Initial stages of FeO growth on Ru(0001)

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Abstract
We study how FeO wüstite films on Ru(0001) grow by oxygen-assisted molecular beam epitaxy at elevated temperatures (800–900 K). The nucleation and growth of FeO islands are observed in real time by low-energy electron microscopy (LEEM). When the growth is performed in an oxygen pressure of $10^{-6}$ Torr, the islands are of bilayer thickness (Fe–O–Fe–O). In contrast, under a pressure of $10^{-8}$ Torr, the islands are a single FeO layer thick. We propose that the film thickness is controlled by the concentration of oxygen adsorbed on the Ru. More specifically, when monolayer growth increases the adsorbed oxygen concentration above a limiting value, its growth is suppressed. Increasing the temperature at a fixed oxygen pressure decreases the density of FeO islands. However, the nucleation density is not a monotonic function of oxygen pressure.

1. Introduction
Noble metals on FeO surfaces exhibit the well-known ‘strong metal support interaction’ (SMSI) in catalysis [1, 2]. Furthermore, different groups have recently demonstrated experimentally [3, 4] and theoretically [5] how an ultrathin FeO film grown on a noble metal surface presents an enhanced catalytic activity. In particular FeO/Pt promotes CO oxidation and other reactions [4–11].

Binary iron oxides can adopt several structures, including FeO, Fe3O4, γ-Fe2O3 and α-Fe2O3. Bulk FeO (wüstite) crystallizes in the cubic NaCl structure [12]. Along the (111) direction, it consists of alternating layers of Fe2+ cations and O2− anions, each arranged in an hexagonal lattice. The distance between adjacent O or Fe atoms in each hexagonal plane is 0.30 nm. FeO is an antiferromagnet with a Néel temperature of 200 K. The Fe atoms within each (111) plane are coupled ferromagnetically and the different Fe planes are coupled antiferromagnetically. Bulk FeO is metastable below 770 K. Nevertheless, when growing iron oxides in thin film form, FeO layers are often encountered in the first stages of growth on metal substrates such as Pt(111) [13, 14], Cu(001) [15] and Ru(0001) [16–18], and on oxide surfaces (Y-stabilized ZrO2(100)–YSZ–, [19]) even when other oxides (usually magnetite) grow at later stages. On Ru(0001), films that are one and two monolayers (ML) thick have an in-plane spacing of 0.32 nm [16–18]. This large expansion relative to the bulk value has been rationalized as required to reduce the dipole of the polar (111) FeO surface [16].

Ultrathin iron oxides on metal substrates have usually been grown by surface scientists using the separate steps of depositing an ultrathin iron film at room temperature followed by oxidation at ~900 K in a molecular oxygen atmosphere. This sequence is repeated if thicker films are desired [14, 16, 20, 21]. An alternative growth method is that based on oxygen-assisted molecular beam epitaxy (O-MBE), where Fe is deposited under a background pressure of oxygen [22]. Thus the surface is covered with oxygen before Fe arrives at the substrate. Recent work has found that the FeO films can be strongly affected by small changes in growth conditions, producing for example either Fe3O4 or FeO [21]. In the cobalt oxides even the crystallographic orientation of an oxide thin film can be selected [23]. Natural questions are then whether the two methods produce the same structures and morphologies and what factors control FeO film growth.

We have previously studied the growth of iron oxides on Ru(0001) by O-MBE, focusing on magnetite islands on complete FeO films [18] and their phase transformations upon...
mild annealing [24]. In this work we study the initial stages of the FeO growth on Ru. We begin by characterizing O-MBE films on Ru(0001) and show that they yield essentially the same FeO phase as produced by oxidizing Fe films [16]. However, we find that the O-MBE films can be bilayer in height, unlike the monolayer islands typically produced at the initial stages of Fe oxidation. To understand why FeO bilayers or monolayers are produced, we use low-energy electron microscopy (LEEM) ([17, 18, 20, 25]) to image the surface during growth in real space. We propose that the oxygen coverage on the Ru substrate controls whether single layer or bilayer films result. And by analyzing the temperature dependence of the FeO island nucleation density, we estimate the activation energy for surface diffusion of the Fe–O growth species.

2. Experimental details

The experiments were carried out in two experimental stations. The first is a commercial Elmitec III LEEM microscope. The second is a multipurpose ultra-high vacuum chamber equipped with a home-made scanning tunneling microscope (STM) [26], a hemispherical analyzer for x-ray photoelectron spectroscopy (XPS) and a conventional low-energy electron diffractometer (STM/XPS/LEED system).

The XPS system comprises an Al/Mg Kα x-ray source and a Phoibos-150 hemispherical analyzer. The spectra were acquired with a pass energy of 20 eV and calibrated relative to the binding energy of Ru 3d5/2 core level. The STM/XPS/LEED system provides a complementary view of the surface morphology by STM, chemical information by XPS and laterally averaged low-energy electron diffraction (LEED). LEEM allows for fast real-space imaging of the surface during growth of the FeO films, as well as selected-area diffraction measurements. Typical LEEM images were acquired at an electron energy (the ‘start voltage’ of the instrument [27]) of 19 eV.

Single-crystal Ru substrates with (0001) orientation were cleaned by exposure to $5 \times 10^{-8}$ Torr oxygen at 1000 K followed by flashing to 1500 K in vacuum (LEEM system) or by repeated cycles of 20 s exposure to $2 \times 10^{-7}$ Torr and flashing to 1500 K in vacuum (STM/XPS/LEED system).

The films were grown by O-MBE by depositing Fe from a 4-mm diameter Fe rod heated by electron bombardment in a variable background pressure of molecular oxygen. The Fe doser was calibrated by measuring the time needed to deposit a 4-mm diameter Fe rod heated by electron bombardment in a variable background pressure of molecular oxygen. The Fe doser was calibrated by measuring the time needed to deposit 1 ML of Fe on Ru(0001) at 1000 K followed by flashing to 1500 K in vacuum (LEEM system) or by repeated cycles of 20 s exposure to $2 \times 10^{-7}$ Torr and flashing to 1500 K in vacuum (STM/XPS/LEED system).

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Figure 1. Characterization of FeO grown by O-MBE. (A) STM image of an FeO bilayer exhibiting a moiré pattern from the misfit between the FeO and Ru lattices. The image size is 147 nm × 70 nm, sample bias is 1.55 V and tunneling current is 2.1 nA. (B) Profile along the white line in (A). (C) Atomic resolution STM image of the FeO bilayer. The image size is 3.7 nm × 3.7 nm, sample bias is 0.24 V and tunneling current is 15 nA. (D) LEED at 60 eV. (E) XPS Fe 2p core level spectrum. The individual components to the fit (red) are also shown: the 2p1/2 and 2p3/2 photoemission peaks (black), with two additional components to account for the broadening due to multiplet splitting (green), and the shake-up satellites (cyan).

3. Results

3.1. Structural and chemical characterization of a FeO bilayer grown by O-MBE

We begin by characterizing FeO films grown by depositing iron on a heated substrate in an oxygen background, O-MBE, and show that they are structurally and chemically equivalent to films grown by oxidizing a previously deposited iron layer. In figure 1 we show STM, LEED and XPS data for a film grown by oxygen-assisted MBE by exposing the substrate at 900 K to an Fe flux of $1.5 \times 10^{-3}$ ML s$^{-1}$ in $10^{-3}$ Torr of oxygen. The substrate presents monoatomic and biatomic steps (of 0.21 and 0.42 nm height, respectively), and it presents a distribution of terraces with widths from tens of nanometers to several micrometers. The STM image (figure 1(A)) shows a nearly complete FeO film, which has a pronounced corrugation with an in-plane periodicity.
energies of 713.0 and 723.9 eV. It is also well known that FeO and other iron oxides [29] we have added two peaks at binding splitting which is known to occur in the XPS spectrum of FeO of 3.5 eV. To account for the broadening due to multiplet (VLEED) [31]. The electron reflectivity is related to the same potential. These measurements at low energy have been referred to as very low-energy electron diffraction (VLEED) [31].

The Fe 2p XPS spectrum recorded from the grown FeO bilayer is quite complex (figure 1(E)). Its shape resembles quite closely that reported for the surface of bulk FeO [28] or FeO grown on Pt [14]. We fitted it considering a genuine photoemission spin–orbit doublet with binding energies of 708.3 eV (Fe 2p\(^{3/2}\)) and 720.8 eV (Fe 2p\(^{1/2}\)) and a linewidth of 3.5 eV. To account for the broadening due to multiplet splitting which is known to occur in the XPS spectrum of FeO and other iron oxides [29] we have added two peaks at binding energies of 713.0 and 723.9 eV. It is also well known that Fe\(^{2+}\) compounds show an intense shake-up satellite structure above the main photoemission lines [28–30]. These satellites are quite evident in the present case and were fitted with two peaks at 716.9 and 729.2 eV.

In summary, all the techniques employed indicate that the FeO films grown by O-MBE are both structurally and chemically the same as those grown by sequential steps of Fe deposition and oxidation.

Figure 2 shows LEEM images during O-MBE growth of FeO. Substrate steps are observed in the initial bare surface (see figure 2(A)). Then oxygen is dosed. At the electron beam energy employed, oxygen adsorbed on the Ru surface produces a decrease in the local electron reflectivity that darkens the image (not shown). When the oxygen density on the surface saturates (i.e. when the reflected intensity stops decreasing), Fe deposition is started. At this point iron oxide islands nucleate both on the substrate terraces and along the substrate steps (see dark areas in figure 2(B)). The islands grow in size (figure 2(C)) until the surface becomes completely covered by a continuous film of FeO (see figure 2(D)). The LEED pattern obtained in the LEEM instrument after growth (figure 2(E)) agrees well with the pattern from the conventional diffractometer (figure 1(E)). Figure 2(F) shows how the electron reflectivity of the FeO surface (i.e. the intensity of the specular beam) varies with electron energy. This is measured by integrating the intensity of a selected area in a sequence of LEEM images acquired with different energies of the incoming electron beam. The zero energy refers to the sample and the electron gun at the same potential. These measurements at low energy have been referred to as very low-energy electron diffraction (VLEED) [31]. The electron reflectivity is related to the unoccupied density of states of the sample (when the density of states is low, the reflectivity is high), and can serve as a fingerprint of a given film or substrate [25]. In particular, we note that the observed electron reflectivity, characteristic of FeO, is not only observed on FeO/Ru (as shown in figure 2 and in [18]) but also on FeO/YSZ [19] and is very different from that of metallic Fe on Ru (see figure 8 of [17]). Given the total amount of iron deposited for a complete film (figure 2(D), 1.4 ML\(_{\text{Fe}}\)) and the difference in lattice spacing between metallic iron and FeO, the FeO film must have a thickness of 2 ML FeO. As the images show only one stage of island nucleation followed by growth, we interpret that the islands initially nucleated under a pressure of 10\(^{-6}\) Torr are of bilayer height (in agreement with the STM observation of figure 1).

3.2. Influence of temperature and oxygen pressure

Next we consider the effect of temperature and oxygen pressure on FeO growth by O-MBE. As mentioned above, Fe
deposition in $10^{-6}$ Torr of oxygen leads to the nucleation and growth of bilayer-height islands, which eventually cover the substrate. This behavior is not affected by temperature in the range of 800–910 K. However, temperature strongly modifies the number of islands nucleated, as shown in figure 3, with a higher temperature leading to fewer but larger islands. While at 910 K there are $3.4 \times 10^7$ islands $\text{cm}^{-2}$, at 800 K there are $1.3 \times 10^9$ islands $\text{cm}^{-2}$. At the highest temperature, most islands nucleate at substrate step edges.

Oxygen pressure has a strong effect on both the island height and the nucleation density. We first discuss the height. Figure 4 shows growth at a lower oxygen background pressure, $10^{-8}$ Torr. At first glance, the image sequence is very similar to growth at the same temperature (800 K) but higher pressure ($10^{-6}$ Torr, figure 2): islands nucleate and then grow until they cover the surface. But there is a crucial difference between them: depositing 1.4 ML$_{\text{Fe}}$ covers the surface with FeO at $10^{-6}$ Torr, but only $\sim 0.7$ ML$_{\text{Fe}}$ is needed at $10^{-8}$ Torr. Furthermore, the electron reflectivity curves from the complete films grown at each different pressure are quite different (compare figures 2(F) and 4(D)), indicating the different nature of the two films. The electron reflectivity of both films is also very different from the electron reflectivity of metallic iron (figure 8 of [17]). Considering the difference of lattice spacings of pseudomorphic iron and the iron oxide, the coverage for complete films corresponds to $\sim 2$ ML$_{\text{FeO}}$ and $\sim 1$ ML$_{\text{FeO}}$ for $10^{-6}$ Torr and $10^{-8}$ Torr, respectively. Thus, the LEEM results imply that the growth of FeO takes place through monolayer-high islands at the lower pressure, and as bilayer-high islands at the higher pressure. We note that we have already reported in [18] that the electron reflectivity was a good fingerprint for regions that are 1 and 2 ML FeO thick as determined by the attenuation of XPS Ru 5d substrate core levels from each region.

To directly show the difference in island height as a function of pressure, figure 5 presents STM images and profiles from the initial stage of the O-MBE growth. In figure 5(A), corresponding to a pressure of $5 \times 10^{-8}$ Torr, islands are observed both on the Ru terraces and wetting the downward side of the Ru monoatomic step. Both island types present moiré patterns (Fe/Ru is pseudomorphic for less than one complete layer on Ru [17]). In contrast, for a higher pressure ($7 \times 10^{-7}$ Torr), the FeO islands are two layers high, but they appear higher than both the lower Ru terrace and the upper terrace on the right side of the image. We note also that on the Ru substrate patches of (2 × 2), presumably due to adsorbed oxygen, can be observed. In consequence, STM confirms the dependence of island height on oxygen pressure first observed by LEEM.

The intermediate pressure of $10^{-7}$ Torr produces a more complex film, as presented in figure 6. The initially nucleated islands are all of bilayer height. However, as they grow, these bilayer islands switch to growing with monolayer height. The electron reflectivity (figure 6(D)) identifies the areas that are FeO bilayers or monolayers. In the completed film (figure 6(C)) the monolayer and bilayer regions are dark and medium gray, respectively.

The effect of temperature on the number of islands nucleated is presented in figure 7 for $10^{-7}$ and $10^{-8}$ Torr. The trend is similar to the previously presented data at the higher pressure ($10^{-6}$ Torr, figure 3): the island density
Figure 5. STM images of growth of FeO under two different pressures: (A), under $5 \times 10^{-8}$ Torr oxygen (sample bias 1.6 V, tunneling current 1.2 nA), and (B), under $7 \times 10^{-7}$ Torr oxygen (sample bias 2.0 V, tunneling current 1.0 nA), respectively. Both images are 50 nm $\times$ 30 nm in size. In both, a green dashed line marks the location of the monoatomic Ru substrate step, and a profile (acquired at a location marked with a white line in each STM image) is shown below.

Figure 6. (A)–(C) LEEM images of FeO film grown on Ru(0001) at 800 K under an oxygen background pressure of $10^{-7}$ Torr. The total amount of deposited iron is 1.1 ML Fe. The field of view was 10 $\mu$m and the electron energy 18.0 eV. The time elapsed was 0, 120 and 744 s, respectively. The schematics below the images illustrate the cross-sectional morphology of the bare substrate (A), bilayer thick FeO (B), and monolayer plus bilayer thick FeO (C). (D) Electron reflectivity as a function of energy from monolayer (red) and bilayer (black) regions of the final film.

decreases with increasing temperature. At a given temperature the island density is the lowest at the intermediate pressure of $10^{-7}$ Torr.

In summary, at $10^{-6}$ Torr, FeO always grows as a bilayer. At $10^{-7}$ Torr, the initial islands are bilayer. However, as the islands expand, they switch and grow as monolayer FeO. Finally, at $10^{-8}$ Torr, only monolayer FeO grows. The number of islands nucleated decreases with temperature and the influence of oxygen pressure is non-monotonic: fewest islands nucleate at an oxygen pressure of $10^{-7}$ Torr.
3.3. FeO growth with a limited supply of oxygen

Additional insight about the FeO growth mechanism can be gained by limiting the supply of oxygen during growth, as we next describe. Instead of a constant background pressure of oxygen, FeO was grown at 800 K on a surface saturated with oxygen by exposure to 6.5 L (1 Langmuir = $10^{-6}$ Torr s) at a pressure of $10^{-7}$ Torr (figure 8(A)). Iron was then dosed on the surface at the same rate as in the previous experiments. This procedure led to the nucleation of bilayer FeO islands, the dark regions in figure 8(B), as confirmed from post-growth reflectivity measurements. Thus oxygen adsorbed on the Ru reacts with the deposited Fe to nucleate FeO islands. Initially these islands grew while depositing additional iron. Then they stopped growing. At this time the substrate steps became decorated and new islands nucleated in the middle of the Ru terraces (figure 8(C)). The interpretation is that eventually there is not enough oxygen available on the Ru surface to support continued growth of stoichiometric FeO. Then iron–oxygen islands with different composition grow. Regardless of their particular composition, the new islands display a markedly different growth behavior. As soon as the change in growth mode was detected, the iron doser was stopped. Then the surface was saturated again with oxygen by dosing an additional 6.5 L. The iron-rich islands in the center of the image mostly vanish (figure 8(D)), leading mainly to the growth of the initial FeO islands and the nucleation of few additional islands.
Figure 8(E) shows the electron reflectivity from the bare substrate regions during cycles of oxygen dosing (gray shaded regions in the plot) followed by Fe dosing (blue shaded regions). Changes in reflectivity can be related to the oxygen concentration on the Ru [32, 33]. The saturation of the surface upon oxygen exposure is detected by a constant reflected intensity from the substrate terraces as the steady-state oxygen coverage at 800 K is reached after ∼60 s. When the oxygen background is removed, the reflected intensity increases linearly with time (see the inset of figure 8(E)). We attribute this increase to oxygen being removed from the surface, either by desorption or by dissolution into the bulk of the crystal [34]. The slope of the reflected intensity versus time increases during Fe deposition, which indicates that oxygen is being removed faster. This can be rationalized by assuming that some fraction of the adsorbed oxygen is being incorporated into the growing FeO islands. When the reflected electron intensity stops changing (point (C) in the inset to figure 8(E)), distinct islands (center of figure 8(C)) nucleate on the substrate. Because of their distinct growth behavior, we interpret these new islands as oxygen-deficient FeO. Stopping the iron dosing and exposure to oxygen replenishes the density of the oxygen on the Ru, as show by the substrate’s electron reflectivity (point (D) in the inset of figure 8(E)) recovering to nearly the value observed at the end of the first oxygen dose (point (A) in the inset to figure 8(E)). More importantly, the smaller, oxygen-deficient islands disappear and the original FeO islands grow. Repetitions of the cycle lead to similar behavior and a net growth of the FeO islands.

4. Discussion

We find that the FeO phase grown by O-MBE is structurally and chemically identical to the oxide produced by depositing and then oxidizing Fe. But the O-MBE technique produced an unexpected result: the morphology of the film changes from bilayer islands that coalesce to form a continuous film at 10⁻⁶ Torr to monolayer islands that grow into a continuous film at 10⁻⁸ Torr. And during growth at an intermediate pressure (10⁻⁷ Torr) the film initially grew as a bilayer but then switched to growing as a monolayer. These results are surprising because the monolayer and bilayer films have a similar composition and structure. So changing the background oxygen pressure does not change the stoichiometry of the oxide, but instead modifies the film morphology (thickness). At the lowest pressures, the supply of molecular oxygen barely keeps up with the iron atoms arriving at the surface, with an arrival ratio of 7:1 (to be compared to 700:1 at the highest pressure employed), and might be assumed to be insufficient for FeO formation. Our observed behavior might be attributed to the Ru substrate, which on the one hand readily dissociates oxygen [35] and on the other serves as a reservoir of oxygen as iron deposition is started on an oxygen saturated substrate. We next propose an explanation for the striking effect of oxygen pressure on morphology.

In O-MBE, the FeO-free Ru substrate is covered by adsorbed oxygen. Figure 8 (section 3.3) shows that FeO grows from adsorbed oxygen reacting with the deposited Fe. The key to understanding the effect of oxygen pressure on FeO thickness comes from comparing the areal density of the adsorbed oxygen with the oxygen density in monolayer and bilayer FeO, respectively, as we next explain. The areal density of oxygen in an FeO monolayer is a factor of 0.72 less than the density of Ru atoms in the surface layer. If the adsorbed oxygen concentration is lower than 0.72 ML Fe, forming monolayer islands of FeO reduces the oxygen density on the ruthenium. On the contrary, if the oxygen density is higher than 0.72 ML Fe, then forming monolayer FeO increases the oxygen density. But this increase in density is hindered. First, there is a limit to the density of oxygen on Ru: one oxygen atom per Ru atom [34]. Second, even for lower densities oxygen–oxygen interactions on Ru are repulsive, as shown by the decrease of the binding energy as a function of coverage [34]. Thus, we propose that if the oxygen density is sufficiently high, the growth of monolayer FeO is hindered because this increases the density of adsorbed oxygen. Instead, FeO bilayers, with an oxygen density of 1.44 ML Fe (due to the two oxygen planes of the bilayer), grow and remove adsorbed oxygen.

So what evidence supports this mechanism? Data from two methods show that the concentration of adsorbed oxygen is near the value (0.72 ML) proposed to select either monolayer or bilayer growth. First, after cooling to room temperature, FeO islands grown in 10⁻⁶ Torr are surrounded by oxygen-covered Ru with a 2 × 2 structure, as evidenced by STM (see figure 5). An oxygen concentration above about 0.75 ML gives a 2 × 2 structure labeled as (2 × 2)–3O [36]. Second, a rough estimate from the reflectivity changes during FeO growth (see appendix) gives a similar oxygen density. We do note, however, that oxygen densities near 0.75 ML seem high for our continuous or sequential exposures to 10⁻⁷ Torr oxygen, for which we estimate doses in the range of 10 L [31, 34, 35, 37, 38].

In 10⁻⁷ Torr, bilayer FeO islands grow initially. But monolayer FeO grows later at this pressure (see figure 6). This can be rationalized by the decreased oxygen concentration on the Ru caused by the smaller sticking coefficient of oxygen on FeO versus Ru. This difference in sticking coefficient suggests that maintaining the oxygen concentration required to complete a uniform bilayer may be difficult at lower oxygen pressures.

The density of FeO islands as a function of temperature and pressure is also striking. While at a given pressure it always decreases with temperature, pressure plays a role, as readily detected in figure 7. On the one hand, the island densities are lower at the intermediate pressure (10⁻⁷ Torr). On the other, the slope in the logarithmic plot of island density versus inverse temperature is more similar for 10⁻⁷ and 10⁻⁶ Torr than for 10⁻⁸ Torr. This latter effect might be related to the bilayer versus monolayer growth regimes. Further study is required to understand this complex behavior.

Meanwhile, we can interpret the results at a given oxygen pressure in terms of the simple nucleation and growth models that have explained the density decrease of metal and semiconductor islands with increasing temperature [39–41]. As the iron atoms arrive at the surface, they probably form
some oxygen–iron species that diffuse on the surface before reaching either an already nucleated FeO island or another oxygen–iron species. In the former case, the island grows; in the latter case, a new island nucleates. This leads to two regimes [39]: the initial nucleation regime, where the number of islands keeps increasing, followed by the growth regime, where the already nucleated islands keep growing. In this simple picture, increasing the temperature causes faster surface diffusion of the Fe–O complexes, allowing them to explore larger areas, which results in fewer nucleated islands.

But we note that even in homoepitaxial, single-component growth, this model can be too simple, and much more so for our heteroepitaxial, bi-component oxide growth. Nevertheless, it is instructive to estimate the main energy barrier involved by assuming the simplest nucleation model [40] for the highest pressure experiments. Then the island area is disregarded (as well as the bilayer thickness) and the critical nucleus is assumed to be a dimer. The relationship between the island density and the diffusion coefficient is then

\[ S = \alpha \theta / D_S, \]

where \( S \) is the island density, \( \theta \) is the coverage and \( D_S \) is the diffusion coefficient. Solving \( D_S \) using the experimentally measured island density gives the plot of figure 9. Assuming that the diffusion of the iron (or iron–oxygen complex) on the surface follows an Arrhenius form \( D_S = D_{S0} \exp(-E_S/kT) \), where \( D_{S0} \) is a pre-factor and \( E_S \) is the diffusion barrier (eV), \( T \) the temperature and \( k \) the Boltzmann constant, the dependency of \( D_S \) should follow the line shown in figure 9. This corresponds to a diffusion barrier of \((5.9 \pm 0.5) \text{ eV})\). This number is much larger than the typical diffusion barriers for surface diffusion on metals, but it is in the expected range for surface diffusion on oxides [42]. Nevertheless we warn that the model is too simplistic and cannot be expected to capture the detailed growth process, as reflected by an unrealistic diffusion pre-factor of \(10^{37} \text{ cm}^2 \text{ s}^{-1} \). As directly observed in figure 7(E), the estimated energy barrier is much smaller (smaller slope) for the lowest pressure of \(10^{-8} \text{ (2.2 eV)}\), while the intermediate pressure value is closer to the high pressure case \((4.5 \text{ eV})\).

5. Summary

We have studied the initial stages of FeO growth on Ru(0001) by the simultaneous deposition of oxygen and iron at elevated temperatures. In an excess of oxygen (at a background pressure of \(10^{-6} \text{ Torr}\), FeO grows by the nucleation and spreading of bilayer thick islands, which eventually coalesce into a complete layer. There is a strong influence of oxygen pressure: at an oxygen pressure 100 times lower, only monolayer FeO grows. At intermediate pressures, the initial oxide is bilayer but eventually monolayer FeO grows. We explain the influence of oxygen pressure by considering how the concentration of oxygen absorbed on the Ru changes as this oxygen is incorporated into the film. Monolayer FeO formation can either decrease or increase the density of adsorbed oxygen. The latter case, which occurs at high concentrations of adsorbed oxygen, increases the concentration above a critical density. This suppresses monolayer growth, leading to exclusive bilayer growth. Increasing the substrate temperature decreases the island density. But the evolution of island density as a function of oxygen pressure is not monotonic, underlying the complexity of the FeO system.

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Appendix. Estimate of concentration from the limited oxygen experiment

We use changes in electron reflectivity to estimate the density of oxygen adsorbed on the Ru during FeO growth. At the electron beam energy used for imaging in figure 8 (19 eV), the reflectivity from the clean Ru is relatively high because a band gap in Ru(0001) results in a low density of unoccupied states. Adsorbed oxygen atoms provide additional scattering channels, which decrease the reflectivity. The changes in electron reflectivity for O/Ru have been studied using a structural method by Pfnür et al [31]. The changes can also be used to track thermal adatom concentrations, as reported for Au [32] and C [33].

Here we estimate the amount of oxygen adsorbed on Ru just before iron deposition is started in the sequential dosing experiment described in section 3.3 (see figure 8). Disregarding the removal of oxygen due to other factors unrelated to the FeO growth (such as desorption or dissolution...
into the Ru), mass conservation dictates that:

$$c_i = \theta_{FeO}c_{FeO} + (1 - \theta_{FeO})c'_i$$

where $\theta_{FeO}$ is the fraction of the surface covered by the islands of FeO at the end of the cycle, $c_{FeO}$ is the density of oxygen in those islands and $c_i, c'_i$ are the densities of adsorbed oxygen on the Ru substrate before and after the growth of the FeO islands, respectively. We refer to all the oxygen densities relative to the Ru substrate (i.e. a density of 1 corresponds to one atom per Ru substrate atom). The coverage of FeO islands is obtained from the amount of iron deposited on the surface. The initial concentration can then be written in terms of the ratio $r = \frac{c'_i}{c_i}$:

$$c_i = \frac{\theta_{FeO}c_{FeO}}{1 - r\theta_{FeO}}.$$}

We assume that the changes in electron reflectivity are proportional to the changes in the adsorbed oxygen density ($c = \alpha(1 - i)$ where $i$ is the local reflected intensity). (The dependence of oxygen density on reflectivity is, though, unlikely to be linear for our large range of concentrations.) Then the ratio $r$ can be estimated without knowing the proportionality constant $\alpha$. From the observed ratio between intensities in the first growth step of figure (8(E), $\frac{c'_i}{c_i} \sim 1.016$, and FeO coverage (estimated from the deposited iron) during the first deposition cycle (0.017 ML/CeO in bilayer form) we obtain an initial oxygen density in that experiment of $c_i \sim 0.75$ ML/Ru.

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