Computational Modeling as a Tool to Optimize and Understand the Atomic Layer Etching Process

Chad Huard, Premkumar Panneerchelvam, and Ankur Agarwal

KLA-Tencor

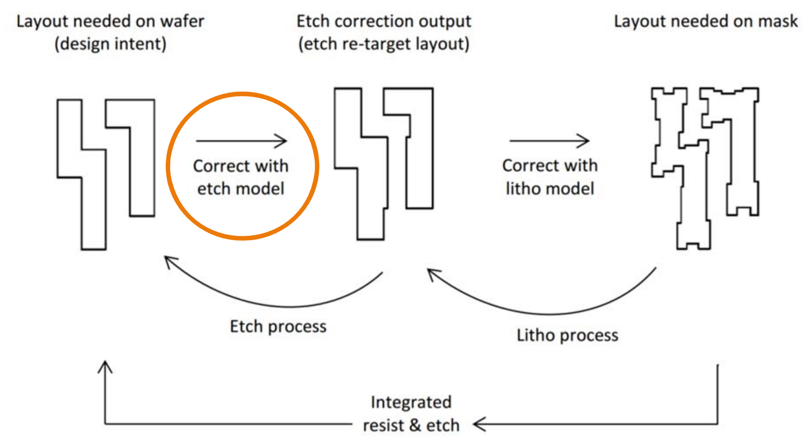
Agenda

- **Q: What can etch modeling provide?**

- Computational etch modeling overview.
- Quantitative vs Qualitative Modeling.
- Etch model validation/calibration.
- Atomic layer etching (ALE).
  - Ar/Cl_2 ALE of silicon.
  - Ar/C_4F_8 ALE of oxide.
- Conclusions.

Requirements for Etch Modeling

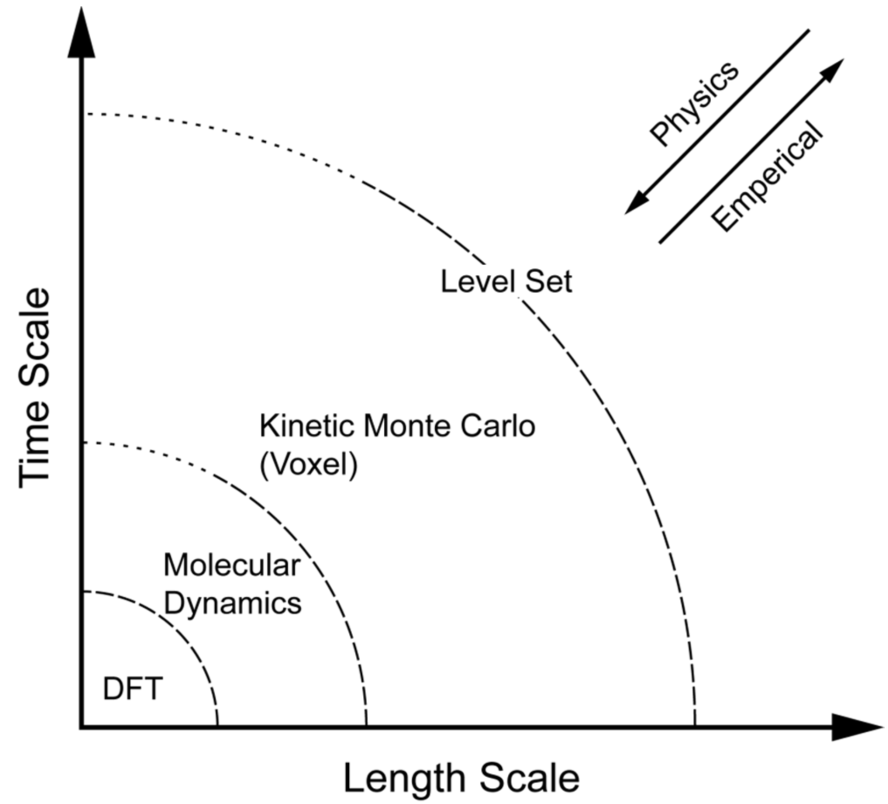
- Q: What can etch modeling provide?
  - Process design / optimization.
  - Process control / feedback.
  - Access operating conditions inaccessible experiments.
  - Determine physical mechanisms responsible for observed behavior.
- Feature profile model must be able to:
  - Accurately model relevant physical processes.
  - Be predictive outside of calibrated conditions.
  - Simulate length/time scales large enough to capture relevant features.
  - Do so in a feasible time period.



- Zavyalova et al. Proc. SPIE 9052, Optical Microlithography XXVII, 905222 (2014)

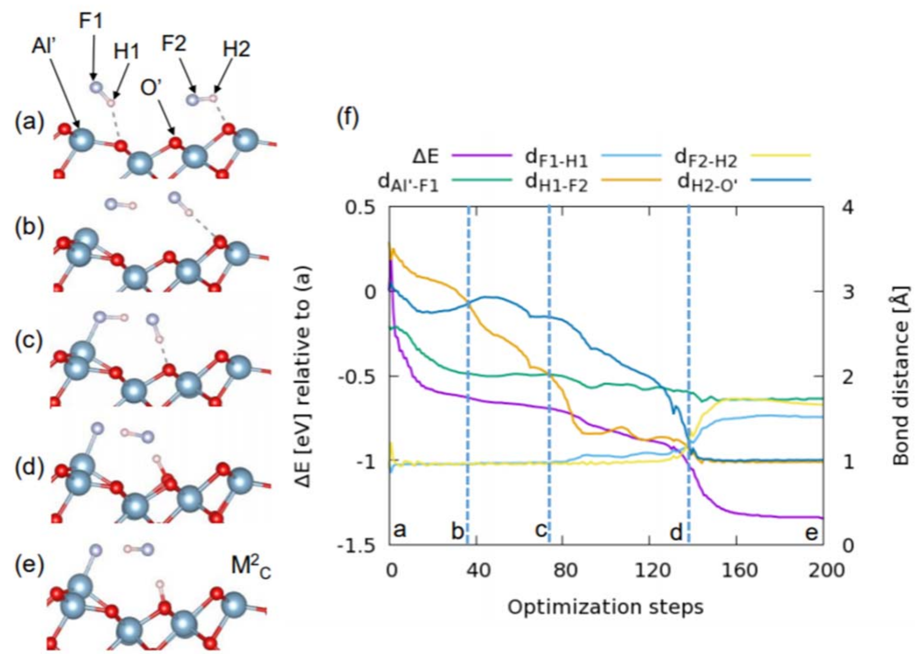
Etch Modeling Schemes

- First principals (DFT, QMD, MD):
  - Few fitting parameters.
  - Lots of physics represented.
  - Slow.
  - Limited simulation area.
- Continuous methods (level set):
  - More empirical assumptions needed.
  - More fitting parameters required.
  - Fast.
  - Large simulation areas possible.



Density Functional Theory for Etch Modeling

- Interaction of two HF molecules with alumina surface.
- At each optimization step energy gradients are calculated using quantum theory.
- Includes all bonding possibilities ‘automatically’ by solving Schrodinger's equation.
- Few fitting parameters.
- Computationally expensive.
- Small domain.
- Sensitive to initial conditions.



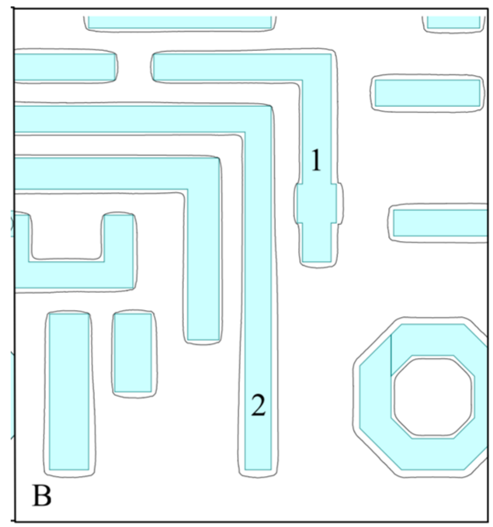
- S. K. Natarajan, and S. D. Elliott. *Chemistry of Materials* Just Accepted Manuscript (2018).

KLA-Tencor

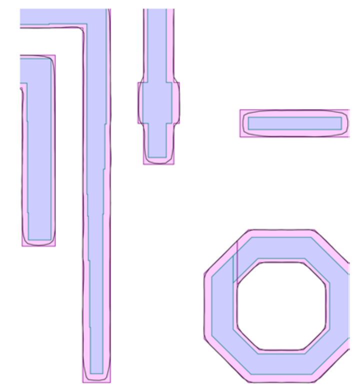
Etch Bias Model

- Etch bias depends(to the first order) on the visible open area from any point.
- A fast model can be constructed which calculates the change in critical dimension by calculating the visible open area at any point.
- This calculation is fast and lends itself to the inverse problem of correcting for etch bias.
- The relationship between etch bias and visible open are is purely empirical.
- This type of model is good for correcting for etch bias, not for predicting etch behavior.

- Etch Bias



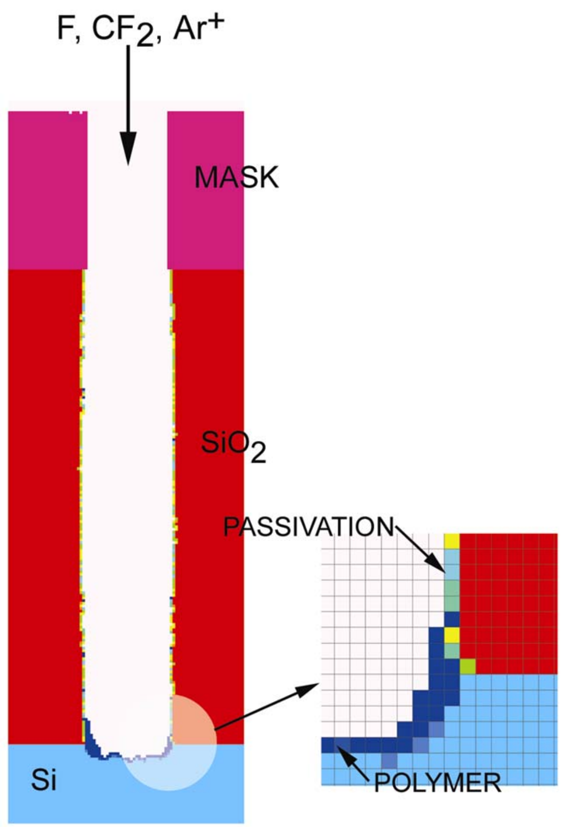
- Etch Bias Correction



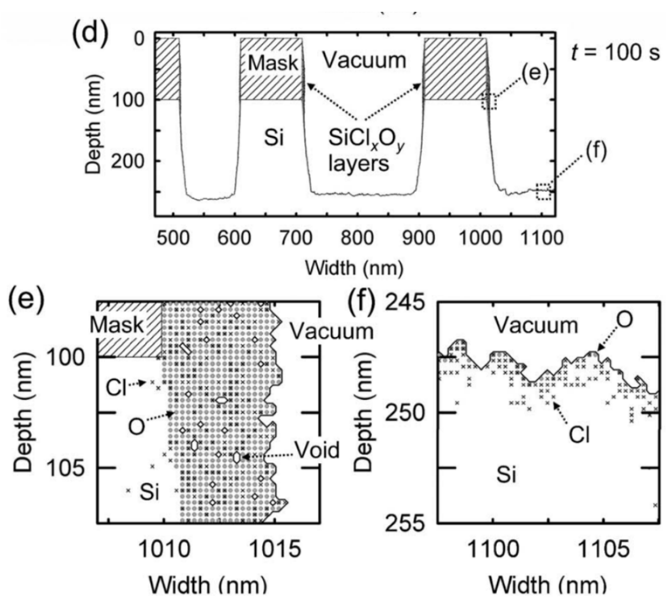
- D. F. Beale, and J. P. Shiely, SPIE 5754, Optical Microlithography XVIII. (2004).

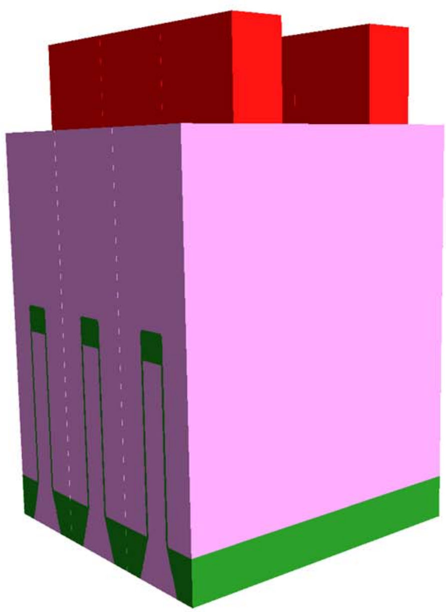
Kinetic Monte Carlo (Voxel) Methods

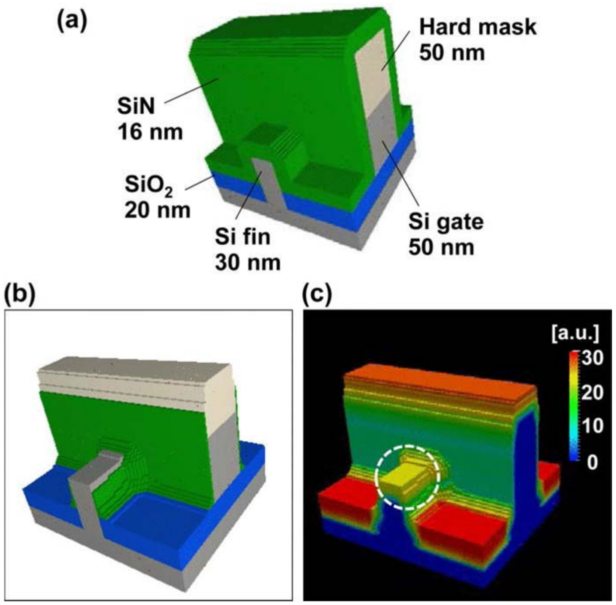
- Simulation domain divided into lattice of computational cells.
- Gas-phase pseudo particles are tracked and react with solid.
- All possible reactions are user defined.
  - Possible to define first-principals (physics based) reaction mechanism.
  - Also possible to define reduced model (empirical) reaction mechanism.
- Ability to address:
  - Large computational domains.
  - Long time scales.
  - User defined level of physics accuracy.



Monte Carlo Etch Codes





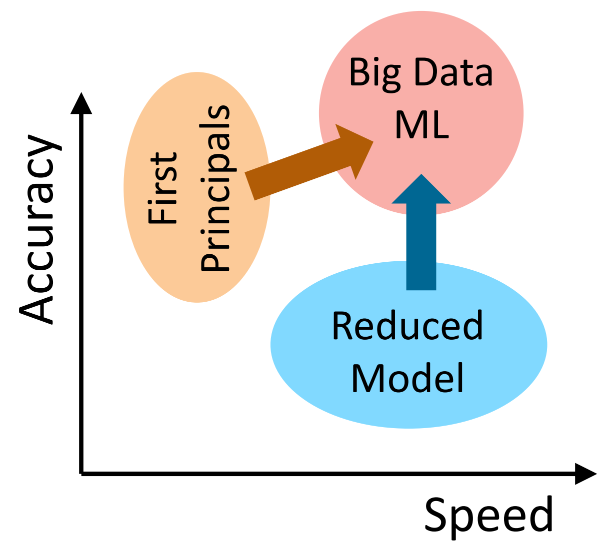


- Y. Osano and K. Ono, *JVST B* **26** 1425 (2008)
- Huard, Kushner et al. AVS 63rd Symposium (Nashville, 2016)
- N. Kuboi, et al., *JVST A* **33** 061308 (2015)

Bilateral Approach to Etch Modeling

- Reduced/empirical models.
- Fully calibrated to experiment.
- Used for
  - Guiding optimization.
  - Reducing # of experiments.
- Must be
  - Quantitatively accurate.
  - Faster than experimental throughput.
  - More scalable than experiments.

- First principals models.
- Based on complete picture of physics.
- Used for
  - Advanced development.
  - Problem solving.
- Must be
  - Qualitatively accurate.
  - Predictive outside of calibration range
  - Able to capture all relevant physics.



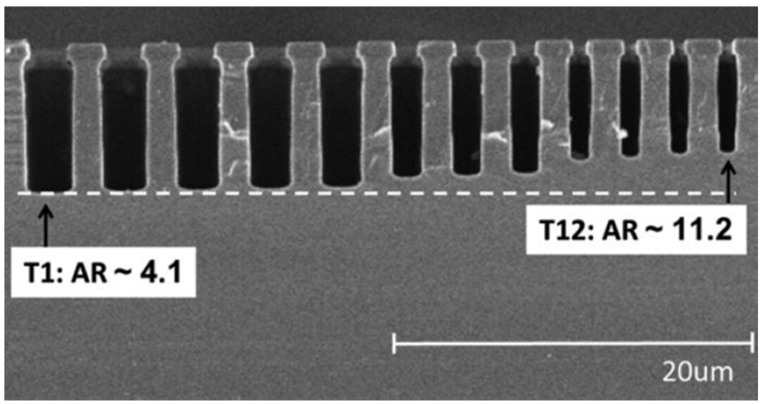
KLA-Tencor

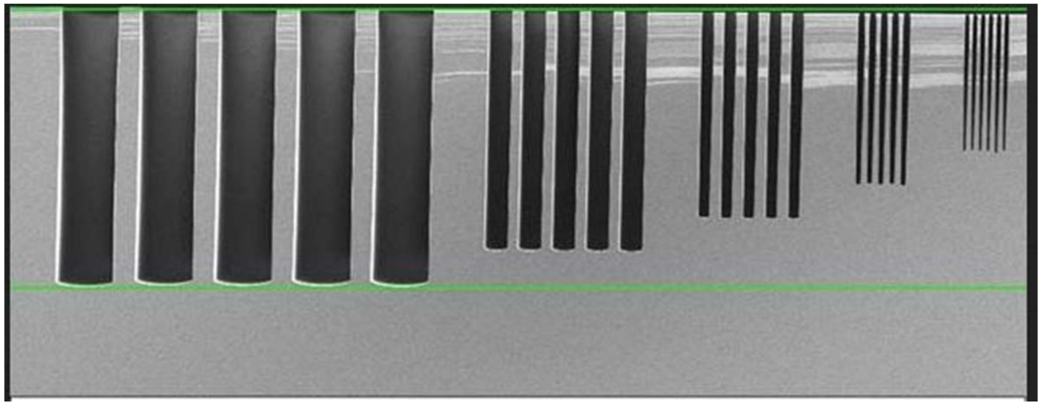
Q: What can etch modeling provide:

A: Fundamental insights

Aspect Ratio Dependent Etching

- In plasma etch processing Aspect Ratio Dependent Etching (ARDE) occurs when etch rate decreases as aspect ratio increases.
- As the dynamic range of features increases, ARDE becomes more problematic.

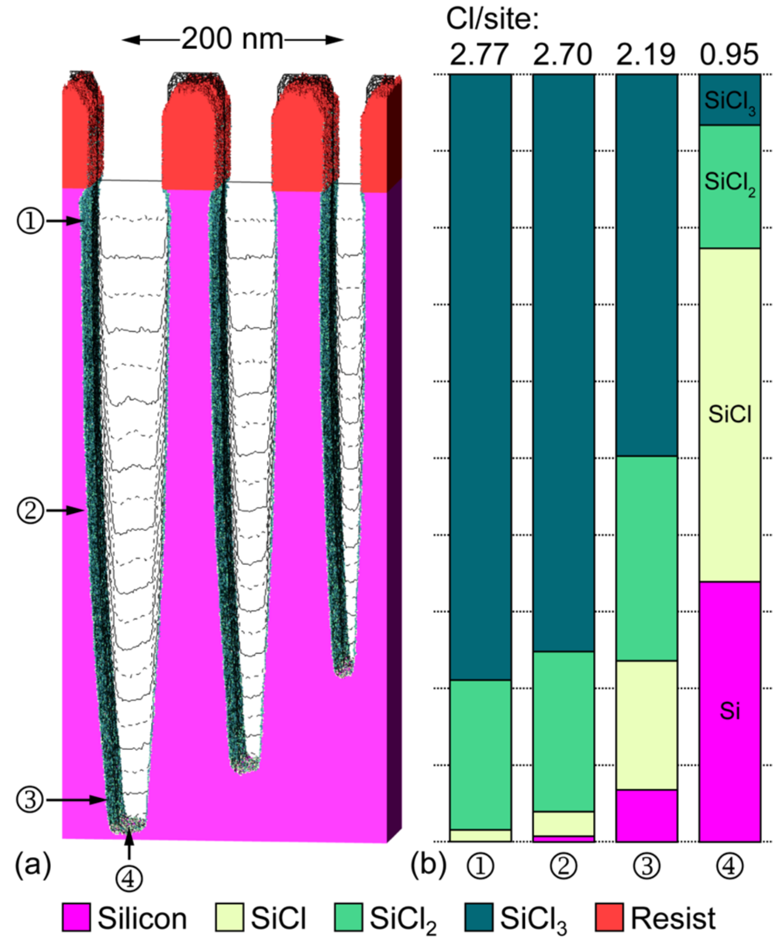




- R. Bates et al. JVSTA 32, 051302 (2014)
- https://cmi.epfl.ch/etch/AMS200.php

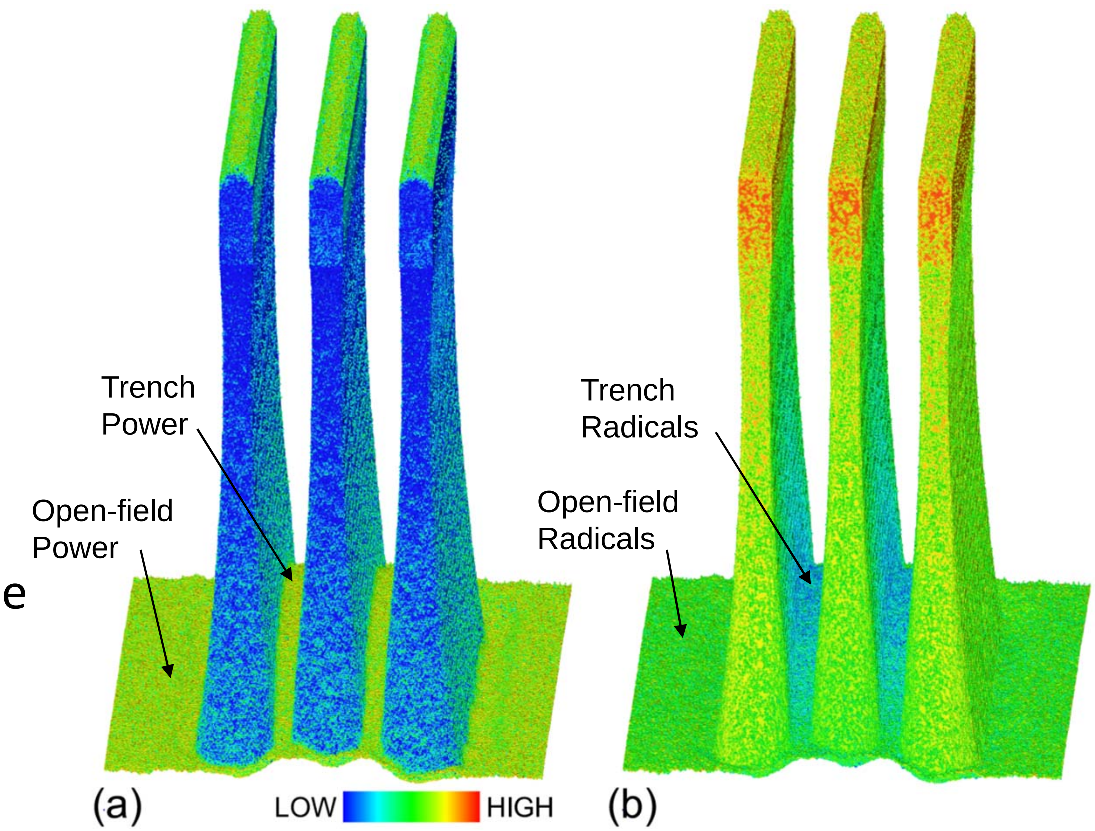
Aspect Ratio Dependent Etching

- Ions are normal incidence.
- Radicals flux is isotropic, transports diffusively.
- ARDE naturally occurs from simulations.
- Investigate using Ar/Cl_2 ICP.
- Additional complications due to differences in side-wall coverage.



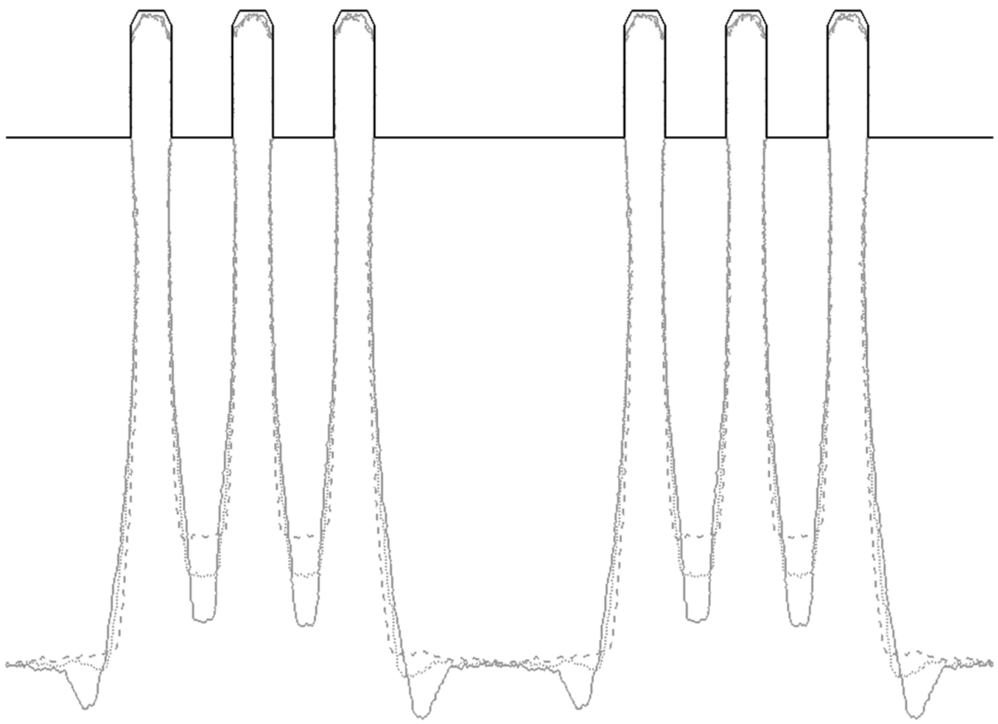
Neutral / Ion Transport

- Power density delivered by ions.
- Power is same in trench as open-field.
- Anisotropic ions are not sensitive to aspect ratio.
- Cl flux is lower in trench than blanket.
- Cl flux also depends on longitudinal position in trench.
- Neutral transport is the dominant cause of ARDE for these conditions.



ANIMATION SLIDE-GIF

Neutral / Ion Transport



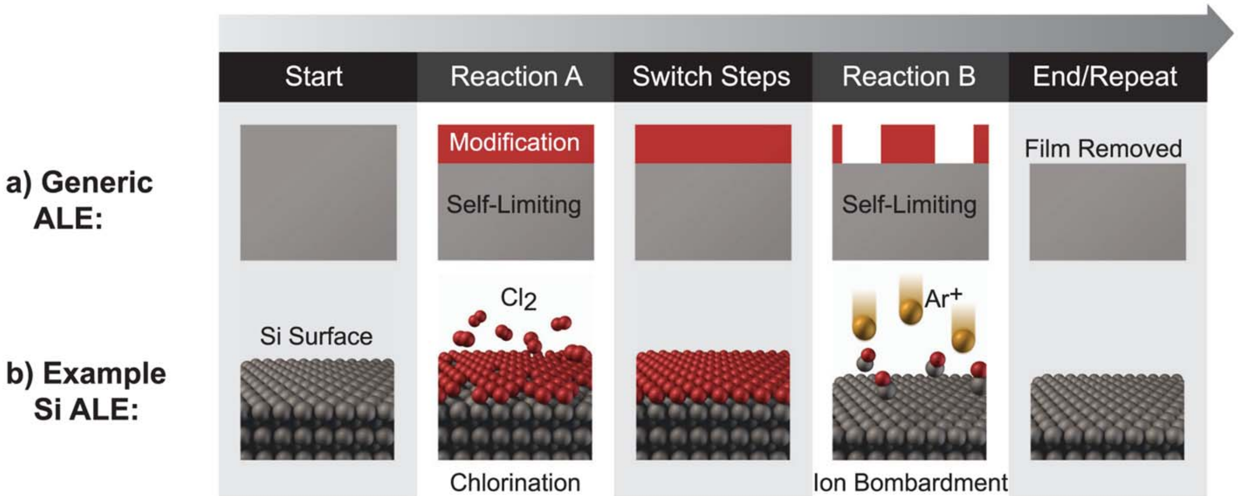
- Etch modeling allows for independent adjustment of neutral to ion flux ratio (Γ_n/Γ_i).
- Increasing Γ_n/Γ_i reduced ARDE, but:
  - Increased tapering.
  - Increased micro-trenching.
  - Reduced etch rate.

Q: What can etch modeling provide:

A: Access to etch conditions not possible in experiment.

Atomic Layer Etching

- Extreme selectivity, high rate and ARDE free etching are difficult to simultaneously achieve.
- Possible solution: Atomic Layer Etching (ALE)
- Example of Si ALE:
- Chlorination of surface Si reduces sputtering threshold of top layer.
- Chlorination (more generally passivation) is self-limited.
- Etching by low energy ion bombardment only removes chlorinated sites.



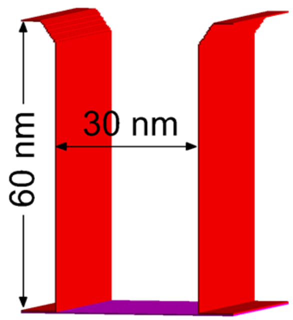
- K. J. Kanarik et al., J. Vac. Sci. Technol. A 33, 20802 (2015).

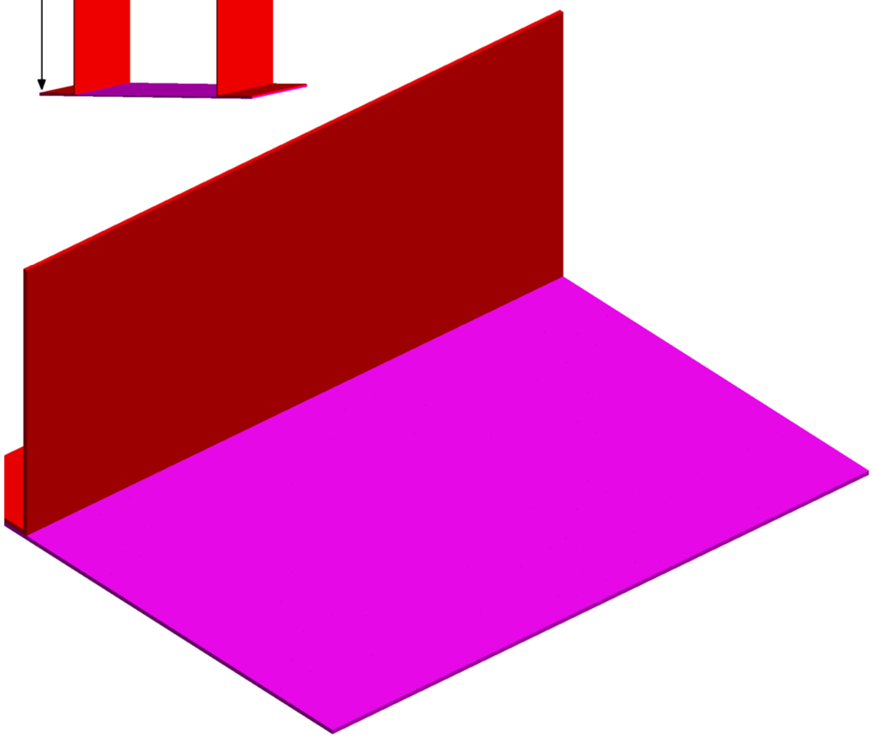
Challenges of ALE of Silicon

- In order to fully benefit from ALE, both passivation and ion bombardment phases must be self limiting.
- In the Ar/Cl_2 etching of Si, this ideally requires:
- Passivation phase:
  - No ion stimulated processes.
  - No thermal etching.
- Ion bombardment phase:
  - Ion energy > sputtering threshold of passivated $SiCl_x$
  - Ion energy < sputtering threshold of bare Si
  - No chlorinating species present (e.g., Cl, Cl^+, Cl_2^+).
- At the basic level, this is accomplished by separating passivation and ion bombardment in time.
- The ideal can not be achieved in experiment, only accessible in etch modeling.

ANIMATION SLIDE-GIF

Ideal ALE of Silicon in Ar/Cl_2 Plasma

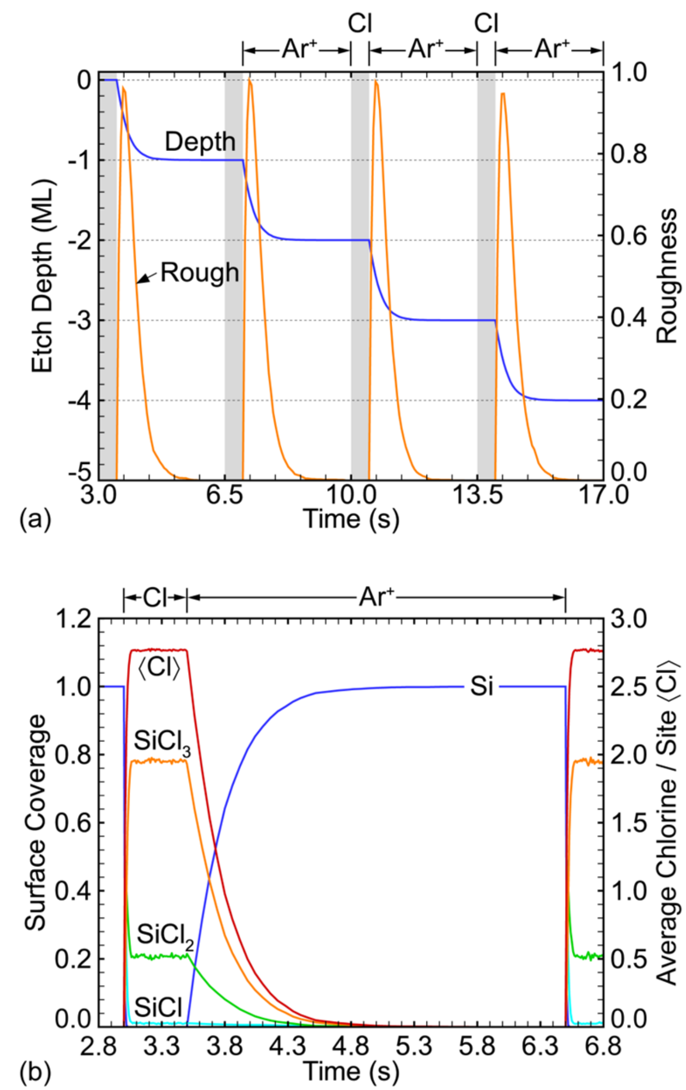




- Passivation phase (Cl):
  - Cl flux.
  - No ions.
- Ion bombardment phase (Ar^+):
  - Ar^+ flux.
  - Ion energy: 24 eV
  - Perfectly anisotropic angular distribution.
  - No passivating species (Cl, Cl^+ or Cl_2^+).
- Feature: 30 nm trench.
- Mesh size = 0.3 nm.
- Monolayer (ML) = 1 mesh layer.
- Note: Animation shows pulses with different time steps to resolve process.

Surface Kinetics in Ideal ALE

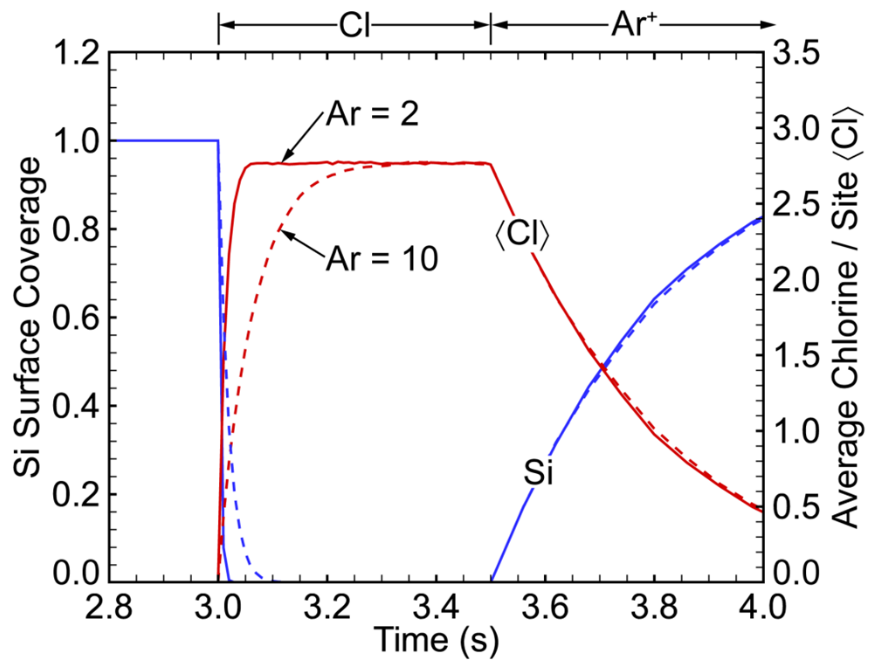
- Ar^+ phase: 3 s
- Cl phase: 0.5 s
- Aspect ratio: 2
- Etch depth shows exactly 1 monolayer (ML) removed in each cycle
- Roughness returns to 0 (perfectly flat etch front) after each pulse.
- Ion bombardment phase returns surface to entirely bare silicon.
- Gas purge times are excluded from the time scale.

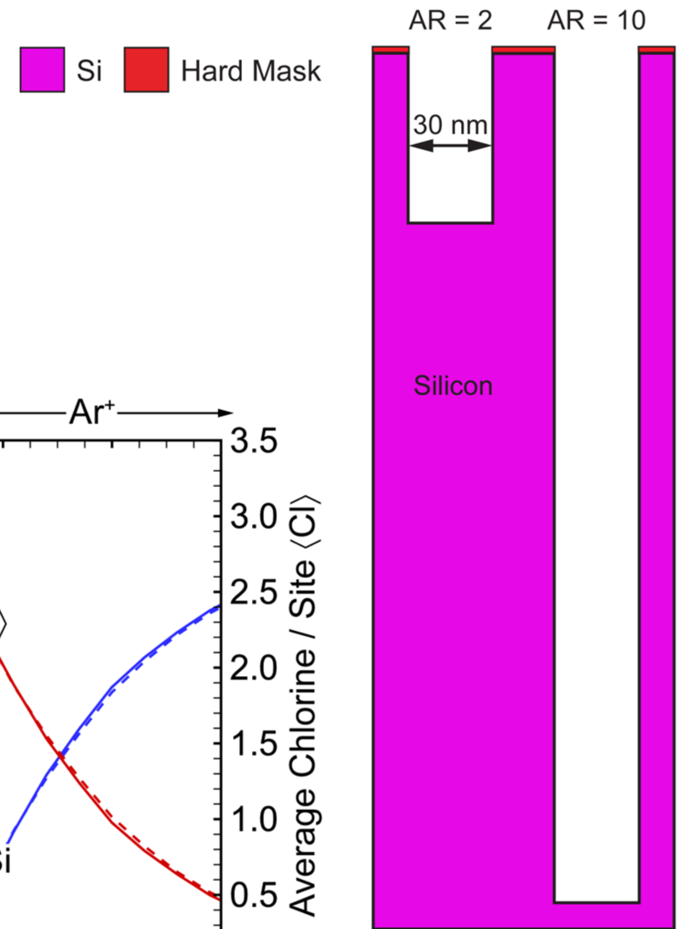


KLA Tencor

Aspect Ratio Dependence of Ideal ALE

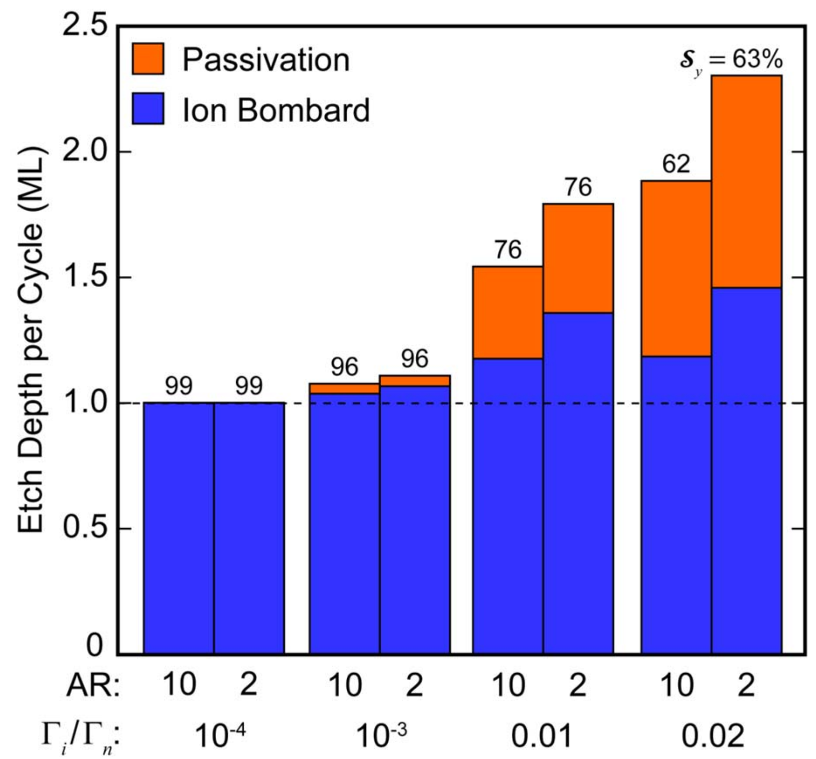
- Aspect ratios: 2 and 10
- Retention of ideal ALE characteristics with aspect ratio independent etch rate.
- AR=10 has significantly longer time to steady state in passivation phase.
- Longer passivation phase results from lower conductance of high AR.
- Nearly identical behavior during ion bombardment due to zero-angle spread of ions.





Impact of Ions During Passivation Phase

- Ideal ALE has no ions during passivation phase.
- The addition of a finite ion to neutral flux (ratio Γ_i/Γ_n) produces:
- > 1 ML etch per cycle (EPC).
- Surface roughness.
- Aspect ratio dependence.
- ALE synergy, S_y, is the percentage of etching done by self-limited processes (as opposed to continuous etching).
- Reduced synergy S_y as continuous etching occurs during passivation.

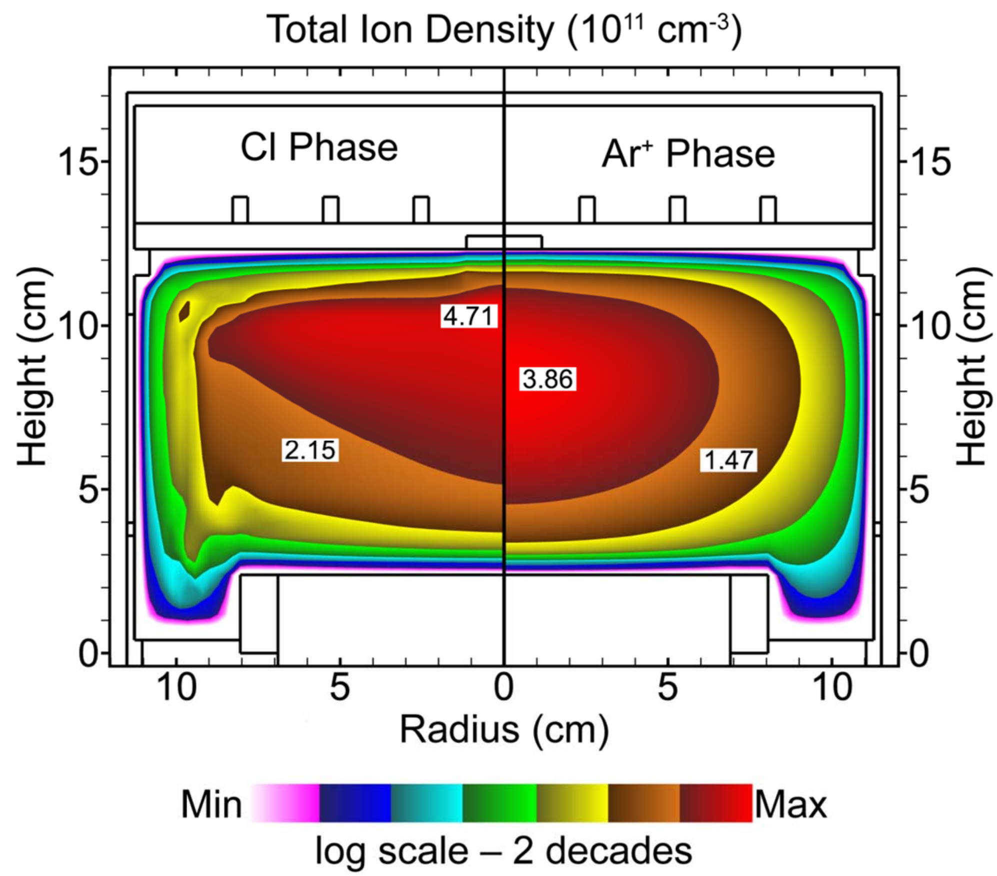


Q: What can etch modeling provide:

A: Efficient, parallel, mapping of large parameter spaces.

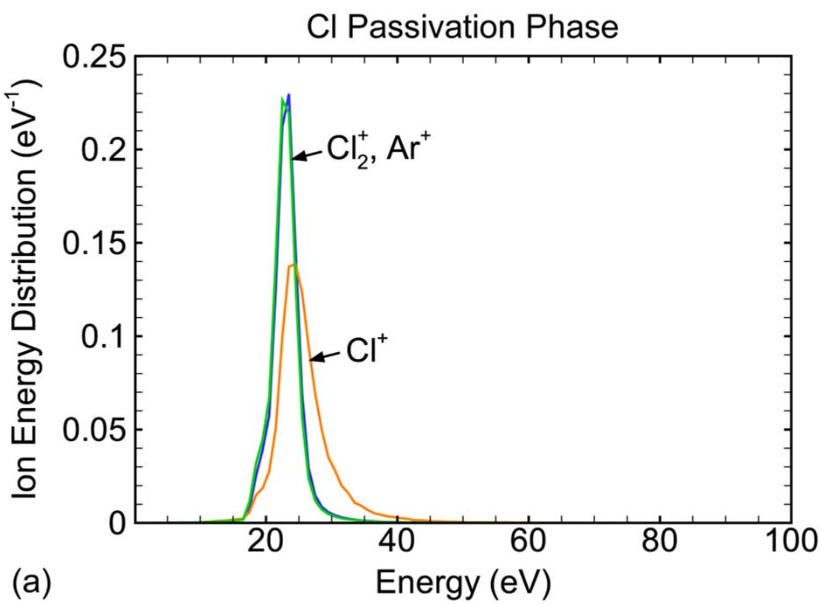
Reactor Scale Properties

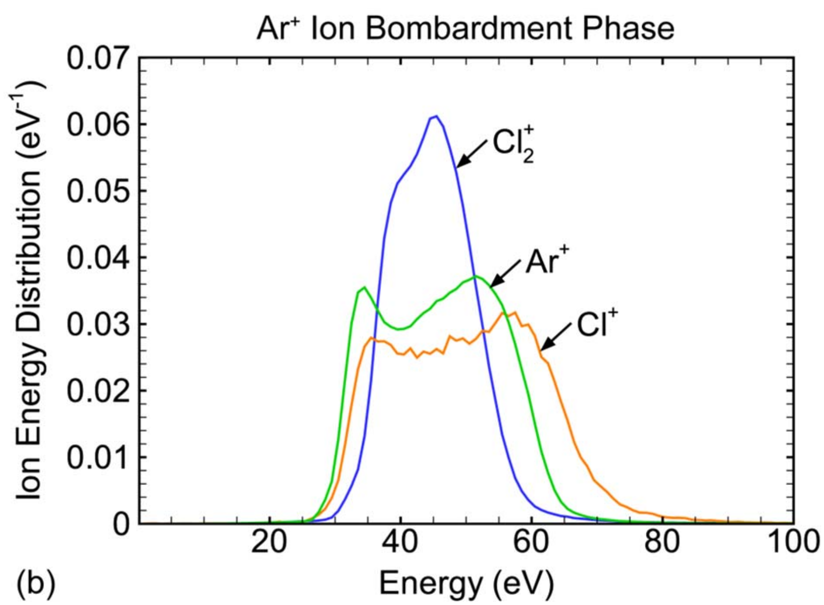
- Reactor scale simulations (HPEM) of an ICP were performed to provide non-ideal ion and radical fluxes, and IEADs.
- Conditions:
  - 20 mTorr, 200 sccm
  - 300 W ICP, 10 MHz
  - Passivation phase:
    - Ar/Cl_2 = 70/30
    - V_{bias} = 0 V
  - Ion bombardment phase:
    - Ar (100 ppm Cl_2)
    - V_{bias} = 30 V, 10 MHz



ALE Plasma Conditions

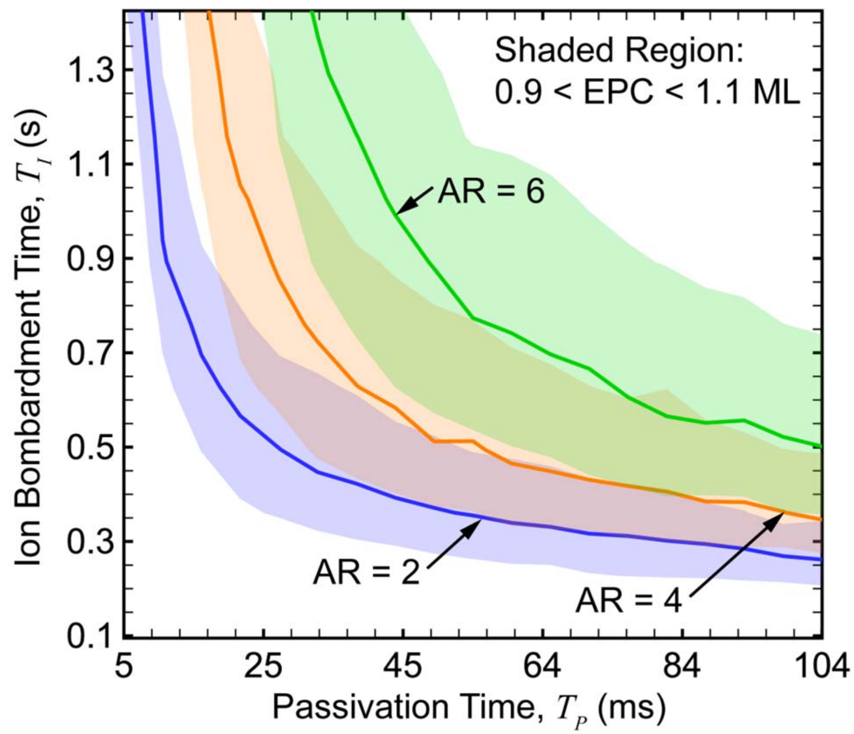
- Passivation phase:
  - Cl 7.0×10^{17} (cm^{-2} s^{-1})
  - Ar^+ 4.9×10^{14}
  - Cl_2^+ 1.1×10^{16}
  - Cl^+ 1.6×10^{15}
- Ion bombardment phase:
  - Cl 7.9×10^{14} (cm^{-2} s^{-1})
  - Ar^+ 2.3×10^{16}
  - Cl_2^+ 2.9×10^{12}
  - Cl^+ 9.2×10^{13}





Pulse Time Optimization

- With ideal conditions, ALE is achieved with any combination of (long enough) passivation and ion bombard times.
- With non-ideal fluxes, passivation and ion bombarding times producing ALE-like behavior (EPC = 1 ML) depend on AR.
- Even with non-ideal reactions, there will be some combination of pulse times yielding EPC=1 ML.
- EPC = 1 ML does not necessarily equate to optimized ALE outcomes (roughness, ARDE)

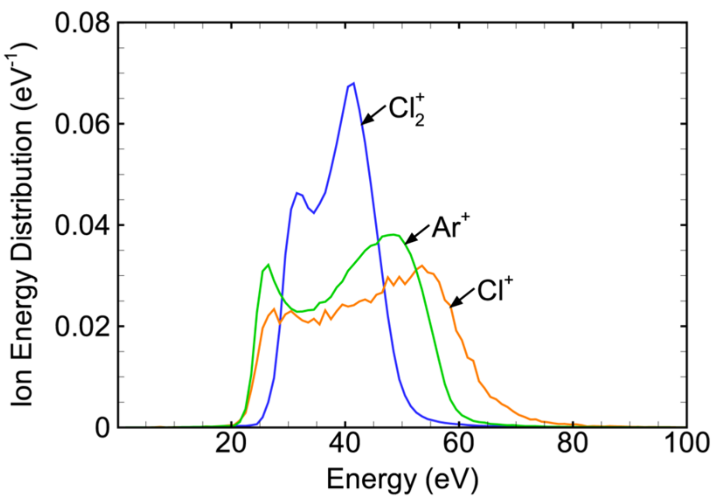


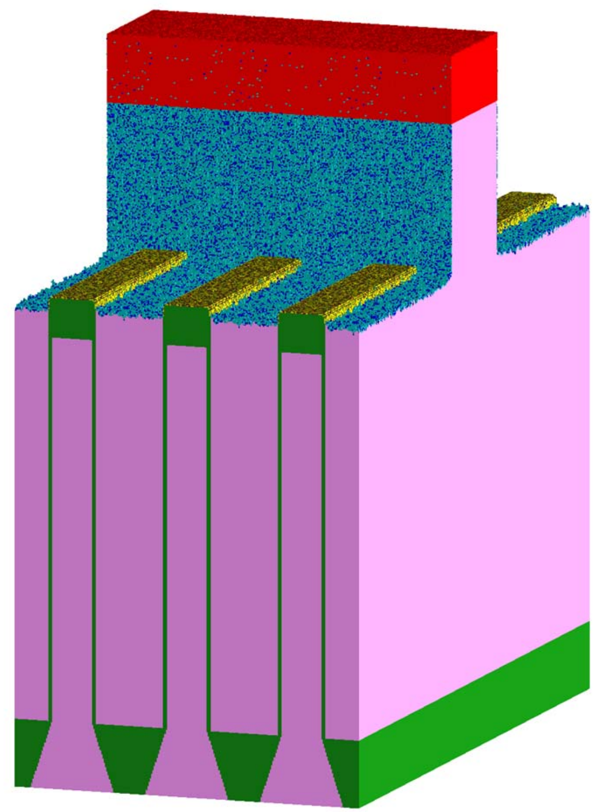
- Etch depth per cycle (EPC) vs pulse times
- Solid line: EPC = 1 ML
- Shaded region: 0.9 < EPC < 1.1 ML

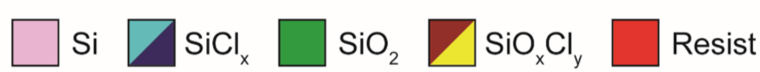
Clearing 3D Corners with Low Bias RIE

- Vbias = 30 V, Ar/Cl2 = 70/30
- Max ion energy: 75 eV
- Etch time: 279 s
- Highly tapered etch profile results in material buildup in corners.

- Material in corners is difficult to remove.
- With 175% over-etch, 3D corners not completely cleared.





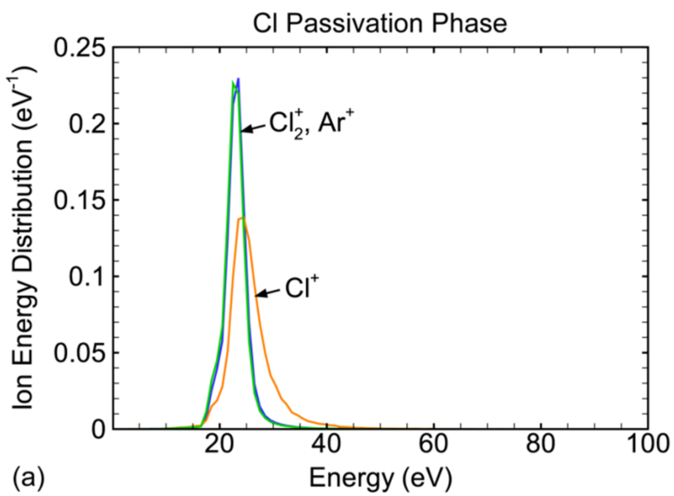


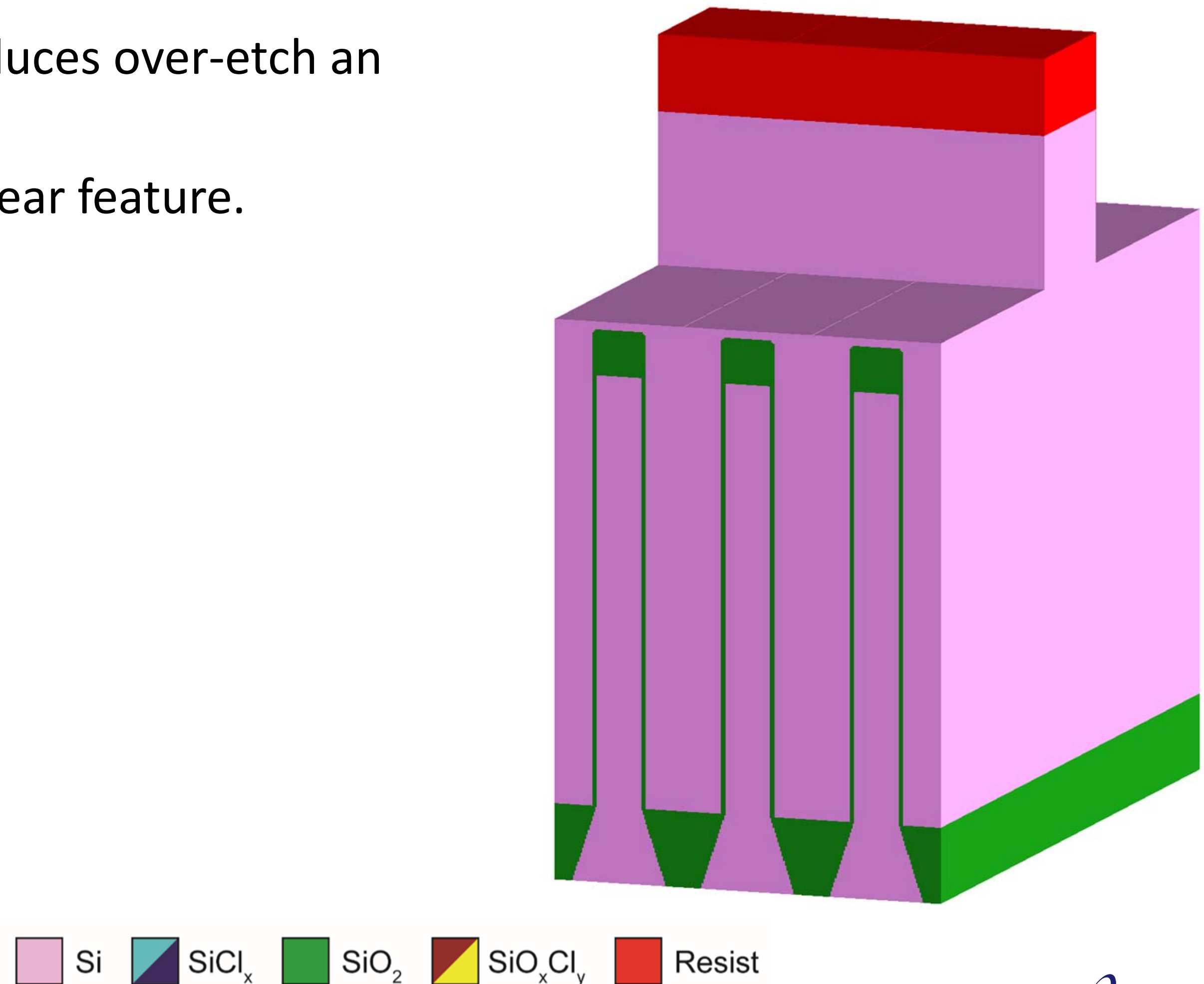
KLA-Tencor

ANIMATION SLIDE-GIF

Clearing 3D Corners with Low Bias RIE

- Optimized ALE removes taper, reduces over-etch an has higher selectivity.
- Only 25% over-etch required to clear feature.
- Penalty is longer etch time.



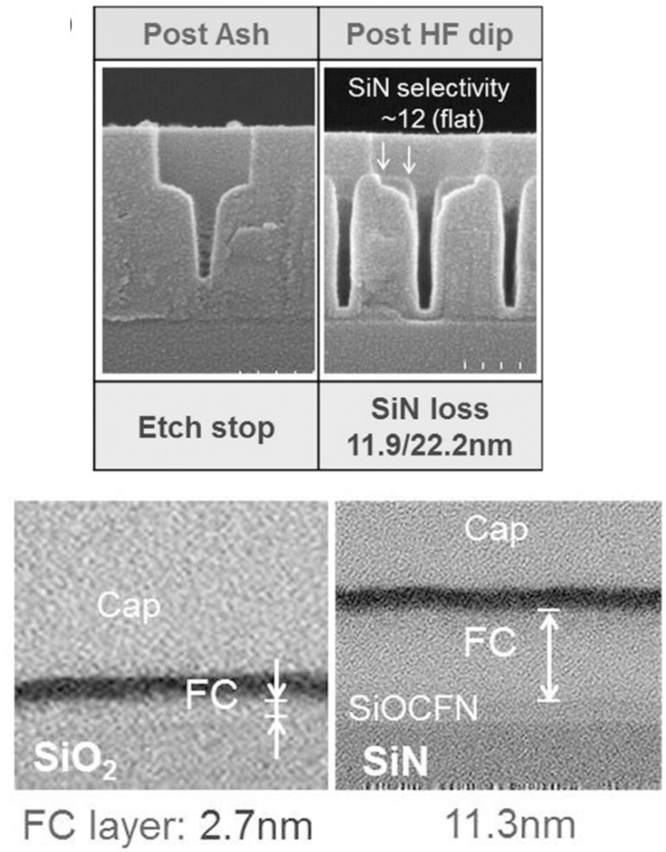


KLA-Tencor

Q: What can etch modeling provide:
A: Understanding/confirming physical etch mechanisms.

Selective Etching in High Aspect Ratio Features

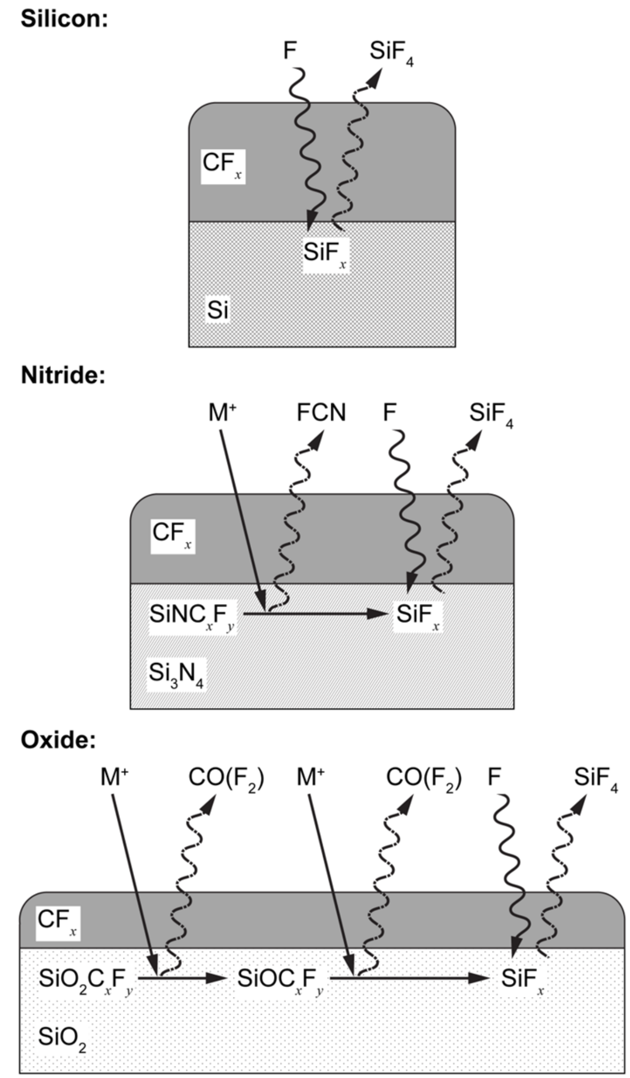
- Selective etching of SiO_2 over Si_3N_4 is critical for manufacturing.
- Selectivity during dielectric plasma etching is based on polymer thickness.
- Si_3N_4 typically has a thicker polymer layer than SiO_2, and so a slower etch rate.
- Thick polymer layers may produced tapered features, critical dimension (CD) loss.
- When aspect ratio increases, CD loss becomes large enough that etch stops.
- Self aligned contact may not complete etch using conventional process.



- M Honda et al, J. Phys. D. 50 234002 (2017)

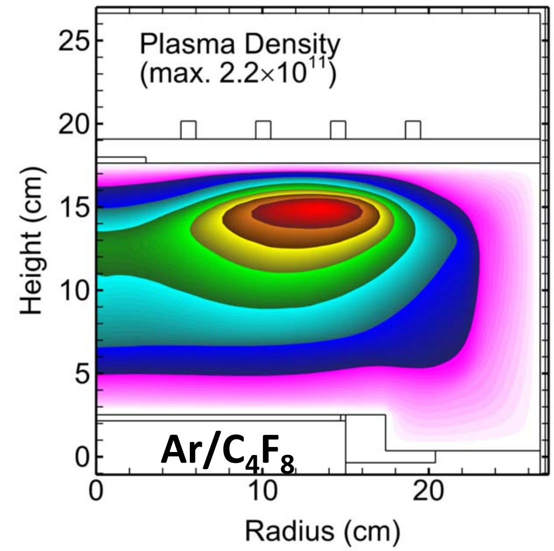
Selective Etching in High Aspect Ratios

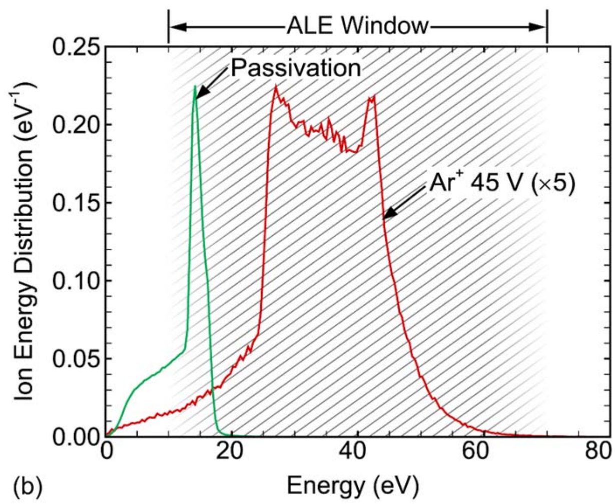
- $SiO_2C_xF_y$ complex formed at the polymer/SiO_2 interface.
- Oxygen is abstracted by ion activated desorption of $CO(F_2)$, forming $SiOC_xF_y$ then SiF_x.
- On nitride only one interfacial species is used, $SINC_xF_y$.
- Nitrogen is abstracted as FCN leaving SiF_x.
- SiF_x can be etched thermally by fluorine radicals, or by chemical sputtering from ion energy.



C_xF_y ALE Plasma Conditions

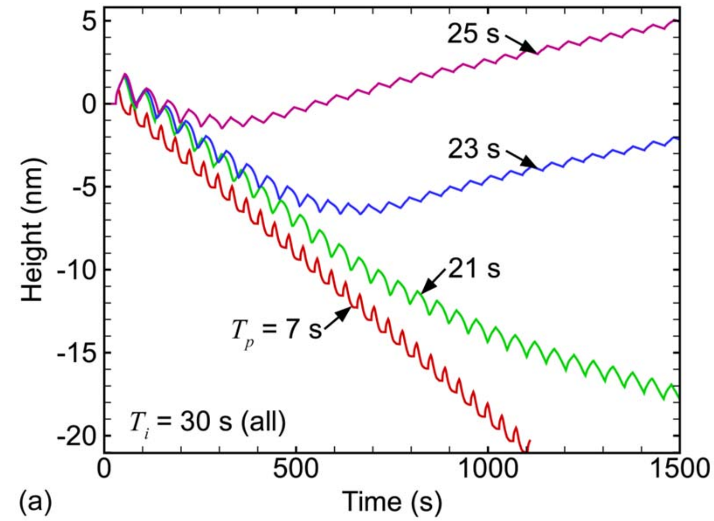
- HPEM executed for Step 1, Step 2
- Step 1: Passivation (T_p)
  - Ar/C_4F_8 = 95/5, 40 mTorr
  - 300 W ICP, 0 V RF bias
- Step 2: Ion Bombardment (T_i)
  - Ar (100 ppm C_4F_8), 40 mTorr
  - 600 W ICP, 45 V RF bias
- Ideal ion bombardment conditions do not include CF_2 or F.



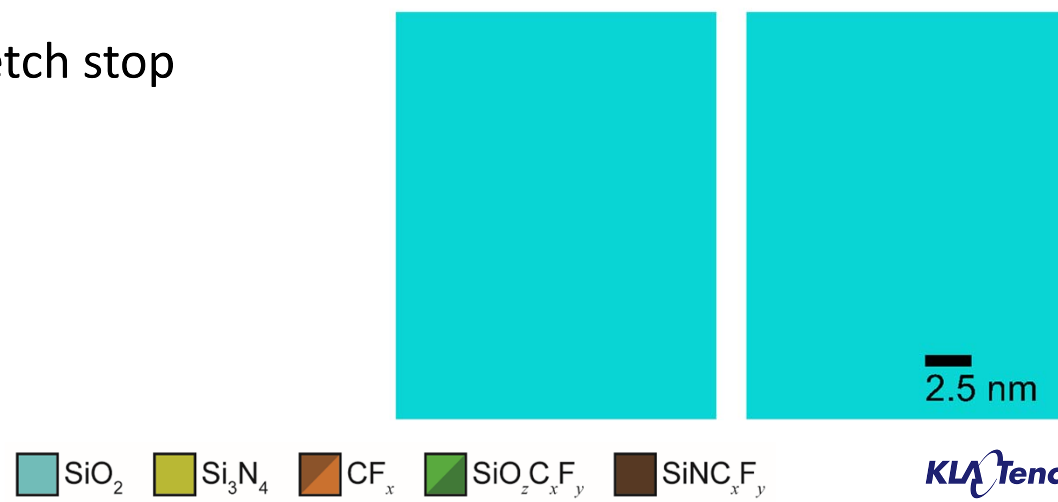


ALE Pulsing on SiO_2 Using Ideal Fluxes

- T_i = length of ion bombardment step
- T_p = length of polymerization step
- Not all conditions result in steady state etching.
- Large T_p results in polymer buildup over time.
- Once polymer thickness reaches critical value, etching stops.
- Fewer pulses are required to reach etch stop with higher T_p.



- T_p = 7 s
- T_p = 23 s

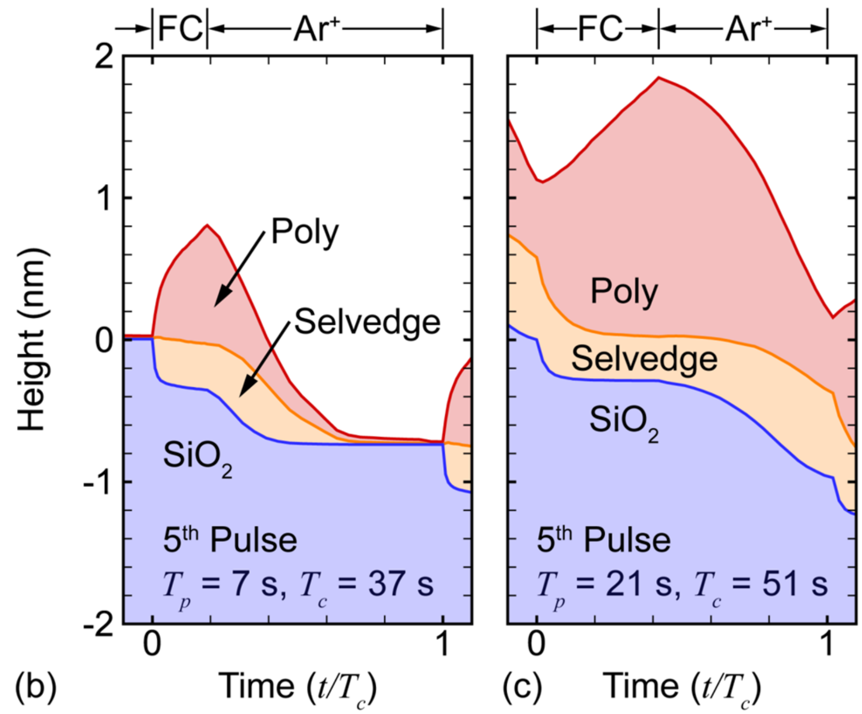


ANIMATION SLIDE-GIF

KLA-Tencor

Ideal ALE Surface Kinetics

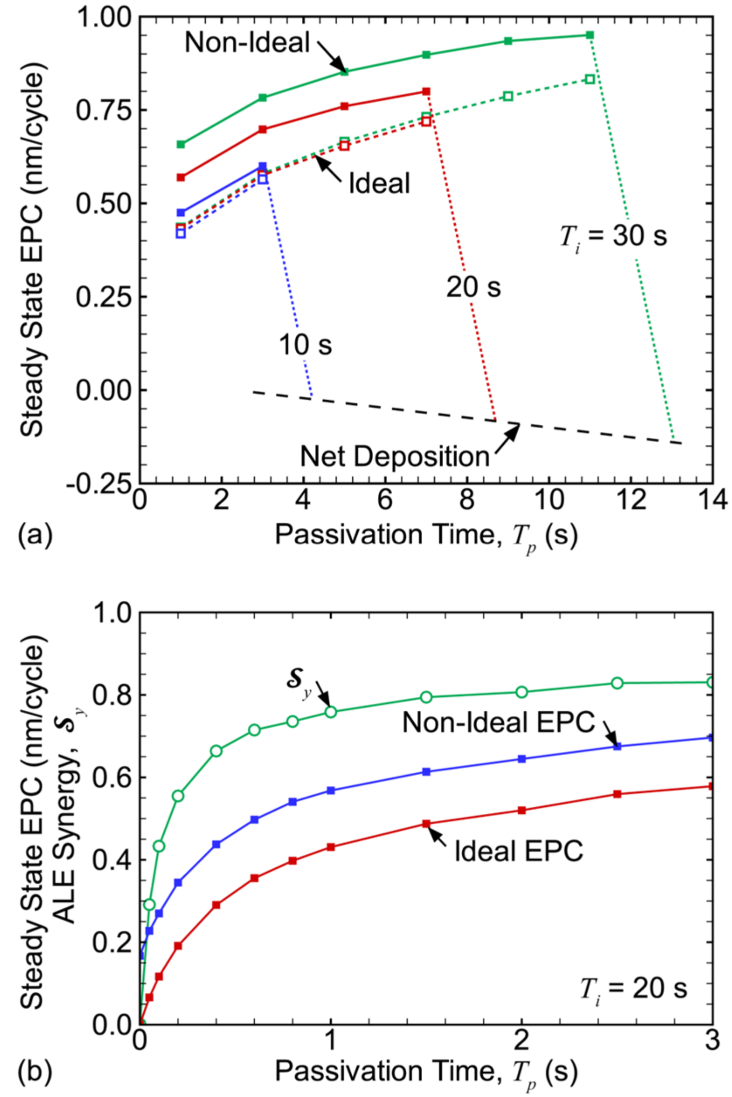
- Pristine SiO_2 is eroded in two self limited phases.
  - During fluorocarbon passivation phase, SiO_2 is converted to selvedge material.
  - During ion bombardment, the polymer is consumed by converting SiO_2 to selvedge, which is subsequently etched.
- With ideal fluxes both phases are self limited.



- For T_p =7 s, the polymer is completely removed by the end of the ion bombardment.
- For T_p = 21 s the polymer not completely removed, eventually building up and causing etch stop.

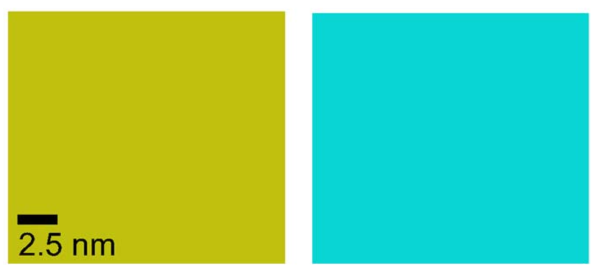
Steady State ALE of SiO_2

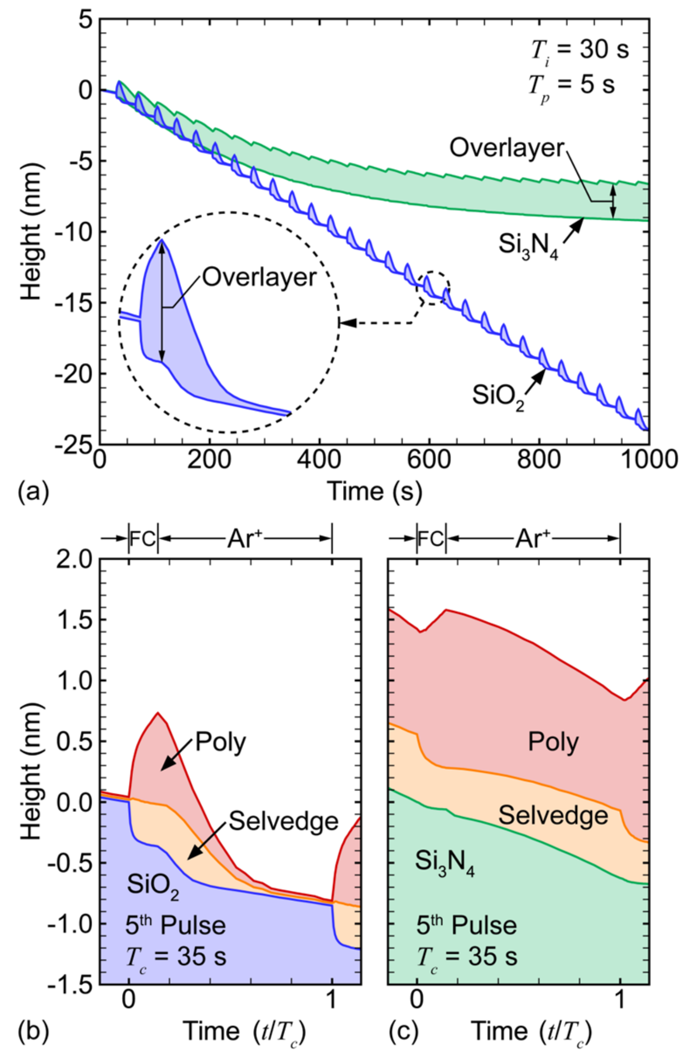
- For ideal ALE, etch-per-cycle (EPC) depends on T_p, but not T_i.
- For non-ideal ALE, EPC depends on both T_p and T_i.
- At low T_p, EPC of ideal ALE goes to zero.
- EPC of non-ideal ALE > 0 at $T_p = 0$ due to continuous etching in ion bombardment phase.
- Synergy is zero at $T_p = 0$, quickly rises to 0.80 at $T_p = 1.5$ s.
- For $T_p > 1.5$ s synergy slowly rises to 0.9 right before etch stop.
- ALE Synergy = EPC / (Ideal EPC)



Steady State ALE of SiO_2

- Using non-ideal fluxes
- Ion bombardment phase is no longer perfectly self limited as small rate of continuous etching occurs.
- For same T_p, Si_3N_4 etch stops while SiO_2 does not.
- Si_3N_4 does not consume as much polymer when etching – thicker polymer slows etching.
- Si_3N_4 has almost continuous etching during both ALE cycles.

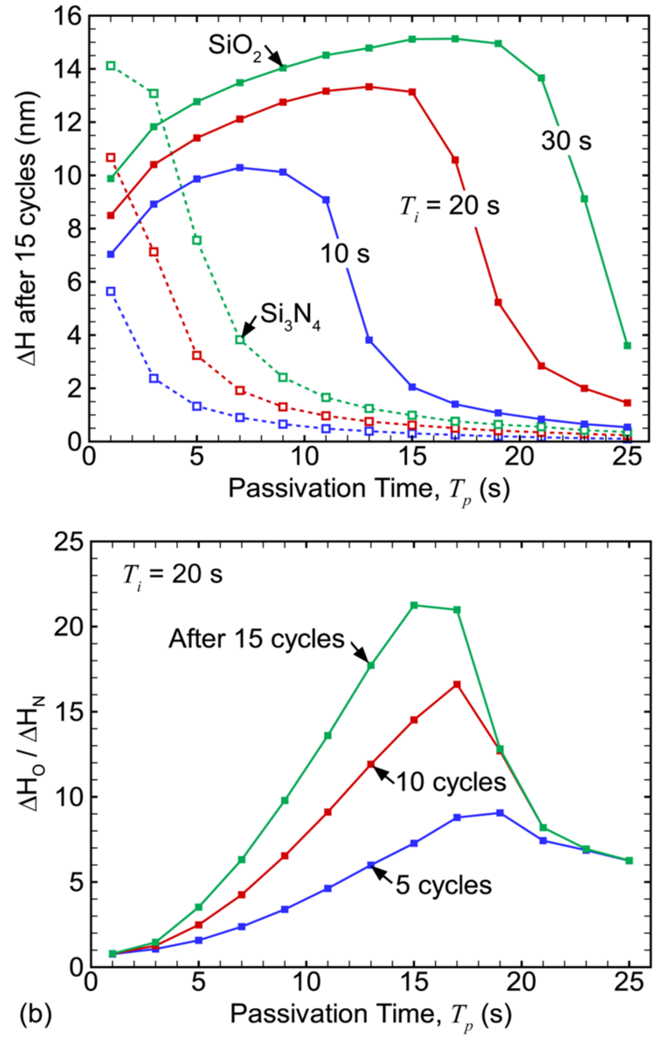




ANIMATION SLIDE-GIF

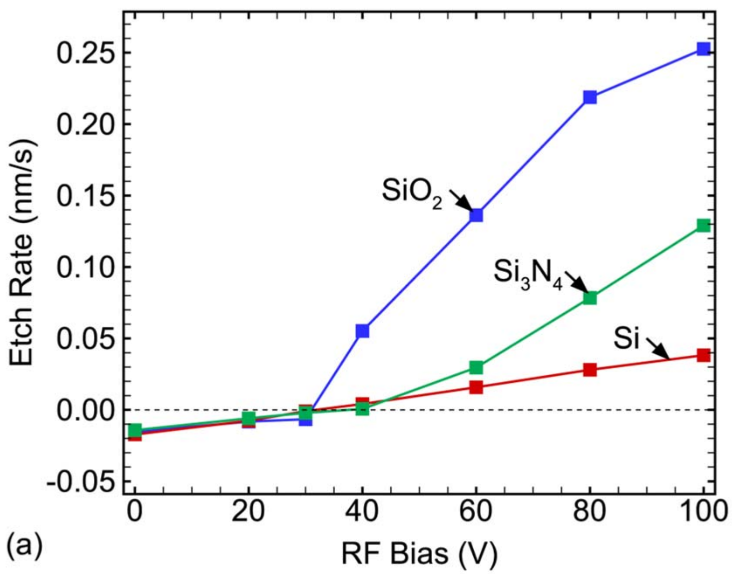
Selectivity of ALE to SiO_2

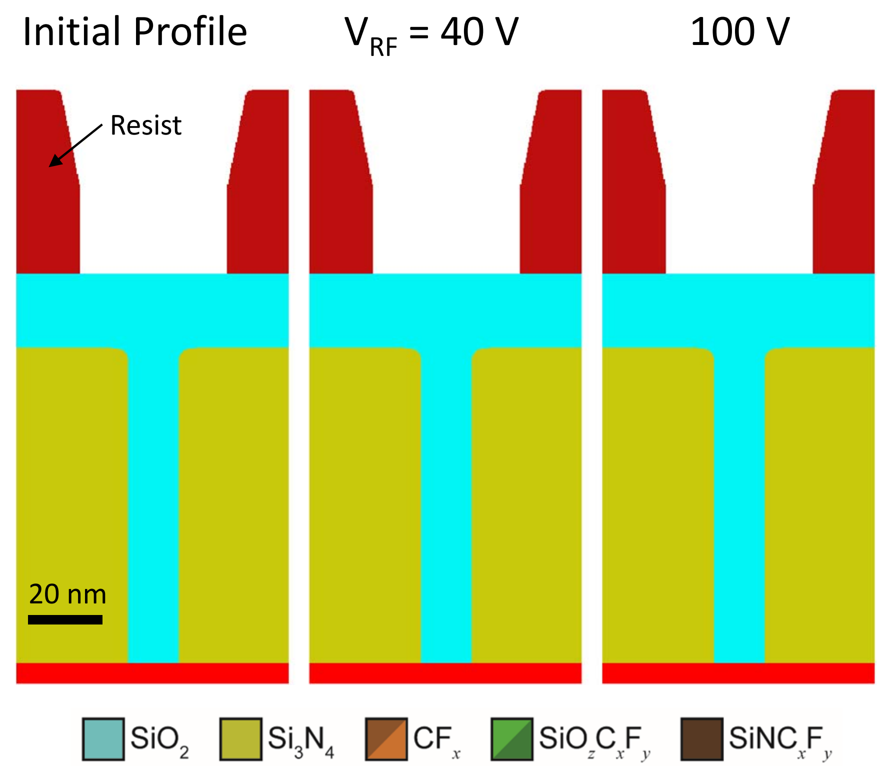
- ΔH - change in height of the target material.
- No values of T_p > 1 s result in steady state etching of Si_3N_4.
- Transient etching accounts for large portion of ΔH for small T_p.
- Selectivity increases with T_p until SiO_2 reaches etch stop.
- Selectivity decreases with fewer pulses.



Self Aligned Contacts

- Continuous etching with V_{RF} = 40 V results in high selectivity, but polymer buildup causes early etch stop.

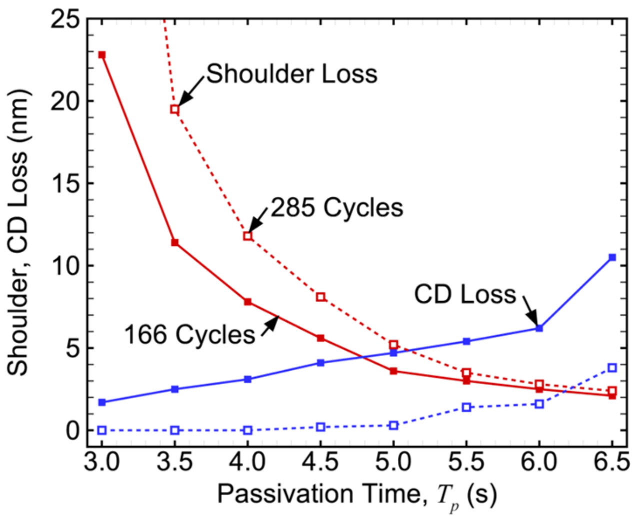


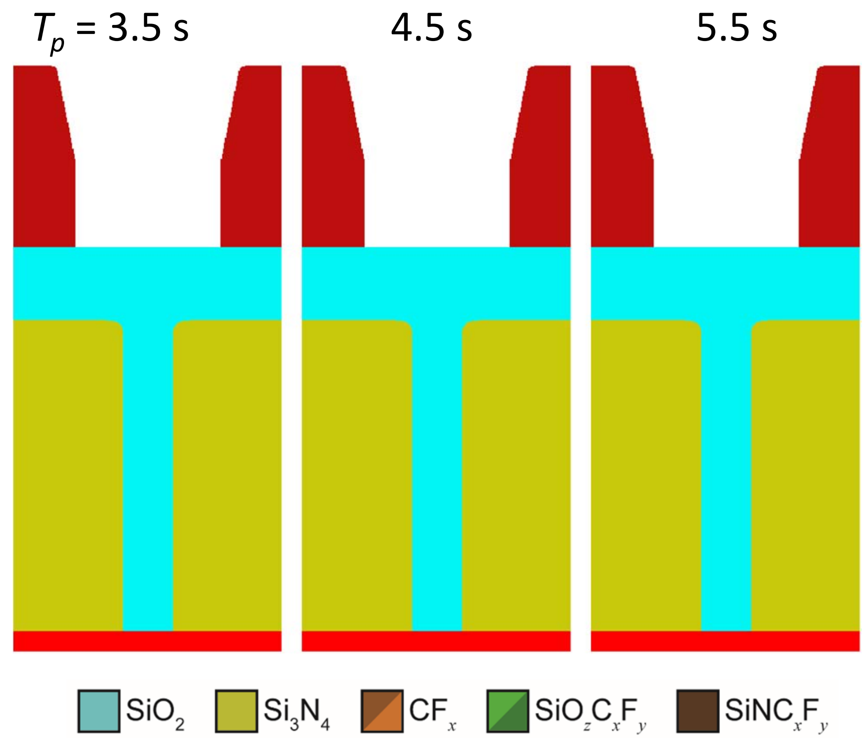


- Increasing V_{RF} to 100 V allows SiO_2 etching to reach contact, but causes significant Si_3N_4 shoulder erosion.

Self Aligned Contacts

- Wide range of ALE conditions can clear the SAC feature with low damage to Si_3N_4 shoulder.
- Longer T_p increases selectivity with less shoulder loss.

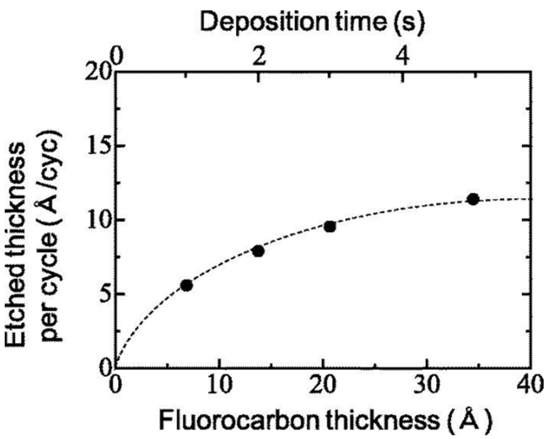


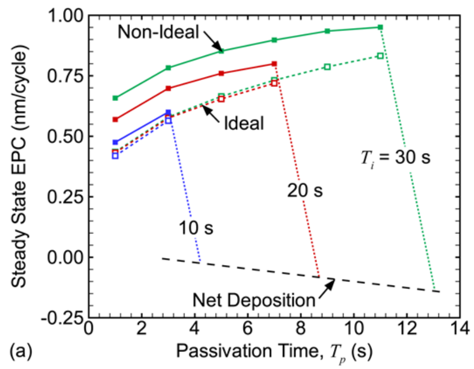


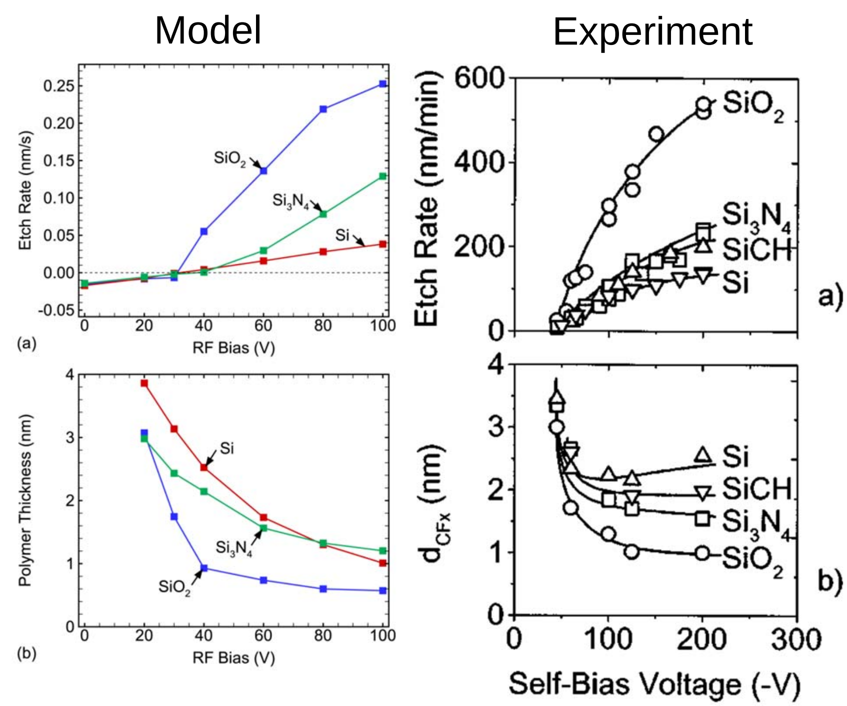
- Longer T_p results in critical dimension (CD) loss at the contact point.
- Increasing over-etch time can reduce CD loss with little change in shoulder loss (for T_p > 5.5 s).

Fluorocarbon Model Validation

- Polymer thickness and etch rate show comparable trends in RF bias as experiment.
- Trend in EPC as a function of passivation time (polymer thickness) comparable to experiment.



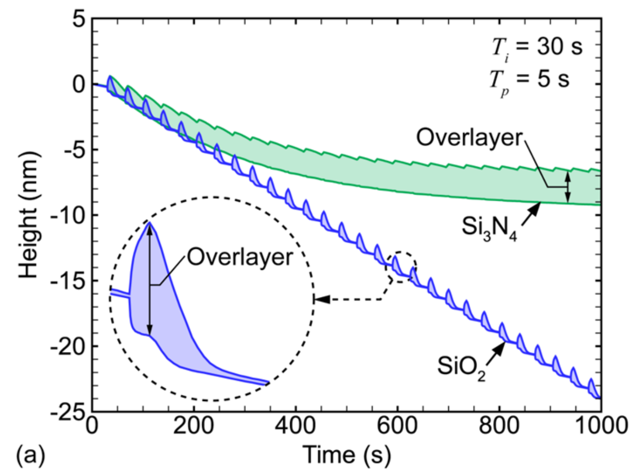




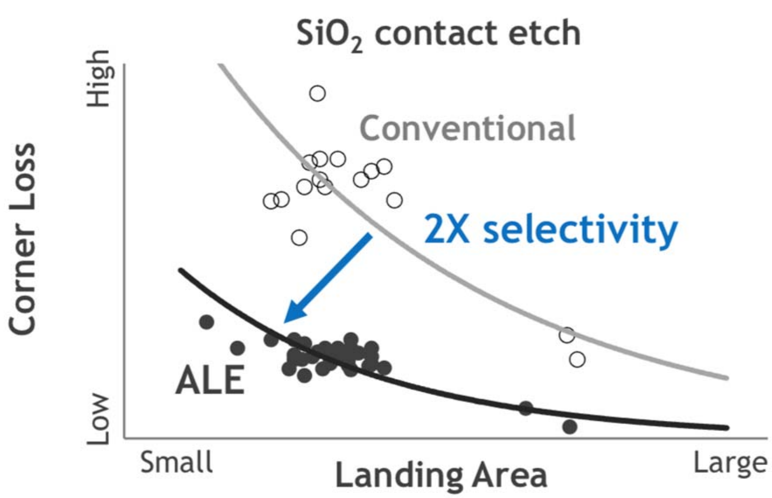
- T. Tsutsumi, et al. *JVST A* 35 01A103 (2017)
- T. Standaert et al., *JVST A* 22, 53 (2004).

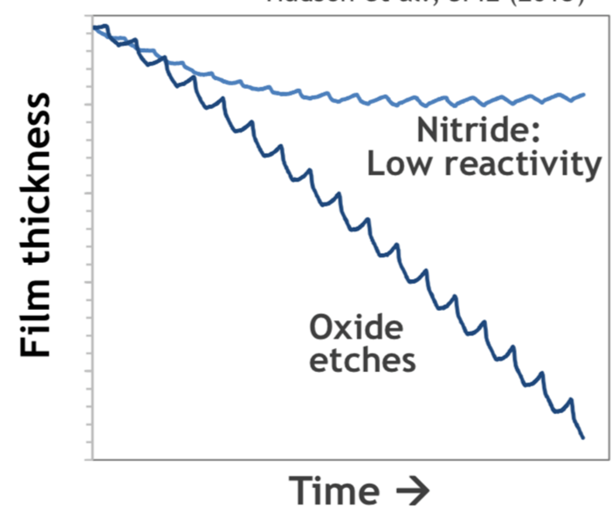
Fluorocarbon ALE Validation

- Trend of transient etching of Si3N4 is seen in experiment.
- Experimental ALE is able to reduce corner loss without reducing landing area.



Hudson et al., SPIE (2015)





- Gottscho, ALE (Denver, 2017).

Concluding Remarks

- Computational etch modeling compliments experiments.
- Modeling offers access to impossible to difficult or impossible to create etch conditions (i.e. ideal ALE etch).
- Modeling can de-couple parameters which are tightly coupled in physical world.
- Modeling can give insight into physical etch mechanisms, which are often difficult to isolate in experiment.
- Modeling can explore a large parameter space efficiently using massive parallelism.
- ALE performance benefits are closely coupled to the self-limited nature of the half-reactions.
- Quasi-ALE of SiO_2 can be achieved using C_4F_8 passivation, but etch per cycle is coupled to passivation time through the polymer thickness.
- ALE of SiO_2 can be highly selective over Si_3N_4 in the steady state, but only after a transient period of reduced (or even inverse) selectivity.

Special Thanks

- Prof. Mark Kushner, for advising my thesis studies and providing access to MCFPM and HPEM for this work.

- Additional Resources:
  - C. M. Huard, et al., "Role of neutral transport in aspect ratio dependent plasma etching of three-dimensional features." *JVST A* **35** 05C301 (2017).
  - Y. Zhang, et al. "Investigation of feature orientation and consequences of ion tilting during plasma etching with a three-dimensional feature profile simulator." *JVST A* **35** 021303 (2017).
  - C. M. Huard, et al., "Atomic layer etching of 3D structures in silicon: Self-limiting and nonideal reactions." *JVST A* **35** 031306 (2017).
  - C. M. Huard, S. J. Lanham, and M. J. Kushner. "Consequences of atomic layer etching on wafer scale uniformity in inductively coupled plasmas." *Journal of Physics D* **51** 155201 (2018).
  - C. M. Huard, et al., "Transient Behavior in Quasi-Atomic Layer Etching of Silicon Dioxide and Silicon Nitride in Fluorocarbon Plasmas" *JVST A* in review (2018)