ESH-Friendly Cleaning and Rinsing of Multi-Material Surfaces and Structures

(*Task Number: : 425.043)*

Co-PIs:

- **Srini Raghavan: Materials Science and Engineering, UA**
- **Manish Keswani: Materials Science and Engineering, UA**
- **Farhang Shadman: Chemical Engineering, UA**

Graduate Students:

- **Chieh-Chun Chiang: Ph.D student; Materials Science and Engineering, UA**

Undergraduate Students:

- **Andrew Jimenez: Chemical Engineering, UA**
- **Michael McBride: Chemical Engineering, UA**

Other Researchers:

- **Reza Dodge: Chemical Engineering, UA**
- **Omid Mahdavi: Micro/Nano Fabrication Center, UA**
- **Jivaan Kishore: Chemical Engineering, UA**

Cost Sharing: $40k from WSP(Arizona TRIF) and $25k from ProSys

Objectives, Method of Approach, Impact

Objective:

- Understand the bottleneck of the rinse process involving small structures, particularly those involving multi-materials
- Develop methods for reducing the water usage by mitigating the rinse bottlenecks

Method of Approach:

- Application of a test structure and testbed
- Process simulation

ESH Impact:

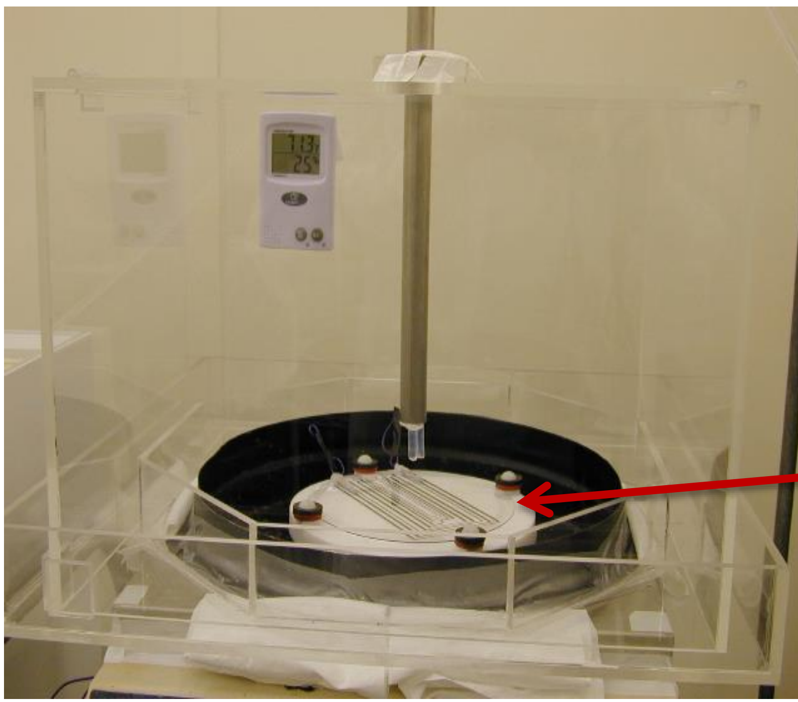
- Robust and efficient rinse processes would have major impact on reducing water and energy usage in fabs

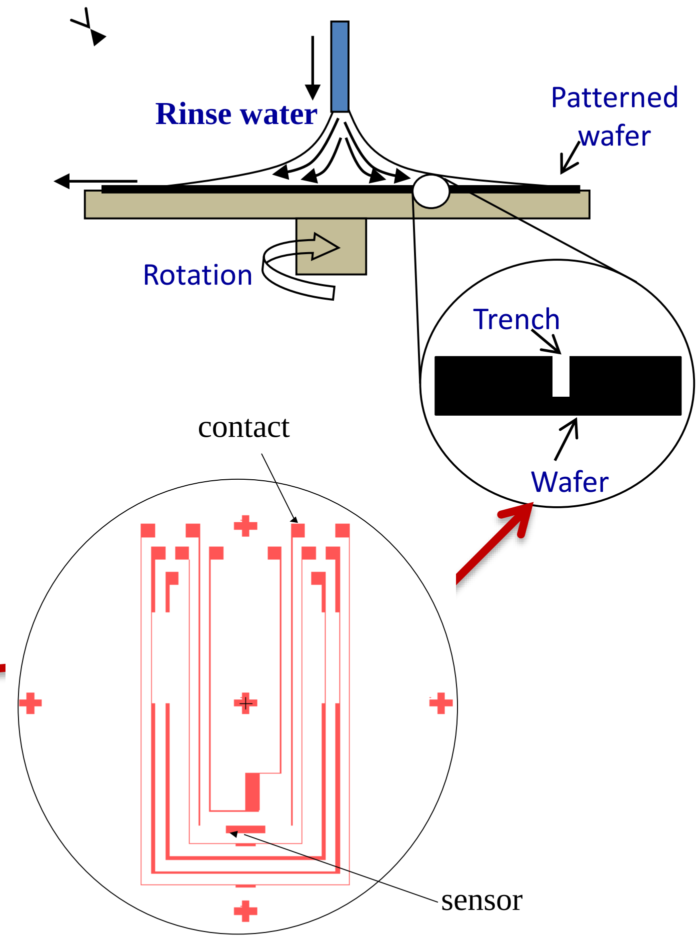
Summary of the Work

During Years 1 and 2 of the Project

1. Testbed for Single-Wafer Spin Rinsing

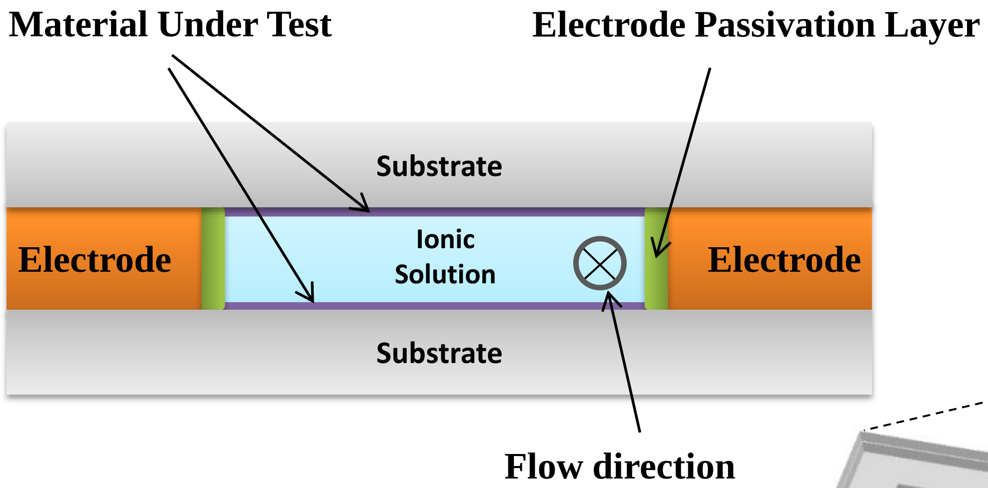
- **Single-wafer spin rinse tool equipped with Electro-Chemical Residue Sensor (ECRS) for wafer-level rinse studies.**
- **Effect of wafer size, flow rate, and feature size.**
- **Methods for minimizing water usage.**

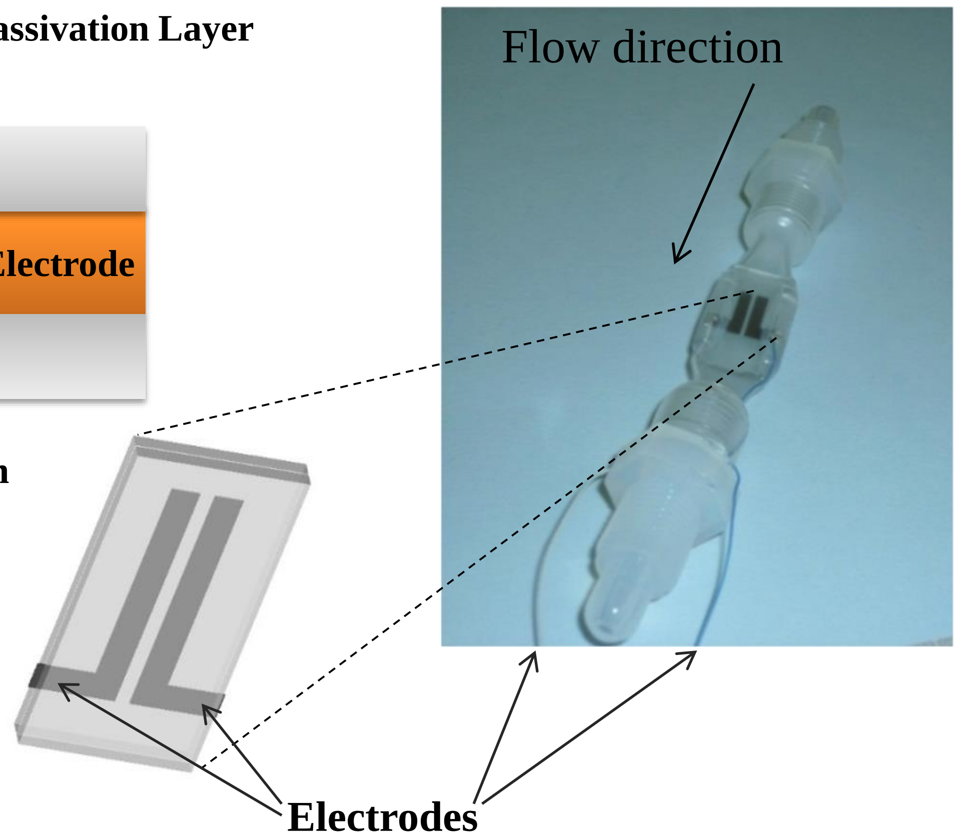




2. Adsorption/Desorption Test Cell

A Novel Device for Direct Measurement of Surface Interactions



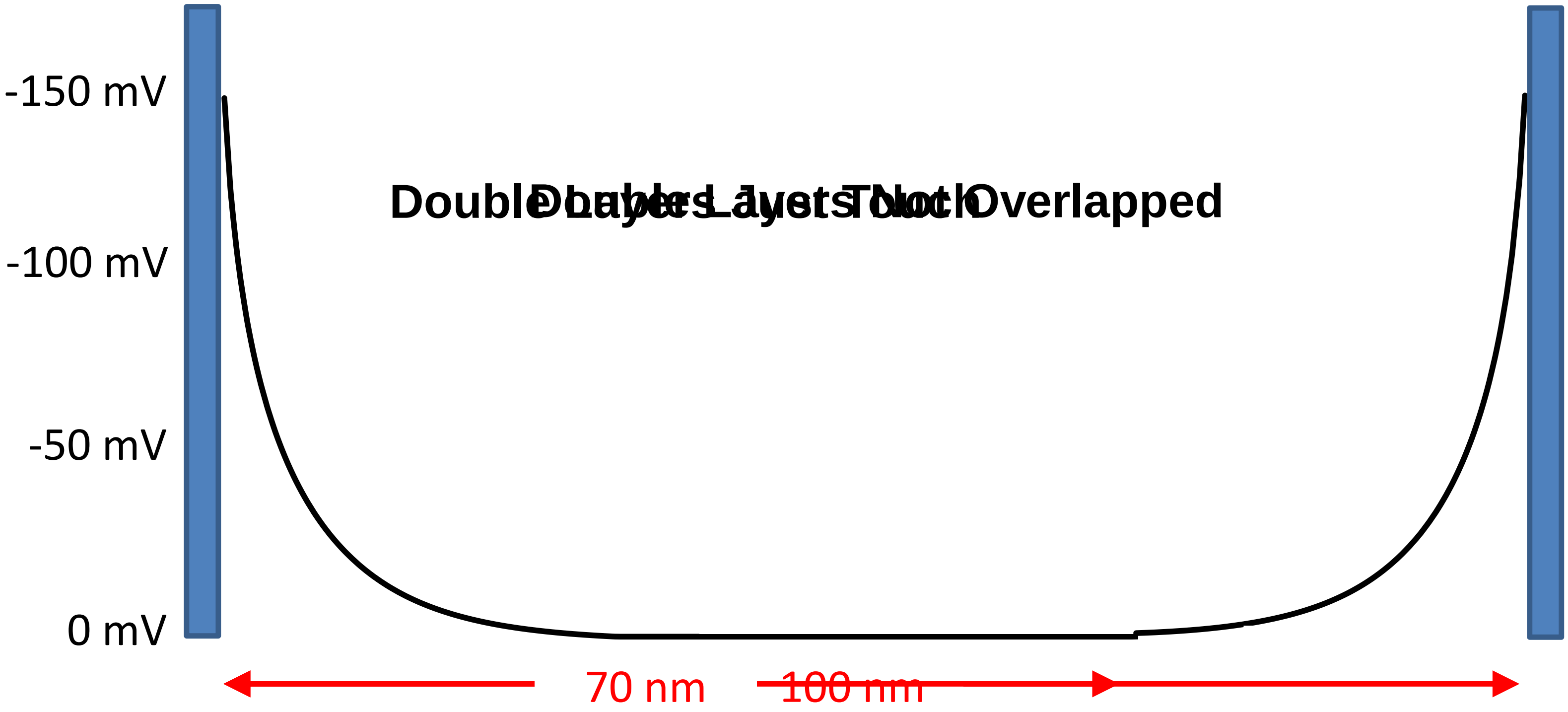


Typical Cell Thickness: 5-25μm
Typical Electrodes Spacing: 0.5-10 mm

Test cell was used to determine the kinetics of adsorption and desorption of NH_4^+ and SO_4^{-2} on Si and SiO_2

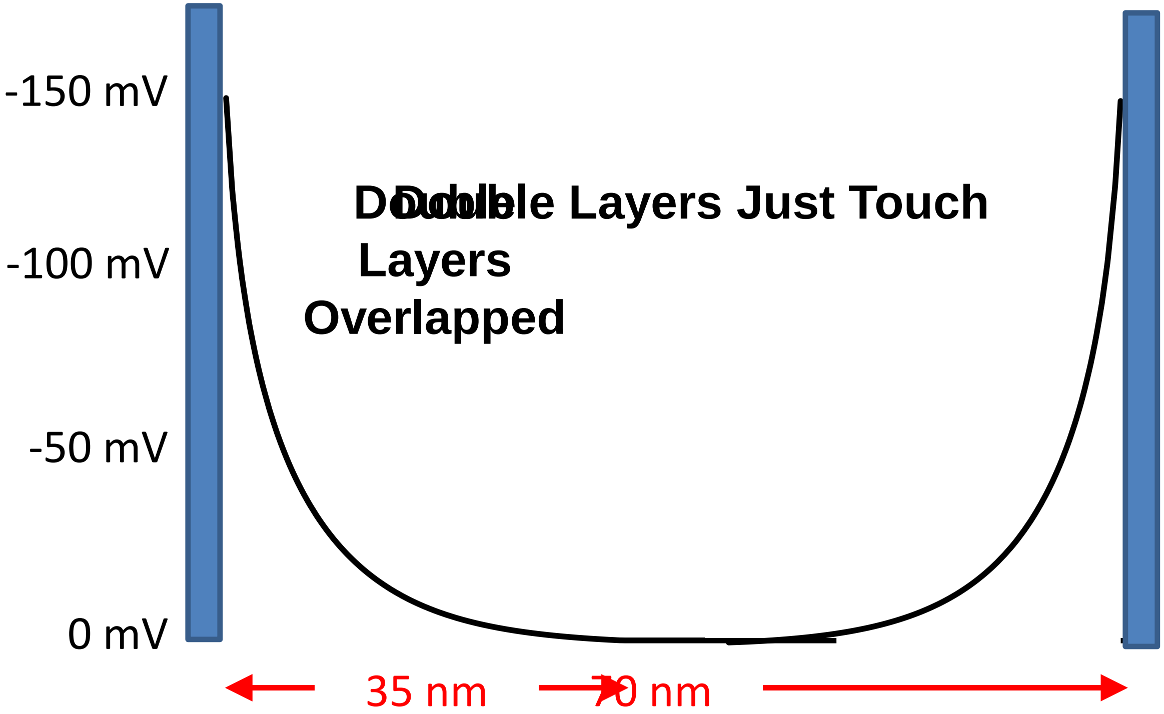
Overlapping of Double layer

Two SiO_2 plates immersed in 0.196 M NH_4OH



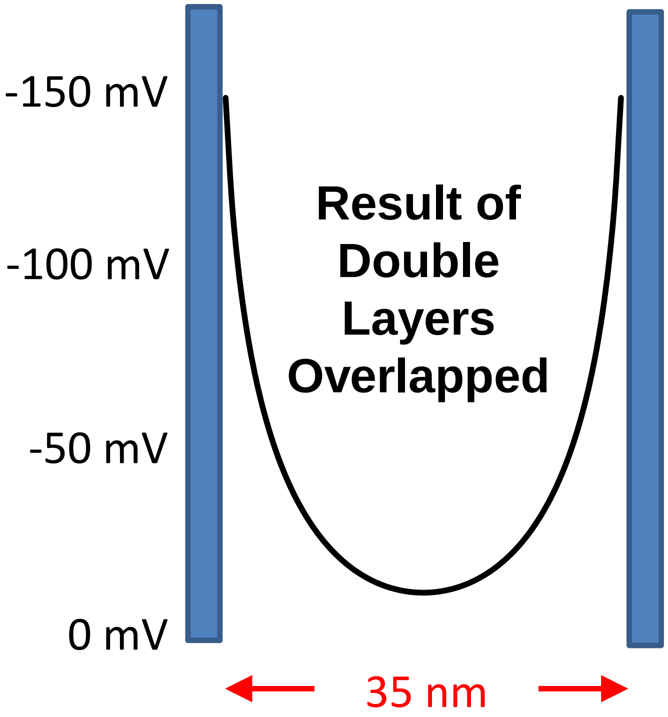
Overlapping of Double layer

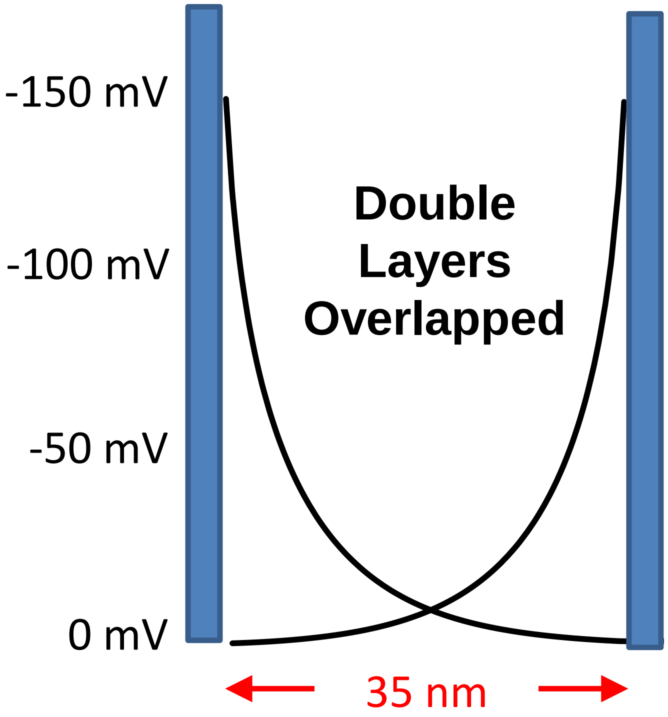
Two SiO_2 plates immersed in 0.196 M NH_4OH



Overlapping of Double layer

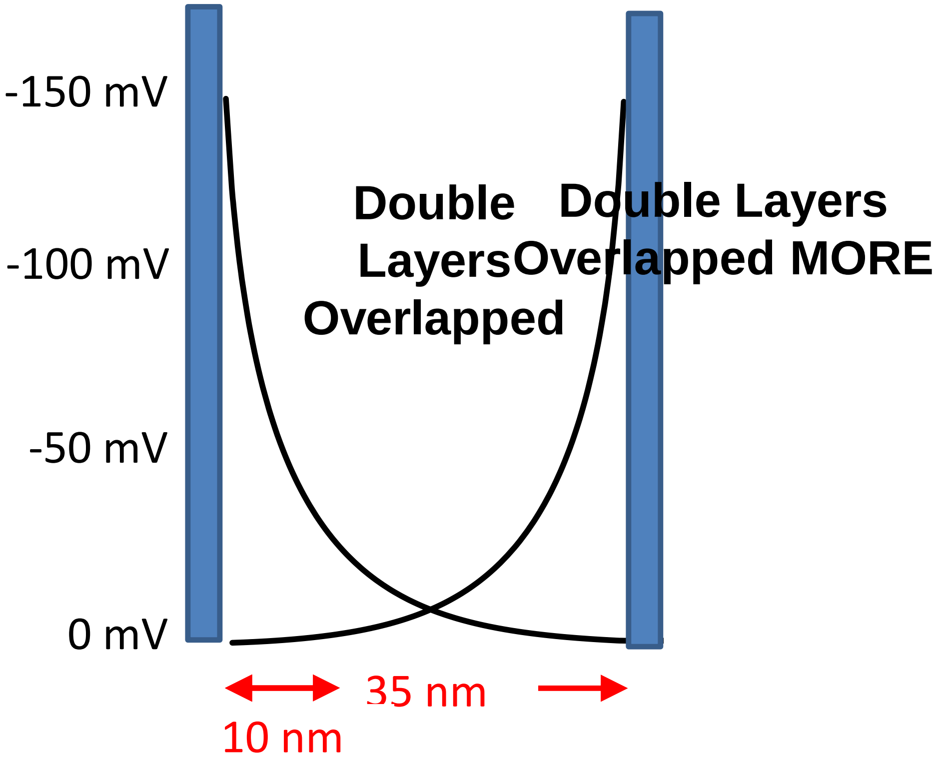
Two SiO_2 plates immersed in 0.196 M NH_4OH





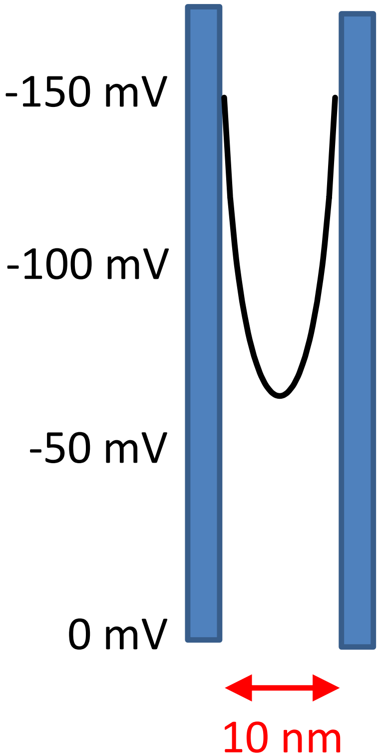
Overlapping of Double layer

Two SiO_2 plates immersed in 0.196 M NH_4OH

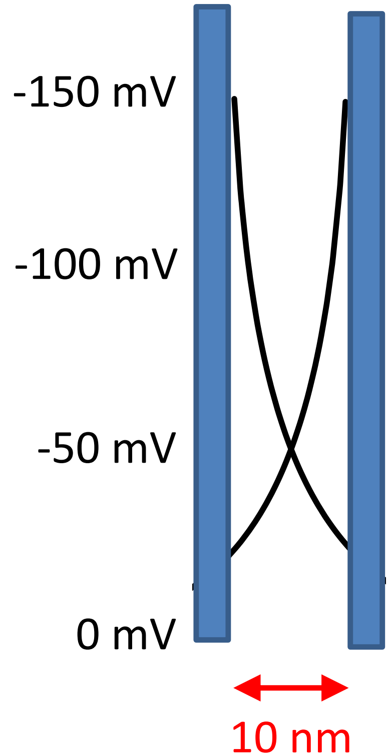


Overlapping of Double layer

Two SiO_2 plates immersed in 0.196 M NH_4OH



Result of Double Layers Overlapped MORE



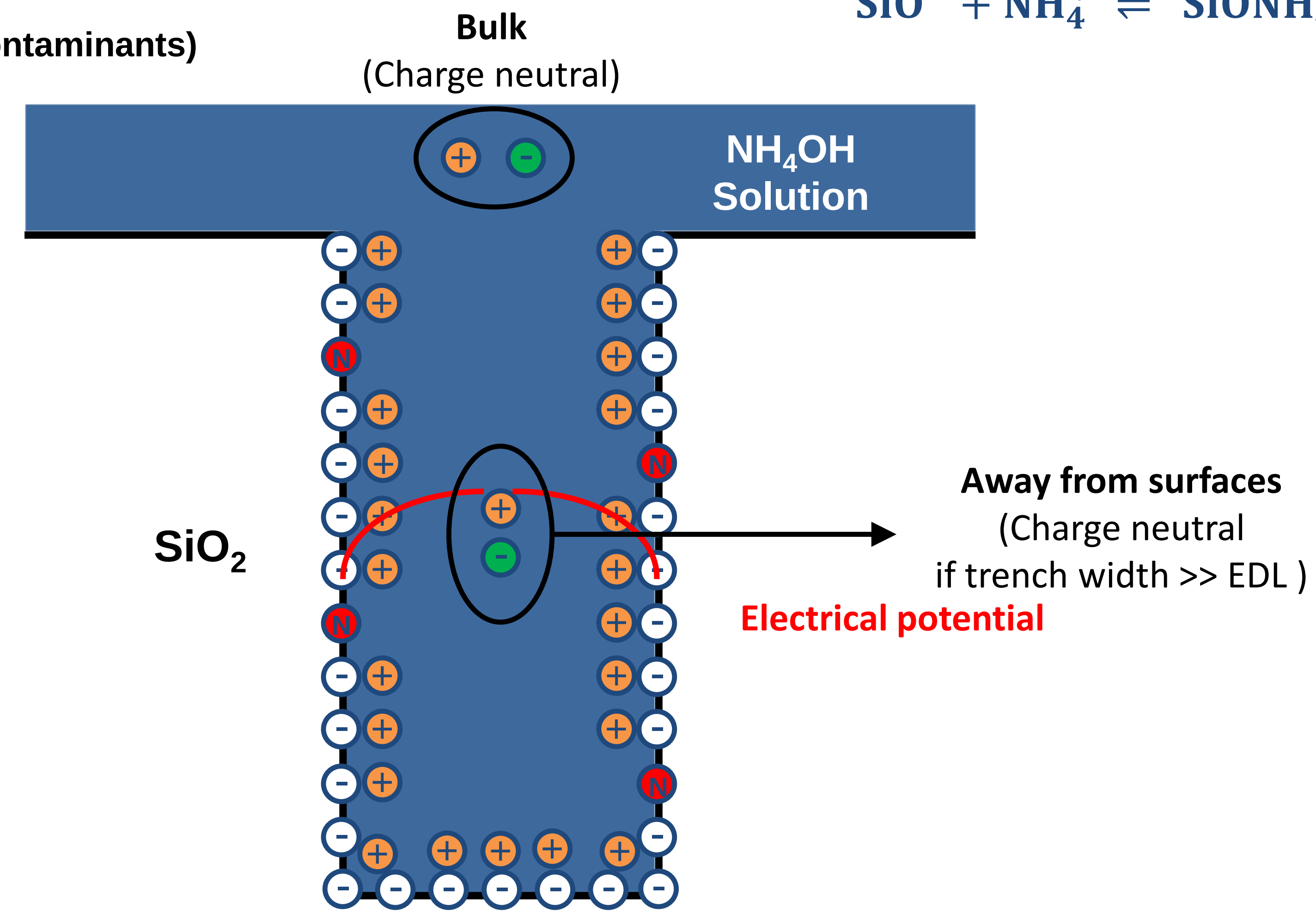
Double Layers Overlapped MORE

Typical Rinse Process

- ⊖ Negatively charged site
- ⊕ Positively charged site
- N Neutral site
- ⊕ NH_4^+ (ionic contaminants)
- ⊕ H^+
- ⊖ OH^-

$$SiOH \rightleftharpoons SiO^- + H^+$$

$$SiO^- + NH_4^+ \rightleftharpoons SiONH_4$$

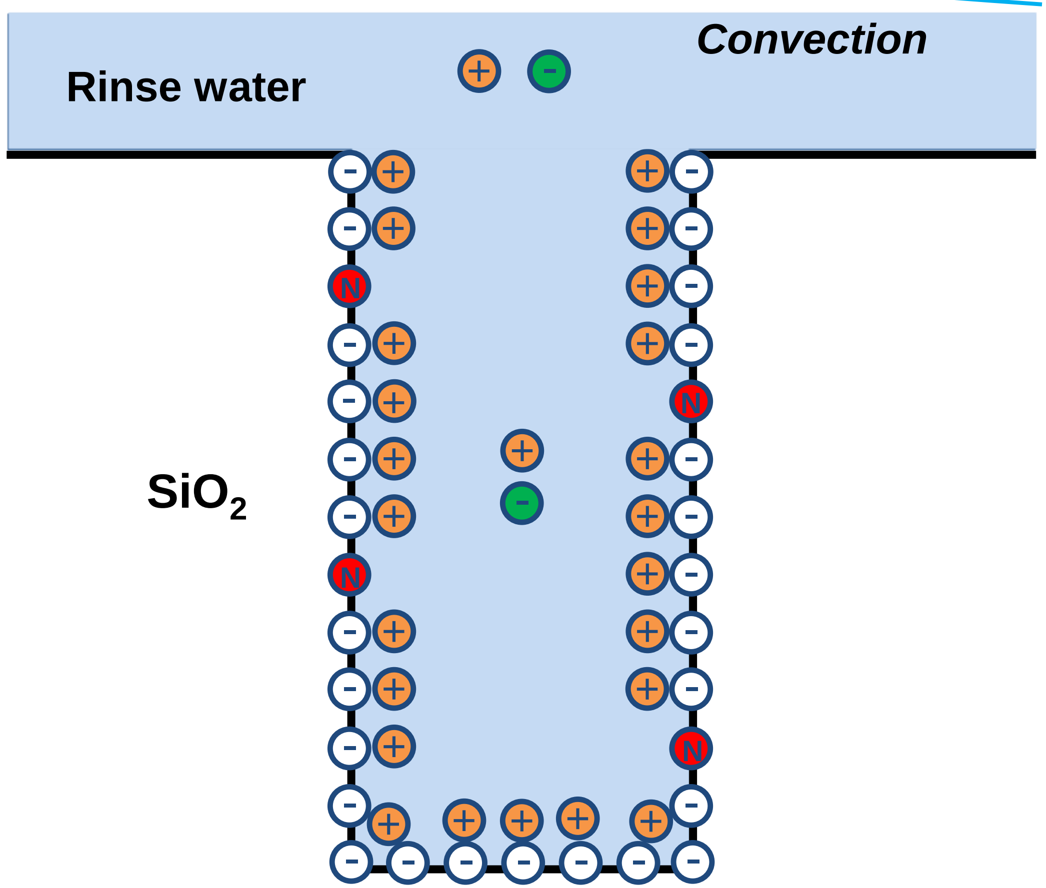


Typical Rinse Process

- Negatively charged site
- Positively charged site
- Neutral site
- NH_4^+ (ionic contaminants)
- H^+
- OH^-

$$SiOH \rightleftharpoons SiO^- + H^+$$

$$SiO^- + NH_4^+ \rightleftharpoons SiONH_4$$

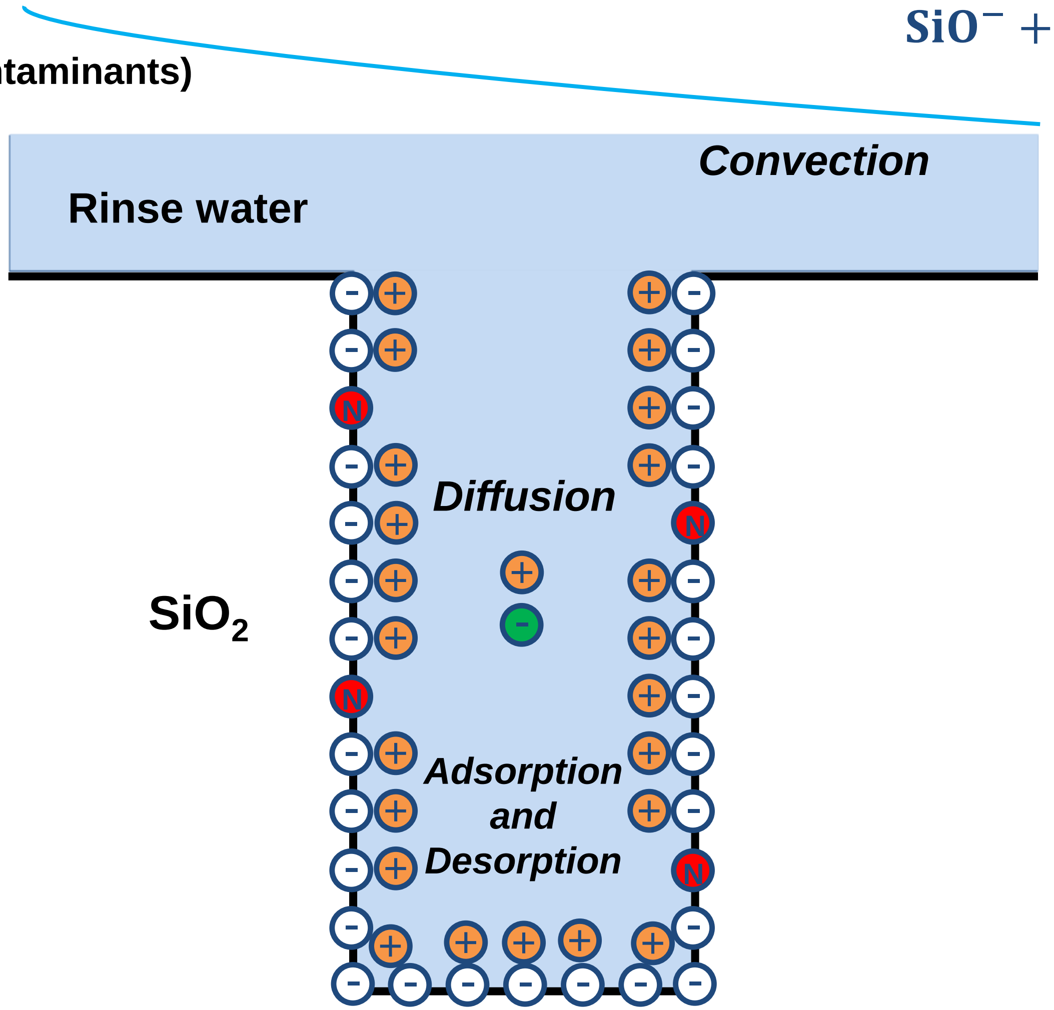


Typical Rinse Process

- Negatively charged site
- Positively charged site
- Neutral site
- NH_4^+ (ionic contaminants)
- H^+
- OH^-

$$SiOH \rightleftharpoons SiO^- + H^+$$

$$SiO^- + NH_4^+ \rightleftharpoons SiONH_4$$

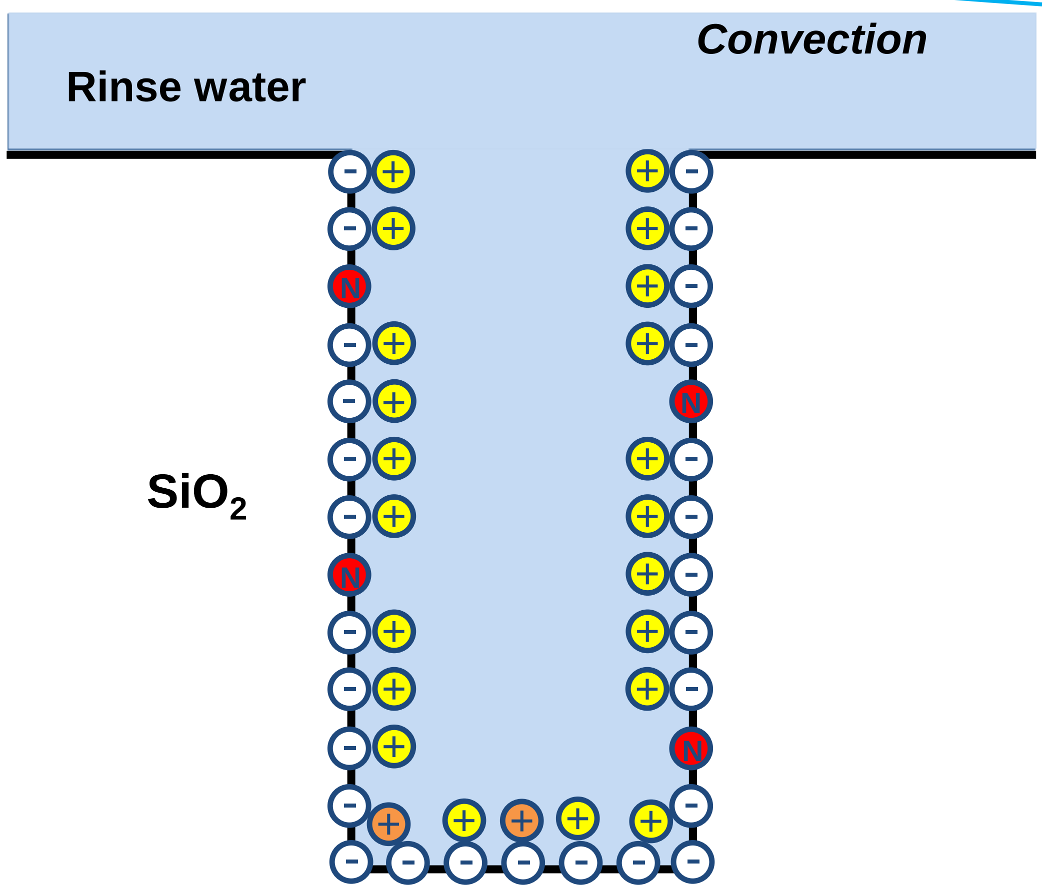


Typical Rinse Process

- Negatively charged site
- Positively charged site
- Neutral site
- NH_4^+ (ionic contaminants)
- H^+
- OH^-

$$SiOH \rightleftharpoons SiO^- + H^+$$

$$SiO^- + NH_4^+ \rightleftharpoons SiONH_4$$



Formulation of Process Simulator

Governing Equations

$$SiOH \underset{k_{Er}}{\overset{k_{Ef}}{\rightleftharpoons}} SiO^- + H^+ \qquad K_E = \frac{k_{Ef}}{k_{Er}} = \frac{C_{SiO^-} C_{H^+}}{C_{SiOH}} = 10^{-7.5}\ M$$

$$SiO^- + NH_4^+ \underset{k_{Mr}}{\overset{k_{Mf}}{\rightleftharpoons}} SiONH_4 \qquad K_M = \frac{k_{Mf}}{k_{Mr}} = \frac{C_{SiONH_4}}{C_{SiO^-} C_{NH_4^+}} = 10^{0.5}\ M$$

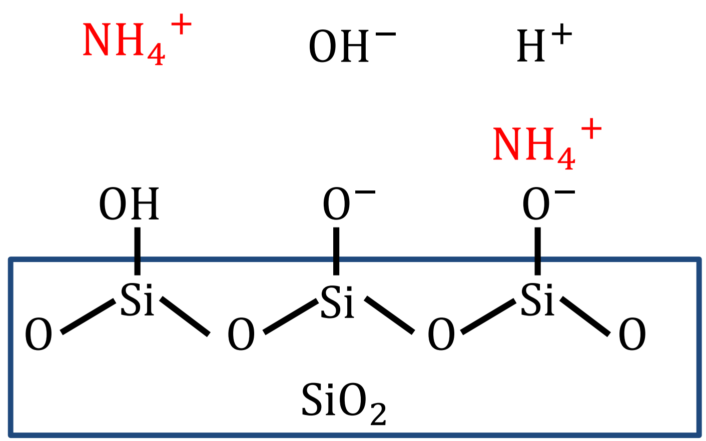
Adsorption/desorption equations:

$$\frac{dC_{SiOH}}{dt} = k_{Er}\, C_{SiO^-} C_{H^+} - k_{Ef}\, C_{SiOH}$$

$$\frac{dC_{SiONH_4}}{dt} = k_{Mf}\, C_{SiO^-}\, C_{NH_4^+} - k_{Mr}\, C_{SiONH_4}$$

Total site density:

$$C_{SiONH_4} + C_{SiOH} + C_{SiO^-} = S_0$$



SiO_2 immersed in aqueous ammonia solution

Formulation of Process Simulator

Governing Equations

Nernst Planck's equations

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i - z_i \mu_i F C_i \nabla \Phi) = R_i$$

$i = NH_4{}^+, H^+, \text{and } OH^-$

Poisson's equation

$$-\nabla^2 \Phi = \frac{F \times \left(z_{NH_4{}^+} C_{NH_4{}^+} + z_{H^+} C_{H^+} + z_{OH^-} C_{OH^-}\right)}{\varepsilon_0 \varepsilon_r}$$

Adsorption/desorption equations

$$\frac{dC_{SiOH}}{dt} = k_{Er}\, C_{SiO^-} C_{H^+} - k_{Ef}\, C_{SiOH}$$

$$\frac{dC_{SiONH_4}}{dt} = k_{Mf}\, C_{SiO^-}\, C_{NH_4{}^+} - k_{Mr}\, C_{SiONH_4}$$

Total site density is fixed

$$C_{SiONH_4} + C_{SiOH} + C_{SiO^-} = S_0$$

B.Cs.

B.Cs.

At mouth of the trench

$$\text{Outward flux of } NH_4{}^+ = k_m\left(C_{NH_4{}^+} - C_{NH_4{}^+\_bulk}\right)$$

$$\text{Outward flux of } OH^- = k_m\left(C_{OH^-} - C_{OH^-\_bulk}\right)$$

$$\text{Outward flux of } H^+ = k_m\left(C_{H^+} - C_{H^+\_bulk}\right)$$

$$\Phi = 0$$

At trench surfaces

$$\text{Inward flux of } NH_4{}^+ = -k_{Mf} C_{NH_4{}^+} C_{SiO^-} + k_{Mr}\, C_{SiONH_4}$$

$$\text{Inward flux of } OH^- = 0$$

$$\text{Inward flux of } H^+ = k_{Ef}\, C_{SiOH} - k_{Er} C_{SiO^-} C_{H^+}$$

$$\sigma_S = -n \cdot (\varepsilon_0 \varepsilon_r \nabla \Phi) = F \times C_{SiO^-}$$

Effective surface charge

Formulation of Process Simulator

Governing Equations

Nernst Planck's equations

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i - z_i \mu_i F C_i \nabla \Phi) = R_i$$

$i = NH_4^+, H^+, \text{and } OH^-$

Poisson's equation

$$-\nabla^2 \Phi = \frac{F \times \left(z_{NH_4^+} C_{NH_4^+} + z_{H^+} C_{H^+} + z_{OH^-} C_{OH^-}\right)}{\varepsilon_0 \varepsilon_r}$$

Adsorption/desorption equations

$$\frac{dC_{SiOH}}{dt} = k_{Er}\, C_{SiO^-} C_{H^+} - k_{Ef}\, C_{SiOH}$$

$$\frac{dC_{SiONH_4}}{dt} = k_{Mf}\, C_{SiO^-}\, C_{NH_4^+} - k_{Mr}\, C_{SiONH_4}$$

Total site density is fixed

$$C_{SiONH_4} + C_{SiOH} + C_{SiO^-} = S_0$$

I.Cs.

I.Cs. prior to rinsing

$C_{NH_4^+} =$ equilibrium profile before rinse

$C_{OH^-} =$ equilibrium profile before rinse

$C_{H^+} =$ equilibrium profile before rinse

$\Phi =$ equilibrium profile before rinse

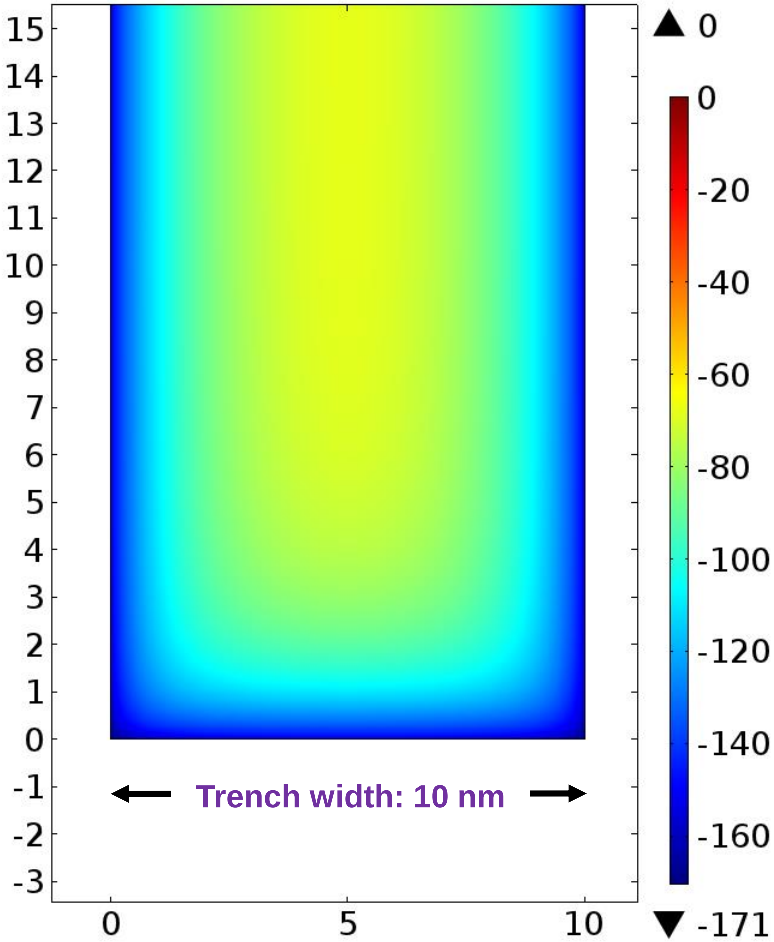
$$C_{SiONH_4} = \frac{C_{SiO^-} C_{NH_4^+}}{K_M}$$

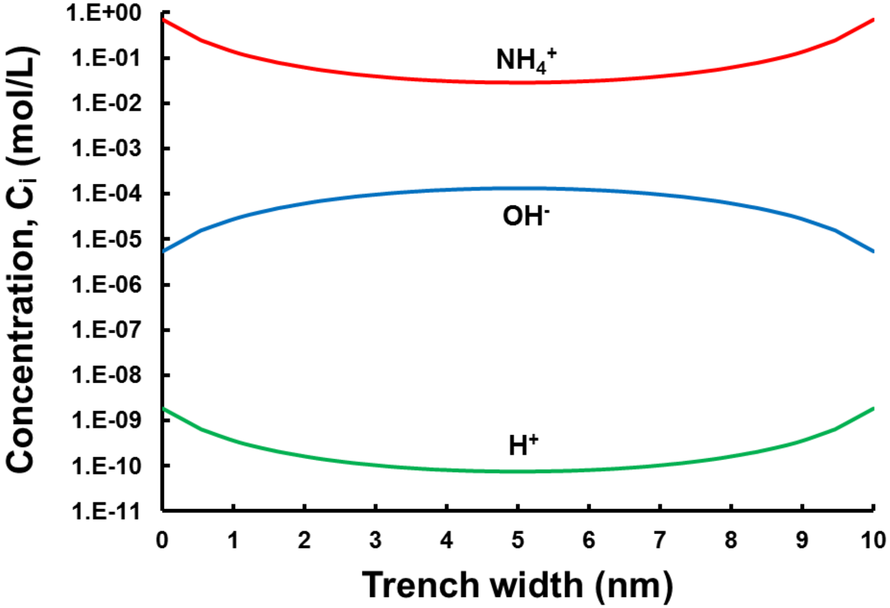
$$C_{SiOH} = K_E C_{SiO^-} C_{H^+}$$

$$C_{SiO^-} = S_0 - C_{SiONH_4} + C_{SiOH}$$

Electrical Potential at the bottom portion of the trench

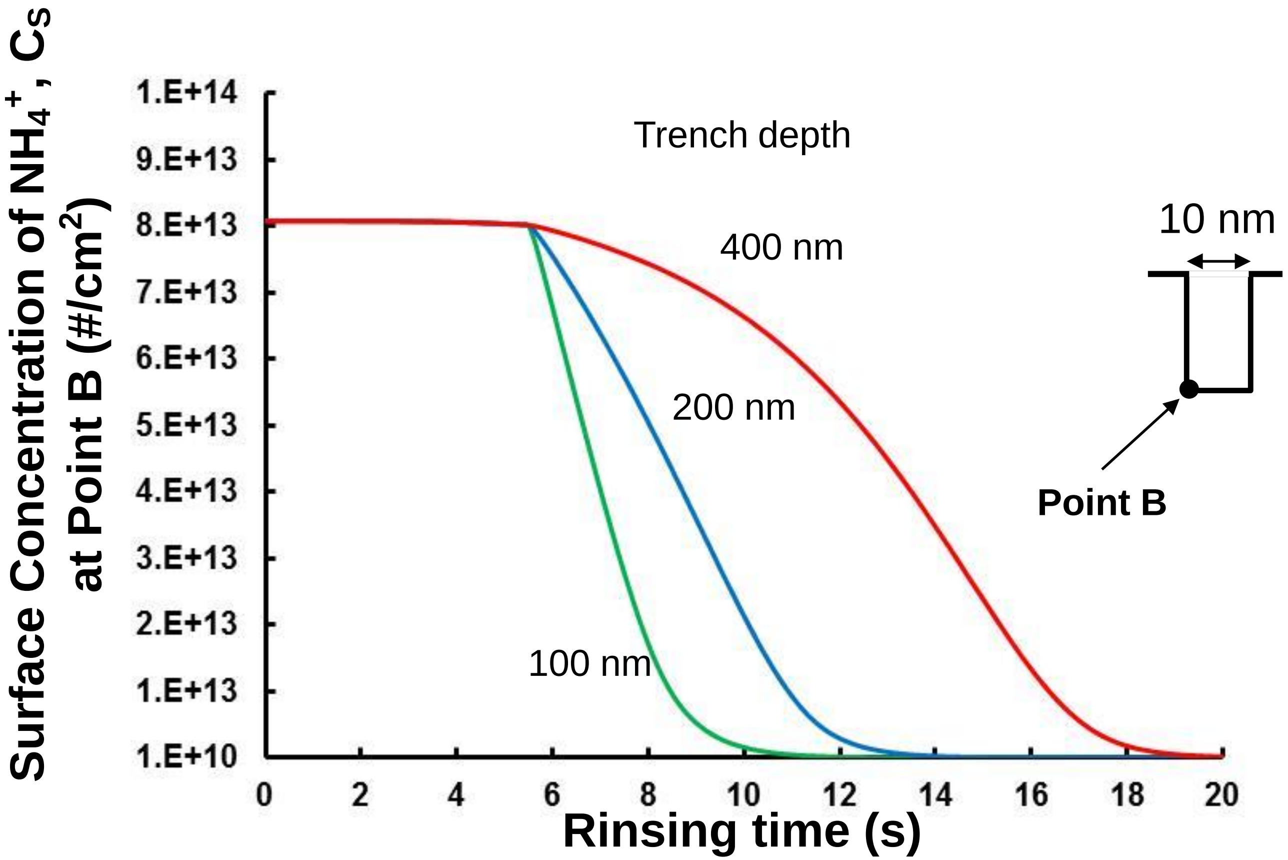
0.196 M NH_4OH





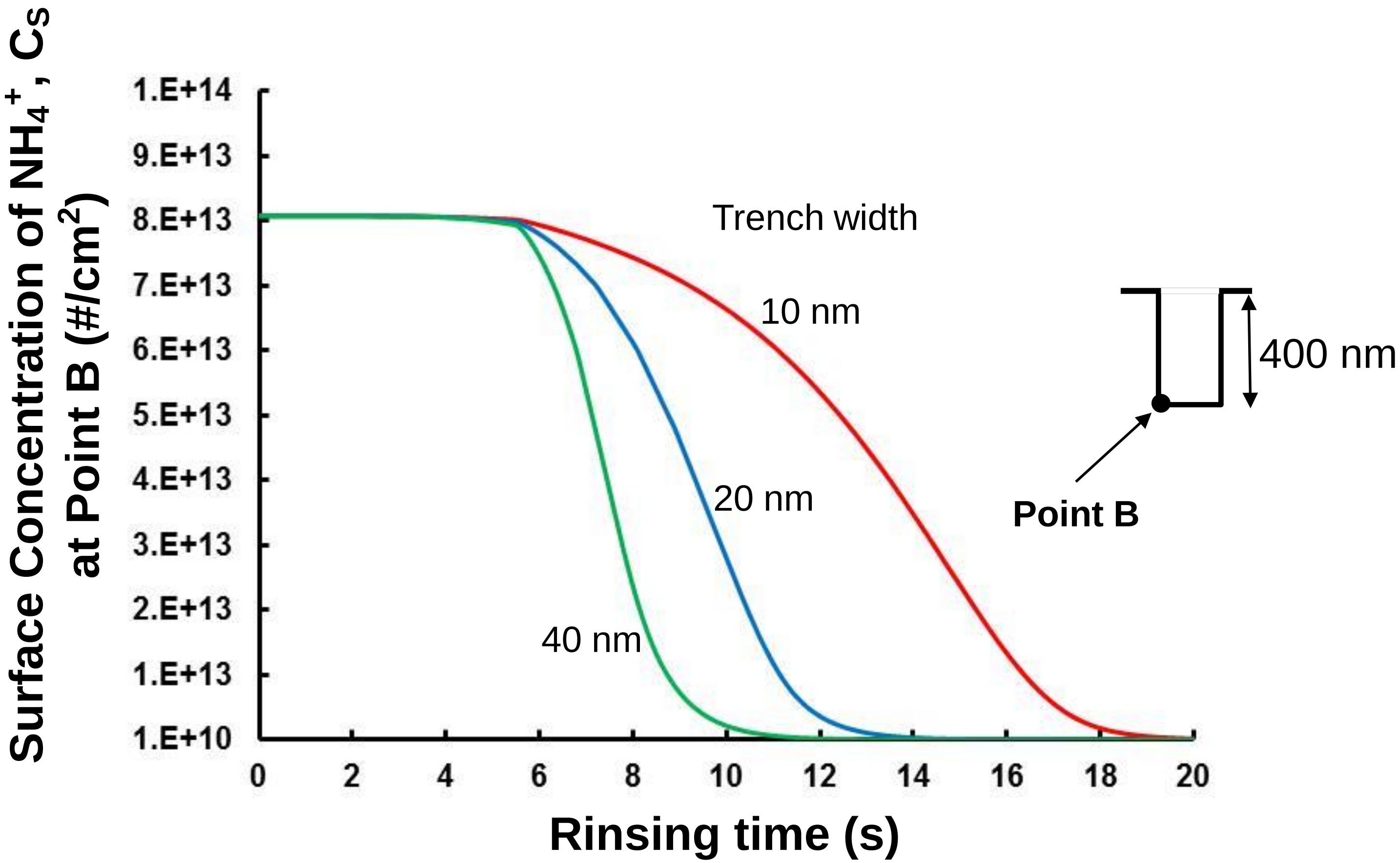
- **Model extension to nm range**
- **Non-zero potential at mid-plane**
- **Double layers overlap**

Effect of Trench Depth on Rinsing Dynamics



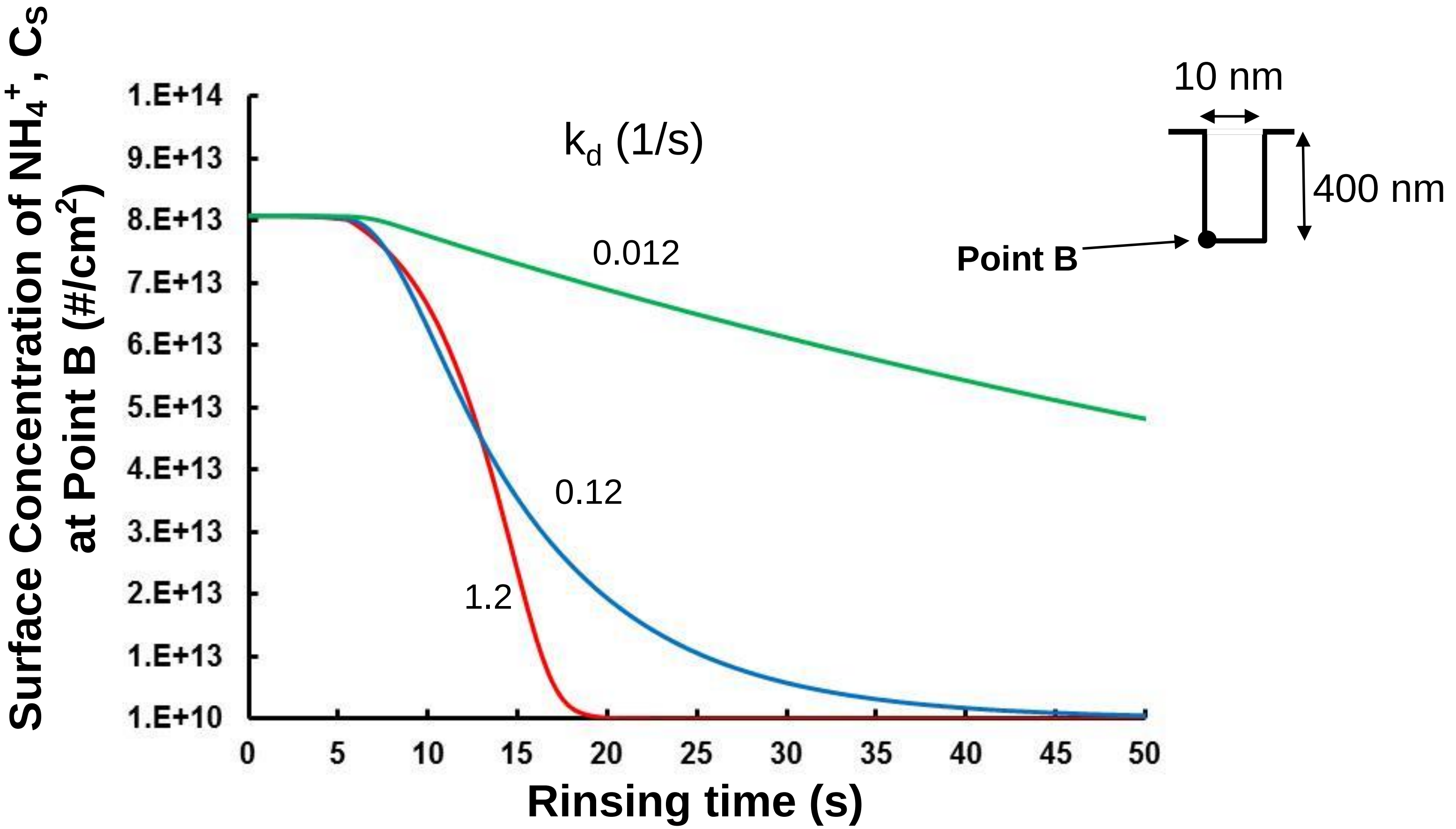
Corners of deep structures are last to clean

Effect of Trench Width on Rinsing Dynamics



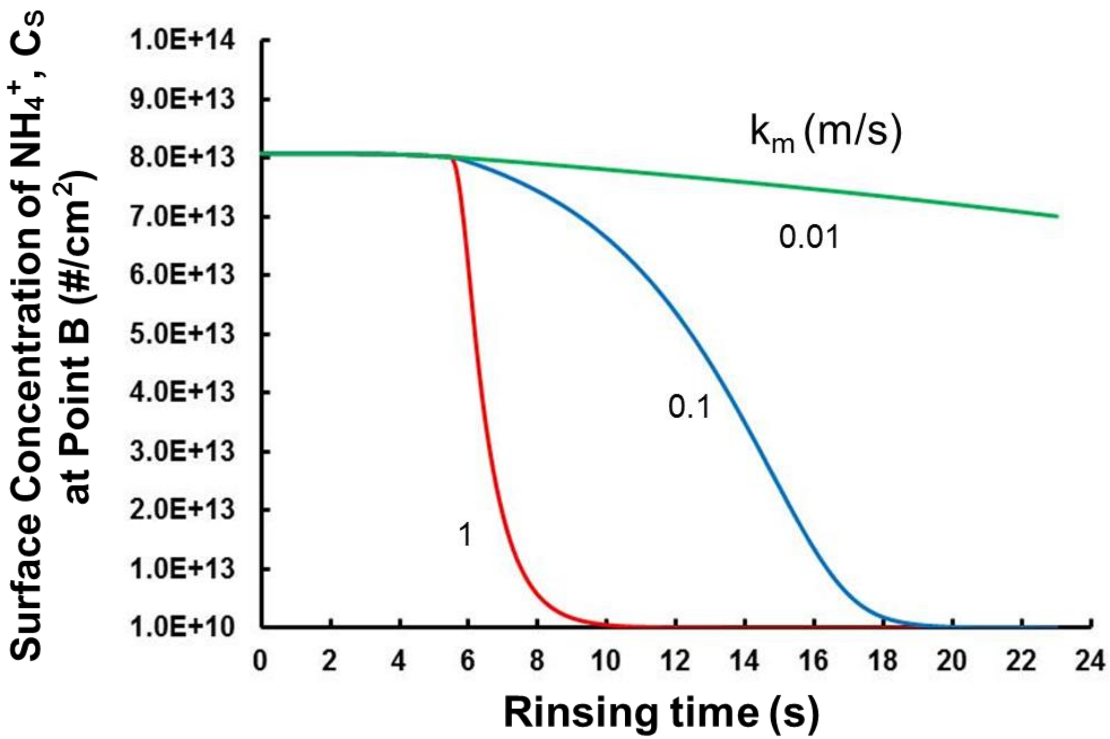
Bottom corners of narrow structures are last to clean

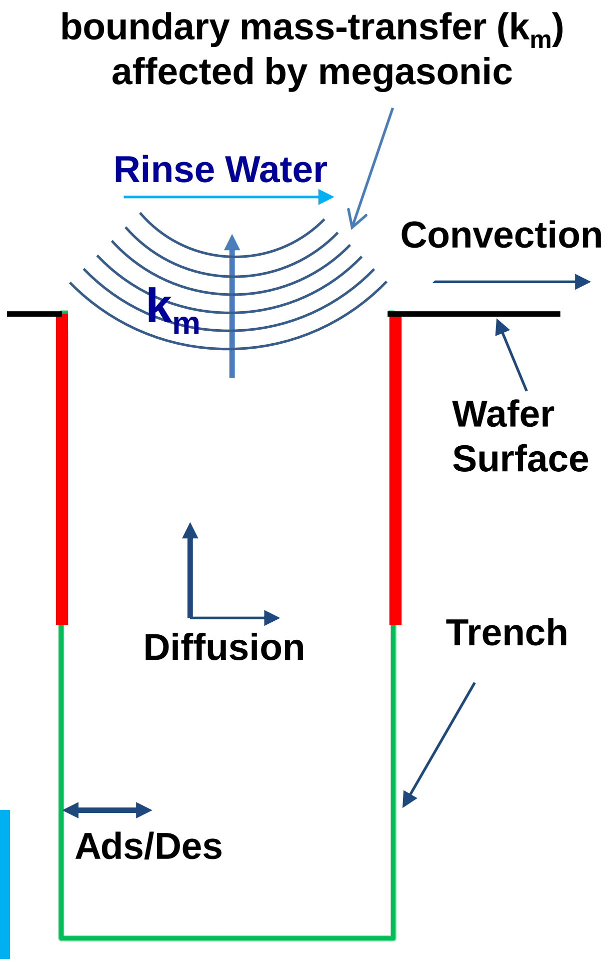
Effect of Desorption Rate Constant on Rinsing Dynamics



Desorption becomes a greater controlling factor as rinse progresses with time

Effect of Mass Transfer Coefficient on Rinsing Dynamics





Enhancement of boundary mass transfer has significant effect on rinse efficiency.

Methods for ESH Gain by Rinse Enhancement

Rinse Operation Parameters:

- **Increase water flow rate:**
  - almost no effect on processes inside fine structures
  - little effect on boundary mass transfer
  - waste of water

- **Increased diffusivity (D):**
  - higher temperature (mild effect)
  - increase in energy usage

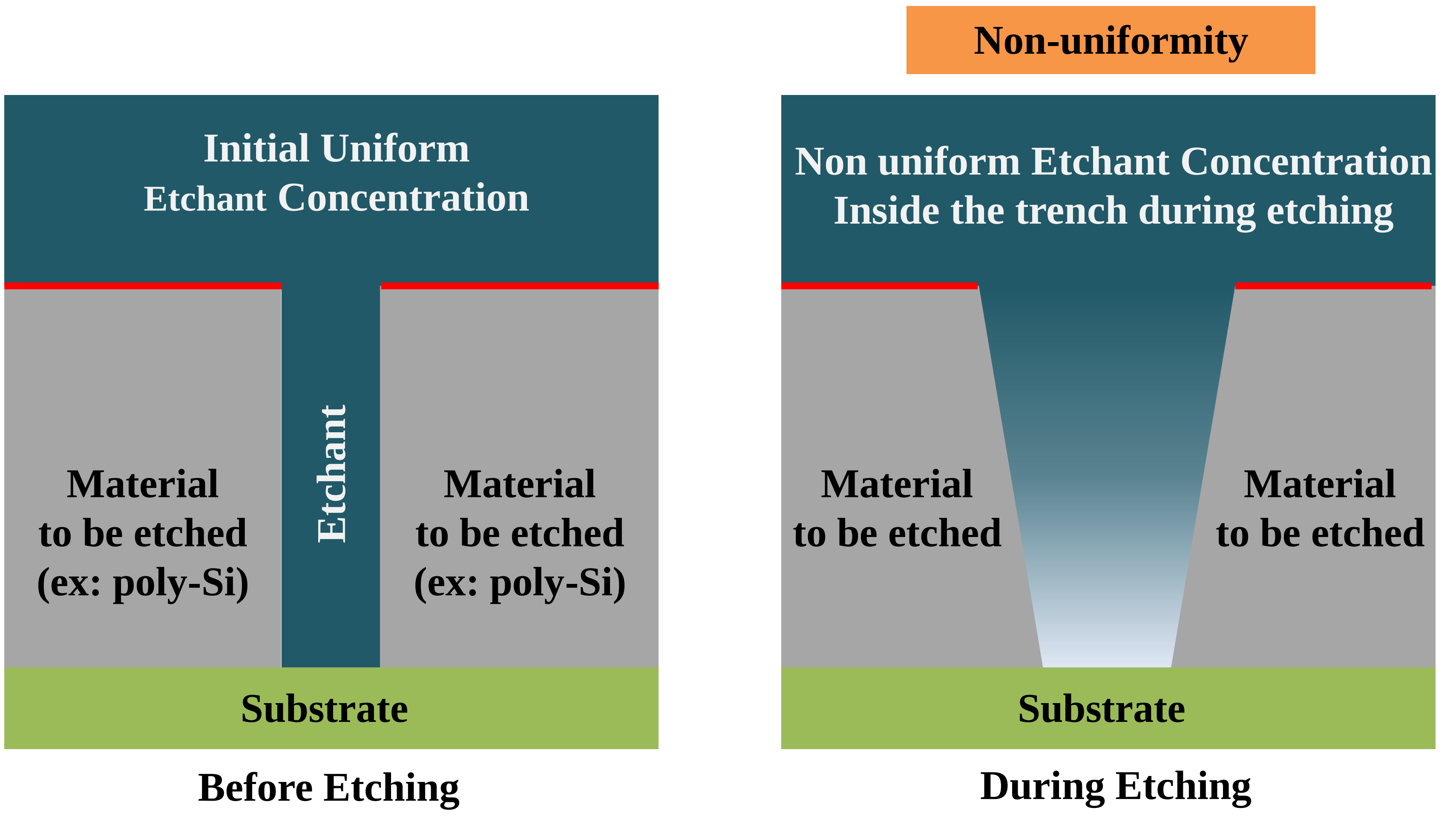
- **Higher desorption (k_d):**
  - higher temperature (mild to strong effect)
  - increase in energy usage

- **Higher boundary mass transfer (k_m):**
  - higher spin rate (low to mild effect)
  - mild megasonic (strong effect);

Extending the Application of Process Simulation:

Dynamics of Etching/Cleaning/Rinsing

Wet Etching in a Simple Trench



Non-Uniformity Problem in Wet Etching

Example: Wet Etching of Poly-Silicon using TMAH

Reaction Mechanism

$$\mathrm{TMAH} \longrightarrow \mathrm{TMA^{+}} + \mathrm{OH^{-}}$$

$$\mathrm{Si} + 2\mathrm{OH^{-}} \longrightarrow \mathrm{Si(OH)_2}^{2+} + 4e^{-}$$

$$\mathrm{Si(OH)_2}^{2+} + 4\mathrm{H_2O} + 4e^{-} \longrightarrow \mathrm{Si(OH)_6}^{2-} + 2\mathrm{H_2}$$

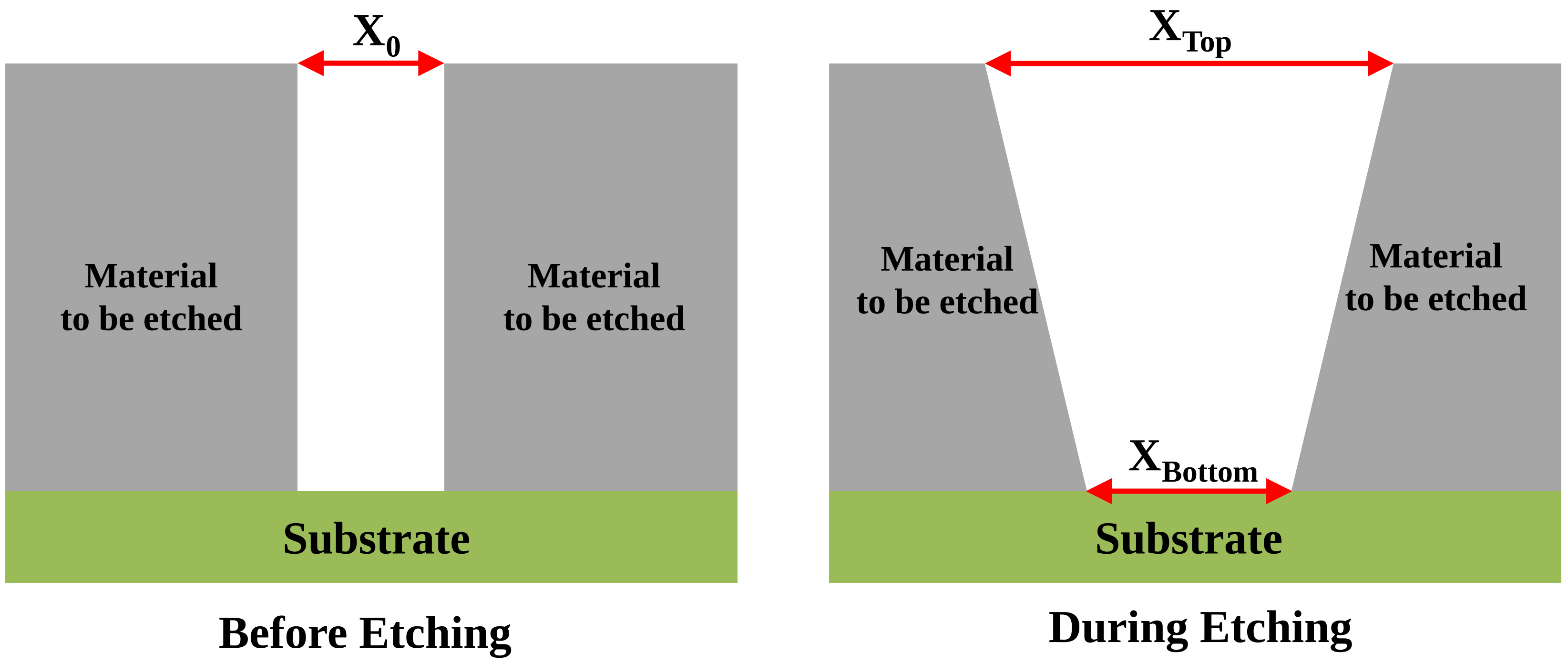
$$\mathrm{Si(OH)_6}^{2-} + \mathrm{TMA^{+}} \longrightarrow \text{final products}$$

Method of approach is this study:

As a test case, a simple poly-Si trench is used:

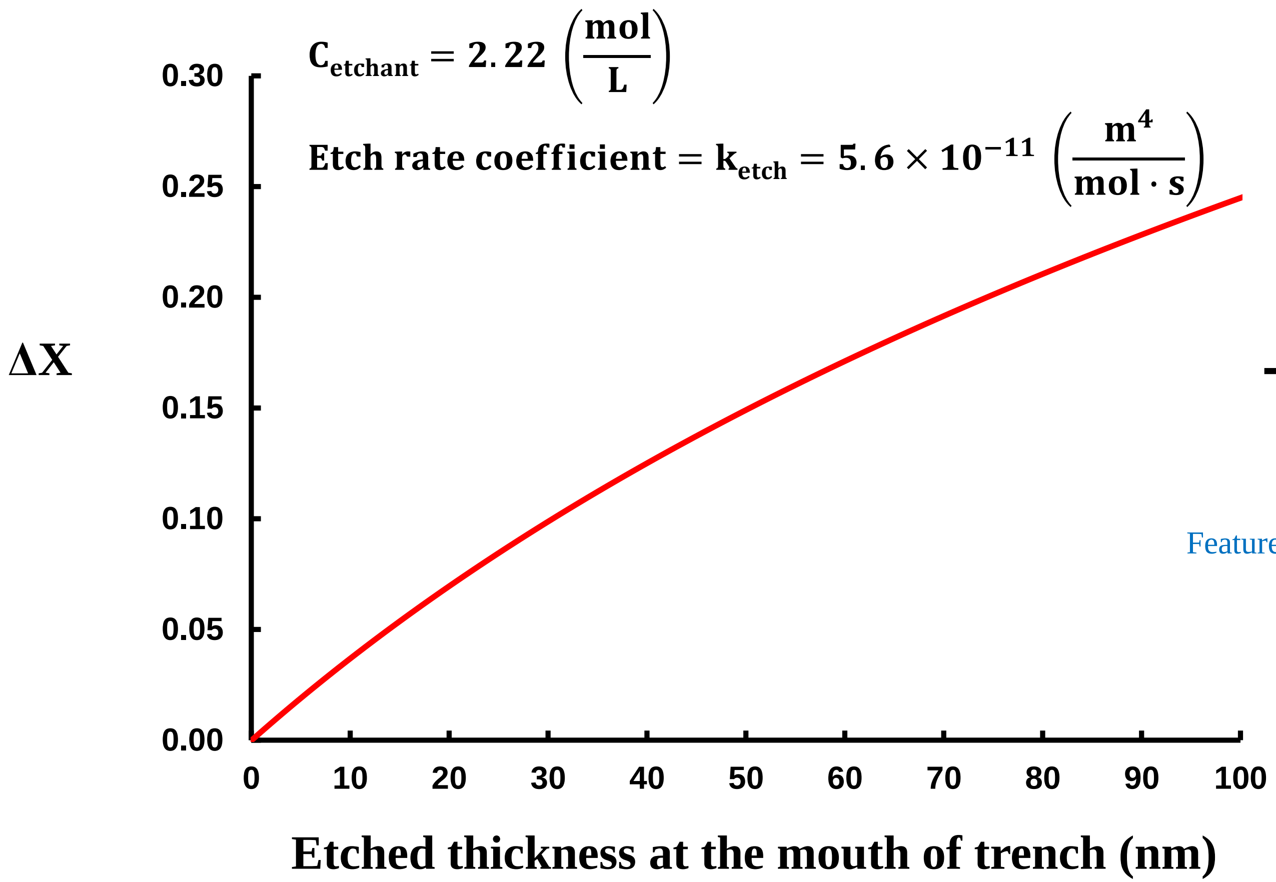
- **To study the mechanisms leading to non-uniformity issue during etching and post-etch rinsing.**
- **To develop a method to mitigate the non-uniform etching problem.**

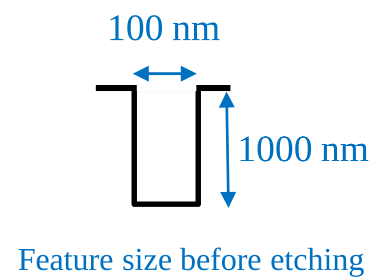
Parameters to Represent Non-Uniformity



$$\Delta X = \frac{X_{Top} - X_{Bottom}}{X_0}$$

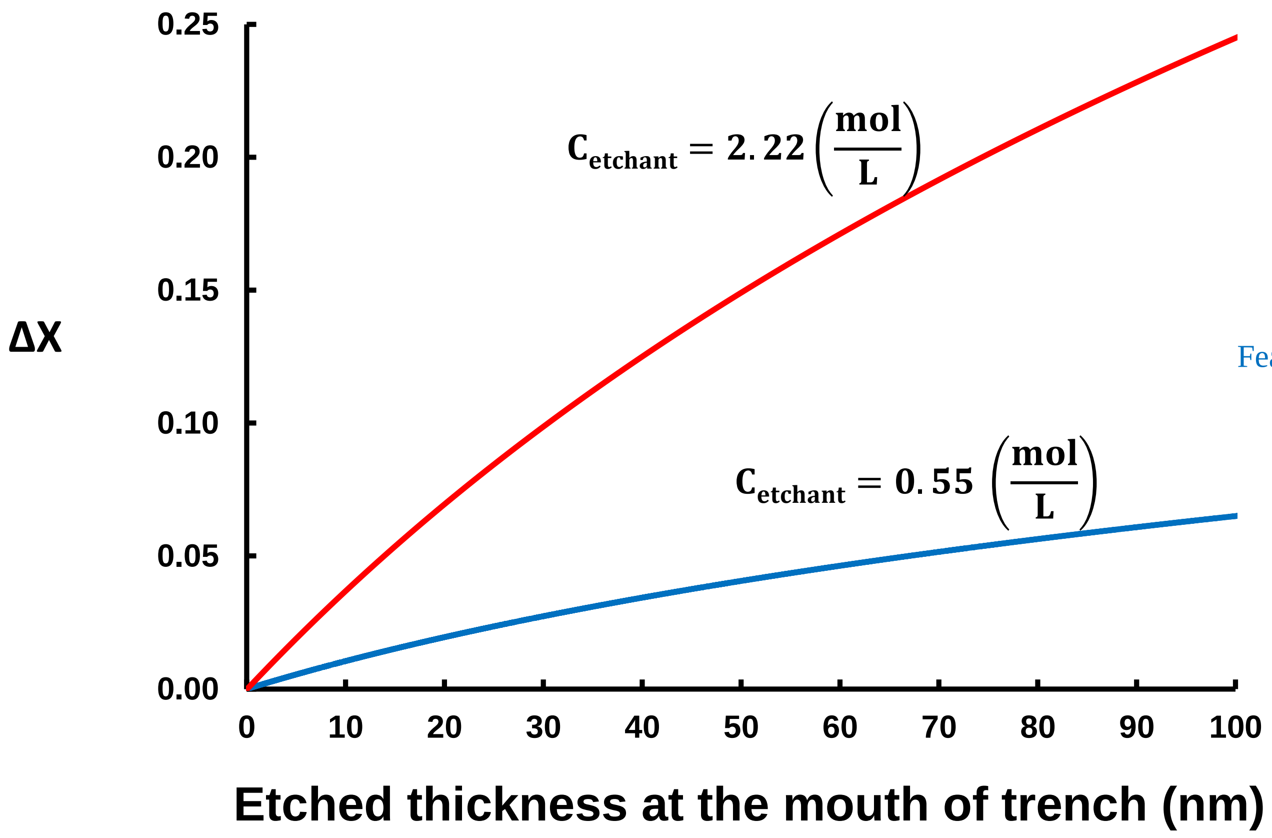
Non-Uniformity in Reference Conditions

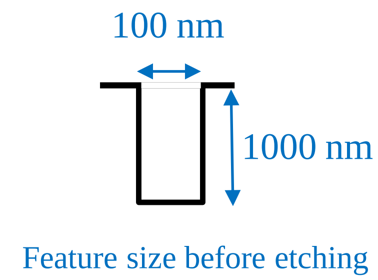




Etch non-uniformity increases with the extent of etch

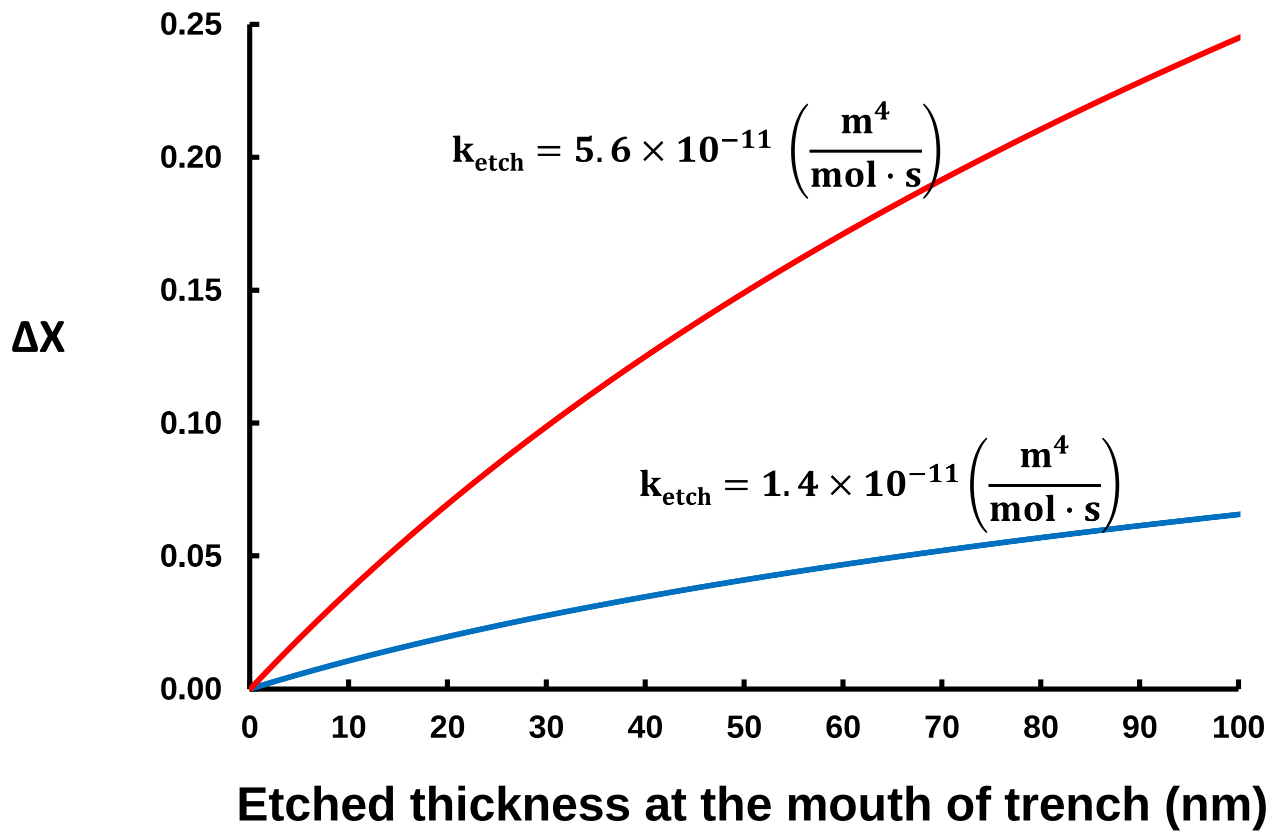
Effect of Etchant Bulk Concentration on Trench Uniformity

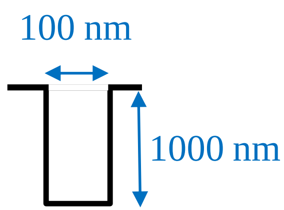




Etch non-uniformity increases with the etchant concentration

Effect of Etch Rate Constant on Trench Uniformity

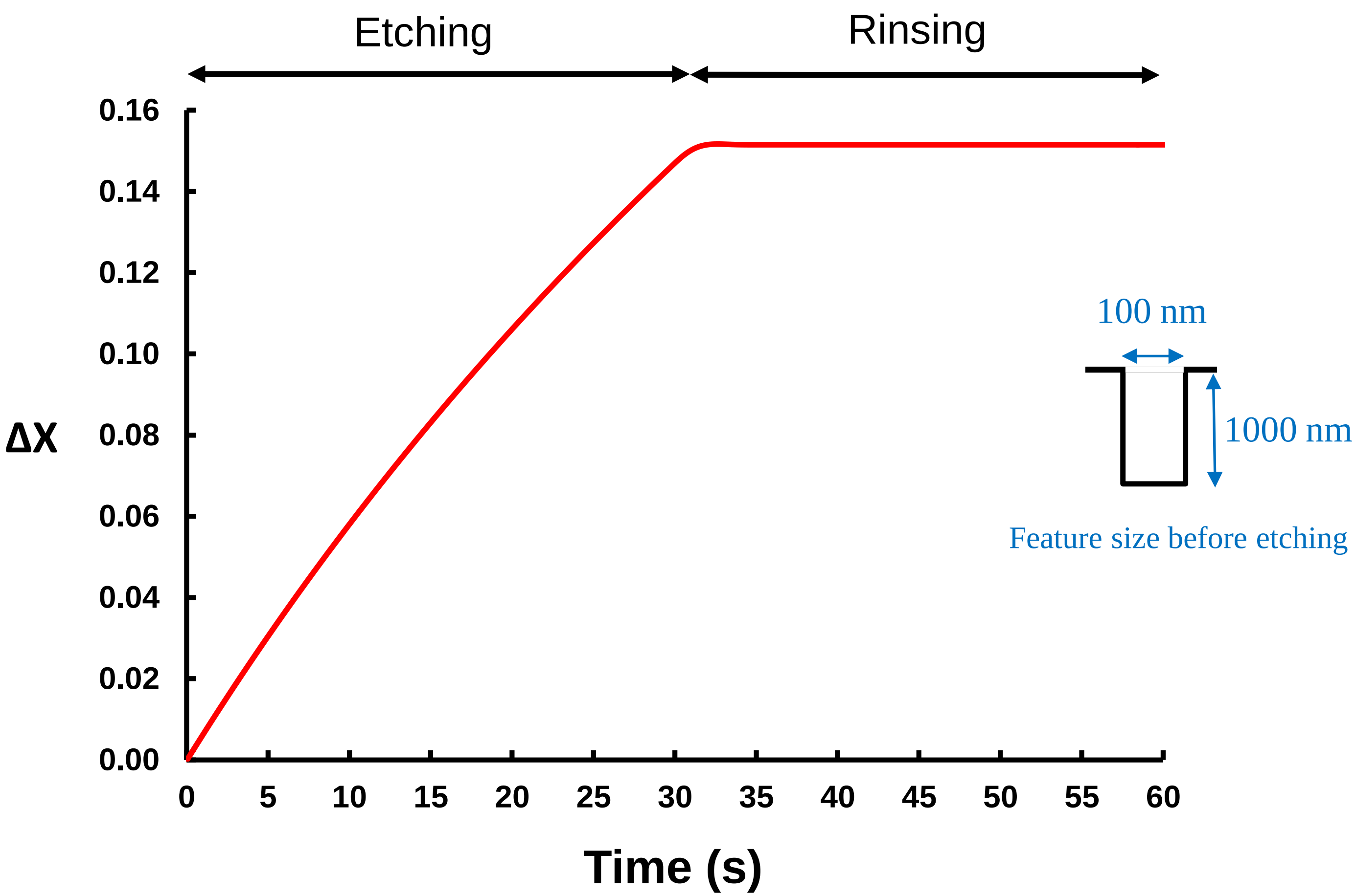




Feature size before etching

Non-uniformity increases with temperature

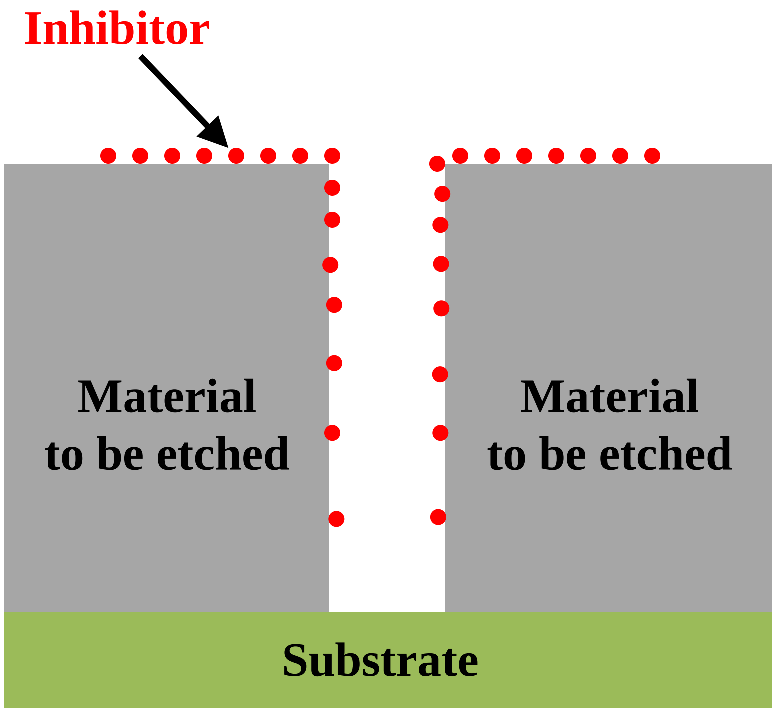
Non-Uniformity in Etching Followed by Rinsing



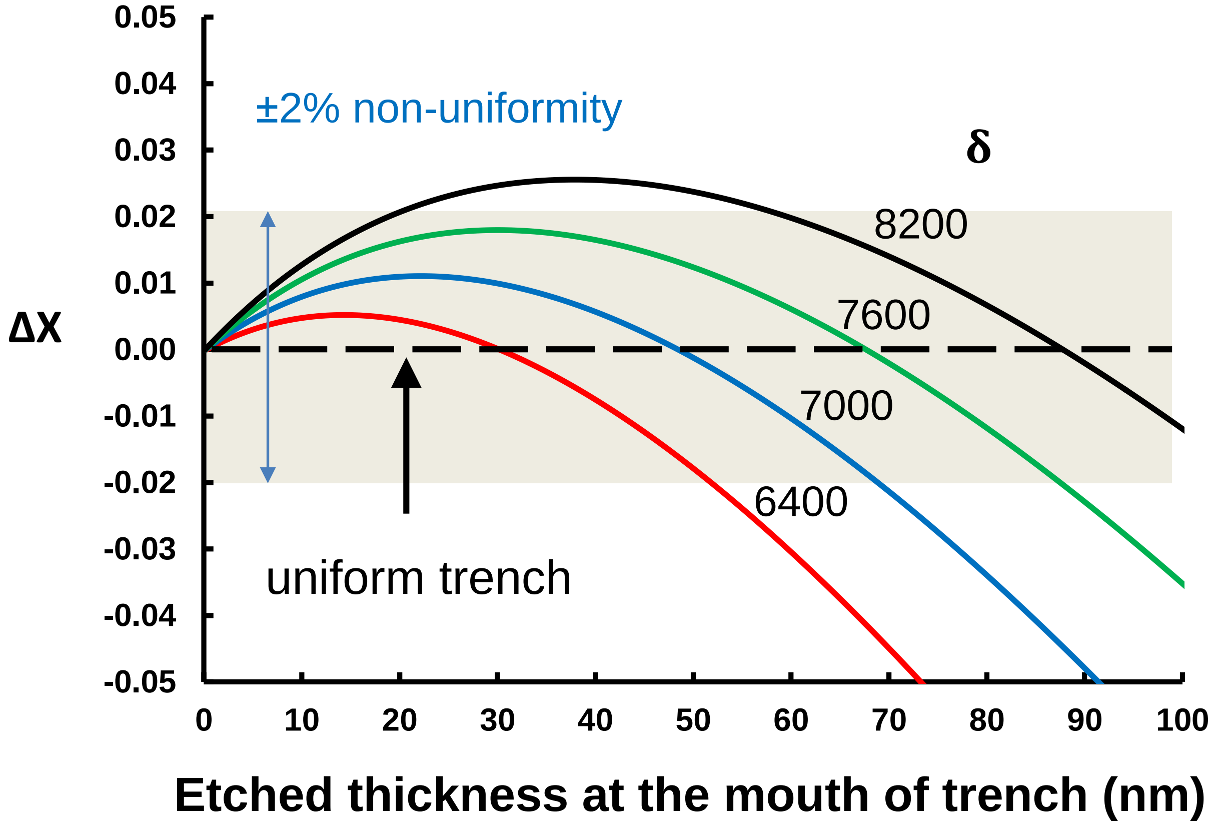
For the case presented here, the contribution of rinse to non-uniformity is small

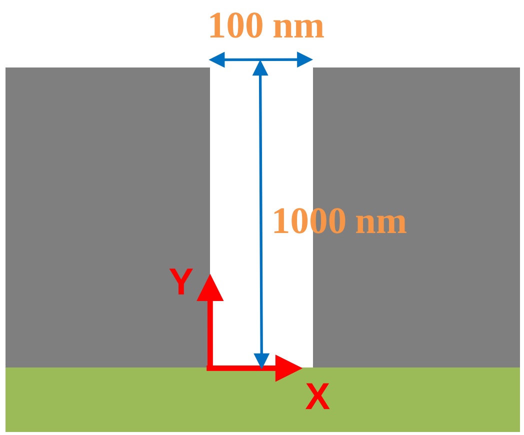
One Method to Obtain Etch Uniformity

- **Suppress the rate where the etchant concentration is high**
- **Application of organic compound as differential inhibitors, similar to suppressors used in electro-plating inside vias and trenches**



Uniformity with the Use of Differential Inhibitors





$$k_{etch} = k_0 \left(1 - \frac{y}{\delta}\right)$$

δ = supression factor

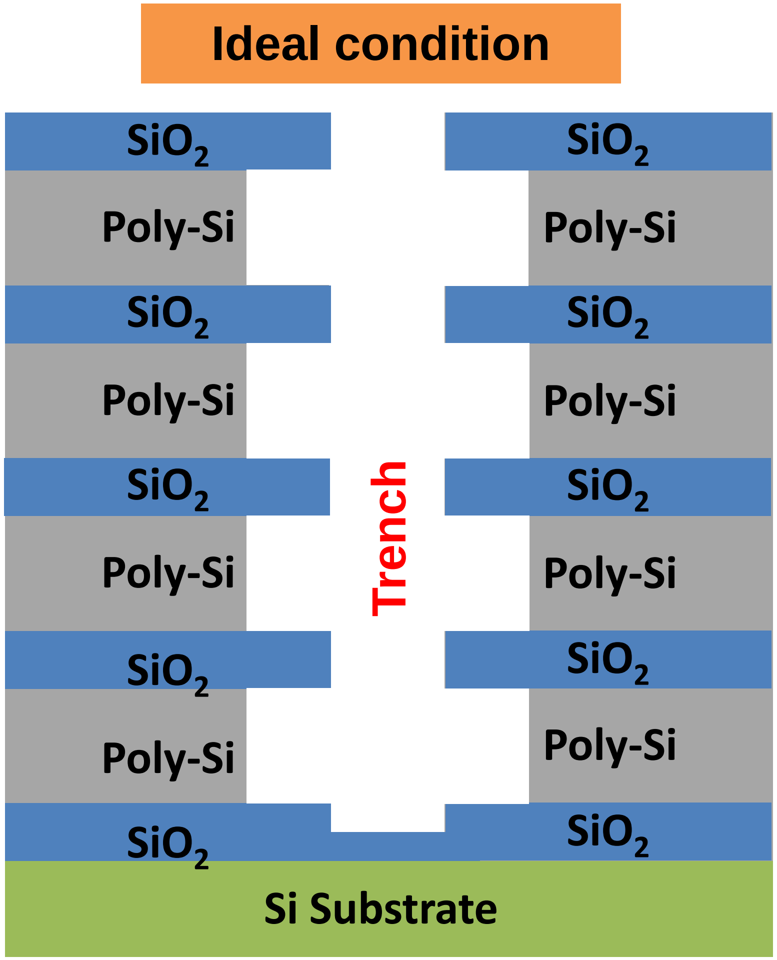
Uniform trench (ΔX < ±2%) with different etched thickness can be obtained by selecting proper inhibitor

Other Examples and Applications

- **Stacked structures used for memory *(example shown on the right)*; uniform (top and bottom) lateral wet etching is a challenge.**

- **Post-etch cleaning of side wall polymers in deep vias and trenches.**

- **Controlled, uniform etching of plasma exposed low-k side walls in the backend.**



Summary and Conclusions

- **A rinse model incorporating Nernst-Planck equation, Poisson's equation in conjunction with site-binding model and surface adsorption/desorption effects was developed.**
- **The simulator developed in the first 2 years is modified and enhanced; applicability to features in nano-meter range is demonstrated *(following feedback from last review)*.**
- **Mass transfer coefficient (k_m) and desorption rate constant (k_d) of contaminant were found to strongly affect rinsing time.**
- **The process simulator has the potential to be applied to different contaminants and different trench materials.**

Summary and Conclusions

- **The issue of non-uniformity in wet etching and post-etch rinsing of structures in patterned wafers was studied.**
- **The non-uniformity was found to be primarily caused by the depletion of the etchant and the concentration gradient inside the features.**
- **A novel approach to reduce non-uniformity to within a specified acceptable range was developed (the details are covered in a filed invention disclosure).**

Industrial Interactions and Acknowledgment

- Ian Brown (TEL) and Wallace Printz (TEL) for technical discussions
- Jivaan Kishore (University of Arizona) for modeling assistance

Publications and Presentations

- **Chiang, C.C., Kishore, J., Raghavan, S., Farhang Shadman "Rinsing of High-Aspect-Ratio Features on Patterned Structure" *Chemical Engineering Science* (submitted in February 2015).**
- **Dodge, M.R. and Shadman, F. "Computer Modeling of Surface Interactions and Contaminants Transport in Microstructures During the Rinsing of Patterned semiconductor Wafers," *Computers and Chemical Engineering* , 68, 182-189 (2014).**
- **Zamani, D., Dhane, K., Mahdavi, O., McBride, M., Yan, J., and Shadman, F. "Surface Cleaning of Small Structures during Spin Rinsing of Patterned Substrates" *Microelectronics Engineering Journal, 108, 57-65 (2013)*.**
- **Chiang, C.C., Raghavan, S., Farhang Shadman "Improving Rinsing Efficiency by Studying Desorption Kinetics of Multivalent Ion on SiO_2 Surface using Electrochemical Impedance Spectroscopy," SRC-TECHCON 2013.**