From Failure to Success: Orthogonal Area-Selective Thin Film Deposition

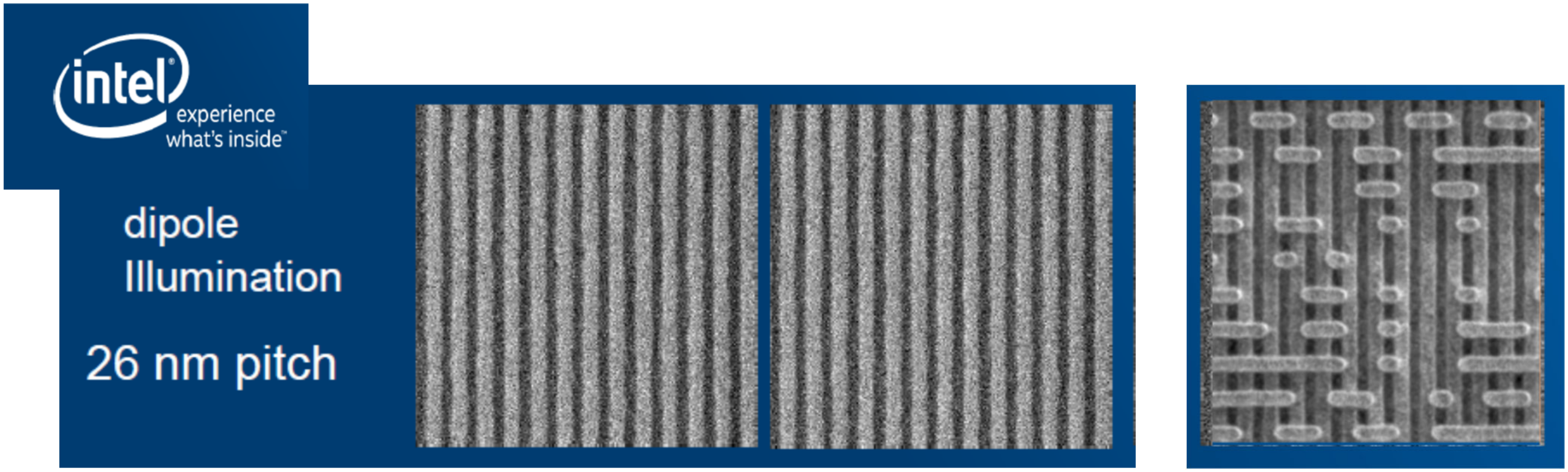
Gregory N. Parsons
Jung-Sik Justin Kim, Hwan Oh, Wenyi Xie, SK Song,
Landon Keller, Hannah Margavio, Holger Saare

Department of Chemical and Biomolecular Engineering
North Carolina State University, Raleigh, NC

SRC Tasks: 2729.001, 2873.001, 3036.001
SRC Seminar
Sept 23, 2021

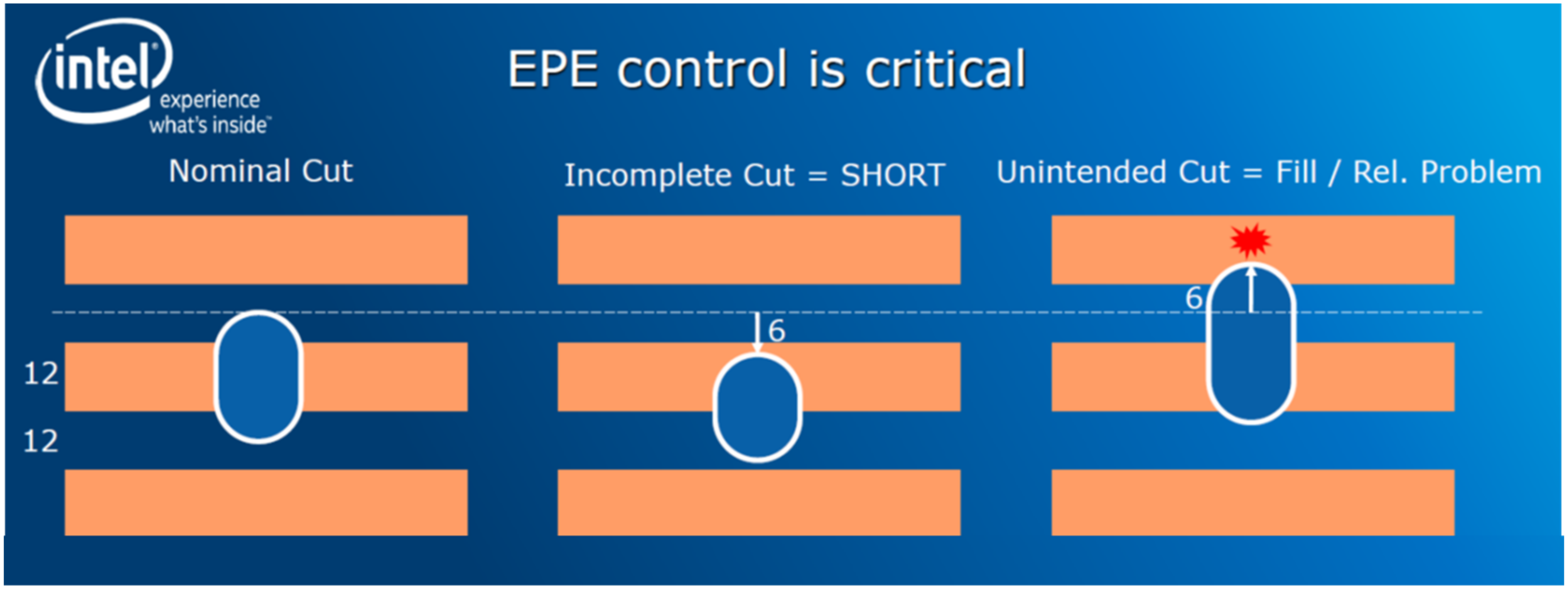
Outline

- Motivation: Deposition-based patterning
- Idea: Orthogonal ASD - Two ASD processes “back-to-back”
- Why we thought our idea would work
  - Success criteria
- Why our original idea was not successful
  - Would the direction have been successful with different boundary conditions?
- How we worked around the problem
  - Discovered a new direction
- What we learned…
  - Success criteria



dipole
Illumination

26 nm pitch



EPE control is critical

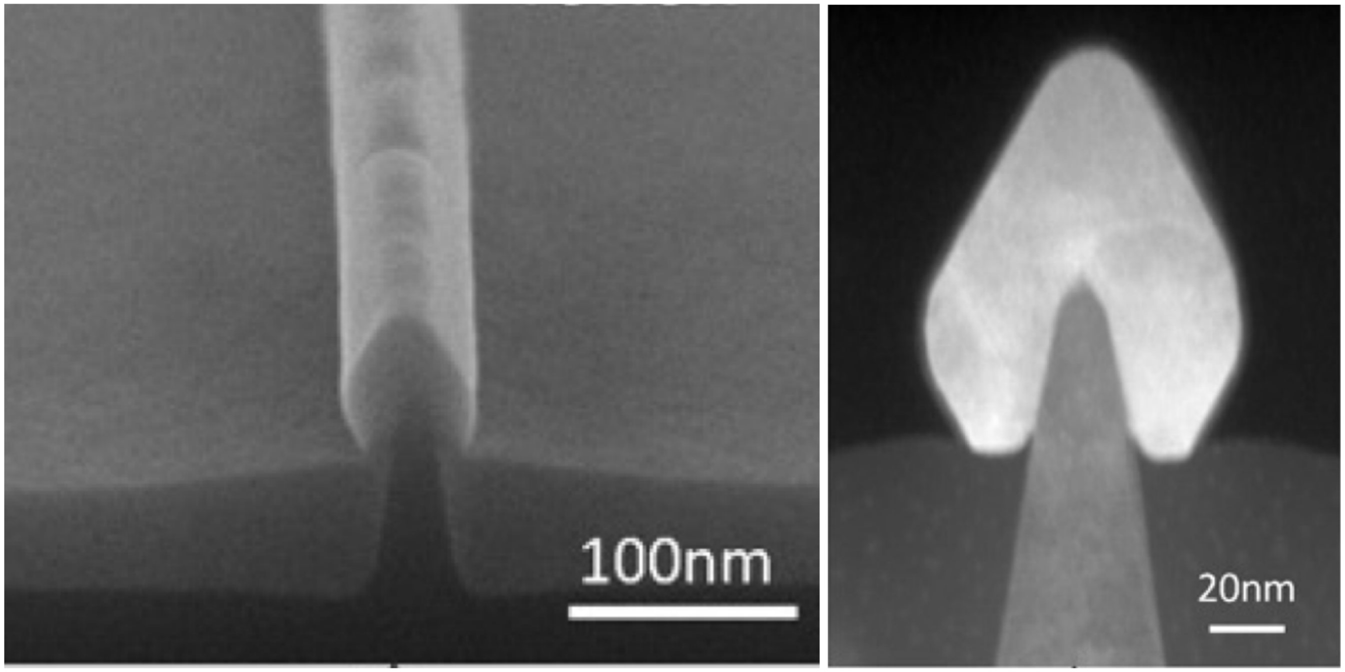
Nominal Cut

Incomplete Cut = SHORT

Unintended Cut = Fill / Rel. Problem

Charles Wallace SPIE Advanced Lithography, EUV, Feb. 24, 2020

Deposition-Based Patterning
Selective Si, SiGe Epitaxy



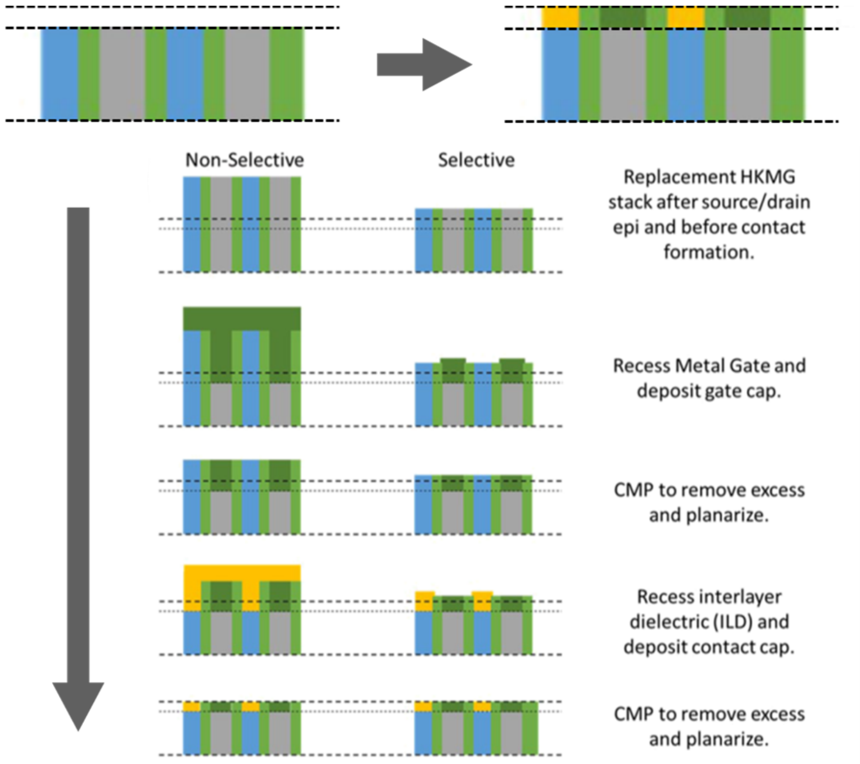
G. Wang et al., *Microelectron. Eng*. (2016)

- Temperature = 700-800°C
- Thermodynamic control of surface termination
- For Back-end ASD: Lower temperatures requires control of reaction kinetics

Back-End Applications for Area Selective Deposition

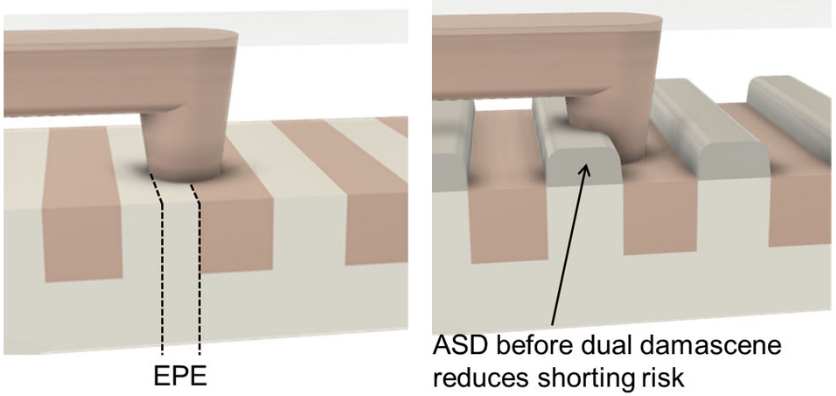
Reduced CMP Overburden for Self-Aligned Gate/Contact (SGOC)

R. Clark et al. APL Mater. 2018



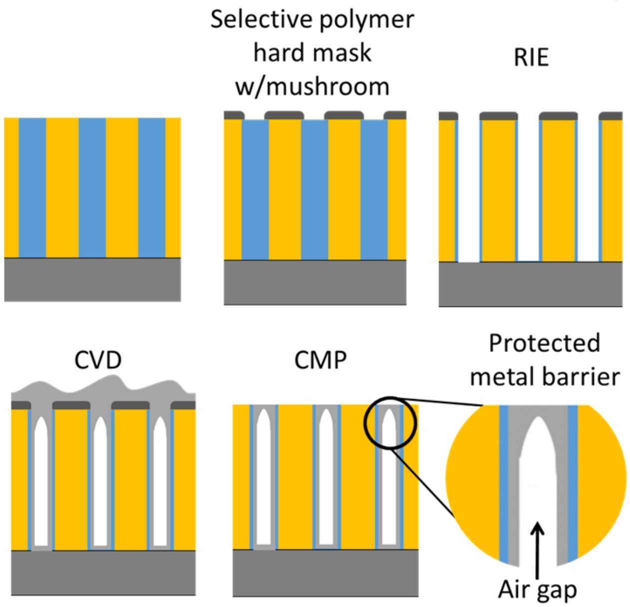
Fully Aligned Via (FAV) for Edge Placement Error (EPE)

G. Parsons, JVSTA 2019

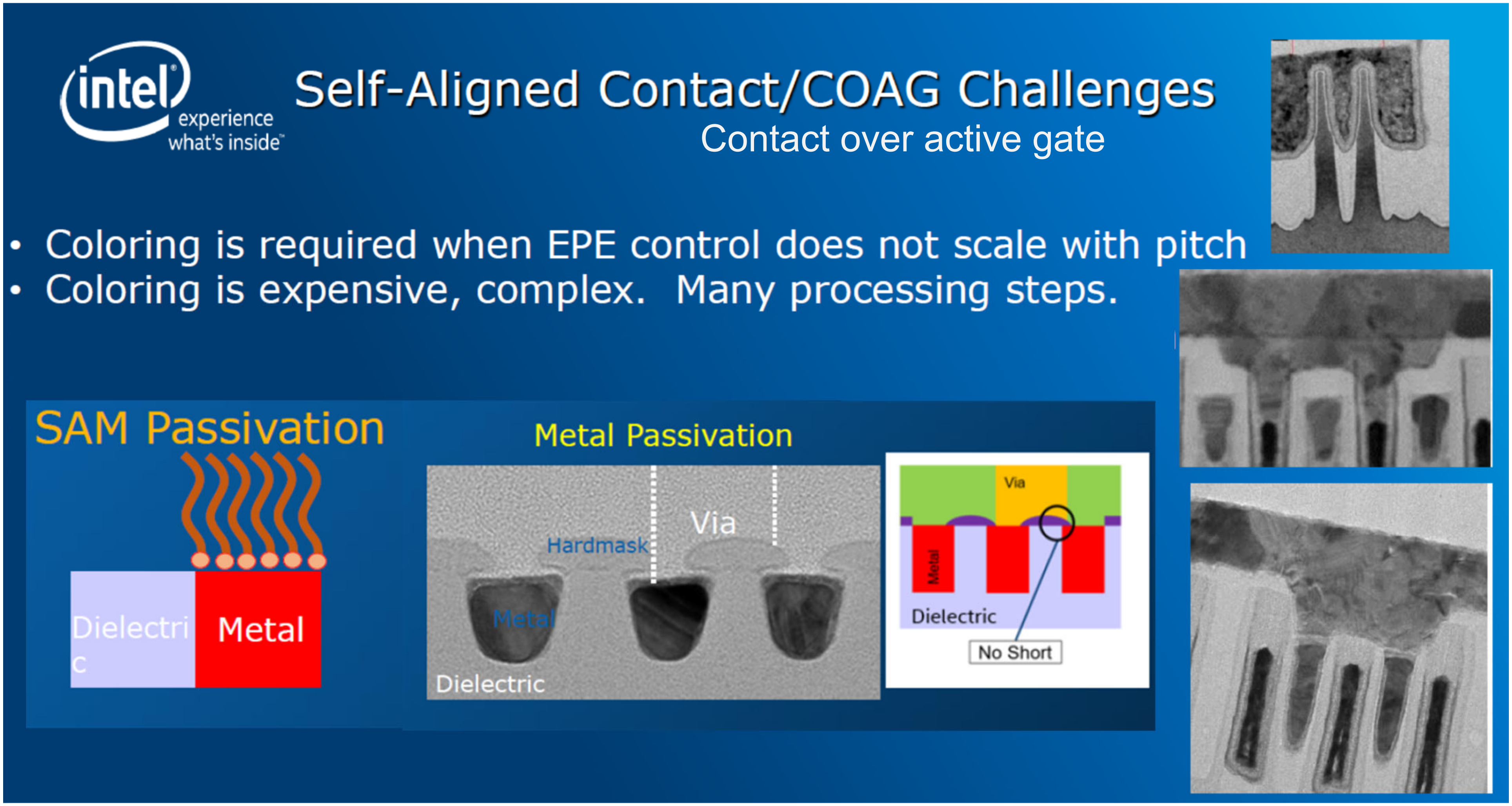


ASD before dual damascene reduces shorting risk

Selective Hard-Masks: Air Gap



- Self-Aligned Block
- Back-end super-via
- Buried power
- Resist augmentation…other….



Self-Aligned Contact/COAG Challenges

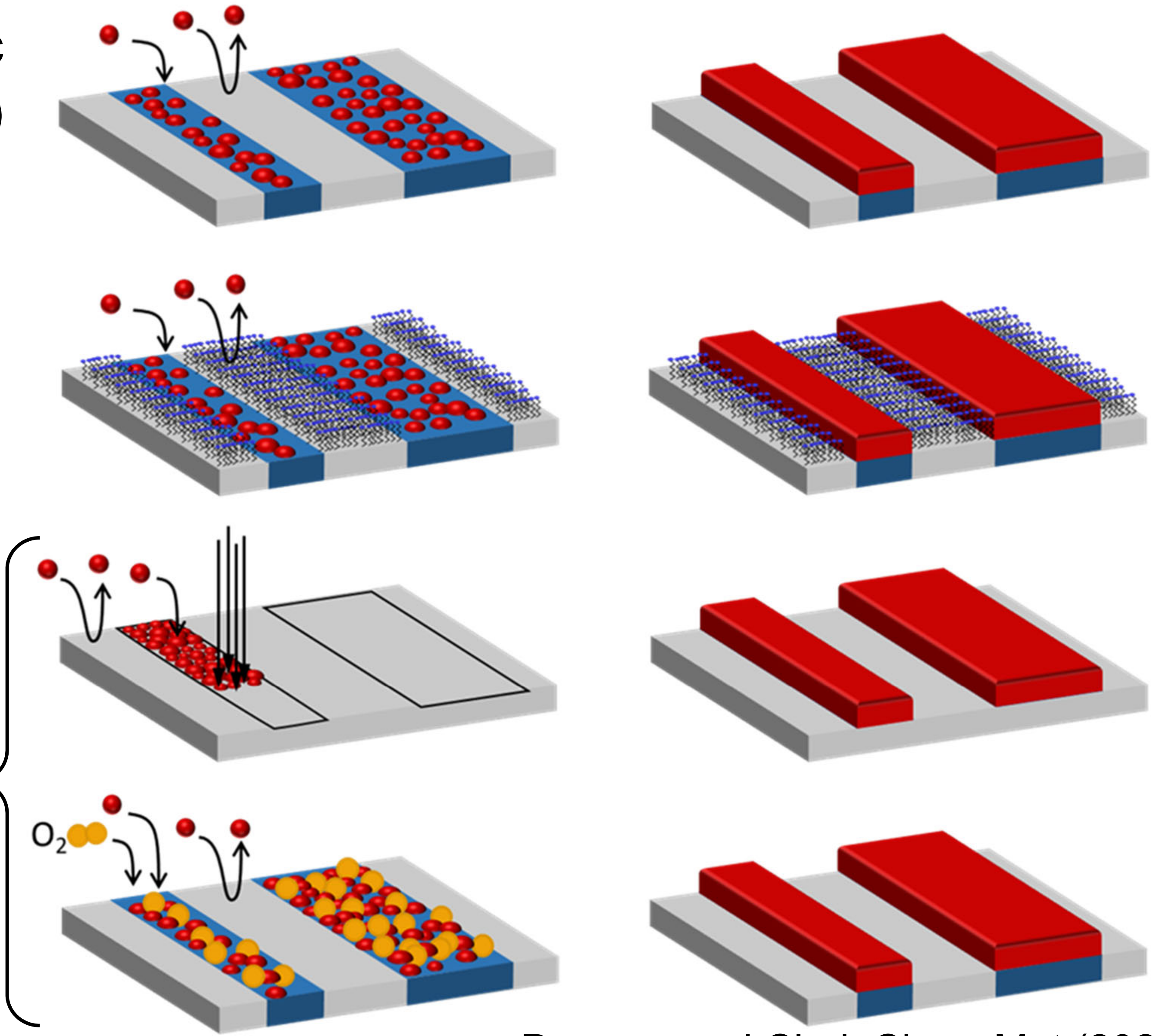
Contact over active gate

- Coloring is required when EPE control does not scale with pitch
- Coloring is expensive, complex. Many processing steps.

SAM Passivation

Metal Passivation

Approaches for Area-Selective Deposition



Intrinsic (clean)

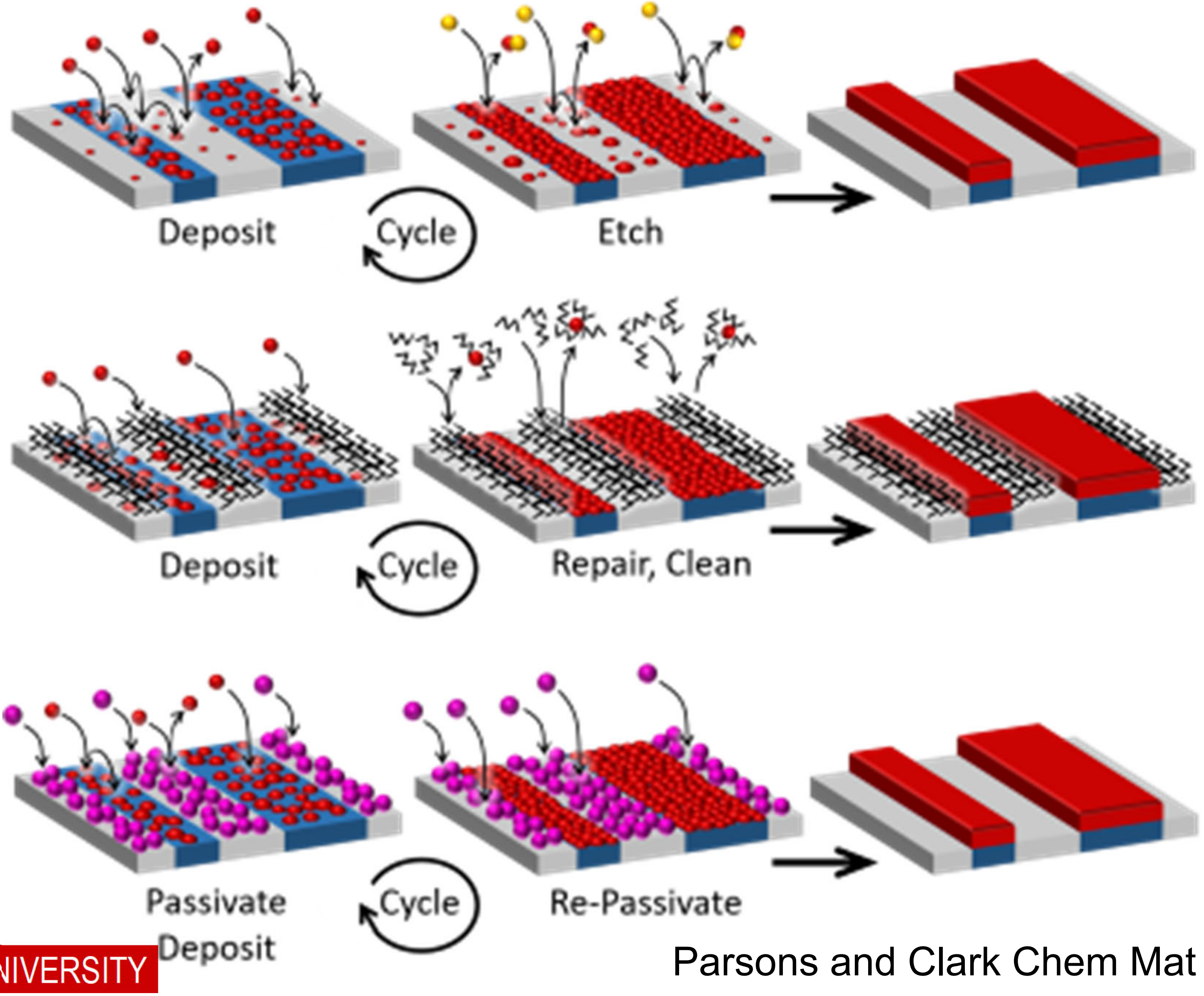
Passivated

Activated

Parsons and Clark Chem Mat (2020)

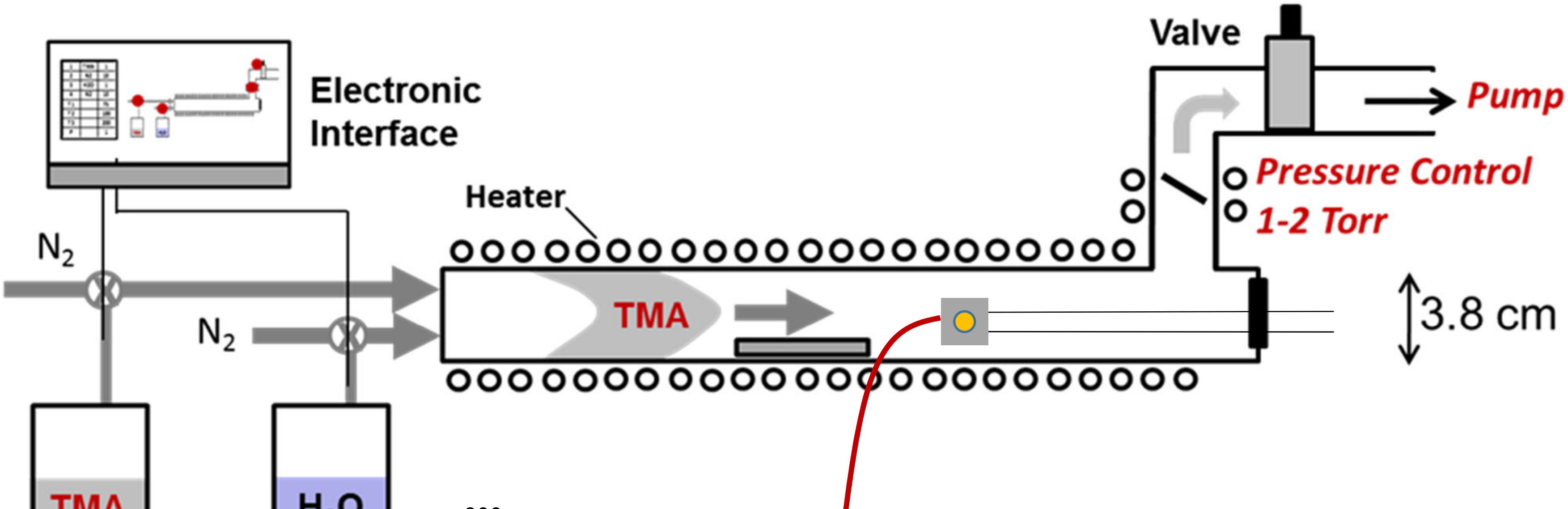
Approaches for Area-Selective Deposition

Multi-Step “Super-Cycle” Methods



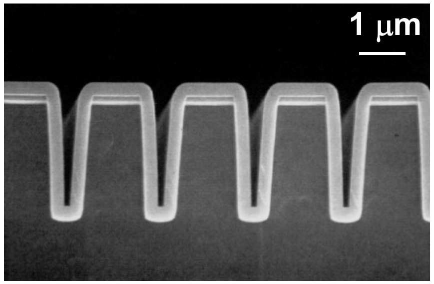
Parsons and Clark Chem Mat (2020)

Parsons Group: Lab-built ALD/ALE Reactors

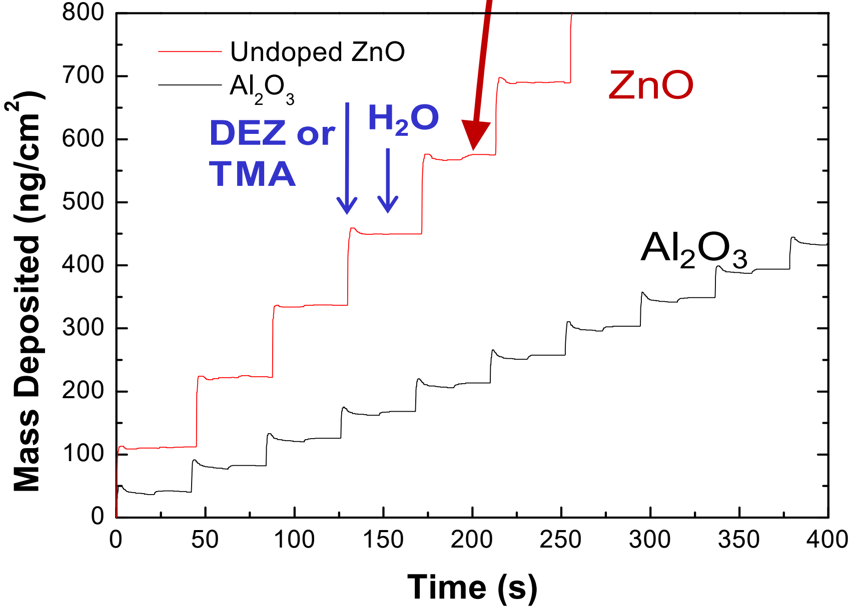


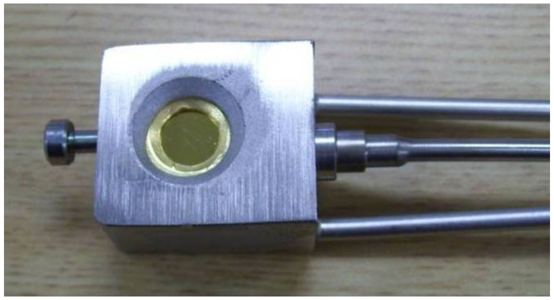
Trimethyl aluminum

Water



Ritala, M. et al., *Chem. Vap. Dep.* **5** 7 (1999)



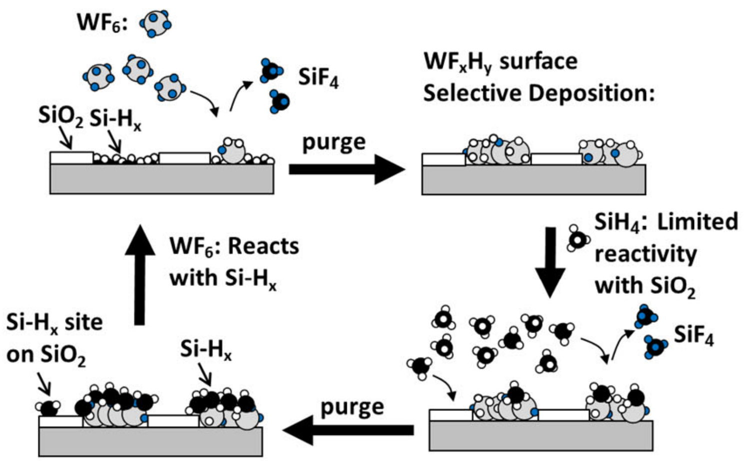


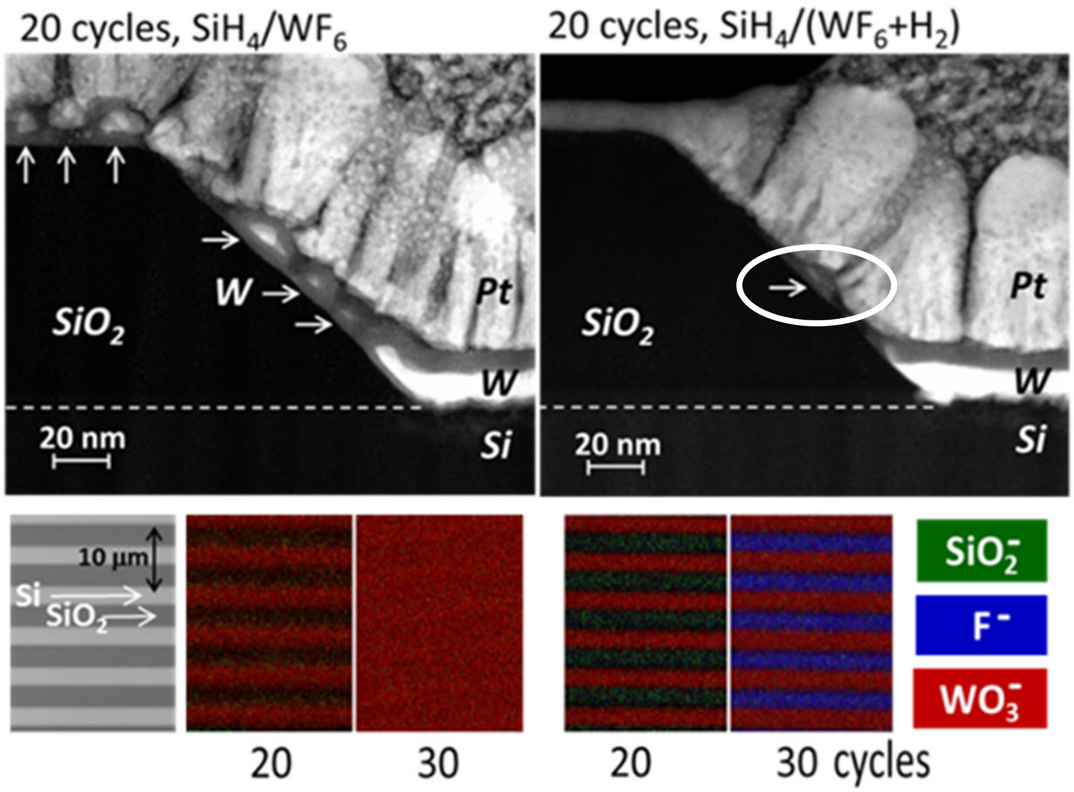
Quartz Crystal Microbalance

W ASD on Si-H vs SiO_2

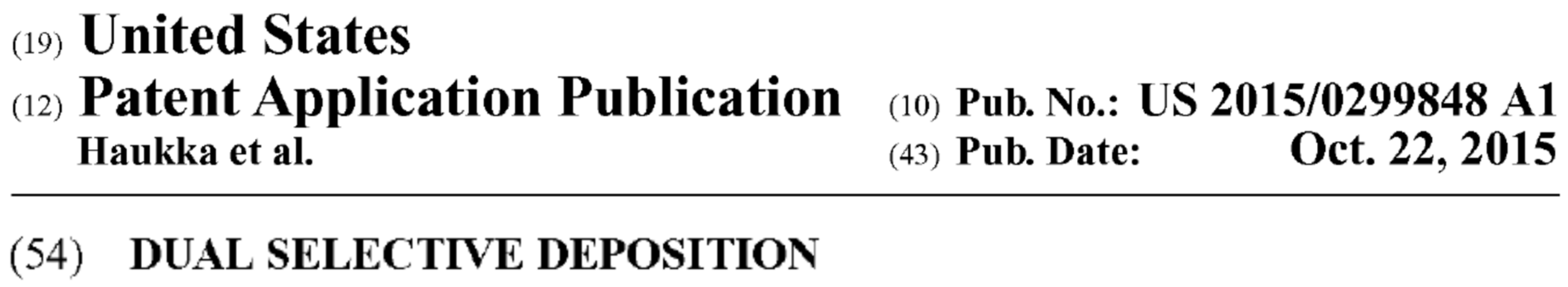
OVERVIEW OF RESEARCH

Project title: Selective Atomic Layer Deposition for Etch-Free Patterning
Investigators: Gregory N. Parsons
University: North Carolina State University
Topic: 2.4 Directed self-assembly of nanomaterials (etch-free patterning)
Date: Nov. 12, 2012





B. Kalanyan et al. Chem Mat (2016)

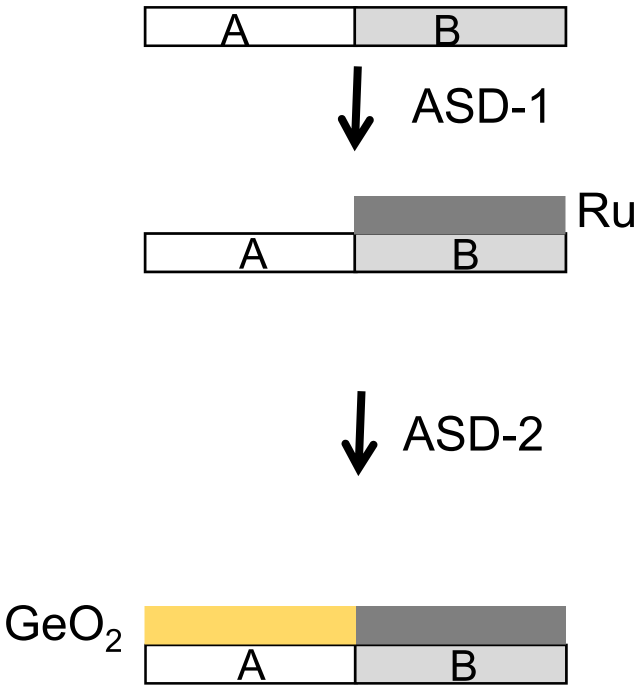


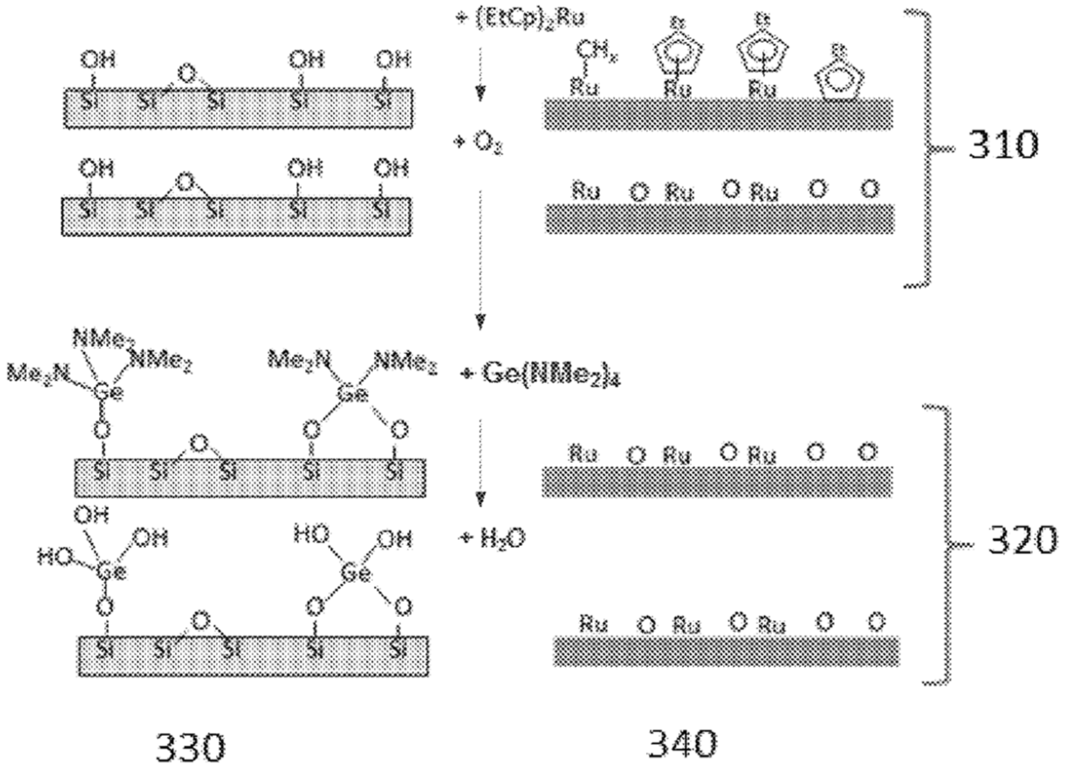
(19) **United States**
(12) **Patent Application Publication**
Haukka et al.

(10) **Pub. No.: US 2015/0299848 A1**
(43) **Pub. Date: Oct. 22, 2015**

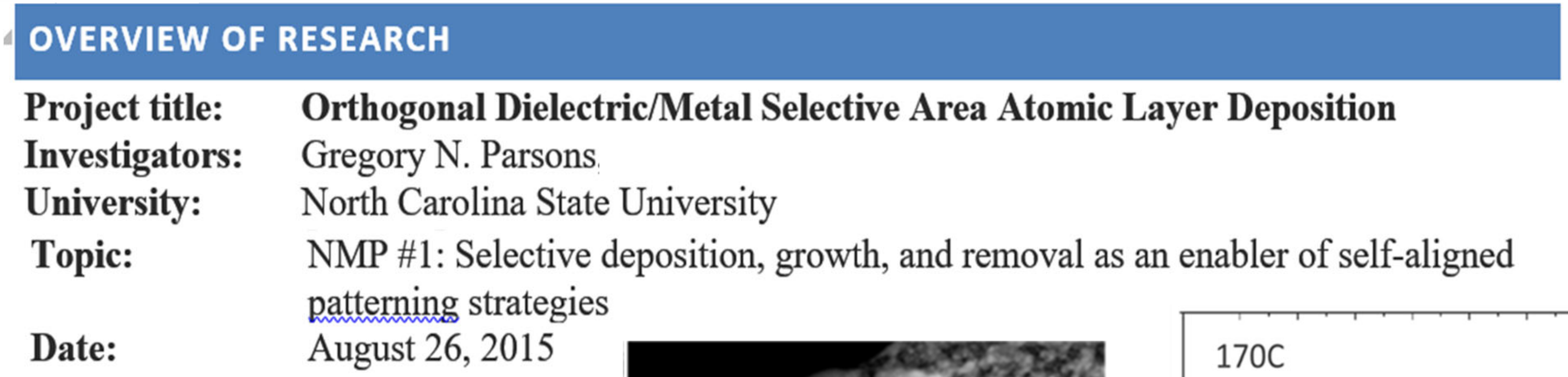
(54) **DUAL SELECTIVE DEPOSITION**

No data included in patent!



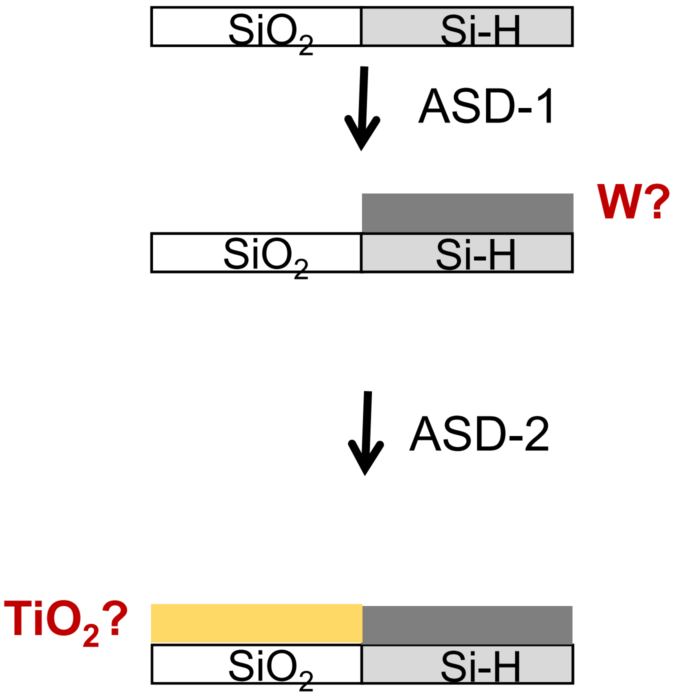


Idea



OVERVIEW OF RESEARCH

Project title: **Orthogonal Dielectric/Metal Selective Area Atomic Layer Deposition**
Investigators: Gregory N. Parsons
University: North Carolina State University
Topic: NMP #1: Selective deposition, growth, and removal as an enabler of self-aligned patterning strategies
Date: August 26, 2015



SiO_2 | Si-H

↓ ASD-1

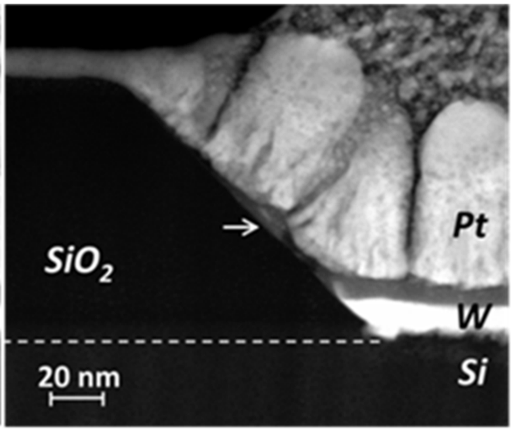
W?

SiO_2 | Si-H

↓ ASD-2

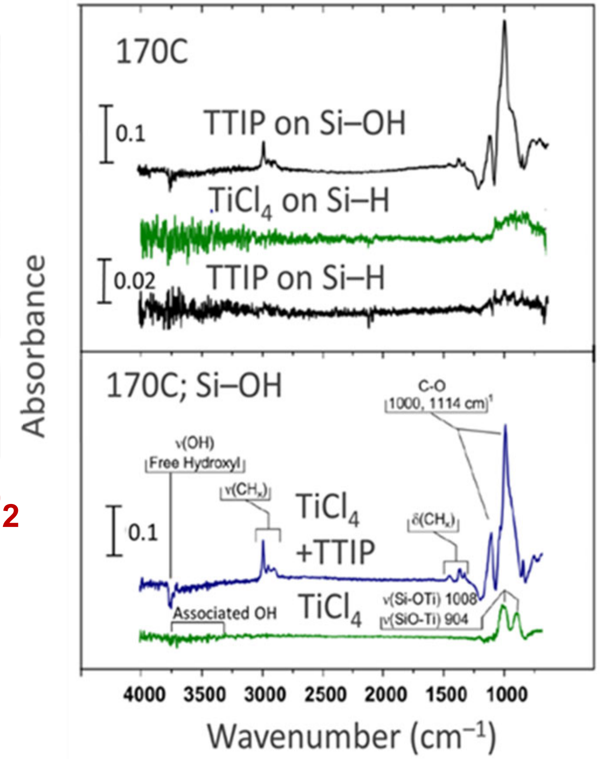
TiO_2?

SiO_2 | Si-H



W ASD on **Si-H vs SiO_2**
B. Kalanyan et al.
Chem Mat (2016)

“Metal-first” approach

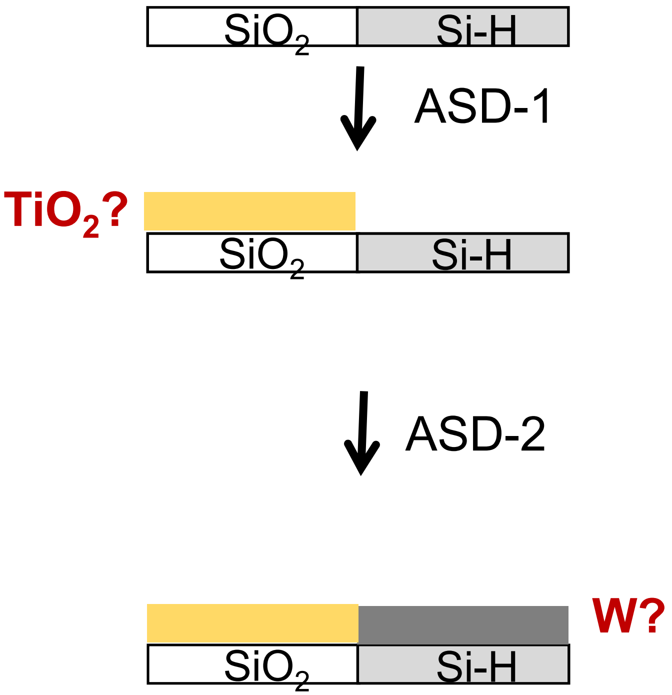


TiO_2 ASD on **SiO_2 vs Si-H**
S. Atanasov et al.
JVSTA (2016)

Idea

OVERVIEW OF RESEARCH

Project title: **Orthogonal Dielectric/Metal Selective Area Atomic Layer Deposition**
Investigators: Gregory N. Parsons
University: North Carolina State University
Topic: NMP #1: Selective deposition, growth, and removal as an enabler of self-aligned patterning strategies
Date: August 26, 2015


SiO_2 | Si-H

ASD-1

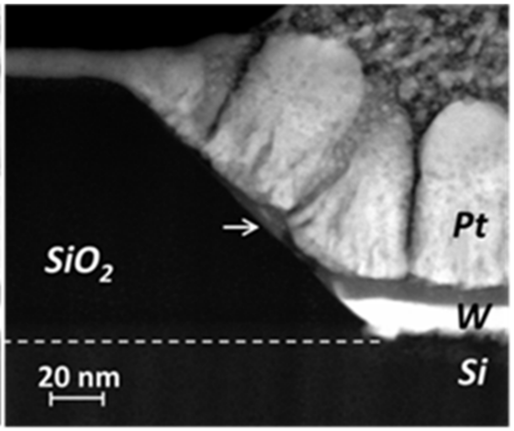
TiO_2?

SiO_2 | Si-H

ASD-2

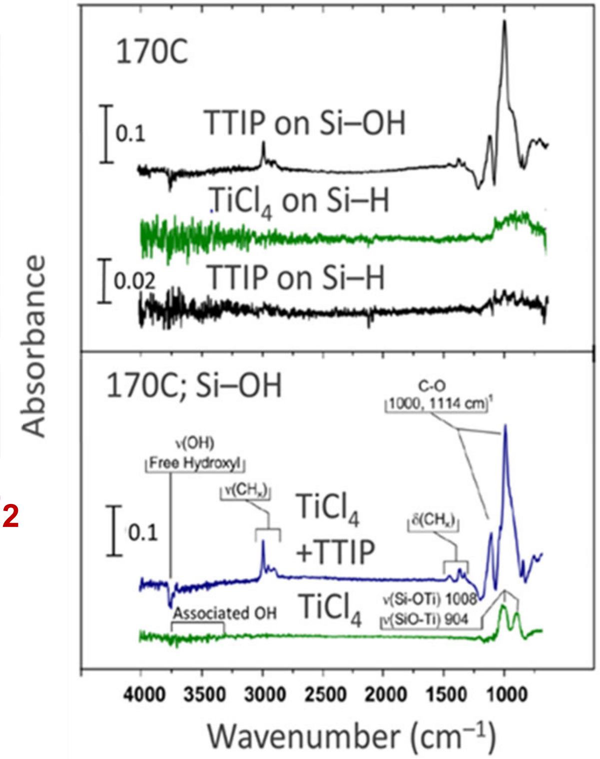
W?

SiO_2 | Si-H



W ASD on **Si-H vs SiO_2**
B. Kalanyan et al.
Chem Mat (2016)

"Dielectric-first" approach



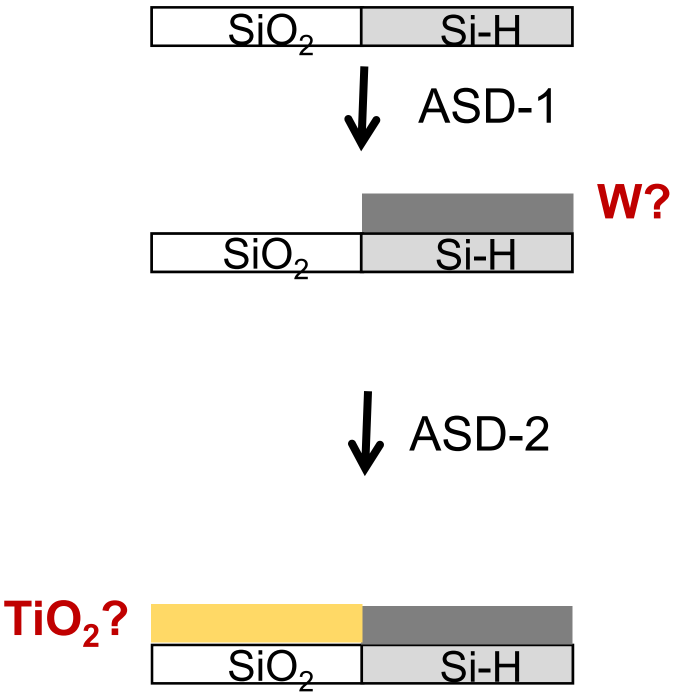
TiO_2 ASD on **SiO_2 vs Si-H**

S. Atanasov et al.
JVSTA (2016)

Success Criteria

1. Create new knowledge about surface reaction processes important for ASD
2. Achieve orthogonal ASD of two materials side-by-side (W and TiO_2) with thickness of 5-10 nm each
3. Build up multiple orthogonal layers, ideally 3 or more layers of each ASD material.

“Metal-First” Approach



SiO_2 | Si-H

ASD-1

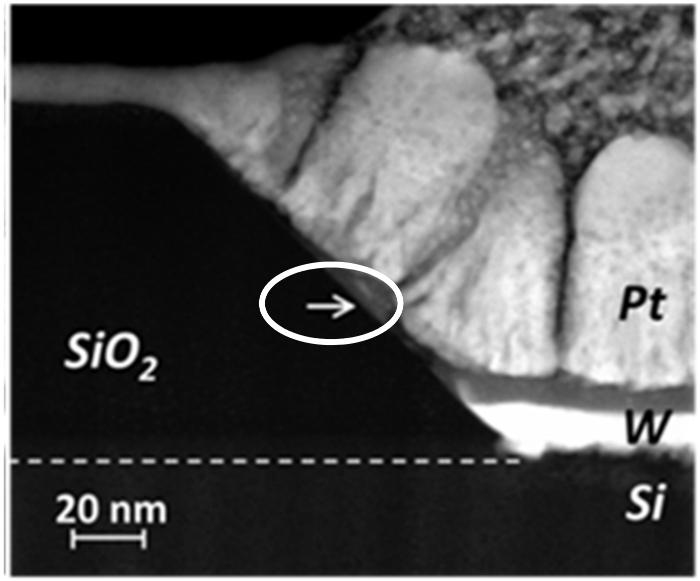
W?

SiO_2 | Si-H

ASD-2

TiO_2?

SiO_2 | Si-H



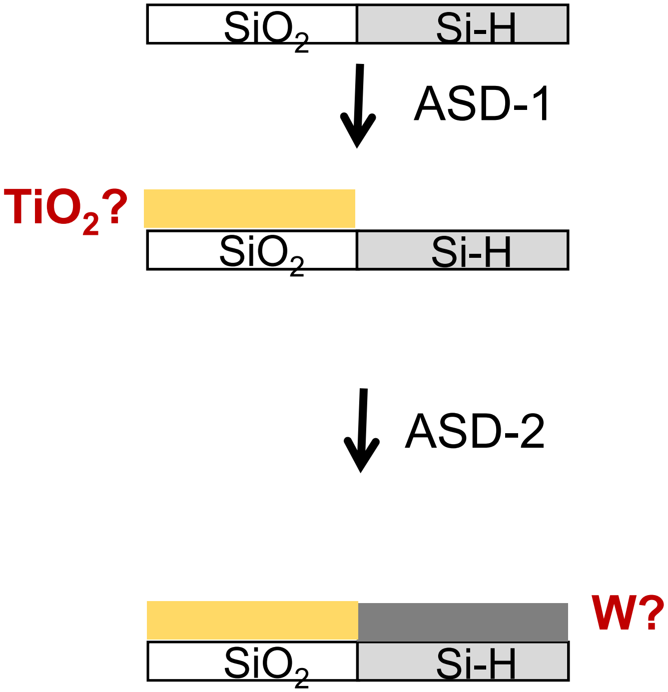
> 10 nm

W ASD on **Si-H vs SiO_2**

TiO_2 grows readily on W

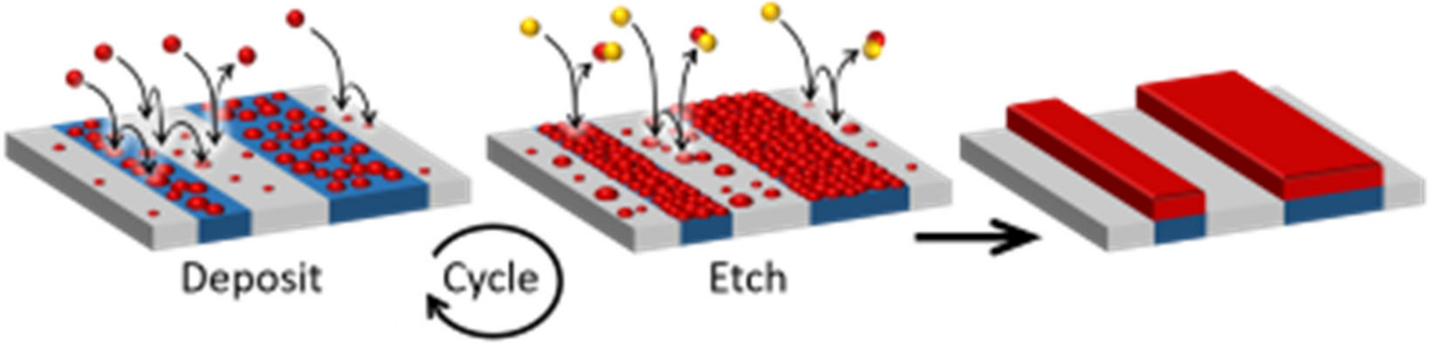
Failure

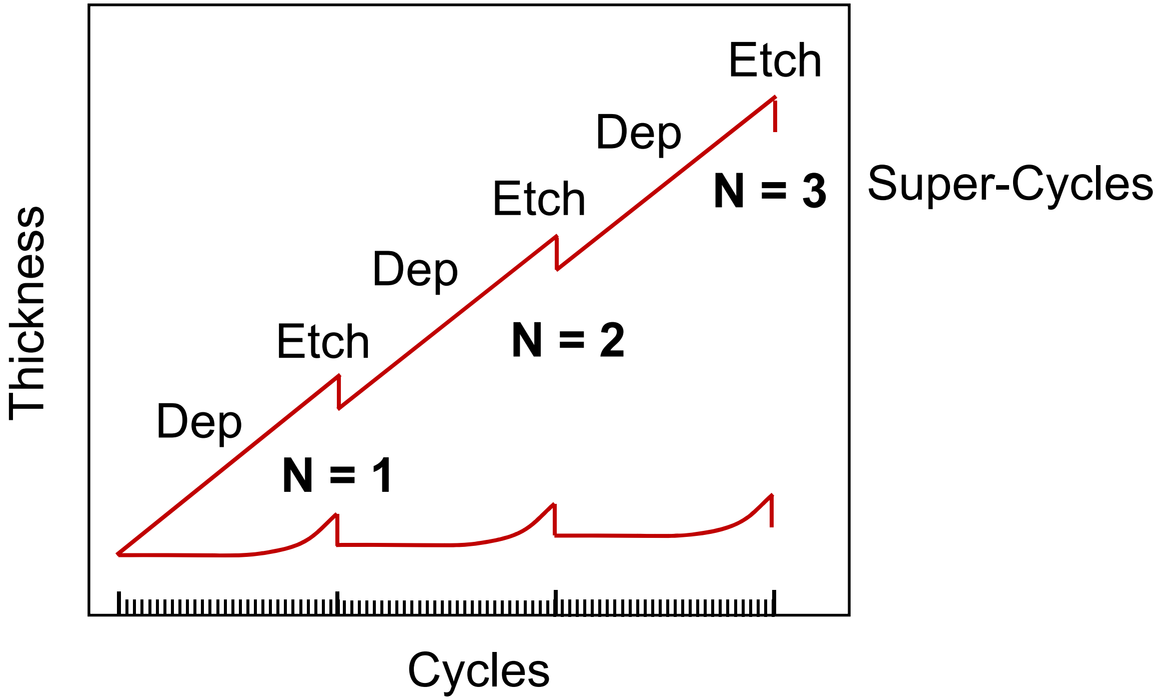
“Dielectric-First” Approach



Approaches for Area-Selective Deposition

Multi-Step "Super-Cycle" Methods



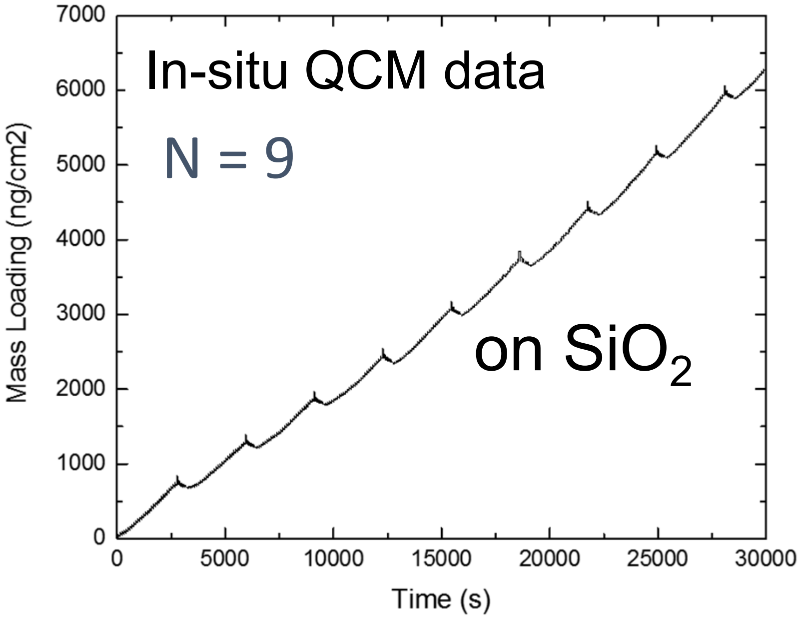


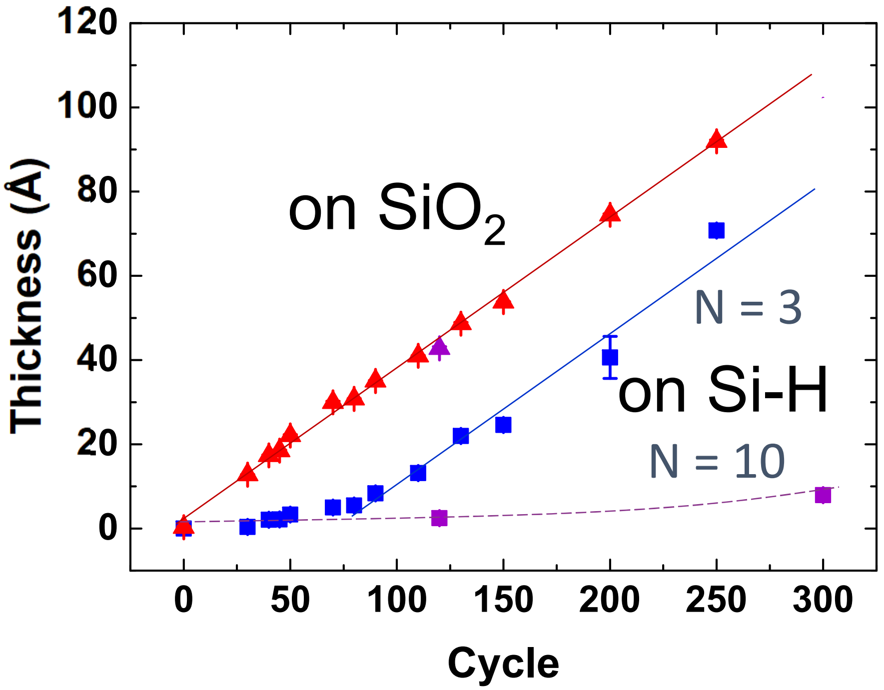
NC STATE UNIVERSITY

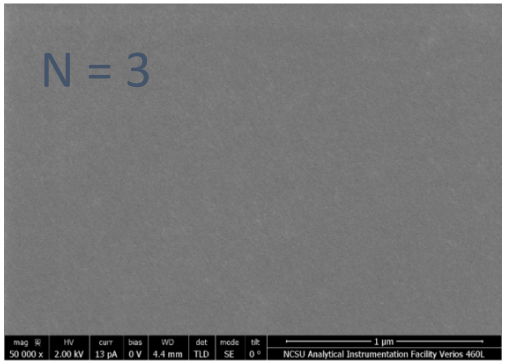
TiO$_2$ ALD + ALE → ASD on SiO$_2$ vs Si-H

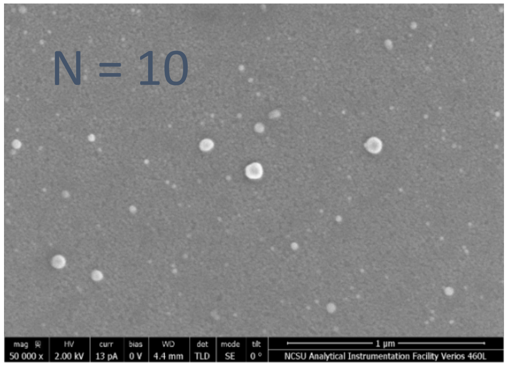
[30x(TiCl$_4$/H$_2$O) + 5x(WF$_6$/BCl$_3$)] x N =10

2017

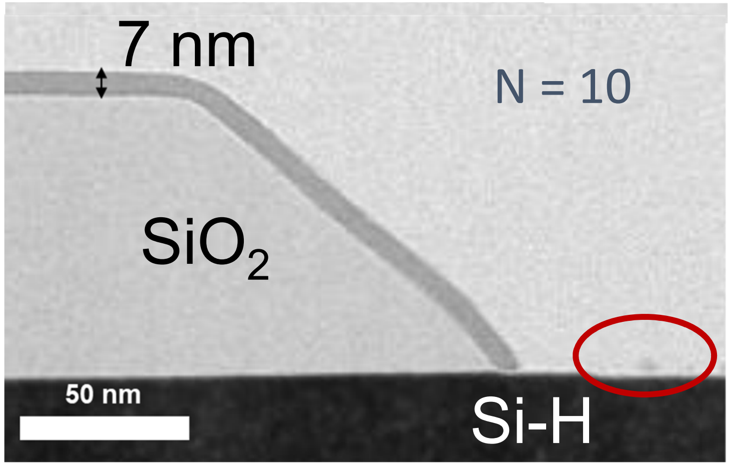




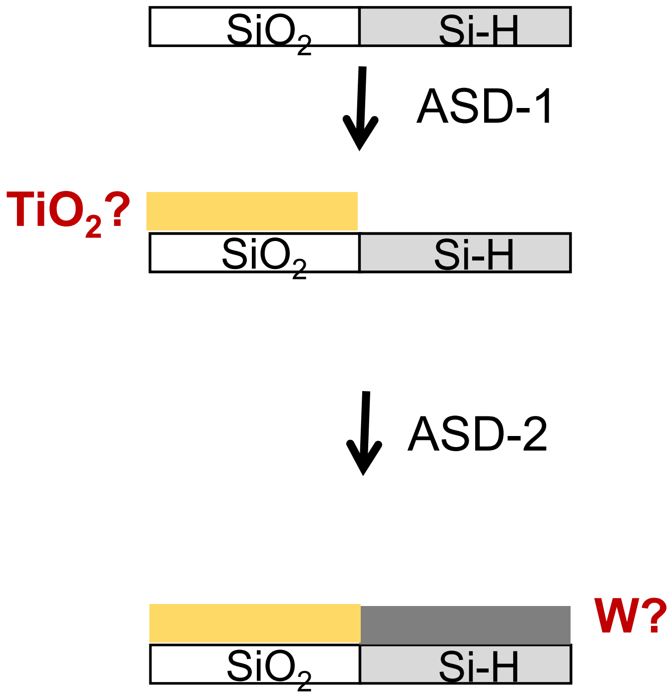




SK Song et al. Chem Mat (2019)



"Dielectric-First" Approach



SiO_2 Si-H

ASD-1

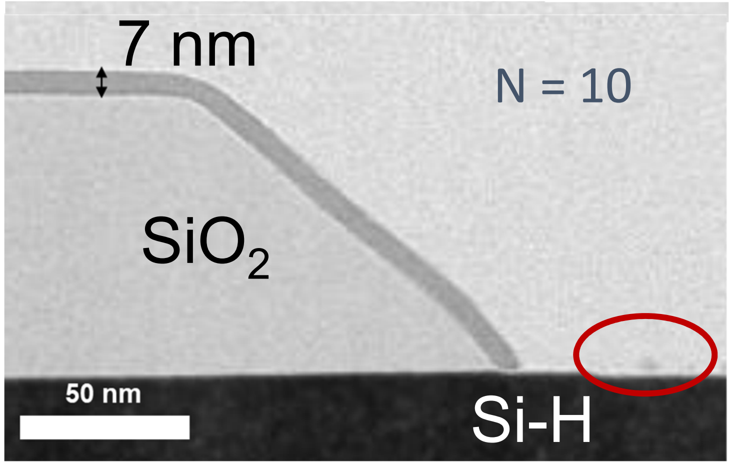
TiO_2?

SiO_2 Si-H

ASD-2

W?

SiO_2 Si-H

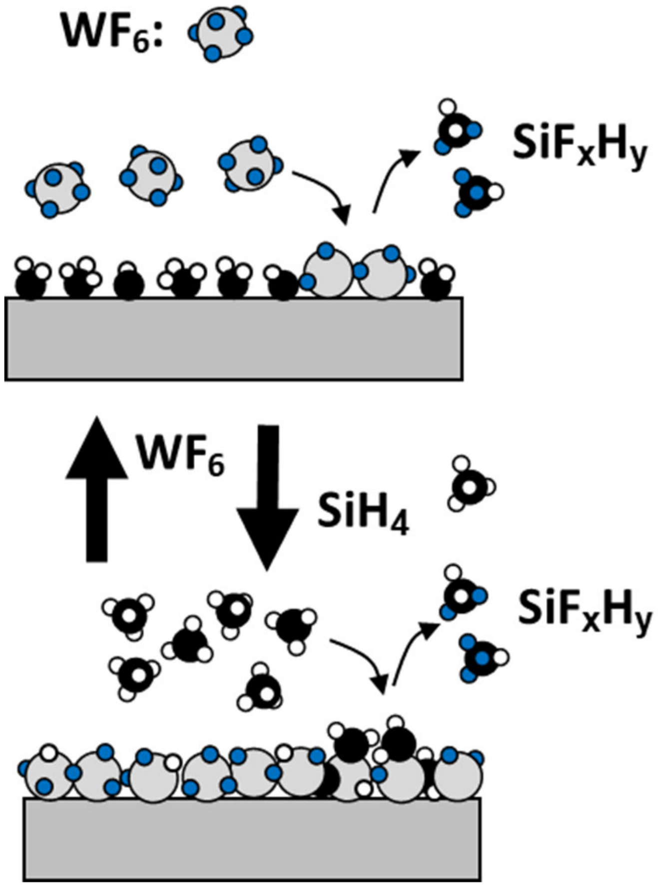


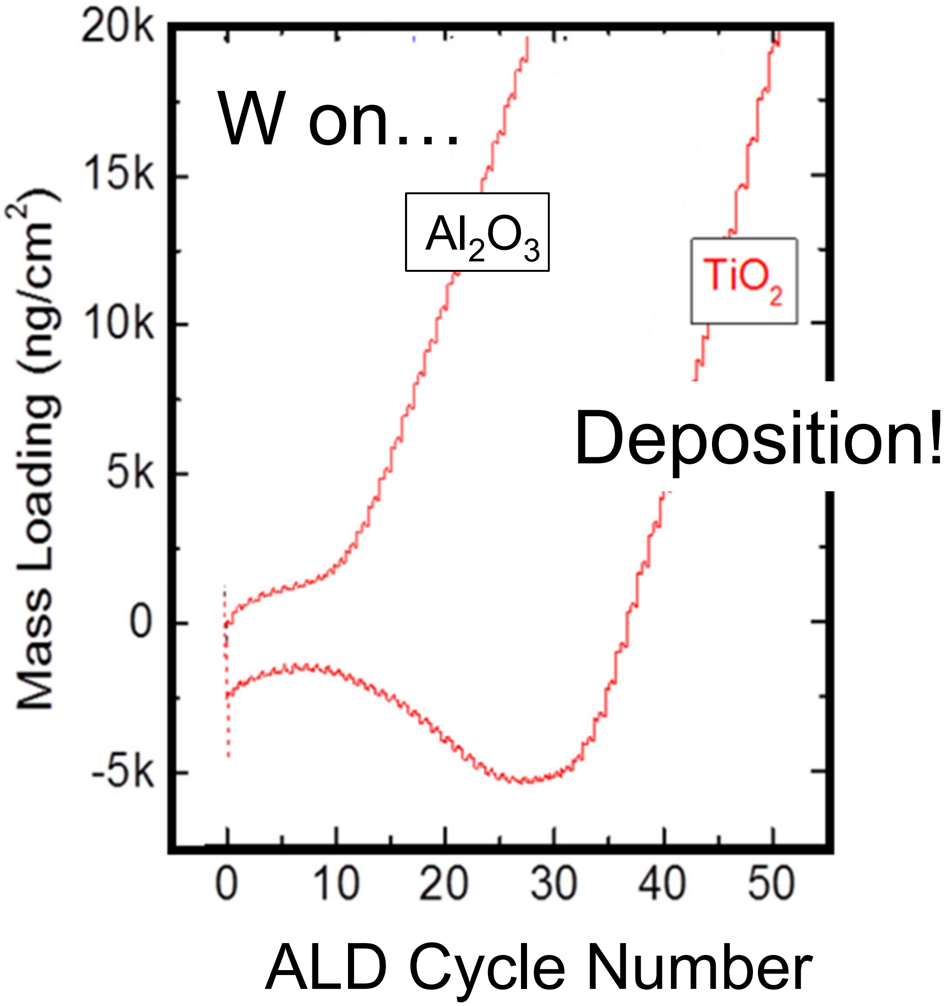
~ 7 nm

TiO_2 ASD on **SiO_2 vs Si-H**

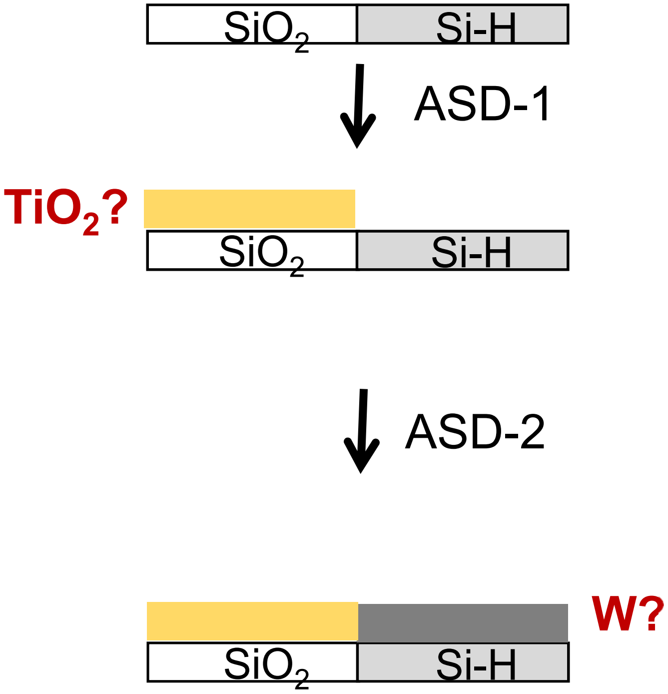
W growth on TiO_2?

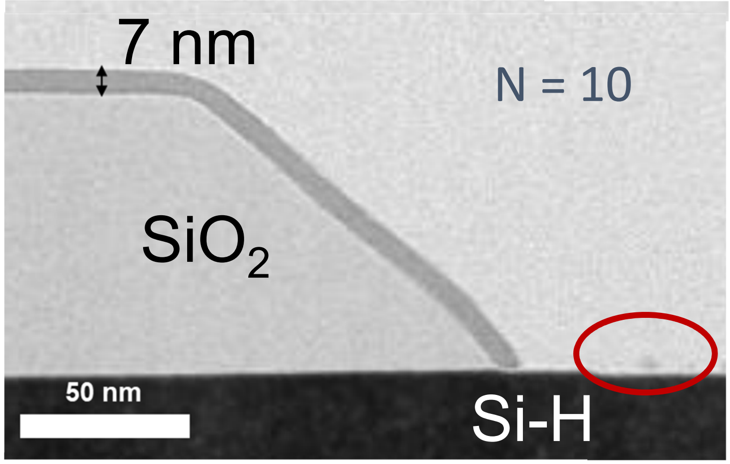
W ASD on Si-H vs TiO_2?

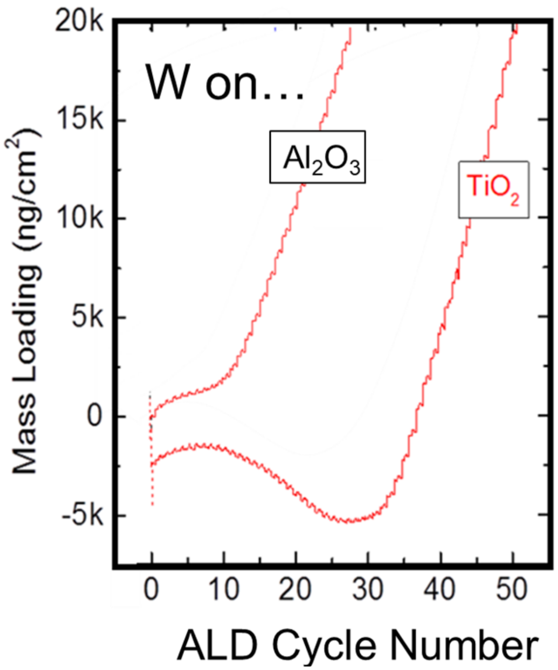




“Dielectric-First” Approach





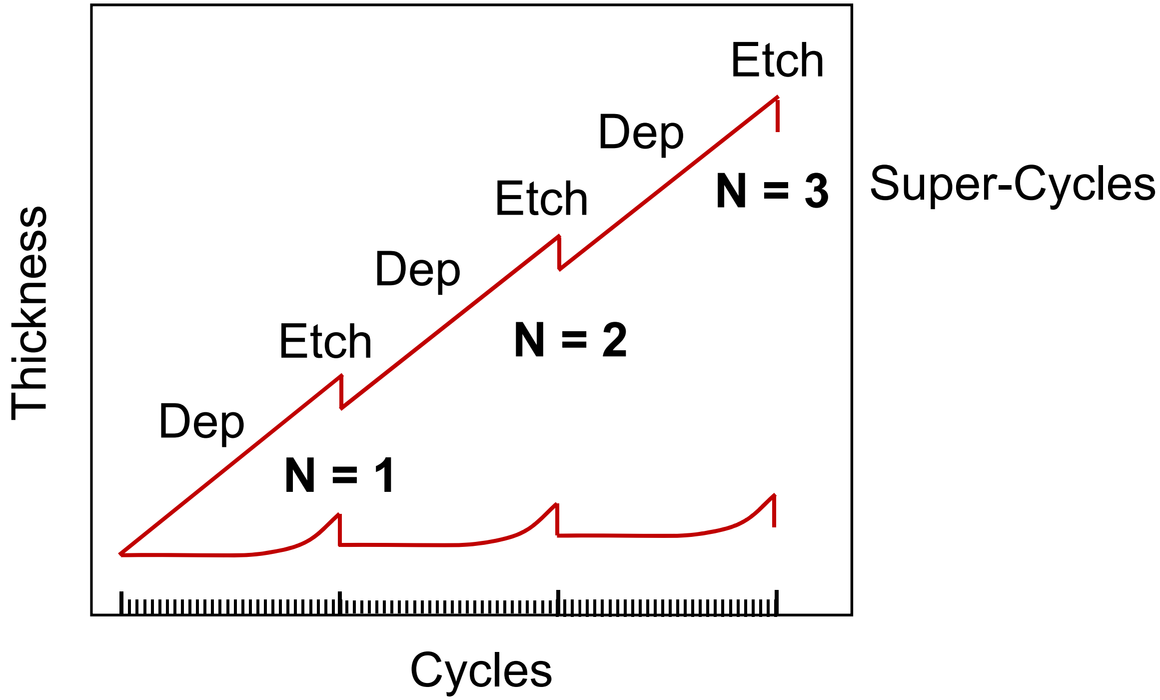


W grows on TiO_2

Failure

What about W ASD via ALD + ALE?

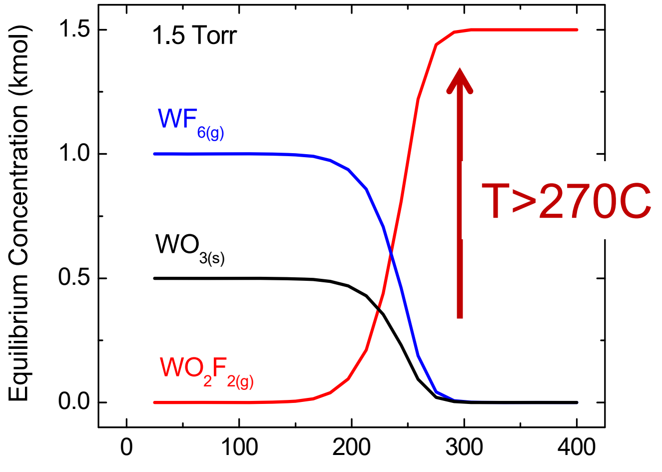
- If we can do W ASD using ALD+ALE, then maybe dielectric first approach could work



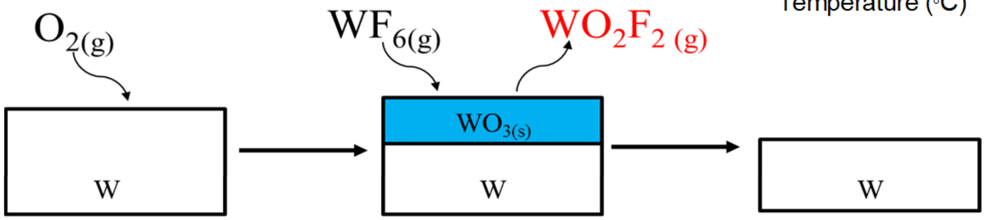
- Need ALE method for W

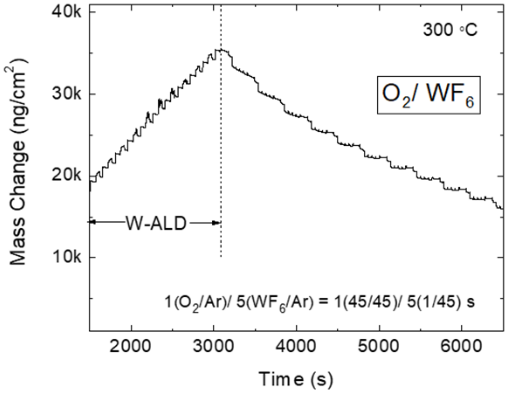
Thermodynamics of Tungsten ALE

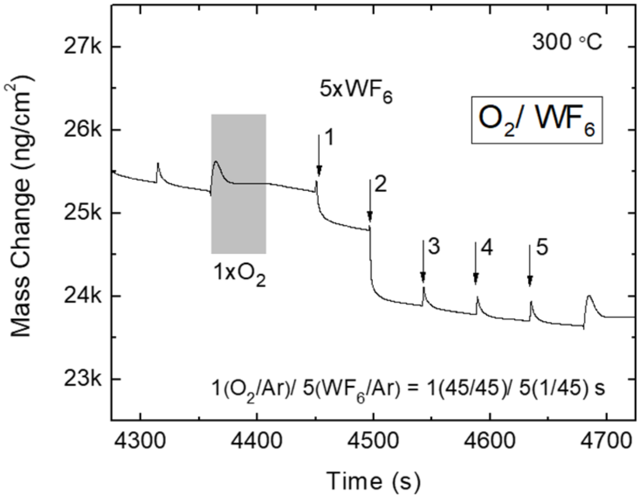
- **Thermochemistry modeling**
  - WO_3(s): oxidized W product
  - WO_2F_2(g): etch product
  - T ≥ 150 °C: WO_2F_2 formed
  - T → 300 °C: WO_3 completely reacted
  - Also works with ozone



- **Two-step thermal W ALE**







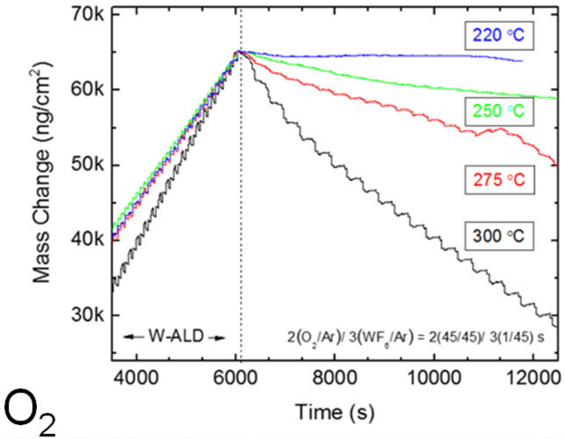
Wenyi Xie et al. JVST A (2020)

W: ALD + ALE = Poor ASD

Good W ALE: O_2/WF_6 at 275C

2018 O_2/WCl_6 at 220C

Wenyi Xie

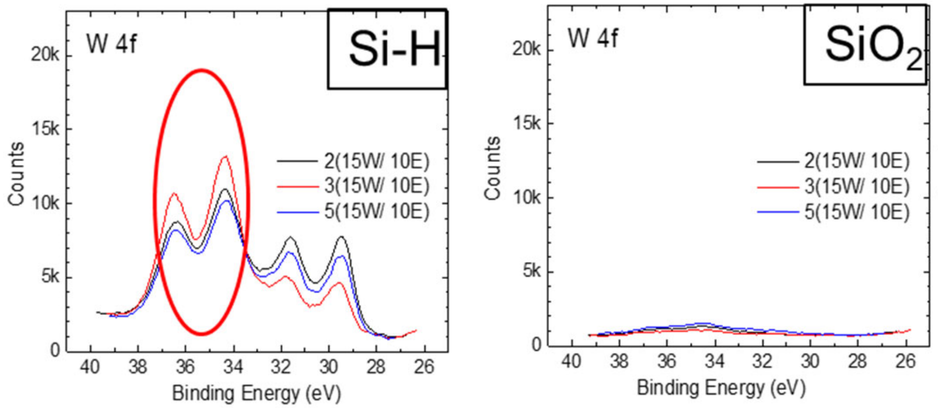


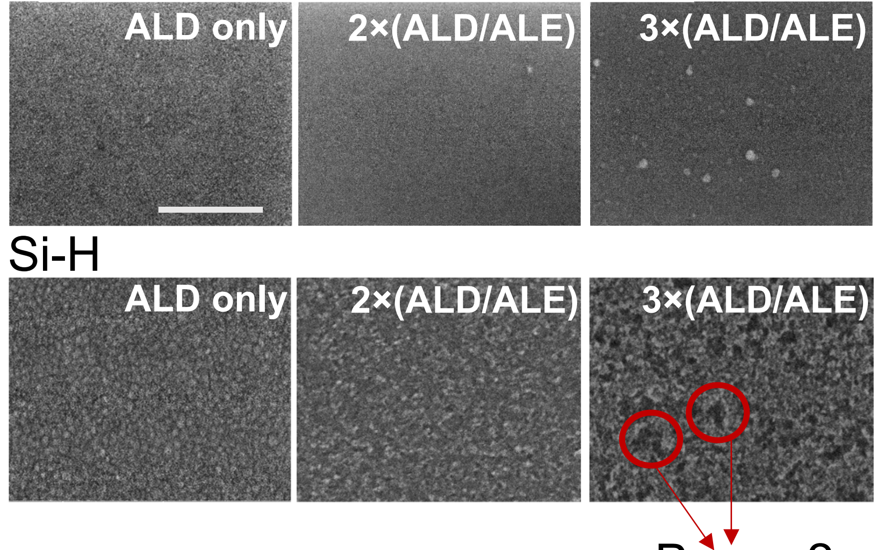
Wenyi Xie & Justin Kim **2019**

Not published

ALD+ALE Super-cycles:

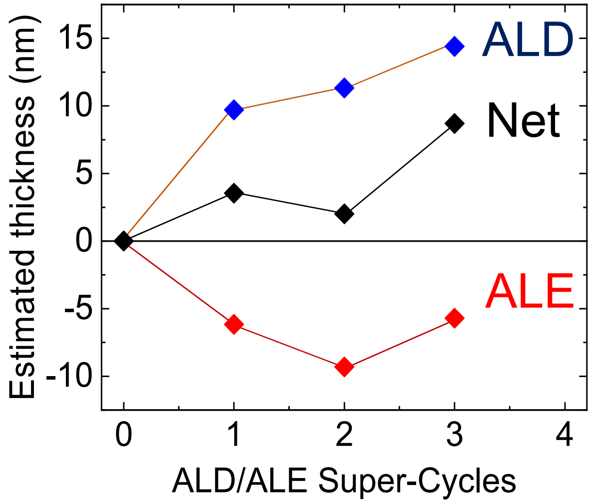
W growth slows on Si-H, ALE slows on SiO_2





Porous?

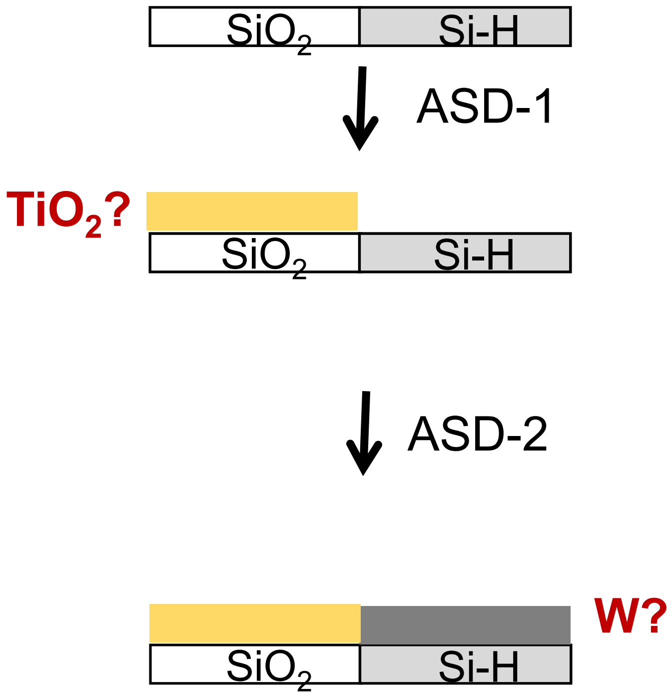
ALD, ALE Rates Inconsistent

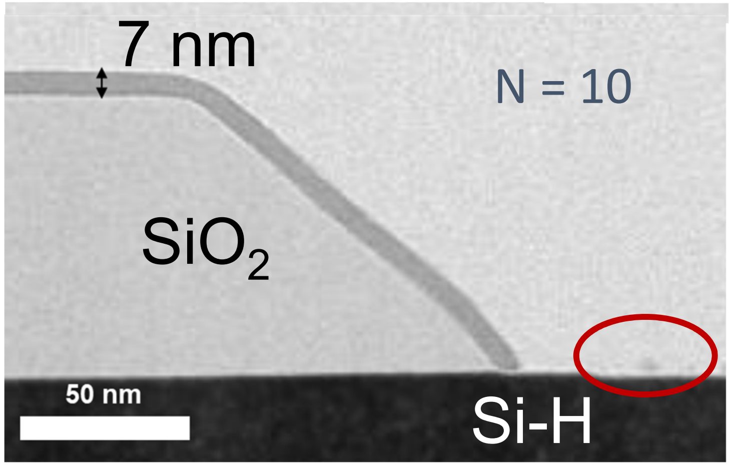


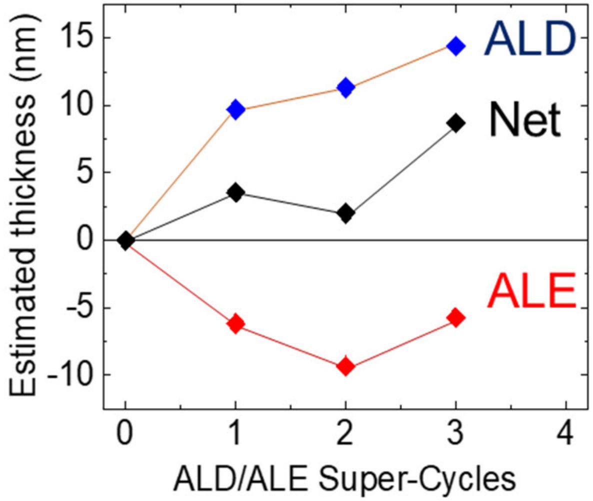
Wenyi Xie & Justin Kim (unpublished)

NC STATE UNIVERSITY

"Dielectric-First" Approach – 2nd try





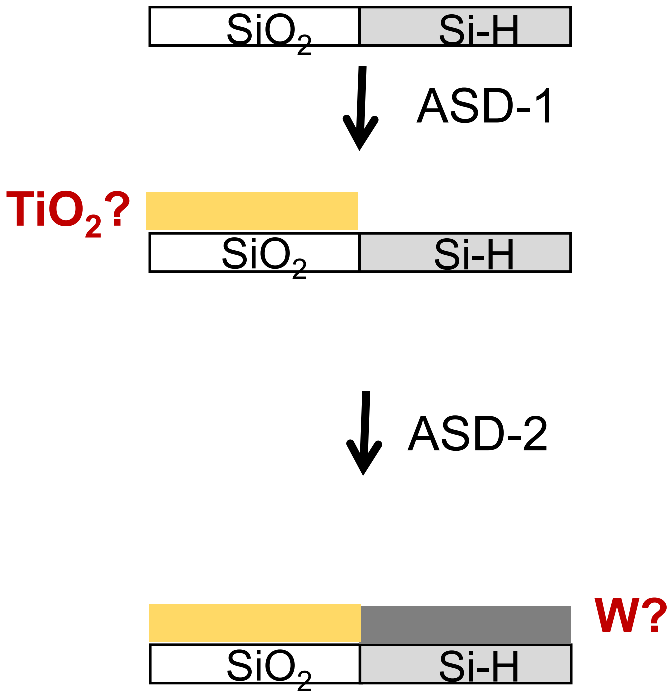


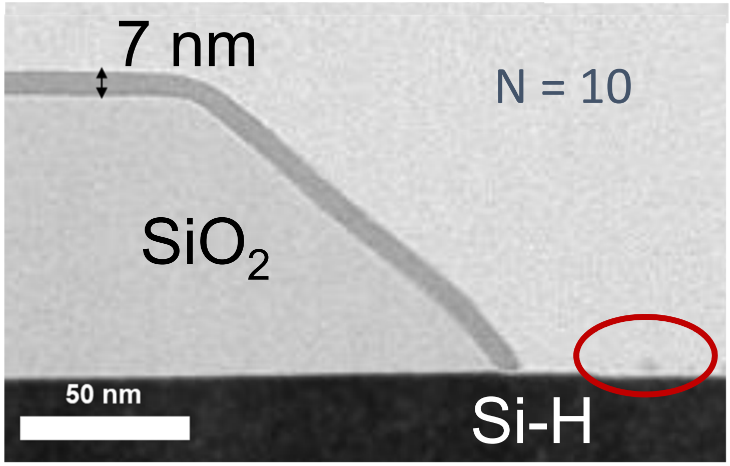
W ASD vis ALD+ ALE doesn't work

Failure

Wenyi Xie & Justin Kim (unpublished)

“Dielectric-First” Approach – 3rd try



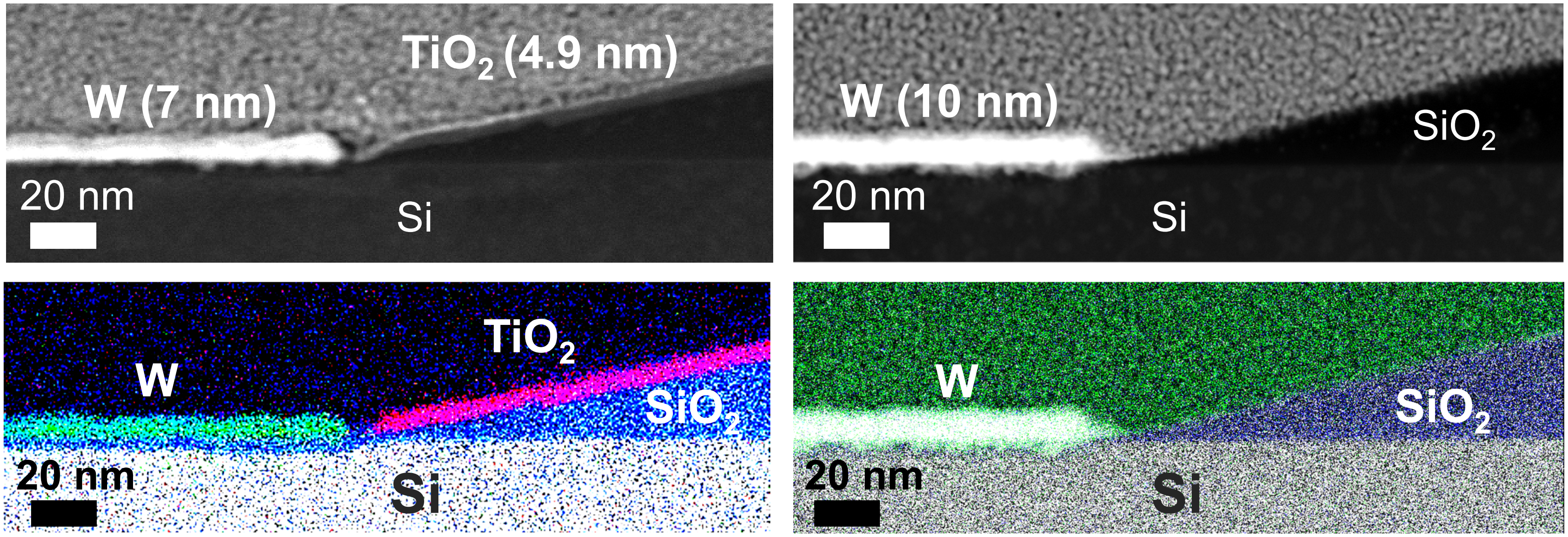


Last chance:

- Do W ALD on TiO_2/Si-H and check nucleation/growth

"Dielectric-First" Approach – 3rd try

TiO_2 ASD @150°C + W ASD @220°C

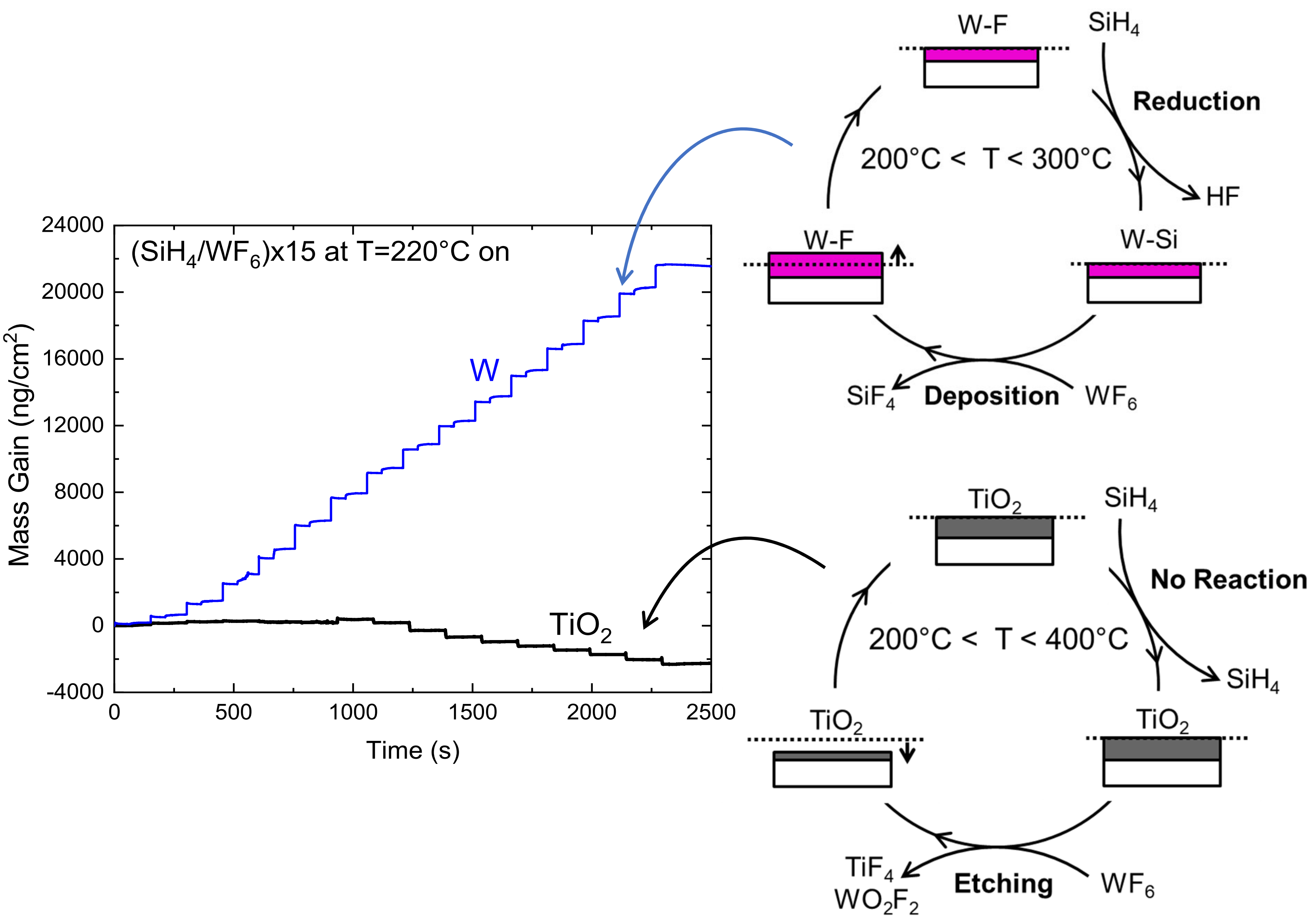


Looks Good!

What is happening?

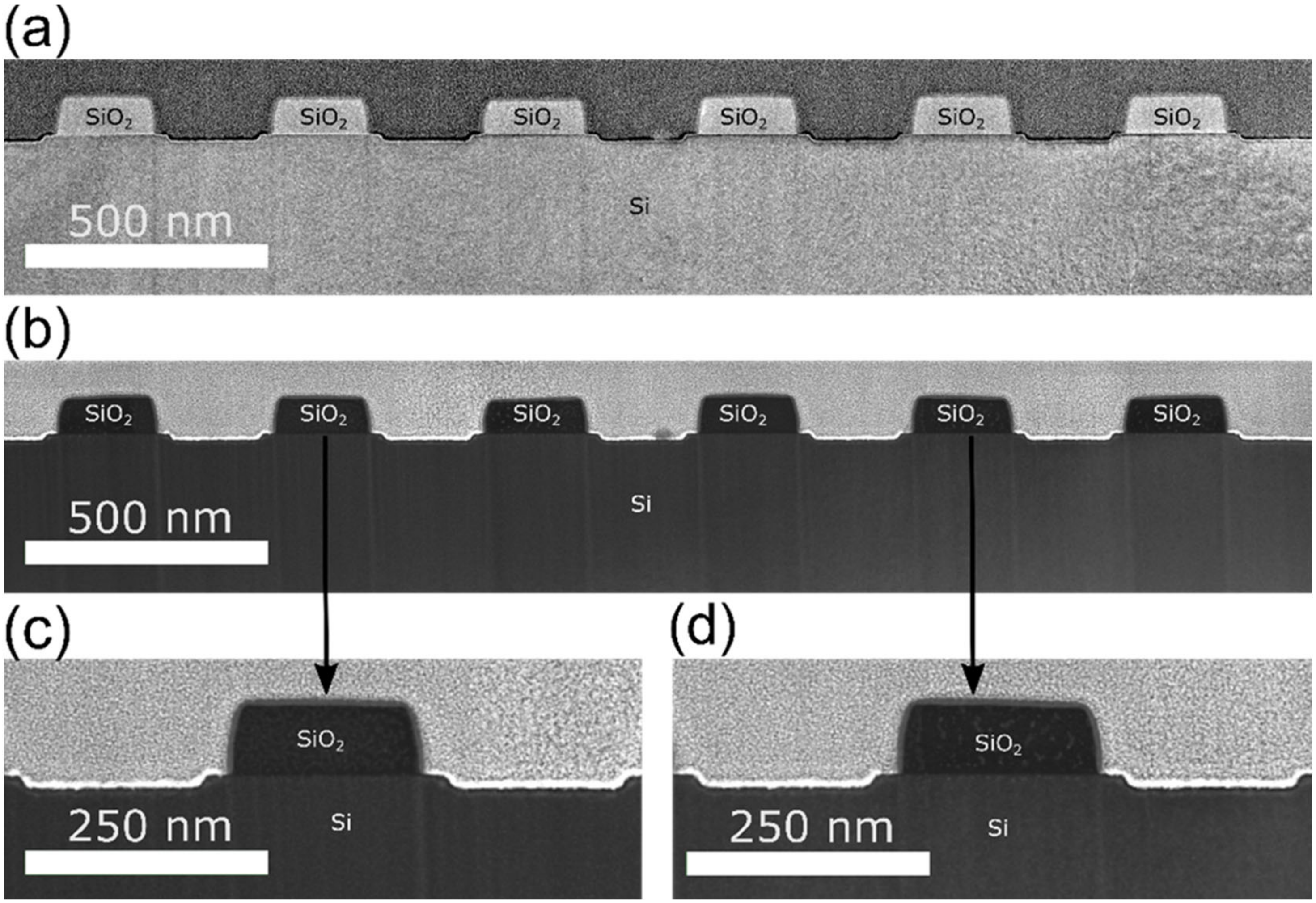
SK Song, J-S Kim et al. ACS Nano (2021)

ASD *via* Simultaneous Adjacent Deposition and Etching



SK Song, J-S Kim et al. ACS Nano (2021)

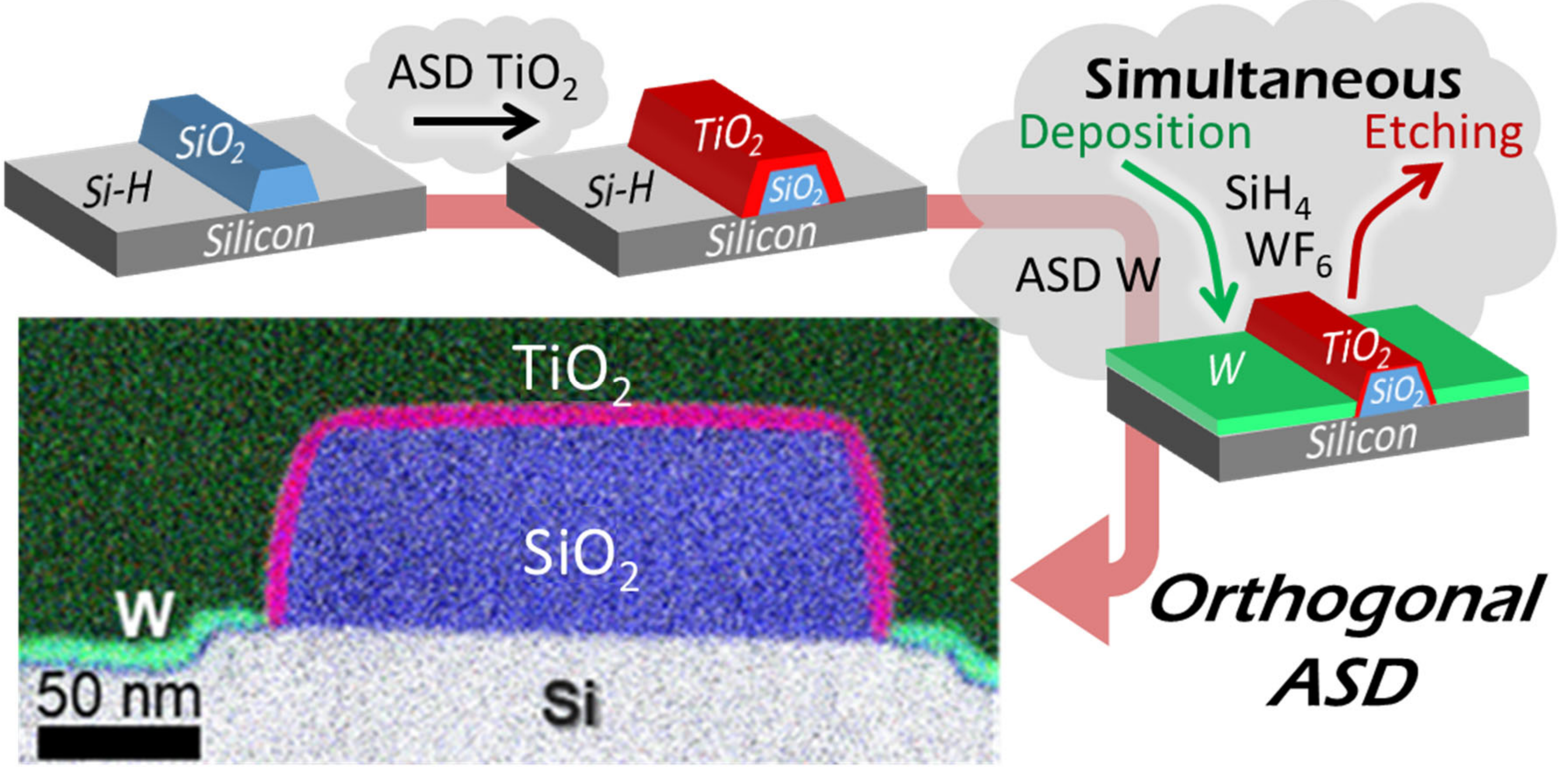
ASD *via* Simultaneous Adjacent Deposition and Etching



SK Song, J-S Kim et al. ACS Nano (2021)

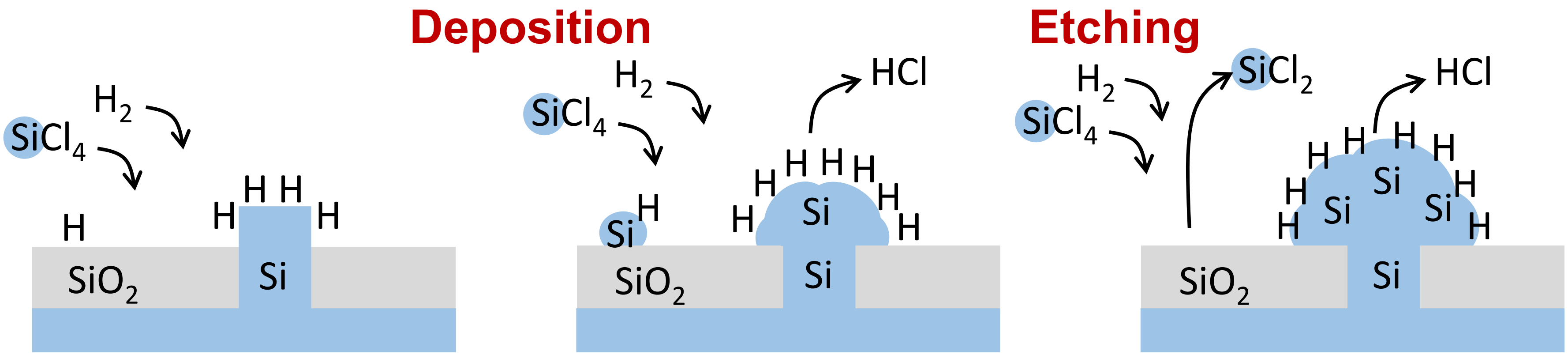
NC STATE UNIVERSITY

ASD *via* Simultaneous Adjacent Deposition and Etching



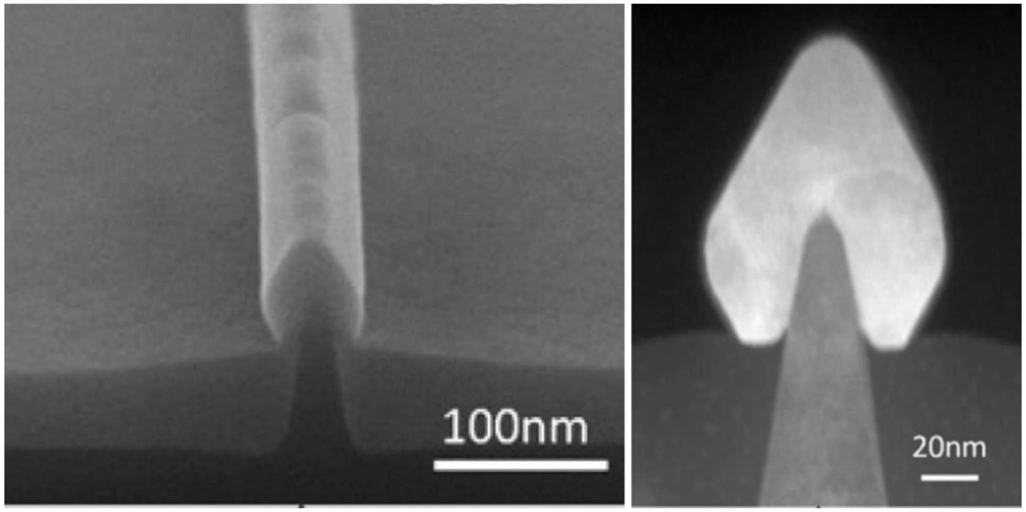
SK Song, J-S Kim et al. ACS Nano (2021)

Selective Si, SiGe Epitaxy: High Temperature, > 700°C



- ASD controlled by reaction thermodynamics
- Deposition precursor is also an etch reactant
- Analogous to our process, T<300°C

G. Wang et al., *Microelectron. Eng*. (2016)



Alternate Possible Low T ASD Materials

SRC Task 3036.001

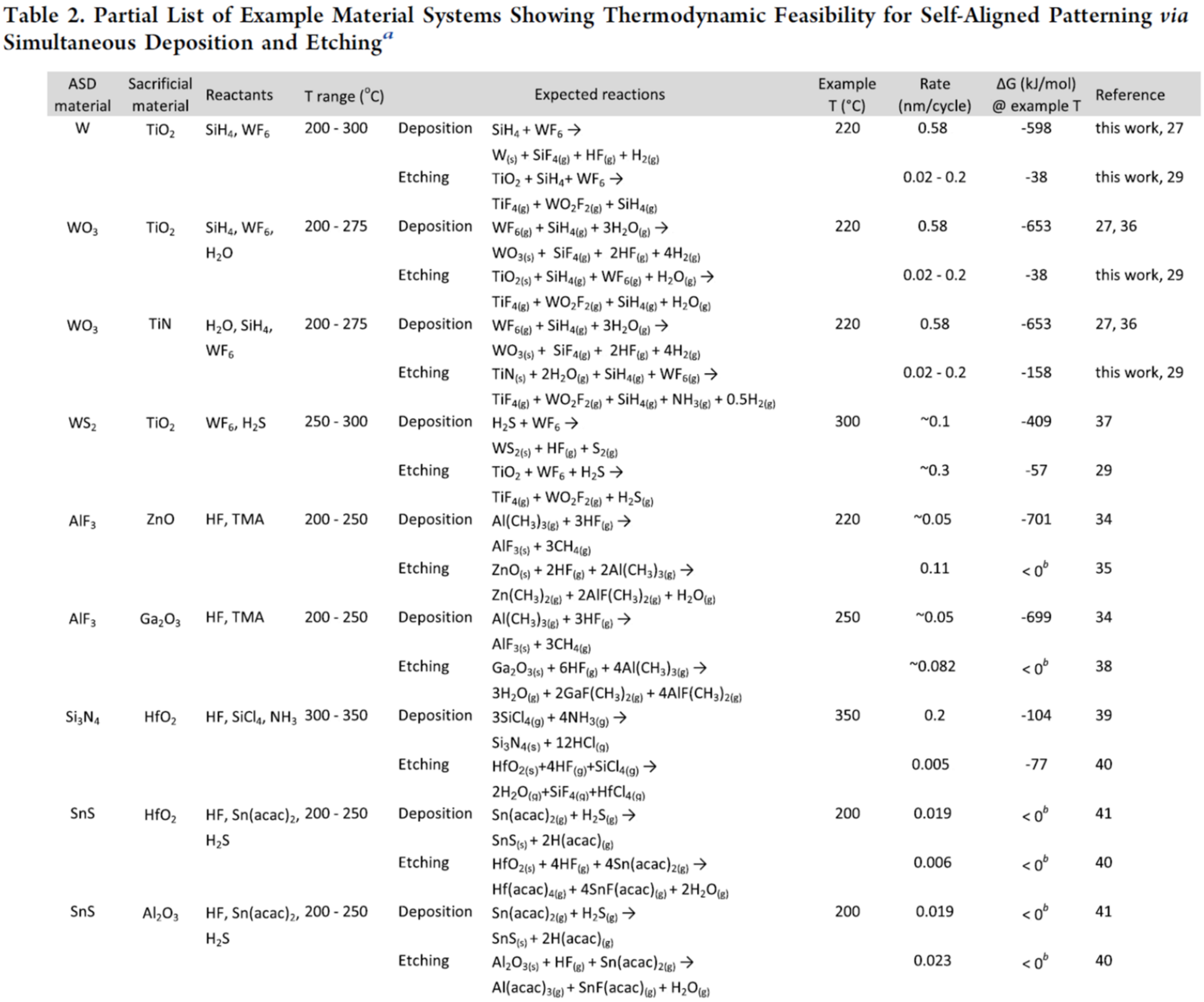


Table 2. Partial List of Example Material Systems Showing Thermodynamic Feasibility for Self-Aligned Patterning *via* Simultaneous Deposition and Etching[a]

ASD material	Sacrificial material	Reactants	T range (°C)		Expected reactions	Example T (°C)	Rate (nm/cycle)	ΔG (kJ/mol) @ example T	Reference
W	TiO_2	SiH_4, WF_6	200 - 300	Deposition	$SiH_4 + WF_6 \rightarrow$ $W_{(s)} + SiF_{4(g)} + HF_{(g)} + H_{2(g)}$	220	0.58	-598	this work, 27
				Etching	$TiO_2 + SiH_4 + WF_6 \rightarrow$ $TiF_{4(g)} + WO_2F_{2(g)} + SiH_{4(g)}$		0.02 - 0.2	-38	this work, 29
WO_3	TiO_2	SiH_4, WF_6, H_2O	200 - 275	Deposition	$WF_{6(g)} + SiH_{4(g)} + 3H_2O_{(g)} \rightarrow$ $WO_{3(s)} + SiF_{4(g)} + 2HF_{(g)} + 4H_{2(g)}$	220	0.58	-653	27, 36
				Etching	$TiO_{2(s)} + SiH_{4(g)} + WF_{6(g)} + H_2O_{(g)} \rightarrow$ $TiF_{4(g)} + WO_2F_{2(g)} + SiH_{4(g)} + H_2O_{(g)}$		0.02 - 0.2	-38	this work, 29
WO_3	TiN	H_2O, SiH_4, WF_6	200 - 275	Deposition	$WF_{6(g)} + SiH_{4(g)} + 3H_2O_{(g)} \rightarrow$ $WO_{3(s)} + SiF_{4(g)} + 2HF_{(g)} + 4H_{2(g)}$	220	0.58	-653	27, 36
				Etching	$TiN_{(s)} + 2H_2O_{(g)} + SiH_{4(g)} + WF_{6(g)} \rightarrow$ $TiF_{4(g)} + WO_2F_{2(g)} + SiH_{4(g)} + NH_{3(g)} + 0.5H_{2(g)}$		0.02 - 0.2	-158	this work, 29
WS_2	TiO_2	WF_6, H_2S	250 - 300	Deposition	$H_2S + WF_6 \rightarrow$ $WS_{2(s)} + HF_{(g)} + S_{2(g)}$	300	~0.1	-409	37
				Etching	$TiO_2 + WF_6 + H_2S \rightarrow$ $TiF_{4(g)} + WO_2F_{2(g)} + H_2S_{(g)}$		~0.3	-57	29
AlF_3	ZnO	HF, TMA	200 - 250	Deposition	$Al(CH_3)_{3(g)} + 3HF_{(g)} \rightarrow$ $AlF_{3(s)} + 3CH_{4(g)}$	220	~0.05	-701	34
				Etching	$ZnO_{(s)} + 2HF_{(g)} + 2Al(CH_3)_{3(g)} \rightarrow$ $Zn(CH_3)_{2(g)} + 2AlF(CH_3)_{2(g)} + H_2O_{(g)}$		0.11	$< 0^b$	35
AlF_3	Ga_2O_3	HF, TMA	200 - 250	Deposition	$Al(CH_3)_{3(g)} + 3HF_{(g)} \rightarrow$ $AlF_{3(s)} + 3CH_{4(g)}$	250	~0.05	-699	34
				Etching	$Ga_2O_{3(s)} + 6HF_{(g)} + 4Al(CH_3)_{3(g)} \rightarrow$ $3H_2O_{(g)} + 2GaF(CH_3)_{2(g)} + 4AlF(CH_3)_{2(g)}$		~0.082	$< 0^b$	38
Si_3N_4	HfO_2	HF, $SiCl_4$, NH_3	300 - 350	Deposition	$3SiCl_{4(g)} + 4NH_{3(g)} \rightarrow$ $Si_3N_{4(s)} + 12HCl_{(g)}$	350	0.2	-104	39
				Etching	$HfO_{2(s)} + 4HF_{(g)} + SiCl_{4(g)} \rightarrow$ $2H_2O_{(g)} + SiF_{4(g)} + HfCl_{4(g)}$		0.005	-77	40
SnS	HfO_2	HF, $Sn(acac)_2$, H_2S	200 - 250	Deposition	$Sn(acac)_{2(g)} + H_2S_{(g)} \rightarrow$ $SnS_{(s)} + 2H(acac)_{(g)}$	200	0.019	$< 0^b$	41
				Etching	$HfO_{2(s)} + 4HF_{(g)} + 4Sn(acac)_{2(g)} \rightarrow$ $Hf(acac)_{4(g)} + 4SnF(acac)_{(g)} + 2H_2O_{(g)}$		0.006	$< 0^b$	40
SnS	Al_2O_3	HF, $Sn(acac)_2$, H_2S	200 - 250	Deposition	$Sn(acac)_{2(g)} + H_2S_{(g)} \rightarrow$ $SnS_{(s)} + 2H(acac)_{(g)}$	200	0.019	$< 0^b$	41
				Etching	$Al_2O_{3(s)} + HF_{(g)} + Sn(acac)_{2(g)} \rightarrow$ $Al(acac)_{3(g)} + SnF(acac)_{(g)} + H_2O_{(g)}$		0.023	$< 0^b$	40

SK Song, J-S Kim et al. ACS Nano (2021)

Summary

- Motivation: Deposition-based patterning
- Original idea: Orthogonal ASD - Two ASD processes “back-to-back”
- Why we thought our idea would work
  - Success criteria
- Why our original idea was not successful
  - Would the direction have been successful with different boundary conditions?
- How we worked around the problem
  - Discovered a new direction
- What we learned…
  - Success criteria

Success Criteria

✓1. Create new knowledge about surface reaction processes important for ASD
   - *Deposition and etching can proceed simultaneously at low temperature on adjacent regions of a patterned substrate using a single set of reactants.*

✓2. Achieve orthogonal ASD of two materials side-by-side (W and TiO_2) with thickness of 5-10 nm each

3. Build up multiple orthogonal layers, ideally 3 or more layers of each ASD material.

Parsons group, friends and sponsors


July 12, 2021

U.S. ARMY

DEVCOM CHEMICAL BIOLOGICAL CENTER

DEVCOM SOLDIER CENTER

DEPARTMENT OF ENERGY UNITED STATES OF AMERICA

DEFENSE THREAT REDUCTION AGENCY UNITED STATES OF AMERICA

NSF

SRC

Lam RESEARCH

CDP

intel

TEL

EMD PERFORMANCE MATERIALS