Mechanism of Thermal Al₂O₃ Atomic Layer Etching Using Sequential Reactions with Sn(acac)₂ and HF

Younghhee Lee, ‡ Jaime W. DucMont, ‡ and Steven M. George* †, ‡

† Department of Chemistry and Biochemistry and ‡ Department of Mechanical Engineering, University of Colorado, Boulder, Colorado 80309, United States

ABSTRACT: Thermal Al₂O₃ atomic layer etching (ALE) can be performed using sequential, self-limiting reactions with tin(II) acetylacetonate (Sn(acac)₂) and HF as the reactants. To understand the reaction mechanism, in situ quartz crystal microbalance (QCM) and Fourier transform infrared (FTIR) measurements were conducted versus temperature. The mass change per cycle (MCPC) increased with temperature from −4.1 ng/(cm² cycle) at 150 °C to −18.3 ng/(cm² cycle) at 250 °C. A kinetic analysis of the temperature-dependent MCPC values yielded an activation barrier for Al₂O₃ ALE of E = 6.6 ± 0.4 kcal/mol. The mass changes after the individual Sn(acac)₂ and HF exposures also varied with temperature. The mass changes after the Sn(acac)₂ exposures were consistent with more Sn(acac)₂ surface reaction products remaining at lower temperatures. The mass changes after the HF exposures were consistent with more AlF₃ species remaining at higher temperatures. The FTIR spectroscopic analysis observed Al₂O₃ etching by measuring the loss of absorbance of Al–O stretching vibrations in the Al₂O₃ film. The infrared absorbance of the acetylacetonate vibration features from Sn(acac)₂ surface reaction products was also smaller at higher temperatures. The correlation between the MCPC values and the acetylacetonate infrared absorbance suggested that the Al₂O₃ ALE rate is inversely dependent on the acetylacetonate surface coverage. In addition, the QCM and FTIR measurements explored the nucleation of the Al₂O₃ ALE. A large mass gain and loss of infrared absorbance of Al–O stretching vibrations after the initial HF exposure on the Al₂O₃ film was consistent with the conversion of Al₂O₃ to AlF₃. FTIR experiments also observed the formation of AlF₃ after the initial HF exposure and the presence of AlF₃ on the surface after each HF exposure during Al₂O₃ ALE. In the proposed reaction mechanism, AlF₃ is the key reaction intermediate during Al₂O₃ ALE. HF converts Al₂O₃ to AlF₃ prior to removal of AlF₃ by Sn(acac)₂.

I. INTRODUCTION
Atomic layer etching (ALE) is a technique that can remove thin films with atomic layer control using sequential, self-limiting surface reactions.¹–³ ALE is the opposite of atomic layer deposition (ALD) which can provide conformal and atomic layer controlled film deposition.⁴ ALD and ALE are both important techniques to provide thin film engineering at the atomic level.⁵–⁶ ALE processes have been previously reported using ion-enhanced or energetic noble gas atom-enhanced surface reactions.¹–³ During these ALE processes, a halogen is first adsorbed on the surface of the material. Ion or noble gas atom bombardment is then used to desorb halogen compounds that etch the material. Based on this process, ALE has been reported for Si, Ge, and compound semiconductors.¹³–¹⁶ ALE has also been demonstrated for a variety of metal oxides and various carbon substrates.²²–²⁴

The ALE of Al₂O₃ was recently reported using sequential, self-limiting thermal reactions with Sn(acac)₂ and HF as the reactants.²⁵ The Al₂O₃ samples were Al₂O₃ atomic layer deposition (ALD) films grown using trimethylaluminum and H₂O. The HF source was HF–pyridine. The linear removal of Al₂O₃ was observed at temperatures from 150 to 250 °C without the use of ion or noble gas atom bombardment. An Al₂O₃ ALE etch rate of 0.27 Å/cycle was measured at 200 °C.²⁵ The ALE etch rates also increased at higher temperatures. The Sn(acac)₂ and HF thermal reactions were both self-limiting versus exposure. The Al₂O₃ films also did not roughen versus the number of Al₂O₃ ALE cycles.²⁵ In addition, the ALE of HfO₂ has also been recently demonstrated using Sn(acac)₂ and HF as the reactants.²⁶

The overall Al₂O₃ etching reaction was proposed to follow the reaction: Al₂O₃ + 6Sn(acac)₂ + 6HF → 2Al(acac)₃ + 6SnF(acac) + 3H₂O.²⁵ In the surface reactions, the Sn(acac)₂ reactant was suggested to donate acac to the substrate to produce Al(acac)₃. The HF reactant was assumed to allow SnF(acac) and H₂O to leave as reaction products.²⁵ An adlayer of AlF₃ was proposed to exist on the Al₂O₃ surface after HF exposures.²⁵ Sn(acac)₂ adsorption products were also believed to exist on the Al₂O₃ surface after Sn(acac)₂ exposures.

Received: January 23, 2015
Revised: April 17, 2015
Published: April 24, 2015
In this study, quartz crystal microbalance (QCM) measurements determined the Al₂O₃ etch rates and the mass changes after individual Sn(acac)₂ and HF exposures versus temperature. The temperature dependence of the mass change per cycle (MCPC) and the individual mass changes during the Sn(acac)₂ and HF exposures helped to formulate a mechanism for Al₂O₃ ALE. In addition, FTIR vibrational spectroscopy analysis monitored the Al₂O₃ etching and characterized the surface species after the Sn(acac)₂ and HF exposures. The combination of these QCM and FTIR studies leads to the understanding of the key reaction intermediates during Al₂O₃ ALE and the reaction mechanism for thermal Al₂O₃ ALE.

II. EXPERIMENTAL SECTION

A. Viscous Flow Reactor Equipped for in Situ QCM Measurements. Al₂O₃ ALE was monitored using in situ QCM experiments in a viscous flow reactor.²⁷ The QCM sensor was an R-cut quartz crystal²⁸ (gold coated and polished, 6 MHz, Colnatec). This QCM sensor was mounted in a baffle sensor head (BSH-150, Inficon) and then sealed with high temperature epoxy (Epo-Tek H21D, Epoxy Technology). All of the QCM measurements were recorded by a film deposition monitor (Maxtek TM-400, Inficon). The reactor temperature was maintained by a PID temperature controller (2604, Eurotherm) at 150–250 °C during the reactions. After changing temperatures, the reactor temperature was allowed to stabilize for at least 2 h before performing new QCM measurements. The pressure in the reactor was measured using a baffle capacitance manometer (Baratron 121A, MKS).

The reactor was pumped using a mechanical pump (Pascal 2015SD, Alcatel). A constant N₂ carrier gas flow of 150 cm³(STP) min⁻¹ was streamed through the reactor. This N₂ gas flow was supplied by three separate mass flow controllers (Type 1179A, MKS). An additional N₂ purge gas flow of 20 cm³(STP) min⁻¹ passed through the QCM housing and prevented deposition on the back side of the QCM sensor. The background pressure in the reactor resulting from the total N₂ gas flow of 170 cm³(STP) min⁻¹ was ~1 Torr.

Al₂O₃ ALE was performed using tin(II) acetylacetonate (Sn(acac)₂, 37–38% Sn, Gelest) and HF–pyridine (70 wt % HF, Sigma-Aldrich) as the reactants. HF–pyridine is known as “Olah’s reagent” and is a convenient reservoir for anhydrous HF.²⁹ The HF pressure from HF–pyridine is 90–100 Torr at room temperature.²⁹ Sn(acac)₂ and HF–pyridine were transferred to stainless steel bubblers in a dry N₂-filled glovebag. The HF–pyridine was lined with a gold coating. The Sn(acac)₂ precursor was maintained at 100 °C and produced a pressure transient of 15–20 mTorr using a pneumatic valve for dosing. The HF–pyridine precursor was held at room temperature and produced a pressure transient of 80 mTorr using two pneumatic valves and one metering valve for dosing.

The Al₂O₃ films were deposited on the QCM sensor by Al₂O₃ ALE. The Al₂O₃ ALE films were grown using at least 100 cycles of Al₂O₃ ALE using TMA (97%, Sigma-Aldrich) and H₂O (deionized water, Chromasolv for HPLC, Sigma-Aldrich). The TMA and H₂O precursors were held at room temperature. The Al₂O₃ films were deposited on the QCM sensor before each ALE reaction.

B. FTIR Spectroscopy Measurements. The in situ FTIR studies were performed in a reactor equipped with an FTIR spectrometer that has been described previously.³⁰ The reactor was pumped using a mechanical pump (TRIVAC D8B, Oerlikon Leybold Vacuum). The FTIR spectrometer (Nicolet 6700 FTIR, Thermo Scientific) utilized a liquid-N₂-cooled mercury cadmium telluride (MCT-B) detector. Dry, CO₂-free air was employed to purge the spectrometer, mirror, and detector setup. Each spectrum consisted of a total of 100 scans at 4 cm⁻¹ resolution from 400 to 4000 cm⁻¹.

The transmission FTIR measurements were performed on high surface area ZrO₂ nanoparticles (99.95%, US Research Nanomaterials Inc.) with an average diameter of 20 nm and high surface area SiO₂ nanoparticles (99.5%, US Research Nanomaterials Inc.) with an average diameter of 15–20 nm. The ZrO₂ nanoparticles absorb infrared radiation between ~400 and 800 cm⁻¹. The SiO₂ nanoparticles absorb infrared radiation between 400 and 650 cm⁻¹, between 700 and 875 cm⁻¹, and between 925 and 1400 cm⁻¹. These absorption regions leave available windows to observe absorbance from the species in Al₂O₃ ALD and Al₂O₃ ALE. The high surface area of these nanoparticles was needed to enhance the signal-to-noise ratio.³¹ Sample preparation involved pressing the ZrO₂ or SiO₂ nanoparticles into a tungsten grid support (Tech-Etch).³²,³³ The tungsten grids had dimensions of 2 × 3 cm². Each grid was 50 μm thick with 100 grid lines per inch.

The tungsten grid could be resistively heated using a DC power supply (6268B, 20 V/20A, Hewlett-Packard). The voltage output of the power supply was controlled by a PID temperature controller (Love Controls 16B, Dwyer Instruments, Inc.). A type K thermocouple was fixed to the bottom of the tungsten grid with epoxy (Cerambond 571, Aremco) that attached and electrically isolated the thermocouple.

A consistent cleaning procedure of the ZrO₂ nanoparticles/grid support was used to produce a reproducible starting surface. Prior to film deposition, the temperature of the sample support was increased to 500 °C for ~2 min to degas and clear adventitious carbon from the ZrO₂ nanoparticles. Since this procedure also depleted the hydroxyl groups from the ZrO₂ nanoparticles, a ~2 s H₂O dose was used to rehydroxylate the surface. This procedure consistently removed any carbon-related vibrational modes and resulted in a clean ZrO₂ starting surface with absorbances attributed only to O–H stretching vibrations and bulk ZrO₂ modes. This cleaning procedure was not utilized for the SiO₂ nanoparticles because rehydroxylation of the SiO₂ surface is very difficult after dehydroxylation.³⁴ The dehydroxylated siloxane surface is hydrophobic and does not easily adsorb H₂O to produce the silanol surface.³⁴

The Al₂O₃ ALE reactions were performed using sequential exposures of Sn(acac)₂ (37–38% Sn, Gelest) and HF–pyridine (70 wt % HF, Sigma-Aldrich). Static dosing of the ALE precursors was utilized to achieve self-limiting behavior on the high surface area particle substrates. Each Sn(acac)₂ exposure consisted of a ~1.0 Torr static dose for 15 s followed by a 120 s purge. Each HF–pyridine exposure consisted of a ~1.5 Torr static dose for 15 s followed by a 120 s purge. The Al₂O₃ films were grown by Al₂O₃ ALD using TMA (97%, Sigma-Aldrich) and H₂O (Chromasolv for HPLC, Sigma-Aldrich). The HF–pyridine, TMA, and H₂O precursors were maintained at room temperature. The stainless steel bubbler containing Sn(acac)₂ was held at 100 °C.

For a direct comparison between the FTIR studies at different temperatures, the sample remained fixed during Al₂O₃ ALD and Al₂O₃ ALE. An Al₂O₃ film was grown using 10 cycles of Al₂O₃ ALD at 200 °C. Subsequently, 10 cycles of Al₂O₃ ALE were performed at 200 °C followed by 8 cycles of Al₂O₃ ALE at both 250 and 300 °C. The FTIR spectra monitored at 250 and 300 °C were recorded during the last two cycles of Al₂O₃ ALE.

III. RESULTS AND DISCUSSION

A. QCM Measurements versus Temperature. Figure 1 displays the mass change during 100 ALE cycles of Al₂O₃ using Sn(acac)₂ and HF reactions at 150, 175, 200, 225, and 250 °C. Some of these QCM results were presented earlier.²⁵ One ALE cycle consisted of a Sn(acac)₂ exposure of 1 s, an N₂ purge of 30 s, a HF exposure of 1 s, and a second N₂ purge of 30 s. This reaction sequence is represented as 1–30–1–30. The initial Al₂O₃ ALD films were grown by 100 cycles of Al₂O₃ ALD using TMA and H₂O with a sequence of 1–20–1–20.

The mass changes versus time during Al₂O₃ ALE are linear for all temperatures. The mass change per cycle (MCPC) increases with temperature from ~4.1 ng/(cm² cycle) at 150 °C to ~18.3 ng/(cm² cycle) at 250 °C.²⁵ These MCPCs correspond to etch rates that vary from 0.14 Å/cycle at 150 °C to 0.61 Å/cycle at 250 °C. The determination of these etch rates is based on the Al₂O₃ ALD film density of 3.0 g/cm³.
Parts a, b, and c of Figure 2 show enlargements of the mass changes during three cycles in the steady-state etching regime for Al₂O₃ ALE at 150, 200, and 250 °C, respectively, in Figure 1. Figure 2a shows a gradual mass decrease after a small mass gain during the Sn(acac)₂ exposure at 150 °C. A small mass gain of ΔM_{Sn} = +0.19 ng/cm² was observed after the Sn(acac)₂ exposure for 1 s at 150 °C. This behavior suggests Sn(acac)₂ adsorption followed by either the removal of reaction products and/or Sn(acac)₂ desorption. In contrast, a mass decrease of ΔM_{HF} = −4.3 ng/cm² was observed after the HF exposure for 1 s at 150 °C. This mass decrease is consistent with the removal of Sn(acac)₂ surface reaction products.

The mass changes are different at 200 °C. After a Sn(acac)₂ exposure for 1 s at 200 °C, Figure 2b shows a mass loss of ΔM_{Sn} = −8.1 ng/cm². In addition, an HF exposure for 1 s leads to a small mass loss of ΔM_{HF} = −0.28 ng/cm². The mass changes continue to evolve at 250 °C. Figure 2c shows a larger mass loss of ΔM_{Sn} = −24.0 ng/cm² after 1 s of Sn(acac)₂ exposure at 250 °C. In contrast, the HF exposure leads to a mass gain instead of a mass loss. A mass gain of ΔM_{HF} = +5.7 ng/cm² was observed after 1 s of HF exposure.

The differences between the mass changes at different temperatures can be qualitatively understood in terms of more stable Sn(acac)₂ surface reaction products at lower temperature and more AlF₃ formation at higher temperatures. If more surface species remain following Sn(acac)₂ exposures at lower temperatures, then there is a mass gain after the Sn(acac)₂ reaction and more surface species that can be lost during the HF reaction. Likewise, larger mass losses after the Sn(acac)₂ exposure and mass gains following the HF exposure at higher temperature can be qualitatively understood in terms of AlF₃ formation. More AlF₃ may form by the reaction of HF with Al₂O₃ at higher temperatures. This AlF₃ layer is then removed by the Sn(acac)₂ exposure and leads to a pronounced mass loss.

Figure 3 shows the MCPC and the ΔM_{Sn}/MCPC ratio during 100 cycles at 200 °C. The MCPC is defined by MCPC = ΔM_{Sn} + ΔM_{HF}. Figure 3a displays ΔM_{Sn}, ΔM_{HF}, and MCPC for the same 100 cycles of Al₂O₃ ALE reaction on the Al₂O₃ surface at 200 °C as shown in Figure 1. The MCPC reaches a
steady-state value of \(-8.4 \text{ ng/(cm}^2 \text{ cycle})\) after a nucleation period requiring 3 cycles of Al\(_2\text{O}_3\) ALE. Figure 3b displays the \(\Delta M_{\text{Sn}}/\text{MCPC}\) ratio during the same 100 cycles. The \(\Delta M_{\text{Sn}}/\text{MCPC}\) ratio reaches a steady-state value of 0.97 after a nucleation interval over 3 cycles of Al\(_2\text{O}_3\) ALE. The \(\Delta M_{\text{Sn}}/\text{MCPC}\) ratio will be used to describe the stoichiometry of the Al\(_2\text{O}_3\) ALE reactions.

\(\Delta M_{\text{Sn}}, \Delta M_{\text{HF}}, \text{MCPC, and the } \Delta M_{\text{Sn}}/\text{MCPC} \) ratio at 150–250 °C are summarized in Table 1. All temperatures display a mass loss, and the mass loss is larger at higher temperatures. The mass change after the Sn(acac)\(_2\) exposure, \(\Delta M_{\text{Sn}}\), is mostly responsible for the temperature dependence of the MCPC. An Arrhenius plot is employed to characterize the temperature dependence. Figure 4a shows the Arrhenius plot for the temperature-dependent MCPC. This Arrhenius plot yields an activation barrier of 6.6 ± 0.4 kcal/mol for Al\(_2\text{O}_3\) ALE.

<table>
<thead>
<tr>
<th>temp (°C)</th>
<th>MCPC</th>
<th>(\Delta M_{\text{Sn}})</th>
<th>(\Delta M_{\text{HF}})</th>
<th>(\Delta M_{\text{Sn}}/\text{MCPC})</th>
<th>(x)</th>
<th>(x/(\text{MCPC}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>−4.1</td>
<td>0.19</td>
<td>−4.3</td>
<td>−0.067</td>
<td>0.74</td>
<td>−3.0</td>
</tr>
<tr>
<td>175</td>
<td>−5.6</td>
<td>−3.2</td>
<td>−2.4</td>
<td>0.57</td>
<td>0.46</td>
<td>−2.6</td>
</tr>
<tr>
<td>200</td>
<td>−8.4</td>
<td>−8.1</td>
<td>−0.28</td>
<td>0.97</td>
<td>0.29</td>
<td>−2.4</td>
</tr>
<tr>
<td>225</td>
<td>−12.3</td>
<td>−14.6</td>
<td>2.3</td>
<td>1.2</td>
<td>0.19</td>
<td>−2.4</td>
</tr>
<tr>
<td>250</td>
<td>−18.3</td>
<td>−24.0</td>
<td>5.7</td>
<td>1.3</td>
<td>0.15</td>
<td>−2.7</td>
</tr>
</tbody>
</table>

\(\Delta M_{\text{Sn}}, \Delta M_{\text{HF}}, \text{MCPC, and the } \Delta M_{\text{Sn}}/\text{MCPC} \) ratio are expressed in units of ng/(cm\(^2\) cycle).

**Table 1.** MCPC, \(\Delta M_{\text{Sn}}, \Delta M_{\text{HF}}, \Delta M_{\text{Sn}}/\text{MCPC}, x, \) and \(x/(\text{MCPC})\) for Al\(_2\text{O}_3\) ALE at Different Temperatures

**B. FTIR Studies of Al\(_2\text{O}_3\) ALE.** In situ FTIR spectra of Al\(_2\text{O}_3\) films grown on ZrO\(_2\) nanoparticles using 10 Al\(_2\text{O}_3\) ALD cycles at 200 °C are shown in Figure 5. These FTIR spectra are referenced to the initial ZrO\(_2\) nanoparticles. The absorbance feature between 800 and 1000 cm\(^{-1}\) is attributed to the Al\(–\)O stretching vibrations in bulk Al\(_2\text{O}_3\). The absorbance of the Al\(–\)O stretching vibrations in amorphous Al\(_2\text{O}_3\) is broad and ranges from ~550 to 1030 cm\(^{-1}\). The breadth of this expected absorbance feature is not observed in Figure 5. The strong absorption from the ZrO\(_2\) nanoparticles at ≤800 cm\(^{-1}\) partially obscures the infrared absorbance of the Al\(–\)O stretching vibrations. The absorbance feature for the Al\(–\)O stretching vibration grows progressively with the Al\(_2\text{O}_3\) ALD cycles.

**Figure 5.** Infrared absorbance showing the growth of Al\(–\)O stretching vibrations in bulk Al\(_2\text{O}_3\) versus the number of Al\(_2\text{O}_3\) ALD cycles at 200 °C. These FTIR spectra were referenced to the initial ZrO\(_2\) nanoparticles.

**Figure 6.** Infrared absorbance showing the loss of Al\(–\)O stretching vibrations in bulk Al\(_2\text{O}_3\) versus the number of Al\(_2\text{O}_3\) ALE cycles at 200 °C. These FTIR spectra were referenced to the initial ZrO\(_2\) nanoparticles.
Infrared absorbance features also appear between 1250 and 1650 cm$^{-1}$ that are attributed to acetylacetonate vibrations from the Sn(acac)$_2$ surface reaction products$^{35,36}$. The absorbance from these acetylacetonate vibrations remains approximately constant after the Sn(acac)$_2$ exposures versus the number of Al$_2$O$_3$ ALE cycles.

The FTIR spectra of the absorbance from the acetylacetonate vibrations during Al$_2$O$_3$ ALE at 200, 250, and 300 °C are shown after Sn(acac)$_2$ and HF exposures in Figures 7a and 7b, respectively. The absorbance from the acetylacetonate surface species, such as SnF(acac)$^*$, Sn(acac)$^*$, or acac$^*$, decreases at higher temperatures after the Sn(acac)$_2$ exposures in Figure 7a. The asterisks are used to indicate surface species. This behavior illustrates that the Sn(acac)$_2$ surface reaction products are more stable at lower surface temperatures.

Figure 7b reveals that the absorbances from the acetylacetonate vibrational features are much lower following the HF exposures. The loss of acetylacetonate vibrational features is expected because HF is believed to react with acetylacetonate species to produce volatile reaction products such as SnF(acac). The absorbance of the remaining acetylacetonate species after HF exposures also decreases dramatically at 300 °C. This behavior indicates that HF exposures are able to remove most of the acetylacetonate species at 300 °C. Based on the peak absorbance for the acetylacetonate vibrational feature at ~1530 cm$^{-1}$, only ≤10% of the acetylacetonate species remain after HF exposures at 300 °C compared with the acetylacetonate species that remain after HF exposures at 200 °C.

C. Studies of Al$_2$O$_3$ ALE Nucleation. QCM and FTIR measurements were employed to study the nucleation of Al$_2$O$_3$ ALE during the first Sn(acac)$_2$ and HF exposures. Figure 8 shows an enlargement of the mass changes during the first two Al$_2$O$_3$ ALE cycles for the various temperatures in Figure 1. The first Sn(acac)$_2$ exposure displays mass gains of $\Delta M_{\text{Sn}} = 52–61$ ng/cm$^2$ at 150–250 °C resulting from Sn(acac)$_2$ surface reaction products on the Al$_2$O$_3$ film such as Sn(acac)$^*$ and acac$^*$. To estimate the coverage of Sn(acac)$_2$ species on the surface, the sites on the Al$_2$O$_3$ surface can be approximated using the density of 3.0 g/cm$^3$ for Al$_2$O$_3$ ALD films. This mass density is equivalent to a number density of $\rho = 1.77 \times 10^{22}$ “Al$_2$O$_3$ units”/cm$^3$. This number density yields an estimate for the number of Al$_2$O$_3$ units on the Al$_2$O$_3$ surface of $p^{2/3} = 6.80 \times 10^{14}$ Al$_2$O$_3$ units/cm$^2$ assuming a square lattice. This coverage of Al$_2$O$_3$ units represents an Al$_2$O$_3$ mass of 115 ng/cm$^2$.

The coverage of Sn(acac)$_2$ can then be approximated based on the mass gain of 61 ng/cm$^2$. This mass gain is equivalent to $1.16 \times 10^{14}$ Sn(acac)$_2$/cm$^2$. The normalized coverage of Sn(acac)$_2$ relative to Al$_2$O$_3$ units on the surface is (1.16 \times 10^{14} \text{Sn(acac)$_2$/cm$^2$})/(6.80 \times 10^{14} \text{Al$_2$O$_3$ units/cm$^2$}) = 0.17 Sn(acac)$_2$/Al$_2$O$_3$ unit. This coverage is reasonable given that Sn(acac)$_2$ may dissociate into Sn(acac)$^*$ and acac$^*$. In addition, the acetylacetonate ligand is bulky and expected to occupy more than one Al$_2$O$_3$ unit on the Al$_2$O$_3$ surface.

The first HF exposure on the Al$_2$O$_3$ surface previously exposed to Sn(acac)$_2$ shows mass gains of $\Delta M_{HF} = 13–17$ ng/cm$^2$ at 150–250 °C. In contrast, the first HF exposure on a fresh Al$_2$O$_3$ surface prior to Sn(acac)$_2$ exposures shows mass gains of $\Delta M_{HF} = 35–38$ ng/cm$^2$ at 150–250 °C. The difference between these mass gains is caused by the amount of Sn(acac)$_2$.
reaction products that are removed by the HF exposures and result in a mass loss.

The coverage of HF or HF reaction products can be approximated based on the mass gain of 38 ng/cm² following HF exposures on fresh Al₂O₃ surfaces. Assuming that HF is the adsorption product, the mass gain is equivalent to 1.14 × 10¹⁵ HF/cm². The normalized coverage of HF species relative to Al₂O₃ units on the surface is (1.14 × 10¹⁵ HF/cm²)/(6.80 × 10¹⁴ Al₂O₃ units/cm²) = 1.68 HF/(Al₂O₃ unit). This estimated HF coverage is larger than the number of Al₂O₃ units on the Al₂O₃ substrate.

The HF may also react with the Al₂O₃ substrate by the following reaction: Al₂O₃ + 6HF → 2AlF₃ + 3H₂O. The reaction of HF with γ-Al₂O₃ to produce AlF₃ has been observed at 250 °C.³⁷ This reaction is predicted to be spontaneous over the temperature range from 150 to 250 °C.³⁸ The Gibbs free energy changes are negative and decrease slightly in absolute magnitude from ΔG° = −63.1 kcal at 150 °C to ΔG° = −53.8 kcal at 250 °C.³⁸

Assuming that AlF₃ is the reaction product, the mass gain of 38 ng/cm² is equivalent to an AlF₃ coverage of 6.93 × 10¹⁴ AlF₃/cm². The normalized coverage of AlF₃ relative to Al₂O₃ units on the surface is (6.93 × 10¹⁴ AlF₃/cm²)/(6.80 × 10¹⁴ Al₂O₃ units/cm²) = 1.02 AlF₃/(Al₂O₃ unit). This estimated AlF₃ coverage is very similar to the number of Al₂O₃ units on the Al₂O₃ substrate.

Subsequent Sn(acac)₂ exposures react with the AlF₃ or HF adlayer, and subsequent HF exposures react with the Al₂O₃ substrate and remove Sn(acac)₂ adsorption products. At 225 and 250 °C, mass losses begin with the second ALE cycle as shown in Figure 8. At 200 and 175 °C, mass losses begin with the third ALE cycle. At 150 °C, mass losses begin with the fourth ALE cycle.

The nucleation of the Al₂O₃ ALE process was also observed by the FTIR studies. Figure 9 shows the FTIR spectra during the first Al₂O₃ ALE cycle. These FTIR spectra are referenced to the initial ZrO₂ nanoparticles. The infrared absorbance corresponding to the Al−O stretching vibration in bulk Al₂O₃ between 800 and 1000 cm⁻¹ decreases slightly with the first Sn(acac)₂ exposure. This decrease is attributed to Sn(acac)₂ adsorbing on the thin Al₂O₃ film and perturbing the Al−O vibrational modes. Pronounced vibrational features associated with acetylacetonate species on the Al₂O₃ substrate at 1250−1650 cm⁻¹ are also observed in Figure 9 after the Sn(acac)₂ exposure.³⁵,³⁶

Figure 9 also shows that an additional reduction occurs in absorbance features corresponding to the Al−O vibrational modes after the first HF exposure. This reduction is consistent with the conversion of some Al₂O₃ to AlF₃. Figure 9 also shows that the vibrational features of the acetylacetonate species are also decreased after the first HF exposure. This decrease is consistent with HF reacting with the Sn(acac)₂ surface reaction products to remove some acetylacetonate species from the Al₂O₃ substrate.

Figure 10 displays the infrared absorbance spectra after the first Sn(acac)₂ exposure and first HF exposure on Al₂O₃ films at 200 °C. In contrast to Figures 5, 6, and 9, these FTIR experiments were performed on SiO₂ nanoparticles. Unlike ZrO₂ nanoparticles that absorb infrared radiation between ~400 and 800 cm⁻¹, SiO₂ nanoparticles absorb infrared radiation between 925 and 1400 cm⁻¹, between 700 and 875 cm⁻¹, and between 400 and 650 cm⁻¹. The SiO₂ nanoparticles have an open window at lower frequency to observe the species involved in Al₂O₃ ALD and Al₂O₃ ALE.

The spectra in Figure 10 were referenced to the SiO₂ nanoparticles and the Al₂O₃ ALD film that coated the SiO₂ nanoparticles. The acetylacetonate features were again observed at 1250−1650 cm⁻¹. In addition, an absorbance feature at 500−800 cm⁻¹ appeared after the first HF exposure. This feature was assigned to the Al−F stretching vibration in the AlF₃ layer that forms from Al₂O₃ during the HF exposure.³⁹,⁴⁰ There was also

![Figure 9](image.png)

**Figure 9.** Infrared absorbance showing the Al−O stretching vibrations in bulk Al₂O₃ and the acetylacetonate vibrational features for the first Sn(acac)₂ and HF exposures at 200 °C. These FTIR spectra were referenced to the initial ZrO₂ nanoparticles.

![Figure 10](image.png)

**Figure 10.** Infrared absorbance after the first Sn(acac)₂ exposure and first HF exposure on an Al₂O₃ film at 200 °C. These FTIR spectra were referenced to the SiO₂ nanoparticles coated with the Al₂O₃ ALD film.
an absorbance loss observed at $\sim 1000 \text{ cm}^{-1}$ that corresponds with the removal of some absorbance from the Al–O stretching vibration in $\text{Al}_2\text{O}_3$ upon $\text{AlF}_3$ formation.

Figure 11 displays the FTIR spectra during $\text{Al}_2\text{O}_3$ ALE at 200, 250, and 300 $^\circ$C. These spectra were again referenced to the SiO$_2$ nanoparticles coated with the $\text{Al}_2\text{O}_3$ ALD film.

Figure 11. Infrared absorbance during $\text{Al}_2\text{O}_3$ ALE at 200, 250, and 300 $^\circ$C recorded after the Sn(acac)$_2$ exposures and HF exposures. These FTIR spectra were referenced to the SiO$_2$ nanoparticles coated with the $\text{Al}_2\text{O}_3$ ALD film.

Figure 12. Difference infrared absorbance during $\text{Al}_2\text{O}_3$ ALE at 200, 250, and 300 $^\circ$C. The difference spectra recorded after the Sn(acac)$_2$ and HF exposures were referenced using the spectra after the previous HF and Sn(acac)$_2$ exposures, respectively.

Figure 12. Difference infrared absorbance during $\text{Al}_2\text{O}_3$ ALE at 200, 250, and 300 $^\circ$C. The difference spectra recorded after the Sn(acac)$_2$ and HF exposures were referenced using the spectra after the previous HF and Sn(acac)$_2$ exposures, respectively.

The absorbance features from acetylacetonate surface species at 1250–1650 cm$^{-1}$ were present after all of the Sn(acac)$_2$ exposures. The acetylacetonate surface species decreased with increasing temperature after both Sn(acac)$_2$ and HF exposures. In addition, most of the acetylacetonate surface species were removed from the surface by the HF exposure at 300 $^\circ$C.

Figure 11 also reveals that a loss from the absorbance feature assigned to the Al–O stretching vibrations in $\text{Al}_2\text{O}_3$ occurs at 200, 250, and 300 $^\circ$C. This loss appears at 825–1050 cm$^{-1}$ because the absorbance gain from the Al–F stretching vibrations of $\text{AlF}_3$ at 500–800 cm$^{-1}$ partially obscures the loss from the Al–O stretching vibrations in $\text{Al}_2\text{O}_3$ at lower frequencies. The spectra after the Sn(acac)$_2$ and HF exposures in the region from 500 to 1050 cm$^{-1}$ were not substantially different at 200 and 250 $^\circ$C. In contrast, the spectra were distinctly different at 300 $^\circ$C where the absorbance from the Al–F stretching vibration is nearly completely removed after the Sn(acac)$_2$ exposure and then reappears after the HF exposure. The spectrum at the bottom of Figure 11 is provided for reference and shows the expected absorbance loss corresponding to the removal of 10 cycles of $\text{Al}_2\text{O}_3$ ALD.

Figure 12 shows the difference infrared absorbance spectra during $\text{Al}_2\text{O}_3$ ALE at 200, 250, and 300 $^\circ$C. Spectra are displayed after both the Sn(acac)$_2$ exposures and HF exposures. These difference spectra correspond to the absolute spectra shown in Figure 11. These difference spectra are referenced with respect to the sample after the previous reactant exposure.

The difference spectra in Figure 12 highlight the absorbance changes that occur during the sequential ALE reactions. The absorbance changes for the acetylacetonate surface species are nearly equal and mirror images of each other after the Sn(acac)$_2$ and HF exposures at 200, 250, and 300 $^\circ$C. In contrast, the absorbance from Al–F vibrations in $\text{AlF}_3$ shows little change at 200 $^\circ$C and nearly mirror image changes after the Sn(acac)$_2$ and HF exposures at 250 $^\circ$C. At 300 $^\circ$C, the absorbance for the Al–F stretching vibrations dramatically appears after the HF exposure and is lost after the Sn(acac)$_2$ exposure.

D. Proposed $\text{Al}_2\text{O}_3$ ALE Reaction Mechanism. Figure 13 shows the schematic for the proposed $\text{Al}_2\text{O}_3$ ALE surface chemistry. This possible picture for $\text{Al}_2\text{O}_3$ ALE is derived from the mass changes during the Sn(acac)$_2$ and HF exposures as determined by the QCM measurements and the vibrational absorbances observed by the FTIR spectroscopy analysis. This scheme does not include species, such as possible acetylacetone species, that do not change during the Sn(acac)$_2$ and HF exposures. This scheme also assumes that the HF reaction produces $\text{AlF}_3$ on the $\text{Al}_2\text{O}_3$ film.

During the Sn(acac)$_2$ reaction shown in Figure 13a, Sn(acac)$_2$ reacts with $\text{AlF}_3$ on the $\text{Al}_2\text{O}_3$ substrate. The reaction between Sn(acac)$_2$ and $\text{AlF}_3$ is probably facilitated by Lewis acid–base interactions. The electron lone pair on Sn(acac)$_2$ acts as a Lewis base. $\text{AlF}_3$ is a strong Lewis acid either as a molecule or as a molecular solid. The reaction between Sn(acac)$_2$ and $\text{AlF}_3$ is assumed to form volatile SnF(acac) and...
Al(acac)₃ reaction products and SnF(acac)* surface species. There is also a possibility that AlF(acac)₂ could be a gas phase reaction product. The gas phase reaction products have not yet been identified using mass spectrometry.

AlF₃ has a negligible vapor pressure at the Al₂O₃ ALE temperatures. A measurable vapor pressure for AlF₃ of ∼1 × 10⁻³ Torr is obtained only at high temperatures of ∼700 °C.⁴⁵ Al(acac)₃ is a stable metal β-diketonate with a high vapor pressure of ∼3 × 10⁻⁴ Torr at 150 °C.⁴⁶−⁴⁸ The sublimation temperature for Al(acac)₃ of ∼200 °C has been derived from thermogravimetric studies.⁴⁷

After the AlF₃ layer is lost resulting from Al(acac)₃ and SnF(acac)₃ product formation, there may be a strong interaction between the SnF(acac)* surface species and the underlying Al₂O₃ substrate. The electron lone pair on SnF(acac)* can again act as a Lewis base and bind on Lewis acid sites on Al₂O₃. This interaction may lead to SnF(acac)* species adsorbed to the Al₂O₃ substrate.

During the HF reaction shown in Figure 13b, HF reacts with the SnF(acac)* surface species and the underlying Al₂O₃ surface to form AlF₃. In addition, HF also provides hydrogen to form H₂O as a reaction product. This reaction removes the oxygen in Al₂O₃. The AlF₃ layer is then ready for the next Sn(acac)₂ reaction.

The overall reaction can be written as

\[
\text{Al}_2\text{O}_3 + 6\text{HF} + 6\text{Sn(acac)}_2 \rightarrow 2\text{Al(acac)}_3 + 6\text{SnF(acac)} + 3\text{H}_2\text{O}
\]

This overall reaction can be separated into the Sn(acac)₂ and HF reactions:

reaction a of Figure 13:

\[
\text{Al}_2\text{O}_3 + 2\text{AlF}_3^* + 6\text{Sn(acac)}_2 \rightarrow 2\text{Al}_2\text{O}_3 + x\text{SnF(acac)} + 2\text{Al(acac)}_3 + (6-x)\text{SnF(acac)}
\]

reaction b of Figure 13:

\[
\text{Al}_2\text{O}_3 | x\text{SnF(acac)} + 6\text{HF} \rightarrow 2\text{Al}_2\text{O}_3 + x\text{SnF(acac)} + 3\text{H}_2\text{O}
\]

These reactions include only species that change during the Sn(acac)₂ and HF exposures. There may be other surface species present, such as acetylacetonate species, that do not change during the Sn(acac)₂ and HF exposures. The asterisks indicate the surface species and the vertical lines are used to separate the various surface species. AlF₃ is the key reaction intermediate. The production of all of the Al(acac)₃ is assumed to occur during reaction a.

The Al₂O₃ shown in eqs 2 and 3 is the amount of Al₂O₃ that is etched during the ALE reactions. Table 1 shows that the amount of Al₂O₃ that is etched during one Al₂O₃ ALE cycle increases with temperature. 2AlF₃* and SnF(acac)* are also the amounts added during the HF and Sn(acac)₂ reactions, respectively. x quantifies SnF(acac)* after the Sn(acac)₂ exposures relative to the amount of Al₂O₃ that is etched in one Al₂O₃ ALE cycle.

The parameter x in eqs 2 and 3 is determined by the ΔMₓ, ΔMₓ and MCPC values. x can be calculated from the ΔMₓ/MCPC ratio using the following equation:

\[
x = \frac{2 \times 84.0 - 102.0(\Delta M_{x}/MCPC))}{236.8}
\]

where 84.0, 102.0, and 236.8 are the molecular weights for AlF₃, Al₂O₃, and SnF(acac), respectively. The temperature dependence of the x values is x = 0.74, 0.46, 0.29, 0.19, and 0.15 at 150, 175, 200, 225, and 250 °C, respectively. These x values are included in Table 1.

The parameter x defines the SnF(acac)* species after the Sn(acac)₂ exposures relative to the amount of Al₂O₃ that is etched in one Al₂O₃ ALE cycle. Consequently, the product x(MCPC) provides a measure of the SnF(acac)* species on the surface after the Sn(acac)₂ exposures. The x(MCPC) values are included in Table 1. These x(MCPC) values are fairly constant at all of the temperatures. This behavior indicates that the
SnF(acac)* coverage is nearly constant at the different temperatures after the Sn(acac)2 exposures.

The difference infrared absorbance spectra in the acetylacetonate region of the spectra in Figure 12 are consistent with a constant coverage of SnF(acac)* species at the different temperatures after the Sn(acac)2 exposures. Figure 12 shows that the changes in the absorbance in the acetylacetonate region after Sn(acac)2 and HF exposures are very similar at 200, 250, and 300 °C. This constant absorbance change can be identified with the SnF(acac)* surface species that are added and then removed during the Sn(acac)2 and HF exposures, respectively, as described by eqs 2 and 3.

The SnF(acac)* coverage after the Sn(acac)2 exposures can be determined from the amount of Al2O3 that is etched in one Al2O3 ALE cycle. For example, the MCPC of ∼5.6 ng/cm² at 175 °C represents a coverage of 3.3 × 10¹³ Al2O3 units/cm². This conversion is based on 1.69 × 10⁻²² g/(Al2O3 unit). This coverage of Al₂O₃ units multiplied by the x value of 0.46 at 175 °C yields a SnF(acac)* coverage of 1.52 × 10¹⁶ SnF(acac)*/cm². The MCPC and x values at the other temperatures also yield similar SnF(acac)* coverages that vary from 1.38 to 1.77 × 10¹⁶ SnF(acac)*/cm².

The nearly constant SnF(acac)* coverage of ∼1.5 × 10¹³ SnF(acac)*/cm² can be compared with the number of Al₂O₃ units on the Al₂O₃ surface of 6.80 × 10¹⁴ Al₂O₃ units/cm². The normalized coverage of SnF(acac)* relative to Al₂O₃ units on the surface is (∼1.5 × 10¹³ SnF(acac)*/cm²)/(6.80 × 10¹⁴ Al₂O₃ units/cm²) = ∼0.022 SnF(acac)*/(Al₂O₃ unit). This normalized coverage is ∼2.2% of an Al₂O₃ unit monolayer. This coverage may represent a saturated layer of SnF(acac)* species on the Al₂O₃ surface. The normalized coverage of ∼2.2% is somewhat low. However, perhaps the SnF(acac)* species bind only on particular Lewis acid sites on the Al₂O₃ surface.

Although the absolute SnF(acac)* coverage derived from the QCM measurements after the Sn(acac)2 exposures is very similar at the different temperatures, the FTIR experiments reveal that the total coverage of acetylacetonate species has a large change with temperature as shown in Figure 7. Figure 4b shows the effective Arrhenius dependence of 1/(integrated absorbance) for the acetylacetonate vibrational features at 200, 250, and 300 °C in Figure 7b after the HF exposures. This effective Arrhenius plot yields an activation barrier of E = 6.2 ± 1.5 kcal/mol. This activation barrier is very similar to the activation barrier of E = 6.6 ± 0.4 kcal/mol derived from the temperature-dependent MCPC values in Figure 4. Nearly identical results were obtained from the effective Arrhenius analysis of the temperature-dependent coverage of acetylacetone species after the Sn(acac)2 exposure.

The correlation between the two Arrhenius plots in Figure 4 suggests that the MCPC is inversely dependent on the coverage of acetylacetonate species remaining on the surface after the HF or Sn(acac)2 exposures. Higher coverages of acetylacetonate species are correlated with lower Al₂O₃ ALE rates. An inverse dependence between MCPC and the coverage of acetylacetonate species would be expected if there is a site-blocking effect of acetylacetonate species on Al₂O₃ ALE. Similar site-blocking effects of acetylacetone species were observed for Pt ALD and Pd ALD.⁴⁸,⁵⁰ The acetylacetonate species could either restrict the fluorination of Al₂O₃ to produce AlF₃ during the HF exposure or the ligand exchange between Sn(acac)₂ and AlF₃ during the Sn(acac)₂ exposure. The dramatic increase in AlF₃ species produced at 300 °C after the HF exposure in Figure 12 argues that the primary site-blocking effect of the acetylacetone species may be on the fluorination reaction.

The proposed reactions for Al₂O₃ ALE are very similar to the reactions proposed earlier for HfO₂ ALE.³⁸ Both Al₂O₃ ALE and HfO₂ ALE display etching rates that increase at higher temperatures. These temperature-dependent etching rates are both believed to be correlated inversely with the acetylacetonate coverage on the substrate after the HF or Sn(acac)2 exposures. The Al(acac)₃ and Hf(acac)₄ etching products are both volatile. Both Al₂O₃ and HfO₂ form stable fluorides upon exposure to HF. The etching rates for Al₂O₃ ALE are somewhat higher than the etching rates for HfO₂ ALE. These differences may be related to the more favorable thermochemistry for Al₂O₃ ALE. The ΔG for the HF reaction with HfO₂ is not as favorable as the ΔG for the HF reaction with Al₂O₃.²⁸

IV. CONCLUSIONS

In situ quartz crystal microbalance (QCM) and Fourier transform infrared (FTIR) spectroscopy measurements were used to explore the mechanism of thermal Al₂O₃ atomic layer etching (ALE) using Sn(acac)₂ and HF as the reactants. The mass change per cycle (MCPC) for Al₂O₃ ALE varied with temperature from −4.1 ng/(cm² cycle) at 150 °C to −18.3 ng/(cm² cycle) at 250 °C. These temperature-dependent etch rates yielded an activation barrier for Al₂O₃ ALE of E = 6.6 ± 0.4 kcal/mol. The mass changes after the Sn(acac)₂ and HF exposures were also dependent on temperature. The mass changes after the Sn(acac)₂ exposures indicated that more Sn(acac)₂ surface reaction products were present at lower temperatures. The mass changes after the HF exposures indicated that more AlF₃ species were present at higher temperatures.

FTIR spectroscopy measurements monitored the Al₂O₃ ALE and quantified the acetylacetone surface species versus temperature. A connection was observed between the MCPC values and the absorbance from the acetylacetone species. The Al₂O₃ ALE rate was inversely dependent on the acetylacetone surface species. This behavior suggested that the acetylacetone surface species may have a site-blocking effect on Al₂O₃ ALE. Difference infrared absorbance spectra also revealed that there was a constant absorbance change in the acetylacetone spectral region at all temperatures. This constant absorbance change may be attributed to the constant coverage of SnF(acac)* species after the Sn(acac)₂ exposures at all temperatures determined by the QCM analysis.

The nucleation of the Al₂O₃ ALE was also explored using QCM and FTIR measurements. The conversion of Al₂O₃ to AlF₃ was consistent with a large mass gain and loss of infrared absorbance of Al–O stretching vibrations after the initial HF exposure on the Al₂O₃ film. The formation of AlF₃ after the initial HF exposure and the presence of AlF₃ on the surface after each HF exposure during Al₂O₃ ALE were also observed by FTIR experiments. These results suggest that AlF₃ is the key reaction intermediate during Al₂O₃ ALE. The HF exposure converts Al₂O₃ to AlF₃, and then the AlF₃ is removed by the Sn(acac)₂ exposure.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: steven.george@colorado.edu.

Notes

The authors declare no competing financial interest.

3656 DOI 10.1021/acs.chemmater.3b00300 Chem. Mater. 2015, 27, 3648–3657
ACKNOWLEDGMENTS

This research was funded by the National Science Foundation (Grant CHE-1306131). Additional personnel support for Y.L. was provided by the Department of Energy through the DOE-BATT program.

REFERENCES