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ABSTRACT: Thermal atomic layer etching (ALE) of Al₂O₃ and HfO₂ using sequential, self-limiting fluorination and ligand-exchange reactions was recently demonstrated using HF and tin acetylacetonate (Sn(acac)₂) as the reactants. This new thermal pathway for ALE represents the reverse of atomic layer deposition (ALD) and should lead to isotropic etching. Atomic layer deposition and ALE can together define the atomic layer growth and removal steps required for advanced semiconductor fabrication. The thermal ALE of many materials should be possible using fluorination and ligand-exchange reactions. The chemical details of ligand-exchange can lead to selective ALE between various materials. Thermal ALE could produce conformal etching in high-aspect-ratio structures. Thermal ALE could also yield ultrasmooth thin films based on deposit/etch-back methods. Enhancement of ALE rates and possible anisotropic ALE could be achieved using radicals or ions together with thermal ALE.

Atomic layer etching (ALE) is a thin film removal technique based on sequential, self-limiting surface reactions that is needed for advanced semiconductor manufacturing.¹ Most previous ALE processes have obtained etching using ion-enhanced or energetic-noble-gas-atom-enhanced surface reactions after adsorbing halogens on the surface of the material.² In contrast, only a few thermal chemical processes have been demonstrated for ALE. Thermal ALE should be able to remove thin films isotropically with atomic layer control. Thermal ALE can be viewed as the reverse of atomic layer deposition (ALD).³ Working together with ALD, thermal ALE will advance the toolset for atomic layer processing.

New pathways for thermal ALE have recently been discovered using sequential, self-limiting thermal reactions. Al₂O₃ ALE has been reported using HF and either tin acetylacetonate (Sn(acac)₂) or Al(CH₃)₃ as the reactants.⁴−⁶ HfO₂ ALE has also been documented using HF and Sn(acac)₂ as the reactants.⁷ Quartz crystal microbalance results for Al₂O₃ ALE using HF and Al(CH₃)₃ at 300 °C are shown in Figure 1.⁶ The removal of Al₂O₃ is linear with the number of Al₂O₃ ALE reaction cycles. The mass change per cycle for Al₂O₃ ALE at 300 °C is ~15.9 ng/(cm² cycle). This mass loss is equivalent to an etch rate of 0.51 Å/cycle.⁶

The etch rate of Al₂O₃ ALE is based on fluorination and ligand-exchange reactions.⁴−⁷ A schematic of the proposed reaction mechanism for Al₂O₃ ALE using Al(CH₃)₃ as the metal precursor is displayed in Figure 2. In the ligand-exchange reaction, the metal precursor accepts fluorine from a metal fluoride surface layer and concurrently transfers its ligand to the metal fluoride. This ligand-exchange can be characterized as a metal-exchange transmetalation reaction between adjacent metal centers.⁸ Etching results if this reaction forms a stable and volatile reaction product.

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Figure 1. Mass change versus number of cycles for Al₂O₃ ALE using sequential HF and Al(CH₃)₃ exposures at 300 °C.
Thermal ALE of various materials

Thermal ALE is analogous to the reverse of ALD, however, this is not quite accurate. Atomic layer deposition reactions are typically very exothermic, and are favorable thermochemical reactions. These thermal reactions are spontaneous with negative ΔG values where G is the Gibbs free energy. Performing the same ALD reactions in reverse should not be possible because of thermodynamic considerations. Thermal ALE requires alternative, self-limiting reactions with different reactants that are exothermic and have negative ΔG values to ensure spontaneity.

Thermal ALE based on fluorination and ligand-exchange reactions represents a broad class of favorable reactions. These reactions should be applicable for etching a wide variety of materials such as metal oxides, nitrides, phosphides, sulfides, arsenides, selenides, and tellurides. Many fluorination sources may be used for the fluorination reactions, such as HF or XeF₂. Thermochemical calculations indicate that fluorination of metal compounds, including metal oxides, is thermochemically favorable. This may be surprising because metal oxides comprise many of the most stable compounds in the Earth’s crust. However, these metal oxides would be metal fluorides if the Earth was covered with seas of HF. The thermochemical free energies for the reaction of fluoride-containing gases with Al₂O₃ at 200 °C are given in Table 1.¹⁰

The ligand-exchange reactions during thermal ALE are metal-exchange transmetalation or redistribution reactions. Ligands are transferred between adjacent metal centers during the ligand-exchange reaction. The proposed transition state for ligand-exchange is a four-center ring. This four-center ring is formed by the metal in the metal precursor and the metal in the metal fluoride, with the fluoride and one ligand from the metal precursor serving as bridging species. Fluorine easily forms bimetallic bridges and stabilizes the four-center ring transition state. A schematic of the proposed four-center ring transition state during the ligand-exchange reaction between Al(CH₃)₃ (trimethylaluminum, TMA) and AlF₃ during Al₂O₃ ALE is shown in Figure 3.

Atomic layer etching reactions for various representative metal compounds are given in Table 2. The thermochemical free energies for the fluorination reactions are given at 200 °C. With the exception of the metal sulfides, selenides, and tellurides, Table 2 illustrates that the fluorination reactions using HF have negative ΔG values and are spontaneous. The fluorination of metal sulfides, selenides, and tellurides have large negative ΔG values and are spontaneous with XeF₂ as the fluorination reagent. The metal precursor in Table 2 is assumed to be Sn(acac)₂. The acac ligand forms volatile metal reaction products with a wide variety of metal elements. Other metal precursors would provide different ligands that may be more selective toward particular metal elements.

Pathways to selectivity

In selective ALE, one material is etched preferentially in the presence of other materials. Selective ALE could occur in the fluorination process or the ligand-exchange process. The fluorine reactants could selectively fluorinate one particular material in a mixture of neighboring materials. Fluorination could also lead to partial selectivity based on different amounts of fluorination. More pronounced ALE selectivity can be achieved in the ligand-exchange process. When the metal precursor accepts fluorine from the metal fluoride layer, the metal precursor donates a ligand to the metal in the metal fluoride and forms a reaction product. Depending on the nature of the ligand, the reaction products formed after ligand-exchange have distinct stabilities and volatilities. Differences in stability and volatility of the reaction products may be used to achieve selective ALE.

Table 3 provides examples of various metal precursor families and the ligand-exchange process during their reaction with metal fluorides, MF₂. Selectivity could be obtained depending on the stability and volatility of the metal reaction product. For example, consider metal precursors for selectivity between Al₂O₃ and ZrO₂. Fluorination should initially form an AlF₃ layer on Al₂O₃ and a ZrF₄ layer on ZrO₂. The metal precursor Al(CH₃)₃ could remove AlF₃ during Al₂O₃ ALE because Al(CH₃)₃ or AlF(CH₃)₂ are stable and volatile metal reaction products. In contrast, Al(CH₃)₃ is not expected to remove ZrF₄ to perform ZrO₂ ALE because Zr(CH₃)₄ or ZrF(CH₃)₄ are not stable metal reaction products.

Recent experiments have revealed selectivity in thermal ALE. Figure 4 shows results for ALE using sequential HF and TMA exposures on TiN, SiO₂, Si₃N₄, Al₂O₃, HfO₂, and ZrO₂ thin films at 300 °C. These films were all etched using identical conditions at the same time. The sequential HF and TMA exposures are able to etch Al₂O₃ and HfO₂. The etching rate...
during Al₂O₃ ALE was 0.45 Å/cycle. The etching rate during HfO₂ ALE was 0.10 Å/cycle. No etching is observed for sequential HF and TMA exposures on TiN, SiO₂, Si₃N₄, or ZrO₂. As expected, HF and TMA can etch Al₂O₃ but not ZrO₂. The etching of HfO₂ and the lack of etching of TiN, SiO₂, and Si₃N₄ can also be understood in terms of the stability and volatility of the metal reaction products.

Besides selectivity in the fluorination or ligand-exchange reactions, there are also other pathways to selectivity. Additional selectivity may be obtained by tuning the substrate temperature. Additional selectivity may be obtained by tuning the substrate temperature. The kinetics of the fluorination or ligand-exchange reactions can lead to different etching rates at different temperatures for various metal precursors. Temperature may also affect the volatility of the metal reaction products.

Selective ALE could also be achieved using molecular adsorbates that bind to one material and not to another. These molecular adsorbates could act as surface blocking groups that would prevent the adsorption of the fluorine precursor or metal precursor. These "molecular masks" could lead to selective ALE. Similar surface blocking effects during ALD have been observed recently by studies of the effect of hfacH on Pt ALD on TiO₂.

### Table 1. Fluorination Reactions for Al₂O₃ and ΔG at 200 °C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ + 6HF → 2AlF₃ + 3H₂O</td>
<td>-58</td>
</tr>
<tr>
<td>Al₂O₃ + 3H₂SO₃</td>
<td>-130</td>
</tr>
<tr>
<td>Al₂O₃ + 3/2SF₄ → 2AlF₃ + 3/2SO₂</td>
<td>-157</td>
</tr>
<tr>
<td>Al₂O₃ + 2Cl₂O₃ + O₂</td>
<td>-224</td>
</tr>
<tr>
<td>Al₂O₃ + 2NO₂</td>
<td>-230</td>
</tr>
<tr>
<td>Al₂O₃ + 3NO₂</td>
<td>-258</td>
</tr>
<tr>
<td>Al₂O₃ + 3O₂</td>
<td>-297</td>
</tr>
</tbody>
</table>

### Table 2. Atomic Layer Etching Reactions for Various Materials and ΔG at 200 °C

**Metal Oxide/HfO₂ ALE**
- overall: HfO₂ + 4 Sn(acac)₂ + 4 HF → Hf(acac)₄ + 4 SnF(acac) + 2 H₂O
- fluoride formation: HfO₂ + 4 HF → HfF₄ + 2 H₂O ΔG = -19 kcal/mol

**Metal Nitride/GaN ALE**
- overall: GaN + 3 Sn(acac)₂ + 3HF → Ga(acac)₃ + 3 SnF(acac) + NH₃
- fluoride formation: GaN + 3 HF → GaF₃ + NH₃ ΔG = -40 kcal/mol

**Metal Phosphide/InP ALE**
- overall: InP + 3 Sn(acac)₂ + 3HF → In(acac)₃ + 3 SnF(acac) + PH₃
- fluoride formation: InP + 3HF → InF₃ + PH₃ ΔG = -39 kcal/mol

**Metal Sulfide/ZnS ALE**
- overall: ZnS + 2 Sn(acac)₂ + 2HF → Zn(acac)₂ + 2 SnF(acac) + H₂S
- fluoride formation: ZnS + 2 HF → ZnF₂ + H₂S ΔG = +6 kcal/mol

**Metal Arsenide/GaAs ALE**
- overall: GaAs + 3 Sn(acac)₂ + 3HF → Ga(acac)₃ + 3 SnF(acac) + AsH₃
- fluoride formation: GaAs + 3 HF → GaF₃ + AsH₃ ΔG = -21 kcal/mol

**Metal Selenide/PbSe ALE**
- overall: PbSe + 2 Sn(acac)₂ + 2HF → Pb(acac)₂ + 2 SnF(acac) + H₂Se
- fluoride formation: PbSe + 2 HF → PbF₂ + H₂Se ΔG = +14 kcal/mol

**Metal Telluride/CdTe ALE**
- overall: CdTe + 2 Sn(acac)₂ + 2HF → Cd(acac)₂ + 2 SnF(acac) + H₂Te
- fluoride formation: CdTe + 2 HF → CdF₂ + H₂Te ΔG = +26 kcal/mol

**Table 3. Fluorination Reactions for Al₂O₃ and ΔG at 200 °C**

![Figure 3. Schematic of the proposed four-center ring transition state during the ligand-exchange reaction between Al(CH₃)₃ and AlF₃ during Al₂O₃ ALE.](image-url)
Table 3. Metal Precursors for Reaction with Metal Fluoride and Metal Reaction Products

| metal precursor family | metal precursor example | ligand-exchange process | metal reaction product from MF<sub>y</sub>
|------------------------|-------------------------|-------------------------|----------------------------------|
| β-diketonate           | Sn(acac)<sub>2</sub>     | accept fluorine, donate acac | M(acac)<sub>y</sub>, or MF<sub>y</sub>(acac)<sub>y</sub>−
| alkyl                  | Al(CH<sub>3</sub>)<sub>3</sub> | accept fluorine, donate CH<sub>3</sub> | M(CH<sub>3</sub>)<sub>y</sub>, or MF<sub>y</sub>(CH<sub>3</sub>)<sub>y</sub>−
| halide                 | SiCl<sub>4</sub>        | accept fluorine, donate chloride | Cl<sub>y</sub>, or MF<sub>y</sub>Cl<sub>y</sub>−
| cyclopentadienyl       | Ni(Cp)<sub>2</sub>      | accept fluorine, donate Cp | M(Cp)<sub>y</sub>, or MF<sub>y</sub>(Cp)<sub>y</sub>−
| silylamide             | Zn(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub> | accept fluorine, donate N(SiMe<sub>3</sub>)<sub>2</sub> | M(N(SiMe<sub>3</sub>)<sub>y</sub>, or MF<sub>y</sub>(N(SiMe<sub>3</sub>)<sub>y</sub>−
| alkoxide               | Al(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> | accept fluorine, donate OCH<sub>2</sub>CH<sub>3</sub> | M(OCH<sub>2</sub>CH<sub>3</sub>)<sub>y</sub>, or MF<sub>y</sub>(OCH<sub>2</sub>CH<sub>3</sub>)<sub>y</sub>−
| amidinate (amd)        | Zn(amd)<sub>2</sub>     | accept fluorine, donate amd | M(amd)<sub>y</sub>, or MF<sub>y</sub>(amd)<sub>y</sub>−

Figure 4. Film thickness versus number of cycles of HF and Al(CH<sub>3</sub>)<sub>3</sub> (trimethylaluminum, TMA) exposures at 300 °C. Thin film materials were Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and TiN.

SURFACE CLEANING BY REMOVAL OF METAL IMPURITIES

Thermal ALE may also be useful in semiconductor fabrication for surface cleaning to remove metal impurities. The gas phase nature of thermal ALE will be particularly important for cleaning nanostructures that are mechanically fragile and can be easily damaged by wet cleaning. The removal of a metal impurity requires that the metal impurity produce a stable and volatile reaction product during the fluorination and ligand-exchange reactions. In contrast, the main surface material does not produce etch products under the same reaction conditions. Surface cleaning is related to selectivity during thermal ALE and should be accomplished with only one or two ALE reaction cycles.

Removal of metal impurities could occur during either the fluorination or ligand-exchange reactions. The fluorination reaction may remove the metal impurity if the metal fluoride is volatile. Volatile metal fluorides include MoF<sub>6</sub> and WF<sub>6</sub>. The ligand-exchange reaction could also remove the metal impurities based on the stability and volatility of the metal reaction products. For example, Al(CH<sub>3</sub>)<sub>3</sub> could remove Al or Hf impurities on SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> surfaces based on the selectivity results presented in Figure 4. The AlF<sub>y</sub> and HfF<sub>y</sub> species produced by fluorination could be removed as volatile AlF(CH<sub>3</sub>)<sub>3</sub> or HfF(CH<sub>3</sub>)<sub>3</sub> reaction products during ligand-exchange. In comparison, the SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> surfaces do not etch, presumably because the Si–F surface species are too stable to undergo ligand-exchange.

CONFORMAL ETCHING IN HIGH-ASPECT-RATIO STRUCTURES

The self-limiting nature of the sequential fluorination and ligand-exchange reactions that define thermal ALE should lead to isotropic etching. If the gas exposures are sufficient to allow the surface reactions to reach completion, then thermal ALE should be able to etch conformally in high-aspect-ratio structures. Conformal etching would complement the ability of ALD to perform conformal deposition in high-aspect-ratio structures. The previous ALE methods based on bombardment by ions or energetic atoms are able to provide anisotropic etching. However, they cannot etch conformally in high-aspect-ratio structures because the ions or energetic atoms require line-of-sight to the surface.

In analogy to ALD in high-aspect-ratio structures, the reactant exposure times during thermal ALE should increase according to the square of the aspect ratio. The purge times to remove unreacted reactant and products will also increase by a similar factor. Another factor influencing the exposure or purge times is the "stickiness" of the reactant. Molecular precursors with large dipole moments, like HF, have long surface residence times and are difficult to purge from the reaction chamber. If they are not removed before introducing the second precursor, then the etching rate could increase rapidly because of chemical vapor etching (CVE).

SMOOTHING AND DEPOSIT/ETCH-BACK METHODS

Thermal ALE provides a novel method for smoothing the surface of a solid substrate. Recent X-ray reflectivity (XRR) studies of Al<sub>2</sub>O<sub>3</sub> ALE and HfO<sub>2</sub> ALE were consistent with surface smoothing occurring during ALE. Smoothing of surfaces is important in the semiconductor industry to obtain flat and damage-free layers. Sputtering with ions or energetic atoms to remove material can leave a rough, damaged surface. Atomic layer etching can be used to remove the damaged layer and smooth the surface.

Surface smoothing can also be used to obtain high quality ultrathin films. For example, these continuous and smooth ultrathin films can be produced by depositing a thicker film and then etching back to obtain a thinner film. This possibility for "deposition/etch-back" is important when nucleation effects lead to roughness in the ultrathin deposited film. As the initial islands formed during nucleation grow and then merge together, they can form a continuous and pinhole-free film at higher thicknesses. Atomic layer etching can then etch this film back and obtain a smoother continuous film than would have been produced by growing to this ultrathin thickness. A schematic illustrating the "deposition/etch-back" method is shown in Figure 5.
thermal etching rate. Radicals could also provide a limited amount of anisotropic etching depending on their directionality and radical recombination rates.

CONCLUSIONS AND PROSPECTS

In this Perspective, we highlighted some of the promising prospects for thermal ALE using sequential, self-limiting fluorination and ligand-exchange reactions. Thermal ALE can complement ALD to provide new capabilities for atomic layer processing based on selective ALE, conformal etching in high-aspect-ratio structures, novel smoothing methods, and possible anisotropic etching with ion or radical enhancement. These new processing capabilities will be important for the construction of nanoscale three-dimensional devices. Many areas should benefit from thermal ALE such as semiconductor and microelectromechanical systems (MEMS) fabrication. We eagerly anticipate the future developments and applications of thermal ALE.

REFERENCES

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