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ABSTRACT: Atomic layer etching (ALE) can result from sequential, self-limiting thermal reactions. The reactions during thermal ALE are defined by fluorination followed by ligand exchange using metal precursors. The metal precursors introduce various ligands that may transfer during ligand exchange. If the transferred ligands produce stable and volatile metal products, then the metal products may leave the surface and produce etching. In this work, selectivity in thermal ALE was examined by exploring tin(II) acetylacetonate (Sn(acac)2), trimethylaluminum (TMA), dimethylaluminum chloride (DMAC), and SiCl4 as the metal precursors. These metal precursors provide acac, methyl, and chloride ligands for ligand exchange. HF-pyridine was employed as the fluorination reagent. Spectroscopic ellipsometry was used to measure the etch rates of Al2O3, HfO2, ZrO2, SiO2, Si3N4, and TiN thin films on silicon wafers. The spectroscopic ellipsometry measurements revealed that HfO2 was etched by all of the metal precursors. Al2O3 was etched by all of the metal precursors except SiCl4. ZrO2 was etched by all of the metal precursors except TMA. In contrast, SiO2, Si3N4, and TiN were not etched by any of the metal precursors. These results can be explained by the stability and volatility of the possible reaction products. Temperature can also be used to obtain selective thermal ALE. The temperature dependence of ZrO2, HfO2, and Al2O3 ALE was examined using Sn(acac)2, TMA, and DMAC as the metal precursors. Sn(acac)2 etched Al2O3 at temperatures ≥250 °C. DMAC etched Al2O3 at higher temperatures ≥225 °C. TMA etched Al2O3 at even higher temperatures ≥250 °C. The combination of different metal precursors with various ligands and different temperatures can provide multiple pathways for selective thermal ALE.

I. INTRODUCTION

Atomic layer etching (ALE) can remove thin films with atomic scale precision using sequential, self-limiting surface reactions. Most reported ALE processes have employed halogenation reactions followed by energetic ion or noble gas atom bombardment to etch the material. Thermal ALE processes have also been developed using sequential exposures of HF and metal precursors. Thermal ALE is the reverse of atomic layer deposition (ALD). Thermal ALE studies have demonstrated Al2O3 ALE, HfO2 ALE, and AlF3 ALE. These thermal ALE investigations have utilized HF and Sn(acac)2 as the reactants. Other recent thermal ALE studies have demonstrated Al2O3 ALE using HF and trimethylaluminum (TMA) as the reactants.

The reactions during thermal ALE are based on gas-phase fluorination and ligand exchange as illustrated in Figure 1. Fluorination first converts the metal-containing compound to the metal fluoride. Most fluorination reactions of metal-containing compounds are thermochromically favorable. The metal precursor then undergoes a ligand-exchange reaction with the metal fluoride. The ligand exchange can be characterized as a metal exchange transmetalation reaction or a redistribution reaction. During the ligand-exchange reaction, the metal precursor can accept fluorine from the metal fluoride. The ligand-exchange reaction can also transfer a ligand from the metal precursor to the metal fluoride. The transition state is believed to be a four-center ring formed by the metal in the metal precursor and the metal in the metal fluoride with fluorine and ligand bridging species.

If the ligand-exchange reaction produces stable and volatile metal products, then the metal products may leave the surface and produce etching. The ligand-exchange reaction may not occur or may not produce etching if the possible metal products are not stable or volatile. This difference between the stability and volatility of the possible metal reaction products can lead to selective etching. Selectivity in thermal ALE may also be achievable based on the stability of the resulting metal fluoride or by tuning the etching temperature.

Selectivity in etching is required to remove one material in the presence of other different materials. Selective ALE has many applications in semiconductor device fabrication and surface cleaning. The selectivity in thermal ALE may be much...
higher than the selectivity during plasma ALE. The selectivity in plasma ALE depends on the energy thresholds for sputtering that are not clearly differentiated for most materials. One example of selectivity in plasma ALE is between SiO2 and Si using fluorocarbon adsorption followed by Ar ion bombardment. Reasonable selectivity is observed for SiO2 etching versus Si etching at an Ar ion energy of 25 eV. However, selectivity is largely lost at the slightly higher ion energy of 30 eV.

In this work, the selectivity in thermal ALE was explored using four different metal precursors for ligand exchange with HF-pyridine as the fluorination precursor. The metal precursors were tin(II) acetylacetonate (Sn(acac)2), trimethylaluminum (TMA), dimethylaluminum chloride (DMAC), and silicon tetrachloride (SiCl4). These metal precursors can transfer acac, methyl, and chloride ligands during the ligand-exchange reaction. These reactions were used to etch Al2O3, HfO2, ZrO2, and TiN thin films on silicon wafers. These six materials are all important in semiconductor device processing. Spectroscopic ellipsometry was then employed to measure the film thicknesses versus number of ALE cycles for each of the six materials. These experiments were able to determine the selectivity of thermal ALE to the different materials using the various metal precursors and the relative etch rates.

Additional experiments explored the selectivity of thermal ALE resulting from substrate temperature. The etching of HfO2, ZrO2, and Al2O3 at different temperatures was explored using SiCl4 as the molecular precursor. Al2O3 ALE was also examined at various temperatures using Sn(acac)2, DMAC, and TMA as the metal precursors. These etching studies revealed that temperature can provide an additional pathway for selective thermal ALE.

II. EXPERIMENTAL SECTION

The thermal ALE reactions were performed in a viscous flow ALD reactor. The reaction temperatures from 150 to 350 °C were maintained by a proportional-integral-derivative (PID) temperature controller (2604, Eurotherm). The pressure was monitored by a capacitance manometer (Baratron 121A, MKS). A constant flow of 150 sccm of ultra high purity (UHP) N2 gas was supplied by mass flow controllers (Type 1179A, MKS). This N2 gas flow produced a base pressure of ~1 Torr in the reactor pumped by a mechanical pump (Pascal 201SSD, Alcatel).

The fluorination reaction employed a HF-pyridine solution (70 wt % HF, Sigma-Aldrich) as the HF source. The HF-pyridine solution has an equilibrium with gaseous HF. The vapor pressure of HF over the HF-pyridine solution is 90–100 Torr at room temperature. Only gaseous HF, without measurable pyridine vapor, is observed in the gas phase. HF derived from the HF-pyridine solution avoids the difficulty of handling high pressure HF gas cylinders. The HF-pyridine solution was transferred to a gold-plated stainless steel bubbler in a dry N2-filled glovebag. The HF-pyridine solution was held at room temperature. The pressure transients of HF derived from the HF-pyridine source were adjusted to ~80 mTorr using a metering bellows-sealed valve (SS-4BMG, Swagelok).

The metal precursors for the ligand-exchange reaction were tin(II) acetylacetonate (Sn(acac)2), 37–38% Sn, Gelest), trimethylaluminum (TMA) (97%, Sigma-Aldrich), dimethylaluminum chloride (DMAC) (97%, Sigma-Aldrich), and silicon tetrachloride (SiCl4) (98%; Gelest). The Sn(acac)2 precursor was maintained at 100 °C. The Sn(acac)2 pressure transients were adjusted to ~20 mTorr using a metering valve. The TMA, DMAC, and SiCl4 precursors were held at room temperature. The TMA and DMAC pressure transients were regulated at ~40 mTorr using metering valves. The SiCl4 pressure transients were defined at ~120 mTorr also using a metering valve. The etch rates reached constant values at longer metal precursor exposures using these pressure transients.

Various thin films on silicon wafers were prepared by SEMATECH to measure the etch rates during thermal ALE. The TiN, Al2O3, HfO2, and ZrO2 films were deposited by semiconductor ALD processes in commercially available tools. Chemical vapor deposition was employed to prepare the SiO2 and Si3N4 films using typical process conditions in a high volume single wafer tool. The thickness of all the initial films was targeted to be ~50 Å. Actual thicknesses were in the range of 39–68 Å as determined by spectroscopic ellipsometry (SE) measurements. The ALE experiments were performed in parallel by placing the Al2O3, HfO2, ZrO2, SiO2, Si3N4, and TiN thin films on silicon wafers in the viscous flow reactor. For each experiment, there was one sample for each of the six materials. The six samples were each 1.25 cm by 1.25 cm in size.

The ALE reactions were performed using an optimized reaction sequence. This reaction sequence is represented as x=30–1−30 and consists of an exposure of metal precursor for x s, 30 s of N2 purge, 1 s of HF exposure derived from the HF-pyridine solution, and 30 s of N2 purge. The ALE reactions using Sn(acac)2 as a metal precursor were performed using a reaction sequence of 1–30–1–30. The ALE reactions using TMA, DMAC, or SiCl4 as the metal precursor were performed using a reaction sequence of 2–30–1–30. The reaction sequence is optimized when an additional increase in the exposure of the metal precursor does not produce a higher etch rate.

The thicknesses of the various films were measured by SE measurements. A spectroscopic ellipsometer (M-2000, J. A. Woollam) measured Ψ and Δ at 240–900 nm with an incidence angle of 75°. The analysis software (CompleteEASE, J. A. Woollam) fitted Ψ and Δ to determine the thicknesses and refractive index of the film. A Sellmeier model was used for fitting the thickness of the Al2O3, HfO2, ZrO2, SiO2, Si3N4, and TiN thin films on silicon wafers in the viscous flow reactor. For each film thickness versus number of ALE cycles, the reported etch rates are accurate to within ±0.01 Å/cycle. Most of the individual least-squares fittings are accurate to within ±0.005 Å/cycle.

The temperature-dependent ALE experiments were performed using an in situ quartz crystal microbalance (QCM) in the viscous flow ALD reactor. The quartz crystal (gold coated and polished, RC crystal, 6 MHz, Phillip Technologies) was placed in a sensor head (BSH-150, Inficon) and then sealed with high temperature epoxy (Epo-Tek H21D, Epoxy technology). The mass changes during the ALE reactions were recorded by a thin film deposition monitor (Maxtek TM-400, Inficon). The initial Al2O3 films on the QCM crystal using Al2O3 ALD with TMA and H2O as the reactants at the same temperature as the ALE reactions.

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III. RESULTS AND DISCUSSION

A. Results for Selectivity Based on Metal Precursor.

The etching results using Sn(acac)$_2$ as the metal precursor are presented in Figure 2. Figure 2a shows the SE measurements of the film thicknesses after 50, 100, 200, and 400 ALE cycles using sequential HF and Sn(acac)$_2$ exposures at 200 °C. The Al$_2$O$_3$, ZrO$_2$, and HfO$_2$ films were etched linearly versus the number of ALE cycles. In contrast, there were no measurable thickness changes for the SiO$_2$, Si$_3$N$_4$, and TiN films. Figure 2b displays the film thickness versus the number of ALE cycles for the Al$_2$O$_3$, ZrO$_2$, and HfO$_2$ films. The slopes from the linear least-squares fittings of the data in Figure 2b yielded etch rates of 0.23 Å/cycle, 0.14 Å/cycle, and 0.06 Å/cycle for the Al$_2$O$_3$, ZrO$_2$, and HfO$_2$ films, respectively. The etch rates of Al$_2$O$_3$ and HfO$_2$ are consistent with earlier reported values.$^7$–$^9$ The etch rate of ZrO$_2$ was determined for the first time.

Additional control experiments were performed on the Al$_2$O$_3$, ZrO$_2$, and HfO$_2$ films to determine if both HF and Sn(acac)$_2$ were necessary for the thermal ALE. Experiments using 200 cycles of HF exposures observed negligible thickness changes for the Al$_2$O$_3$, ZrO$_2$, and HfO$_2$ films. In addition, sequential exposures of HF and acetylacetone (acacH, Sigma-Aldrich >99%) did not lead to the etching of Al$_2$O$_3$ at 200 °C. Without the metal acetylacetonate precursor, acetylacetone alone does not yield thermal ALE.

Both the metal and the ligands on the metal precursor were changed for the results for TMA shown in Figure 3. Figure 3a displays the film thickness after 25, 50, 100, and 200 ALE cycles using sequential HF and TMA exposures at 300 °C. The Al$_2$O$_3$ and HfO$_2$ films were etched linearly versus the number of ALE cycles. There were negligible thickness changes during 200 ALE cycles for the ZrO$_2$, SiO$_2$, Si$_3$N$_4$, and TiN films. The film thicknesses versus the number of ALE cycles for the Al$_2$O$_3$, HfO$_2$, and ZrO$_2$ films are shown in Figure 3b. Etch rates of 0.45 Å/cycle and 0.10 Å/cycle were measured for the Al$_2$O$_3$ and HfO$_2$ films, respectively. The etch rate of Al$_2$O$_3$ is in agreement with the value measured earlier by quartz crystal microbalance (QCM) and SE experiments.$^{11}$ The etch rate of HfO$_2$ using HF and TMA was determined for the first time. A negligible etch rate of 0.01 Å/cycle was determined for the ZrO$_2$ film.

The metal remained Al and the ligands on the metal precursor were either chlorine or methyl for the results for DMAC that are displayed in Figure 4. Figure 4a shows the film thickness after 10, 25, 50, and 100 ALE cycles using sequential HF and DMAC exposures at 250 °C. Linear etching was observed for the ZrO$_2$, HfO$_2$, and Al$_2$O$_3$ films versus the
number of ALE cycles. No measurable thickness changes were observed for the SiO$_2$, Si$_3$N$_4$, and TiN films. The film thicknesses versus the number of ALE cycles are displayed for the ZrO$_2$, HfO$_2$, and Al$_2$O$_3$ films in Figure 4b. Etch rates of 0.96 Å/cycle, 0.77 Å/cycle, and 0.32 Å/cycle were determined for the ZrO$_2$, HfO$_2$, and Al$_2$O$_3$ films, respectively.

The metal was changed to Si and the ligands on the metal precursor were chlorine for the results for SiCl$_4$ that are shown in Figure 5. Figure 5a displays the film thicknesses after 50, 100, 200, and 400 ALE cycles using sequential HF and SiCl$_4$ exposures at 350 °C. The ZrO$_2$ and HfO$_2$ films were etched linearly versus the number of ALE cycles. In contrast, there were no measurable thickness changes during 400 ALE cycles for the Al$_2$O$_3$, SiO$_2$, Si$_3$N$_4$, and TiN films. Figure 5b displays the film thickness versus the number of ALE cycles for the ZrO$_2$, HfO$_2$, and Al$_2$O$_3$ films. Etch rates of 0.14 Å/cycle and 0.05 Å/cycle were measured for the ZrO$_2$ and HfO$_2$ films, respectively. The etch rate of Al$_2$O$_3$ was negligible.

The etching results for SiCl$_4$ shown in Figure 5 were performed under self-limiting conditions. To confirm self-limiting behavior, etch rates were measured versus increasing exposure times of SiCl$_4$ while keeping the HF exposure time constant at 1.0 s. These results are shown in Figure 6a. The etch rates for both ZrO$_2$ and HfO$_2$ are self-limiting versus SiCl$_4$ exposure. The etch rates are constant at progressively larger SiCl$_4$ exposure times. The etch rates at each SiCl$_4$ exposure time were determined using at least 3–4 measured film thicknesses after different numbers of ALE cycles.

The etch rates were also determined versus increasing exposure times of HF while maintaining a constant SiCl$_4$ exposure time of 2.0 s. These results are displayed in Figure 6b. The etch rate for HfO$_2$ is self-limiting versus HF exposures. In addition, the etch rate for ZrO$_2$ begins to level off at higher HF exposures. The slight increases at larger HF exposures for ZrO$_2$ can be attributed to the difficulty purging HF from the reactor after longer HF exposures. Residual HF remaining in the reactor will lead to chemical vapor etching (CVE) during the SiCl$_4$ exposure. Similar influences of CVE on thermal ALE have been observed earlier after longer HF exposures.$^8,9$

Al$_2$O$_3$ ALE is self-limiting using HF and Sn(acac)$_2$ exposures$^8$ or HF and TMA exposures.$^{11}$ HfO$_2$ ALE is also known to be self-limiting using HF and Sn(acac)$_2$ exposures.$^9$ Additional studies have confirmed that Al$_2$O$_3$ ALE is self-limiting using HF and DMAC exposures. ZrO$_2$ ALE using HF and Sn(acac)$_2$ exposures, HfO$_2$ or ZrO$_2$ ALE using HF and DMAC exposures and HfO$_2$ ALE using HF and TMA exposures were run under the same self-limiting reaction conditions as employed for Al$_2$O$_3$ ALE.
The reaction $\text{HfO}_2 + 4\text{HF}(g)$ is thermochemically favorable. The reaction $\text{Al}_2\text{O}_3 + 350^\circ\text{C} 2\text{H}_2\text{O}(g)$ has $\Delta G$ values of $-8.9, -9.6, -12.1, -15.2,$ and $-16.0 \text{kcal/mol}$ at 200, 250, 300, and 350 °C, respectively. These $\Delta G$ values may also be the favored metal reaction product derived from $\text{HfF}_4$. The resulting $\text{HfF}_4$ and $\text{ZrF}_4$ reaction products are not volatile. $\text{AlF}_3$ and $\text{HfF}_4$ sublimes at 1276, 970, and 912 °C, respectively.

The subsequent ligand-exchange reactions can produce stable and volatile reaction products for most of the metal precursors with the $\text{AlF}_3$, $\text{HfF}_4$, and $\text{ZrF}_4$ metal fluorides. For example, for the $\text{Sn(acac)}_2$ results shown in Figure 2, $\text{Sn(acac)}_2$ can accept F and donate acac to produce volatile SnF(acac) and metal products with acac ligands. This ligand exchange is facilitated by the ability of fluorine to form bimetallic bridges. For the $\text{TMA}$ results displayed in Figure 3, TMA can etch $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$. In contrast, TMA can not etch $\text{ZrO}_2$. The methyl ligand from TMA can form stable metal methyl compounds with Al and Hf. TMA can accept F from $\text{AlF}_3$ and donate CH$_3$ to produce volatile AlF(CH$_3$)$_2$ from TMA and metal products with methyl ligands from $\text{AlF}_3$. The possible four-center transition state for the ligand-exchange reaction between TMA and $\text{AlF}_3$ is shown in Figure 7a. The vapor pressure of AlF(CH$_3$)$_2$ is 80 Torr at 100 °C. $\text{AlF}_3$ has been characterized as a tetramer in the gas phase. $\text{AlF}_3$ may also be the favored metal reaction product derived from $\text{AlF}_3$. TMA can also accept F from $\text{HfF}_4$ and donate CH$_3$ to produce volatile AlF(CH$_3$)$_2$. Hf reaction products with methyl ligands.

Figure 6. (a) Etch rates for $\text{ZrO}_2$ and $\text{HfO}_2$ versus $\text{SiCl}_4$ exposure time with constant HF exposure time of 1.0 s. (b) Etch rates for $\text{ZrO}_2$ and $\text{HfO}_2$ versus HF exposure time with constant $\text{SiCl}_4$ exposure time of 2.0 s.

Figure 7. Possible four-center transition states for (a) TMA with $\text{AlF}_3$, (b) TMA with $\text{ZrF}_4$, (c) DMAC with $\text{ZrF}_4$, and (d) SiCl$_4$ with $\text{ZrF}_4$. For the TMA results displayed in Figure 3, TMA can etch $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$. In contrast, TMA can not etch $\text{ZrO}_2$. The methyl ligand from TMA can form stable metal methyl compounds with Al and Hf. TMA can accept F from $\text{AlF}_3$ and donate CH$_3$ to produce volatile AlF(CH$_3$)$_2$ from TMA and metal products with methyl ligands from $\text{AlF}_3$. The possible four-center transition state for the ligand-exchange reaction between TMA and $\text{AlF}_3$ is shown in Figure 7a.
Hf(CH₃)₄ is known to be larger than Zr(CH₃)₄. The Hf–CH₃ bond energy is also larger than the Zr–CH₃ bond energy. 10 Zr(CH₃)₄ has been prepared but decomposes even at low temperatures ≤15 °C.11 The lack of etching of ZrO₂ by sequential HF and TMA exposures may result from no methyl ligand transfer from TMA to ZrF₄ in the possible four-center transition state displayed in Figure 7b.

Although TMA did not etch ZrO₂, DMAC was able to etch ZrO₂, effectively as shown in Figure 4. The difference between TMA and DMAC is the chloride ligand on DMAC. The chloride ligand may form Al–Cl–Zr bridge species that facilitate etching. 12 These Al–Cl–Zr bridge species are illustrated in the proposed four-center transition state for ligand exchange between DMAC and ZrF₄ in Figure 7c. The chloride ligand may also promote the stability or volatility of the Zr reaction products. DMAC is known to be a good fluoride acceptor and chloride donor when reacting with Hf and Zr fluorides. 30 Hf and Zr form stable volatile metal chlorides. HfCl₄ and ZrCl₄ sublime at 317 and 331 °C, respectively. 18 The presence of Cl in the metal precursor may also stabilize the etch products. ZrCl₄(CH₃)₂ and ZrCl₄(CH₃)₂ are much more stable than Zr(CH₃)₄. 34

Figure 5 shows that SiCl₄ is also able to etch ZrO₂. Together with the results for DMAC, these results argue that the chloride ligand is responsible for forming stable and volatile Zr reaction products. The possible four-center transition state for ligand exchange between SiCl₄ and ZrF₄ is displayed in Figure 7d. This ligand exchange would again form stable and volatile Zr chlorides.

The most surprising result in Figure 5 is the lack of Al₂O₃, etching by SiCl₄, ZrO₂, and HfO₂ were both etched by sequential SiCl₄ and HF exposures. Zr and HF are both known to form volatile metal chlorides. Al can also form volatile metal chlorides such as AlCl₃. The lack of Al₂O₃ etching by SiCl₄ led to the exploration of alternative explanations involving the reaction thermochemistry. The thermochemistry of the ligand exchange was determined assuming complete ligand exchange to form SiF₄ and the fully chlorinated metal in the original metal fluoride.

The thermochemical results for the ligand exchange between SiCl₄ and AlF₃, ZrF₄, and HfF₄ are given in Figure 8. These results reveal that the ligand exchange between SiCl₄ and ZrF₄, or HfF₄ is thermochromically favorable at >200 °C. In contrast, the ligand exchange between SiCl₄ and AlF₃ is not thermochromically favorable at any temperature shown in Figure 8. These results are consistent with the results in Figure 5. ZrF₄ and HfF₄ can both undergo ligand exchange with SiCl₄ at 350 °C because these reactions are spontaneous with ΔG ≈ −10 kcal/mol. On the other hand, Al₂O₃ cannot be etched at 350 °C because the ligand exchange between SiCl₄ and AlF₃ is not spontaneous with ΔG ≈ +26 kcal/mol.

In contrast to the results for Al₂O₃, HfO₂, and ZrO₂, SiO₂ and Si₃N₄ were not etched by any of the metal precursors under the reported reaction conditions. The formation of SiF₄ from SiO₂ and Si₃N₄ by reaction with HF is thermochromically favorable. The reaction SiO₂ + 4HF(g) → SiF₄(g) + 2H₂O(g) has ΔG values of −140, −130, and −120 kcal/mol at 200, 250, and 300 °C, respectively. 17 The reaction Si₃N₄ + 12HF(g) → 3SiF₄(g) + 4NH₃(g) has ΔG values of −159.9, −153.2, and −146.5 kcal/mol at 200, 250, and 300 °C, respectively.17 Both of these reactions produce SiF₄ as a reaction product. SiF₄ is extremely volatile. However, neither SiO₂ nor Si₃N₄ is etched spontaneously by HF. The fluorination of SiO₂ or Si₃N₄ does not proceed all the way to SiF₄. In agreement with these results, HF does not etch SiO₂ in the absence of H₂O. 35,36

Another explanation for the lack of etching of SiO₂ and Si₃N₄ is that the ligand-exchange reactions for Si–F species are not favorable. The Si–F bond is very strong. The Si–F bond in F₃Si has a bond strength of 167 kcal/mol. 37 The activation energy for breaking the Si–F bond may be too high for an effective ligand-exchange reaction. Large Si–F bond strengths also lead to large activation energies for the hydrolysis of SiF₄. 38

Ligand exchange may also not occur for the Si-compounds because the resulting reaction products are unstable. Si(IV) favors coordination numbers of four or six. The production of Si(acac)₄ when using Sn(acac)₂ as the metal precursor is not possible because this complex requires eight coordination. The requirements for Si acetylacetonates lead to a monodentating acac ligand or a cationic product such as Si(acac)₃.39 In contrast, Si could form stable Si(CH₃)₄ when using TMA as the metal precursor. Si could also form Si(CH₃)₂ or SiCl₄ when using DMAC as the metal precursor. Consequently, the lack of etching of SiO₂ and Si₃N₄ is probably explained by the high activation barrier to break Si–F bonds during ligand exchange.

TiN was also not etched by any of the metal precursors. The formation of TiF₃ from TiN by HF is thermochromically favorable. The reaction TiN + 3HF(g) → TiF₃ + NH₃(g) has ΔG values of −40.3, −37.0, and −33.8 kcal/mol at 200, 250, and 300 °C. 17 The ligand-exchange reaction between TiF₃ and Sn(acac)₂ may also be possible. The production of Ti(acac)₃ from TiN when using Sn(acac)₂ should be feasible based on earlier studies that have prepared Ti(acac)₃. 40 In contrast, the production of Ti(CH₃)₃ from TiF₃ when using TMA as the metal precursor is not expected because there are no previous reports for Ti(CH₃)₃ in the literature. Likewise, the production of TiCl₃ from TiF₃ when using DMAC or SiCl₄ as the metal precursor may not be viable because TiCl₃ has low volatility with a boiling point of 960 °C. 18

In addition to the absence of stable or volatile Ti(III) reaction products, the lack of etching of TiN may be explained by a TiNₐ oxide, or TiO₂ layer on the TiN surface. 31,32 In this case, HF would be required to fluorinate a Ti(IV) surface species.
This reaction is nearly thermochemically neutral.\textsuperscript{17} The formation of Ti(acac)\textsubscript{4} when using Sn(acac)\textsubscript{2} as the metal precursor for ligand exchange is also not favorable. Producing Ti(acac)\textsubscript{4} is not possible because this reaction product requires eight coordination. Ti(IV) acetylacetonate compounds favor six coordination with complexes such as Ti(=O)\textsubscript{2} (acac)\textsubscript{2} and TiCl\textsubscript{2}(acac)\textsubscript{2}.

The production of Ti(CH\textsubscript{3})\textsubscript{4} from TiF\textsubscript{4} when using TMA as the metal precursor is also not expected because Ti(CH\textsubscript{3})\textsubscript{4} decomposes at low temperatures <78 °C.\textsuperscript{34} In contrast, the production of TiCl\textsubscript{4} or TiCl\textsubscript{3}F\textsubscript{x} y from TiF\textsubscript{4} when using DMAC or SiCl\textsubscript{4} as the metal precursor is possible because TiCl\textsubscript{4} is a stable and volatile molecule. On the basis of these chemical arguments, the negligible etching of TiN by Sn(acac)\textsubscript{2}, TMA, DMAC, or SiCl\textsubscript{4} is attributed to either the absence of stable or volatile Ti(III) reaction products or the difficulty of fluorinating Ti(IV) surface species using HF.

**C. Selectivity Based On Temperature.** Temperature is also an important variable for selective thermal ALE. The temperature-dependent etch rates of ZrO\textsubscript{2}, HfO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3} using sequential HF and SiCl\textsubscript{4} exposures are shown in Figure 9.

![Figure 9](Image)

Figure 9. Etch rates of ZrO\textsubscript{2}, HfO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3} versus temperature using SiCl\textsubscript{4} as the metal precursor.

None of the three metal oxides is etched at 250 °C. The etch rates for ZrO\textsubscript{2} and HfO\textsubscript{2} become measurable at 300 °C. The etch rates at 350 °C were obtained from Figure 5. The etch rate of ZrO\textsubscript{2} is larger than HfO\textsubscript{2} at both 300 and 350 °C. The etch rate of Al\textsubscript{2}O\textsubscript{3} is not measurable at any of the three temperatures.

The results in Figure 9 are consistent with the thermochemical calculations in Figure 8. The ligand-exchange reaction between SiCl\textsubscript{4} and AlF\textsubscript{3} is unfavorable at all the temperatures shown in Figure 8. The ligand-exchange reaction between SiCl\textsubscript{4} and ZrF\textsubscript{4} or HfF\textsubscript{4} is feasible at >200 °C. The increasing negative \( \Delta G \) for the ligand-exchange reaction between SiCl\textsubscript{4} and ZrF\textsubscript{4} or HfF\textsubscript{4} in Figure 8 is in agreement with the increasing etch rates at >250 °C displayed in Figure 9. The ZrO\textsubscript{2} etch rate is higher than the HfO\textsubscript{2} etch rate even though their predicted \( \Delta G \) values are nearly equivalent. There must be additional kinetic factors that determine the actual etch rates.

Temperature and various metal precursors can also be used to tune the etch rate of a particular material. For example, the etch rates for Al\textsubscript{2}O\textsubscript{3} ALE using various metal precursors are compared at different reaction temperatures in Figure 10. The ALE results for Sn(acac)\textsubscript{2} as the metal precursor were obtained earlier using a reaction sequence of 1–30–1–30.\textsuperscript{8} The ALE results for TMA as the metal precursor were also measured earlier using a reaction sequence of 2–30–1–30.\textsuperscript{11} The ALE results for DMAC as the metal precursor were obtained using a reaction sequence of 2–30–1–30. Each etch rate was measured using the mass change per cycle (MCPC) and the density of the Al\textsubscript{2}O\textsubscript{3} film obtained by XRR.

The Al\textsubscript{2}O\textsubscript{3} etching has different threshold temperatures for each metal precursor. The Al\textsubscript{2}O\textsubscript{3} etch rates all increase at higher temperatures after exceeding the threshold temperature. Figure 10a shows that Sn(acac)\textsubscript{2} etched Al\textsubscript{2}O\textsubscript{3} at temperatures ≥150 °C. In comparison, Figure 10b indicates that DMAC etched Al\textsubscript{2}O\textsubscript{3} at higher temperatures ≥225 °C. Figure 10c shows that TMA etched Al\textsubscript{2}O\textsubscript{3} at even higher temperatures ≥250 °C. The different temperature thresholds may be attributed to varying activation barriers for the ligand-exchange reactions. The different temperature thresholds for the etching may provide another method for obtaining selective thermal ALE.

**IV. CONCLUSIONS**

Selective thermal ALE can be accomplished by using different metal precursors for ligand exchange. This study explored selectivity in ALE using Sn(acac)\textsubscript{2}, TMA, DMAC, and SiCl\textsubscript{4} as the metal precursors. These different metal precursors transfer acac, methyl, and chloride ligands during ligand exchange. Etching can occur if these ligands form stable and volatile reaction products during the ligand-exchange reaction. Differences between the stability and volatility of the possible reaction products can lead to selective etching.

This study examined the etching of Al\textsubscript{2}O\textsubscript{3}, HfO\textsubscript{2}, ZrO\textsubscript{2}, SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}, and TiN thin films on silicon wafers. All of the metal precursors etched HfO\textsubscript{2}. All of the metal precursors also etched Al\textsubscript{2}O\textsubscript{3} except SiCl\textsubscript{4}. ZrO\textsubscript{2} was etched by all of the metal precursors except TMA. In contrast, none of the metal precursors could etch SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}, and TiN. The explanation for these results was based on the stability and volatility of the possible reaction products. The lack of etching of Al\textsubscript{2}O\textsubscript{3} by SiCl\textsubscript{4} was explained based on thermochemical considerations.

Selective thermal ALE can also be achieved by tuning the reaction temperature. The etching of ZrO\textsubscript{2}, HfO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3}...
using SiCl₄ as the metal precursor was consistent with thermochemical calculations. Temperature can be used to adjust the ZrO₂ etch rate relative to the HfO₂ etch rate using SiCl₄ as the metal precursor. The combination of different metal precursors and variable temperature can also tune the etch rate for Al₂O₃ ALE over a wide range of temperature. The combination of different metal precursors with various ligands and different temperatures will provide pathways for selective thermal ALE. The selectivity in thermal ALE will complement the selectivity in ALD to provide for maskless processing. This selectivity will be important for atomic level processing to fabricate advanced semiconductor devices.

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**Notes**

The authors declare no competing financial interest.

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