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

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Outline

1. Al_2O_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

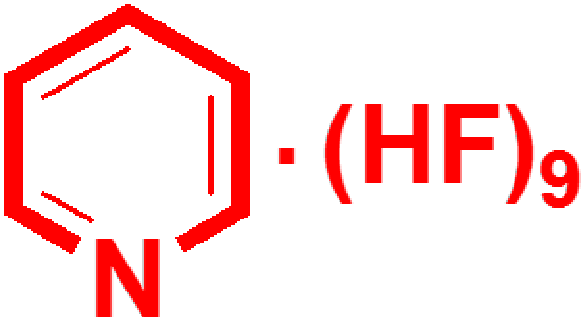
Need **spontaneous**, sequential, **self-limiting** thermal reactions that **remove** with atomic control.

Spontaneous requires thermochemically favorable.

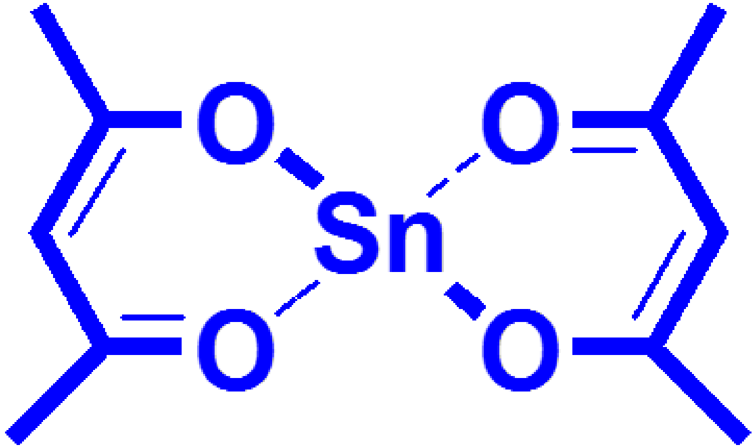
Self-limiting requires saturation of surface reaction.

Removal requires volatility of reaction product.

Al_2O_3 ALE Using HF-Pyridine & $Sn(acac)_2$ as Reactants



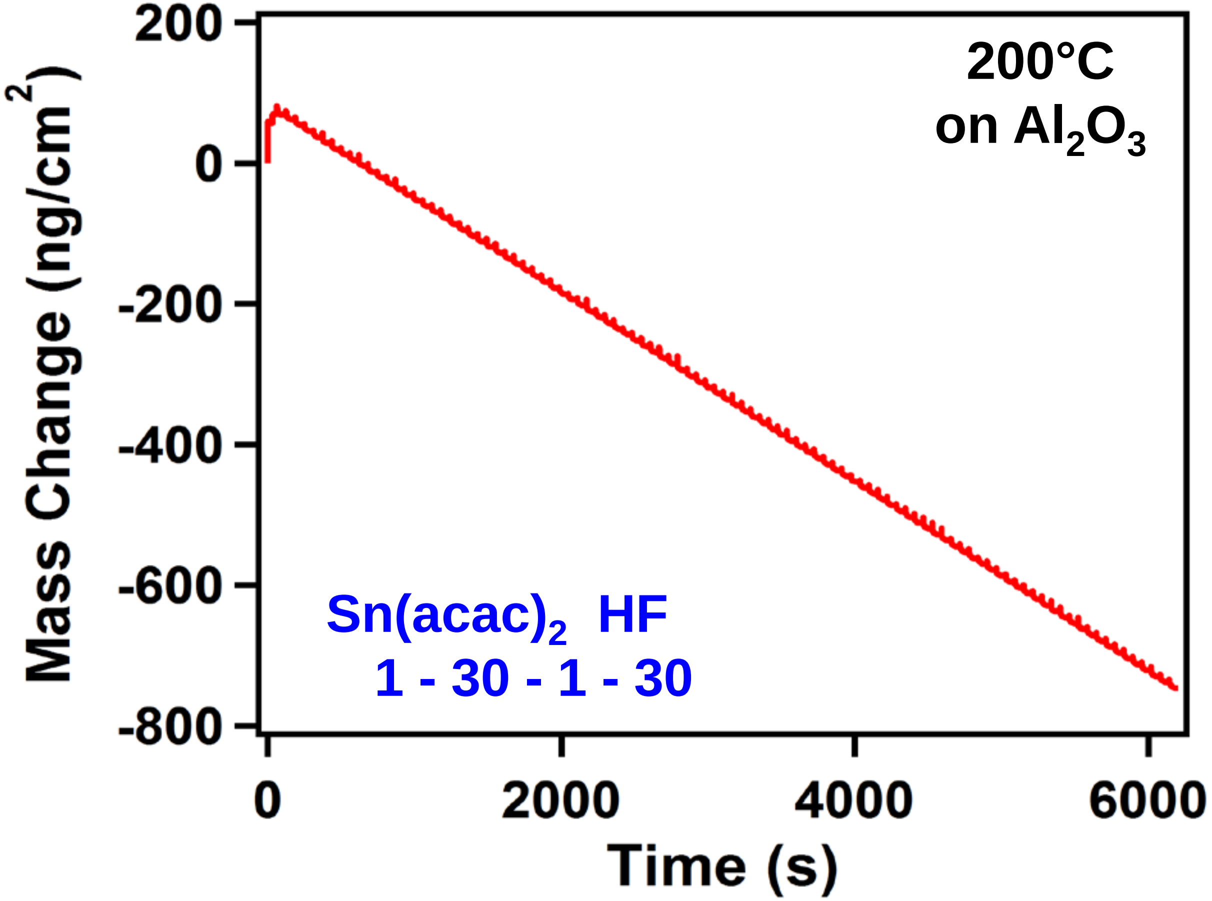
HF-Pyridine



$Sn(acac)_2$

Y. Lee & S.M. George, *ACS Nano* ***9***, 2061 (2015).

Al_2O_3 ALE Using HF & $Sn(acac)_2$



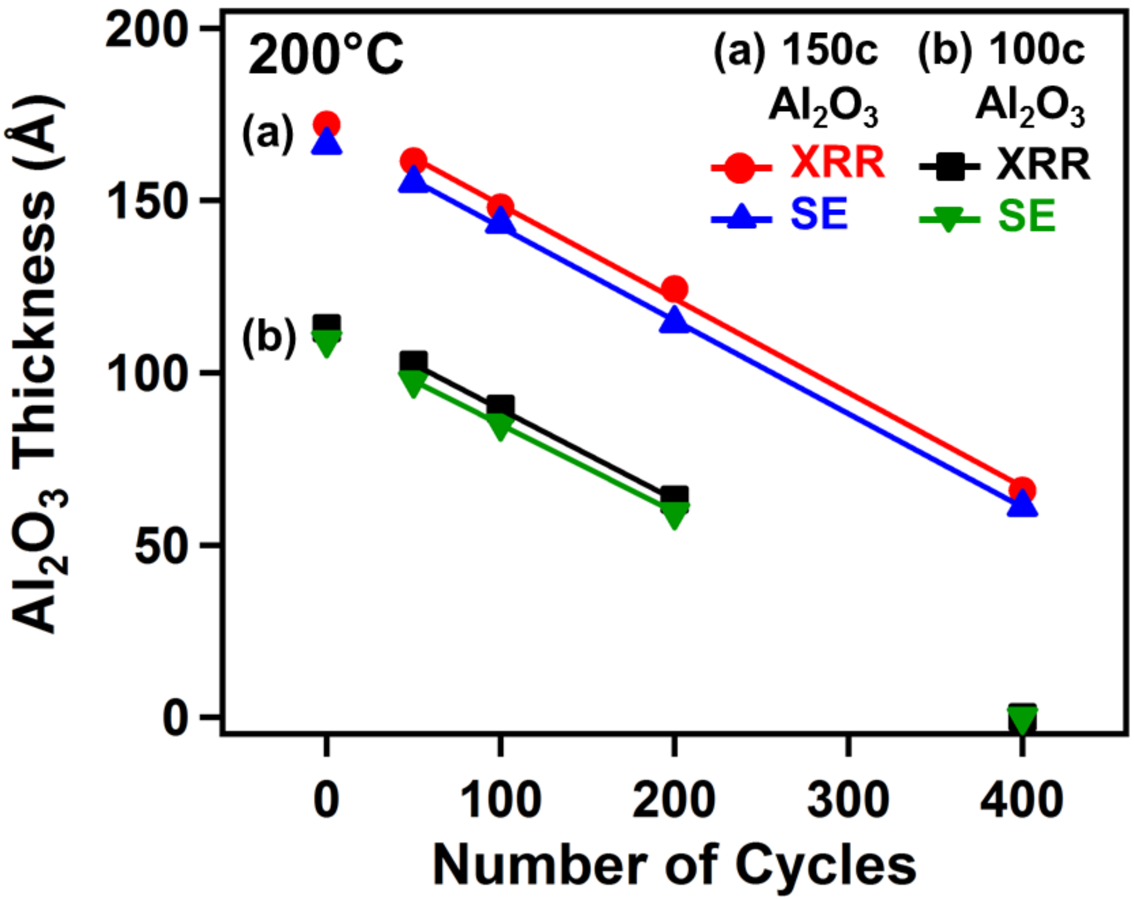
100 ALE cycles

Mass change per cycle = $-8.4\ ng/cm^2$

Etch rate = 0.28 Å/cycle

Y. Lee & S.M. George, *ACS Nano* ***9,*** 2061 (2015).

Linear Decrease of Al_2O_3 Film Thickness vs Number of Al_2O_3 ALE Cycles

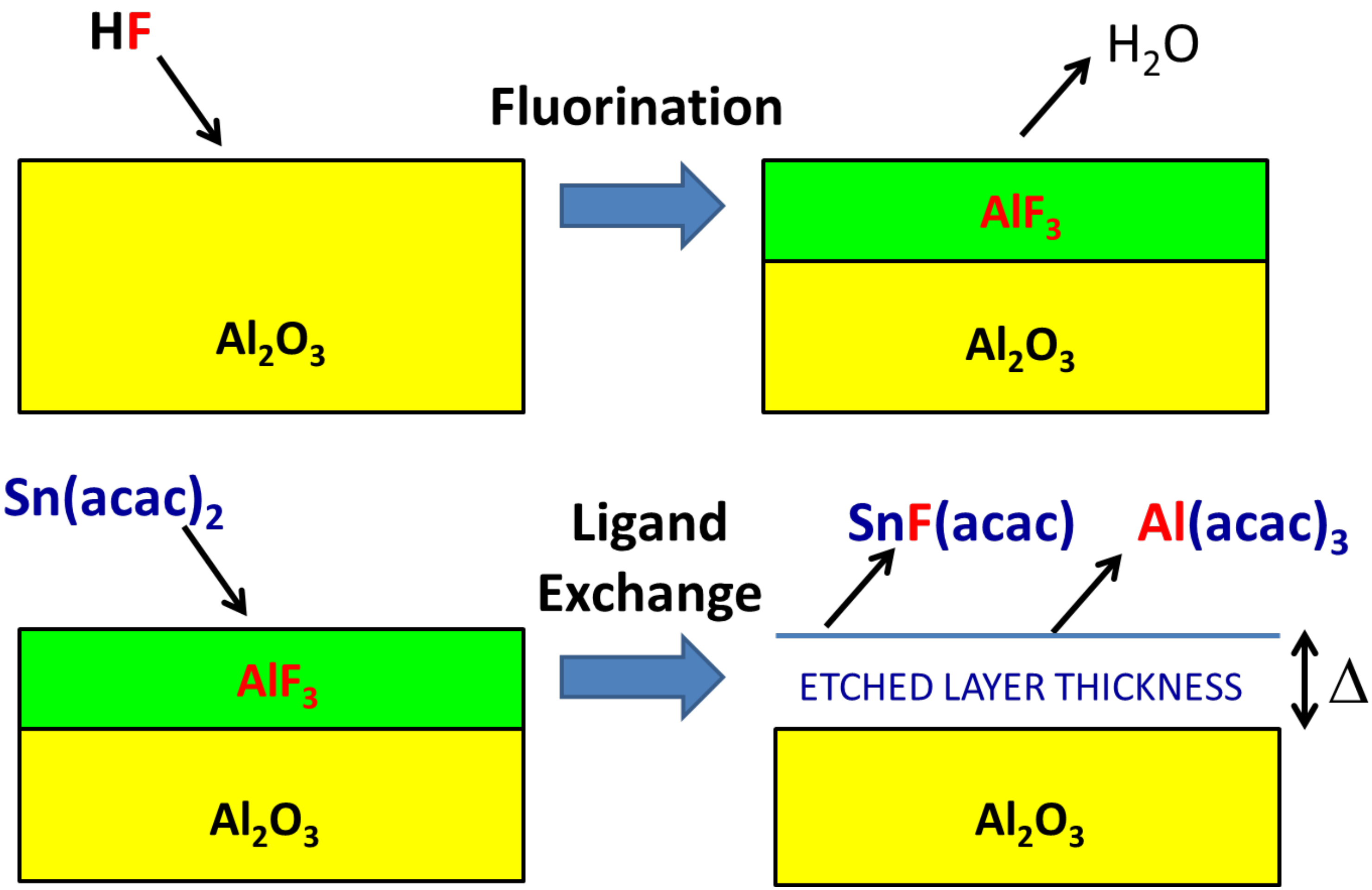


XRR measurements yield etch rate = 0.27 Å/cycle

Confirm with spectroscopic ellipsometry (SE)

Y. Lee & S.M. George, *ACS Nano* ***9***, 2061 (2015).

Al_2O_3 ALE via Fluorination & Ligand Exchange



Metal Precursors for ALE

Requirements for Metal Precursor:

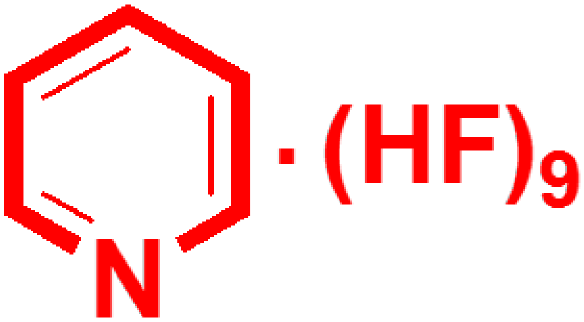
1. Accept fluorine from metal fluoride
2. Donate ligand to metal in metal fluoride
3. Metal reaction product is stable & volatile

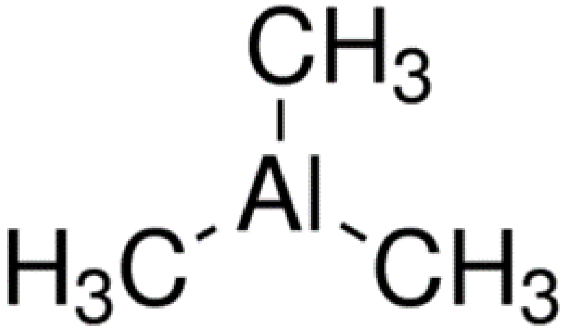
Possible Metal Precursor:

Same precursor as used for ALD of etched material

e.g. $Al(CH_3)_3$ for Al_2O_3 ALE

Al_2O_3 ALE Using HF-Pyridine & $Al(CH_3)_3$ as Reactants



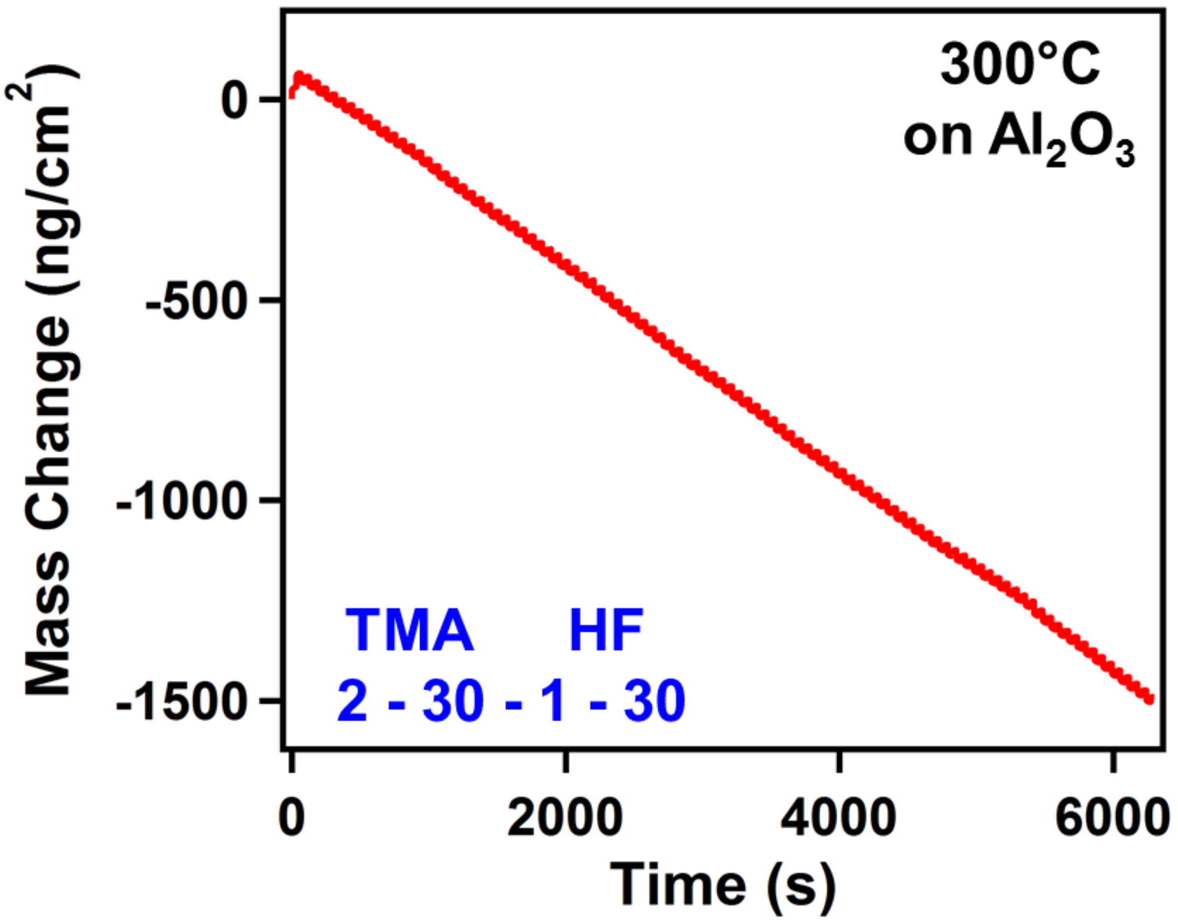


HF-Pyridine

$Al(CH_3)_3$

Y. Lee, J.M. DuMont & S.M. George, *Chem. Mater. (In Press).*

Al_2O_3 ALE Using HF & $Al(CH_3)_3$



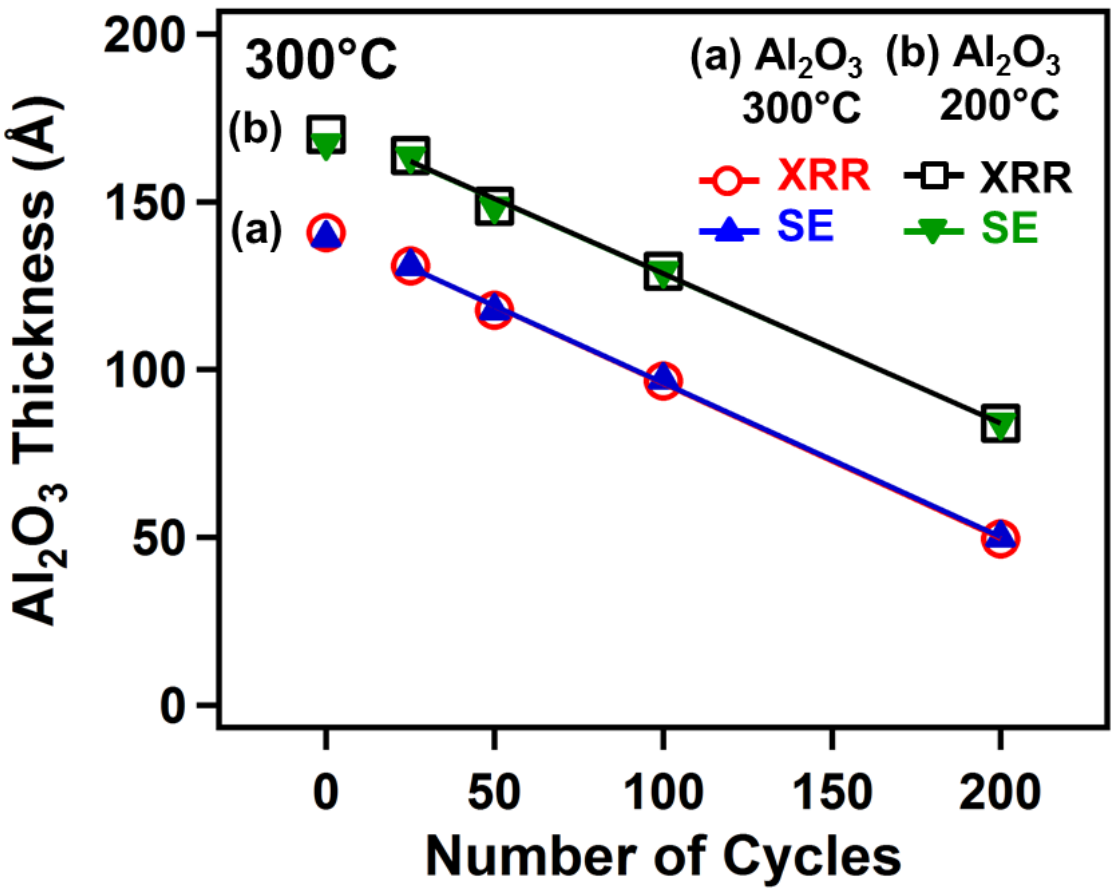
100 ALE Cycles

Mass change per cycle = -15.9 ng/cm^2

Etch rate = 0.51 Å/cycle

Y. Lee, J.M. DuMont & S.M. George, *Chem. Mater. (In Press).*

Linear Decrease of Al_2O_3 Film Thickness vs Number of Al_2O_3 ALE Cycles

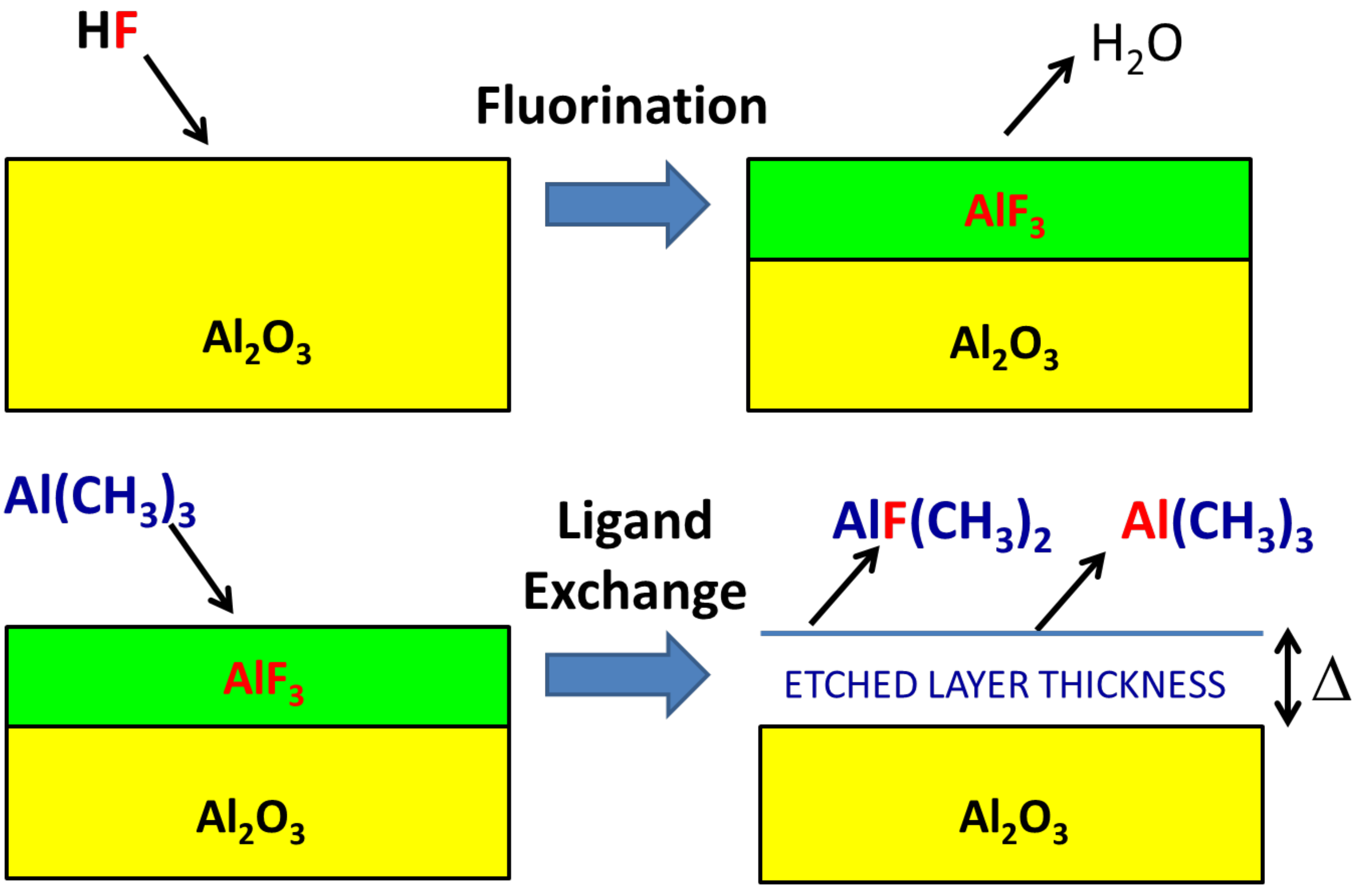


XRR measurements yield etch rate = 0.46 Å/cycle

Confirm with spectroscopic ellipsometry (SE)

Y. Lee, J.M. DuMont & S.M. George, *Chem. Mater. (In Press).*

Al_2O_3 ALE via Fluorination & Ligand Exchange



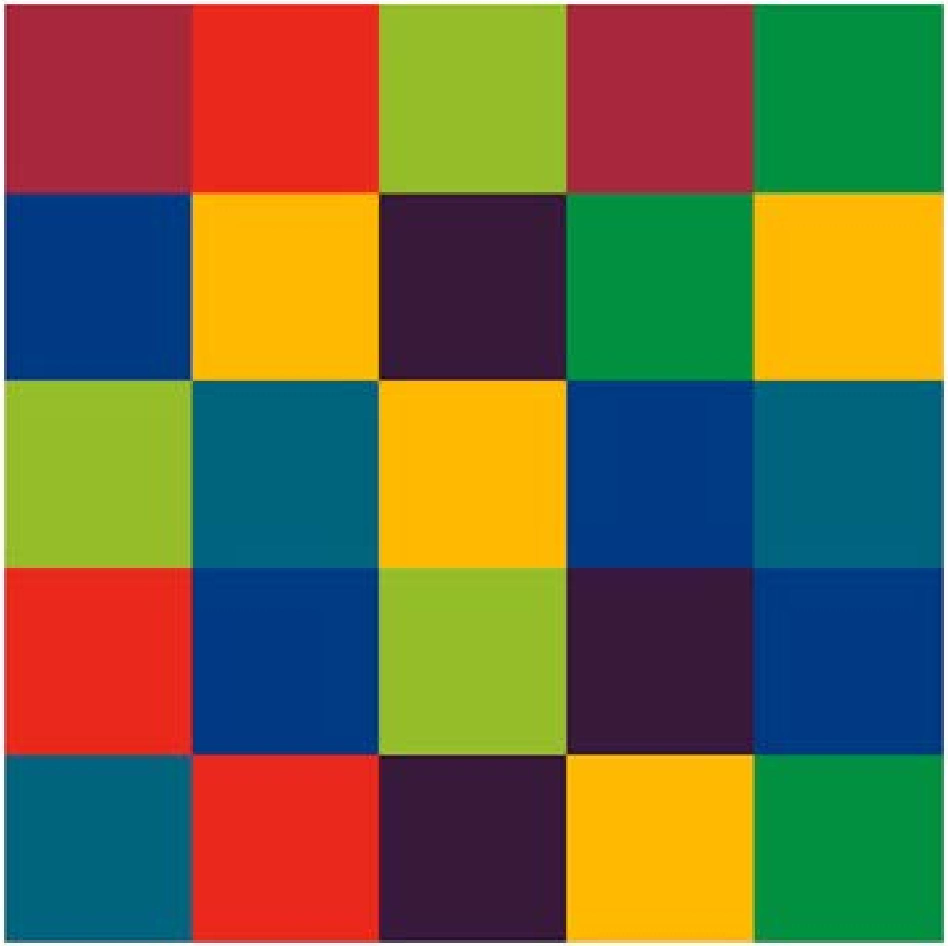
Outline

1. Al_2O_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.

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

*Adapted from C.T. Carver et al., *ECS J. Solid State Sci. Technol.* **4**, N5005 (2015).

Selectivity During ALE

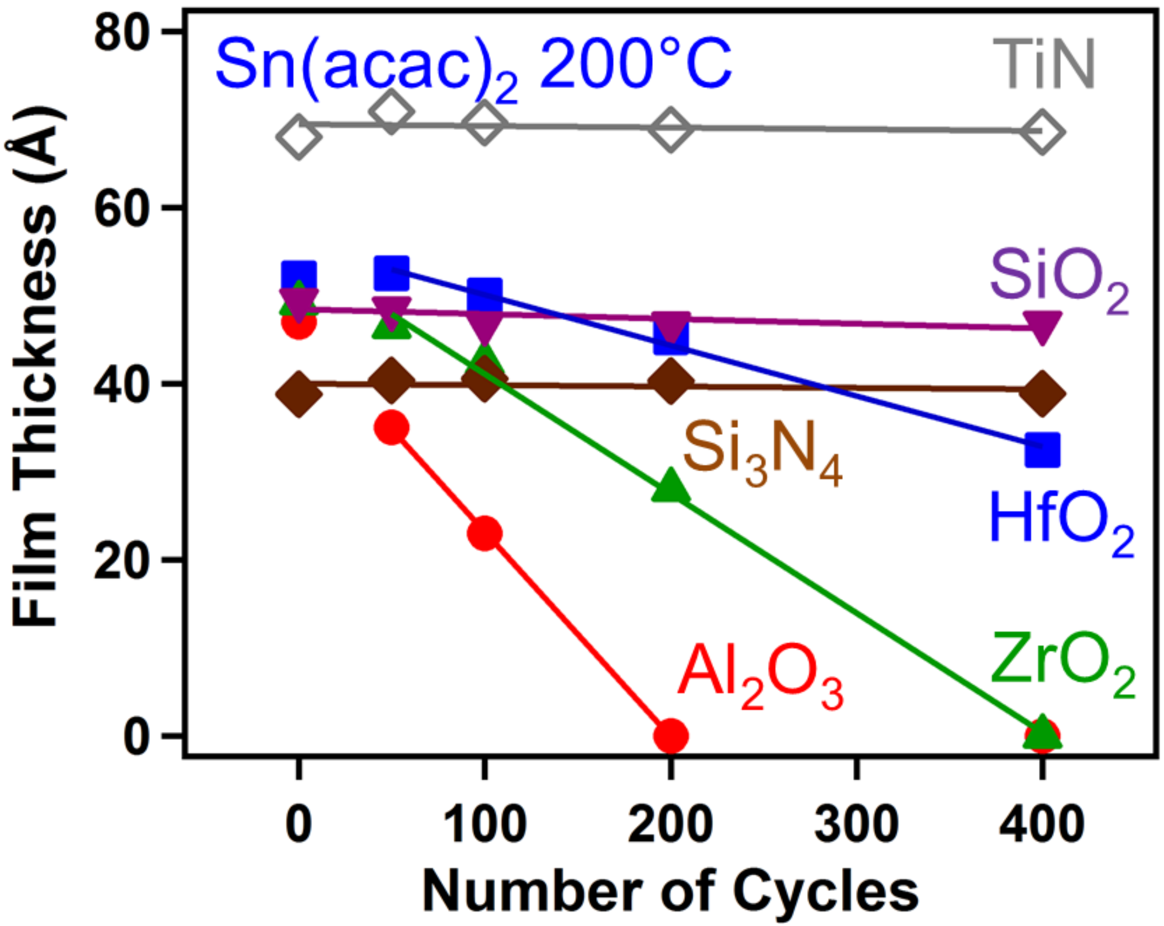
Requirements for Metal Precursor:

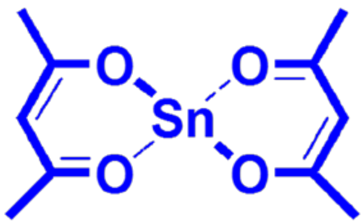
1. Accept fluorine from metal fluoride
2. Donate ligand to metal in metal fluoride
3. Metal reaction product is stable & volatile

Strategy for Selectivity:

Use metal precursors with ligands that yield stable & volatile reaction products with target metals

ALE Using HF & $Sn(acac)_2$



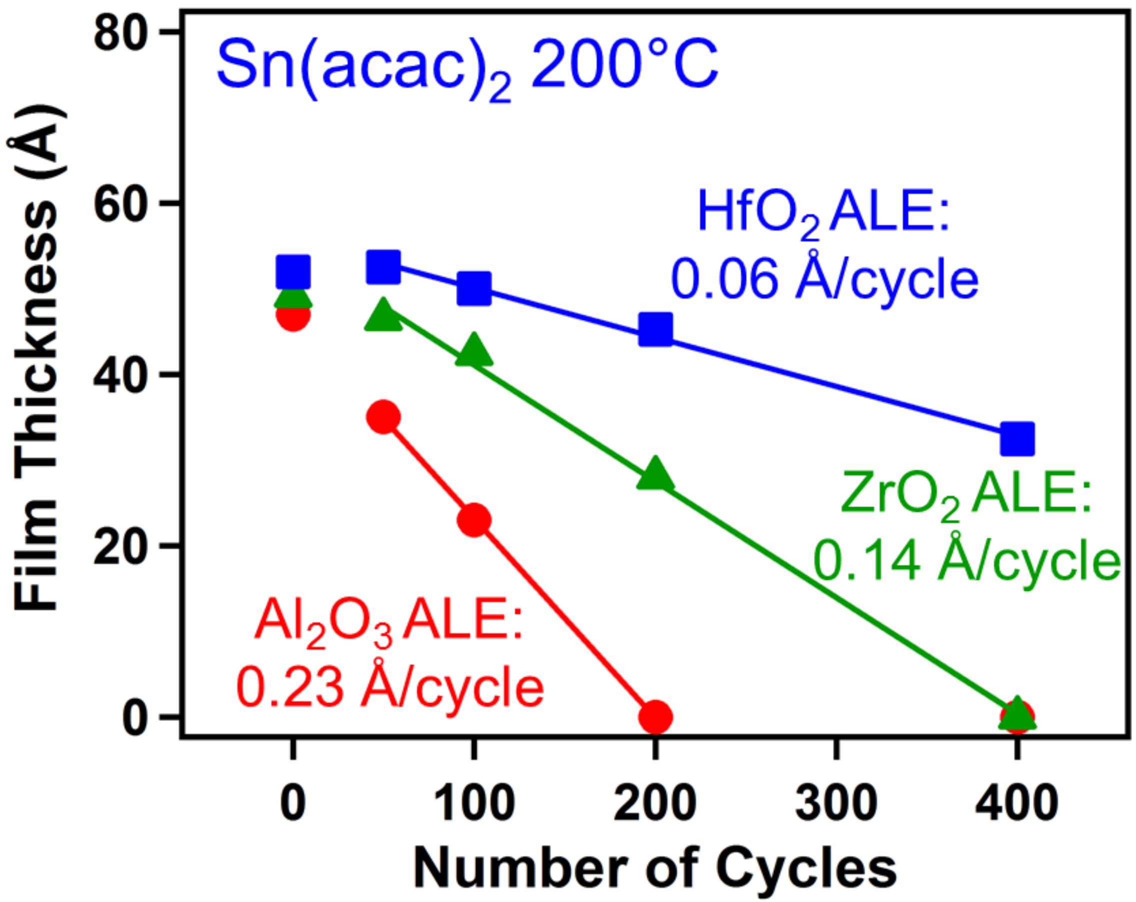


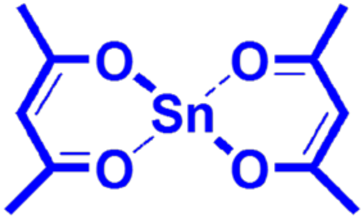
Selective etching of Al_2O_3, HfO_2 & ZrO_2.

Al, Hf & Zr form stable & volatile acac complexes.

Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, TiN

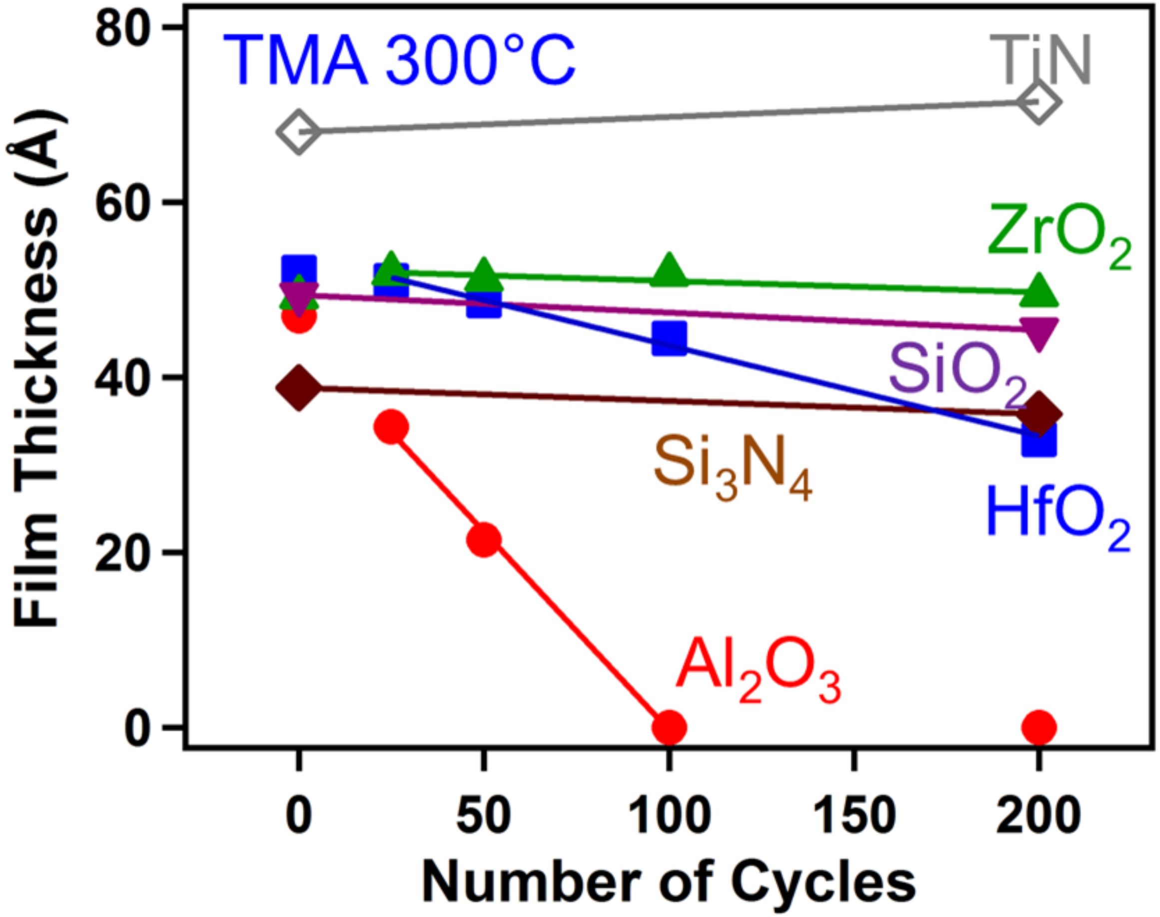
Al_2O_3, HfO_2 & ZrO_2 ALE Using HF & $Sn(acac)_2$

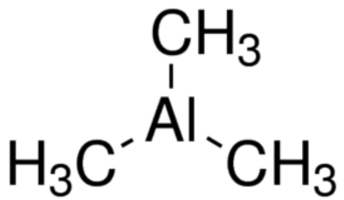




Al_2O_3, HfO_2, ZrO_2

ALE Using HF & $Al(CH_3)_3$ (TMA)



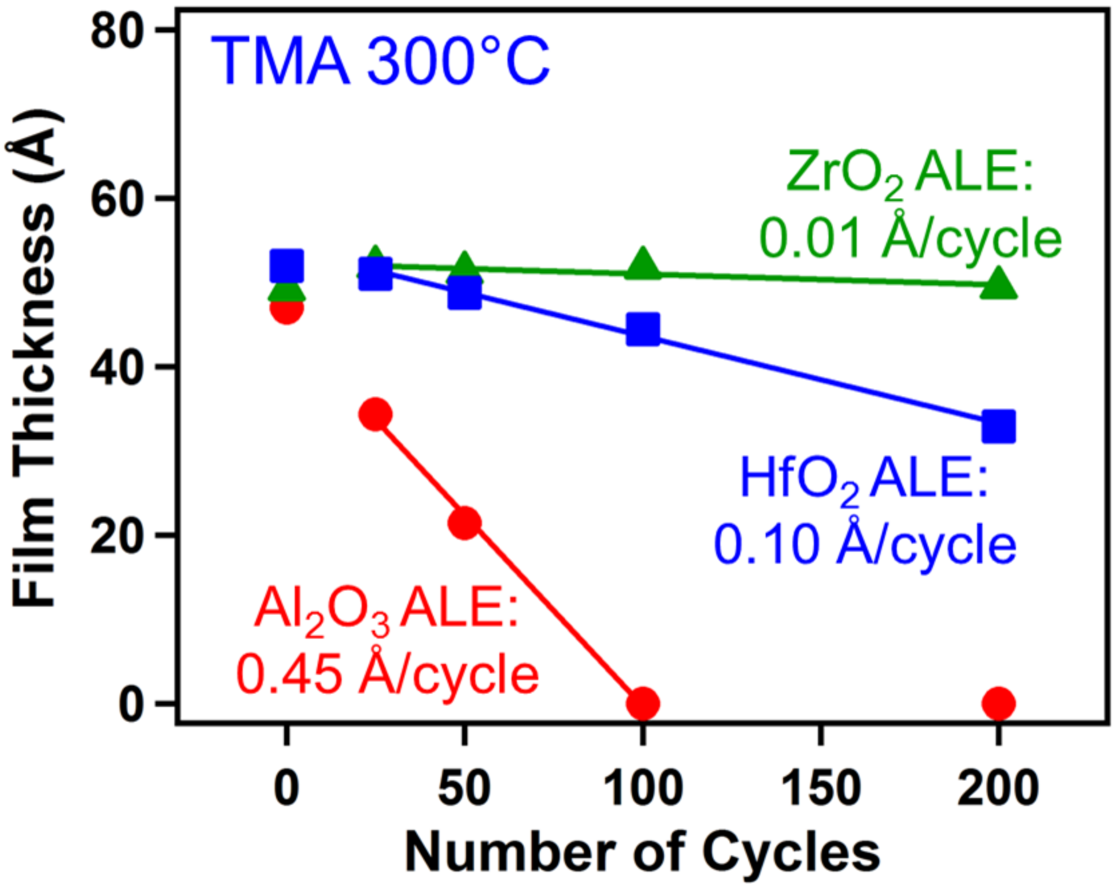


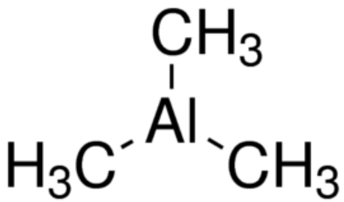
Selective etching of Al_2O_3 & HfO_2.

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

Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, TiN

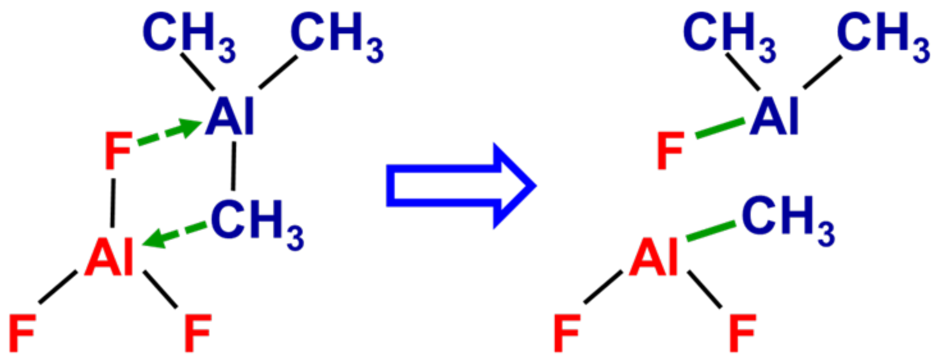
Al_2O_3, HfO_2 & ZrO_2 ALE Using HF & $Al(CH_3)_3$ (TMA)



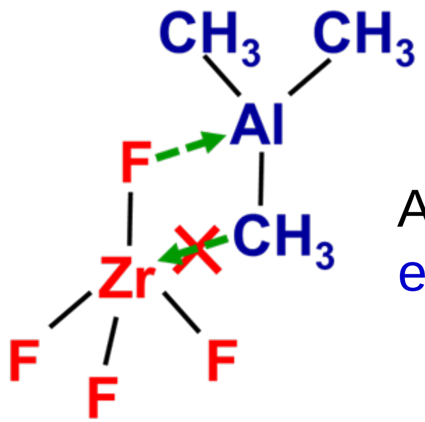


Al_2O_3, HfO_2, ZrO_2

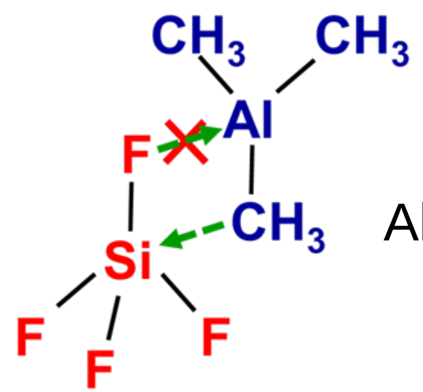
Understanding Selectivity



Al_2O_3 ALE with $Al(CH_3)_3$.
Ligand-exchange.
Stable Al-CH_3 reaction product.

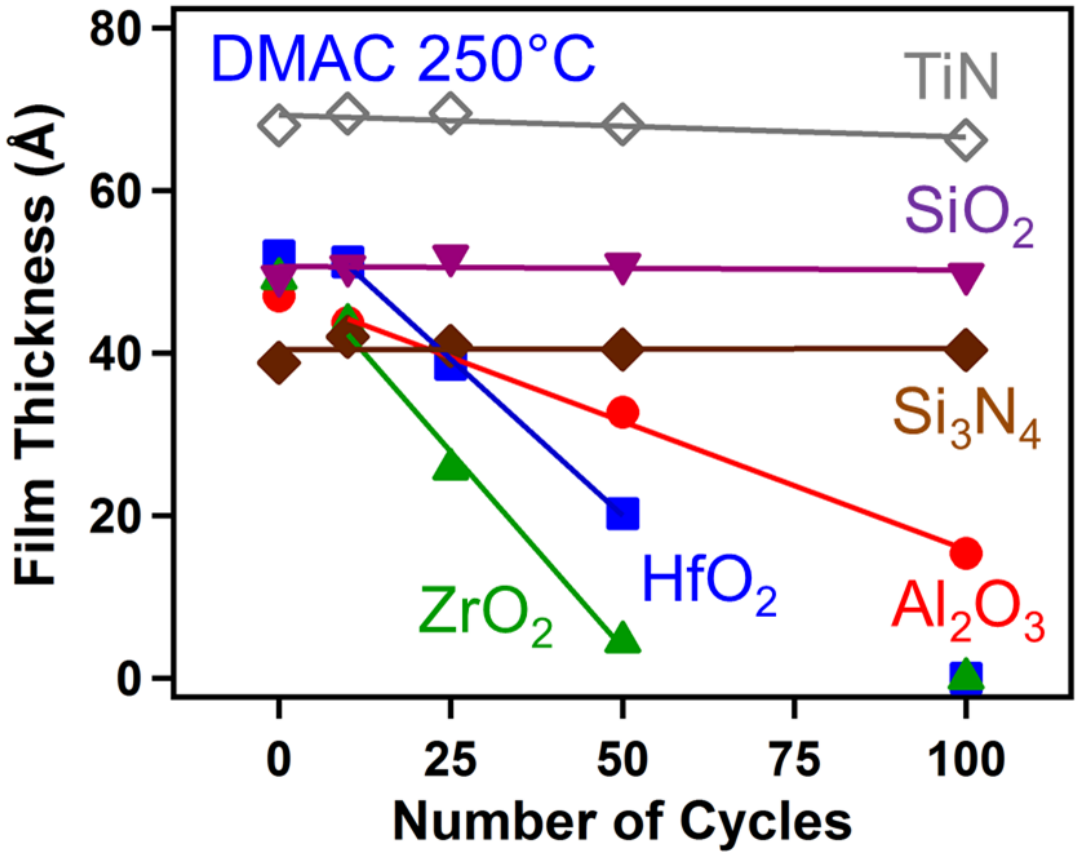


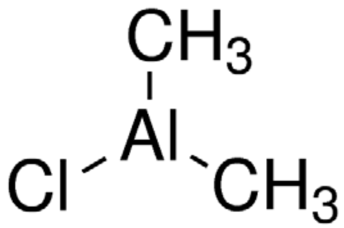
ZrO_2 ALE with $Al(CH_3)_3$. No ligand-exchange. Unstable Zr-CH_3 reaction product.



SiO_2 ALE with $Al(CH_3)_3$. No ligand-exchange. Si-F bond too stable.

ALE Using HF & $AlCl(CH_3)_2$ (DMAC)



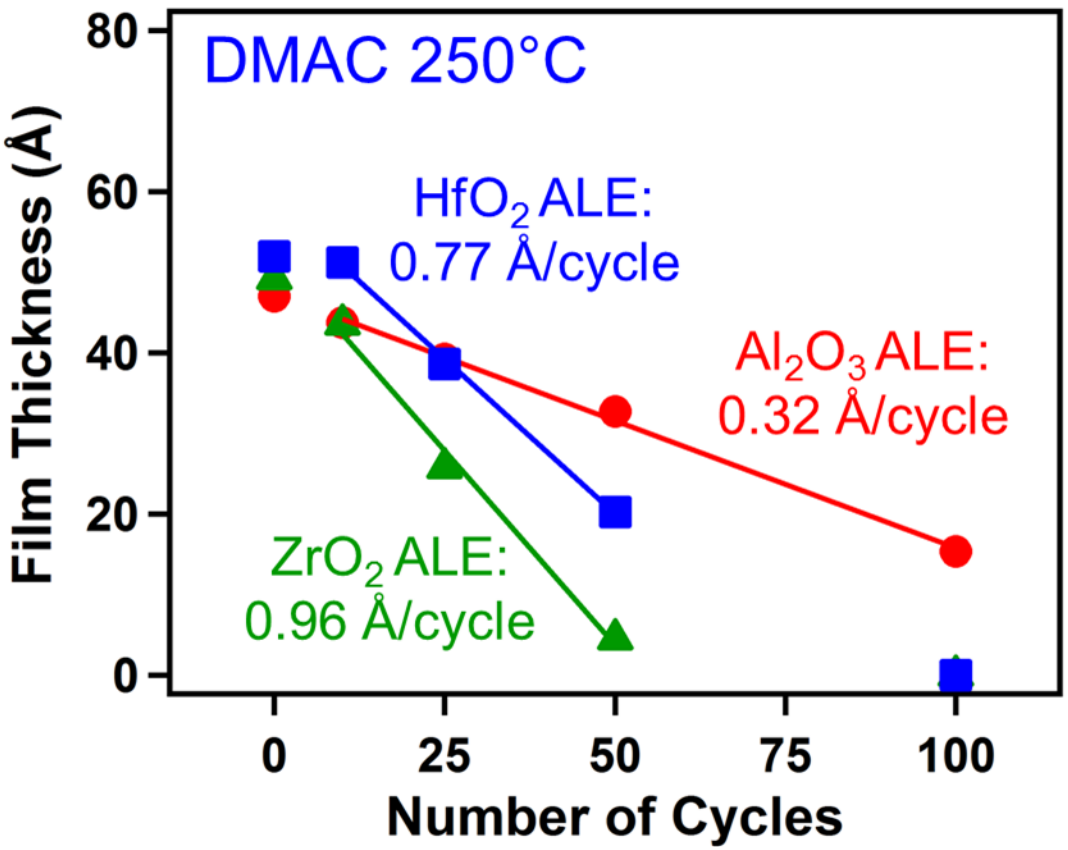


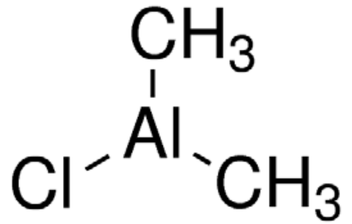
Selective etching of Al_2O_3, ZrO_2 & HfO_2.

Al, Zr & Hf form stable & volatile complexes with chloride or methyl groups.

Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, TiN

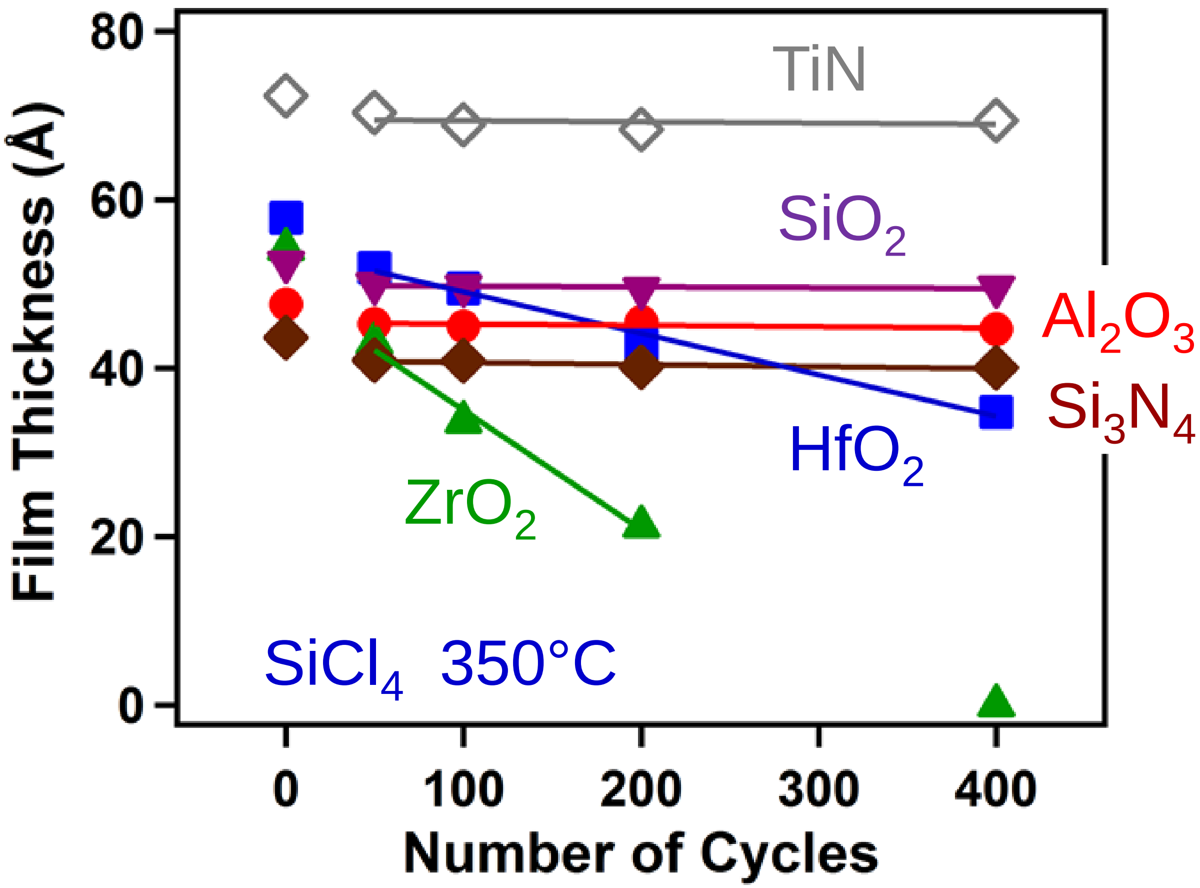
Al_2O_3, HfO_2 & ZrO_2 ALE Using HF & $AlCl(CH_3)_2$ (DMAC)

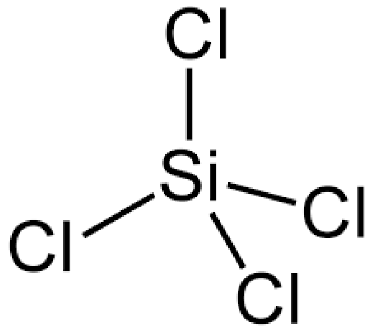




Al_2O_3, HfO_2, ZrO_2

ALE Using HF & $SiCl_4$



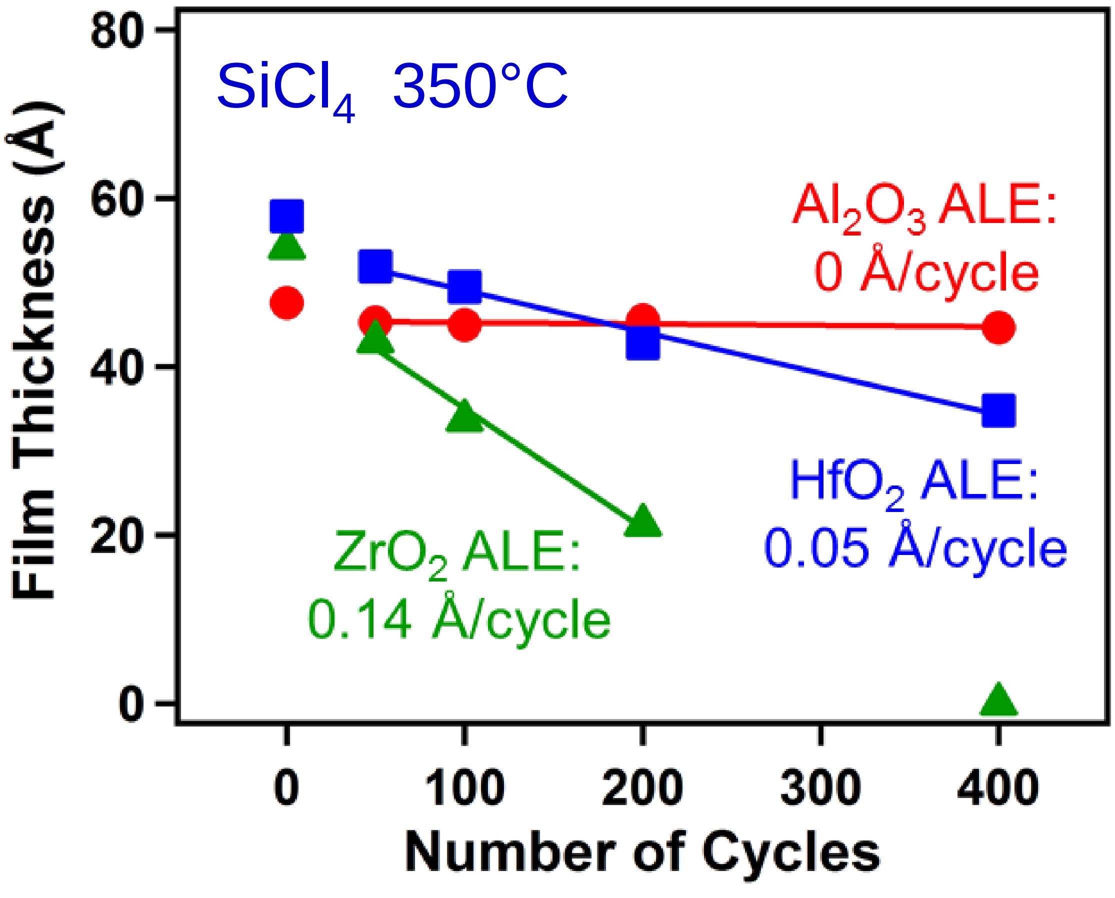


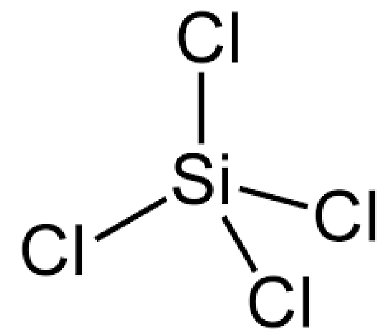
Selective etching of ZrO_2 & HfO_2.

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

Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, TiN

Al_2O_3, HfO_2 & ZrO_2 ALE Using HF & $SiCl_4$

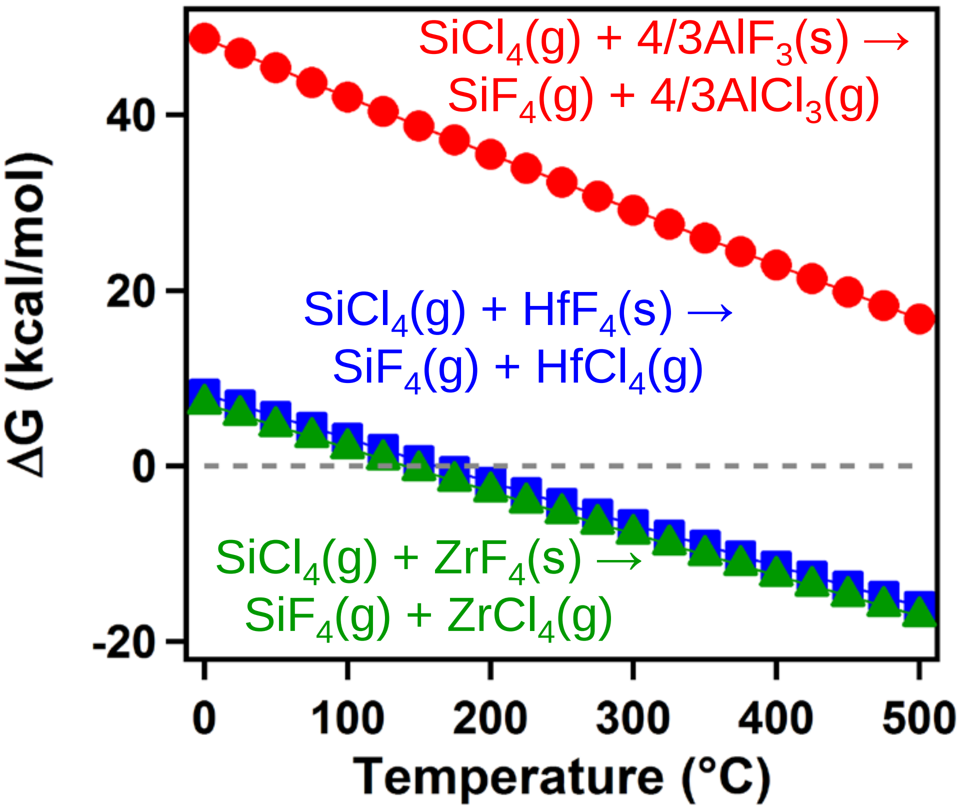




Why no etching of Al_2O_3 with $SiCl_4$?

Al_2O_3, HfO_2, ZrO_2

Ligand-Exchange Thermochemistry Explains No Al_2O_3 ALE



Positive ΔG for $SiCl_4$ ligand-exchange for Al_2O_3 ALE.

$\Delta G = 0$

Negative ΔG for $SiCl_4$ ligand-exchange >150°C for HfO_2 & ZrO_2 ALE.

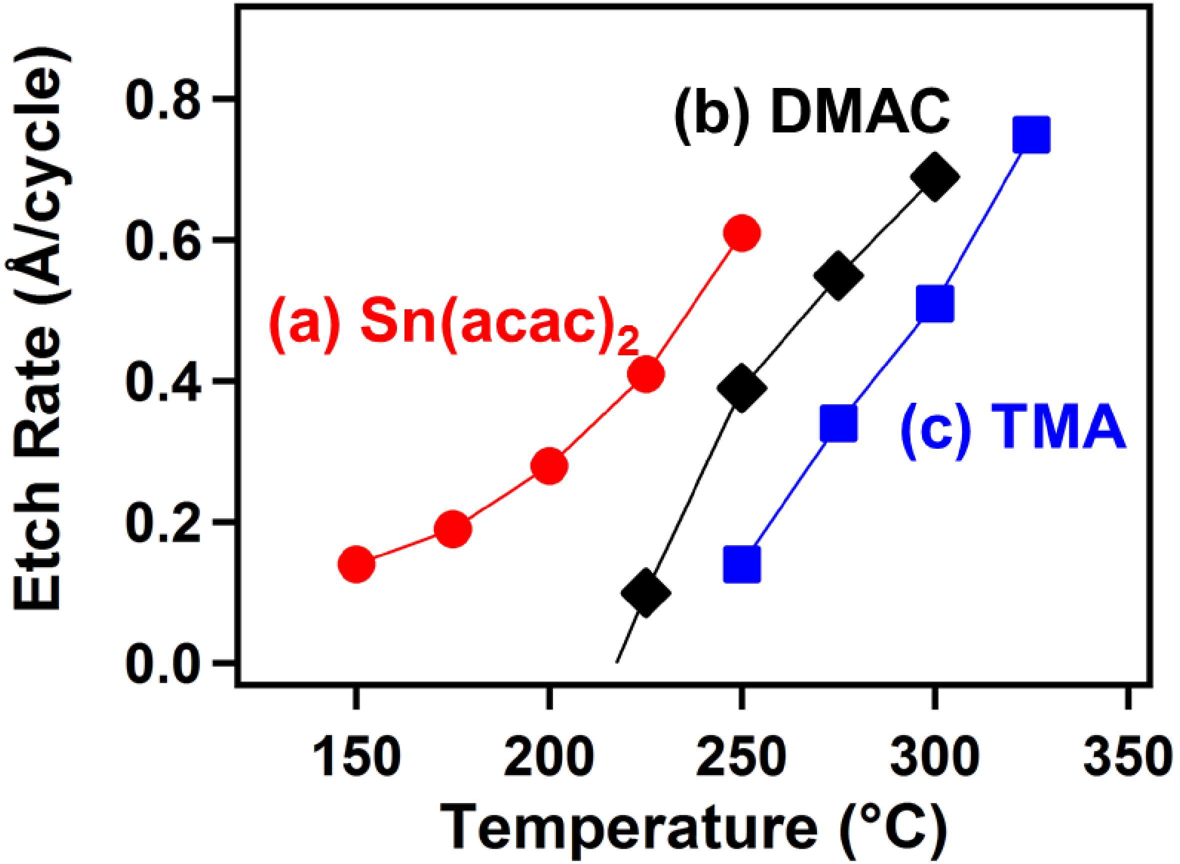
Outline

1. Al_2O_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.

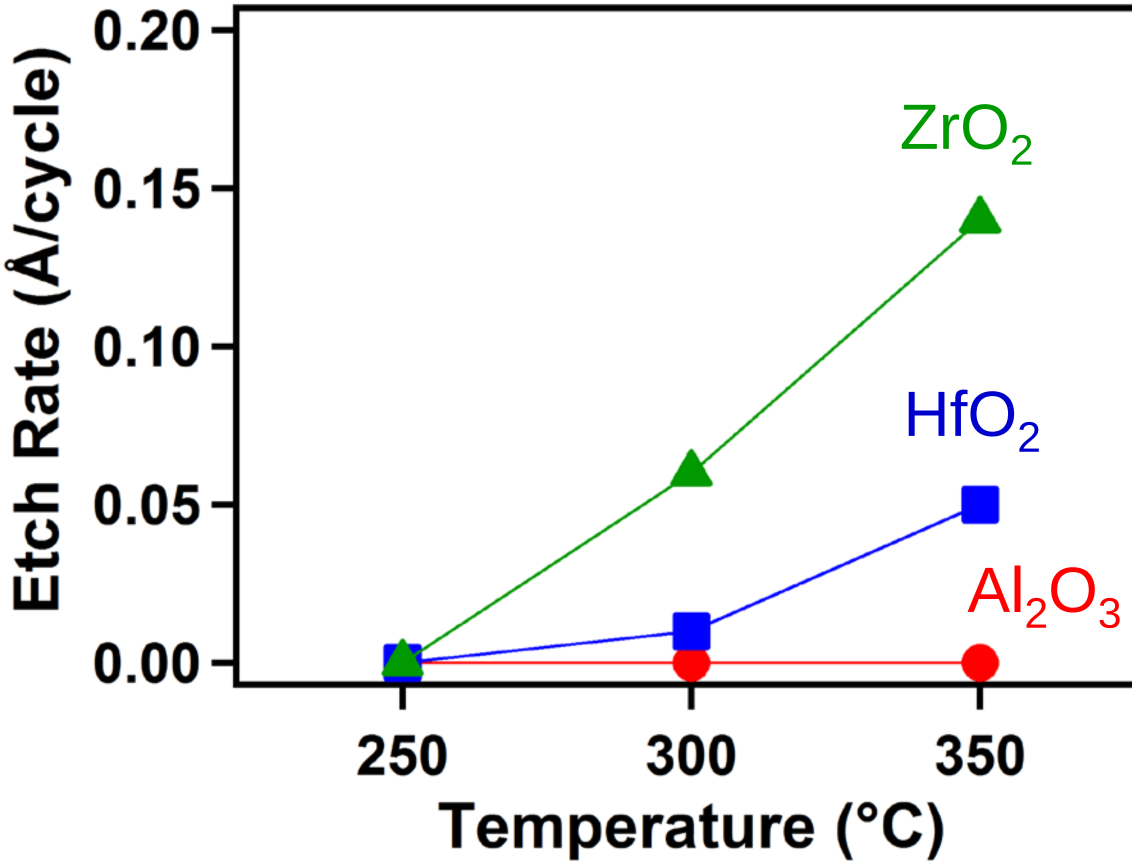
3. Selectivity in ALE based on temperature.

Selectivity Based on Temperature for Al_2O_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



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.