In-Situ Cleaning of Sn EUV Sources

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- **Etch Rates and Cleaning of Collector**
- **Sputtering Predictions**
- **MLM Surface Analysis by SIMS**
- **MLM EUVR Results**
- **Modeling**
- **Conclusions**

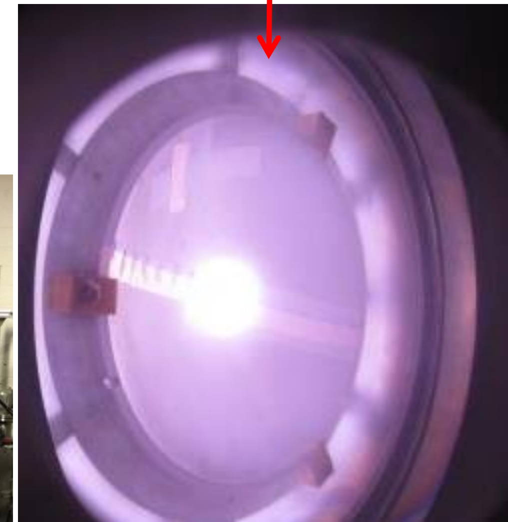
Rationale for Plasma at Collector

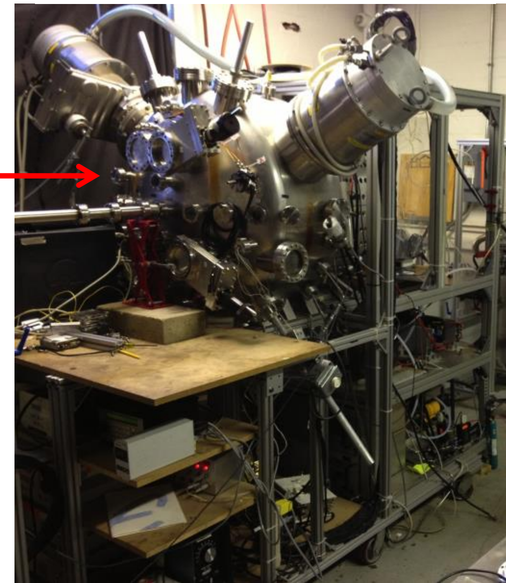
- EUV plasmas expel high-energy Sn ions and neutrals.
- Current buffer gas mitigation must be supplemented by Sn cleaning.
- Solution: Hydrogen Plasma Cleaning. $Sn + 4H \rightarrow SnH_4$ (g)
- An external radical source would suffer from recombination at the walls as radicals are blown into system.
- Additionally, the radical delivery system for such a setup could block the collector.
- The flux from a point-source radical generator decreases as $1/r^2$.
- Ideal scenario: create radicals at collector surface, where they are needed.
- This can be accomplished by using the collector as antenna to create a plasma at the surface.

Experimental Apparatus

- 5 Masked Samples are placed on 790 cm^2 steel dummy collector.
- Magnetron sputtering used to coat entire dummy collector with Sn in SCOPE chamber.
- Collector installed in CPMI's XTS 13-35 source chamber (XCEED).
- 300W supply run for 2 hrs, 130mTorr, 500sccm H_2 flow.

Collector-driven plasma in XCEED



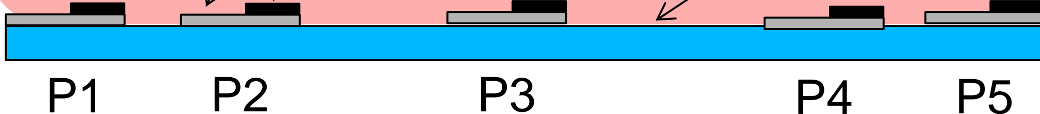


H_2 Plasma

Sn Coated Witness Plate

Mask

Dummy Collector

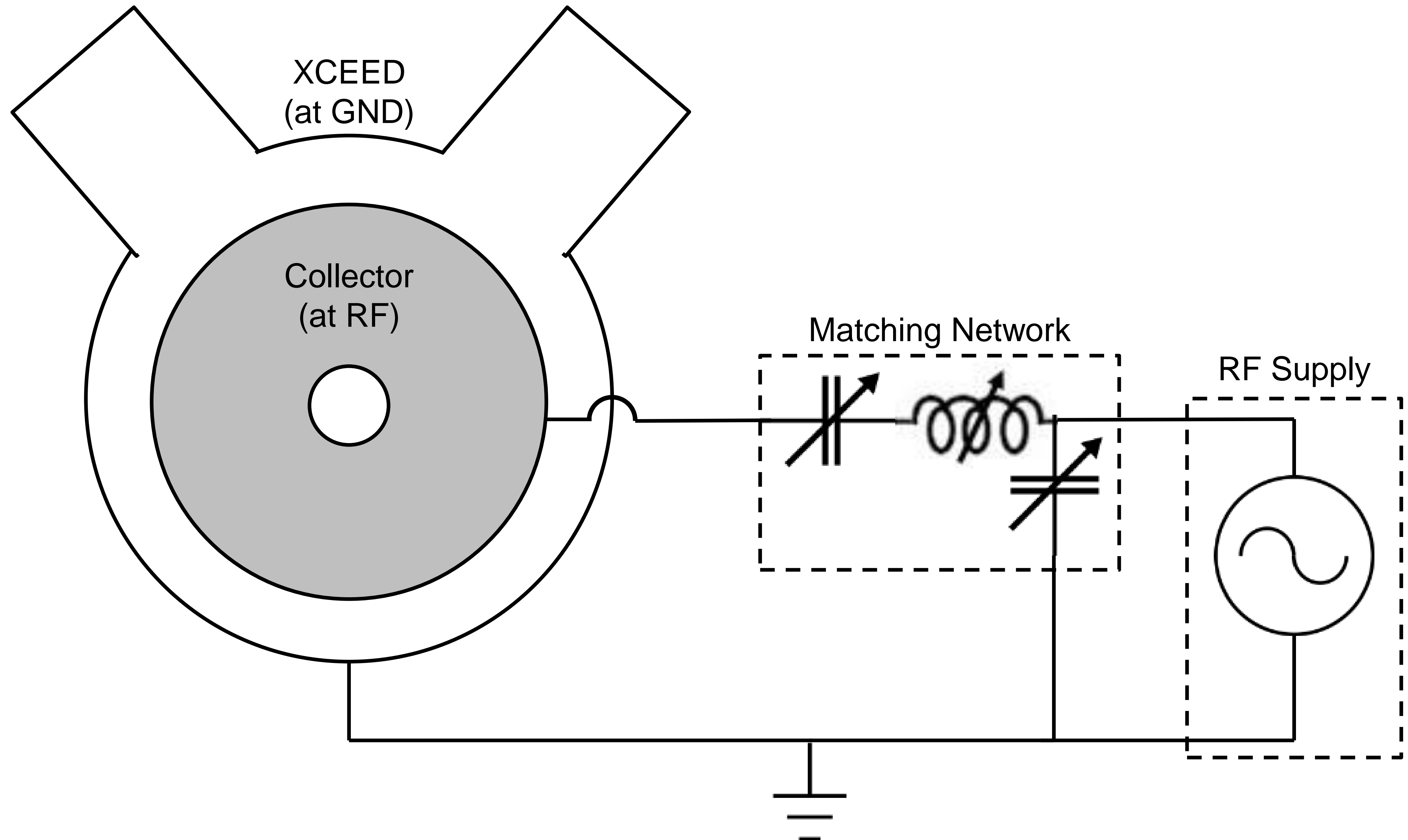


P1 P2 P3 P4 P5

Matching Network

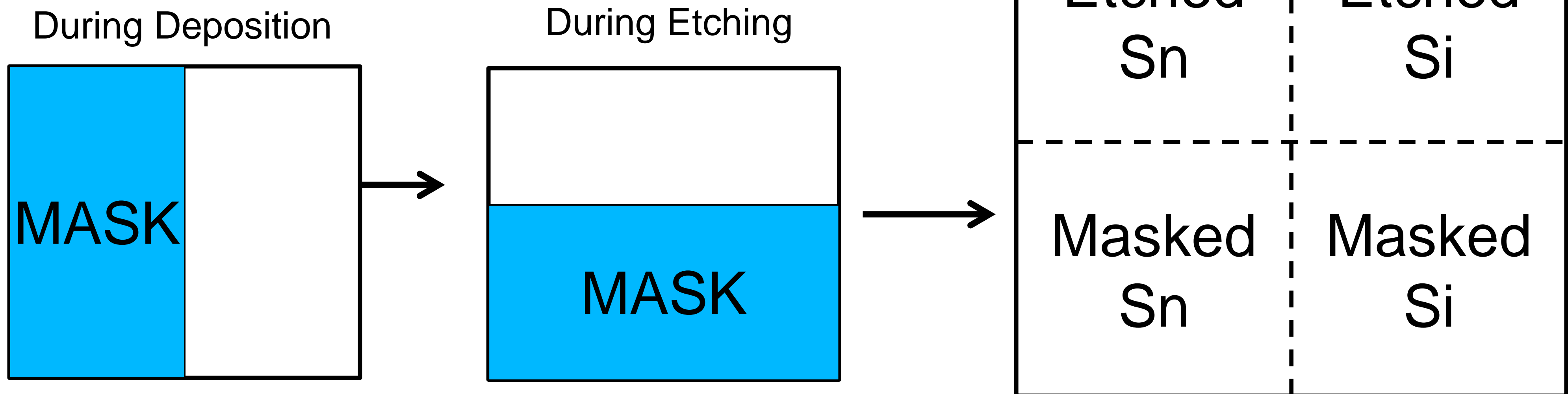
300 W
13.56 MHz
RF-Generator

Circuit Diagram



Sample Masking Procedure

- Si samples (approx. 1 cm^2)placed on disk to enable measurement in characterization machines.
- Half-sample masked for deposition.
- Mask rotated 90º during etching.
- Etch depth measured by profilometer (step between Etched Sn and Masked Sn)

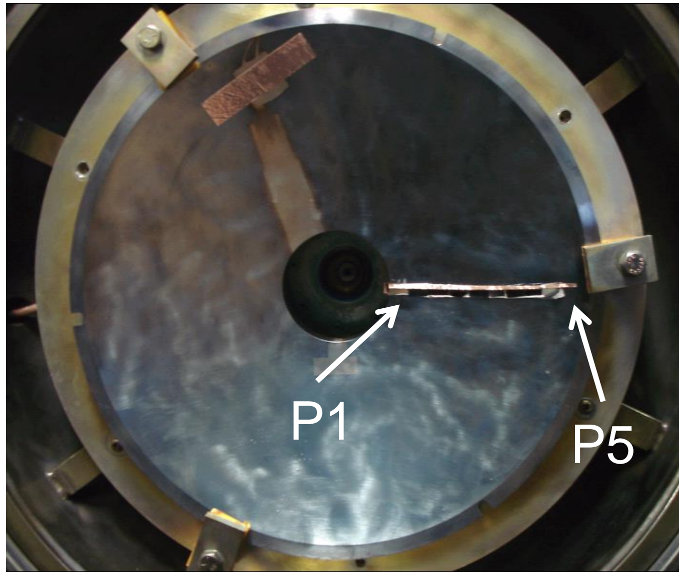


Etched Sn: Deposited with Sn, Exposed during Etching
Masked Sn: Deposited with Sn, Exposed during Etching

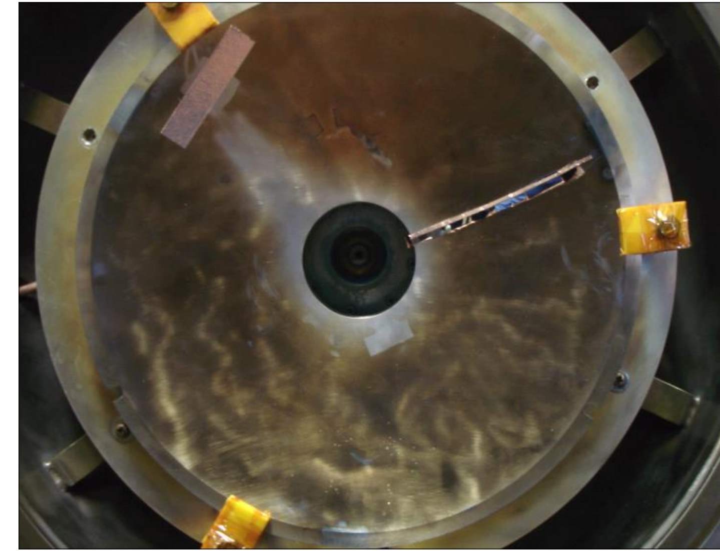
Etched Si: Masked during Deposition, Exposed during Etching
Masked Si: Masked during Deposition, Masked during Etching

Dummy Collector Images (20nm Sn Deposition)[7]

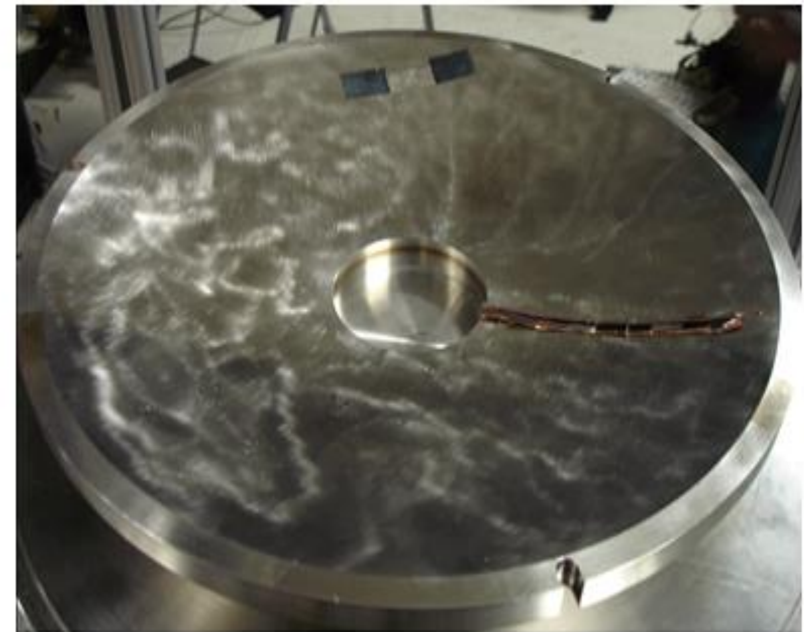
Before Etching



4 min Etching

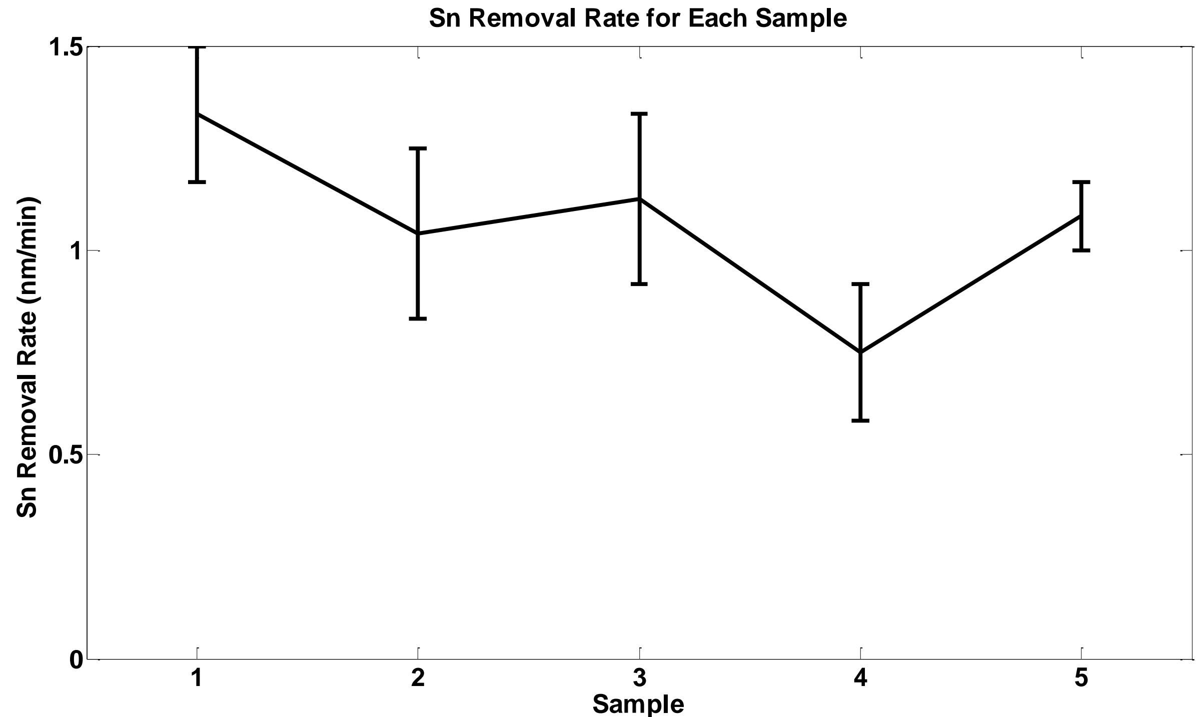


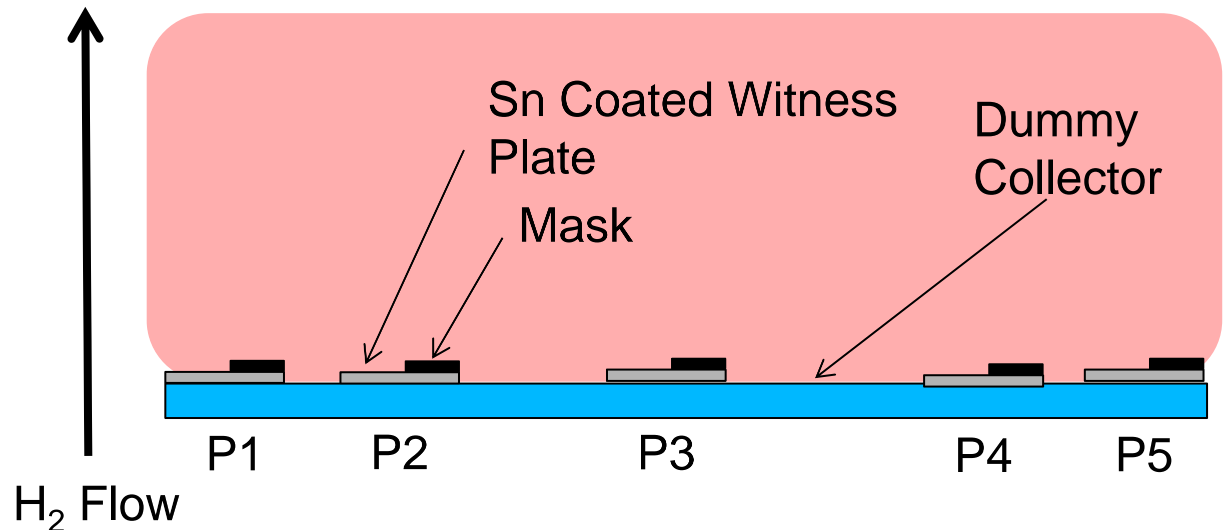
After Etching



Removal Rates of Sn on Si Samples

- Removal Rate varies by position.
- Dependent on radical density and ability to remove SnH_4.
- Samples 1 and 5 are close to edges of dummy collector. Less surrounding Sn, and etched SnH_4 can enter voids to be removed.
- Higher local electric fields at center → More radicals
- Geometry causes Sample 1 to see the highest flow rate.
- So we can clean…but would we harm a real MLM surface?





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Voltage Curve on Dummy Collector

- Capacitive plasmas are current-limited by the ability of ions to carry current through the sheath.
- Self-biasing occurs to increase the magnitude of the average sheath voltage, allowing the sheath to draw enough ions. Will this cause sputtering on a real MLM?
- Average Value = DC bias ~= 300V. V_{plasma} ~= 50V (measured with Langmuir Probe).

Sputtering Expectations

- Average sheath potential drop: 350eV.
- Sputtering Yields calculated with SRIM.
- Expected sputtering rates are small for Si and 0 for Mo and Ru.

$$Ion\ Flux = \Gamma = n_e v_i \qquad Sputtering\ Rate = \Gamma\ x\ Yield\ x \frac{1}{density}$$

350 eV Ions

	Si	**Mo**	**Ru**
Sputtering Yield	0.021 at/ion	0	0
Sputtering Rate	0.036 nm/min	0	0
Thickness Sputtered after 2 hours	4.4 nm	0	0
Thickness Sputtered after 45 min	1.6 nm	0	0

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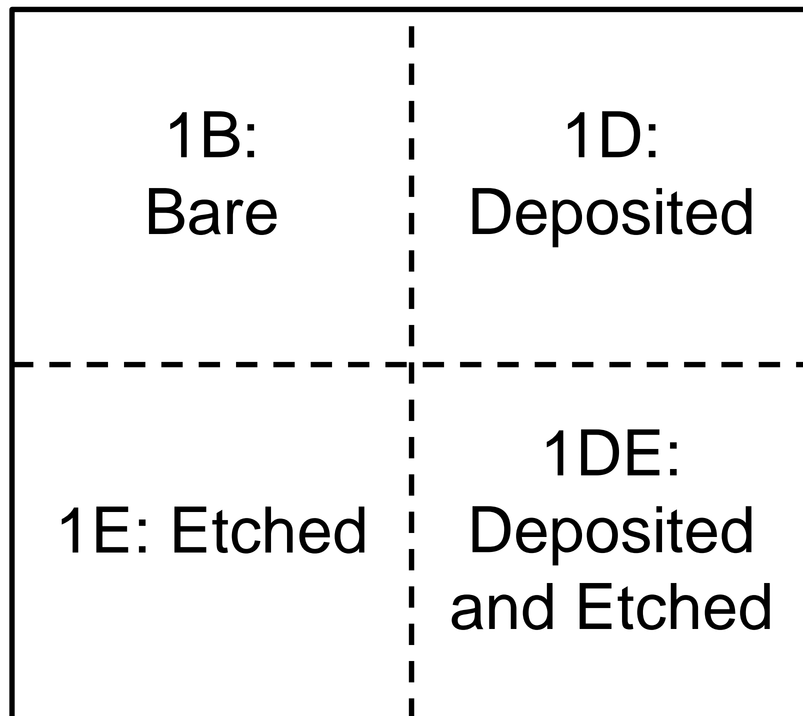
SIMS Depth Profiling Experiment

- Two different multilayer mirror samples: Cap Layer A and Cap Layer B.
- Each cut into four pieces:
  - One piece left bare (B)
  - One piece deposited, not etched (D)
  - One piece etched, not deposited (E)
  - One piece deposited and etched (DE)
- Sample analysis done with SIMS depth profiling. 12keV oxygen ions used to bore through sample; secondary ions measured with mass spectrometer.



- Deposition: <20nm
- Etching: 45 min.
- Given the experimental removal rates, complete etching should be achieved.
- SIMS: 100nA ion current, 500 μm^2 scan size.

Example: Cap A Non-Deposited

Cap A: Bare

O2+, 12kV, 100nA, PosSec, FA2, CD2, Rast 500 um, InFld 150 um

28Si

98Mo

30Si

Cap Layer

Apparent difference due to different ionization yields for Si and Mo.

Multilayers are observed in the Si and Mo lines, but as sputtering continues, the sample heats and the layers mix.

Counts Per Second

1E+7
1E+6
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0

0 500 1000 1500 2000 2500

Depth (a. u.)

Cap A: Etched

O2+, 12kV, 100nA, PosSec, FA3, CD2, Rast 500 um, InFld 150 um

28Si

98Mo

30Si

Cap Layer

Counts Per Second

1E+8
1E+7
1E+6
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0

0 500 1000 1500 2000 2500

Depth (a. u.)

Cap A Deposited

Cap A: Deposited

O2+, 12kV, 100nA, PosSec, FA2, CD2, Rast 500 um, InFld 150 um

Counts Per Second: 1E+0, 1E+1, 1E+2, 1E+3, 1E+4, 1E+5, 1E+6, 1E+7

Depth (a. u.): 0, 500, 1000, 1500, 2000, 2500

28Si
98Mo
30Si
120Sn
Cap Layer

Cap A: Deposited & Etched

O2+, 12kV, 100nA, PosSec, FA3, CD2, Rast 500 um, InFld 150 um

Counts Per Second: 1E+0, 1E+1, 1E+2, 1E+3, 1E+4, 1E+5, 1E+6, 1E+7

Depth (a. u.): 0, 500, 1000, 1500, 2000, 2500

28Si
98Mo
30Si
120Sn
Cap Layer

SIMS Analysis: Cap A MLM Sample

- Cap A "bump" near the beginning of the depth profiles is approximately the same thickness in B, D, E, DE.
- Depth is back-calculated from time assuming constant sputter rate. Though this gives only a rough estimate, features of the same material and same size should appear the same in each scan.

Bare
~100 a.u.
Si layers
1E+06
1E+05
28Si
98Mo

Etch
~100 a.u.
1E+07
1E+06
28Si
98Mo

Dep.
~100 a.u.
1E+06
1E+05
28Si
98Mo
120Sn
30Si

Dep, then Etch
~100 a.u.
1E+07
1E+06
28Si
98Mo

- Even on close inspection, E and DE are nearly identical. Sn should have protected MLM from etching for part of the DE etch; E had no Sn protection. Capping layer appears same thickness in B, D, E, and DE.

Conclusion: No sputtering observed.

Cap B Non-Deposited

Cap B: Bare

O2+, 12kV, 200nA, PosSec, FA2, CD2, Rast 500 um, InFld 150 um

High current

98Mo

Counts Per Second

1E+8, 1E+7, 1E+6, 1E+5, 1E+4, 1E+3, 1E+2, 1E+1, 1E+0

0, 500, 1000, 1500, 2000, 2500

Depth (a. u.)

Cap B: Etched

O2+, 12kV, 100nA, PosSec, FA3, CD2, Rast 500 um, InFld 150 um

98Mo

Counts Per Second

1E+8, 1E+7, 1E+6, 1E+5, 1E+4, 1E+3, 1E+2, 1E+1, 1E+0

0, 500, 1000, 1500, 2000, 2500

Depth (a. u.)

Cap B Deposited

Cap B: Deposited

O2+, 12kV, 100nA, PosSec, FA2, CD2, Rast 500 um, InFld 150 um

98Mo

120Sn

Counts Per Second

1E+7
1E+6
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0

0 500 1000 1500 2000 2500

Depth (a. u.)

Cap B: Deposited & Etched

O2+, 12kV, 100nA, PosSec, FA3, CD2, Rast 500 um, InFld 150 um

98Mo

120Sn

Counts Per Second

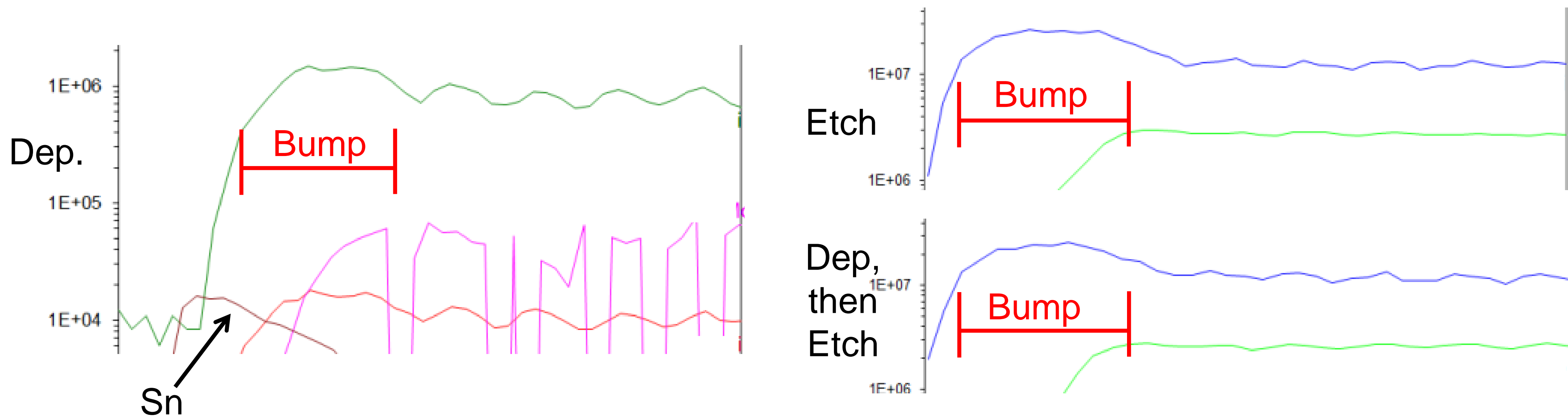
1E+8
1E+7
1E+6
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0

0 500 1000 1500 2000 2500

Depth (a. u.)

SIMS Analysis: Cap B

- Again, Sn is removed. E and DE are nearly identical.
- The same "bump" appears near the beginning of the depth profiles. It is hypothesized that this "bump" is part of a capping layer.
- "Bump" is same thickness in D, E, DE. Cap is not removed or damaged. Underlying MLM structure is untouched.



Conclusion: No sputtering observed.

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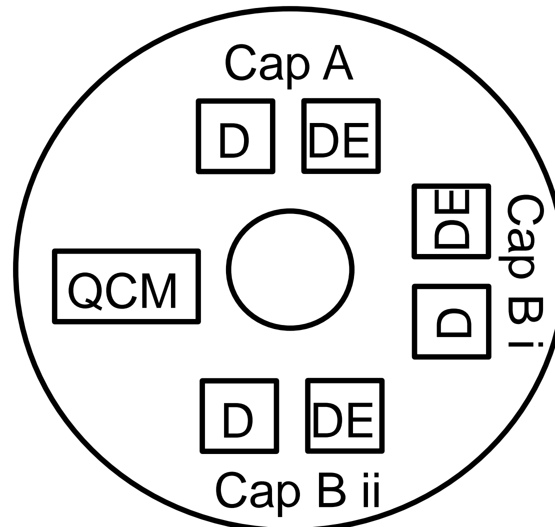
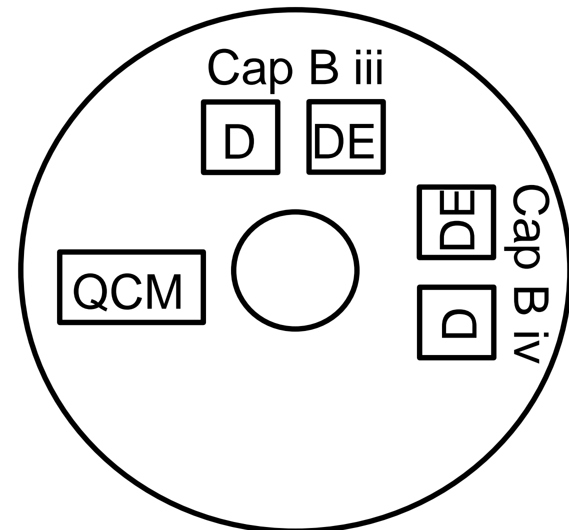
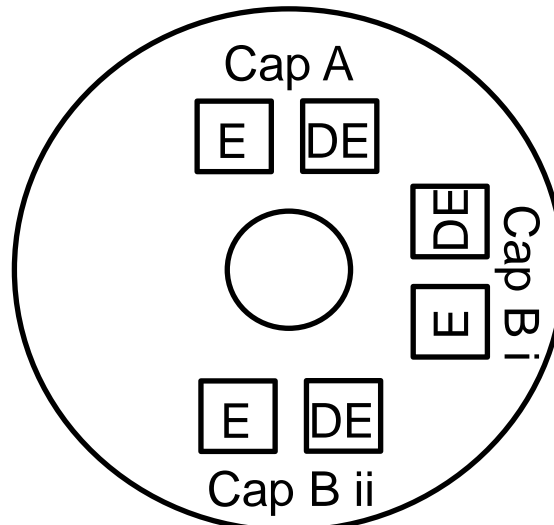
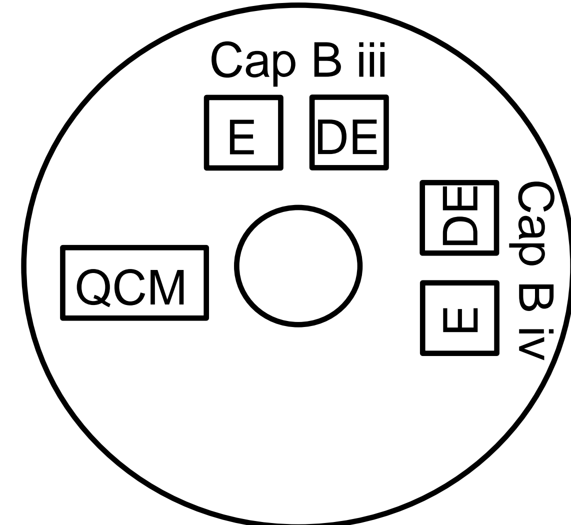
MLM EUVR Experiments

- A real EUV source will not be performing SIMS measurements. The true test is to measure EUVR.
- Can we restore reflectivity to Sn-coated MLM samples? And can we avoid destroying it for bare samples exposed to our plasma?
- 1 set of Cap A samples and 4 sets of Cap B samples analyzed.
- 5 samples per set: Control, Bare, Etched, Deposited, Deposited & Etched.
- Control was never removed from sample holder. “Bare” was opened, picked up, and handled whenever other samples were handled, to see if sample handling and atmosphere affected results.
- Deposition: ~20nm. Etching Time: 45 mins.
- EUVR measured by Dr. Eric Gullikson on LBNL’s Advanced Light Source.

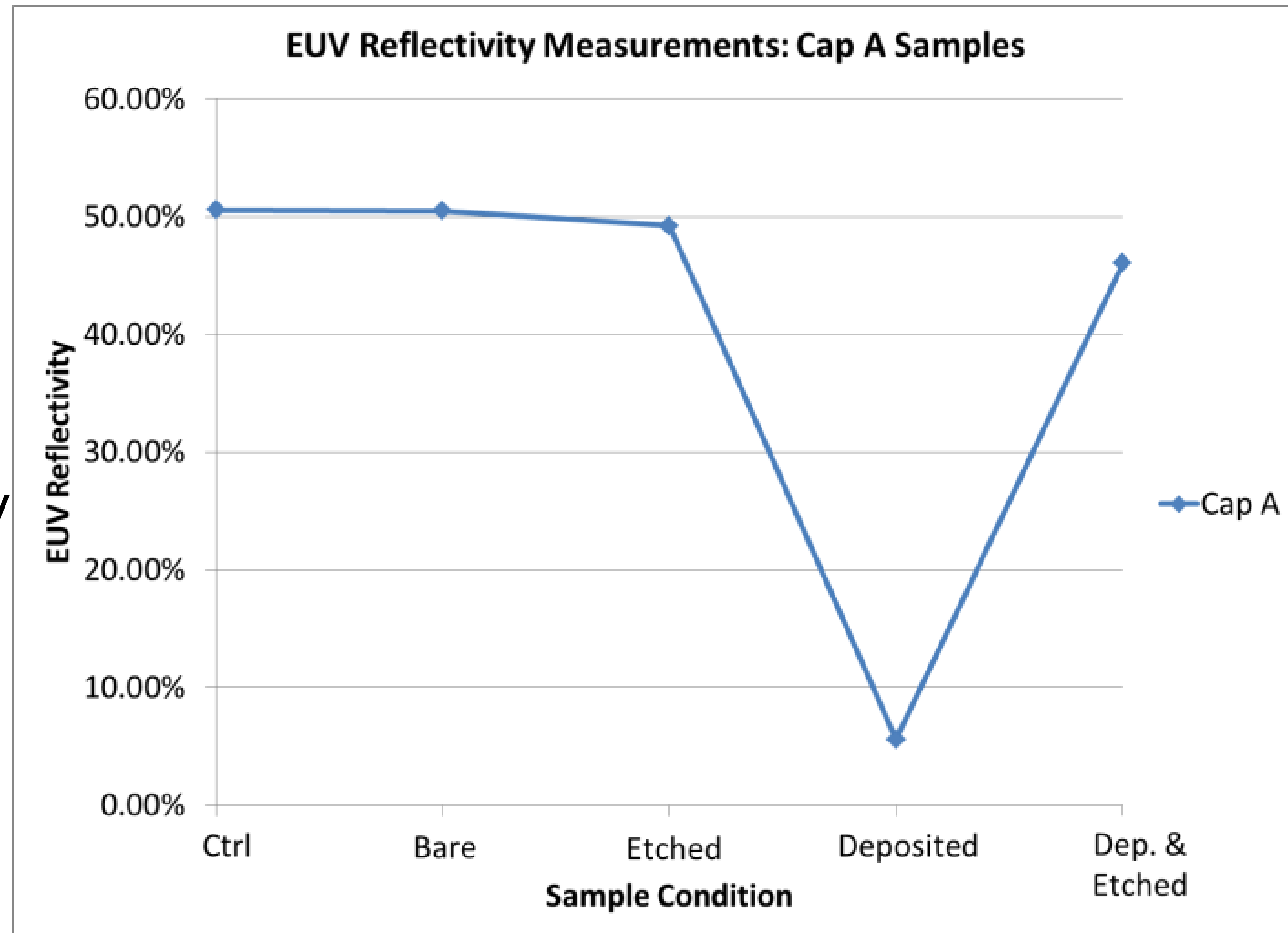
Experiment Setup

- 2 runs of samples: one with the Cap A set and two Cap B sets, and one with two Cap B sets.

	Run 1	Run 2
In SCOPE deposition chamber		
In XCEED etching chamber		

Cap A EUVR Results

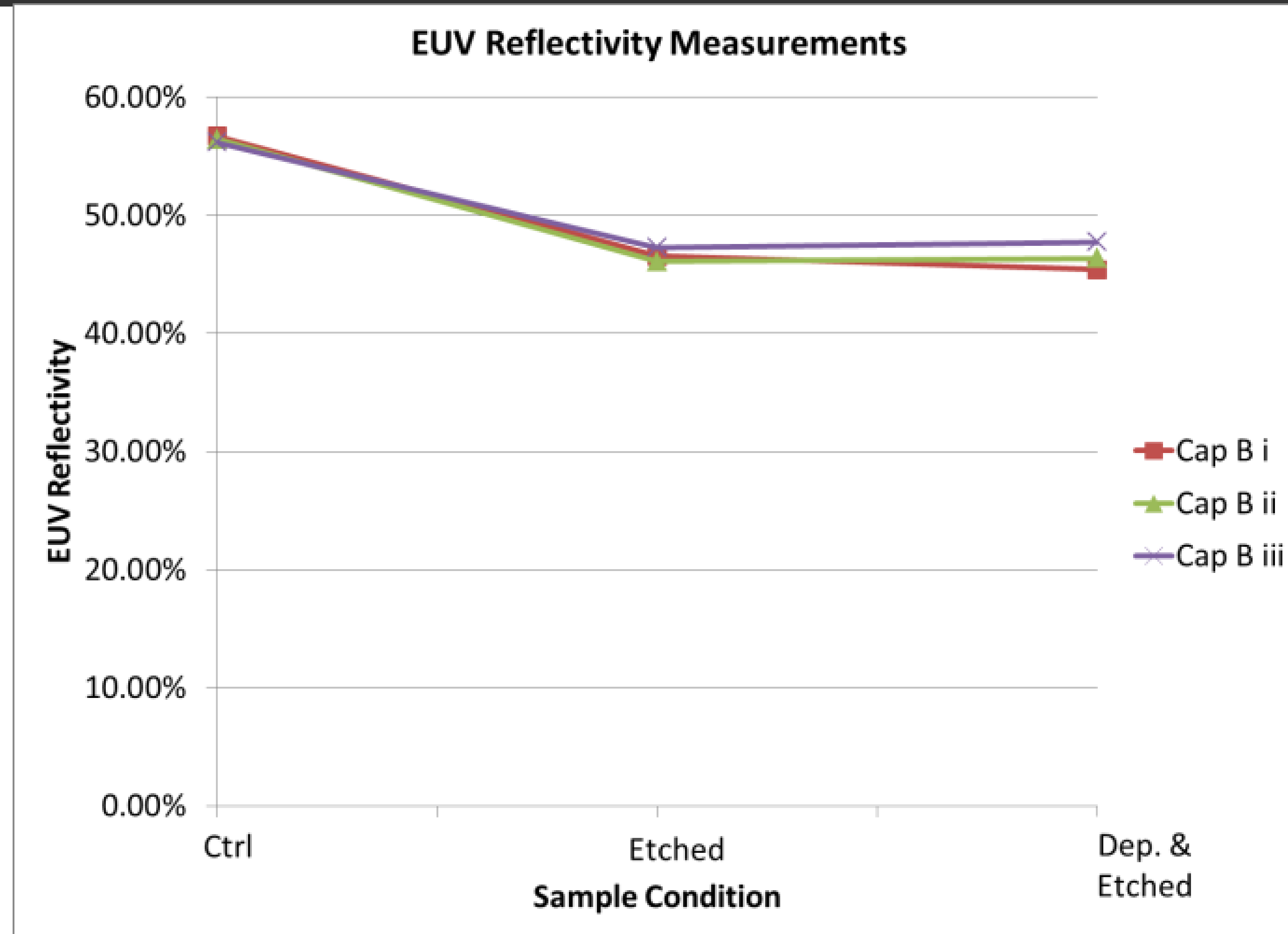
- Bare and Control are nearly identical; samples not hurt by handling.
- After 45min of exposure to etching plasma, EUVR is very slightly decreased (from 50.5% to 49.1%).
- Sn deposition causes EUVR to plummet.



- Cleaning restores most reflectivity (restored from 5.6% to 46.1%).

Cap B EUVR Results

- Cap B i, ii, and iii do not have Bare or Deposited Measurements (due to shutdown of ALS).

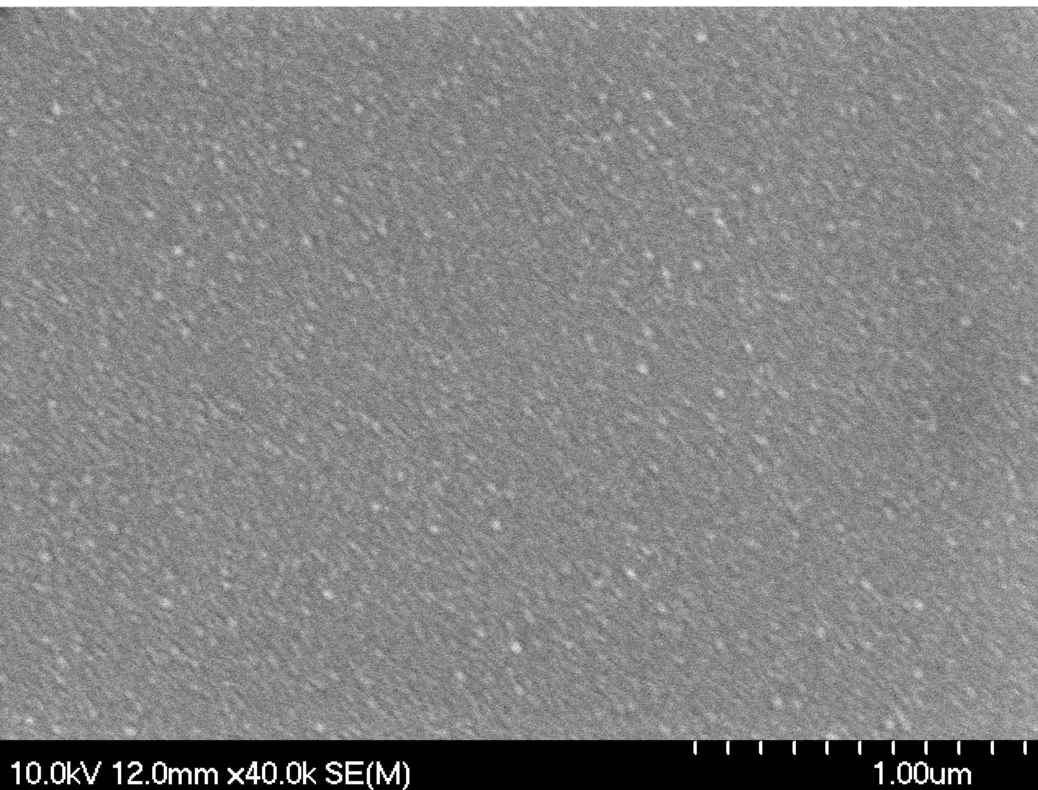


- Reflectivity loss is greater for Cap B samples than Cap A samples.
- Etched samples went from about 56% to about 46-47%.
- Post-cleaning reflectivity is restored to approximately same levels (46-47%).

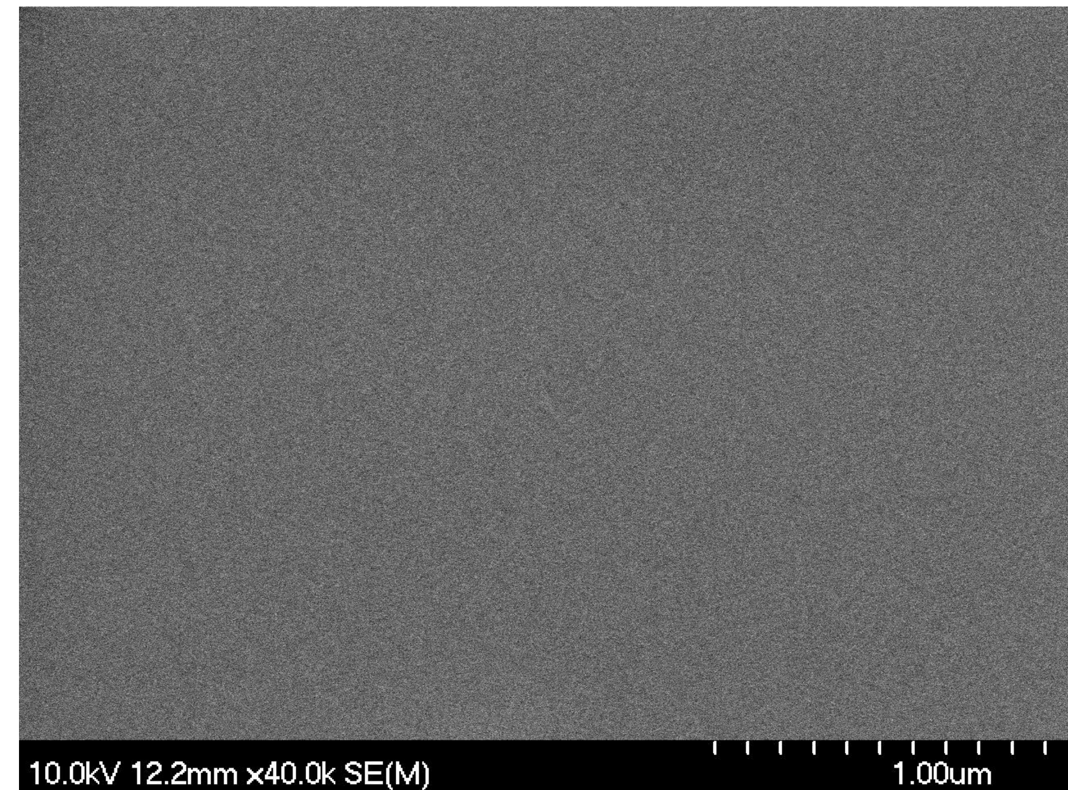
SEM Images: Etch Completion

- Did etching complete?
- Yes. For example, Cap B iii DE sample is bare and pristine.
- For comparison, Cap A Deposited sample is covered with small Sn particles.

Cap A Sample after Deposition

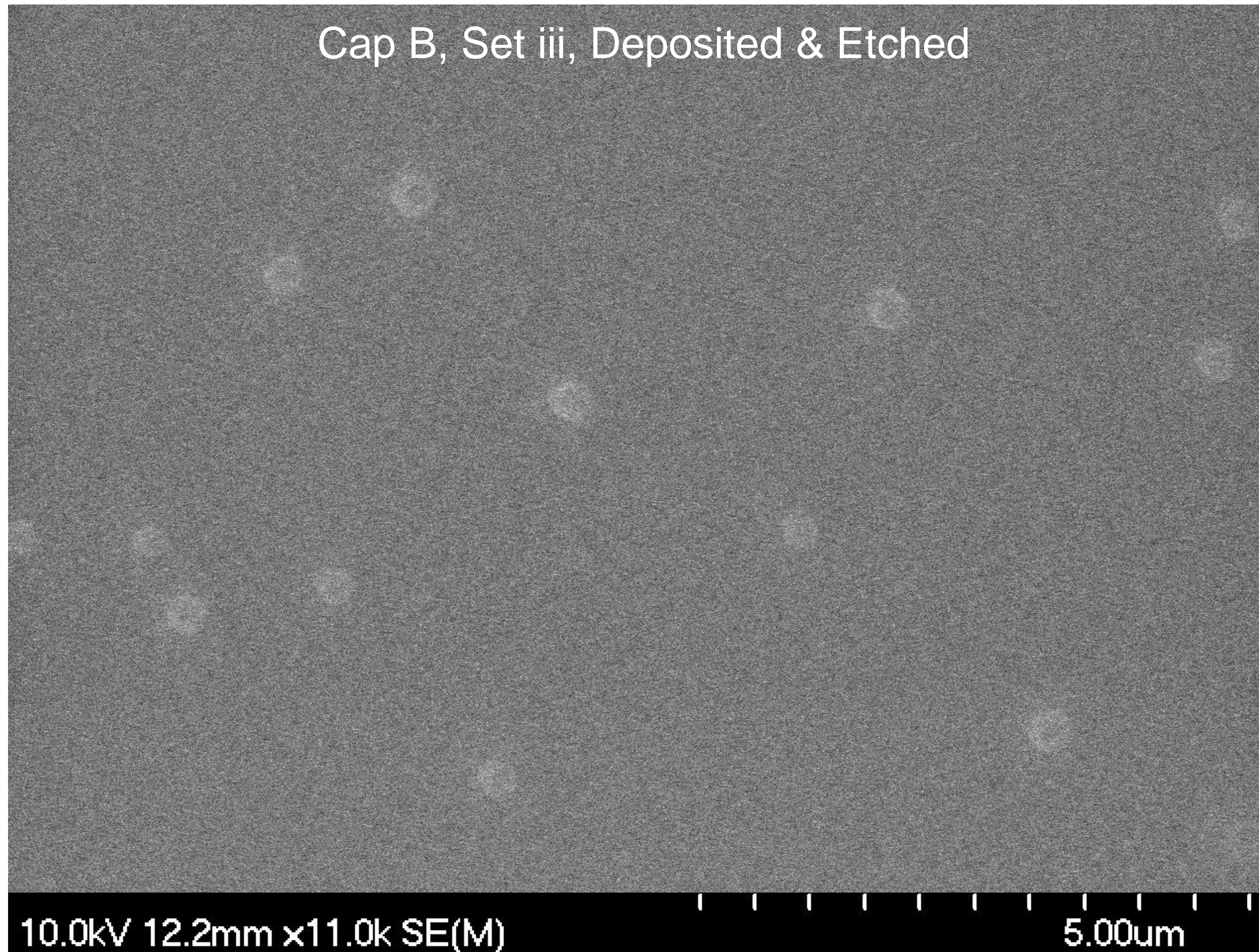


Cap B iii Sample after Deposition and Etch Cleaning



Implantation/Blistering on Cap B

- Zooming out on the Cap B iii DE sample (11kx) reveals some bubble-like structures. These could be due to blistering.

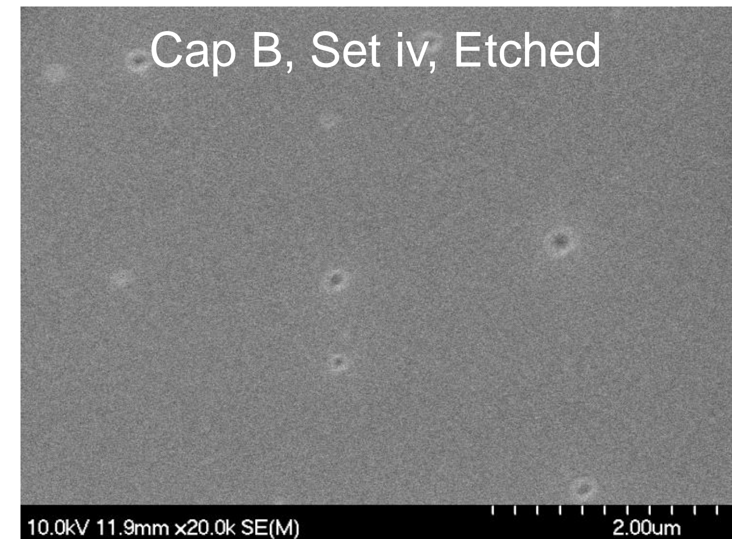


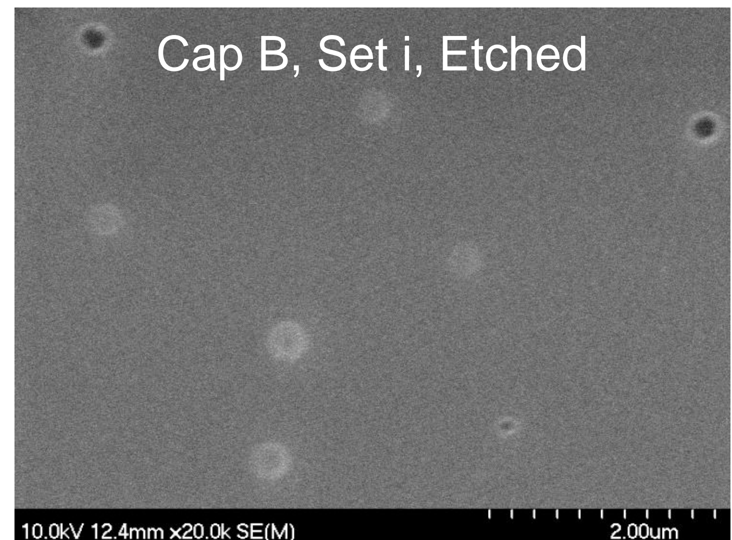
Blistering

- Cap B bare samples exposed to etching also show blistering. After 45 minutes of etching, some of the blisters have popped.

Cap B, Set ii, Etched

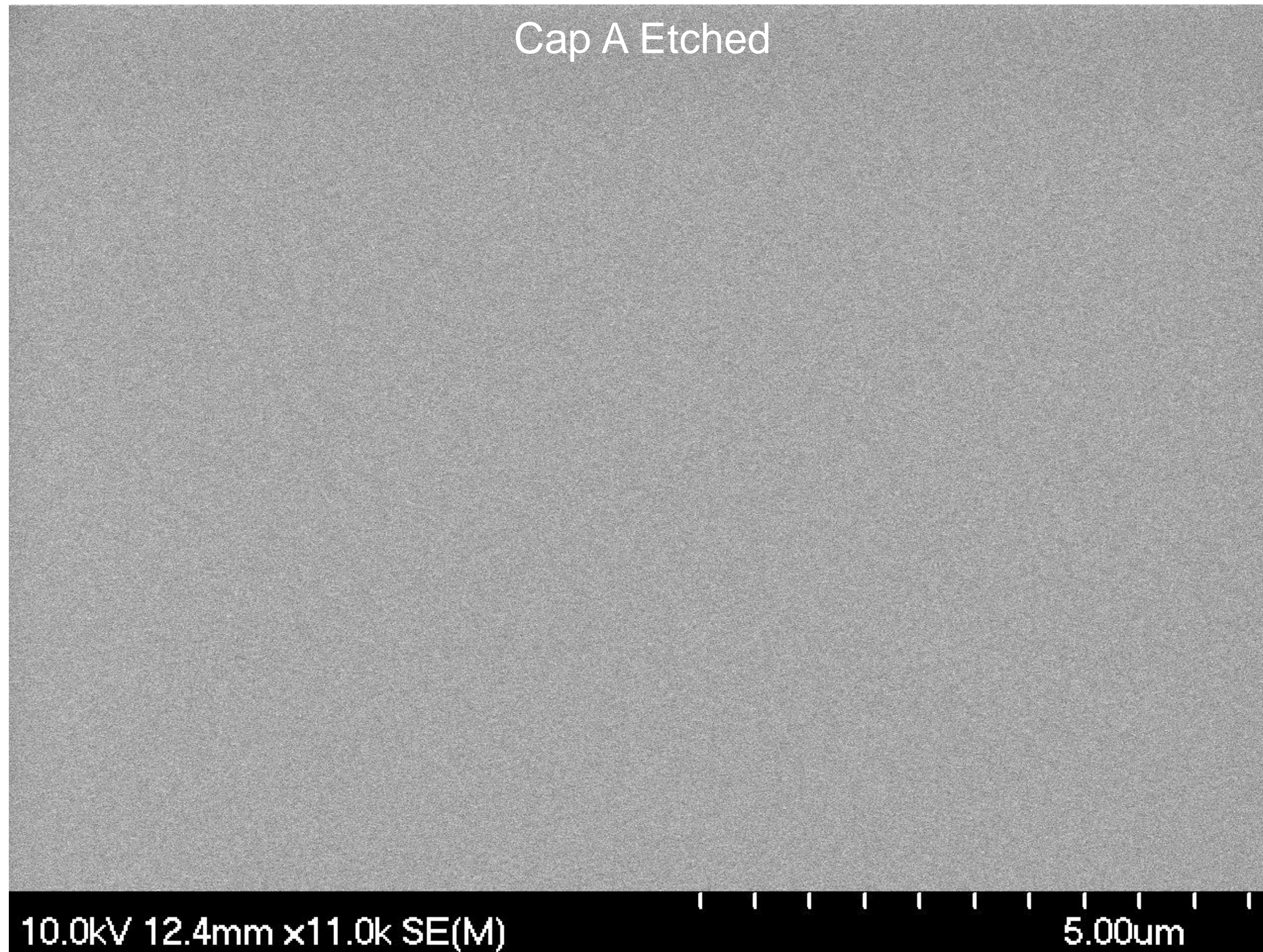
10.0kV 12.2mm x11.0k SE(M) 5.00um





No Blistering on Cap A

- However, blisters are not seen on Cap A.



Blistering

- Cap Layer B is known to be more susceptible to oxidation than Cap Layer A.
- Some oxygen contamination will be present in the etching chamber due to leaks.
- Blistering occurs when hydrogen ions implant in the surface and form bubbles. Oxidation of the cap layer surface increases the potential for blistering.
- Therefore, it makes sense that blistering is seen on Cap Layer B.
- Blistering reduces reflectivity and could be responsible for the larger reflectivity drop on samples with Cap Layer B.
- No blistering is present on Cap Layer A.
- Potential for Cap B blistering could be lowered by lowering ion energy.

MLM Sample Conclusions

- After 45 min. of etching, the bare Cap Layer A sample had only a very slight (~1%) reflectivity drop.
- After etching, Sn-coated Cap Layer A sample reflectivity was restored to about 46%, approximately 4.5% below the initial value.
- Cap Layer B bare samples suffer a reflectivity drop from about 56% to 46% after etching. Reflectivity of Sn-coated Cap Layer B samples is restored to the same level.
- SEM images indicate that etching completed. Some blistering is present in samples with Cap Layer B. Blistering could explain the drop in EUVR that occurs in Cap Layer B samples after etching.
- However, EUVR results show an ability to restore most reflectivity, especially for Cap Layer A samples. Additionally, EUVR loss of a bare Capy Layer A MLM sample after 45 minutes was only about 1%.

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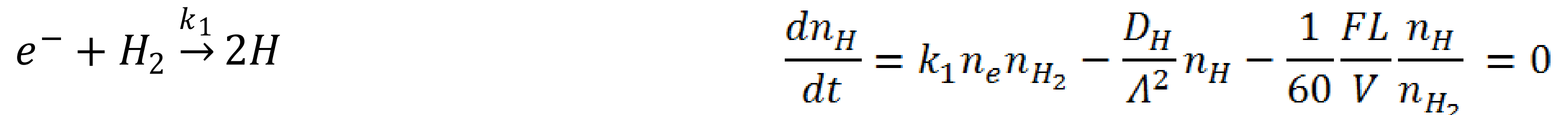
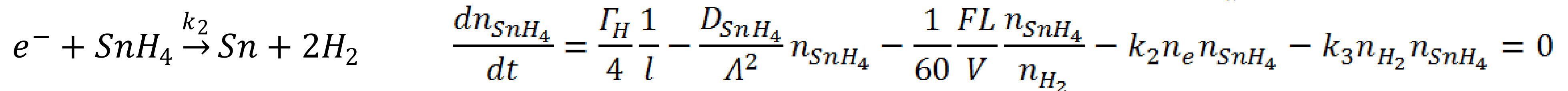
Modeling: Equations and Theory

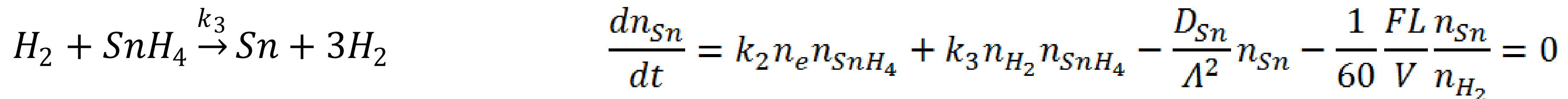
- For steady-state, rate equations may be set to 0 and solved computationally for the particle densities.



$$e^- + H_2 \xrightarrow{k_1} 2H \qquad \frac{dn_H}{dt} = k_1 n_e n_{H_2} - \frac{D_H}{\Lambda^2} n_H - \frac{1}{60}\frac{FL}{V}\frac{n_H}{n_{H_2}} = 0$$



$$e^- + SnH_4 \xrightarrow{k_2} Sn + 2H_2 \qquad \frac{dn_{SnH_4}}{dt} = \frac{\Gamma_H}{4}\frac{1}{l} - \frac{D_{SnH_4}}{\Lambda^2} n_{SnH_4} - \frac{1}{60}\frac{FL}{V}\frac{n_{SnH_4}}{n_{H_2}} - k_2 n_e n_{SnH_4} - k_3 n_{H_2} n_{SnH_4} = 0$$



$$H_2 + SnH_4 \xrightarrow{k_3} Sn + 3H_2 \qquad \frac{dn_{Sn}}{dt} = k_2 n_e n_{SnH_4} + k_3 n_{H_2} n_{SnH_4} - \frac{D_{Sn}}{\Lambda^2} n_{Sn} - \frac{1}{60}\frac{FL}{V}\frac{n_{Sn}}{n_{H_2}} = 0$$

- $k_x n_y n_z$: Gain or Loss due to Chemical Reaction
- $\frac{D_x}{\Lambda^2} n_x$: Loss from Diffusion
- $\frac{1}{60}\frac{FL}{V}\frac{n_H}{n_{H_2}}$: Loss due to Convected Flow
- $\frac{\Gamma_H}{4}\frac{1}{l}$: Gain of SnH_4 due to Etching

- L: Loschmidt Number (2.69×10^{19}), the number of molecules in 1 sccm
- V: Cell Volume, $l \ x \ w \ x \ d$

- The densities can be used to determine fluxes and, from there, the removal rate.

$$\Gamma_x = n_x \bar{v}_x$$

$$\Gamma_{to\ surface} = \frac{n_x \bar{v}_x}{4}$$

$$R_{removal} = R_{etch} - R_{deposition} = \frac{1}{n_{surf}}\left(\frac{\Gamma_H}{16} - \frac{\Gamma_{SnH_4}}{4} - \frac{\Gamma_{Sn}}{4}\right)$$

Extra factor of 4 because 4 radicals are required to etch one Sn

Future Modeling

- Still ironing out equations from previous page to make sure everything is correct.
- After this, model will expand to multiple cells.
- Example: for cell x in a multiple-cell model where all cells are in a line, the equations would be:

$$\frac{dn_{H\,x}}{dt} = k_1 n_e n_{H_2} + \frac{1}{\Lambda^2}\left(\frac{D_H n_{H\,x-1} + D_H n_{H\,x+1}}{4} - D_H n_{H\,x}\right) + \frac{1}{60V n_{H_2}}\left(F_{in} L n_{H\,x-1} - F_{out} L n_{H\,x}\right) = 0$$

$$\frac{dn_{SnH_4\,x}}{dt} = \frac{\Gamma_H}{4}\frac{1}{l} + \frac{1}{\Lambda^2}\left(\frac{D_{SnH_4} n_{SnH_4\,x-1} + D_{SnH_4} n_{SnH_4\,x+1}}{4} - D_{SnH_4} n_{SnH_4\,x}\right) + \frac{1}{60V n_{H_2}}\left(F_{in} L n_{SnH_4\,x-1} - F_{out} L n_{SnH_4\,x}\right) - k_2 n_e n_{SnH_4\,x} - k_3 n_{H_2} n_{SnH_4\,x} = 0$$

$$\frac{dn_{Sn}}{dt} = k_2 n_e n_{SnH_4\,x} + k_3 n_{H_2} n_{SnH_4\,x} + \frac{1}{\Lambda^2}\left(\frac{D_{Sn} n_{Sn\,x-1} + D_{Sn} n_{Sn\,x+1}}{4} - D_{Sn} n_{Sn\,x}\right) + \frac{1}{60V n_{H_2}}\left(F_{in} L n_{Sn\,x-1} - F_{out} L n_{Sn\,x}\right) = 0$$

- Flow and diffusion from other cells are added.
- More plasma reactions can also be included.
- Surface reactions could also be added.
- This will become complicated; further progress could require an FEM model.

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- We have shown the ability to remove Sn and restore EUV reflectivity by using a 300mm dummy collector as a plasma antenna without evidence of surface sputtering.
- For Sn-coated Cap A MLM, reflectivity was restored to 46.1% after cleaning (original reflectivity 50.5%).
- After 45 minutes of exposure to etching plasma, a bare Cap A MLM only lost 1.26% EUVR (from 50.5% to 49.2%).
- Cap B EUVR largely restored as well, though SEM images indicate some blistering.
- Blistering did not occur on Cap A sample.
- A model of Sn etching and removal continues to be developed.
- Moving towards the future, we will explore new plasma topologies (to raise ne and lower ion energy), operations at higher pressures, and modeling of the physical processes at work.

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