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Characterization of nanocrystalline $\alpha$-Fe$_2$O$_3$ thin films grown by reactive evaporation and oxidation of iron

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Abstract
Iron oxide thin films, with an $\alpha$-Fe$_2$O$_3$ phase, were deposited by two techniques. The first was evaporation of iron in vacuum, followed by oxidation through annealing in air. The second was reactive evaporation of iron in an oxygen atmosphere. This was also followed by annealing in air. The structural, morphological and chemical properties of the films were investigated. All films were polycrystalline with nano-sized crystallites. Structural characterization showed that the films deposited by the first technique had to be annealed at 400 °C to obtain fully oxidized $\alpha$-Fe$_2$O$_3$. On the other hand, the films deposited by the second technique already had the $\alpha$-Fe$_2$O$_3$ phase before annealing. Morphological analysis showed that the films deposited by vacuum evaporation had considerable surface roughness and grain sizes that monotonically increased with annealing temperature. However, reactively evaporated films had smoother surfaces and larger grains, with a maximum grain size obtained in the annealing temperature range 300–400 °C. Surface chemical analysis indicated that the surfaces of the films consisted of FeO$_2$ and Fe$_2$O$_3$, although the latter oxide was the predominant one.

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1. Introduction

The iron–oxygen system contains several oxides, including hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$) and wustite (FeO). Hematite and wustite are antiferromagnetic, whereas the other two oxides are ferromagnetic. $\alpha$-Fe$_2$O$_3$ is the thermodynamically stable phase of Fe$_2$O$_3$. It has very attractive properties, such as high quantum yield, good thermodynamic stability at high temperatures, non-toxicity, low cost and abundance [1]. Moreover, it has an optical band gap (~2.2 eV) that lies in the visible range. Thus, it has attracted considerable interest for several applications, including gas sensing, electrochromism, catalysis, photocatalysis, corrosion, solar energy conversion devices and the photodissociation electrolysis of water [1–4].

Thin films of Fe$_2$O$_3$ have been prepared by a variety of techniques, such as molecular beam epitaxy [5–8], sputtering [9–11], pulsed laser deposition [12], atomic layer deposition [13], spray pyrolysis [3, 14], chemical and metal organic deposition [2, 4, 15–18], sol–gel deposition [19] and electron-beam deposition [20].

A simple and low-cost method of obtaining Fe$_2$O$_3$ thin films is through the oxidation of iron. Three iron oxidation techniques have been developed. The first technique is the oxidation of bulk iron substrates [21–23]. Another technique is the reactive evaporation of iron in an oxygen atmosphere [24–27]. The third technique is the post-deposition annealing of iron thin films in an oxygen atmosphere [25, 26, 28–31]. These studies were limited in many ways. Firstly, most of them were confined to the investigation of ultrathin films (usually monolayers) [25, 26, 28–30]. Such ultrathin films will not be practical for applications, such as gas sensing, photocatalysis or photovoltaics. Secondly, the effect of annealing evaporated iron thin films was systematically investigated only for iron monolayers deposited on molybdenum, and annealed in the temperature range from 200 to 100 °C [29]. Thirdly, from a characterization point of view, these studies focused either on structural analysis using x-ray diffraction (XRD) or on chemical analysis using x-ray photoelectron spectroscopy.

This work focuses on the preparation of $\alpha$-Fe$_2$O$_3$ thin films using evaporation of iron. Our motivation for carrying
out this work was the importance of this material and the simplicity of the technique. We prepared α-Fe₂O₃ thin films using two methods. The first method is the evaporation of iron in vacuum, followed by oxidation of iron via annealing in air. In the second method, iron was reactively evaporated in an oxygen atmosphere. This was also followed by annealing in air. The properties of the films deposited by the two methods were evaluated using structural, morphological and chemical characterization techniques. We attempt, in this work, to provide a comparison between the two methods, to systematically investigate the effect of annealing temperature and also to correlate the properties of the films using various characterization techniques.

2. Experiment

The starting material was solid iron granules (Alfa Aesar, purity 99.999%). Evaporation was carried out by electron-beam deposition using a 4 kW electron gun in a Leybold L560 box coater that was evacuated by a turbomolecular pump. The material was slowly outgassed before evaporation. The system was pumped to a base pressure of 4 × 10⁻⁴ Pa. The films were deposited on fused silica and tantalum substrates. The substrates were rotating during deposition, and the source-to-substrate distance was 40 cm. Three sets of films were deposited. The first set (RW films) was deposited on unheated substrates in vacuum. The other two sets were deposited in an oxygen atmosphere, at an oxygen partial pressure of 0.1 Pa. The other two sets were deposited in an oxygen atmosphere, at an oxygen partial pressure of 0.1 Pa. The second set (RO films) was deposited on unheated substrates, whereas the third set (HO films) was deposited on substrates that were heated to 300 °C. The deposition rate (0.2 nm s⁻¹) and thickness of the films were controlled by a quartz crystal thickness monitor. After deposition, the films were annealed in a horizontal tube furnace in air in the temperature range 200–500 °C in steps of 100 °C, and for 4 h for each annealing temperature. After annealing, the samples were cooled down to room temperature while they were still in the furnace.

The thickness of the films was measured using a surface profiler (Ambios XP-2). The thickness was also verified optically. The structure of the films was investigated by XRD using a Shimadzu XRD-6000 diffractometer, employing Cu Kα (1.54 Å) radiation. XRD was performed for films deposited on fused silica substrates. The surface morphology of the films was examined by tapping mode atomic force microscopy (AFM; Veeco Innova diSPM). The sample surface was probed with a silicon tip of 10 nm radius oscillating at its resonant frequency of 300 kHz. The scan area was 2 × 2 μm², and the scan rate was 1 Hz. AFM images were obtained for films deposited on fused silica substrates. The chemical composition of the films was studied using x-ray photoelectron spectroscopy (XPS), and was performed in a VG Scientific ESCALAB MKII spectrometer equipped with an Al Kα (1486.6 eV) x-ray source. Prior to the XPS analysis, the samples were transferred in air to the XPS analysis chamber. The C 1s peak of hydrocarbon contamination, at a binding energy (BE) of 284.5 eV, was used as an energy reference. During the XPS analysis, the samples were maintained at ambient temperature at a pressure of 5 × 10⁻⁷ Pa. XPS was performed on samples deposited on tantalum substrates, since the charging effects will be smaller for these substrates.

3. Results

3.1. Structural properties

The XRD patterns of the films deposited and post-annealed under different experimental conditions are depicted in figures 1 and 2. Identification of materials and phases, and
peak assignments were based on data from the International Center for Diffraction Data (ICDD)\(^1\). The films were polycrystalline with no preferred orientation, except those of pure iron. Figure 1 shows the effect of annealing on iron thin films deposited in vacuum (RW films). The as-deposited films exhibited oriented growth along the (110) direction of the cubic structure of elemental iron. No iron oxides were observed (within the detection limits of XRD). The same behavior was observed when these films were annealed at 200 °C. However, upon annealing at 300 °C, a mixture of iron and iron oxide (\(\alpha\)-Fe\(_2\)O\(_3\)) was formed, indicating the onset of oxidation. Complete oxidation was achieved at 400 °C, where no traces of elemental iron were observed. The oxide films had a predominant (104) growth direction. The XRD patterns of as-deposited reactively evaporated films (RO and HO films) are shown in figure 2. Annealing did not affect these patterns. No peaks due to elemental iron were detected, indicating complete oxidation of the as-deposited films. All peaks belong to the \(\alpha\)-Fe\(_2\)O\(_3\) phase. The films deposited on heated substrates (HO films) exhibited two preferred orientations, namely (104) and (110).

The crystallite size (\(L\)) of the films was calculated using the Scherrer equation (\(L = 0.9\lambda/(\beta \cos \theta)\)), where \(\lambda\) is the x-ray wavelength, \(\beta\) is the full-width at half-maximum of the diffraction peak and \(\theta\) is the angle corresponding to the diffraction peak. The most intense peak in every XRD pattern was used to calculate the crystallite size. The calculated crystallite sizes are given in table 1. Pure iron thin films (RW films) had the lowest crystallite size, which was significantly enhanced when the films were oxidized. Reactively evaporated films had similar values for the crystallite size: 14.5 ± 0.4 nm for RO films and 14.7 ± 0.2 nm for the HO films. These crystallite sizes reflect the nanocrystalline nature of the films.

\(^1\) ICDD files: (01-087-0722) for elemental iron; (01-071-5088) for \(\alpha\)-Fe\(_2\)O\(_3\).

### Table 1. Crystallite size as calculated from XRD spectra. \(T_a\), annealing temperature; RW, films evaporated in vacuum; RO, films deposited on unheated substrates in oxygen; HO, films deposited on heated substrates in oxygen.

<table>
<thead>
<tr>
<th>(T_a) (°C)</th>
<th>RW</th>
<th>RO</th>
<th>HO</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>10.2</td>
<td>14.1</td>
<td>15.0</td>
</tr>
<tr>
<td>200</td>
<td>10.2</td>
<td>14.5</td>
<td>14.6</td>
</tr>
<tr>
<td>300</td>
<td>13.3</td>
<td>14.9</td>
<td>14.9</td>
</tr>
<tr>
<td>400</td>
<td>14.9</td>
<td>14.5</td>
<td>14.5</td>
</tr>
<tr>
<td>500</td>
<td>14.4</td>
<td>14.6</td>
<td>14.6</td>
</tr>
</tbody>
</table>

The thickness of as-deposited iron films that were evaporated in vacuum (RW films) was 110 nm. This value was slightly reduced to 100 nm upon annealing at 200 °C. A drastic change occurred when the films were annealed at 300 °C, where the thickness increased to 220 nm. This could be attributed to oxide formation. Thereafter, the thickness slightly increased with annealing temperature to a value of 230 nm at 500 °C. The thickness of the films deposited on unheated substrates under an oxygen atmosphere (RO films) was 245 nm. The thickness of these films did not change (<2% variation) as they were annealed up to 500 °C. Similarly, the thickness of the films deposited on heated substrates in an oxygen atmosphere (HO films) was 145 nm, and did not show any variation with annealing. The lower thickness of the films deposited on heated substrates may be attributed to the lower sticking efficiency of iron at higher substrate temperatures [29].

### 3.2. Morphological properties

AFM was used to characterize the morphology and film growth mode and also to estimate the surface root-mean-square roughness (\(R_{rms}\)) and the lateral (surface) grain size. Representative three-dimensional AFM images of iron oxide thin films are shown in figure 3. The effect of annealing...
on the lateral grain size is shown in figure 4. The morphology of the as-deposited vacuum-evaporated iron films (RW films) was characterized by irregular grains (figure 3(a)) with an $R_{\text{rms}}$ value of 2.0 nm. Annealing these films at 200 $^\circ$C reduced $R_{\text{rms}}$ to 1.7 nm without a significant change in morphology. Annealing at 300 $^\circ$C resulted in oriented vertical growth of the grains (figure 3(b)) accompanied by a significant increase in $R_{\text{rms}}$ to 5.3 nm. Further annealing up to 500 $^\circ$C did not change the morphology, although $R_{\text{rms}}$ progressively increased to 7.2 nm. The lateral grain size of the RW films monotonically increased with the annealing temperature, as shown in figure 4. The conversion into vertical growth may be attributed to the increase in thickness. A similar behavior was observed in aluminum-doped zinc oxide thin films [32]. Moreover, the increase in lateral grain size was due to the fusion of adjacent grains when sufficient energy is provided by the annealing process [33].

The morphology of the reactively deposited (RO and HO) films is also shown in figure 3. The as-deposited films had a columnar microstructure (figure 3(c)). Upon annealing at 300 $^\circ$C, the grain boundaries coalesced, resulting in a denser structure (figure 3(d)). However, when the films were annealed at 500 $^\circ$C, their morphology turned back to a columnar microstructure. These morphological changes were reflected in the lateral grain size, as shown in figure 4. The columnar microstructure at 500 $^\circ$C may be explained on the basis of the Thornton grain structure zone model [34], which predicts such a structure for $0.3 < T/T_m < 0.5$, where $T_m$ is the melting point of the material. In our case, $T = 773$ K and $T_m = 1840$ K. The validity of this model is supported by the XRD results, which indicated that these films consisted of a single phase material (Fe$_2$O$_3$). These films had similar values of $R_{\text{rms}}$ that did not change significantly with annealing temperature: $R_{\text{rms}} = 2.8 \pm 0.3$ nm for RO films and $R_{\text{rms}} = 2.5 \pm 0.2$ nm for HO films.

### 3.3. Chemical properties

A typical XPS wide survey scan is shown in figure 5, and it reveals that the only elements present were the constituent elements (Fe and O) and adventitious carbon. In addition to the wide survey scans, detailed high-resolution spectra were obtained in the Fe 2p and O 1s core level regions. The Fe 2p spectrum is shown in figure 6(a). A high-resolution Fe 2p$_{3/2}$ spectrum is shown in figure 6(b). The Fe 2p$_{3/2}$ spectrum had a highly asymmetric line shape due to the presence of several oxidation states and satellites. Likewise, the asymmetry of the O 1s peak (figure 7) was due to the presence of chemisorbed oxygen. In order to investigate the presence of different oxidation states of iron, the Fe 2p$_{3/2}$ spectrum was resolved into constituent components using a Gaussian/Lorentzian mixed function employing Shirley background correction, as shown...
Figure 5. A typical XPS wide survey scan of the films.

Figure 6. XPS spectra in the Fe 2p core level region: (a) the full spectrum showing the spin–orbit splitting (Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$) and the shake-up satellite, and (b) resolution of the Fe 2p$_{3/2}$ peak into two components corresponding to the two oxidation states of iron.

in figure 6(b). The weight ($W$) of a component was found by dividing the area under that component by the total area under the Fe 2p$_{3/2}$ peak. Initially, we attempted to resolve the Fe 2p$_{3/2}$ into three components (Fe$^0$, Fe$^{2+}$, Fe$^{3+}$). However, the metallic component (Fe$^0$) was only found in the as-deposited RW films, with a very small weight of 0.02. Thus, the Fe 2p$_{3/2}$ peak was resolved into two components (Fe$^{2+}$ and Fe$^{3+}$). These components were not well separated due to strong multiplet splitting [29]. The BEs, weight and full-width at half-maximum ($\Gamma$) of the two components are listed in table 2. The spin–orbit splitting ($\delta_{2p}$) between the Fe 2p$_{1/2}$ and the Fe 2p$_{3/2}$ peaks is also given in table 2. Its value was very close to that reported in the literature [3, 22].

Figure 7. Resolution of the XPS O 1s spectrum into an LBE component corresponding to the Fe–O bond and an HBE component corresponding to chemisorbed oxygen.

The O 1s spectra were resolved into two components (figure 7). The first is a low-binding-energy (LBE) component, which corresponds to oxygen bonded to iron. The second is a high-binding-energy (HBE) component, which corresponds to chemisorbed oxygen. The BE, weight and full-width at half-maximum of each component are given in table 2. On average, the HBE component was 12% of the total O 1s peak for films deposited on unheated substrates (RW and RO films). Its value was significantly reduced to 6% for films deposited on heated substrates (HO films). The intensity of this component is partly proportional to the amount of adsorbed water, which in turn is expected to increase with the porosity of the films. This is consistent with the compact nature of the HO films, as revealed by their lower thickness.

4. Discussion

The iron–oxygen system has several oxides with different oxidation states and crystalline structures. The lowest oxidation state (Fe$^{2+}$) corresponds to FeO, which has a rocksalt structure [20]. In magnetite (Fe$_3$O$_4$), iron can have oxidation states Fe$^{2+}$ and Fe$^{3+}$ [35], and has a cubic spinel structure [20]. The third oxide is Fe$_2$O$_3$, in which iron has the oxidation state Fe$^{3+}$. This oxide exists in three forms. The first form is hematite (α-Fe$_2$O$_3$), which has a stable corundum rhombohedral hexagonal structure [13, 20]. The second form is maghemite (γ-Fe$_2$O$_3$), which has a cubic spinel structure [20]. The third form is β-Fe$_2$O$_3$, which has a body-centered cubic structure [14]. Of the three forms, the α phase is known as the most stable material [14], whereas the other two phases are metastable. These oxides transform into each other depending on the ambient conditions such as temperature and oxygen partial pressure [36]. For example, the γ-Fe$_2$O$_3$ phase is unstable and transforms into α-Fe$_2$O$_3$ when heated above 350 °C [6]. It was also observed that at 500 °C and low oxygen content in the gas phase (~1 mbar), Fe$_3$O$_4$ was formed, whereas in an oxygen-rich atmosphere Fe$_2$O$_3$ was favored [17, 24]. Annealing Fe$_2$O$_4$ films in air at 400 °C yields α-Fe$_2$O$_3$ films [24], whereas annealing α-Fe$_2$O$_3$ films in vacuum yields Fe$_3$O$_4$ films [31].

The crystallinity of thin films is influenced by several factors, including (i) the deposition technique, (ii) substrate
nature and crystallinity, (iii) substrate temperature, (iv) deposition rate, (v) oxygen partial pressure and (vi) annealing temperature, atmosphere and heating rate. A compilation showing the effects of these parameters on the crystallinity of iron oxide thin films is given in Table 2. Therefore, it is not unusual to find widely scattered results on the crystalline structure of thin films of a given material. Our XRD results are consistent with previous studies on iron oxide thin films grown by thermal evaporation and oxidation, all of which resulted in the formation of polycrystalline films [24, 31]. Chiba et al. [31] found that pure iron films transform into α-Fe₂O₃ upon annealing in air at 400 °C. The effect of deposition under an oxygen atmosphere was investigated by Fujii et al. [24], who derived the phase diagram for the formation of iron oxides as a function of the substrate temperature and oxygen partial pressure. Their results showed that more oxidized phases were obtained at low substrate temperatures \( T_s \) and high oxygen partial pressure \( p(O_2) \).

In particular, for \( T_s \leq 300 \) °C and \( p(O_2) = 1.0 \times 10^{-3} \) mbar, only α-Fe₂O₃ was formed. Our XRD results indicated that the reactively evaporated films (RO and HO films) had the \( α-Fe₂O₃ \) phase without the need for annealing. Moreover, annealing did not improve the crystallinity of these films. The multiple growth directions for films deposited on the heated substrates were due to the increased mobility of the atoms on the substrate’s surface. The \( α-Fe₂O₃ \) phase could be obtained from vacuum-evaporated films (RW films) only after annealing the films at 400 °C, upon which the films had the same structure as the as-deposited HO films.

The morphological analysis of the films indicated that although annealing did not influence the crystallite size or surface roughness of the RO and HO films, it had a profound effect on the lateral grain size, where the largest grain size was obtained after annealing at 300–400 °C. The RW films had larger values of surface roughness with lower grain size. Roughness can be beneficial in some applications that require a large surface to volume ratio, such as catalysis and sensing. XPS has been used extensively in the chemical analysis of iron oxides. This was driven by three motivations. Firstly, it is important to determine the oxidation states of iron and construct the band structure of iron oxides. Secondly, from an applications point of view, iron oxides are used in several surface-based applications such as catalysis and sensing. Thirdly, iron oxide surfaces are of great importance in corrosion studies [28]. XPS is a surface technique that can probe a few top layers of the films. It can yield valuable information about the oxidation state of iron since it is sensitive to core-level shifts. There have been some difficulties in interpreting XPS data related to iron oxides. These difficulties have been attributed to four factors. Firstly, the correlation effects among the Fe 3d and O 2p states give rise to complicated multiplet structures [8]. Secondly, it is very difficult to prepare clean surfaces with controlled stoichiometry, and XPS spectra are easily influenced by the presence of contamination such as water and hydrocarbons at the surface [8]. Thirdly, the BEs were found to depend on the thickness of the oxide films. Variations of as much as 0.5 eV have been reported for films of different thicknesses [26]. In the case of oxidation, this is explained as follows. At first, FeO is formed; then as the oxide thickness increases, Fe₂O₃ and Fe₃O₄ form on top of the FeO layer [22]. Fourthly, several levels were used as the BE reference, such as the gold Au 4f/2 [21, 25], the carbon C 1s (although with different BEs) [3, 22], the molybdenum Mo 3d₅/₂ [29] and the oxygen O 1s [8, 14, 35].

The iron 2p level consists of two sublevels (2p₁/₂ and 2p₃/₂) due to spin–orbit splitting. The reported values of the BEs of the Fe 2p₁/₂ level depend on the oxidation state of the iron. The reported values of the BE of Fe 2p₁/₂ in metallic iron \((Fe^0)\) are in the range 706.7–707.4 eV [21–23, 29]. The reported values for the BEs of Fe 2p₁/₂ in the Fe²⁺ state are in the range 709.3–710.0 eV [7, 21–23, 28–30]. The reported values for the BEs of Fe 2p₁/₂ in the Fe³⁺ state are in the range 710.6–711.6 eV [7, 8, 21–23, 28–30]. Moreover, the Fe 2p₁/₂ level in FeO and Fe₂O₃ is characterized by the presence of
Table 3. Comparison of the crystalline structure of iron oxide thin films deposited by various techniques. ALD, atomic layer deposition; CVD, chemical vapor deposition; DCS, DC sputtering; IBAD, ion beam-assisted deposition; MBE, molecular beam epitaxy; MOCVD, metal organic chemical vapor deposition; NA, not applicable; PECDV, plasma enhanced chemical vapor deposition; PLD, pulsed laser deposition; poly: polycrystalline; \( p(\text{O}_2) \), oxygen partial pressure during oxidation; RFS, RF sputtering; RT, unheated substrate; SP, spray pyrolysis; \( T_s \), substrate temperature; \( T_a \), annealing temperature (in air).

<table>
<thead>
<tr>
<th>Method</th>
<th>Substrate Source material</th>
<th>( p(\text{O}_2) ) (Pa)</th>
<th>( T_s ) (°C)</th>
<th>Crystallinity</th>
<th>Phase</th>
<th>( T_a ) (°C)</th>
<th>Phase</th>
<th>Crystallinity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>Evaporation</td>
<td>Glass</td>
<td>Fe</td>
<td>–</td>
<td>RT</td>
<td>–</td>
<td>400</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>Poly</td>
<td>[31]</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Glass, Si</td>
<td>Fe</td>
<td>1.3 \times 10^{-2}</td>
<td>200</td>
<td>Amorphous</td>
<td>700</td>
<td>amorphous</td>
<td>–</td>
<td>[27]</td>
</tr>
<tr>
<td>IBAD</td>
<td>Glass, Si</td>
<td>Fe</td>
<td>6.4 \times 10^{-2}</td>
<td>200</td>
<td>Amorphous</td>
<td>700</td>
<td>Fe(_2)O(_3)</td>
<td>Poly</td>
<td>[27]</td>
</tr>
<tr>
<td>DCS</td>
<td>Glass, Ni</td>
<td>Fe</td>
<td>7–27 \times 10^{-2}</td>
<td>100–200</td>
<td>Poly</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>–</td>
<td>–</td>
<td>[11]</td>
</tr>
<tr>
<td>RFS</td>
<td>Glass(^a)</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>–</td>
<td>RT</td>
<td>Poly</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>–</td>
<td>–</td>
<td>[9]</td>
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<tr>
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<td>–</td>
<td>RT</td>
<td>Poly</td>
<td>FeO, Fe(_2)O(_3), Fe(_3)O(_4) (^b)</td>
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<td>–</td>
<td>[10]</td>
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<tr>
<td>PLD</td>
<td>Si, LiAlO(_3)</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>0–7</td>
<td>400</td>
<td>Poly</td>
<td>( \alpha, \gamma )-Fe(_2)O(_3) (^c)</td>
<td>–</td>
<td>–</td>
<td>[12]</td>
</tr>
<tr>
<td>MBE</td>
<td>MgO, Al(_2)O(_3)</td>
<td>Fe</td>
<td>(&lt;7 \times 10^{-3})d</td>
<td>225–500</td>
<td>Epitaxial</td>
<td>( \alpha )-Fe(_2)O(_3), Fe(_2)O(_4) (^e)</td>
<td>–</td>
<td>–</td>
<td>[6]</td>
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<tr>
<td>MBE</td>
<td>MgO</td>
<td>Fe</td>
<td>3.3 \times 10^{-3}(d)</td>
<td>225–500</td>
<td>Epitaxial</td>
<td>( \gamma )-Fe(_2)O(_3)</td>
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<td>–</td>
<td>[6]</td>
</tr>
<tr>
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<td>365</td>
<td>Amorphous</td>
<td>–</td>
<td>300–800</td>
<td>( \alpha, \gamma )-Fe(_2)O(_3)(^f)</td>
<td>Poly</td>
<td>[4]</td>
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<td>CVD</td>
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<td>Fe precursor</td>
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<td>200–400</td>
<td>Poly</td>
<td>( \beta )-Fe(_2)O(_3)</td>
<td>–</td>
<td>–</td>
<td>[15]</td>
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<tr>
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<td>Glass</td>
<td>Fe precursor</td>
<td>50–200(g)</td>
<td>500–600</td>
<td>Poly</td>
<td>( \alpha )-Fe(_2)O(_3), Fe(_2)O(_4) (^e)</td>
<td>–</td>
<td>–</td>
<td>[16]</td>
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<tr>
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<td>Si</td>
<td>Fe precursor</td>
<td>40(d)</td>
<td>450–600</td>
<td>Poly</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>–</td>
<td>–</td>
<td>[18]</td>
</tr>
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<td>PECVD</td>
<td>Al(_2)O(_3)</td>
<td>Fe precursor</td>
<td>80–350</td>
<td>Poly</td>
<td>( \alpha )-Fe(_2)O(_3), Fe(_2)O(_4) (^e)</td>
<td>450–650</td>
<td>–</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>ALD</td>
<td>Glass, Si</td>
<td>Fe precursor</td>
<td>130–380</td>
<td>Poly</td>
<td>( \alpha, \gamma )-Fe(_2)O(_3) (^e)</td>
<td>–</td>
<td>–</td>
<td>[13]</td>
<td></td>
</tr>
<tr>
<td>SP</td>
<td>Si</td>
<td>Fe precursor</td>
<td>NA</td>
<td>200–400</td>
<td>Poly</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>–</td>
<td>–</td>
<td>[14]</td>
</tr>
</tbody>
</table>

\(^a\) Other substrates (Ta, Au, mylar) were also used.

\(^b\) Depending on RF power.

\(^c\) Depending on \( p(\text{O}_2) \).

\(^d\) ECR plasma.

\(^e\) Depending on substrate and/or substrate temperature.

\(^f\) Depending on annealing temperature.

\(^g\) In units of sccm.

\(^h\) Other substrates (MgO, Al\(_2\)O\(_3\)) were also used.
a shake-up satellite at a BE of 715–716 eV for FeO [21, 29] and 719.0–719.8 eV for Fe$_2$O$_3$ [7, 21, 29, 30]. These satellites are frequently used as fingerprints to identify the iron oxide phases [8]. Magnetite (Fe$_3$O$_4$) contains 1/3 Fe$^{3+}$ ions and 2/3 Fe$^{2+}$ ions [30], and has no satellite structure [21]. Detailed values for the BEs in the Fe 2p$_{3/2}$ region are given in [21]. The O 1s spectrum in iron oxides consists of two components. The first LBE component corresponds to the Fe–O bond. It was reported that this component has a BE of 529.8–530.6 eV, independent of the oxidation state of iron [8, 21, 22, 29, 30]. The second HBE component corresponds to a BE of $\geq 532$ eV, and is attributed to chemisorbed oxygen or adsorbed water [22, 29].

Our XPS results indicate that the surfaces of iron films are oxidized when exposed to air. Exposure of iron to oxygen, even at room temperature, results in the adsorption of oxygen and the formation of a few monolayers of Fe$^{3+}$ and Fe$^{4+}$ oxides [22, 29]. The satellites observed were characteristic of Fe$_3$O$_4$. The lack of the satellites characteristic of FeO, and the appearance of the Fe$^{2+}$ component in the XPS spectra, reveal the presence of Fe$_3$O$_4$ on the surfaces of the films. Although the XRD results showed that the annealing of iron resulted in the formation of Fe$_3$O$_4$, the XPS results indicated that the surfaces of the films contained both Fe$_3$O$_4$ and Fe$_2$O$_3$ species, albeit with a predominant Fe$_2$O$_3$ component. The presence of the two oxide phases on the surfaces of the films reflects the high reactivity of iron toward oxygen.

5. Conclusions

Thin films of the $\alpha$-Fe$_2$O$_3$ phase of iron oxide were prepared by two methods. In the first method, iron films were prepared by evaporating iron in vacuum, and subsequently the films were annealed in air, in the temperature range 200–500 °C, to oxidize them. Full oxidation was achieved when the films were annealed at 400 °C. The crystallite size of these films increased from 10.2 nm, for pure iron, to 14.4 nm for oxide films. The surface roughness of the films increased from 2.0 nm for pure iron films to 7.2 nm for oxidized films. The lateral grain size progressively increased with annealing temperature from 20 nm for the as-deposited films to 50 nm for the films annealed at 500 °C. In the second method, iron was reactively evaporated under an oxygen partial pressure of 0.1 Pa, both on unheated substrates and on substrates heated to 500 °C. Through reactive evaporation, the as-deposited films already had the $\alpha$-Fe$_2$O$_3$ phase without further annealing. However, annealing was carried out, over the same temperature range, to investigate its effects on the properties of the films, and for comparison with the films deposited using the first method. Reactively evaporated films had the same crystallite size of about 15 nm and the same surface roughness of about 2.5 nm; both properties did not change with the annealing temperature. However, the lateral grain size was dependent on both the substrate temperature and annealing temperature, attaining a maximum value of 65 nm for the films deposited on unheated substrates and further annealed at 300 °C. In addition, reactive deposition on heated substrates resulted in more compact films with growth along several crystalline directions. The surfaces of all films exhibited the presence of both Fe$_3$O$_4$ and Fe$_2$O$_3$ iron oxides. This was attributed to the high reactivity of iron toward oxygen. Thus, from a structural and a process viewpoint, reactive deposition on unheated substrates (RO films) seems to be a very convenient method for preparing $\alpha$-Fe$_2$O$_3$ thin films. This is because it does not require substrate heating, and the films had a similar surface roughness and crystallite size to those deposited on heated substrates. They also had the largest lateral grain size when annealed at 400 °C. Deposition on heated substrates resulted in more compact films with higher as-deposited grain size. Vacuum evaporation (RW films) requires post-deposition annealing at 400 °C to obtain $\alpha$-Fe$_2$O$_3$; however, they provide films with higher surface roughness, which may be beneficial for certain applications.

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References