Preparation and characterization of ultra-thin iron oxide films on a Mo(100) surface

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Abstract

The synthesis and characterization of ultra-thin films of iron and iron oxides on a Mo(100) surface, have been carried out under ultrahigh vacuum conditions in the 100–1500 K substrate temperature range. The oxides were prepared by both post-oxidation of pure Fe ultra-thin films and by evaporating Fe onto the Mo surface in oxygen ambient (in situ oxidation). The characterization of the iron oxide films, with respect to the chemical states and composition, was made using X-ray photoelectron spectroscopy as well as temperature programmed desorption. By varying the molybdenum substrate temperature and the oxygen background pressure during either the post- or the in situ oxidation process, oxide films consisting of virtually pure phases of Fe$_2$O$_3$ and FeO can be successfully obtained as well as intermediate phases including Fe$_3$O$_4$. In addition, discrete phase changes were found corresponding to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ at ~550 K and Fe$_3$O$_4$ to FeO at ~750 K by means of thermally induced oxygen loss.

Keywords: Ceramic thin films, Iron, Iron oxide, Metal–oxide interface, Oxidation; Soft X-ray photoelectron spectroscopy; Thermal desorption spectroscopy

1. Introduction

Iron and its oxides are important in many scientific and technological applications. Material interests include corrosion studies as well as magnetic properties of iron/iron oxides in high density recording media. Iron oxide is used as a catalyst in industrially important reactions such as ammonia synthesis, dehydrogenation of butene to butadiene and dehydrogenation of ethylbenzene to styrene.

Thin films and ultra-thin films of oxides often occur in natural and synthetic processes. Surface studies utilizing thin films of oxides supported on refractory metal substrates have important advantages over their bulk analogues. These include improved temperature control and reduced surface charging associated with charged particle techniques [1,2].

The synthesis of oxide films possessing multiple phases presents an exciting challenge in surface studies. Iron oxide thin films have been synthesized primarily by oxidation of iron substrates [3–7] or iron overlayers (both by post-oxidation of an overlayer [8–11] and layer-by-layer oxidation and anneal cycles [12–16]). Other methods include electrochemically formed oxides [17] as well as reactive vapor deposition in an oxygen background [18]. The oxida-
tation process has been studied using methods such as quantitative oxygen adsorption, low energy electron diffraction, Auger, photoelectron, ion scattering and electron energy loss spectroscopies [3–18]. These studies, in general, have shown that increasing the O₂ exposure at 300 K results in the following sequence of surface species: chemisorbed oxygen, FeO, Fe₂O₄, and at higher O₂ exposures, Fe₂O₃. Depending on the growth method and conditions used, various iron species have been produced. While these species usually coexist in mixed phases and are not well characterized, some ordered films have been synthesized [12–16,18].

In this paper we will first present our results on ultra-thin iron films prepared on Mo(100). We will then discuss the growth of oxide films which were prepared using both post-oxidation of pure iron films and deposition of iron in a background of O₂ (reactive vapor deposition) onto a Mo(100) surface. We will demonstrate that essentially pure phases of Fe₂O₃, Fe₃O₄, and FeO can be synthesized. We will also discuss evidence for the presence of oxidation precursor species as well as phase changes involving the reduction of the higher oxides.

2. Experimental

The ultra-high vacuum surface analysis chamber (base pressure ≤ 4 × 10⁻¹⁰ Torr) employed in this experiment had capabilities for X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and temperature programmed desorption (TPD). A complete description of the system’s capabilities has been given previously [19]. The XPS spectra were taken using a MgKα radiation source (1253.6 eV) and a precision hemispherical energy analyzer with detection normal to the surface. The energy dispersion of the spectrometer was calibrated using the known values of the Mg(1s) (1309.0 eV) and Mg(2p) (49.6 eV) core-level binding energies for a ~ 200 ML (monolayer) film of pure Mg on clean Mo(100). The spectrometer work function was then determined by referencing to the Mo(3d₅/₂) substrate binding energy at 227.7 eV. The core levels are reported from the peak maxima and have an experimental error of ± 0.03 eV.

The sample holder consisted of two Ta wires mounted on a liquid nitrogen cooling reservoir and spot-welded onto the back face of the Mo(100) crystal. The substrate sample could be resistively heated to 1600 K and cooled by conduction to 90 K. An e⁻-beam heater was used to flash the sample up to 2300 K. Sample temperatures were monitored using a W–5%Re/W–26%Re thermocouple.

Cycles of oxidation in 2 × 10⁻⁷ Torr of oxygen at 1200 K and annealing in vacuum at 2000 K were used to clean the Mo(100) substrate. After several cycles, the level of impurities was found to be less than 1 at% by AES and the sample exhibited a sharp (1 × 1) LEED pattern. The Fe ultra-thin films were prepared by thermal evaporation of a high purity Fe wire wrapped tightly around a W filament. The filament was thoroughly outgassed until AES, following the deposition of Fe, indicated the absence of any impurities in the overlayer. The evaporation flux of Fe was allowed to stabilize for two minutes before each deposition. By varying the time of vapor deposition, the coverage of Fe could be accurately changed. The iron flux and coverage was determined by using TPD area analysis in conjunction with a break in a plot of AES intensity ratios upon completion of one monolayer. The deposition rate used in this work was 0.5 ML per minute (one ML corresponds to the Mo(100) surface atomic density). The oxide films were synthesized using a variable leak valve which delivered research grade (≥ 99.998%) oxygen.

3. Results

3.1. Fe on Mo(100)

The TPD spectra of increasing Fe coverage on Mo(100) are shown in Fig. 1. The Fe films were grown at a substrate temperature of ~ 300 K and showed no O, C or S impurities in AES. Two distinct desorption states are observed in the spectra and are designated as β₁ and β₂. The growth of Fe on Mo(100) was also followed using AES. A plot of Fe versus Mo AES signal intensity (not shown) exhibits an increase in slope after two minutes of Mo(100) exposure to the Fe flux. The XPS core level of the Fe(2p₃/₂) peak was also followed as a func-
Fig. 1. TPD spectra of metallic Fe desorption from Mo(100) as a function of deposition time; (a) 90 s; (b) 120 s; (c) 240 s; (d) 300 s; (e) 360 s and (f) 480 s. The deposition temperature was 300 K and the heating rate was 10 K/s.

Fig. 2. Fe(2p) XPS spectra of post-oxidized Fe(20 ML)/Mo(100) films at 473 K as a function of oxygen exposure. The spectra were acquired at ~ 300 K.

Fig. 3 and Fig. 4 give the XPS Fe(2p) and O(1s) showing the annealing effect on the oxide film grown at 473 K after exposure to 360 L of oxygen. Up to 790 K, there is little change in the Fe(2p) peak shape but a slight reduction in the Fe(2p) overall binding energy. At 900 K, the appearance of a small shake-up feature at ~ 716 eV can be seen. This feature becomes clearly developed at an annealing temperature of 1126 K. The core-level peak is also much narrower than that observed for previous annealing temperatures and exhibits a binding energy of 709.6 eV.

3.2. Oxygen adsorption on Fe(~ 20 ML)/Mo(100)

The XPS spectra of the Fe(2p) region (Fe(2p\text{1/2}) and Fe(2p\text{3/2})) of a ~ 20 ML iron film deposited and subsequently oxidized at 473 K on Mo(100) are shown in Fig. 2. Upon the deposition of Fe in vacuo at 473 K, only a single state was observed for Fe\text{0}(2p\text{3/2}) at 706.7 eV, with a small shake-up feature observed at ~ 711 eV. After dosing 90 L of O\text{2} at 473 K, three states of Fe are apparent. A metallic state at 706.7 eV remains in conjunction with peaks at ~ 709.5 and ~ 710.5 eV. Increasing the oxygen exposure reduces the lower binding energy component and shifts the overall peak maxima to higher binding energy. This spectrum did not change greatly after further exposures to oxygen in vacuo at 473 K. A peak maxima of 530.1 eV was found for the associated O(1s) spectra at 360 L (see Fig. 4), and is consistent with the expected range of values for oxygen in the O\text{2−} state. The Mo(3d\text{5/2}) substrate signal remained constant at 227.7 eV for all of the spectra shown in Fig. 2.

Preliminary LEED results have indicated that the first two ML of Fe grow pseudomorphically on Mo(100), yielding sharp (1 X 1) LEED patterns upon annealing the film to 500 K. After the annealing of films greater than 2 ML, the LEED pattern observed exhibited streaked patterns which indicated the clustering of overlayers into three-dimensional islands. The present results correlate well with previous detailed studies of the growth and structural characteristics of ultra-thin Fe films on W(100), W(110) [20] and Mo(110) [21].
Fig. 3. Fe(2p) XPS of Fe(20 ML)/Mo(100) film exposed to 360 L of oxygen at 473 K and subsequently annealed to the indicated temperatures. The spectra were acquired at ~300 K.

By an annealing temperature of 1280 K, the spectral intensity is reduced, yet exhibits similar features to that observed at 1126 K.

The O(1s) spectra associated with those of iron in Fig. 3, are shown in Fig. 4 and can be attributed to oxygen in the O$^{2-}$ state. The O(1s) peak does not shift greatly until an annealing temperature of 1126 K is reached. At this annealing temperature, the O(1s) binding energy is 530.5 eV. After annealing to 1280 K, the O(1s) shifts slightly higher, yet does not decrease in intensity as significantly as that of the corresponding iron spectra. At temperatures below 1100 K, the Mo substrate (3d_{5/2}) remained at a constant intensity and binding energy of 227.7 eV. However, upon annealing to 1126 K, the Mo peak was slightly broadened towards higher binding energy. After the film was annealed to 1280 K, the Mo core-level spectra exhibited an increase in the main peak intensity, with an obvious shoulder at higher binding energy.

The post-oxidation of a ~20 ML thin Fe film was repeated with a substrate temperature of 1000 K. Fig. 5 shows the evolution of the oxide formed under these conditions. Upon exposure to 450 L, the metallic state has been nearly removed and an oxide.

Fig. 4. O(1s) XPS of Fe(20 ML)/Mo(100) film exposed to 360 L of oxygen at 473 K and subsequently annealed to the indicated temperatures. The spectra were acquired at ~300 K.

Fig. 5. Fe(2p) XPS spectra of post-oxidized Fe(20 ML)/Mo(100) films at 1000 K as a function of oxygen exposure. The spectra were acquired at ~300 K.
feature appears at 709.5 eV with a small peak at \( \sim 716 \) eV. After greatly increasing the oxygen exposure, the peak binding energy increases to only 709.6 eV. The associated O(1s) spectra (not shown) all have a core-level value of 530.4 eV. The Mo(3d_{5/2}) peak persisted at 227.7 eV for the post-oxidation of Fe at 1000 K.

### 3.3. Deposition of Fe in oxygen ambient

Fig. 6 shows the Fe(2p) spectra of 10 ML iron oxide films grown in increasing backgrounds of \( \text{O}_2 \). The films were deposited at a rate of 0.5 ML/min (as calibrated for metallic Fe from TPD and AES results referenced to the Mo(100) substrate density) and a substrate temperature of 300 K. As the oxygen background is increased, the higher binding energy oxide states increase with a concomitant decrease in the metallic state. At a synthesis pressure of \( 2.5 \times 10^{-8} \) Torr the Fe(2p) peak exhibits a broad feature. However, increasing the background pressure of oxygen to \( 5 \times 10^{-8} \) Torr results in a narrow peak at 709.6 eV with a distinct shake-up feature. A further increase in the background pressure results in a broadening of the Fe(2p) peak and a shift to higher binding energy. The O(1s) spectra follow a similar trend to those of the post-oxidized films with comparable Fe(2p) spectra. The Mo(3d_{5/2}) remained constant at 227.7 eV for each growth condition in Fig. 6.

Each of the films grown in Fig. 6 were also characterized by TPD. To acquire the TPD, the sample temperature was resistively ramped at a rate of 10 K/s. The iron signal is that of \( m/e = 56 \), and the oxygen signal arises from \( m/e = 16 \) in order to observe the desorption of all of the iron and/or oxygen containing species. (Note that there was no evidence for \( \text{NH}_3 \) or \( \text{CH}_4 \) species in XPS or TPD.) Fig. 7 shows the iron as well as oxygen TPD. The iron desorption peaks appear at comparable temperatures to those of metallic iron in Fig. 1 up to a synthesis pressure of \( 2.5 \times 10^{-8} \) Torr. At a growth pressure of \( 2.5 \times 10^{-8} \) Torr, the TPD peak begins an obvious broadening towards higher temperatures. At \( 1 \times 10^{-7} \) Torr and greater pressures, the higher temperature component of the Fe TPD peak (above 1400 K) grows until it is the largest feature at \( 5 \times 10^{-6} \) Torr, and a peak in the oxygen TPD begins to appear at the same temperature. It should be noted that there is an oxygen desorption feature beginning around 750 K and ending at \( \sim 950 \) K for the TPD of films.
grown at $2.5 \times 10^{-8}$ Torr and lower pressures. There were no lower temperature desorption features in the oxygen or iron TPD.

Increasing the background to $1 \times 10^{-5}$ Torr at 300 K (not shown) only increases the Fe(2p) binding energy to 710.6 eV with a slight increase in the oxide component of the TPD. This iron core-level binding energy is comparable to that observed for the post-oxidized films, yet falls short of the published binding energy observed for the most oxygen-rich iron oxide ($\text{Fe}_3\text{O}_4$) (consisting of only $\text{Fe}^{3+}$ ions exhibiting a core-level binding energy of $\sim 711$ eV). Since chemisorption of oxygen is much stronger at lower temperatures, the sticking probability and the possibility of incorporating more oxygen into the film are both increased. A set of experiments similar to the previous ones performed at 300 K were carried out at 100 K in order to increase the effective oxygen background without destroying vacuum conditions.

Fig. 8 shows the Fe(2p) XPS spectra of these films as a function of increasing oxygen background at 100 K. It is obvious that oxygen incorporation occurs to a much greater extent for the films grown at lower temperature. By a background pressure of $1 \times 10^{-8}$ Torr, the film consists of a mixture of the oxides in conjunction with a small metallic component. At a growth pressure of $5 \times 10^{-8}$, no metallic features remain and the Fe(2p) spectrum exhibits a peak with a core-level binding energy of 710.8 eV. A small shake-up peak is also observed at $\sim 718$ eV. As the pressure is increased to $1 \times 10^{-5}$ Torr, the peak reaches a maximum binding energy of 710.9 eV. To confirm that further oxidation of iron was not possible, a 30 ML film was grown under similar conditions ($1 \times 10^{-5}$ Torr at 100 K), annealed to room temperature and then lowered into a high-pressure cell [19]. In the high pressure cell, the sample was exposed to 100 Torr of oxygen at room temperature for 30 min. The sample was analyzed immediately following the oxidation and found to have the same Fe(2p) spectra (a maximum binding energy of 710.9 with a well defined shake-up feature), however, the Mo(100) substrate exhibited some oxidation as well.

Fig. 9 gives the corresponding O(1s) spectra as a function of the oxygen background. These spectra are markedly different from those seen in the previous experiments and are rich with features related to the in situ oxidation process. At a synthesis pressure of $5 \times 10^{-9}$ Torr, the O(1s) peak has a broad peak width (FWHM of 3.5 eV) with an overall binding...
energy of $\sim 530.7$ eV. At $1 \times 10^{-8}$ Torr, all of the components grow in intensity with a similar FWHM. However, at a growth pressure of $5 \times 10^{-8}$ Torr, the high binding energy components decrease and the lower binding energy component dominates the spectrum. The resulting peak gave a FWHM of 2 eV and a binding energy of 529.8 eV. As the oxygen background pressure is increased to $1 \times 10^{-6}$ Torr, a high binding energy O(1s) component becomes apparent again. This component grows at higher pressures and is accompanied at $5 \times 10^{-6}$ Torr by a small peak at $\sim 534.6$ eV; the low binding energy portion of this peak has decreased significantly. Again, the associated Mo(100) core-level values remained constant at 227.7 eV throughout the in situ oxidation experiments carried out at 100 K.

Similar to the films grown in situ at 300 K, the films in Figs. 8 and 9 were studied by TPD. The iron TPD, shown in Fig. 10, are very similar to those seen in Fig. 7. For oxidation backgrounds of $5 \times 10^{-9}$ and $1 \times 10^{-8}$ Torr, the spectra appear essentially metallic in nature. At an oxidation pressure of $5 \times 10^{-8}$ Torr and greater, two features are evident, the lower temperature peak appears at the metallic desorption temperature. As the oxygen pressure is increased, similar features are observed, but the overall desorption peak area decreases.

The complementary set of oxygen TPD is shown in Fig. 11. Some of the features seen here were also seen in the films grown at 300 K. Similar to the results in Fig. 7, the film grown at $5 \times 10^{-9}$ Torr does not exhibit a desorption peak at high temperatures. Well resolved high temperature peaks are observed above $5 \times 10^{-5}$ Torr and correspond to the highest temperature peaks observed in the iron TPD. The high temperature tail likely arises from degassing associated with the resistive leads which heat the sample, as does the initial spike in the TPD at $\sim 130$ K. As seen previously, a desorption feature between 800 and 1000 K is observed for the films grown at $5 \times 10^{-9}$ and $1 \times 10^{-8}$ Torr. This feature disappears at higher synthesis pressures. The desorption feature beginning at $\sim 250$ K and ending at $\sim 550$ K grows slowly with increasing oxygen background until a synthesis pressure of $1 \times 10^{-6}$ Torr is reached. At this point this feature begins to grow rapidly. A third feature at $\sim 700$ K becomes evident at a synthesis pressure of $1 \times 10^{-5}$ Torr and has quickly become a prominent state at $1 \times 10^{-5}$ Torr.
In order to understand the thermal behavior as well as aid in the characterization of the TPD results of the films grown in a background of oxygen, a series of XPS experiments were carried out as a function of annealing temperature. The Fe(2p) and O(1s) XPS results for a film grown in an oxygen background of $1 \times 10^{-6}$ Torr at 100 K are shown in Fig. 12 and Fig. 13. At 100 K, the Fe(2p) exhibits a core-level value of $\sim 710.7$ eV. This value is slightly lower than that of a film grown under the same conditions previously (Fig. 8), however, upon annealing to 200 K, the film shows the same peak position of 710.9 eV with a shake-up feature at $\sim 719$ eV. The peak remains constant until 500 K at which it can be seen to be slightly broadened toward lower binding energy. At 600 K, the peak is broadened and obviously shifted to lower binding energy. The overall peak maximum is at 710.3 eV at this temperature and the $\sim 719$ eV shake-up feature is no longer evident. At temperatures of 900 and 1000 K, the Fe(2p) peak has become narrower and further shifted to a lower binding energy of 709.6 eV. Upon annealing to 1300 K, the peak has decreased in intensity and has shifted slightly upwards to 709.8 eV.

The O(1s) spectra (in Fig. 13) exhibit the same features as that seen previously in Fig. 9. The core-level binding energy is 529.8 eV with a high binding energy shoulder. This shoulder is nearly gone upon annealing to 400 K. From 600–700 K, the O(1s) binding energy shifts upward to yield a value of 530.1 eV. The core level at 900–1000 K is 530.4 eV. Finally, after reaching an annealing temperature of 1300 K, the oxygen signal is significantly decreased and exhibits a binding energy of 530.7 eV.

4. Discussion

4.1. Core-level shifts in Fe and $Fe_xO_y$

There are several complications involved in identification of different iron oxides and their relative amounts in samples using core-level XPS. With respect to the pure stoichiometric phases of iron oxide,
FeO consists of exclusively Fe$^{2+}$ ions while Fe$_2$O$_3$ contains only Fe$^{3+}$ ions. One third of the iron ions in Fe$_2$O$_3$ are in the Fe$^{2+}$ state while the remaining are Fe$^{3+}$. However, a continuum of stoichiometries may be present depending upon the existing conditions. The Fe$^{2+}(2p)$ state has a highly asymmetric line shape due to high binding energy satellite features. Similarly, the Fe$^{3+}(2p)$ core levels are not well separated and also exhibit broad features due to strong multiplet splitting and shake-up phenomena. Efforts to deconvolute the spectra have been hampered by disagreement in the interpretation of the line broadening features. Other complexities include effects such as initial/final state effects, surface charging, interface properties of thin films, and defects as well as chemical modifications [2]. The large range of values for core-level shifts of FeO species observed in the literature seems to have resulted from faulty sample preparation techniques as well as inadequate reference levels. (The reference level for the spectra presented is the metallic Mo(100) substrate which remained constant for all of the experiments except those above 1000 K, as will be later discussed.) These errors include contaminated samples such as air exposed samples. Without sufficient cleaning, this results in surface hydroxides. Efforts to remove contamination using reducing species or extensive argon sputtering can result in a change of the surface phase to a lower oxide state. Attempts at subsequent oxidation can produce different phases depending upon temperature and pressure conditions. Also, post-oxidation of iron films usually creates a film of varying stoichiometry with thickness. Spectra from oxide films prepared in this manner may well exhibit features of several oxide species, depending upon the thickness of the film and the surface sensitivity of the experiment. Vurens and co-workers [16] have shown that the surfaces of higher oxides of iron are not stable in vacuo over a period of hours at room temperature, but are reduced via the loss of oxygen. In order to verify the type of surface present and identify its core level, secondary surface techniques have been very helpful, whereas bulk techniques have often been misleading due to differences in the bulk and surface compositions.

After calibration of the spectrometer, a pure ~40 ML Fe film was found to have a binding energy of 706.7 eV. This value is the same as a previously reported result [22] and fits well within the average of other results (706.8 eV) [9,23–26]. Earlier studies of a clean ordered film of FeO yielded a Fe$^{2+}$ binding energy of 709.5 eV [16]. Other results have yielded an average value of 709.6 eV for Fe$^{2+}$ [9,22–26]. Owing to our experimental observations, we also attribute this peak position to be due to Fe$^{2+}$ in FeO. Extensive oxidation (low temperatures, high pressures of O$_2$) of Fe gave a maximum core-level value of 710.9 eV in our experiments. We attribute this value to be due to Fe$^{3+}$ in Fe$_2$O$_3$, which is in good agreement with an average of previous studies (711.0 eV) [16,22–26].

4.2. Fe on Mo(100)

The two desorption states seen in the iron TPD spectra (Fig. 1), can be attributed to multilayer desorption ($\beta_1$) and monolayer desorption ($\beta_2$). The saturation of the $\beta_2$ peak and the onset of the $\beta_1$ peak corresponds to the completion of a monolayer film. (This was also confirmed with a break in the Fe/Mo Auger intensity ratios.) Leading edge analysis of the multilayer peak, which begins at ~1150 K and exhibits zero-order kinetics, yields a desorption activation energy of ~87 kcal/mol. This value agrees well with the bulk Fe sublimation energy of ~85 kcal/mol. The small separation between the $\beta_1$ and $\beta_2$ states indicates that the Fe–Mo interaction at the interface is only slightly stabilized relative to bulk Fe–Fe interactions.

In correlation with this, only a small (~0.10 eV) Fe(2p$_{3/2}$) XPS core-level shift to lower binding energy was observed for submonolayer Fe films. (The core-level binding energy of a ~40 ML Fe film was found to be 706.7 eV.) Since this value approaches experimental error, no conclusions will be made, but it should be noted that this shift may arise from transfer of electronic density as observed previously for interactions of other transition metal overlayers [27].

4.3. Post-oxidation of Fe

As was briefly stated in the introduction, essentially all of the previous studies of Fe oxide formation have involved post-oxidation of metallic Fe. For comparison and contrast, we have presented our
observations for the oxidation of Fe ultra-thin films deposited on Mo(100). In this case, we have shown the XPS results for ~20 ML films of Fe being post-oxidized by a background of O$_2$ at 473 and 1000 K.

At 473 K, the diffusion coefficient of oxygen into metallic Fe is high enough for the formation of all of the higher oxides of Fe. Yet, it should be expected that a post-oxidized film would consist of oxide strati with the highest oxygen content at the surface and lower oxygen levels deeper within the film [3]. The resulting XPS spectra exhibit a convolution of this inhomogeneity within the photoelectron escape depth.

The pure iron film in Fig. 2 has a core level of 706.7 eV. After an oxygen exposure of 90 L, Fe$^0$ clearly remains present. The shoulder at ~709.5 eV is attributed to Fe$^{2+}$ which is in coexistence with Fe$^{3+}$ (Fe$^{3+}$ is manifested above 710 eV). Increasing the oxygen exposure removes the metallic species and results in an overall shift to higher binding energy. This is interpreted to result from an increase in the Fe$^{3+}$ to Fe$^{2+}$ ratio due to development of the higher oxides Fe$_2$O$_4$ and Fe$_2$O$_3$. After exposure to 360 L of oxygen, the overall stoichiometry within the surface region detected is estimated to be near that of Fe$_2$O$_4$ based on the associated peak width and position. However, this spectrum likely arises from an overlayer richer in Fe$^{3+}$ ions than in the subsurface region. This film probably consists of an overlayer of Fe$_2$O$_3$, on Fe$_2$O$_4$ as seen previously [3].

The above film was studied as a function of annealing temperature (Fig. 3). The shift back to lower binding energy is attributed to a decrease of the oxygen to iron ratio in the iron oxide overlayer. The thermal loss of oxygen will be discussed in a later section. The small shake-up feature at ~716 eV becomes clearly developed at 1126 K and has been attributed to an Fe$^{2+}$ shake-up. It should also be noted that the peak at 709.6 eV has become significantly narrower with a related increase in intensity. This change can be attributed to the merging of the Fe$^{2+}$ and Fe$^{2+}$ states as well as the thermal loss of some oxygen. The composition at this point is again FeO. The Mo substrate signal associated with the 1126 K film has slightly broadened to higher binding energy, indicating the formation of some MoO$_x$ species at the FeO/Mo(100) interface due to the loss of oxygen via higher oxides. As will be discussed further, the reduction of the peak intensity at 1280 K arises, in part, from the partial desorption of the iron oxide overlayer from Mo(100), as well as interdiffusion of MoO$_x$ species. Analysis of the peak shape at 1280 K suggests the presence of some Fe$^0$ which has arisen from FeO reduction by the Mo substrate.

After reaching 1126 K in the associated O(1s) spectra (Fig. 4), a shift to higher binding energy of 530.5 eV is attributed to two phenomena. First, this shift arises from O$^{2-}$ associated with only Fe$^{3+}$ ions. In the films annealed at lower temperatures, the O$^{2-}$ is coordinated with both Fe$^{2+}$ ions as well as the more electropositive Fe$^{3+}$ ions. Secondly, some oxygen has migrated to the substrate as evidenced by the Mo(3d$_{5/2}$) spectra. At an annealing temperature of 1280 K, the oxygen peak continues to shift to higher binding energy, yet is not reduced in intensity as significantly as the corresponding Fe(2p) spectra. This observation is explained to be a result of the interdiffusion and subsequent reduction of some FeO by the Mo substrate observed above 1200 K. A significant fraction of the O(1s) peak at 1280 K is associated with MoO$_x$. The behavior of MoO$_x$ species will be discussed in further detail in a later section of this report.

Due to a decreased sticking coefficient for oxygen at higher temperatures, greater oxygen exposures are necessary to remove the metallic Fe feature in films oxidized at 1000 K (Fig. 5). The maximum core-level position, obtained for the Fe peak, is 709.6 eV under these conditions. This peak position, as well as the shake-up feature at ~716 eV, is again attributed to Fe$^{2+}$ and an Fe$^{2+}$ satellite, respectively. The associated O(1s) spectra all exhibited 530.4 eV peak positions indicating that oxygen was associated with only Fe$^{2+}$ for the films oxidized at 1000 K. This value is in agreement with the FeO film obtained by annealing the post-oxidized film in Figs. 3 and 4 above 1000 K and indicates that at 1260 L, the film consists of essentially stoichiometric FeO. These observations indicate that Fe$^{3+}$ is not stable under these growth conditions as compared to the films shown in Fig. 2. These results also agree with previous studies which have shown that FeO is the most stable iron oxide phase at the surface under vacuum conditions and 1000 K [3,28].
4.4. In situ oxidation of Fe at 300 K

The post-oxidized films were grown in order to observe the oxidation of iron thin films as well as to develop a comparison with previous studies carried out using post-oxidation methods. Yet, in order to grow an oxide film with a well defined homogeneous composition, it is necessary to deposit the iron in a steady background of oxygen [2].

As the oxygen partial pressure in the chamber is increased, during deposition of 10 ML films at 300 K, the evolution of the oxide from the metal can be seen in the corresponding iron core levels (Fig. 6). The metallic feature at 706.7 eV does not disappear until a synthesis pressure of $5 \times 10^{-8}$ Torr is reached. At this background pressure, the film consists of only FeO as confirmed by the relatively narrow peak width, the binding energy and the shake-up satellite. An increase in the background pressure shifts the peak to higher binding energy, decreases the overall intensity of the peak, increases the FWHM and subdues the shake-up satellite. This results from the evolution of Fe$^{3+}$ species as the stoichiometry shifts from FeO towards Fe$_3$O$_4$. The shake-up structure becomes "smeared-out" as the Fe$^{3+}$ core level begins to overlap with the low binding energy side of the Fe$^{2+}$ shake-up, and the Fe$^{3+}$ shake-up (at about 719 eV) begins to overlap with the high binding energy side of the Fe$^{2+}$ shake-up. The fact that the substrate Mo(3d$_{5/2}$) remained constant at 227.7 eV for each growth condition in Fig. 6 indicates that the interface is relatively abrupt, with little or no MoO$_2$ species formed.

The TPD in Fig. 7 indicate that most of the iron desorbed is metallic in nature at growth pressures of $5 \times 10^{-8}$ Torr and below. However, at $5 \times 10^{-8}$ Torr, the XPS data in Fig. 6 indicate that the film consists of essentially pure FeO. Similarly, there is no peak in the oxygen TPD above 1400 K. As shown previously, this arises from the fact that a significant amount of the iron oxide is reduced by the Mo(100) substrate during the TPD process (above 1100 K), giving rise to metallic Fe. It should be noted that several MoO$_x$ species may desorb in the 1400–2200 K temperature range [29,30] with the higher temperature MoO$_x$ desorptions occurring for lower oxygen exposures to Mo. These desorptions may contribute to the oxygen peak signal as well as the high temperature tail (at $\sim 1550$ K [30]). Also, a significant O(1s) signal remains after TPD, indicative of MoO$_x$ remaining on the surface. The high temperature shoulder in the iron TPD of films grown at $2.5 \times 10^{-8}$ Torr and above, is attributed to FeO$_x$ desorption.

The oxygen desorption feature beginning around 750 K and ending at $\sim 950$ K for the TPD of films grown at $2.5 \times 10^{-8}$ Torr and lower pressures is associated with the initial presence of metallic Fe in XPS. This peak was also found in the films grown at 100 K which contained large metallic components. At present, the nature of this peak is not known, but at least two possibilities exist. This state may arise from a recombinative desorption of CO from contamination on the metallic iron. This is supported by the fact that CO does not chemisorb from iron oxide [15] but will dissociatively adsorb on iron metal [31,32]. However, the CO desorption maxima are $\geq 100$ K below that observed in this case [31,32]. Also, we observed no evidence of carbon contamination with XPS. Yet, CO desorption is still a possibility considering the low XPS cross section for carbon, the inhomogeneous sites available for CO recombinative desorption and the relatively small desorption area of the peak. A second possibility is that of a desorption arising from a chemisorbed oxygen state associated with unoxidized iron. It is known that bulk iron undergoes delayed oxidation, in which a certain number of O$_x$ chemisorption states, having chemisorption species more stable than the oxide anion, must be populated before the rate of oxidation becomes significant [33]. However, this desorption has not been previously observed [3]. (This may be a consequence of the oxidation method used, as will be discussed in a later section.)

4.5. In situ oxidation of Fe at 100 K

For the oxide film grown in an O$_2$ background of $5 \times 10^{-9}$ Torr at 100 K, the iron XPS data indicate that the film contains a large metallic component. This is further confirmed by the purely metallic nature of the associated Fe thermal desorption peak (Fig. 10). The associated O(1s) XPS data indicate the presence of two or more oxygen species from the broad peak width (FWHM of 3.5 eV). As seen in the Fe(2p) XPS, some of this oxygen must be in the
form of an oxide (either Fe$^{2+}$ or Fe$^{3+}$ species). Due to the overall O(1s) peak position and the trend in the Fe(2p) spectra, the Fe$^{2+}$ oxide likely forms before the higher oxides and therefore has the greatest contribution to the O(1s) envelope. However, we have shown that the O(1s) binding energy from FeO is only $\sim 530.4$ eV. Therefore, the broad oxygen peak must contain a different oxygen component at a higher binding energy. Previous studies involving the oxidation of iron have observed the formation of chemisorbed oxygen, which acts as a precursor species for oxide formation [3,7–11,25,33,34]. In XPS studies, this species has been reported to appear as a O(1s) high binding energy shoulder [9,34]. Therefore we attribute part of the high O(1s) binding energy component to chemisorbed $\text{O}_2$.

At an oxygen synthesis pressure of $5 \times 10^{-8}$ Torr, the film consists of nearly all Fe$_2$O$_3$ as evidenced by the high binding energy of the Fe(2p) peak, narrow peak width and strong Fe$^{3+}$ shake-up feature at $\sim 718$ eV. As the pressure is increased to $1 \times 10^{-6}$ Torr, the peak reaches a maximum binding energy of 710.9 eV. This value is taken to be that of a pure Fe$_2$O$_3$ film. The associated O(1s) peak shows that the Fe$^{2+}$ oxide states have been diminished with a narrowing of the FWHM. The O(1s) 529.8 eV binding energy arises from $\text{O}_2^-$ ions associated with only Fe$^{3+}$ ions and can be associated with a pure Fe$_2$O$_3$ state.

The iron TPD spectra, for films grown at pressures $\geq 5 \times 10^{-8}$ Torr, originate from oxide films lacking metallic components, however, they exhibit a low temperature shoulder arising from metallic desorption. As discussed previously, this is a consequence of the reduction of some oxide species by the Mo(100) surface above 1200 K. TPD is a dynamic experiment, and the higher temperature peak arises from desorption of the oxide which has not yet been reduced upon reaching the heat of sublimation of the oxide. The heat of sublimation of the higher temperature oxide peak can be calculated from the peak maximum and is $\sim 91$ kcal/mol. Similarly, a peak appears in the oxygen TPD corresponding to the oxide desorption.

It should be observed, that at higher oxygen background pressures, the overall Fe desorption peak is decreased. This is in agreement with a reduction in the Fe(2p) XPS intensity as well as a decrease in the low binding energy component of the O(1s) XPS at higher oxygen pressures. These observations indicate that the overall iron flux was attenuated $\sim 30\%$ at the higher oxygen pressures.

In the films grown in an oxygen background at 100 K, there are two oxygen desorption features that were not observed for those grown at 300 K. The first can be seen as the oxygen feature between $\sim 250$ and $\sim 500$ K in Fig. 11. This feature corresponds to the XPS high binding energy component which broadens the O(1s) peak at higher growth pressures. (This is verified by the annealing experiments in Fig. 13 where this feature is greatly diminished at 400 K and absent at 500 K.) As stated previously, we assign this to be due to a chemisorbed species. However, it must be stated that a small amount of water desorption was observed in the 150–300 K region (probably as a result of the recombination of a hydroxyl contaminant species). This would contribute some to the $m/e = 16$ TPD and is expected to be observed as part of the broadening of the O(1s) peak. (OH$^-$ species created on Fe from water vapor exhibit a O(1s) peak at 532 eV [35].)

The accumulation of the chemisorbed oxygen species is tentatively assigned to arise from $\text{O}_2$, which has been "trapped" within a fully oxidized crystallite. This is supported by the rapid growth of this state once the iron has reached the maximum oxidation composition (Fe$_2$O$_3$ – at pressures $\geq 5 \times 10^{-8}$ Torr). Similar desorption states would not be expected from a post-oxidation experiment. Thermal desorption of oxygen from powdered Fe$_2$O$_3$ has been previously observed under atmospheric conditions [36]. This previous study found a desorption state between 473 and 573 K, which exhibited second-order kinetics. In a similar experiment, the homonuclear exchange reaction

$$^{16}\text{O}_2 + ^{18}\text{O}_2 \rightarrow 2^{16}\text{O}^{18}\text{O}$$

was found to take place on powdered Fe$_2$O$_3$ within this temperature range [37].

A different oxygen feature appears in the oxygen XPS and TPD at synthesis pressures above $1 \times 10^{-6}$ Torr. In the TPD spectra, a prominent peak is evident at $\sim 700$ K and corresponds to the development of a peak at 534.6 eV in the associated O(1s) XPS of Fig. 9. This peak is attributed to a "trapped" molecular oxygen species in the oxide film. The oxygen
core-level value is much too high to be attributed to a chemisorbed atomic species or hydroxylated species. It is, however, found near that of condensed water. Yet, water desorption from Fe$_2$O$_3$ [38], sputtered Fe$_2$O$_3$ [37], and iron oxide thin films [15] occurs below 250 K. Similarly, various hydroxides synthesized from water on Fe(110) decomposed below 315 K [39]. Lu and co-workers observed possible evidence, in high resolution electron energy loss spectra, for a “highly perturbed nondissociated O–O adsorbed species” on Fe(100) [6]. This species persisted to ~700 K. It is not known if this is indeed the same species observed in the experimental results presented here. Previous attempts to observe a molecular oxygen precursor on polycrystalline Fe films at 25 K using XPS were unsuccessful [10]. This may be as a result of the small number of chemisorbed molecular oxygen species present using post-oxidation methods.

The thermal treatment of a film grown in 1 x 10$^{-6}$ Torr of oxygen at 100 K, indicates that the oxide film undergoes several phase changes before desorption. The Fe(2p) spectrum at 100 K is at a slightly lower binding energy than that observed in Fig. 8. However, upon annealing to 200 K, the peak shifts to 710.9 eV. Similarly, the O(1s) component at 529.8 eV grows slightly as the amount of chemisorbed O$_2$ decreases. This indicates that the depletion of chemisorbed oxygen may arise from desorption, as well as the filling of some oxygen vacancies in the Fe$_2$O$_3$ grown at 100 K. (Incorporation of oxygen from chemisorbed O$_2$ to oxide oxygen has been shown to be a nonactivated process [32].) Up to an annealing temperature of 400 K, the film exhibits well-defined Fe$_2$O$_3$ features. From 600–700 K, the Fe(2p) peak is broad and exhibits no shake-up features. We attribute these peaks to Fe$_3$O$_4$. Upon reaching an annealing temperature of 900 K, the Fe(2p) feature is characteristic of FeO. These phase changes are in close agreement with previous results [3]. At 1000 K, MoO$_3$ begins to form at the interface. Above 1200 K MoO$_3$ begins to diffuse into the iron overlayer and reduces the Fe signal in the corresponding thermal desorption experiments. This effect is likely responsible for the abnormally high oxygen and iron core-level binding energies at 1300 K. We were unable to attribute any of the oxygen desorption features to the phase changes observed in the XPS. We believe that the reduction of the higher oxides comes from oxygen diffusion to the Mo(100) interface and finally into the substrate to form MoO$_x$.

5. Conclusions

Iron oxide films were grown by post-oxidation and in situ oxidation methods. In situ oxidation methods are expected to yield films with better homogeneity when compared to those grown by post-oxidation of iron thin films. Metallic iron exhibited a Fe(2p$_{3/2}$) peak at 706.7 eV. By deposition of Fe (at 0.5 ML/min) in a background of oxygen, essentially pure phases of iron oxide could be grown. Deposition of Fe in 5 x 10$^{-8}$ Torr at a substrate temperature of 300 K and subsequent annealing to 500 K resulted in the formation of an FeO film. This film exhibited a Fe(2p$_{3/2}$) peak position at 709.6 eV with a shake-up feature at ~716 eV. The FeO associated O(1s) peak was at 530.4 eV. Iron deposition in 1 x 10$^{-6}$ Torr at 100 K and annealed to 400 K yielded a film of Fe$_2$O$_3$. A corresponding Fe(2p$_{3/2}$) XPS feature was found at 710.9 eV with a shake-up feature at ~719 eV. The O(1s) feature with Fe$_2$O$_3$ was at 529.8 eV. Annealing the Fe$_2$O$_3$ film to 700 K yielded a film with stoichiometry near Fe$_3$O$_4$. The Fe(2p$_{3/2}$) core level associated with Fe$_3$O$_4$ was ~710.3 eV and did not exhibit any shake-up features. An O(1s) binding energy of ~530.1 eV was attributed to Fe$_2$O$_3$. Several desorption peaks were found in the oxygen TPD spectra of films grown in situ at 100 K and are tentatively attributed to chemisorbed atomic species as well as an adsorbed molecular species. Discrete phase changes are observed for the thermal reduction of the oxides by the Mo(100) substrate.

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References