Understanding Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination & Ligand-Exchange Reactions

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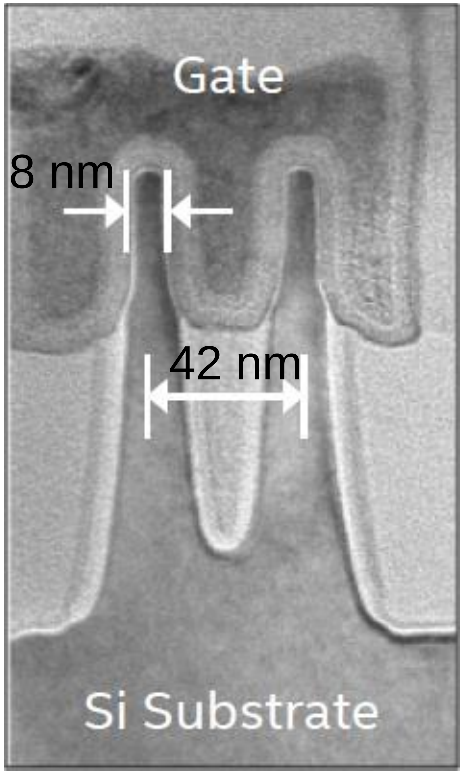
University of Colorado Boulder

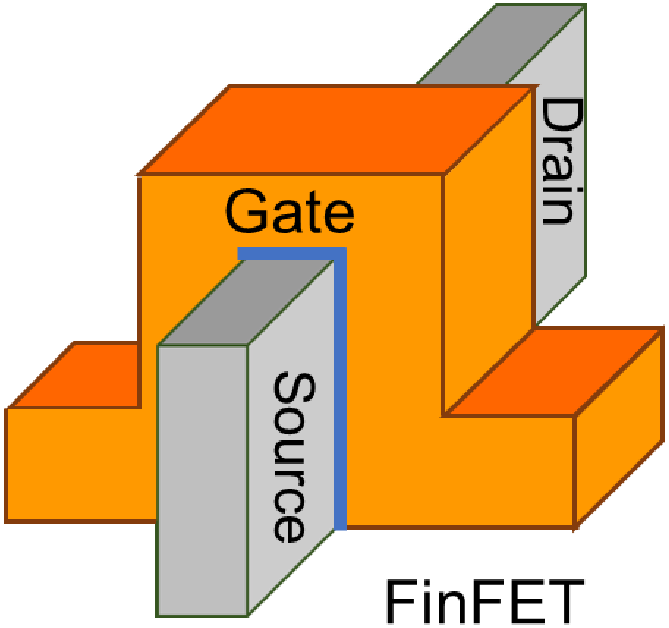
2nd Area Selective Deposition Workshop 2017

Atomic Layer Etching

Need precise & damage-free etching, enabling 3D process at atomic scale.



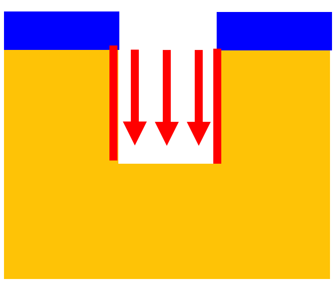
14 nm FinFET by Intel



S. M. George & Y. Lee,
ACS Nano **2016**, 10 (5), 4889

Various ALE Approaches

Energetic ALE:
halogenation
& energetic
bombardment

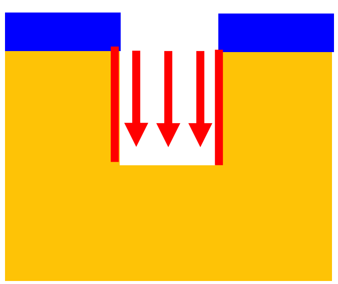


Anisotropic
Etching

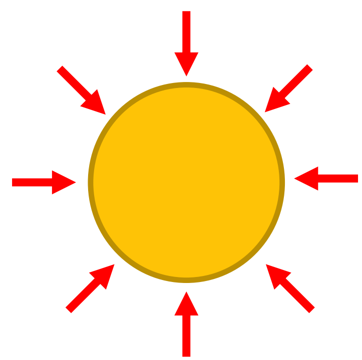
Various ALE Approaches

Energetic ALE:
halogenation
& energetic
bombardment

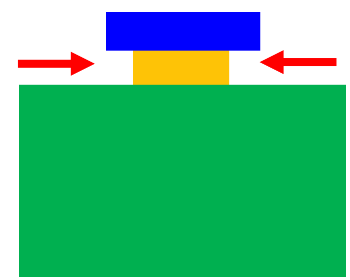
Thermal ALE:
"Reverse ALD"
sequential & self-limiting
surface reactions



Anisotropic
Etching

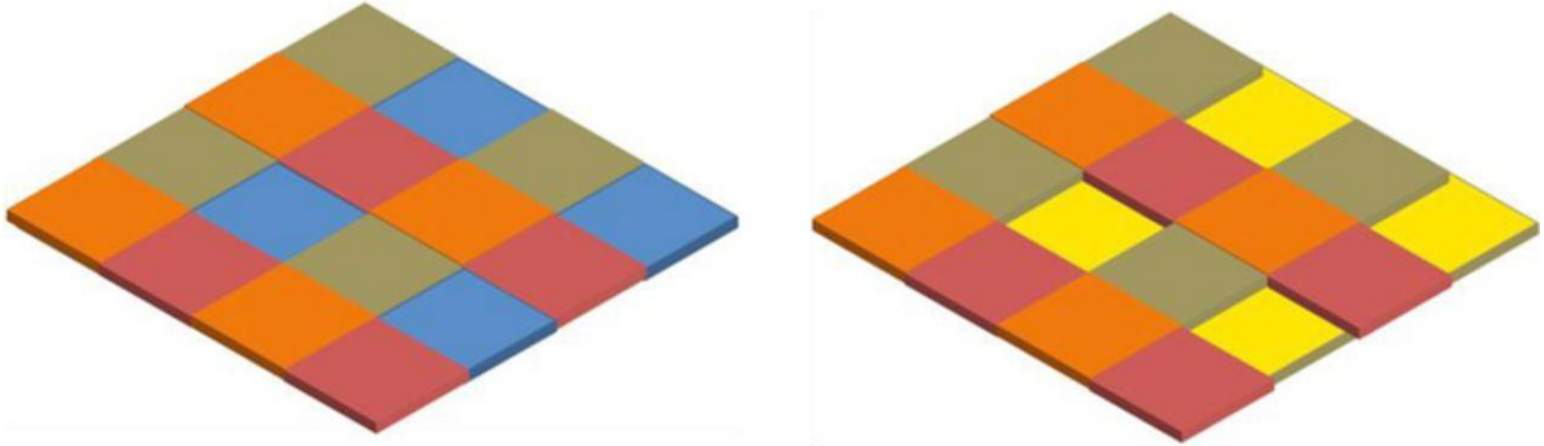


Isotropic
Etching



Undercut
Etching

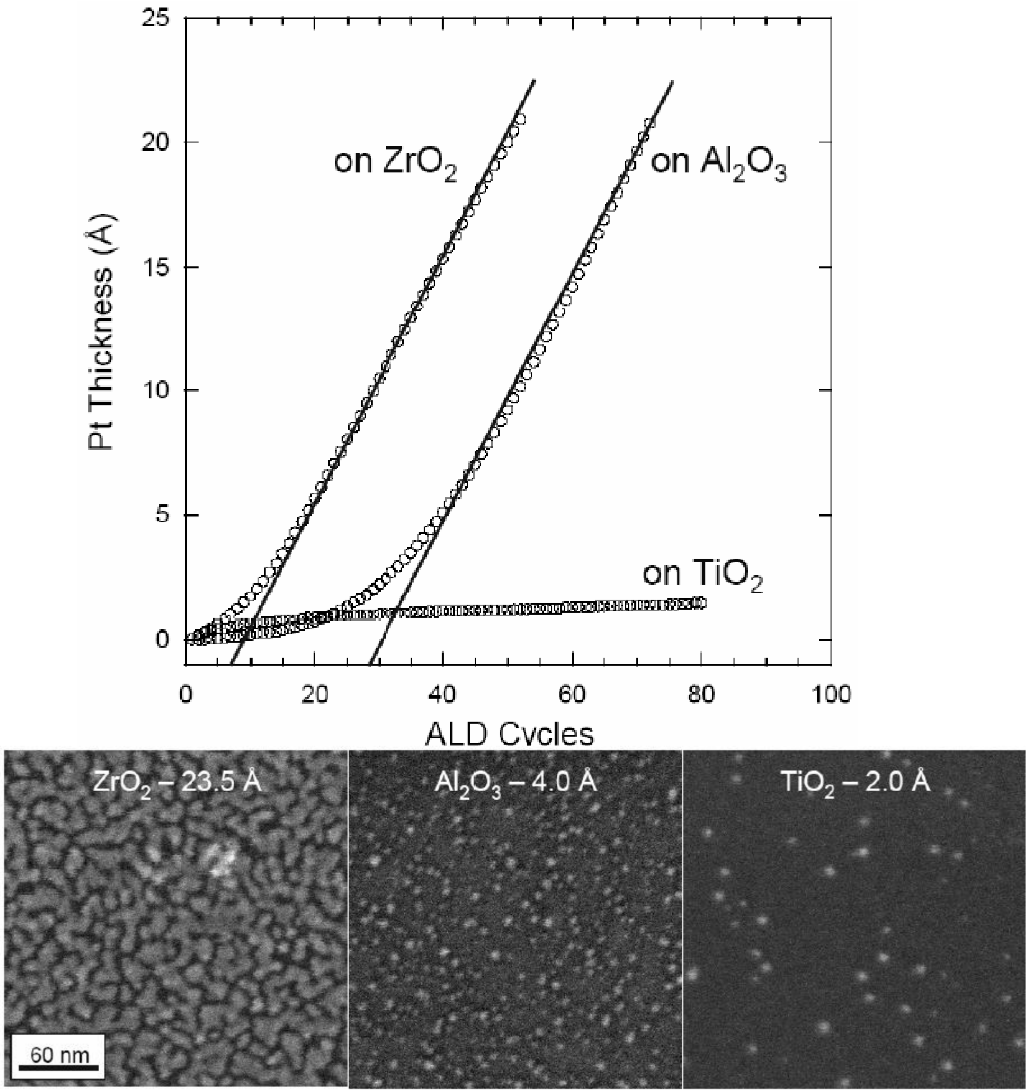
Selectivity in ALE



- Need to remove one material not other materials
- No damage to underlying material

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

ALE May Help Area Selective Deposition



Better selectivity by removing unwanted ALD nucleation

J. W. Elam *et al.*, *ECS Transactions* **3**, 271 (2007)

Outline

- Al_2O_3 & HfO_2 ALE using HF & $Sn(acac)_2$
- Al_2O_3 ALE using HF & TMA
- Selectivity in ALE using $Sn(acac)_2$, $Al(CH_3)_3$, $AlCl(CH_3)_2$, and $SiCl_4$ as metal reactants.
- Selectivity in ALE based on temperature

Outline

- Al_2O_3 & HfO_2 ALE using HF & $Sn(acac)_2$
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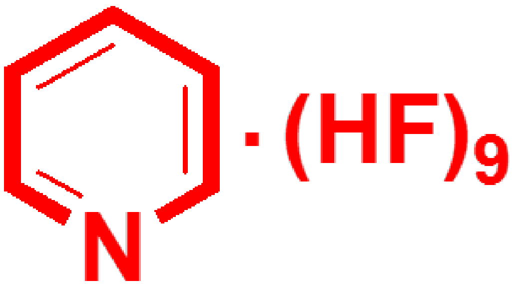
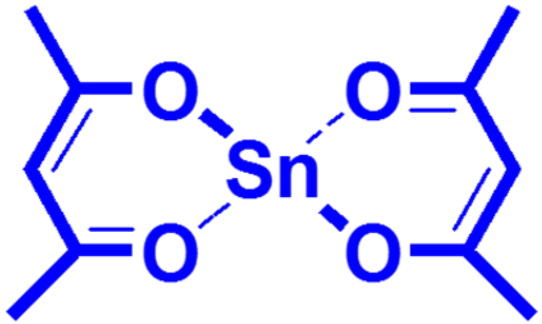
- Selectivity in ALE based on temperature

HF-Pyridine & $Sn(acac)_2$ Reactants





HF-pyridine

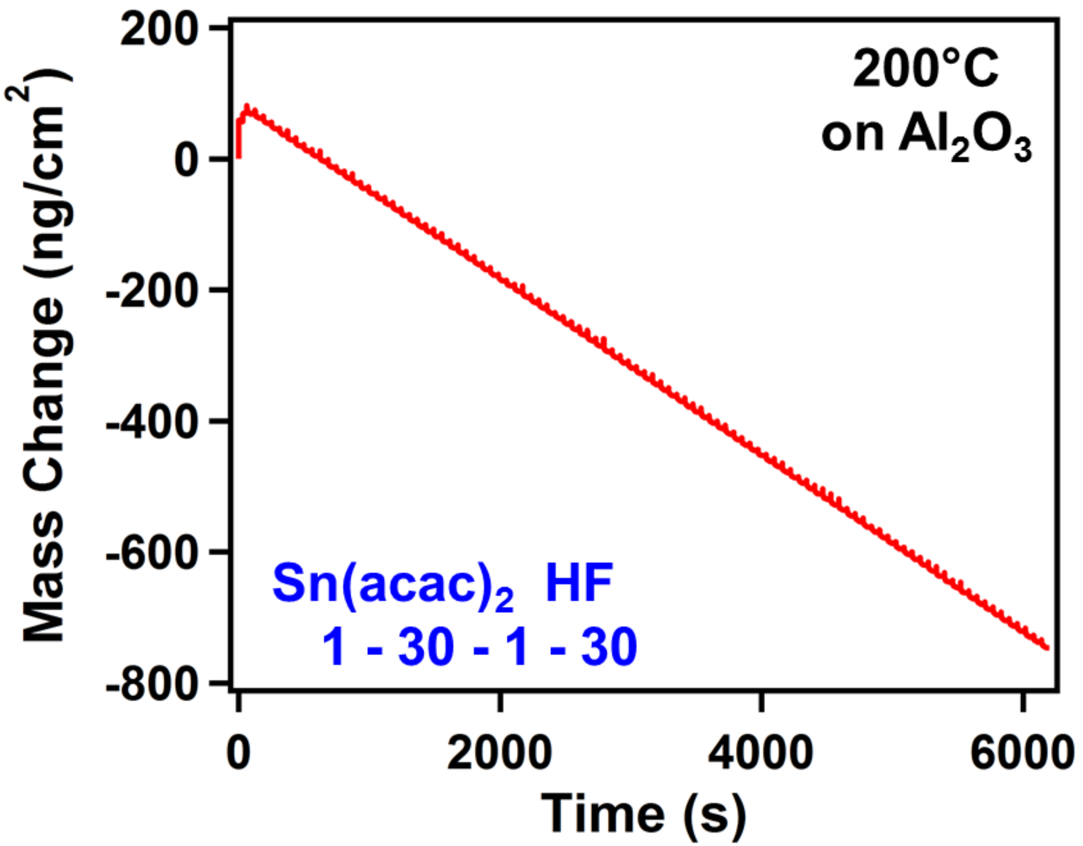
Safer HF precursor

$Sn(acac)_2$

Volatile & reactive fluorine acceptor

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

Linear Etching of Al_2O_3 Using $Sn(acac)_2$ & HF Monitored by QCM

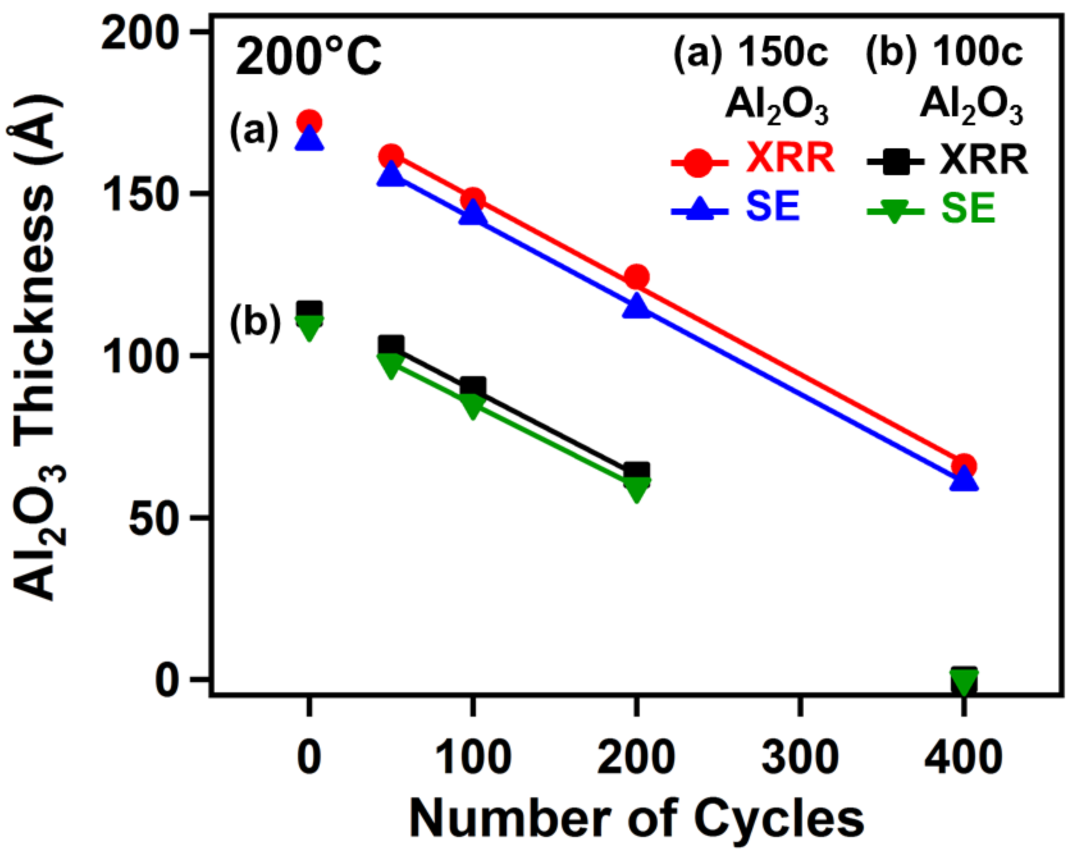


Mass Change per Cycle (MCPC) = -8.4 ng/(cm^2 cycle)

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

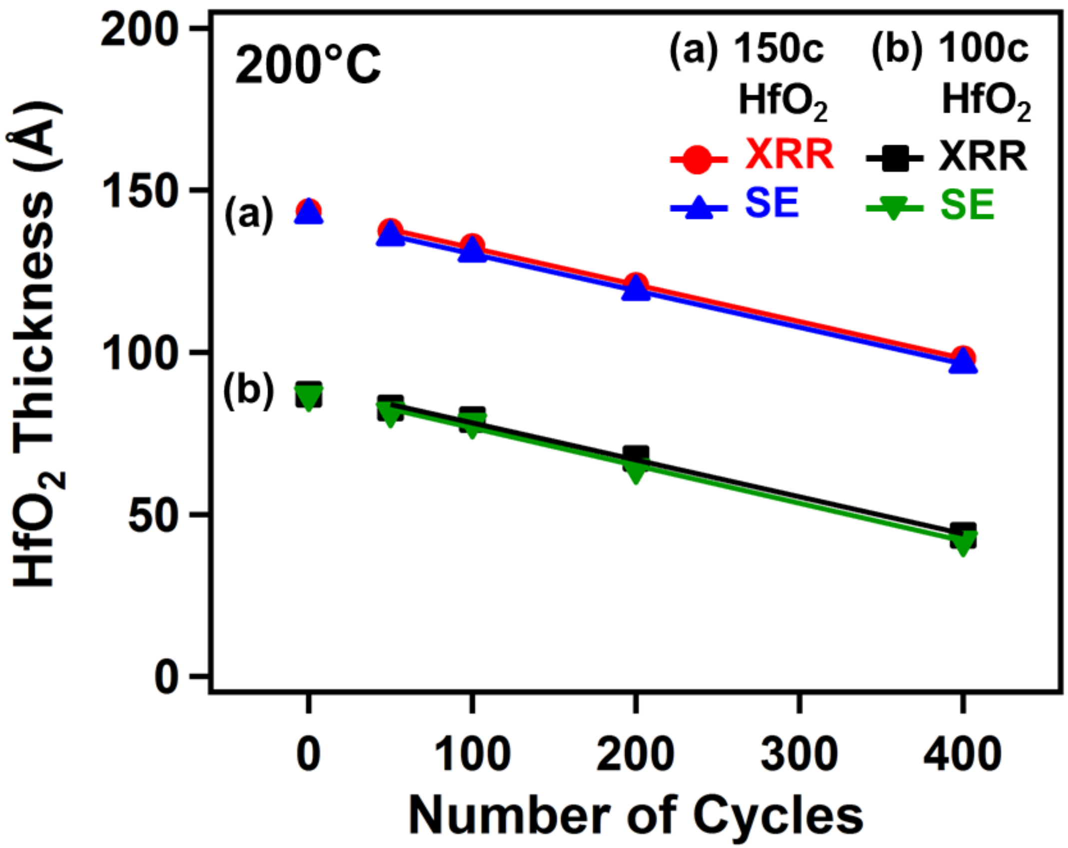


Etch rate
= 0.27 Å/cycle

Unchanged
Density &
Refractive index

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

Linear Decrease of HfO_2 Film Thickness vs. Number of HfO_2 ALE Cycles

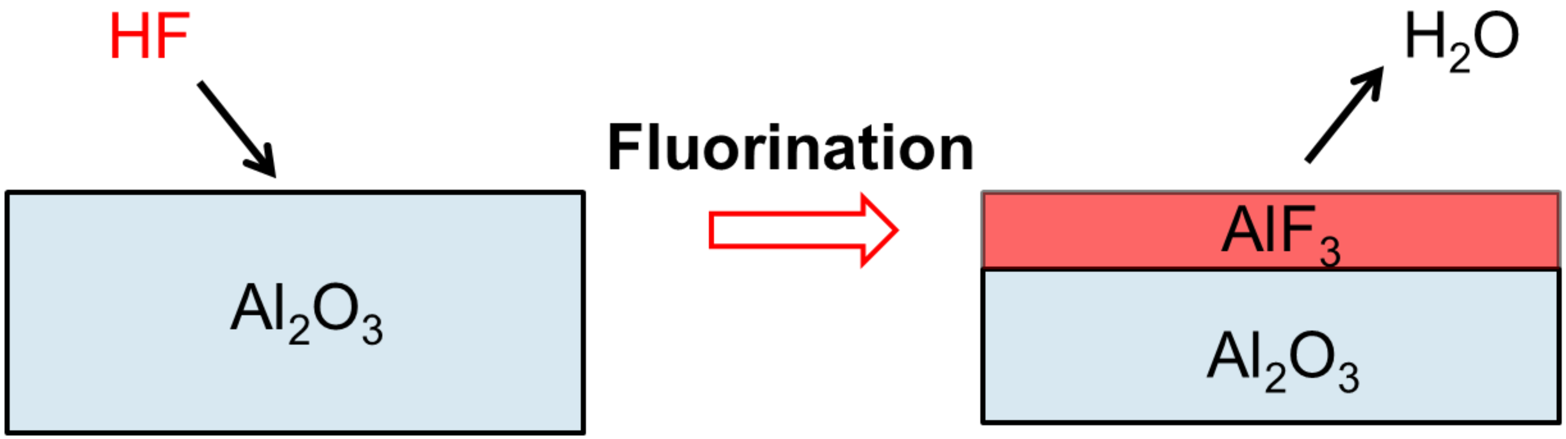


Etch rate
= 0.11 Å/cycle

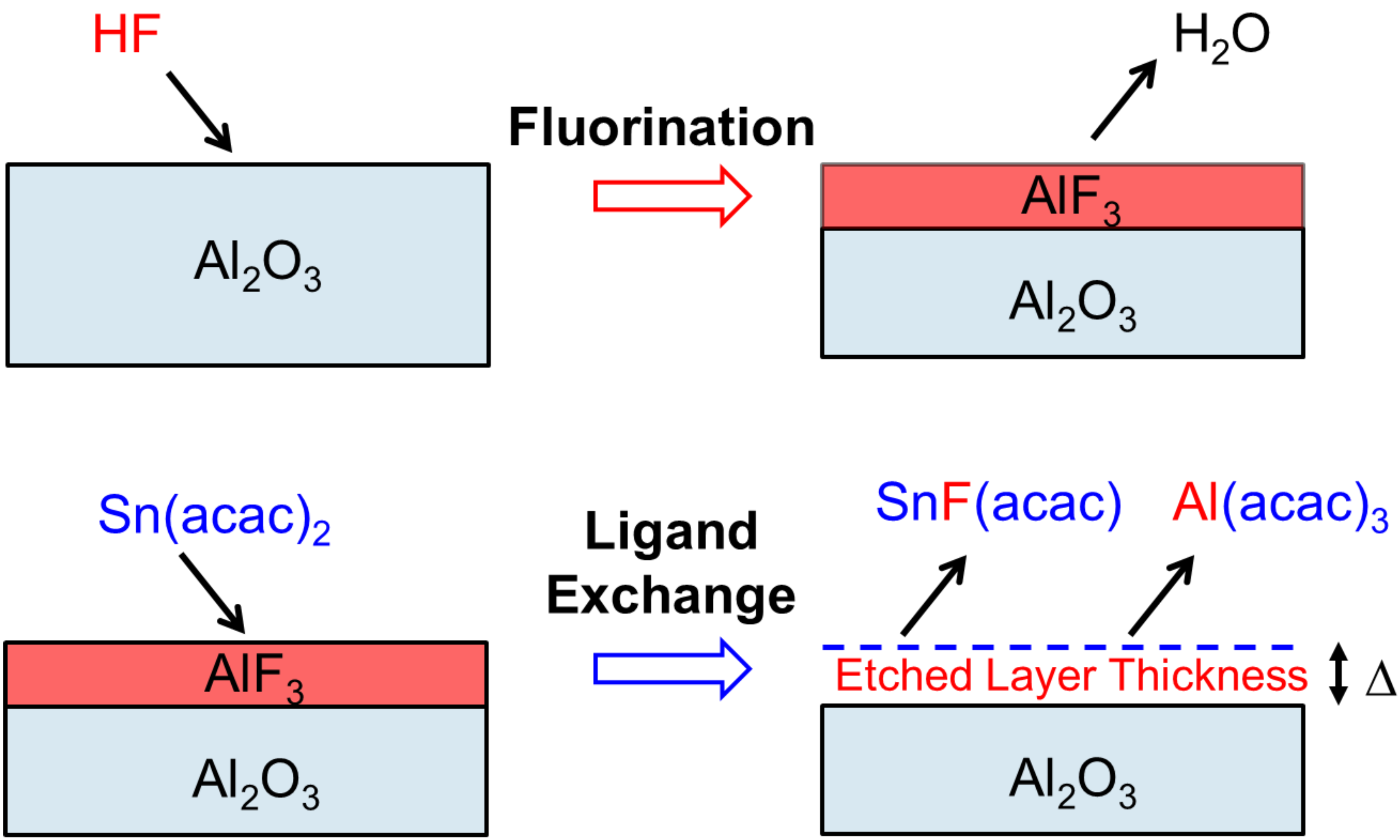
Unchanged
Density &
Refractive index

Y. Lee, J.W. DuMont & S.M. George,
ECS J. Solid State Sci. Technol. **4,** N5013 (2015)

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



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



Metal Reactants for ALE

Requirements for Metal Reactants:

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

Possible Metal Reactant:

Same reagent as used for ALD of etched material

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

Outline

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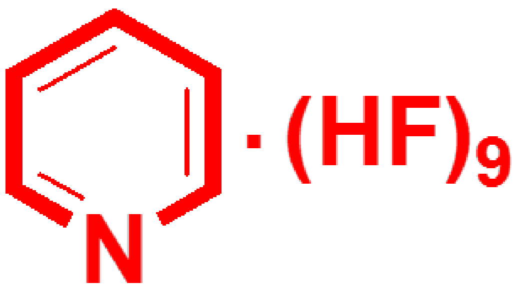
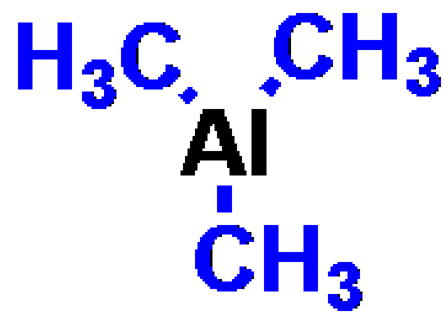
- Al_2O_3 ALE using HF & TMA
- Selectivity in ALE using $Sn(acac)_2$, $Al(CH_3)_3$, $AlCl(CH_3)_2$, and $SiCl_4$ as metal reactants.
- Selectivity in ALE based on temperature

HF-Pyridine & Trimethylaluminum Reactants



HF-pyridine

Safer HF precursor



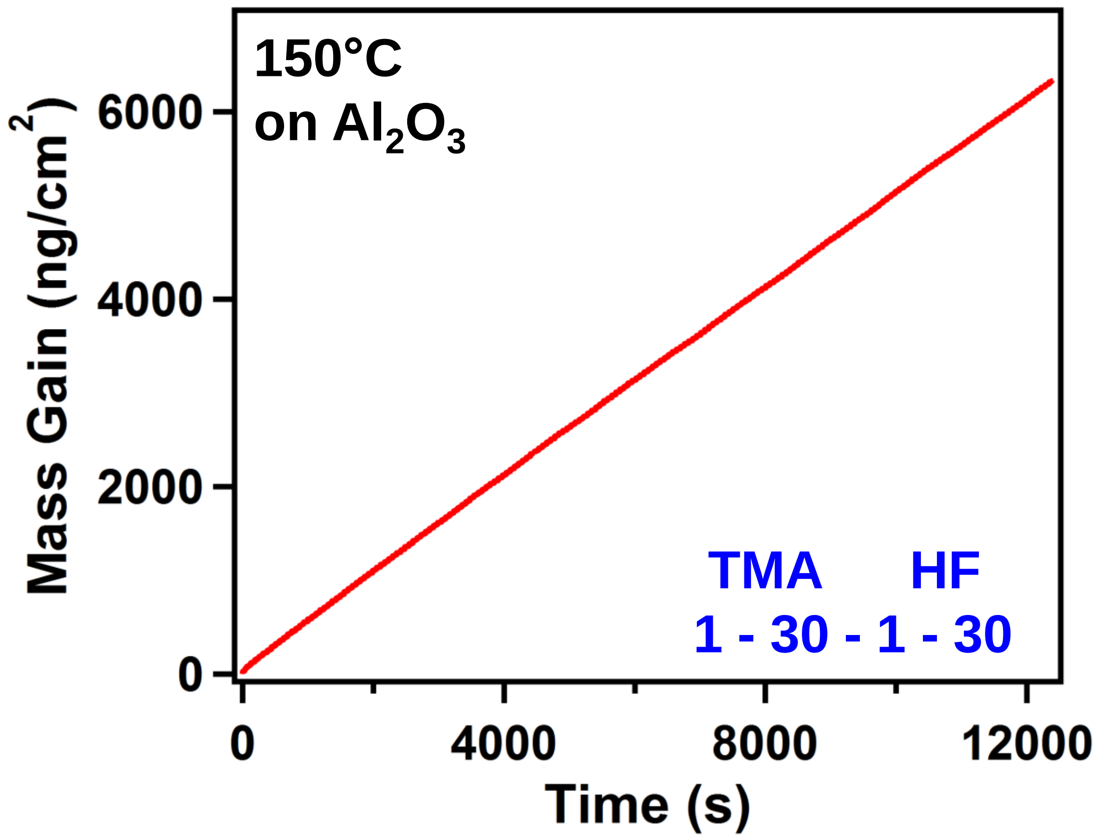
TMA

Volatile & reactive fluorine acceptor

Same precursor for AlF_3 ALD

Y. Lee, J.W. DuMont, A.S. Cavanagh & S.M. George, *J. Phys. Chem. C* **119**, 14185 (2015)

Linear Growth of AlF_3 Using TMA & HF Monitored by QCM

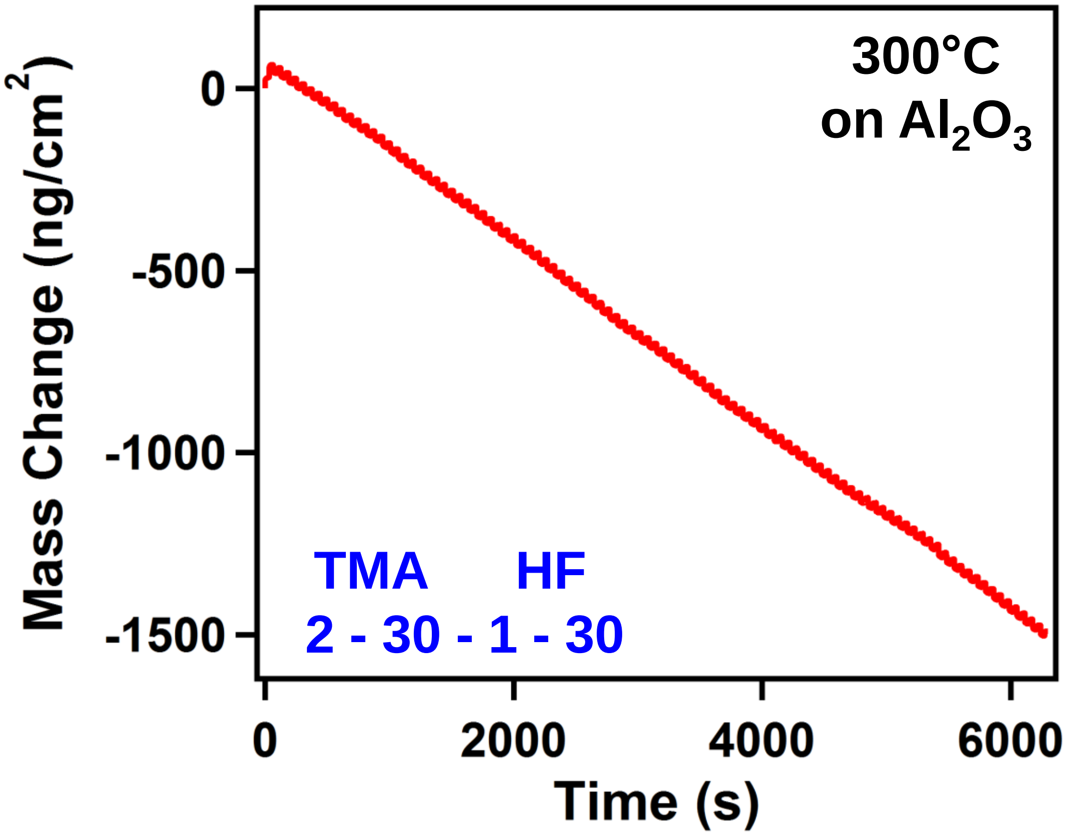


Mass Gain per Cycle (MGPC) = 31 ng/(cm^2 cycle)

Growth Rate = 1.1 Å/cycle

Y. Lee, J.W. DuMont, A.S. Cavanagh & S.M. George, *J. Phys. Chem. C* **119**, 14185 (2015)

Linear Etching of Al_2O_3 Using TMA & HF Monitored by QCM

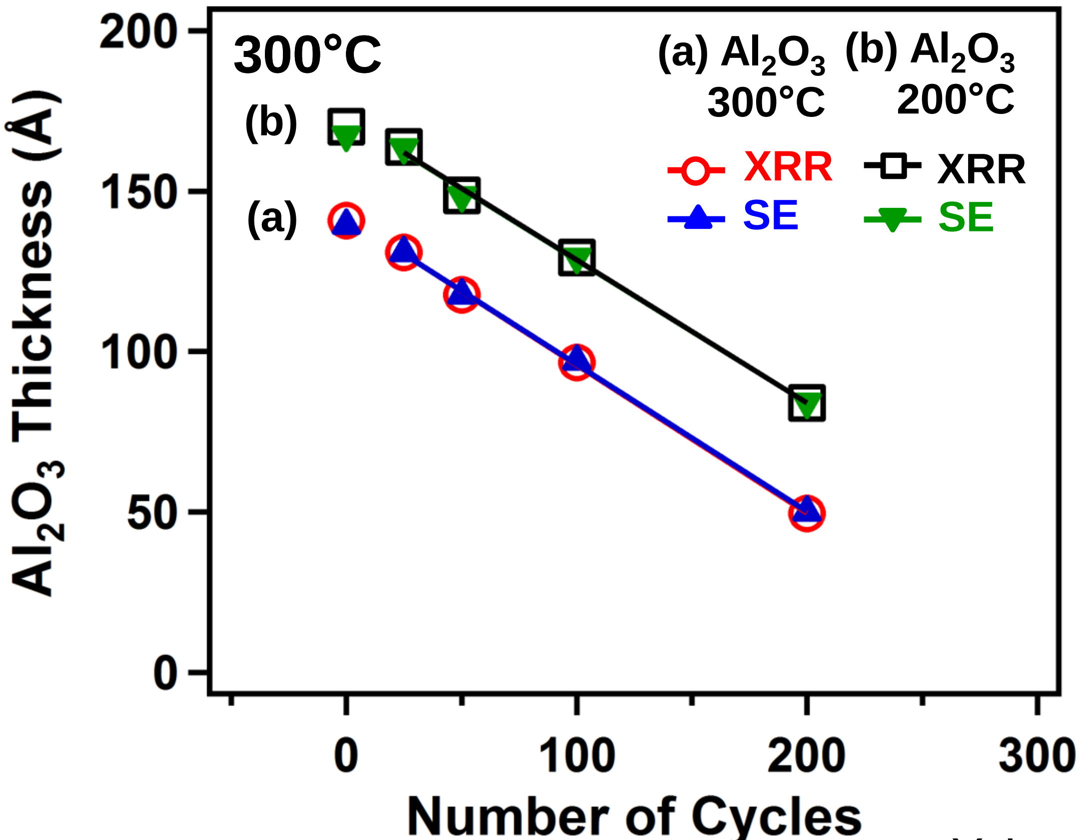


Mass Change per Cycle (MCPC) = -16 ng/(cm^2 cycle)

Etch Rate = 0.51 Å/cycle

Y. Lee, J.W. DuMont & S.M. George, *Chem. Mater.* **28,** 2994 (2016)

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

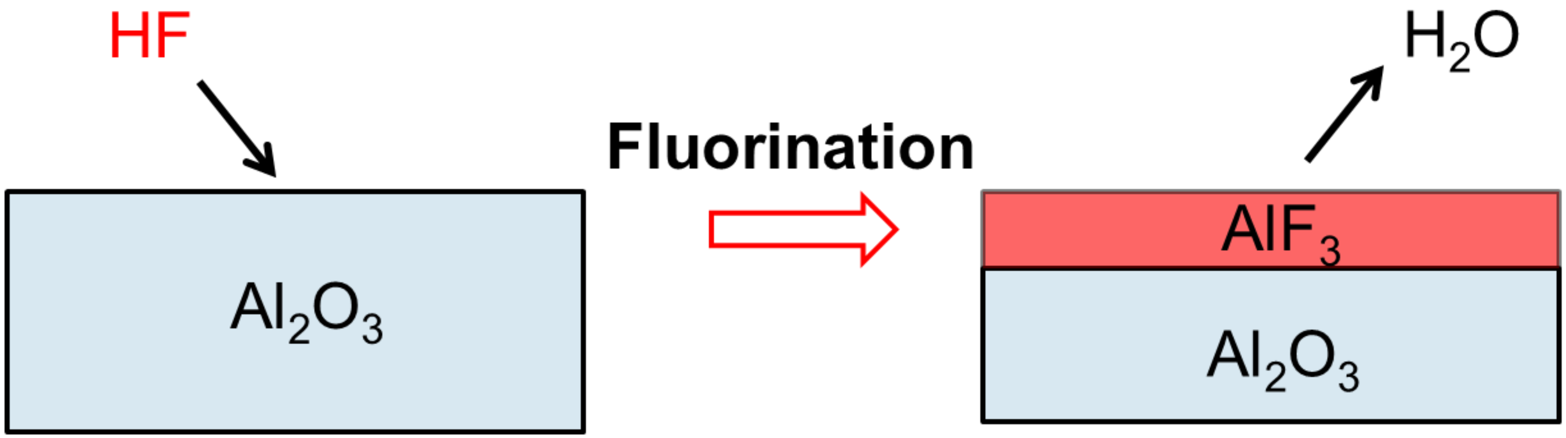


Etch rate = 0.45-0.46 Å/cycle

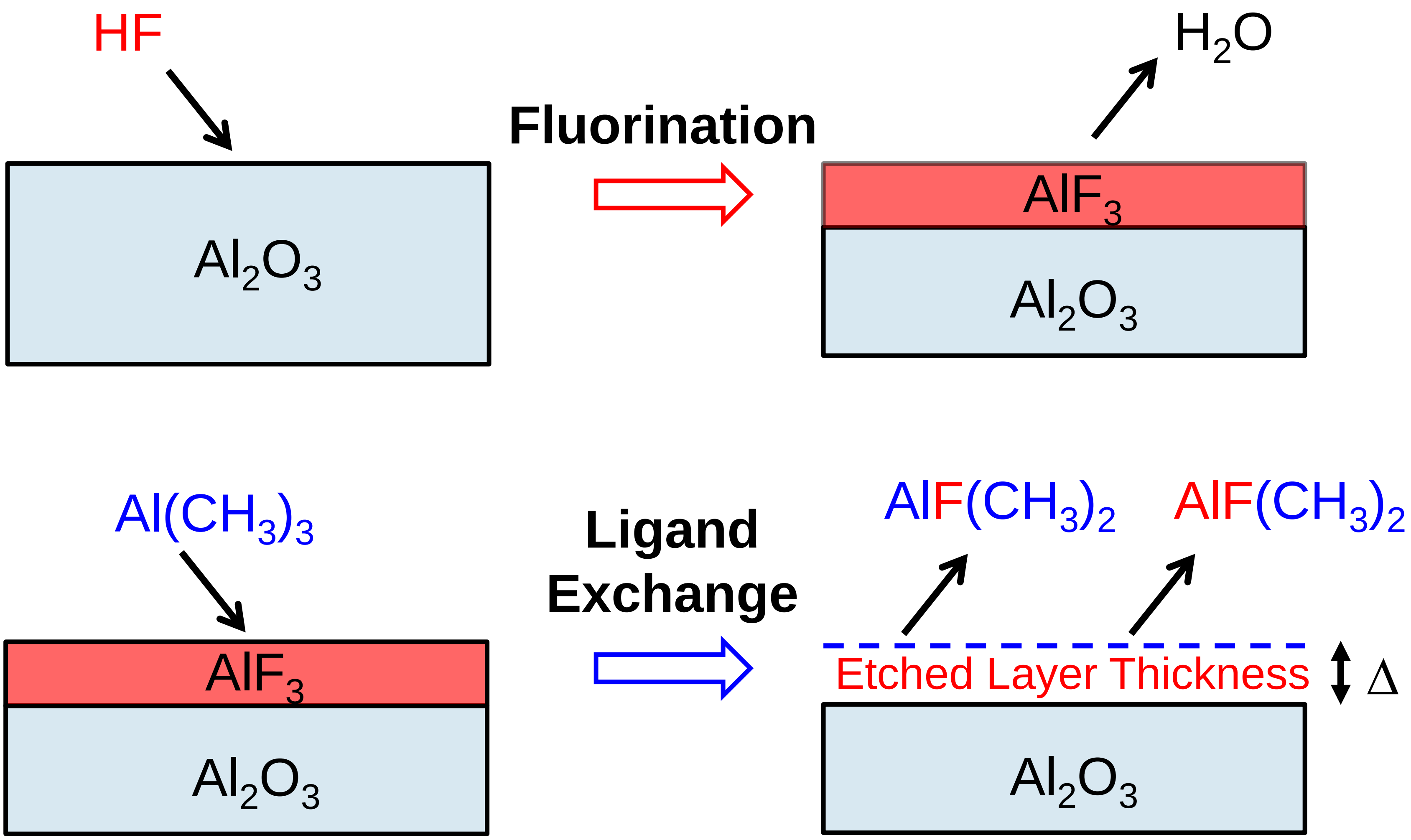
Unchanged Density & Refractive index

Y. Lee, J.W. DuMont & S.M. George, *Chem. Mater.* **28,** 2994 (2016)

Scheme for Al_2O_3 ALE via Fluorination & Ligand Exchange



Scheme for Al_2O_3 ALE via Fluorination & Ligand Exchange



Understanding Fluorination

$Al_2O_3 + 6HF(g) \rightarrow 2AlF_3 + 3H_2O(g)$
$\Delta G = -58.4$ kcal/mol at 200 °C,
AlF_3 sublimes at 1276 °C

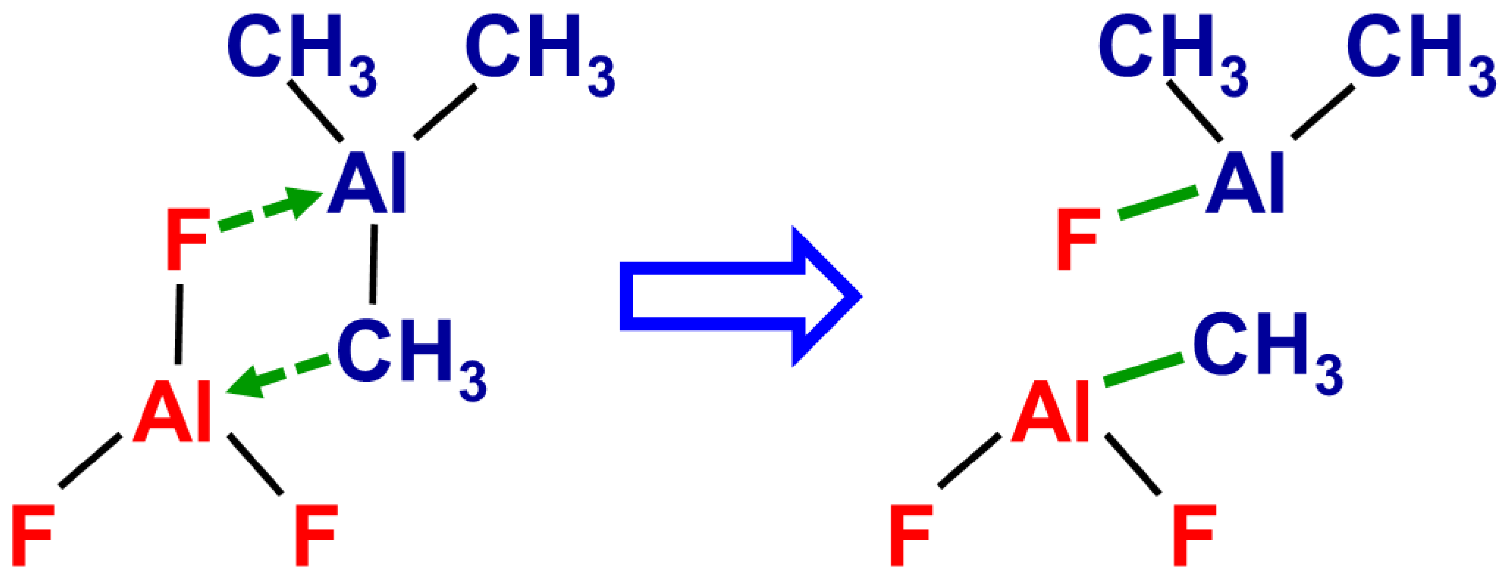
$HfO_2 + 4HF(g) \rightarrow HfF_4 + 2H_2O(g)$
$\Delta G = -19.1$ kcal/mol at 200 °C,
HfF_4 sublimes at 970 °C

$ZrO_2 + 4HF(g) \rightarrow ZrF_4 + 2H_2O(g)$
$\Delta G = -18.4$ kcal/mol at 200 °C,
ZrF_4 sublimes at 912 °C

Fluorination of Al_2O_3, HfO_2 & ZrO_2 is thermochemically favorable

AlF_3, HfF_4 & ZrF_4 are not volatile

Understanding Ligand-Exchange



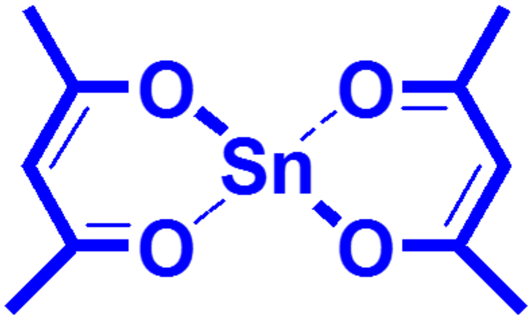
Favorable Al-CH_3 bond

Stable & volatile etch product

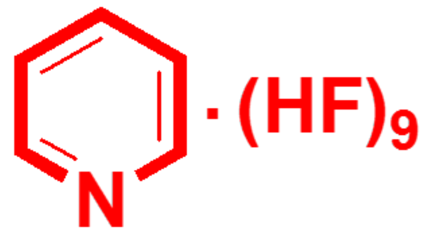
Outline

- Al_2O_3 & HfO_2 ALE using HF & $Sn(acac)_2$
- Al_2O_3 ALE using HF & TMA
- Selectivity in ALE using $Sn(acac)_2$, $Al(CH_3)_3$, $AlCl(CH_3)_2$, and $SiCl_4$ as metal reactants.
- Selectivity in ALE based on temperature

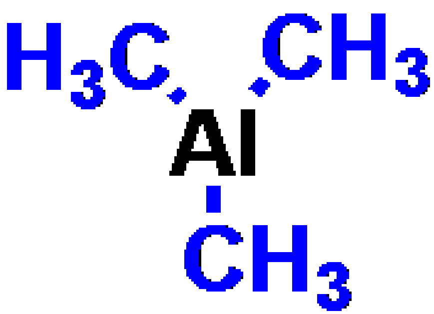
Metal Precursors & HF-Pyridine



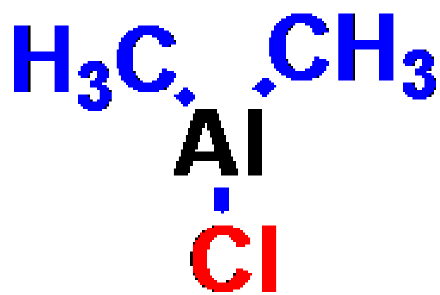
$Sn(acac)_2$



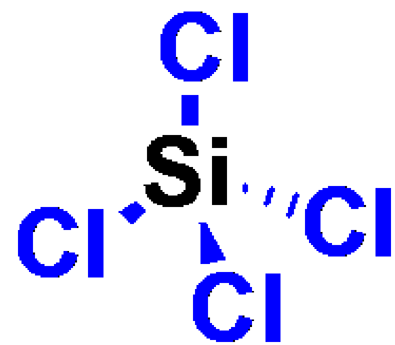
HF-Pyridine



TMA

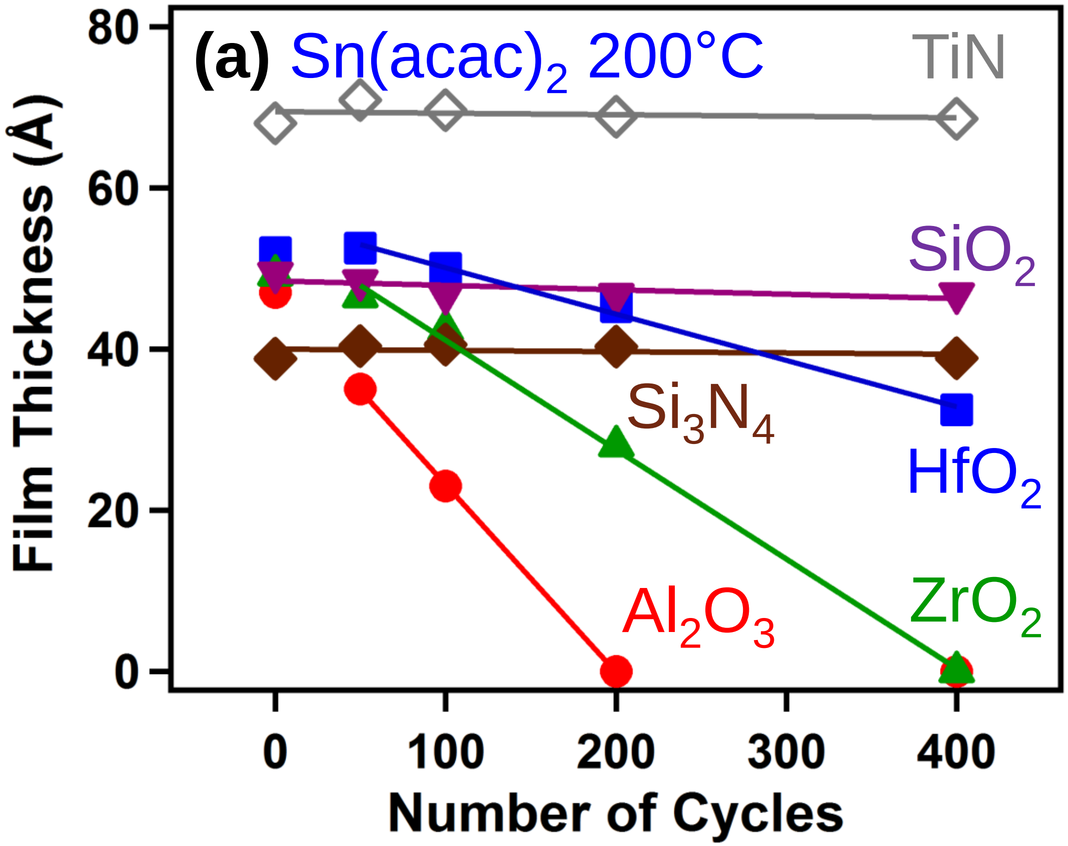


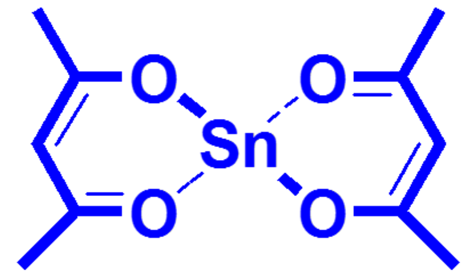
DMAC



$SiCl_4$

ALE Using HF & $Sn(acac)_2$

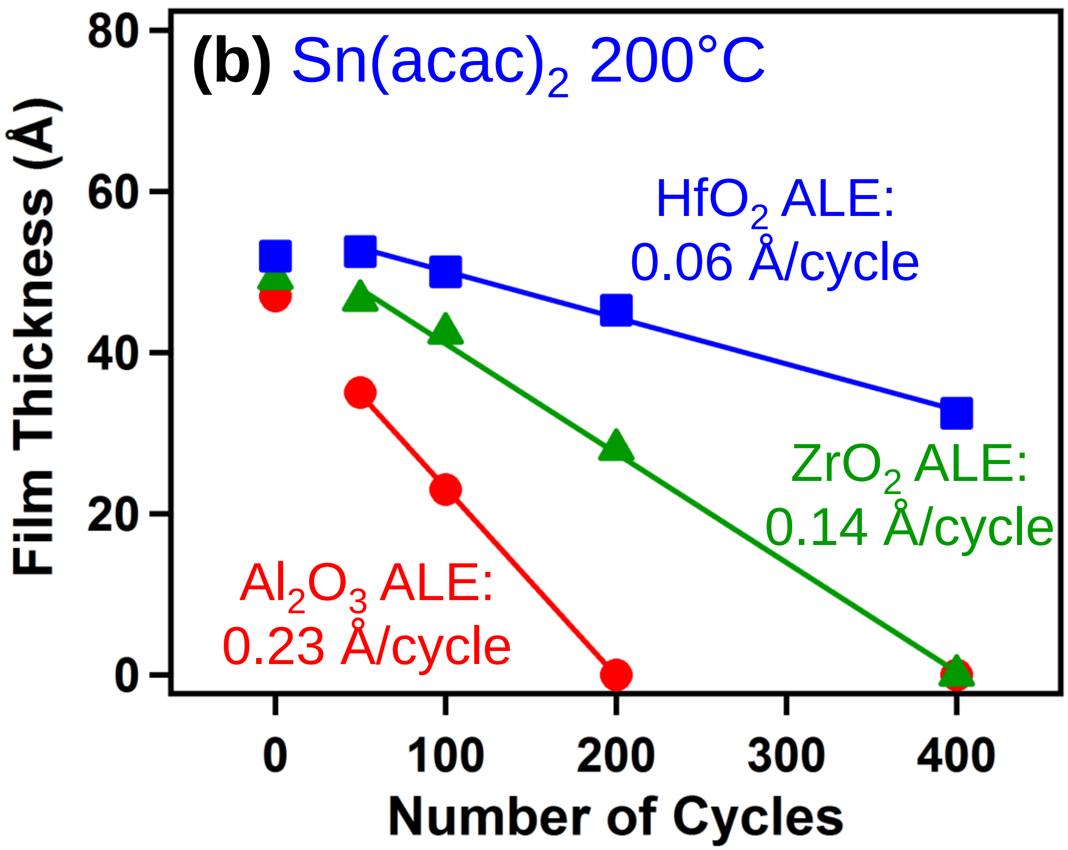


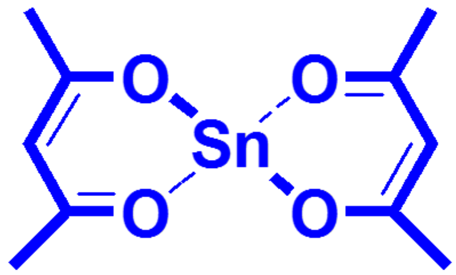


Al, Hf & Zr form stable & volatile acac complexes.

Y. Lee, C. Huffman & S.M. George, *Chem. Mater.* **28,** 7657 (2016)

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



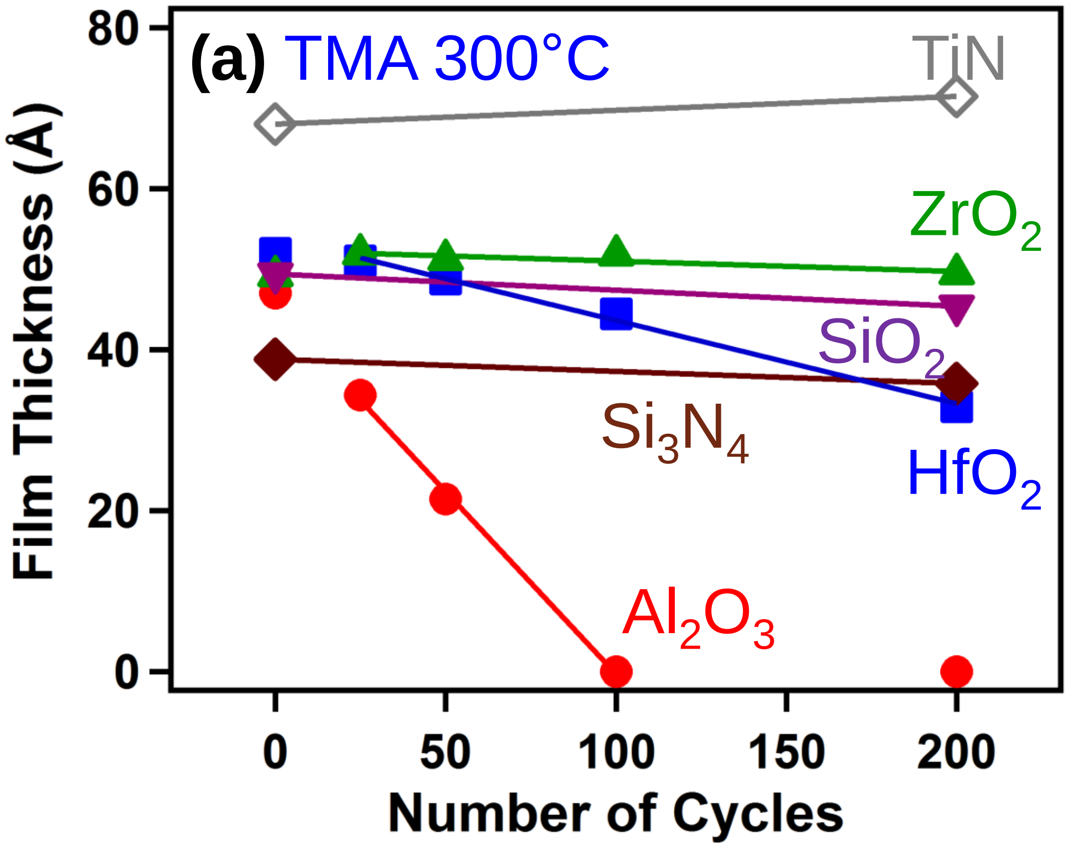


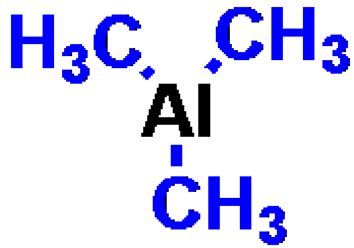
Etch rates:

Al_2O_3>ZrO_2>HfO_2

Y. Lee, C. Huffman & S.M. George, *Chem. Mater.* **28,** 7657 (2016)

ALE Using HF & TMA

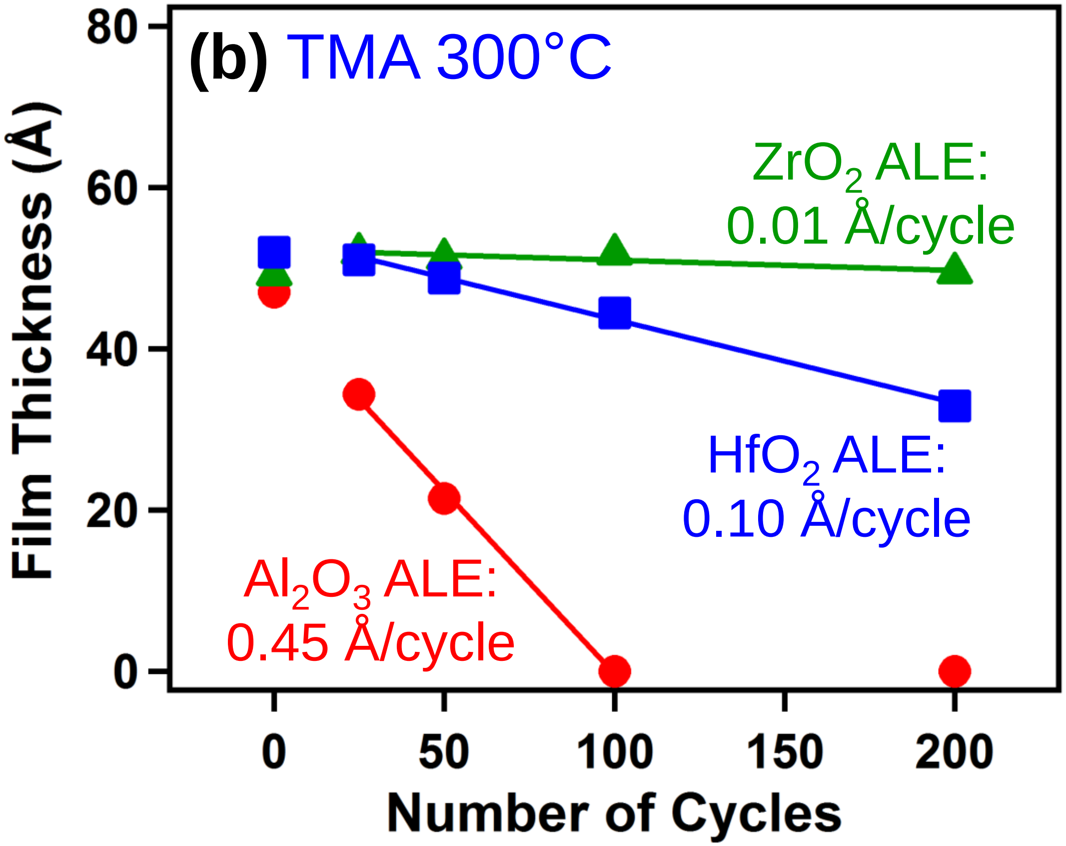


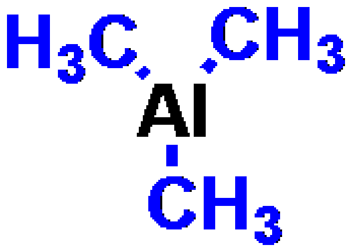


Al & Hf form stable & volatile complexes with methyl ligands.

Y. Lee, C. Huffman & S.M. George,
Chem. Mater. **28,** 7657 (2016)

Al_2O_3, HfO_2 & ZrO_2 ALE Using HF & TMA





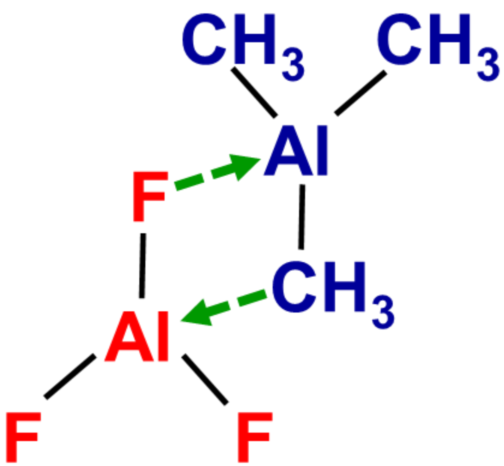
Etch rates:

Al_2O_3>HfO_2>ZrO_2

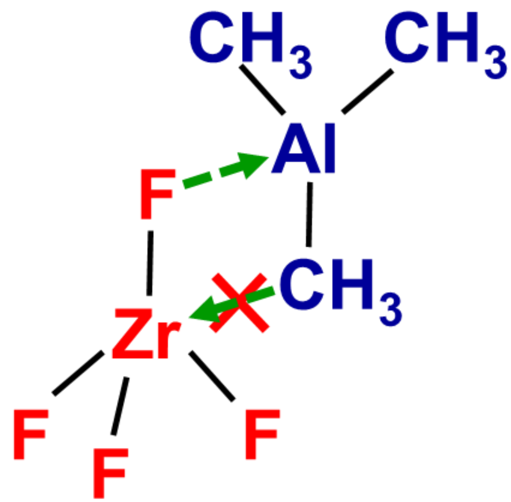
Y. Lee, C. Huffman & S.M. George,
Chem. Mater. **28,** 7657 (2016)

Understanding Selectivity (1)

(a) TMA/Al_2O_3



(b) TMA/ZrO_2

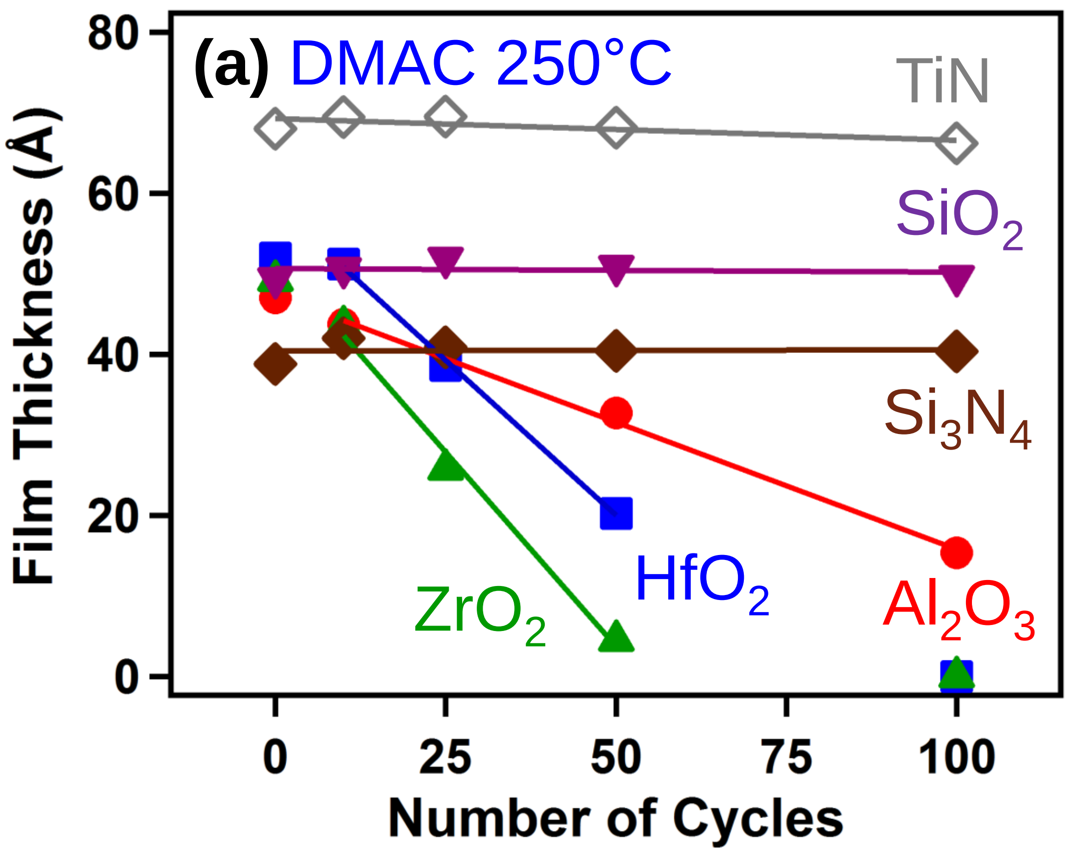


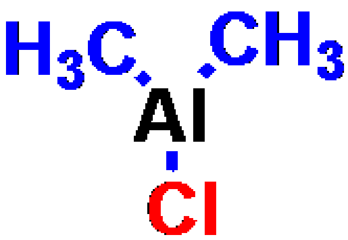
Al_2O_3 ALE with $Al(CH_3)_3$.

No ZrO_2 etching with $Al(CH_3)_3$.

No ligand-exchange. Unstable Zr-CH_3 reaction product.

ALE Using HF & DMAC

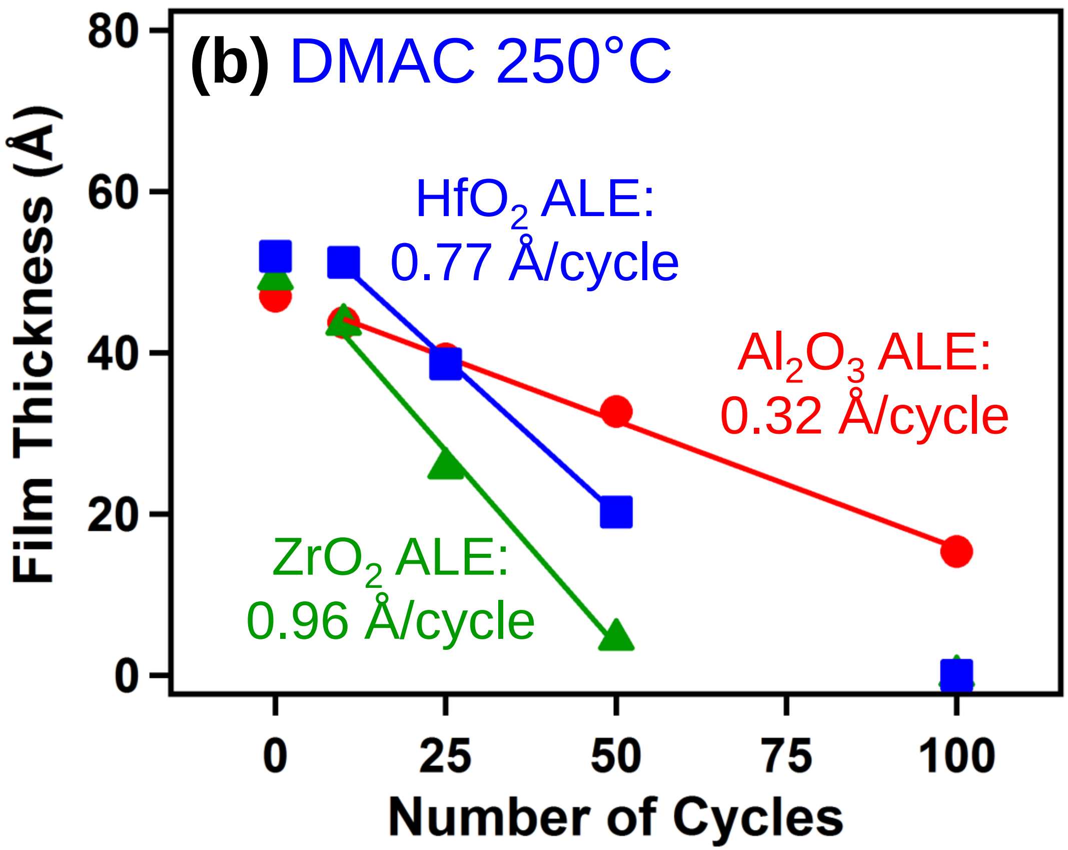


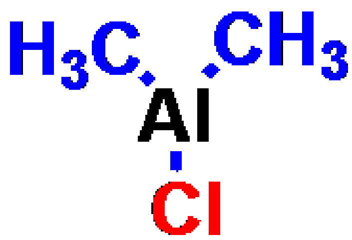


Al, Zr & Hf form stable & volatile complexes with chloride or methyl ligands.

Y. Lee, C. Huffman & S.M. George, *Chem. Mater.* **28,** 7657 (2016)

Al_2O_3, HfO_2 & ZrO_2 ALE Using HF & DMAC



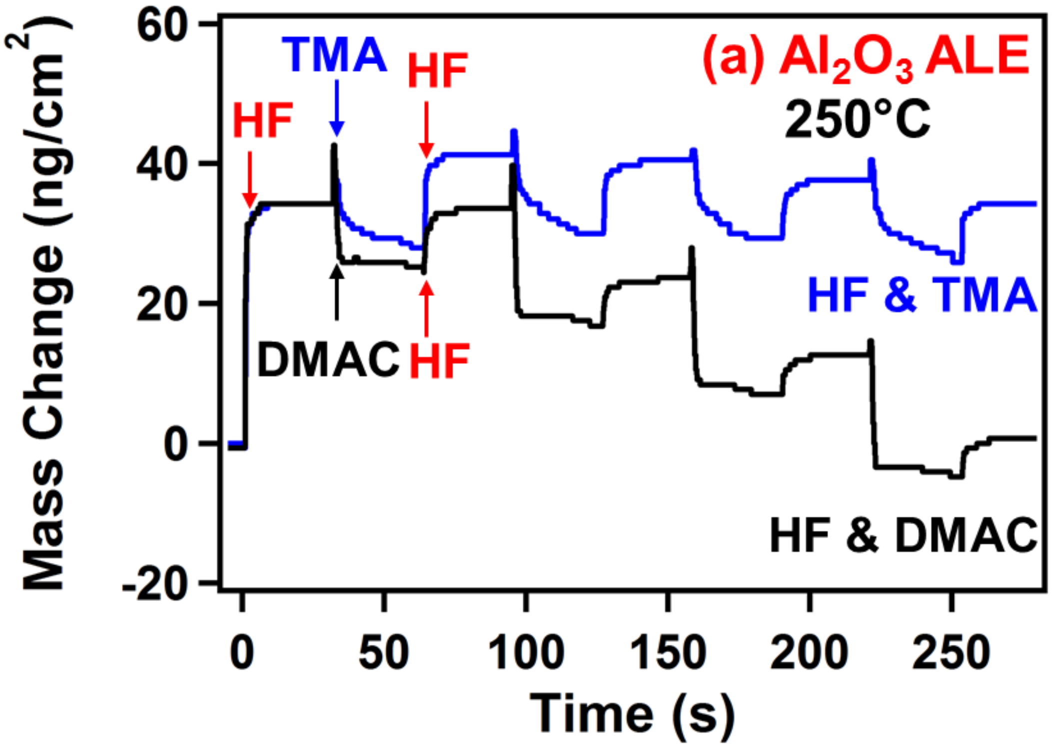


Etch rates:

ZrO_2>HfO_2>Al_2O_3

Y. Lee, C. Huffman & S.M. George,
Chem. Mater. **28,** 7657 (2016)

Al_2O_3 ALE Using HF & TMA vs. HF & DMAC

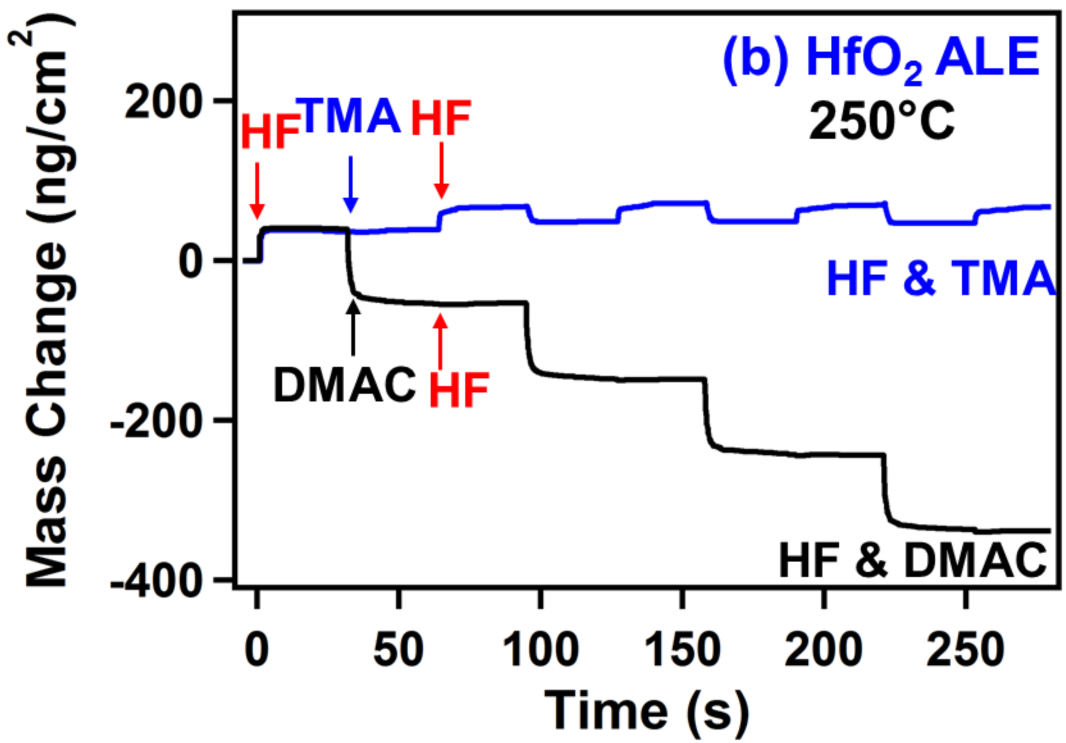


Al_2O_3 ALE
with HF & TMA

Al_2O_3 ALE
with HF & DMAC:
Cl help etching

Y. Lee & S.M. George,
(In Preparation)

HfO_2 ALE Using
HF & TMA vs. HF & DMAC

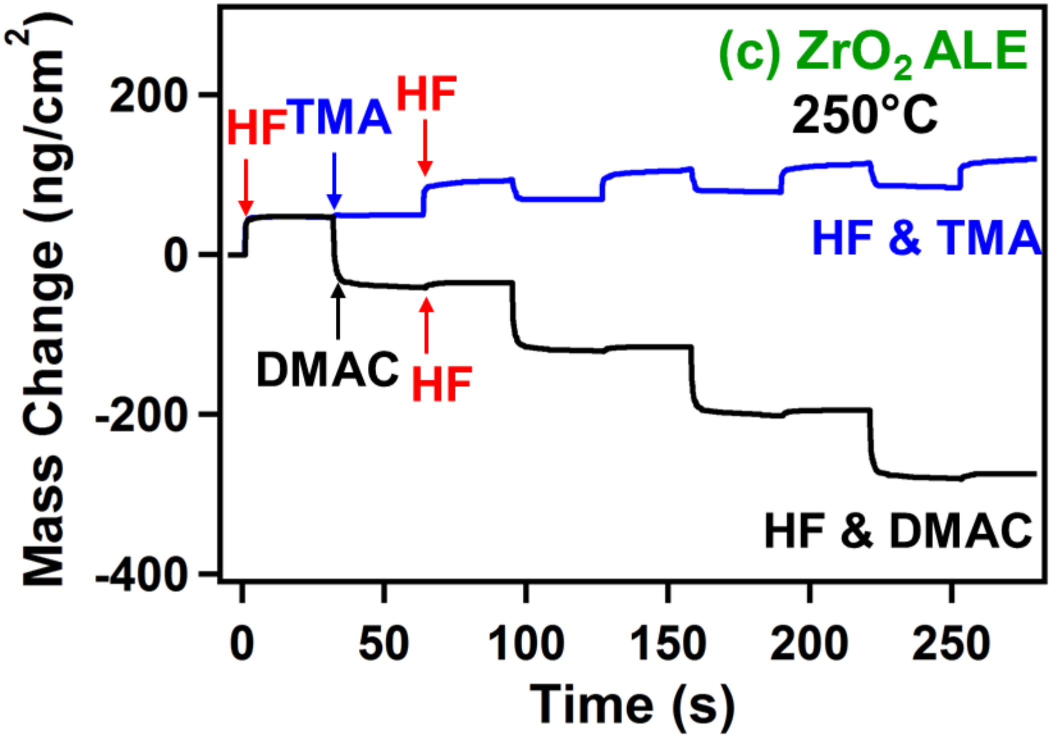


Slight etching of HfO_2
MCPC = −5 ng/cm^2
with HF & TMA:
Hf-CH_3 is
somewhat stable

HfO_2 ALE
HF & DMAC:
Hf-Cl is stable

Y. Lee & S.M. George,
(In Preparation)

ZrO_2 ALE Using HF & TMA vs. HF & DMAC

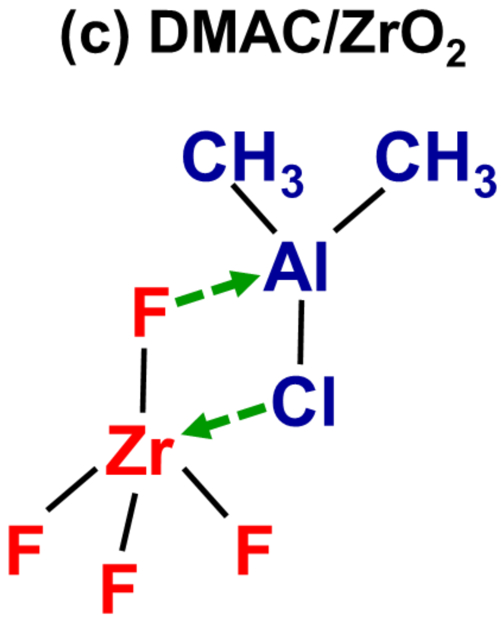


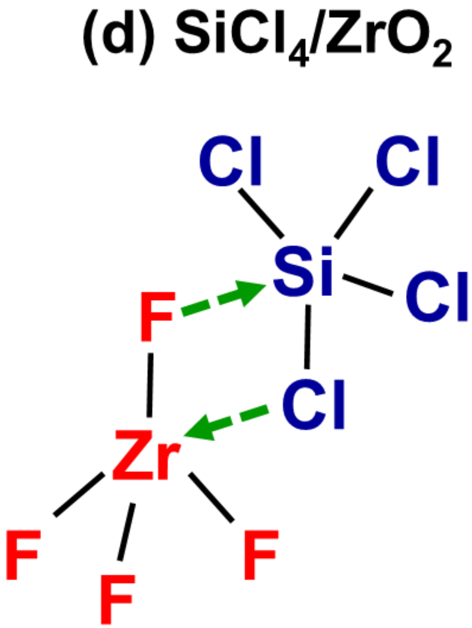
No etching of ZrO_2
MCPC = +5 ng/cm^2
with HF & TMA:
Zr-CH_3 is not stable

ZrO_2 ALE
HF & DMAC:
Zr-Cl is stable

Y. Lee & S.M. George,
(In Preparation)

Understanding Selectivity (2)

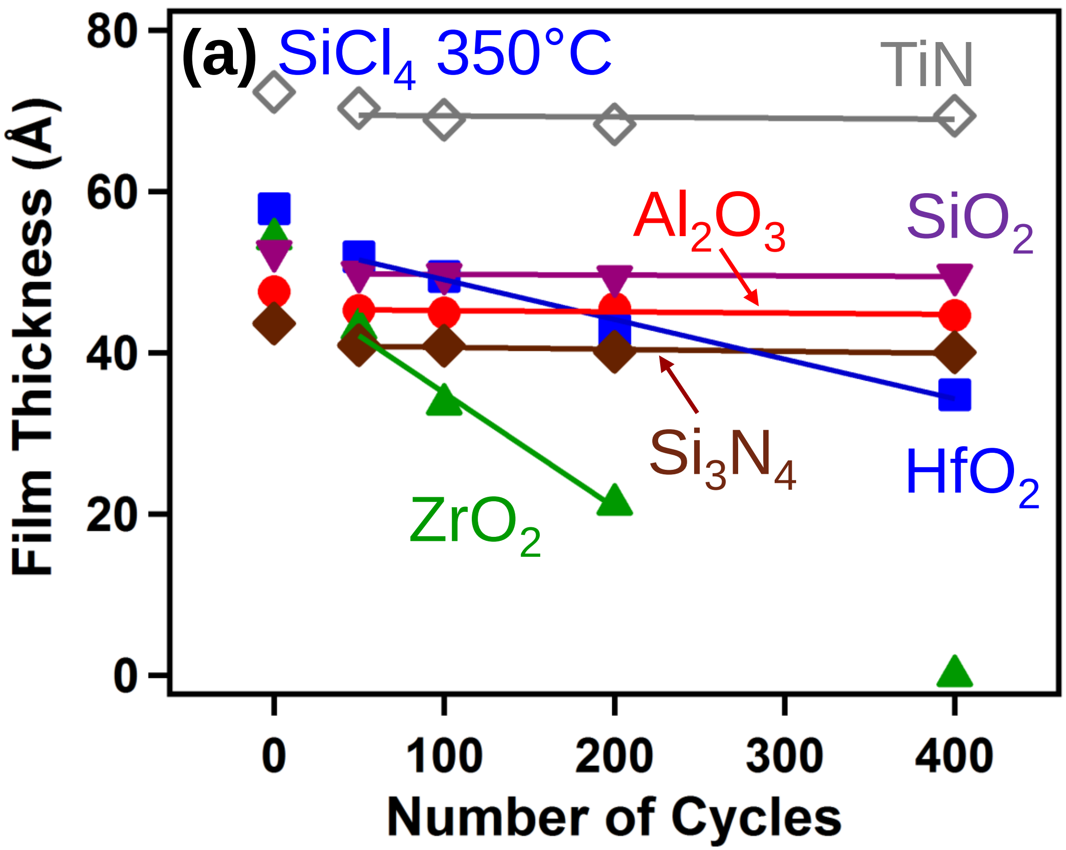


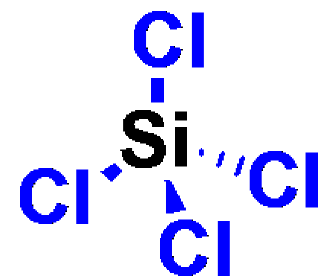


ZrO_2 ALE with DMAC or $SiCl_4$

Ligand-exchange. Stable Zr-Cl reaction product.

ALE Using HF & $SiCl_4$

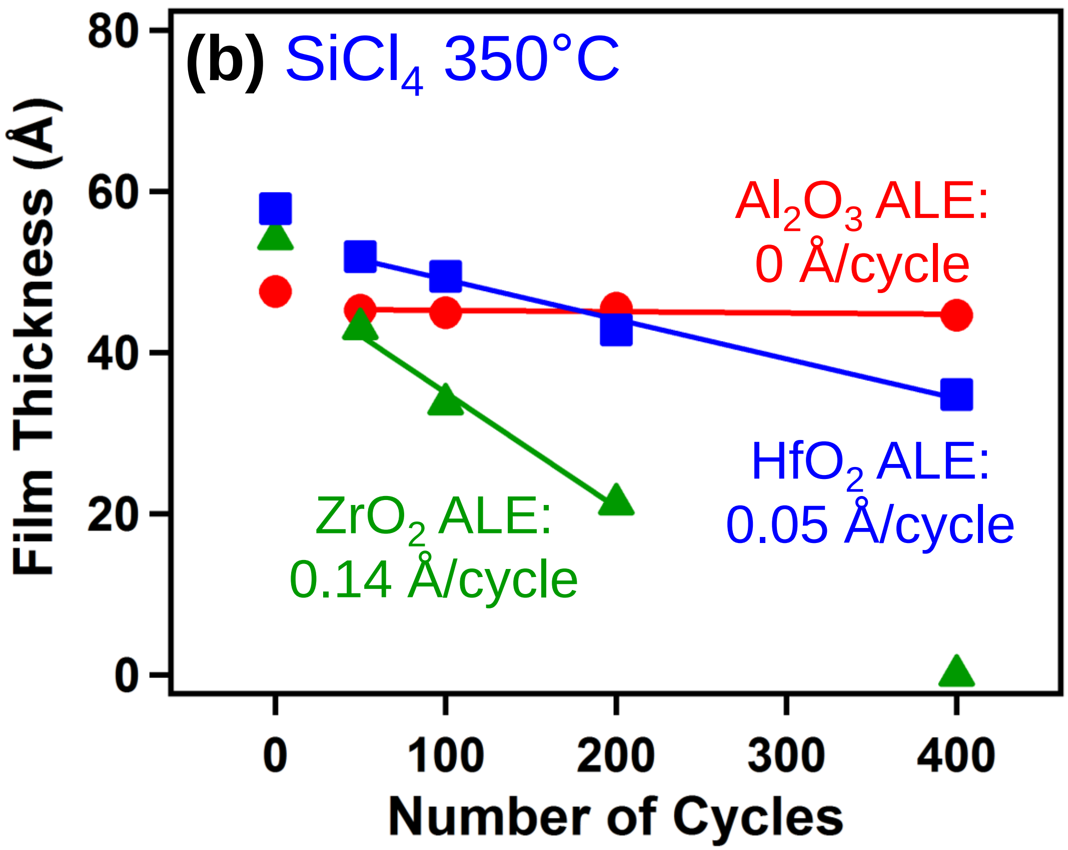


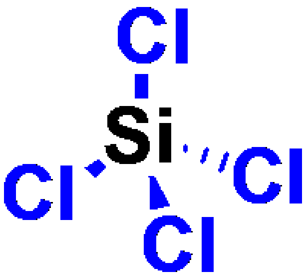


Zr & Hf form stable & volatile complexes with chloride ligands.

Y. Lee, C. Huffman & S.M. George, *Chem. Mater.* **28,** 7657 (2016)

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





Etch rates:

ZrO_2>HfO_2>Al_2O_3

No etching of Al_2O_3 with $SiCl_4$

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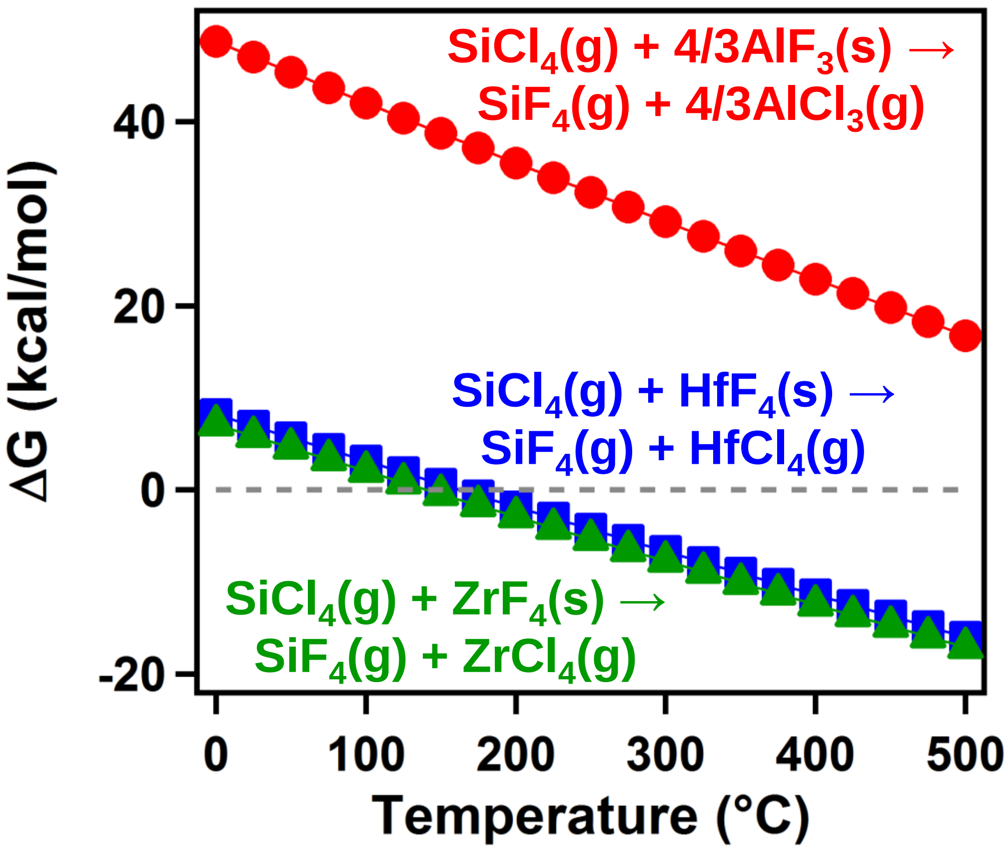
Ligand-Exchange Thermochemistry Explains No Al_2O_3 ALE



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

⇦ ΔG = 0

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

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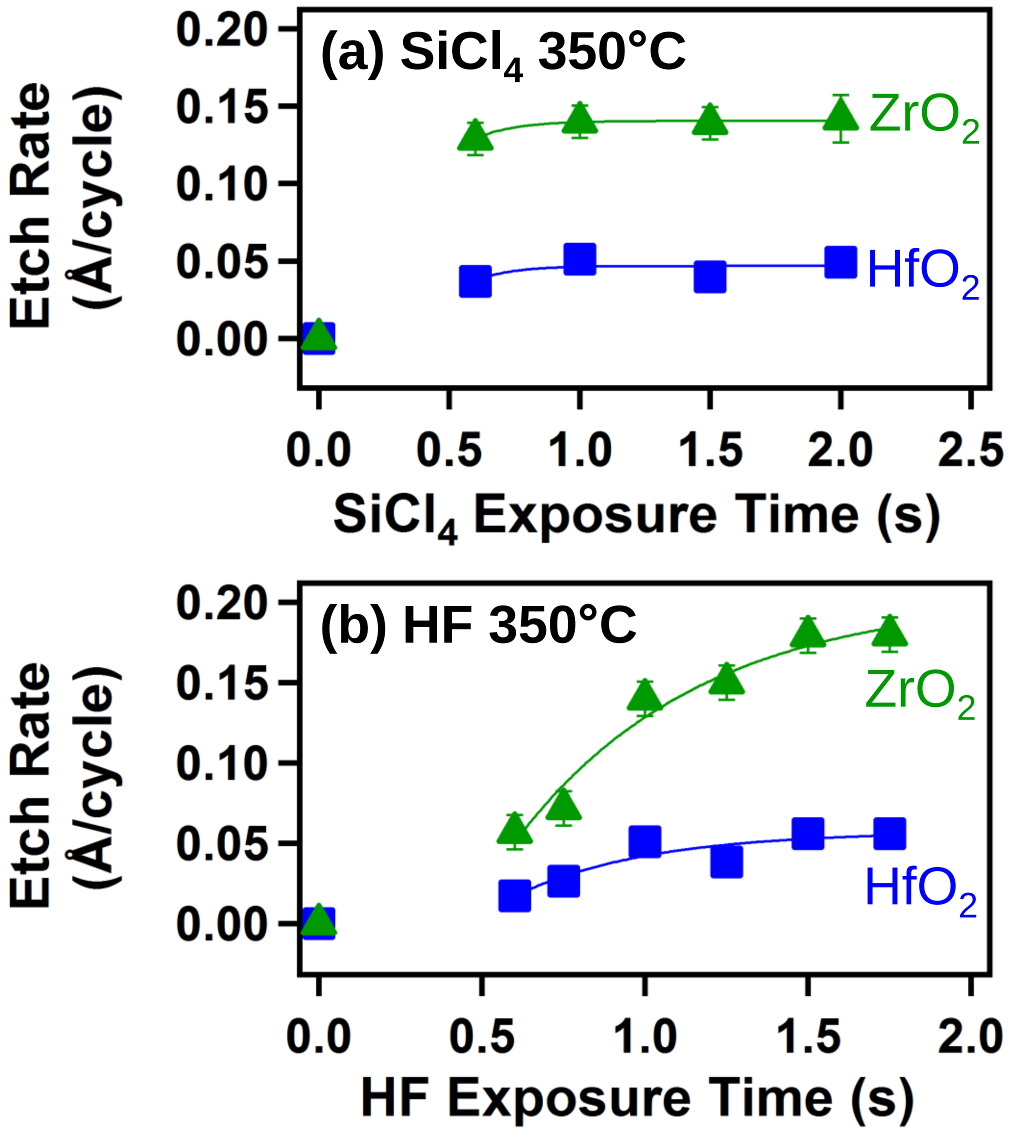
Self-Limiting Reactions



Vary $SiCl_4$
HF at 1 s

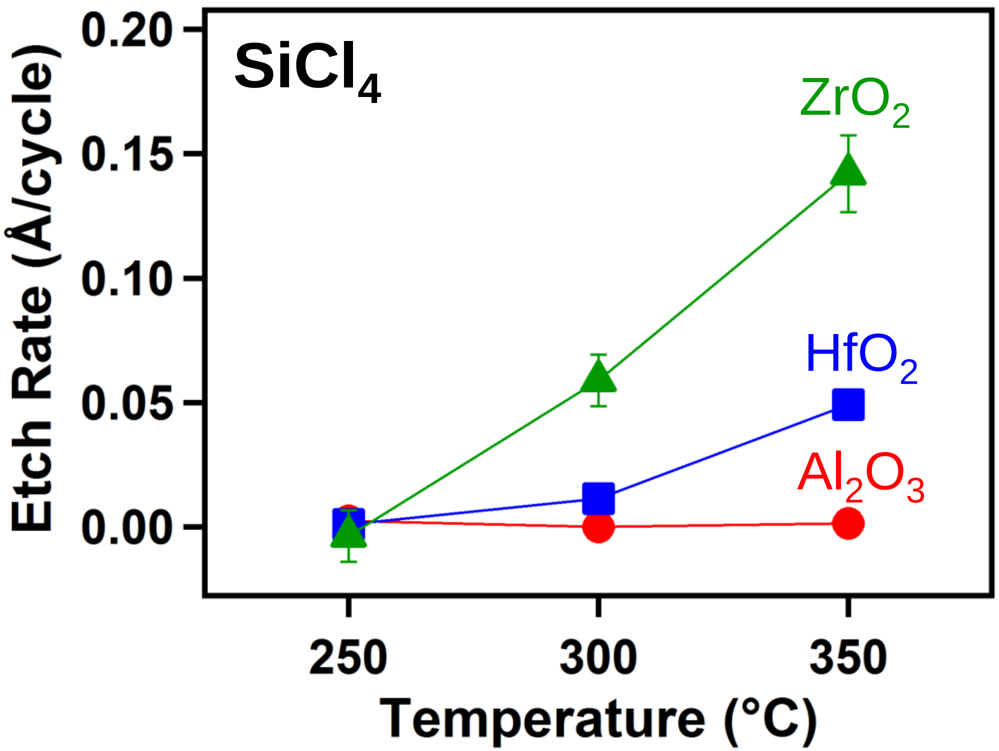
Vary HF
$SiCl_4$ at 2 s

Both $SiCl_4$ & HF reactions are self-limiting.

Outline

- Al_2O_3 & HfO_2 ALE using HF & $Sn(acac)_2$
- Al_2O_3 ALE using HF & TMA
- Selectivity in ALE using $Sn(acac)_2$, $Al(CH_3)_3$, $AlCl(CH_3)_2$, and $SiCl_4$ as metal reactants.
- Selectivity in ALE based on temperature

Selectivity Based on Reaction Temperature: ALE Using $SiCl_4$ as Metal Precursor



Temperature provides additional pathway for selective ALE

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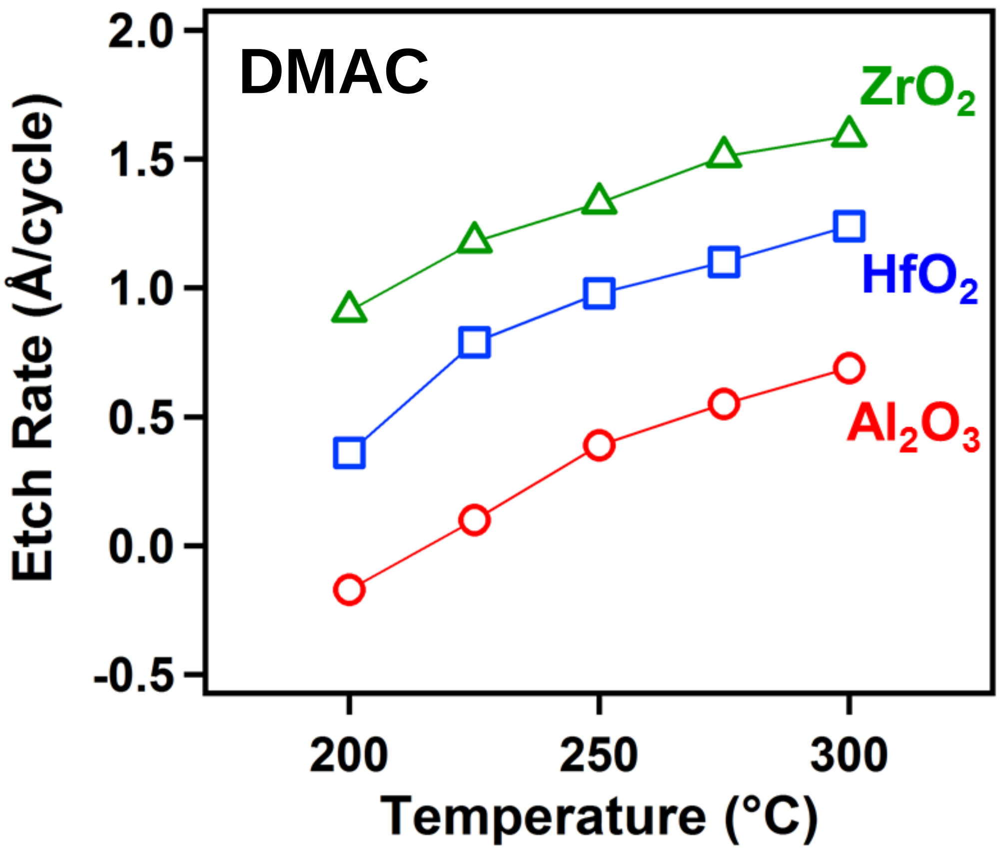
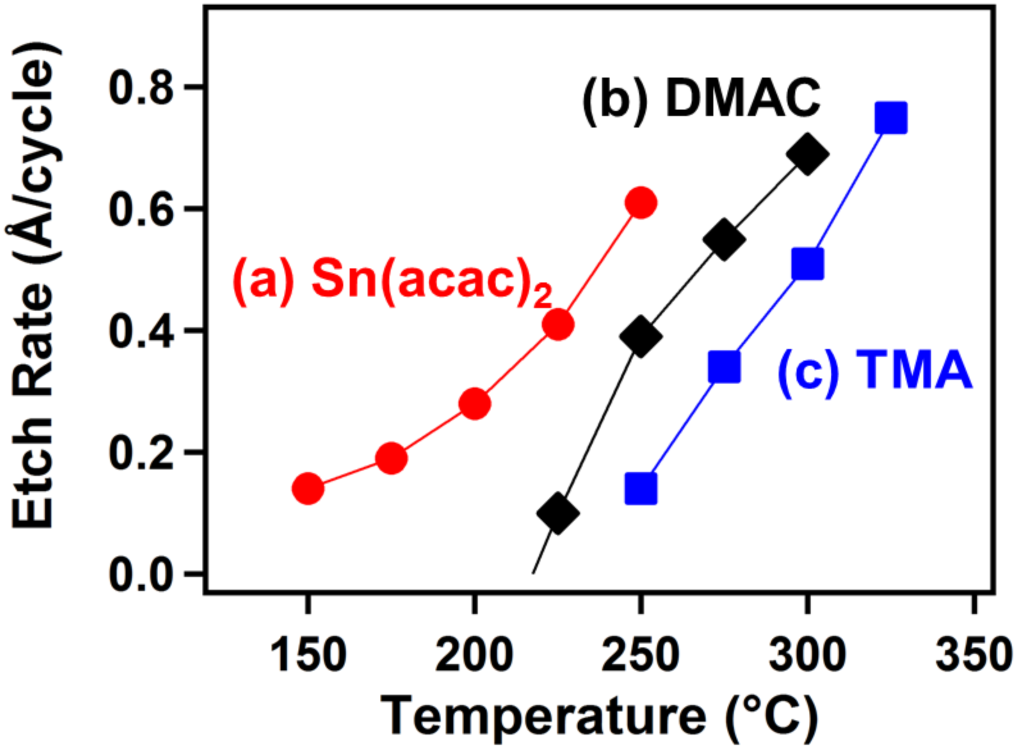
Selectivity Based on Reaction Temperature: ALE Using DMAC as Metal Precursor



Temperature provides additional pathway for selective ALE

Y. Lee & S.M. George, *(In Preparation)*

Selectivity Based on Reaction Temperature: Al_2O_3 ALE Using Different Metal Precursors



Different etch rates at various temperatures for different metal precursors

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Summary for Selectivity

Metal Precursor	Al_2O_3	HfO_2	ZrO_2	SiO_2	Si_3N_4	TiN	Etch Rate
$Sn(acac)_2$	YES	YES	YES	NO	NO	NO	$Al_2O_3 > ZrO_2 > HfO_2$
DMAC, $AlCl(CH_3)_2$	YES	YES	YES	NO	NO	NO	$ZrO_2 > HfO_2 > Al_2O_3$
TMA, $Al(CH_3)_3$	YES	YES	NO	NO	NO	NO	$Al_2O_3 > HfO_2 > ZrO_2$
$SiCl_4$	NO	YES	YES	NO	NO	NO	$ZrO_2 > HfO_2 > Al_2O_3$

Conclusions

- Thermal ALE possible using sequential, self-limiting fluorination & ligand-exchange reactions.
- Thermal ALE using HF & metal precursors such as $Sn(acac)_2$, $Al(CH_3)_3$, $AlCl(CH_3)_2$ & $SiCl_4$.
- Selective ALE is possible based on stability & volatility of reaction products.
- Temperature provides additional pathway for selective ALE.

Acknowledgments

SRC Semiconductor Research Corporation

intel

NSF

Craig Huffman:
SEMATECH wafers