Volatile Etch Species Produced during Thermal Al₂O₃ Atomic Layer Etching

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ABSTRACT: The thermal atomic layer etching (ALE) of Al₂O₃ can be achieved using sequential fluorination and ligand-exchange reactions. Although previous investigations have characterized the etch rates and surface chemistry, no reports have identified the volatile etch products. This study explored the volatile etch species during thermal Al₂O₃ ALE at 300 °C using quadrupole mass spectrometry (QMS). HF was the fluorination reactant; Al(CH₃)₃ (trimethylaluminum (TMA)) and AlCl(CH₃)₂ (dimethylaluminum chloride, (DMAC)) were the metal precursors for ligand exchange. When TMA was used as the metal precursor after the fluorination of Al₂O₃ powder, the QMS measurements revealed that the main ion species were consistent with dimers of AlF(CH₃)₂ (dimethylaluminum fluoride (DMAF)) with itself (DMAF + DMAF) or with TMA (DMAF + TMA). These ion species were observed after loss of a methyl group as Al₂F₃(CH₃)₄⁺ at m/z = 137 and AlF(CH₃)₂AlF⁺ at m/z = 133, respectively. In addition, an ion species consistent with a trimer was also observed as AlF(CH₃)₄⁺ at m/z = 213. Very similar results were observed for TMA exposures on AlF₃ powder. Comparable results were also obtained using DMAC as the metal precursor for ligand exchange. In contrast, SiCl₄ and TiCl₄ are not successful metal precursors because they do not lead to thermal Al₂O₃ ALE at 300 °C. QMS measurements revealed no Al-containing etch species after SiCl₄ and TiCl₄ exposures on AlF₃ powder. However, SiF₆Cl₂⁺ and TiF₆Cl₂⁺ species were observed which suggested that ligand-exchange reactions can occur without the release of Al-containing etch species. Density functional theory (DFT) and coupled cluster singles, doubles, and perturbative triples (CCSD(T)) calculations were performed to support the preference for dimer products. The theoretical results confirmed the stability of the dimer species and showed that dimers with two Al–F–Al bridging bonds are the most stable and dimers with two Al–CH₃–Al bridging bonds are the least stable. In addition, the calculations suggested that dimers with terminal CH₃ ligands are most able to desorb from the surface because these dimers need to break weak Al–CH₃–Al bridging bonds. Transmission electron microscopy (TEM) studies confirmed the thermal Al₂O₃ ALE of Al₂O₃ films on W powders. The TEM images revealed that the etch process was uniform and conformal after various numbers of thermal Al₂O₃ ALE cycles using HF and TMA as the reactants.

I. INTRODUCTION

Atomic layer etching (ALE) uses sequential, self-limiting surface reactions to remove material with atomic level precision.¹ Plasma and thermal ALE are two types of ALE. Plasma ALE is based on surface modification and then removal of the surface modified layer using energetic species via sputtering.² Plasma ALE yields anisotropic etching. In contrast, thermal ALE is based on thermal reactions and can remove material without the need of sputtering.³ Thermal ALE can be viewed as the reverse of atomic layer deposition (ALD).³,⁴ Thermal ALE and ALD are both isotropic processes that are needed for atomic layer processing. ALD is a mature technology with an origin many decades ago. Thermal ALE is a recent development that was discovered less than five years ago. The understanding of thermal ALE is still in its nascent stage.

The first thermal ALE was performed on Al₂O₃ using sequential fluorination and ligand-exchange reactions.²,³ HF was the fluorination reactant, and Sn(acac)₂ was the metal precursor used for ligand exchange.²,⁵ The thermal ALE of other materials, such as HfO₂ and AlN, was also developed using HF and Sn(acac)₂ as the reactants.⁶,⁷ Subsequent work showed that thermal Al₂O₃ ALE could also be accomplished using HF and Al(CH₃)₃ (trimethylaluminum (TMA)).⁸,⁹ This demonstration was significant because TMA is also the main metal precursor for Al₂O₃ ALD.¹⁰ In addition, Al₂O₃ ALE or AlF₃ ALD could be obtained using HF and TMA depending on the substrate temperature.⁸,¹¹ Other mechanisms for thermal ALE have also been discovered based on the conversion of the surface layer of the material.¹²,¹³ After conversion, the new surface layer can be etched using fluorination and ligand exchange. The “conversion-etch” mechanism has been developed for thermal ZnO and SiO₂ ALE.¹²,¹³ In addition, a variation of the “conversion-etch” mechanism was employed for thermal W ALE where the surface of W was first oxidized to a WO₃ layer.¹⁴ Subsequently,
the WO$_3$ surface layer was converted to B$_2$O$_3$ using BCl$_3$ prior to the spontaneous etching of B$_2$O$_3$ to produce a volatile fluoride using HF.$^{14}$

Oxidation was also used for thermal TiN ALE.$^{15}$ In this case, the surface of TiN was first oxidized to TiO$_2$ using ozone. The TiO$_2$ surface layer was then spontaneously etched by fluorination with HF to produce a volatile fluoride. $^{15}$ Thermal Si ALE is another version of oxidation and “conversion etch”. $^{16}$ The silicon substrate is first oxidized to form a SiO$_2$ surface layer. Subsequently, the SiO$_2$ surface layer is converted to Al$_2$O$_3$ prior to the etching of Al$_2$O$_3$ using fluorination and ligand exchange. $^{16}$

Other fluorination reactants besides HF have also been developed for thermal ALE. SF$_6$ was employed for thermal VO$_2$ ALE using SF$_6$ for fluorination and Sn(acac)$_2$ as the metal precursor for ligand exchange. $^{17}$ XeF$_2$ was used for thermal GaN ALE using XeF$_2$ for fluorination and BCl$_3$ for ligand exchange. $^{18}$ Other metal precursors have also been utilized for ligand exchange after the fluorination reaction during thermal ALE. SiCl$_4$ (silicon tetrachloride) and TiCl$_4$ (titanium tetrachloride) have been used together with HF for fluorination to achieve thermal ZrO$_2$ and HfO$_2$ ALE. $^{9,19}$ AlCl(CH$_3$)$_2$ (dimethylaluminum chloride, (DMAC)) has also been used together with HF for fluorination to obtain thermal ZrO$_2$ and HfO$_2$ ALE. $^{9}$

Most of the understanding of thermal ALE has been derived from quartz crystal microbalance (QCM) measurements of film mass, Fourier transform infrared (FTIR) studies of surface species, and X-ray reflectivity (XRR) and spectroscopic ellipsometry (SE) investigations of film thickness. This previous work has established etch rates and identified the surface species after the various sequential reactions. The volatile etch products resulting from the sequential reactions have been inferred based on the surface chemistry. However, there has been no direct confirmation of the volatile etch products.

In this work, a custom-built reactor with in situ quadrupole mass spectrometry (QMS) was used to identify the volatile species produced during thermal ALE on powder samples. The QMS studies focused on thermal Al$_2$O$_3$ ALE using HF as the fluorination reactant. Various metal precursors were explored for the ligand-exchange reaction including TMA, DMAC, SiCl$_4$, and TiCl$_4$. Similar experiments were also conducted using AlF$_3$ to avoid using HF to fluorinate Al$_2$O$_3$. To confirm the QMS observations, density functional theory (DFT) and coupled cluster (CC) calculations were also performed on the possible etch products. In addition, transmission electron microscopy (TEM) was used to verify the thermal ALE of Al$_2$O$_3$ using HF and TMA.

II. EXPERIMENTAL SECTION

Thermal ALE Chemistry. The fluorination reaction during thermal Al$_2$O$_3$ ALE was studied using HF–pyridine (~30% pyridine, ~70% HF, Sigma-Aldrich) and 500 mg of Al$_2$O$_3$ powder (40–50 nm APS, Nanophase). The Al$_2$O$_3$ powder had a high surface area of 32–40 m$^2$/g to produce a large quantity of volatile reaction products. In addition, the high surface area of the Al$_2$O$_3$ powder greatly exceeded the surface area of the chamber walls. The ligand-exchange reactions on HF-fluorinated Al$_2$O$_3$ powder and AlF$_3$ powder (99.8%, Sigma-Aldrich) were performed using Al(CH$_3$)$_3$ (97%, Sigma-Aldrich), SiCl$_4$ (99%, Sigma-Aldrich), TiCl$_4$ (99.0% Sigma-Aldrich), and AlCl(CH$_3$)$_2$ (97%, Sigma-Aldrich) as the metal precursors.

In situ quadrupole mass spectrometry (QMS) analysis of the fluorination and ligand-exchange reactions was performed at 300 °C under static dosing conditions. The HF pressure was provided by a HF–pyridine solution. The HF vapor pressure over the HF–pyridine solution was 90–100 Torr at room temperature. The pyridine vapor pressure is also negligible. The fluorination reaction with Al$_2$O$_3$ powder, 9 Torr of HF was held statically in the reaction chamber for 60 s before purging. For the ligand-exchange reactions, 9 Torr of either Al(CH$_3$)$_3$, SiCl$_4$, TiCl$_4$, or AlCl(CH$_3$)$_2$ was also maintained in the chamber statically for 60 s. Every precursor exposure was followed by a purging sequence of 120 s of static purge, 240 s of viscous N$_2$ purge, and final 120 s of static purge to prevent cross-contamination between reactant precursors.

The QMS sampling was performed during the reactant exposures. At the onset of the reactant exposure, a pneumatic valve was opened between the reaction chamber and the QMS ionization region, and the QMS scans were repeated continuously for 60 s. Each QMS scan from $m/z = 0$ to 300 required 6 s. Ten scans were conducted during the 60 s exposure. The QMS spectra were largely unchanged after the second scan. The first scan could be affected by adsorbed gases on the powder sample and the chamber walls that are present after atmospheric exposures when loading the samples. The results shown in this paper were obtained from the eighth or ninth scan during the 60 s exposure.

Reactor for Quadrupole Mass Spectrometer (QMS) Analysis. The in situ QMS studies were performed in a custom reactor. The reactor consists of a stainless steel tube that is 1.5 in. diameter × 19 in. long (Figure 1A). A precursor manifold containing six precursor lines and one N$_2$ purge line is separated from the reaction chamber by a pneumatically actuated bellows valve to allow for static dosing and purging (Figure 1B). To avoid cross-contamination, each precursor is separated from the reaction chamber by a pneumatically actuated bellows valve to allow for static dosing and purging. The valve is opened between the reaction chamber and the QMS ionization region, and the QMS scans were repeated continuously for 60 s. Each QMS scan from $m/z = 0$ to 300 required 6 s. Ten scans were conducted during the 60 s exposure. The QMS spectra were largely unchanged after the second scan. The first scan could be affected by adsorbed gases on the powder sample and the chamber walls that are present after atmospheric exposures when loading the samples. The results shown in this paper were obtained from the eighth or ninth scan during the 60 s exposure.

Figure 1. Schematic of ALE reactor with in situ QMS: (A) main reactor with ceramic heater; (B) valve separating precursor manifold from main reactor; (C) powder sample holder; (D) additional valve; (E) aperture separating reactor from ionizer region; (F) N$_2$ purging of aperture region with mass flow controller and valve; (G) QMS analyzer; (H) RF generator; (I) secondary electron multiplier; (J) differential-pumped ionizer region; and (K) turbomolecular pump.
The thickness of Al2O3 was performed using an FEI Tecnai T12 instrument operated at 100 kV in bright field resolution.

Transmission electron microscopy (TEM) analysis was used to study the morphology of Al2O3 ALD coatings on Si substrates. TEM images were obtained as the Al2O3 ALD coatings were progressively grown.

An additional nitrogen gas flow controller was used to purge the reaction chamber through a T-joint to allow separate N2 purging of the aperture region (Figure 1F). This purging ensures that the reactants and product gases are completely removed from the aperture region between each reaction.

Detection of the volatile products was accomplished using a HiQuad QMG 700 QMS (Pfeiffer Vacuum). The HiQuad system is composed of the QMA 400 analyzer inside a 2.5 in. diameter stainless steel tube (Figure 1G) and the QMH 400-5 high-frequency generator (Figure 1H). The QMA 400 analyzer consists of a crossbeam ion source with two tungsten filaments, a quadrupole mass filter (8 mm diameter by 200 mm long molybdenum rods), and both Faraday and secondary electron multipliers (Figure 1I).

The mass spectrometer analyzer is situated perpendicular to the incoming gas stream. The crossbeam ion source has an open design that allows quick response to changes in the gas composition. This geometry also minimizes exposure to the corrosive gas species and increases the signal-to-noise ratio for detection of the volatile etch products. The QMH 440-5 RF generator provides a mass range of 1–512 amu necessary for the detection of large etch species with high sensitivity and resolution.

The QMS scans from m/z = 0 to 300 were performed continuously for 60 s during the reactant exposures. The scans were typically ended at m/z = 300 because the mass signals above m/z = 300 were negligible. The ionization region of the chamber (Figure 1J) and lines leading to the ionization region were maintained at 180 °C. This high temperature prevents condensation of the volatile etch products. The ionization region is pumped with a turbomolecular pump (Figure 1K).

Characterization of Thermal Al2O3 ALD Using TEM.

Transmission electron microscopy (TEM) analysis was performed using an FEI Tecnai T12 instrument operated at 100 kV in bright field mode. The TEM characterized the thickness of Al2O3 films on W powder. The W powder was crystalline with particle sizes ranging from 0.6 to 1 μm (99.9%, Sigma-Aldrich). TEM images were obtained as the Al2O3 ALD films were progressively etched using sequential HF and Al(CH3)3 exposures at 300 °C. The TEM images revealed the uniformity and conformality of the Al2O3 films on the W powder.

Computational Details. Examination of the ligand-exchange reactions of Al2O3 with HF and AlF3 with Al(CH3)3, as well as the dimerization reactions, was performed using a combination of quantum chemical and thermochemical calculations. All calculations, unless otherwise noted, were performed using Gaussian 16. Unrestricted DFT calculations were performed at the UMN15/6-31g level of theory to optimize the molecular structures and determine the harmonic frequencies.

Initial calculations were performed on one of the possible dimer products, di-μ-fluoridotetrafluorodialuminum. These calculations showed that using tighter convergence tolerances for the SCF and geometry optimization changed the free energies results by <0.01 eV. As a result, the default convergence thresholds of 3 × 10−4 hartree/bohr for the root mean-squared (RMS) force per atom and 1.2 × 10−3 bohr for the RMS displacement per atom were used for all calculations reported in this work. Accurate energy calculations were performed using the unrestricted coupled cluster singles, doubles, and perturbative triples (UCCSD(T))/6-31g level of theory at the DFT optimized geometries.

The structural and vibrational information from UMN15 calculations was used to calculate the thermal correction arising from translational, rotational, and vibrational degrees of freedom at finite temperature. For a detailed description of the methods used to calculate these contributions, see Chapter 11 in ref 30. The frequencies were scaled with a factor of 0.979 following previous instructions. All calculations were performed on the RMACC Summit supercomputer.

III. RESULTS AND DISCUSSION

Fluorination of Al2O3 Powder Using HF. H2O is the predicted reaction product for the fluorination reaction of Al2O3 with HF.

Figure 2. Proposed mechanism for Al2O3 thermal ALD based on sequential reactions using HF as the fluorination reactant and Al(CH3)3 as the metal precursor for ligand exchange.

\[
\text{Al}_{2}\text{O}_3 + \text{HF} \rightarrow \text{HF} \rightarrow \text{AlF}_{3} + \text{H}_2\text{O}
\]

Al2O3 with HF. This reaction is shown in Figure 2 and can be written as

\[
\text{Al}_{2}\text{O}_3(s) + 6\text{HF}(g) \rightarrow 2\text{AlF}_3(s) + 3\text{H}_2\text{O}(g) \quad (1)
\]

To investigate this fluorination reaction using QMS, 500 mg of Al2O3 powder was exposed to 9 Torr of HF at 300 °C. Figure 3 shows the mass spectrum results for the products produced during the fluorination reaction.

As predicted by the proposed mechanism in Figure 2, the predominant reaction product observed in Figure 3 is H2O at m/z = 18. The presence of F+ at m/z = 19 is also observed in
Figure 3 shows the mass spectrum produced during this ligand-exchange reaction of Al(CH₃)₃ with AlF₃. This reaction was examined by exposing 9 Torr of Al(CH₃)₃ to the HF-fluorinated Al₂O₃ powder. The peaks at m/z = 15 is higher than expected from the TMA fragmentation pattern because TMA can produce CH₄ by reaction with HF on the surface of the HF-fluorinated Al₂O₃ powder. The largest mass fragment is observed at m/z = 57 corresponding to Al(CH₃)₅⁺. The peaks at m/z = 42, 27, and 15 correspond to Al(CH₃)³⁺, Al⁺, and CH₃⁺, respectively. The parent molecular ion is observed at m/z = 72 for Al(CH₃)₅⁺ and has a small relative abundance of 1.8%. These peaks for Al(CH₃)₅⁺ are observed because excess Al(CH₃)₃ reactant was used to ensure a complete reaction with the HF-fluorinated Al₂O₃ powder.

In addition to the mass peaks for the TMA reactant, the predicted product for the ligand-exchange reaction between TMA and AlF₃ is DMAF. DMAF is believed to be the volatile etch product because DMAF has a vapor pressure of 80 Torr at 100 °C. DMAF should be observed at m/z = 76. However, Figure 4 shows that only a very small signal is observed at m/z = 76. The peak at m/z = 76 has a low relative abundance of 1.9%.

Instead of observing a significant peak at m/z = 76 for DMAF, larger peaks at m/z = 133, 137, and 213 are observed in Figure 4. These peaks at m/z = 133, 137, and 213 correspond to the molecular ions Al₁F₆(CH₃)³⁺, Al₁F₆(CH₃)⁵⁺, and Al₁F₆(CH₃)⁷⁺, respectively. The parent molecular ion at m/z = 213 corresponds to Al₁F₆(CH₃)⁷⁺. This peak could result from the ionization of Al₁F₆(CH₃)⁷⁺. This trimer etch product is similar to a trimer of DMAF that has lost one CH₃ group.

DMAF forms after two ligand-exchange reactions of TMA with AlF₃. A dimer formed from two DMAF molecules could also form after one ligand-exchange reaction of TMA with AlF₃. A dimer formed from two DMAF molecules. The molecular ion at m/z = 137 corresponding to Al₁F₆(CH₃)⁵⁺ may originate from Al₁F₆(CH₃) and TMA. However, Figure 4 shows that there is no signal observed at m/z = 80 for Al₁F₆(CH₃). If the molecular ion at m/z = 137 is formed from Al₁F₆(CH₃) and TMA, then no volatile Al₁F₆(CH₃) desorbs by itself and appears in the mass spectrum.

Figure 5 shows the proposed structures for the molecular ions Al₁F₆(CH₃)³⁺, Al₁F₆(CH₃)⁵⁺, and Al₁F₆(CH₃)⁷⁺ at m/z = 133, 137, and 213, respectively. The bridge bonds between the Al metal centers are shown by the dashed lines.

The dimers and trimer of DMAF could form on the surface and then desorb as dimers and trimers. Alternatively, the dimers and trimers could form in the gas phase after DMAF desorbs as a monomer from the surface. To distinguish between these two possibilities, additional experiments were performed under different reaction conditions. The formation of the dimers and trimers in the gas phase should be more favorable at higher partial pressures of DMAF. Dimers and trimers should be less probable at much lower partial pressures of TMA and product DMAF.

Experiments were performed under viscous flow conditions at much lower TMA pressures. 500 mg of Al₂O₃ powder was initially fluorinated with HF to form an HF-fluorinated Al₂O₃ surface. TMA was then flowed continuously through the
Because of the stability of CH₃ bridge bonding between the Al₃F(CH₃)₄ dimer of DMAF with itself (DMAF + DMAF) is also
ion current for the peak at m/z 133, 137, and 213 respectively. The ion currents were less than the ion currents during the static exposures. In addition, the ion current for the m/z = 137 peak was higher than the ion current for the m/z = 133, 137, and 213 respectively. The ion currents were less than the ion currents during the static exposures. In addition, the ion current for the m/z = 137 peak was higher than the ion current for the m/z = 133, 137, and 213 peaks at the much lower TMA pressure of 300 mTorr. The comparison of the ions detected after the ligand-exchange reaction on HF-fluorinated Al₂O₃ powder in Figure 6a shows the molecular ions of Al₂(CH₃)₃ and Al₂F(CH₃)₃ after leaving a gas nozzle at 80 °C. DMAP also is detected as a tetramer in freezing benzene. There is a possibility that the dimer and trimer molecular ions are derived from larger multimers of DMAF. However, the possible molecular ions at higher mass that would be consistent with a tetramer or other multimer were negligible.

**Ligand-Exchange Reaction between Al(CH₃)₃ and AlF₃**

The fluorination of Al₂O₃ with HF produces a surface layer of AlF₃ or AlO₂F₃ oxyfluorides. The previous section explored the ligand-exchange reaction between Al(CH₃)₃ and HF-fluorinated Al₂O₃ powder. For a comparison of the ligand-exchange reaction on HF-fluorinated Al₂O₃ and AlF₃ experiments can be performed using AlF₃ powder. Substituting AlF₃ powder for HF-fluorinated Al₂O₃ powder avoids the HF fluorination of Al₂O₃. The AlF₃ powder can also reveal the differences between the ligand exchange of Al(CH₃)₃ on AlF₃ and HF-fluorinated Al₂O₃ that may contain a surface layer of AlF₃ or AlO₂F₃ oxyfluorides.

The reaction of TMA with AlF₃ powder was performed in the same manner as the reaction of Al(CH₃)₃ with HF-fluorinated Al₂O₃ powder. 500 mg of AlF₃ powder was placed in the stainless steel mini-conflet nozzle and contained by the stainless steel mesh. The AlF₃ powder was exposed to TMA at a pressure of 9 Torr at 300 °C. The volatile products were then detected by the in situ QMS using the same conditions employed for the HF-fluorinated Al₂O₃ powder.

The comparison of the ions detected after the ligand-exchange reaction of TMA with HF-fluorinated Al₂O₃ or AlF₃ is displayed in Figure 6. Figure 6a shows the molecular ions detected during the ligand exchange between TMA and HF-fluorinated Al₂O₃ powder. Figure 6b shows the molecular ions detected during the ligand exchange between TMA and AlF₃ powder. The two mass spectra are very similar. The ion signal at m/z = 15 corresponding with CH₄ is larger for TMA reacting with the HF-fluorinated Al₂O₃ powder in Figure 6a compared with TMA reacting with the AlF₃ powder in Figure 6b. The residual HF present in the chamber after HF exposures to form HF-fluorinated Al₂O₃ may react with TMA to produce additional CH₄. In addition, the same ions consistent with the ionization of dimer products at m/z = 133 and 137 and trimer products m/z = 213 are produced when
experiments, 500 mg of AlF₃ powder was placed in the stainless steel mini-conflat sample holder and exposed to 9 Torr of AlCl(CH₃)₂ at 300 °C. Figure 7 shows the QMS results. The large peak at m/z = 28 amu is from the fragmentation of AlCl(CH₃)₂ and is attributed to AlH⁺. Peaks at m/z = 92, 57, 42, and 14 are also associated with the cracking pattern for AlCl(CH₃)₂.

In addition to the mass peaks for AlCl(CH₃)₂ and its fragmentation pattern, sizable peaks are also observed at m/z = 133, 137, and 213 in Figure 7. The peaks at m/z = 133 and 137 correspond to the Al₃F₃Cl(CH₃)₄⁺ and Al₂F₂Cl(CH₃)₂⁺ molecular ions. The peak at m/z = 213 corresponds to the Al₃F₃Cl(CH₃)₄⁺ molecular ion. These peaks are in agreement with the spectra in Figures 4 and 6 for the ligand exchange of TMA with either HF-fluorinated Al₂O₃ or AlF₃. The similarity of the results for TMA and DMAC argues that the dominant ligand-exchange reaction is the ligand transfer of CH₃ from either TMA or DMAC to AlF₃.

There are also some mass peaks that are consistent with ligand transfer of Cl from DMAC to AlF₃. Figure 8 shows an expanded scale of the mass spectrum from m/z = 150 to m/z = 300 amu after the ligand-exchange reaction between DMAC and AlF₃. The peak at m/z = 153 corresponds to the ionization of the Al₃F₃Cl(CH₃)₄⁺ dimer to produce the Al₃F₃Cl(CH₃)₄⁺ molecular ion after losing one CH₃ group. The peak at m/z = 157 corresponds to the ionization of the Al₂F₂Cl(CH₃)₂⁺ dimer to produce the Al₂F₂Cl(CH₃)₂⁺ molecular ion after losing one CH₃ group. The Al₂F₂Cl(CH₃)₂⁺ and Al₂F₂Cl(CH₃)₂⁺ ions have relative abundances of 1.55% and 0.75%, respectively. The peak at m/z = 233 is believed to correspond to the ionization of the Al₃F₃Cl(CH₃)₄ trimer to produce the Al₃F₃Cl(CH₃)₄⁺ molecular ion. These assignments were confirmed by the natural isotopic abundances for chlorine. The isotopic distributions were generated using the Scientific Instrument Services, Inc., isotope distribution calculator. The proposed structures of these molecular ions are shown in Figure 9. The bridge bonds between the Al metal centers are again shown by the dashed lines.

Additional smaller peaks are also present in Figure 8. The peak clusters at m/z = 165, 169, 173, and 177 correspond to molecular ions from mixed-oxy-halogen dimers. These ions are
attributed to Al₂OCl(CH₃)₄⁺ at m/z = 165, Al₂OFCl(CH₃)₃⁺ at m/z = 169, Al₂OF₂Cl(CH₃)₂⁺ at m/z = 173, and Al₂F₃OCl(CH₃)⁺ at m/z = 177. The AlF₃ powder likely contains a surface oxide that provides the oxygen for these mixed-oxy-halogen dimers. These species were not observed earlier after TMA exposures on AlF₃ powder. Therefore, chlorine from DMAC may be necessary to form these mixed-oxy-halogen dimers. There are also small peaks at m/z = 181, 183, 185, 187, and 197 that may be derived from fragments of larger mixed-halogen trimers.

**Reaction between SiCl₄ and TiCl₄ with AlF₃.** Previous studies have revealed that SiCl₄ and TiCl₄ are unable to etch HF-fluorinated Al₂O₃.⁹,¹⁹ These results were explained by reaction thermochemistry. The ligand-exchange reaction between SiCl₄ and AlF₃ is not thermochemically favorable. The reaction ⁴/₃AlF₃ + SiCl₄(g) → ⁴/₃AlCl₃(g) + SiF₄(g) has a positive standard free energy change of ΔG° = +29 kcal at 300 °C.⁵⁰ Similarly, the ligand-exchange reaction between TiCl₄ and AlF₃ is also thermochemically unfavorable. The reaction ⁴/₃AlF₃ + TiCl₄(g) → ⁴/₃AlCl₃(g) + TiF₄(g) has a positive standard free energy change of ΔG° = +71 kcal at 250 °C.⁵⁰

The reactions of SiCl₄ and TiCl₄ with AlF₃ were explored using *in situ* QMS studies to confirm that SiCl₄ and TiCl₄ do not yield Al-containing etch products during ligand-exchange reactions with AlF₃.

The experiments were performed by placing 500 mg of AlF₃ powder in the stainless steel mini-conflat sample holder. The AlF₃ powder was then exposed to 9 Torr of SiCl₄ at 300 °C. Figure 10a shows the mass spectrum of SiCl₄ in the reactor with no AlF₃ powder. This mass spectrum is equivalent to the reference spectrum for SiCl₄ from the NIST database. The mass spectrum after SiCl₄ exposure to the AlF₃ powder is shown in Figure 10b. The results in Figure 10b are nearly equivalent to the mass spectrum for SiCl₄ in Figure 10a. The natural isotopic abundances for both chlorine and silicon affect the mass spectrum for SiCl₄.

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not etch HF-fluorinated Al2O3.9 Although there are no Al-containing reaction products, there are some additional smaller peaks in Figure 10b that are not in the mass spectrum of SiCl4. Figure 10c shows the mass spectrum in Figure 10b with the mass spectrum for SiCl4 removed using the peak at m/z = 133 for calibration. The removal of the SiCl4 mass spectrum reveals two clusters of peaks at m/z = 117 and m/z = 152.

The peaks in the cluster at m/z = 152 correspond to SiFCl3+. These peaks could be formed by a single ligand-exchange reaction between SiCl4 and the AlF3 surface. This ligand transfer between SiCl4 and AlF3 would also form AlClF2 on the surface. This ligand-exchange product is not volatile. There are also peaks in the mass spectrum in Figure 10c in a cluster at m/z = 117. This cluster corresponds to SiFCl2+. The SiFCl2+ is likely the result of SiFCl3+ fragmentation. SiFCl3 and HCl could also be formed by the reaction of SiCl4 with residual HF in the reactor. However, there is no mass signal at m/z = 35 or 37 in Figure 10c after the removal of the SiCl4 mass spectrum.

Experiments were also performed for TiCl4 interacting with AlF3. Similar to SiCl4, TiCl4 does not produce Al-containing etch products. However, there are halogen-exchange species formed by reaction with the AlF3 surface. Figure 11a shows the mass spectrum for TiCl4 in the reactor with no AlF3 powder. This mass spectrum matches the reference spectrum for TiCl4 in the NIST database. Figure 11b shows the mass spectrum after exposing 500 mg of AlF3 powder to 9 Torr of TiCl4 at 250 °C. The main species observed in Figure 11b are from TiCl4 and its respective fragments. The natural isotopic abundances for both chlorine and titanium lead to the mass clusters observed in the mass spectrum for TiCl4.

Figure 11c shows the mass spectrum in Figure 11b with the mass spectrum for TiCl4 removed using the peak at m/z = 153 for calibration. The removal of the TiCl4 mass spectrum reveals peaks associated with TiFCl3 resulting from a single ligand-exchange reaction between TiCl4 and the AlF3 surface. The cluster of peaks at m/z = 172 is assigned to TiFCl3+. Subsequent fragmentation of TiFCl3+ yields clusters of peaks at m/z = 137, 102 and 70, corresponding to TiFCl2+, TiFCl+, and Cl+2, respectively. Additional peaks at m/z = 67 and 19 correspond to TiF+ and F+, respectively.

Characterization of Thermal Al2O3 ALE Using Transmission Electron Microscopy (TEM). TEM was used to confirm that HF and Al(CH3)3 etch Al2O3 at 300 °C. 100 cycles of Al2O3 ALE was first deposited on W powder using static exposures of Al(CH3)3 and H2O at 200 °C. The static exposures were at 9 Torr for 60 s. The sample was then removed and imaged using TEM. The 100 cycles of Al2O3 ALE resulted in ~16 nm of conformal Al2O3 on the W particles as shown in Figure 12a.

The reactor temperature was then increased to 300 °C, and 50 cycles of thermal Al2O3 ALE was performed using 9 Torr and 60 s static exposures of HF and Al(CH3)3. The resulting products were monitored using in situ QMS. The products were consistent with the products previously observed while etching the HF-fluorinated Al2O3 powder as displayed in Figure 4. The powder sample was then removed from the reactor and imaged using TEM. After 50 thermal Al2O3 ALE cycles, the thickness of the Al2O3 coating was reduced to a thickness of ~13 nm as shown by the TEM image in Figure 12b. The Al2O3 thickness is still smooth and conformal on the W powder. The conformality demonstrates that the thermal Al2O3 ALE is isotropic on these Al2O3 films on the W powder.

The same sample was placed back into the reactor and exposed to another 50 cycles of thermal Al2O3 ALE cycles at 300 °C. The Al2O3 coating was further reduced to a thickness of ~5 nm as displayed by the TEM image in Figure 13a. The Al2O3 thickness remains smooth and conformal on the W powder, consistent with isotropic thermal Al2O3 ALE. The same sample was placed back into the reactor and exposed to another 50 cycles of thermal Al2O3 ALE cycles at 300 °C. After these additional cycles, the Al2O3 coating was completely removed by the thermal Al2O3 ALE as displayed by the TEM image in Figure 13b.

Computational Analysis. Calculations were performed to investigate the stability of the proposed Al2F2(CH3)4 and Al2F2(4(CH2)3)4 dimer products compared with the monomer products. The reaction of Al(CH3)3 with AlF3 was initially studied to determine whether an activation barrier was present during ligand exchange and whether the ligand-exchange reaction was energetically favorable. A schematic of this reaction is shown in Figure 14. The free energy difference, ΔG, at T = 300 °C was calculated between the Al(CH3)3 and AlF3 reactants and the predicted monomer products. The monomer products were DMAF and AlF2(CH3)3. The free energy difference was also calculated between the Al(CH3)3 and AlF2 reactants and the intermediate during the ligand-exchange reaction.

The DFT structural optimizations did not reveal an activation barrier between the reactants and products. The

Figure 11. (a) Mass spectrum of TiCl4 in reactor with no AlF3. (b) Mass spectrum after ligand-exchange reaction between TiCl4 and AlF3 powder at 300 °C. (c) Mass spectrum from (b) with the TiCl4 mass spectrum removed using the peak at m/z = 153 for reference.
thermochemistry calculations determined that the intermediate dimer complex between TMA and AlF$_3$ during ligand exchange is lower in free energy than the AlF$_3$ and Al(CH$_3$)$_3$ reactants by $\Delta G$(300 °C) = −0.763 eV as shown in Figure 14. The intermediate dimer complex during ligand exchange is shown prior to any rearrangement. In comparison, the AlF(CH$_3$)$_2$ and AlF$_2$(CH$_3$)$_2$ monomer products are lower in free energy than the AlF$_3$ and Al(CH$_3$)$_3$ reactants by $\Delta G$(300 °C) = −0.678 eV. The intermediate dimer complex is lower in free energy than the monomer products by $\Delta G$(300 °C) = −0.085 eV.

These results are consistent with the QMS observation of volatile dimer species as the main products during the ligand-exchange reaction between TMA and AlF$_3$. The rearrangement of F atoms and CH$_3$ groups within the intermediate dimer complex may also lead to free energies for isomers that are even lower than $\Delta G$(300 °C) = −0.763 eV shown in Figure 14. These more stable dimer complexes are even more likely to favor the observation of volatile dimer species as etch products.

Theoretical calculations were used to examine the stability of all possible structures formed from the dimerization of the products from the reaction between AlF$_3$ and Al(CH$_3$)$_3$. The possible dimer structures are shown in Figure 15. Their $\Delta G$(300 °C) values and identifying names are given in Table 1. The $\Delta G$ values at 300 °C for all dimers were calculated by stoichiometrically balancing the starting reactants, AlF$_3$ and Al(CH$_3$)$_3$, and the given dimer. In other words, $X$ and $Y$ were determined for the general reaction $XAIF_3 + YAIC(CH_3)_3 \rightarrow$ dimer in question. As an explicit example, the balanced
reaction for the formation of the Al2F2(CH3)4 dimer in Figure 15 is $\frac{2}{3}$AlF3 + $\frac{4}{3}$Al(CH3)3 → Al2F2(CH3)4.

Organizing all the possible dimer combinations by terminal groups and bridging pairs revealed interesting correlations. The dimer molecules containing fluorine bridge bonds were significantly more stable than those containing methyl bridge bonds. This trend is consistent with the ability of fluorine to form bimetallic bridge bonds.51 The free energy of formation for dimers grows more positive, i.e., unfavorable, with the addition of each methyl bridging ligand. This instability is partially caused by the entropic cost of immobilizing methyl ligands in the bridging positions.

The observation of volatile products will be dependent on the stability of the dimer and the ability of the dimer to leave

Table 1. Possible Dimers versus Number of F and CH3 Species for All Possible Structures of F and CH3 in Bridge or Terminal Positions

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<tr>
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The identifier refers to Figure 15. $\Delta G$ is the free energy of formation of the dimer from the AlF3 and Al(CH3)3 reactants.

Figure 14. Free energy diagram showing reactants, the intermediate dimer complex, and products for ligand-exchange reaction between Al(CH3)3 and AlF3. $\Delta G$ values were calculated using optimized geometries and frequencies from UMN15 with energies from UCCSD(T).

Figure 15. All possible dimer structures and their respective $\Delta G$ values organized by bridging pairs and terminal groups. The $\Delta G$ values were determined by subtracting the free energies of the AlF3 and Al(CH3)3 reactants, multiplied by the appropriate stoichiometric coefficients, from the free energy of the dimer product. For example, the balanced reaction for the formation of the Al2F2(CH3)4 dimer in Figure 15g is $\frac{2}{3}$AlF3 + $\frac{4}{3}$Al(CH3)3 → Al2F2(CH3)4.
the surface. The Al$_2$F$_2$ dimer species displayed in Figure 15a (di-$\mu$-fluorido-tetrafluorodialuminum) is unlikely to be observed under the thermal Al$_2$O$_3$ ALE reaction conditions. AlF$_3$ has a high melting temperature of 1290 °C. This high stability is attributed to the strong Al–F–Al bridge bonding between AlF$_3$ molecules. The fully fluorinated terminal positions of the Al$_2$F$_2$ dimer will also have Al–F–Al bonds to surface Al atoms. The strength of these Al–F–Al bonds will hinder the desorption of the Al$_2$F$_2$ dimer.

The Al$_2$(CH$_3$)$_6$ dimer species illustrated in Figure 15u (di-$\mu$-methyl-tetramethyldialuminum) is also not likely to be observed under the thermal Al$_2$O$_3$ ALE reaction conditions. The Al–CH$_3$–Al bridge bonding between Al(CH$_3$)$_3$ molecules is much weaker than Al–F–Al bridge bonding. The Al$_2$(CH$_3$)$_6$ dimer species is also not stable at higher temperatures.35

The expected volatile products are dimers with Al–F–Al bridge bonds and CH$_3$ ligands in the terminal positions. The Al–F–Al bridge bonds lead to dimer stability. The CH$_3$ ligands in the terminal positions enable the dimer to leave the surface. Based on these two observations, the ideal dimer with both stability and the ability to leave the surface would be Al$_2$F$_2$Me$_4$ illustrated in Figure 15g (di-$\mu$-fluorido-tetramethyldialuminum).

Figure 15 can also illustrate how rearrangement of F atoms and CH$_3$ groups within a dimer complex to form various isomers can lead to lower free energies. For example, the F atoms and CH$_3$ groups in Al$_2$F$_2$Me$_4$ can be rearranged to yield Figure 15s (di-$m$-methyl-trans-dimethyldi fluoridoluminum), Figure 15m (m-$m$-methyl-fluorido-trimethylfluorido-dialuminum), or Figure 15g (di-$m$-fluorido-tetramethyldialuminum). The free energies of these isomers shown in Figures 15s, 15m, and 15g are $\Delta G(300$ °C) = +0.47, −0.80, and −1.73 eV, respectively. During rearrangement from Figure 15s to Figure 15g, the F atoms will move to obtain the more stable bridging positions in the dimer.

The ion currents of the various observed dimers are consistent with dimers that have Al–F–Al bridge bonds and CH$_3$ ligands in the terminal positions. Figure 16 shows the ion currents for the dimers for the ligand-exchange reaction between TMA and HF-fluorinated Al$_2$O$_3$ surface at 300 °C as a function of number of CH$_3$ groups in the dimer. The dashed line is intended only to guide the eye. The F is always placed in an Al–F–Al bridge bond prior to a terminal position in the dimer. The lowest ion signal is for Al$_2$F$_2$ displayed in Figure 15a (di-$\mu$-fluorido-tetrafluorodialuminum). This dimer can not easily leave the surface because of strong Al–F–Al bonds.

The highest ion signals are for Al$_2$FMe$_3$ ($\mu$-methyl-$\mu$-fluoridotetramethylaluminum) shown in Figure 15n and Al$_2$F$_2$Me$_4$ (di-$\mu$-fluoridotetramethylaluminum) displayed in Figure 15g. These dimers have one or two strong Al–F–Al bridge bonds and four terminal CH$_3$ ligands that facilitate desorption from the AlF$_3$ surface. The ion currents decrease as F atoms are progressively placed in the terminal positions for Al$_2$F$_2$Me$_4$ shown in Figure 15f (di-$\mu$-fluorido-trimethylfluoridoluminum), Al$_2$F$_2$Me$_2$ displayed in Figures 15d and 15e (di-$\mu$-fluorido-cis-dimethylfluoridoaluminum and di-$\mu$-fluorido-trans-dimethylfluoridoaluminum), and Al$_2$F$_3$Me$_2$ illustrated in Figure 15b (di-$\mu$-fluoriodimethylfluoridoluminum).

Based on the theoretical and QMS results, the dominant species leaving the HF-fluorinated Al$_2$O$_3$ surface during the ligand-exchange reaction with TMA are Al$_2$F($\text{CH}_3$)$_3$ shown in Figure 15n ($\mu$-methyl-$\mu$-fluoridotetramethylaluminum) and Al$_2$F$_2$($\text{CH}_3$)$_4$ displayed in Figure 15g (di-$\mu$-fluorido-tetramethyldialuminum). Upon ionization, these dimers lose a CH$_3$ group and are detected as Al$_2$F($\text{CH}_3$)$_2$ at $m/z$ = 133 and Al$_2$F$_2$($\text{CH}_3$)$_3$ at $m/z$ = 137. The Al$_2$F$_3$($\text{CH}_3$)$_3$ trimer is also expected to have three Al–F–Al bridge bonds and four terminal CH$_3$ ligands as shown in Figure 5. This trimer is detected as Al$_2$F$_3$($\text{CH}_3$)$_3$ at $m/z$ = 213.

IV. CONCLUSIONS

In situ QMS was used to characterize the volatile etch species produced during the fluorination and ligand-exchange reactions during thermal Al$_2$O$_3$ ALE. The thermal Al$_2$O$_3$ ALE was performed using HF and Al(CH$_3$)$_3$ (trimethylaluminum, TMA) at 300 °C. The QMS measurements showed that H$_2$O is the predominant product produced during the fluorination of Al$_2$O$_3$ powder with HF. During the ligand-exchange reaction between TMA and HF-fluorinated Al$_2$O$_3$ powder, the QMS results revealed prominent molecular ions at Al$_2$F($\text{CH}_3$)$_2$ at $m/z$ = 133 and Al$_2$F$_2$($\text{CH}_3$)$_3$ at $m/z$ = 137. These molecular ions are believed to result from dimers of AlF($\text{CH}_3$)$_2$ (dimethylaluminum fluoride (DMAF) with itself (DMAF + DMAF) or with TMA (DMAF + TMA) after the loss of a methyl group. Another important molecular ion is a trimer detected as Al$_2$F$_3$($\text{CH}_3$)$_3$ at $m/z$ = 213.

Nearly equivalent results were observed for TMA exposures on AlF$_3$ powder. This equivalence indicates that the surface of HF-fluorinated Al$_2$O$_3$ powder and the surface of AlF$_3$ powder are nearly identical for the TMA ligand-exchange reaction. Thermal Al$_2$O$_3$ ALE was confirmed by TEM studies of Al$_2$O$_3$ ALD films on W wafers. TEM images before and after various numbers of thermal Al$_2$O$_3$ ALE cycles using HF and TMA as the reactants revealed that the etch process was uniform and conformal.

By use of AICI($\text{CH}_3$)$_2$ (dimethylaluminum chloride, (DMAC)) as the metal precursor for ligand exchange on AlF$_3$ powder, the main molecular ions observed by QMS were the dimers Al$_2$F($\text{CH}_3$)$_2$ at $m/z$ = 133 and Al$_2$F$_2$($\text{CH}_3$)$_3$ at $m/z$ = 137 and the trimer Al$_2$F$_3$($\text{CH}_3$)$_3$ at $m/z$ = 213. Mixed-halogen products, such as the dimers Al$_2$FCl($\text{CH}_3$)$_2$ at $m/z$ = 153 and Al$_2$F$_2$Cl($\text{CH}_3$)$_3$ at $m/z$ = 157 and the trimer
Al$_2$F$_4$(CH$_3$)$_2$, or Al$_2$F$_5$(CH$_3$)$_3$ dimers with 3, 4, or 5 methyl groups. Boulder for startup funds used to pay for allocations on the State University. The authors thank the University of Colorado 1532236), the University of Colorado Boulder, and Colorado the National Science Foundation (ACI-1532235 and ACI- the RMACC Summit supercomputer, which is supported by QMS results showing that the ion signals from the ligands. [AlClF$_2$] species formed after the ligand-exchange reaction are not able to desorb from the AlF$_3$ surface. Quantum chemical calculations verified that dimer products are energetically more stable than monomer products. In addition, dimer products with two Al–F–Al bridging bonds are the most stable and dimers with two Al–CH$_3$–Al bridging bonds are the least stable. These results also suggest that dimers with terminal CH$_3$ ligands are most able to desorb from the surface because these dimers need to break weak Al–CH$_3$–Al bridging bonds. This suggestion was supported by the QMS results showing that the ion signals from the Al$_2$F$_3$(CH$_3$)$_3$ or Al$_2$F(CH$_3$)$_4$ dimers with 4 or 5 methyl groups are much higher than the ion signals from the Al$_2$F$_4$(CH$_3$)$_4$, Al$_2$F$_5$(CH$_3$)$_2$, or AlF$_3$(CH$_3$)$_4$ dimers with 3, 4, or 5 fluorine ligands.

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
This research was funded by the Lam Research Corporation. Additional support was provided by the National Science Foundation (CHE-1609554 and CHE-1800584). The authors are also grateful to the Defense Advanced Research Projects Agency (DARPA) for seed funds to build the custom reactor with *in situ* QMS. J.E.T.S. gratefully acknowledges support from a fellowship through The Molecular Sciences Software Institute under NSF Grant AC11547580. This work utilized the RMACC Summit supercomputer, which is supported by the National Science Foundation (ACI-1532235 and ACI-1532236), the University of Colorado Boulder, and Colorado State University. The authors thank the University of Colorado Boulder for startup funds used to pay for allocations on the Summit supercomputer.

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