Atomic layer etching (ALEt) of HfO2 was performed using sequential, self-limiting thermal reactions with Sn(acac)2 and HF as the reactants. The HF source was a HF-pyridine solution. The etching of HfO2 was linear with atomic level control versus number of Sn(acac)2 and HF reaction cycles. The HfO2 ALEt was measured at temperatures from 150–250 °C. Quartz crystal microbalance (QCM) measurements determined that the mass change per cycle (MCPC) increased with temperature from −6.7 ng/(cm2·cycle) at 150 °C to −11.2 ng/(cm2·cycle) at 250 °C. These MCPC values correspond to etch rates from 0.070 Å/cycle at 150 °C to 0.117 Å/cycle at 250 °C. X-ray reflectivity analysis confirmed the linear removal of HfO2 and measured an HfO2 ALEt etch rate of 0.11 Å/cycle at 200 °C. Fourier transform infrared (FTIR) spectroscopy measurements also observed HfO2 ALEt using the infrared absorbance of the Hf-O stretching vibration. FTIR analysis also revealed absorbance features consistent with HfF4 or HfF6, surface species as a reaction intermediate. The HfO2 etching is believed to follow the reaction: HfO2 + 4Sn(acac)2 + 4HF → Hf(acac)4 + 4SnF(acac) + 2H2O. In the proposed reaction mechanism, Sn(acac)2 donates acac to the substrate to produce Hf(acac)4. HF allows Sn(acac)2 to add to the substrate to produce Hf(acac)4. Hf(acac)4 is then etched by HF to produce Sn(acac)2 and H2O to leave as reaction products. The thermal ALEt of many other metal oxides, as well as metal nitrides, phosphides, sulfides and arsenides, should be possible by a similar mechanism.

Experimental

Viscous flow reactor equipped for in situ QCM measurements.—

The ALEt reactions were performed in a viscous flow ALD reactor. The reaction temperatures varied from 150–250 °C. A proportional-integral-derivative (PID) temperature controller (2604, Eurotherm) maintained the temperature to within ±0.04 °C. The pressure was measured in the reactor using a capacitance manometer (Baratron 121A, MKS). The ALD reactor was equipped with an in situ quartz crystal microbalance (QCM). An RC-cut quartz crystal (gold coated and polished, 6 MHz, Colnatec) was positioned in a sensor head (BSH-150, Inficon). The sensor head was then sealed with high temperature epoxy (Epo-Tek H21D, Epoxy technology). A thin film deposition monitor (Maxtek TM-400, Inficon) was used to record the QCM measurements.

Sequential exposure of tin(II) acetylacetonate (Sn(acac)2), 37–38% Sn, Gelest) and HF-pyridine (70 wt% HF, Sigma-Aldrich) were employed for the HfO2 ALEt reactions. These precursors are shown in Figure 1. Use of gaseous HF from HF-pyridine enables the safe handling of anhydrous HF. HF-pyridine is a liquid at room temperature and is known as Olah’s reagent. The HF-pyridine solution has an equilibrium with gaseous HF. Our mass spectrometer analysis has shown that HF dominates the vapor pressure of HF-pyridine. Our

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The transmission FTIR measurements were performed on high surface area SiO2 nanoparticles (99.5%, US Research Nanomaterials Inc.) with an average diameter of 15–20 nm. The high surface area of these particles improved the signal-to-noise ratio compared with a flat sample.36 Sample preparation involving pressing the SiO2 nanoparticles into a tungsten grid support (Tech-Etch).36,37 The tungsten grids were 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, 20V/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 attached to the bottom of the tungsten grid with Epoxy (Cernamond 571, Aremco) that served to attach and electrically isolate the thermocouple during the experiment.

The HfO2 films were grown with HfO2 ALD using TDMAH and H2O at 200°C. The HfO2 ALEt reactions were performed using sequential exposures of Sn(acac)2 and Hf. Static dosing of both the ALD and ALEt precursors was utilized to achieve self-limiting behavior on the high surface area SiO2 particles. During HfO2 ALD, each TDMAH exposure consisted of a ~1.0 Torr static dose for 30 s followed by a 240 s purge. For the H2O reaction, each exposure consisted of a ~1.0 Torr static dose for 30 s followed by a 240 s purge.

During HfO2 ALEt, each Sn(acac)2 exposure consisted of a ~1.0 Torr static dose for 30 s followed by a 240 s purge. For the Hf reaction, each HF exposure consisted of a ~1.0 Torr static dose for 30 s followed by a 240 s purge. For these FTIR experiments, the Hf-pyridine and H2O precursors were maintained at room temperature. The stainless steel bubbler containing Sn(acac)2 was held at 100°C. The stainless steel bubbler containing ALEt was held at 70°C.

The Hf2F7 films were deposited using HfF4 ALD with sequential exposures of TDMAH and HF at 150°C. The Hf2F7 films were grown on a fresh HfO2 ALD film that was prepared using three HfO2 ALD cycles with TDMAH and H2O as the reactants. Static dosing of the reactants was utilized to achieve self-limiting behavior of the surface reactions on the high surface area SiO2 particles. During Hf2F7 ALD, each TDMAH exposure consisted of a ~1.0 Torr static dose for 30 s followed by a 240 s purge. Each HF exposure consisted of a ~1.0 Torr static dose for 30 s followed by a 240 s purge.

Results and Discussion

FTIR spectroscopy measurements.—The in situ transmission FTIR measurements of HfO2 ALEt were performed in a reactor equipped with an FTIR spectrometer.35 The FTIR spectrometer (Nicolet 6700 FTIR from Thermo Scientific) utilized a high-sensitivity liquid-N2-cooled mercury cadmium telluride (MCT-B) detector. The spectrometer, mirror, and detector were purged with dry, CO2-free air. A total of 100 scans at 4 cm⁻¹ resolution from 400 to 4000 cm⁻¹ were recorded for each collected spectrum.

Figure 2. Mass change versus time for HfO2 ALEt using sequential Sn(acac)2 and HF exposures at 200°C.
HfO₂ surface at 200 °C. The initial HfO₂ film on the QCM sensor was deposited using 100 cycles of HfO₂ ALD with TDMAH and H₂O as the reactants at 200 °C. One ALEt cycle was defined by a Sn(acac)₂ dose of 1.0 s, a N₂ purge of 30 s, a HF dose of 1.0 s, and a second N₂ purge of 30 s. This reaction sequence is designated as 1-30-1-30. The pressure transients during the Sn(acac)₂ and HF exposures were 20 mTorr and 80 mTorr, respectively.

The etching of the HfO₂ film in Figure 2 is linear and is consistent with a mass change per cycle (MCPC) = −11.1 ng/(cm² cycle). This MCPC corresponds to an etch rate of 0.116 Å/cycle based on the HfO₂ ALD film density of 9.6 g/cm³ that was measured by XRR analysis. All of the ALEt cycles display a mass loss as a result of etching the HfO₂ film except during the first ALEt cycle. The first cycle shows mass gains of ΔM_sn = 71 ng/cm² and ΔM_HF = 6 ng/cm².

The mass gain for ΔM_sn on the first cycle is assigned to Sn(acac)₂ adsorption on the HfO₂ surface. The Sn(acac)₂ could either adsorb associatively as Sn(acac)₂ ∗ or dissociatively as Sn(acac)+ and (acac)−. The asterisks designate a surface species. The mass gain for ΔM_HF on the first cycle is explained by HF adsorption or the formation of HfF₂ or HfF₃ species by the reaction of HF with the underlying HfO₂ surface. The reaction HfO₂ + 4HF → HfF₄ + 2H₂O is spontaneous with ΔG = −19 kcal at 200 °C. This first cycle establishes the initial Sn(acac)₂ and HF, HfF₄, or HfFx species on the HfO₂ substrate.

Figure 3 displays an enlargement of the mass changes versus time at 200 °C for three cycles in the steady state linear etching regime in Figure 2. There is a gradual mass decrease after a small mass gain coinciding with the Sn(acac)₂ exposure. This behavior suggests Sn(acac)₂ desorption and/or removal of reaction products. A mass change of ΔM_sn = −4.8 ng/cm² was observed after 1.0 s of Sn(acac)₂ exposure. A mass change of ΔM_HF = −6.3 ng/cm² was observed after 1.0 s of HF exposure. The experimental variation of these mass changes was measured over 50 HfO₂ ALEt cycles. The standard deviation on the ΔM_sn and ΔM_HF mass changes was <0.1 ng/cm².

Figure 4 shows the MCPC and the ΔM_sn/MCPC ratio during 100 cycles of HfO₂ ALEt at 200 °C. The MCPC is defined by MCPC = ΔM_sn + ΔM_HF. The standard deviation on the MCPC was also <0.1 ng/cm². Figure 4a displays ΔM_sn, ΔM_HF and MCPC for the same 100 cycles of HfO₂ ALEt on the HfO₂ film at 200 °C as shown in Figure 2. The MCPC varies from approximately 17ng/(cm² cycle) to 11ng/(cm² cycle) over the second to fifth ALEt cycles. The MCPC decreases to a steady-state value of about 0.78 ng/(cm² cycle) after ~20 HfO₂ ALEt cycles. These first 20 HfO₂ ALEt cycles prior to reaching the steady state values define the nucleation regime.

Figure 4b displays the ΔM_sn/MCPC ratio during the same 100 cycles as shown in Figure 4a. This ΔM_sn/MCPC ratio varies from 0.78 to 0.64 over the second to fifth ALEt cycles. The ratio then slowly decreases to a steady-state value of 0.43 after the first ~20 HfO₂ ALEt cycles in the nucleation regime. This ΔM_sn/MCPC ratio will be used to determine the stoichiometry of the ALEt surface reactions. The standard deviations on the ΔM_sn/MCPC ratio was <0.005.

Figure 5 examines the self-limiting nature of the Sn(acac)₂ and HF reactions during HfO₂ ALEt at 200 °C. These MCPC values were measured versus different reactant exposure times. Figure 5a shows the ratio of mass change per cycle (MCPC) after the HF exposure (ΔM_HF) and mass change per cycle (MCPC) versus number of ALEt cycles at 200 °C.

Figure 5b displays the mass change per cycle (MCPC) versus exposure time for (a) Sn(acac)₂ and (b) HF.
the self-limiting behavior of the Sn(acac)_2 reaction using different Sn(acac)_2 exposure times with a single 1.0 s exposure of HF. A constant N_2 purge of 30 s was used after each exposure. This reaction sequence can be denoted as x-30-1-30. The MCPC versus Sn(acac)_2 exposure time decreases quickly and levels off at MCPC = −11 ng/(cm^2 cycle).

Figure 5b examines the self-limiting behavior of the HF reaction using different HF exposure times with a single 1.0 s exposure of Sn(acac)_2. This reaction sequence can be denoted as 1-30-1-30. The MCPC versus HF exposure time decreases and does not level off after longer HF exposure times. The HF reaction does not appear to be self-limiting versus HF exposure. The lack of self-limiting behavior for the HF exposure may indicate that the HF reaction has not reached saturation. Much larger HF exposures may be necessary to complete the surface reaction.

Another possibility is that the larger HF exposures lead to larger HF background pressures and longer HF residence times in the reactor. If some HF residual pressure remains during the Sn(acac)_2 exposure, then the HfO_2 substrate can be continuously etched with HF and Sn(acac)_2 by chemical vapor etching (CVE). CVE is the reverse of chemical vapor deposition (CVD) and occurs when the two precursors are not responsible for the mass change. This correspondence indicates that the mass change during the Sn(acac)_2 reaction is primarily responsible for the temperature dependence of the mass loss during HfO_2 ALEt.

The MCPC values in Figure 8a correlate with the mass change of the Sn(acac)_2 reaction at 150°C, 175°C, 200°C and 250°C. The differences in the mass change after 100 cycles for these temperatures are determined by the mass changes in the nucleation regime during the first 20 HfO_2 ALEt cycles.

The ΔMSn, ΔMHF, and MCPC values at the various reaction temperatures are shown in Figure 8b. All HfO_2 ALEt reactions were performed using a reaction sequence of 1-30-1-30 on initial HfO_2 films. Figure 8a shows that ΔMSn displays a slight mass gain at 150°C and progressively larger mass losses at higher temperatures. In contrast, ΔMHF displays mass losses over the entire temperature range. The mass losses are slightly less at higher temperatures.

Figure 8b reveals that the MCPC increases with temperature between 150 and 200°C. The MCPC values are nearly equivalent at 200, 225 and 250°C. The MCPC values are nearly equivalent at 200, 225 and 250°C. The MCPC values are nearly equivalent at 200, 225 and 250°C.
**XRR, XPS and SE measurements.**— Ex situ XRR studies also examined HfO$_2$ ALEt. These XRR experiments employed HfO$_2$ ALD films with a thickness of 144 Å that were grown on Si(100) wafers. These HfO$_2$ ALD films were deposited using 150 cycles of TDMAH and H$_2$O at 200°C with a reaction sequence of 1-20-1-20. Figure 9 shows XRR scans of the HfO$_2$ ALD films on the Si wafers versus number of Sn(acac)$_2$ and HF reaction cycles at 200°C. The XRR scans have been displaced from each other for clarity. These XRR scans reveal uniform and smooth HfO$_2$ films.

Figure 9a displays the XRR scan of the initial HfO$_2$ ALD film grown on Si(100) wafers. The HfO$_2$ ALD film thickness of 144 Å can be obtained by fitting the reflected X-ray intensity versus incident angle. Figure 9b, 9c, 9d, and 9e show XRR scans of the etched HfO$_2$ film after 50, 100, 200, and 400 ALEt cycles at 200°C, respectively. The HfO$_2$ thicknesses decrease with increasing number of ALEt cycles. This decreasing film thickness leads to the decrease in the modulation of the X-ray intensity versus angle with higher numbers of ALEt cycles.

The etched HfO$_2$ films are smooth and do not roughen versus HfO$_2$ ALEt. The XRR measurements yielded a roughness of the initial HfO$_2$ ALD film of ~6 Å. The surface roughness then decreased to ~3-4 Å after 50, 100, 200, and 400 ALEt cycles. The ALEt process is able to smooth the surface of the initial HfO$_2$ films. The error in these XRR surface roughness measurements is ~1 Å. The position of the critical angle of all the etched HfO$_2$ films is also constant. This constant critical angle indicates that there is no change of the film density during the ALEt reactions.

**Table I.** $\Delta M_{Sn}$, $\Delta M_{HF}$, MCPC, $\Delta M_{Sn}/$MCPC, $x$, and $x$(MCPC) for HfO$_2$ ALEt at different temperatures. $\Delta M_{Sn}$, $\Delta M_{HF}$, MCPC and $x$(MCPC) are expressed in units of ng/(cm$^2$ cycle).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>MCPC</th>
<th>$\Delta M_{Sn}$</th>
<th>$\Delta M_{HF}$</th>
<th>$\Delta M_{Sn}$/MCPC</th>
<th>$x$</th>
<th>$x$(MCPC)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>−6.7</td>
<td>0.37</td>
<td>−7.1</td>
<td>1.1</td>
<td>−7.6</td>
</tr>
<tr>
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<td></td>
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<td>−1.7</td>
<td>−6.6</td>
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</tr>
<tr>
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<td></td>
<td>−11.1</td>
<td>−4.8</td>
<td>−6.3</td>
<td>0.43</td>
<td>0.69</td>
</tr>
<tr>
<td>225</td>
<td></td>
<td>−11.9</td>
<td>−6.1</td>
<td>−5.8</td>
<td>0.51</td>
<td>0.62</td>
</tr>
<tr>
<td>250</td>
<td></td>
<td>−11.2</td>
<td>−5.6</td>
<td>−5.6</td>
<td>0.50</td>
<td>0.63</td>
</tr>
</tbody>
</table>

**Figure 10.** X-ray reflectivity (XRR) and spectroscopic ellipsometry (SE) measurements of HfO$_2$ film thickness versus number of HfO$_2$ ALEt cycles for initial HfO$_2$ ALD films grown using (a) 150 HfO$_2$ ALD cycles and (b) 100 HfO$_2$ ALD cycles.
index for the HfO2 film remained at n = 2.07-2.09 after 50, 100, 200, and 400 ALEt cycles.

XRR measurements were also performed on HfO2 ALD films with a thickness of 87 Å that were grown on Si(100) wafers. These HfO2 ALD films were deposited at 200°C using 100 cycles of TDMAH and H2O with a reaction sequence of 1-20-1-20. Figure 10b displays the film thickness versus number of Sn(acac)2 and HF reaction cycles at 200°C. The XRR measurements yield an HfO2 ALEt etch rate of 0.11 Å/cycle. The SE measurements also yield an etch rate of 0.12 Å/cycle with an initial HfO2 ALD film thickness of 87 Å. The initial thickness of the HfO2 film is again not employed to determine the etch rate because of the mass gain that occurs on the first ALEt cycle and the nucleation regime that occurs during the first 20 ALEt cycles.

X-ray photoelectron spectroscopy (XPS) analysis was used to determine the elements on the HfO2 film after HfO2 ALEt. The XPS analysis measured Sn 3d5/2 XPS signals of 0.47-0.61 at% and F 1s XPS signals of 4.0-4.1 at% after 200 or 400 Al2O3 ALEt cycles after the HF exposure. These XPS signals are consistent with residual Sn(acac)2 adsorption products and the formation of HfF4 or HfFx surface species. The Sn and F XPS signals were removed to below the XPS detection limit after Ar ion sputtering for 2 minutes. This sputtering time also removes adventitious carbon from the surface. In situ FTIR Spectroscopy measurements.—In situ FTIR spectra of HfO2 ALD films grown using 10 cycles of TDMAH and H2O at 200°C are shown in Figure 11. These FTIR spectra are difference spectra referenced to the initial SiO2 particles. FTIR Spectroscopy measurements.—In situ FTIR spectra of HfO2 ALD films grown using 10 cycles of TDMAH and H2O at 200°C are shown in Figure 11. These FTIR spectra are difference spectra referenced to the initial SiO2 particles. These spectra were recorded after the Sn(acac)2 exposure. Decreasing absorbance for the Sn(acac)2 absorption products is also observed in Figure 12 in the range between 1250–1750 cm⁻¹. These vibrational features are derived from the acetylacetonate (acac) constituents. The features are consistent with either Sn(acac)2, SnF(acac)⁺ or acac⁺ adsorbed on the HfO2 substrate.

Nucleation behavior and proposed HfF2 formation.—Figure 13 displays an enlargement of the mass changes from Figure 7 during the first two ALEt cycles on HfO2 films. The first Sn(acac)2 exposure shows mass gains of ΔMΔA = 68–72 ng/cm² at 150–250°C resulting from adsorption products of Sn(acac)2 such as Sn(acac)⁺ and acacH⁺. To estimate the coverage of Sn(acac)2⁺ species on the surface, the sites on the HfO2 surface can be approximated using the HfO2 density of 9.6 g/cm³. This mass density is equivalent to a number density of ρ = 2.7 × 10²² “HfO2 units”/cm³. This number density yields an estimate for the number of “HfO2 units” on the HfO2 surface of ρ⁰ = 9.10 × 10¹⁴ “HfO2 units”/cm² assuming a square lattice. This coverage of “HfO2 units” represents an HfO2 mass of 320 ng/cm². The coverage of Sn(acac)2⁺ can then be approximated based on the mass gain of 72 ng/cm². This mass gain is equivalent to 1.37 × 10¹⁴ Sn(acac)2 molecules/cm². The normalized coverage of Sn(acac)2⁺ species relative to “HfO2 units” on the surface is 1.37 × 10⁴ Sn(acac)2 molecules/cm²/9.10 × 10¹⁴ “HfO2 units”/cm² = 0.15 Sn(acac)2 species/HfO2 unit. This coverage is reasonable given that Sn(acac)2 may dissociate into Sn(acac)⁺ and acacH⁺. In addition, the acac ligand is bulky and expected to occupy more than one “HfO2 unit” on the HfO2 surface.
The first HF exposure on the surface previously exposed to Sn(acac)₂ shows mass gains of ∆M_\text{HF} = 3.8 ng/cm² at 150–250°C. These mass gains may be affected by the loss of Sn(acac)₂ adsorption products. The mass gains following HF exposures on an initial HfO₂ film can be used to estimate the coverage of HF or HF reaction products. A mass gain of 37.8 ng/cm² is observed after HF exposures on an initial HfO₂ film at 200°C in Figure 6a. Assuming that HF is the adsorption product, this mass gain is equivalent to 1.14 × 10^{15} HF molecules/cm². The normalized coverage of HF species relative to "HfO₂ units" on the surface is 1.14 × 10^{15} HF molecules/cm²/9.10 × 10^{14} "HfO₂ units"/cm² = 1.25 HF/HfO₂ unit.

The first HF exposure on the surface previously exposed to Sn(acac)₂ shows mass gains of ∆M_\text{HF} = 1.25 HF/HfO₂ unit. Assuming either HF or HfF₄ products, the estimated coverages after the HF exposure are comparable with the number of "HfO₂ units" on the HfO₂ substrate. These coverages are consistent with the rapid and self-limiting fluorination of the HfO₂ surface.

Because the loss in absorbance from HfO₂ and the gain in absorbance from HfF₄ or HfFx surface species occurs in the same frequency range, difference FTIR spectra were examined during the first HF and first Sn(acac)₂ exposures on the initial HfO₂ film to distinguish the HfF₄ or HfFx surface species produced by the first HF exposure. The first HF exposure produces a gain in absorbance between 500–650 cm⁻¹ and a loss in absorbance between 650–925 cm⁻¹. The reference spectrum for this FTIR spectrum was the initial HfO₂ film on the SiO₂ nanoparticles. The loss of absorbance between 650–925 cm⁻¹ and the gain in absorbance between 500–650 cm⁻¹ is attributed to the conversion of HfO₂ to HfF₄ or HfFx surface species. The reference spectrum for this FTIR spectrum was the previous FTIR spectrum recorded after the HF exposure. This loss of absorbance is expected from the Sn(acac)₂ reaction with the HfF₄ or HfFx surface species.

With the first HF exposure, a portion of the Hf-O absorbance feature decreases between 625–800 cm⁻¹. There is also another absorbance decrease between ~800–900 cm⁻¹. These changes may correspond with the conversion of Hf-O stretching vibrations to Hf-F stretching vibrations.
Figure 16. These FTIR spectra are referenced to the initial HfO2 film on the SiO2 nanoparticles. FTIR spectra versus number of HfF4 ALD cycles are displayed in cycles of HfO2 ALD on the SiO2 nanoparticles. The reference spectrum was the FTIR spectrum after 10 cycles of HfO2 ALD on the SiO2 nanoparticles. The difference spectrum after removal of 10 cycles of HfO2 ALD from the reference spectrum was the previous FTIR spectrum after the HF exposure. Figure 15 shows the schematic for the proposed HfO2 ALEt surface chemistry. This possible picture for HfO2 ALEt 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 includes only surface species that change during the Sn(acac)2 and HF exposures. This scheme also assumes that the HF reaction produces HfF4 on the HfO2 film.

期间，HfF4是关键的反应中间体。HfF4层与HfO2薄膜反应形成SnF(acac)和Hf(acac)4产物，然后沉淀在HfO2底材表面最终形成挥发性的SnF(acac)和Hf(acac)4产物。这些反应包括表面物种在HfO2 ALD期间的反应。

In addition, HF also provides hydrogen to form H2O as a reaction product. This reaction removes the oxygen in HfO2. The HfF4 layer on the HfO2 substrate to form volatile SnF(acac) and Hf(acac)4 product formation, there may be a strong interaction between SnF(acac)+ surface species and the underlying HfO2 substrate. This interaction may lead to some SnF(acac)+ species adsorbed to the HfO2 substrate.

During the HF reaction (B), HF reacts with some of the SnF(acac)+ surface species and the underlying HfO2 surface to form a HfF4 layer. In addition, HF also provides hydrogen to form H2O as a reaction product. This reaction removes the oxygen in HfO2. The HfF4 layer is then ready for the next Sn(acac)2 reaction.

The overall proposed reaction can be expressed as:

\[ \text{HfO}_2 + 4\text{HF} + 4\text{Sn(acac)} \rightarrow \text{SnF(acac)} + 4\text{HF} + 4\text{HF} = \text{HfF}_4 + 4\text{SnF(acac)} + 2\text{H}_2\text{O} \]  [1]

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

(A) \[ \text{HfO}_2(\text{HfF}_4^+) + 4\text{Sn(acac)}_2 \rightarrow \text{SnF(acac)} + 4\text{HF} + (4 - x) \text{SnF(acac)} \]  [2]

(B) \[ \text{HfO}_2(x\text{SnF(acac)} + 4\text{HF} \rightarrow \text{HfF}_4^+ + x\text{SnF(acac)} + 2\text{H}_2\text{O} \]  [3]

These reactions include only the species that 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. Note that HfF4 is the key reaction intermediate. The production of all the Hf(acac)4 is assumed to occur during reaction (A). Hf(acac)4 is a stable metal β-diketonate with a vapor pressure of ~0.1 Torr at 150 °C.51,52

The HfF4 shown in Equations 2 and 3 is the amount of HfO2 that is etched in one HfO2 ALEt cycle. \( x \) quantifies the coverage of SnF(acac)+ on the surface after the Sn(acac)2 exposures relative to the amount of HfO2 that is etched in one HfO2 ALEt cycle. \( x \) can be determined from the \( \Delta M_{\text{Sn}}/\text{MCPC} \) ratio using the equation:

\[ x = (254.5 - 210.5(\Delta M_{\text{Sn}}/\text{MCPC}))/236.8 \]  [4]

where 254.5, 210.5 and 236.8 are the molecular weights for HfF4, HfO2 and SnF(acac), respectively. The \( x \) values are 1.1, 0.90, 0.69, 0.62, and 0.63 at 150, 175, 200, 225 and 250 °C, respectively. Table I lists all the \( x \) and MCPC values.

\( x \) defines the SnF(acac)+ species after the Sn(acac)2 exposures relative to the amount of HfO2 that is etched in one HfO2 ALEt cycle. Consequently, the product x(MCPC) provides a measure of the SnF(acac)+ surface species after the Sn(acac)2 exposures. The x(MCPC) values are included in Table I. These x(MCPC) values are fairly constant at all the temperatures. This behavior indicates that the SnF(acac)+ coverage is nearly constant at all the temperatures after
Figure 17. Schematic of proposed surface chemistry for HfO<sub>2</sub> ALEt showing (A) Sn(acac)<sub>2</sub> reaction and (B) HF reaction.

the Sn(acac)<sub>2</sub> exposures. This coverage may represent a saturated monolayer for SnF(acac)<sup>*</sup> on the HfO<sub>2</sub> surface.

The proposed reactions for HfO<sub>2</sub> ALEt are similar to the reactions proposed earlier for Al<sub>2</sub>O<sub>3</sub> ALEt. Both HfO<sub>2</sub> ALEt and Al<sub>2</sub>O<sub>3</sub> ALEt display etching rates that increase at higher temperatures. These temperature dependent etching rates are believed to be correlated inversely with the acetylacetonate coverage remaining on the substrate after the Sn(acac)<sub>2</sub> exposure. The Hf(acac)<sub>4</sub> and Al(acac)<sub>3</sub> etching products are both volatile. The vapor pressure of Hf(acac)<sub>4</sub> at 150 °C is ∼0.1 Torr. The vapor pressure of Al(acac)<sub>3</sub> at 150 °C is ∼3-4 Torr. Both HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> form stable fluorides upon exposure to HF. However, the Hf(acac)<sub>4</sub> etching product may become unstable at >100 °C. The ΔG for the HF reaction with HfO<sub>2</sub> is also not as favorable as the ΔG for the HF reaction with Al<sub>2</sub>O<sub>3</sub>. These factors may lead to etching rates for Al<sub>2</sub>O<sub>3</sub> ALEt that are higher than the etching rates for HfO<sub>2</sub> ALEt.

Extensions to other materials and advantages of thermal ALEt.—The ALEt of other materials should be possible using sequential, self-limiting thermal reactions with Sn(acac)<sub>2</sub> and HF as the reactants. The prospective materials include other metal oxides, metal nitrides, metal phosphides, metal sulfides and metal arsenides. The Sn(acac)<sub>2</sub> and HF reactants should be generally useful because Sn(acac)<sub>2</sub> can readily react with fluorine to form SnF(acac). Sn-F bond formation is favorable because tin has a high affinity for fluorine. The reaction of Sn(acac)<sub>2</sub> with fluorine to form SnF(acac) enables Sn(acac)<sub>2</sub> to release an acac ligand to the surface. Metals easily form complexes with acac ligands and have comparable stabilities. The hydrogen from HF can also combine with either oxygen, nitrogen, phosphorous, sulfur or arsenic from the metal oxide, metal nitride, metal phosphide, metal sulfide or metal arsenide to form H<sub>2</sub>O, NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>S or AsH<sub>3</sub>, respectively. The ALEt of elemental metals should also be possible by first oxidizing the metal and then etching the resulting metal oxide. Alternatively, elemental metals could be directly fluorinated to form the metal fluoride and then the metal fluoride could be removed by Sn(acac)<sub>2</sub>.

There are advantages to the thermal ALEt approach compared with ALEt based on halogen adsorption and ion or energetic neutral noble atom bombardment. The thermal ALEt approach avoids any damage to the underlying substrate resulting from high energy ions or energetic neutrals. The ALEt based on ion or neutral noble atom bombardment requires line-of-sight to the substrate. This requirement can be used advantageously to minimize undercutting with directional ions or energetic neutral atoms during ALEt. However, this line-of-sight requirement is limited to the small surface areas that are subjected to ion or neutral noble atom bombardment. In contrast, the thermal ALEt approach will be useful for etching larger samples. The thermal ALEt approach will also be important for etching high surface area samples and high aspect ratio structures.

Conclusions

HfO<sub>2</sub> ALEt was demonstrated using Sn(acac)<sub>2</sub> and HF as the reactants. The sequential, self-limiting thermal reactions of Sn(acac)<sub>2</sub> and HF etched HfO<sub>2</sub> linearly with atomic level precision. HfO<sub>2</sub> ALEt was observed at temperatures from 150–250 °C. The Sn(acac)<sub>2</sub> reaction was self-limiting versus reactant exposure as revealed by QCM studies. However, the HF reaction was weakly self-limiting presumably because of a high residence time for HF and chemical vapor etching (CVE) caused by the presence of both Sn(acac)<sub>2</sub> and HF in the reactor.

The QCM studies measured MCPC values of −6.7, −8.3, −11.1, −11.9, and −11.2 ng/(cm<sup>2</sup> cycle) at 150, 175, 200, 225, and 250 °C, respectively. These mass changes per cycle correspond to etch rates of 0.070, 0.087, 0.116, 0.124, and 0.117 Å/cycle at 150, 175, 200, 225 and 250 °C, respectively. The linear removal of HfO<sub>2</sub> was confirmed by XRR analysis. The XRR studies measured HfO<sub>2</sub> ALEt etch rates of 0.11 Å/cycle at 200 °C. The HfO<sub>2</sub> films also were smoothed by HfO<sub>2</sub> ALEt. HfO<sub>2</sub> ALEt was also observed by FTIR spectroscopy analysis that monitored the loss of absorbance from the Hf-O stretching vibrations.
vibration of bulk HfO2 versus number of Sn(acac)2 and HF reaction cycles. FTIR analysis also monitored absorbance features that were consistent with HfF4 or HfFx surface species as a reaction intermediate. The HfO2 etching is believed to follow the reaction: HfO2 + 4Sn(acac)2 + 4HF \rightarrow Hf(acac)4 + 4SnF(acac)2 + 2H2O. In the proposed reaction mechanism, HfF4 or HfFx is the key reaction intermediate. The Sn(acac)2 reactant donates acac to the HfF4 or HfFx adlayer on the HfO2 substrate to produce Hf(acac)4. The HF reactant forms the HfF4 or HfFx reaction intermediate from HfF4 and allows SnF(acac)2 and H2O to leave as reaction products. The ALEt of many other metal oxides besides HfO2 should also be possible using sequential Sn(acac)2 and HF exposures. This ALEt reaction mechanism should also be applicable for the ALEt of metal nitrides, metal phosphides, metal arsenides and elemental metals.

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