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Mechanisms of Thermal Atomic Layer Etching

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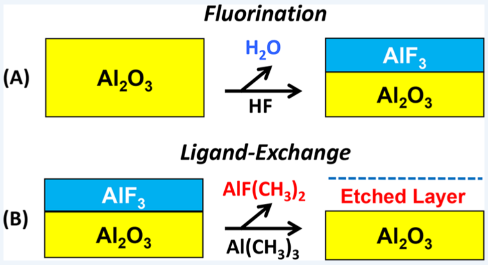

CONSPECTUS: Atomic layer control of semiconductor processing is needed as critical dimensions are progressively reduced below the 10 nm scale. Atomic layer deposition (ALD) methods are meeting this challenge and produce conformal thin film growth on high aspect ratio features. Atomic layer etching (ALE) techniques are also required that can remove material with atomic layer precision. ALE processes are defined using sequential, self-limiting reactions based on surface modification and volatile release. Plasma ALE methods employ energetic ion or neutral species to release the modified material anisotropically using sputtering. In contrast, thermal ALE processes utilize gas species to release the modified material isotropically using thermal reactions. Thermal ALE can be viewed as the "reverse of ALD".

There are a number of mechanisms for thermal ALE that have developed over the last five years. This Account will first examine the fluorination and ligand-exchange mechanism for thermal ALE. This mechanism is applicable for many metal oxide and metal nitride materials. Subsequently, the "conversion etch" mechanisms will be explored that are derived from the conversion of the surface of the substrate to a new material. The "conversion etch" mechanisms are needed when the initial material does not have a viable etching pathway via fluorination and ligand-exchange or when the material has a volatile fluoride. The thermal ALE mechanisms founded on either oxidation or halogenation of the initial substrate will then be examined with an emphasis on metal thermal ALE. Lastly, thermal ALE mechanisms will be considered that are based on self-limiting surface ligands or temperature modulation mechanisms. These various mechanisms offer a wide range of pathways to remove material isotropically with atomic layer control.

Thermal ALE will be required to fabricate advanced semiconductor devices. This fabrication will increasingly occur beyond the limits of lithography and will extend into the third dimension. The situation is like Manhattan during the advent of skyscrapers. When there was no more room on the ground, building started to move to the third dimension. Three-dimensional devices require a sequential series of deposition and etching steps to build the skyscraper structures. Some etching needs to be vertical and anisotropic to make the elevator shafts. Other etching needs to be horizontal and isotropic to form the hallways. The mechanisms of thermal ALE will be critical for the definition of isotropic ALE processes.

Reaching beyond the limits of lithography will also increase the need for maskless processing. The mechanisms of thermal ALE lead to strategies for selective etching of one material in the presence of many materials. In addition, area-selective deposition can benefit from the ability of thermal ALE to enhance deposition on the desired growth surfaces by removing deposition from other surrounding surfaces. Looking ahead, thermal ALE will continue to provide unique capabilities and will grow in importance as a nanofabrication processing technique.

1. INTRODUCTION

With continued miniaturization, atomic layer processing is increasingly important for nanofabrication. There is a need for atomic layer control for both deposition and removal of material. Sequential, self-limiting surface reactions provide the foundation for atomic layer deposition (ALD) and atomic layer etching (ALE). ALD is a well-established technique that underlies semiconductor device fabrication and many other applications.[1] ALE is a relative newcomer that is still in the developmental stage.[2,3]

ALE can be subdivided into two categories: plasma ALE[2,4] and thermal ALE.[5] Both plasma and thermal ALE utilize sequential surface modification and removal reactions. Plasma ALE removes surface species with energetic ions or neutral atoms.[2,4] Because of the directionality of the energetic ions and neutral atoms, plasma ALE yields anisotropic etching that is needed to fabricate high aspect ratio features.[2] In contrast, the randomness of gas species and the self-limiting nature of thermal ALE reactions produce isotropic and conformal etching.[6,7]

Thermal ALE can be viewed as the reverse of ALD.[1,8] Both thermal ALE and ALD rely on binary surface reaction sequences.

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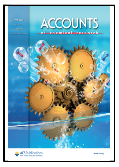

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A schematic for thermal ALE based on surface modification and volatilization reactions is shown in Figure 1. The first surface modification reaction produces an altered surface layer. The second reaction then liberates volatile etch products from this altered surface layer. Ideally, both of these surface reactions are self-limiting. The repetition of these surface modification and volatilization reactions defines the thermal ALE process.

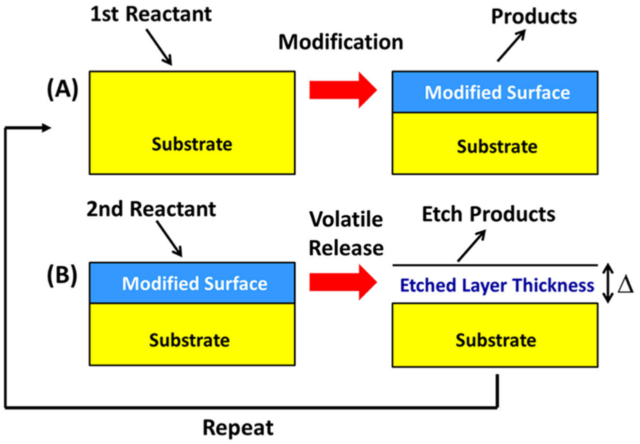

Figure 1. Schematic of ALE process based on sequential surface modification and volatile release reactions.

This Account considers the mechanisms of ALE processes that are only dependent on temperature or involve thermal annealing. ALE processes that involve ions or energetic neutral atoms for the volatile release process are not considered in this survey. Some plasma processes that are utilized only for surface modification are included in this Account. The goal is to introduce the many possible pathways for thermal ALE and to inspire the development of new mechanisms.

2. FLUORINATION AND LIGAND-EXCHANGE MECHANISM

The main thermal ALE mechanism for metal oxides is based on fluorination and ligand-exchange reactions.[9] Fluorination is the surface modification reaction. Fluorination is thermochemically favorable because most metal fluorides are more stable than their corresponding metal oxides.[9] One difficulty with fluorination is that some metal fluorides are volatile. These metal oxides require a different thermal ALE mechanism.

Ligand-exchange is the reaction that volatilizes the modified surface. Ligand-exchange is a metal-exchange transmetalation reaction between adjacent metal centers.[10,11] Ligand-exchange reactions are useful to replace fluorine in the metal fluoride with ligands that break the strong metal−fluorine−metal bridge bonding that stabilizes the metal fluoride.[12] This ligand replacement leads to volatile complexes that can desorb from the surface.

2.1. Thermal Al_2O_3 ALE

The first fluorination and ligand-exchange reaction utilized HF and $Sn(acac)_2$ as the reactants for Al_2O_3 ALE.[5] The original intent of using these reactants was to grow SnF_2 by an ALD process on an Al_2O_3 ALD surface. However, these reactions were observed to etch the Al_2O_3 instead of depositing SnF_2.[5] Figure 2 shows quartz crystal microbalance (QCM) results that observed the linear loss of mass versus number of Al_2O_3 ALE cycles at 200 °C. The mass loss of -8.4 ng/(cm^2 cycle) is equivalent to an etch rate of 0.28 Å/cycle.[5] These results suggested that a new class of reactions similar to the "reverse of ALD" was possible to remove material.

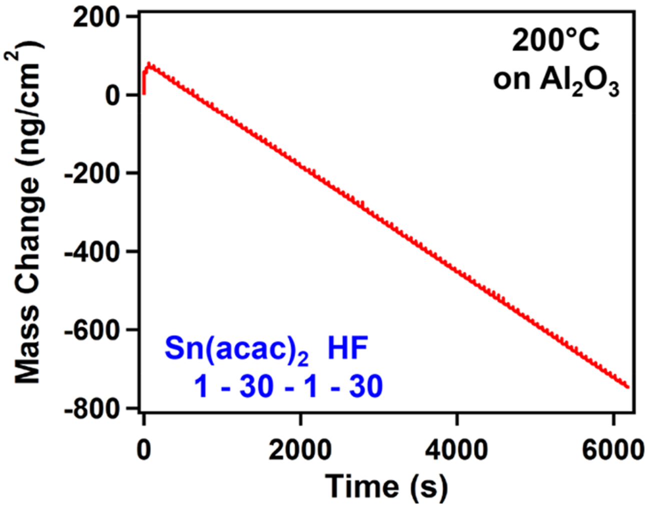

Figure 2. Mass change versus time during Al_2O_3 ALE at 200 °C using HF and $Sn(acac)_2$ as the reactants. Reproduced with permission from ref 5. Copyright 2015 American Chemical Society.

Subsequent studies explored the mechanism of Al_2O_3 ALE with HF and $Sn(acac)_2$.[13] These investigations identified the growth of surface fluoride and loss of Al_2O_3 during the HF exposure. Likewise, the loss of surface fluoride was monitored during the $Sn(acac)_2$ exposure.[13] The ligand-exchange reaction transfers acac ligands to the AlF_3 surface layer. Presumably, SnF(acac) remains volatile after the ligand-exchange reaction. The Al species probably become volatile as $AlF(acac)_2$ or $Al(acac)_3$ after multiple ligand-exchange reactions or redistribution of acac ligands on the surface.

Additional studies explored other precursors for the ligand-exchange reaction. Trimethylaluminum (TMA) was observed to etch Al_2O_3 together with HF for the fluorination reaction.[14] These results were remarkable because TMA is the main precursor for Al_2O_3 ALD using H_2O as the oxygen precursor.[15] With only the change of H_2O to HF, the TMA reactant can etch Al_2O_3. The ligand-exchange reaction between TMA and AlF_3 is shown in Figure 3. This reaction produces $AlF(CH_3)_2$ (dimethylaluminum fluoride, DMAF) from the TMA reactant.[6,14] In addition, $AlF(CH_3)_2$ may also be the volatile etch product from the AlF_3 surface after two ligand-exchange reactions or redistribution of CH_3 ligands on the surface.[6]

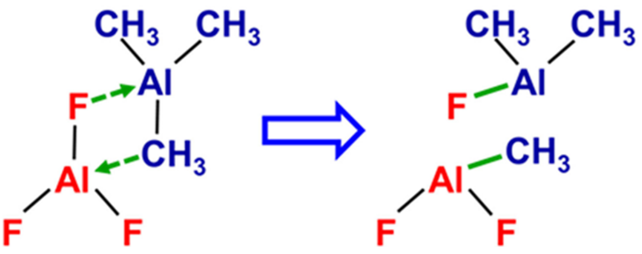

Figure 3. Ligand-exchange reaction between AlF_3 and $Al(CH_3)_3$. Reproduced with permission from ref 9. Copyright 2016 American Chemical Society.

The overall reaction for Al_2O_3 ALE using HF and TMA can be written as

$$Al_2O_3 + 6HF + 4Al(CH_3)_3 \rightarrow 6AlF(CH_3)_2 + 3H_2O \quad (1)$$

This reaction can be divided into individual HF and TMA reactions:[14]

$$(A) Al_2O_3|Al_2O_3^* + 6HF \rightarrow Al_2O_3|2AlF_3^* + 3H_2O \quad (2)$$

$$(B) Al_2O_3|2AlF_3^* + 4Al(CH_3)_3 \rightarrow Al_2O_3^* + 6AlF(CH_3)_2 \quad (3)$$

The Al_2O_3 that is etched during the ALE reactions is designated by $Al_2O_3^*$. The asterisks indicate the surface species and the vertical lines separate the various species. A schematic for Al_2O_3 ALE is also displayed in Figure 4.

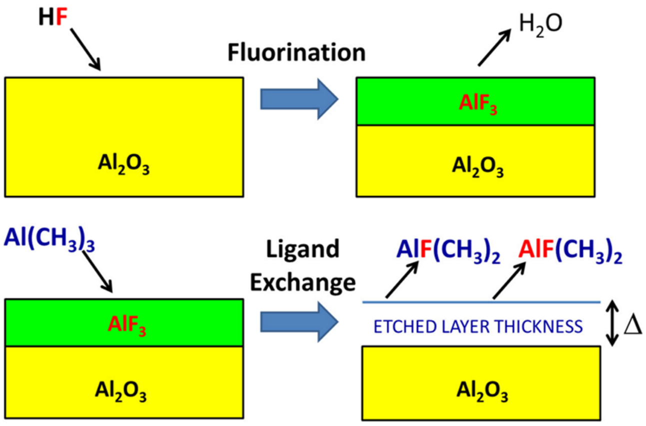

Figure 4. Schematic of Al_2O_3 ALE based on fluorination with HF and ligand-exchange with $Al(CH_3)_3$.

Mass spectrometry studies confirmed the presence of $AlF(CH_3)_2$ etch products.[6] However, DMAF was observed as the dimer of DMAF with itself (DMAF/DMAF) or with TMA (DMAF/TMA).[6] These dimers are favored because of strong bridge bonding between fluorine and the Al metal centers. Fluorine forms stronger bridge bonds between the Al metal centers than CH_3.[6] Knowledge of the bridge bonding strengths suggests that fluorine forms bridge bonds in the dimers and CH_3 ligands are in the terminal positions. The terminal CH_3 ligands facilitate desorption of the dimer from the surface.[6]

Temperature also was a key variable for Al_2O_3 ALE. The HF and TMA reactants led to Al_2O_3 ALE at >250 °C.[14,16] The etch rates were progressively larger at higher temperatures where the sequential reactant exposures yield etching by fluorination and ligand-exchange.[14] The HF and TMA reactants could also produce AlF_3 ALD at $T < 250$ °C where the sequential reactant exposures led to metal fluoride growth by an ALD process.[16] Competition between Al_2O_3 ALE and AlF_3 ALD was also observed in studies on SiO_2 nanoparticles.[17]

There is also competition between Al_2O_3 ALE and AlF_3 growth when using HF and TMA as the reactants during rapid Al_2O_3 ALE.[18] For rapid Al_2O_3 ALE, there is no purge time, and the HF and TMA exposures overlap in time and produce AlF_3 CVD.[18] The subsequent TMA exposure outside of the overlap with HF is then able to spontaneously etch AlF_3.[16] After removing the AlF_3 CVD layer, TMA can proceed to remove the AlF_3 layer on the surface of the Al_2O_3 substrate. The spontaneous etch of AlF_3 by TMA allows rapid Al_2O_3 ALE to be performed with a short cycle time without a purge.

Additional experimental studies explored the fluorination of Al_2O_3 by HF.[19] Higher HF pressure increased the Al_2O_3 fluorination and the Al_2O_3 etch rate. Fluoride thicknesses up to 5−6 Å were measured for higher HF pressures of 4−8 Torr.[19] These high HF pressures yielded Al_2O_3 etch rates of ~2.5 Å/cycle at 300 °C.[19] Theoretical studies have also examined the fluorination of Θ-Al_2O_3 by HF.[20] These investigations revealed that a self-limiting fluoride coverage is obtained on Θ-Al_2O_3. The experimental studies were consistent with a fluoride composition of Al_2OF_4.[19]

2.2. Other Materials, Reactants, and Effect of Film Structure

The fluorination and ligand-exchange mechanism is applicable for many other metal oxides including HfO_2 and ZrO_2.[7,21,22] In addition to $Sn(acac)_2$ and TMA, many different metal precursors such as $AlCl(CH_3)_2$ (dimethylaluminum chloride (DMAC)), $SiCl_4$ and $TiCl_4$, have been effective for the ligand-exchange reaction.[7,22,23] These metal precursors provide various ligands, such as acac, CH_3, and Cl. Different degrees of etching selectivity are derived from these ligands.

Etching selectivity results for TMA are shown in Figure 5a.[23] Together with HF for fluorination, TMA is able to etch Al_2O_3

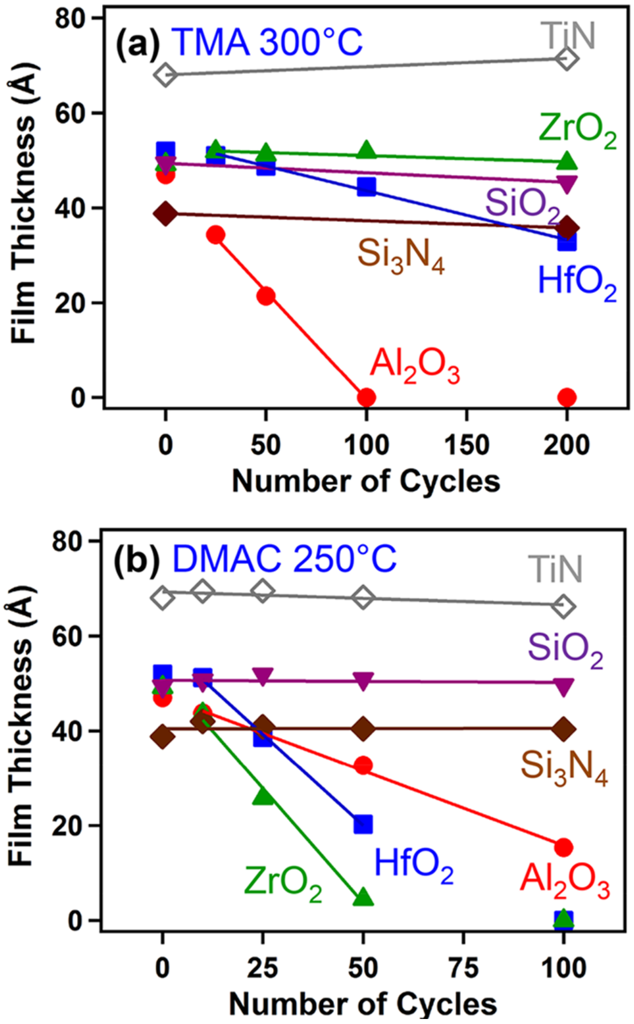

Figure 5. Film thickness versus number of ALE cycles for various materials using HF as fluorine reactant and (a) TMA or (b) DMAC as metal precursor for ligand-exchange. Reproduced with permission from ref 23. Copyright 2016 American Chemical Society.

and HfO_2. However, TMA is not able to etch TiN, ZrO_2, SiO_2, or Si_3N_4. Al_2O_3 is able to etch because $AlF(CH_3)_2$ is a stable and volatile etch product. HfO_2 etches at a lower rate, presumably because possible etch products such as $HfF(CH_3)_3$ or $Hf(CH_3)_4$ are not as stable and volatile as $AlF(CH_3)_2$. In comparison, ZrO_2 etches at a negligible rate. The differences between HfO_2 and ZrO_2 are surprising because the properties of Hf and Zr are usually similar. However, $Hf(CH_3)_4$ has a higher stability than $Zr(CH_3)_4$ and the Hf-CH_3 bond energy is larger than the Zr-CH_3 bond energy.[24,25]

Another example of selectivity for DMAC is displayed in Figure 5b.[23] In similarity to the results for TMA in Figure 5a, Al_2O_3 and HfO_2 are etched by DMAC together with HF for fluorination. These results are anticipated because TMA and DMAC both have CH_3 ligands for the ligand-exchange reaction. In addition, DMAC is able to etch ZrO_2. The ability of DMAC to etch ZrO_2 is believed to be linked to the Cl ligand on DMAC. A ligand-exchange reaction between DMAC and the fluoride layer on ZrO_2 can transfer Cl ligands that can form stable and volatile Zr complexes.

Stronger fluoride precursors than HF may be needed for thermochemically favorable fluorination. SF_4 and XeF_2 are two stronger fluorination reactants that have been explored for thermal ALE. SF_4 was demonstrated for Al_2O_3 ALE and VO_2 ALE.[26] Metal nitrides can also be etched using thermal ALE based on fluorination and ligand-exchange reactions. XeF_2 was reported to be necessary for GaN ALE.[27] In contrast, SF_4 and HF were not successful for GaN ALE.[27] The difficulty in etching GaN may be related to the crystallinity of the GaN films. However, AlN ALE was observed for crystalline AlN films using HF and $Sn(acac)_2$ as the reactants.[28]

The effect of film crystallinity has been studied for amorphous and crystalline HfO_2, ZrO_2, and $HfZrO_4$ films.[29] The amorphous films all etched faster than the crystalline films under the same reaction conditions. HfO_2 ALE results for amorphous and crystalline HfO_2 films using HF and $TiCl_4$ as the reactants at 250 °C are displayed in Figure 6.[29] Crystallinity reduces the etch rate. This reduction may be related to the higher density of the crystalline films. Fluorination of the metal oxides results in a volume expansion. This volume expansion may be easier for the amorphous films.[29]

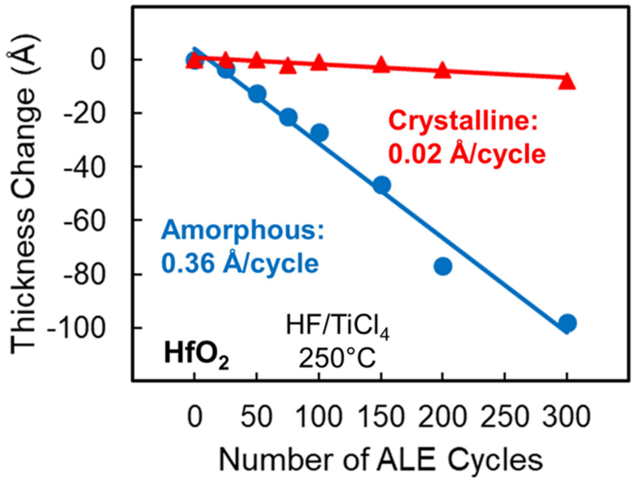

Figure 6. Thickness change versus number of ALE cycles for crystalline and amorphous HfO_2 using HF and $TiCl_4$ as reactants. Reproduced with permission from ref 29. Copyright 2020 American Vacuum Society.

3. CONVERSION MECHANISMS

Many materials do not have a direct pathway for thermal ALE based on fluorination and ligand-exchange reactions. Some metal oxides will form a volatile fluoride and etch spontaneously. Other metal fluorides after fluorination may not easily form stable and volatile etch products with various metal precursors. For example, Figure 5 showed that the TMA and DMAC metal precursors were not able to etch TiN, SiO_2, or Si_3N_4 under the reaction conditions employed at 250 or 300 °C.[23] These materials do not have accessible pathways to stable and volatile etch products.

One possible strategy for these materials is to use a metal precursor to convert the surface of the original metal oxide to another metal oxide. This conversion process occurs because the original metal oxide is not as stable as the resulting metal oxide. The stability of the metal oxides can be determined by their heats of formation. In addition, Ellingham diagrams or thermochemical calculations can be used to predict the possible conversion of one oxide to another more stable oxide. A metal nitride can also be converted to another more stable nitride.

3.1. Conversion, Fluorination, and Ligand-Exchange

The conversion mechanism was initially observed for ZnO ALE using HF and TMA.[30] QCM studies revealed much larger mass losses during TMA exposures than expected from ligand-exchange reactions. These large mass losses suggested that TMA converts the surface of the ZnO substrate to a more stable Al_2O_3 surface layer. The Al_2O_3 surface layer can then be fluorinated and subsequently removed by the TMA ligand-exchange reaction. The TMA can continue to convert the underlying ZnO surface to Al_2O_3. A schematic illustrating the ZnO ALE surface chemistry via the conversion, fluorination, and ligand-exchange mechanism is shown in Figure 7.[30]

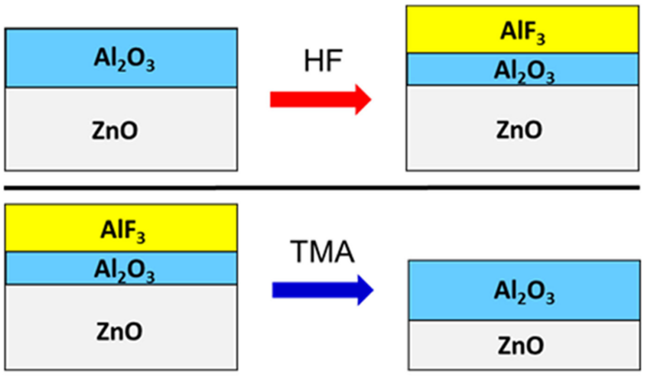

Figure 7. Schematic for ZnO ALE using HF and TMA as reactants. TMA removes AlF_3 layer by ligand-exchange and then converts the surface of underlying ZnO to an Al_2O_3 surface layer. Reproduced with permission from ref 30. Copyright 2017 American Chemical Society.

Another example of the conversion, fluorination, and ligand-exchange mechanism is thermal SiO_2 ALE using HF and TMA.[31] TMA is able to convert the surface of SiO_2 to Al_2O_3. This conversion process requires higher pressures of TMA than the TMA pressures of ~40 mTorr that were utilized in the TMA results shown in Figure 5a.[23] At reactant pressures of 1.0 and 4.0 Torr, SiO_2 etch rates were 0.18 and 0.27 Å/cycle, respectively.[31] Corresponding Fourier transform infrared (FTIR) spectroscopy studies confirmed the conversion of Si−O stretching vibrations to Al−O stretching vibrations. The FTIR investigations also observed greater conversion at higher reactant pressures. A schematic of thermal SiO_2 ALE via conversion to Al_2O_3 or aluminum oxide silicate is shown in Figure 8.[31]

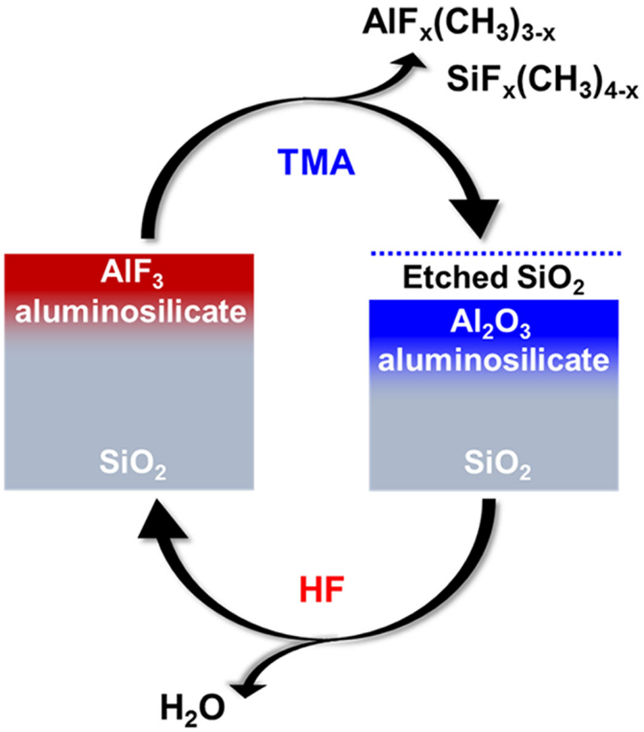

Figure 8. Schematic for SiO_2 ALE using TMA and HF as reactants. TMA removes AlF_3 layer by ligand-exchange and then converts surface of underlying SiO_2 to an Al_2O_3 surface layer. Reproduced with permission from ref 31. Copyright 2017 American Chemical Society.

3.2. Conversion and Fluorination to Volatile Fluoride

Another class of conversion reactions produce metal oxides that spontaneously etch to produce volatile fluorides after fluorination. These conversion reactions readily lead to pathways for thermal ALE. One useful reactant for conversion and fluorination to a volatile fluoride is BCl_3. BCl_3 can convert metal oxides to B_2O_3 because B_2O_3 is a very stable metal oxide. In addition, B_2O_3 can be etched spontaneously using HF.[32] The spontaneous etch products are believed to be BF_3 and $B(OH)F_2$.

WO_3 ALE using BCl_3 and HF is an example of an ALE process that may occur via conversion and fluorination to a volatile fluoride. The proposed mechanism for WO_3 ALE is shown in Figure 9.[32] The surface of WO_3 is first converted to a B_2O_3 surface layer by BCl_3 exposure. Subsequently, the B_2O_3 surface layer is spontaneously etched by HF. The underlying WO_3 is not spontaneously etched by HF and serves as an etch stop. Mass spectrometry studies are needed to confirm this etching mechanism.

4. OXIDATION MECHANISMS

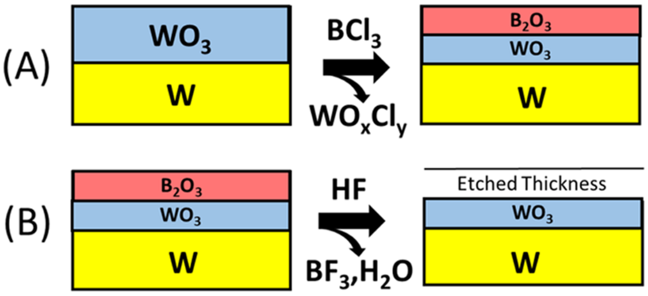

Figure 9. Schematic for WO_3 ALE using BCl_3 and HF as reactants. BCl_3 converts the surface of WO_3 to a B_2O_3 surface layer. HF then spontaneously etches the B_2O_3 surface layer. Reproduced with permission from ref 32. Copyright 2017 American Chemical Society.

Oxidation is a useful step for many thermal ALE pathways. Oxidation changes the oxidation number of the element that may be critical to obtain the correct oxidation state for the stable, volatile etch product. Oxidation can oxidize elemental metals to metal oxides. Elemental metals have an oxidation state of zero. Many volatile metal etch products have the metal oxidation state in 2+, 3+, or 4+. Oxidation can also convert metal nitrides to metal oxides. Many metal nitrides have the metal in the 3+ oxidation state. However, many stable etch products require the metal in the 4+ oxidation state.

4.1. Oxidation and Fluorination to Volatile Fluoride

TiN ALE using O_3 and HF as the reactants is an example of oxidation and fluorination to a volatile fluoride.[33] The oxidation state of Ti in TiN is 3+. The oxidation state for most stable volatile Ti complexes is 4+. TiN can be oxidized to TiO_2 using ozone. This oxidation converts the Ti oxidation state to 4+. After the oxidation of TiN to TiO_2, the TiO_2 surface layer can be spontaneously etched using HF. A schematic of TiN ALE is displayed in Figure 10.[33] TiN etch rates of 0.2 Å/cycle were measured at 250 °C. The TiN etch rate was also self-limiting versus O_3 and HF exposure times.[33]

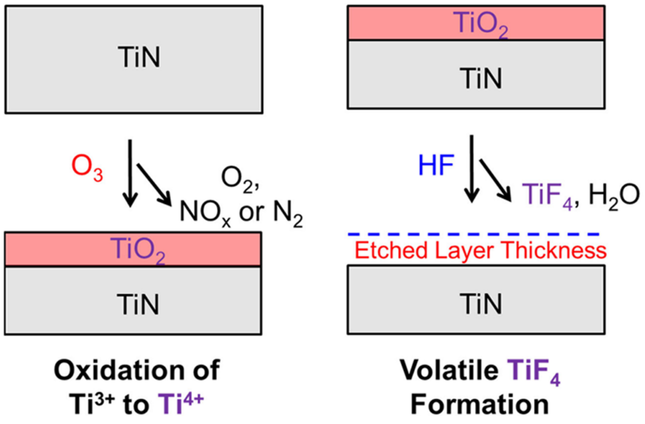

Figure 10. Schematic for TiN ALE using O_3 and HF as reactants. O_3 oxidizes TiN to TiO_2. HF then spontaneously etches the TiO_2 surface layer. Reproduced with permission from ref 33. Copyright 2017 American Chemical Society.

W ALE using O_2 and WF_6 is another example of oxidation and fluorination to a volatile fluoride.[34] For W ALE, the W surface is first oxidized to WO_3 using O_2. This oxidation changes the oxidation state of W from 0 to 6+. Subsequently, WF_6 is able to etch the WO_3 surface layer by forming volatile WO_xF_y species. This W ALE procedure is consistent with previous studies where WF_6 was observed to spontaneously etch WO_3 at >180 °C during WO_3 ALD.[35,36]

4.2. Oxidation, Conversion, Fluorination, and Ligand-Exchange

Oxidation can also be used together with conversion to define other thermal ALE mechanisms. The oxidation and conversion pathway is critical to define thermal Si ALE.[37] For thermal Si ALE, Si is first oxidized to produce a surface SiO_2 layer. Subsequently, the surface SiO_2 layer is converted to Al_2O_3 or an aluminum oxide silicate using TMA at higher pressures as discussed in Section 3.1. The Al_2O_3 or aluminum oxide silicate is then removed by fluorination and ligand-exchange reactions as discussed in Section 2.1. A schematic for thermal Si ALE is shown in Figure 11.[37]

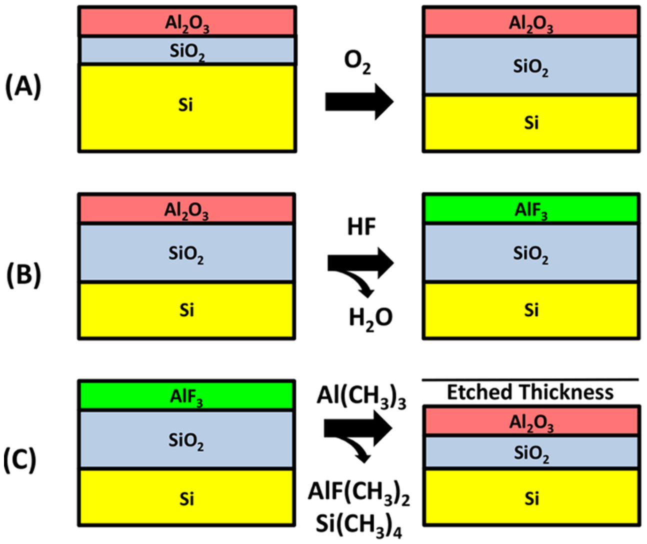

Figure 11. Schematic for Si ALE using O_2, HF, and $Al(CH_3)_3$. O_2 oxidizes Si to SiO_2. HF converts the top Al_2O_3 layer to AlF_3. $Al(CH_3)_3$ removes the AlF_3 surface layer by a ligand-exchange reaction and then converts SiO_2 to Al_2O_3. Reproduced with permission from ref 37. Copyright 2018 American Chemical Society.

Results for Si ALE based on spectroscopic ellipsometry studies are displayed in Figure 12.[37] Si ALE using a O_2, HF, and TMA reaction sequence yields a Si etch rate of 0.4 Å/cycle at 290 °C.[37] The ellipsometric investigations also monitor a SiO_2 layer with a thickness of ~11 Å that exists on the Si surface during Si ALE. This SiO_2 layer is continuously formed from Si oxidation and then converted to an Al_2O_3 or aluminum oxide silicate surface layer by the TMA exposure prior to removal by fluorination and ligand-exchange reactions.

Si_3N_4 ALE can also be accomplished using the oxidation, conversion, fluorination and ligand-exchange mechanism.[38] Because Si_3N_4 is more difficult to oxidize than Si, O_3 is preferable to O_2 for the oxidation reaction. Similar etch rates are measured for Si_3N_4 ALE and Si ALE under comparable reaction conditions with O_3 as the oxidant for Si_3N_4 ALE and O_2 as the oxidant for Si ALE. A Si_3N_4 etch rate of 0.47 Å/cycle was measured at 290 °C using an O_3−HF−TMA reactant sequence.[38]

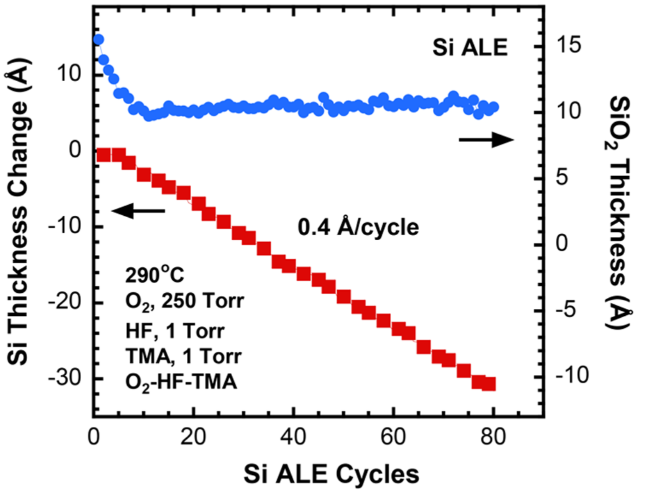

Figure 12. Si ALE using O_2, HF, and $Al(CH_3)_3$ as reactants at 290 °C. Si etching occurs with an etch rate of 0.4 Å/cycle, while the top SiO_2 layer remains constant at ~11 Å. Reproduced with permission from ref 37. Copyright 2018 American Chemical Society.

4.3. Oxidation, Conversion, and Fluorination to Volatile Fluoride

Oxidation can also be combined with conversion and fluorination to a volatile fluoride to define another thermal ALE mechanism. This pathway was utilized for thermal W ALE.[32] The W substrate was first oxidized using ozone to form a WO_3 surface layer. The WO_3 surface layer was then removed using BCl_3 and HF as the reactants as discussed in Section 3.2. BCl_3 converts the WO_3 surface layer to a B_2O_3 surface layer. HF can then spontaneously etch the B_2O_3 surface layer. A schematic showing this three-step process is given in Figure 13.[32]

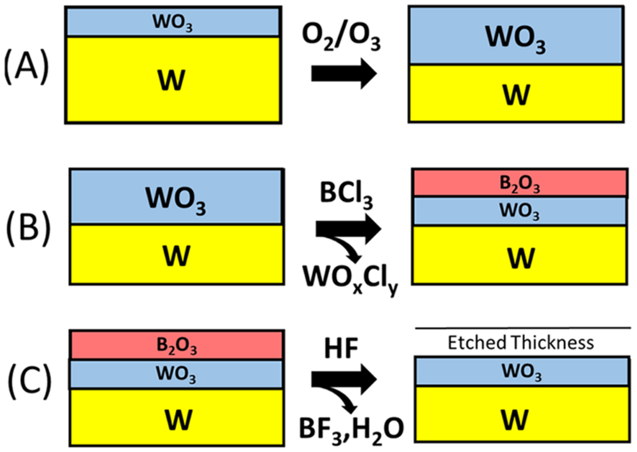

Figure 13. Schematic for W ALE using O_2/O_3, BCl_3, and HF. O_2/O_3 oxidizes W to WO_3. BCl_3 converts WO_3 to B_2O_3. HF then spontaneously etches B_2O_3. Reproduced with permission from ref 32. Copyright 2017 American Chemical Society.

In situ spectroscopic ellipsometry measurements monitored both the WO_3 surface layer and the underlying W film thickness during W ALE. Figure 14 shows the WO_3 and W thicknesses during W ALE at 207 °C.[32] The WO_3 thickness displayed in Figure 14a oscillates as the WO_3 layer is increased in thickness by O_3 exposures and then etched by BCl_3/HF exposures. While the WO_3 thickness is oscillating, the underlying W film thickness decreases linearly as W is progressively converted into WO_3. The results in Figure 14b yield a W etch rate of 2.44 Å/cycle.[32] Additional experiments determined that the individual O_3, BCl_3, and HF exposures were self-limiting.[32]

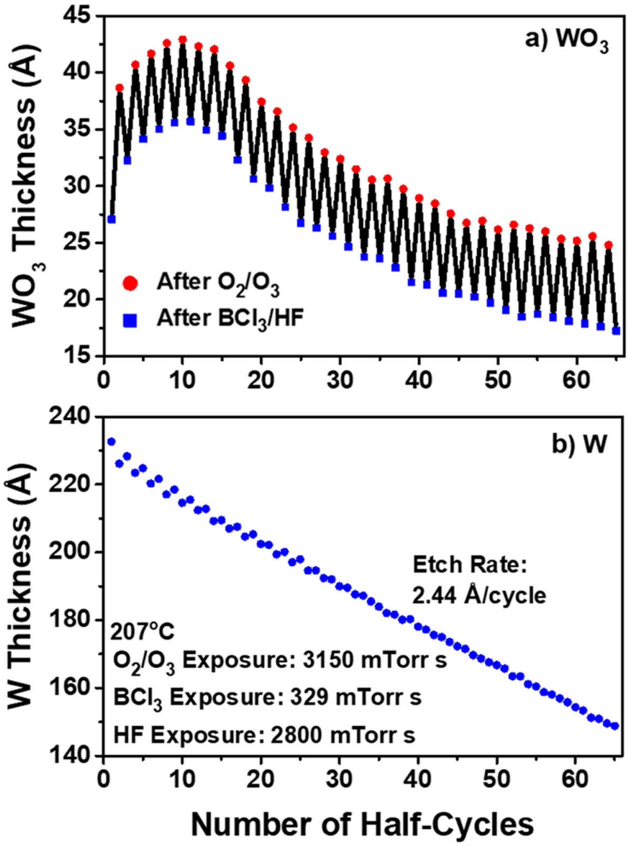

Figure 14. W ALE using O_2/O_3, BCl_3, and HF as reactants at 207 °C. (a) WO_3 thickness increases after O_2/O_3 exposure and decreases after BCl_3/HF exposure. (b) W etching occurs with an etch rate of 2.44 Å/cycle. Reproduced with permission from ref 32. Copyright 2017 American Chemical Society.

4.4. Oxidation and Ligand Volatilization

Oxidation is critical for thermal metal ALE. Oxidation increases the oxidation state of the metal. Subsequently, various ligands can extract the oxidized metal and produce a metal complex that is both stable and volatile. Copper thermal ALE is an example of this mechanism using oxidation with O_2 or O_3 to increase the Cu oxidation number and yield Cu_2O or CuO, respectively.[39] The Cu_2O is then believed to interact with hexafluoroacetylacetone (hfacH) in a disproportionation reaction to form volatile $Cu(hfac)_2$ and elemental Cu.[39] This process produced an etch rate of 0.9 Å/cycle at 275 °C.[39] Alternatively, the CuO is thought to interact with hfacH to produce $Cu(hfac)_2$ and H_2O.[39] This process yielded an etch rate of 84 Å/cycle at 275 °C.[39]

Metal ALE using oxidation and ligand volatilization has also been performed using an O_2 plasma to oxidize the metal. Fe, Cu, Co, Pd, and Pt have been oxidized using an O_2 plasma to change the oxidation state of the metal.[40] Subsequently, the metal oxide has been removed using various organic ligands such as formic acid.[40] The metal etch rates varied from 5 Å/cycle for Pt to 42 Å/cycle for Fe.[40] The etch rates also were proportional to the oxide thicknesses produced by the O_2 plasma.[40]

5. HALOGENATION MECHANISMS

Halogenation is another key step for the thermal ALE of metals. Like oxidation, halogenation changes the oxidation state of the metal. This change may be necessary for the metal to obtain the correct oxidation state to yield stable, volatile etch products. The metal complexes will have an oxidation state determined by the number of halide ligands. In addition, the metal complexes will also contain additional two-electron donor ligands to obey the "18 electron rule" or "16 electron rule".[41]

Guidelines to determine stable metal complexes are given by the Covalent Bond Classification (CBC) method.[42] X ligands are one-electron donors such as halogens like Cl. L ligands are two-electron donors like PR_3 or NR_3. The stable metal complex has an initial number of d-electrons. The metal will add electrons by binding X and L ligands to obtain 18 or 16 electrons in its outer shell.[42] For example, Ni has 10 d-electrons, and Ni complexes typically have NiX_2L_3 or NiX_2L_2 configurations. One approach for Ni ALE is to create volatile nickel compounds that are either NiX_2L_3 or NiX_2L_2 formed by sequential surface reactions.

5.1. Halogenation and Ligand Volatilization

Halogenation followed by ligand exposure has been demonstrated for Co ALE.[43] The pathway to volatilization involved chlorination using Cl_2 to form $CoCl_x$ surface species. The oxidation state of cobalt was increased by chlorination. Subsequently, hfacH exposures are believed to extract the oxidized Co species by forming $Co(hfac)_xCl_y$ volatile complexes. A schematic showing this halogenation and ligand volatilization process is given in Figure 15.[43] Co etch rates were determined using scanning electron microscopy of Co film cross sections before and after Co ALE. The Co etch rates varied from 2 Å/cycle at 140 °C to 16 Å/cycle at 185 °C.[43]

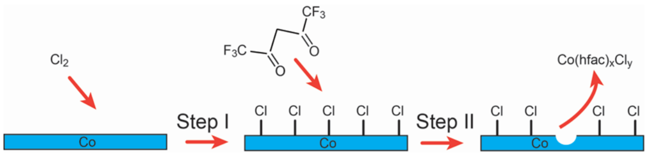

Figure 15. Schematic of Co ALE with Cl_2 and hfacH as reactants. Cl_2 chlorinates the Co surface in Step I. hfacH removes $Co(hfac)_2Cl_2$ in Step II. Reproduced with permission from ref 43. Copyright 2019 American Vacuum Society.

5.2. Chlorine/Fluorine Ligand Exchange

Halogenation is also an effective mechanism for thermal ALE if the fluorides and chlorides of materials have different volatilities. In the first step, a self-limiting fluorination process can be used to form a stable fluoride layer on the substrate. In the second step, a chlorine/fluorine ligand-exchange process can be employed to yield volatile chloride species. This chlorine/fluorine ligand-exchange mechanism was utilized to define TiO_2 ALE with WF_6 and BCl_3 as the reactants.[44] The TiO_2 ALE process was viable at temperatures ≤170 °C because the fluoride is stable but the chloride is volatile.[44] A TiO_2 etch rate of ~0.6 Å/cycle was observed at 170 °C. In contrast, TiO_2 was etched spontaneously by WF_6 at higher temperatures because the fluoride is volatile.[44] TiO_2 ALE has also been used together with TiO_2 ALD for area-selective TiO_2 ALD.[45]

6. SELF-LIMITING SURFACE LIGAND MECHANISMS

Some materials are etched by precursors where the buildup of species on the surface from the precursor eventually stops the etching. The species that limit the etching can then be removed by a second precursor to define the ALE process. An example of this self-limiting surface ligand mechanism is AlF_3 ALE using $Sn(acac)_2$ and HF as the reactants.[46] $Sn(acac)_2$ can undergo a ligand-exchange reaction with AlF_3. This ligand-exchange reaction is believed to produce volatile SnF(acac) from $Sn(acac)_2$. In addition, the ligand-exchange reaction also yields $AlF_2(acac)$ on the surface.

The etching of AlF_3 by $Sn(acac)_2$ is self-limiting and is known to saturate with acac species on the surface.[46] A subsequent HF exposure is required to maintain the AlF_3 ALE process. The HF exposure is thought to lead to the fluorination reaction: $AlF_2(acac) + HF(g) \rightarrow AlF_3 + acacH(g)$. This fluorination reaction reforms the AlF_3 surface and allows the AlF_3 ALE process to continue versus $Sn(acac)_2$ and HF exposures.

Another related example is ZnO ALE using acetylacetone (acacH) and O_2 plasma as the reactants.[47] acacH is proposed to etch ZnO by forming $Zn(acac)_2$ and H_2O. However, the ZnO surface also becomes covered by acacH adsorption products that limit the reaction. The subsequent O_2 plasma reaction then removes these acacH adsorption products and allows the ZnO ALE to continue versus sequential acacH and O_2 plasma exposures. A schematic of the proposed mechanism for ZnO ALE is shown in Figure 16.[47] ZnO etch rates varied from 0.5 to 1.3 Å/cycle at temperatures between 100 and 250 °C.[47]

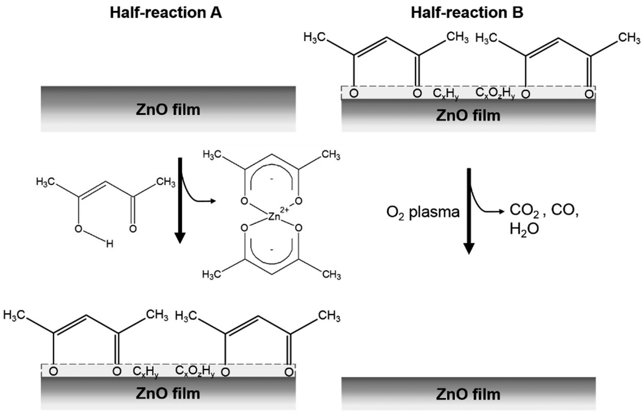

Figure 16. Schematic of ZnO ALE using acacH and O_2 plasma as reactants. acacH produces $Zn(acac)_2$ and also forms self-limiting acac surface ligands in reaction A. O_2 plasma removes acac surface ligands in reaction B. Reproduced with permission from ref 47. Copyright 2018 American Chemical Society.

7. TEMPERATURE MODULATION MECHANISMS

Another class of thermal ALE reactions is based on temperature annealing. A surface modification reaction is first performed at lower temperature. Subsequently, the surface modified layer is desorbed by heating to higher temperature. The temperature is then returned to the initial temperature to repeat the thermal ALE process.

For example, a thermal modulation mechanism for Si_3N_4 ALE is based on the formation of an $(NH_4)_2SiF_6$ layer on the Si_3N_4 surface.[48] This ammonium salt layer can be formed by exposure of a hydrofluorocarbon plasma to the Si_3N_4 surface at 20 °C. Subsequently, the substrate is thermally annealed to 150 °C to desorb the $(NH_4)_2SiF_6$ layer.[48] A schematic of Si_3N_4 ALE using this temperature modulation mechanism is shown in Figure 17.[48] This Si_3N_4 ALE process produced a Si_3N_4 etch rate of 16 Å/cycle.[48]

A temperature modulation mechanism has also been employed for Si ALE.[49] The Si surface is first oxidized to a SiO_2 layer using an O_2 plasma. The SiO_2 layer is then converted to an $(NH_4)_2SiF_6$ layer using a NH_3/NF_3 plasma. Subsequently, the substrate is thermal annealed to desorb the ammonium salt layer.[49] In addition, MoS_2 ALE has been performed using an O_2 plasma to form an amorphous MoO_3 monolayer on the MoS_2 surface at 200 °C.[50] Subsequently, the MoO_3 monolayer can be desorbed by thermal annealing to 500 °C.[50]

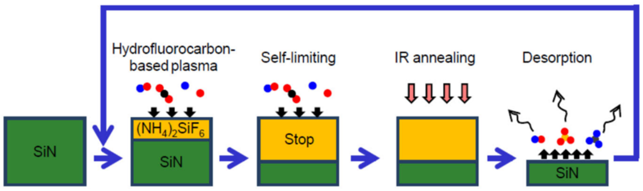

Figure 17. Schematic of SiN ALE using surface modifying hydrofluorocarbon plasma and thermal annealing. Reproduced with permission from ref 48. Copyright 2017 IOP Publishing.

8. CHALLENGES AND FUTURE PROSPECTS

Thermal ALE has developed rapidly over the last five years. The Intel etch group proposed the possibility of thermal ALE using sequential, self-limiting surface reactions in their seminal perspective in 2015.[3] Many materials, including metal oxides and metal nitrides, can now be etched using thermal ALE mechanisms. A current important challenge is the development of thermal ALE mechanisms for metals. Another critical goal for thermal ALE is selectivity between various materials. Many studies have illustrated that the different ligands involved in ligand-exchange reactions can provide pathways for selectivity.[23] Investigations of new ligands for thermal ALE are needed to expand the options for selectivity between different materials. In addition, a deeper understanding of thermal ALE requires spectroscopic analysis of the species formed on the surface and the volatile products released to the gas phase.

Thermal ALE will become increasingly critical for nanofabrication as dimensions continue to shrink and devices become more three-dimensional. A key application for thermal ALE will be fabrication of advanced devices such as FinFETs and gate-all-around FETs.[51] Plasma ALE and thermal ALE will need to be used together to provide anisotropic and isotropic etching. There also may be possibilities for hybrid approaches where low energy ions may remove self-limiting surface species during thermal ALE.[28] These hybrid approaches may be able to allow thermal ALE to display anisotropic properties similar to those of plasma ALE.

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Notes

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■ REFERENCES

(1) George, S. M. Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110*, 111−131.

(2) Kanarik, K. J.; Lill, T.; Hudson, E. A.; Sriraman, S.; Tan, S.; Marks, J.; Vahedi, V.; Gottscho, R. A. Overview of Atomic Layer Etching in the Semiconductor Industry. *J. Vac. Sci. Technol., A* **2015**, *33*, 020802.

(3) Carver, C. T.; Plombon, J. J.; Romero, P. E.; Suri, S.; Tronic, T. A.; Turkot, R. B. Atomic Layer Etching: An Industry Perspective. *ECS J. Solid State Sci. Technol.* **2015**, *4*, N5005−N5009.

(4) Oehrlein, G. S.; Metzler, D.; Li, C. Atomic Layer Etching at the Tipping Point: An Overview. *ECS J. Solid State Sci. Technol.* **2015**, *4*, N5041−N5053.

(5) Lee, Y.; George, S. M. Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF. *ACS Nano* **2015**, *9*, 2061−2070.

(6) Clancey, J. W.; Cavanagh, A. S.; Smith, J. E. T.; Sharma, S.; George, S. M. Volatile Etch Species Produced During Thermal Al_2O_3 Atomic Layer Etching. *J. Phys. Chem. C* **2020**, *124*, 287−299.

(7) Lee, Y.; George, S. M. Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures. *J. Phys. Chem. C* **2019**, *123*, 18455−18466.

(8) Faraz, T.; Roozeboom, F.; Knoops, H. C. M.; Kessels, W. M. M. Atomic Layer Etching: What Can We Learn from Atomic Layer Deposition? *ECS J. Solid State Sci. Technol.* **2015**, *4*, N5023−N5032.

(9) George, S. M.; Lee, Y. Prospects for Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions. *ACS Nano* **2016**, *10*, 4889−4894.

(10) Osakada, K. Transmetalation. In *Fundamentals of Molecular Catalysis, Current Methods in Inorganic Chemistry*, Vol. 3; Kurosawa, H., Yamamoto, A., Eds.; Elsevier Science: Amsterdam, 2003, pp 233−291.

(11) Lockhart, J. C. Redistribution and Exchange Reactions in Groups 2B-7B. *Chem. Rev.* **1965**, *65*, 131−151.

(12) Roesky, H. W.; Haiduc, I. Fluorine as a Structure-directing Element in Organometallic Fluorides: Discrete Molecules, Supramolecular Self-Assembly and Host-guest Complexation. *J. Chem. Soc., Dalton Trans.* **1999**, 2249−2264.

(13) Lee, Y.; DuMont, J. W.; George, S. M. Mechanism of Thermal Al_2O_3 Atomic Layer Etching Using Sequential Reactions with $Sn(acac)_2$ and HF. *Chem. Mater.* **2015**, *27*, 3648−3657.

(14) Lee, Y.; DuMont, J. W.; George, S. M. Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions. *Chem. Mater.* **2016**, *28*, 2994−3003.

(15) Puurunen, R. L. Surface Chemistry of Atomic Layer Deposition: A Case Study for the Trimethylaluminum/water Process. *J. Appl. Phys.* **2005**, *97*, 121301.

(16) Lee, Y.; DuMont, J. W.; Cavanagh, A. S.; George, S. M. Atomic Layer Deposition of AlF_3 Using Trimethylaluminum and Hydrogen Fluoride. *J. Phys. Chem. C* **2015**, *119*, 14185−14194.

(17) DuMont, J. W.; George, S. M. Competition Between Al_2O_3 Atomic Layer Etching and AlF_3 Atomic Layer Deposition Using Sequential Exposures of Trimethylaluminum and Hydrogen Fluoride. *J. Chem. Phys.* **2017**, *146*, 052819.

(18) Zywotko, D. R.; Faguet, J.; George, S. M. Rapid Atomic Layer Etching of Al_2O_3 Using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum with No Purging. *J. Vac. Sci. Technol., A* **2018**, *36*, 061508.

(19) Cano, A. M.; Marquardt, A. E.; DuMont, J. W.; George, S. M. Effect of HF Pressure on Thermal Al_2O_3 Atomic Layer Etch Rates and Al_2O_3 Fluorination. *J. Phys. Chem. C* **2019**, *123*, 10346−10355.

(20) Natarajan, S. K.; Elliott, S. D. Modeling the Chemical Mechanism of the Thermal Atomic Layer Etch of Aluminum Oxide: A Density Functional Theory Study of Reactions during HF Exposure. *Chem. Mater.* **2018**, *30*, 5912−5922.

(21) Lee, Y.; DuMont, J. W.; George, S. M. Atomic Layer Etching of HfO_2 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF. *ECS J. Solid State Sci. Technol.* **2015**, *4*, N5013−N5022.

(22) Lee, Y.; George, S. M. Thermal Atomic Layer Etching of HfO_2 Using HF for Fluorination and $TiCl_4$ for Ligand-Exchange. *J. Vac. Sci. Technol., A* **2018**, *36*, 061504.

(23) Lee, Y.; Huffman, C.; George, S. M. Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions. *Chem. Mater.* **2016**, *28*, 7657−7665.

(24) Skinner, H. A. The Thermochemistry of Organometallic Compounds. *J. Chem. Thermodyn.* **1978**, *10*, 309−320.

(25) Wu, Y. D.; Peng, Z. H.; Chan, K. W. K.; Liu, X. Z.; Tuinman, A. A.; Xue, Z. L. Computational and Experimental Studies on the Thermolysis Mechanism of Zirconium and Hafnium Tetraalkyl Complexes. Difference Between Titanium and Zirconium Complexes. *Organometallics* **1999**, *18*, 2081−2090.

(26) Gertsch, J. C.; Cano, A. M.; Bright, V. M.; George, S. M. SF_4 as the Fluorination Reactant for Al_2O_3 and VO_2 Thermal Atomic Layer Etching. *Chem. Mater.* **2019**, *31*, 3624−3635.

(27) Johnson, N. R.; Hite, J. K.; Mastro, M. A.; Eddy, C. R.; George, S. M. Thermal Atomic Layer Etching of Crystalline GaN Using Sequential Exposures of XeF_2 and BCl_3. *Appl. Phys. Lett.* **2019**, *114*, 243103.

(28) Johnson, N. R.; Sun, H. X.; Sharma, K.; George, S. M. Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-limiting Hydrogen Fluoride and $Sn(acac)_2$ Reactions and Enhancement by H_2 and Ar Plasmas. *J. Vac. Sci. Technol., A* **2016**, *34*, 050603.

(29) Murdzek, J. A.; George, S. M. Effect of Crystallinity on the Thermal Atomic Layer Etching of Hafnium Oxide, Zirconium Oxide and Hafnium Zirconium Oxide. *J. Vac. Sci. Technol., A* **2020**, *38*, 022608.

(30) Zywotko, D. R.; George, S. M. Thermal Atomic Layer Etching of ZnO by a "Conversion-Etch" Mechanism Using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum. *Chem. Mater.* **2017**, *29*, 1183−1191.

(31) DuMont, J. W.; Marquardt, A. E.; Cano, A. M.; George, S. M. Thermal Atomic Layer Etching of SiO_2 by a "Conversion-Etch" Mechanism Using Sequential Reactions of Trimethylaluminum and Hydrogen Fluoride. *ACS Appl. Mater. Interfaces* **2017**, *9*, 10296−10307.

(32) Johnson, N. R.; George, S. M. WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Mechanisms. *ACS Appl. Mater. Interfaces* **2017**, *9*, 34435−34447.

(33) Lee, Y.; George, S. M. Thermal Atomic Layer Etching of Titanium Nitride Using Sequential, Self-Limiting Reactions: Oxidation to TiO_2 and Fluorination to Volatile TiF_4. *Chem. Mater.* **2017**, *29*, 8202−8210.

(34) Xie, W. Y.; Lemaire, P. C.; Parsons, G. N. Thermally Driven Self-Limiting Atomic Layer Etching of Metallic Tungsten Using WF_6 and O_2. *ACS Appl. Mater. Interfaces* **2018**, *10*, 9147−9154.

(35) Strobel, A.; Schnabel, H. D.; Reinhold, U.; Rauer, S.; Neidhardt, A. Room Temperature Plasma Enhanced Atomic Layer Deposition for TiO_2 and WO_3 Films. *J. Vac. Sci. Technol., A* **2016**, *34*, 01a118.

(36) Tagtstrom, P.; Martensson, P.; Jansson, U.; Carlsson, J. O. Atomic Layer Epitaxy of Tungsten Oxide Films Using Oxyfluorides as Metal Precursors. *J. Electrochem. Soc.* **1999**, *146*, 3139−3143.

(37) Abdulagatov, A. I.; George, S. M. Thermal Atomic Layer Etching of Silicon Using O_2, HF, and $Al(CH_3)_3$ as the Reactants. *Chem. Mater.* **2018**, *30*, 8465−8475.

(38) Abdulagatov, A. I.; George, S. M. Thermal Atomic Layer Etching of Silicon Nitride Using an Oxidation and "Conversion Etch" Mechanism. *J. Vac. Sci. Technol., A* **2020**, *38*, 022607.

(39) Mohimi, E.; Chu, X. Q. I.; Trinh, B. B.; Babar, S.; Girolami, G. S.; Abelson, J. R. Thermal Atomic Layer Etching of Copper by Sequential Steps Involving Oxidation and Exposure to Hexafluoroacetylacetone. *ECS J. Solid State Sci. Technol.* **2018**, *7*, P491−P495.

(40) Chen, J. K. C.; Altieri, N. D.; Kim, T.; Chen, E.; Lill, T.; Shen, M. H.; Chang, J. P. Directional Etch of Magnetic and Noble Metals. II. Organic Chemical Vapor Etch. *J. Vac. Sci. Technol., A* **2017**, *35*, 05c305.

(41) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Oxford University Press: New York, NY, 2016.

(42) Green, M. L. H. A New Approach to the Formal Classification of Covalent Compounds of the Elements. *J. Organomet. Chem.* **1995**, *500*, 127−148.

(43) Konh, M.; He, C.; Lin, X.; Guo, X. Y.; Pallem, V.; Opila, R. L.; Teplyakov, A. V.; Wang, Z. J.; Yuan, B. Molecular Mechanisms of Atomic Layer Etching of Cobalt with Sequential Exposure to Molecular Chlorine and Diketones. *J. Vac. Sci. Technol., A* **2019**, *37*, 021004.

(44) Lemaire, P. C.; Parsons, G. N. Thermal Selective Vapor Etching of TiO_2: Chemical Vapor Etching via WF_6 and Self-Limiting Atomic Layer Etching Using WF_6 and BCl_3. *Chem. Mater.* **2017**, *29*, 6653−6665.

(45) Song, S. K.; Saare, H.; Parsons, G. N. Integrated Isothermal Atomic Layer Deposition/Atomic Layer Etching Supercycles for Area-Selective Deposition of TiO_2. *Chem. Mater.* **2019**, *31*, 4793−4804.

(46) Lee, Y.; DuMont, J. W.; George, S. M. Atomic Layer Etching of AlF_3 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and Hydrogen Fluoride. *J. Phys. Chem. C* **2015**, *119*, 25385−25393.

(47) Mameli, A.; Verheijen, M. A.; Mackus, A. J. M.; Kessels, W. M. M.; Roozeboom, F. Isotropic Atomic Layer Etching of ZnO Using Acetylacetone and O_2 Plasma. *ACS Appl. Mater. Interfaces* **2018**, *10*, 38588−38595.

(48) Miyoshi, N.; Kobayashi, H.; Shinoda, K.; Kurihara, M.; Watanabe, T.; Kouzuma, Y.; Yokogawa, K.; Sakai, S.; Izawa, M. Atomic Layer Etching of Silicon Nitride Using Infrared Annealing for Short Desorption Time of Ammonium Fluorosilicate. *Jpn. J. Appl. Phys.* **2017**, *56*, 06HB01.

(49) Song, E. J.; Kim, J. H.; Kwon, J. D.; Kwon, S. H.; Ahn, J. H. Silicon Atomic Layer Etching by Two-Step Plasma Process Consisting of Oxidation and Modification to Form $(NH_4)_2SiF_6$, and Its Sublimation. *Jpn. J. Appl. Phys.* **2018**, *57*, 106505.

(50) Zhu, H.; Qin, X. Y.; Cheng, L. X.; Azcatl, A.; Kim, J.; Wallace, R. M. Remote Plasma Oxidation and Atomic Layer Etching of MoS_2. *ACS Appl. Mater. Interfaces* **2016**, *8*, 19119−19126.

(51) Lu, W. J.; Lee, Y.; Gertsch, J. C.; Murdzek, J. A.; Cavanagh, A. S.; Kong, L. S.; del Alamo, J. A.; George, S. M. In Situ Thermal Atomic Layer Etching for Sub-5 nm InGaAs Multigate MOSFETs. *Nano Lett.* **2019**, *19*, 5159−5166.