SiO_2 Dry Etching with Ru Hardmasks: Verticality and >100 Selectivity

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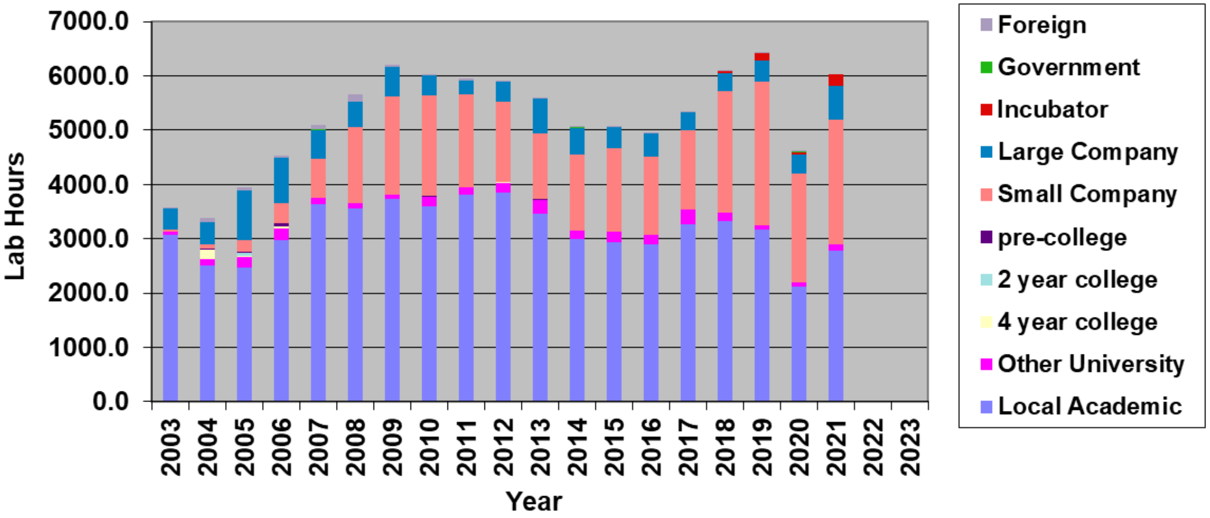
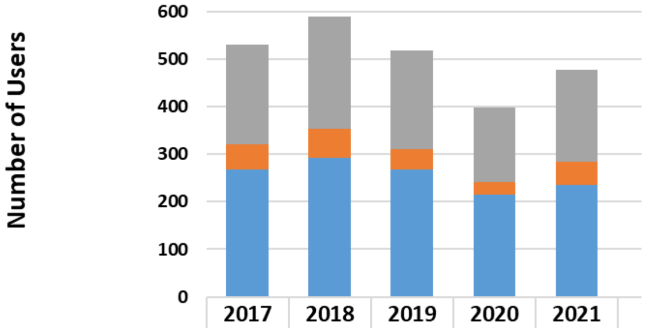
U.C. Santa Barbara Nanofab



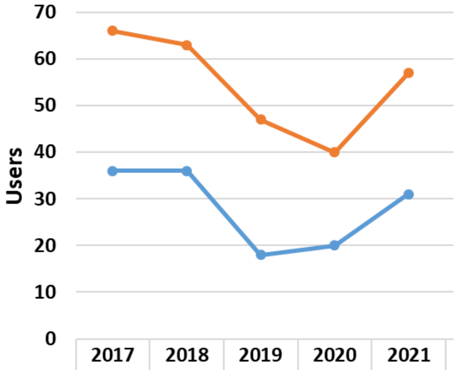
- COVID shutdown:
  2 week closure
- III-V’s, quantum, superconducting, unusual materials
  - Photonics is strongest

Number of Users



	2017	2018	2019	2020	2021
Industrial	209	236	208	156	193
Other Academic	53	62	42	27	50
UC Academic	268	292	268	215	235

Remote ‘Fab Users

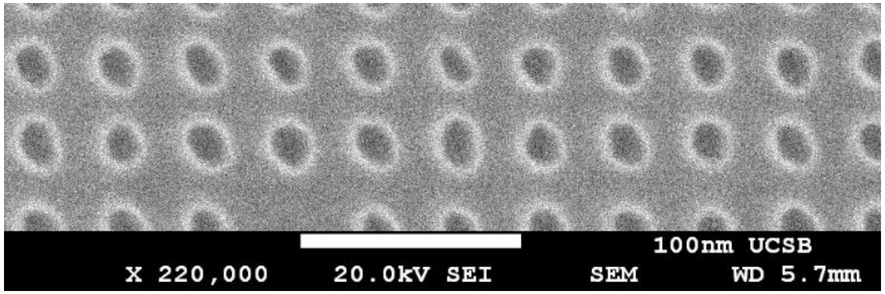


	2017	2018	2019	2020	2021
New Remote	36	36	18	20	31
Remote Users	66	63	47	40	57

- Remote Fabrication:
  - 6 staff on remote ‘fab
  - Critical learning and process development
  - Process Qualification/SPC

SiO_2 etching: current practices

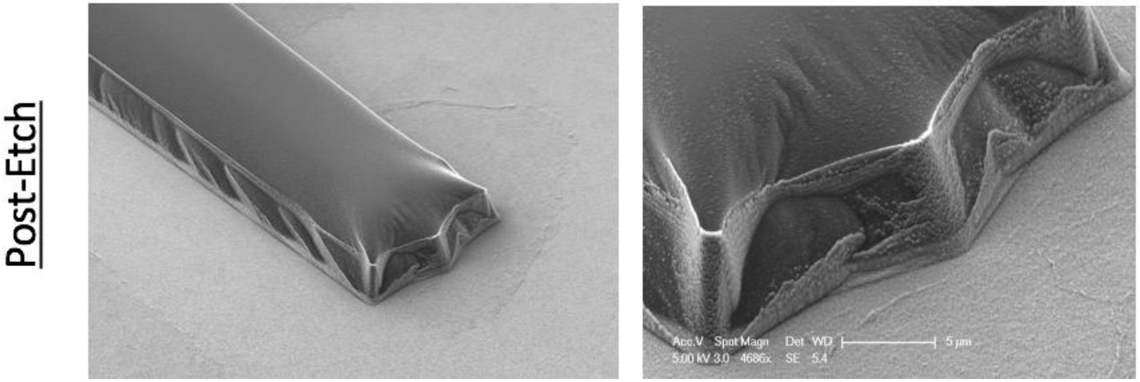
- CHF_3, CF_4 are typical etchants, some O_2 to mitigate polymer
- Found that pure CHF_3 turns ~20nm circles into strange shapes due to polymer roughness

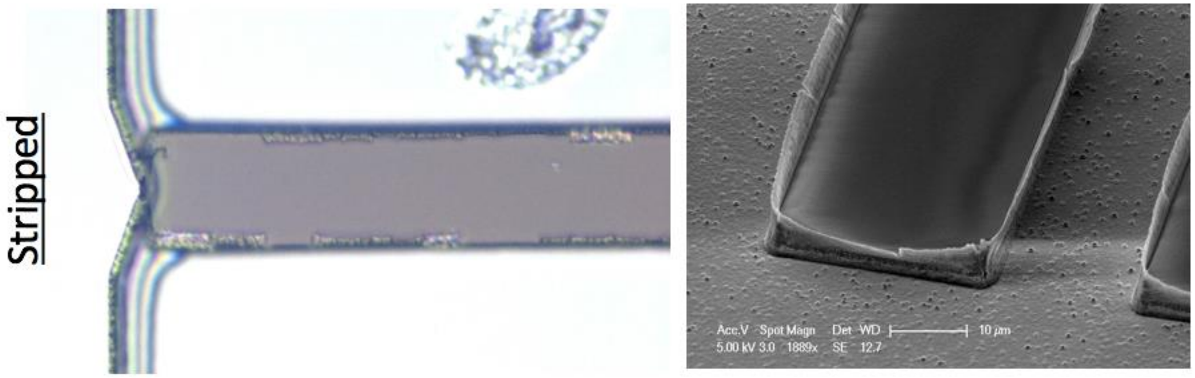


- Verticality is difficult without high selectivity
- High selectivity is difficult without high CHF_3
  - Can’t achieve <20nm roughness and deep features

SiO_2 etching: current practices

- CHF_3 (100%) polymer w/ photoresist

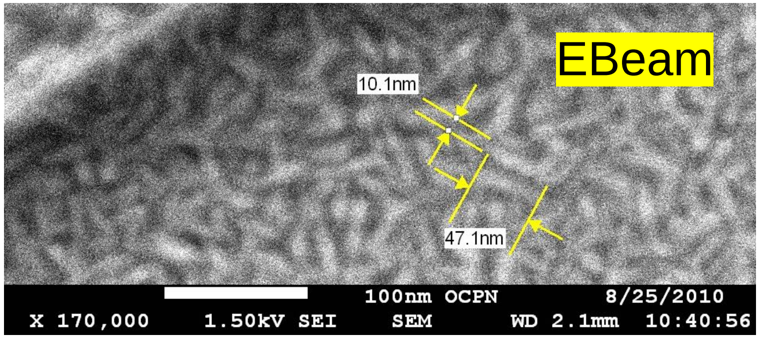


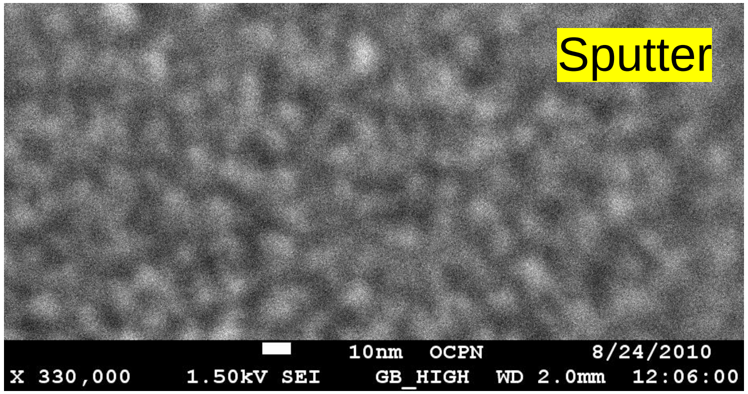


SiO_2 etching: current practices

- Chromium hard-mask
  - Good selectivity ≥30, works
  - EBeam Evap. has large ~50nm grains
    - Sputter has smaller ~10nm grains
- Cr dry etches in ICP of $Cl_2/O_2 \approx 70/30\%$
  - Strong loading effects
  - Nitrogen plasma discharge creates unetchable CrN
  - Occasionally wouldn't dry etch properly, leaving residues
  - Etches into underlying Si/SiO_2
  - Begins etching as soon as Cl_2 introduced

Cr grain size





Why Ruthenium?

- ALD Ru – developed as MOSFET gate, high-conductivity conformal seed layer for Cu plating etc.
- Installed as possible MOSFET gate for researchers

- Literature shows a simple O_2-based etch/strip with high-selectivity, thermally stable, hard material
- We hypothesized that the non-volatile fluorides might make a good F-based etch mask.
  - RuF_3 and RuF_4 are non-volatile (melt >500° C)
  - RuF_5, RuF_6, RuF_8 are volatile (melt <90° C)

Ru etching

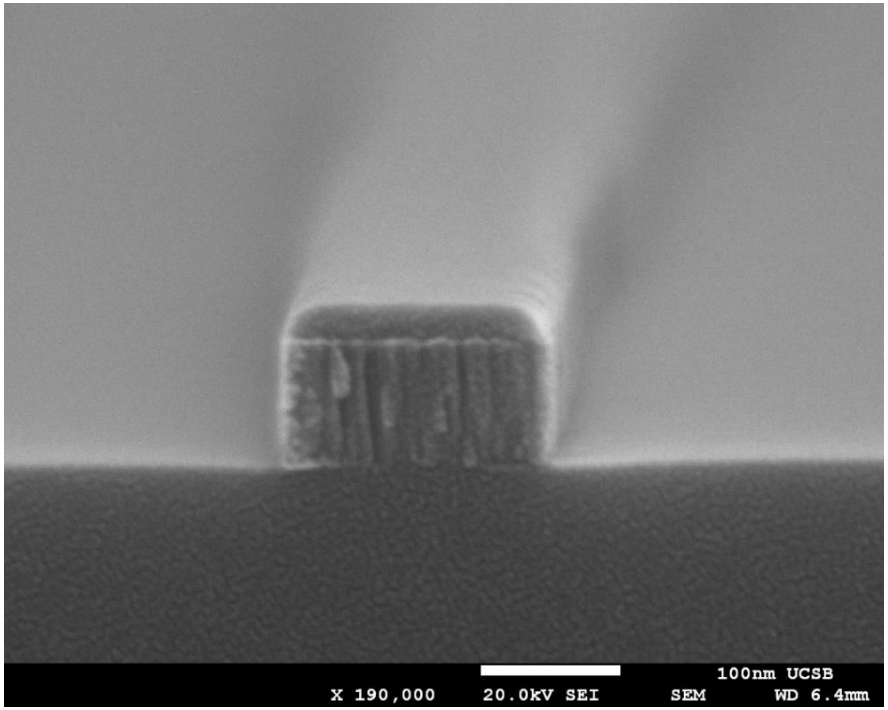
- Ru etches in O_2, very slowly
  - RuO_4 is gas at RT
- Addition of Cl_2 (5-10%) increases etch rate
  - For low-Cl_2 %, believe that Cl_2 increases O_2 radical density
- O_2-based etch provides very high selectivity to Si,SiO_2 underlayers
- Easy dry-chemical strip (in-situ possible)

- Compare with Chromium
  - Requires 20-30% Cl_2
  - Etches via CrO_xCl_y formation
    - $CrCl_x$ and CrO_x non-volatile with high melting point
  - Etches the underlying SiO_2/Si
  - Wet-removal not always possible

Ruthenium Hard Mask

- 100nm Sputtered Ru
  - Smoother than ALD!
- HSQ mask + EBL
- O_2=40 sccm, Cl_2=2 sccm, 0.5 Pa, ICP/Bias=900/50 W
- Overetched by 25%
  - No SiO_2 etching at all.

- HSQ etches slowly in O_2
  - Un-annealed selectivity ~10
  - Primarily driven by ion bombardment (faceting)



Ru adhesion layer

- In some cases, Ru adhesion needed to be increased.

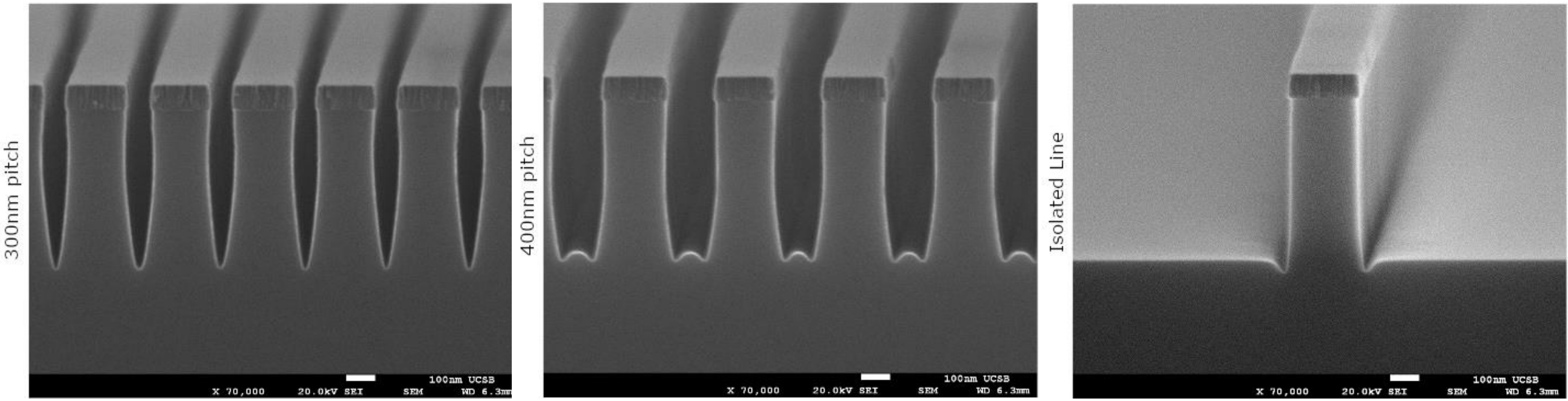
- We used ALD TiN ~5nm
  - Sputtered Ti adhesion would likely also work.
- For most work, we can omit the adhesion layer with no ill-effects.

Baseline SiO_2 Etch

- CF_4 flow = 60 sccm, total maintained
- Pressure = 5 mTorr,
- Bias power = 75 W
- ICP = 950 W (not varying)

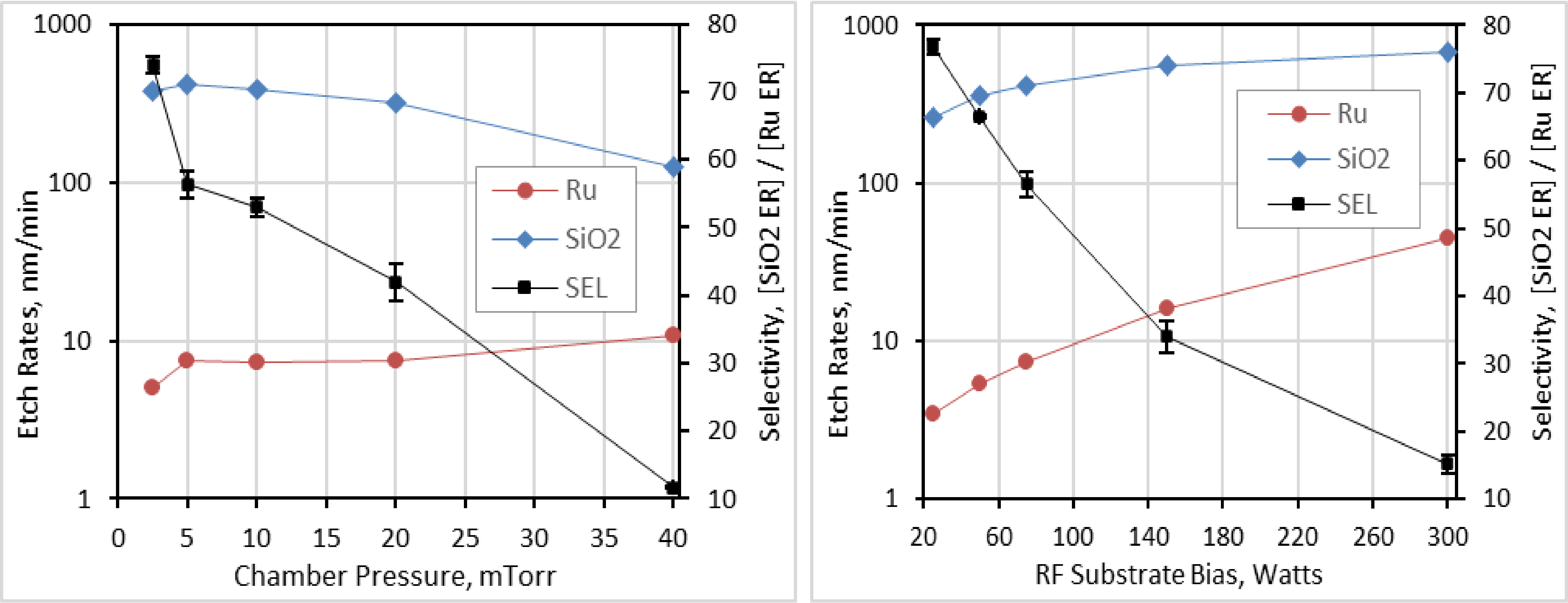
Selectivity: ~55

250nm wide ridges, varying pitch/gap:



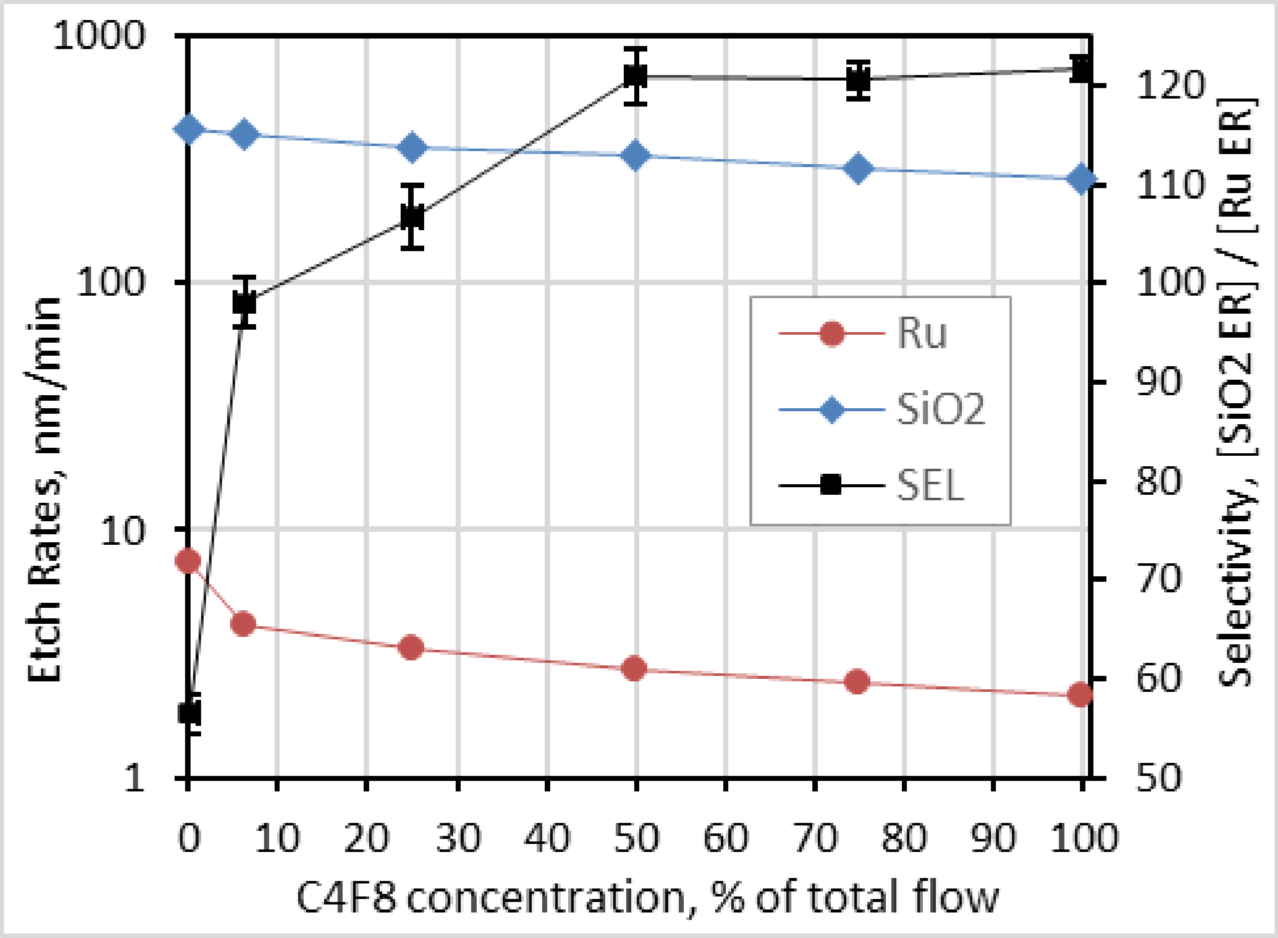
ΔPressure, ΔBias

- ↑ Pressure: SiO_2 rate ↓↓ , Ru rate ↑
- ↑ Bias: SiO_2 rate ↑ , Ru rate ↑↑



C_4F_8 Etching

- ↑↑ Selectivity, due to Ru rate ↓↓ in first 5 sccm
- $RuF_{2\text{-}3}$ formation – non-volatile fluoride



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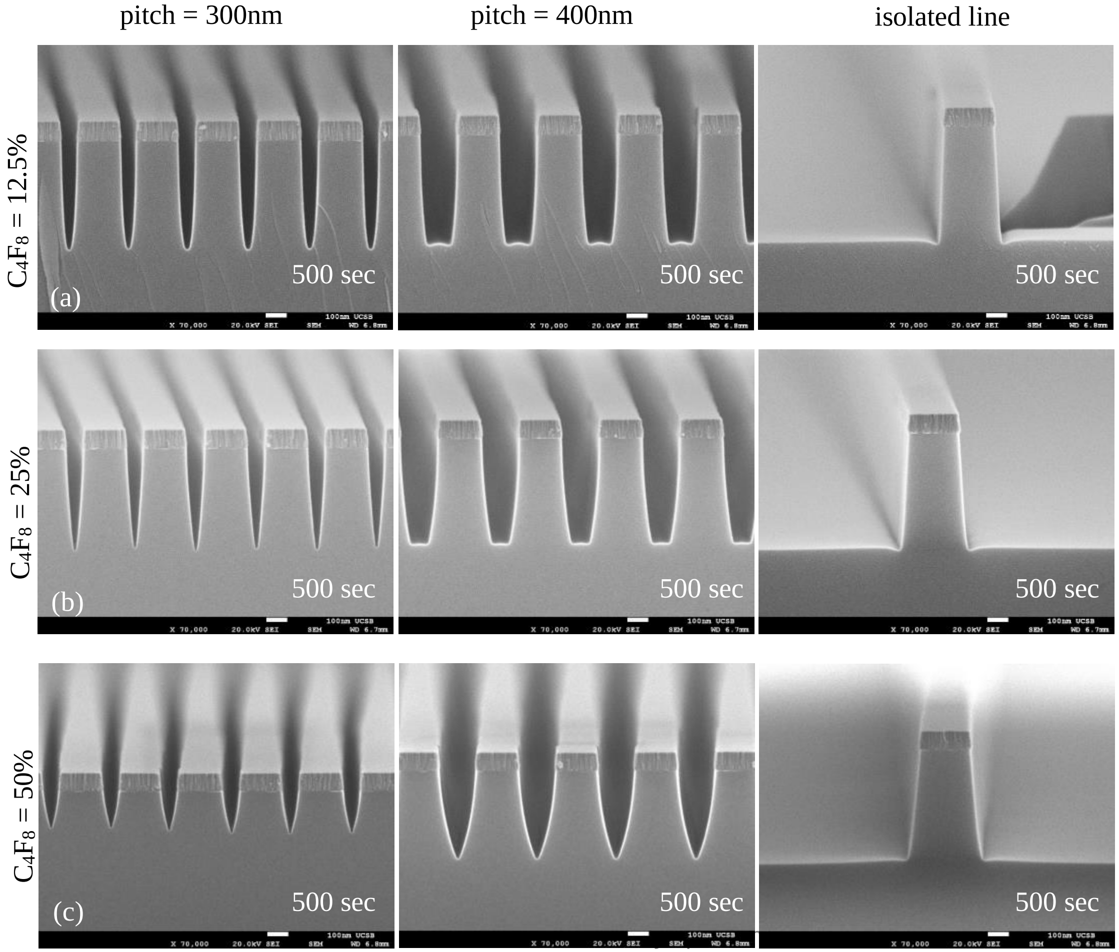


Increased Selectivity

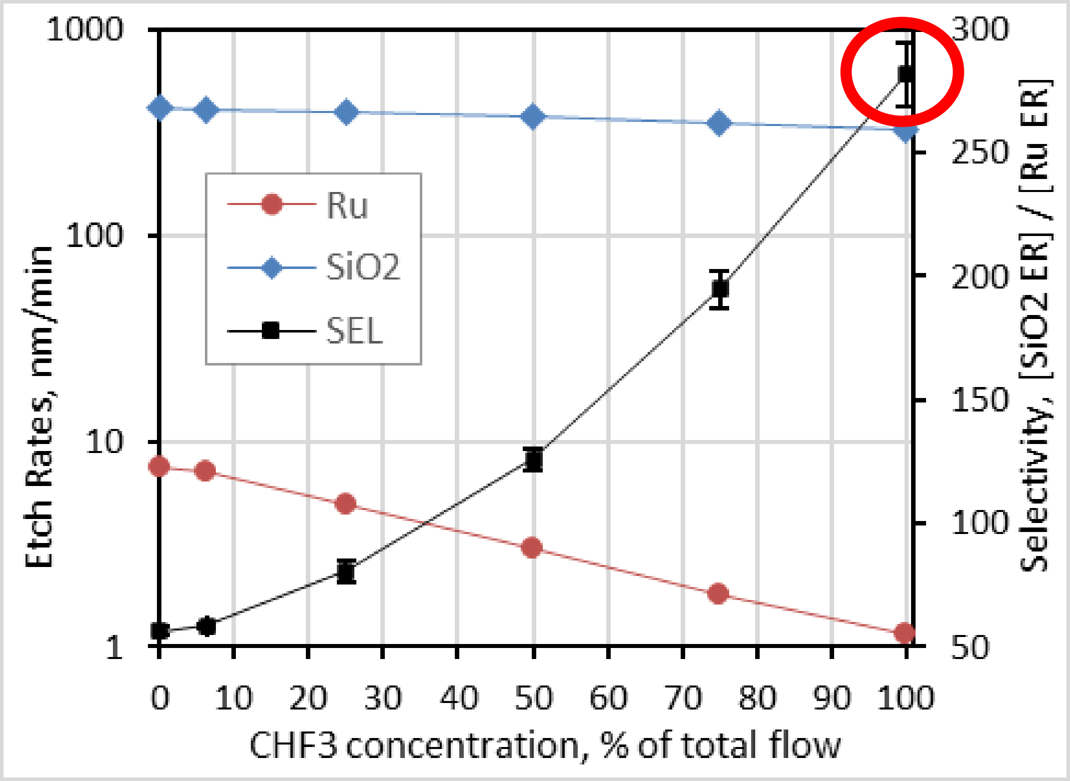
> 100

> 100

~120

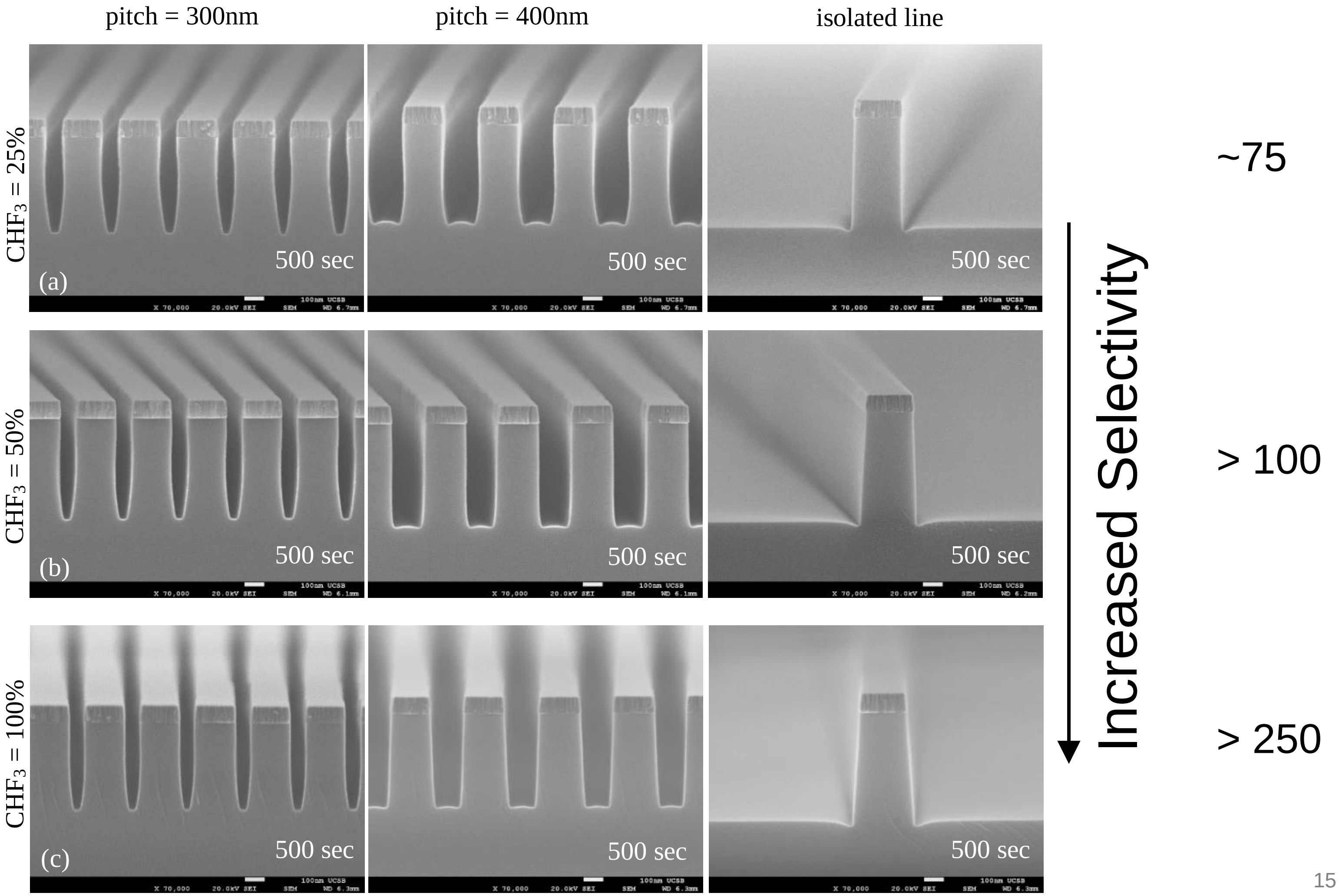
CHF_3 Etching

- CHF_3: Ru rate ↓↓ , Selectivity >> 200 for 100%
- $RuF_{2\text{-}3}$ formation – hard, non-volatile fluoride
- Ru Delamination at CHF3 > 50sccm – required TiN adhesion layer to prevent.



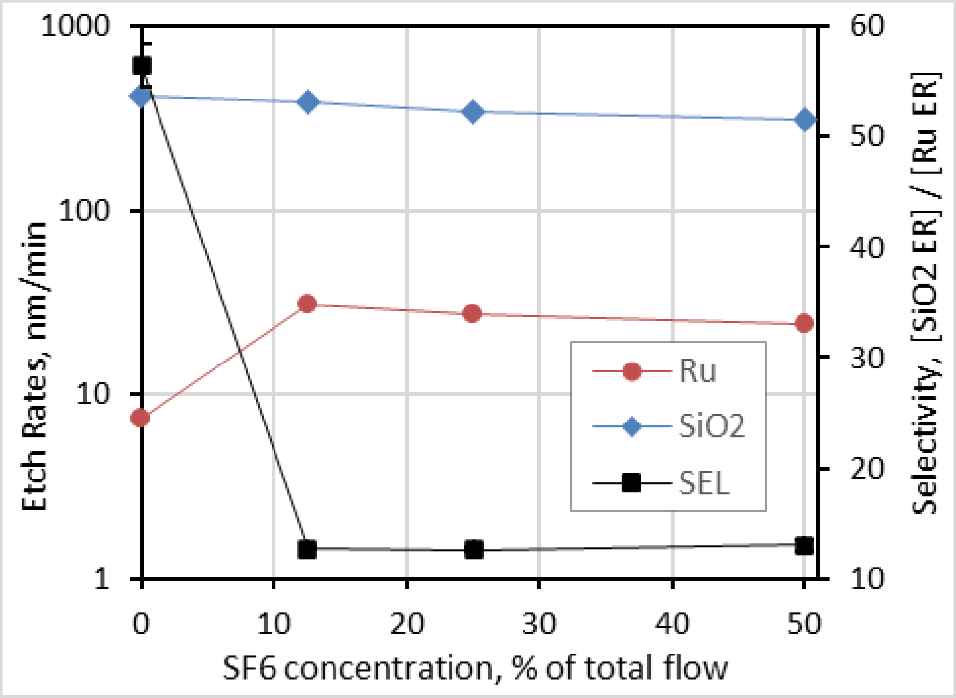
CHF_3 Etching

- CHF_3: Ru rate ↓↓ , Selectivity >> 200 for 100%



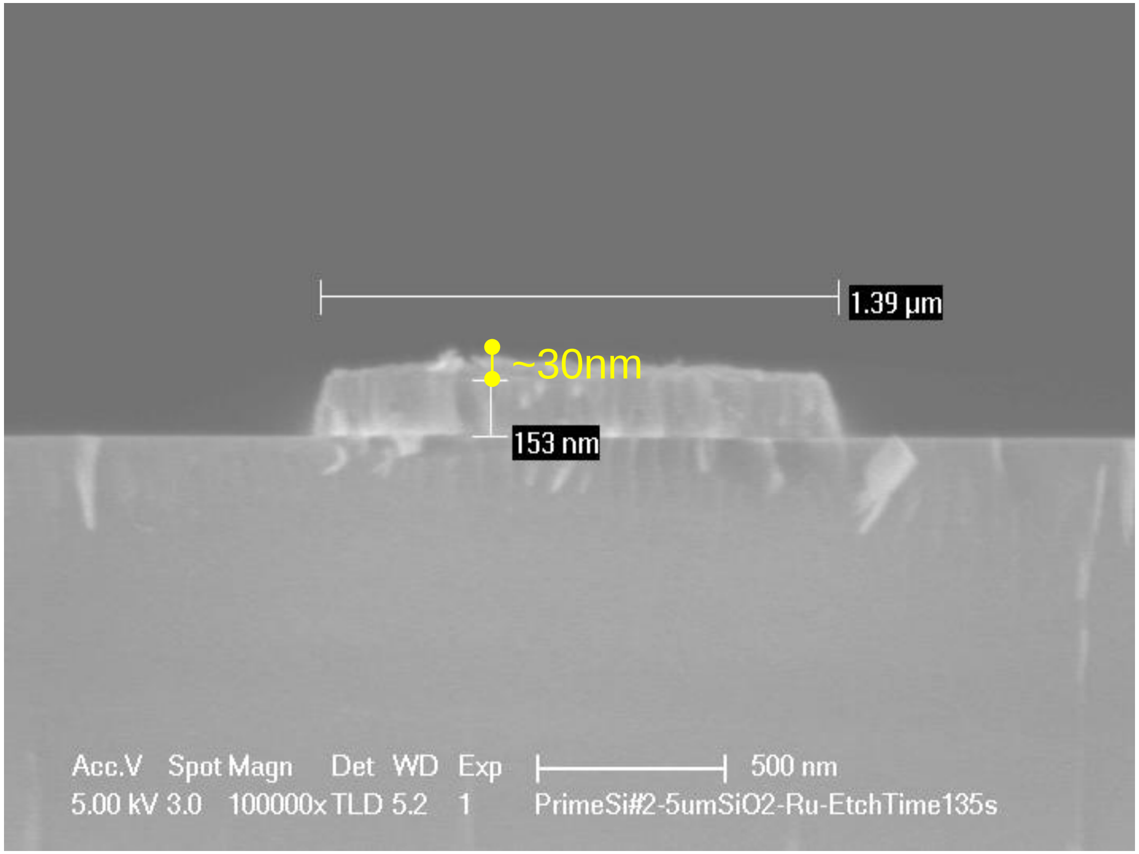
SF_6 Results

- Ru rate ↑ , SiO2 rate —
- High Fluorine concentration, allows for formation of high-F compounds with low melting points
  - RuF5 – 86.5° C
  - RuF6 – 54° C



Transferred to I-Line PR's

- Low selectivity, Ru:PR ≈ 0.2
- Can use thinner Ru layers due to high SiO_2:Ru selectivity



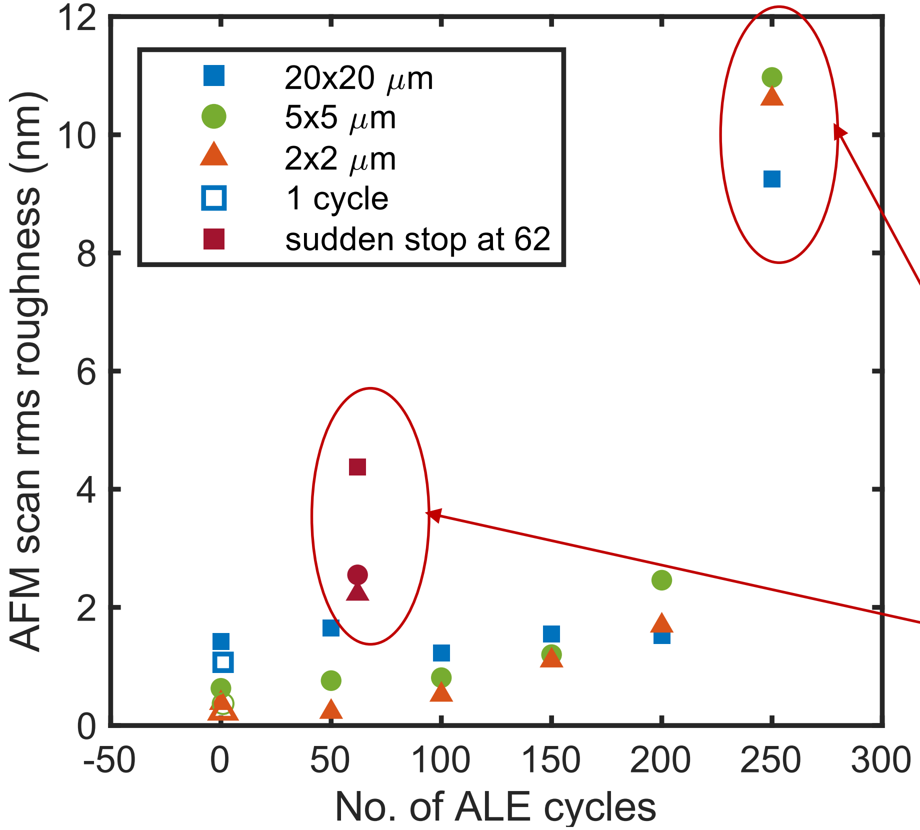
Conclusions

- Ru-masked SiO_2 etching:
  - Patterned and removed with high-selectivity O_2 etch (+ 5% Cl_2)
    - Does not attack underlying Si or SiO2 layers
  - Easiest way to achieve highly vertical SiO_2/SiN etching.
  - Selectivity up to 250 (pure CHF_3)
    - Requires Ti-based adhesion layer.

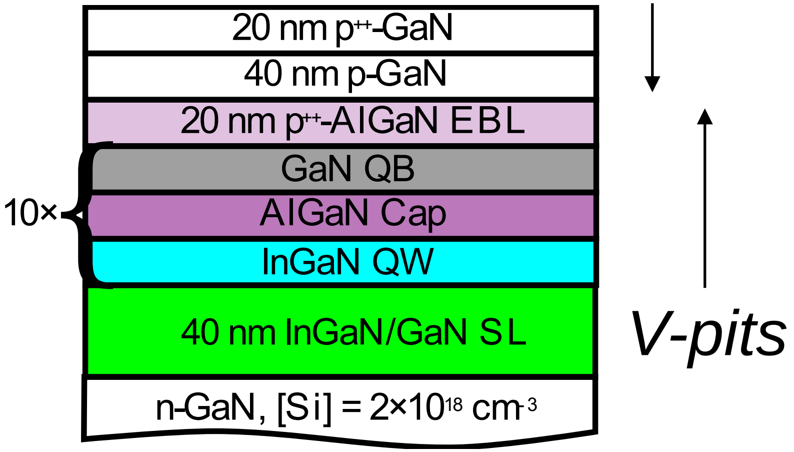
- Further work: Osmium?
  - etches in O_2 alone, but leaves residue, rate is low.
    - Add F-based and ↑ rate.
    - Add Cl2, and ↓ rate
    - Opposite of Ru – perhaps good for Cl2-based etching?
  - No papers on etching Osmium? One textbook from the 60’s.
  - $6k for *Os* sputter target. *Ru* target was ~$3k.

Oxford Cobra GaN ALE

- Surface roughness relatively constant down to ~44nm etch depth



Etching top p-GaN layers

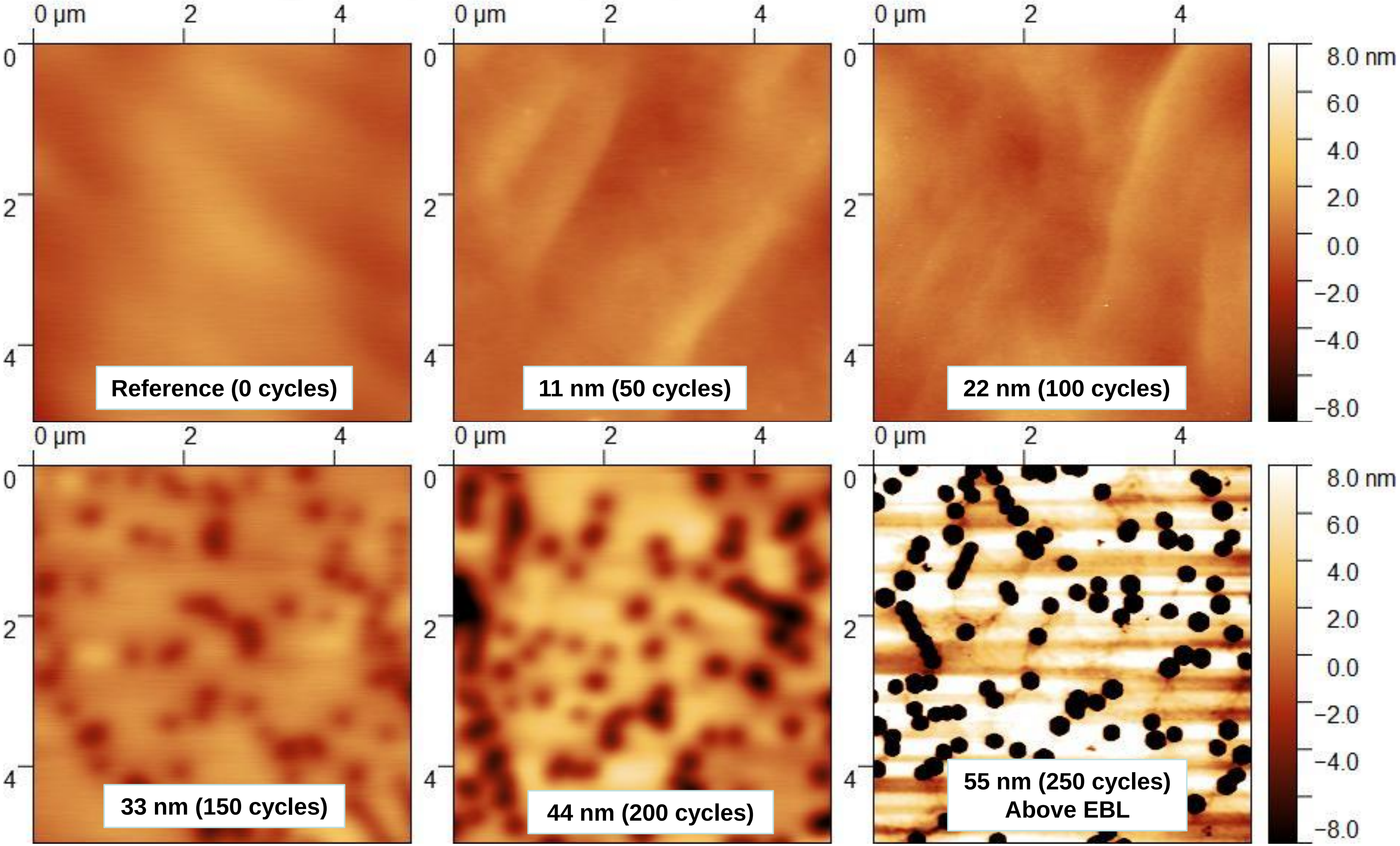

20 nm p^{++}-GaN
40 nm p-GaN
20 nm p^{++}-AlGaN EBL
10× GaN QB
AlGaN Cap
InGaN QW
40 nm InGaN/GaN SL
n-GaN, [Si] = 2×10^{18} cm^{-3}

V-pits

Roughness from exposing of buried V-pits.

Error in pressure resulting in sudden stop mid-etch

AFM Images (5 x 5 μm)



Reference (0 cycles)

11 nm (50 cycles)

22 nm (100 cycles)

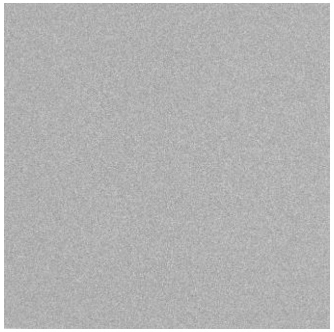
33 nm (150 cycles)

44 nm (200 cycles)

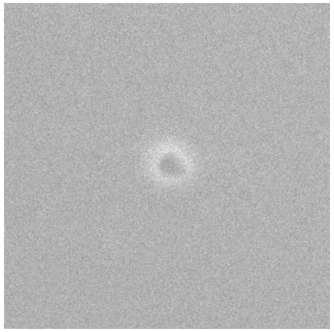
55 nm (250 cycles)
Above EBL

Raith Velion FIB

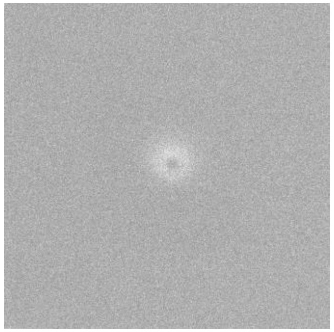
Raith Velion FIB



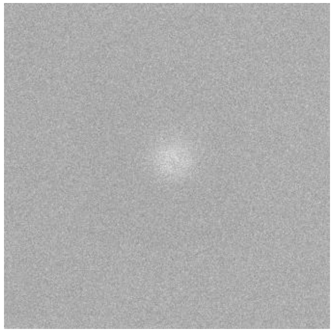
Unpatterned
Membrane
50nm thick Si_3N_4



75nm nanopore FIB

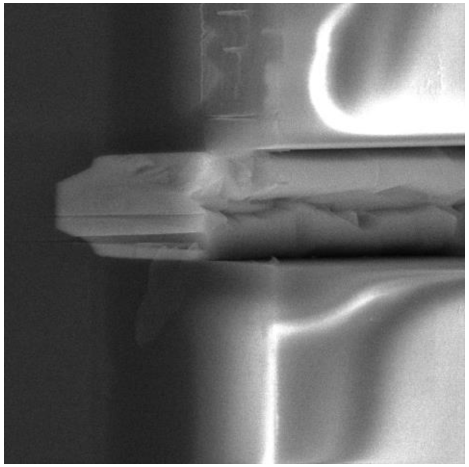


1µm x 1µm area
Shrinks to 38nm

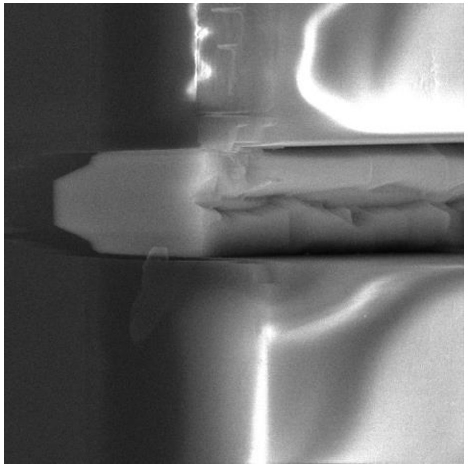


1µm x 1µm area
Closed off

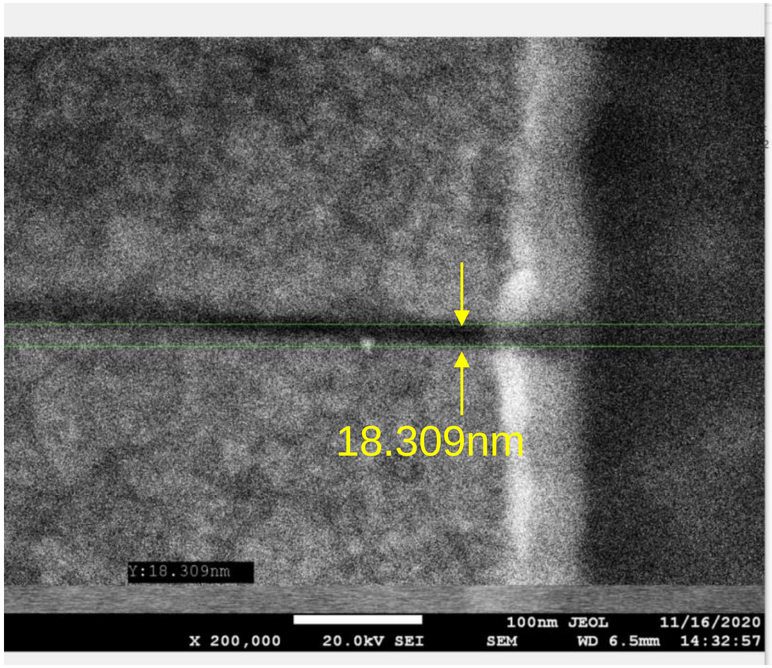
III-V-on-Silicon Ridge laser facets



As cleaved before milling



After ion beam milling



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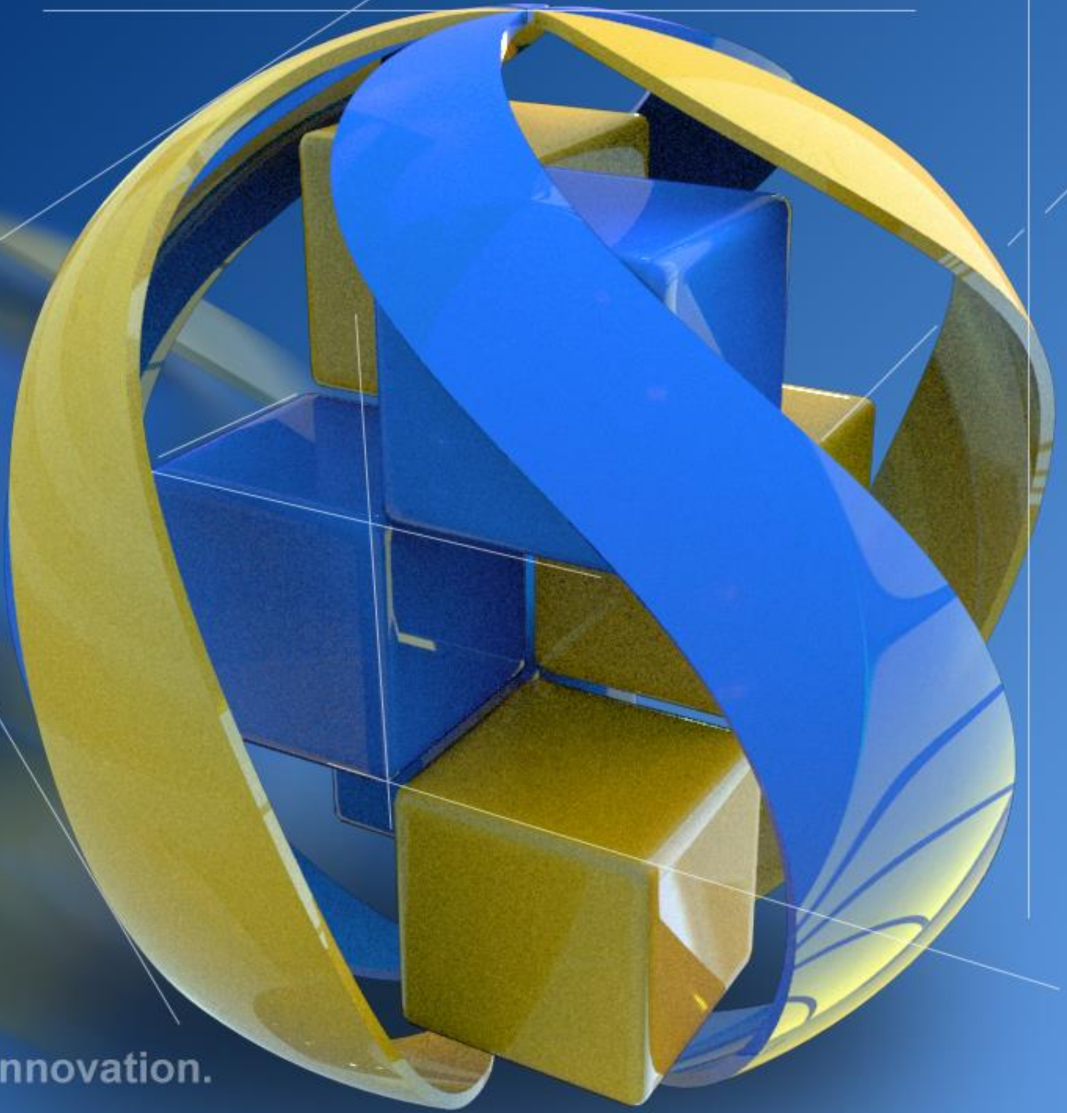

Remote 'Fab Services:
demis@ucsb.edu

The convergence of research and innovation.