Selectivity in Atomic Layer Etching Using Sequential, Self-Limiting Thermal Reactions

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1. Al$_2$O$_3$ ALE using HF and Sn(acac)$_2$ or Al(CH$_3$)$_3$ as metal precursors.

2. Selectivity using Sn(acac)$_2$, Al(CH$_3$)$_3$, AlCl(CH$_3$)$_2$ and SiCl$_4$ as metal precursors.

3. Selectivity in ALE based on temperature.
Requirements for Sequential, Self-Limiting Thermal Reactions for ALE

Need **spontaneous**, sequential, **self-limiting** thermal reactions that **remove** with atomic control.

**Spontaneous** requires thermochemically favorable. **Self-limiting** requires saturation of surface reaction. **Removal** requires volatility of reaction product.
Al$_2$O$_3$ ALE Using HF-Pyridine & Sn(acac)$_2$ as Reactants

$\text{Al}_2\text{O}_3$ ALE Using HF & Sn(acac)$_2$

100 ALE cycles
Mass change per cycle = -8.4 ng/cm$^2$
Etch rate = 0.28 Å/cycle

Linear Decrease of Al₂O₃ Film Thickness vs Number of Al₂O₃ ALE Cycles

![Graph showing the decrease in Al₂O₃ film thickness with the number of cycles at 200°C.](graph_image)

**XRR measurements yield etch rate = 0.27 Å/cycle**

Confirm with spectroscopic ellipsometry (SE)

Al₂O₃ ALE via Fluorination & Ligand Exchange
Metal Precursors for ALE

Requirements for Metal Precursor:
1. Accept fluorine from metal fluoride
2. Donate ligand to metal in metal fluoride
3. Metal reaction product is stable & volatile

Possible Metal Precursor:
Same precursor as used for ALD of etched material
e.g. Al(CH$_3$)$_3$ for Al$_2$O$_3$ ALE
Al₂O₃ ALE Using HF-Pyridine & Al(CH₃)₃ as Reactants

Al$_2$O$_3$ ALE Using HF & Al(CH$_3$)$_3$

100 ALE Cycles
Mass change per cycle = -15.9 ng/cm$^2$
Etch rate = 0.51 Å/cycle

Linear Decrease of Al$_2$O$_3$ Film Thickness vs Number of Al$_2$O$_3$ ALE Cycles

XRR measurements yield etch rate = 0.46 Å/cycle

Confirm with spectroscopic ellipsometry (SE)

Al$_2$O$_3$ ALE via Fluorination & Ligand Exchange

HF $\rightarrow$ Fluorination $\rightarrow$ H$_2$O

Al$_2$O$_3$ $\rightarrow$ AlF$_3$ $\rightarrow$ Al$_2$O$_3$

Al(CH$_3$)$_3$ $\rightarrow$ Ligand Exchange $\rightarrow$ AlF(CH$_3$)$_2$

AlF$_3$ $\rightarrow$ AlF(CH$_3$)$_2$ $\rightarrow$ Al(CH$_3$)$_3$

ETCHED LAYER THICKNESS $\rightarrow$ $\Delta$
Outline

1. Al₂O₃ ALE using HF and Sn(acac)₂ or Al(CH₃)₃ as metal precursors.

2. Selectivity using Sn(acac)₂, Al(CH₃)₃, AlCl(CH₃)₂ and SiCl₄ as metal precursors.

3. Selectivity in ALE based on temperature.
Selective ALE for Different Materials

Different materials represented by various colors*

Goal to etch just one material in a background of other materials

Selectivity determined by stability & volatility of reaction products

Selectivity During ALE

Requirements for Metal Precursor:
1. Accept fluorine from metal fluoride
2. Donate ligand to metal in metal fluoride
3. Metal reaction product is stable & volatile

Strategy for Selectivity:
Use metal precursors with ligands that yield stable & volatile reaction products with target metals
ALE Using HF & Sn(acac)$_2$

Selective etching of Al$_2$O$_3$, HfO$_2$ & ZrO$_2$.

Al, Hf & Zr form stable & volatile acac complexes.
Al$_2$O$_3$, HfO$_2$ & ZrO$_2$ ALE Using HF & Sn(acac)$_2$
ALE Using HF & Al(CH₃)₃ (TMA)

Selective etching of Al₂O₃ & HfO₂.

Al & Hf form stable & volatile complexes with methyl groups.

Al₂O₃, HfO₂, ZrO₂, SiO₂, Si₃N₄, TiN
Al₂O₃, HfO₂ & ZrO₂ ALE Using HF & Al(CH₃)₃ (TMA)

TMA 300°C

- **Al₂O₃ ALE**: 0.45 Å/cycle
- **HfO₂ ALE**: 0.10 Å/cycle
- **ZrO₂ ALE**: 0.01 Å/cycle

Al₂O₃, HfO₂, ZrO₂
Understanding Selectivity

\[ \text{Al}_2\text{O}_3 \text{ ALE with } \text{Al}((\text{CH}_3)_3). \]
Ligand-exchange. Stable Al-CH\(_3\) reaction product.

\[ \text{ZrO}_2 \text{ ALE with } \text{Al}((\text{CH}_3)_3). \text{ No ligand-exchange. Unstable Zr-CH}_3 \text{ reaction product.} \]

\[ \text{SiO}_2 \text{ ALE with } \text{Al}((\text{CH}_3)_3). \text{ No ligand-exchange. Si-F bond too stable.} \]
ALE Using HF & AlCl(CH₃)₂ (DMAC)

Selective etching of Al₂O₃, ZrO₂ & HfO₂.

Al, Zr & Hf form stable & volatile complexes with chloride or methyl groups.
Al$_2$O$_3$, HfO$_2$ & ZrO$_2$ ALE Using HF & AlCl(CH$_3$)$_2$ (DMAC)
ALE Using HF & SiCl₄

SiCl₄ 350°C

Zr & Hf form stable & volatile complexes with chloride groups.

Selective etching of ZrO₂ & HfO₂.

Al₂O₃, HfO₂, ZrO₂, SiO₂, Si₃N₄, TiN
Al$_2$O$_3$, HfO$_2$ & ZrO$_2$ ALE Using HF & SiCl$_4$

Why no etching of Al$_2$O$_3$ with SiCl$_4$?
SiCl\(_4\) (g) + HfF\(_4\) (s) → SiF\(_4\) (g) + HfCl\(_4\) (g)

SiCl\(_4\) (g) + ZrF\(_4\) (s) → SiF\(_4\) (g) + ZrCl\(_4\) (g)

SiCl\(_4\) (g) + 4/3AlF\(_3\) (s) → SiF\(_4\) (g) + 4/3AlCl\(_3\) (g)

**Ligand-Exchange Thermochemistry Explains No Al\(_2\)O\(_3\) ALE**

Positive \(\Delta G\) for SiCl\(_4\) ligand-exchange for Al\(_2\)O\(_3\) ALE.

\(\Delta G = 0\)

Negative \(\Delta G\) for SiCl\(_4\) ligand-exchange >150°C for HfO\(_2\) & ZrO\(_2\) ALE.
1. $\text{Al}_2\text{O}_3$ ALE using HF and $\text{Sn}($acac$)_2$ or $\text{Al}($CH$_3$)$_3$ as metal precursors.

2. Selectivity using $\text{Sn}($acac$)_2$, $\text{Al}($CH$_3$)$_3$, $\text{AlCl}($CH$_3$)$_2$ and $\text{SiCl}_4$ as metal precursors.

3. Selectivity in ALE based on temperature.
Selectivity Based on Temperature for Al$_2$O$_3$ ALE Using Different Metal Precursors

Different etch rates at various temperatures for different metal precursors.
Selectivity Based on Temperature for ALE Using SiCl$_4$ as Metal Precursor

![Graph showing etch rate vs. temperature for ZrO$_2$, HfO$_2$, and Al$_2$O$_3$.](image-url)
Conclusions

1. Thermal ALE possible using sequential, self-limiting fluorination & ligand-exchange reactions.

2. Thermal ALE using HF and either Sn(acac)$_2$, Al(CH$_3$)$_3$, AlCl(CH$_3$)$_2$ or SiCl$_4$ as metal precursors.

3. Selective ALE is possible. Depends on stability and volatility of reaction products.

4. Temperature provides additional pathway for selective ALE.