Atomic Layer Deposition of Fe$_2$O$_3$ Using Ferrocene and Ozone

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ABSTRACT: Growing interest in Fe$_2$O$_3$ as a light harvesting layer in solar energy conversion devices stems from its unique combination of stability, nontoxicity, and exceptionally low material cost. Unfortunately, the known methods for conformally coating high aspect ratio structures with Fe$_2$O$_3$ leave a glaring gap in the technologically relevant temperature range of 170–350 °C. Here, we elucidate a self-limiting atomic layer deposition (ALD) process for the growth of hematite, α-Fe$_2$O$_3$, over a moderate temperature window using ferrocene and ozone. At 200 °C, the self-limiting growth of Fe$_2$O$_3$ is observed at rates up to 1.4 Å/cycle. Dense and robust thin films grown on both fused quartz and silicon exhibit the expected optical bandgap (2.1 eV). In situ mass spectrometric analysis reveals the evolution of two distinct cyclic reaction products during the layer-by-layer growth. The readily available and relatively high vapor pressure iron precursor is utilized to uniformly coat a high surface area template with aspect ratio ~150.

1. INTRODUCTION

Hematite (rhombohedral, α-Fe$_2$O$_3$) is the most common form of iron(III)oxide. An exceedingly stable substance, the familiar red polymorph is the principal constituent in rust. Hematite has been used throughout history in pottery and as a pigment and, more recently, has attracted attention for its electrical and optical properties. As a semiconductor, Fe$_2$O$_3$ is a potentially useful solar absorber and water oxidation catalyst.1,2

Growing interest in Fe$_2$O$_3$ as a light harvesting layer in solar energy conversion devices stems from its unique combination of stability, nontoxicity, and exceptionally low material cost. Although the 2.1 eV bandgap of hematite is not ideal for single-junction solar energy conversion devices, its potential in multijunction photovoltaics (PV) and photochemical conversion applications makes it an attractive target. The indirect bandgap material is a seemingly efficient light collector with peak absorptivity exceeding 10$^5$ cm$^{-1}$. Still, collecting 90% of incident photons with energy greater than the indirect gap would require a relatively thick film (~1 μm). Given that the hole diffusion length within α-Fe$_2$O$_3$ is most often reported to be 2–20 nm,3,4 utilizing a significant fraction of the incident solar flux will require alternative photoelectrode designs, ones that are characterized by both high surface areas and short charge–collection distances. Such designs will almost certainly entail nanoscale structuring.

By utilizing self-limiting surface reactions, atomic layer deposition (ALD) offers a general route to thin films that is uniquely suited to nanoscale structuring.5 The technique is more appropriately classified as a surface-synthesis strategy comprising alternating chemical reactions that sequentially functionalize a substrate. Unlike other physical or chemical vapor deposition techniques, ALD employs self-limiting reactions that result in the growth of one atomic layer (or less) per A–B cycle. This elegant approach to material growth provides exquisite control over the thickness and composition of thin films. By its nature, ALD grows conformal films that have been shown to uniformly and reproducibly coat nanoscale architectures with aspect ratio in excess of 1000.6,7 Several studies have shown the utility of ALD in the fabrication of nanostructured photovoltaics.8–13 This study extends the range of high-aspect-ratio-compatible ALD processes suitable for the next generation of electro-optic devices.

The ALD of α-Fe$_2$O$_3$ was first demonstrated by alternating exposure to tris-(2,2,6,6-tetramethyl-3,5-heptanedionato)iron(III) (Fe(thd)$_3$) and ozone (O$_3$).14 While the self-limiting nature of the surface reaction was established, the process suffers from an exceptionally low growth rate (~0.1 Å/cycle) and a small iron precursor vapor pressure, both of which limit its applicability to high aspect ratio coating. Subsequent reports of Fe$_2$O$_3$ formation via ALD include sequential substrate exposure to iron(III) tert-butoxide (Fe$_2$(O'Bu)$_6$) and water15 as well as ferrocene (Fe(Cp)$_2$) pulsed alternately with molecular oxygen (O$_2$) at...
high temperature.\textsuperscript{16,17} While the Fe\textsubscript{2}(O\textsubscript{3}Bu)\textsubscript{6} system has been shown to coat porous membranes with aspect ratio of 100, the narrow temperature window (130–170 °C) incites significant carbon incorporation. Fe(Cp)\textsubscript{2} has previously been used in condensation of Fe(Cp)\textsubscript{2} on the reactor walls. The reaction tube constructed of a stainless steel of 5 cm to hold the substrates for purity O\textsubscript{2}. A growth rate of 1.4 Å/cycle was reported for temperatures less than 500 °C, but differs substantially (0.6 Å/cycle) in porous membranes. Regardless, the known methods for conformally coating high aspect ratio structures with Fe\textsubscript{2}O\textsubscript{3} leave a glaring gap in the technologically relevant temperature range of 170–350 °C. The ready application of a self-limiting, Fe\textsubscript{2}O\textsubscript{3} ALD process utilizing commercially available, high vapor pressure precursors would stimulate the field.

In this Article, we describe a method for growing Fe\textsubscript{2}O\textsubscript{3} by ALD using Fe(Cp)\textsubscript{2} and O\textsubscript{3}. As compared to previous reports of ALD using Fe(Cp)\textsubscript{2} in combination with O\textsubscript{2}, the use of \textit{O}3 enables growth over a much wider temperature range (100–250 °C). Furthermore, dense thin films that show only a single crystalline phase as grown are observed. Finally, the relatively large partial pressure of Fe(Cp)\textsubscript{2} (∼100 Pa at 80 °C) enables conformal deposition of Fe\textsubscript{2}O\textsubscript{3} on high aspect ratio structures. While this is the first full report of ALD using these precursors, we note that one sentence was published during our studies that refers to ALD using Fe(Cp)\textsubscript{2} and O\textsubscript{3}.\textsuperscript{18} The authors report only the growth rate, 0.2 Å/cycle, one that differs markedly from those described herein.

2. EXPERIMENTAL SECTION

Fe\textsubscript{2}O\textsubscript{3} ALD was performed using a viscous flow ALD reactor constructed of a stainless steel flow tube with an inside diameter of 5 cm to hold the substrates for film growth.\textsuperscript{19} Ultrahigh purity (99.999%) nitrogen carrier gas continuously passed through the flow tube at a mass flow rate of 60 sccm and a pressure of 1.6 Torr. A constant reactor temperature was maintained by two temperature controllers connected to resistive heating elements attached to the outside of the reactor. Fe\textsubscript{2}O\textsubscript{3} ALD was performed using alternating exposures to Fe(Cp)\textsubscript{2} (Aldrich, >98%) and O\textsubscript{3} (∼10 wt % in 500 sccm ultrahigh purity O\textsubscript{2}). The Fe(Cp)\textsubscript{2} was held in a stainless steel bubbler maintained at 80 °C, while the tubing connecting the bubbler to the ALD reactor was maintained at 200 °C to prevent condensation of Fe(Cp)\textsubscript{2} on the reactor walls. The reaction tube and samples were heated to 200 or 250 °C as specified in the text. Ultrahigh purity nitrogen at a mass flow rate of 20 sccm was sent through the bubbler during Fe(Cp)\textsubscript{2} exposures and was diverted to bypass the bubbler following Fe(Cp)\textsubscript{2} exposures. Additional oxygen sources evaluated for Fe\textsubscript{2}O\textsubscript{3} ALD included deionized water, hydrogen peroxide (Aldrich, 50 wt %), and O\textsubscript{2} (ultrahigh purity, 500 sccm). The ALD reactor was equipped with a quadrupole mass spectrometer (QMS, Stanford Research Systems RGA300) located downstream of the samples in a differentially pumped chamber separated from the reactor tube by a 35 μm orifice and evacuating using a 50 L/s turbomolecular pump.

The ALD timing sequences can be expressed as \( t_1 - t_2 - t_3 - t_4 \), where \( t_1 \) is the exposure time for the first precursor, \( t_2 \) is the purge time following the first exposure, \( t_3 \) is the exposure time for the second precursor, \( t_4 \) is the purge time following the exposure to the second precursor, and all units are given in seconds (s).

The Fe\textsubscript{2}O\textsubscript{3} films were deposited on Si(100) and fused quartz substrates. Prior to loading, the substrates were cleaned in an ultrasonicator using acetone and then isopropanol and blown dry using nitrogen. After loading, the substrates were allowed to outgas in the ALD reactor for 10 min at the deposition temperature in 1.6 Torr of flowing ultrahigh purity nitrogen. Next, the substrates were cleaned in situ using a 180 s exposure to O\textsubscript{3} in O\textsubscript{2} at a mass flow rate of 500 sccm.

Scanning electron microscopy (SEM) images were acquired using a Hitachi S4700 SEM with a field emission gun electron beam source, and an energy dispersive X-ray (EDX) detector for elemental analysis. X-ray diffraction (XRD) measurements were taken on a Rigaku Miniflex Plus diffractometer with Cu Kα radiation. Ellipsometric measurements of the Fe\textsubscript{2}O\textsubscript{3} films deposited on Si(100) surfaces were performed using a J.A. Woollam Co. M2000 variable angle spectroscopic ellipsometer (VASE). Thin film thickness and density were also derived from fits to X-ray reflectivity (XRR) spectra acquired on a custom-built tool. The relative thickness of films grown on fused quartz was derived from X-ray fluorescence (XRF) measurements made using an Oxford Instruments ED2000. UV−vis−NIR reflection-corrected absorption spectra were derived from measurements employing a Varian Cary 5000 with integrating sphere accessory (DRA-2500). Silica aerogel films (∼9 μm thickness, aspect ratio 150) built on conductive glass platforms and micromachined Si trench wafers (aspect ratio 4) were coated with Fe\textsubscript{2}O\textsubscript{3}.

3. RESULTS AND DISCUSSION

Self-Limiting Growth Kinetics. The self-limiting nature of each half-cycle defines ALD as a surface-selective synthesis strategy and is paramount to the uniform coating of high aspect ratio structures. A true ALD process (with no CVD component) will exhibit saturating surface reactions such that in the limit of long precursor exposures a plateau in the growth rate is observed. Under our experimental conditions of constant precursor delivery in time, the exposure is strictly proportional to dose time. At 200 °C, both reactions are self-limiting and fit well to a Langmuir adsorption model, Figure 1.

The maximum growth rate in Figure 1a is limited by the selection of a subsaturating O\textsubscript{3} exposure, chosen in the interest of time. We note that this selection does not undermine the conclusion that can be drawn, that the Fe(Cp)\textsubscript{2} half-reaction is self-limiting at 200 °C. Under careful scrutiny, the growth rate dependence on ferrocene exposure reveals a mild slope in the long dose limit. Although many ALD precursors show “soft” saturation in the very high exposure limit,\textsuperscript{20–22} the case of Fe(Cp)\textsubscript{2} in these studies is particularly intriguing due to the reported acceleration of Fe(Cp)\textsubscript{2} decomposition on vessels coated with Fe and C.\textsuperscript{23} The result is an autocatalytic process in which the Fe(Cp)\textsubscript{2} decomposition products (containing Fe and C) stimulate the decomposition of Fe(Cp)\textsubscript{2} itself. The catalytic effect is so great that the kinetics of thermolysis have been measured at temperatures as low as 400 °C in Fe−C coated vessels.\textsuperscript{23} This study is in discord with previous reports of ALD employing Fe(Cp)\textsubscript{2} and O\textsubscript{2} at 350–500 °C.\textsuperscript{16,17} In published work examining the self-limiting nature of the Fe(Cp)\textsubscript{2} ALD surface reaction, reported only at 350 °C, the presence of a CVD component is unclear. Our experience with Fe(Cp)\textsubscript{2} at higher temperatures indicates that ALD growth at 250 °C is also practical although slightly less self-limiting. Fe\textsubscript{2}O\textsubscript{3} ALD at temperatures above 300 °C using either O\textsubscript{2} or O\textsubscript{3} resulted in variable and sporadic growth rates and sometimes yielded visibly nonuniform, rough films. Other oxygen sources were explored under the
200 °C growth conditions. Alternating exposure to Fe(Cp)$_2$ and H$_2$O (60 s exposures) produces negligible growth. Attempts to deposit thin films using H$_2$O$_2$ (60 s) or pure O$_2$ (240 s) resulted in films of comparable quality, but depositions were slow and variable as compared to growth with O$_3$. Growth at temperatures as low as 100 °C using O$_3$ was also observed resulting in growth rates of ~0.3 Å/cycle but required very long purge times (90 s).

Under the standard ALD growth conditions at 200 °C, relatively large exposures of ~10$^7$ L (1 L = 1 × 10$^{-6}$ Torr s) of both Fe(Cp)$_2$ and O$_3$ are required to reach saturated growth conditions on planar surfaces. These exposures are orders of magnitude greater than for typical ALD reactions, but are not without precedent. For example, reported ALD processes for SiN$_2$ and SiO$_2$ require ~10$^6$ and >10$^9$ L, respectively. For practical purposes, the vapor pressure of Fe(Cp)$_2$ may be increased by raising the precursor temperature, thereby reducing the length of the A cycle. A larger partial pressure of O$_3$, in contrast, may require quasi-static (stop-flow) operation or a higher initial O$_3$ concentration. With respect to photoelectrochemical applications, in which useful film thickness are typically less than 10 nm, the deposition rate (in time) is currently acceptable. Furthermore, for infiltrating nanoporous materials with very large aspect ratios, the infiltration kinetics can be diffusion limited so that the unusually low reactivities of the Fe(Cp)$_2$ and O$_3$ are of little consequence.

Despite the self-limiting ALD process, film growth shows a reproducible dependence on the distance from the precursor inlet, Figure 2.

Although uncommon for ALD processes, a distance dependence on growth rate is not irreconcilable with self-limiting growth. Several growth mechanisms may explain this distance dependence. A first-order decomposition rate of one or both chemical precursors in the reactor tube will produce an exponentially decaying concentration gradient of precursor. The direct deposition of these decomposition products into thin films is one possibility, although it is inconsistent with the self-limiting nature of the half-reactions that were measured within 24 cm from the inlet, Figure 1. A second possibility is that the decomposition products are volatile, creating a quasi-steady state concentration profile of gas-phase precursors and decomposition products down the length of the reactor tube. Given the relative stability of ferrocene at these modest temperatures, metal precursor involvement in this mechanism is unlikely but cannot be excluded. In contrast, previous reports of the catalytic decomposition of O$_3$ over metal oxide surfaces, including Fe$_2$O$_3$, strongly support the possibility of an axial O$_3$ concentration gradient. A third, more complex mechanism, in which decomposition products further inhibit or accelerate surface reaction kinetics, is also feasible. Water seems to be a possibility here, as relative humidity has been shown to alter the decomposition rate.
of O$_3$ over Fe$_2$O$_3$. There is also evidence from mass spectroscopy studies (see below) that a slow evolution of reaction products occurs upon Fe(Cp)$_2$ dosing.

**Surface Reaction Mechanism.** In situ QMS measurements were employed to help elucidate the mechanism for Fe$_2$O$_3$ ALD using Fe(Cp)$_2$ and O$_3$. A survey of $m/z$ ratios 1–200 revealed the primary products of the Fe(Cp)$_2$ reaction with the O$_3$-prepared surface to be $m/z = 66$ and 80, which (along with their characteristic mass cracks) are consistent with release of cyclopentadiene (HCp) and cyclopentadienone, respectively. HCp has been previously observed in similar metal–Cp ALD reactions, so its signature during the Fe(Cp)$_2$ reaction is not surprising. The second reaction product, cyclopentadienone, is postulated on the basis of the slow and identical evolution of the following (in order of decreasing fraction): $m/z = 80$, 52, 26, 37, 51, 25, and 79. Cyclopentadienone is a feasible reaction product, although highly reactive and previously unreported in ALD chemistry. During the O$_3$ reaction, $m/z = 44$ and 18 show the signature of combustion products and are evolved with a ratio of approximately 2:1, as may be expected from the burning of remaining surface-bound hydrocarbon-based ligands. Unfortunately, the slow reaction saturation kinetics combined with an inhomogeneous reactor coating (and therefore chemistry) prevent a more quantitative analysis of surface chemistry.

**Thin-Film Growth.** Robust, transparent thin films of Fe$_2$O$_3$ were grown homogeneously on both fused quartz and Si(100) between 100 and 250 °C. Excellent fits to ellipsometric spectra of all thickness were obtained by modeling a Cauchy dispersion layer over the wavelength range not absorbed by Fe$_2$O$_3$ (700–1000 nm). This method was further corroborated by comparison to thicknesses determined using literature values of the full spectrum (380–1000 nm) complex refractive index for Fe$_2$O$_3$ provided with the ellipsometric software. While excellent fits were obtained in the thin film limit, the full spectrum approach is less attractive due to the changing imaginary component of the complex index of refraction as a function of film crystallinity (see absorptivity discussion below). Finally, X-ray reflectivity (XRR) was employed to infer the thickness, density, and roughness of a pair of films of thickness 7 and 13 nm. Agreement between XRR and ellipsometric derived thickness to within 3% was obtained for both films when the bulk density (5.27 g/cm$^3$) is best fit to 96% and 100% respectively. A roughness of 1–2 nm is derived from fits to XRR data for both films on fused quartz.

Linear growth was observed as a function of the number of ALD cycles on Si(100), Figure 3. On Si(100), there was no nucleation delay, as evidenced by the y-intercept crossing near the origin. Ellipsometry of the Fe$_2$O$_3$ films is problematic on fused quartz substrates due to reflection of the probe beam from the back of the substrate as well as the semitransparent nature of both substrate and thin film. To compare the growth rate on the different substrates, FeK$\alpha$ XRF was acquired for the fused quartz samples and compared to adjacent films on Si(100). When appropriately scaled, the XRF intensity produced a best fine line parallel to the thickness result on Si(100). The x-axis offset in relative thickness suggests a 16-cycle nucleation delay on fused quartz.

A summary of growth characteristics is presented in Table 1 where the Fe(Cp)$_2$/O$_3$ process is compared to previously reported iron oxide ALD processes.

**Properties of Fe$_2$O$_3$ Films.** Iron oxide phase identification was performed using XRD. A component analysis of common iron oxide phases including hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), and wustite (FeO) is feasible on the basis of the signature XRD patterns of each. In agreement with

**Table 1. Growth Characteristics of Iron Oxide by ALD**

<table>
<thead>
<tr>
<th>iron precursor</th>
<th>O source</th>
<th>self-limiting</th>
<th>growth temp (°C)</th>
<th>growth rate (Å/cycle)</th>
<th>reference</th>
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<tr>
<td>Fe(thd)$_3$</td>
<td>O$_3$</td>
<td></td>
<td></td>
<td>186</td>
<td>0.14</td>
</tr>
<tr>
<td>Fe$_2$(O'Bu)$_6$</td>
<td>H$_2$O</td>
<td></td>
<td></td>
<td>140</td>
<td>0.26</td>
</tr>
<tr>
<td>Fe(Cp)$_2$</td>
<td>O$_3$</td>
<td></td>
<td></td>
<td>350°</td>
<td>0.6–1.4</td>
</tr>
<tr>
<td>Fe(Cp)$_3$</td>
<td>O$_3$</td>
<td></td>
<td></td>
<td>200</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Self-limiting behavior untested in the long-dose limit.*
ellipsometric analysis, no crystallinity was detected by diffraction for films less than 14 nm. Above this thickness, XRD patterns that match rhombohedral, polycrystalline α-hematite (PDF 00-033-0664) were observed for films grown at 250 °C, Figure 4.

Figure 5. (a) Photograph of an 18 nm thick Fe₂O₃ film grown on fused quartz at 250 °C and (b) reflection-corrected absorption spectra of 6.7 nm (red), 12.6 nm (blue), and 15.3 nm (green) Fe₂O₃ thin films on fused quartz.

Figure 6. (a) SEM image of a conformal Fe₂O₃ thin film grown at 250 °C on a Si trench wafer. The scale bar on each of the three close-up images is 100 nm. (b) Cross-sectional SEM image of a 9 μm thick silica aerogel film coated with Fe₂O₃ by ALD and subsequently cleaved. The image is overlaid with Fe Kα intensity as measured by cross-sectional EDX (red line).
lack of diffraction peaks in thin films grown at 200 °C suggests a predominantly amorphous material, although some crystalline character (not resolved by our XRD) is postulated on the basis of the evolution of structure in the complex index of refraction spectra as observed by ellipsometry.

In contrast to previous reports of Fe₂O₃ ALD by alternating Fe(Cp)₂ with molecular oxygen (O₂) at the self-limiting temperature, thin films grown with O₃ are not of mixed phase. The strongly oxidizing oxygen source in the present system likely precludes the mixing of less oxidized forms of iron such as magnetite (Fe₃O₄). That the presence of O₃ yields higher oxidation states of iron is further supported by previous reports of ALD using Fe(thd)₃ with O₃ in which only hematite was observed.

Quantitative compositional analysis of a thin film grown at 200 °C was performed using Rutherford backscattering spectroscopy (RBS) and the amount of H quantified by hydrogen forward scattering (HFS). The atomic ratio of the primary film constituents Fe:O is observed to be 1:0.61, which is consistent with a slightly oxygen-rich stoichiometry of Fe₂O₃.3. The primary impurity is hydrogen, which is present in 7 ± 1 atomic % and suggests the possibility of some iron(III) oxide—hydroxide incorporation, for example, FeO(OH). The remaining impurity in the film (<1 atomic %) is consistent with Nb, the major metal deposited on our shared ALD tool. Carbon appeared at the film surface but was not detected in the film (C detection limit of the method is 4 atomic %). Here again, the film quality appears to benefit from O₃ this time as a result of the probable oxidation of carbon-containing residues that may otherwise contaminate the films during the relatively low temperature growth.

The optically transparent and homogeneous thin films exhibited an intense red-orange “rust” color characteristic of hematite, Figure 5a. Reflection-corrected extinction spectra at several thin film thicknesses, Figure 5b, revealed strong and structured absorptivity out to approximately 600 nm (2.1 eV), in agreement with literature reports.

The absorptivity was observed to decrease slightly, and several spectral features grew in as the film increased in thickness. At least four distinct spectral features are observed in the thickest film, while films less than 14 nm thick showed similar but more subtle structure. The position of each peak (223, 315, 375, and 535 nm) is in excellent agreement with transitions calculated for hematite, Figure 5b, clearly illustrates the uniform and deeply penetrating coating characteristics using the FeCp₂/O₃ ALD process. As the largest pores in the aerogel are less than 60 nm, an aspect ratio greater than 150 is calculated.

A comparison of thin film properties produced by the FeCp₂/O₃ ALD process relative to those for previously reported iron oxide routes, Table 2, reveals several pertinent differences. The exclusion of less oxidized forms of iron is pertinent for photoelectrochemical applications in particular. Indeed, air annealed Fe₂O₃ thin films grown by ALD using Fe(Cp)₂ and ozone have recently been utilized in regenerative photoelectrochemical cells.

### Growth on High-Aspect-Ratio Templates

The ability to coat high-aspect-ratio structures conformally demonstrates the potential of this process for use in photoelectrochemical applications in which great light harvesting is beneficial. Long dose times were used to grow thin hematite films on both Si trench wafers and thick-film silica aerogels. Scanning electron microscopy (SEM) and cross-sectional energy dispersive X-ray spectroscopy (EDX) were used to verify the conformity and penetration of iron oxide into the porous structures. A cross-section SEM of a cleaved Si trench wafer (aspect ratio 4) reveals a conformal thin film on all surfaces of the convoluted substrate, Figure 6a.

Oblique angle, high magnification images further corroborate ellipsometric and XRR evidence for smooth and dense films. A 9 μm thick porous silica framework was also coated by ALD and subsequently fractured for analysis. The cross-sectional EDX spectrum of Fe Kα overlaying the thick porous structure, Figure 6b, clearly illustrates the uniform and deeply penetrating coating characteristics using the FeCp₂/O₃ ALD process. As the largest pores in the aerogel are less than 60 nm, an aspect ratio greater than 150 is calculated.

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### Table 2. Physical Properties of Iron Oxide Grown by ALD

<table>
<thead>
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<th>iron precursor</th>
<th>O source</th>
<th>crystalline phases observed</th>
<th>achieved aspect ratio</th>
<th>reference</th>
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<tr>
<td>Fe(thd)₃</td>
<td>O₃</td>
<td>α-Fe₂O₃</td>
<td>not reported</td>
<td>14,34</td>
</tr>
<tr>
<td>Fe₂(OBu)₆</td>
<td>H₂O</td>
<td>not reported</td>
<td>100</td>
<td>18,30</td>
</tr>
<tr>
<td>Fe(Cp)₂</td>
<td>O₂</td>
<td>mixed</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>Fe(Cp)₂</td>
<td>O₃</td>
<td>α-Fe₂O₃</td>
<td>&gt;150</td>
<td>herein</td>
</tr>
</tbody>
</table>

### 4. CONCLUSIONS

We have elucidated a self-limiting ALD process for the growth of hematite, α-Fe₂O₃, over a moderate temperature window using ferrocene and ozone. The system is likely to be particularly well suited to photoelectrochemical applications due to the unique convergence of ample ALD growth per cycle and resulting thin film quality. Alternating exposure to molecular precursors at 200 °C enables deposition of Fe₂O₃ films with a growth rate greater than 1 Å /cycle. The dense and robust films that result exhibit an optical bandgap of 2.1 eV and modest surface roughness. Uniformly coated high-aspect-ratio templates further demonstrate the self-saturating nature of each reaction and suggest the possibility of further utility in the future.

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