ETCHING AND POST ETCHING PROCESSES OF POROUS AND CONVENTIONAL SIO_2 IN FLUOROCARBON BASED CHEMISTRIES

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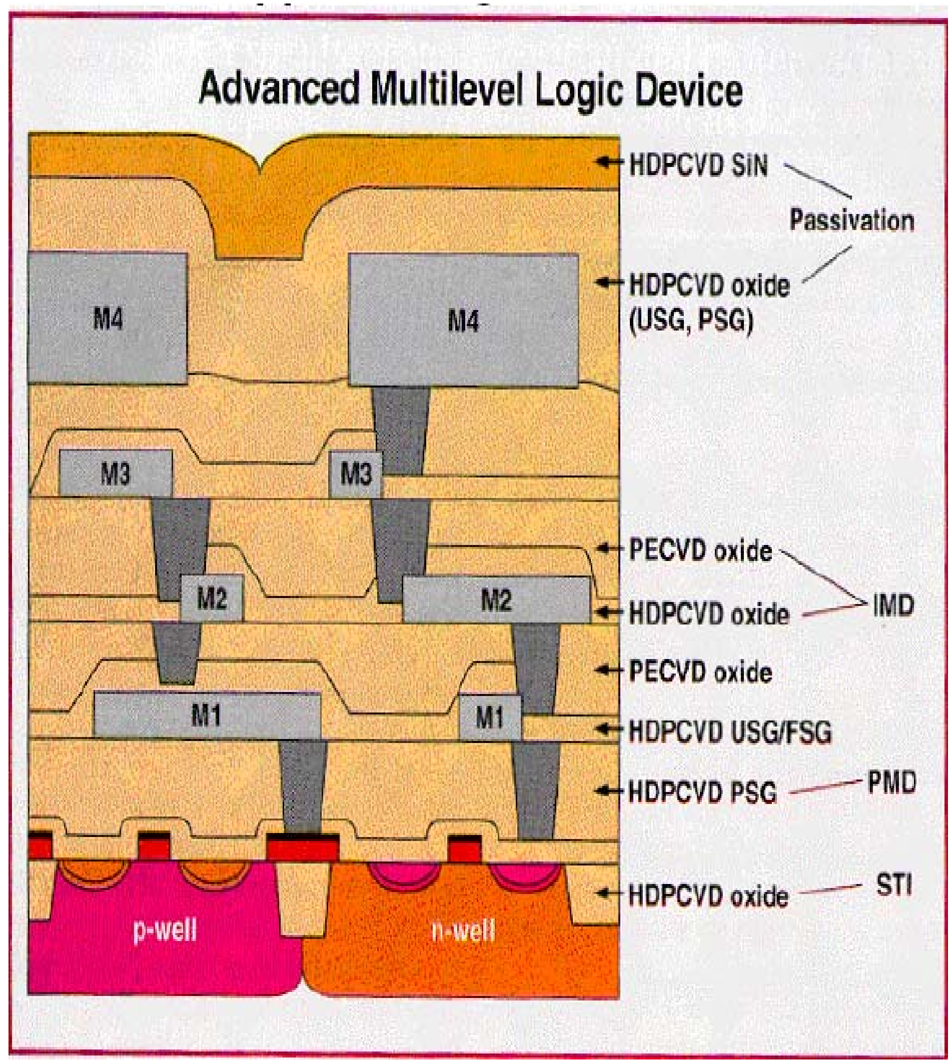
AGENDA

- Surface reaction mechanisms and validation
  - Fluorocarbon etching of SiO_2/Si
  - Oxygen etching of organic polymer
- Fully integrated process simulation
  - Etching, Cleaning, IMPVD of conventional SiO_2 in complex gas mixtures
- High aspect ratio (HAR) fluorocarbon etching of porous SiO_2
- Ar/O_2 strip of polymer and IMPVD of porous SiO_2 HAR profiles
- Concluding Remarks

MULTILEVEL DEVICES

- **The levels of interconnects in ICs will increase to 8-9 over the next decade.**
- **This will increase the delay in the signal propagation, due to resistance in the lines and capacitance between lines (RC delay).**
- **This has lead the focus onto low dielectric constant materials.**



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POROUS SILICON DIOXIDE

- Porous SiO_2 (xerogels) have low-k properties due to lower mass density resulting from (vacuum) pores.

  - Typical porosities: 30-70%
  - Typical pore sizes: 2-20 nm

- Porous SiO_2 (P-SiO_2) is, from a process development viewpoint, an ideal low-k dielectrics.

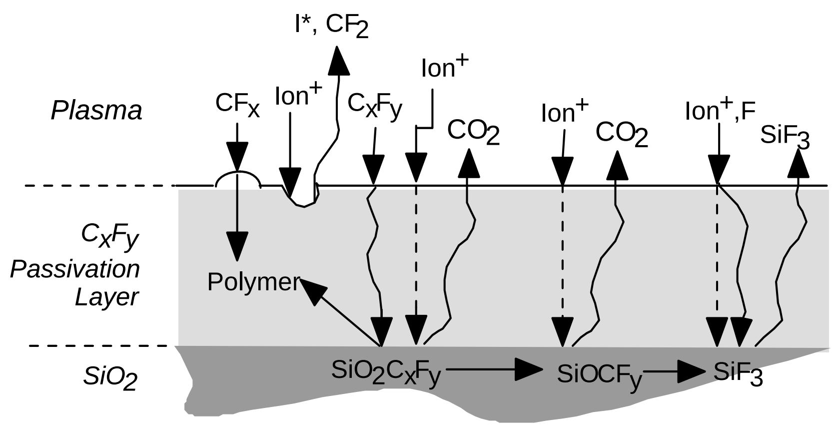
  - Extensive knowledge base for fluorocarbon etching of conventional non-porous (NP-SiO_2).

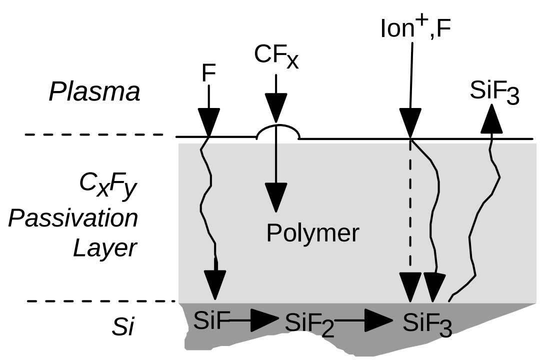
  - No new materials (though most P-SiO_2 contains some residual organics)

  - No new integration requirements

SURFACE REACTION MECHANISM

- CF_x and C_xF_y radicals produce the passivation layer which regulates delivery of precursors and activation energy.
- Chemisorption of CF_x produces a complex at the oxide-polymer interface. 2-step ion activated (through the polymer layer) etching of the complex consumes the polymer.





- Activation scales inversely with polymer thickness; polymer thickness scales inversely with bias.
- In Si etching, CF_x is not consumed, resulting in thicker polymer layers.
- Si reacts with F to release SiF_x.

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ASIDE ON REACTION MECHANISMS

- A reaction mechanism is simply a set of reactions with fundamental coefficients and probabilities, which should not depend on the chemistry.
- The chemistry merely determines the magnitude of the fluxes but not the reaction pathways.
- An etch mechanism valid for C_2F_6 plasmas should, with no change, also be valid for C_4F_8 or CHF_3 plasma.
- Development of reaction mechanisms across different chemistries should *result in more reliable mechanisms*.

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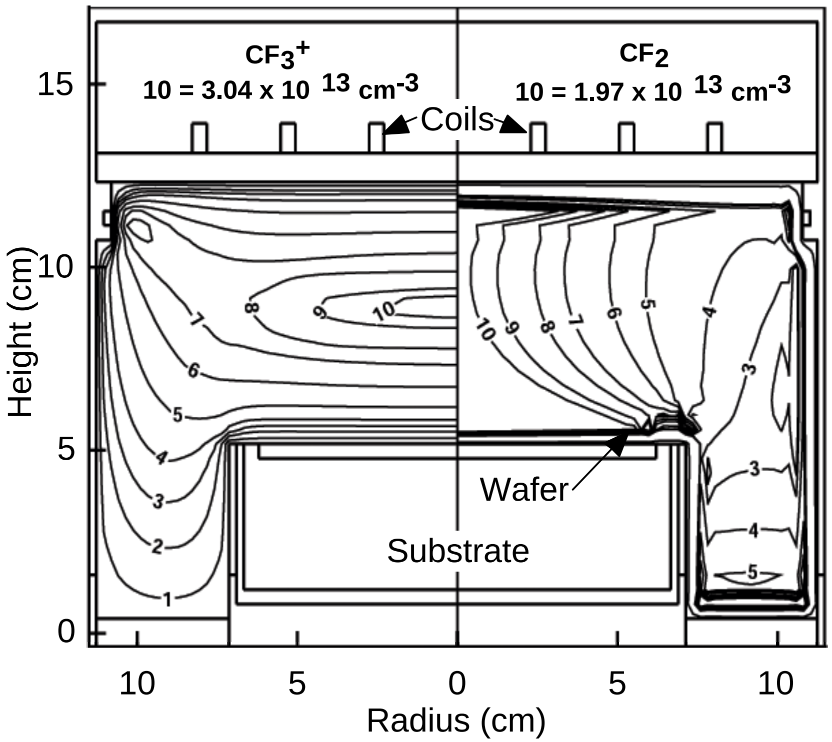
TYPICAL PROCESS CONDITIONS



- **Process conditions**
  - **Power: 1400 W**
  - **Pressure: 6 mTorr**
  - **rf self-bias: 0-150 V**
  - **Gas flow rate: 40 sccm**

Species	Flux ($cm^{-2}\,s^{-1}$)	
	C_2F_6	CHF_3
CF_3^+	9.32×10^{15}	2.78×10^{15}
CF_2^+	1.45×10^{16}	5.70×10^{15}
F^+	2.88×10^{16}	2.39×10^{16}
F_2^+	3.16×10^{14}	6.34×10^{14}
$C_2F_4^+$	6.68×10^{13}	2.87×10^{11}
$C_2F_5^+$	1.85×10^{13}	7.41×10^{11}
CHF_2^+	-	1.59×10^{14}
H_2^+	-	1.17×10^{15}
H^+	-	8.42×10^{14}
CF_2	2.71×10^{16}	8.24×10^{15}
CF	2.07×10^{16}	5.48×10^{15}
F	5.35×10^{16}	1.56×10^{16}
H	-	1.15×10^{16}
C_2F_3	9.57×10^{11}	3.50×10^{09}
C_2F_4	4.66×10^{12}	3.91×10^{11}

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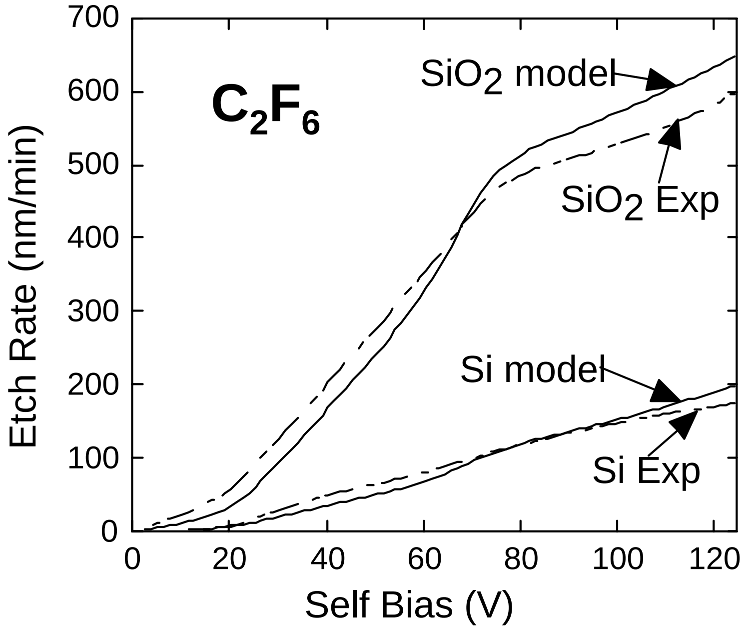

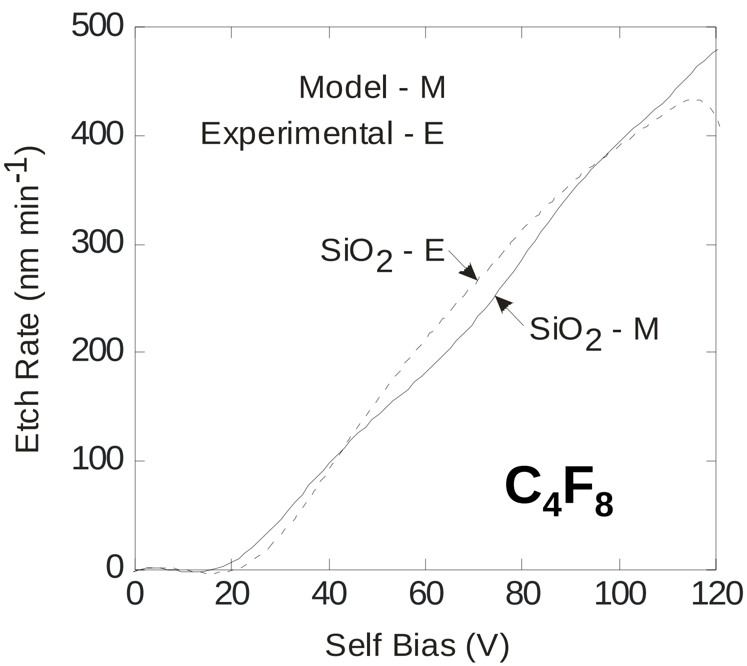

VALIDATION: C_2F_6 and C_4F_8

- **The mechanism was validated by comparison to experiments by Oehrlein *et al* using C_2F_6 and C_4F_8 chemistry.[1]**

- **Threshold for SiO_2 etching was well captured at self-bias ≈ 20 V. For Si the etch rates were lower due to thicker polymer in C_2F_6 chemistry.**

[1] J. Vac. Sci.Technol. A **17**, 26 (1999), private communications

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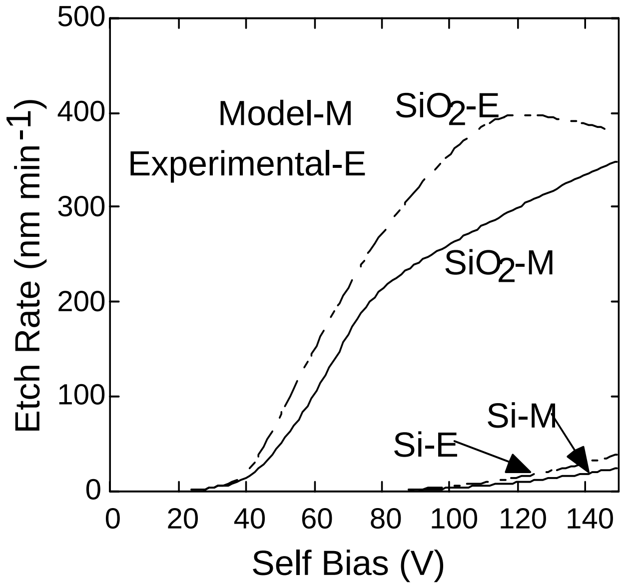
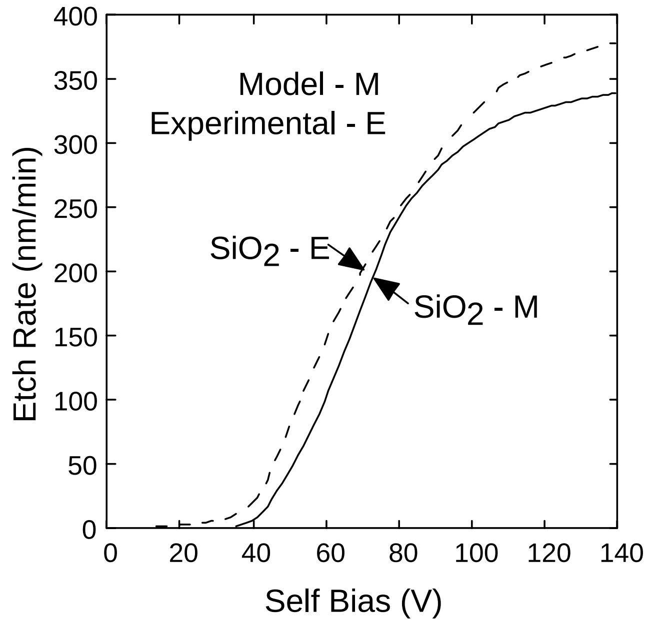
VALIDATION: CHF_3





- Threshold for SiO_2 and Si etching were well captured at self-bias of 40 V and 100 V respectively for CHF_3.
- Differences between model and experiments for SiO_2 are attributed to H radicals forming hydrocarbon polymer chains.
- Different polymer is accounted for by modifying sputtering rates to account for the mass differences.

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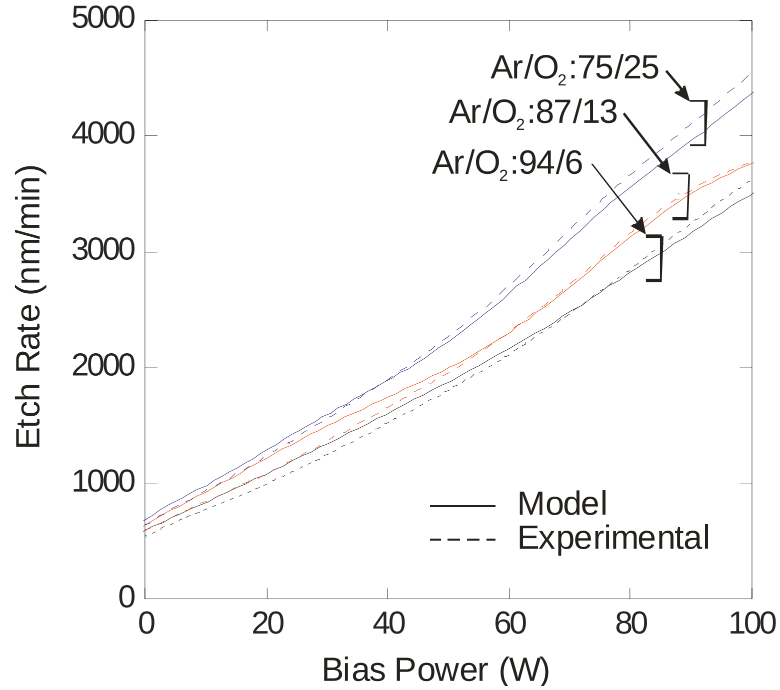
OXYGEN ETCHING OF ORGANIC POLYMERS

- Ar/O_2 is typically used for polymer stripping after fluorocarbon etching and resist removal.
- Little polymer removal is observed with oxygen radical chemistries suggesting ion activation.

$$P(s) + I(g) \rightarrow P^*(s)$$
$$P^*(s) + O(g) \rightarrow COF_x(g)$$

- Algorithms based on this mechanism were developed (and validated) for the MCFPM.
- ICP Power: 600 W (13.56 MHz)
- Pressure: 4 mTorr
- Bias power: 0-100 W (3.4 MHz)



Exp: Standaert *et al* JVSTA_19_435_2001

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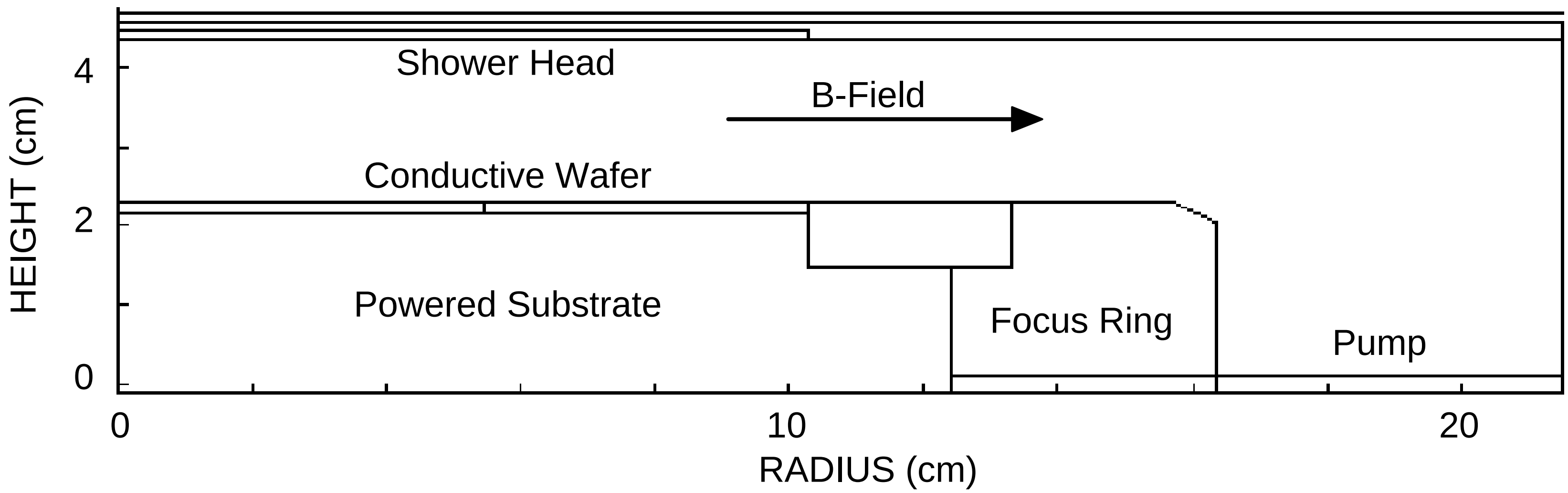
SiO_2 ETCHING IN MERIE REACTOR

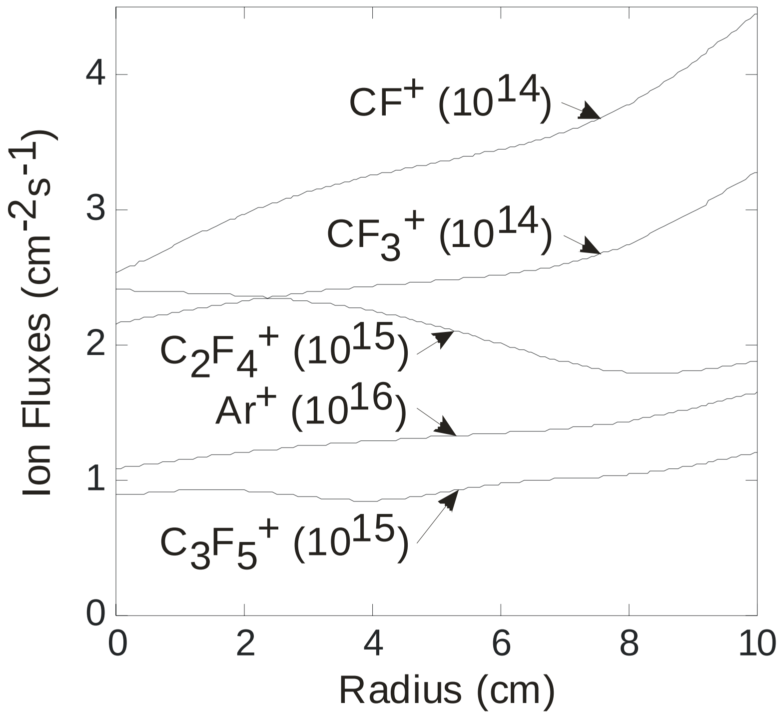
- **Etch mechanisms were applied to SiO_2 etching in fluorocarbon chemistries in a TEL-DRM-like reactor.**

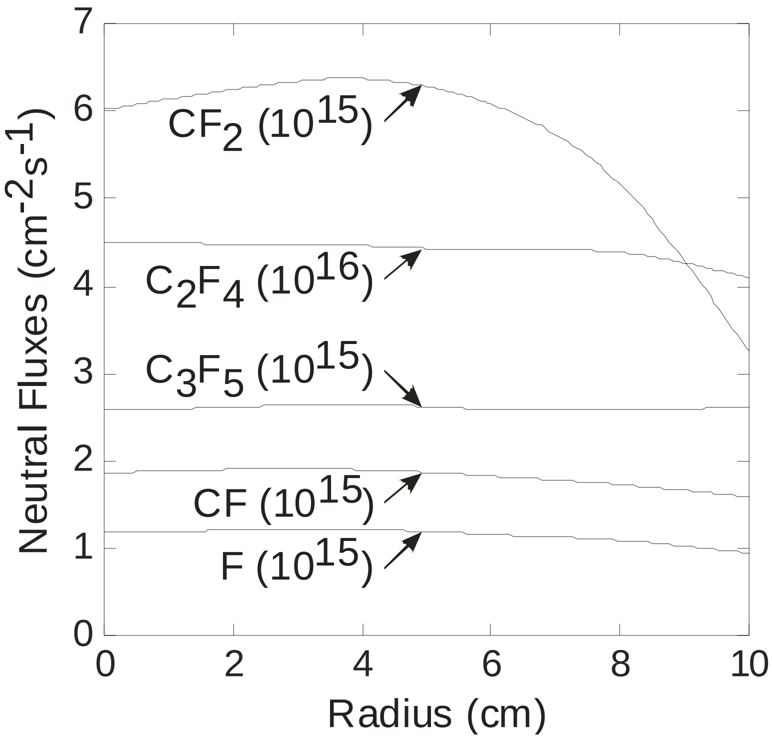


- **With reaction mechanisms developed for:**
  - **Fluorocarbon SiO_2 etching**
  - **CF_x polymer etching/removal**
  - **Metal deposition by IMPVD (J. Lu, SRC supported UIUC graduate)**

a fully integrated process can now be simulated based on first principles.

FLUXES: Ar / O_2 / C_4F_8 = 200/5/10 sccm, 2000 W

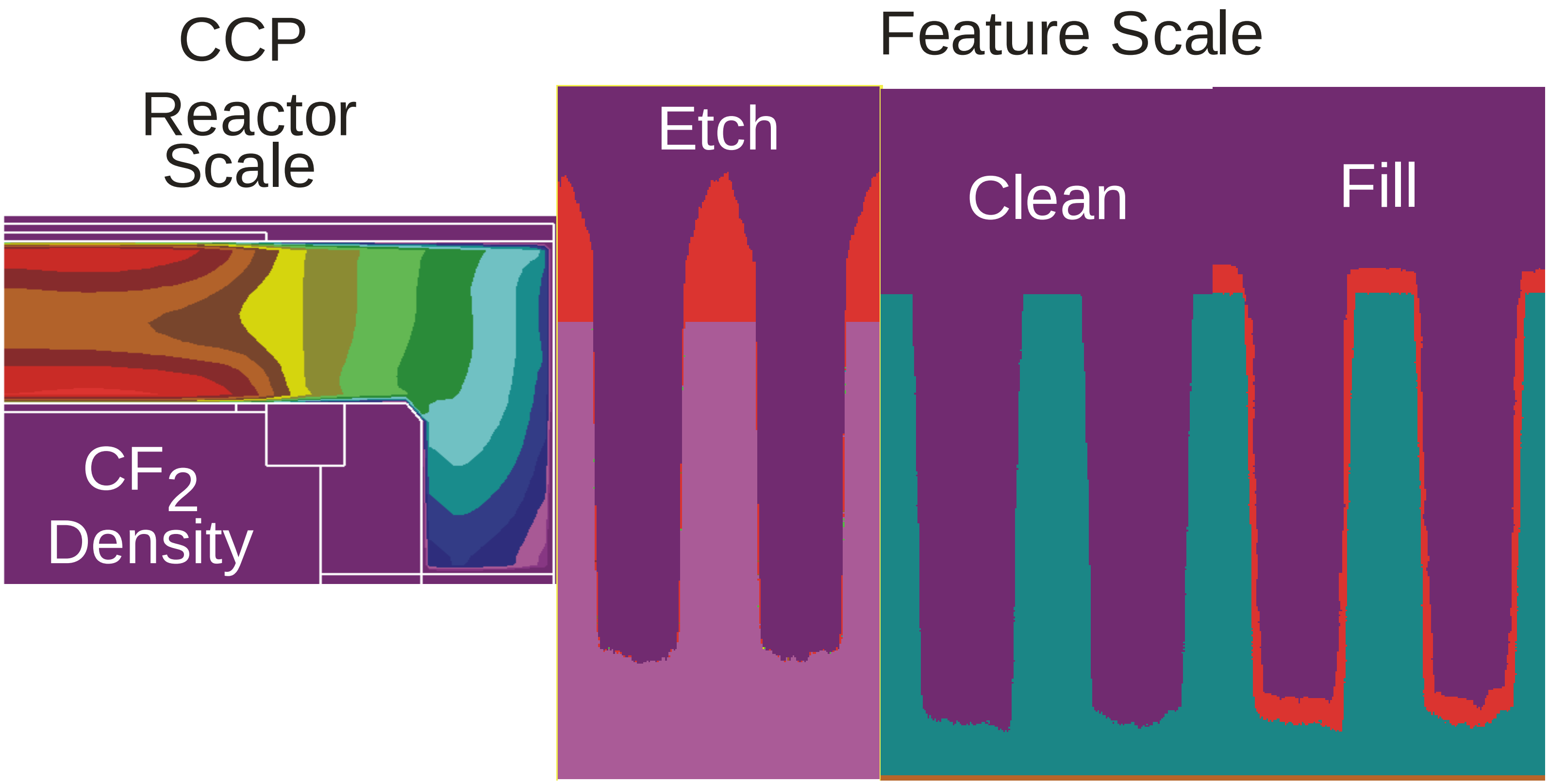




- **Ar: 200 sccm**
- **O_2: 5 sccm**
- **C_4F_8: 10 sccm**
- **Power: 2000 W**
- **Pressure: 40 mTorr**

- **Dominant Ions: Ar^+, $C_2F_4^+$**
- **Dominant Neutral: C_2F_4, CF_2**

INTEGRATED MODELING



- **Ar / O_2 / C_4F_8 = 200/5/10 sccm, 2000 W, 40 mTorr**

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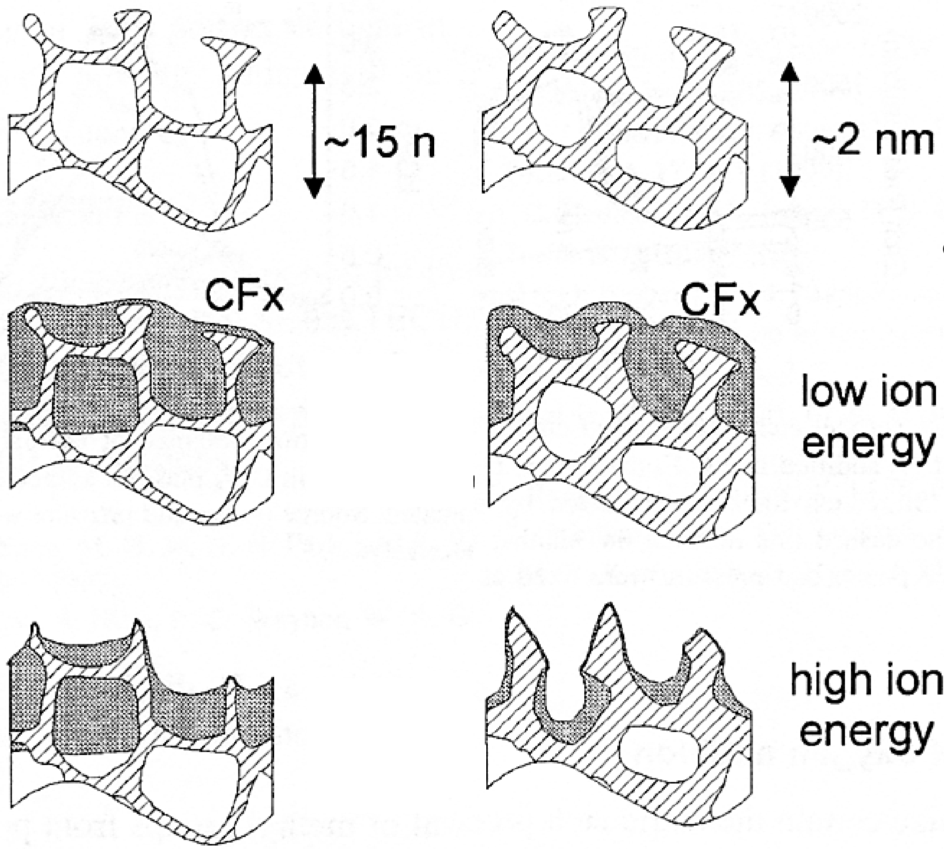
WHAT CHANGES WITH POROUS SiO_2?

- The "opening" of pores during etching of P-SiO_2 results in the filling of the voids with polymer, creating thicker layers.
- Ions which would have otherwise hit at grazing or normal angle now intersect with more optimum angle.



- An important parameter is L/a (polymer thickness / pore radius).

- Adapted: Standaert, JVSTA 18, 2742 (2000)

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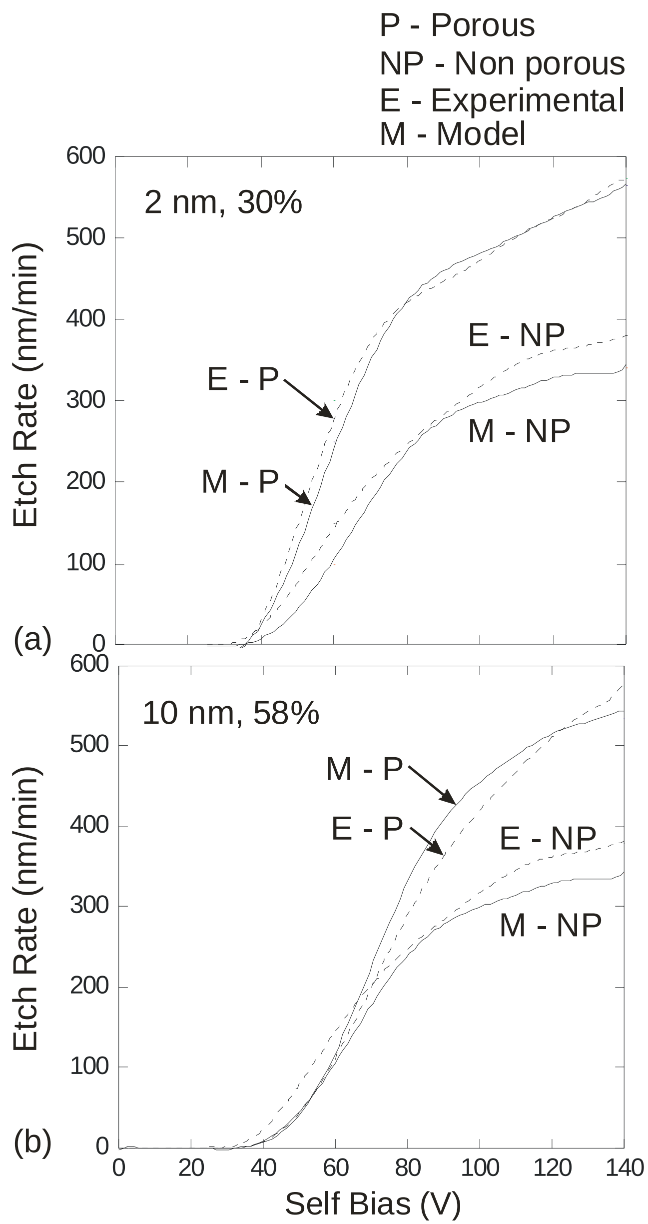
POROUS SiO_2



- **Pores are characterized by porosity, interconnectivity and average radius.**

- **Validation performed for:**
  - **2 nm pore radius, 30% porosity**
  - **10 nm pore radius, 58% porosity**

- **Process conditions (ICP):**
  - **Power: 1400 W (13.56 MHz)**
  - **Pressure: 10 mTorr**
  - **rf self-bias: 0-150 V**

- **Etch rates of P-SiO_2 are higher than for NP-SiO_2 due to lower mass densities.**

Exp: Oehrlein *et* al, J. Vac. Sci.Technol. A **18**, 2742 (2000)

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PORE-DEPENDENT ETCH RATES

- **To isolate the effect of pores on etch rate, corrected etch rate is defined as**

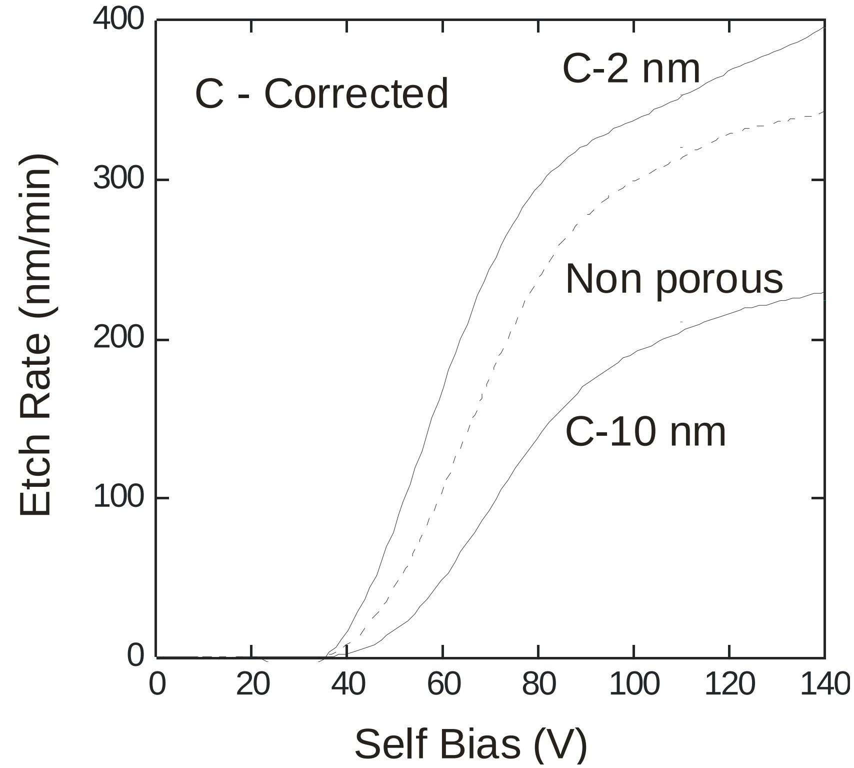
$$\textbf{Etch Rate (ER)}_{\text{corrected}} = \textbf{ER}_{\text{regular}} \times (1 - p),$$

$$p = \text{porosity}$$

- **If etching depended only on mass density, corrected etch rates would equal that of NP- SiO_2.**

- **2 nm pores L/a $\geq$1 : ER_{cor} > ER_{NP}. Favorable yields due to non-normal incidence may increase rate.**

- **10 nm pores L/a $\leq$ 1 : ER_{cor} < ER_{NP}. Filling of pores with polymer decrease rates.**



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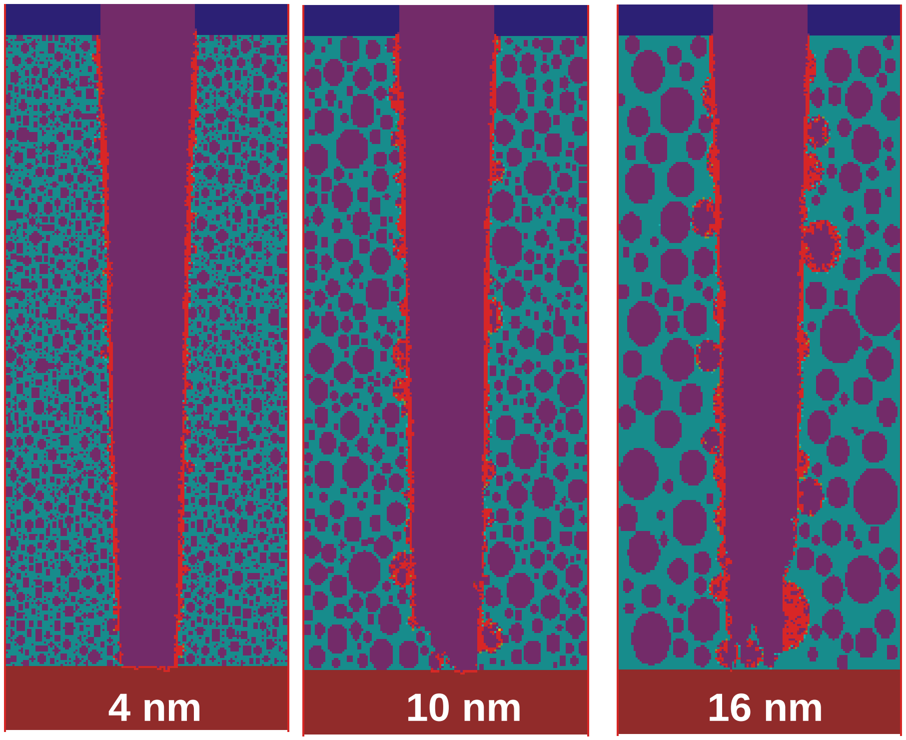
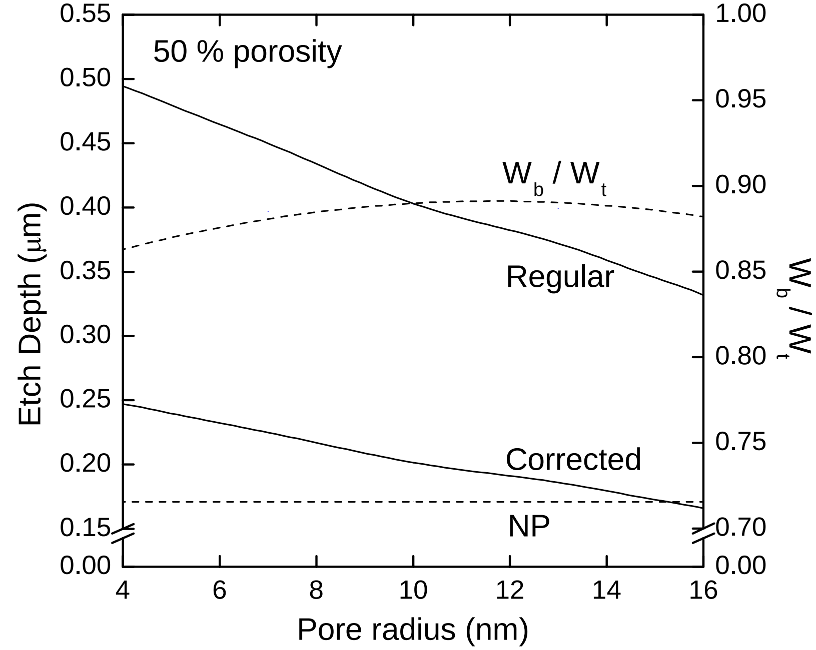
EFFECT OF PORE RADIUS ON HAR TRENCHES





- **With increase in pore radius, L/a decreases causing a decrease in etch rates with pore radius.**
- **Thick polymer layers eventually lead to mass corrected etch rates falling below NP-SiO_2. There is little variation in the taper.**

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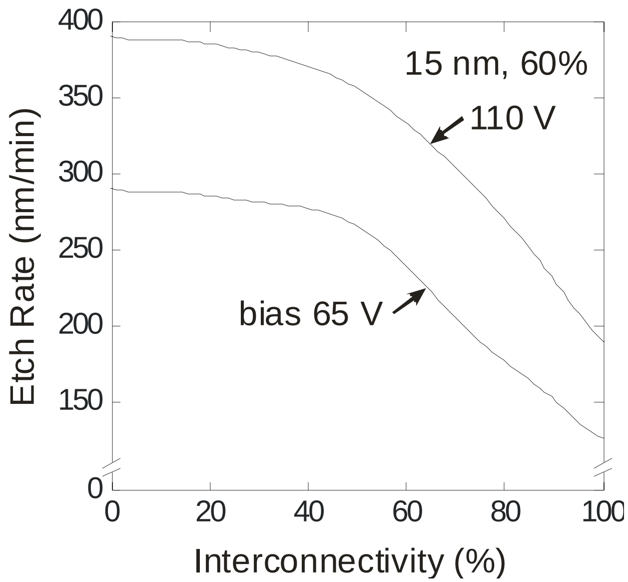

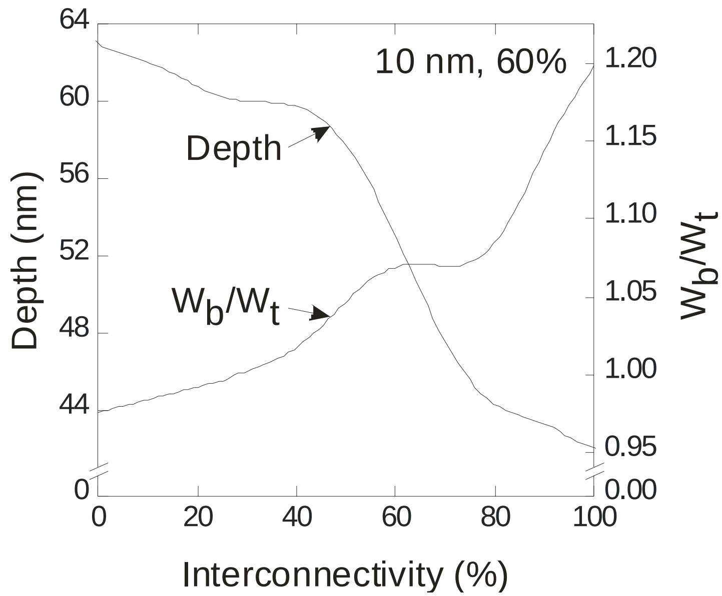

POROUS INTERCONNECTIVITY

- Etch rates decrease with increasing interconnectivity.
- Although the fractal dimension is small, the effective polymer thickness (by pore filling) increases with increasing interconnectivity.
- Due to there being more pore openings in the sidewalls, bowing occurs at high interconnectivities, which also leads to slower etching.

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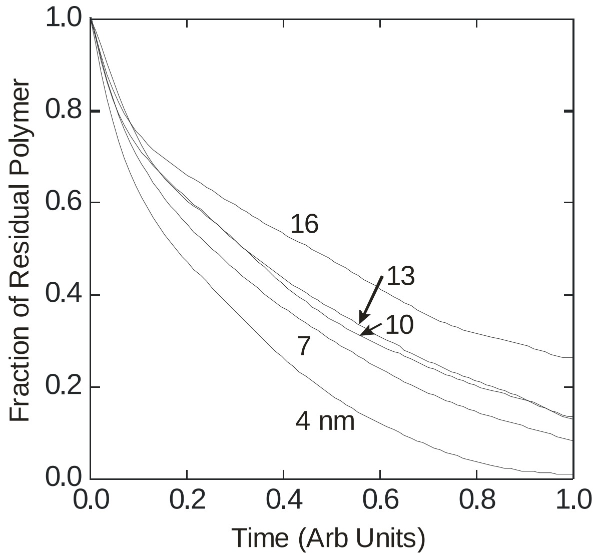
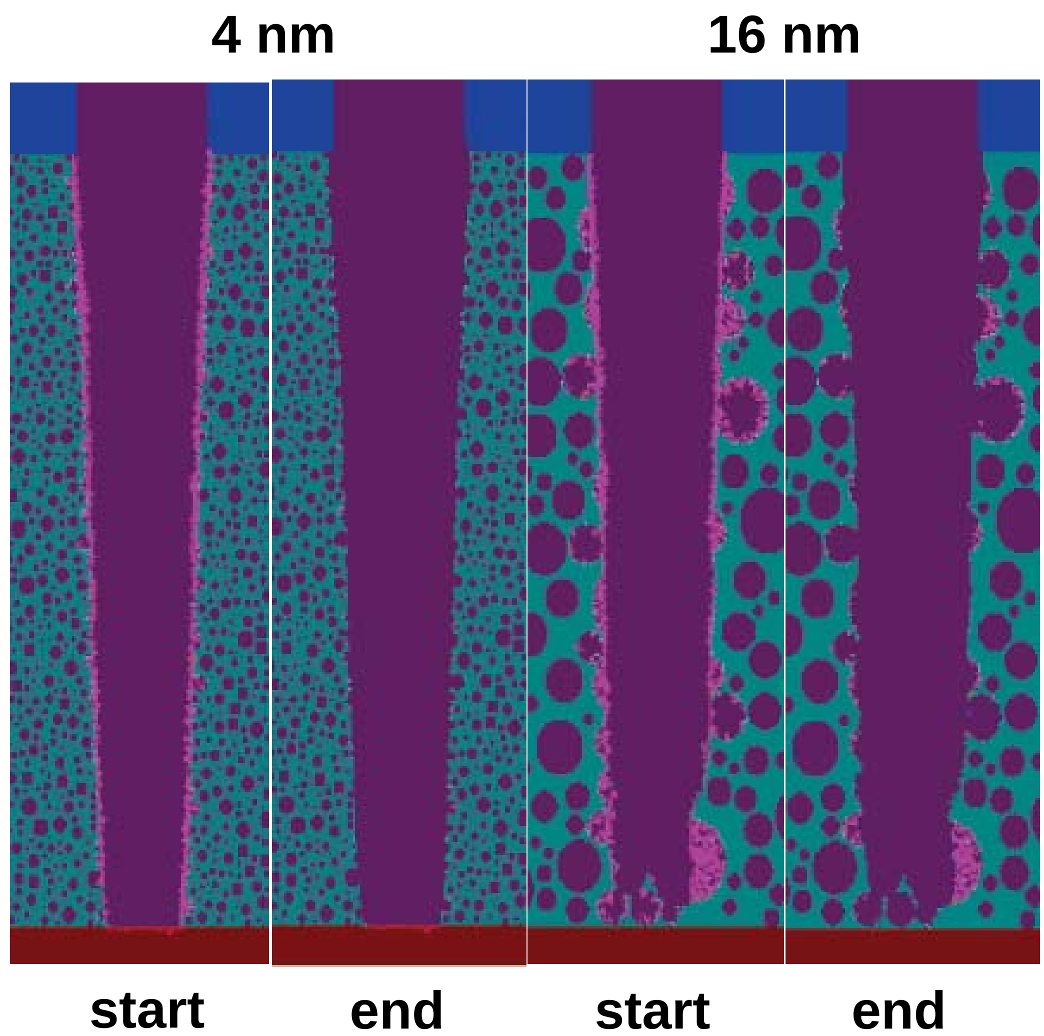
EFFECT OF PORE RADIUS ON STRIPPING





- **Larger pores are harder to clean due to unfavorable view angles**

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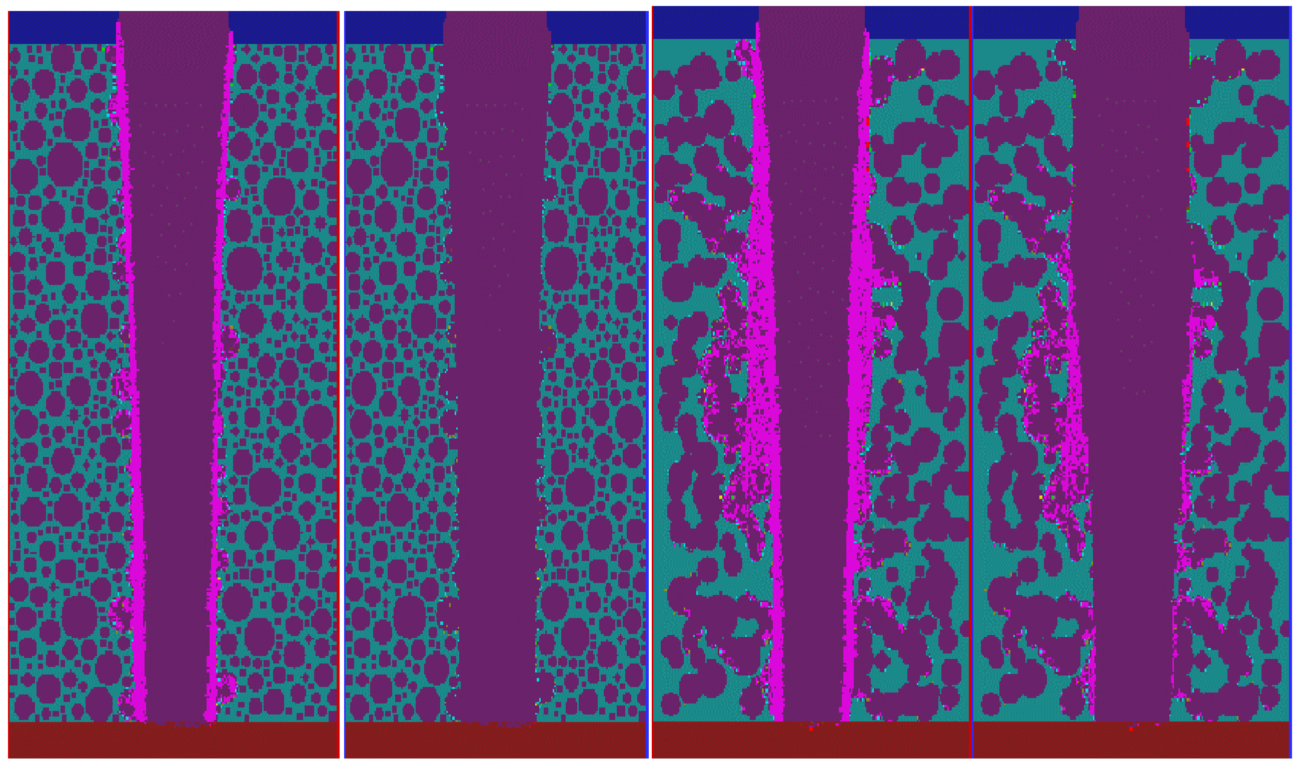
EFFECT OF INTERCONNECTIVITY ON STRIPPING

- Cleaning is inefficient with interconnected pores.
- Higher interconnectivity leads to larger shadowing of ions.



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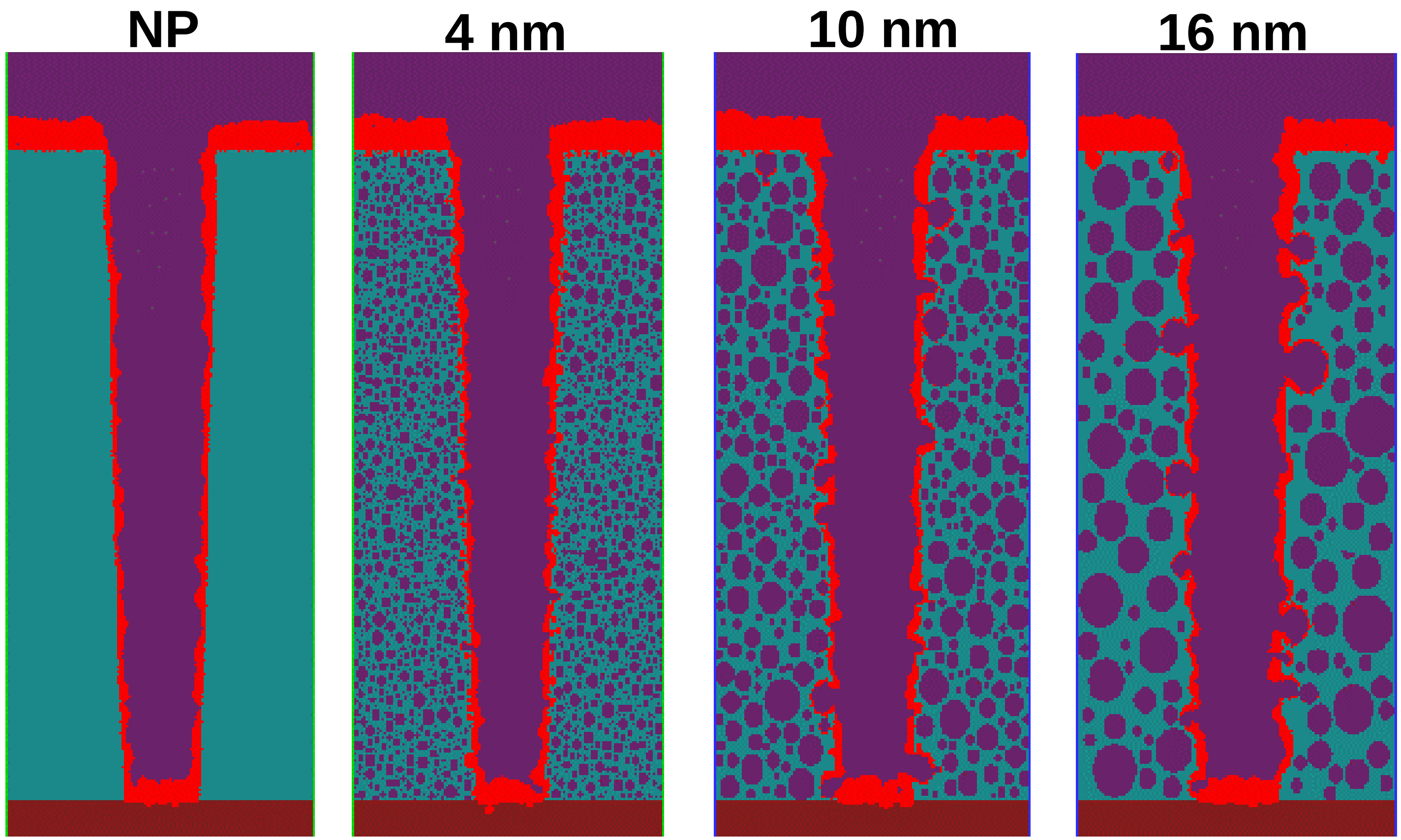
POST ETCH: FILL



- **Voids are created or initiated during filling due to presence of pores and leads to non-conformal filling. Presence of voids are pronounced for bigger pores.**

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CONCLUSIONS

- Etching of P-SiO_2 obeys similar scaling laws as NP-SiO_2. Etch rate increases for smaller pores and slows for larger pores (at high porosities) and at high interconnectivities.

- L/a determines etch rate variation of P-SiO_2. Polymer filling increases for interconnected pores.

- Organic polymer etching increase linearly with bias; and is only sensitive to O_2 at low O_2 fractions.

- Large pores and interconnected pores are harder to clean due to shadowing of the surfaces from ion fluxes.

- Copper deposition using IMPVD was studied as a surrogate to seed layer deposition (and/or barrier coating). Voids are created in or initiated by pores.