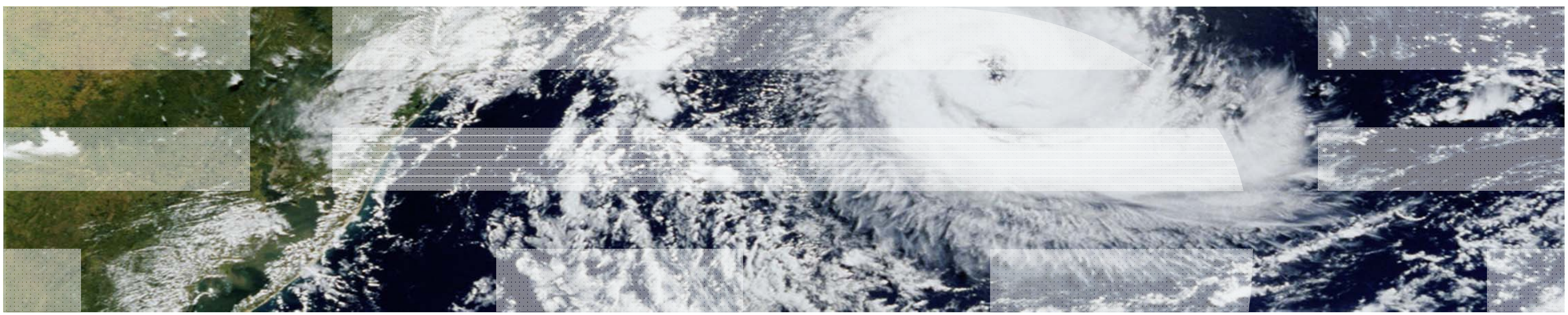
Methods to Enable Plasma Etching of Transition Metals with Atomic Scale Precision

N. Marchack, B. Walusiak, K. Hernandez[†], J.M. Papalia, S.U. Engelmann and E. A. Joseph

IBM Research, Yorktown Heights, NY
[†]*University of Texas at Dallas, Richardson, TX*



NCCAVS Plasma Applications Group Workshop on Atomic Layer Etching
August 20th, 2018
Milpitas, California, USA

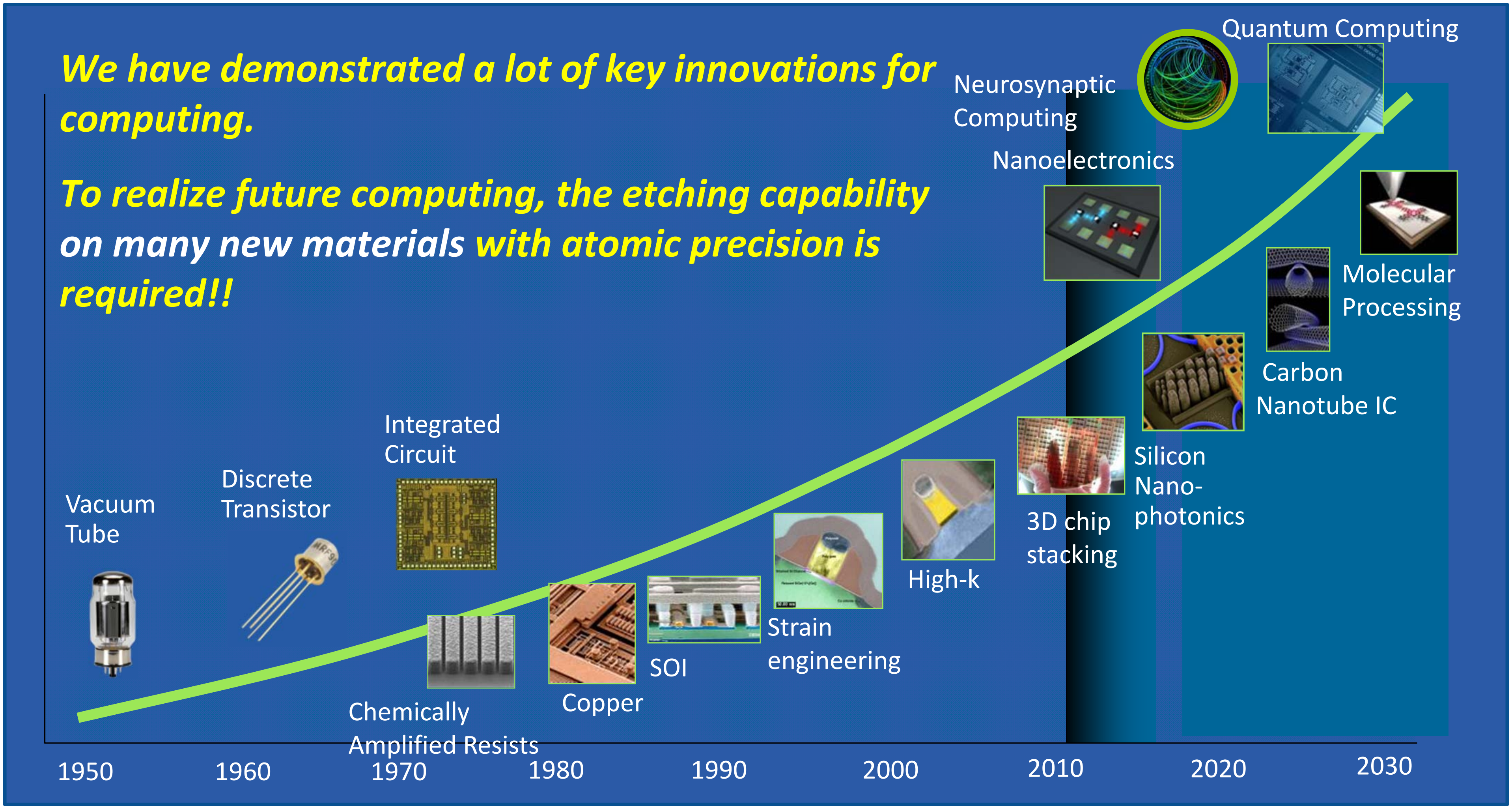
Overview

- Cyclic Approaches for Transition Metal Patterning
- Cl_2/H_2 Approach to TaN and TiN
  - Synergy Study and Deviations from Ideal Case
  - Knobs for Profile and CD Control
- Effect of Carrier Gas – Ar vs. He
  - Process Uniformity
  - Surface Composition
  - Redeposition effects on Profile
- Conclusions

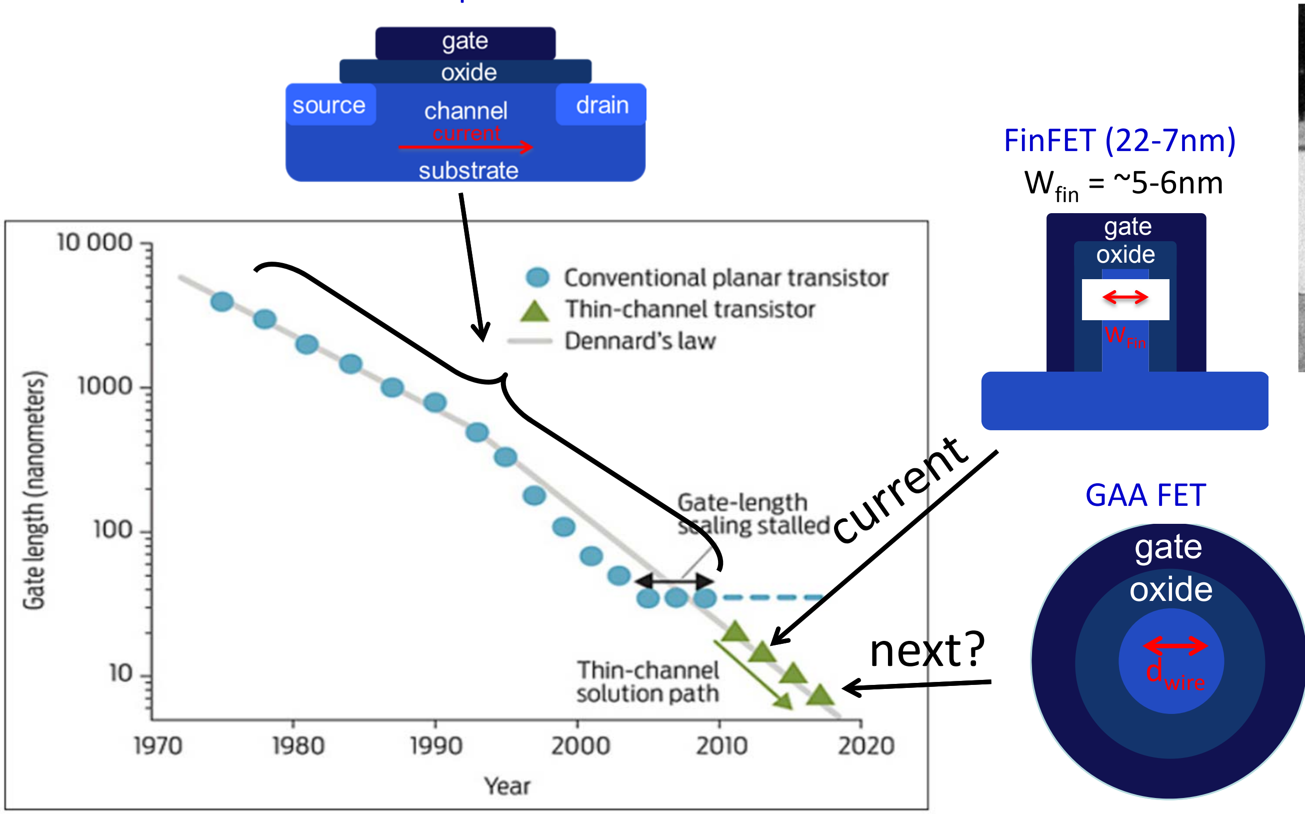
Strategy of IBM's Computing Innovation

We have demonstrated a lot of key innovations for computing.

To realize future computing, the etching capability on many new materials with atomic precision is required!!

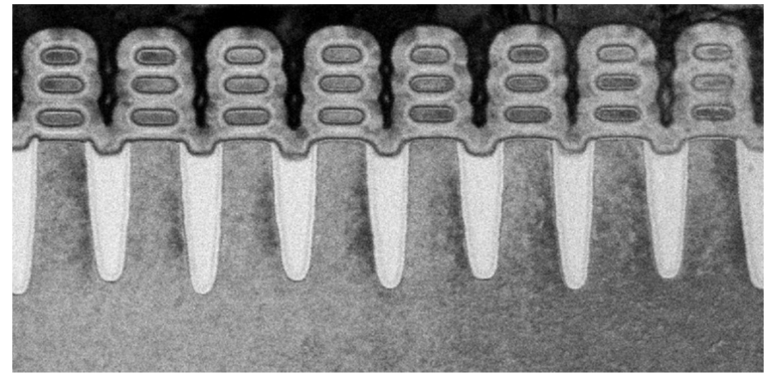


Continued scaling of MOSFET



IEEE Spectrum, Nov. 2011, pg. 50

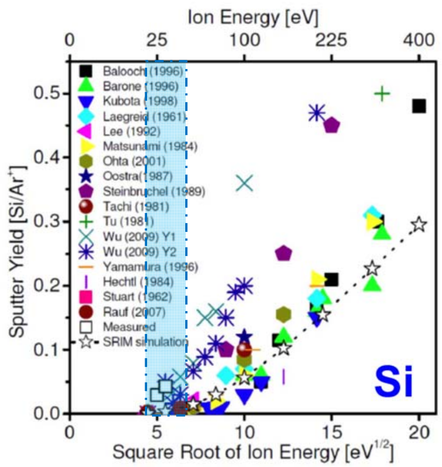
***5nm solution** (June 2017 IBM/Samsung/GF)*

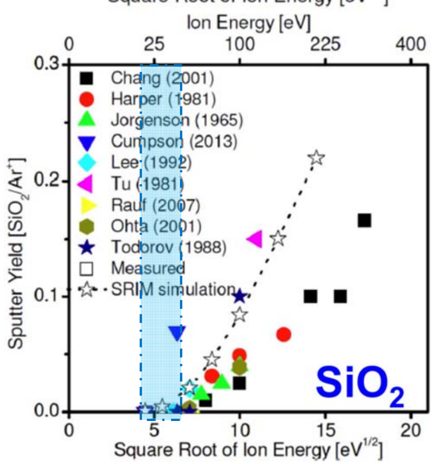


- Shrinkage of MOSFET
  - Moore's law
  - Dennard's scaling
    - Increase density
    - Lower power operation
    - Faster switching
- Industry is facing single digit node
  - W_{fin} = ~5-6nm for 10 and 7nm node
  - ~10 atomic layers of Si
- Novel geometries, materials for 5nm node and beyond

Methods for Atomic Layer Precision Control

Controlling selectivity by ion energy

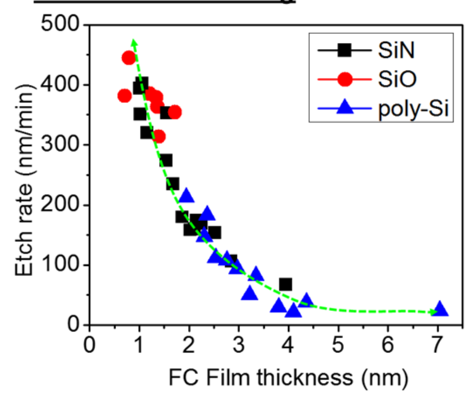




Oehrlein et al. ECS J. Solid State Sci. Technol. 2015; 4 (6) N5041-N5053

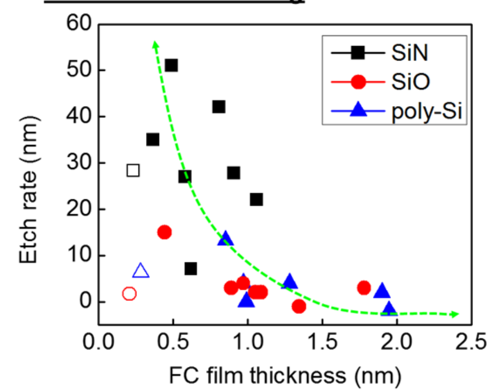
Controlling selectivity by surface chemistry

Selective SiO etching



M. Schaepkens et al., JVST. A 17, 26 (1999).

Selective SiN etching



Engelmann et al., JVSTB submitted (2017).

- **Tailoring surface chemistry is an essential method to reach atomic layer control**
- **Ion Energy control is another critical way to enable atomic scale precision**

→ Combination of Chemistry and Energy threshold chosen specifically to enable reactant activation and removal of one material selective to all others

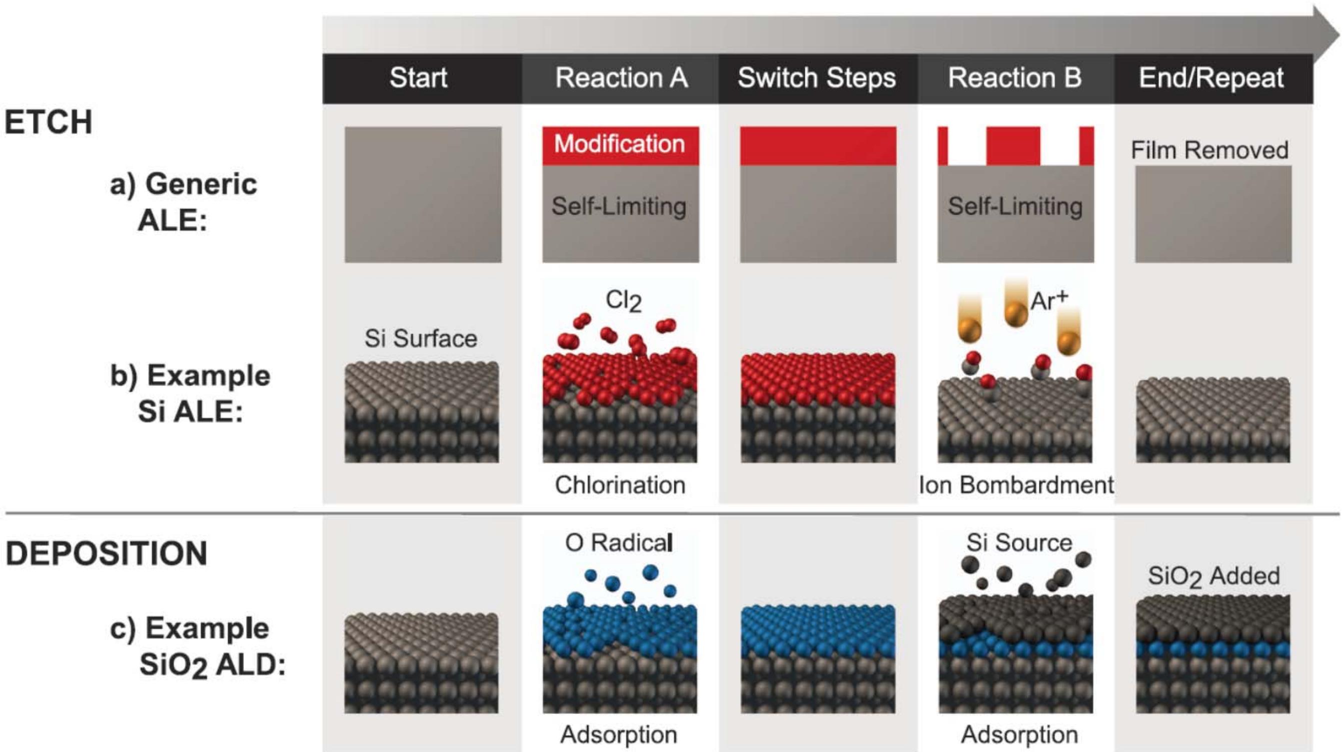
Engelmann, et al., JVSTB 35, 051803-1 (2017)

Control of surface chemistry by Cyclic etching

- Cyclic processing for Atomic Layer Etching
  - Surface adsorption/modification of reactive species
  - Volatilization of at very low energy inert ions (typically lower than sputtering threshold)

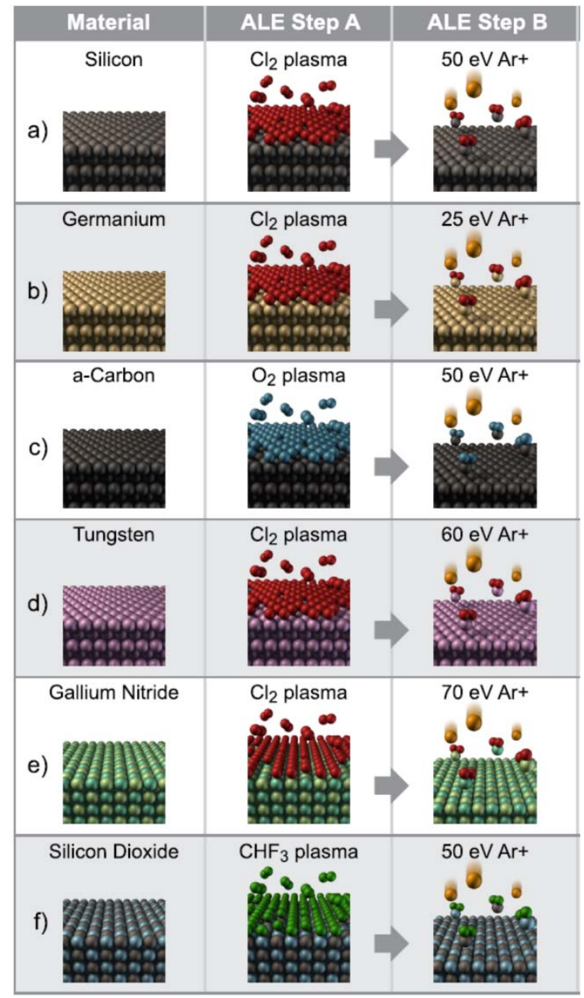
- Etch process control by “self-limiting” reaction at surface

[1] Kanarik, JVSTA (2017)
[2] Kanarik, JVSTA (2015)



Concept of gas pulsing cyclic etch[1]

Examples [2]

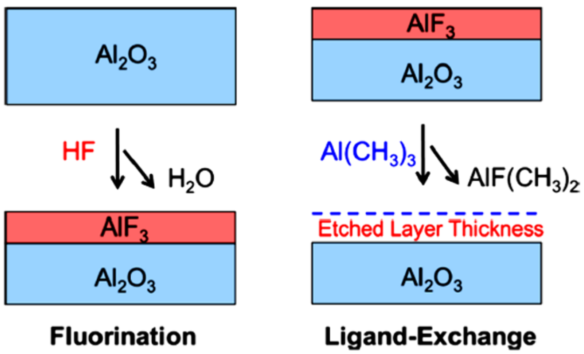


“ALE” Approaches - Overview

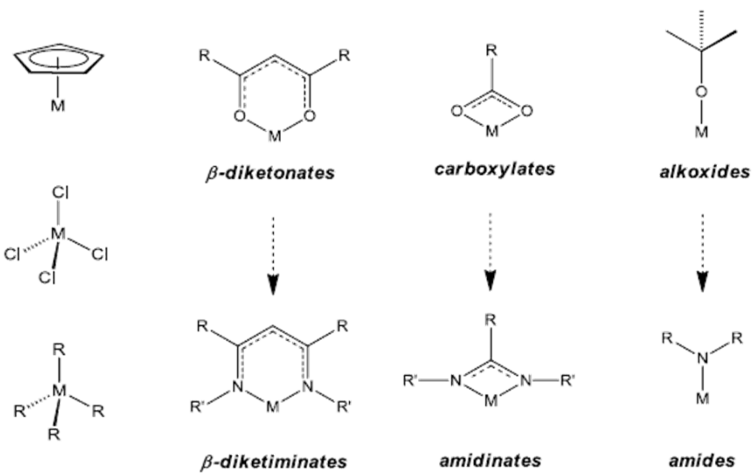
	ALE (reverse ALD)	Flux Control – Quasi ALE
Method	Cyclic process with self-limited adsorption and etch steps; complementary to established ALD processes	Continuous plasma during all cyclic processing steps, depositing plasma layer and reacting layer energetically at top surface
Advantage	High precision, true self limitation, uniformity	Wide process temperature range, faster process time, synergy with PE-ALD learning
Disadvantage	Throughput, physical wafer movement (some systems), process temperature limitations	Plasma damage, true self-limitation deposit not known at this point, design of precursor gas needs understanding of ALE plasma decomposition
Examples	Si ALE by Cl_2 and Ar (neutral beam or ions), Cyclic TMA + HF → Conversion Etch	Cyclic etch of oxide by fluorocarbon/Ar plasma discharges

Source: *S. U. Engelmann et al., ECS J. Solid State Sci. Technol. 2015 4(6): N5054-N5060*

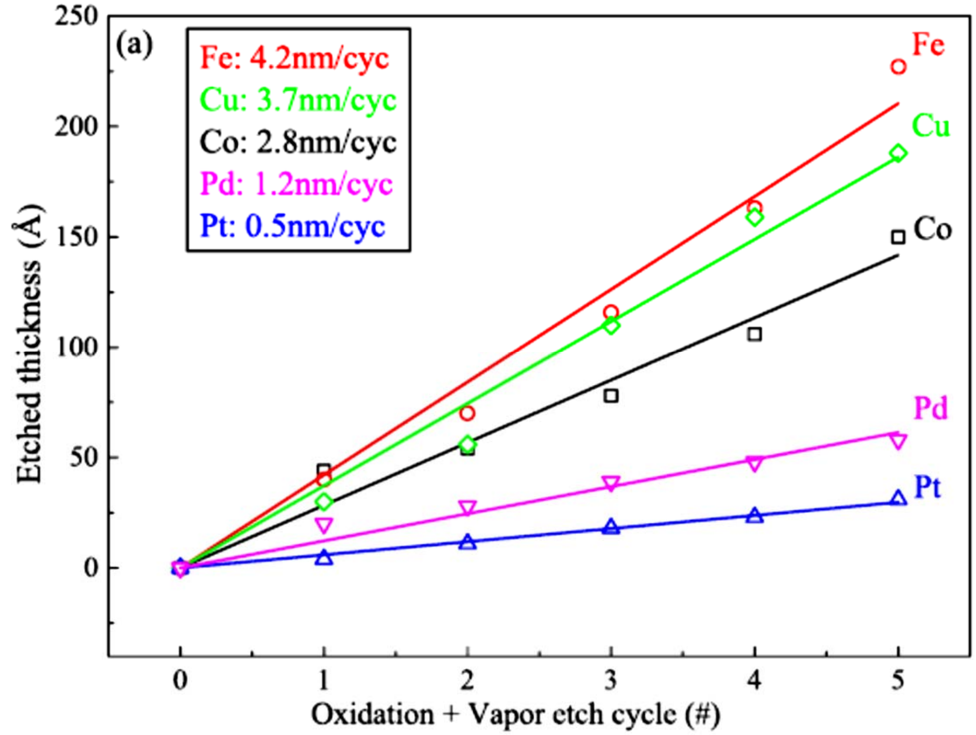
ALE Approaches for Metal (Composite) Films



(Lee, Huffman & George, Chem. Materials, 2016)



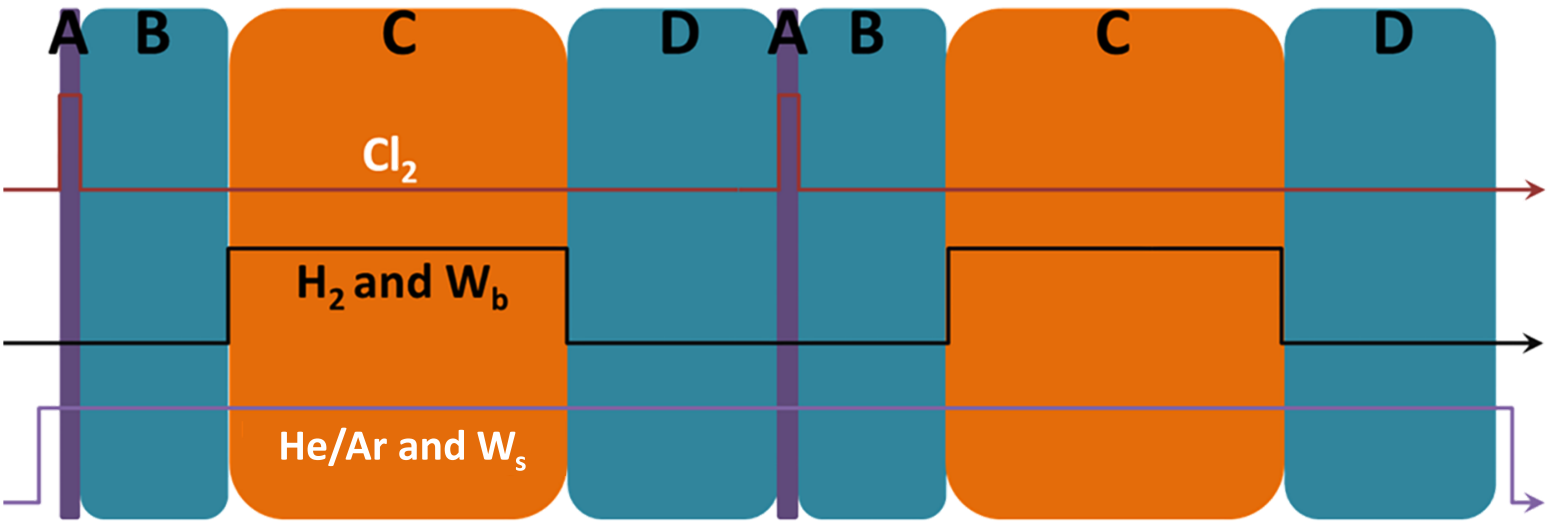
(B. Turkot, Sematech ALE Workshop, April 21, 2014).



(Chen et al., JVST A, 2017)

- **Cyclic approach recognized as necessary for delineation of complex reactions, esp. in a plasma environment!**

Experimental Setup - Cyclic Etch Approach



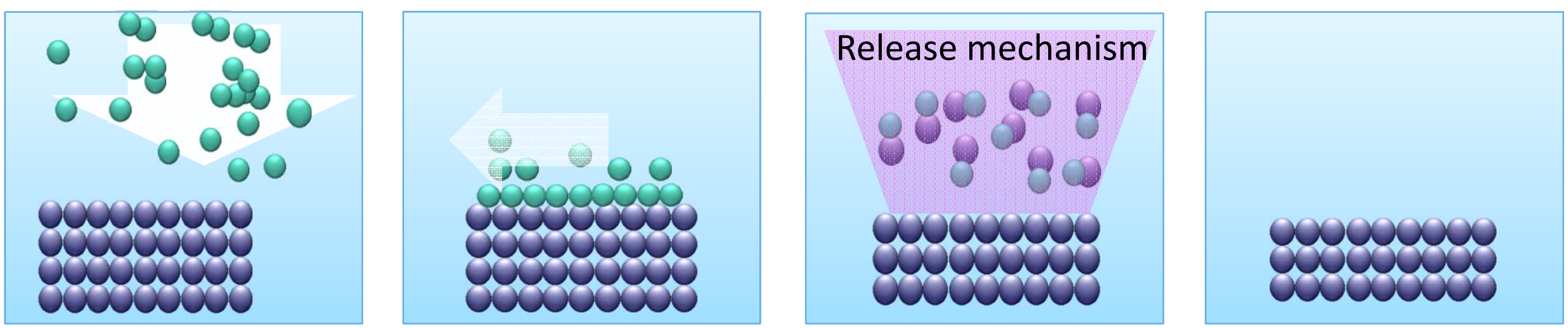
A = Cl_2 Introduction (2s)
B = Purge (15s)
C = Bias (H_2 optional) (20s)
D = Purge (2s)

A. Surface Layer reaction

B. Purge excess reactant

C. Reaction mechanism release

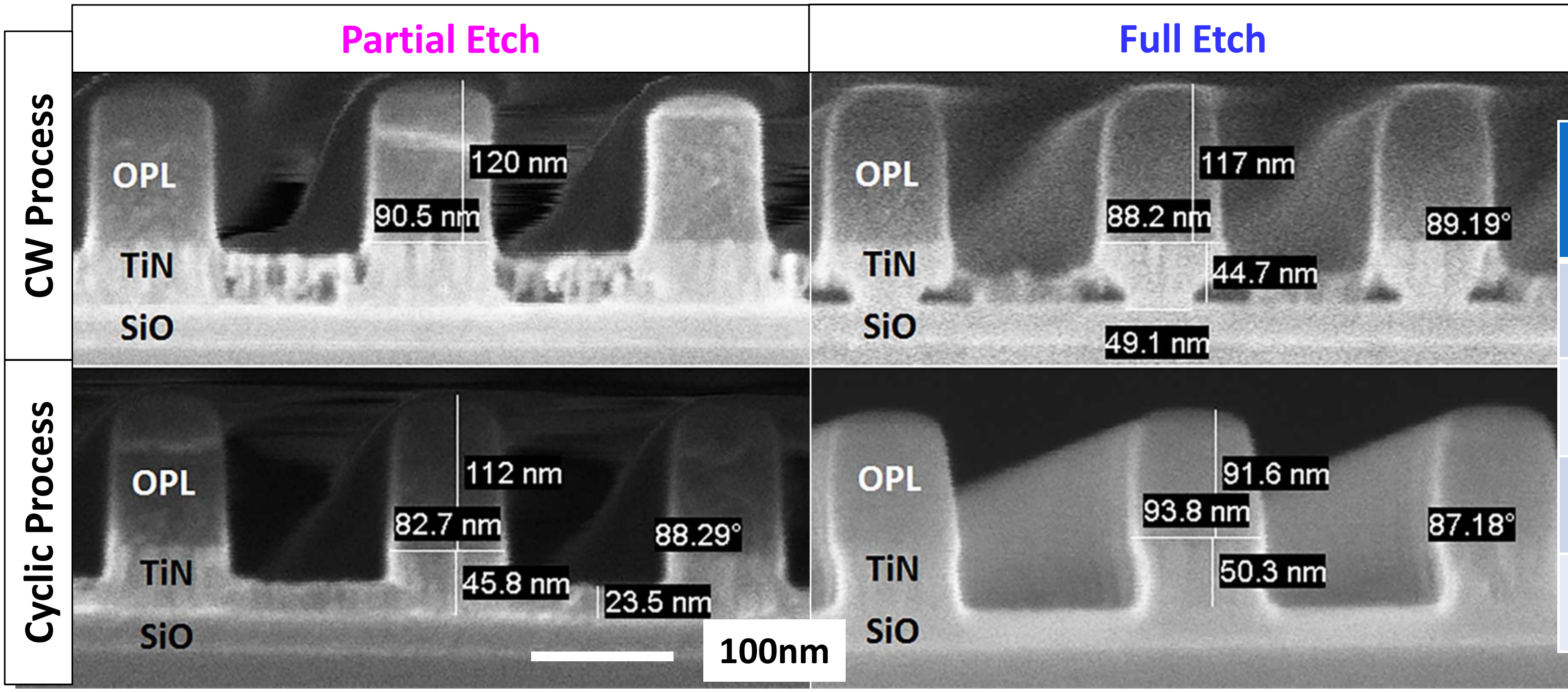
D. Byproduct Purge



- He chosen as background gas to reduce physical sputtering component, remains on during entire duration of process.

Huffman et al, 2015 VLSI-TSA TSS15

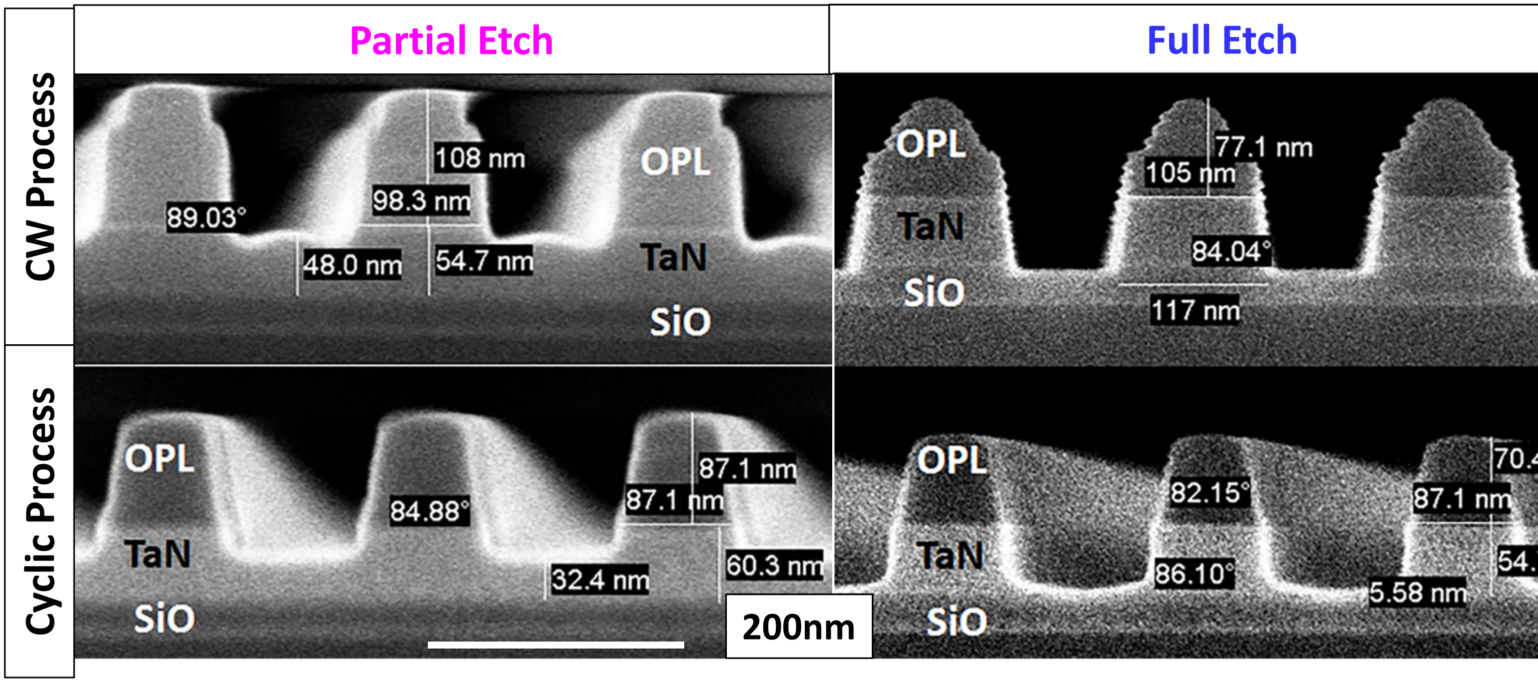
TiN – Comparison of CW Process to Cyclic Etch (No H_2)



	CD (nm)	SWA (°)	ER (nm/Cycle)
CW (Partial)	91	84	
CW (Full)	88	76	
Cyclic (P)	83	89	7.3
Cyclic (F)	94	N/A	>5.5*

- Residue apparent in trench bottoms for CW process for both partial and full etch conditions.
- Cyclic Etch Process shows ER (per cycle) well above "ALE" standards.

TaN – Comparison of CW Process to Cyclic Etch (No H_2)

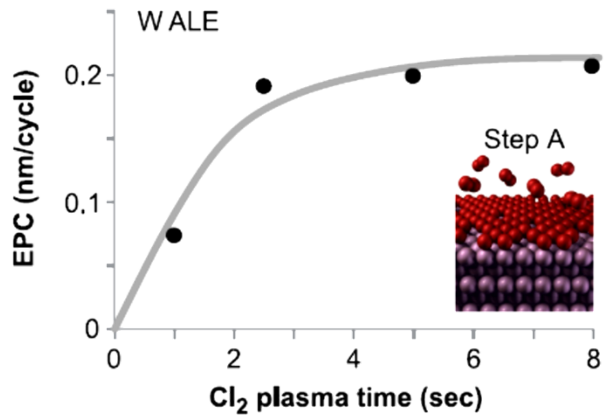


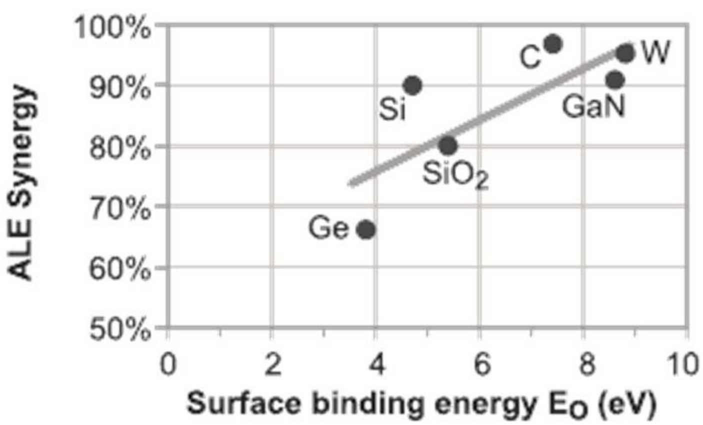
	CD (nm)	SWA (°)	ER (nm/ Cycle)
CW (Partial)	98	65	2.5 nm/s
CW (Full)	117	84	3.1 nm/s
Cyclic (P)	87	79	**4.7**
Cyclic (F)	93	86	**3.5**

- **Veiling of OPL (due to redep) is less apparent for TaN etched using the cyclic process.**
- **Sidewall angle on deeper etch is more vertical (less redep).**

Synergy Assessment – Application to TiN and TaN

$$\text{ALE synergy \% } (S) = \frac{\text{EPC} - (\alpha + \beta)}{\text{EPC}} \times 100\%.$$





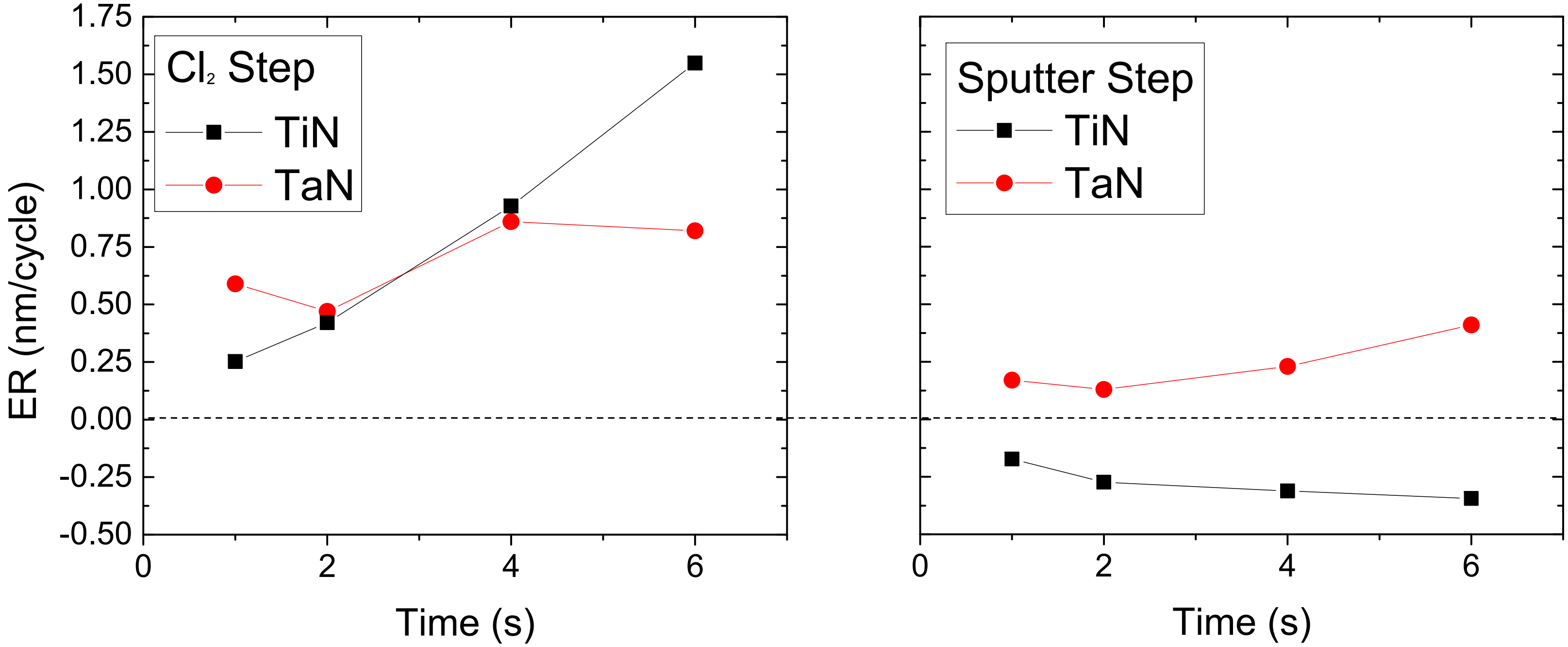
(Kanarik et al., JVST A, 2017)

Material	Bond	ΔHf_{298} (kJ/mol)	Surface Binding Energy (eV)
TiN	Ti-N	464	4.89 (Ti), 4.94 (TiN)**
	Ti-Cl	494	
	Ti-O	662	
TaN	Ta-N	611	8.1 (Ta)
	Ta-Cl	544	
	Ta-O	805	

(Ranjan et al., JVST A, 2001)

- **ALE synergy appears correlated to surface binding energy – potentially favoring TaN over TiN for more "ideal" ALE process.**
- **Reaction with Cl_2 for TiN expected to be more favorable ($\Delta Hf_{Ti\text{-}Cl} > \Delta Hf_{Ti\text{-}N}$) than TaN.**

Synergy Assessment

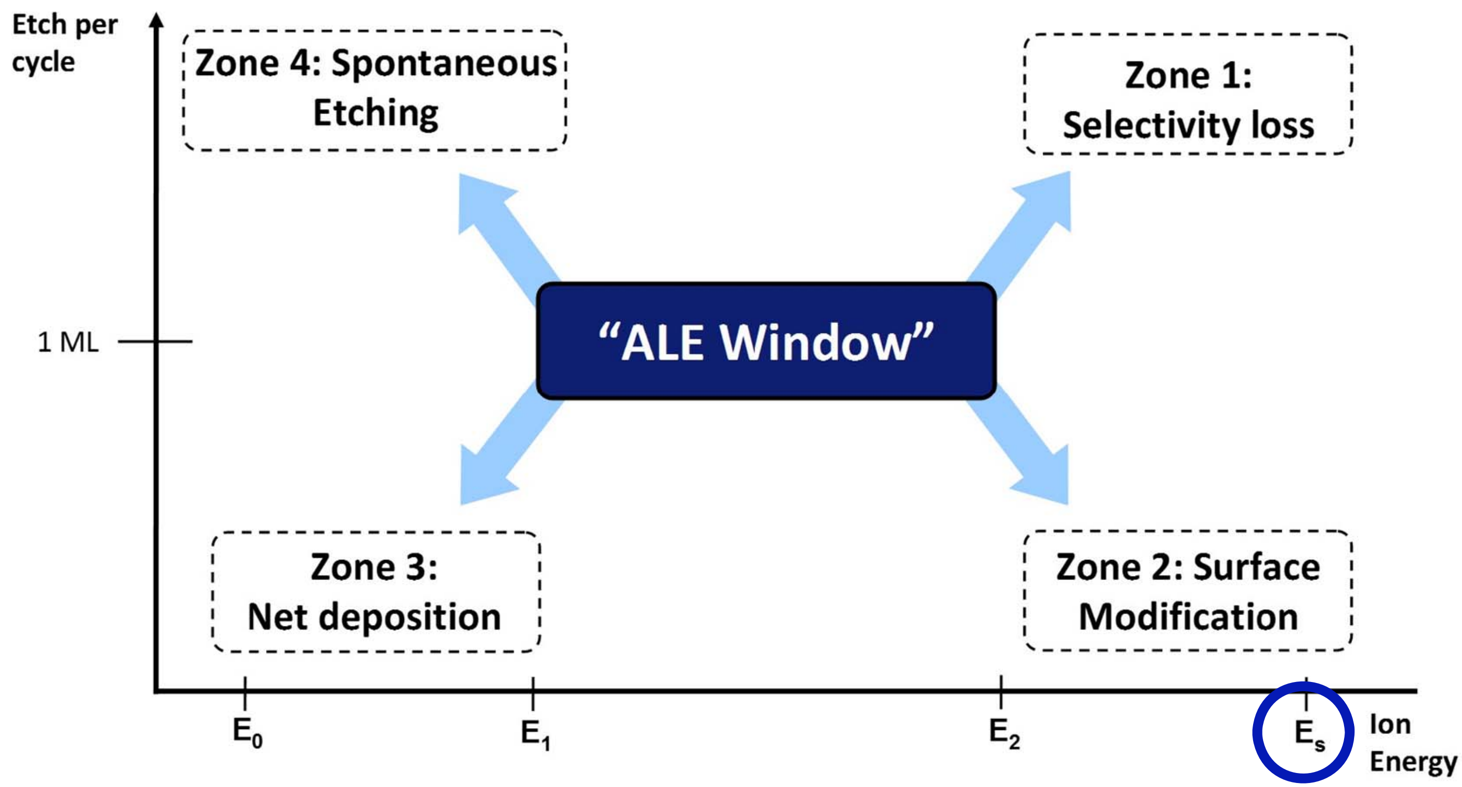


$$S_{TaN} \sim \frac{6 - (0.84 + 0.41\ )}{6} \leq 79\%$$

- **TiN does not show saturation behavior even for Cl_2 pulse time of 6s.**
- **Synergy calculations approximate due to "quasi-ALE" nature, however numbers are in line w/ literature (albeit at ERs ~ one order of magnitude larger…)**

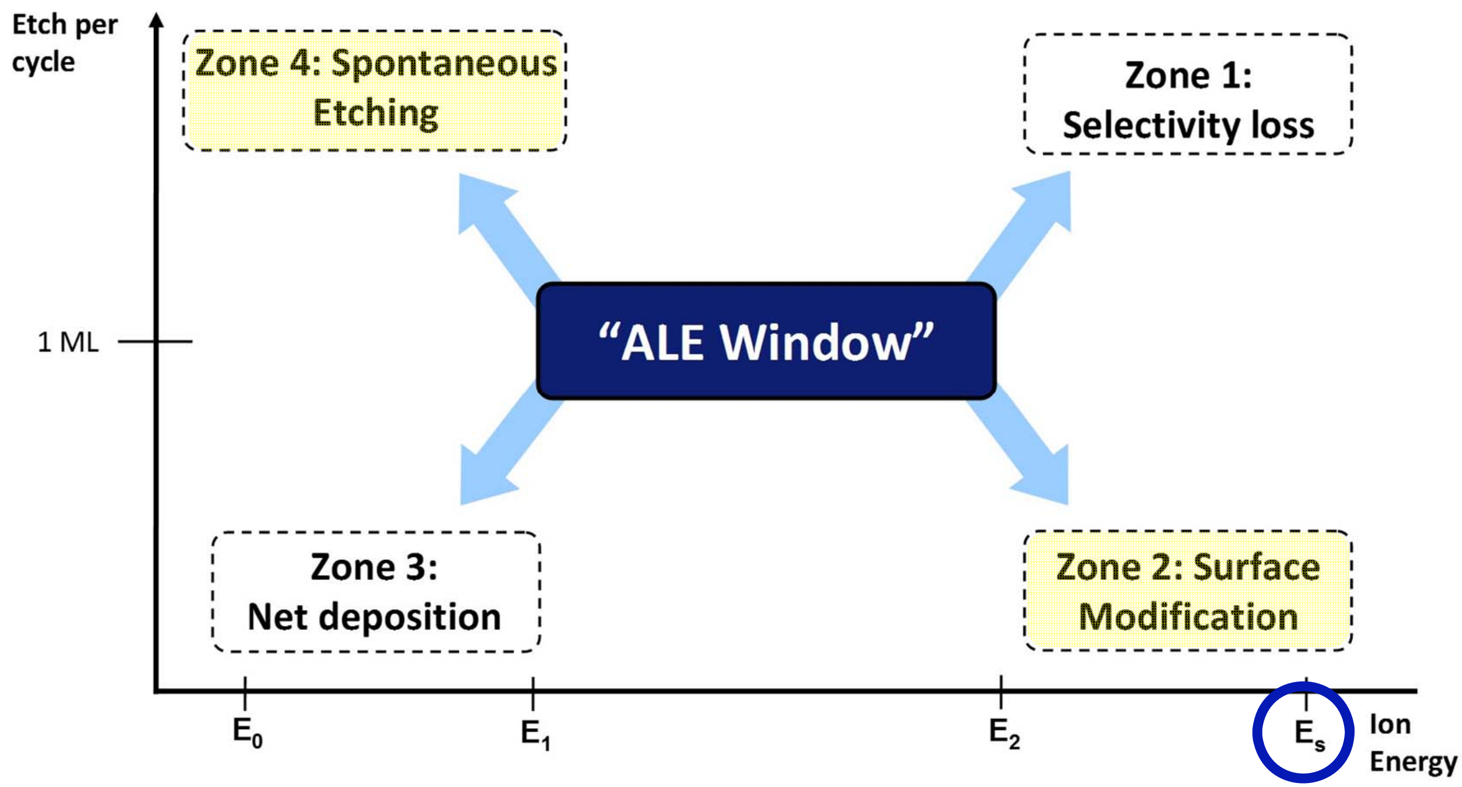
PE-ALE Process Space

- **ALE “window” driven by:**
  - Energy of desorption process
  - Plasma chemistry and radical physi/chemisorption
- **TiN exhibits non-ideal behavior**
  - Based on Zone 4 and Zone 2 process limitations

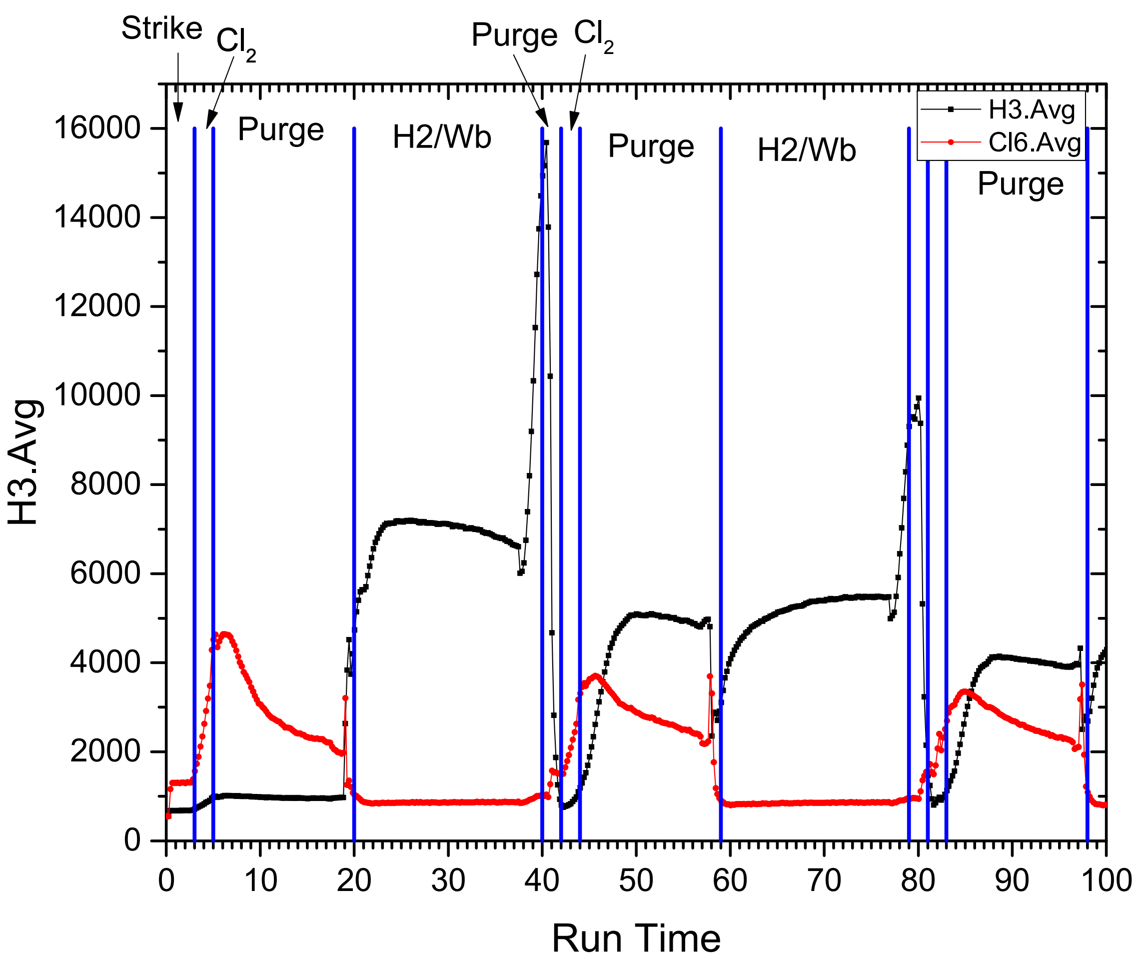


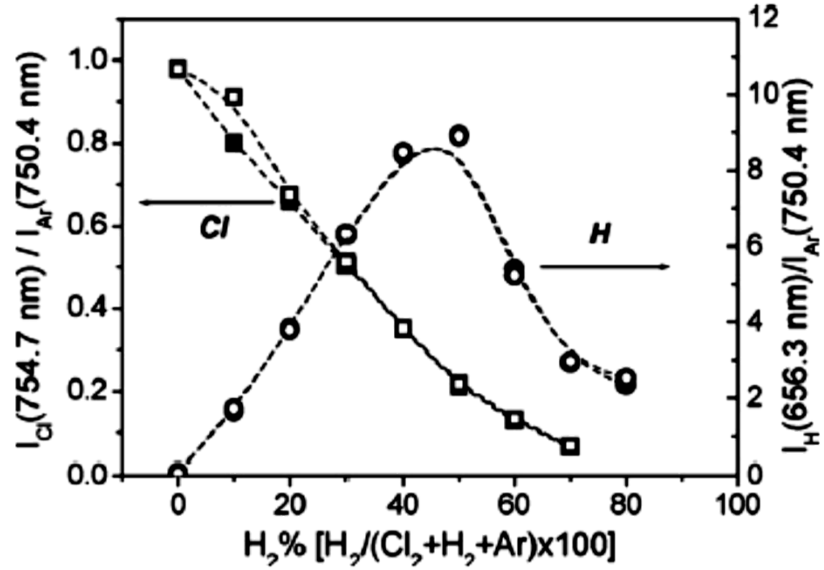
PE-ALE Process Space

- **ALE “window” driven by:**
  - Energy of desorption process
  - Plasma chemistry and radical physi/chemisorption
- **TiN exhibits non-ideal behavior**
  - Based on Zone 4 and Zone 2 process limitations



TiN Cyclic Etch – Effect of H_2 Addition



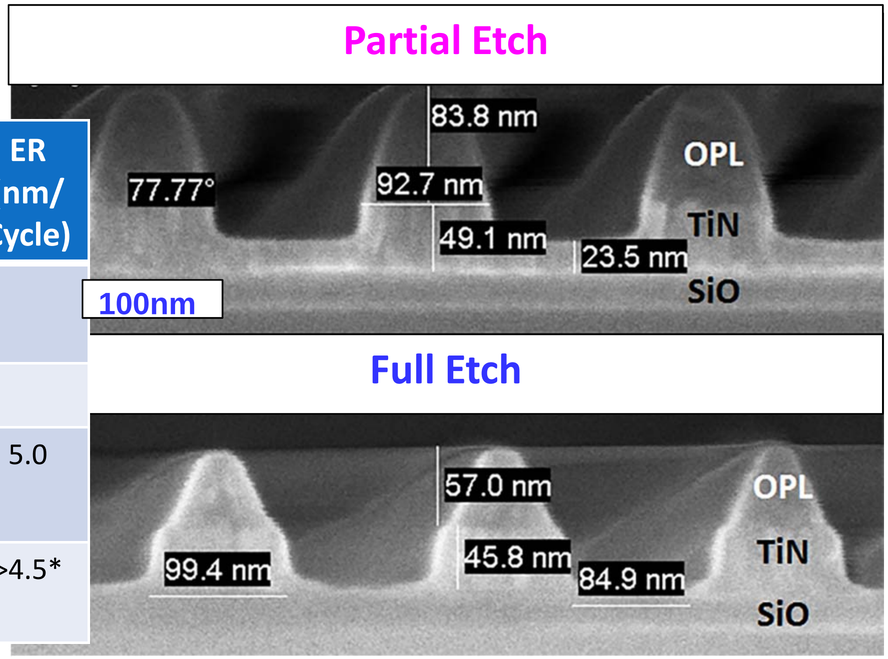


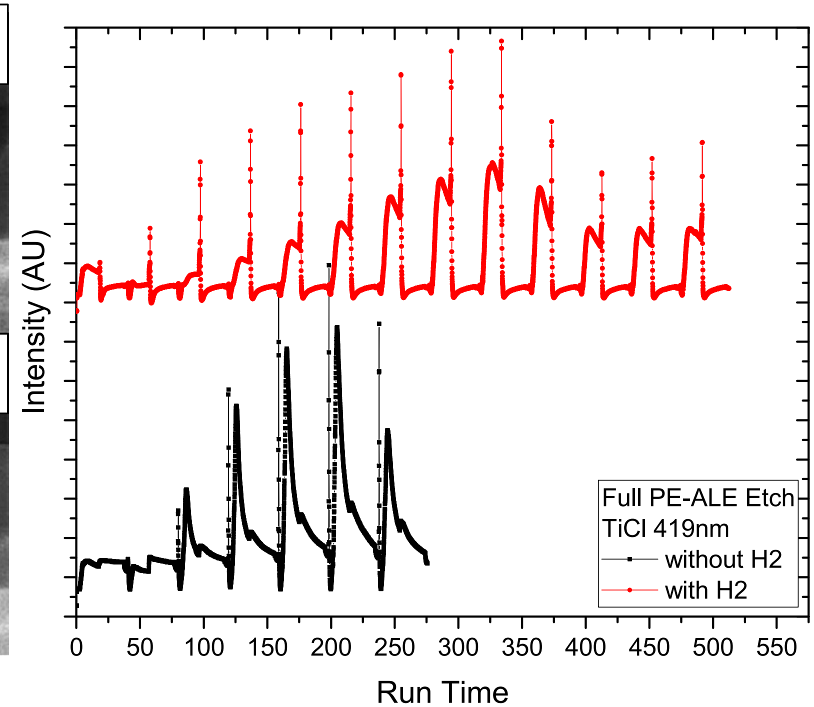
(Gatilova et al., JVST A 2009)

- **Cl_2 residence time appears to exceed allotted purge time.**
- **Introduction of H_2 causes drop of Cl_2 signal to baseline.**

TiN Cyclic Etch – Effect of H_2 Addition

	CD (nm)	SWA (°)	ER (nm/ Cycle)
CW (Partial)	91	84	
CW (Full)	88	76	
Cyclic w/ H_2 (P)	93	82	5.0
Cyclic w/ H_2 (F)	99	74	>4.5*

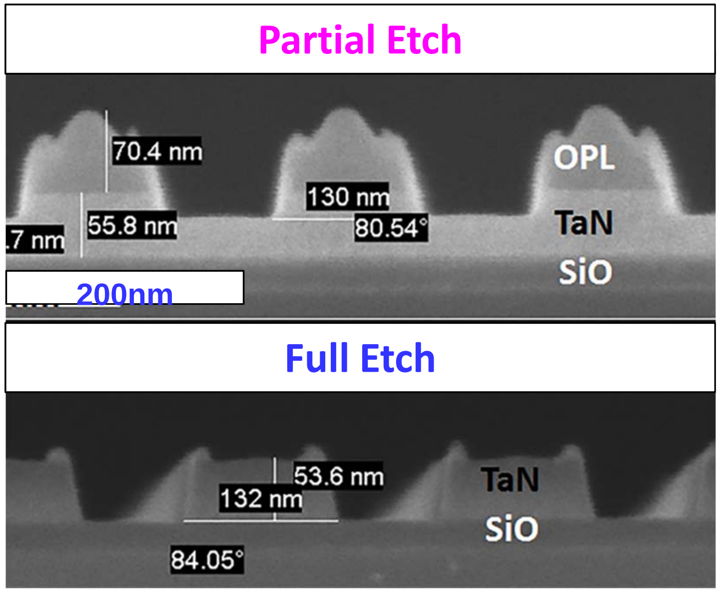


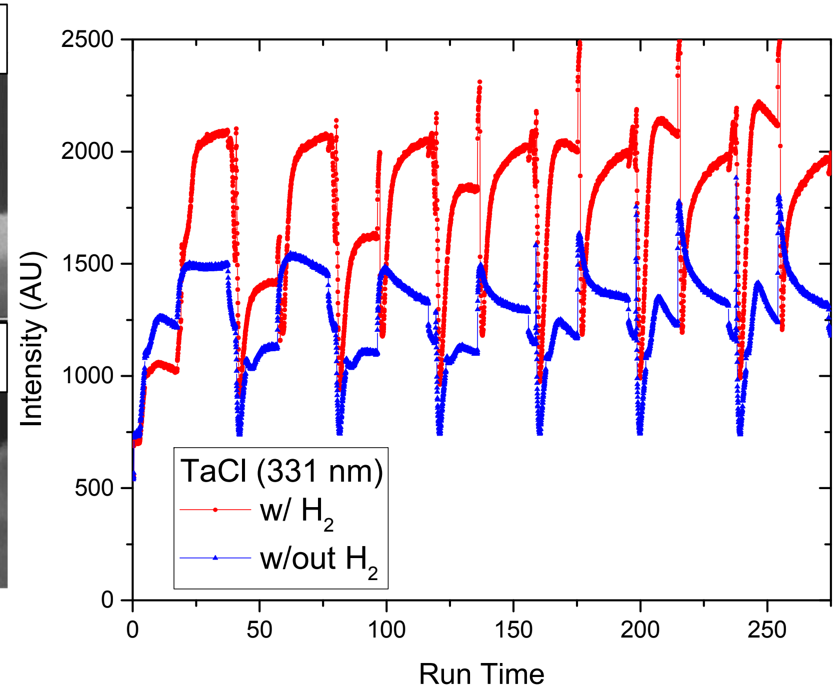


- Mask loss mainly due to H_2 addition
- ER/cycle is lower with H_2 addition
- OES comparison indicates that H_2 addition is affecting reaction of Cl_2

TaN Cyclic Etch – Effect of H_2 Addition

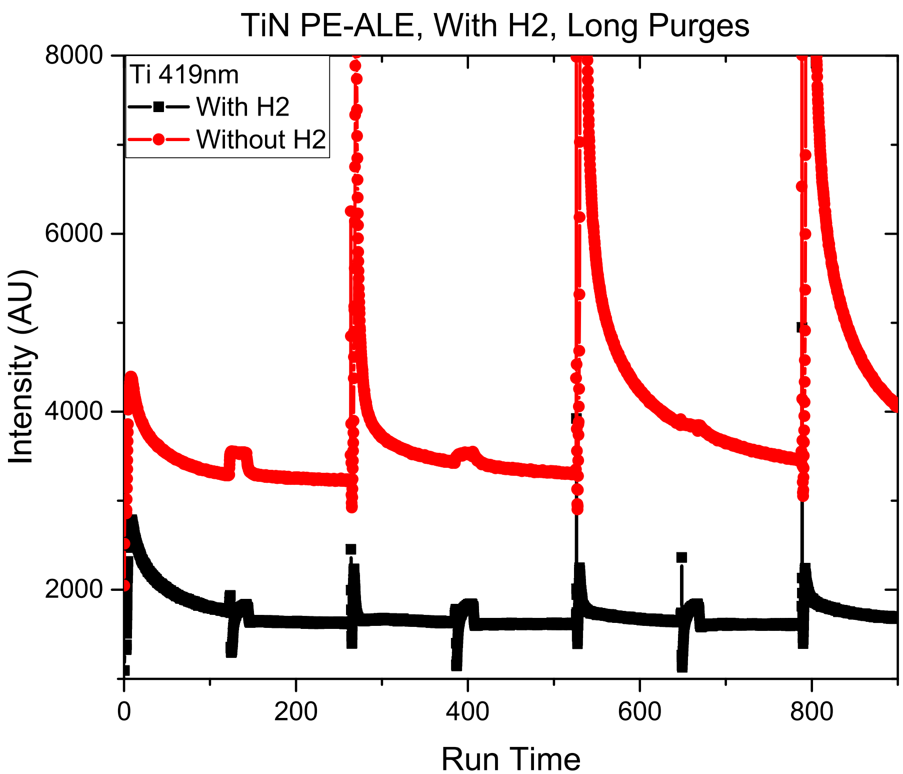
	CD (nm)	SWA (°)	ER (nm/ Cycle)
CW (Partial)	98	65	2.5 nm/s
CW (Full)	117	84	3.1 nm/s
Cyclic w/ H_2 (P)	130	84	7
Cyclic w/ H_2 (F)	132	84	6.1

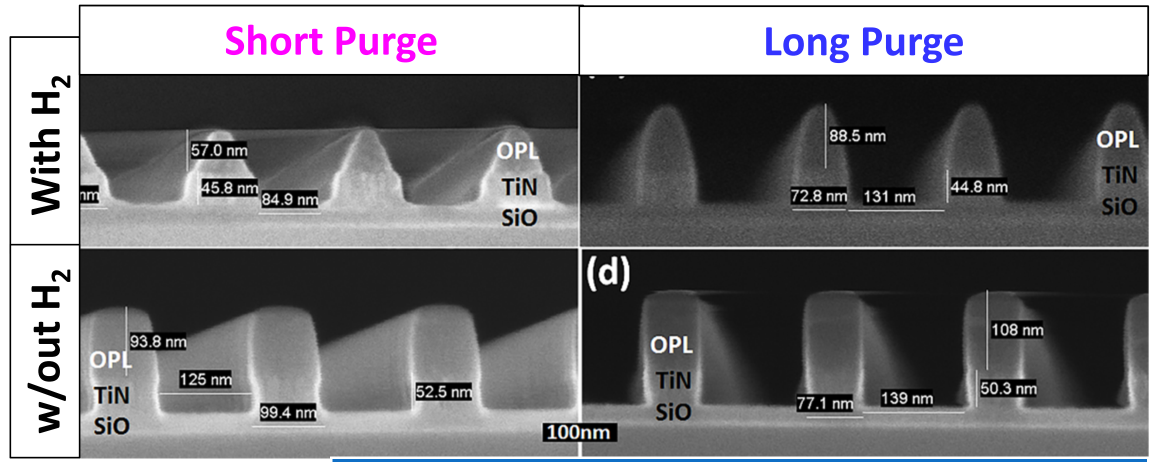




- Mask loss mainly due to H_2 addition
- Veiling of OPL becomes more pronounced, due to increase in sputtering component.

Effect of Residence/Purge Times – Effect on TiN Profile



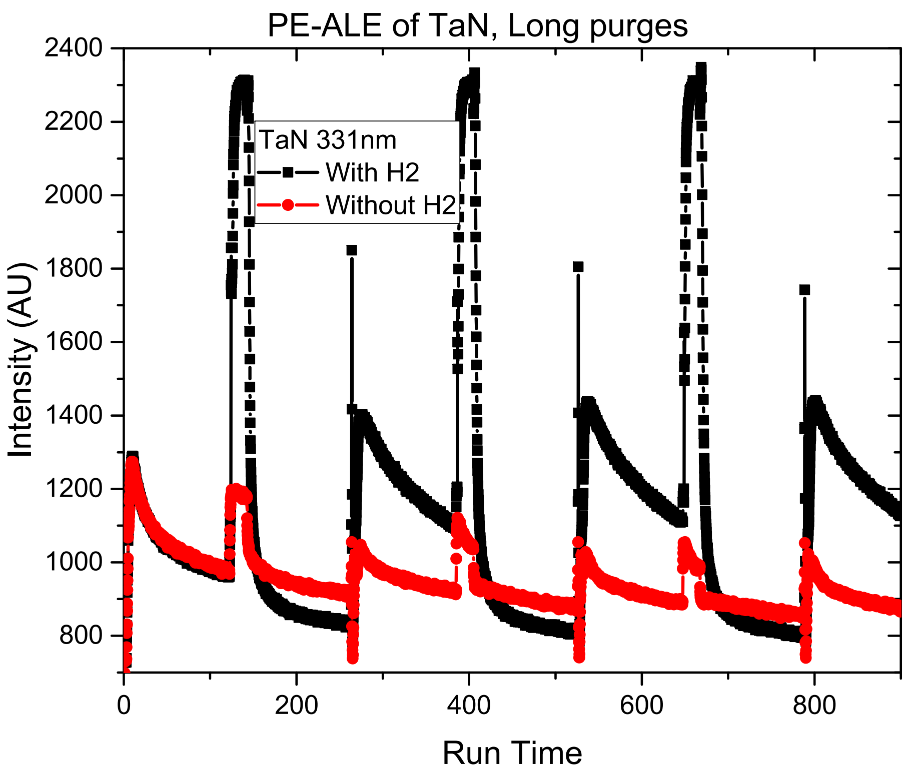


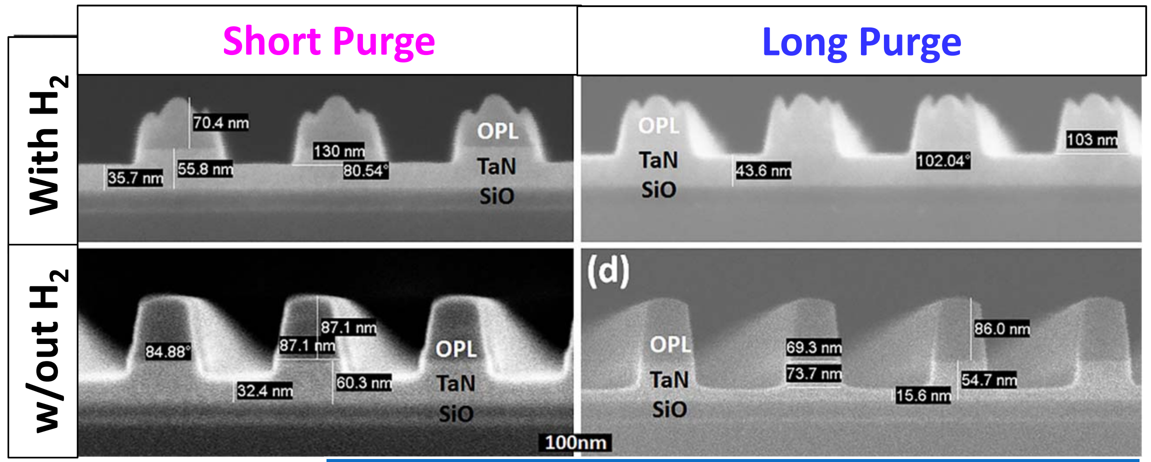
CD measurements (space-width @ 200nm pitch)

Sample	CD (nm)	ER (nm/cycle)	OPL Left (nm)
With H_2 Short purge	99	>4.5	57
With H_2 Long purge	**73**	8	**89**
Without H_2 Short purge	99	>5.5	94
Without H_2 Long purge	**77**	7	**108**

- **Increasing purge times results in significant improvement of mask retention.**
- **ER/cycle increases due to extended reaction of Cl_2 with TiN, lateral component also increased.**

Effect of Residence/Purge Times – Effect on TaN Profile





CD measurements (space-width @ 200nm pitch)

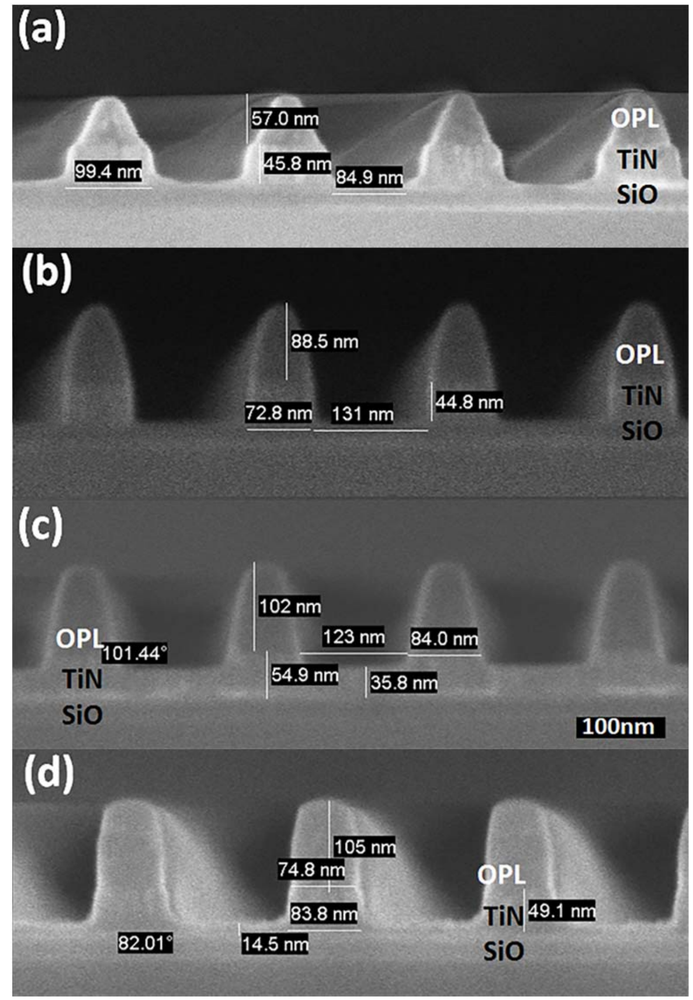
Sample	CD (nm)	ER (nm/cycle)	OPL Left (nm)
With H_2 Short purge	123	6-7	74
With H_2 Long purge	**103**	3.0	70
Without H_2 Short Purge	111	4-5	83
Without H_2 Long Purge	**73.7**	5.2	86

- **For TaN, increasing purge times results in lower ER/cycle**
- **CD change (isotropic etch) is most apparent effect.**

Deconvolution of Purge Time Effect

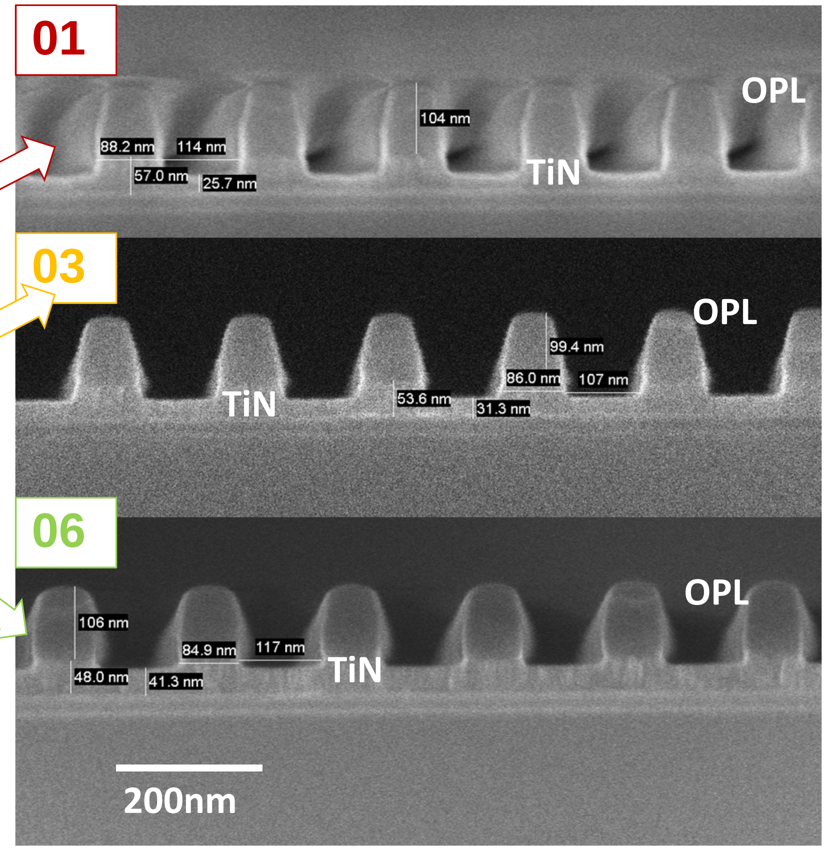
TiN Cyclic Etch w/ H_2 Addition					
Sample	**CD-Pre (nm)**	**CD-Post (nm)**	**ER * (nm / cycle)**	**# of Cycles**	**OPL Left**
Both Purges Short **(A)**	103	85	~5	13	57
Both Purges Long **(B)**	97	73	~8	7	89
Long H_2 Purge Only **(C)**	98	84	**2.5**	8	102
Long Cl_2 Purge Only **(D)**	97	65	>10	10	81

- **Only increasing duration of H_2 purge results in etch rate reduction, if Cl_2 is held constant.**



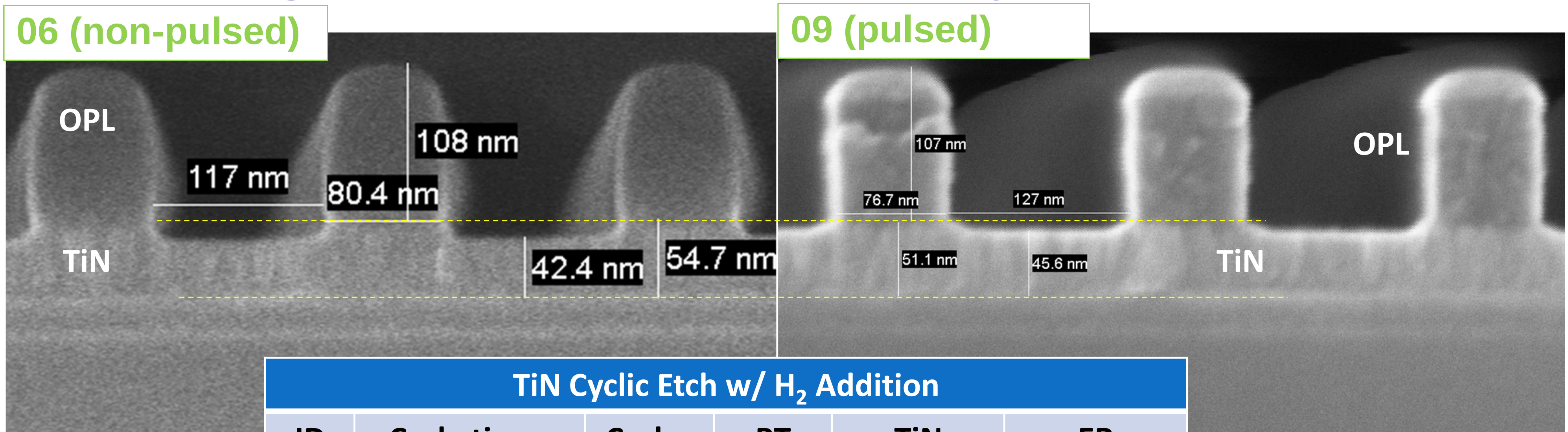
ER/cycle Control Using Cl_2 Exposure and Purge Times

TiN Cyclic Etch w/ H_2 Addition					
ID	**Cycle times**	**Cycles**	**BT Cycles**	**TiN Etched**	**ER (nm/cycle)**
01	2,**15**,20,120	12	2	31.3	3.1
02	2,**10**,20,120	12	2	25.7	2.6
03	2,**5**,20,120	12	2	21.3	2.1
04	2,**1**,20,120	12	2	23.4	2.3
05	**1**,1,20,120	12	2	23.4	2.3
06	**0.5**,1,20,120	12	2	12.3	**1.2**



- **Etched amount per cycle can be reduced to ~1nm/cycle by controlling Cl_2 pulse time and "purge" time before H_2 exposure.**

Plasma Pulsing to Further Reduce Etch Rate Per Cycle



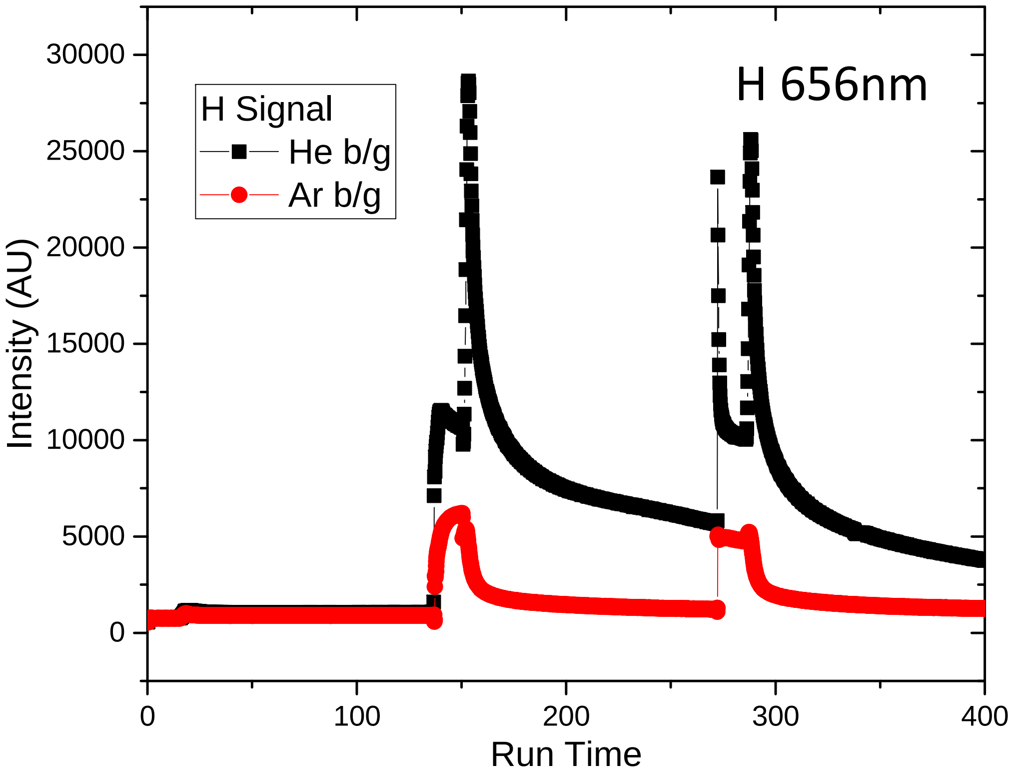
TiN Cyclic Etch w/ H_2 Addition					
ID	Cycle times	Cycles	BT Cycles	TiN Etched	ER (nm/cycle)
06	**0.5**,1,20,120	12	2	12.3	**1.2**
09	**0.5**,1,20,120*	12	2	5.5	**0.6**

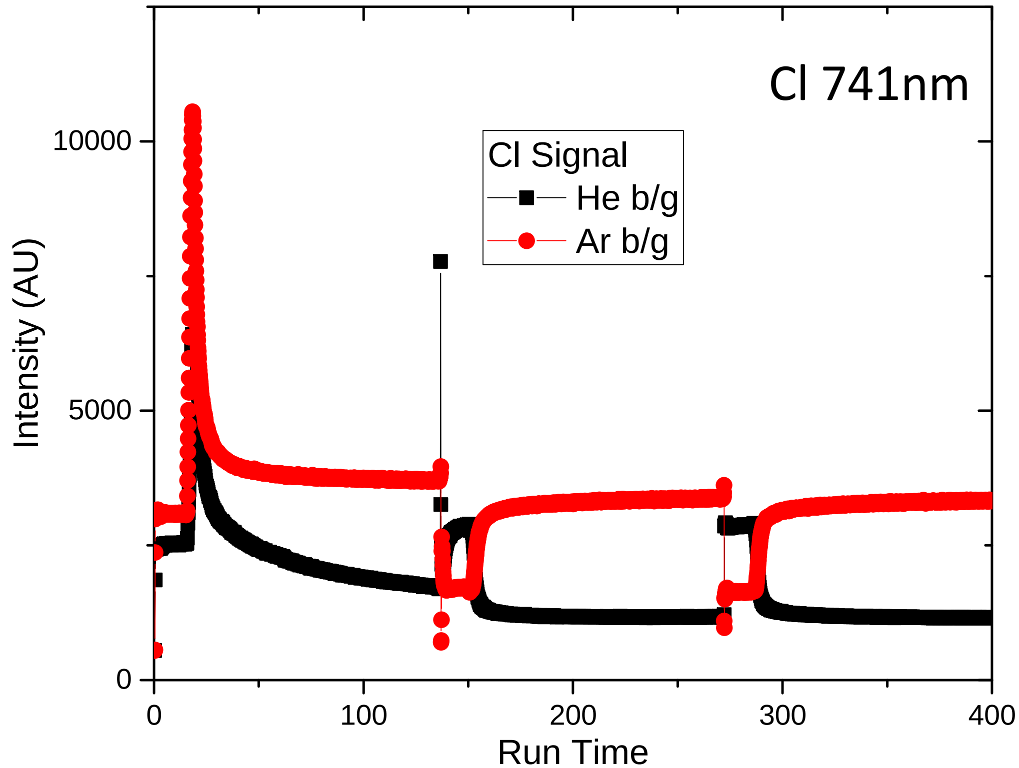
- **Use of synchronous plasma pulsing @ 60% DC results in a decrease of 50% in ER.**
- **Need to assess effect for extended step times!**

Overview

- Effect of Carrier Gas – Ar vs. He
  - Process Uniformity
  - Surface Composition
  - Effect of Carrier Wafer
  - Redeposition effects on Profile

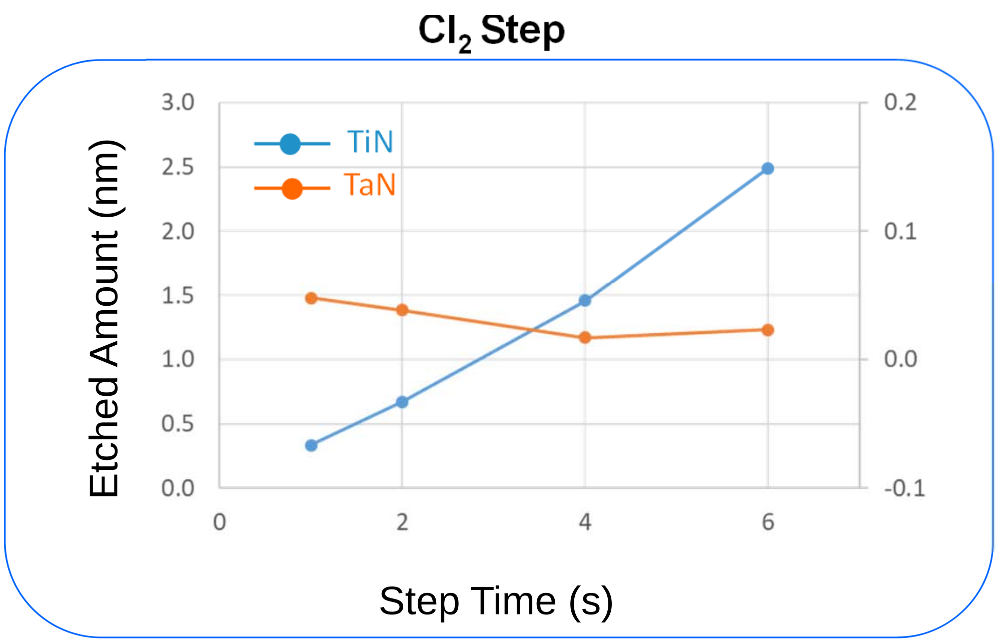
Effect of He vs. Ar as the background gas

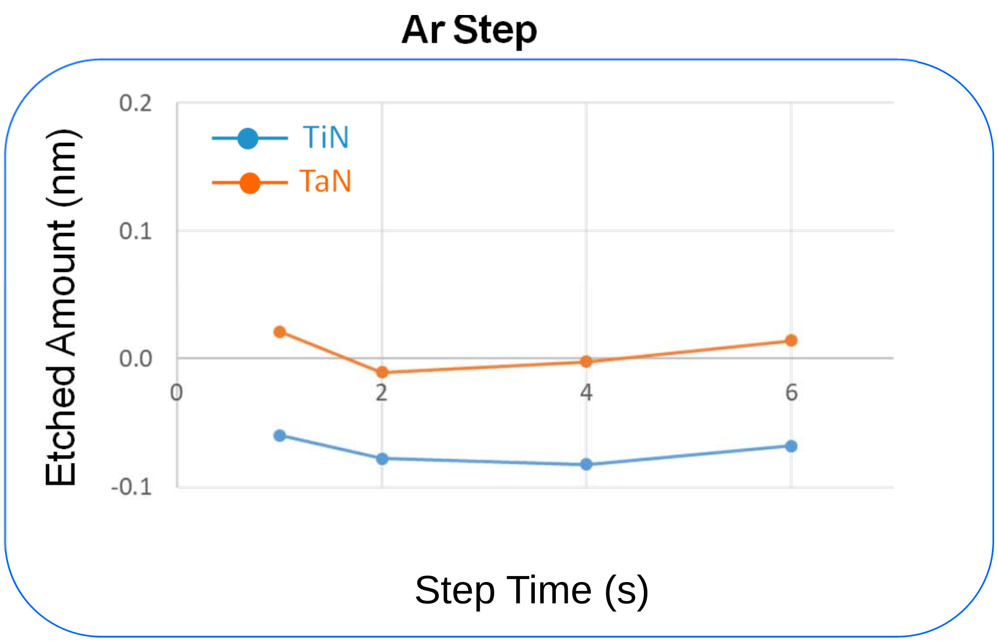




- **He was selected as a carrier gas to reduce the sputtering component**
- **Preliminary OES results suggest Cl may be vacated more effectively by Ar than He.**

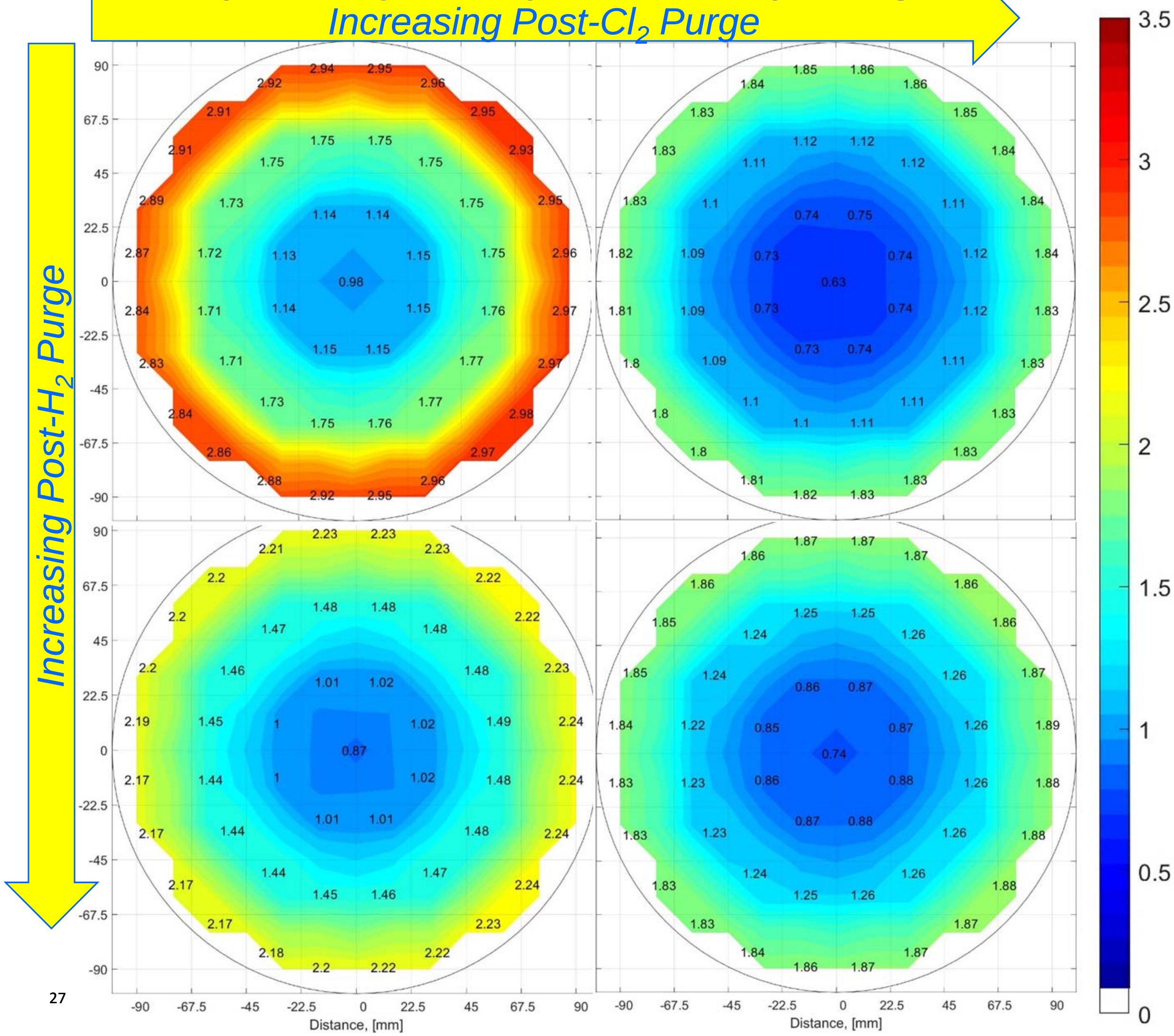
Individual Step Assessment – Ar background





- **Similar to He background, TiN etches spontaneously in Cl_2 under this plasma condition.**
- **No sputtering observed for either material.**

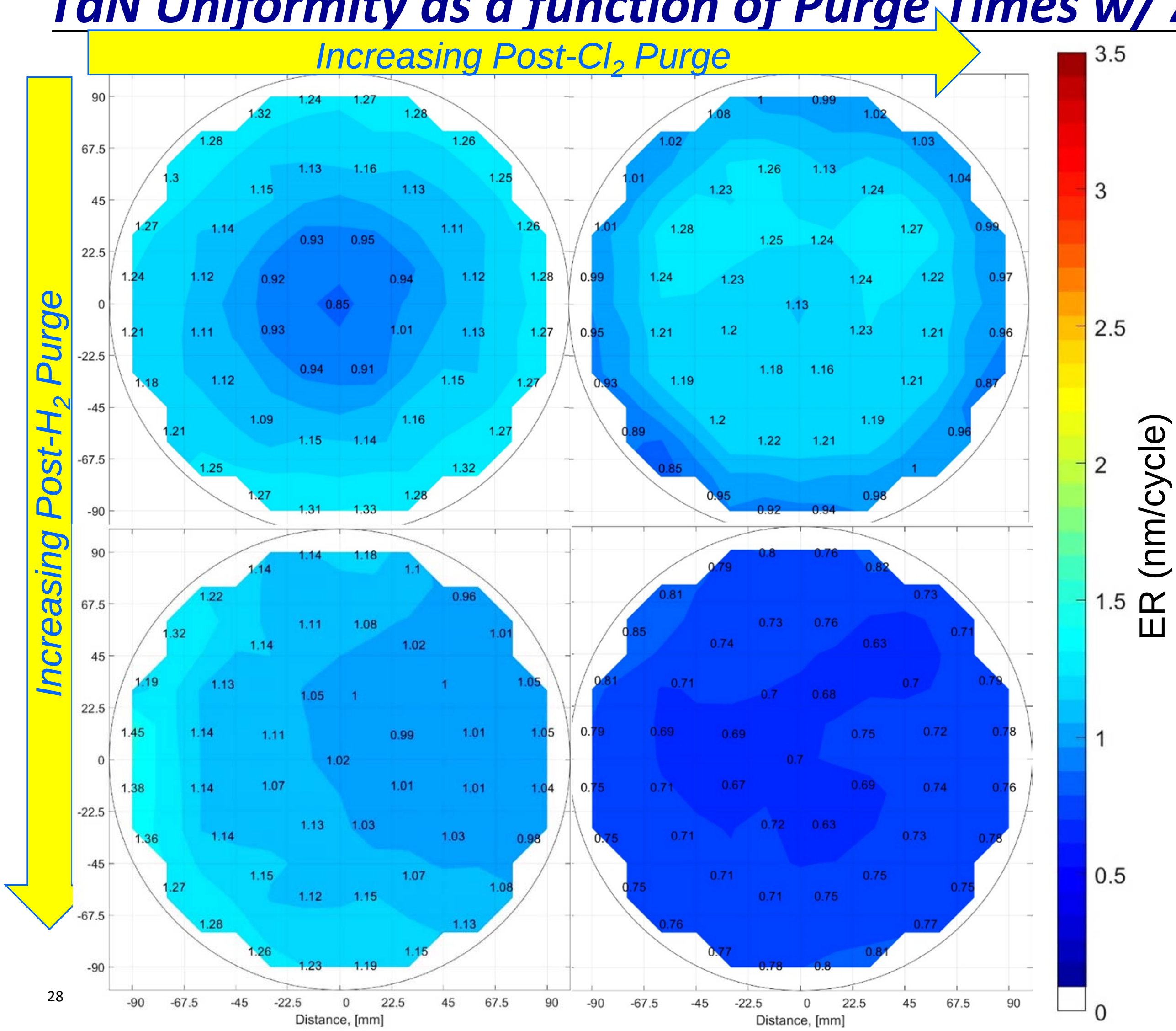
TiN Uniformity as a function of Purge Times w/ Ar Background



Post Cl_2 purge (s)	Post H_2 purge (s)	ER (nm/cyc)	StDev (%)
15	2	2.2	33.5
120	120	1.5	27.5
15	120	1.7	28.1
120	2	1.4	32.6

- **Opposite effect seen compared to He background – the ER decreases w/ increasing Cl_2 purge.**
- **Suggests Ar could contribute to purging Cl_2 more efficiently.**

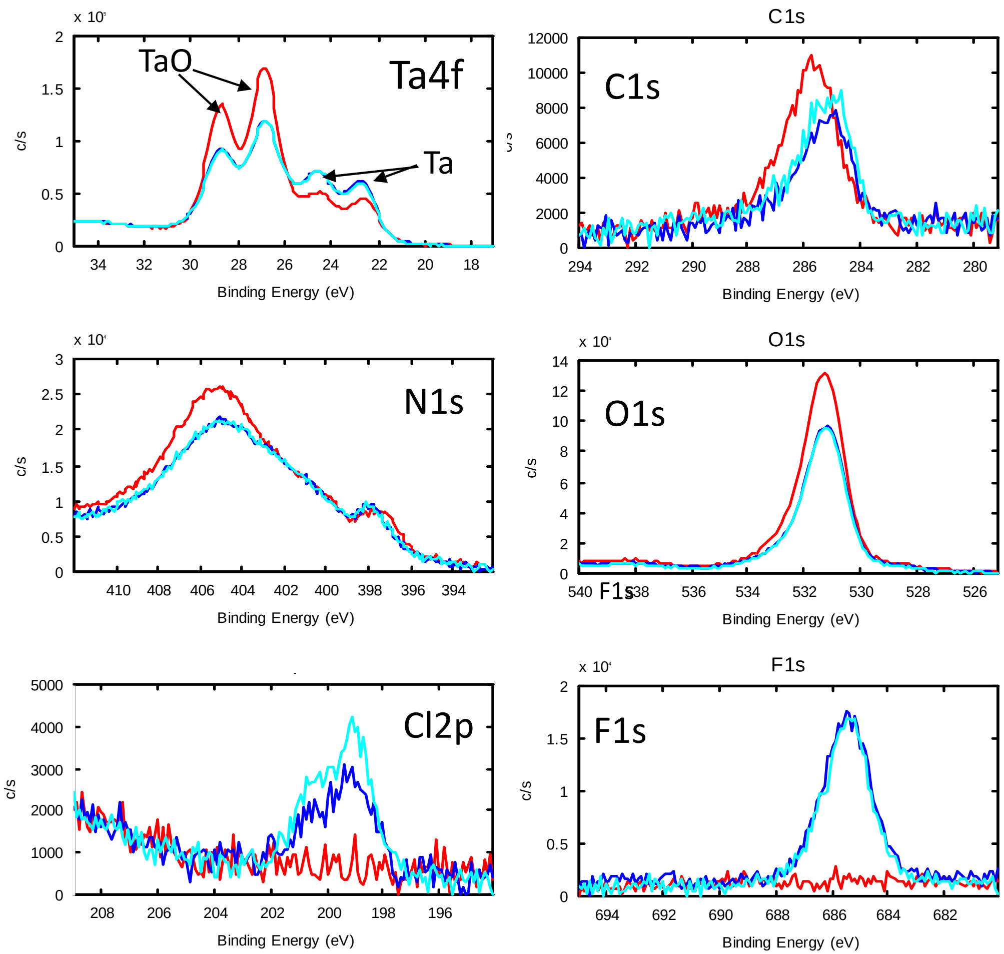
TaN Uniformity as a function of Purge Times w/ Ar Background



Post Cl_2 purge (s)	Post H_2 purge (s)	ER (nm/cyc)	StDev (%)
15	2	1.2	11.2
120	120	**0.7**	6.4
15	120	1.1	9.9
120	2	1.1	11.9

- **Improved across-wafer uniformity for cyclic TaN etch.**
- **Focus on TaN in remainder of study.**

Surface Composition of Blanket TaN

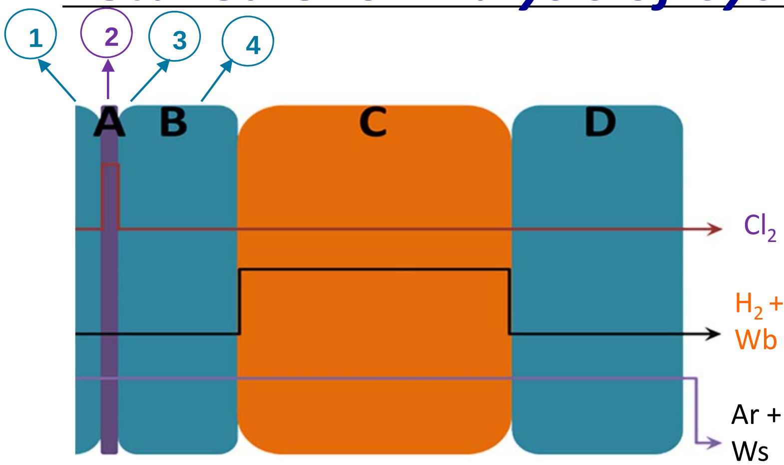


Pre-Etch
Cyclic, Long H_2 Purge (2,15,20,120) – 5 cycles
Cyclic, Long Cl_2 Purge (2,120,20,2) – 5 cycles

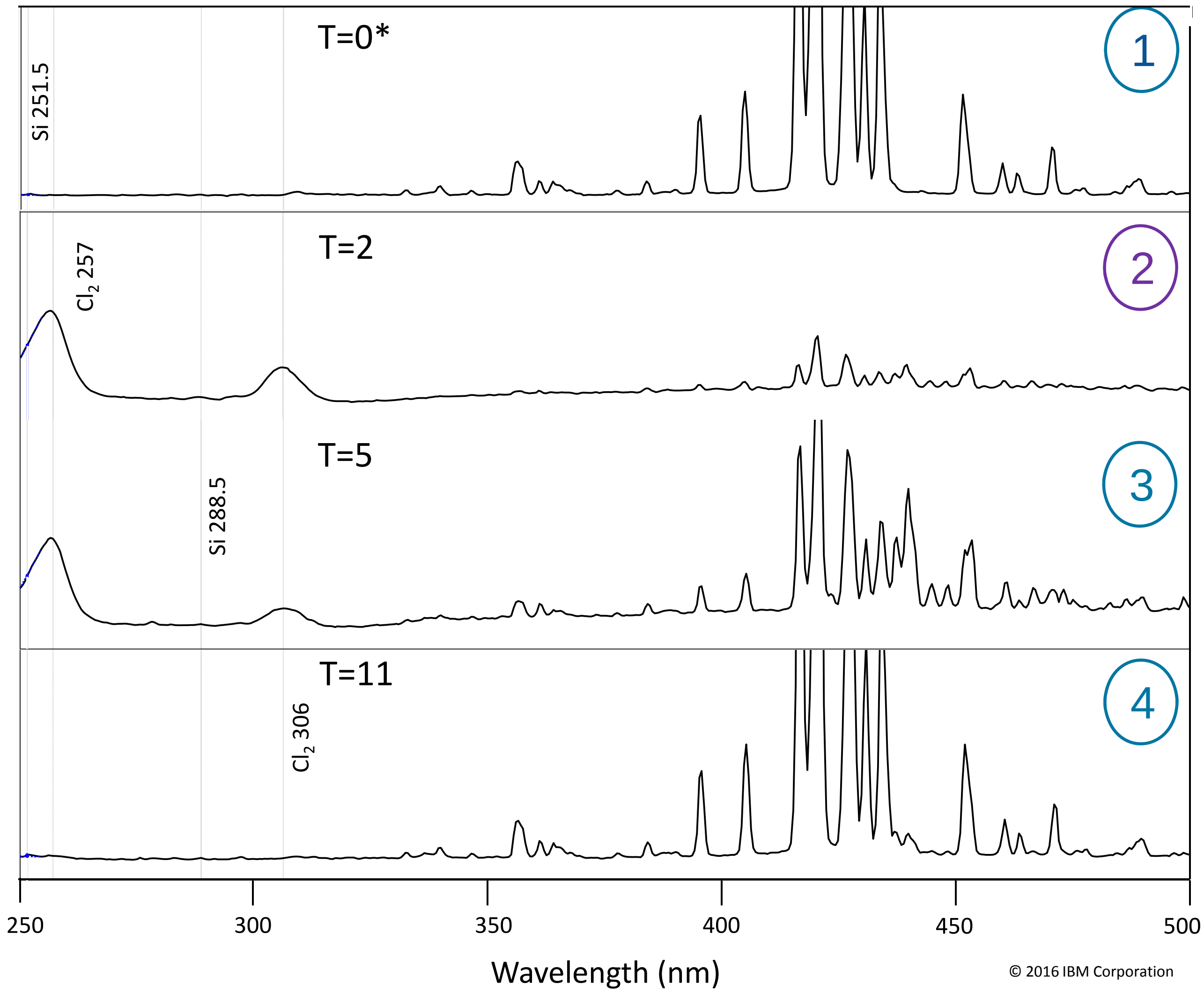
Element	Pre-Etch	Long Cl Purge	Long H_2 Purge
Ta	31	32	32
C	13	11	11
N	3	3	3
O	53	47	46
Cl	0	1	2
F	0	6	6

- **No significant differences seen in surface composition as a function of purge time.**
- **Etched films show reduced oxygen content corresponding to increase in relative intensity of metallic Ta.**

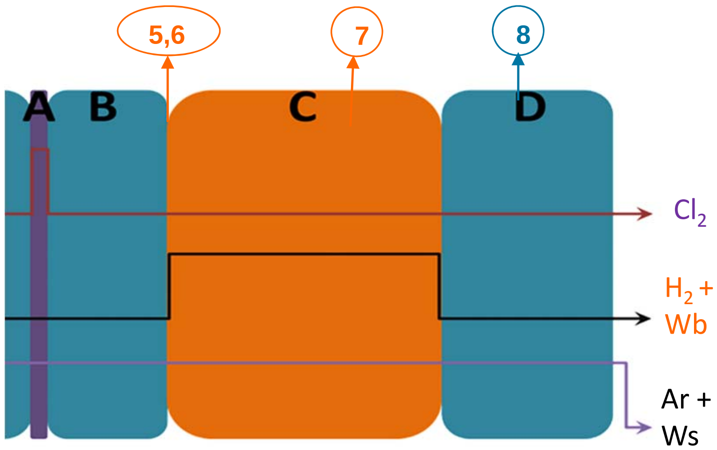
Detailed OES Analysis of Cyclic Process

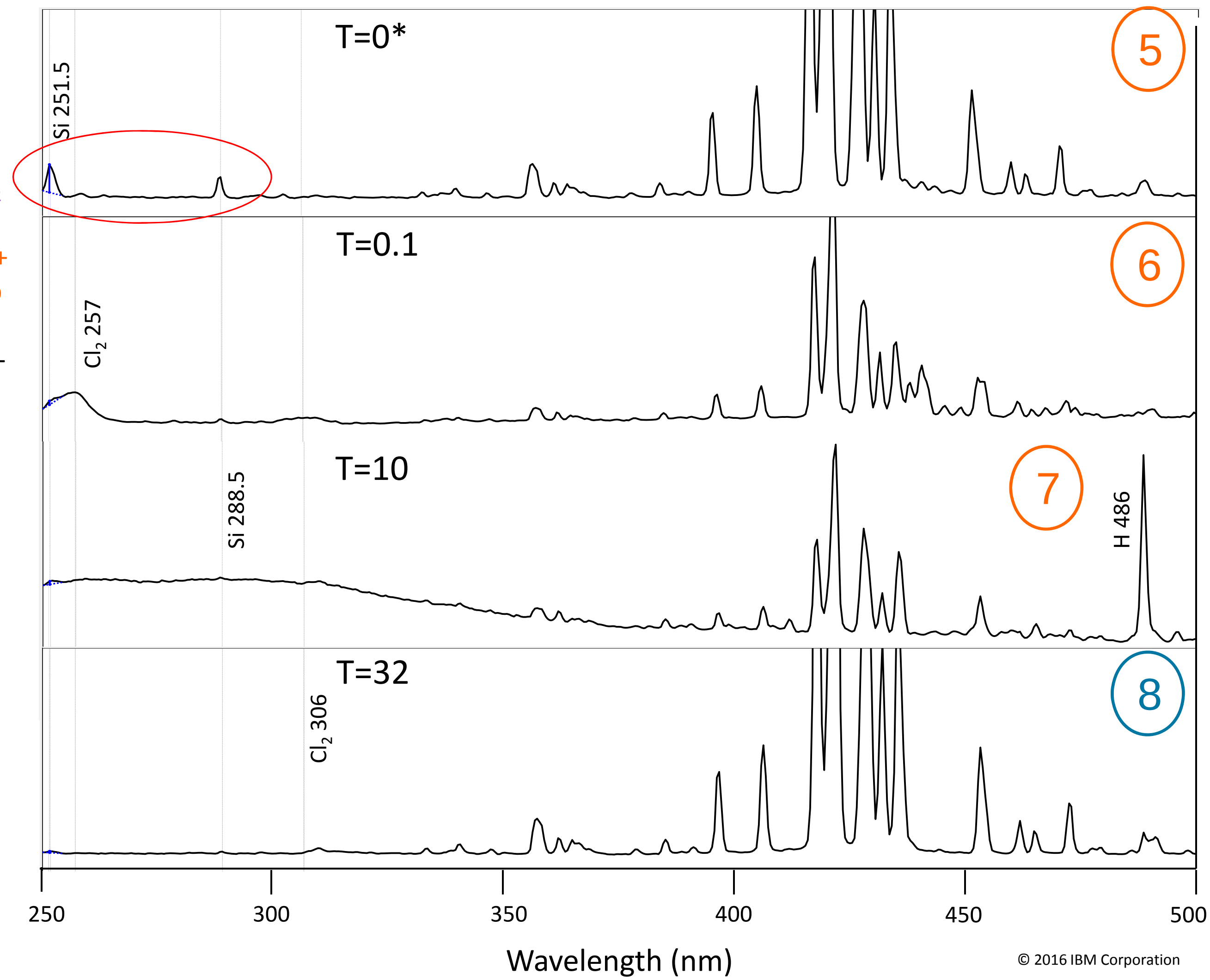


- As Cl_2 is introduced to the discharge relative intensity of background Ar gas drops (2).
- As Cl_2 is evacuated, its peaks become diminished (3), and subsequently intensity of Ar lines increases again (4).



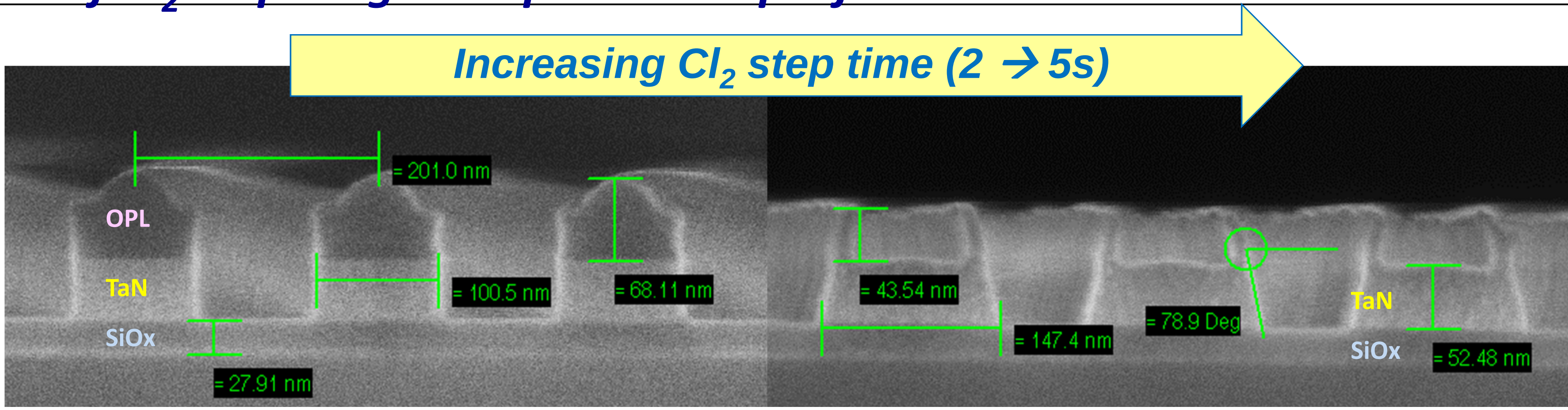
Detailed OES Analysis of Cyclic Process

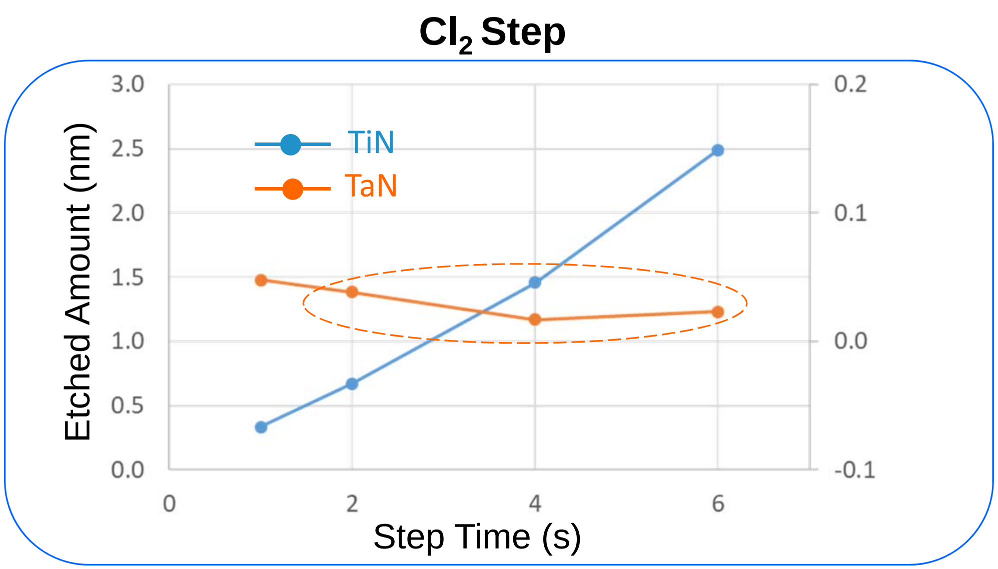




- **At onset of H_2/Wb step (5), matching network readjusts and Si excitation is seen. Cl_2 subsequently appears (6)**
- **Broad rise in UV seen during H_2 step and appearance of 486nm emission (7). As H_2 is purged, Ar dominates again (8).**

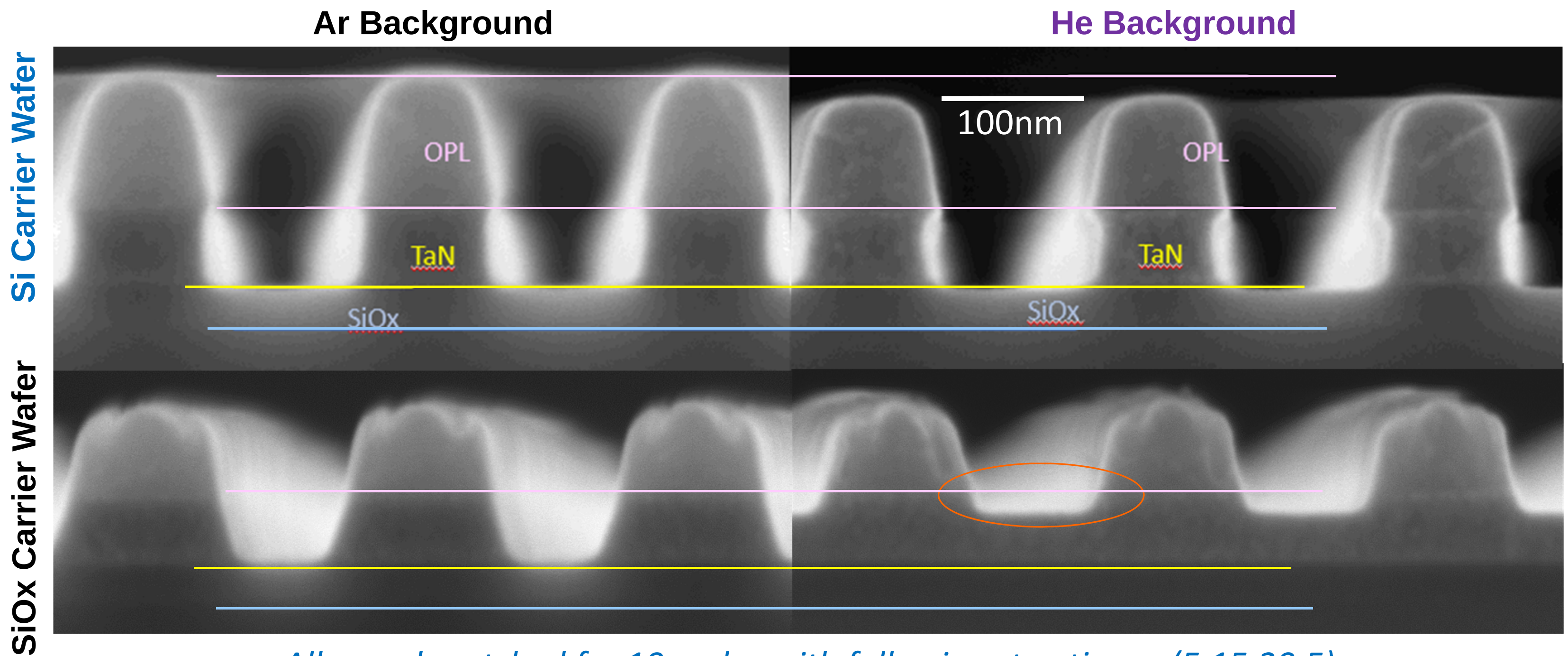
Effect of Cl_2 step length on patterned profiles





- For patterned samples, increased difficulty seen in breakthrough of native TaON layer, added brief CF_4 based step.
- Subsequently, on a coupon (~1/4 of 200mm wafer), large discrepancy seen in profiles with increased Cl_2 step length.
- However, blanket ER data shows no dependence on Cl_2 step length.

Carrier Wafer Effect



All samples etched for 10 cycles with following step times: (5,15,20,5)

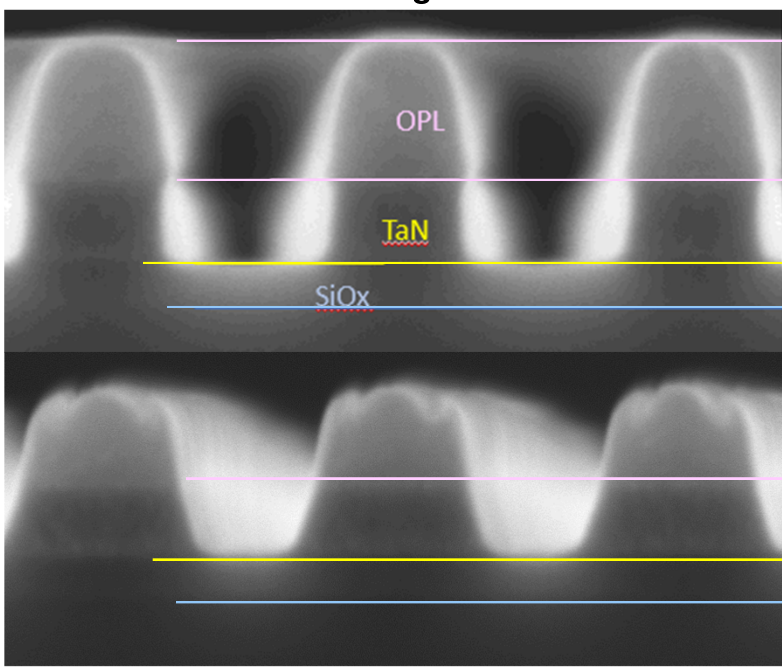
- **For the case of Si carrier wafer, OPL retention is worse in case of He background, more lateral etch of TaN observed.**
- **For SiO_x carrier wafer, OPL retention is worse than Si carrier and profiles become slanted.**

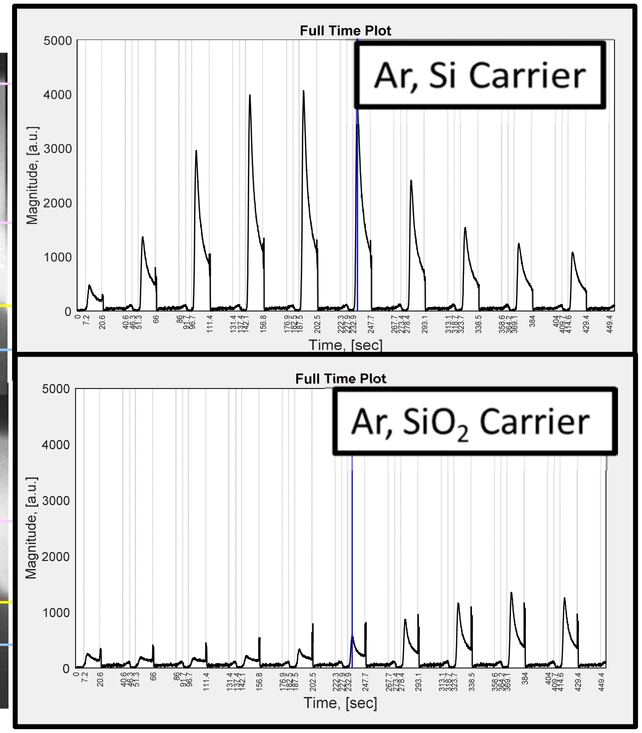
Carrier Wafer Effect

Ar Background

Si Carrier Wafer

SiOx Carrier Wafer





Ta 331nm as a function of time

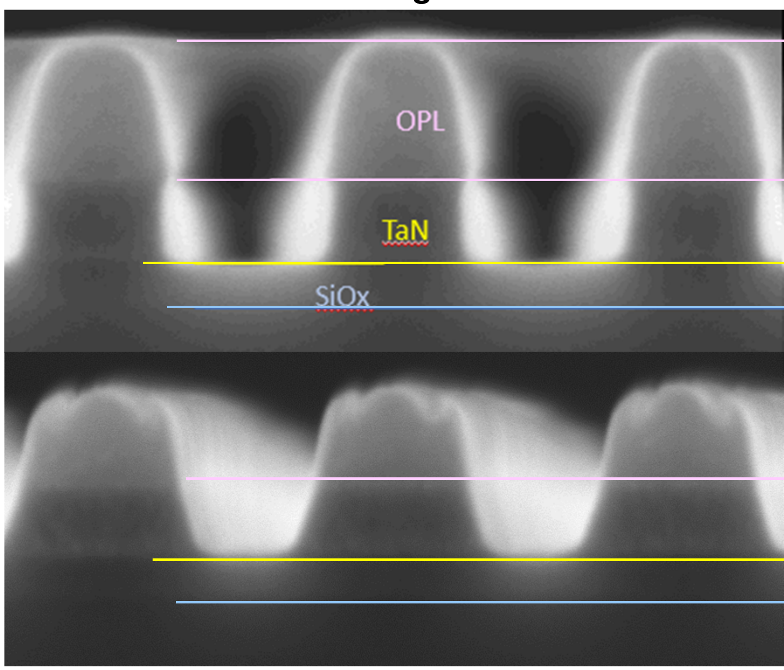
- For the case of Si carrier wafer, OPL retention is worse in case of He background, more lateral etch of TaN observed.
- For SiO_x carrier wafer, OPL retention is worse than Si carrier and profiles become slanted.

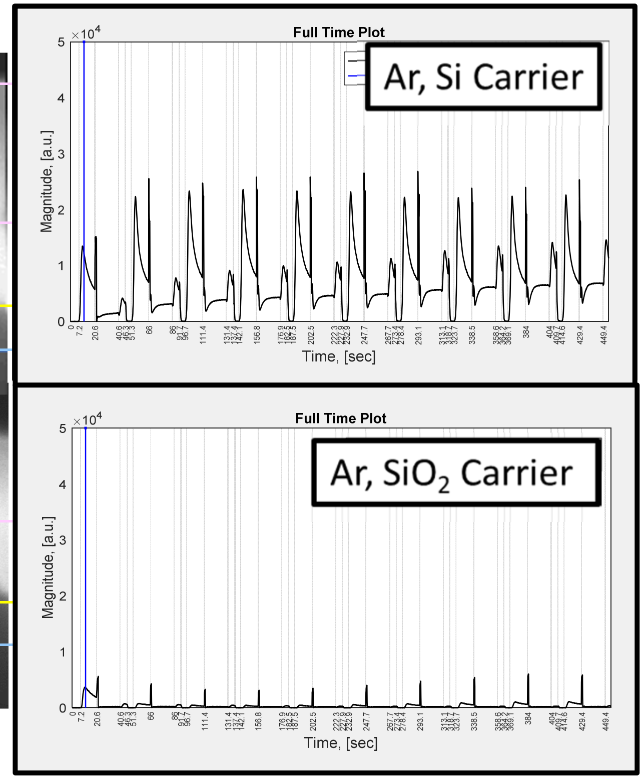
Carrier Wafer Effect

Ar Background

Si Carrier Wafer

SiOx Carrier Wafer



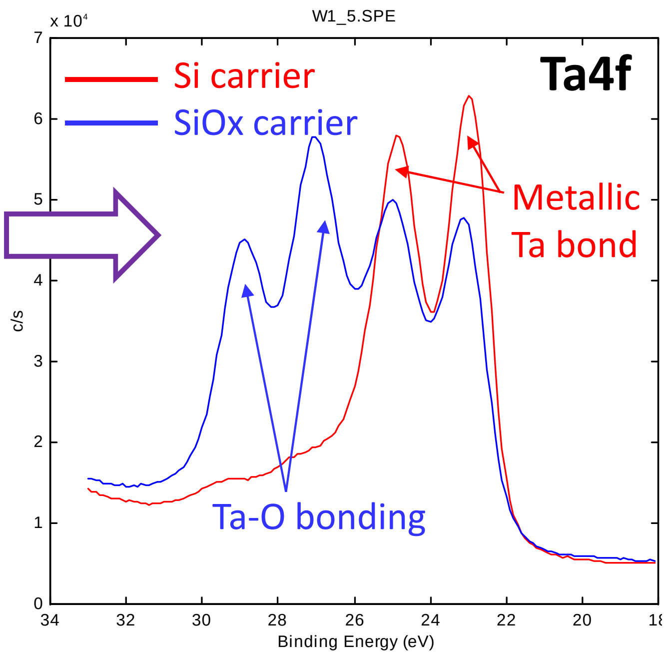


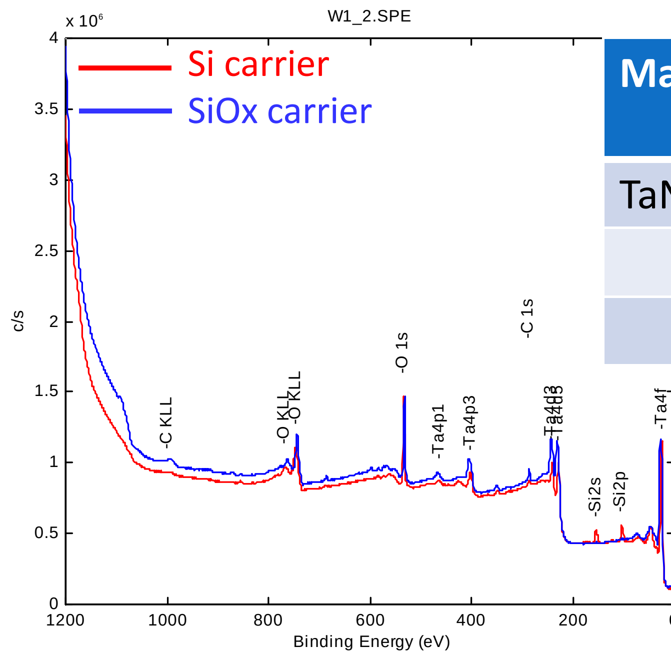
Si 251nm as a function of time

- For the case of Si carrier wafer, OPL retention is worse in case of He background, more lateral etch of TaN observed.
- For SiO_x carrier wafer, OPL retention is worse than Si carrier and profiles become slanted.

Surface Composition Dependence on Carrier Wafer

¼ wafer
BT + 3 cycles
(5,15,20,5)

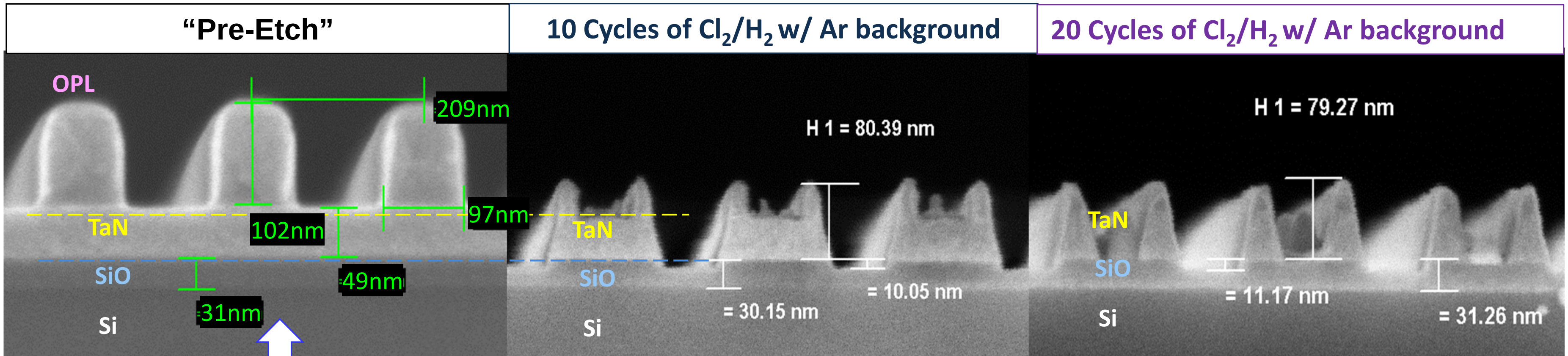




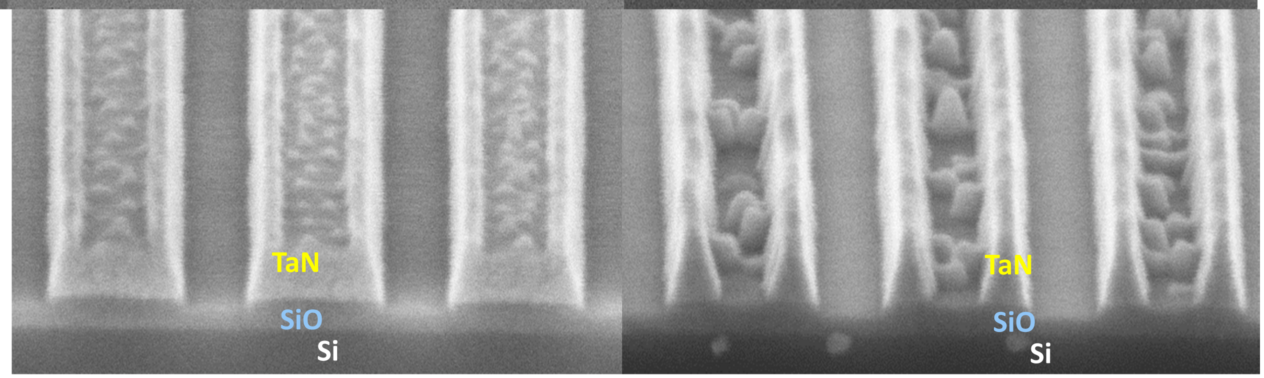
Material	Bond	ΔHf_{298} (kJ/mol)
TaN	Ta-N	611
	Ta-Cl	544
	Ta-O	805

- **Pronounced Ta-O bonding seen after 3 cycles of etching using SiOx carrier.**
- **Survey scans confirm presence of Si on surface for Si carrier (observed in OES).**
- **Ta-O formation in line with thermodynamic data.**

Utilizing Redeposition Effects



Note: this sample was exposed to 10 cycles of Cl_2/H_2 (Ar) without the CF_4 based breakthrough.

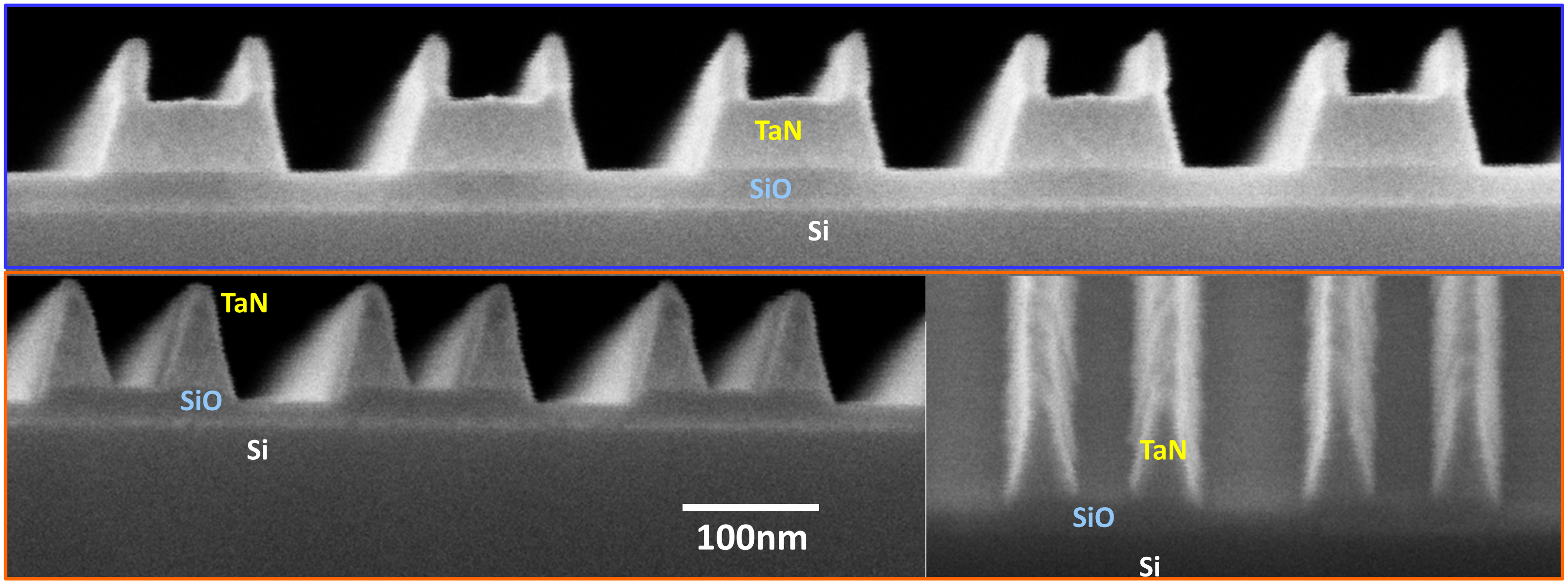


- **Fencing effect and OPL loss was caused by exposure of OPL mask to cyclic process.**
- **Used to create "pitch split" effect from single lithographic feature.**

Utilizing Redeposition Effects

Ar background
BT + 10 cycles

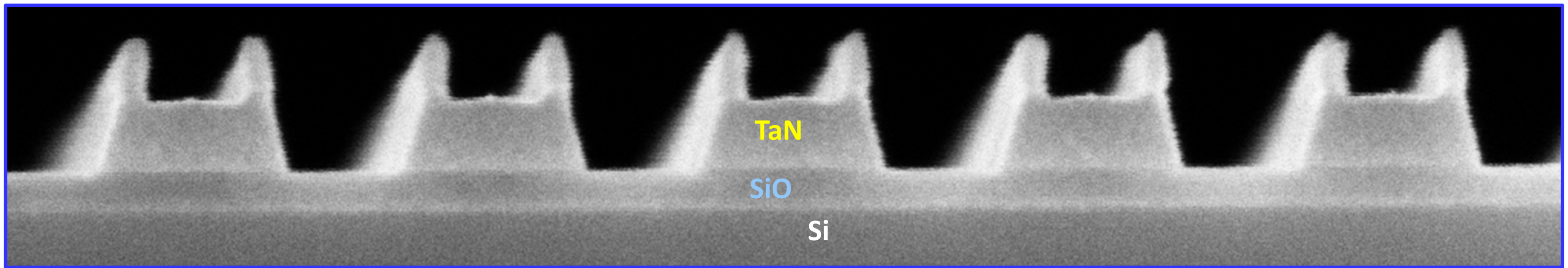
Ar background
BT + 20 cycles



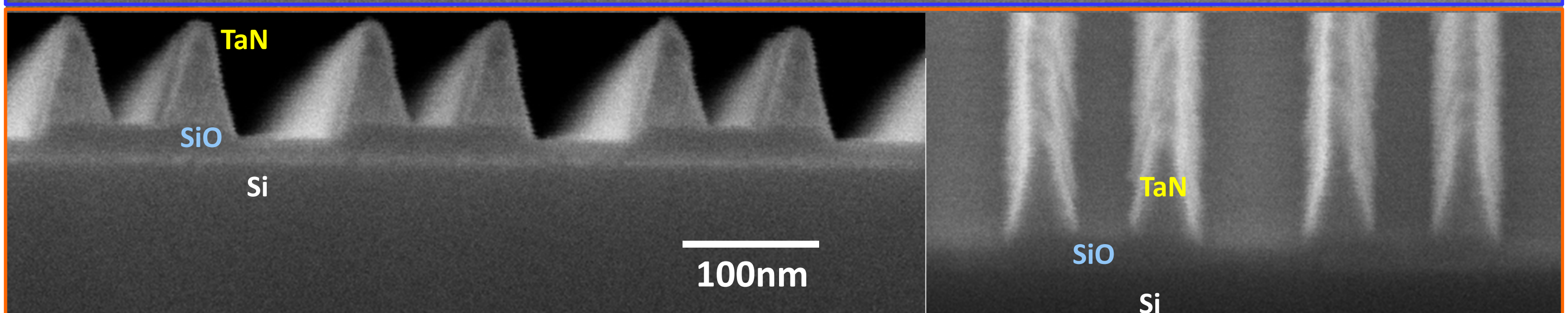
- **Experimental result reproduced after “pre-exposure” of OPL mask to cyclic etch process.**

Utilizing Redeposition Effects

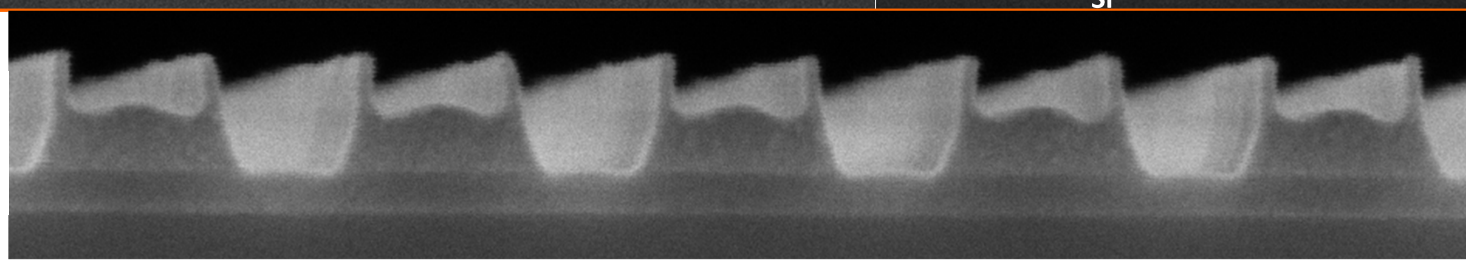
Ar background
BT + 10 cycles



Ar background
BT + 20 cycles



He background
BT + 13 cycles
(Thick SiOx carrier)



- **Experimental result reproduced after "pre-exposure" of OPL mask to cyclic etch process.**
- **Later found that thickness of SiOx on carrier wafer also played role.**

Conclusions

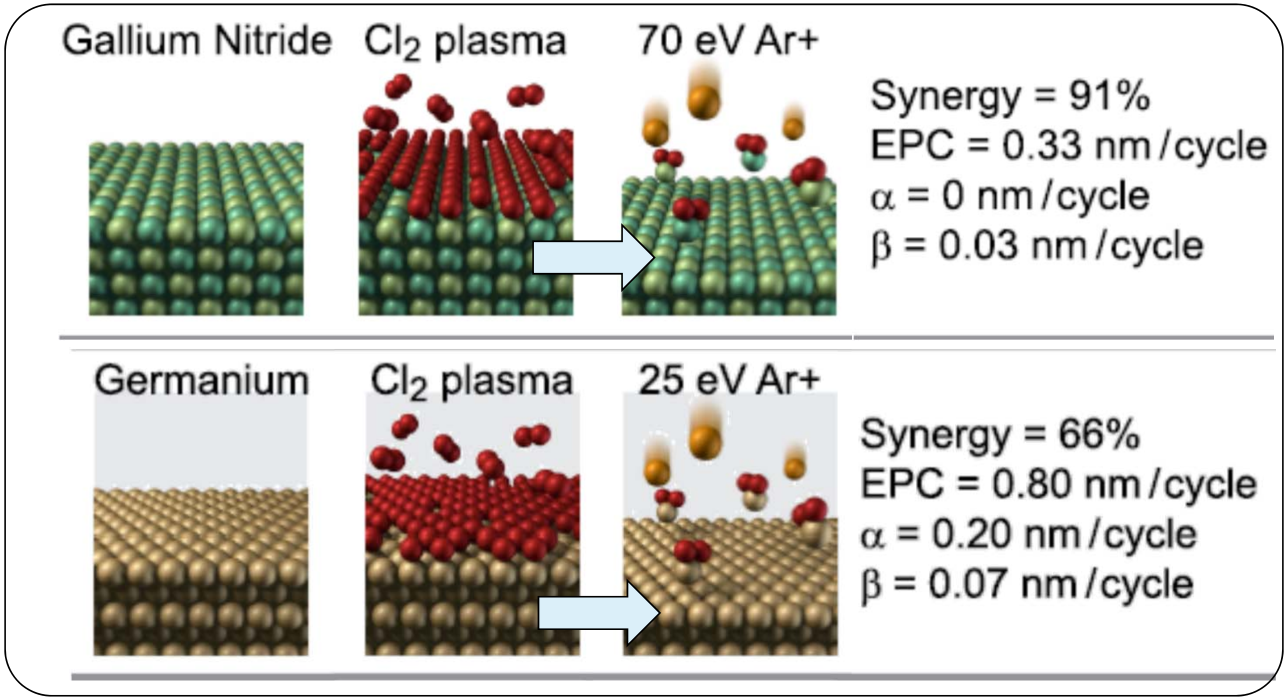
- Flux-controlled Quasi-ALE process using Cl_2 and H_2 demonstrated on TiN and TaN using OPL masks.
- Cyclic etching approach offers several benefits – less sputtering/redeposition, additional knobs for control of profile/CD.
- Key differences in He vs. Ar background gas that need to considered (e.g. when operating in spontaneous etch regime).
- Loading effects/mask interaction also play important role when trying to apply quasi-ALE to patterned features!

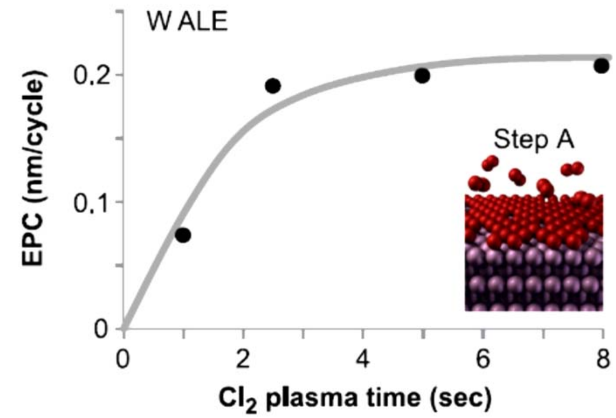
Acknowledgments

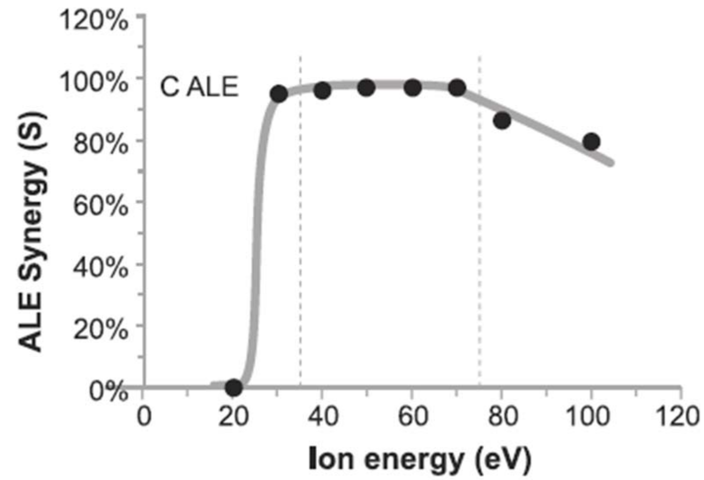
- All results shown have been produced in the Microelectronics Research Laboratory (MRL) at the TJ Watson Research Center, Yorktown Heights.
- Authors would like to thank TJ Watson management for their support of our efforts.
- Thanks to Robert Bruce and Hongwen Yan for fruitful discussions.

Synergy Assessment

$$\text{ALE synergy \% }(S) = \frac{\text{EPC} - (\alpha + \beta)}{\text{EPC}} \times 100\%.$$



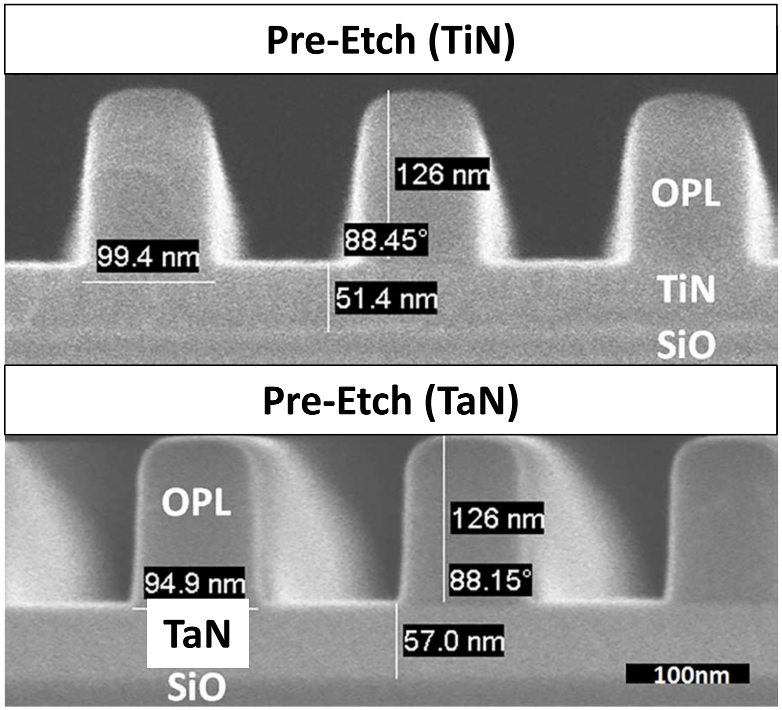


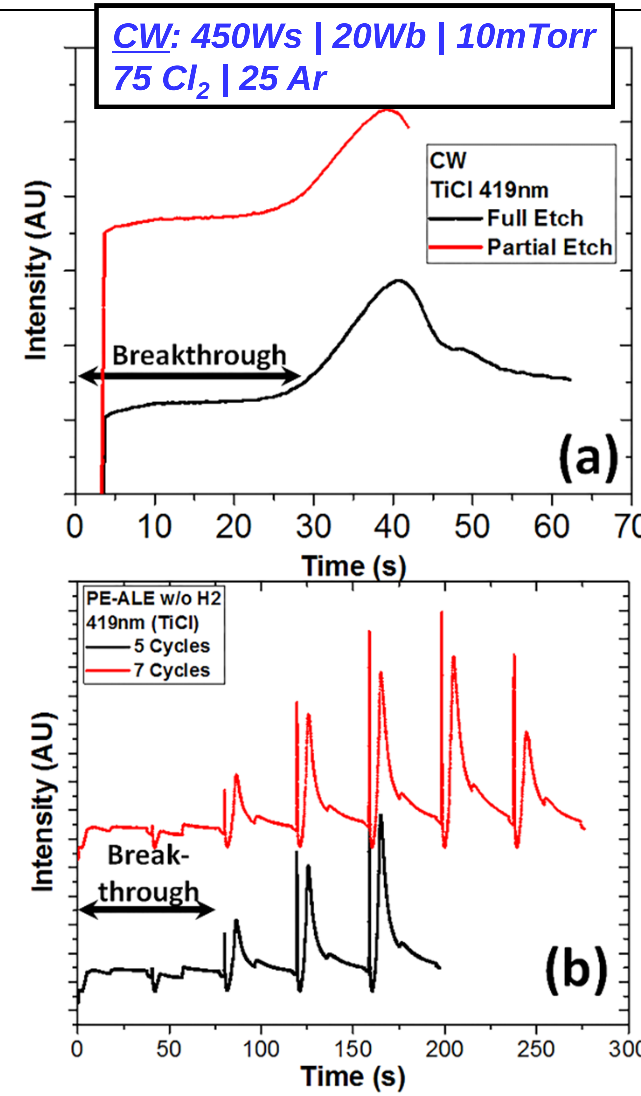


- **Synergy is a measure of deviation from ideal behavior.**
- **Linked to surface energy of materials.**

(Kanarik et al., JVST A, 2017)

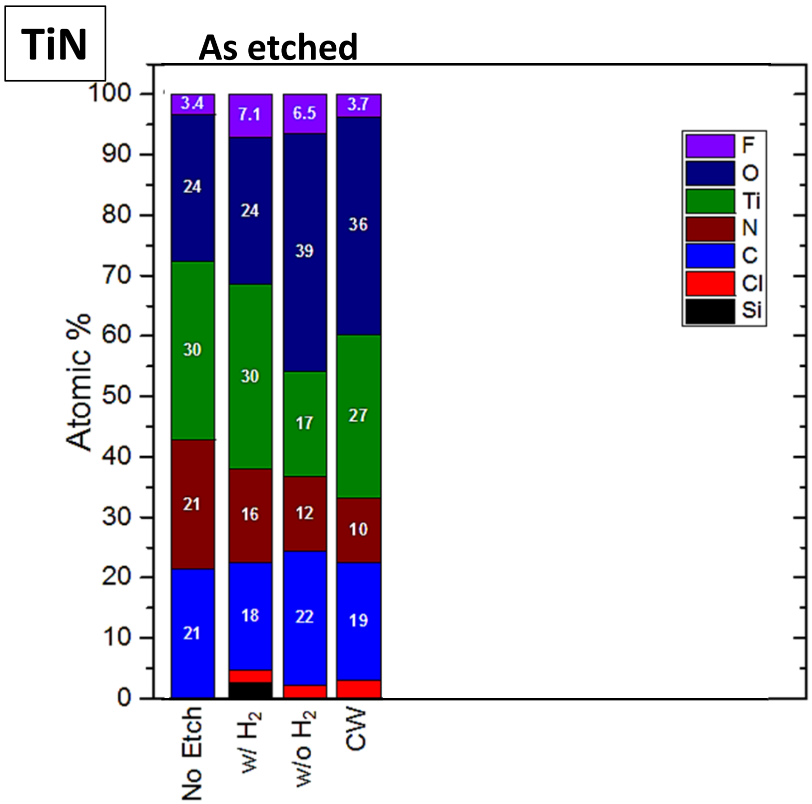
Role of Surface Oxidation





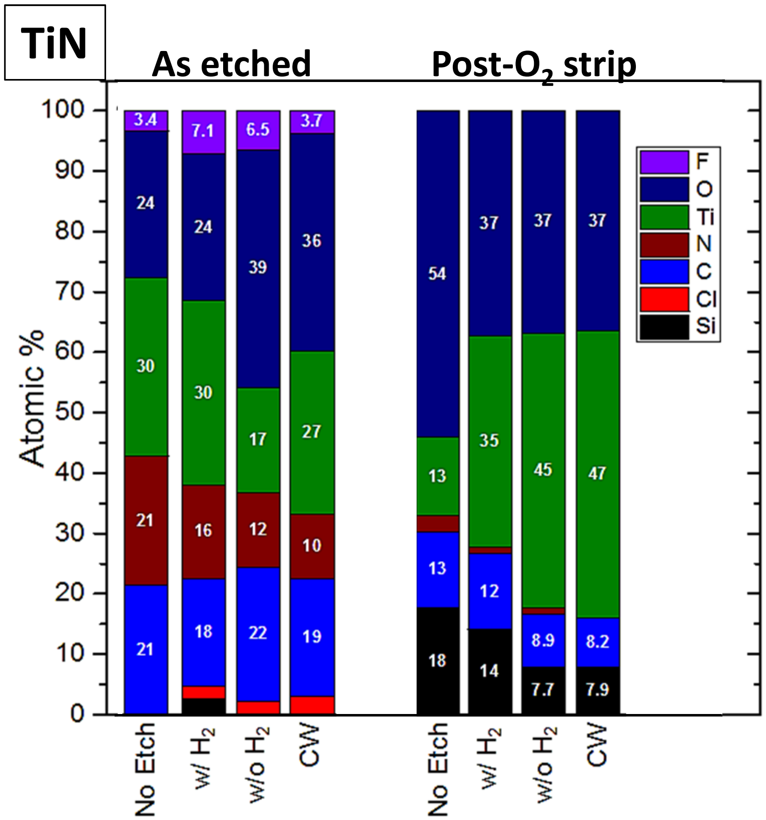
- **Breakthrough delay observed for TiN and TaN, both CW and cyclic etch processes.**
- **Oxidation of surface attributed to the OPL mask open (N_2/O_2)**

Surface Chemistry Effects



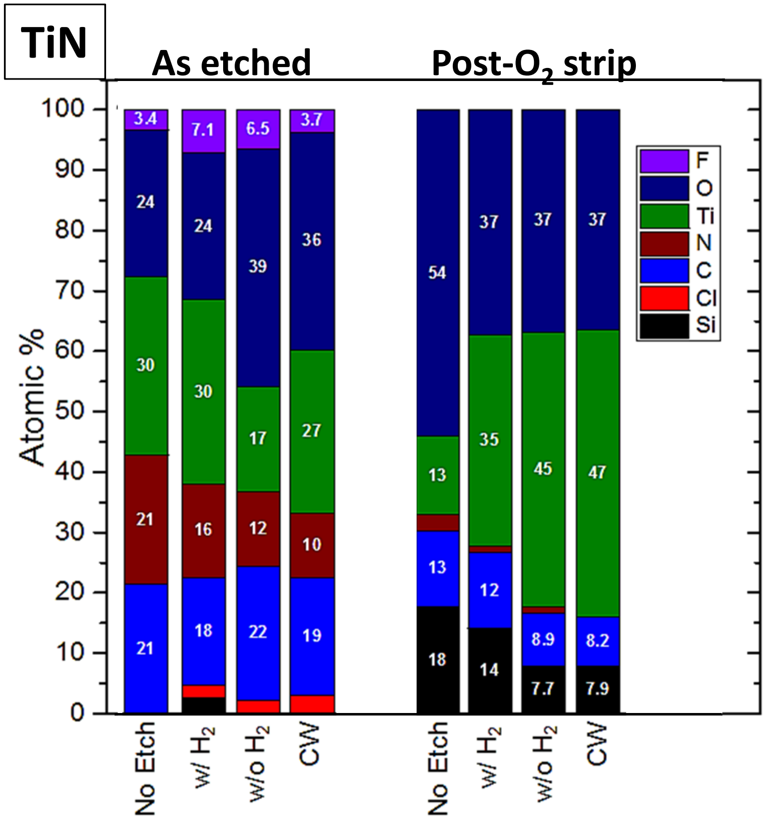
- Cyclic Etch process (w/ H_2) show best retention of Ti:N ratio compared to CW.

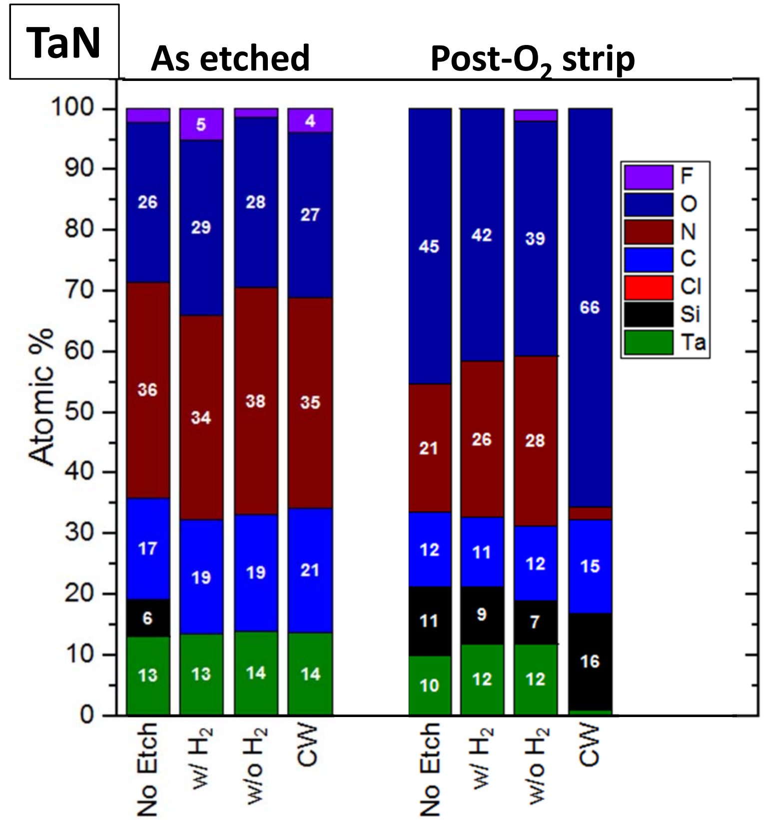
Surface Chemistry Effects



- Cyclic Etch process (w/ H_2) show best retention of Ti:N ratio compared to CW.

Surface Chemistry Effects





- ❑ **Cyclic Etch process (w/ H_2) show best retention of Ti:N ratio compared to CW.**
- ❑ **For TaN, cyclic etch shows significantly less oxidation post O_2 strip.**