Status Talk: ALD & ALE

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CHyN
Center for Hybrid Nanostructures

Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

My Introduction

Rakshith Venugopal

Bachelor of Science, (Physics, Chemistry, Mathematics) 2019 - 2022
at CHRIST University, Bangalore, India
Graduated Top of Class: 1.00 GPA

Master of Science, Physics, 2022 - Current
Center for Hybrid Nanostructures, University of Hamburg,
Thesis: ”Atomic Layer Etching of SiO_2 using Ar/SF_6 Plasma”

PEALD Coating of Thin Films

ALD-assisted VO_2 for memristor devices

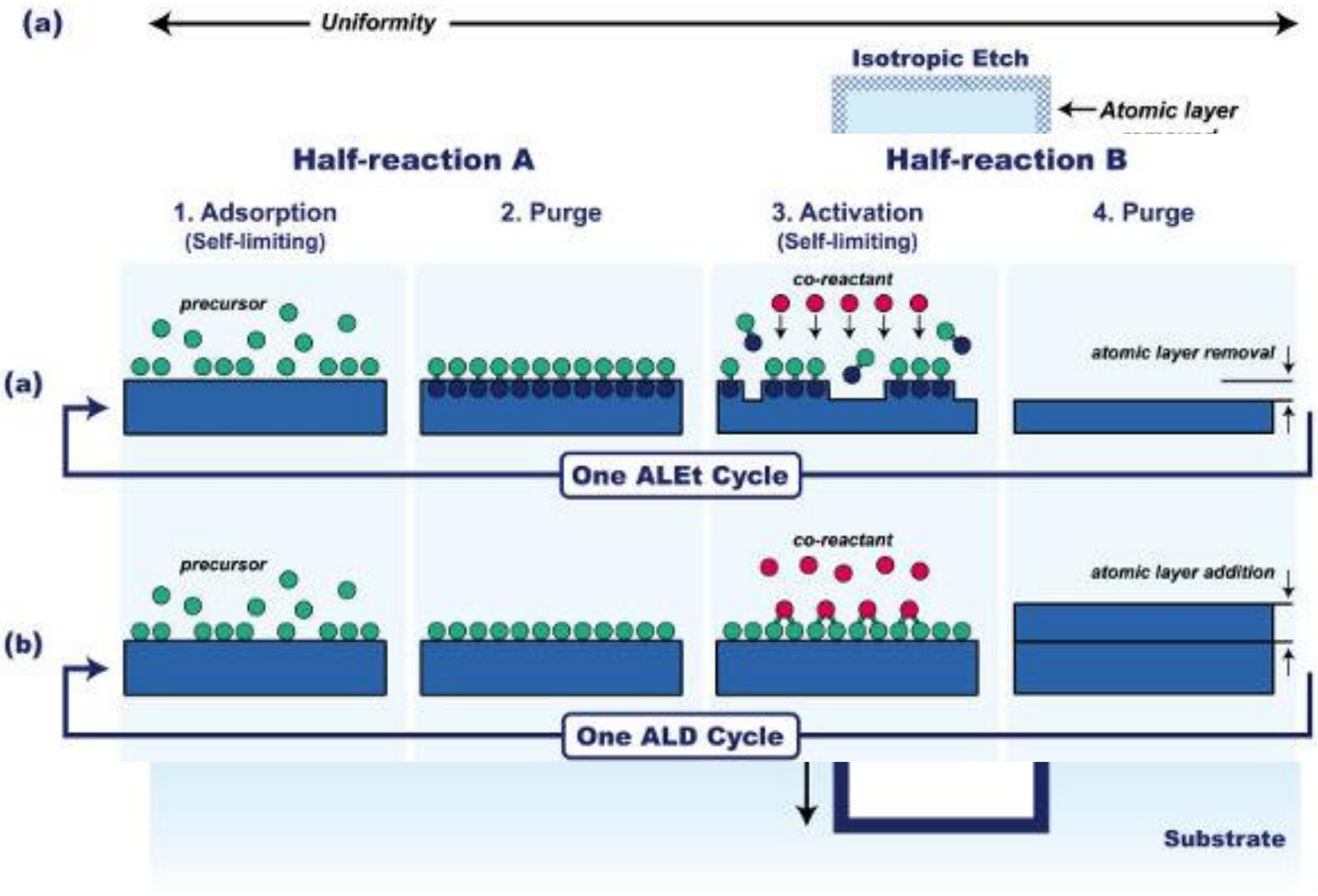
Atomic Layer Etching of SiO_2

Position Sensitive Detector

Atomic Layer Deposition vs Atomic Layer Etching

Atomic Layer Etching (ALEt)

- Self-limiting half-reactions
- One atomic layer **removal**
- Etching gas + energy source
- Lower temperatures
- Anisotropic/ Isotropic



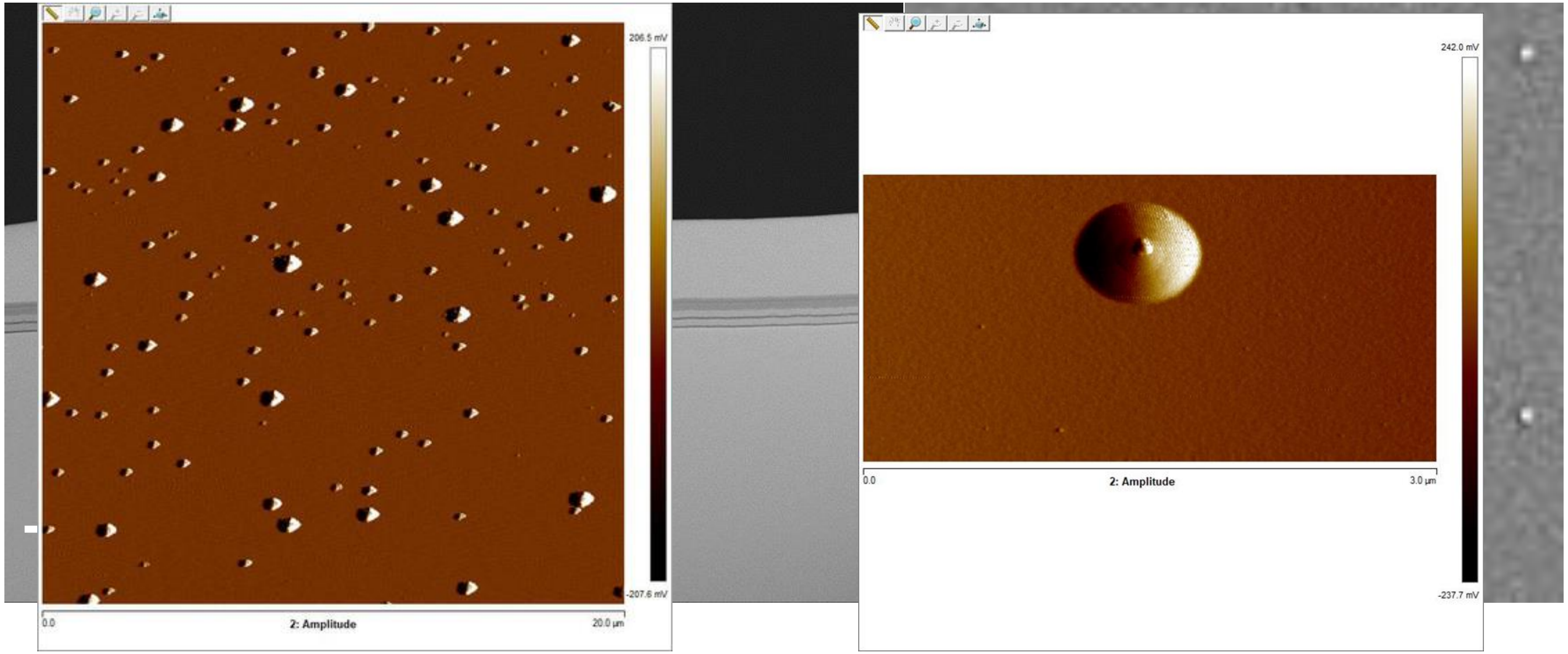
Atomic Layer Deposition (ALD)

- Self-limiting half-reactions
- One atomic layer **addition**
- Precursor + co-reactant
- Moderate to High temperatures
- Conformal coating

Source: nanomanufacturing.nl/ALE/

Blister Study on PEALD Grown thin films

Blisters on Thin Films



AFM scan of Si + AlN (182 cycles)~10 nm

First Samples

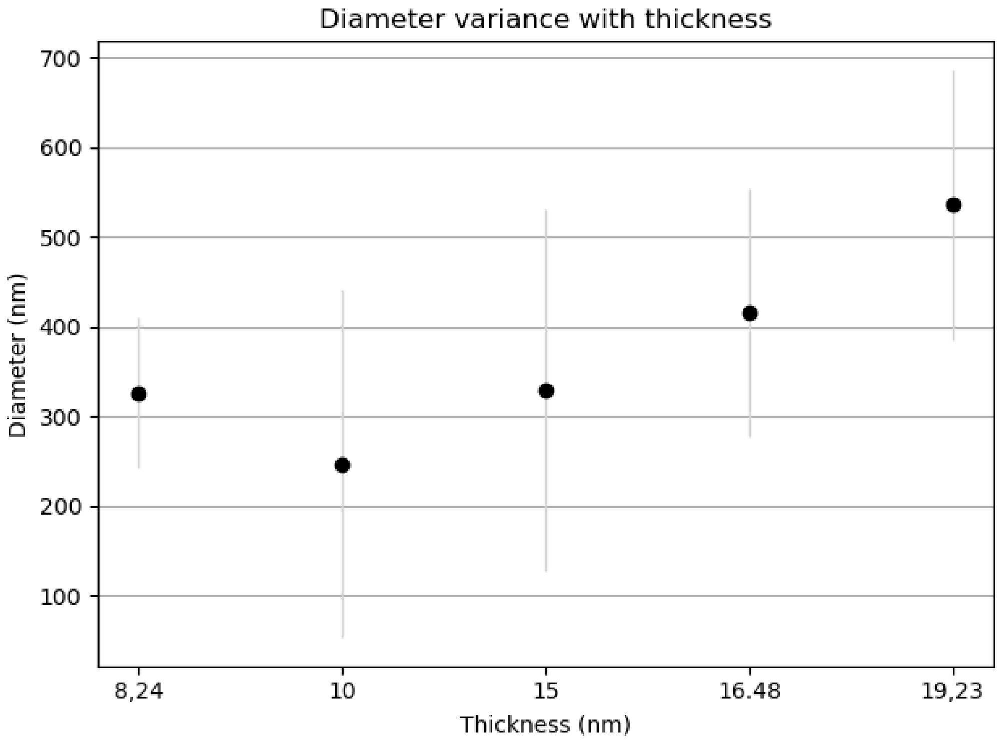
Substrate + Coating	Blisters?
Si + AlN	Yes
Si + NbTiN	No
Si + AlN + NbTiN	Yes
Nb + NbTiN	No
Nb + AlN	No
Nb + AlN + NbTiN	Yes
Nb + (AlN + NbTiN) X 2	Yes

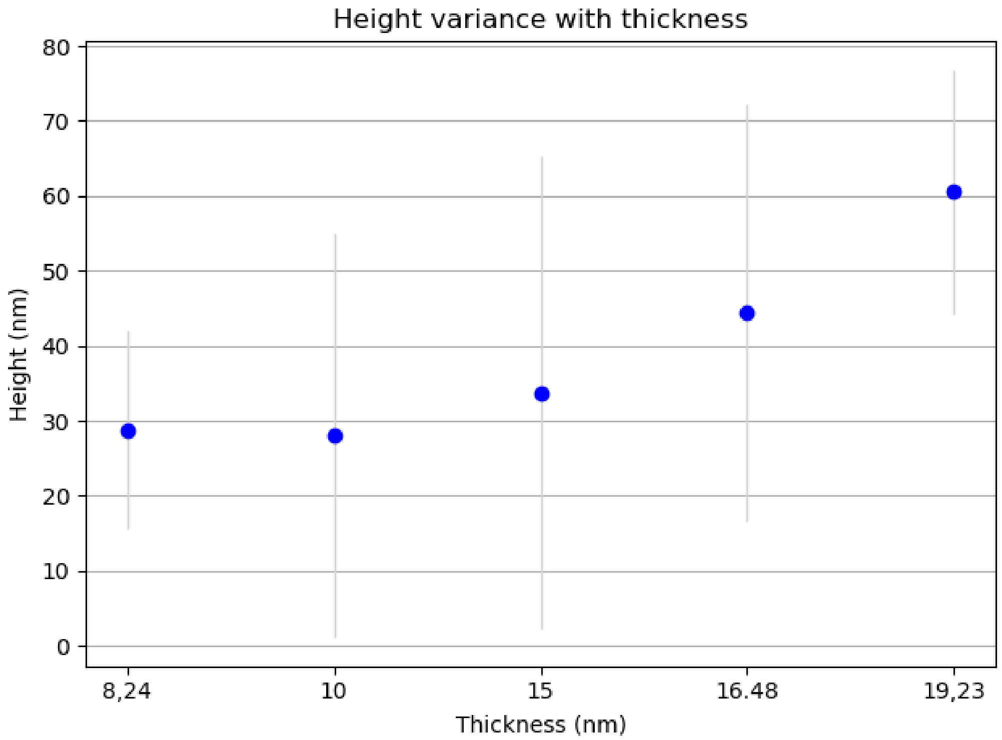
- Formation of blisters could be attributed to presence of H[13], defects in substrate/local delamination due to stress[14].
- Formation of blisters was attributed to the coating of AlN at a higher temperature.
- Increasing thickness of AlN also increases density of blisters

Abbreviations

Si : Silicon
AlN: Aluminium Nitride
NbTiN : Niobium Titanium Nitride
Nb : Niobium

Blister Diamater and Height with thickness of AlN

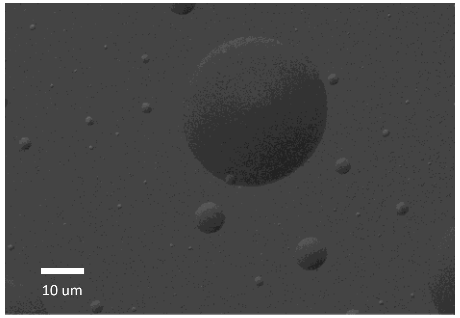




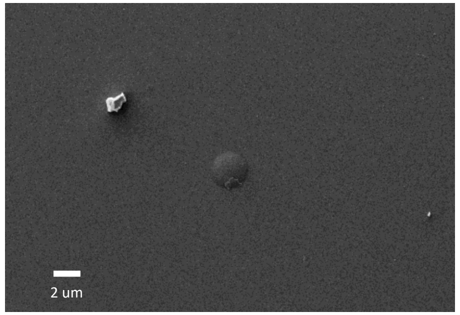
Further Studies

Aluminum Nitride at different Temperatures

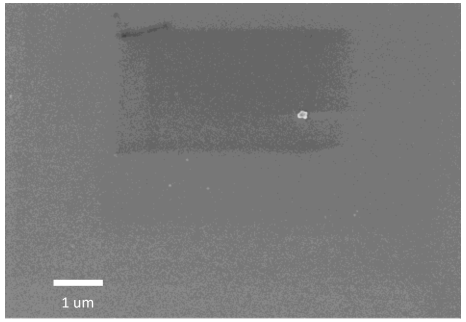
@105 °C



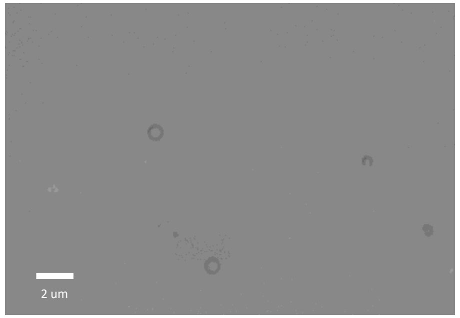
@125 °C



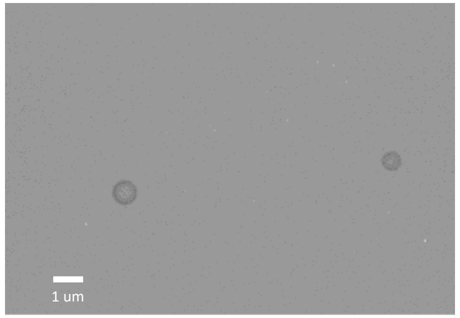
@150 °C



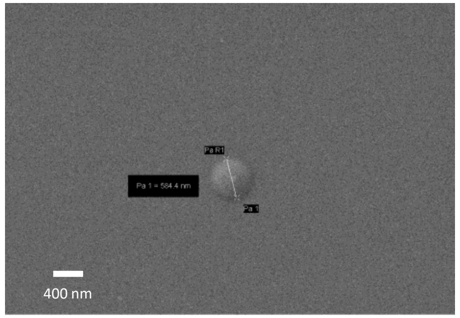
@170 °C



@200 °C



@250 °C



Temperature (°C)	Blisters?
105	Yes
125	Yes
150	No
170	Yes
200	Yes
250	Yes

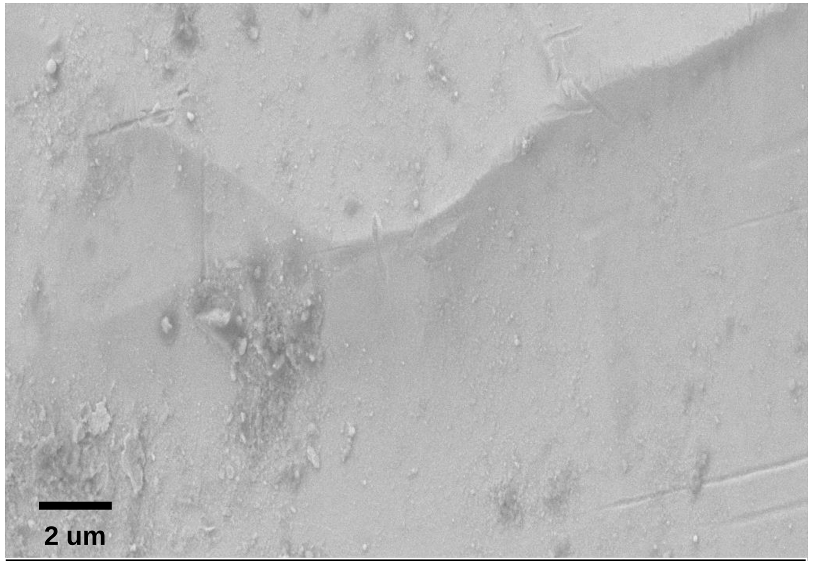
But, coating at 175 later yielded no blisters.

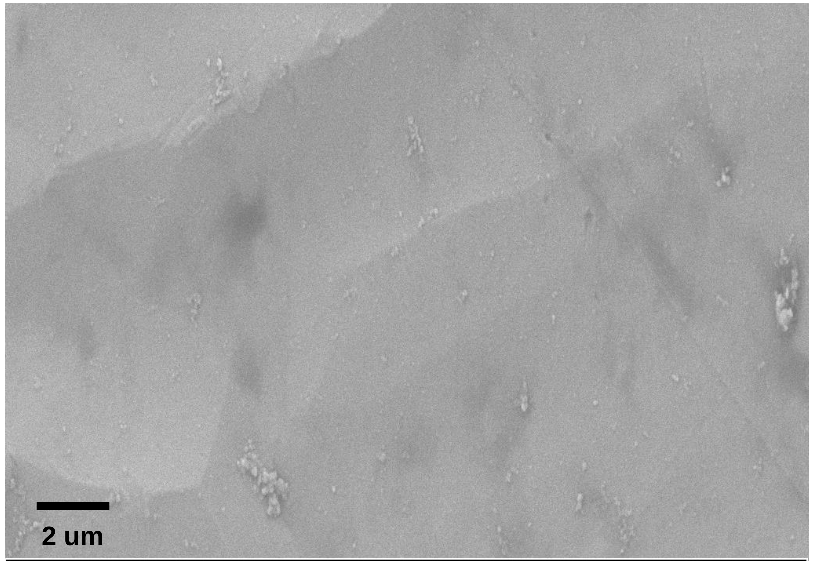
Coating on Niobium substrate

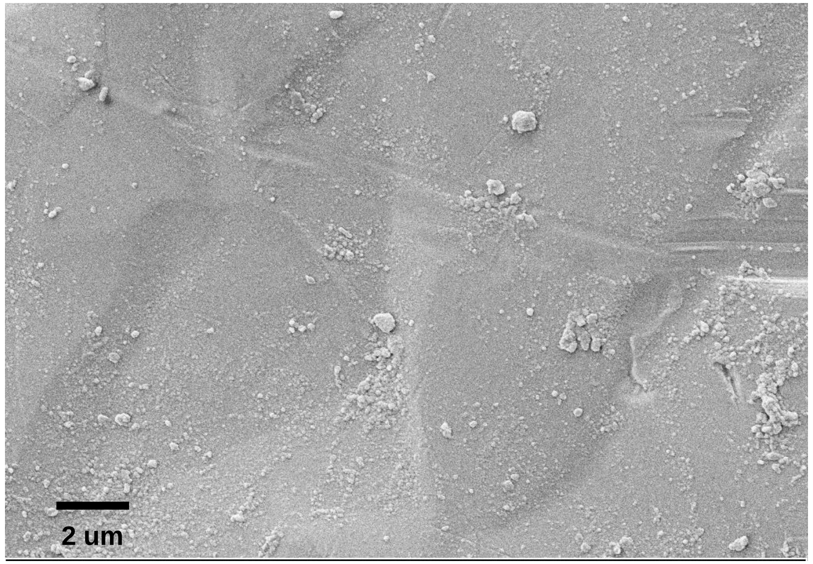
AlN (350 cycles)
@ 175 °C

AlN (350 cycles)
@ 175 °C + 30 hours

AlN (273 cycles) + NbTiN
(81 cycles) @ 175 °C







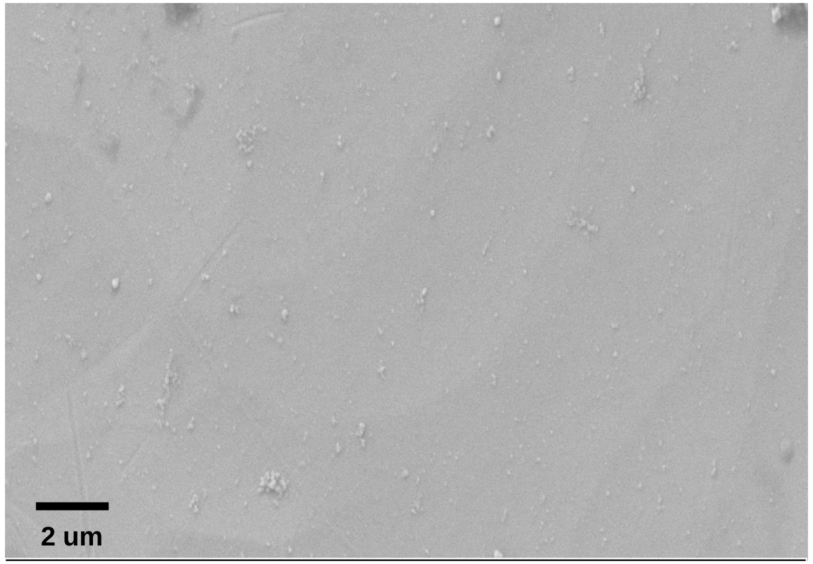
No Blister Formation on Niobium substrate!

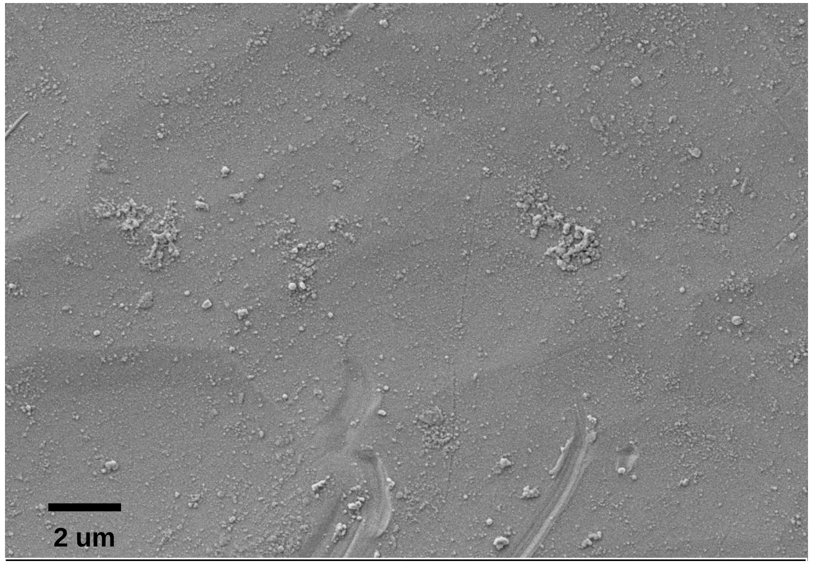
Coating on Niobium substrate

NbTiN (100 super cycles)
@ 175 °C

NbN (100 cycles)
@ 175 °C

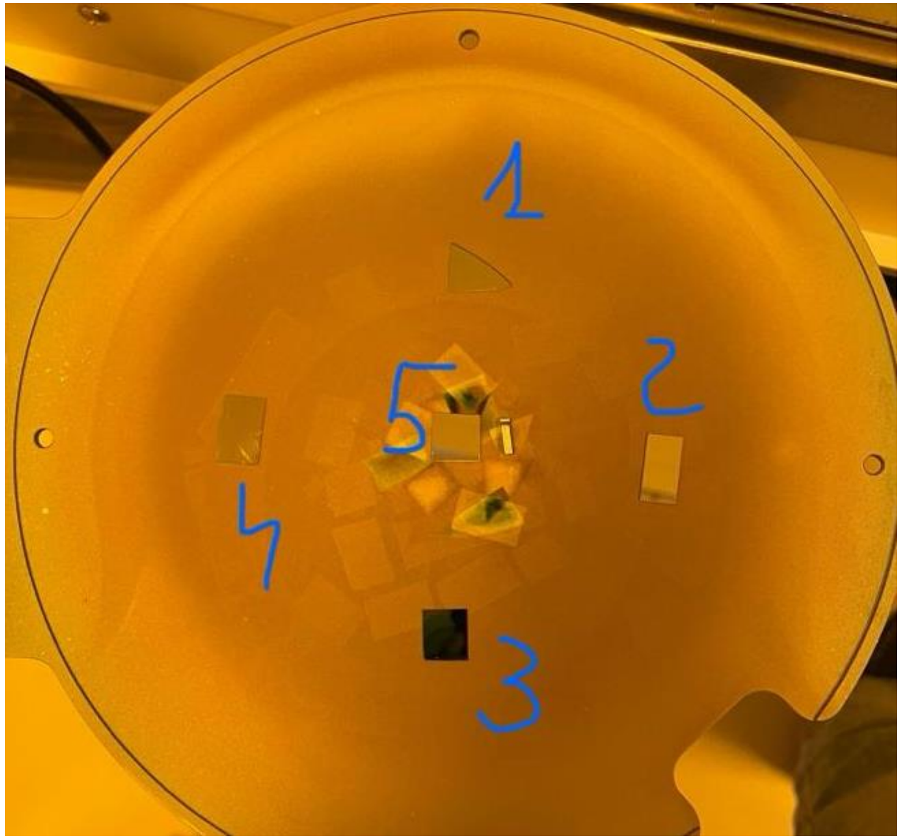
NbTiN (100 super cycles) +
AlN (350 cycles)@ 175 °C





No Blister Formation on Niobium substrate!

Study of Blisters on different substrates at 175 °C



Coating	Blisters on Substrate (At 175 °C)		
	On Si	On AlN	On Nb
TiN	No	No	-
NbN	No	Yes	No
AlN + NbTiN	Yes	-	No
AlN	No	-	No
NbTiN	No	Yes	No

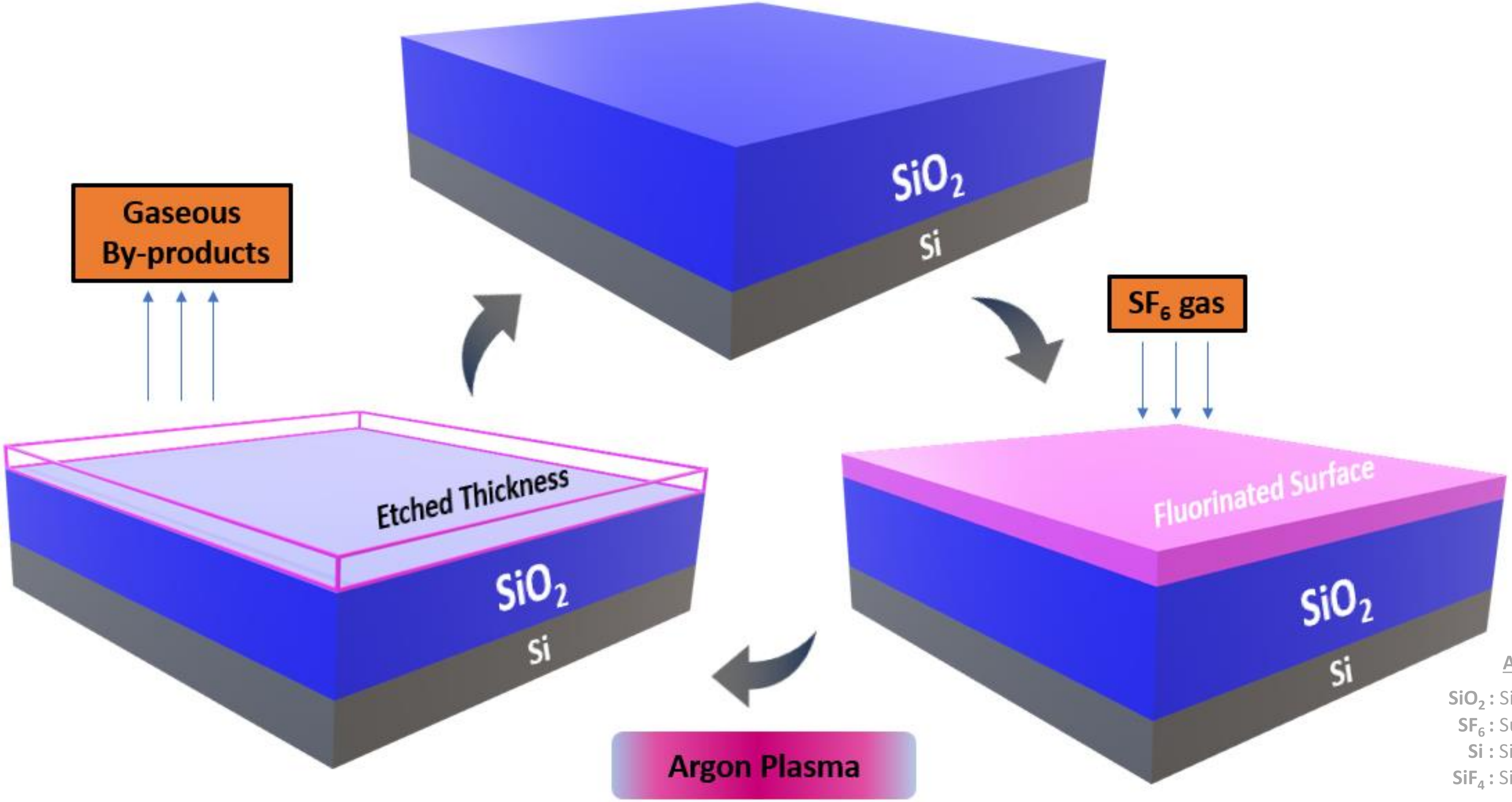
Position dependent study to determine if plasma distribution has an important role → <u>No conclusive result from any position on the holder</u>

Summary & Outlook

- Appearance of Blisters could be attributed to presence of H gas or defects in Si
- Aluminum Nitride seems to be the main cause of the blisters
- Thicker coating of Aluminum Nitride ~ More blisters
- No blisters on newly coated Niobium substrates
- Position of the sample in the chamber is independent of results
- Lower Temperatures/Sweet spot? To reduce blisters?
- Changed O-Ring gave fewer blisters

Master Thesis: Atomic Layer Etching of SiO_2 using Ar/SF_6 Plasma

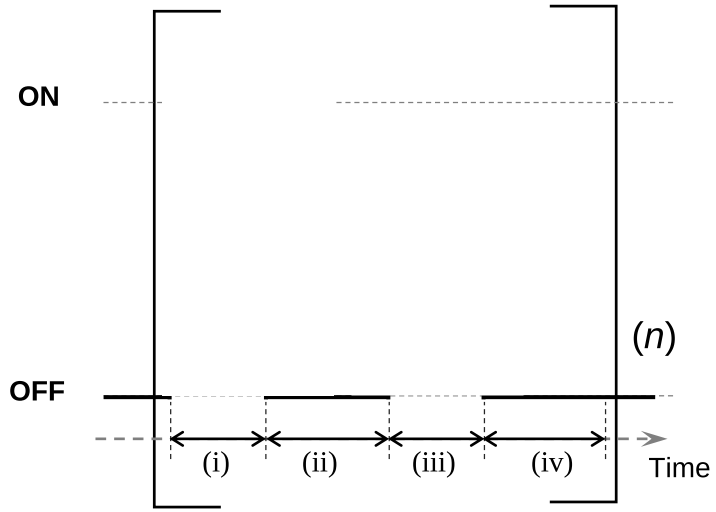
Atomic Layer Etching Process



Abbreviations

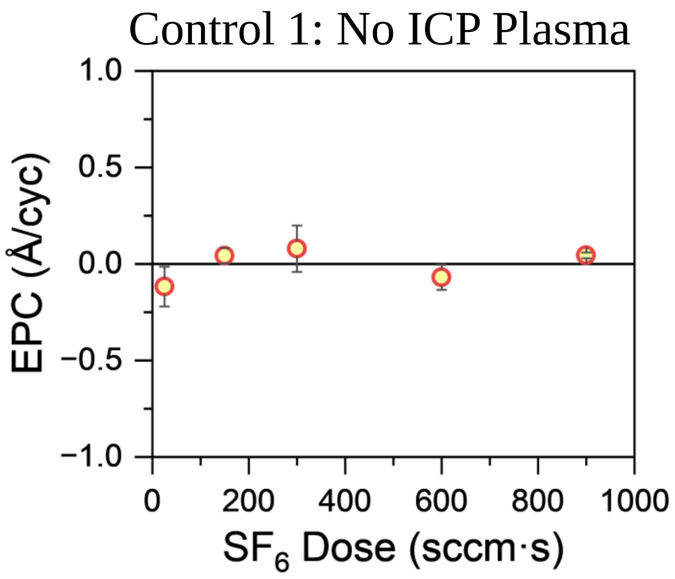
SiO$_2$: Silicon Dioxide
SF$_6$: Sulfur Hexafluoride
Si : Silicon
SiF$_4$: Silicon Tetrafluoride

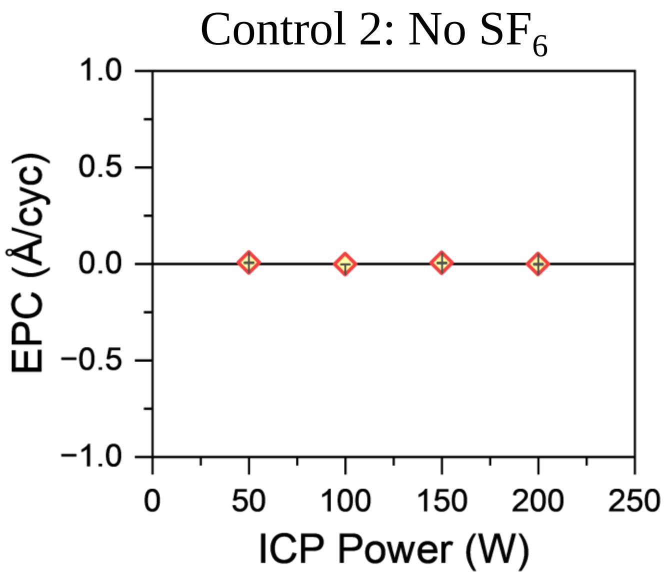
Control Experiments

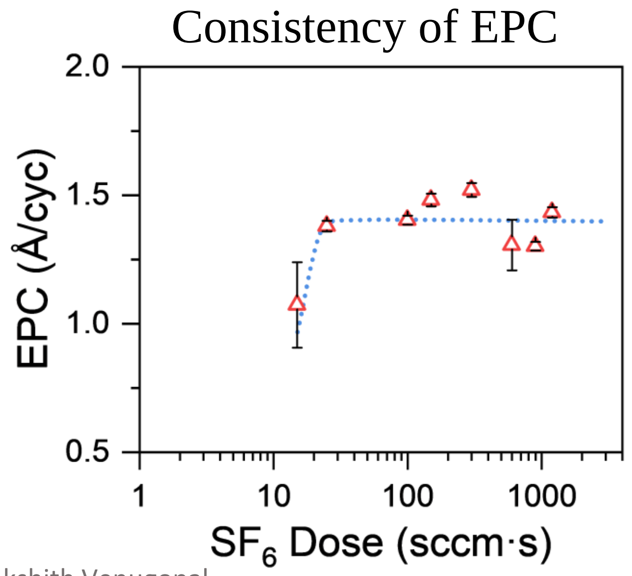


Schematic of the Cyclic ALE Process

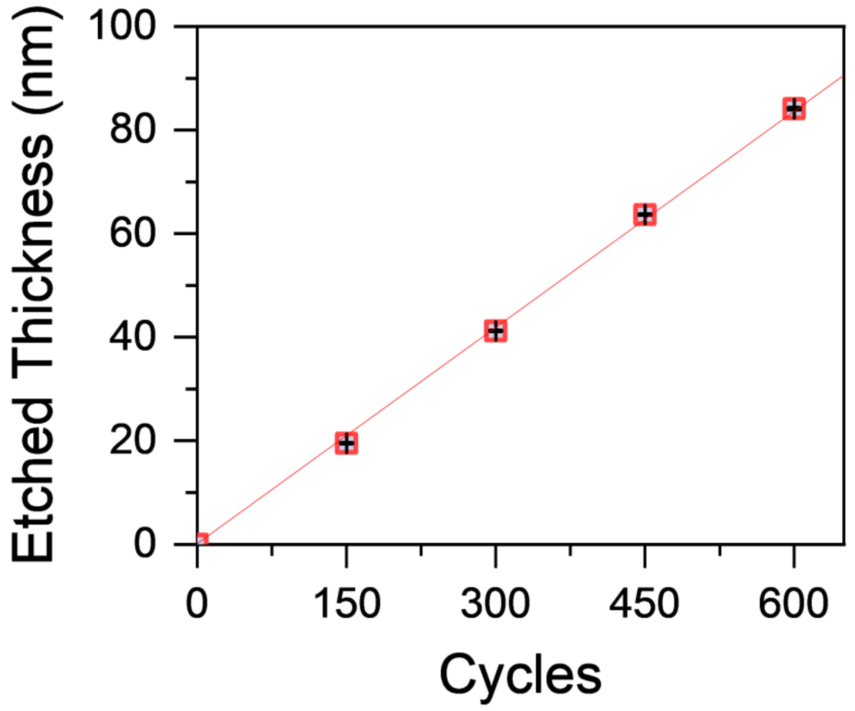
Step	Time (s)	Parameter
i	5	SF_6 :variable sccm
ii	30	Ar: 100 sccm
iii	60	Ar: 100 sccm/100 W
iv	30	Ar: 100 sccm
iv	30	Ar: 100 sccm



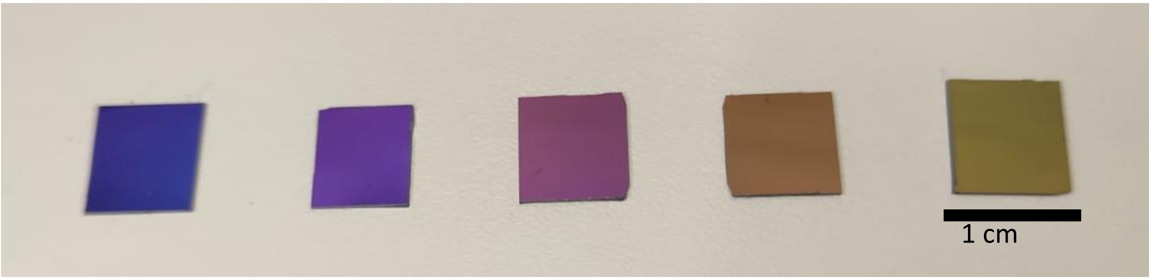




Consistency of Process across cycles



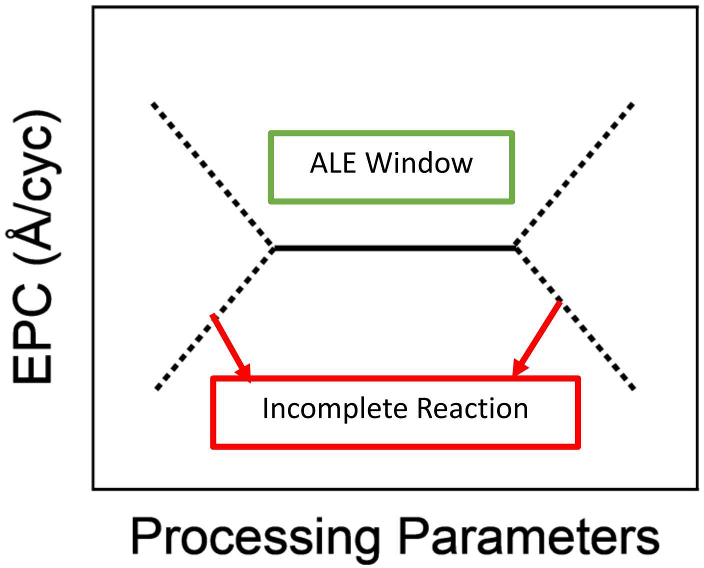
Etched Thickness



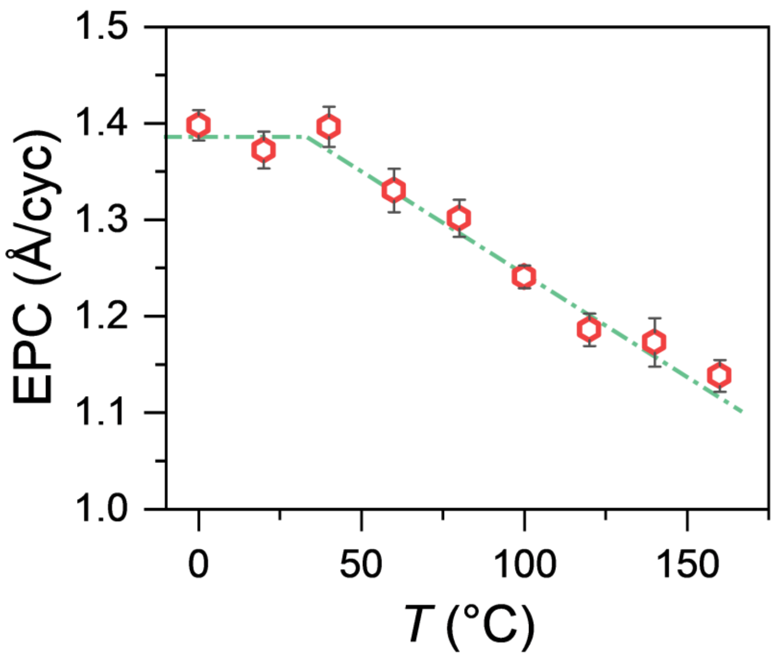
0 nm | 20 nm | 40 nm | 60 nm | 80 nm

Etch Per cycle (EPC) : $\frac{Thickness\ Etched}{Cycles}$ = **1.4 ± 0.1** Å/cycle

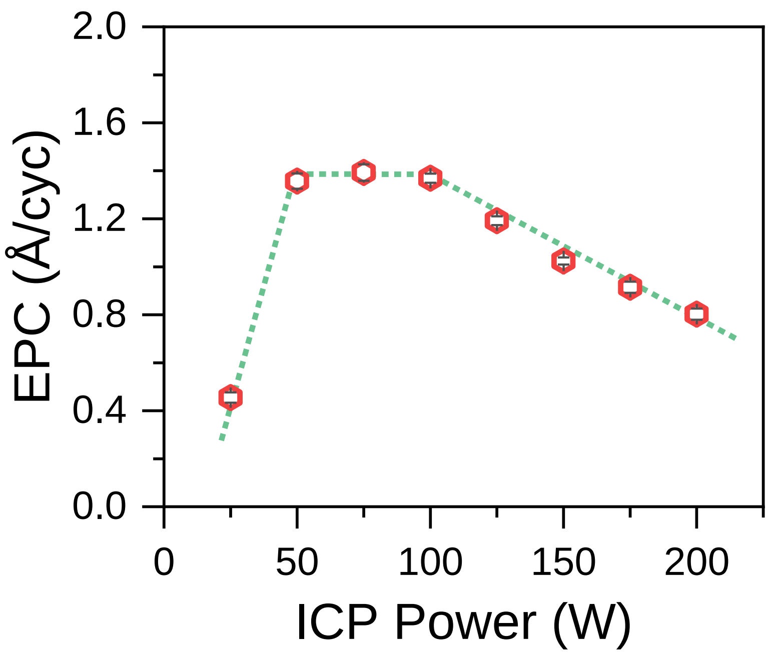
ALE Window



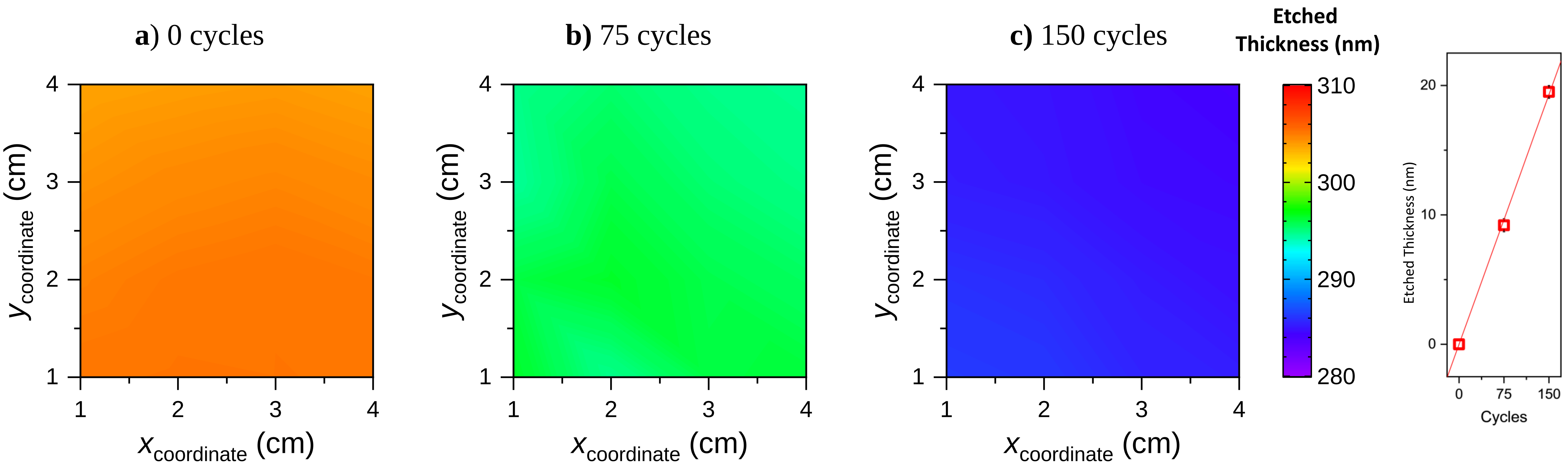
Temperature vs EPC



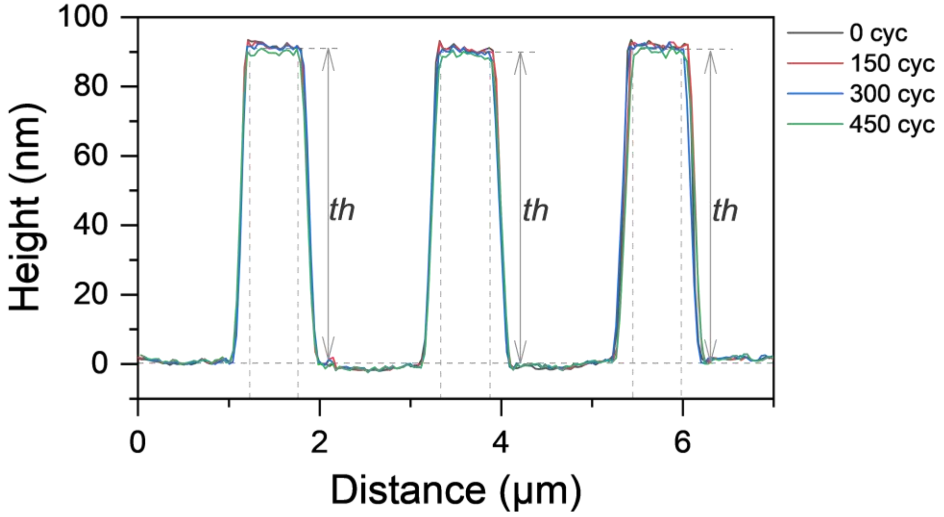
ICP Power vs EPC

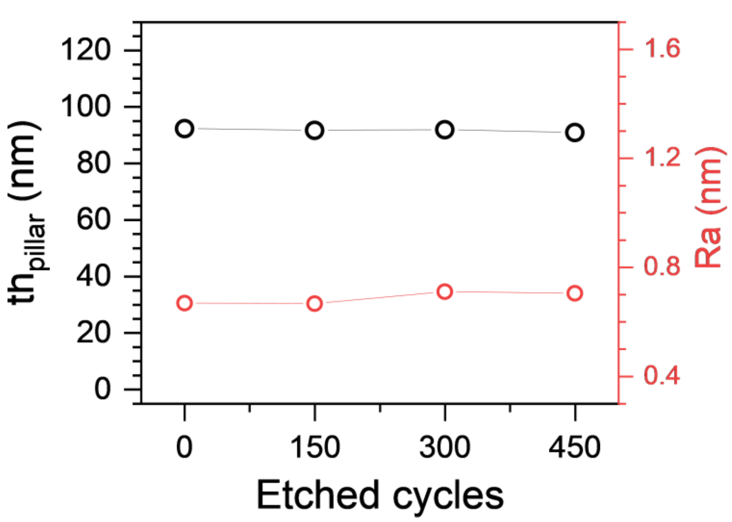


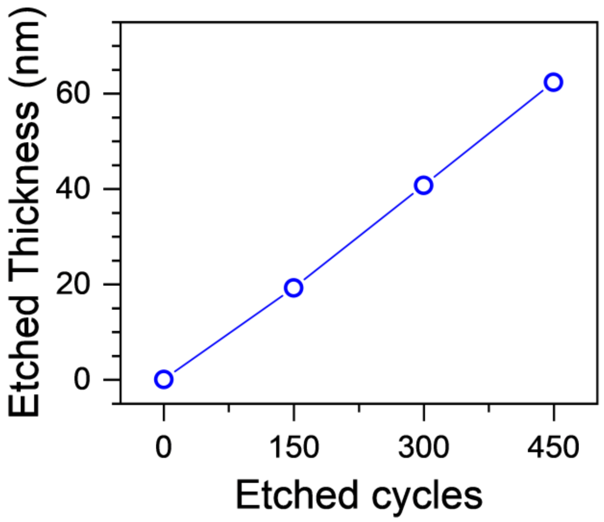
Uniformity Test

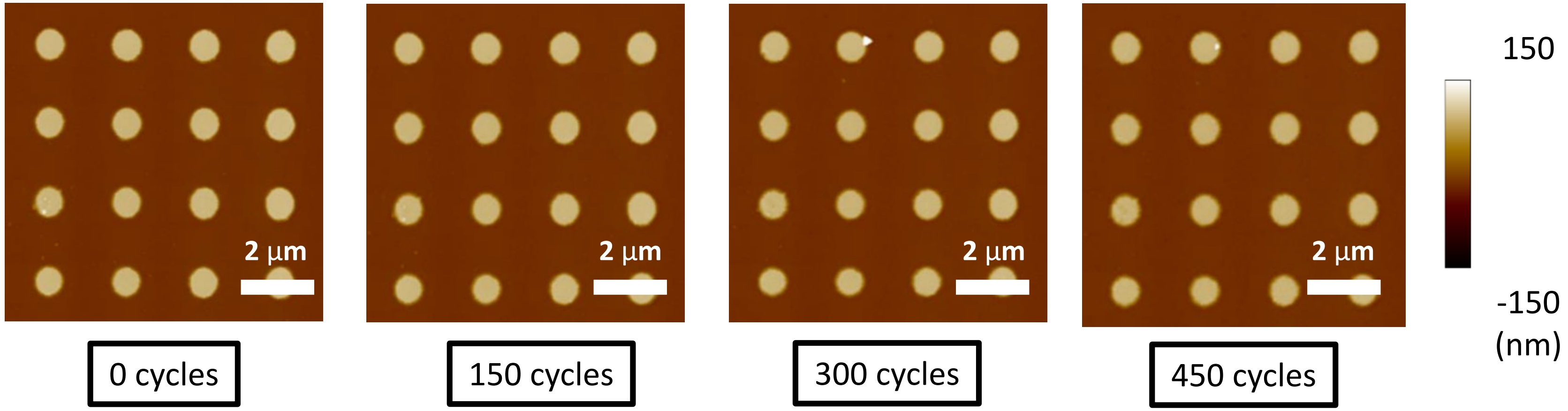


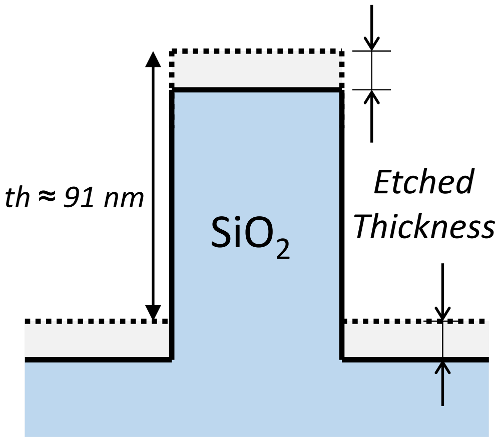
Anisotropic Etching (Directional ALE)





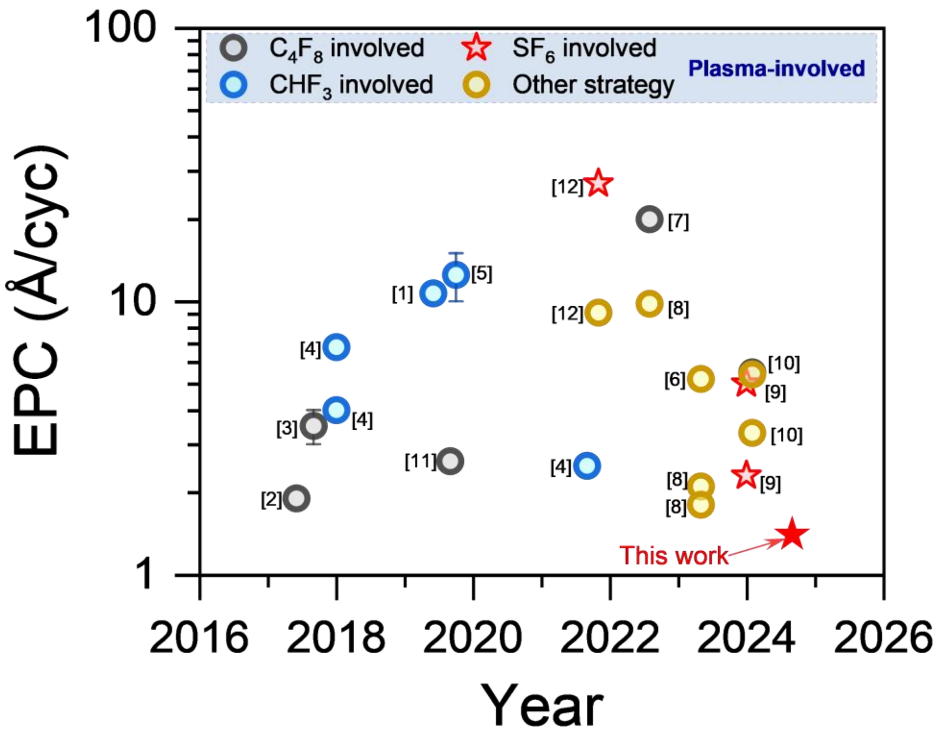




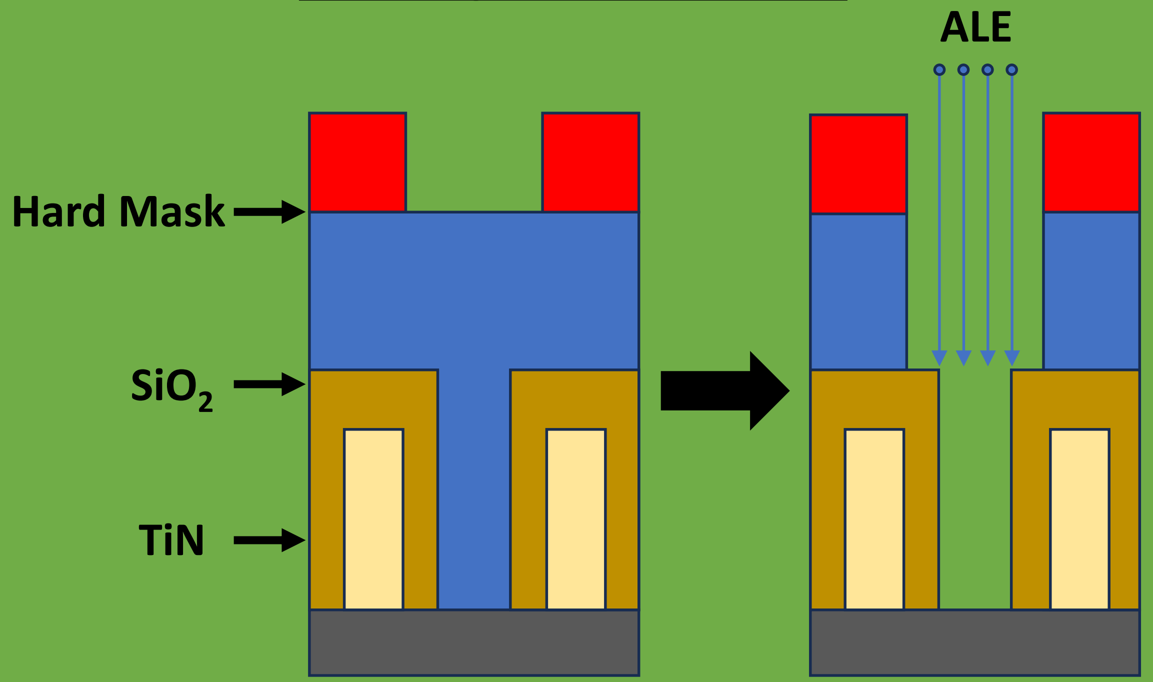


ALE & the Semiconductor Industry

Comparison of our work with others



Etching for 3D NAND



Arts, K., et al. *Plasma Sources Science and Technology*, *31*(10), p.103002.

- **High Aspect Ratio Etching**
- **Etch Selectivity over TiN**

Summary & Outlook

- Reliable and scalable ALE for SiO_2 using sequential SF_6 and Ar plasma
- Etch Rate of ~ **1.4 ± 0.1** Å/cycle
- Uniform etching over large scale substrates
- Low temperature
- High Aspect Ratio Directional etching
- Tests in the PEALD chamber to combine ALD and ALE in a single chamber
- Showcased in a talk at SEMICON EUROPA 2024

Skills

- Plasma Enhanced Atomic Layer Deposition (PEALD)
  - Process Optimisation and Device Maintenance
- Scanning Electron Microscope (SEM)
- Atomic Force Microscopy (AFM)
- Raman Spectroscopy
- Cleanroom Nanofabrication and Lithographic Process
- Physical Vapor Deposition (PVD)
- Reactive Ion Etching (RIE)
- Atomic Layer Etching (ALE)
- OriginPro
- C++
- Python

Achievements

- ***Peng, J., Zhao, P., Venugopal, R., Deneke, K., Haugg, S., Blick, R. and Zierold, R., 2024. Thermal Sight: A Position-Sensitive Detector for a Pinpoint Heat Spot. Small Science, 4(8), p.2400091.***
- ***"ALD-assisted VO_2 for Memristor Application" Status: Accepted***
- ***"Atomic Layer Etching of SiO_2 using sequential SF_6 gas and Ar Plasma", https://arxiv.org/abs/2412.20653***
- *Student grant of 9000 € for "Attempted replication of LK99"; July 2023 to August 2024*

Thank you!

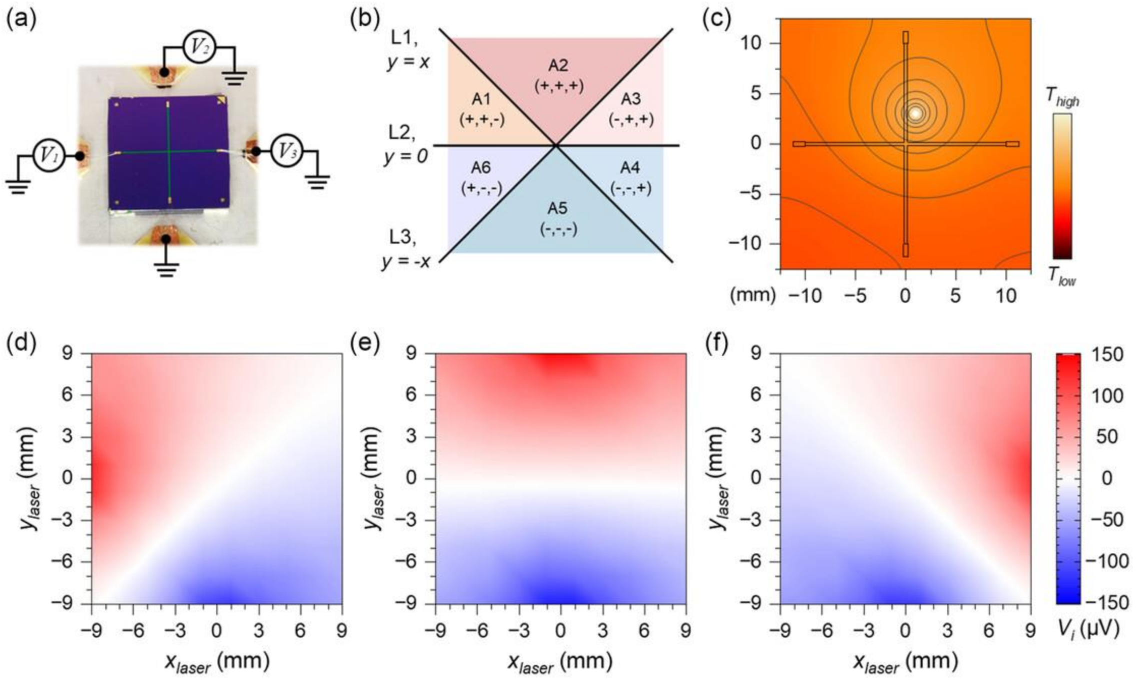
References

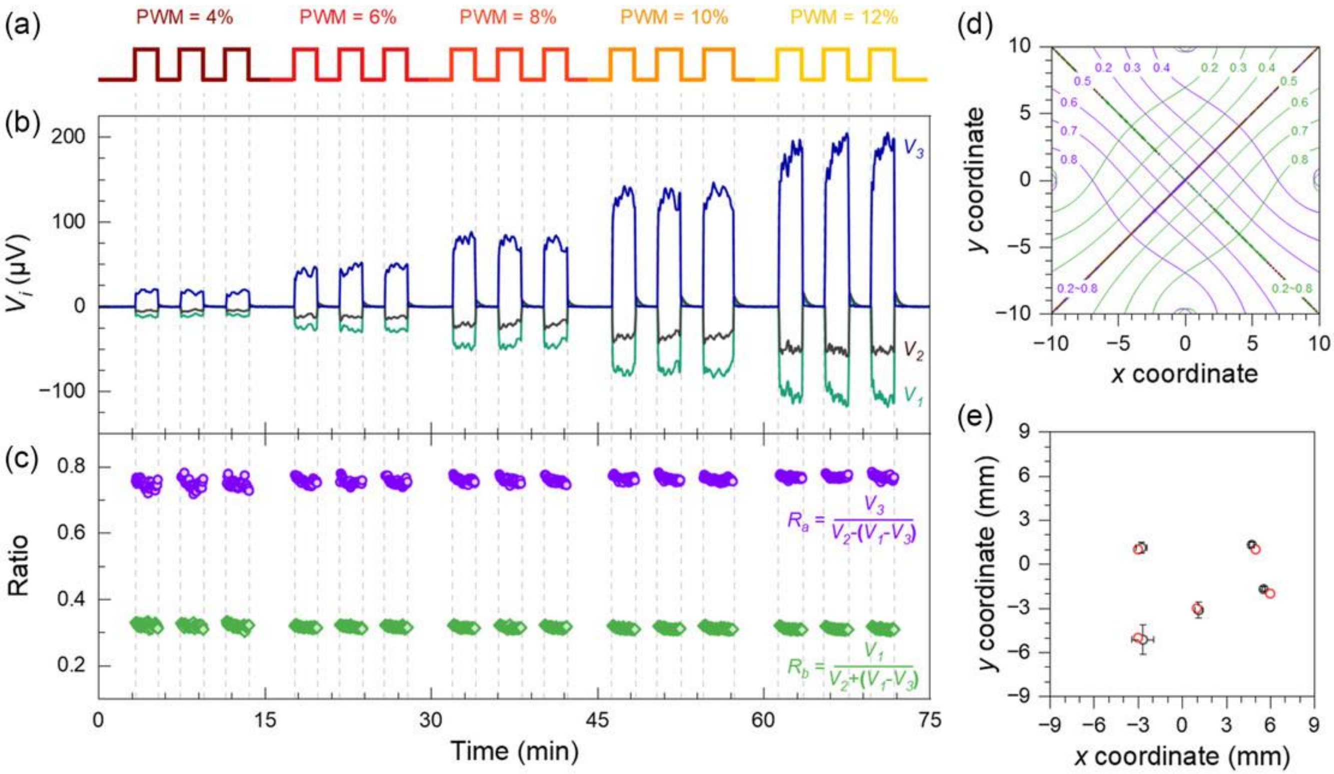
[1] Metzler, D., et al., *Characterizing fluorocarbon assisted atomic layer etching of Si using cyclic Ar/C_4F_8 and Ar/CHF_3 plasma*. The Journal of Chemical Physics, 2016. **146**(5): p. 052801.
[2] Gasvoda, R.J., et al., *Surface Phenomena During Plasma-Assisted Atomic Layer Etching of SiO_2*. ACS Applied Materials & Interfaces, 2017. **9**(36): p. 31067-31075.
[3] Koh, K., et al., *Quasi atomic layer etching of SiO_2 using plasma fluorination for surface cleaning*. Journal of Vacuum Science & Technology A, 2017. **36**(1): p. 01B106.
[4] Dallorto, S., et al., *Balancing ion parameters and fluorocarbon chemical reactants for SiO_2 pattern transfer control using fluorocarbon-based atomic layer etching*. Journal of Vacuum Science & Technology B, 2019. **37**(5).
[5] Kim, S.Y., I.-S. Park, and J. Ahn, *Atomic layer etching of SiO_2 using trifluoroiodomethane*. Applied Surface Science, 2022. **589**: p. 153045.
[6] Lee, Y.S., et al., *Purgeless atomic layer etching of SiO_2*. Journal of Physics D: Applied Physics, 2022. **55**(36): p. 365203.
[7] Kim, Y., et al., *Plasma Atomic Layer Etching of SiO_2 and Si_3N_4 with Low Global Warming $C_4H_3F_7O$ Isomers*. ACS Sustainable Chemistry & Engineering, 2023. **11**(16): p. 6136-6142.
[8] Osonio, A., et al., *Topographically-selective atomic layer etching of SiO_2 using radical fluorination of the surface followed by Ar ion bombardment*. Japanese Journal of Applied Physics, 2023. **62**(12): p. 121001.
[9] Kanarik, K.J., et al., *Predicting synergy in atomic layer etching*. Journal of Vacuum Science & Technology A, 2017. **35**(5).
[10] Kanarik, K.J., et al., *Predicting synergy in atomic layer etching*. Journal of Vacuum Science & Technology A, 2017. **35**(5).
[11] Gasvoda, R.J., et al., *Surface prefunctionalization of SiO2 to modify the etch per cycle during plasma-assisted atomic layer etching*. Journal of Vacuum Science & Technology A, 2019. **37**(5): p. 051003.
[12] Miyoshi, N., et al., *Atomic layer etching of SiO_2 with self-limiting behavior on the surface modification step using sequential exposure of HF and NH_3*. Journal of Vacuum Science & Technology A, 2021. **40**(1): p. 012601.
[13] Zhao, S., Yuan, G., Zhang, D., Xu, P., Li, G. and Han, W., 2021. Formation and elimination mechanism of thermal blistering in Al2O3/Si system. *Journal of Materials Science*, *56*(31), pp.17478-17489.
[14] Xie, DG., Wang, ZJ., Sun, J. *et al. In situ* study of the initiation of hydrogen bubbles at the aluminium metal/oxide interface. *Nature Mater* **14**, 899–903 (2015). https://doi.org/10.1038/nmat4336

Backup Slides

Position Sensitive Detector

- Contributing Author



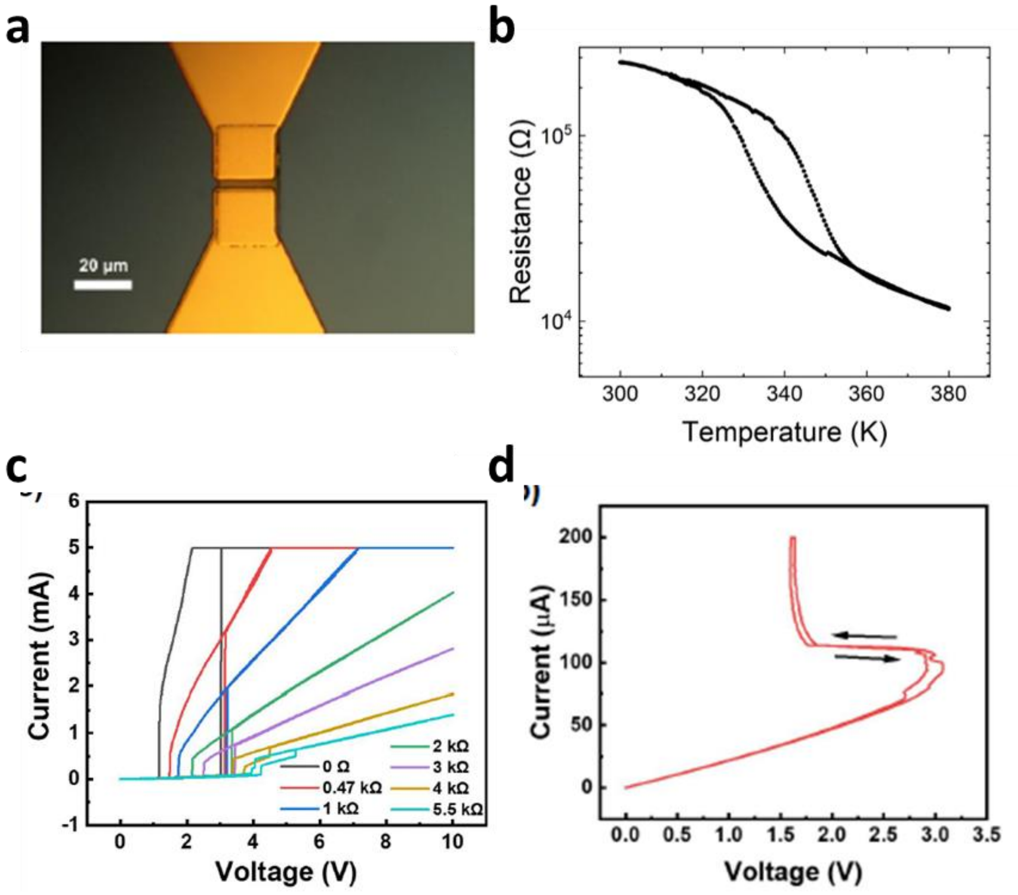


Contributed: Device measurements, calibration, Python decoding voltage signals for position

Peng, J., Zhao, P., Venugopal, R., Deneke, K., Haugg, S., Blick, R. and Zierold, R., 2024. Thermal Sight: A Position-Sensitive Detector for a Pinpoint Heat Spot. Small Science, 4(8), p.2400091.

ALD grown VO_2 for memristor

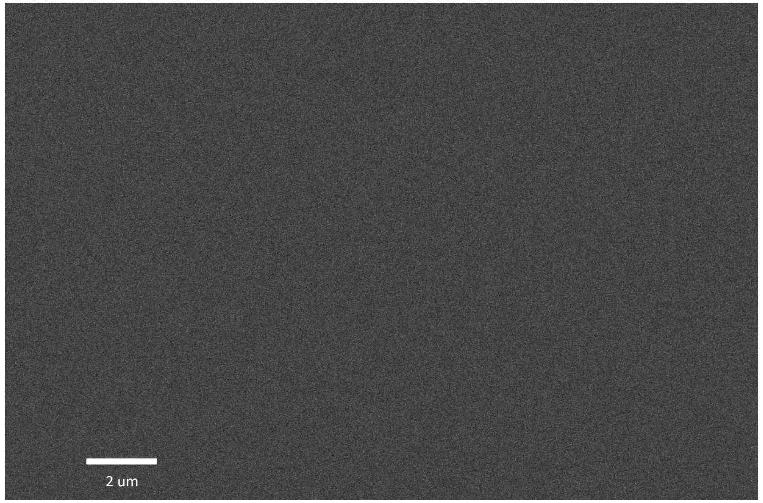
- Contributing author



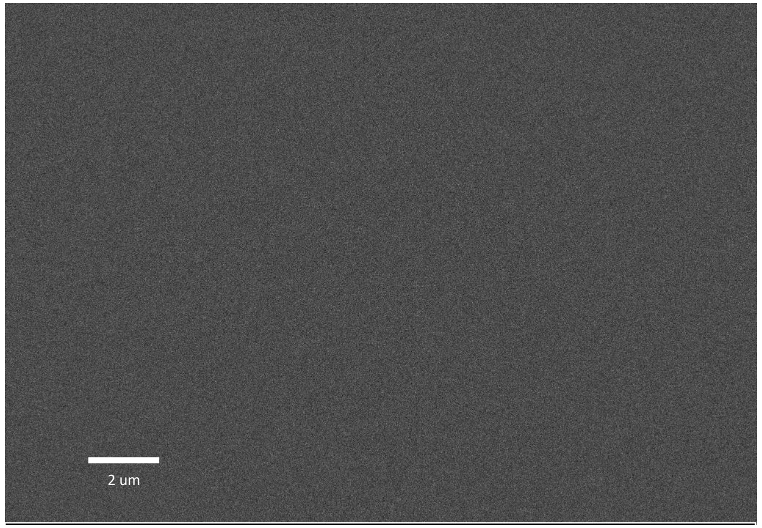
Contribution: Device fabrication and lithographic processes

TiN

Temperature: 175 C

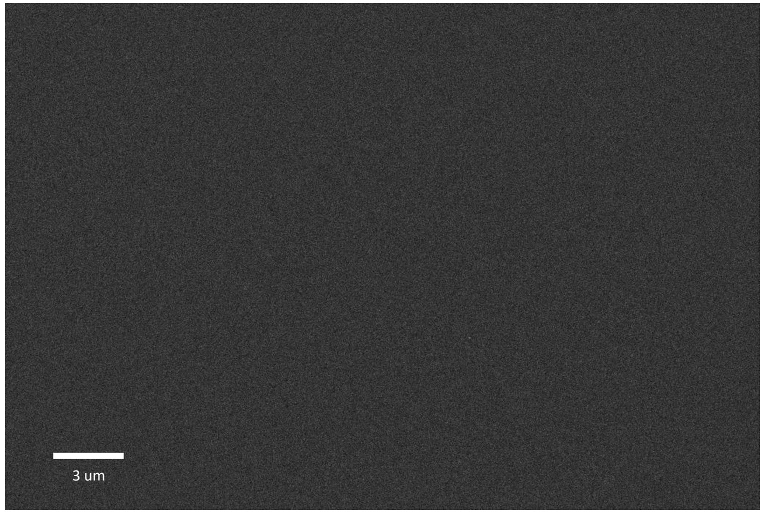


On Si



79 cycles

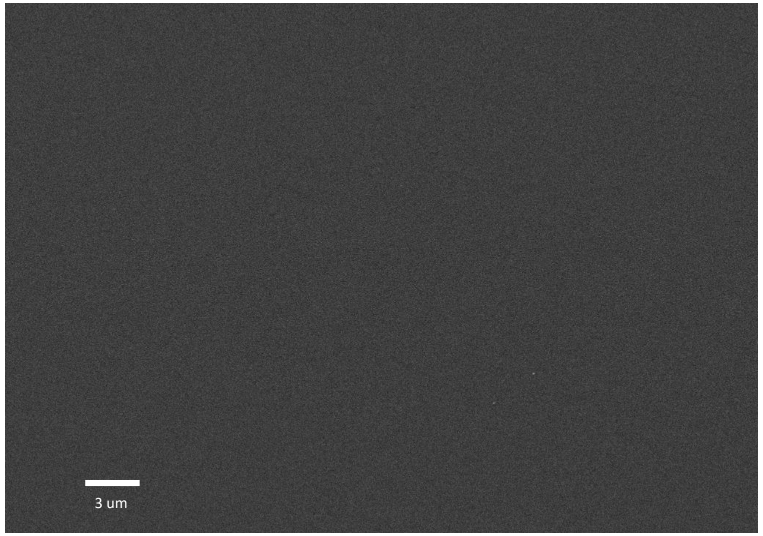
158 cycles



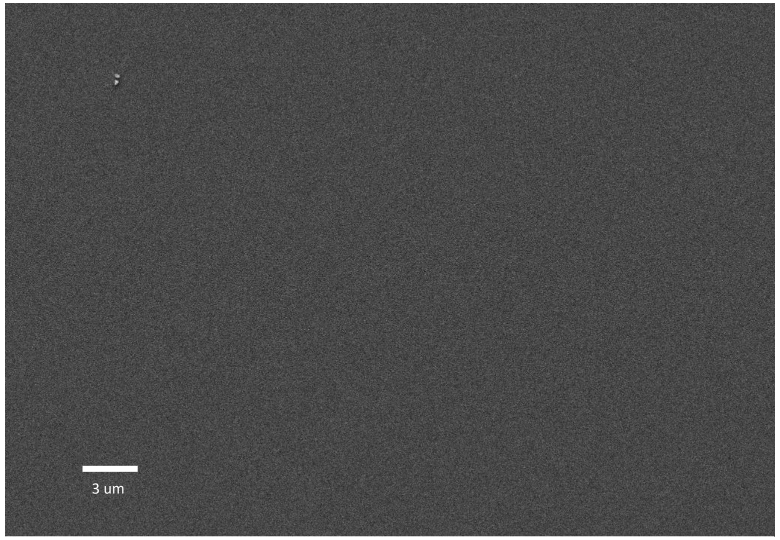
On AlN

NbN

Temperature: 175 C

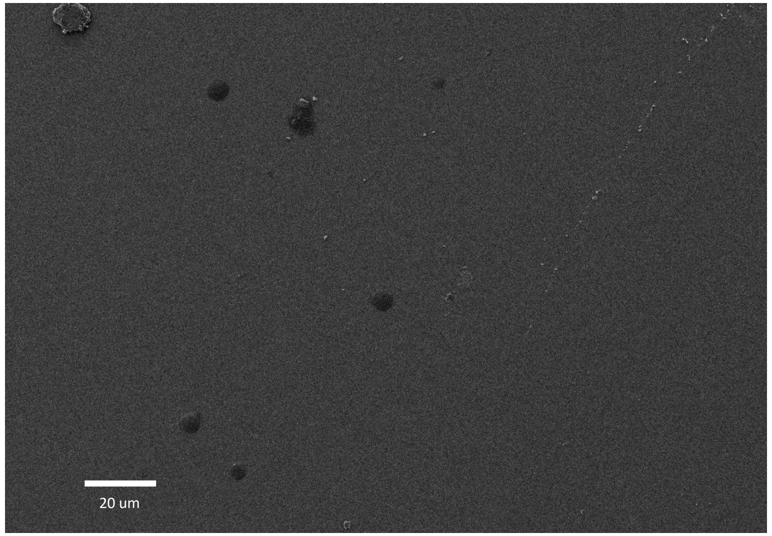


On Si

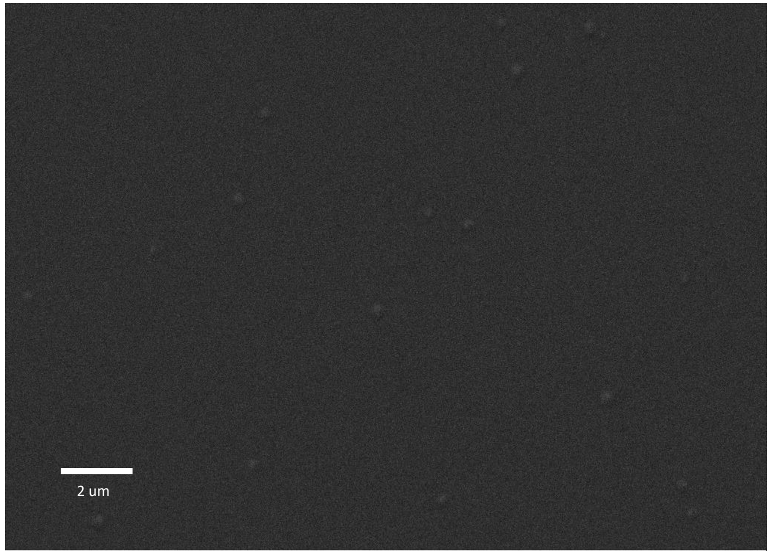


100 cycles

200 cycles

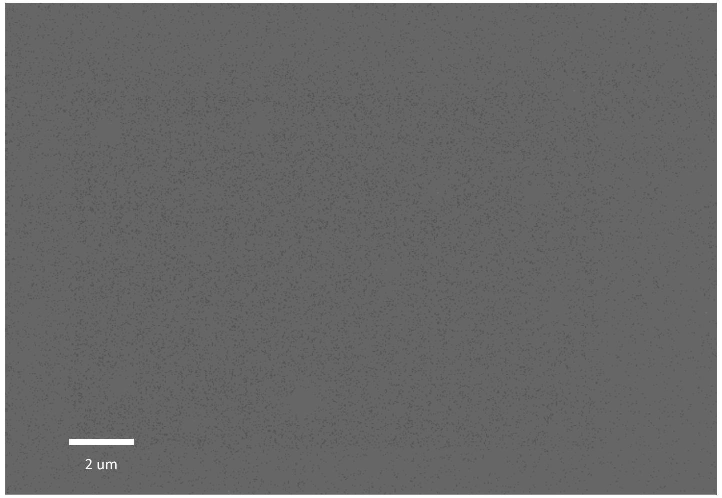


On AlN

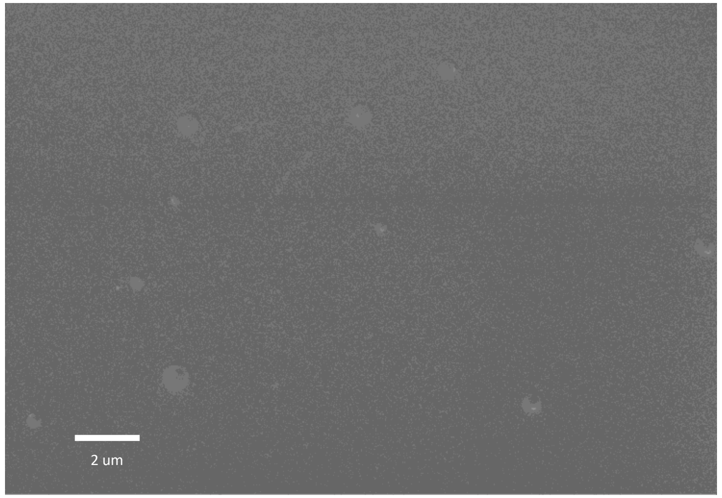


AlN + NbTiN

Temperature: 175 C

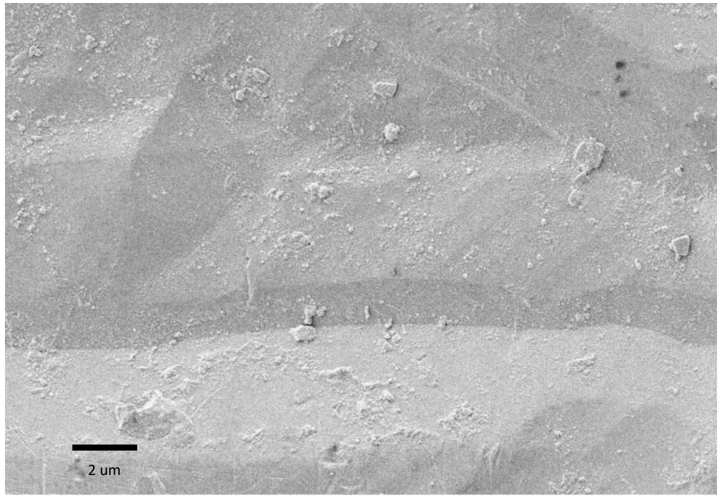


On Si

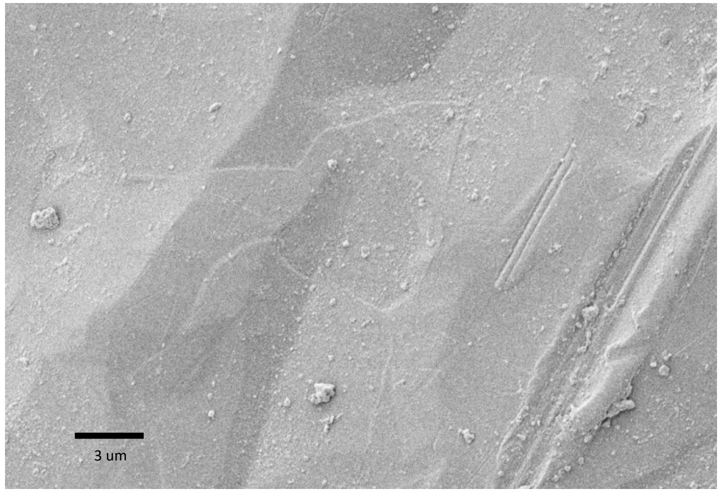


100 Super-Cycles

85 Super-Cycles



On Nb

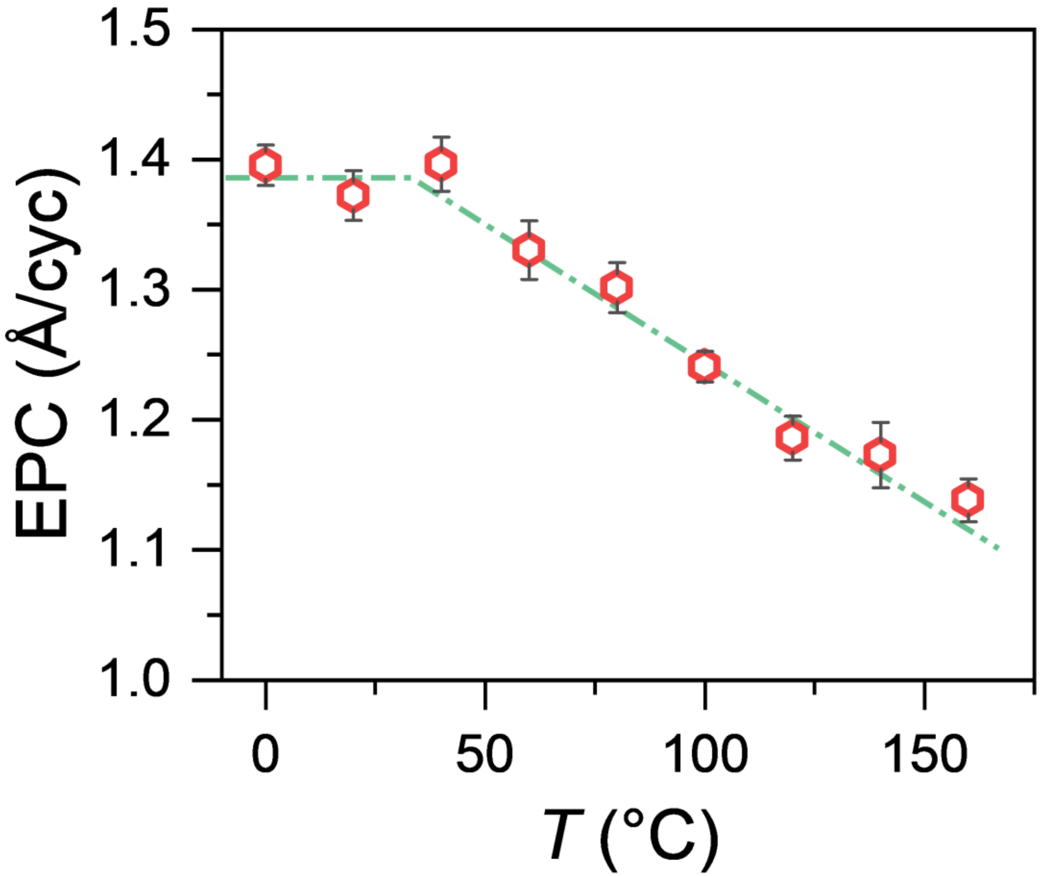


Mechanism Study using DFT and Molecular Dynamics

Collaborators: Dr. Nian Ran, Prof. Jianjun Liu

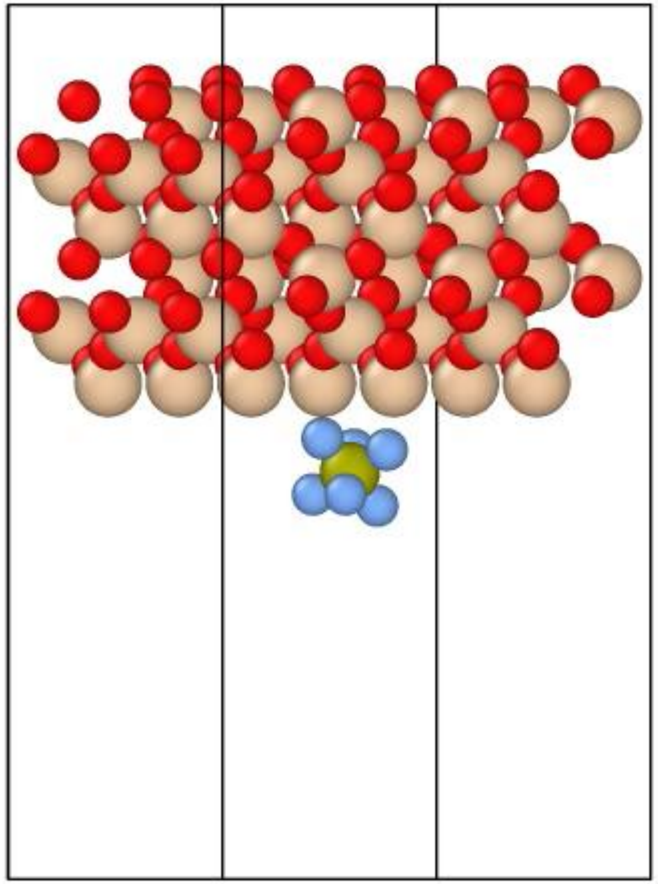
Molecular Dynamics to Study Temperature Vs EPC

Temperature Vs EPC

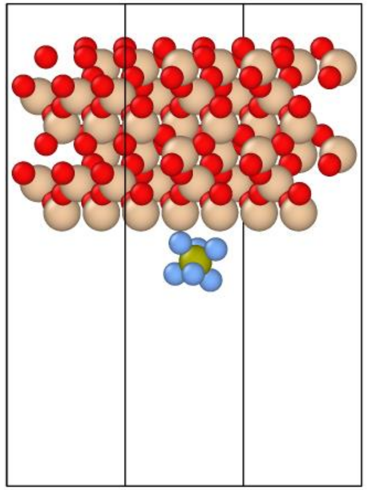


❖ Higher Temperatures: Lower Etch Rates
❖ Lower Temperatures: Constant Etch Rates

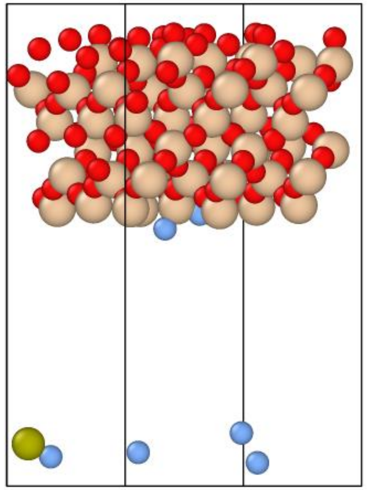
Molecular Dynamics (300K) (Si Atom)



0 – 500 ps



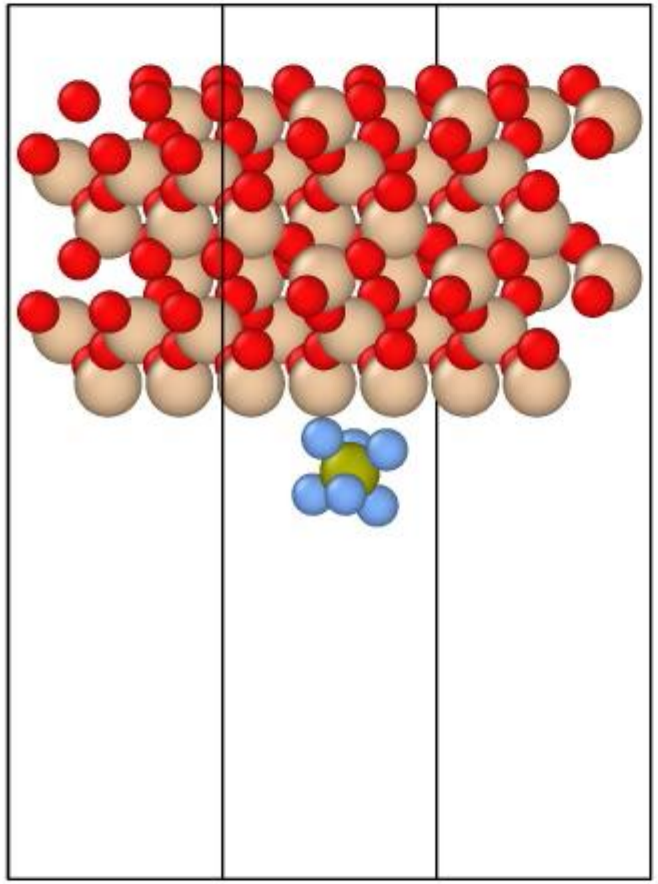
0 ps



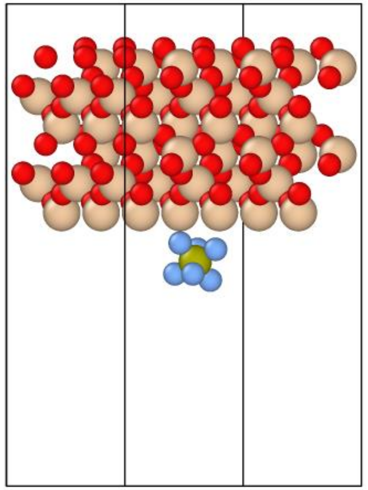
9999 ps

❖ Fluorine attachment indicates higher Fluorine coverage at lower temperatures.

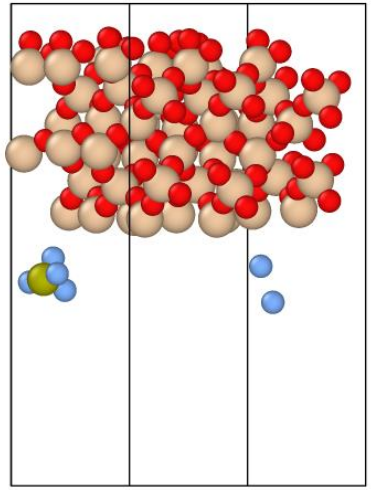
Molecular Dynamics (450K) (Si Atom)



0 – 500 ps



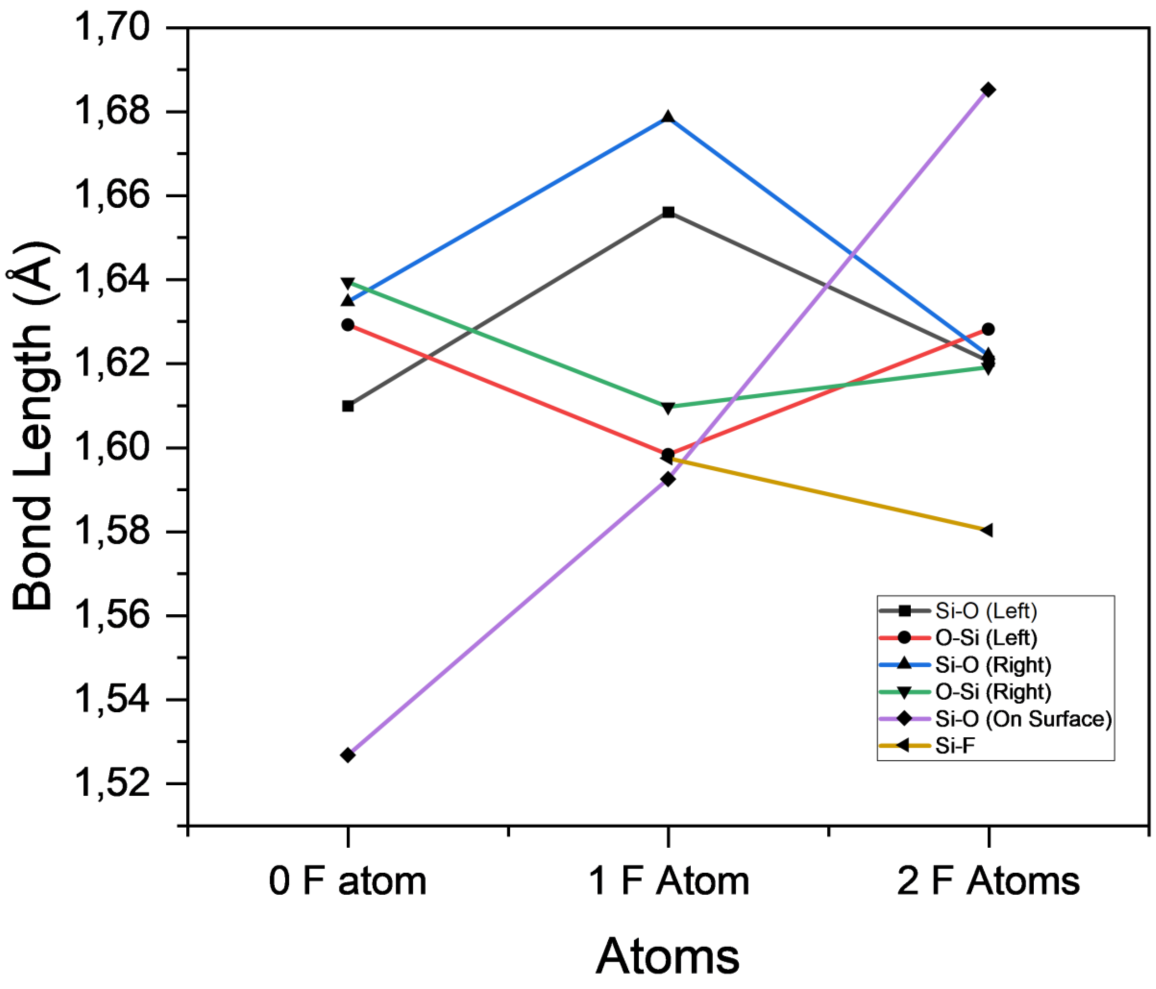
0 ps



9999 ps

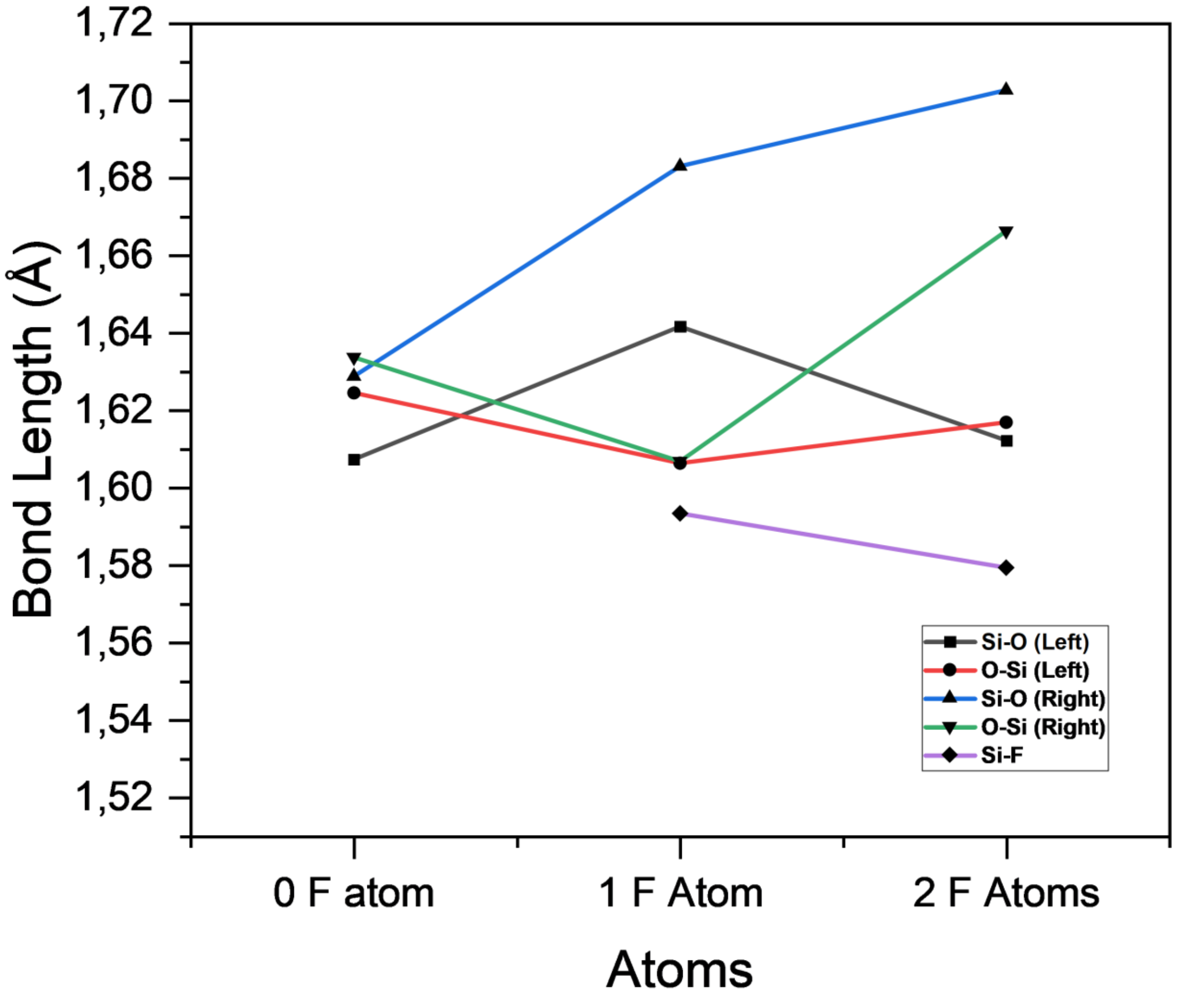
- ❖ No attachment of F atoms on the surface
- ❖ Indicates at higher temperature the Fluorine coverage is lower

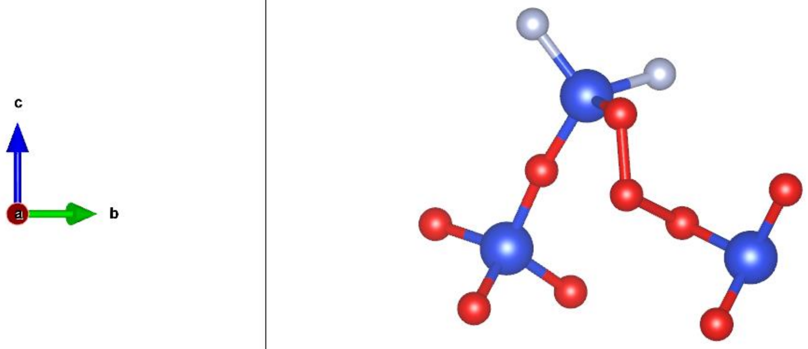
DFT for Bond Length Changes



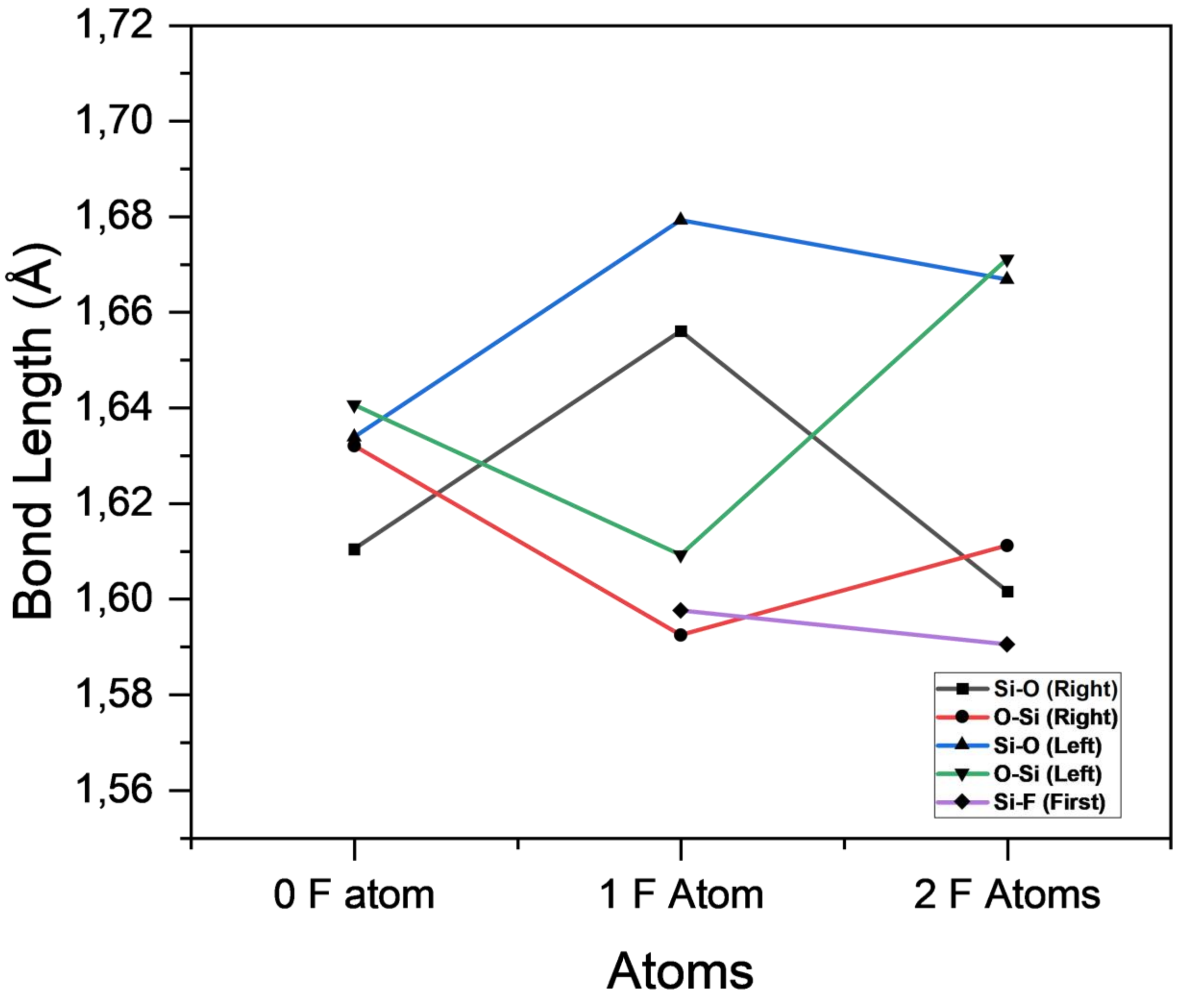
❖ O-Si bond length increasing indicates weakening

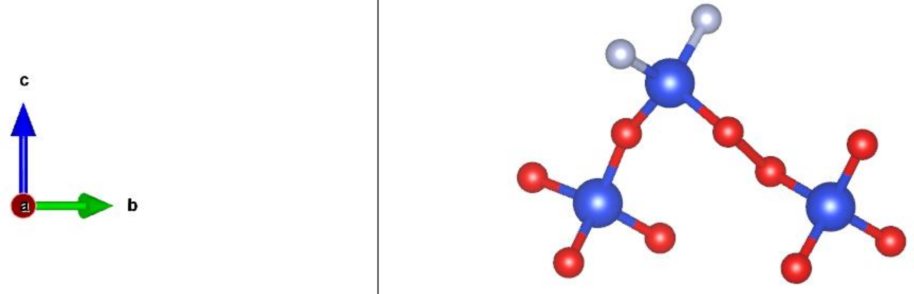
DFT Bond Length Changes: Defect 2

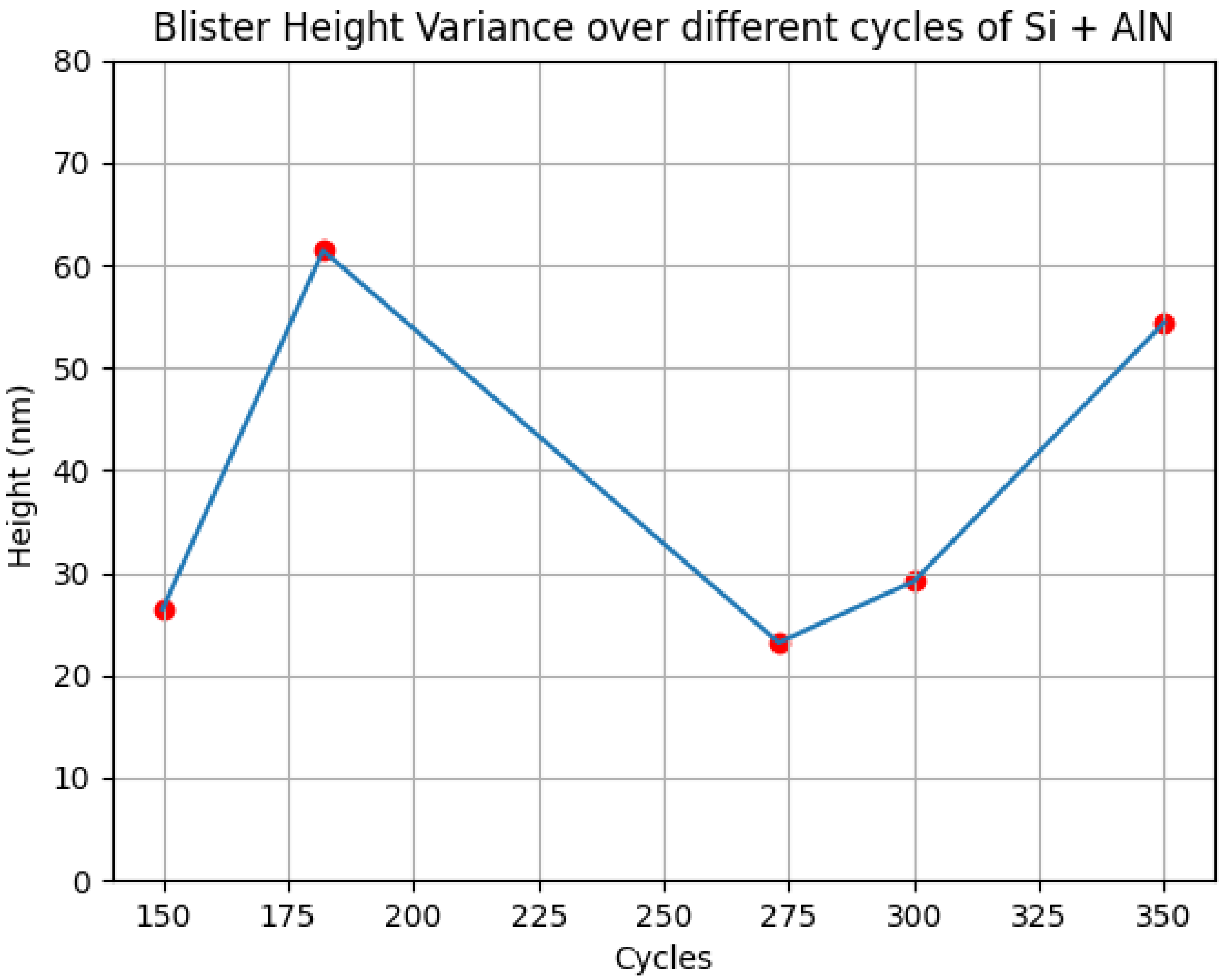


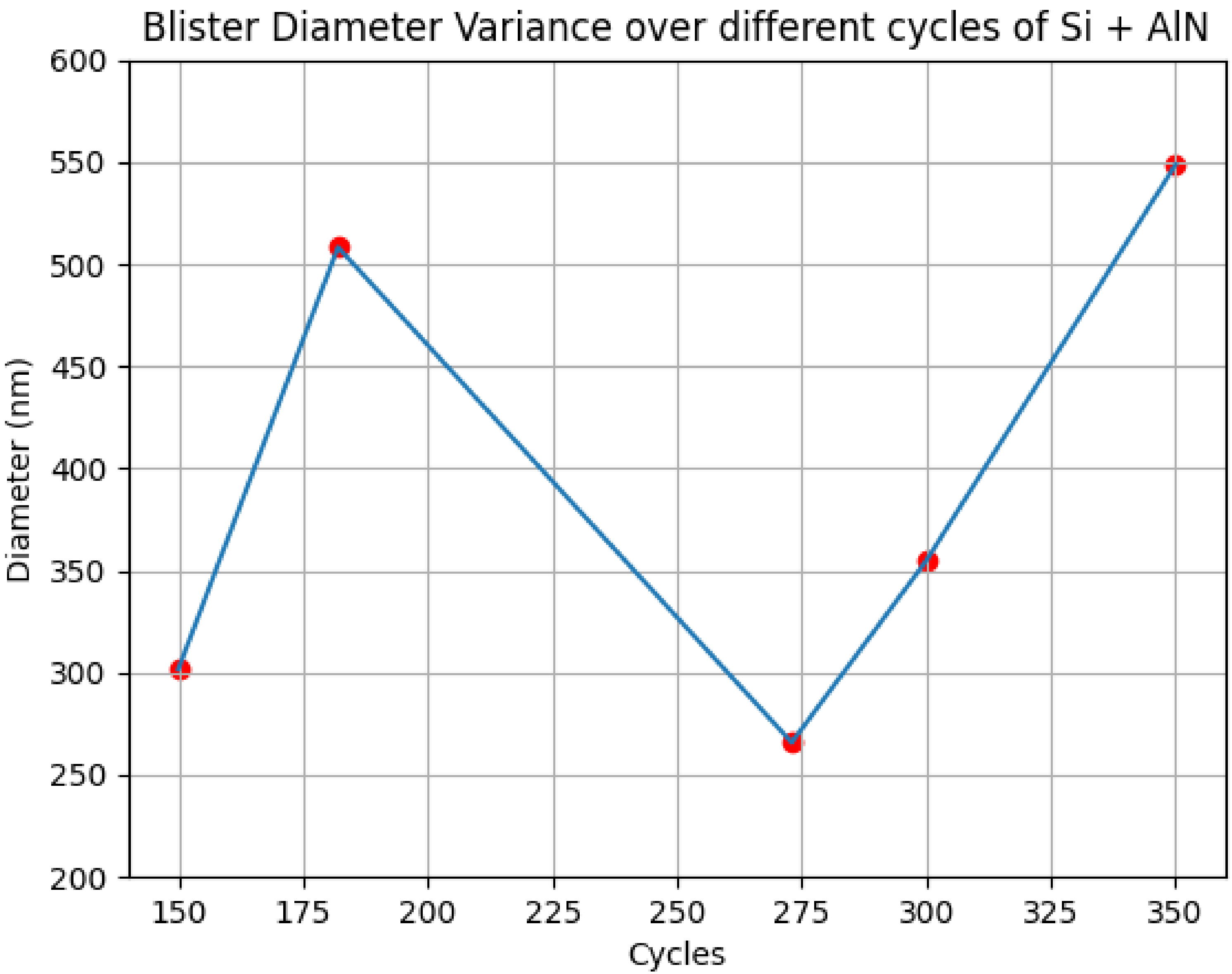


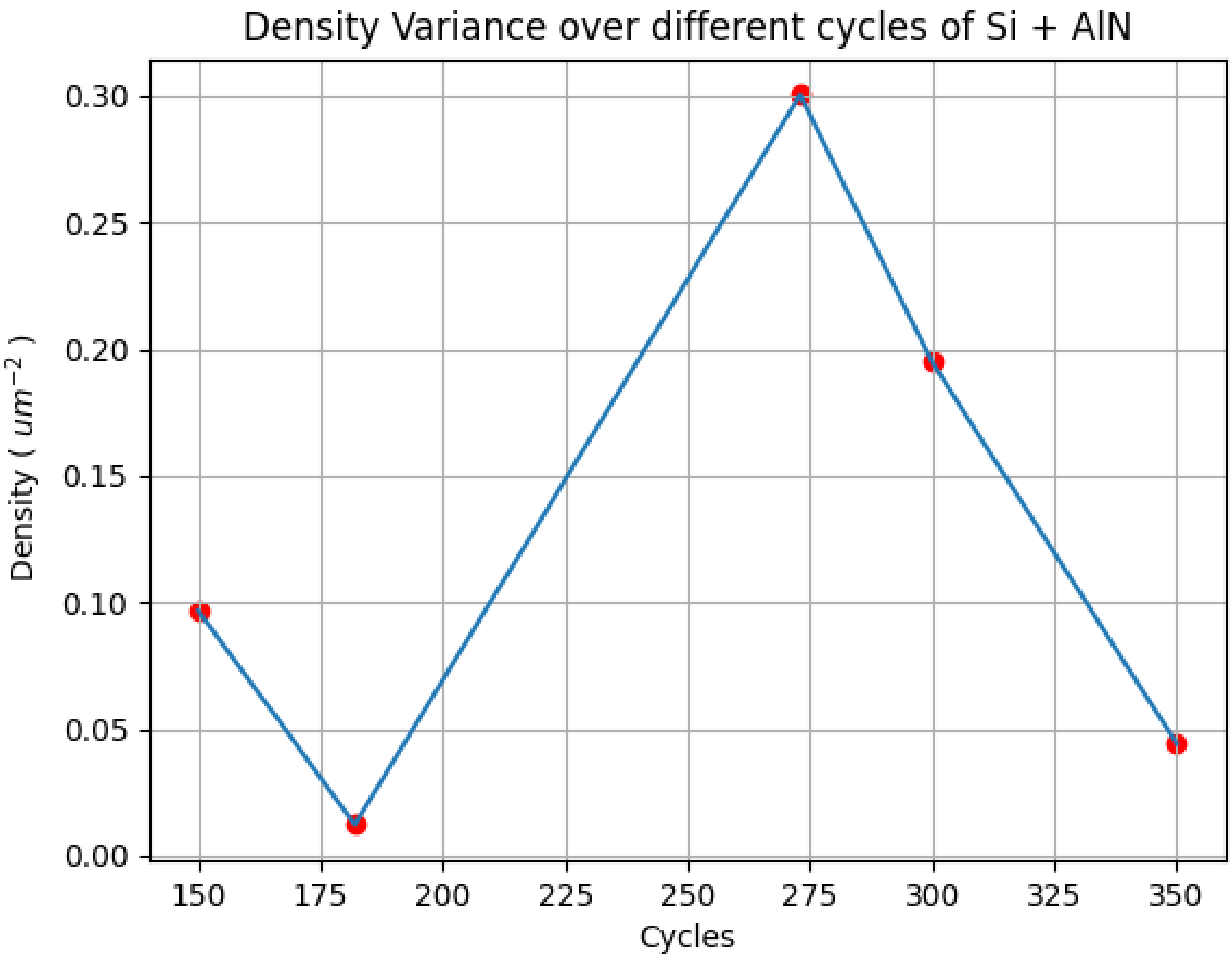
DFT Bond Length Changes: Defect 1





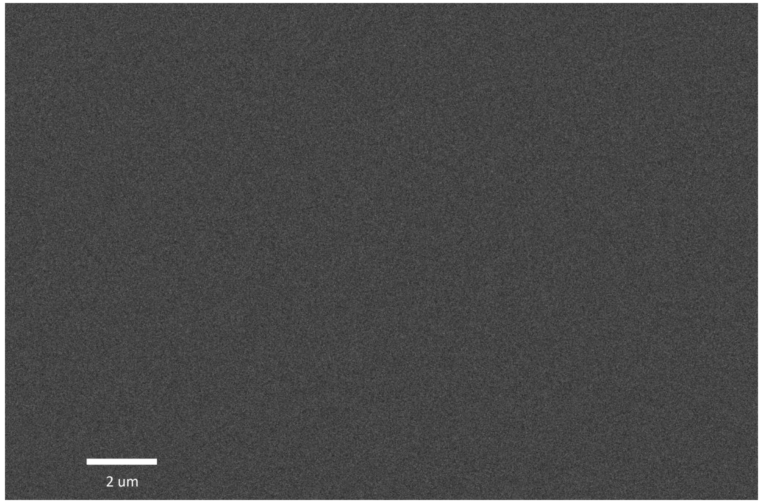

Blister Height Variance over different cycles of Si + AlN
Height (nm)
0
10
20
30
40
50
60
70
80
150
175
200
225
250
275
300
325
350
Cycles


Blister Diameter Variance over different cycles of Si + AlN
Diameter (nm)
600
550
500
450
400
350
300
250
200
150
175
200
225
250
275
300
325
350
Cycles

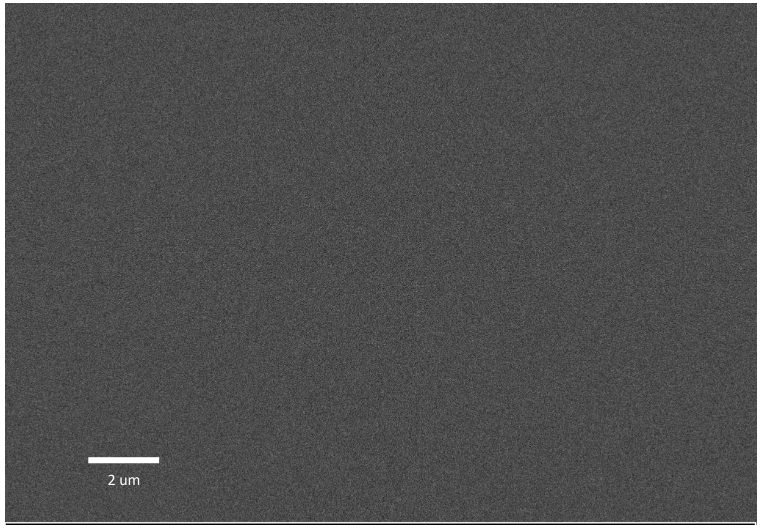

Density Variance over different cycles of Si + AlN
Density (um^{-2})
0.00
0.05
0.10
0.15
0.20
0.25
0.30
150
175
200
225
250
275
300
325
350
Cycles

TiN

Temperature: 175 C



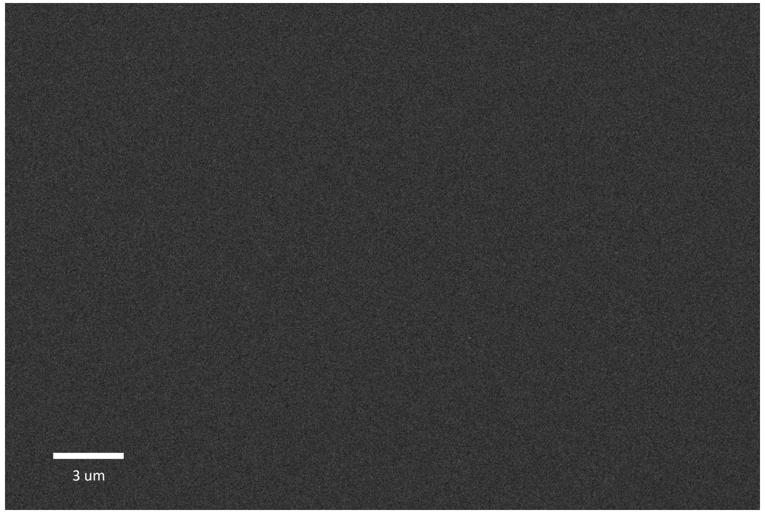
On Si



79 cycles

Are blisters thickness dependent?

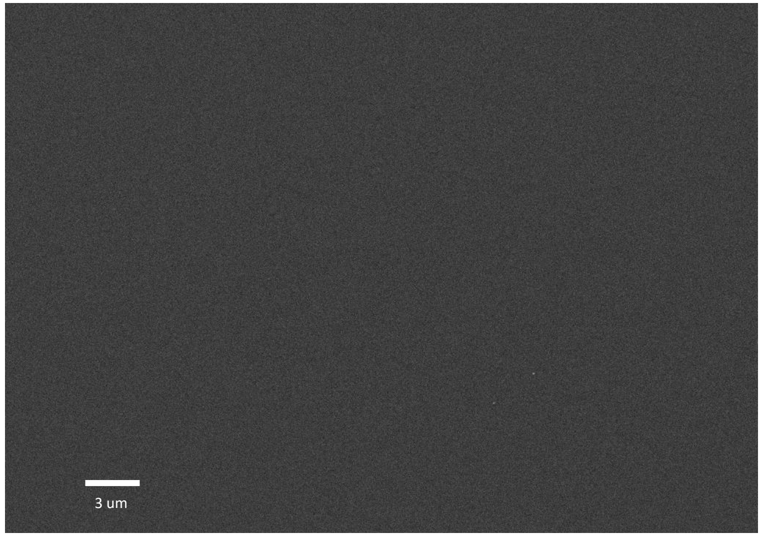
158 cycles



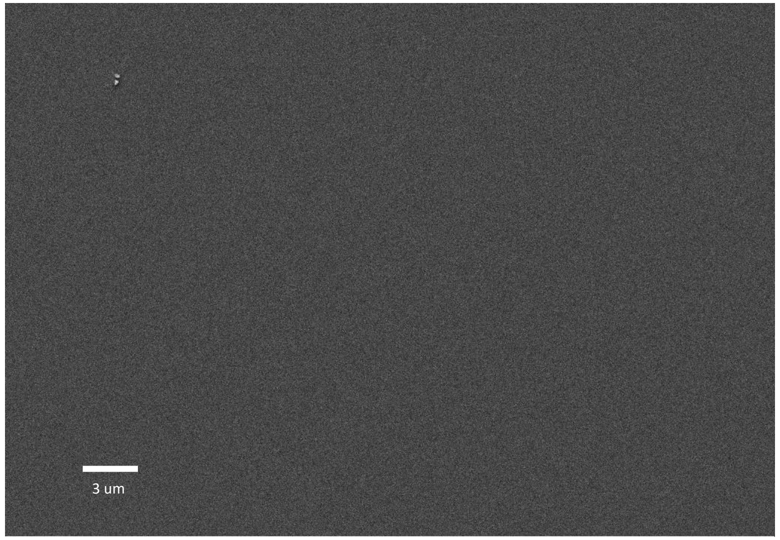
On AlN

NbN

Temperature: 175 C

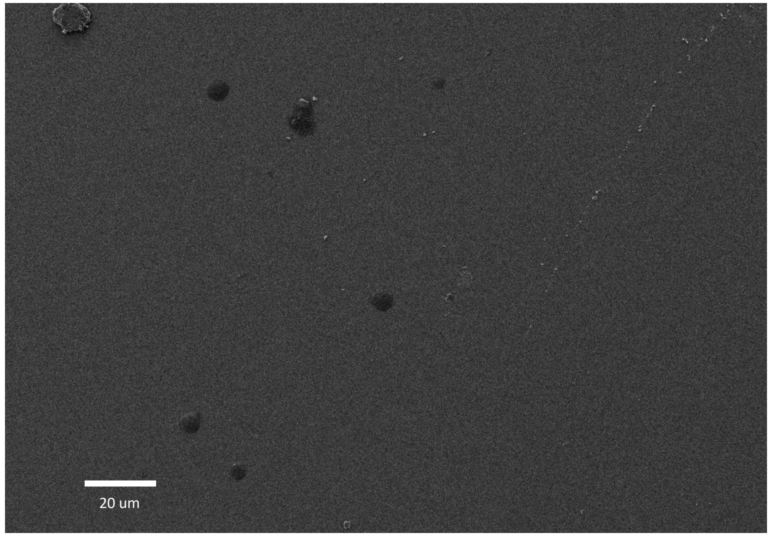


On Si

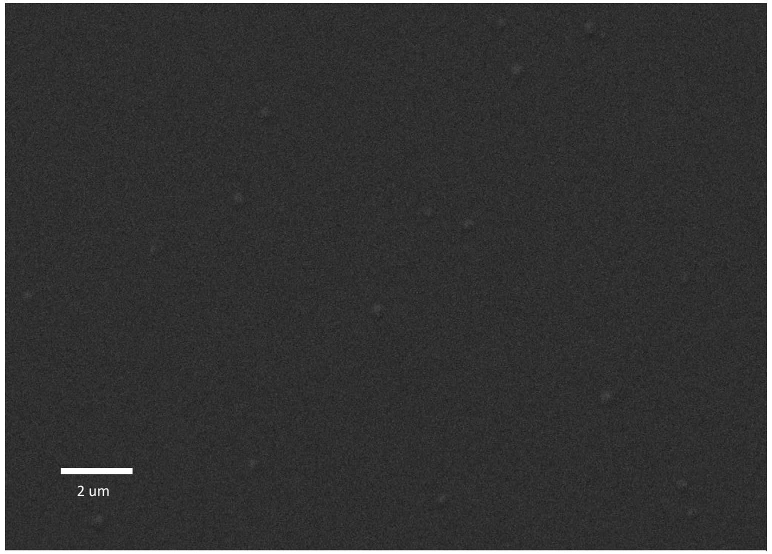


100 cycles

200 cycles

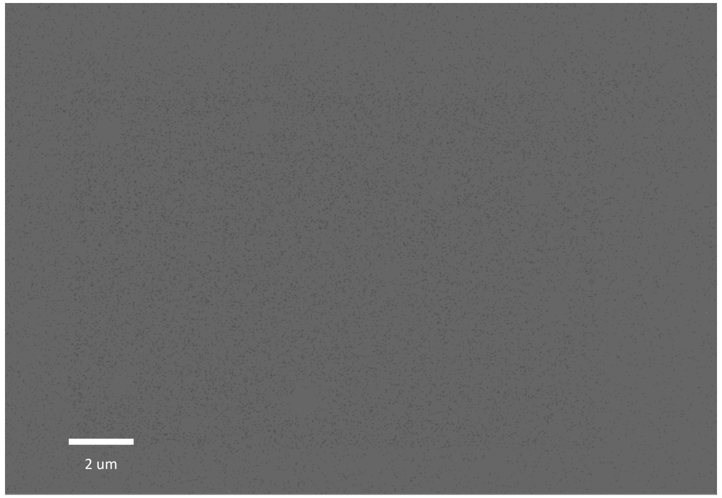


On AlN

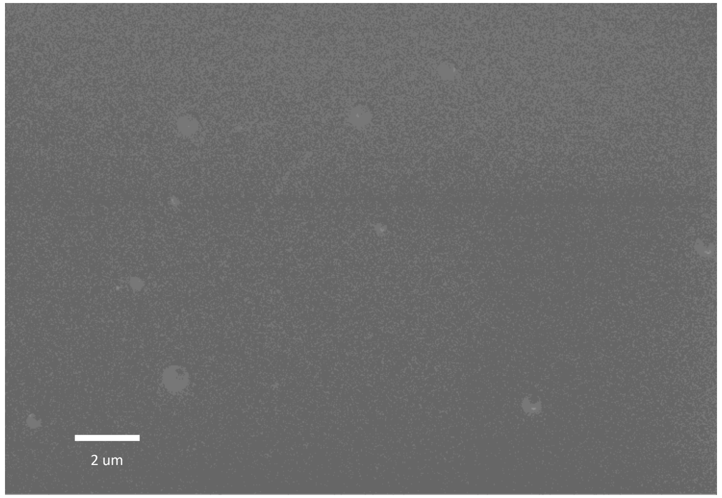


AlN + NbTiN

Temperature: 175 C

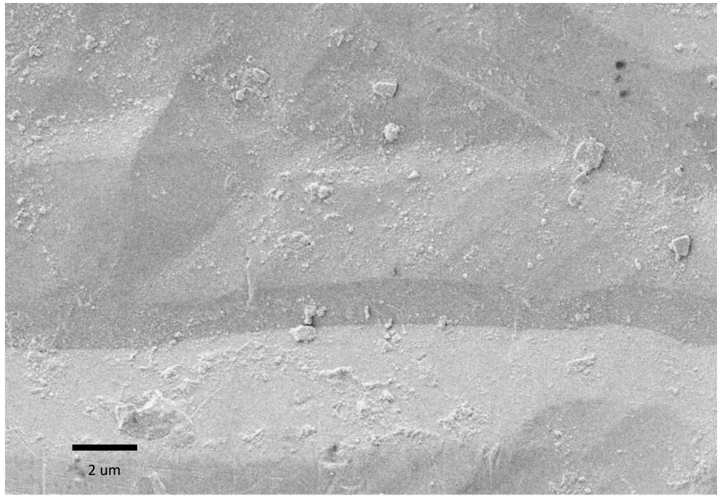


On Si



100 Supercycles

85 supercycles



On Nb