe.

Type-iii edges are clearly distinct from the other two. The most striking difference is the strong bias dependence of the apparent height of the feature compared to the surrounding FeO film, as shown in Fig. 2d. A sharp change from dark to bright occurs between +0.3 and +0.6 V, signaling the onset of non-metallic character. This observation is suggestive of a structure where Fe ions are present in a distinctly different environment compared to the 2-, 3-, and 4-fold coordinated species observed for the pristine film and in O-rich and O-deficient line defects, where Fe in all cases interacts directly with the Pt substrate [18,31]. Without resolving atomic features, we can only speculate about the structure of the *type-iii* line defects, but considering again the arrangement and locations of high-symmetry domains in the vicinity of the line defect (Fig. 2d), we can determine the arrangement of atoms directly adjacent to it. A plausible model is shown in Fig. 3c, consisting of a row of tetrahedrally-coordinated Fe ions. We propose that this type of 3D O-coordination environment, which decouples the Fe from the Pt surface, is responsible for the observed non-metallic behavior of the species. Like the *type-i* and *type-ii* line defects, this structure also incorporates excess O. Consideration, as with the other types, of formation of a closed triangular domain, this particular model incorporates twice as much oxygen, or $2/3$ its length in atoms (note that the edges can be constructed as those bounding an O vacancy dislocation loop, incorporating an oxygen *deficiency* of $1/3$ [18], with an extra row of O atoms added, giving the resulting $2/3$ oxygen excess).

3.3 FeO_2 trilayer islands

The bright islands observed in STM images at all O exposures, and which saturate the surface at the highest used O exposure, are assigned to patches of FeO_2 trilayer islands. By high-resolution STM, combined with DFT calculations, we are able to provide insight into the

details of these structures. Fig. 4a,b show STM images of four closely-spaced islands. We note that each island is located at an FCC domain of the FeO moiré structure (marked by squares in the images), and that these islands are separated by bare FeO. That is, the FeO₂ does not form a contiguous layer, at least at low O exposures. As is visible in Fig. 4a,b as well as in the higher-resolution images in Fig. 4c,d, at relatively high bias voltages, distinct atomic protrusions are observed which show a tendency toward $\sqrt{3}\times\sqrt{3}R30^\circ$ arrangement. At lower bias voltage, the (1×1) hexagonal lattice of the FeO₂ becomes visible, and the protrusions observed at high bias are found to be coincident with this lattice. Registry analysis, shown in Fig. 4e, using the positions of Fe atoms at nearby TOP domains, shows these protrusions to be coincident with the O sub-lattice of the surrounding FeO, i.e. between three Fe ions and, at the FCC domain, above *hcp* hollow sites of the Pt(111) surface.

We therefore interpret the STM images as showing the uppermost O layer of the FeO₂. Location of these O atoms above *hcp* hollow sites, and location of the Fe atoms above *fcc* hollow sites implies placement of the lower O layer directly atop surface Pt atoms, an arrangement which was previously found to be most favorable in calculations by Giordano *et al.* [28] The bright protrusions observed at the O positions are assigned to H adatoms resulting from reaction of water with the FeO₂, forming OH groups. Rapid hydroxylation of trilayer FeO₂ by traces of water in the background gas was recently reported by Johansson *et al.* [44] on the basis of XPS measurements. Although the heating treatment applied to the sample should have removed most H adatoms formed during O exposure, exposure to water from the background gas following the treatment and while the sample was in the STM for imaging can still be significant. The corresponding structure, depicted schematically in Fig. 4f, can be viewed as resulting essentially from intercalation of O beneath the FeO film at FCC moiré domains, such that the Fe and upper O layer remain contiguous with the surrounding film.

Our DFT calculations support this interpretation of the STM data. Fig. 5a shows the optimized structure formed by placement of 27 interfacial O atoms between Pt(111) substrate and FeO film at the FCC domain of the moiré unit cell. The O atoms are found to be stable at the atop Pt sites.

We note that due to the insertion of these interfacial O atoms, Fe atoms and topmost O atoms at the FCC domain are lifted by 0.93 Å and 1.00 Å, respectively, when compared against the optimized pristine FeO / Pt(111) thin film structure. The topmost layer of O atoms, protruding furthest from the surface where the interfacial O layer was added, appear in the simulated STM image (simulated based on the Tersoff-Hamann approximation [45]) in Fig. 5b as bright islands similar to those observed in the experiments. The particular stability of the FeO₂ structure at FCC domains was reflected in a simulation of a continuous FeO₂ trilayer, where an entire layer of interfacial O atoms has been added, i.e. O atoms were added at all domains of the FeO moiré structure (not shown). This structure was found not to be stable, with interfacial O atoms at HCP and TOP domains shifting away from *fcc* and *hcp* hollow sites and causing severe distortion of the structure. This observation again points toward the particular stability of adsorption of interfacial O directly atop Pt, limiting the FeO₂ to islands at FCC domains.

It has previously been postulated that the $\sqrt{3}\times\sqrt{3}R30^\circ$ arrangement of bright protrusions observed in STM images of the FeO₂ trilayer islands result from spontaneous relaxation of Fe ions away from the surface, and thus the $\sqrt{3}\times\sqrt{3}R30^\circ$ structure was considered as an intermediate state in the transformation of the FeO(111) into the Fe₂O₃(0001) film [28]. Our calculations show no evidence for this type of relaxation, but they do support the proposal that these features arise from H adatoms. A stable structure was found in calculations where H atoms were added, as shown in Fig. 6a. The H adatoms reside atop oxygen in the topmost O layer, and give rise to bright protrusions in the simulated STM image, as seen in Fig. 6b.

3.4 FeO nanoislands

Our experiments utilized an atomic oxygen source to produce the structures studied, and previous studies have either had to employ high O₂ pressures [6,28,29,44] or NO₂ [44] in order to introduce excess oxygen to the FeO films. Nanometer-scale FeO islands, on the other hand, have been found to oxidize more readily, with O-rich features appearing after O₂ exposures in the 10⁻⁶ mbar range [26]. High-resolution images of FeO islands grown on Pt(111) as described

previously [26], following exposure to 1.3×10^{-6} mbar O_2 at 475 K, are shown in Fig. 7. These islands exhibit bright patches assigned to trilayer FeO_2 which are imaged with atomic resolution. Importantly, the patches show the same characteristics as those formed on the continuous FeO film with atomic oxygen: they are located at FCC domains and show atomic protrusions corresponding to the topmost O layer. In addition, some of the O atoms also appear brighter than others, indicating the presence of H adatoms (OH groups).

In addition to the oxidized edges, which react directly with CO [22,24,27], and the line defects which enable reversals of the island edge terminations [26], the FeO_2 trilayer patches formed on these FeO islands can themselves act as O sources. DFT calculations by Giordano *et al.* indeed showed that the reaction of CO with O atoms at a boundary between the FeO_2 structure and bare Pt(111) surface can be very facile [46]. Accordingly, the islands seen in Fig. 7 exhibit at least two possible catalytically active sites.

3.5 Implications

Finally, we briefly comment on the implications of the presented data. First, we find it noteworthy that the structure of the bright O adatom dislocations on FeO / Pt(111), i.e. the *type-i* defects exhibiting 4-fold coordinated Fe atoms, is indeed identical to those observed previously on FeO / Pd(111), where they often occurred as loops [31]. This result is relevant, because it justifies retroactively the assignments of the edge-terminations on Pt(111)-supported FeO nanoislands (see ref. [26] & [27]), which completely relied on the assignment of the bright rows on FeO / Pt(111) being O adatom dislocations, although this was at that time established solely for the FeO / Pd(111) system.

Second, regarding the “ FeO_2 trilayer structure”, we stress that the presented STM results point to an incomplete FeO_2 trilayer on FeO / Pt(111), even when high O_2 pressures were used. This is consistent with previous experimental results [29], and the presented new DFT+U calculations also support this point of view. This means that the O-rich FeO / Pt(111), characterized by FeO_2 patches at FCC domains, is heterogeneous, and the FeO– FeO_2 interface must be considered an

inherent feature of this system. Accordingly, to explain the catalytic activity of O-rich FeO / Pt(111), for example towards low-temperature CO oxidation [6,28,29], the FeO–FeO₂ interface must be also considered as possible host of the active sites. Although this possibility has been noted [29], it has not been addressed by DFT calculations. Likewise, the FeO–FeO₂ interface might be of high relevance for explaining the fast hydroxylation of the “FeO₂ trilayer structure” [44], a proposition which still needs to be studied more in depth.

4. Conclusions

In our STM experiments we have looked in detail at the structures formed upon oxidation of a Pt(111)-supported FeO monolayer. Small amounts of excess O are accommodated by formation of domains of inverted FeO orientation, the boundaries of which are O-rich. Three different boundary types are observed, two of which are similar to those observed previously in reduced FeO / Pt(111) and oxidized FeO / Pd(111), involving essentially planar 2-fold and 4-fold coordinated Fe species. The third type of boundary is unique in exhibiting distinctly non-metallic properties, and these are proposed to consist of 1D-chains of Fe ions in bulk-like coordination environments.

Our investigation of the “FeO₂ trilayer structure”, which provides the dominant mechanism for storage of excess O in the FeO film, has shed new light on its atomic structure. The features consist of islands, localized at FCC domains, where excess oxygen atoms are incorporated beneath the FeO film and atop Pt atoms. Thus, the “FeO₂ trilayer structure” on Pt(111) is incomplete, and the FeO–FeO₂ interface must be considered an inherent feature of this system. The islands are also found to exhibit bright protrusions assigned to H adatoms adsorbed atop the topmost O atoms, probably resulting from the reaction of residual water with the “FeO₂ trilayer structure”.

In our DFT modeling and STM simulations we have addressed the “FeO₂ trilayer structure”. We found good agreement with the experimental results, confirming that FeO₂ trilayer islands are formed on the FCC domains. Moreover, the DFT modeling supports the proposal that the

$\sqrt{3}\times\sqrt{3}R30^\circ$ arrangement of bright protrusions observed in STM images of the FeO_2 trilayer islands arises from H adatoms.

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Fig. 1. a) STM image (65 mV, 3 nA) of the FeO monolayer film on Pt(111). Symbols mark the three different high-symmetry domains ($\square$ = FCC, $\circ$ = Top, $\triangle$ = HCP). b,c,d) STM images of the FeO film after exposure to increasing doses of atomic oxygen (O_2 background pressure set to 1×10^{-8} mbar), followed by brief annealing at 500 K. b) (0.9 V, 0.2 nA) 90 sec, c) (1.0 V, 0.3 nA) 180 sec, d) (2.0 V, 0.2 nA) 480 sec.

Fig. 2. Line defects formed by oxidation of the FeO film. a) Large-scale STM image (2.6 V, 0.2 nA) showing the three distinct types of line defects observed, all of which form boundaries between FeO domains of opposite orientation. Under these imaging conditions, bright areas of the moiré pattern correspond to FCC-type domains. The central part of the image shows a domain of inverted orientation relative to the areas of the film at left and upper right. Yellow diamonds show the moiré unit cell in the different regions. b) Atomic-scale STM image (0.88 V, 0.4 nA) of the bright and dark “metallic” defects denoted *type-i* and *type-ii*, respectively. *Type-i* appears as a chain of bright atomic protrusions while *type-ii* appears as a chain of depressions of vacancies. c) A different region, showing *type-i* and *type-ii* line defects. Note the offset in position of FCC domains on either side of the *type-ii* boundary. d) STM images (0.3 nA) at different sample bias voltages of the *type-iii* line defect, exhibiting non-metallic behavior.

Fig. 3. Proposed models for the three types of line defects observed on the oxidized FeO film. a) *type-i* domain exhibiting 4-fold coordinated Fe atoms. b) *type-ii* domain exhibiting 2-fold coordinated O atoms. c) *type-iii* domain exhibiting tetrahedrally-coordinated Fe atoms. Note the difference in orientation of the domain boundary in this case compared to the others (yellow unit cells).

Fig. 4. FeO₂ trilayer islands. a) and b) show STM images of four FeO₂ trilayer islands, each occupying one domain of the FeO moiré structure, acquired at different bias voltages. c) and d) show smaller scale STM images of one island. Bright protrusions are observed at high bias voltages (c) while the atomic lattice of the island is observed at low bias (d). e) STM image of the same island shown in c) and d), with a superimposed grid corresponding to the Fe sub-lattice of the film. f) Atomic model for the FeO₂ trilayer island at an FCC domain. The Fe layer and upper O layer are in registry with the surrounding FeO film while an extra O layer is added at the interface, bound atop Pt atoms.

Fig. 5. a) Top (upper panel) and cross-section (lower panel) views of the optimized, DFT+U-based Pt(111)-supported FeO₂ trilayer structure. Interfacial O atoms have been placed only in the FCC domain, in accord with experimental findings. b) Simulated STM image at a bias voltage of +0.4 V. The bright protrusions arise from protruding O atoms in the FeO₂ trilayer. The unit cell used in the calculations is indicated by the white, dashed diamond.

Fig. 6. a) Top (upper panel) and cross-section (lower panel) views of the optimized, DFT+U-based Pt(111)-supported hydroxylated FeO₂ trilayer structure. Interfacial O atoms have been placed only in the FCC domain. b) Simulated STM image at a bias voltage of +0.4 V. The bright protrusions arise from hydroxyls formed on the trilayer island. The unit cell used in the calculations is indicated by the white, dashed diamond.

Fig. 7. STM images of FeO islands on Pt(111), showing formation of FeO₂ trilayer patches at FCC type domains. The islands were prepared by molecular O₂ exposure (1×10^{-6} mbar) at 473 K.

Graphical abstract