Thermal Atomic Layer Etching of Al₂O₃, HfO₂, and ZrO₂ Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures

Published as part of The Journal of Physical Chemistry virtual special issue "Hai-Lung Dai Festschrift".

Younghhee Lee and Steven M. George

Department of Chemistry, University of Colorado, Boulder, Colorado 80309, United States

ABSTRACT: Atomic layer etching (ALE) of Al₂O₃, HfO₂, and ZrO₂ was accomplished using sequential exposures with hydrogen fluoride (HF) as the fluorination reagent and dimethylaluminum chloride (DMAC, AlCl(CH₃)₂) as the metal reactant for ligand exchange. DMAC could provide either CH₃ or Cl ligands for the ligand-exchange reaction. The presence of the Cl ligand on DMAC led to efficient HfO₂ and ZrO₂ etching attributed to the formation of stable and volatile chloride species. In situ quartz crystal microbalance (QCM) measurement observed mass changes during Al₂O₃, HfO₂, and ZrO₂ ALE reactions at 200–300 °C. Al₂O₃, HfO₂, and ZrO₂ were etched linearly versus number of HF and DMAC sequential exposures. The QCM analysis confirmed that the HF and DMAC reactions were self-limiting versus reactant exposure. The QCM studies observed mass changes per cycle (M CPC) of −12.2 ng/(cm² cycle), −94.1 ng/(cm² cycle), and −75.6 ng/(cm² cycle) for Al₂O₃, HfO₂, and ZrO₂ ALE, respectively, at 250 °C. These M CPC correspond to Al₂O₃, HfO₂, and ZrO₂ etch rates of 0.39 Å/cycle, 0.98 Å/cycle, and 1.33 Å/cycle, respectively. In comparison, the AlF₃, HfF₄, and ZrF₄ surface layers were estimated to have thicknesses of 3.0 Å, 3.3 Å, and 4.4 Å on Al₂O₃, HfO₂, and ZrO₂, respectively. The magnitudes of these fluoride thicknesses have the same ordering as the etch rates for Al₂O₃, HfO₂, and ZrO₂ ALE, respectively. X-ray reflectivity (XRR) and spectroscopic ellipsometry measurements verified the etch rates for Al₂O₃ ALE. XRR analysis also confirmed smoothening of the etched Al₂O₃ film. The etch rates for Al₂O₃, HfO₂, and ZrO₂ ALE increased with temperature from 200 to 300 °C. A comparison of Al₂O₃, HfO₂, and ZrO₂ ALE using either HF and DMAC or HF and trimethylaluminum (TMA, Al(CH₃)₃) revealed that higher etch rates were observed for DMAC for all three materials. Cross-sectional transmission electron microscopy (TEM) studies also revealed that Al₂O₃ ALE on masked Al₂O₃ substrates was isotropic and selective in the presence of SiN and SiO₂. Because of the ability of DMAC to provide either CH₃ or Cl ligands during the ligand-exchange reaction, DMAC should be a very useful metal reactant for the thermal ALE of various materials.

I. INTRODUCTION

Atomic layer etching (ALE) is based on sequential, self-limiting surface reactions that remove a thin film with atomic level precision. Plasma ALE processes using sequential halogenation and bombardment by energetic inert ions or neutrals have been developed to accomplish anisotropic etching for >25 years. In contrast, thermal ALE for isotropic etching has been developed more recently using sequential fluorination and ligand-exchange reactions. Thermal ALE is useful to etch materials selectively with atomic layer control without damaging the underlying film. The first report of thermal Al₂O₃ ALE employed fluorination and ligand-exchange reactions with HF and Sn(acac)₂ as the reactants. The thermal ALE proceeds with the formation of a metal fluoride layer and the sequential removal of the metal fluoride by ligand exchange with a metal reactant. The HF and Sn(acac)₂ exposure sequence was also able to etch HfO₂, AlF₃, AlN, and ZrO₂. Another metal reactant, trimethylaluminum (TMA), was used together with HF to etch Al₂O₃ and HfO₂. TiCl₄ was used as the metal reactant together with HF to etch HfO₂ and ZrO₂. The use of different metal reactants for ligand exchange, such as Sn(acac)₂, TMA, DMAC, SiCl₄, and TiCl₄, had demonstrated selective etching of various materials by providing different ligands such as acac, CH₃, and Cl⁻. In the ligand-exchange reaction, the metal reagent accepts F⁻ from the metal fluoride and donates a ligand to the metal fluoride. One metal atom from the metal reagent, M, with ligand, L, and the other metal atom from the metal fluoride, M', with the fluoride ligand, F⁻, participate in the formation of a four-center transition state. This transition state is stabilized by Lewis acid–base interactions. The M atom in the metal reagent is commonly a Lewis acid. The F⁻ in the metal fluoride acts as a Lewis base. F⁻ favors the formation of fluoride bridging structures with two metal centers (M–F–M'). Because the M' atom in the metal fluoride is often a Lewis acid, a ligand

Received: May 20, 2019
Revised: July 3, 2019
Published: July 3, 2019
that can serve as a Lewis base is desirable for ligand transfer. The ligand transfer is favorable when the ligand is capable of forming a bridging structure (M—L—M').

TMA is one of the most useful metal reagents for Al₂O₃ atomic layer deposition (ALD) due to its high reactivity and high volatility. The reactivity and vapor pressure of dimethylaluminum chloride (Al₂Cl₆) are similar to TMA. The boiling points of DMAC and TMA are nearly the same at 126 and 130 °C, respectively. The use of DMAC for ALD is very promising because both CH₃ and Cl ligands on DMAC are available for ligand exchange. Many metal chlorides in groups 4–6 and groups 13–15 including AlCl₃, HfCl₄, and ZrCl₄ are stable and volatile. Many metal alkyls such as TMA and diethylzinc in groups 12–15 are also stable and volatile. Both stability and volatility are important for the reaction products to leave the surface after the ligand-exchange reaction. Metal reactants having different ligands, such as DMAC, can be versatile for the thermal ALD of various materials.

The Cl ligand has a stronger ability to form a bridging structure (M—L—M') than the CH₃ ligand. AlCl₃ is a solid at room temperature and undergoes sublimation at 180 °C. The dissociation energy for the AlCl₃ dimer (Al₂Cl₆ ↔ 2AlCl₃) is E₂ = 29.0 kcal/mol. In contrast, Al(CH₃)₃ is liquid with boiling point less than 130 °C. The dissociation energy of the TMA dimer (Al₂(CH₃)₆ ↔ 2Al(CH₃)₃) is E₂ = 20.2 kcal/mol. DMAC can form a dimeric structure analogous to a four-center transition state during the ligand-exchange reaction because of its Cl ligand. Although both Cl and CH₃ are possible in a bridging structure, Cl in the Al—Cl—Al bridging structure is much more favorable. A dimeric DMAC molecule in the gas phase was confirmed by electron diffraction and mass spectrometry. No measurable dissociation of dimeric DMAC was observed at 92–135 °C. In contrast, TMA shows ~50% dissociation at 150 °C and exists mostly as a monomer at 215 °C.

In this paper, in situ quartz crystal microbalance (QCM) measurements examined the thermal ALD of Al₂O₃, HfO₂, and ZrO₂ using sequential exposures of H₂ and DMAC at 200–300 °C. The etch rates and mass changes during the individual HF and DMAC reactions were investigated during thermal Al₂O₃, HfO₂, and ZrO₂ ALD at different temperatures. X-ray reflectivity (XRR) and spectroscopic ellipsometry analyses were also utilized to measure the film thicknesses versus number of ALD cycles to confirm the etch rates. DMAC was compared with TMA as a metal reactant to understand the role of the Cl ligand in DMAC. Cross-sectional transmission electron microscopy (TEM) studies after Al₂O₃ ALD on masked Al₂O₃ substrates were also employed to determine if thermal Al₂O₃ ALD using HF and DMAC was selective and isotropic.

II. EXPERIMENTAL SECTION

II.A. In Situ QCM Studies in a Viscous Flow Reactor.

The ALD and ALD reactions were performed in the same viscous flow, hot wall reactor. An in situ measurement of the mass change was conducted using a quartz crystal microbalance (QCM) in the reactor. The quartz crystal (gold coated and polished, 6 MHz RC, Colnatec) was placed in a sensor head (BS11-150, Inficon) and sealed with high-temperature epoxy (Epo-Tek H21D, Epoxy technology). The mass changes during the ALD and ALD reactions were measured by a thin-film deposition monitor (Maxtek TM-400, Inficon) with a mass resolution of 0.375 ng/cm².

Each reaction temperature at 200, 225, 250, 275, and 300 °C was maintained with a proportional-integral-derivative (PID) temperature controller (2604, Eurotherm) that held the set point temperature to within ±0.04 °C. Change of the temperature required 2 h of stabilization to minimize the effect of temperature fluctuations during the QCM measurements. The pressure in the reactor was monitored by a bakeable capacitance manometer (Baratron 121A, MKS).

A constant flow of 150 sccm of ultra high purity (UHP) N₂ gas into the reactor was regulated by mass flow controllers (Type 1179A, MKS). An additional flow of 20 sccm of N₂ gas defined using a metering bellows-sealed valve (SS-4BMG, Swagelok) prevented deposition on the backside of the QCM crystal. The total N₂ gas flow of 170 sccm produced a base pressure of ~1 Torr in the reactor. The reactor was pumped by a mechanical pump (Pascal 201SSD, Alcatel).

The Al₂O₃, HfO₂, and ZrO₂ ALD reactions were accomplished using sequential exposures of DMAC (97%, Sigma-Aldrich) and HF derived from HF–pyridine (70 wt %, Sigma-Aldrich). The use of HF from the HF–pyridine solution enabled the safer handling of anhydrous HF. Mass spectroscopy has confirmed that a negligible pyridine partial pressure is present over the HF–pyridine solution. A vapor pressure of 90–100 Torr for HF over the HF–pyridine solution has been measured at room temperature. The HF–pyridine solution was transferred to a gold-plated stainless steel bubbler in a dry N₂-filled glovebag. The HF–pyridine and DMAC reactants were maintained at room temperature. DMAC and HF exposures produced pressure transients of 40 mTorr and 80 mTorr, respectively, on top of the base pressure of ~1 Torr in the reactor.

The Al₂O₃ films were grown on the QCM crystal with Al₂O₃ ALD using TMA (97%, Sigma-Aldrich) and H₂O (Chromasolv for HPLC, Sigma-Aldrich). The HfO₂ and ZrO₂ ALD reactions were conducted using tetrakis(dimethylamido) hafnium (TDMAH, 99.99%, Sigma-Aldrich) and tetrakis(ethylmethylamido) zirconium (TEZAM, 99.99%, Sigma-Aldrich), respectively, together with H₂O. The TMA and H₂O reactants were maintained at room temperature. The bubbler temperatures for TDMAH and TEMAZ were 67 and 112 °C, respectively.

II.B. X-ray Reflectivity and Spectroscopic Ellipsometry. Ex situ X-ray reflectivity (XRR) scans were recorded by a high-resolution X-ray diffractometer (Bede D1, Jordan Valley Semiconductors) using Cu Kα (λ = 1.5403 Å) radiation. The filament voltage and current in the X-ray tube were 40 kV and 35 mA, respectively. A 10 arcsec step size and a 5 s acquisition time were used for recording all XRR scans with a range of 300–6000 arcsec. The analysis software (Bede REFS, Jordan Valley Semiconductors) fitted the XRR scans to determine film thickness, film density, and surface roughness.

Ellipsometry was performed using a spectroscopic ellipsometer (M-2000, J. A. Woollam) with a range of 240–1700 nm and an incidence angle of 75°. The analysis software (CompleteEASE, J. A. Woollam) determined the thicknesses and refractive index of the film by fitting the Ψ and Δ values based on a Sellmeier model.

For the XRR and ellipsometry studies, Al₂O₃ ALD films were also grown on boron-doped Si(100) wafers (p-type, Silicon Valley Microelectronics). The bare Si substrates were sliced into samples with dimensions of 2.5 cm × 2.5 cm prior.
to the $\text{Al}_2\text{O}_3$ ALD. These samples were then used as the substrates for the $\text{Al}_2\text{O}_3$ ALE studies.

III. RESULTS AND DISCUSSION

III.A. In Situ QCM Measurements for Thermal $\text{Al}_2\text{O}_3$ ALE. Figure 1 shows the mass change observed by QCM measurements during 100 cycles of $\text{Al}_2\text{O}_3$ ALE at 250 °C using sequential exposures of DMAC and HF. The $\text{Al}_2\text{O}_3$ film on the QCM crystal was prepared by 100 cycles of $\text{Al}_2\text{O}_3$ ALD using TMA and $\text{H}_2\text{O}$ at 250 °C. Each ALE cycle was defined by a DMAC dose of 2 s, a first $\text{N}_2$ purge of 30 s, a HF dose of 1.0 s, and a second $\text{N}_2$ purge of 30 s. This reaction sequence is denoted as 2–30–1–30.

The mass change versus time in Figure 1 is linear with a mass change per cycle (MCPC) of $-12.2$ ng/(cm² cycle). This MCPC corresponds to an etch rate of 0.39 Å/cycle based on the $\text{Al}_2\text{O}_3$ ALD film density of 3.1 g/cm³ obtained by XRR measurements. All $\text{Al}_2\text{O}_3$ ALE cycles show mass loss except during the first ALE cycle. Mass gains of $\Delta M_{\text{DMAC}} = 54$ ng/cm² and $\Delta M_{\text{HF}} = 22$ ng/cm² were observed during the first cycle.

The mass gain for $\Delta M_{\text{DMAC}}$ during the first DMAC exposure is caused by the formation of $\text{AlCl}_3^*$ and $\text{AlCl}_4^*$ surface species on the initial hydroxylated $\text{Al}_2\text{O}_3$ substrate. The asterisks designate surface species. HF then reacts with the $\text{AlCl}_3^*$ and $\text{AlCl}_4^*$ surface species to form $\text{AlF}_3$ surface species. HF can also react with the underlying $\text{Al}_2\text{O}_3$ film to form an $\text{AlF}_3$ or $\text{AlF}_2\text{O}_3$ surface layer. The fluorination reaction $\text{Al}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O}$ is thermodynamically favorable with a standard free energy change of $\Delta G^\circ = -54$ kcal/mol at 250 °C. This first reaction cycle creates the initial $\text{AlF}_3$ or $\text{AlF}_2\text{O}_3$ layer on the $\text{Al}_2\text{O}_3$ substrate.

Figure 2 displays the mass changes during three sequential $\text{Al}_2\text{O}_3$ ALE cycles at 250 °C in the steady state region of Figure 1. Each ALE cycle leads to repeatable mass changes. The DMAC exposure leads to a rapid mass decrease followed by little additional change during the purge time. A mass gain of $\Delta M_{\text{HF}} = 5$ ng/cm² was observed after 1.0 s of HF exposure. This mass gain is attributed to the reaction of HF with $\text{AlCl}_3^*$ and $\text{AlCl}_4^*$ surface species to form $\text{AlF}_3$ surface species in addition to the fluorination of $\text{Al}_2\text{O}_3$ to form an $\text{AlF}_3$ or $\text{AlF}_2\text{O}_3$ surface layer. This $\text{AlF}_3$ or $\text{AlF}_2\text{O}_3$ surface layer is then removed by the ligand-exchange reaction during the subsequent DMAC exposure.

Figure 3 shows the MCPC and the $\Delta M_{\text{DMAC}}$/MCPC ratio during the 100 cycles of $\text{Al}_2\text{O}_3$ ALE at 250 °C shown in Figure 1. The variation in the $\Delta M_{\text{DMAC}}$, $\Delta M_{\text{HF}}$, and MCPC values is ±0.3 ng/(cm² cycle) over the 100 cycles. The $\Delta M_{\text{DMAC}}$ and $\Delta M_{\text{HF}}$ mass changes are constant except during the first few cycles. The MCPC is expressed by MCPC = $\Delta M_{\text{DMAC}}$ + $\Delta M_{\text{HF}}$. 

Figure 2. Enlargement of linear region of Figure 1 showing the individual mass changes during the sequential DMAC and HF exposures at 250 °C using the reaction sequence of 2–30–1–30.

Figure 3. (a) Mass change after the DMAC exposure ($\Delta M_{\text{DMAC}}$), mass change after the HF exposure ($\Delta M_{\text{HF}}$), and mass change per cycle (MCPC) versus number of ALE cycles at 250 °C. (b) $\Delta M_{\text{DMAC}}$/MCPC ratio versus number of ALE cycles.
ΔM_{DMAC}. Figure 3a displays MCPC, ΔM_{DMAC}, and ΔM_{HF} for the 100 Al_{2}O_{3} ALE cycles at 250 °C. MCPC = -12.2 ng/(cm² cycle) was obtained in steady state after a short nucleation period. Figure 3b shows the ΔM_{DMAC}/MCPC ratio during the same 100 Al_{2}O_{3} ALE cycles. A ΔM_{DMAC}/MCPC ratio = 1.4 was obtained in steady state. This ΔM_{DMAC}/MCPC ratio can be used to clarify the mechanism of the Al_{2}O_{3} ALE reaction.\(^{8,10-12,14}\)

In situ QCM experiments also examined the self-limiting nature of the Al_{2}O_{3} ALE reactions during DMAC and HF exposures at 250 and 300 °C. Figure 4a and 4b show the mass changes monitored as a function of exposure time for DMAC and HF, respectively, at 250 and 300 °C. Figure 4a shows ΔM_{DMAC}, the mass change after the DMAC exposure, with different DMAC exposure times using a single 1.0 s exposure of HF. This reaction sequence can be expressed as: Al_{2}O_{3} + 3HF → AlF_{3} + HCl + 2CH_{4}. Similar results were observed for AlF_{3} ALD using TMA and HF as the reactants at T < 250 °C. At temperatures >250 °C, the same TMA and HF reactants yield Al_{2}O_{3} ALE.\(^{15}\)

Figure 5 shows a 1 s HF exposure at 250 °C. This self-limiting behavior is consistent with an AlF_{3} or AlF_{2}O_{3} surface layer passivating the Al_{2}O_{3} film.\(^{38,29}\) Additional results for ΔM_{HF} displayed in Figure 4b also confirmed similar self-limiting behavior at 300 °C. The mass gain reaches near saturation at ΔM_{HF} = 11 ng/(cm² cycle) after a 0.75 s HF exposure at 300 °C.

Figure 5 displays the mass changes during 100 Al_{2}O_{3} ALE cycles at 200, 225, 250, 275, and 300 °C with the reaction sequence of 2–30–1–30. The initial Al_{2}O_{3} ALD films were grown using 100 cycles of Al_{2}O_{3} ALD at the same temperatures as the ALE reactions. The mass changes versus time during Al_{2}O_{3} ALE show linear etching at 225–300 °C. The MCPC changes with temperature from -3.2 ng/(cm² cycle) at 225 °C to -21.3 ng/(cm² cycle) at 300 °C. These MCPCs are equivalent to etch rates that increase from 0.10 Å/s at 225 °C to 0.69 Å/s at 300 °C. These etch rates are again determined using the Al_{2}O_{3} ALD film density of 3.1 g/cm³.

Figure 5 also shows that a mass gain is observed at 200 °C. This mass gain is attributed to AlF_{3} ALD. The growth of AlF_{3} using DMAC and HF can be written as AlCl(CH_{3})_{2} + 3HF → AlF_{3} + HCl + 2CH_{4}. Similar results were observed for AlF_{3} ALD using TMA and HF as the reactants at T < 250 °C. At temperatures >250 °C, the same TMA and HF reactants yield Al_{2}O_{3} ALE.\(^{15}\)

The mass changes during the first two Al_{2}O_{3} ALE cycles were investigated to understand the surface species after the sequential DMAC and HF exposures on the hydroxylated Al_{2}O_{3} film. Figure 6 displays an enlargement of the mass changes during the first two Al_{2}O_{3} ALE cycles at the different temperatures in Figure 5. The first DMAC exposure in Figure 6 displays mass gains of ΔM_{DMAC} = 47–56 ng/cm² at 200–300 °C. These mass gains are attributed to the reaction of DMAC with AlOH\(^{+}\) surface species and described by AlOH\(^{+}\) + AlCl(CH_{3})_{2} → AlOAlCl\(^{+}\)(CH_{3})\(^{+}\) + CH_{4}. The mass gains during DMAC exposures are higher than ΔM_{TMA} = 27–32 ng/cm² observed during TMA exposure on initial hydroxylated Al_{2}O_{3} films at 250–325 °C.\(^{12}\) These higher mass gains are consistent with the presence of AlCl\(^{+}\) species, in addition to AlCH_{3}\(^{+}\) species, when using DMAC.

The first HF exposure in Figure 6 displays mass gains of ΔM_{HF} = 20–22 ng/cm² at 200–300 °C. These mass gains
during the first HF exposure result from the reaction of HF with AlCl\textsubscript{4}\textsuperscript{-} and AlCl\textsuperscript{3} species in addition to the fluorination of the Al\textsubscript{2}O\textsubscript{3} substrate. The reaction of HF with AlCl\textsuperscript{3} and Al(\textch{CH}_3)\textsuperscript{3} surface species leads to a smaller mass loss and can be expressed as AlCl\textsuperscript{3} + 2H\textch{CH}_3 \to 2AlF\textsuperscript{3} + HCl + CH\textsubscript{4}. The fluorination of AlCl\textsuperscript{3} to AlF\textsuperscript{3} is thermochemically favorable. The reaction AlCl\textsubscript{3} + 3HF \to AlF\textsubscript{3} + 3HCl has a standard free energy change of $\Delta G^\circ = -61$ kcal/mol at 250°C.\textsuperscript{30}

HF can also fluorinate the Al\textsubscript{2}O\textsubscript{3} substrate and form an AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} surface layer.\textsuperscript{5,9} The fluorination reaction leads to mass gain that is larger than the mass loss resulting from the reaction of HF with AlCl\textsubscript{4} and AlCl\textsuperscript{3} species. The fluorination reaction Al\textsubscript{2}O\textsubscript{3} + 6HF \to 2AlF\textsubscript{3} + 3H\textsubscript{2}O is spontaneous at 200–300°C. The standard free energy changes are negative with values of $\Delta G^\circ = -88$ kcal/mol at 200°C and $\Delta G^\circ = -49.1$ kcal/mol at 300°C.\textsuperscript{30}

Figure 6 also shows that the fluorination of Al\textsubscript{2}O\textsubscript{3} to form an AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} surface layer is fairly constant at different temperatures. The comparable mass changes at different temperatures suggest a similar AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} layer thickness. Previous experiments of HF exposures on hydroxylated Al\textsubscript{2}O\textsubscript{3} substrates also showed constant mass gains of $\Delta M_{HF}$ = 35–38 ng/cm\textsuperscript{2} at 150–250°C.\textsuperscript{12}

After the creation of the AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} layer by HF, the next DMAC exposure removes the AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} layer by ligand exchange as demonstrated by the mass losses shown in Figure 6. The DMAC and HF cycles show a mass loss in the second cycle for temperatures at 250–300°C. The DMAC and HF cycles at 225°C show a mass loss at the fourth AL cycle. Figure 6 indicates that more removal of AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} by DMAC at higher temperatures results in a larger mass gain for the subsequent fluorination of Al\textsubscript{2}O\textsubscript{3} by HF. Similar behavior was observed during Al\textsubscript{2}O\textsubscript{3} ALE using TMA and HF exposures.

Figure 7 shows the $\Delta M_{DMAC}$, $\Delta M_{HF}$, and MCPC values at 200–300°C in the steady state etching region. The $\Delta M_{DMAC}$, $\Delta M_{HF}$, MCPC, and etch rate values are summarized in Table 1. The same reaction sequence of 2–30–1–30 was employed for all Al\textsubscript{2}O\textsubscript{3} ALE reactions. $\Delta M_{DMAC}$ shows increasing mass losses at higher temperatures. In contrast, $\Delta M_{HF}$ shows increasingly larger mass gains at higher temperatures. Figure 7b reveals that the temperature dependence of MCPC follows the temperature dependence of $\Delta M_{DMAC}$. More removal of AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} by DMAC exposure leads to the higher etch rate of Al\textsubscript{2}O\textsubscript{3} at higher temperature. Higher $\Delta M_{HF}$ at higher temperature compensates for the removal of AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} to maintain a nearly constant AlF\textsubscript{3} or AlF\textsubscript{4}O\textsubscript{2} thickness.

### III.B. Ex Situ XRR and SE Measurements for Thermal Al\textsubscript{2}O\textsubscript{3} ALE

Al\textsubscript{2}O\textsubscript{3} ALE was also studied using ex situ XRR and SE measurements. Al\textsubscript{2}O\textsubscript{3} ALD films were grown on Si(100) wafers using 150 cycles of TMA and H\textsubscript{2}O at 250°C with a reaction sequence of 1–20–1–20. Figure 8a shows the film thicknesses of the initial Al\textsubscript{2}O\textsubscript{3} film and the Al\textsubscript{2}O\textsubscript{3} film after 10, 25, 50, 100, and 200 ALE cycles at 250°C. The accuracy of these film thickness measurements is ±0.5 Å. The initial Al\textsubscript{2}O\textsubscript{3} ALD films grown at 250°C have a thickness of 151 Å. The film thickness is then reduced linearly versus number of ALE cycles with an etch rate of 0.31 Å/cycle. The spectroscopic ellipsometry (SE) measurements on these same Al\textsubscript{2}O\textsubscript{3} films also yield an etch rate of 0.31 Å/cycle. The etch rates determined by XRR and SE are comparable to the etch rate of 0.39 Å/cycle obtained by the in situ QCM experiments at 250°C.

Figure 8b shows the root-mean-square (RMS) roughness of the Al\textsubscript{2}O\textsubscript{3} ALD films obtained from the XRR analysis. The accuracy of these surface roughness measurements is ±0.3 Å. The initial Al\textsubscript{2}O\textsubscript{3} ALD film has a roughness of ~5 Å. The Al\textsubscript{2}O\textsubscript{3} films become smoother versus Al\textsubscript{2}O\textsubscript{3} ALE cycles. The surface roughness reduces to ~2.5 Å after 10 ALE cycles. The surface roughness then reduces further to ~1.5 Å after 100–200 ALE cycles. These uncertainty in these XRR surface roughness measurements is ±0.5 Å. Similar surface smoothening versus number of ALE cycles has been observed during Al\textsubscript{2}O\textsubscript{3} ALE using HF and Sn(acac)$_2$. Al\textsubscript{2}O\textsubscript{3} ALE using HF and TMA, ZnO ALE using HF and TMA, and H\textsubscript{2}O ALE using HF and Sn(acac)$_2$. 

---

**Table 1**: Summary of $\Delta M_{DMAC}$, $\Delta M_{HF}$, MCPC, and etch rate values

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta M_{DMAC}$ (ng/cm²)</th>
<th>$\Delta M_{HF}$ (ng/cm²)</th>
<th>MCPC (ng/cm²)</th>
<th>Etch Rate (Å/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>35</td>
<td>38</td>
<td>0.22</td>
<td>0.31</td>
</tr>
<tr>
<td>225</td>
<td>40</td>
<td>42</td>
<td>0.24</td>
<td>0.32</td>
</tr>
<tr>
<td>250</td>
<td>45</td>
<td>47</td>
<td>0.25</td>
<td>0.33</td>
</tr>
<tr>
<td>275</td>
<td>50</td>
<td>52</td>
<td>0.26</td>
<td>0.34</td>
</tr>
<tr>
<td>300</td>
<td>55</td>
<td>57</td>
<td>0.27</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Table 1. MCPC, Etch Rate, $\Delta M_{\text{DMAC}}$ and $\Delta M_{\text{HF}}$ for Thermal Al$_2$O$_3$, HfO$_2$, and ZrO$_2$ ALD at Different Temperatures$^a$

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature ($^\circ$C)</th>
<th>MCPC ng/(cm$^2$ cycle)</th>
<th>Etch Rate (Å/cycle)</th>
<th>$\Delta M_{\text{DMAC}}$ ng/(cm$^2$ cycle)</th>
<th>$\Delta M_{\text{HF}}$ ng/(cm$^2$ cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>225</td>
<td>-3.2</td>
<td>0.10</td>
<td>-3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>250</td>
<td>-12.2</td>
<td>0.39</td>
<td>-17.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>275</td>
<td>-17.1</td>
<td>0.55</td>
<td>-26.1</td>
<td>9.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>300</td>
<td>-21.3</td>
<td>0.69</td>
<td>-32.5</td>
<td>11.2</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>200</td>
<td>-34.6</td>
<td>0.36</td>
<td>-28.5</td>
<td>-6.1</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>225</td>
<td>-76.0</td>
<td>0.79</td>
<td>-72.8</td>
<td>-3.2</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>250</td>
<td>-94.1</td>
<td>0.98</td>
<td>-93.6</td>
<td>-0.5</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>275</td>
<td>-105.4</td>
<td>1.10</td>
<td>-107.0</td>
<td>1.7</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>300</td>
<td>-118.8</td>
<td>1.24</td>
<td>-120.6</td>
<td>1.8</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>200</td>
<td>-52.1</td>
<td>0.91</td>
<td>-50.8</td>
<td>-1.3</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>225</td>
<td>-67.5</td>
<td>1.18</td>
<td>-69.1</td>
<td>1.6</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>250</td>
<td>-75.6</td>
<td>1.33</td>
<td>-79.1</td>
<td>3.4</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>275</td>
<td>-85.8</td>
<td>1.51</td>
<td>-95.0</td>
<td>9.3</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>300</td>
<td>-90.5</td>
<td>1.59</td>
<td>-103.3</td>
<td>12.8</td>
</tr>
</tbody>
</table>

$^a$Accuracy of MCPC, $\Delta M_{\text{DMAC}}$, and $\Delta M_{\text{HF}}$ is ±0.3 ng/(cm$^2$ cycle).

\[\text{Al}_2\text{O}_3 + 6\text{HF} + 4\text{AlCl}_3 \rightarrow 2\text{AlF}(_2\text{H})_3 + 4\text{AlCl}_2\text{CH}_3 + 3\text{H}_2\text{O}\] (1)

This overall reaction can be split into the HF and DMAC reactions:

\[(A) \text{Al}_2\text{O}_3|\text{AlF}_3^+ + 6\text{HF} \rightarrow \text{Al}_2\text{O}_3|2\text{AlF}_3^+ + 3\text{H}_2\text{O}\] (2)

\[(B) \text{Al}_2\text{O}_3|2\text{AlF}_3^+ + 4\text{AlCl}_3\text{CH}_3 \rightarrow \text{Al}_2\text{O}_3^+ + 2\text{AlF}(_2\text{H})_3 + 4\text{AlCl}_2\text{CH}_3\] (3)

Figure 8. (a) X-ray reflectivity and spectroscopic ellipsometry measurements of Al$_2$O$_3$ film thickness versus number of Al$_2$O$_3$ ALD cycles. (b) Al$_2$O$_3$ film roughness versus number of Al$_2$O$_3$ ALD cycles for initial Al$_2$O$_3$ ALD films.

III.C. Proposed Mechanism of Thermal Al$_2$O$_3$ ALE.

Figure 9 illustrates the proposed reaction mechanism for thermal Al$_2$O$_3$ ALE using sequential HF and DMAC exposures. This mechanism is based on the mass changes during the HF and DMAC exposures as observed by the QCM measurements. During the fluorination reaction (A), HF reacts with AlCH$_3^+$ and AlCl$_3^+$ surface species to form AlF$_3^+$ surface species and CH$_4$ and HCl reaction products. HF also fluorinates the underlying Al$_2$O$_3$ film to form an AlF$_4$ or AlF$_5$O$_x$ surface layer and H$_2$O reaction products.

During the ligand-exchange reaction (B), DMAC removes the AlF$_3$ or AlF$_5$O$_x$ surface layer on the Al$_2$O$_3$ substrate and is expected to form volatile AlF(CH$_3$)$_2$ and AlFCI(CH$_3$)$_2$ reaction products. Mass spectrometry studies are needed to confirm these etch products. DMAC and one of the possible etch products, AlF(CH$_3$)$_2$, AlFCI(CH$_3$)$_2$ are shown as dimers. AlF(CH$_3$)$_2$ has a vapor pressure of 80 Torr at 100 °C. AlF(Ch$_3$)$_2$ is expected to be volatile. AlCl(Ch$_3$)$_2$ may also react with the underlying Al$_2$O$_3$ substrate to form AlCl$_4^+$ and Al(Ch$_3$)$_4^+$ after the elimination of AlF$_3^+$ species.

The simplest overall reaction assuming CH$_4$ ligand transfer during the ligand-exchange reaction can be written as

\[\text{Al}_2\text{O}_3 + 6\text{HF} + 4\text{AlCl}_3 \rightarrow 2\text{AlF}(_2\text{H})_3 + 4\text{AlCl}_2\text{CH}_3 + 3\text{H}_2\text{O}\] (1)

This overall reaction can be split into the HF and DMAC reactions:

\[(A) \text{Al}_2\text{O}_3|\text{AlF}_3^+ + 6\text{HF} \rightarrow \text{Al}_2\text{O}_3|2\text{AlF}_3^+ + 3\text{H}_2\text{O}\] (2)

\[(B) \text{Al}_2\text{O}_3|2\text{AlF}_3^+ + 4\text{AlCl}_3\text{CH}_3 \rightarrow \text{Al}_2\text{O}_3^+ + 2\text{AlF}(_2\text{H})_3 + 4\text{AlCl}_2\text{CH}_3\] (3)

The amount of Al$_2$O$_3$ that is etched during the ALD reaction cycle is given by Al$_2$O$_3$ in eqs 2 and 3. The vertical lines are meant to separate the surface species. 2AlF$_3^+$ is the amount of AlF$_3$ corresponding with the amount of Al$_2$O$_3$ that is etched during the ALD reaction cycle.

The reactions described by eqs 1–3 may be incomplete because DMAC may also interact with the etched surface. The reaction of DMAC with Al$_2$O$_3$ could form both AlCH$_3^+$ and AlCl$_3^+$ surface species. DMAC may also interact with AlF$_3$ surface species remaining due to incomplete etching. This interaction may lead to F/Cl exchange.

In comparison to this thermal Al$_2$O$_3$ ALD process, plasma Al$_2$O$_3$ ALD has also been demonstrated using sequential exposures of BC$_3$ gas to chlorinate the Al$_2$O$_3$ surface and bombardment by energetic neutral Ar beams to remove the surface chloride species. The Ar beams were formed by
neutralizing Ar⁺ ion beams from an inductively coupled plasma ion gun. Al₂O₃ etch rates of ~1 Å/cycle were obtained using a grid voltage of 100 V for the Ar⁺ ion beams.²⁵

III.D. In Situ QCM Measurements for Thermal ALE of HfO₂ and ZrO₂. HfO₂ and ZrO₂ ALE were also studied by QCM measurements using sequential DMAC and HF exposures at 200–300 °C. The initial HfO₂ ALD films on the QCM sensor were grown using TDMAP and H₂O as the reactants.²⁵ The initial ZrO₂ ALD films were grown using TEMAZ and H₂O as the reactants.²⁵ The reaction sequence for the HfO₂ and ZrO₂ ALD was 1–40–1–40. Figure 10 shows the mass change during 100 cycles of HfO₂ and ZrO₂ ALE at 250 °C using the DMAC and HF reaction sequence of 2–30–1–30.

Figure 10a and 10b reveal that the mass changes are linear versus the number of sequential DMAC and HF exposures. The mass changes versus number of reaction cycles in Figure 10a and 10b yield MCPC = −94.1 ng/(cm² cycle) for HfO₂ ALE and MCPC = −75.6 ng/(cm² cycle) for ZrO₂ ALE, respectively. These MCPCs are consistent with etch rates of 0.98 Å/cycle for HfO₂ ALE and 1.33 Å/cycle for ZrO₂ ALE.

Figure 11 displays the mass changes during three sequential cycles of HfO₂ and ZrO₂ ALE at 250 °C. These three cycles are from enlargements of the linear etching regions of HfO₂ and ZrO₂ ALE shown in Figure 10. Figure 11a shows the mass changes coinciding with the DMAC and HF exposures for HfO₂ ALE. The mass loss during the DMAC exposure for 2.0 s is very prompt with little additional change during the purge time. A mass change of ΔM₁DMAC = −93.6 ng/(cm² cycle) was observed after the DMAC exposure. This mass decrease is consistent with the removal of the HfF₄ surface layer on the HfO₂ substrate. DMAC is able to transfer either Cl or CH₃ ligands. The ligand exchange of Cl from DMAC to HfF₄ to form HfCl₄ or HfCl₄·Fₓₓₓₓ mixed halogen species is most likely. HfCl₄ is stable and volatile at 250 °C. The vapor pressure of HfCl₄ is 1 Torr at 190 °C.²⁷ Hf(CH₃)₄ may be volatile but has limited stability at high temperature.²⁷ Very little is known about HfCl₄·Fₓₓₓₓ mixed halogen species.

The mass change after the HF exposure for 1.0 s is very small at ΔM₂HF = −0.5 ng/(cm² cycle). In contrast, the fluorination of HfO₂ to HfF₄ by HF should produce a mass increase. The molar masses of HfO₂ and HfF₄ are 210.5 g/mol and 254.5 g/mol, respectively. The negligible mass change for ΔM₂HF suggests that the concurrent fluorination of the HfCl₄* species by HF to form a HF* species must produce a mass loss. The balance of the mass gain and loss during fluorination then would result in a small mass change.

Figure 11b shows the mass changes during the DMAC and HF exposures for ZrO₂ ALE. The mass loss during the DMAC exposure for 2.0 s is again very rapid. A mass change of ΔM₁DMAC = −79.1 ng/(cm² cycle) was observed after the DMAC exposure. This mass decrease is consistent with the removal of the ZrF₄ surface layer on the ZrO₂ substrate. In comparison, previous studies revealed that TMA and HF exposures could not etch ZrO₂.²⁵ These results were explained by the instability of Zr(CH₃)₄ at high temperature.²⁷ In contrast, DMAC can transfer Cl ligands and form ZrCl₄ or ZrCl₄·Fₓₓₓₓ mixed halogen species. ZrCl₄ is stable and volatile at 250 °C. The vapor pressure of ZrCl₄ is 1 Torr at 190 °C.²⁷

Figure 10. Mass change versus time during 100 cycles of (a) HfO₂ ALE and (b) ZrO₂ ALE at 250 °C using the reaction sequence of 2–30–1–30.
Figure 11. Enlargement of mass change versus time in Figure 10 for three sequential DMAC and HF exposures in the steady state, linear etching region at 250 °C during: (a) HfO₂ ALE and (b) ZrO₂ ALE.

Almost nothing has been reported about ZrClₓFₓ₋₁₋ₓ mixed halogen species.

The mass change after the HF exposure for 1.0 s is small at ΔMHF = -3.4 ng/(cm² cycle). The fluorination of ZrO₂ to ZrFₓ should produce a mass gain. The molar masses of ZrO₂ and ZrFₓ are 123.2 g/mol and 167.2 g/mol, respectively. A small mass change argues that the simultaneous reaction of HF with ZrClₓ species to form ZrFₓ⁻¹ species must produce a mass loss. The balance between mass gain and mass loss leads to a small mass increase.

Both HfO₂ and ZrO₂ ALE reactions displayed self-limiting reactions. The self-limiting behavior was examined by monitoring mass changes versus exposure for each reactant. ΔMDMAC, ΔMHF, MCPC, and the etch rate for HfO₂ and ZrO₂ ALE at the different temperatures are summarized in Table I. Etch rates for HfO₂ and ZrO₂ ALE were calculated using the MCPCs and the XRR densities of 9.6 g/cm³ for HfO₂ ALD film and 5.7 g/cm³ for ZrO₂ ALD film, respectively.

III.E. Proposed Mechanism of Thermal HfO₂ and ZrO₂ ALE. Figure 12 shows the proposed reaction mechanism for thermal MO₂ (M = Hf or Zr) ALE. This mechanism is based on the mass changes during the HF and DMAC exposures as obtained by the QCM measurements. During the fluorination reaction (A), HF reacts with MClₓ⁻¹⁻ₓ surface species to form MFₓ⁻¹⁻ₓ surface species and HCl reaction products. HF also reacts with the underlying MO₂ film to form an MFₓ⁻¹⁻ₓ surface layer and H₂O reaction products. During the ligand-exchange reaction (B), DMAC reacts with the MFₓ⁻¹⁻ₓ surface layer on the MO₂ substrate to form volatile MClₓ⁻¹⁻ₓ and MFₓ⁻¹⁻ₓ mixed halogen species and ALF(CH₃)₃ reaction products.

HfClₓ⁻¹⁻ₓ and ZrClₓ⁻¹⁻ₓ are volatile solids having sublimation temperatures of 317 and 331 °C, respectively. Vapor pressures of HfClₓ⁻¹⁻ₓ and ZrClₓ⁻¹⁻ₓ are ~1 Torr at 190 °C. Mixed fluoride/chloride species such as MF₅Clₓ⁻¹⁻ₓ or MFₓ⁻¹⁻ₓClₓ may also be etch products if they have a high enough vapor pressure. The etch products with M–CH₃ bonds such as MF₅Clₓ(CH₃)y⁻¹⁻ₓ or MFₓ⁻¹⁻ₓClₓ(CH₃)y⁻¹⁻ₓ may be possible, but the M–Cl bond is much more stable than the M–CH₃ bond. Figure 12 includes only MClₓ⁻¹⁻ₓ surface species because of the higher stability of the M–Cl bond compared with the M–CH₃ bond. Chemical equations could also be written for the surface chemical reactions that are similar to eqs 2 and 3.

Plasma HfO₂ and ZrO₂ ALE have also been performed using sequential exposures of BCl₃ gas to chlorinate the HfO₂ and ZrO₂ surfaces and bombardment by energetic neutral Ar beams to desorb the surface chloride species. Plasma beams were formed by neutralizing Ar⁺ ion beams. HfO₂ and ZrO₂ etch rates of ~1 Å/cycle were obtained using the sequential BCl₃ and energetic neutral Ar beam exposures.

III.F. Etch Rates and Fluoride Thicknesses for Thermal Al₂O₃, HfO₂, and ZrO₂ ALE. Figure 13 shows the etch rates for thermal Al₂O₃, HfO₂, and ZrO₂ ALE using DMAC and HF at different temperatures. These etch rates were determined from the MCPCs measured by in situ QCM studies using the density of the metal oxides to convert between mass and thickness. The etch rates increase versus temperature from 200 to 300 °C. The relative etch rates also vary with the metal oxides according to ZrO₂ > HfO₂ > Al₂O₃. The etch rates for Al₂O₃ ALE increased from 0.10 Å/cycle to 0.69 Å/cycle at temperatures from 225 to 300 °C. The etch rates for HfO₂ ALE increased from 0.36 Å/cycle to 1.24 Å/cycle at temperatures from 200 to 300 °C. The etch rates for ZrO₂ ALE increased from 0.91 Å/cycle to 1.59 Å/cycle at temperatures from 200 to 300 °C.

The thicknesses of the metal fluorides on Al₂O₃, HfO₂, and ZrO₂ during thermal ALE are also consistent with the relative etch rates. In the previous study of Al₂O₃ ALE, the mass gain of 34 ng/cm² after HF exposures on fresh Al₂O₃ ALD surfaces...
Figure 13. Etch rates for $\text{Al}_2\text{O}_3$, $\text{HfO}_2$, and $\text{ZrO}_2$ ALE at different temperatures using DMAC and HF.

was employed to calculate the thickness of the $\text{AlF}_3$ layer. These calculations revealed that 1.7 Å of $\text{Al}_2\text{O}_3$ was converted to an $\text{AlF}_3$ layer with a thickness of 3.0 Å during thermal $\text{Al}_2\text{O}_3$ ALE.\(^9\)

In comparison, HF exposures on initial $\text{HfO}_2$ substrates showed mass gains of $\Delta M_{\text{HF}} = 36–41 \text{ ng/cm}^2$ at 150–300 °C. The fluorination reaction $\text{HfO}_2 + 4\text{HF} \rightarrow \text{HfF}_4 + 2\text{H}_2\text{O}$ will result in a mass increase of 12% from 210.5 amu for $\text{HfO}_2$ to 254.5 amu for $\text{HfF}_4$. The average value of $\Delta M_{\text{HF}} = 39 \text{ ng/cm}^2$ corresponds to the conversion of 186.6 $\text{ng/cm}^2$ of $\text{HfO}_2$ to 225.6 $\text{ng/cm}^2$ of the $\text{HfF}_4$ layer. Based on the density of 9.6 $\text{g/cm}^3$ for $\text{HfO}_2$, the mass of 186.6 $\text{ng/cm}^2$ for $\text{HfO}_2$ is equivalent to a $\text{HfF}_4$ thickness of 1.9 Å. Similarly, based on the density of 6.8 $\text{g/cm}^3$ for $\text{HfF}_4$, the mass of 225.6 $\text{ng/cm}^2$ for $\text{HfF}_4$ is equivalent to a $\text{HfF}_4$ thickness of 3.3 Å.

HF exposures on initial $\text{ZrO}_2$ substrates displayed mass gains of $\Delta M_{\text{HF}} = 45–50 \text{ ng/cm}^2$ at 200–300 °C. The fluorination reaction $\text{ZrO}_2 + 4\text{HF} \rightarrow \text{ZrF}_4 + 2\text{H}_2\text{O}$ will result in a mass increase of 36% from 123.2 amu for $\text{ZrO}_2$ to 167.2 amu for $\text{ZrF}_4$. The average value of $\Delta M_{\text{HF}} = 48 \text{ ng/cm}^2$ corresponds to the conversion of 134.4 $\text{ng/cm}^2$ of $\text{ZrO}_2$ to 182.4 $\text{ng/cm}^2$ of the $\text{ZrF}_4$ layer. Based on the density of 5.7 $\text{g/cm}^3$ for $\text{ZrO}_2$, the mass of 134.4 $\text{ng/cm}^2$ for $\text{ZrO}_2$ is equivalent to a $\text{ZrF}_4$ thickness of 2.4 Å. Similarly, based on the density of 4.1 $\text{g/cm}^3$ for $\text{ZrF}_4$, the mass of 182.4 $\text{ng/cm}^2$ for $\text{ZrF}_4$ is equivalent to a $\text{ZrF}_4$ thickness of 4.4 Å.

The values for the fluoride thicknesses are in the same relative order as the values for the etch rates at 250 °C. The fluoride thicknesses are 3.0, 3.3, and 4.4 Å for $\text{Al}_2\text{O}_3$, $\text{HfO}_2$, and $\text{ZrO}_2$, respectively. The etch rates are 0.39, 0.98, and 1.33 Å/cycle at 250 °C for $\text{Al}_2\text{O}_3$, $\text{HfO}_2$, and $\text{ZrO}_2$, respectively. The correlation between the fluoride thicknesses and the etch rates was also observed for $\text{Al}_2\text{O}_3$ ALE versus HF pressure.\(^9\) Higher HF pressures led to thicker $\text{AlF}_3$ film thicknesses and higher $\text{Al}_2\text{O}_3$ etch rates.\(^9\)

II.G. Comparison between DMAC and TMA for Thermal $\text{Al}_2\text{O}_3$, $\text{HfO}_2$, and $\text{ZrO}_2$ ALE. Figure 14 compares DMAC and TMA for thermal $\text{Al}_2\text{O}_3$, $\text{HfO}_2$, and $\text{ZrO}_2$ ALE at 250 °C. Figure 14a shows the comparison of the mass changes versus time during four sequential cycles using either DMAC or TMA together with HF for $\text{Al}_2\text{O}_3$ ALE. Following the initial nucleation, sequential HF and TMA exposures etch the $\text{Al}_2\text{O}_3$ film with an etch rate of $-4.2 \text{ ng/cm}^2$. In contrast, sequential HF and DMAC exposures etch the $\text{Al}_2\text{O}_3$ film at a much faster etch rate of $-12.2 \text{ ng/cm}^2$. The larger etch rate for DMAC is attributed to the Cl ligand on DMAC. The Cl ligand yields a more efficient ligand-exchange reaction. The individual mass changes for DMAC and TMA measured by the QCM are also consistent with Cl present on the surface after the DMAC exposure during $\text{Al}_2\text{O}_3$ ALE.

Figure 14b shows the comparison of the mass changes versus time during four sequential cycles using either DMAC or TMA together with HF exposures for $\text{HfO}_2$ ALE. The QCM results reveal that sequential HF and TMA exposures lead to negligible $\text{HfO}_2$ etching in agreement with previous studies.\(^7\) In contrast, sequential HF and DMAC exposures etch the $\text{HfO}_2$ film with a mass loss of $-94.1 \text{ ng/cm}^2$ or 0.98 Å/
cycle. This selectivity results from the ability of DMAC to provide a Cl ligand during ligand exchange. As discussed earlier, Hf–Cl bonds are stable, and HfCl₂ is volatile. Hf–C bonds are also weaker, and Hf(CH₃)₄ is unstable at higher temperatures.

Figure 14c shows the comparison of the mass changes versus time during four sequential cycles using either DMAC or TMA together with HF for ZrO₂ ALE. Similar to the comparison in Figure 14b, HF and TMA do not etch ZrO₂ in agreement with previous results. In contrast, sequential HF and DMAC exposures etch the ZrO₂ film with a mass loss per cycle of MCPC = −75.6 ng/cm² or 1.33 Å/cycle. This selectivity again results from the ability of DMAC to transfer a Cl ligand during the ligand-exchange reaction. Zr–Cl bonds are stable, and ZrCl₄ is volatile as mentioned earlier. Zr–C bonds are also weaker, and Zr(CH₃)₄ is unstable at higher temperatures.

III. H. Etching of Masked Al₂O₃ Substrates. The selectivity of thermal Al₂O₃ ALE was also demonstrated by using sequential exposures of HF and DMAC to etch a masked Al₂O₃ substrate. The mask was SiN₃; the etched material was Al₂O₃; and the etch stop was SiO₂. Figure 15a shows a schematic of the test structure used to demonstrate selective etching by thermal Al₂O₃ ALE. Because thermal ALE is isotropic, the Al₂O₃ film underlying the SiN mask should be etched resulting from the nondirectional nature of thermal ALE. This undercutting is illustrated in Figure 15a.

Figure 15b reveals the transmission electron microscopy (TEM) image of the masked substrate after 1000 cycles of Al₂O₃ ALE using HF and DMAC at 250 °C. The initial structure consists of a plasma-enhanced chemical vapor deposition (PECVD) SiN patterned mask with a thickness of 46 nm on an Al₂O₃ film with a thickness of 28 nm on a thermal SiO₂ film. The Al₂O₃ film not covered by the SiN mask is etched by thermal Al₂O₃ ALE. There is undercut etching of Al₂O₃ beneath the SiN mask because thermal ALE is isotropic. The thermal Al₂O₃ ALE is selective and does not etch the SiN or SiO₂ films in agreement with previous results.

The Al₂O₃ ALE is reasonably isotropic. The 1000 cycles of Al₂O₃ ALE remove a 277 Å vertical thickness of Al₂O₃ in the unmasked region. The length of the horizontal lateral etch depth undercutting the SiN mask is 221 Å. The etching is not perfectly isotropic. The difference between the 277 Å vertical and 221 Å horizontal etch lengths may be dependent on gas conductance. The precursor exposures may not be self-limiting in the shadowed volumes underneath the SiN mask.

IV. CONCLUSIONS

The thermal ALE of Al₂O₃, HfO₂, and ZrO₂ was demonstrated using sequential exposures of HF and DMAC. DMAC is an effective metal reactant for thermal ALE using fluorination and ligand-exchange reactions because either CH₃ or Cl ligands can be transferred in the ligand-exchange reactions. Al₂O₃, HfO₂, and ZrO₂ ALE were studied at temperatures from 200 to 300 °C using QCM experiments. These QCM studies revealed that the mass loss during Al₂O₃, HfO₂, and ZrO₂ ALE was linear versus number of HF and DMAC exposures. In contrast, ZrO₂ and HfO₂ ALE were negligible using HF and TMA exposures. TMA only has CH₃ ligands that can transfer in the ligand-exchange reaction, and Zr(CH₃)₄ and Hf(CH₃)₄ etch products are not stable.

The etch rates for Al₂O₃, HfO₂, and ZrO₂ ALE using HF and DMAC increased at higher temperatures. At 250 °C, the mass change per cycle of Al₂O₃ was −12.2, −93.6, and −79.1 ng/(cm² cycle) or etch rates of 0.39, 0.98, and 1.33 Å/cycle were measured for Al₂O₃, HfO₂, and ZrO₂ ALE using HF and DMAC. In comparison, the AlF₃, HfF₄, and ZrF₄ surface layers after the HF exposure were estimated to have a thickness of 3.0 Å, 3.3 Å, and 4.4 Å on Al₂O₃, HfO₂, and ZrO₂, respectively. The magnitudes of these fluoride thicknesses have the same ordering as the etch rates for Al₂O₃, HfO₂, and ZrO₂ ALE, respectively. A similar correlation between fluoride thickness and etch rate was observed recently during studies of the effect of HF pressure on Al₂O₃ ALE using HF and TMA.

XRR and SE studies confirmed the linear etching and the etch rates using HF and DMAC. XRR analysis also revealed the smoothing of the etched Al₂O₃ film. A comparison of Al₂O₃, HfO₂, and ZrO₂ ALE using either HF and DMAC or HF and TMA demonstrated that higher etch rates were observed with DMAC for all three materials. The etch of masked Al₂O₃ substrates also showed that Al₂O₃ ALE was reasonably isotropic and selective to Al₂O₃ in the presence of the SiN mask and SiO₂ etch stop. The ability of DMAC to provide either CH₃ or Cl ligands during the ligand-exchange reaction should be useful for the thermal ALE of a variety of materials.
ACKNOWLEDGMENTS

This research was funded by Intel Corporation through a Member Specific Research Project administered by the Semiconductor Research Corporation. Additional funding was obtained from the National Science Foundation (CHE-1609554). The authors thank Andreas Fischer and Thorsten Lill of Lam Research for the masked Al₂O₃ substrates and for TEM imaging of these substrates after thermal Al₂O₃ ALD.

REFERENCES

(18) CRC Handbook of Chemistry and Physics; CRC Press: Cleveland, 2018.
(30) HSC Chemistry, HSC Chemistry S.1: Outokumpu Research Oy: Pori, Finland.