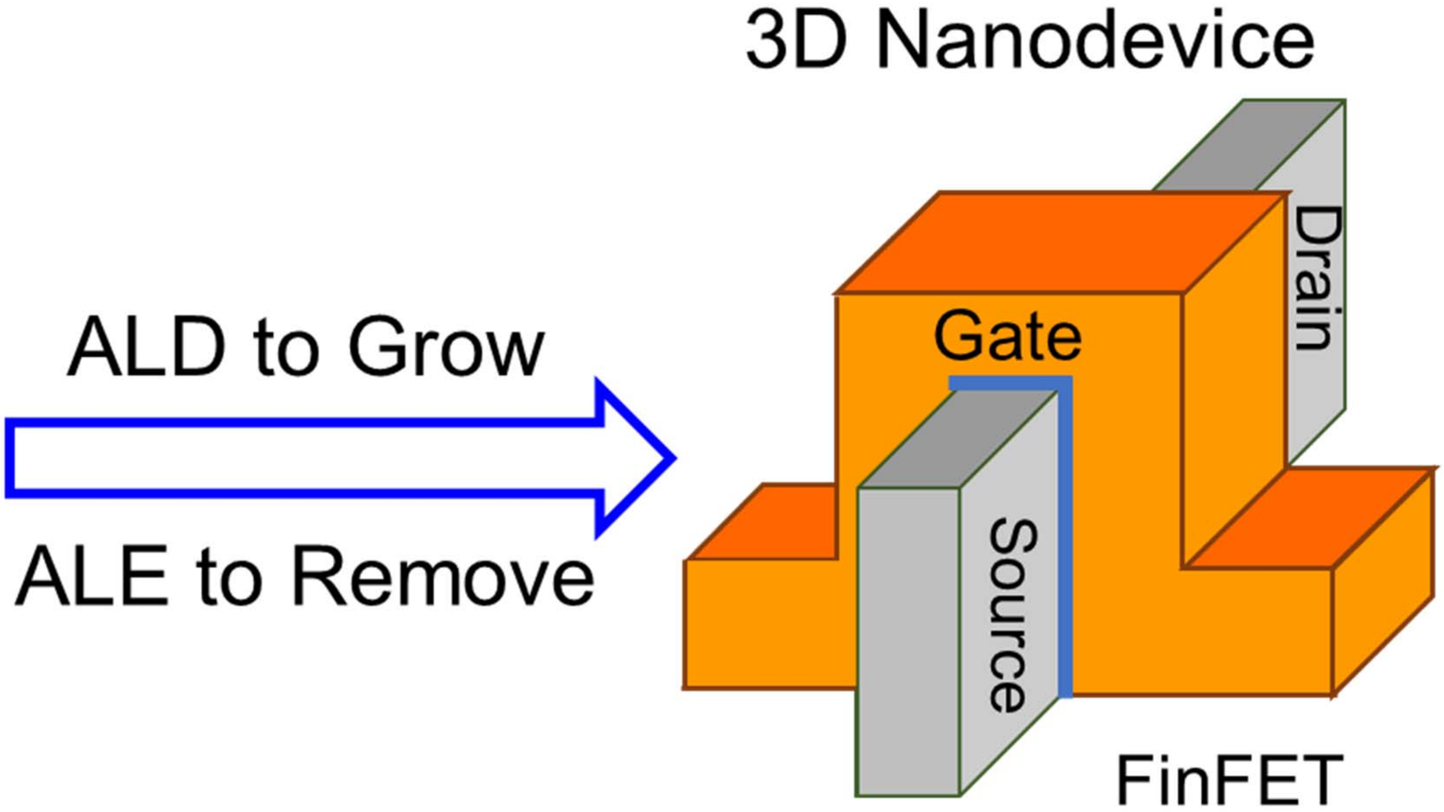
Mechanisms for Thermal Atomic Layer Etching

Steven M. George
Dept. of Chemistry, University of Colorado
Boulder, Colorado 80309
Steven.George@Colorado.edu

Advanced Semiconductor Fabrication Requires Atomic Layer Processing



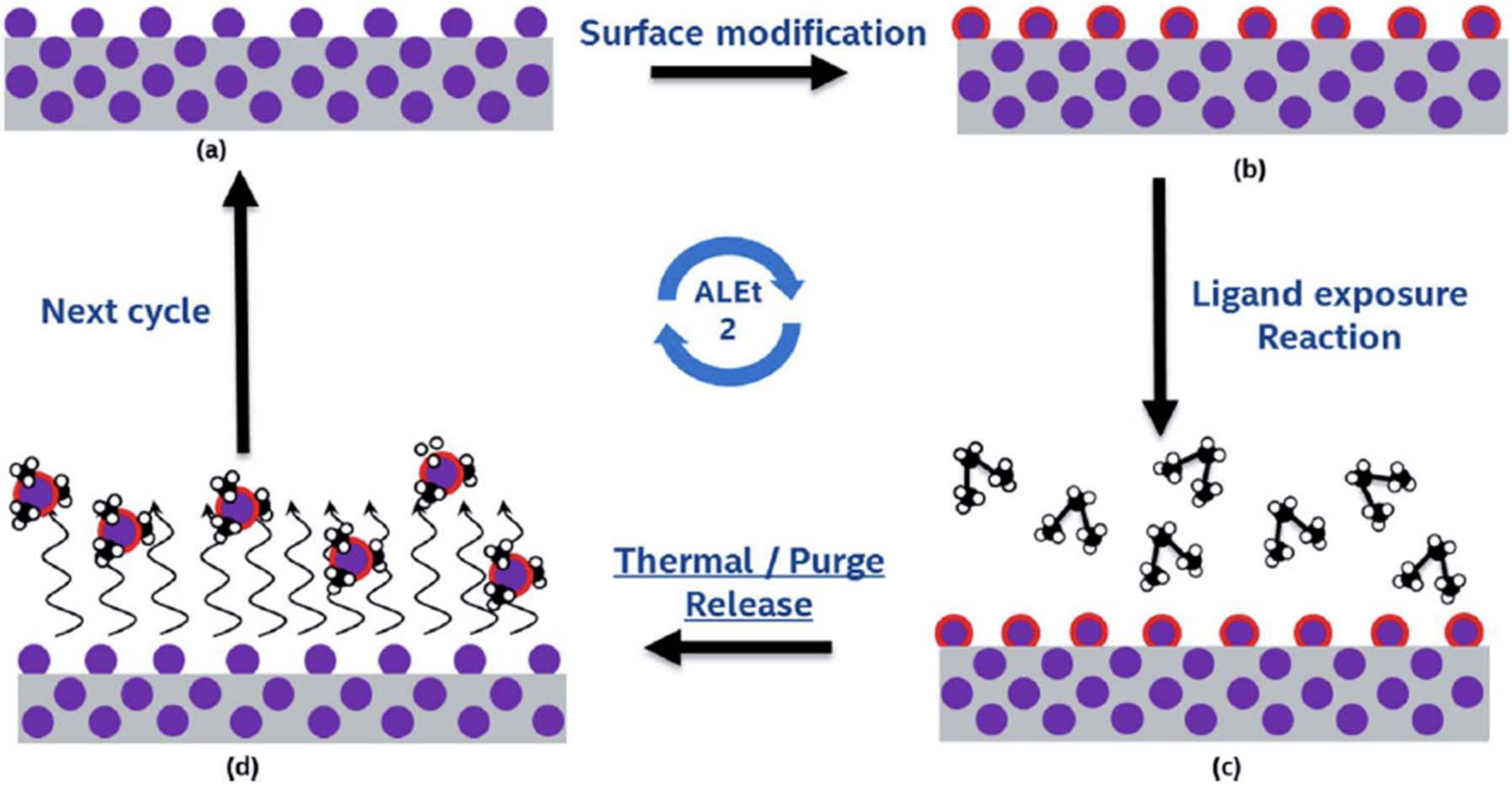
ALD to Grow

ALE to Remove

3D Nanodevice

FinFET

Thermal ALE Using Sequential, Self-Limiting Surface Reactions



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

Requirements for Thermal ALE

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

Spontaneous requires favorable thermochemistry.

Self-limiting requires saturation of surface reaction.

Removal requires volatility of reaction product.

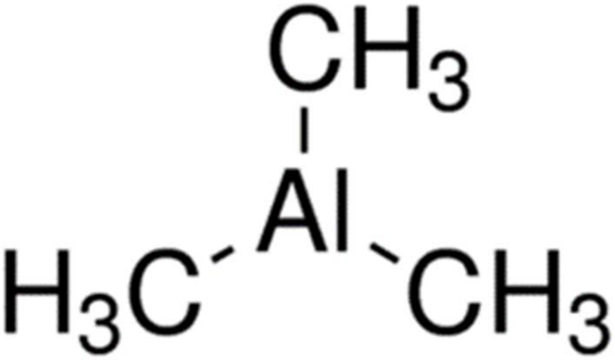
Mechanisms for Thermal ALE of Metal Oxides, Metal Nitrides & Elemental Metals

1. Fluorination & Ligand-Exchange: Al_2O_3 ALE Using $Al(CH_3)_3$ & HF

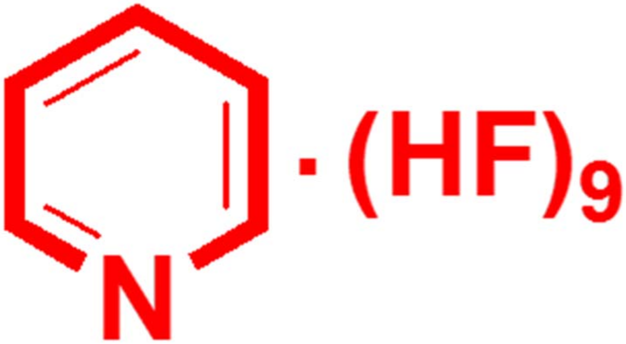
2. Oxidation & Fluorination to Volatile Fluoride: TiN ALE Using O_3 & HF

3. Oxidation, Conversion & Fluorination to Volatile Fluoride: W ALE Using O_3, BCl_3 & HF

1. Fluorination & Ligand-Exchange: Al_2O_3 ALE Using $Al(CH_3)_3$ & HF

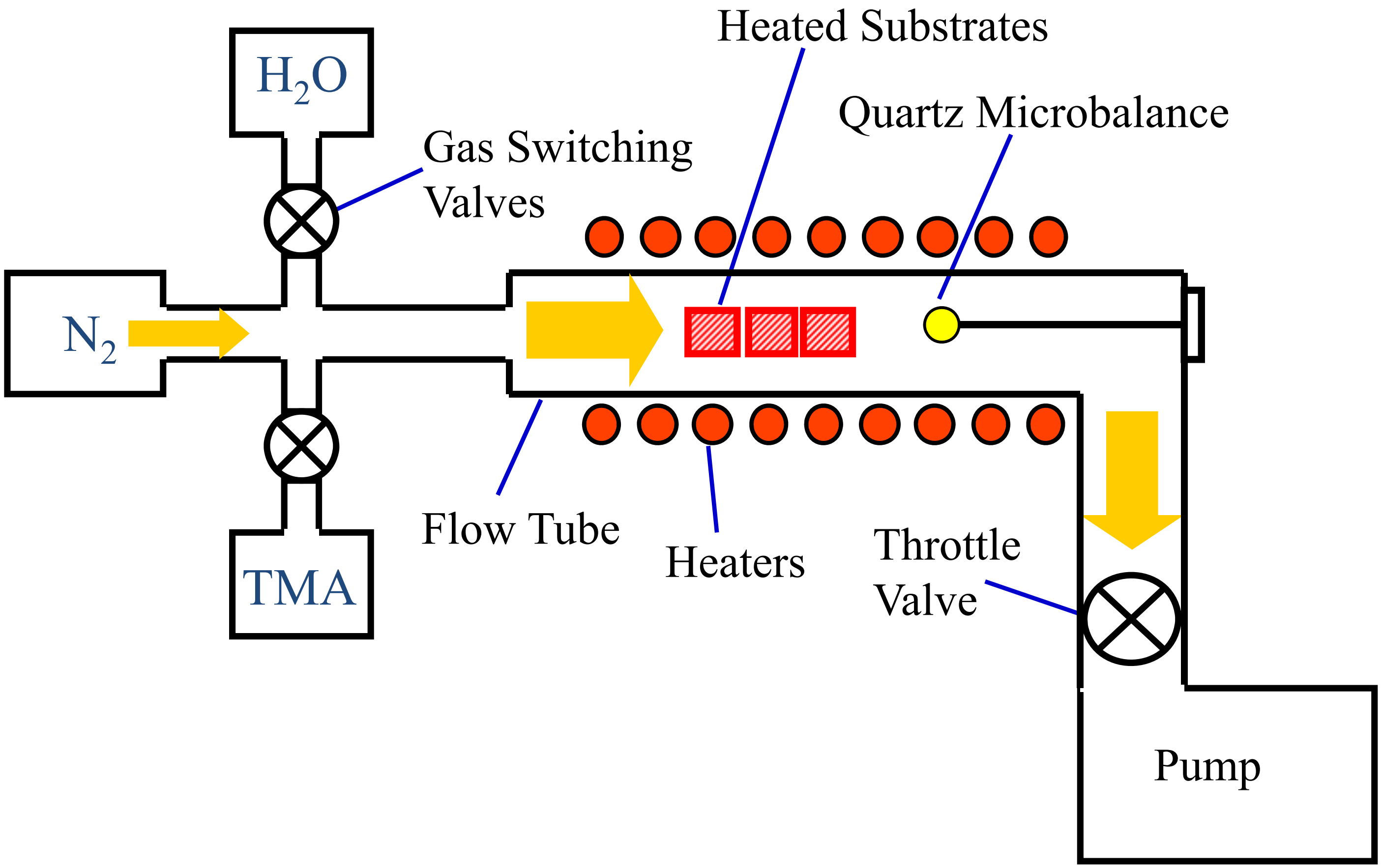


$Al(CH_3)_3$ (TMA)



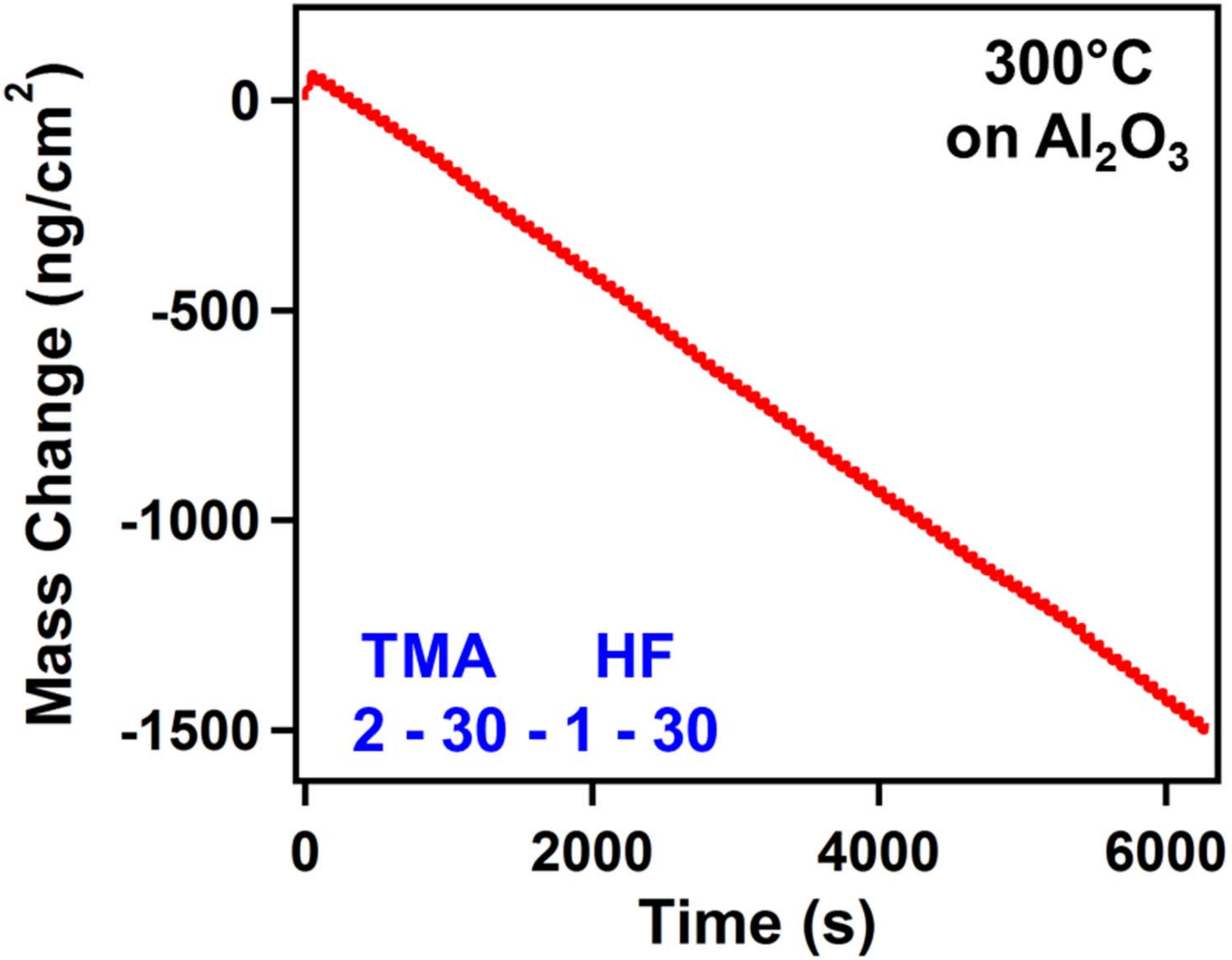
HF-Pyridine

QCM Studies in Hot Wall, Viscous Flow Reactor



J.W. Elam et al., *Rev. Sci. Instrum.* **73**, 2981 (2002).

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



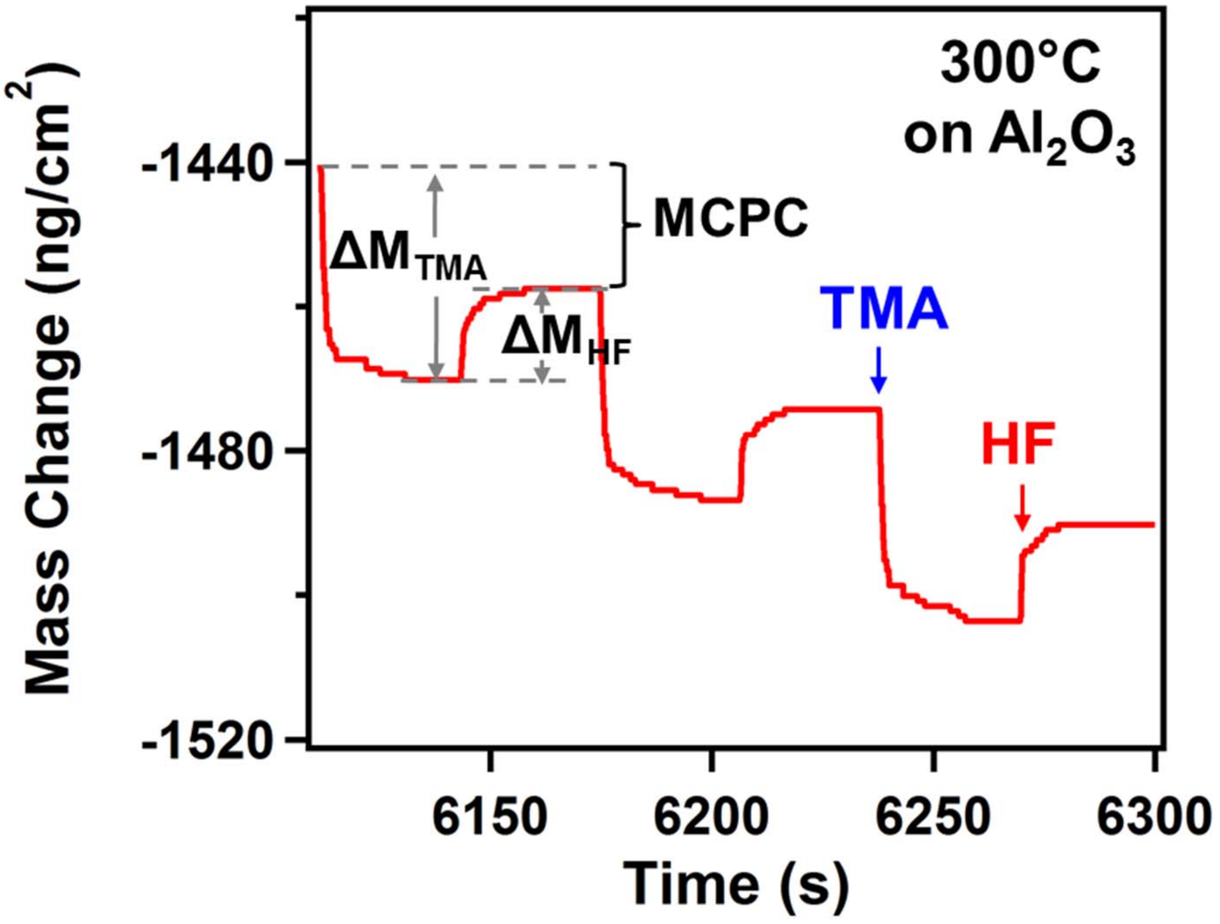
100 ALE Cycles

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.* **28**, 2994 (2016).

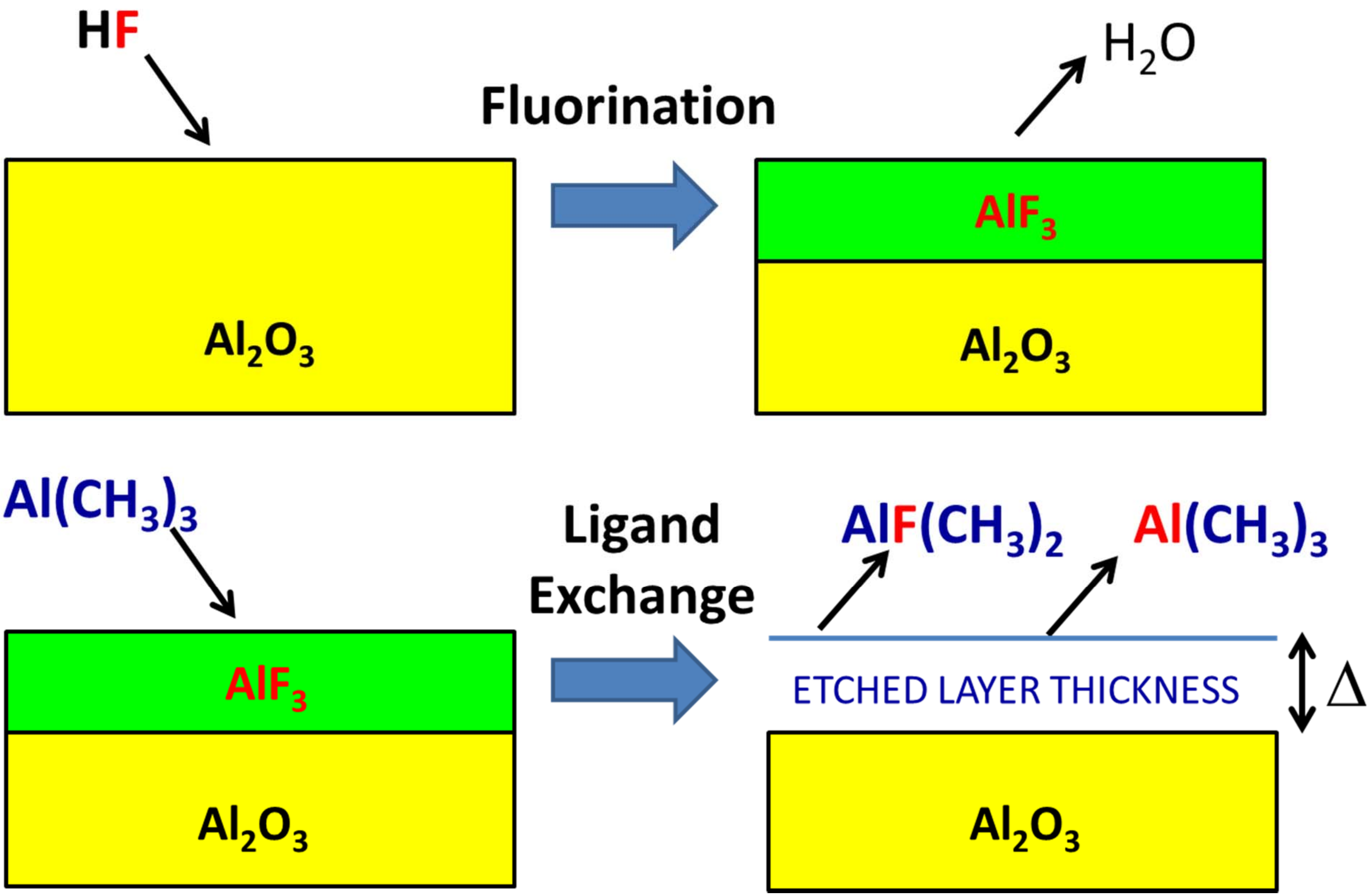
Mass Loss During $Al(CH_3)_3$ and HF Exposures for 3 Cycles of Al_2O_3 ALE



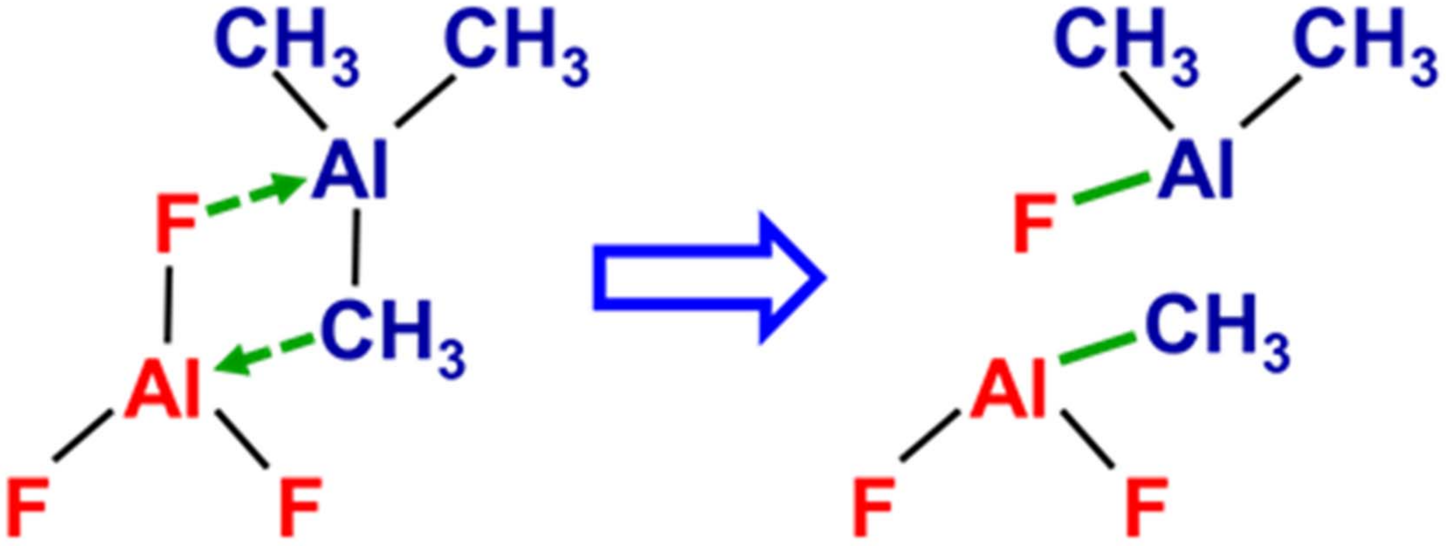
Constant mass changes with each reactant exposure

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

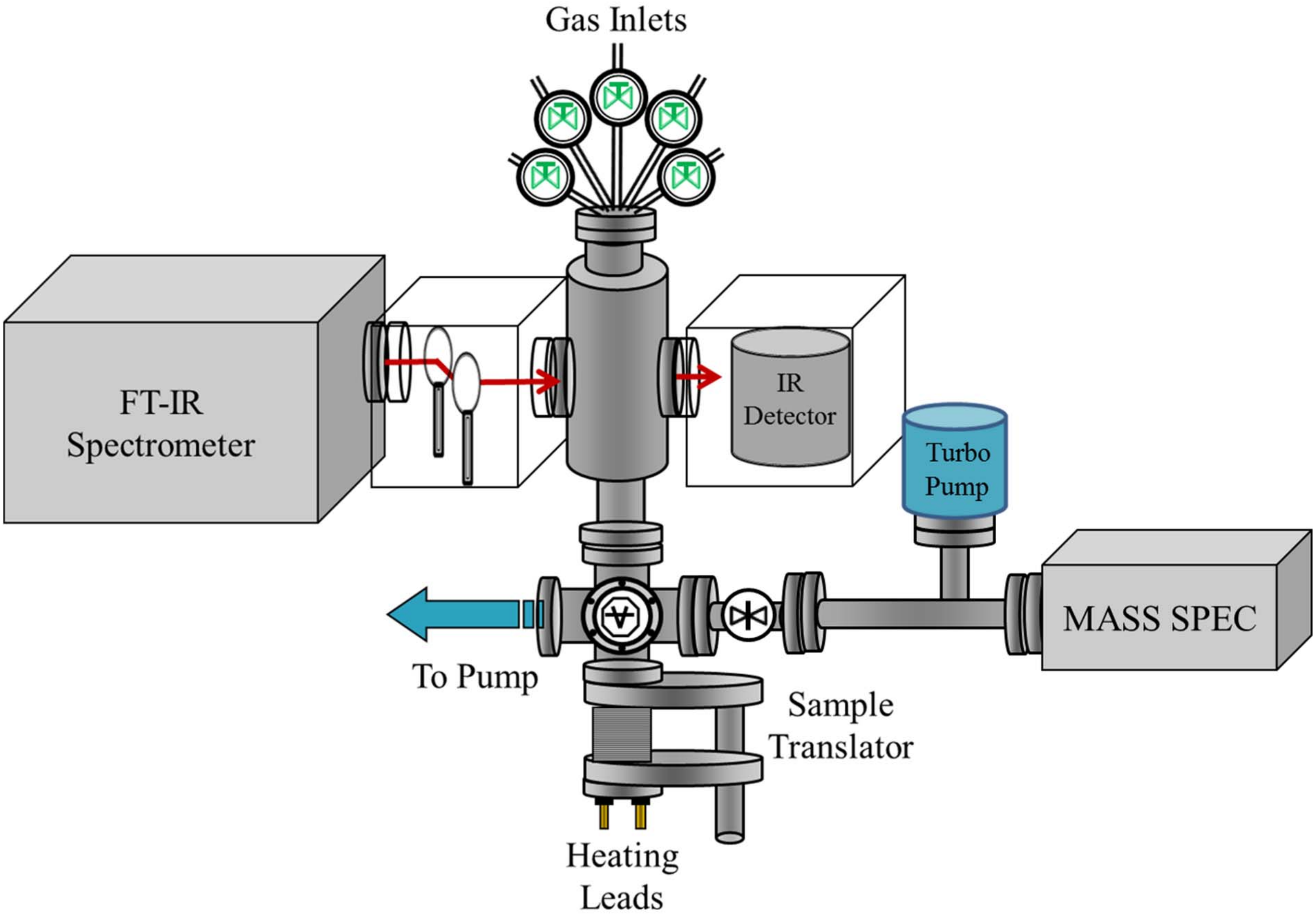
Al_2O_3 ALE via Fluorination & Ligand Exchange



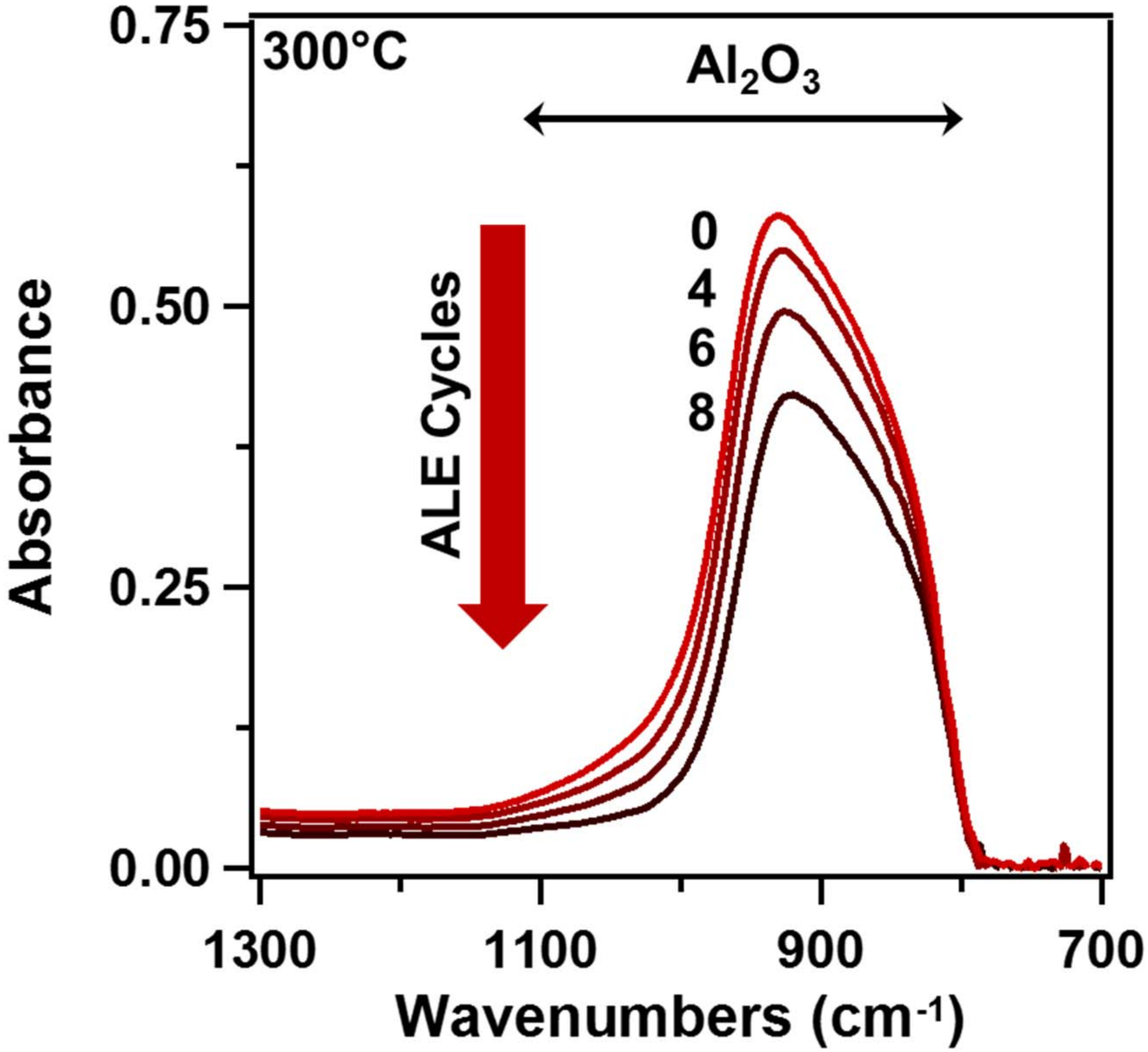
Ligand-Exchange Involves (1) Transfer of Fluorine from Metal Fluoride to Metal Precursor and (2) Transfer of Ligand from Metal Precursor to Metal Fluoride



FTIR Spectroscopy Studies of ALE Surface Species & Etched Material



FTIR Spectroscopy Measurement of Al_2O_3 Etching vs ALE Cycles

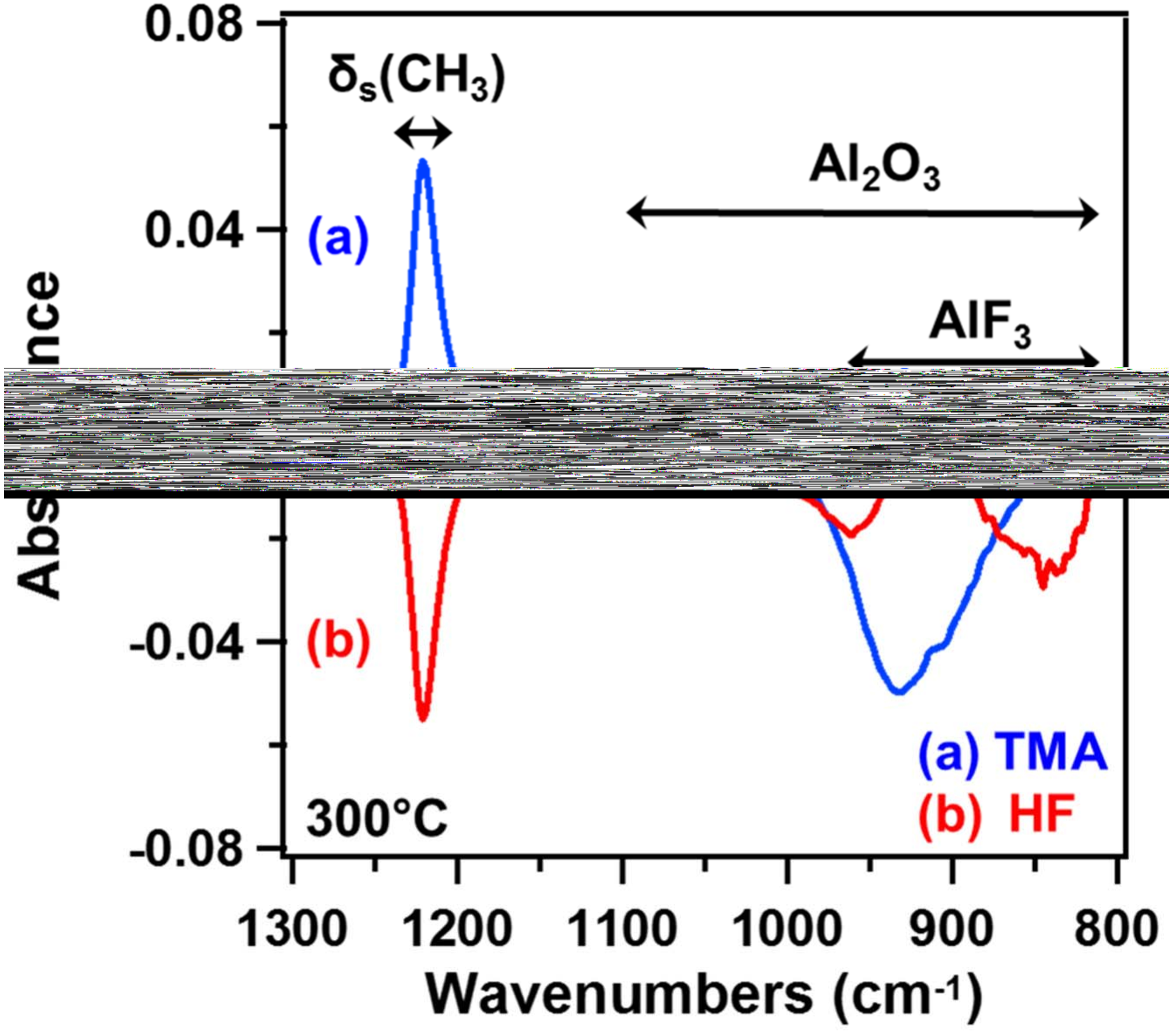


Al_2O_3 ALE with TMA & HF

Observe loss in absorbance during ALE

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

Difference Spectra During TMA & HF Exposures



[redacted]

TMA removes absorbance for Al-F stretch in AlF_3

HF removes absorbance for Al-O stretch in Al_2O_3 & produces Al-F stretch in AlF_3

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

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

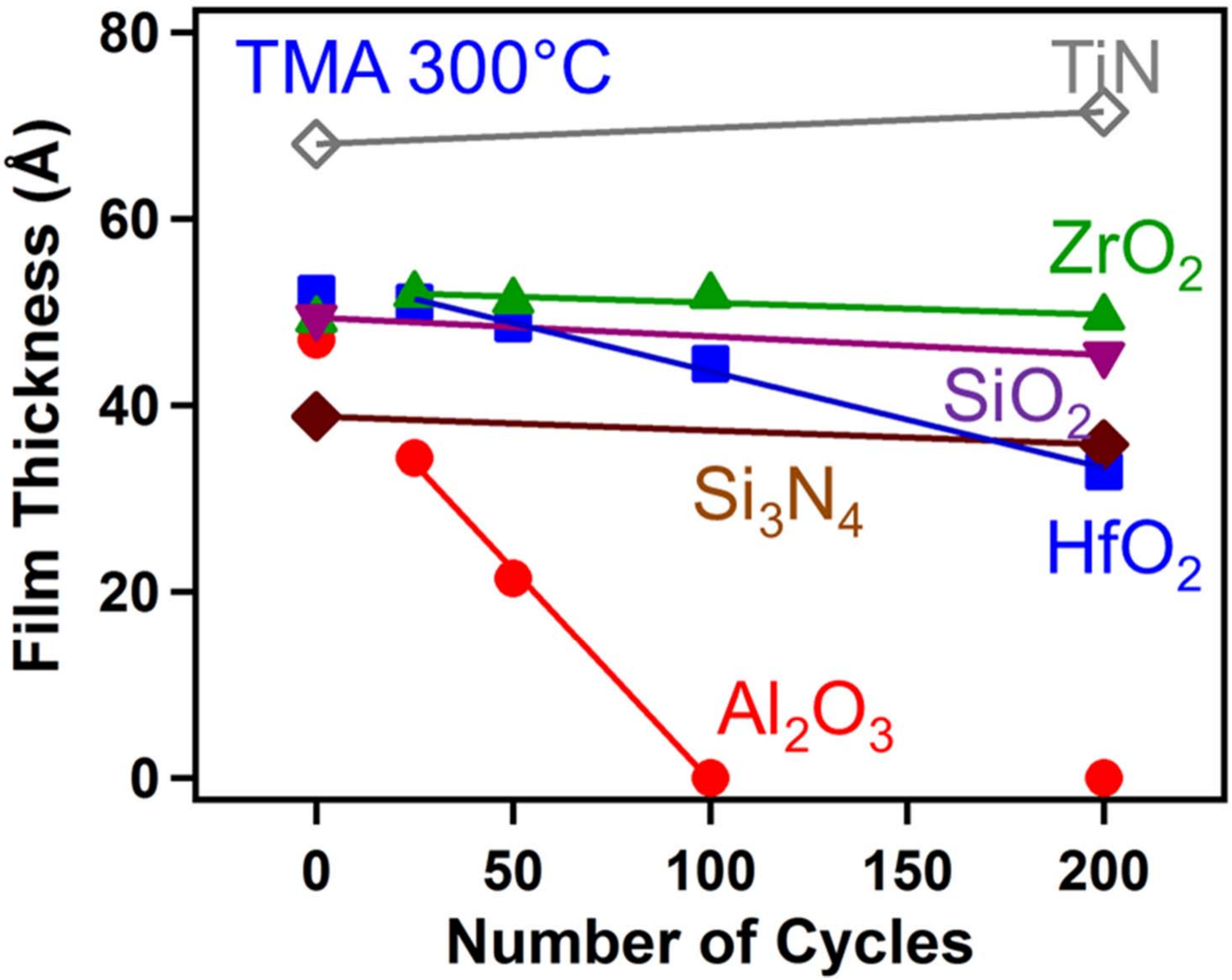
Requirements for Metal Precursor:

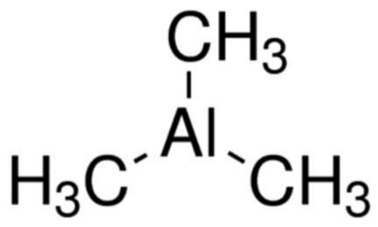
1. Accept fluorine from metal fluoride
2. Donate ligand to metal in metal fluoride
3. Metal reaction product is stable & volatile

Strategy for Selectivity:

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

Selective ALE Using $Al(CH_3)_3$



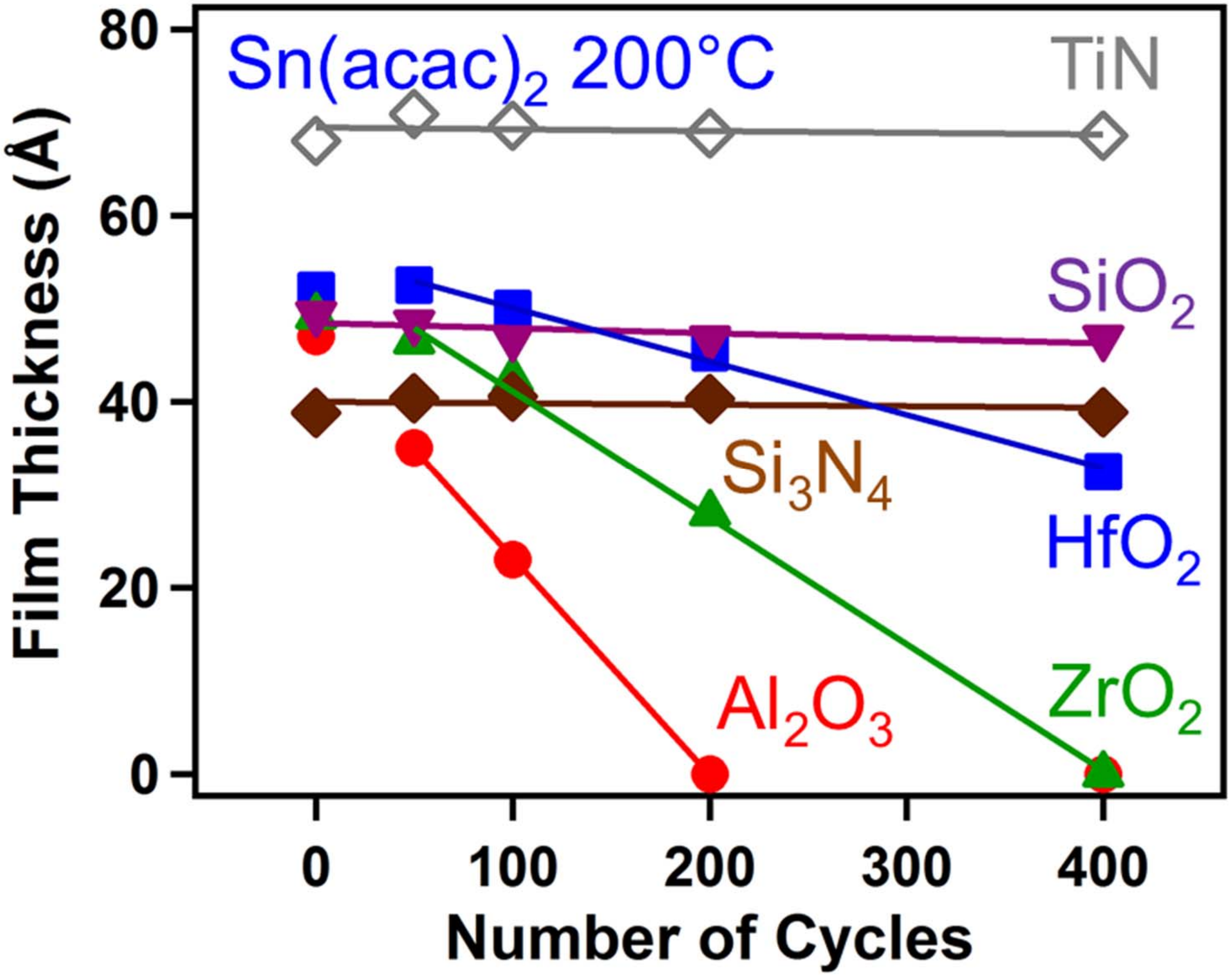


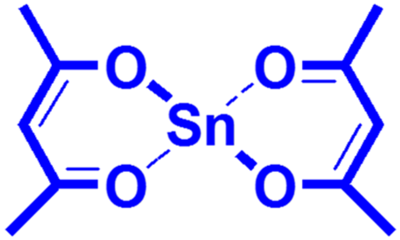
Selective etching of Al_2O_3 & HfO_2.

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

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

Selective ALE Using $Sn(acac)_2$





Selective etching of Al_2O_3, HfO_2 & ZrO_2.

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

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

Thermal ALE Using Fluorination & Ligand-Exchange

Overall Reactions Using Sn(acac)$_2$ & HF:

Metal Oxide

$HfO_2 + 4\ Sn(acac)_2 + 4\ HF \rightarrow Hf(acac)_4 + 4\ SnF(acac) + 2\ H_2O$

Metal Arsenide

$GaAs + 3\ Sn(acac)_2 + 3\ HF \rightarrow Ga(acac)_3 + 3\ SnF(acac) + AsH_3$

Metal Nitride

$GaN + 3\ Sn(acac)_2 + 3HF \rightarrow Ga(acac)_3 + 3\ SnF(acac) + NH_3$

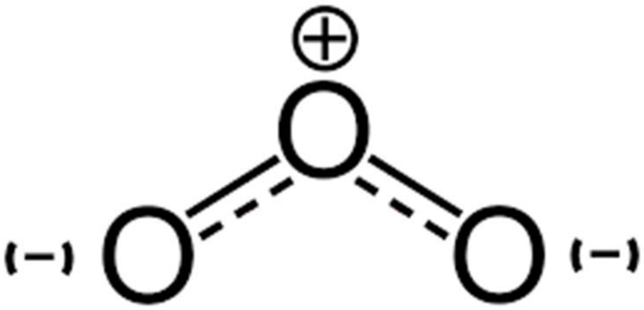
Metal Phosphide

$InP + 3\ Sn(acac)_2 + 3HF \rightarrow In(acac)_3 + 3\ SnF(acac) + PH_3$

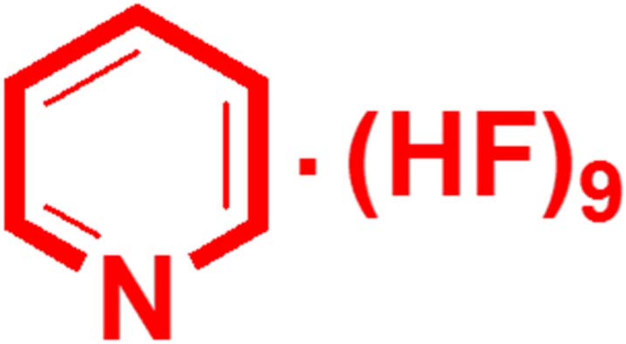
Metal Selenide

$PbSe + 2\ Sn(acac)_2 + 2\ HF \rightarrow Pb(acac)_2 + 2\ SnF(acac) + H_2Se$

2. Oxidation & Fluorination to Volatile Fluoride: TiN ALE Using O_3 & HF



Ozone



HF-Pyridine

TiN not Etched by Fluorination & Ligand-Exchange Reactions

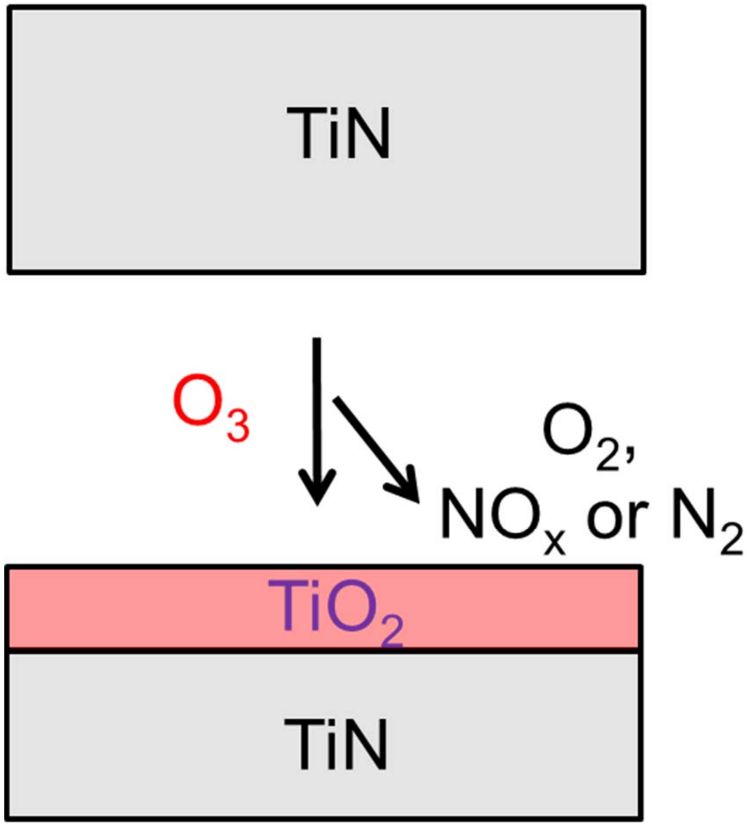
TiN fluorinated to TiF_3. Ti in 3+ oxidation state.

Problem: Ti^{3+} does not have stable, volatile products during ligand-exchange.

→ Ti^{4+} has stable, volatile products.

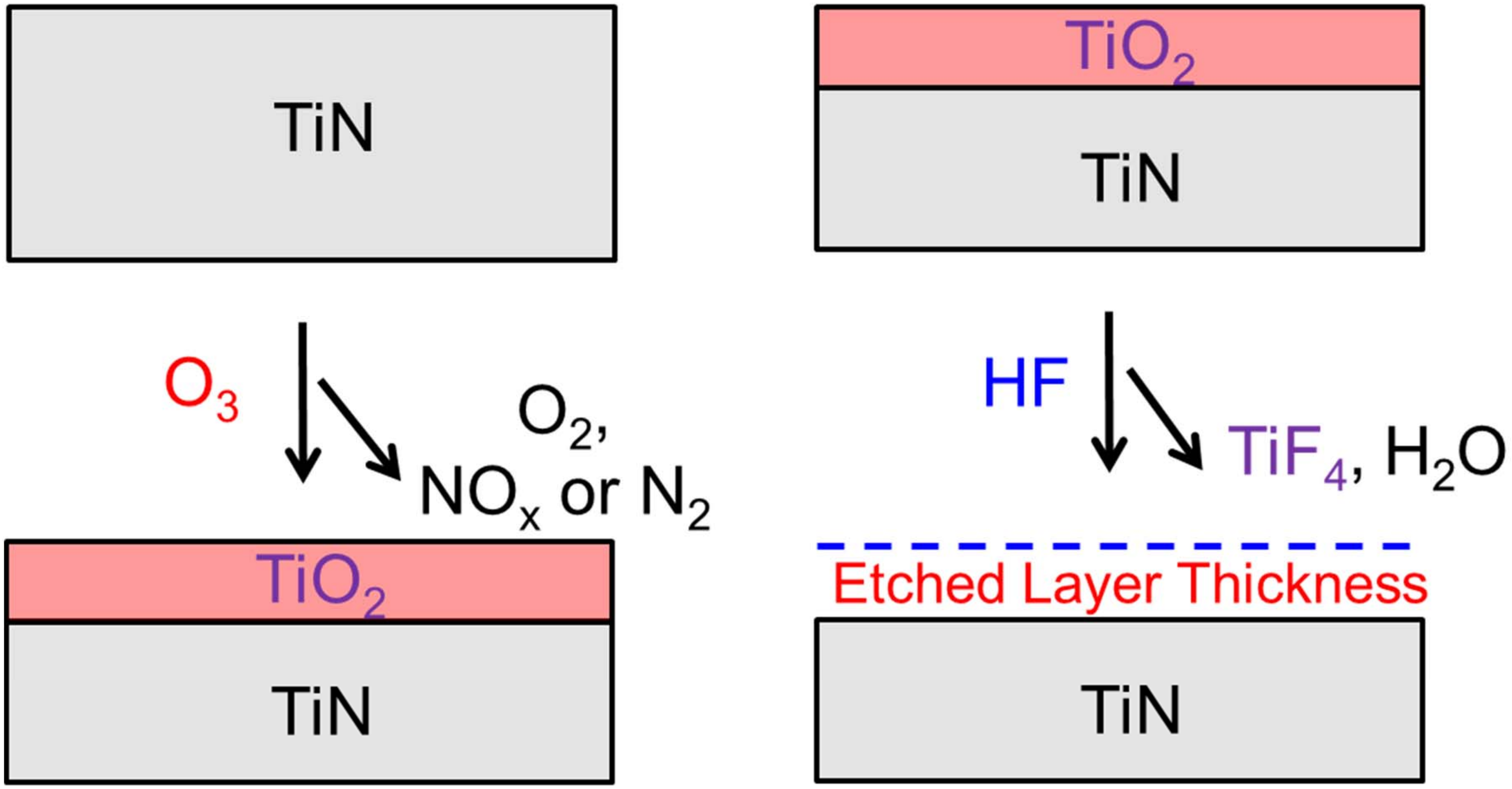
New Strategy: Oxidize TiN to TiO_2 with Ti in 4+ oxidation state. Then can spontaneously etch TiO_2 with TiF_4 as reaction product.

Reaction Mechanism for TiN ALE Using O_3 & HF



Oxidation of Ti^{3+} to Ti^{4+}

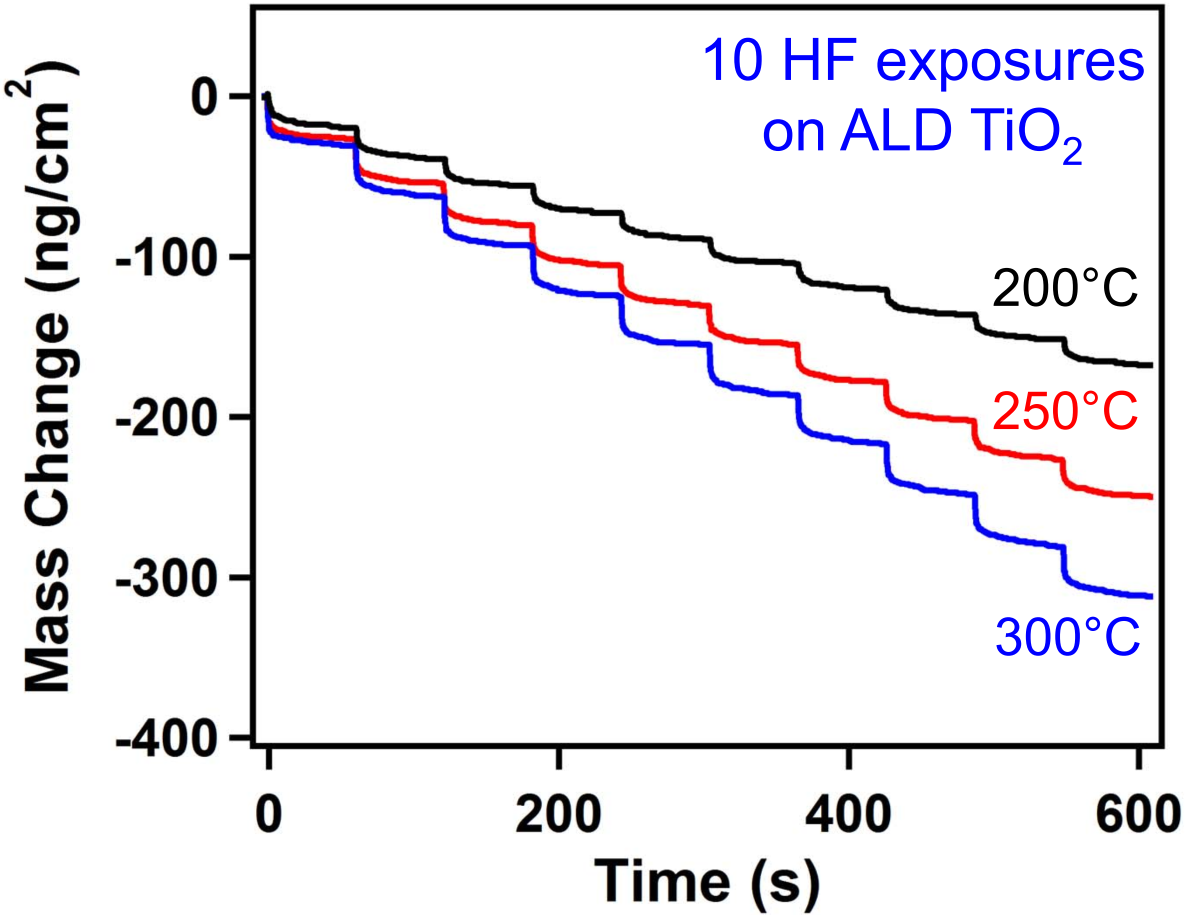
Reaction Mechanism for TiN ALE Using O_3 & HF



Oxidation of Ti^{3+} to Ti^{4+}

Volatile TiF_4 Formation

Spontaneous Etching of TiO_2 by HF Exposures at 200−300°C



Mass Changes per 1s HF exposure:

−17 ng/cm^2

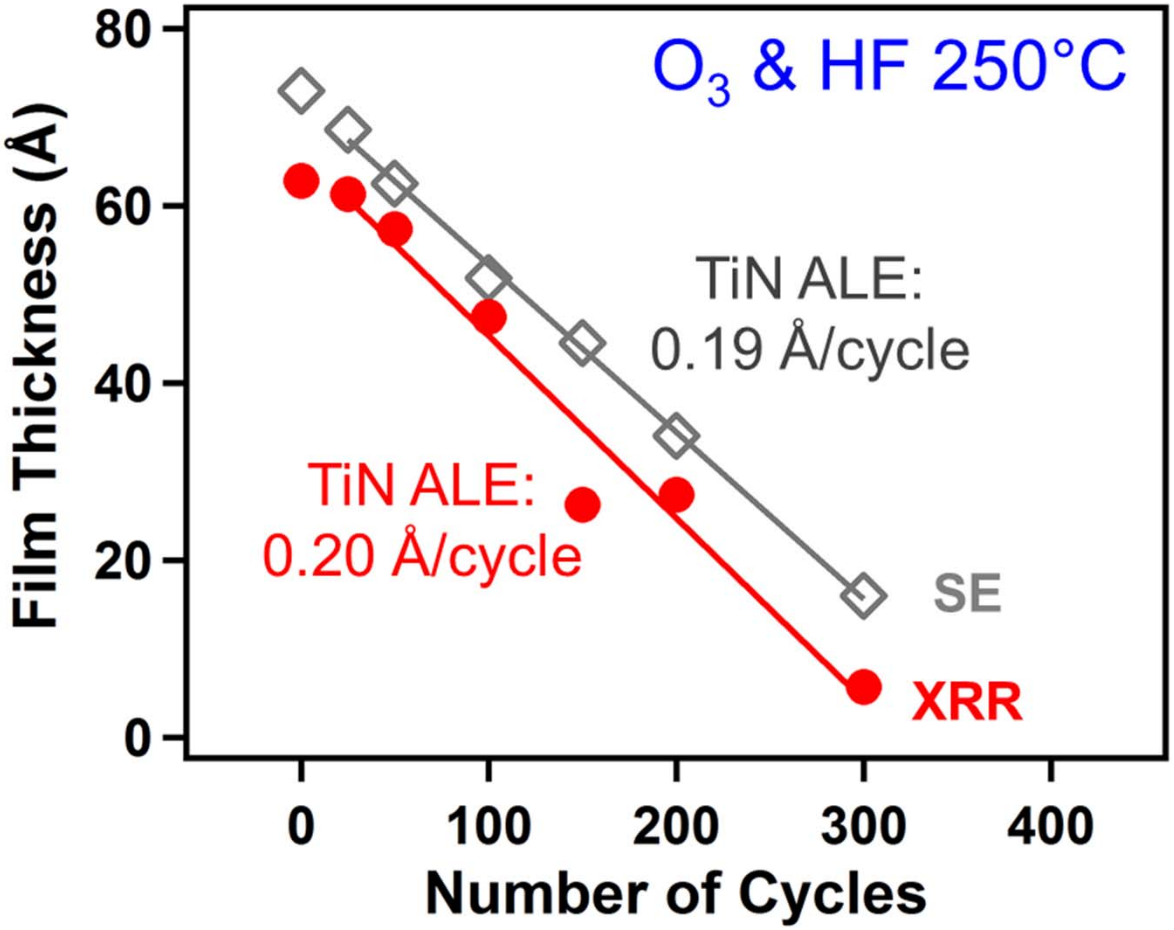
−25 ng/cm^2

−32 ng/cm^2

$TiO_2(s) + 4HF(g) \rightarrow TiF_4(g) + 2H_2O(g)$

Y. Lee & S.M. George, *Chem. Mater.* **29**, 8202 (2017).

TiN Film Thickness vs. Number of ALE Cycles Using O_3 & HF



Linear Etching

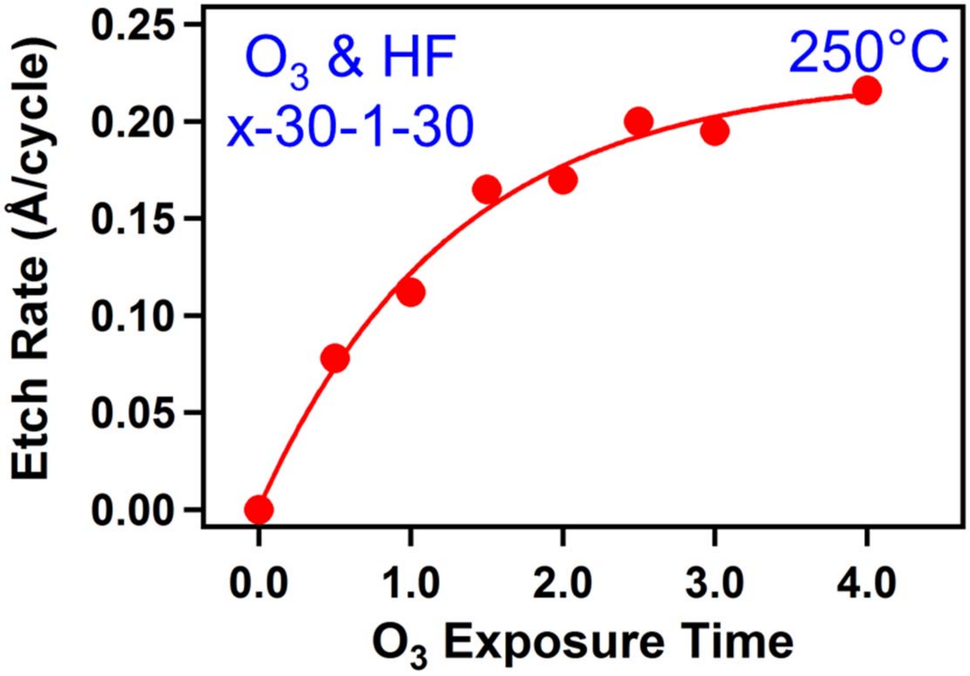
Etch Rate:
0.19-0.20 Å/cycle

Y. Lee & S.M. George, *Chem. Mater.* **29**, 8202 (2017).

Self-Limiting Behavior for TiN ALE

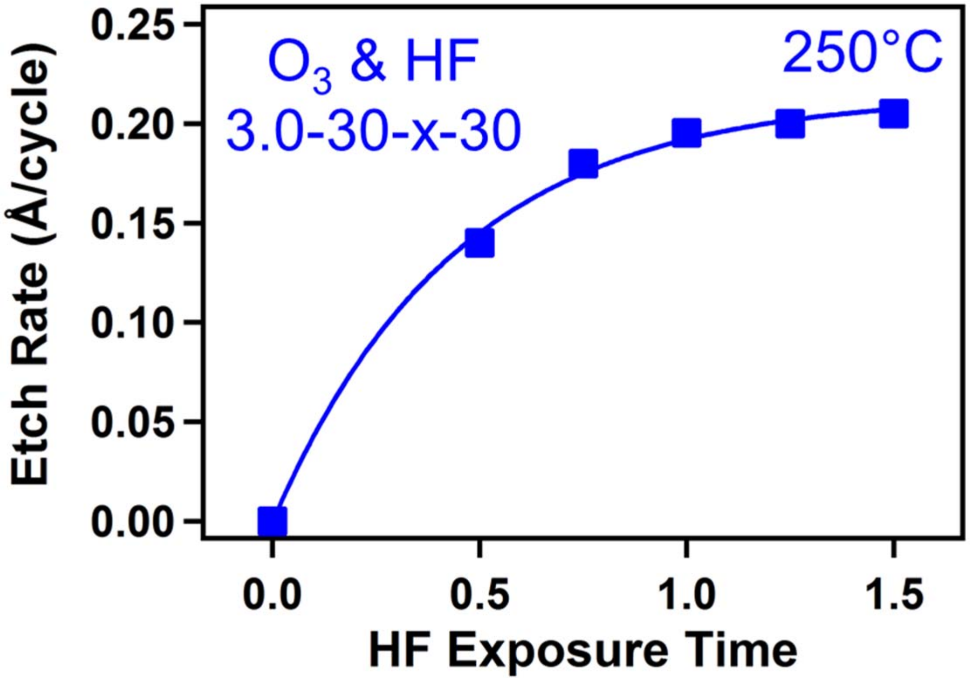
Self-limiting O_3 reaction:

$TiN + 3O_3 \rightarrow TiO_2 + NO + 3O_2$



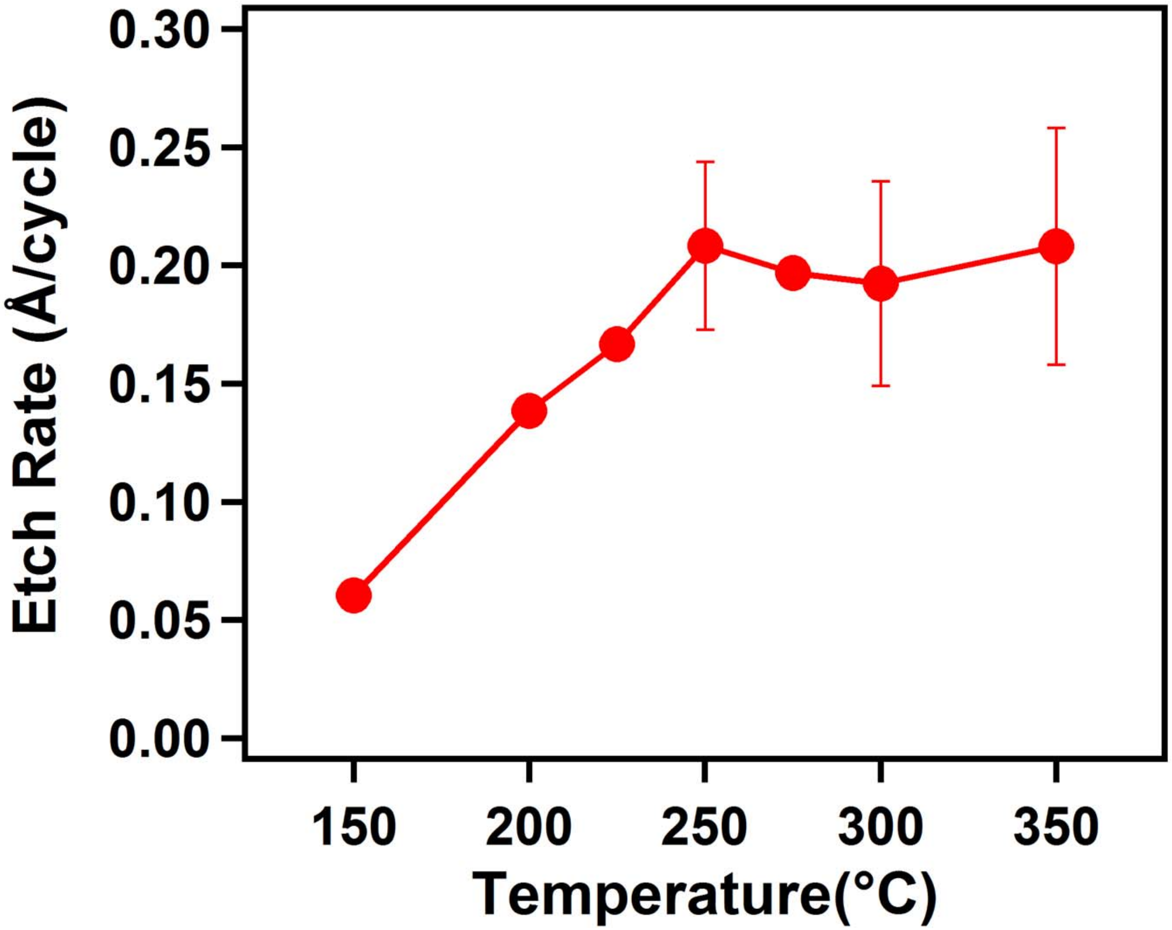
Self-limiting HF reaction:

$TiO_2 + 4HF \rightarrow TiF_4 + 2H_2O$



Y. Lee & S.M. George, *Chem. Mater.* **29**, 8202 (2017).

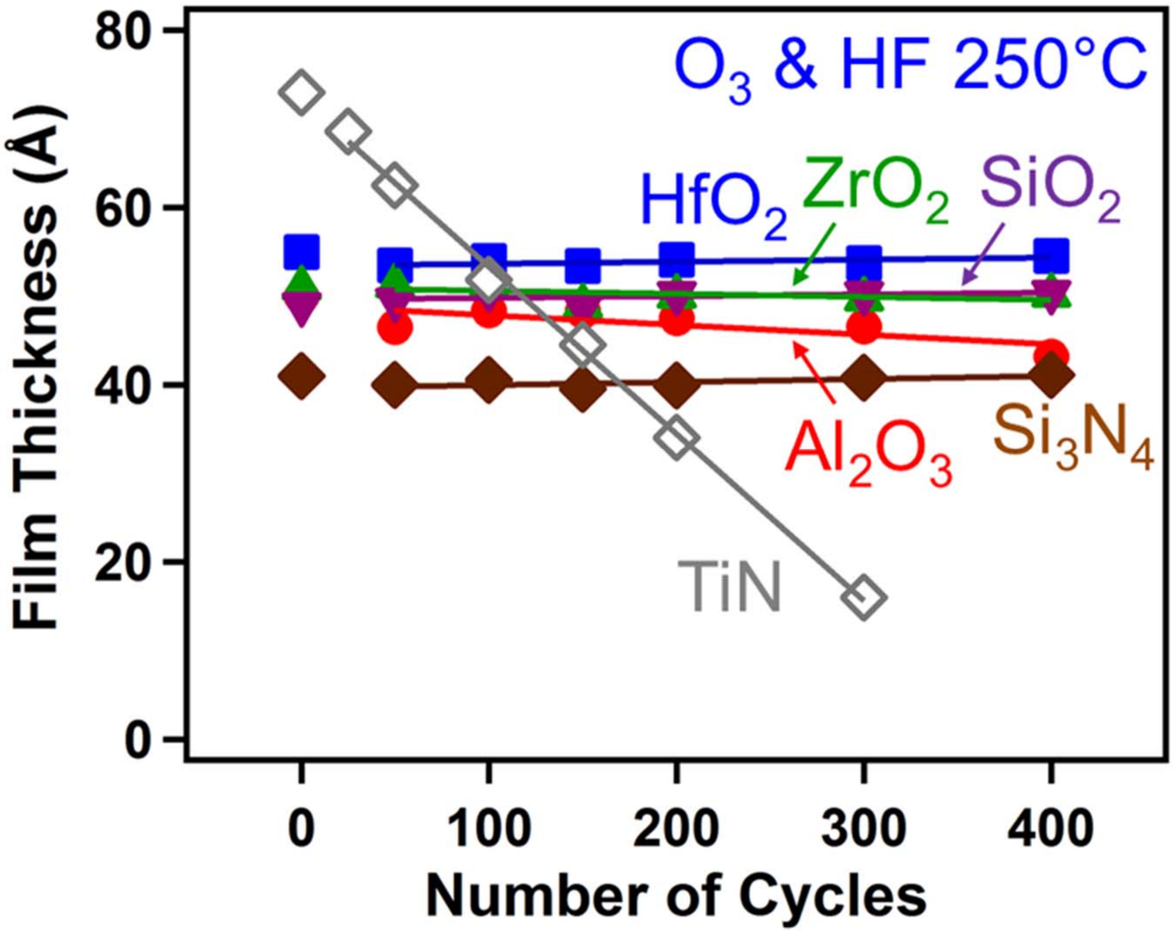
Temperature Dependence of Etch Rate for TiN ALE



Etch rate for TiN ALE : 0.2 Å/cycle at ≥ 250°C

Y. Lee & S.M. George, *Chem. Mater.* **29**, 8202 (2017).

Selectivity of TiN ALE Using O_3 & HF



Selective Etching
of TiN

Y. Lee & S.M. George, *Chem. Mater.* **29**, 8202 (2017).

Thermal ALE Using Oxidation & Fluorination to Volatile Fluoride

Overall Reactions Using O_3 & SF_4:

Metal Nitride

$TiN + 3\ O_3 + SF_4 \rightarrow TiF_4 + NO + 3\ O_2 + SO_2$

Metal Sulfide

$WS_2 + 7\ O_3 + 3/2\ SF_4 \rightarrow WF_6 + 7/2\ SO_2 + 7\ O_2$

Metal Selenide

$MoSe_2 + 9\ O_3 + 3/2\ SF_4 \rightarrow MoF_6 + 2\ SeO_3 + 9\ O_2 + 3/2\ SO_2$

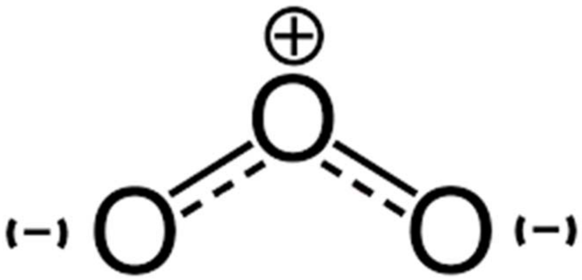
Metal Carbide

$NbC + 7/2\ O_3 + 5/4\ SF_4 \rightarrow NbF_5 + CO + 7/2\ O_2 + 5/4\ SO_2$

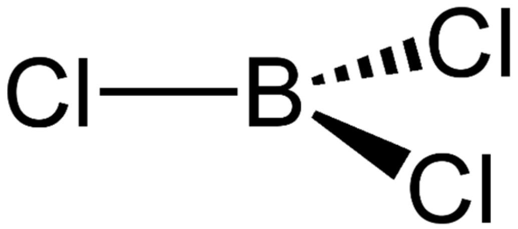
Elemental Metal

$Ta + 5/2\ O_3 + 5/4\ SF_4 \rightarrow TaF_5 + 5/2\ O_2 + 5/4\ SO_2$

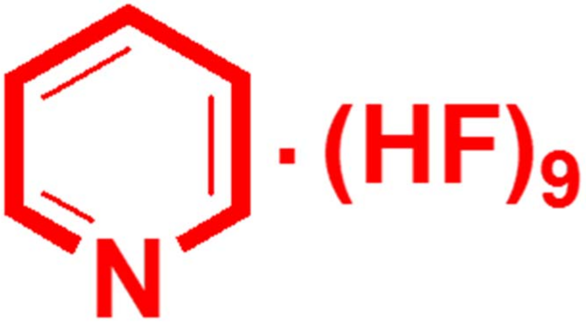
3. Oxidation, Conversion & Fluorination to Volatile Fluoride: W ALE Using O_3, BCl_3 & HF



Ozone



BCl_3



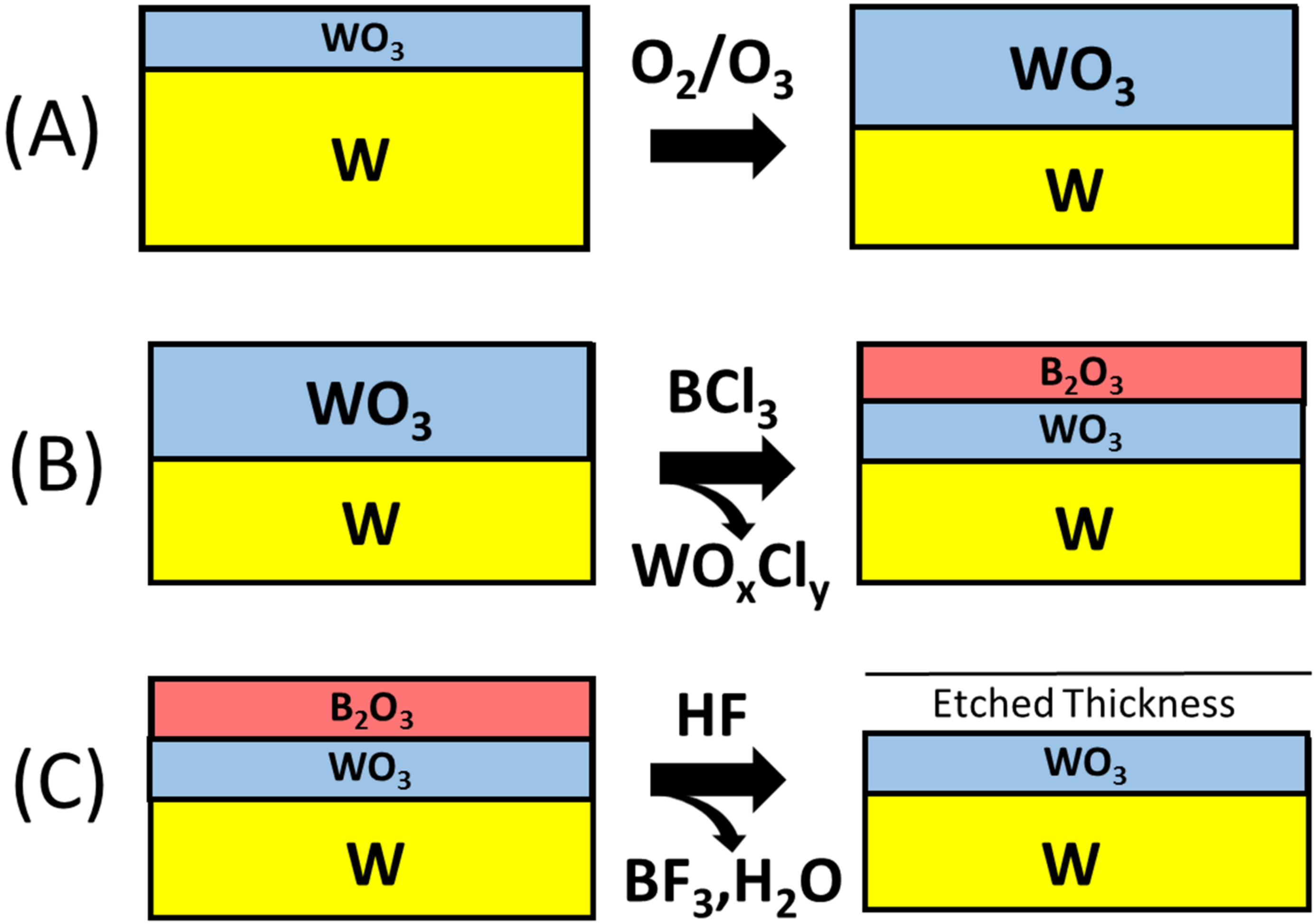
HF-Pyridine

Metal ALE Difficult Using Fluorination & Ligand-Exchange Reactions

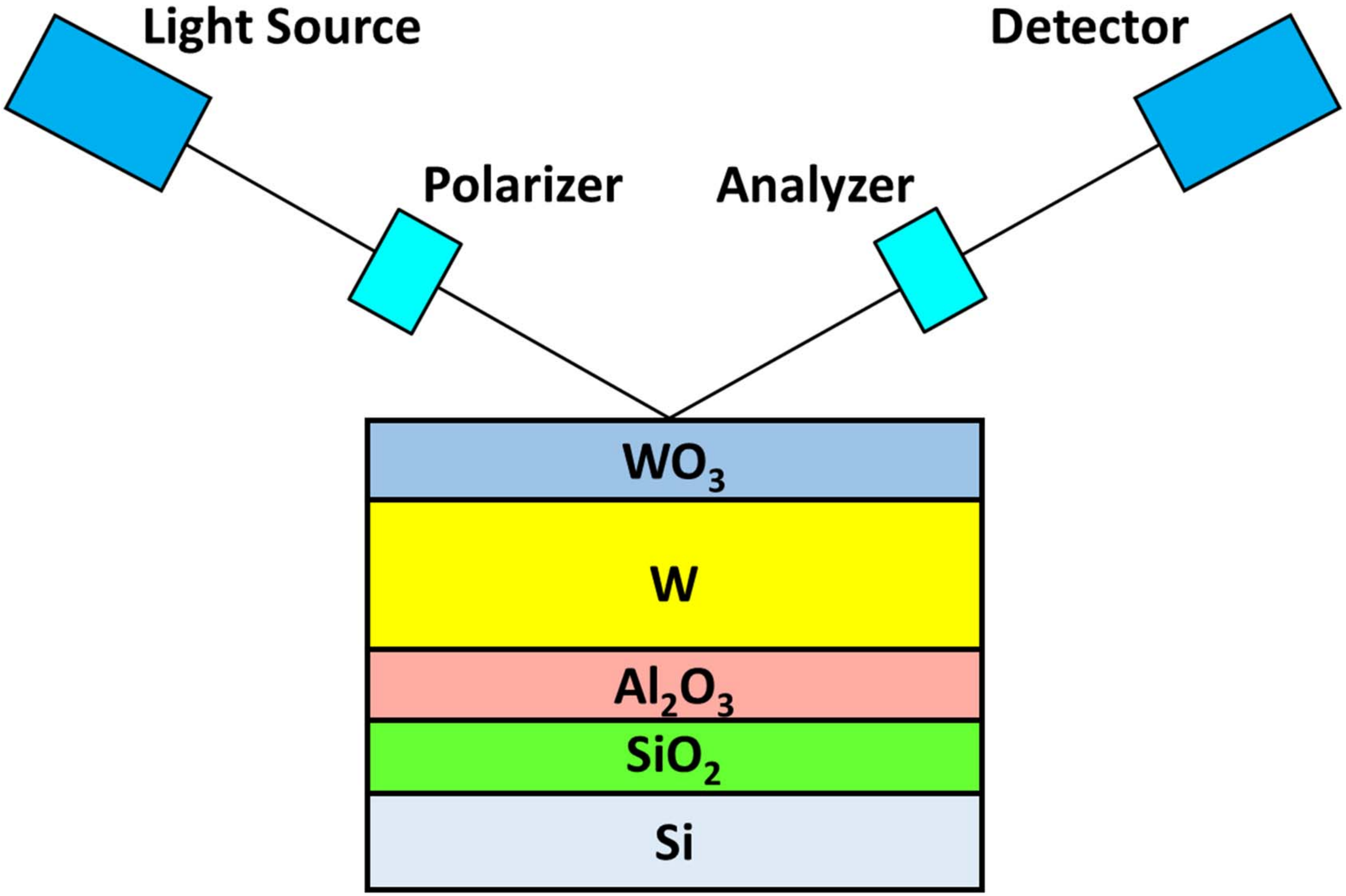
Problems: (1) Many metals have volatile fluorides; (2) Fluorination too exothermal and yields metal fluoride layer too thick for ALE; (3) Stable & volatile reaction products difficult during ligand exchange.

Alternatives: New thermal ALE mechanisms based on "Oxidation-Conversion-Fluorination".

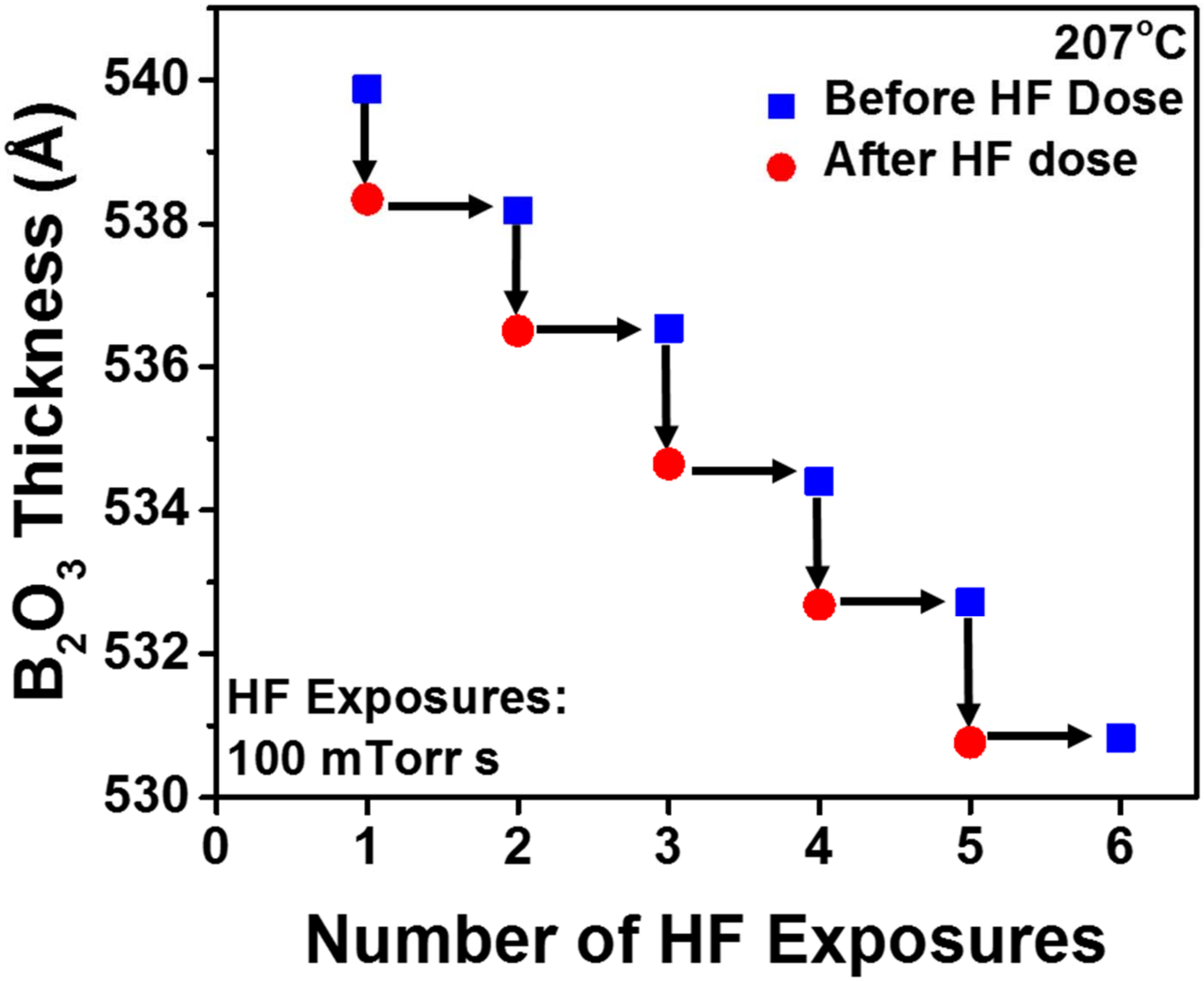
W Thermal ALE Using “Oxidation-Conversion-Fluorination” Mechanism



Ellipsometer Can Monitor Both WO_3 and W Film Thicknesses



B_2O_3 Spontaneously Etched With HF

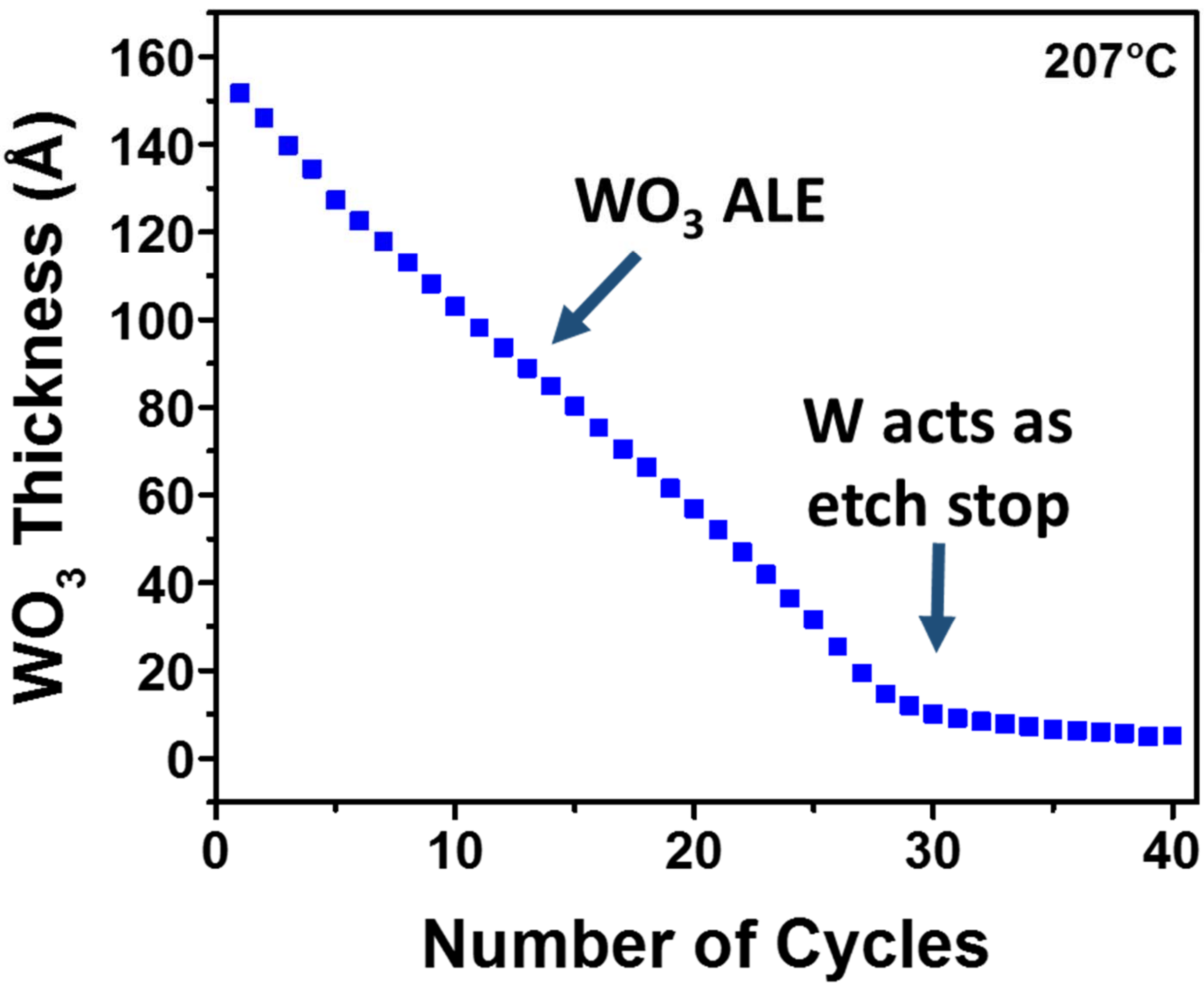


HF exposures: 100 mTorr for 1 s

B_2O_3 films spontaneously etched at ~2 Å per HF exposure

N.R. Johnson & S.M. George, *ACS Appl. Mater. Interfaces* **9**, 34435 (2017).

WO_3 ALE with BCl_3 & HF at 207°C



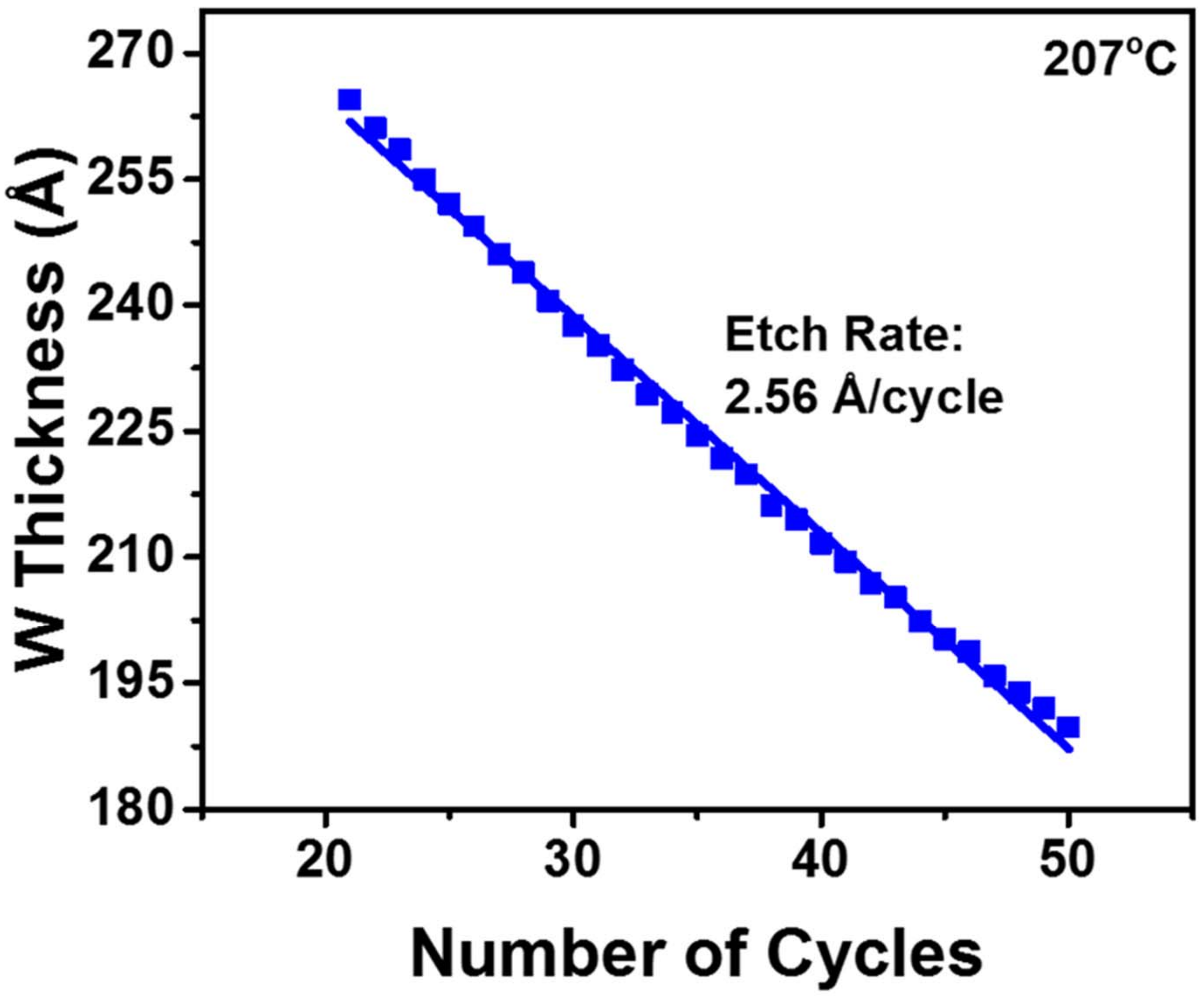
Initial WO_3 samples prepared by oxidizing W ALD films with 600 W O_2 plasma at 280°C

Etch rate of 4.19 Å/cycle

Tungsten is an etch stop for BCl_3/HF etch process

N.R. Johnson & S.M. George, *ACS Appl. Mater. Interfaces* **9**, 34435 (2017).

W ALE with O_3, BCl_3 and HF at 207°C



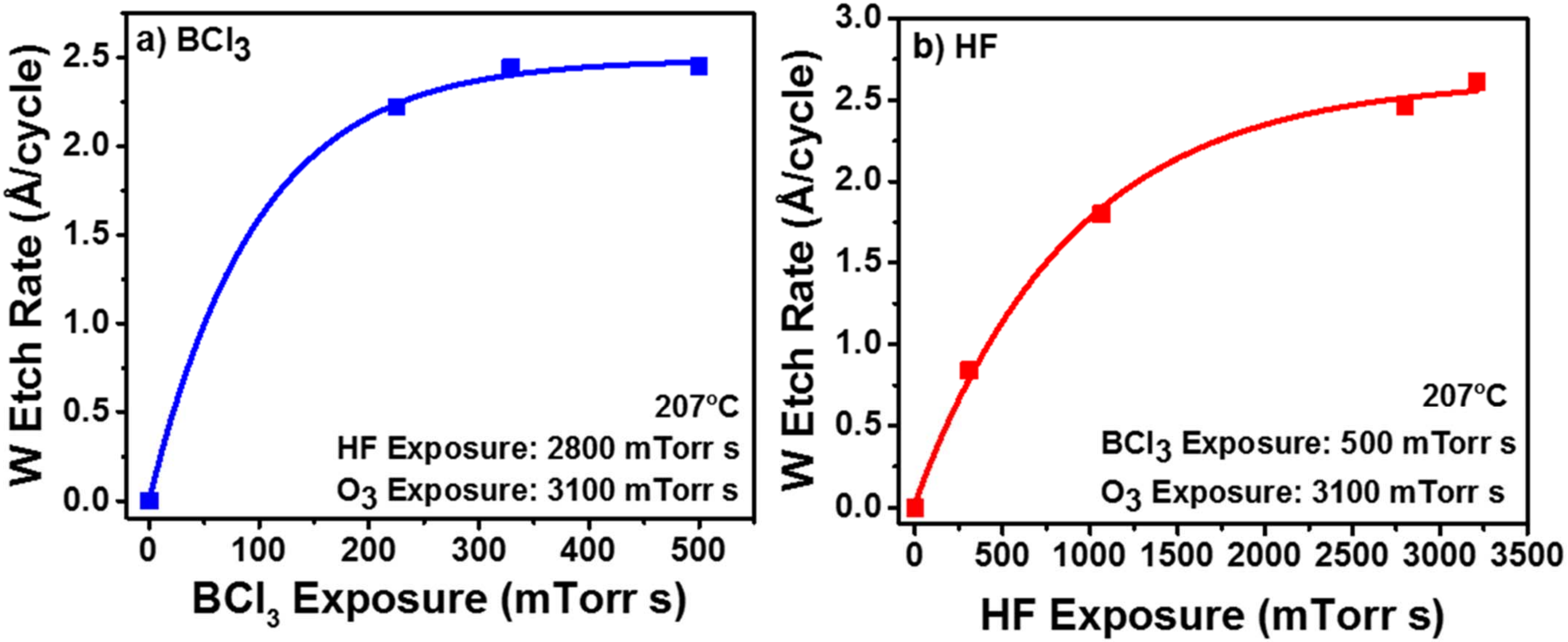
Linear W ALE

Etch rate of 2.56 Å/cycle is slightly less than one unit cell length for body-centered cubic W of 3.19 Å

N.R. Johnson & S.M. George, *ACS Appl. Mater. Interfaces* **9**, 34435 (2017).

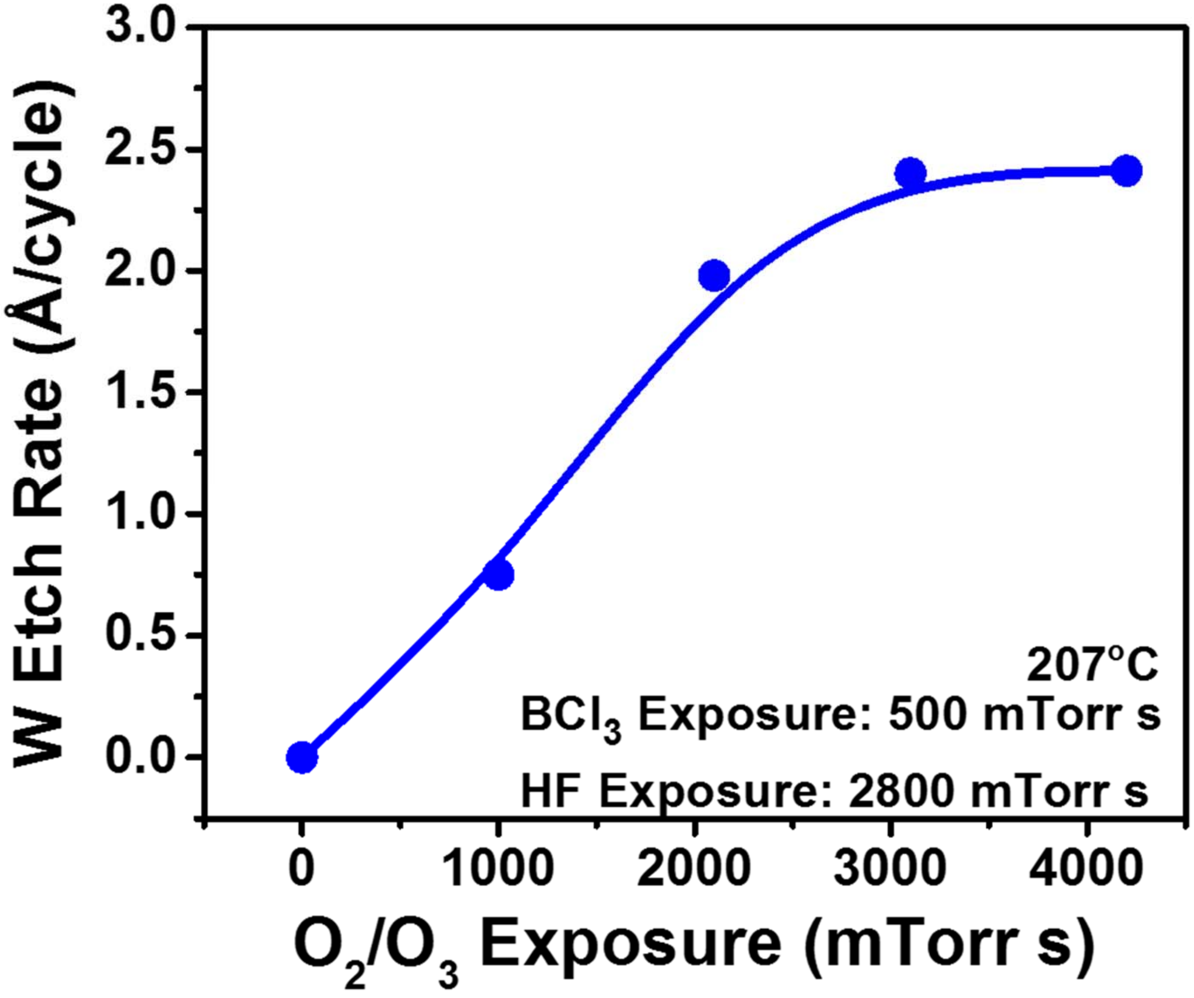
Self-Limiting BCl_3 & HF Reactions

Self-limiting exposures are 500 mTorr s for BCl_3 & 2800 mTorr s for HF. Self-limiting etch rate is 2.45 Å/cycle.



N.R. Johnson & S.M. George, *ACS Appl. Mater. Interfaces* **9**, 34435 (2017).

Self-Limiting O_3 Reaction

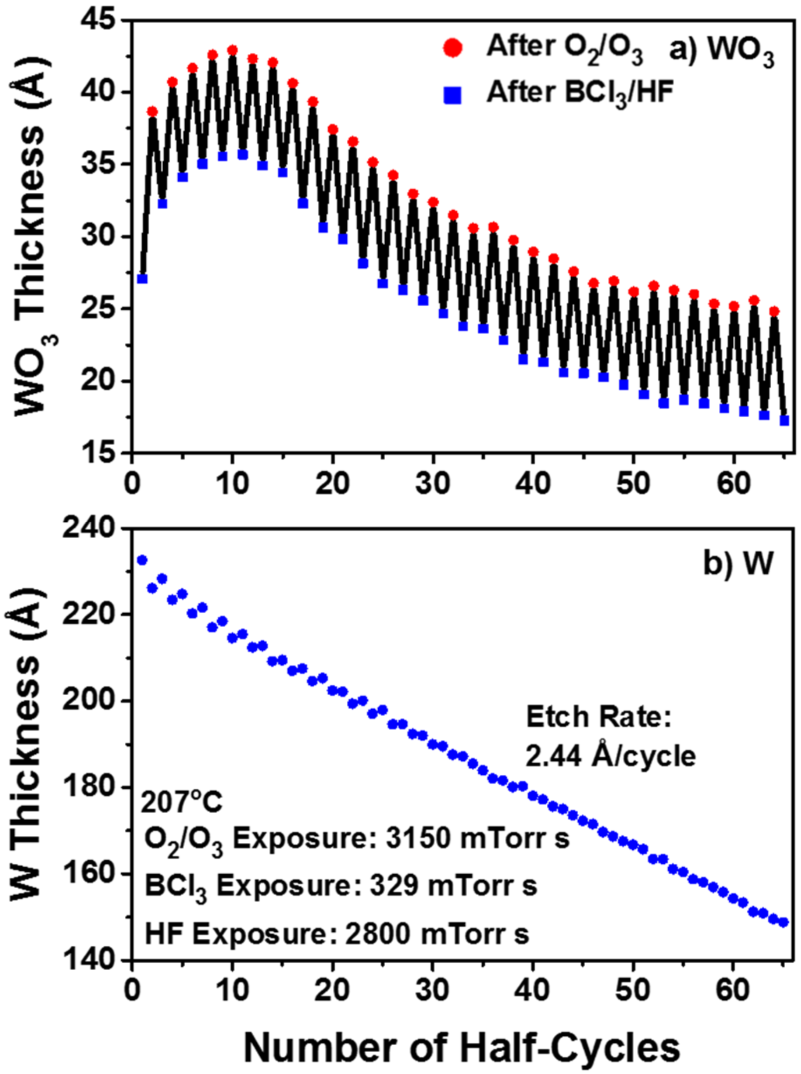


Self-limiting O_3 exposure is 3100 mTorr s

Self-limiting etch rate is 2.44 Å/cycle

N.R. Johnson & S.M. George, *ACS Appl. Mater. Interfaces* **9**, 34435 (2017).

WO_3 & W Thicknesses During W ALE Using O_3, BCl_3 & HF

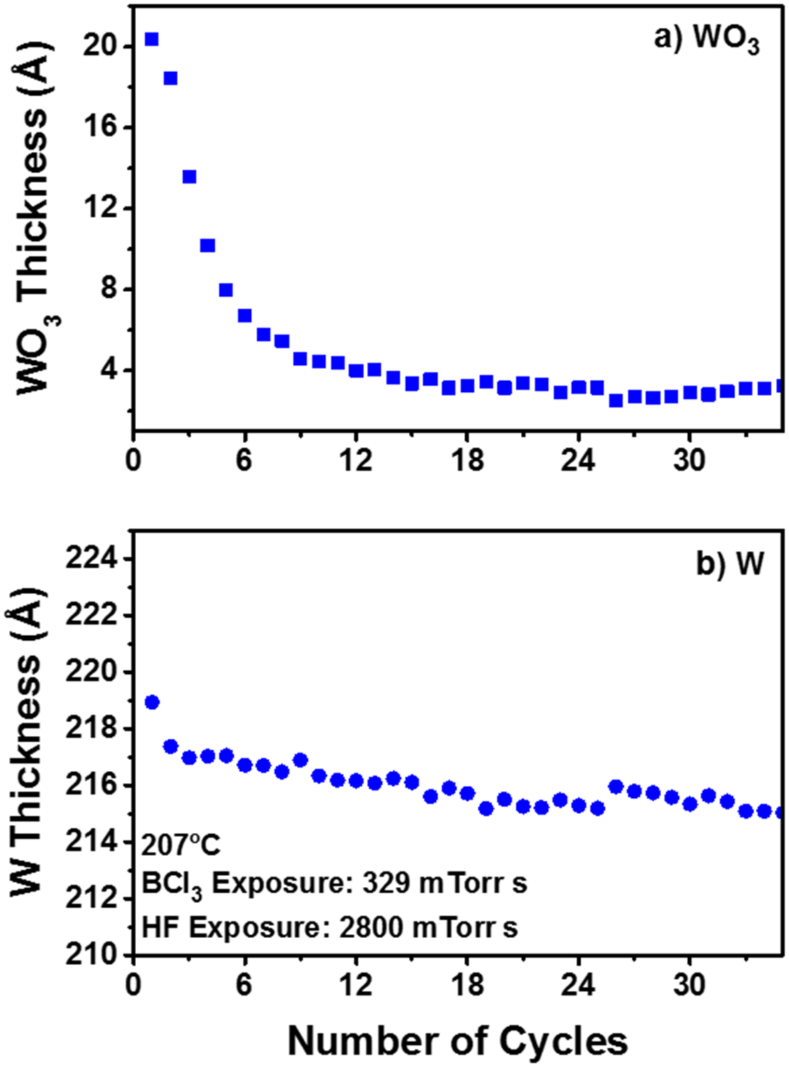


WO_3 thickness oscillates with sequential O_3 oxidation & BCl_3/HF etch reactions

W thickness reduced linearly with number of O_3 oxidation & BCl_3/HF etch reactions. Etch rate = 2.44 Å/cycle

N.R. Johnson & S.M. George, *ACS Appl. Mater. Interfaces* **9**, 34435 (2017).

Removal of WO_3 Thickness on W after W ALE



WO_3 thickness can be reduced after W ALE using sequential BCl_3 & HF exposures

W thickness remains nearly constant during sequential BCl_3 & HF exposures

N.R. Johnson & S.M. George, *ACS Appl. Mater. Interfaces* **9**, 34435 (2017).

Thermal ALE Using Oxidation, Conversion & Fluorination to Volatile Fluoride

Oxide Conversion Reactions Using BCl_3:

Iron Oxide

$Fe_2O_3 + 2\ BCl_3(g) \rightarrow B_2O_3 + 2\ FeCl_3(g)$

Germanium Oxide

$GeO_2 + 4/3\ BCl_3(g) \rightarrow 2/3\ B_2O_3 + GeCl_4(g)$

Molybdenum Oxide

$MoO_3 + 2/3\ BCl_3(g) \rightarrow 1/3\ B_2O_3 + MoO_2Cl_2(g)$

Vanadium Oxide

$VO_2 + 4/3\ BCl_3(g) \rightarrow 2/3\ B_2O_3 + VCl_4(g)$

Gallium Oxide

$Ga_2O_3 + 2\ BCl_3(g) \rightarrow B_2O_3 + 2\ GaCl_3(g)$

Surface Chemistry for Thermal ALE of Metal Oxides, Metal Nitrides & Elemental Metals

1. Al_2O_3 ALE with $Al(CH_3)_3$ & HF as reactants.
   Fluorination & ligand-exchange mechanism.
2. TiN ALE with O_3 & HF as reactants.
   Mechanism based on oxidation & fluorination to volatile fluoride.
3. W ALE with O_3, BCl_3 & HF as reactants.
   Mechanism based on oxidation, coversion & fluorination to volatile fluoride.

Acknowledgements

Nick Johnson–Funded by SRC through the Nanomanufacturing Materials and Processes Thrust (GRC Task 2659.001).

Younghee Lee –Funded by SRC through Member-Specific Research project from Intel (MSR-Intel Task 2643.001).