**Oxidation Pathways in Bicomponent Ultrathin Iron Oxide Films**

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**ABSTRACT:** The reactive growth of ultrathin Fe oxide films on Ru(0001) has been studied and characterized using low-energy electron microscopy, diffraction, and laterally resolved spectroscopies. Under exposure to molecular oxygen at 900 K, we observed the growth of a bicomponent film composed of micrometer-sized flat triangular Fe₃O₄ (magnetite) islands on a FeO (wüstite) wetting layer. Subsequent oxidation using NO₂ at 600 K resulted in the chemical transformation of the initially grown film to a Fe₂O₃ composition but still in bicomponent form. The triangular magnetite islands evolve to γ-Fe₂O₃ (maghemite), and the surrounding layer is converted to α-Fe₂O₃ (hematite). The evolution of both members of the bicomponent iron oxide films, wüstite to hematite and maghemite to maghemite, can be understood by considering that both are topotactic transformations occurring by the diffusion of iron in octahedral sites to react with oxygen on the film’s surface.

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**INTRODUCTION**

Oxides are promising functional materials because their physical properties can be tailored by tuning their stoichiometry and structure. In particular, binary iron oxides range from reasonable conductors (magnetite) to insulators and from ferrimagnets to antiferromagnets. Consequently, understanding the transformations from one phase into another, as well as the influence of external parameters on the observed changes, is a long-standing theme in iron oxide research, with implications in fields as diverse as corrosion, geophysics, and catalysis.

Wüstite (FeO), magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and hematite (α-Fe₂O₃) are the most common binary iron oxides. FeO, the only Fe²⁺ binary oxide, has the cubic NaCl structure, and is an antiferromagnet below 200 K. Magnetite, the oldest magnetic material known, is a mixed valence Fe³⁺/Fe²⁺ iron oxide with an inverse spinel structure, which is predicted to be a half-metal. The maghemite and hematite allotropes only contain Fe³⁺ ions. Maghemite presents the same inverse spinel-related structure as magnetite, albeit with some additional vacancies at the octahedral sites, and is insulating and ferrimagnetic. Hematite, the most stable phase in ambient conditions, is a rhombohedral iron oxide with the corundum structure, and a weak ferromagnet due to canted antiferromagnetism. Table 1 summarizes some of their properties relevant for this work.

The growth of these iron oxides in thin or ultrathin film form has been successfully performed on different metal surfaces, such as Pt(111), Cu(100), Ru(0001), Au(111), or Ag(100). The growth is typically performed by depositing a few atomic layers of iron and oxidizing them afterward. By using molecular oxygen in ultrahigh vacuum (UHV), i.e., pressures below 10⁻⁵ mbar, as an oxidizing agent, the resulting oxides grow in a characteristic, reproducible sequence: the thinnest films that wet the metal substrate completely are FeO(111). Magnetite islands nucleate in thicker films also with (111) orientation. Either an increase of the oxygen pressure to the mbar range or the use of stronger oxidizing agents (such as NO₂) allows for the growth of hematite films. Surprisingly, reports on ultrathin maghemite films are scarce.

The different transformations of iron oxides in bulk form have been the subject of many studies. For example, the topotactic transformation between magnetite and maghemite was initially discussed in terms of the migration of iron cations through the material. In contrast, there are only a few reports of the transformation of ultrathin iron films upon further oxidation or annealing, such as the change between FeO and Fe₂O₃ on Pt(111) and the transformation between magnetite and hematite on Ag(111) and on W(110). However, an unequivocal identification of the iron oxides in very thin film form is a challenging task, since a single spectroscopic or structural measurement does not provide enough information to identify all the possible iron oxides. Therefore, an experimental approach combining microscopy, structural methods, and spectroscopic techniques, is desirable. We have previously grown by molecular beam epitaxy (MBE) bicomponent iron oxide films of FeO/Fe₂O₃ on Ru(0001). We characterized them by low-energy electron microscopy...
Table 1. Summary of Iron Oxide Characteristics (Adapted from refs 1 and 4)\textsuperscript{a}

<table>
<thead>
<tr>
<th>oxide name</th>
<th>formula</th>
<th>oxygen lattice</th>
<th>nominal iron valence</th>
<th>magnetic order</th>
<th>O–O lateral distance (nm)</th>
<th>LEED periodicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>wustite</td>
<td>FeO</td>
<td>fcc</td>
<td>2+</td>
<td>afm</td>
<td>0.305</td>
<td>1 × 1</td>
</tr>
<tr>
<td>magnetite</td>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td>fcc</td>
<td>2+/3+</td>
<td>ferri</td>
<td>0.297</td>
<td>2 × 2</td>
</tr>
<tr>
<td>maghemite</td>
<td>γ-Fe\textsubscript{2}O\textsubscript{3}</td>
<td>fcc</td>
<td>3+</td>
<td>ferri</td>
<td>0.295</td>
<td>2 × 2</td>
</tr>
<tr>
<td>hematite</td>
<td>α-FeO</td>
<td>hcp</td>
<td>3+</td>
<td>canted afm</td>
<td>0.295</td>
<td>$\sqrt{3} \times \sqrt{3}R30^\circ$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In all cases, the LEED periodicity, relative to the oxygen anion in-plane unit cell, for the unreconstructed bulklike structure is given for the (111) surface of the fcc-based structures and for the (0001) surface for hematite. afm: antiferromagnetic. ferri: ferrimagnetic.

(LEEM)\textsuperscript{17} and photoemission microscopy (PEEM),\textsuperscript{18} using a combination of laterally resolved X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD), and low-energy electron diffraction (LEED). In the present work, we aim at understanding how the previously studied bicomponent films of FeO/Fe\textsubscript{3}O\textsubscript{4} are transformed during the oxidation by NO\textsubscript{2}. By using a combination of nanometer-resolution characterization tools, we provide insight into the different transformation pathways of the various iron oxides. This knowledge can help to tailor the fabrication of nanostructured thin films with well-defined composition for particular catalytic or spintronic applications.

\section*{EXPERIMENTAL SECTION}

The experiments were carried out employing the spectroscopic and photoemission low-energy microscope (Elmitec SPEEM III) at the Nanospectroscopy beamline of the Elettra storage ring.\textsuperscript{19,20} The instrument, which combines LEEM and PEEM, is equipped with a hemispherical energy analyzer with the option of selecting either an electron beam or the X-ray beam at the beamline as an illumination source. The electron beam allows for regular LEEM use, including fast real-space imaging of the surface during growth of the oxide films, and selected-area diffraction measurements. Using X-rays as an illumination, i.e., in PEEM, the instrument can perform selected-area XPS by detection of the emitted photoelectrons, laterally resolved XAS spectra using the secondary electrons emitted following the different processes that occur after the X-ray illumination, or spatially resolved emission images at selected electron and photon energies. From sequences of the latter, scanning the incident photon or the analyzed electron energies, XPS or XAS spectra can be measured from surface regions as small as 40 nm, although in our experiments signal-to-noise requirements require integration over micrometer-sized areas. The two possible helicities of the X-ray beam can be selected to perform XMCD measurements. The X-ray beam is fixed relative to the sample at an angle of 16° with the film plane, so the XAS measurements are mostly sensitive to the in-plane magnetization.

Iron oxide thin films were grown on a Ru(0001) single crystal substrate using O\textsubscript{2}-assisted MBE. Ru was previously cleaned by exposure to 5 × 10\textsuperscript{-8} mbar oxygen at 1000 K, followed by flashing to 1500 K in a vacuum. First, iron was deposited from an iron rod heated by electron bombardment in a background pressure of molecular oxygen of 5 × 10\textsuperscript{-7} mbar keeping the substrate temperature at 900 K. Subsequently, the films were characterized at room temperature by using LEEM, LEED, XPS, and XAS. In subsequent steps, background pressures in the range of 1 × 10\textsuperscript{-8} to 5 × 10\textsuperscript{-7} mbar of NO\textsubscript{2} were allowed into the UHV chamber while keeping the temperature of the substrate at 500 K and the resulting films were again characterized. In both cases, molecular oxygen and NO\textsubscript{2} the gases were introduced in the experimental chamber by means of a capillary that increased the exposure to the gas at the sample position by a factor of 2. The NO\textsubscript{2} pressure corresponds to the (uncorrected) reading of the ionization gauge of the experimental chamber. The amount of iron deposited is given relative to the density of a monolayer of close-packed layer of Ru(0001) (ML\textsubscript{Ru}).

\section*{RESULTS}

\subsection*{Film Structure: Low-Energy Electron Microscopy and Diffraction}

The growth of iron oxides using O\textsubscript{2}-assisted MBE at 900 K and with an Fe flux of 0.12 ML/min on clean Ru (Figure 1A) proceeds by the initial growth of small FeO islands, ...
2 Fe–O layers in height,\(^{18}\) that are visible in Figure 1B. The islands grow (Figure 1C) until they form a continuous film. Further Fe deposition produces a change in the LEEM contrast (Figure 1D and E) followed by the nucleation of micrometer wide triangular islands (Figure 1F). In this bicomponent film, the electron reflectivity and the low-energy electron diffraction patterns from the wetting layer and the large islands differ.

In a low-energy electron microscope without an energy filter, the only possible way to obtain information about the electronic state of the sample consists of changing the energy of the electron beam used for illumination. When in LEEM mode, this allows obtaining the selected-area reflectivity from different areas of the film.\(^ {21}\) Theoretically, the electron reflectivity is related to the local density of unoccupied states: the lower the density, the higher the reflectivity. Multiple scattering complicates the picture, and at very low energies, the electron reflectivity is not easy to interpret in the absence of band structure calculations.\(^ {22}\) Nevertheless, even in the absence of a theoretical interpretation, the simplicity of electron reflectivity measurements in LEEM makes the technique very useful for fingerprinting different surface structures. In Figure 2, we present the reflectivity curves of the as-grown wetting layer (A) and large triangular islands (B). As previously reported, the wetting layer curve is a fingerprint for FeO, while the one from the triangular islands corresponds to magnetite.\(^ {17}\)

The LEEM instrument allows acquiring LEED patterns from micrometer-sized selected areas on the surface (in the current setup, the smallest aperture for micro-LEED is 2 \(\mu\)m in diameter). Each different iron oxide phase presents a characteristic LEED pattern. Recorded from the different parts of the layer, LEED patterns are presented in Figure 3. While a 1 \(\times\) 1 pattern is expected from wüstit, a 2 \(\times\) 2 pattern should correspond to either maghemite or magnetite due to the presence of iron layers with that unit cell between the oxygen layers along the (111) direction.\(^ {23}\) In agreement with our previous work,\(^ {17,18}\) the LEED patterns recorded from the two well-defined zones observed in the oxygen-grown films are different and they are also different from the Ru substrate LEED pattern. The pattern from the as-grown wetting layer (Figure 3B) presents, in addition to the integer beams, several satellite spots that indicate the presence of a coincidence pattern between the film and the substrate, i.e., a moiré pattern. The integer beams correspond to a hexagonal unit cell of 0.32 \(\pm\) 0.04 nm. For FeO, the satellite spots correspond to a real-space distance of 1.8 \(\pm\) 0.2 nm, close to the periodicity of the moiré pattern observed by STM.\(^ {6}\) At the island (Figure 3C), the integer spots are at the same position as the wetting layer, so the unit cell remains the same. However, the periodicity of the moiré is much larger (smaller spacing in reciprocal space), with a distance of 5.2 \(\pm\) 0.5 nm. In addition, weak 2 \(\times\) 2 spots can be observed at specific energies and correspond to either magnetite or maghemite.\(^ {23}\)

NO\(_2\) exposure did not bring about obvious changes in the topography of the bicomponent film. There are, however, changes in the image contrast, as can be seen comparing the electron reflectivity curves before and after NO\(_2\) exposure in Figure 2. Furthermore, NO\(_2\) exposure changes the LEED pattern of the wetting layer and the islands. And both regions have different patterns, showing that the film remains bicomponent. No satellite spots are detected probably due to a reduction in the crystallographic order of the film, as also evidenced in the broader LEED spots shown in Figure 3E and F. As shown in Figure 3, the wetting layer pattern (E) presents

![Figure 2. Electron reflectivity: (A) wetting layer, as-grown; (B) island, as-grown; (C) wetting layer, oxidized; (D) island, oxidized.](image)

![Figure 3. LEED patterns: (B) wetting layer, as-grown; (C) island, as-grown; (E) wetting layer, oxidized; (F) island, oxidized. (B and C) 48 eV electron energy; (E and F) 30 eV electron energy. Real space images of as-grown (A) and oxidized (D) islands were collected at 3 and 19 eV, respectively. The FOV is 4 \(\mu\)m.](image)
a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure, while the island (F) still presents a 2 $\times$ 2 pattern. The oxygen–oxygen lateral distances are slightly contracted to 0.30 $\pm$ 0.04 and 0.29 $\pm$ 0.04 nm, and there is a small 3$^\circ$ rotation between the island pattern and the wetting layer pattern (which in turn is aligned with all the previous LEED patterns).

In summary, before NO$_2$ oxidation, the bicomponent iron-oxide film presents reflectivity curves and LEED patterns that are, respectively, characteristic of FeO (wetting layer) and magnetite (islands). After oxidation, the electron reflectivity and LEED patterns still indicate a bicomponent film but with LEED patterns characteristic of hematite (wetting layer) and either magnetite or maghemite (islands).

**Film Composition and Chemical State: XPS and XAS.**

XPS is commonly used to characterize iron oxides. In particular, Fe 2p core level spectra are typically used and the respective shapes and binding energies are, thus, well-known. In our case, the XPS spectra of different phases are extracted from series of images acquired at a range of 90–120 eV kinetic energy with a photon energy of 825 eV. We obtain the XPS Fe spectra by integrating the image intensity inside or outside the triangular islands, providing the spectra shown in Figure 4, which shows the XPS Fe 2p spectra recorded before and after the NO$_2$ treatment.

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**Figure 4.** Fe 2p XPS spectra: (A) wetting layer, as-grown; (B) island, as-grown; (C) wetting layer, oxidized; (D) island, oxidized. The spectra have been fit using mixed Gaussian–Lorentzian lines (80–20%, respectively) and a combined Shirley-linear background. sat.: shakeup peak. m.s.: multiplet splitting.

The spectrum recorded from the wetting layer (Figure 4A) is virtually the same as the one reported for FeO$_4^-$ and it has been fitted using an spin orbit doublet and several other components arising from multiplet splitting and shakeup structures. The data support the assertion that the wetting layer is FeO with only Fe$^{3+}$. The main photoemission lines in the Fe 2p spectrum recorded from a triangular island (Figure 4B) appear at higher binding energies than those observed in the spectrum of the wetting layer, indicating that the average Fe oxidation state in the island is higher than that of Fe in the wetting layer. We best-fitted it to two spin–orbit doublets assignable to Fe$^{2+}$ and Fe$^{3+}$, plus an evident shakeup satellite shifted by 3.7 eV from the main photoemission Fe$^{2+}$ peak which is usually taken as a fingerprint of Fe$^{2+}$. Taken together, the results indicate that the island iron phase is a mixed-valence Fe$^{2+}$/Fe$^{3+}$ oxide, consistent with the occurrence of magnetite. In fact, the spectrum is similar to those reported for various forms of magnetite (bulk magnetite, nanoparticles, or thin layers). Magnetite can exist in different degrees of stoichiometry, and therefore, spectra recorded from different nonstoichiometric forms of magnetite can show slightly different XPS spectra shapes, arising from different Fe$^{2+}$/Fe$^{3+}$ ratios (see Figure 9 in ref 26). This can explain, to some extent, the differences found between the XPS magnetite spectra reported in the literature (in the current experiments we have no direct control on the stoichiometry of the phases of the films and thus one could not expect to have precisely the spectrum characteristic of pure, stoichiometric magnetite).

The XPS Fe 2p spectra from the wetting layer and from the triangular island after exposure to NO$_2$ are also shown in Figure 4C and D, respectively [we also acquired XPS N 1s spectra to check for the possible incorporation of nitrogen into the iron oxide film, and no nitrogen signal was detected (not shown)]. Neither spectra have the shape characteristic of magnetite. In fact, the spectra of the oxidized iron films do not exhibit the typical Fe$^{3+}$ shakeup structure in the high binding energy side of the Fe 2p$_{3/2}$ line. Instead of this, another broad peak separated by approximately 8–9 eV from the main photoemission Fe 2p$_{3/2}$ peak is observed. This latter peak is a characteristic shakeup satellite appearing in the spectra of exclusively Fe$^{3+}$-containing oxides. All the results clearly indicate that the NO$_2$ treatment favored the oxidation of both the FeO wetting layer and Fe$_3$O$_4$ island to iron phases containing mostly Fe$^{3+}$.

Both $\alpha$ and $\gamma$ oxides, only with Fe$^{3+}$, have photoemission spectra similar to the oxidized film. That is, all the spectra have the same Fe$^{3+}$ shakeup peak and the Fe 2p$_{3/2}$ core level peaks are at the same binding energy. Although variations in the main Fe 2p$_{3/2}$ shape due to a change in the multiplet splitting components or changes in the intensity of the Fe$^{3+}$ shakeup satellite have sometimes been claimed to allow distinguishing both phases, we consider the differences between the wetting layer and island as too subtle to give a reliable identification of one or another type of oxide.

Summarizing, the XPS data of the as-grown bicomponent iron oxides indicate that the wetting layer is exclusively composed by FeO and that the triangular islands are composed by a mixed-valence Fe$^{2+}$/Fe$^{3+}$ oxide (compatible with the occurrence of magnetite). After the NO$_2$ treatment, the iron films still present two distinct components but now the wetting layer and the islands are composed of Fe$^{3+}$-containing oxides. However, XPS does not allow assigning them unequivocally to either $\alpha$-Fe$_2$O$_3$ or $\gamma$-Fe$_3$O$_4$.

XAS can be used to gain insight into the oxidation state and local structure around the iron cations in the various iron oxides. Furthermore, the L$_{2,3}$ XAS spectra of the iron oxides are all well-known, including those for magnetite having different stoichiometries, and can be used as fingerprints for identification purposes. In the present work, the displayed XAS spectra were obtained integrating the image intensity inside or outside the triangular islands.

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Figure 5 shows the XAS spectra (Fe L\textsubscript{2,3} absorption edges) of the initially grown iron oxides, from the wetting layer (A) and from a triangular island (B), respectively. The island spectrum exhibits the characteristic shape of Fe\textsubscript{3}O\textsubscript{4}. The shoulder before the L\textsubscript{3}-edge maximum at 707.5 eV arises from the different contributions of the Fe\textsuperscript{2+,3+} and Fe\textsuperscript{3+} cations occupying the octahedral and tetrahedral positions, respectively, of the inverse spinel-related structure of this oxide.\textsuperscript{30−33} The XAS spectrum recorded from the wetting layer at the Fe L\textsubscript{2,3}-edges does not show the shoulder near the L\textsubscript{3}-edge maximum and is very similar to that reported for FeO.\textsuperscript{30} The XAS results are, therefore, fully consistent with those obtained by XPS.

After the NO\textsubscript{2} treatment, the XAS spectra recorded from the island and the wetting layer both show noticeable differences from those recorded from the initially grown oxides. The most distinguishing feature from the oxidized regions is the pronounced shoulder or pre-L\textsubscript{3} edge peak at 705.8 eV (Figure 5C and D), which is characteristic of Fe\textsubscript{2}O\textsubscript{3} oxides.\textsuperscript{30} This shoulder arises mainly from the presence of Fe\textsuperscript{3+} cations in octahedral sites. It has been reported\textsuperscript{29} that this pre-edge peak is most intense and appears more separated from the main peak of the L\textsubscript{3}-edge in hematite than in maghemite, something which does not occur here so evidently. This also contrasts with the LEED data which, as explained above, suggests the formation of a hematite-like oxide on the wetting layer after NO\textsubscript{2} treatment. We will come back to discuss this point later. However, the XAS data recorded from the NO\textsubscript{2}-exposed films are consistent with the XPS data in the sense that they show the formation of Fe\textsuperscript{3+} oxides both within and around the islands.

Further information can be obtained from the oxygen K-edges, which are presented in Figure 6 for the island. The signal-to-noise ratio of the oxygen K-edge XAS spectra from the wetting layer was too low for a reliable determination of the composition, probably due to the reduced thickness (from the attenuation of the Ru 3d core level signal,\textsuperscript{18} we estimate that the wetting layer is around two FeO layers thick while the island is five FeO layers high) of the wetting layer as compared to the island together with the low Z of oxygen. Using the same method as that used for the iron edge, island spectra were acquired before and after the NO\textsubscript{2} oxidation. The two spectra show three different features, the first at 530 eV, the second at 535−545 eV, and the third at 548 eV. The structures of the two O K-edge spectra are in good agreement with that reported in previous work\textsuperscript{34,35} where multiple scattering analysis was used to simulate the oxygen K-edge XAS spectra rendered by the different iron oxides. The main difference is notable in the shoulder found after the first peak, being more prominent in spectrum A than in B. This feature reflects transitions from oxygen antibonding 2p states to the empty Fe d-bands, and its small variation has been interpreted in the literature as a change in the O−Fe structure.\textsuperscript{35} It indicates that the as-grown island corresponds to magnetite while the oxidized island corresponds to maghemite.

**Magnetic Properties: XMCD.** Since wüstite and hematite are both antiferromagnetic and maghemite and magnetite are ferrimagnetic, XMCD can be a useful tool to help in the identification of the different oxides formed at the various oxidation steps used in this work. It is well-known that the ferrimagnetic compounds will give a dichroic signal when illuminated with X-rays having different circular polarizations while the antiferromagnetic oxides (either above or below the Neél temperature) will not. To such an end, we have used XMCD-PEEM.\textsuperscript{36} Collecting XAS images with opposite helicities and subtracting them pixel by pixel gives the XMCD images of as-grown islands and oxidized islands of Figure 7. These images were taken at the photon energies that correspond to the different features observed in the XAS spectra (red and blue

![Figure 6. O K-edge absorption spectra of iron oxide islands: (A) as-grown island; (B) oxidized island.](image)
Fe$^{3+}$ cations, respectively, located in the octahedral sites, while the edge, at 705.8 and 707.5 eV, arise mostly from the Fe$^{2+}$ and the $\{011\}$ direction of the substrate. The photon beam (yellow arrow in the middle scheme) direction makes an angle of 50.1° with the images’ x-axis. The photon beam is oriented along the [011] direction of the substrate.

All islands show dichroic contrast, so they have, both before and after NO$_2$ oxidation, a significant in-plane local magnetization. However, the wetting layer appears with a uniform gray intensity, both before and after NO$_2$ exposure, indicating the absence of magnetic dichroic contrast in that region of the film.

The XMCD spectra have been obtained using the procedure reported in ref 18. The spectrum from the as-grown island (Figure 8A) shows the typical features of the XMCD signal of magnetite, characterized by three well-defined peaks at each L-edge$^{32,37,38}$ and, thus, is a further confirmation that the islands are magnetite. More precisely, the two negative peaks at the L$_1$-edge, at 705.8 and 707.5 eV, arise mostly from the Fe$^{2+}$ and Fe$^{3+}$ cations, respectively, located in the octahedral sites, while the positive peak at 706.7 eV is associated with the tetrahedral Fe$^{3+}$ cations. The positive and negative orientation of the XMCD peaks originates from the antiferromagnetic coupling between the octahedral and tetrahedral sublattices of the inverse-spinel structure of magnetite. This indicates that the magnetite islands, despite their thickness (≈1 nm)$^{18}$ maintain their ferrimagnetic order. It is worth mentioning, however, that the intensity of the peak associated with the octahedral Fe$^{2+}$ ions is slightly larger here than that observed in the case of bulk magnetite.$^{38}$ These differences can be interpreted in terms of additional contributions from the underlying FeO wetting layer$^{39}$ or attributed to the formation of an incomplete unit cell.$^{40}$

The XMCD spectrum of the NO$_2$-oxidized island is also presented in Figure 8B. As in the case of magnetite, the L$_3$-edge also shows two negative peaks, in this case at 707.0 and 708.7 eV, and a positive one at 707.9 eV. However, the relative intensity of the two negative peaks is completely different from that observed in the XMCD spectrum of magnetite and approaches that reported for γ-Fe$_2$O$_3$.$^{33,41}$ This arises from the absence of Fe$^{2+}$ in the maghemite structure and from the occurrence of vacancies within its octahedral network. The existence of peaks having opposite alternate orientations in the XMCD signal is again indicative of the occurrence of ferrimagnetic order.

The interest of the XMCD results lies in the fact that, on one hand, they confirm the composition of the islands carried out with the rest of the techniques employed in this work, being particularly helpful in the identification of magnetite in the NO$_2$-oxidized islands. On the other hand, they show the lack of ferri- or ferromagnetic order in the wetting layer after NO$_2$ exposure. This lack of ferromagnetic order, the presence of iron Fe$^{3+}$ shown by XPS and XAS, and the LEED pattern recorded from the wetting layer after NO$_2$ oxidation all point to the transformation of the as-grown FeO into a hematite-like oxide.

**DISCUSSION**

The as-grown films have been discussed previously.$^{6,17,18}$ and their composition (wüstite for the wetting layer and magnetite for the large islands) is in agreement with Fe oxide grown on Pt(111).$^4$ The FeO structure is composed of alternating compact planes of iron and oxygen, with an in-plane distance of 3.2 Å for the first two FeO layers (Figure 9A). Our XPS data show a Fe$^{2+}$ valence state. Furthermore, the XAS data are similar to those reported for FeO and no XMCD contrast is observed. A lack of XMCD contrast of the wetting layer can be due to absence of magnetic order or to antiferromagnetic order. While bulk FeO has a Néel temperature below room temperature, we must point out that there is no experimental confirmation of the magnetic ordering of an ultrathin wüstite film on a metal substrate (the structure reported for the magnetic FeO on Fe(110) is quite different from wüstite$^{42}$).

Identifying the large islands in the iron oxide films grown with molecular oxygen as magnetite (Figure 9B) is well-established: the 2 × 2 LEED pattern, the XPS spectra with a mixed Fe$^{2+}$/Fe$^{3+}$ character, and the Fe L$_3$-edge and O K-edge XAS spectra uniquely identify the islands as magnetite. The in-plane spacing
of the magnetite and the wetting layer are the same. Thus, the magnetite islands are strained relative to their in-plane bulk value. This is explained if the islands rest on the FeO wetting layer instead of extending down to the Ru substrate.

After oxidation with NO₂, the film topography is not changed in a major way, as observed by LEEM: the films are still composed of a continuous wetting layer and large, mostly triangular, flat islands. However, the composition of the wetting layer and the triangular islands has changed markedly.

In the islands, the 2 × 2 pattern is maintained, although with a smaller lattice spacing than before, 0.29 nm, and with a small rotation of the LEED pattern of 3°. On the contrary, the Fe 2p XPS signal has changed. The features related to Fe³⁺ ions have disappeared, and there is a shakeup satellite characteristic of Fe⁵⁺. This indicates that, upon oxidation, magnetite could have changed to any of the Fe₂O₃ phases. Although in ref 7 only hematite was considered because it is the stable iron oxide in the bulk (with magnetite and the e-Fe₂O₃ phases being metastable), such an argument is not applicable on an ultrathin film where metastable phases might easily be rendered stable as already reported in ref 43 for FeO. Hematite can be discarded because of the 2 × 2 LEED pattern (hematite would give a √3 × √3R30°). This assignment is confirmed by the Fe and O XAS spectra, which are typical of maghemite and clearly different from magnetite. Finally, the islands still show XMCD contrast, indicating that they have ferrimagnetic order. Maghemite is the only binary ferrimagnetic iron oxide with Fe⁵⁺ cations. Therefore, the islands obtained by postoxidation of magnetite at 600 K are unequivocally identified as maghemite.

The wetting layer iron oxide is also modified by the NO₂ oxidation. The LEED pattern now shows a reduced spacing of 0.30 nm and a √3 × √3R30° pattern (Figure 3E). As shown on the different oxide schematics, Figure 9, this pattern suggests that the film is now a hematite-like oxide. This determination is further supported by the XPS spectra, where features typical of a Fe³⁺ oxide are observed. The absence of an XMCD signal points to an antiferromagnetic or superparamagnetic oxide. The XAS spectra are more ambiguous, as they show some features that can be associated to an Fe⁵⁺ oxide but do not correspond clearly to hematite (which presents a much more prominent pre-edge peak). One possible explanation is that the XAS signal comes from the full thickness of the film, while the XPS data are acquired at an electron kinetic energy with a short mean free path close to one Fe–O layer. Then, the difference between the XPS and XAS spectra would point to an incomplete oxidation of the full film thickness with the surface being completely converted to an hematite-like film, while the film close to the Ru/oxide interface would still be closer to FeO.

Overall, the oxidation of the original bicomponent oxide (FeO/Fe₃O₄) gives rise then to another bicomponent oxide, now formed by the two allotropes of Fe₂O₃ (α/γ). The reason for the different oxidation pathways most probably lies in the low temperature employed through the process. The different oxide structures are based on either an fcc (for wüstite, magnetite, and maghemite) or an hcp anion lattice (hematite). Also, while magnetite and maghemite have iron cations both in octahedral and tetrahedral positions, the iron in both wüstite and hematite only occupies octahedral positions. It is known that the most stable iron oxide under oxidizing conditions is hematite, with maghemite being metastable. The transformation of magnetite to maghemite is topotactic: the same local arrangement of atoms is maintained, and only some iron cations in octahedral positions (eight per three unit cells) have to diffuse to the surface of the islands to react with available oxygen. In agreement with this argument, cation diffusion is supposed to be the main venue of iron oxide transformations in the bulk. In contrast, the transformation of magnetite or maghemite into hematite requires (i) a change in the oxygen anion lattice from fcc to hcp and (ii) the removal of tetrahedral cations from the lattice. All together, it is clear that in these experiments the magnetite to hematite transformation is kinetically hindered.

However, the wetting layer transforms from an FeO structure to a hematite-like film. This can be understood with the same argument used for the magnetite–maghemite transformation: both FeO and hematite have only octahedral cations. Although the anion lattices are different (fcc for FeO vs hcp for hematite), the difference requires at least three oxygen—iron layers (for two layers, the sequence in an fcc or hcp lattice is the same). As the films are around two layers thick, this limitation does not apply. Starting with FeO, all the octahedral positions are occupied with Fe (see Figure 9E). If one-third of the cations diffuse to the film’s surface to react with further oxygen (provided by the NO₂), the FeO structure evolves (Figure 9F) to that of hematite (Figure 9G), again topotactically. The same mechanism, diffusion of the iron cations in octahedral positions, could thus explain the transformation of magnetite to maghemite and the transformation of the ultrathin films of FeO to hematite. These results shed some light into the old
In summary, we have characterized the oxidation by NO2 of bicomponent iron oxide films. While the initial film, grown by O2-assisted MBE, is composed of a wetting layer of FeO and large islands of Fe3O4, the oxidized film is composed of a hematite-like wetting layer with maghemite islands. The wetting layer and islands are characterized by LEED, XPS, XAS, and XMCD. Both the wetting layer and island transformations can be understood by the diffusion of iron cations in octahedral positions to the surface of the film, where they react with oxygen provided by NO2. Both transformations are topotactic.

Our study indicates the possibility of obtaining different bicomponent iron oxides in ultrathin form in the same substrate by means of a choice of the experimental parameters. This behavior allows tuning the ultrathin iron oxides to exploit their catalytic and magnetic properties.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Spanish Ministry of Science and Innovation (MICYT) under Project Nos. MAT2009-14578-C03-01, MAT2009-14578-C03-02, and MAT2010-21156-C03-02, by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Contract No. DE-AC04-94AL85000, and by the European Union through 226716-ELISA. M.M. and B.S. thank the MICINN for supporting them through FPI fellowships.

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