

# In-Situ Cleaning of Sn EUV Sources

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- **Collector Cleaning Theory**
- **3D Flow Modeling**
- **Radical Probe & 0D Modeling of H Radicals**
- **Experimental Plans for Measuring the Probability of Etching and the Probability of Redeposition**
- **Beyond EUV (6.7 nm) Optics**
- **Beyond EUV (6.7 nm) Source**
- **Conclusions**

- Sn removal depends not only on etching by H radicals, but on SnH<sub>4</sub> dissociation and redeposition.
- Therefore, understanding of transport of SnH<sub>4</sub> is necessary. Described by diffusion-advection equation:

$$\frac{\partial n}{\partial t} = 0 = -\nabla \cdot (Dn) + \mathbf{v} \cdot \nabla n$$

- To solve this, we need:
  - Velocity profile  $\mathbf{v}$  (SnH<sub>4</sub> will assume profile of H<sub>2</sub> flow)
  - Radical Flux
  - Probability of Etching } → SnH<sub>4</sub> Inlet Boundary Condition
- Probability of Redeposition → SnH<sub>4</sub> Outlet Boundary Condition
- Etch rate given by radical flux and probability of etching. Subtract deposition rate to get net removal rate.

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# Modeling of H<sub>2</sub> Flow: Complete

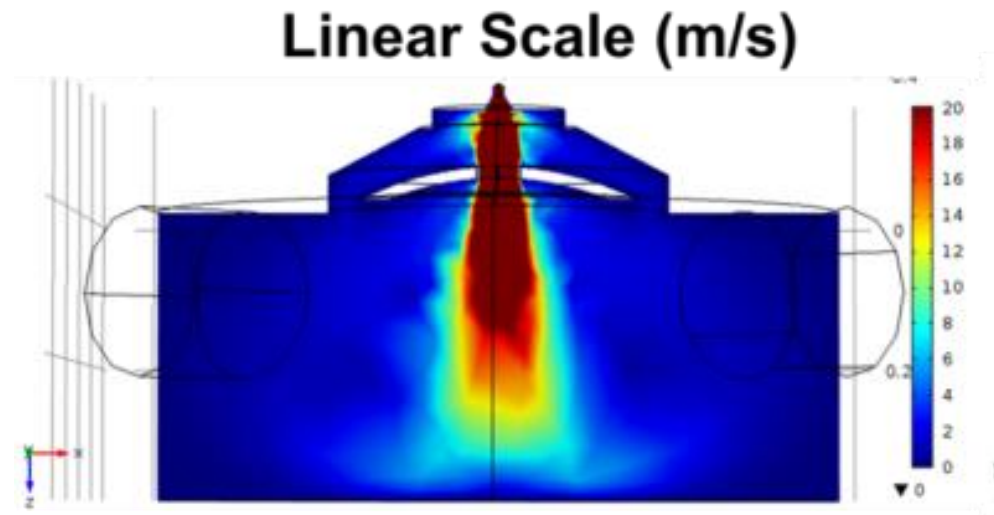
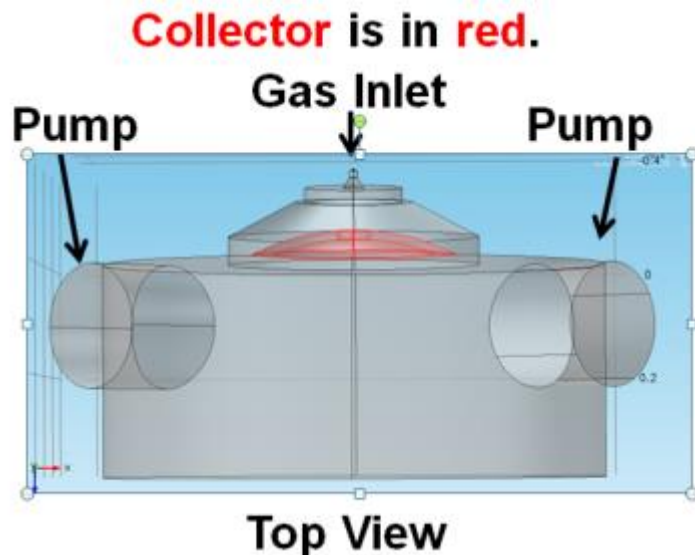
- Bulk gas is mostly H<sub>2</sub> (by orders of magnitude)
- Assumption: Flow in chamber can be decoupled from species and solved simply for H<sub>2</sub>; the few non-H<sub>2</sub> particles will take on the H<sub>2</sub> velocity profile.
- Solve Navier-Stokes Equations for H<sub>2</sub> in XCEED.

$$\rho \frac{\partial \mathbf{u}}{\partial t} - \nabla \cdot \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p = \mathbf{F}$$

$$\nabla \cdot \mathbf{u} = 0$$

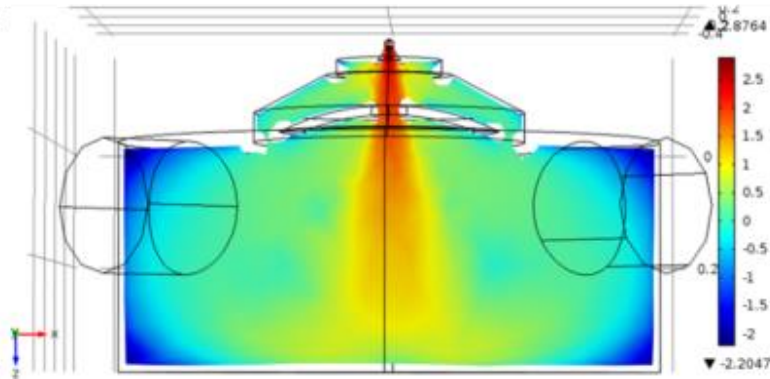
- Velocity profiles shown below.

1.3 Torr, 3200 sccm (current operating conditions)

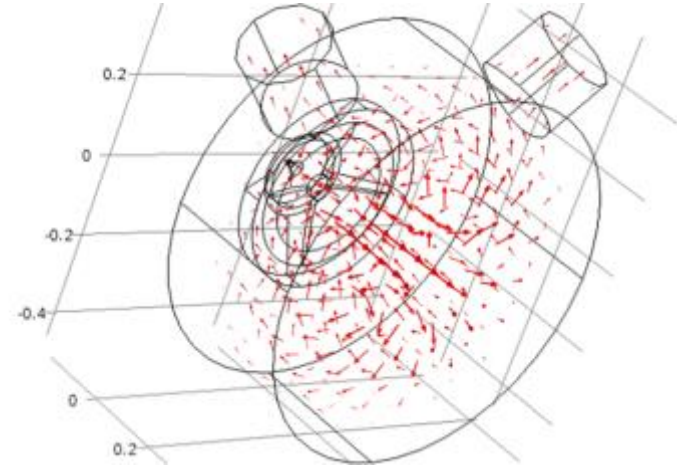


# H<sub>2</sub> Flow (Continued)

1.3 Torr, 3200 sccm  
Log Scale

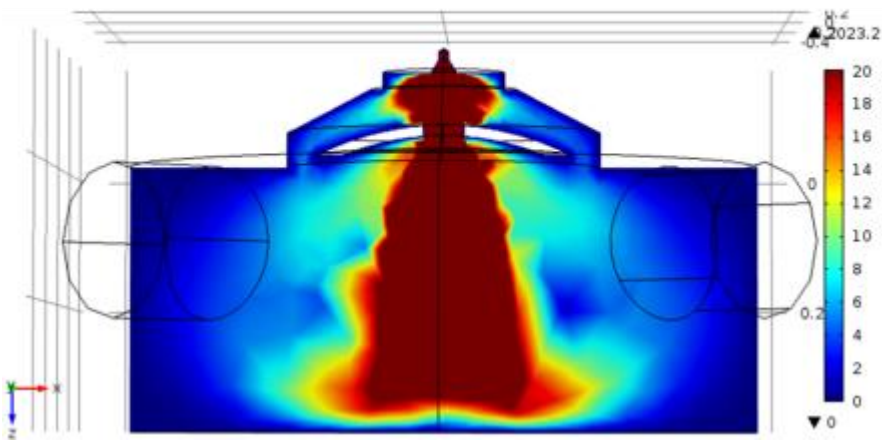


3D Arrow Profile

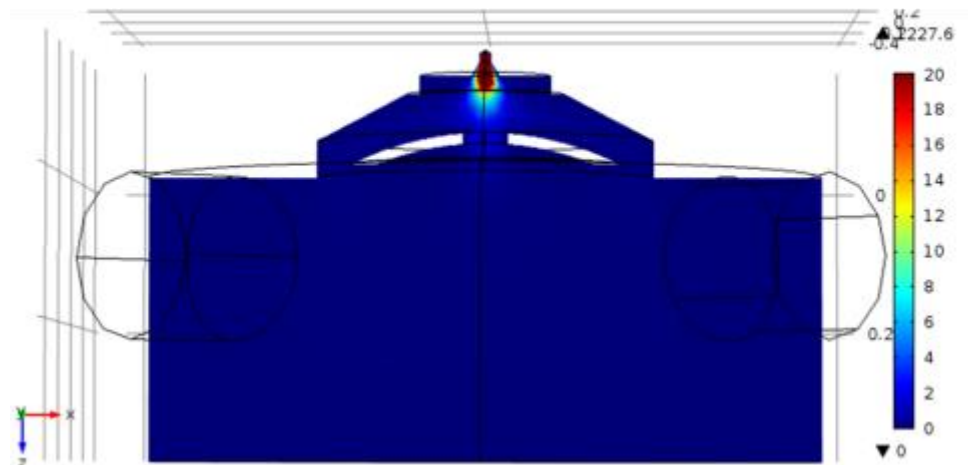


If pressure or flow change, velocity profile changes as expected:

260 mTorr, 3200 sccm



1.3 Torr, 1000 sccm



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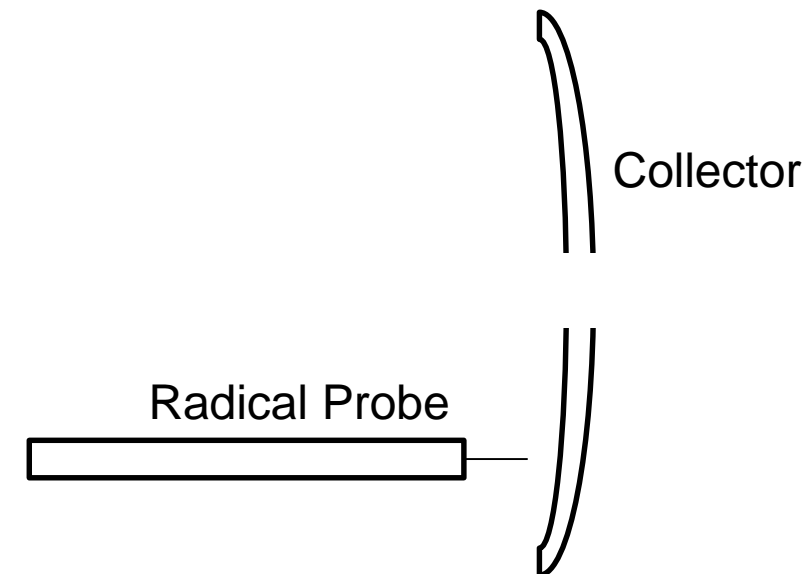
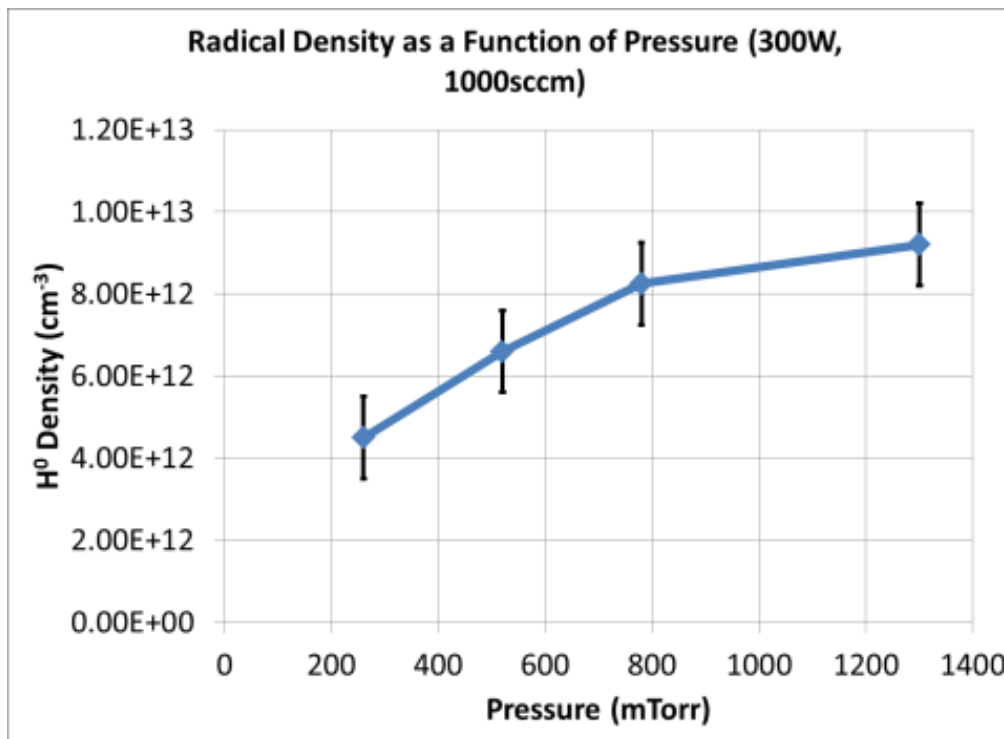


# Radical Probe

- Catalytic probe: heats up due to radical recombination on catalyst surface.

$$Power = mc_p \frac{dT}{dt} = \frac{1}{2} W \gamma \Gamma A$$

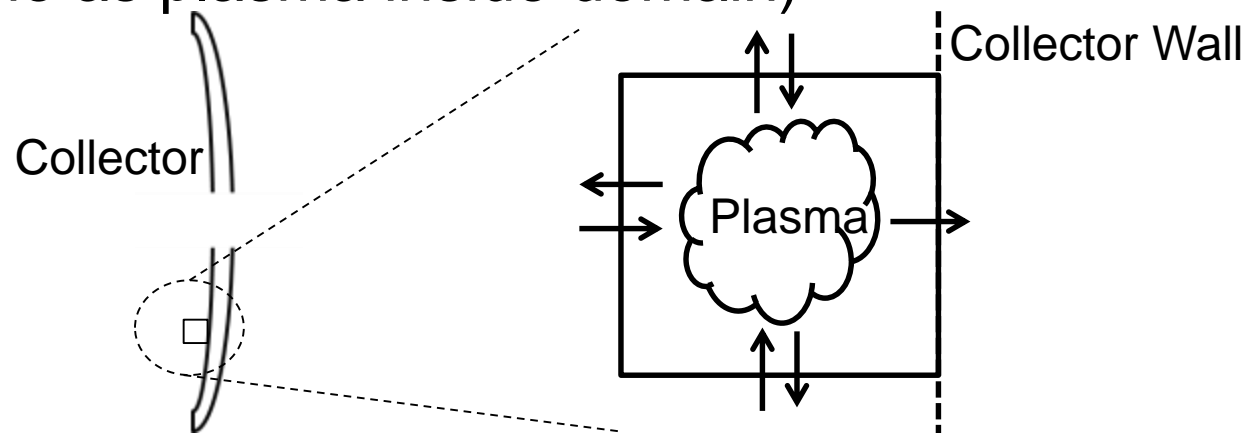
- A=probe area; W=Energy from Recombination;  $\Gamma$ =Radical Flux,  $\gamma$ =Recombination probability





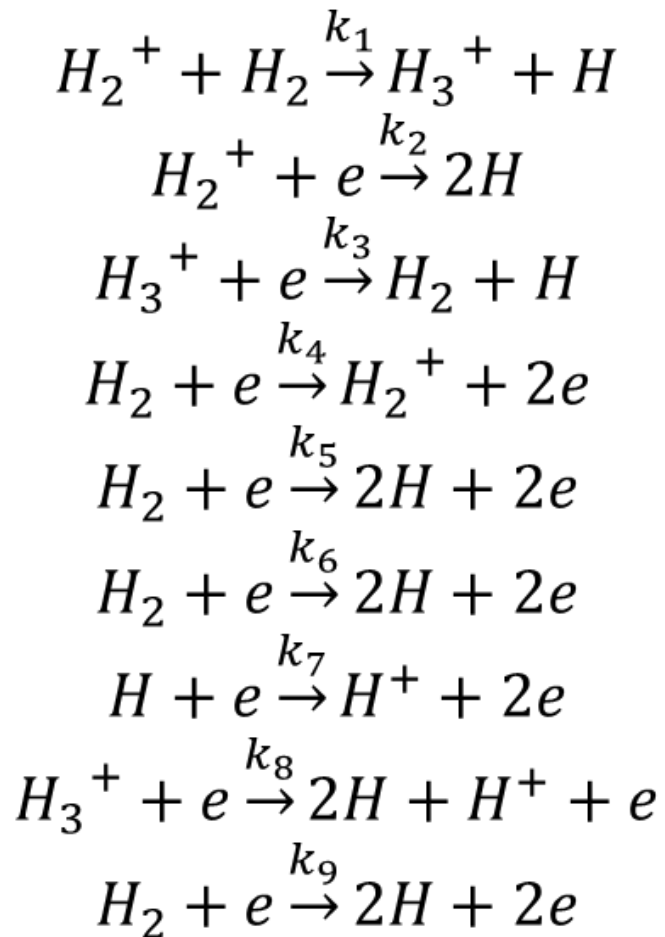
# Radical Probe Validation: 0D Model

- Plasma Chemistry Model: Reactions  $\rightarrow$  Rate Equations
- Given  $n_e$  and  $T_e$ , what densities of ions and radicals are produced?
- Domain size:  $1\text{cm}^3$
- Assumptions:
  - Plasma is uniform inside cube (valid for the small domain)
  - One face touches collector; ions and radicals lost to collector
  - No gain/loss through other faces (plasma next to the domain is approximately same as plasma inside domain)
  - Quasineutrality



# Reactions

- Rate coefficients  $k$  either found directly in literature or calculated up from reaction cross-sections.
- Rate coefficients  $k$  will be dependent on  $T_e$ .



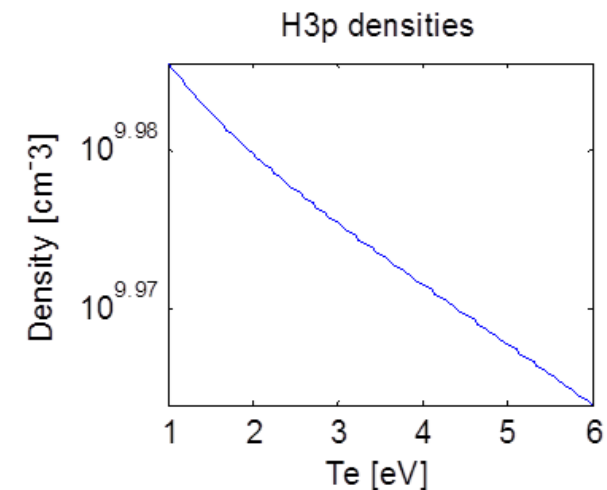
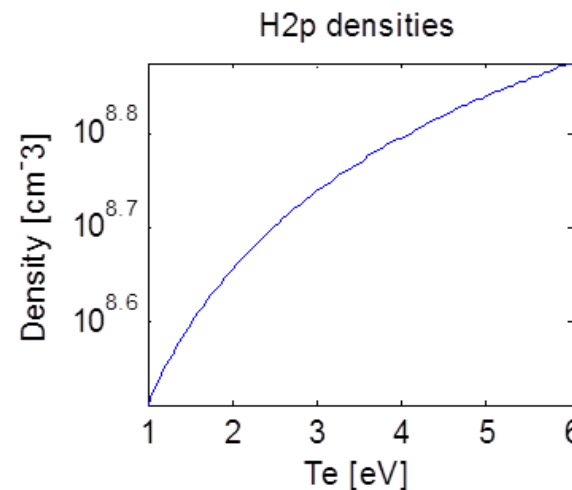
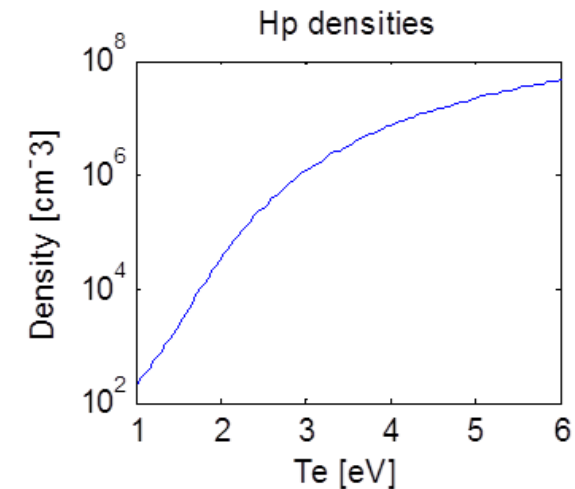
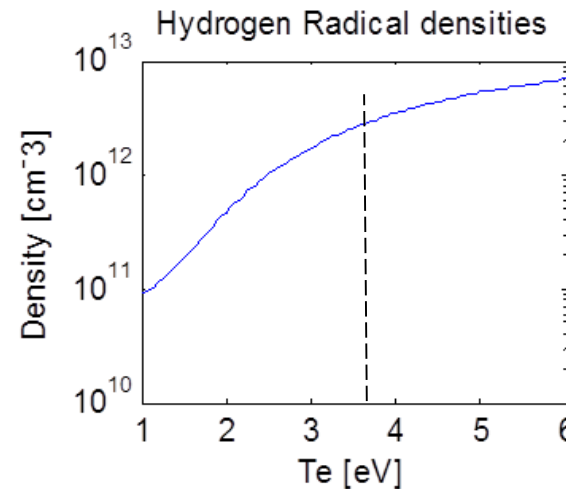
# Equations

- Rate of Change = Gain - Loss
- For steady-state, rate is set to 0.
- Equations solved with ode45 in MATLAB until steady-state is reached.

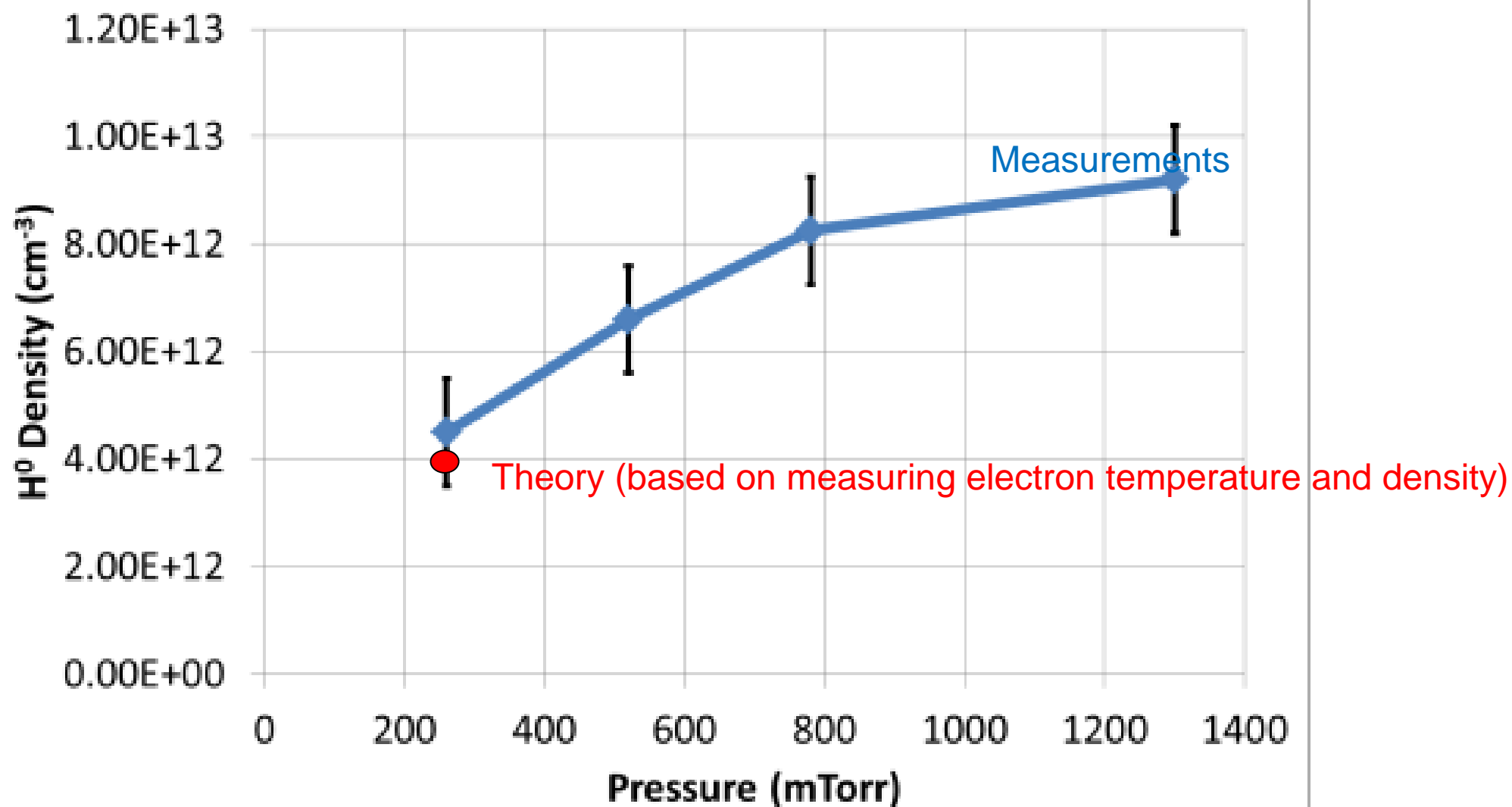
$$\begin{aligned} \frac{dn_H}{dt} &= k_1 n_{H_2} n_{H_2^+} + 2k_2 n_e n_{H_2^+} + k_3 n_e n_{H_3^+} + 2(k_5 + k_6) n_{H_2} n_e + 2k_8 n_e n_{H_3^+} \\ &\quad + 2k_9 n_{H_2} n_e - k_8 n_H n_e - \frac{A n_H v_{H,th}}{V} \\ \frac{dn_{H^+}}{dt} &= k_7 n_H n_e + k_8 n_e n_{H_3^+} - \frac{A}{V} n_H v_{H^+,Bohm} \\ \frac{dn_{H_2^+}}{dt} &= n_e - n_{H^+} - n_{H_3^+} \\ \frac{dn_{H_3^+}}{dt} &= k_1 n_{H_2} n_{H_2^+} - k_3 n_e n_{H_3^+} - k_8 n_e n_{H_3^+} - \frac{A}{V} n_H v_{H_3^+,Bohm} \end{aligned}$$

# Results

- $n_e$ ,  $T_e$  measured with Langmuir probe at 260mTorr (to allow for low-pressure regime for collisionless sheath equations)
- $n_e=10^{10}\text{cm}^{-3}$ ,  $T_e=4.5\text{eV}$
- 0D Model at  $n_e=10^{10}\text{cm}^{-3}$ :
- 4.5eV:  $n_{\text{H}}=4.4\times 10^{12}\text{cm}^{-3}$
- Well within error bar of radical probe measurement ( $4.5 \pm 1 \times 10^{12} \text{ cm}^{-3}$ )
- Conclusion:  
Radical Probe works; it is a reliable experimental diagnostic.



Radical Density as a Function of Pressure (300W, 1000sccm)

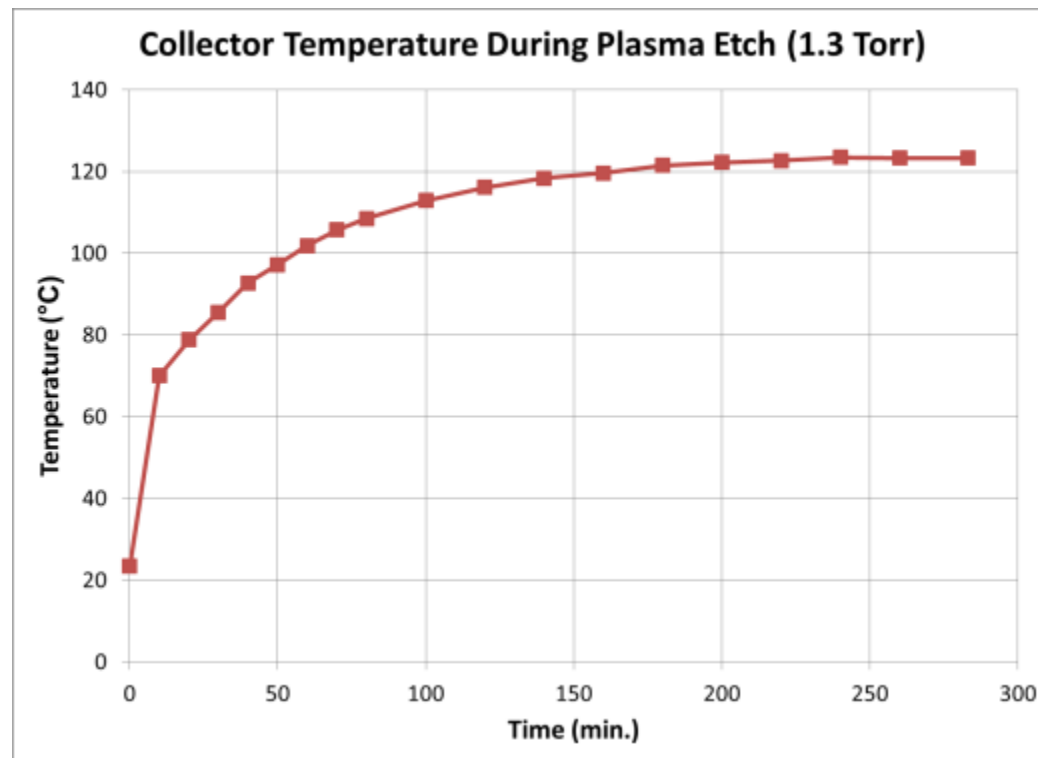


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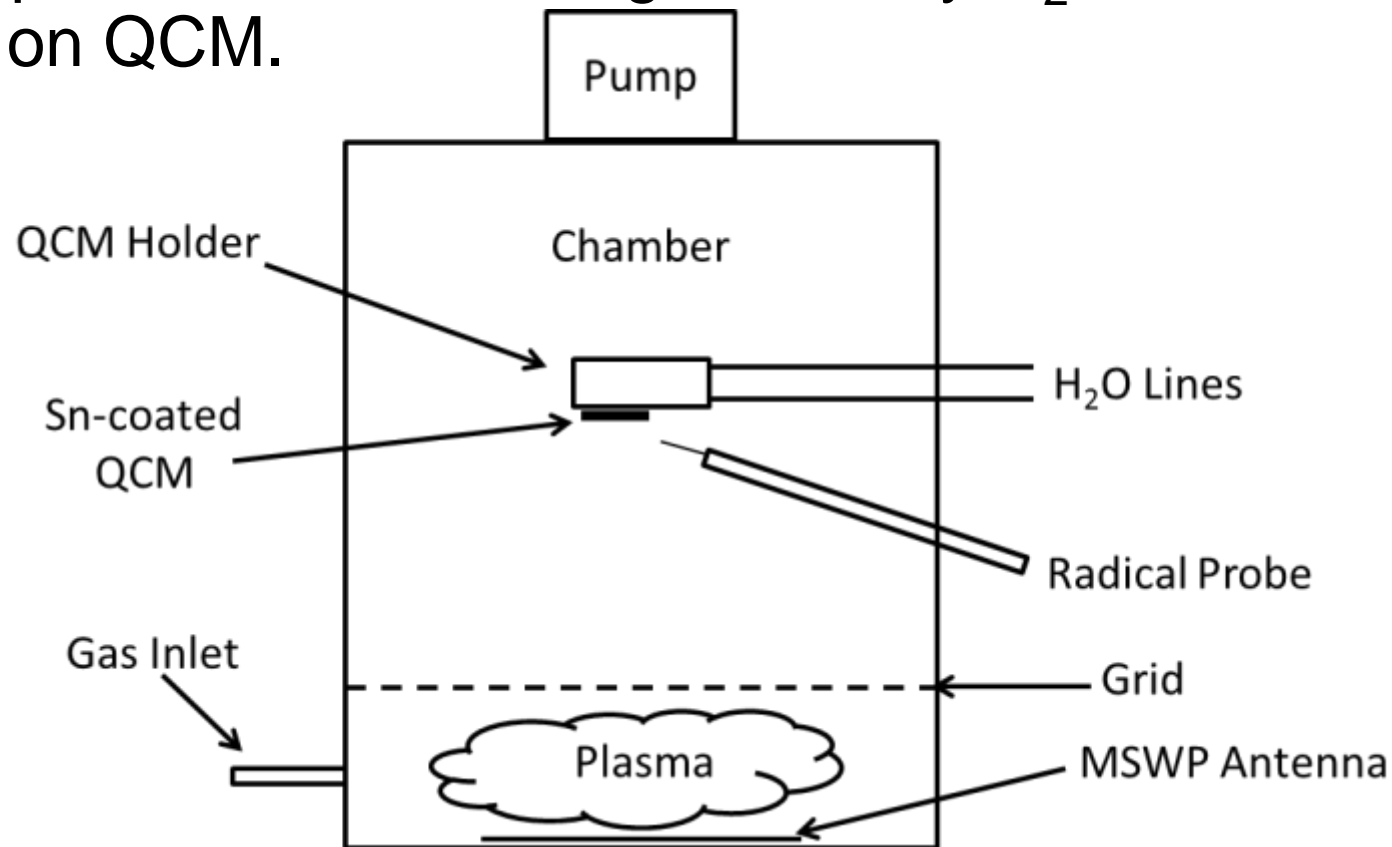
# Future Experiments

- Scan radical probe radially over collector → radial  $n_H$  profile
- Also, need  $P(\text{etching})$  and  $P(\text{redeposition})$ .
- $P(\text{redeposition})$  is dependent on temperature;  $P(\text{etching})$  may be as well.
- Temperature can be measured on collector. Will need to perform the probability experiments as a function of temperature.



# Probability of Etching

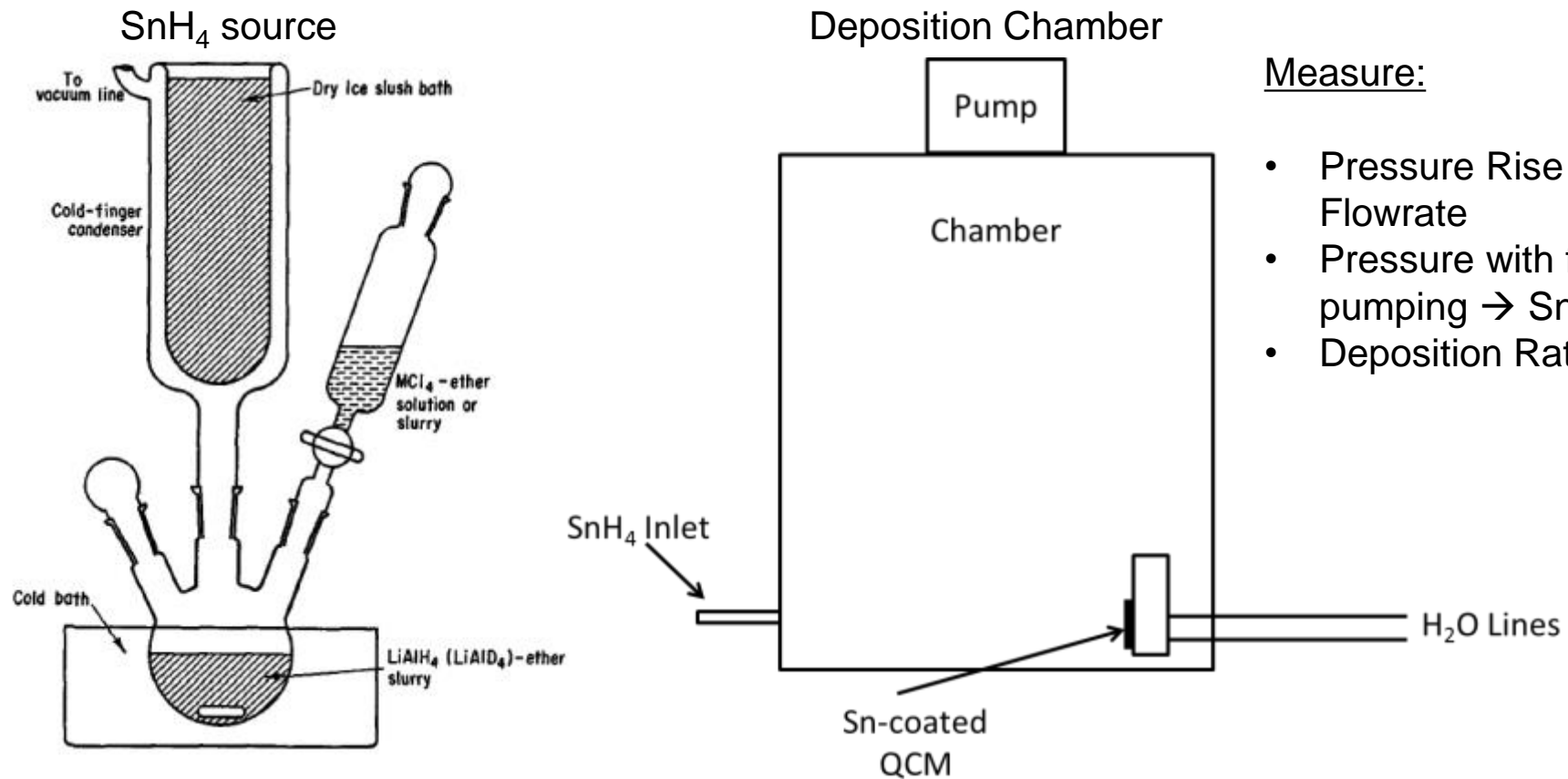
- Sn-coated QCM to measure etch rate
- QCM is small; no other source of Sn  $\rightarrow$  No redeposition
- Temperature-controlled
- Remote plasma source with grid  $\rightarrow$  only  $H_2$  and radicals incident on QCM.





# Probability of Redeposition

- Flow  $\text{SnH}_4$  into chamber; measure deposition on temperature-controlled Sn-coated QCM.
- However,  $\text{SnH}_4$  will need to be produced.
- One way:  $\text{SnCl}_4 + \text{LiAlH}_4 \rightarrow \text{LiCl} + \text{AlCl}_3 + \text{SnH}_4$
- Possible Setup for  $\text{SnH}_4$  Synthesis and Deposition:



Norman, et al., 1968

## Measure:

- Pressure Rise Time  $\rightarrow$   $\text{SnH}_4$  Flowrate
- Pressure with flow and pumping  $\rightarrow$   $\text{SnH}_4$  Density
- Deposition Rate on QCM

# MSWP Chamber to be Used for Experiments

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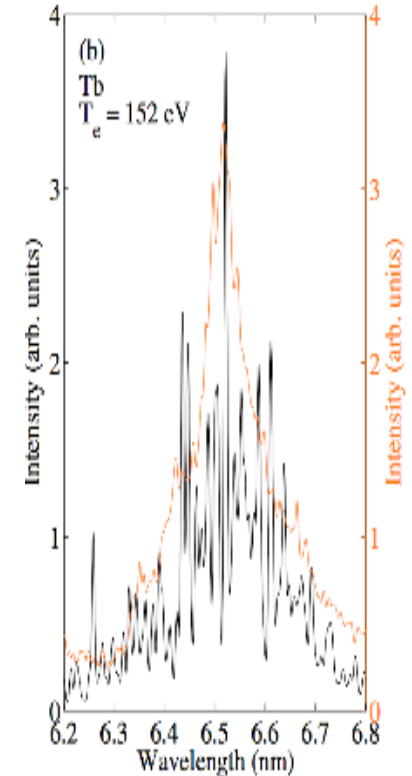
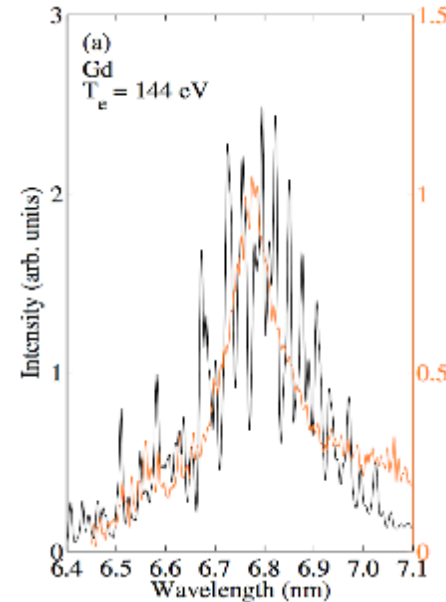
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# Beyond EUV

## Transition to 6.X nm light

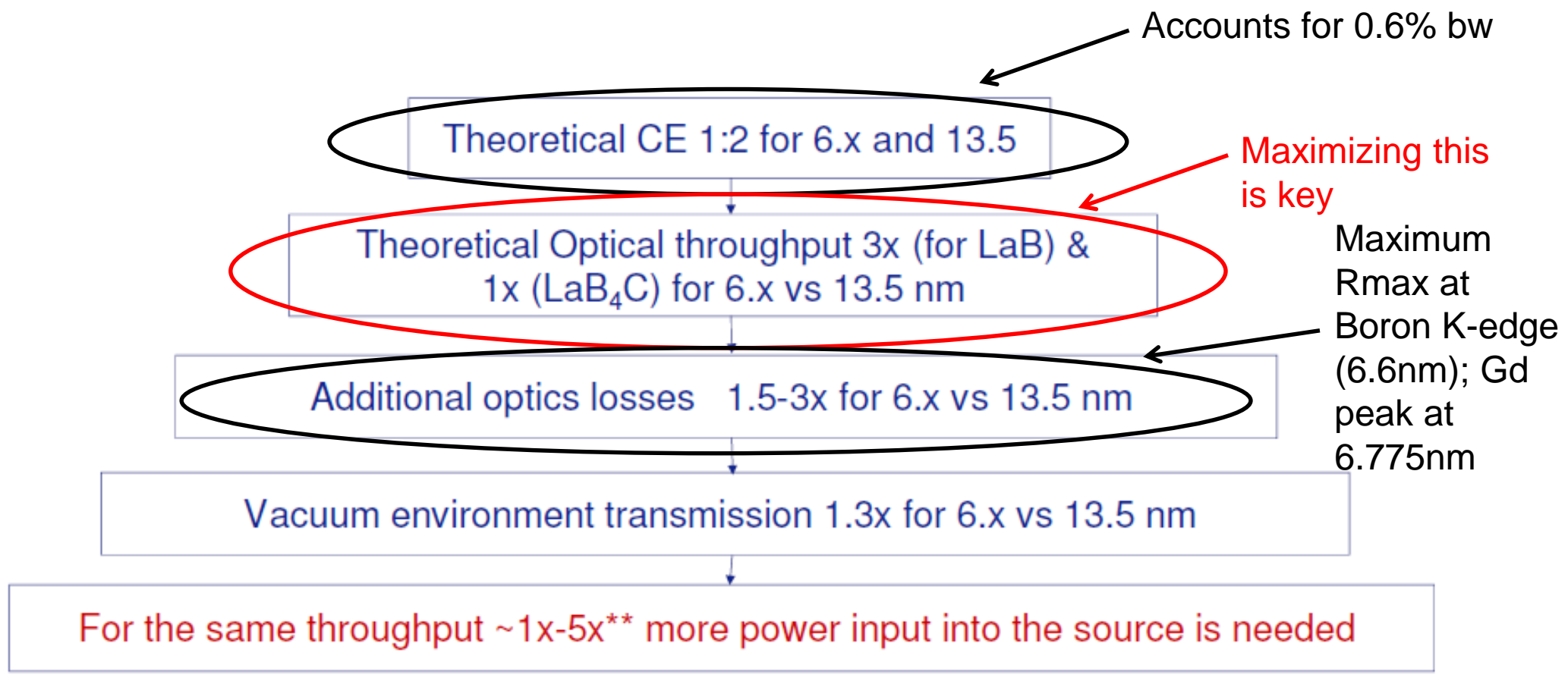
- Two fuels of importance: Gd , Tb
- Gd peak : 6.775 nm
- Tb peak : 6.515 nm
- La/B, LaN/B , LaN/B<sub>4</sub>C frontrunner multilayer mirrors.
- Boron has K-absorption edge at 6.6nm.
- Theoretical  $R_{\max}$  is high (~80%), but bandwidth is low (0.6%)
- However, real mirrors have yet to reach above 60%.
- This hinders development of BEUV.



Kilban and O'Sullivan, 2010

For **peak intensity Tb is better than Gd.**  
For **peak MLM reflectivity Gd is better than Tb.**

# Feasibility of 6.7nm



\* Resist sensitivity is taken comparable \*\* Uncertainty in ML performance is very high

ASML & Zeiss, SPIE 2012

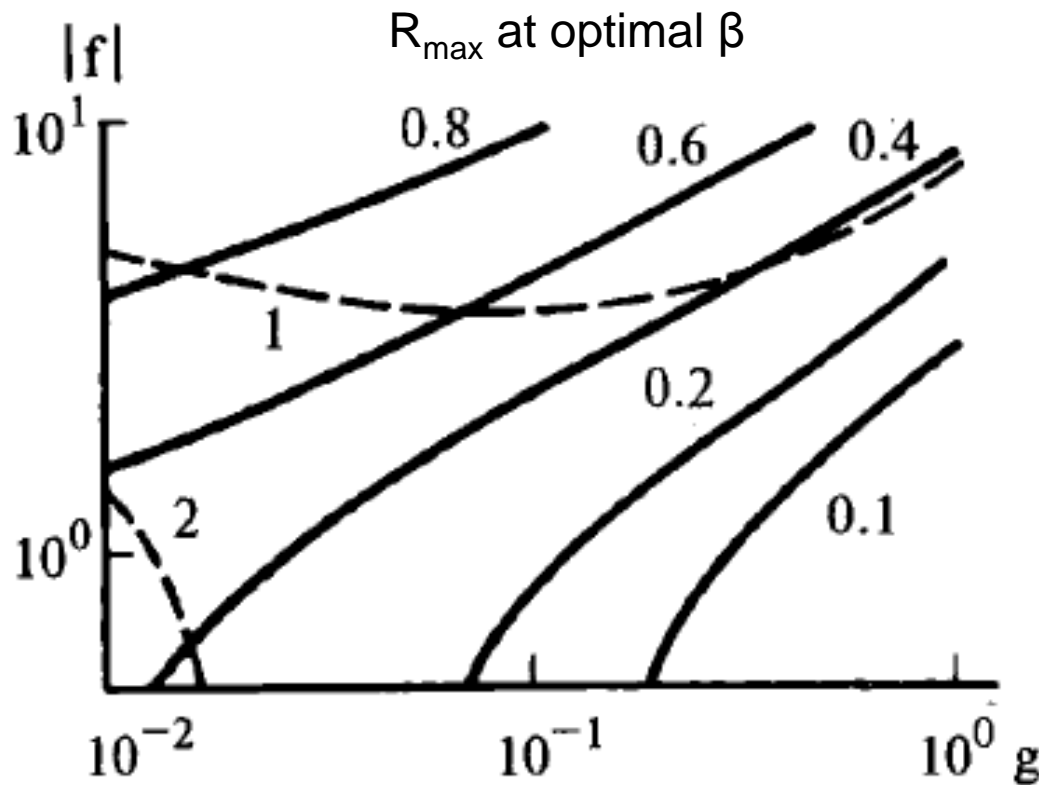
**If we can maximize the reflectivity, 6.7nm stands a shot.**

# How an MLM Works

- Bragg Reflection
- Reflectivity is function of  $f$ ,  $g$ ,  $\beta$
- Optimal  $\beta$ :  $\tan \pi \beta_* = \pi(\beta_* + g)$ .

Reflector	$\epsilon_1$	$l_1$	$\beta = \frac{l_1}{l_2}$
Spacer	$\epsilon_2$	$l_2$	

$$f = \frac{\text{Re}(\epsilon_1 - \epsilon_2)}{\text{Im}(\epsilon_1 - \epsilon_2)} \quad g = \frac{\text{Im} \epsilon_2}{\text{Im}(\epsilon_1 - \epsilon_2)}$$

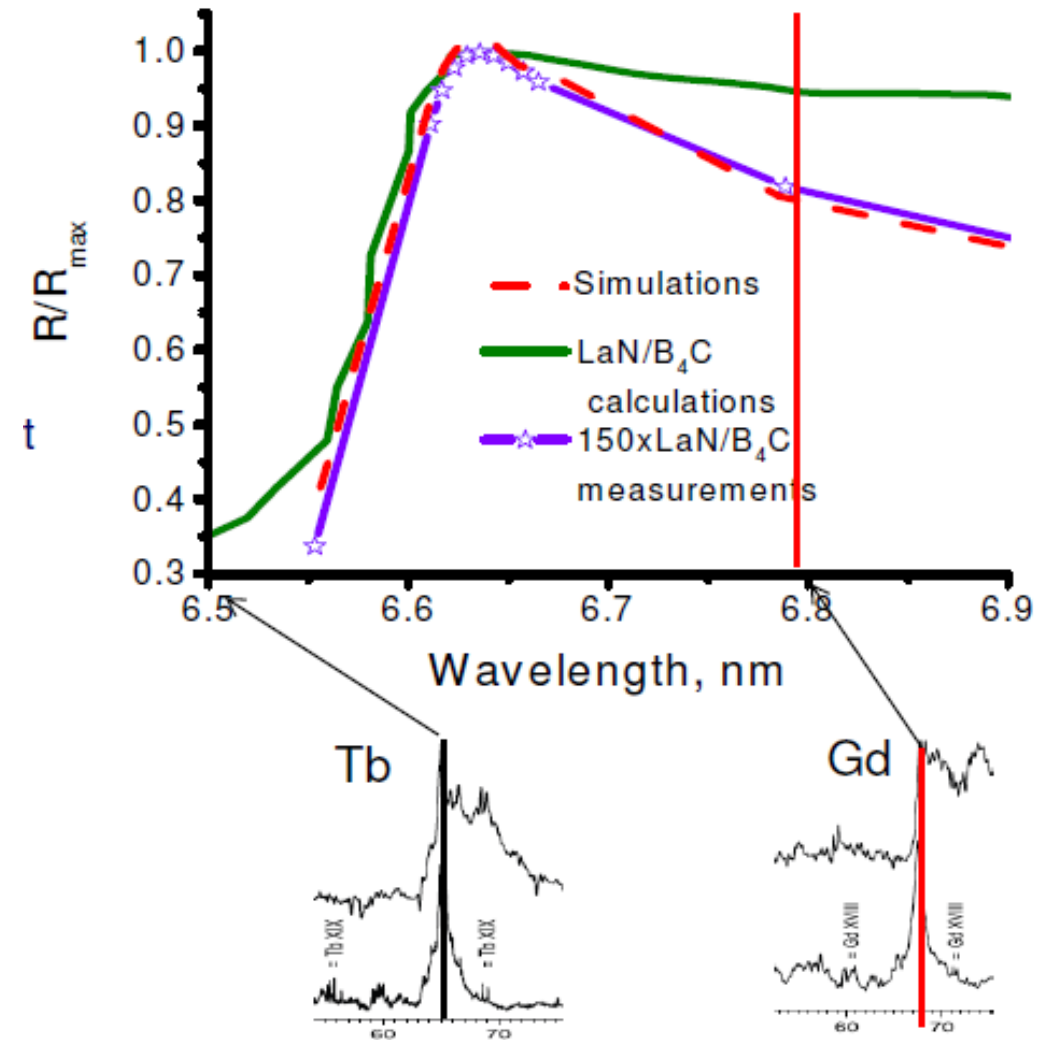


Kozhevnikov, 1995

- Minimize  $g$ : low  $\text{Im}(\epsilon_2)$ . Spacer should have lowest possible absorption.
- Maximize  $f$ : High  $\text{Re}(\epsilon_1 - \epsilon_2)$ . High permittivity contrast between materials.
- Ratio of  $l_1/l_2$ : Solving  $\tan \pi \beta_* = \pi(\beta_* + g)$  yields optimal  $\beta$ .
- High  $f$  also leads to high bandwidth (low resolving power).

# Wavelength “Mismatch”

- Spacer material is chosen for having an absorption edge just below wavelength of interest.
- Boron has K-absorption edge at 6.6nm
- Just above absorption edge,  $\text{Im}(\epsilon_2)$  is very small.
- Gd peak at 6.775nm;  $\text{Im}(\epsilon_2)$  a bit higher here  $\rightarrow$  reflectivity lower.

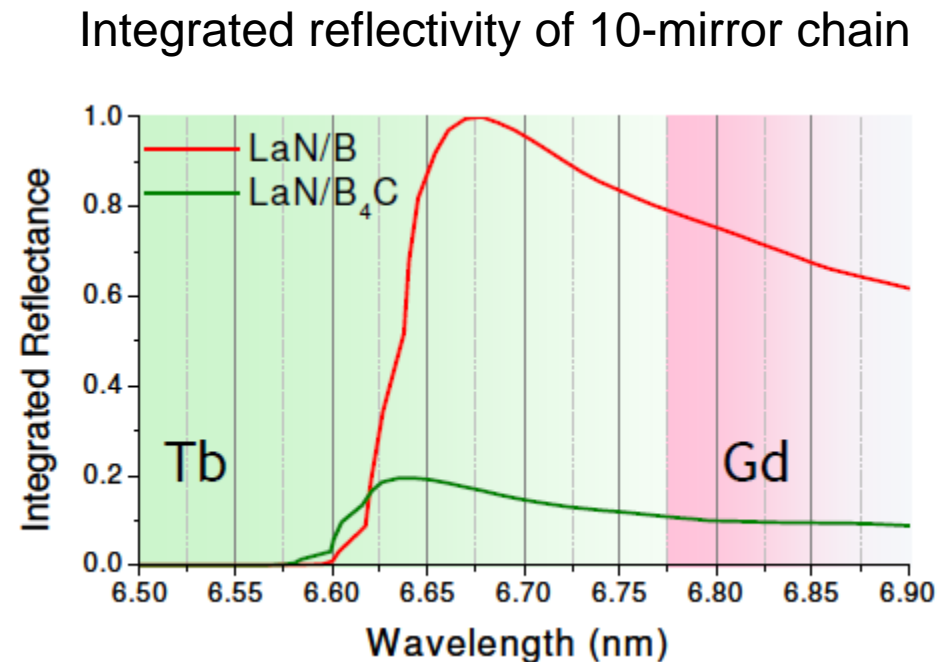
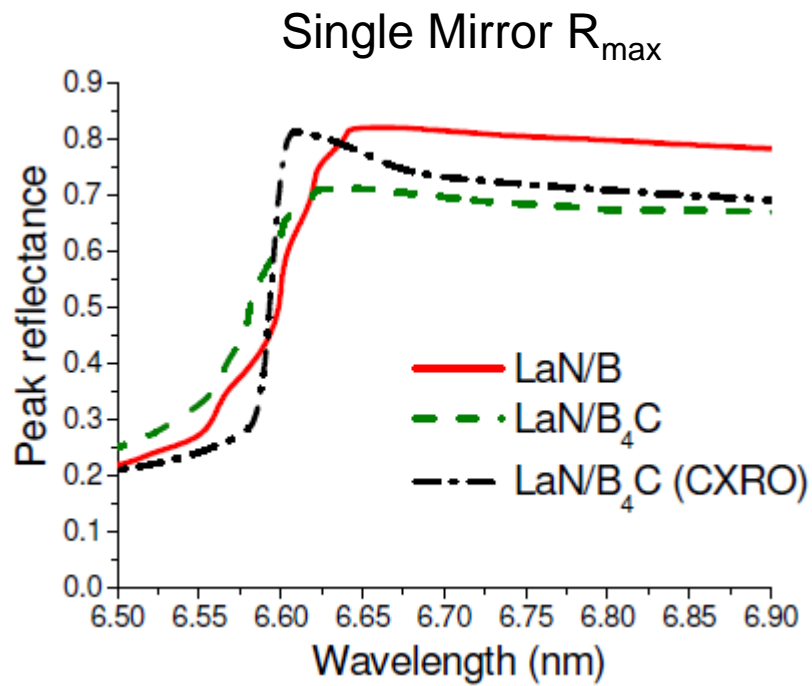


Makhotkin et al., 2012



# Importance of Every Percentage

- Every reflectivity percentage counts.
- For example, La/B mirrors have theoretical peak R only slightly above that of theoretical peak of La/B<sub>4</sub>C.
- However, after going through a 10-mirror chain, that small difference removes a great deal of BEUV power.



Makhotkin, 2013





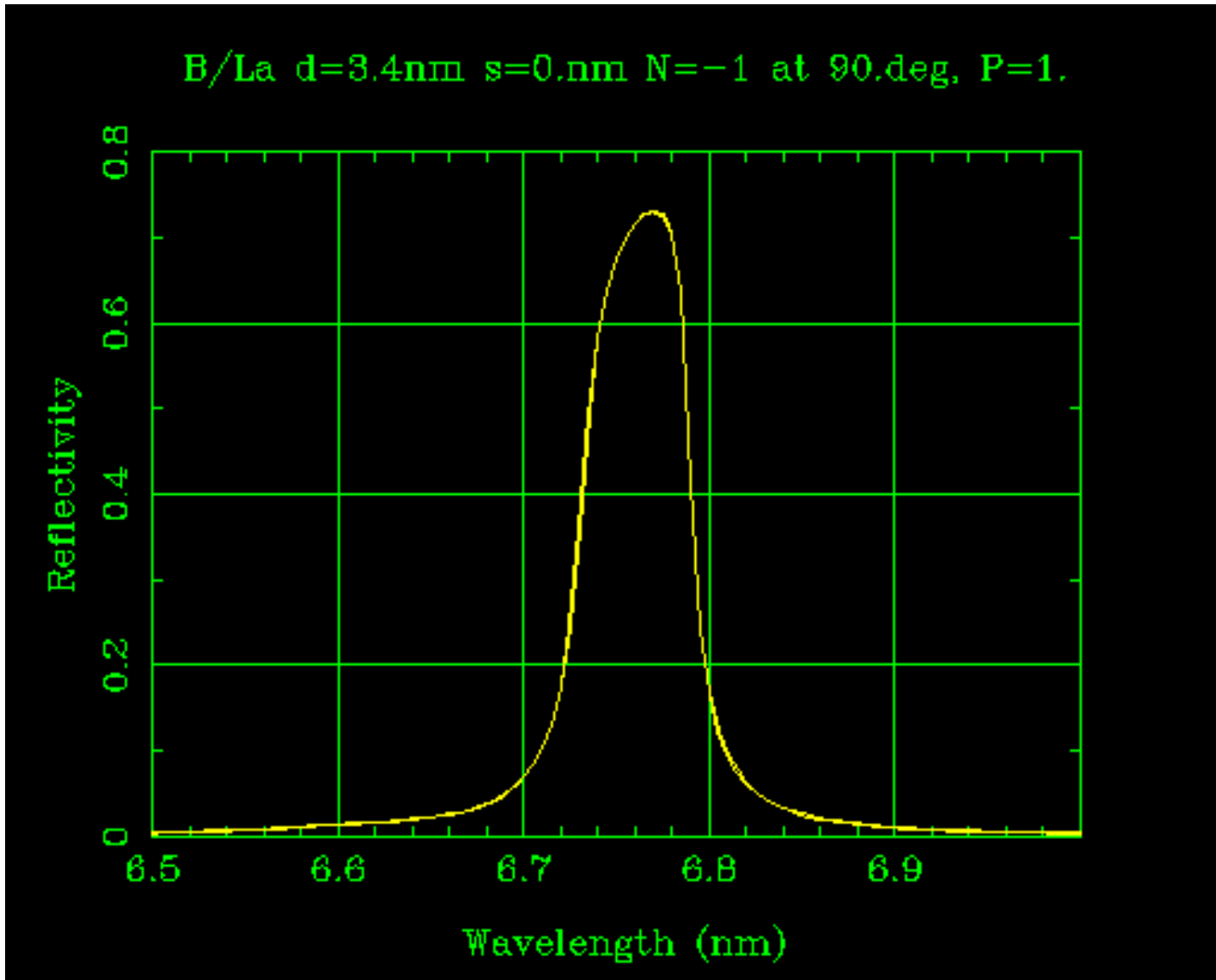
# Ways to Increase Real MLM Reflectivity

- Roughness and intermixing reduce permittivity contrast and reduce reflectivity.
  - Reduce intermixing: lower temperature, use compounds (such as LaN) that reduce reactivity.
  - Reduce roughness: use high mobility deposition (magnetron sputtering)
  - Ideal: ALD, potentially with ion polishing (a la Wulfhekel)
- B deposition more difficult than B<sub>4</sub>C deposition, but B is more desirable (less-absorbing).
- Density Control
  - Density can be varied by deposition technique
  - Lowering density of spacer (boron) lowers its absorption
  - Potentially deposit some boron hydride film or B interspersed with H<sub>2</sub> bubbles



# Density Effect

Example: semi-infinite mirror, Gd peak, La/B,  $\beta=0.35$ ,  $\rho_B=2.37\text{g/cm}^3$  (normal density)

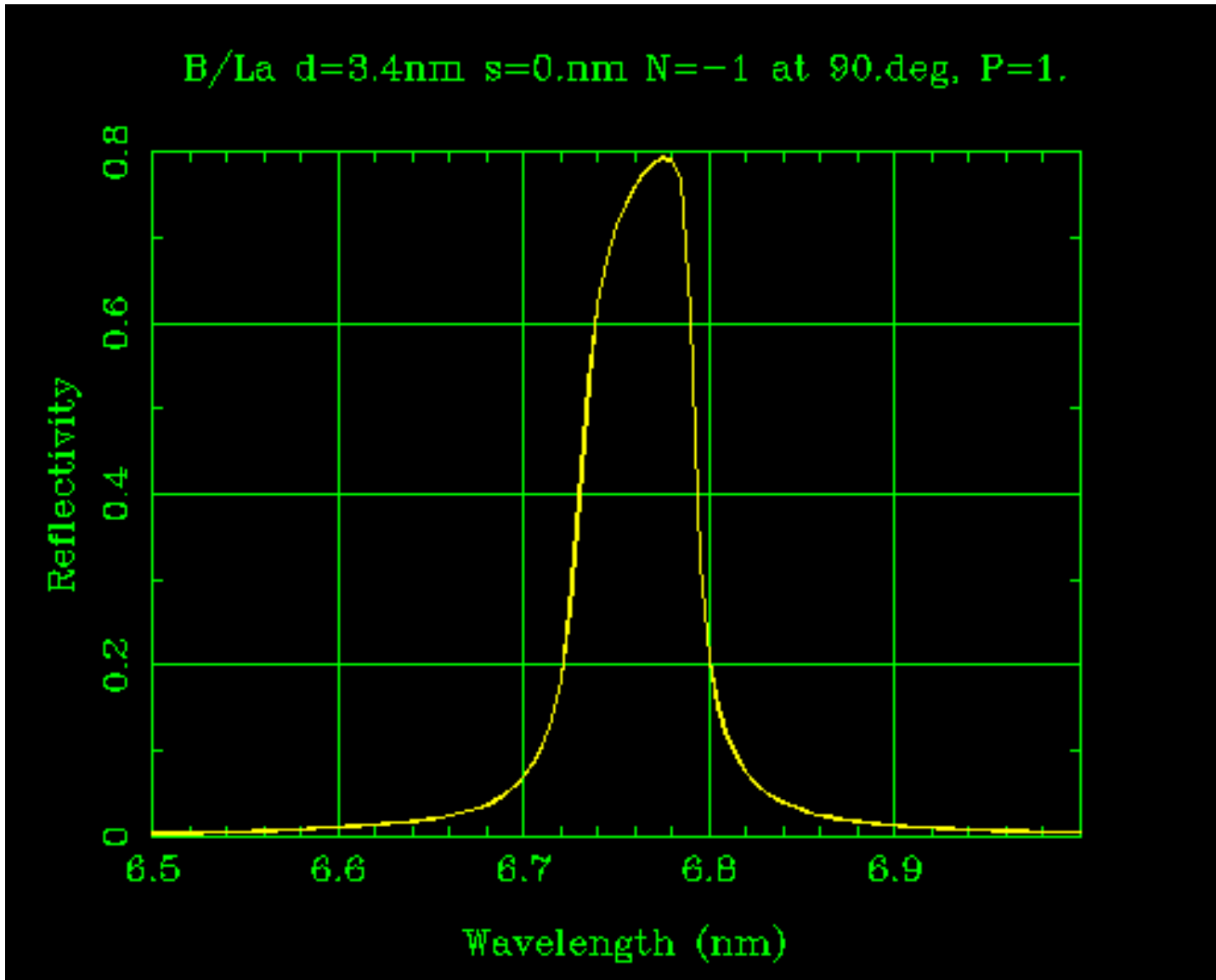


Calculated on LBNL website <[http://henke.lbl.gov/optical\\_constants/multi2.html](http://henke.lbl.gov/optical_constants/multi2.html)>



# Density Effect

Semi-infinite mirror, Gd peak, La/B,  $\beta=0.35$ ,  $\rho_B=1.15\text{g/cm}^3$



Note the reflectivity jump! Can we achieve this kind of density reduction?



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# Beyond EUV Source

## Source Problems

- Disadvantages: Gd and Tb have high melting temperatures (1,312°C, 1,356°C respectively)
- Require solid fuel injection
- Fuel must be dense enough to have high CE , yet transmittance is an issue.
- Fuel must be large enough to utilize full laser spot.

## Solution

- Form hydrocarbon particle with Gd/Tb embedded
- H/C have low 6.5 nm absorption cross section
- IR transmittance of most hydrocarbons > 90%
- Resulting spherical fuel large enough to absorb all IR energy but metal density low enough to allow EUV transparency.

Element	Absorption Cross Section (cm <sup>2</sup> /mg)	Energy (eV)	Wavelength (nm)
Hydrogen	1.68	190	6.5
Carbon	6.27	190	6.5
Nitrogen	10.65	190	6.5
Oxygen	17.99	190	6.5
Gadolinium	23.74	185	6.7
Terbium	28.03	190	6.5



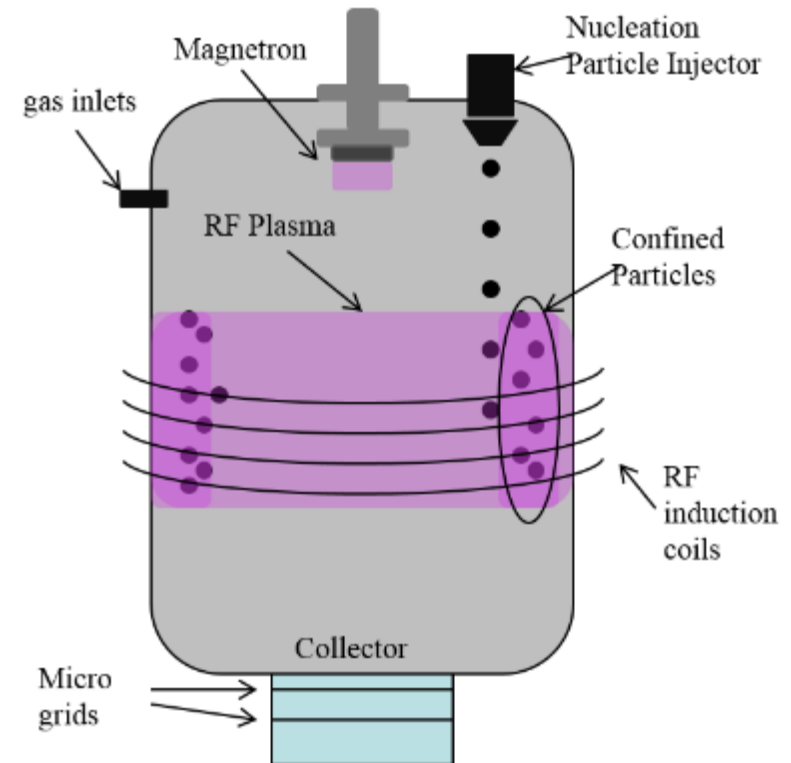
## Possible Methods

- Pulsed laser ablation of solid or gas target.
- Microplasma with gas or solid electrode.
- Plasma spray synthesis (spray pyrolysis) with oxygen-free environment.
- **Magnetron sputtering in hydrocarbon atmosphere.**
  1. Not only is a magnetron simple and flexible, but particle size is mostly dependent on confinement time in plasma.
  2. Also, because of charging of particles in the dusty plasma, agglomeration is likely lower.
- Particles would be made in a separate chamber, collected in a portable chamber and attached to existing EUV chamber.

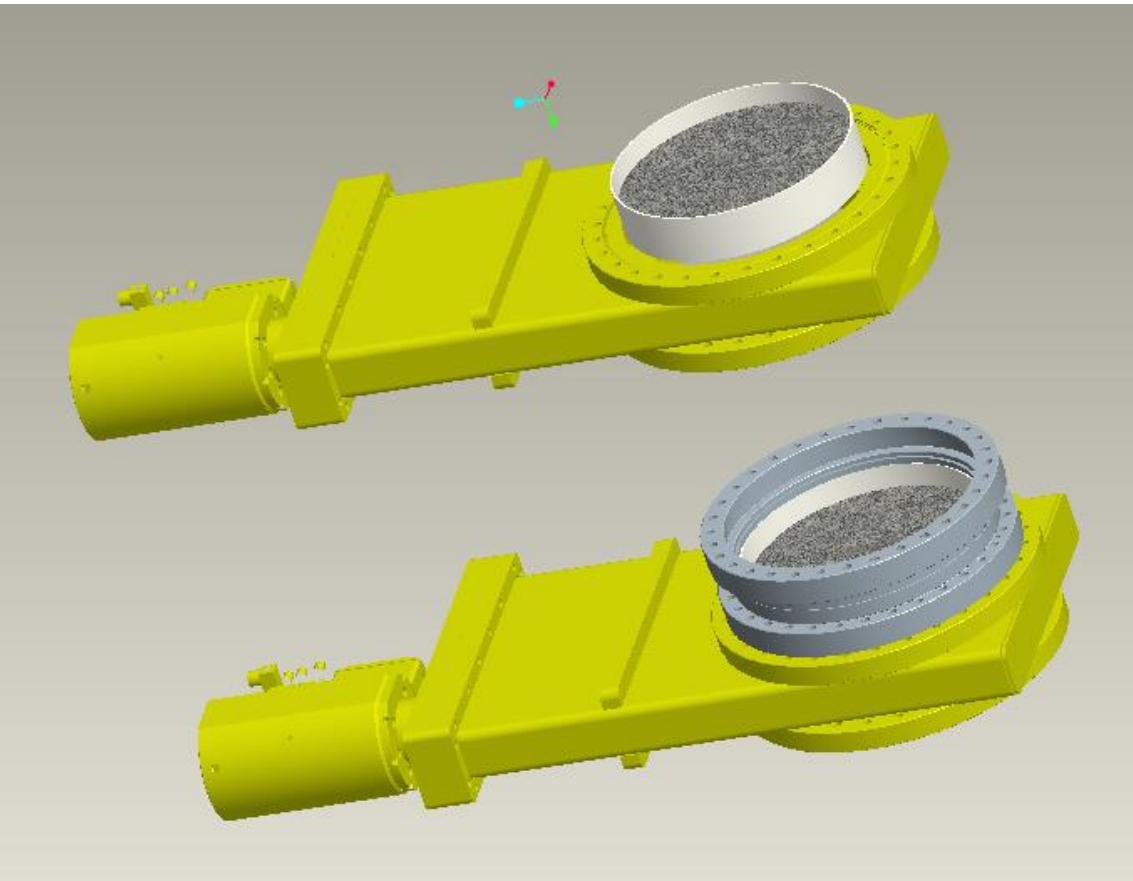


## Magnetron Synthesis Method: Dusty Particles

- System consists of Gd/Tb magnetron target and an Ar/methane inductively coupled plasma.
- Initial hydrocarbon particles (100 nm diameter polyethylene spheres) are injected to provide nucleation sites for hydrocarbon monomers and Gd/Tb.
- Hydrocarbon monomers ionize and form branched polymers due to plasma polymerization on the surface of the polyethylene spheres.
- Gd/Tb is assumed to sputter and embed in the particles.
- Bottom “Collector” consists of microgrids that filter out particles larger and smaller than desired size.



## Particle Collector design



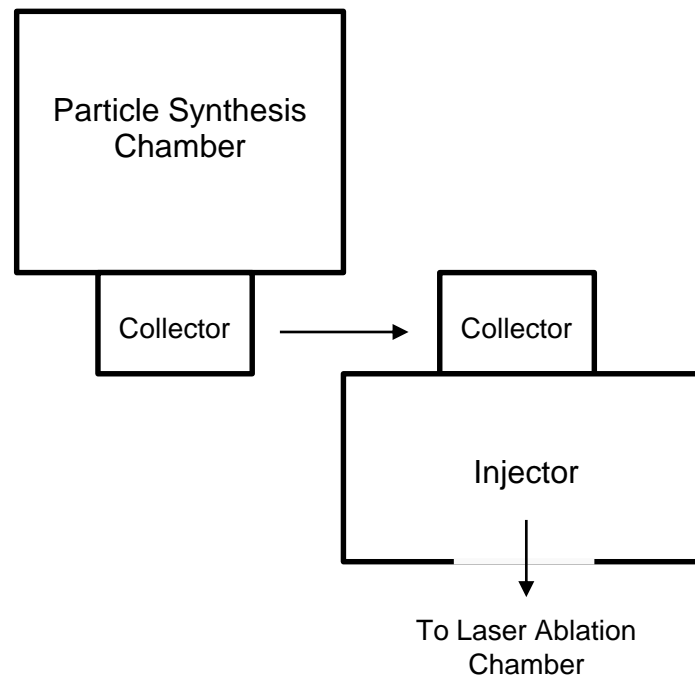
- Series of two grids with circular apertures.
- First grid allows particles greater than chosen size through. Larger particles are pumped out after particle synthesis complete.
- Second grid allows smaller particles than chosen size through. Pump below this grid takes away smaller particles.
- When completed, two gate valves above and below grids are closed in order to transport particles to injector system.



# Beyond EUV

## Possible Delivery Methods

- Suspend particles in liquid.
- Piezo-electric shaker coupled with an impeller.
- Overall system designed shown below.



# Conclusions

- A theoretical framework has been developed for  $\text{SnH}_4$  removal.
- Flow velocity profiles for use in diffusion-advection of  $\text{SnH}_4$  have been computed.
- Radical probe measurements show nonlinear increase in radical density with pressure.
- 0D plasma chemistry model has been used to validate the radical probe as an experimental diagnostic.
- Currently, poor MLM reflectivity hinders BEUV development.
- Reflectivity can be raised by improving deposition techniques, enabling ALD, and reducing density of deposited B films.
- A new approach for a BEUV source has been proposed.
- With good MLM and source technology, BEUV may be able to succeed.



# Acknowledgments

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- Thanks to undergraduate assistants Valentin Castro and Shanna Bobbins.



# References for Figures

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