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

(Task Number: : 425.043)

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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:
  - ✓ Minimization of rinse bottleneck
  - ✓ On-line “end point detection”

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

1. Comprehensive Process Simulator for Development of Low-Water Rinse Methods

Process modeling is needed to:

- **Analyze data and understand the process**
- **Search for new methods and better operating conditions**

Process Simulator: Concept and Formulation

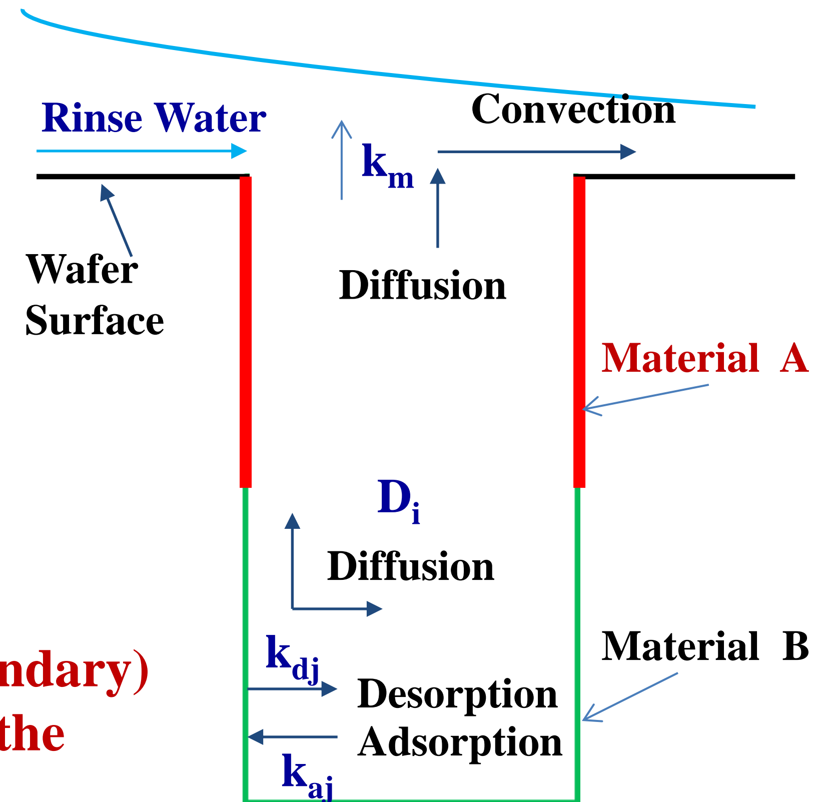
Multi-component transport:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i + z_i F \mu_i c_i \nabla \varphi) - u \nabla c_i$$

Surface adsorption and desorption:

$$\frac{\partial c_{sj}}{\partial t} = k_{aj} c_i (s_{0j} - c_{sj}) - k_{dj} c_{sj}$$

Flux out of the trench: $F_i = k_m (c_i - c_{bi})$



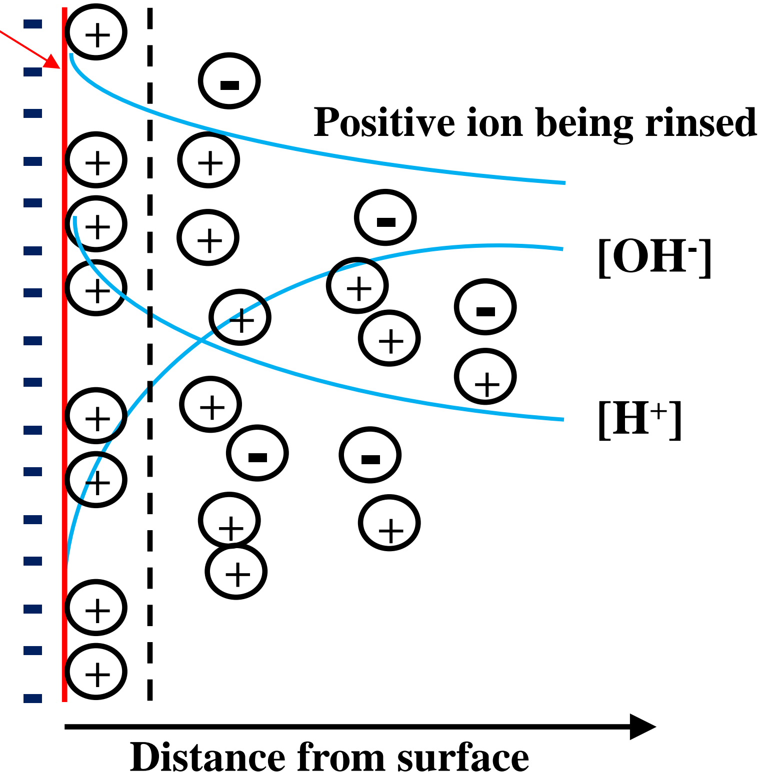
- k_m **(mass transfer coefficient in the boundary) is a known function of flow velocity on the wafer surface.**
- **New simulator handles multi-material layers with different properties.**

Surface and Space Charge Effects

Poisson equation: $\nabla^2 \varphi = -\frac{\rho}{\epsilon}$

Charge density: $\rho = F \sum_i z_i c_i$

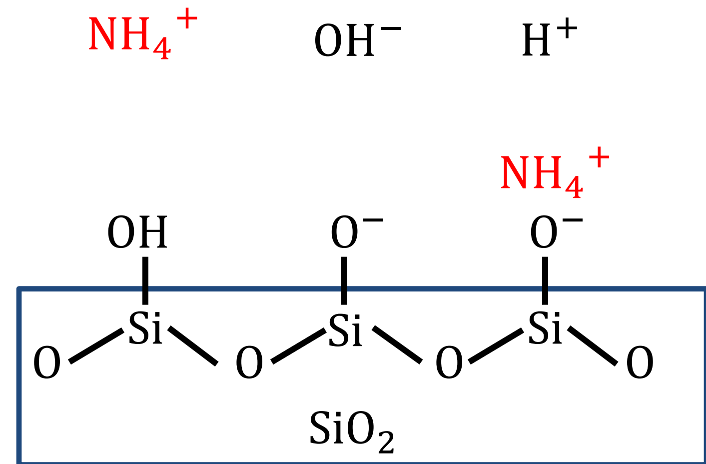
- New simulator takes into account the detailed effects of the electrified interface on the rinse process.



Interaction of surface charge and ionic species

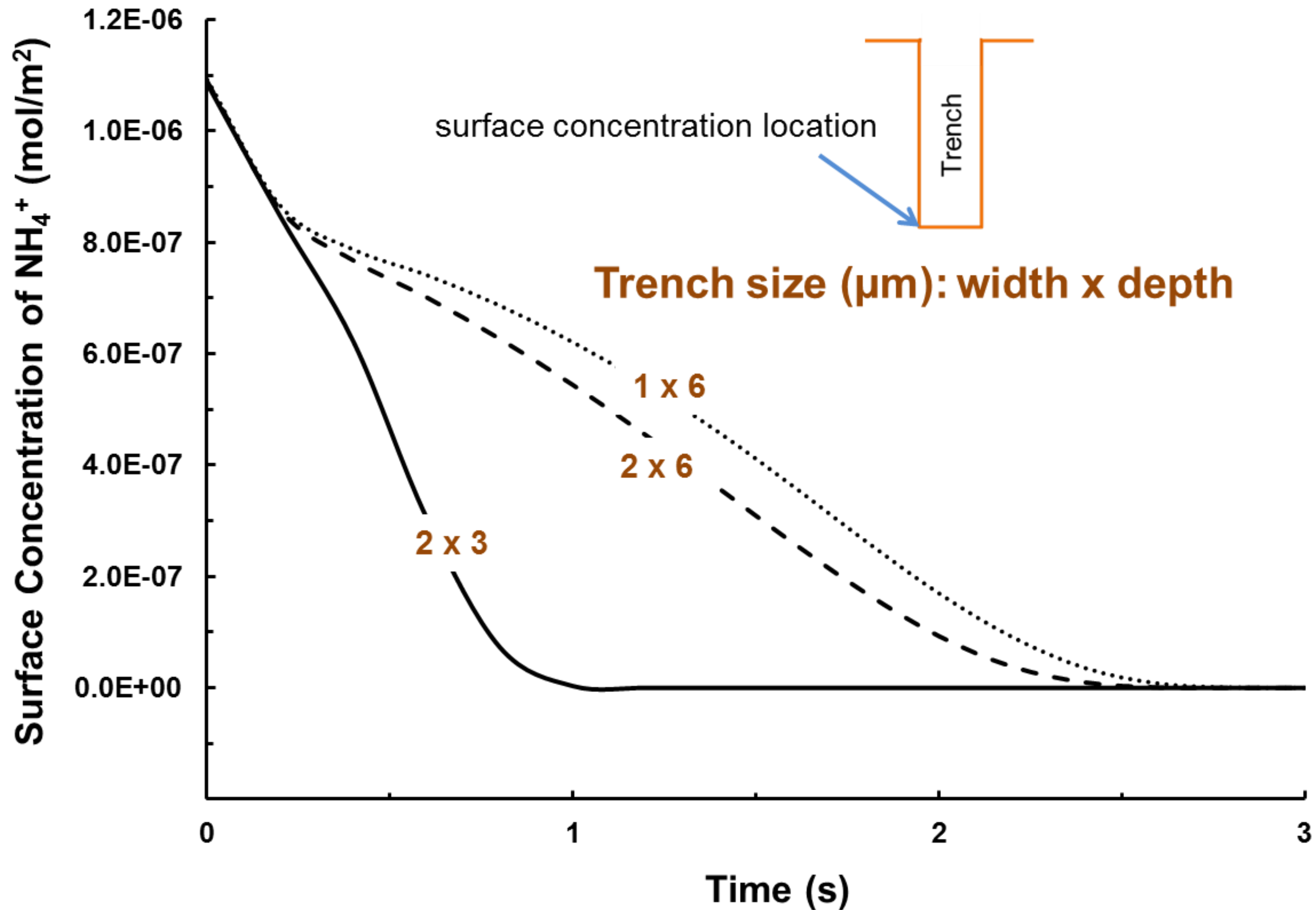
Example of Simulator Application:
Removal of Ammonia from SiO_2 Surface

The key surface and liquid reactions occurring during the rinse:



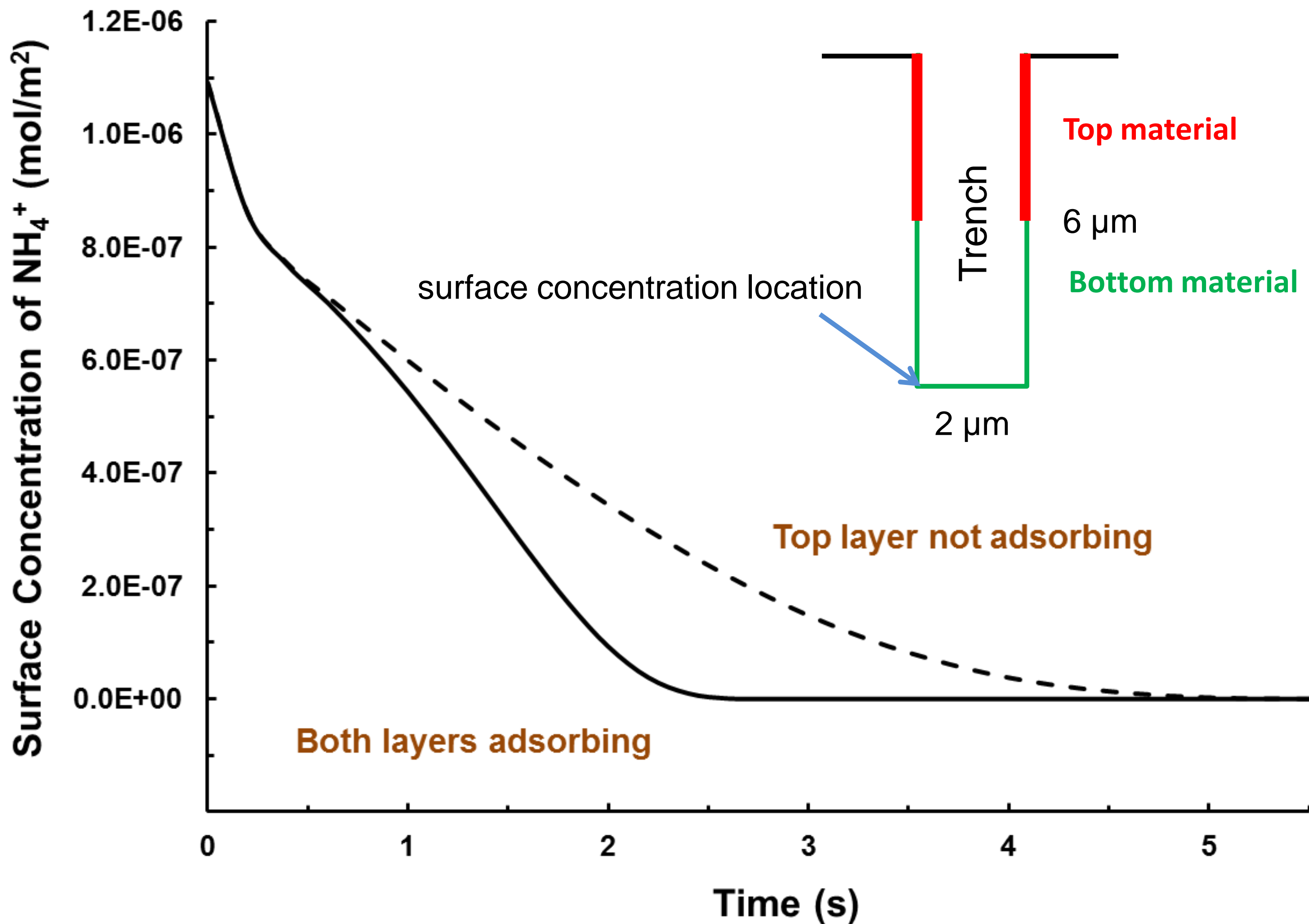
SiO_2 immersed in aqueous ammonia solution

Effect of Trench Dimensions on Rinsing Dynamics



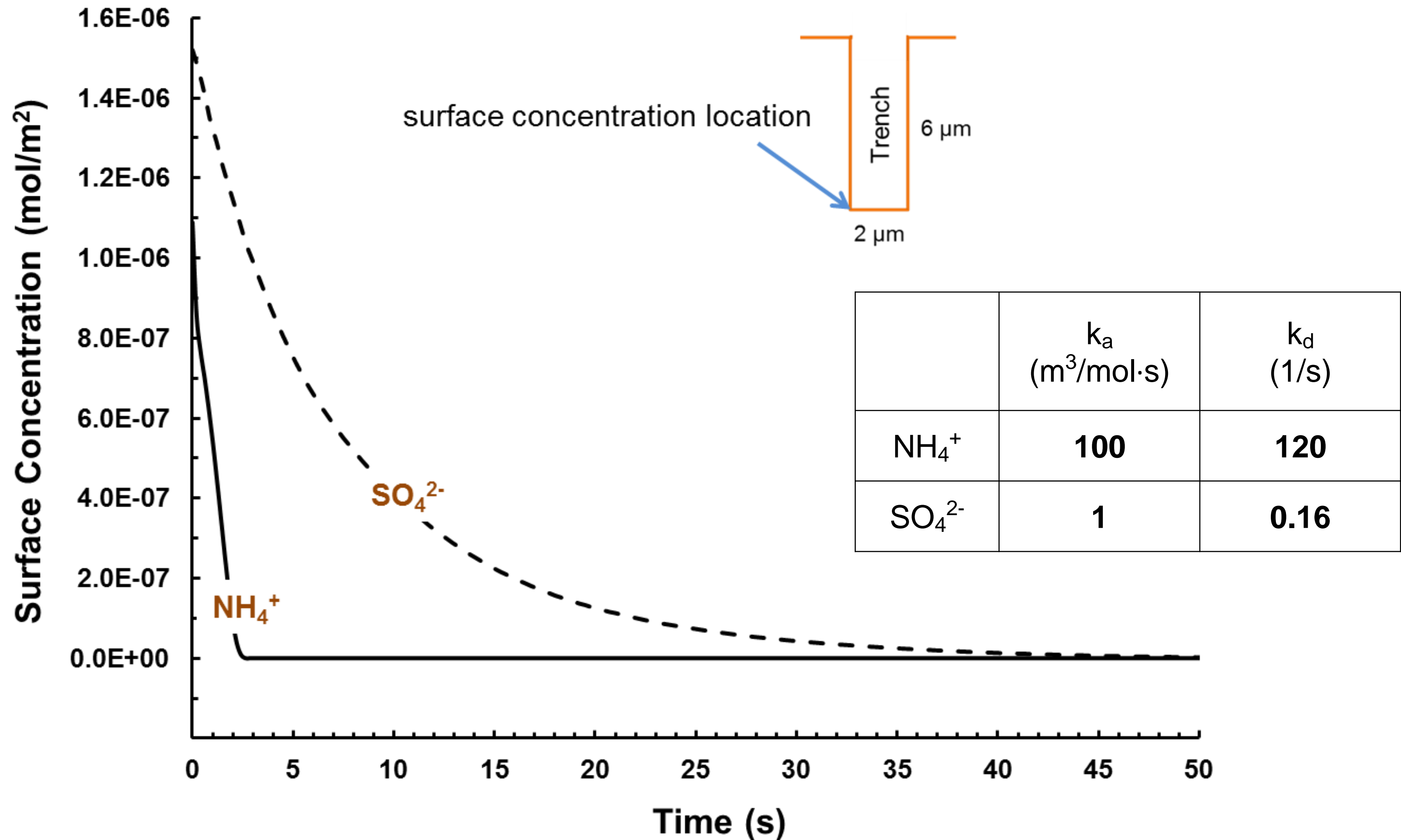
Rinse rate depends strongly on the trench depth (less strongly on the trench width)

Effect of Multi-Material on Rinsing Dynamics



Adsorption on the bottom layers dominates the rinse process

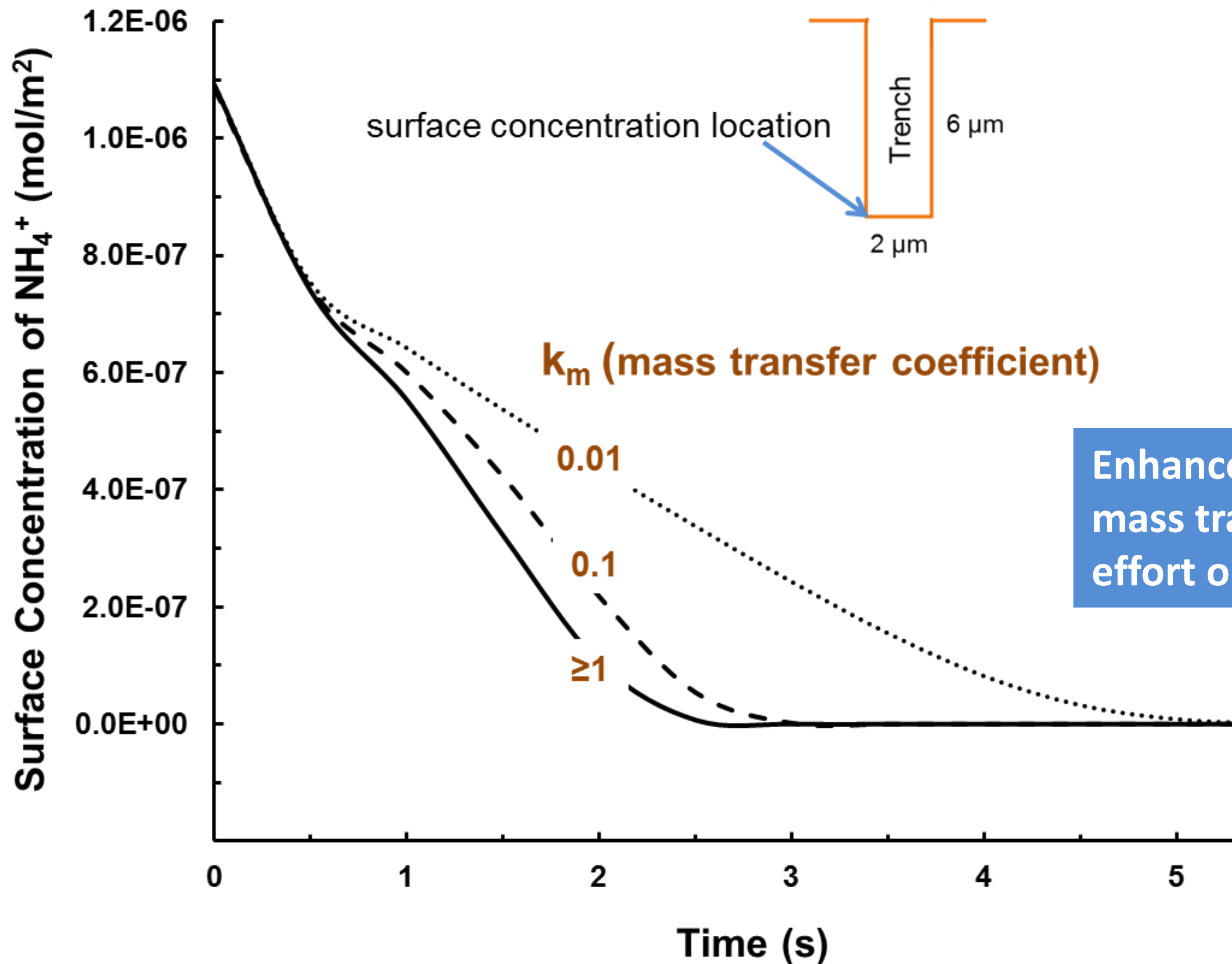
Effect of Impurity Adsorption and Desorption Properties



	k_a (m^3/mol·s)	k_d (1/s)
NH_4^+	**100**	**120**
SO_4^{2-}	**1**	**0.16**

Ions, such as sulfate, with high k_a and low k_d, chemisorb and require long rinse times

Effect of Boundary Mass Transfer on Rinse Dynamics



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

Methods for ESH Gain by Rinse Enhancement

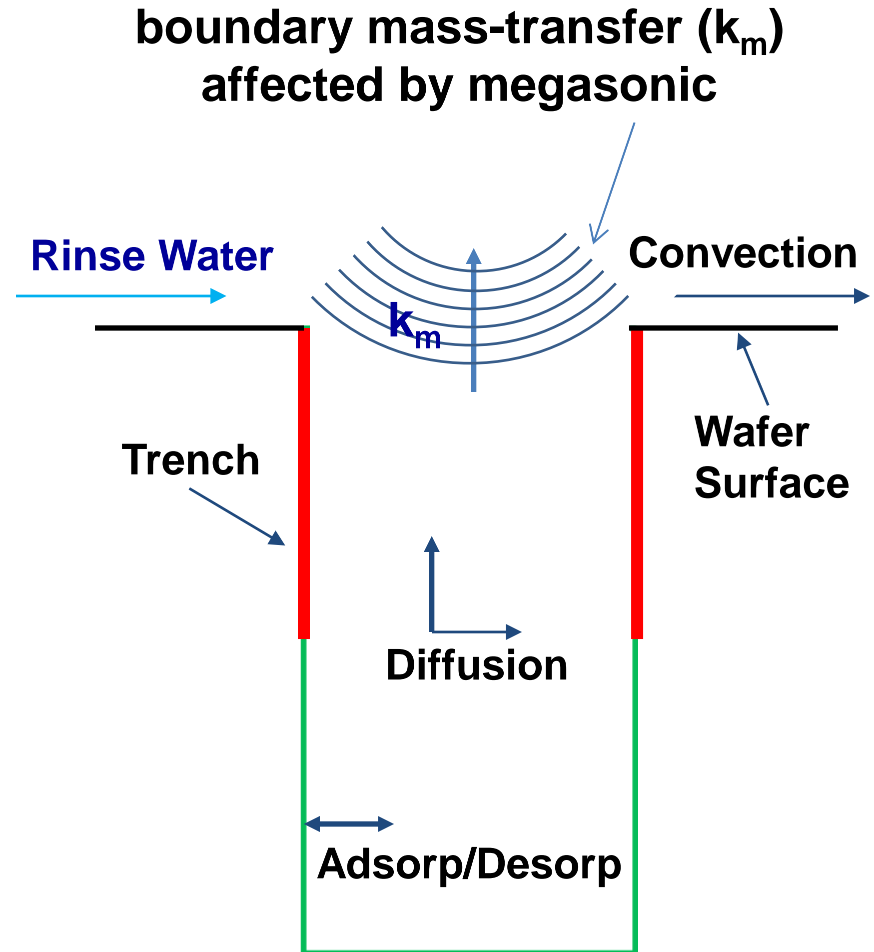
Rinse Operation Parameters:

- **Increase water flow rate:**
  almost no effect for fine structures;
  waste of water

- **Increased diffusivity (D):**
  higher temperature (mild effect)

- **Higher desorption (k_d):**
  higher temperature (mild effect)

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



2. End-Point Detection: A Key Step in Water Use Minimization

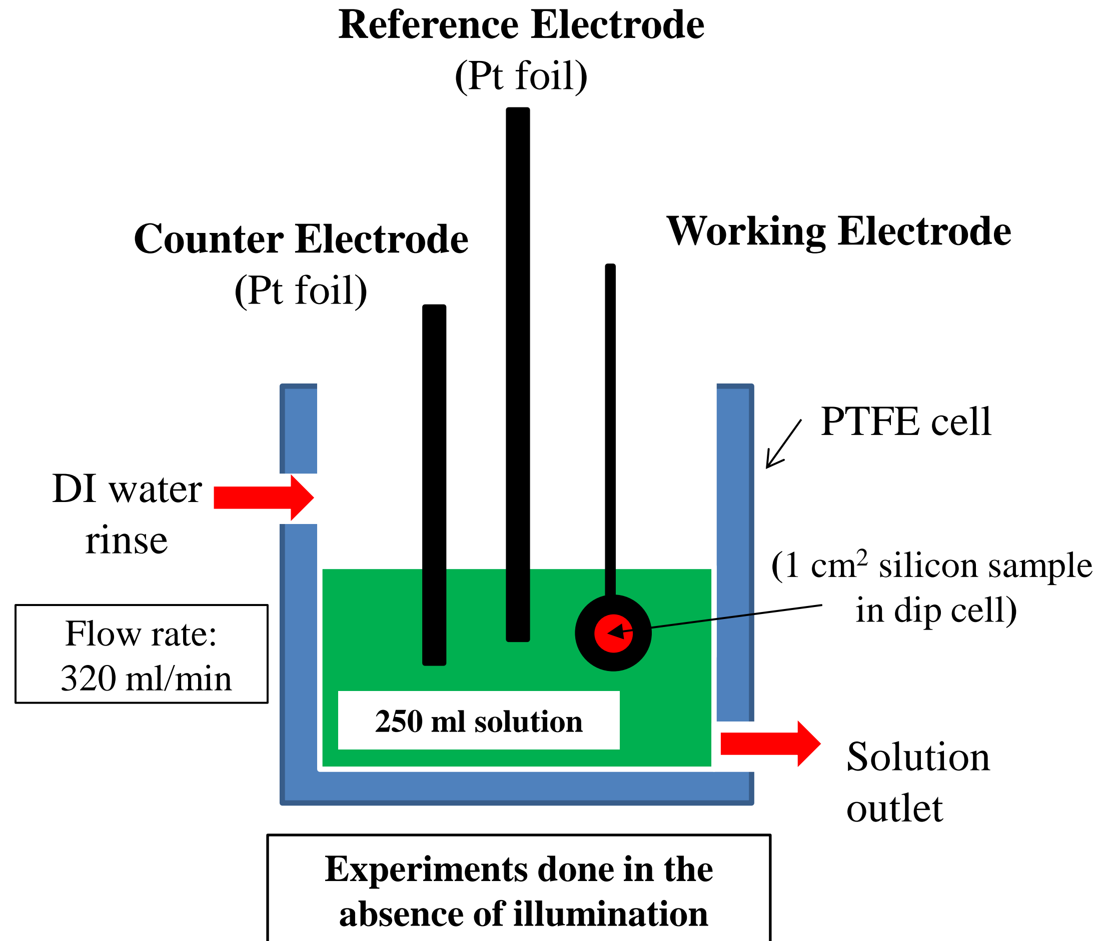
Case Study: Rinsing of silicon immersed in DHF

Materials and Methods

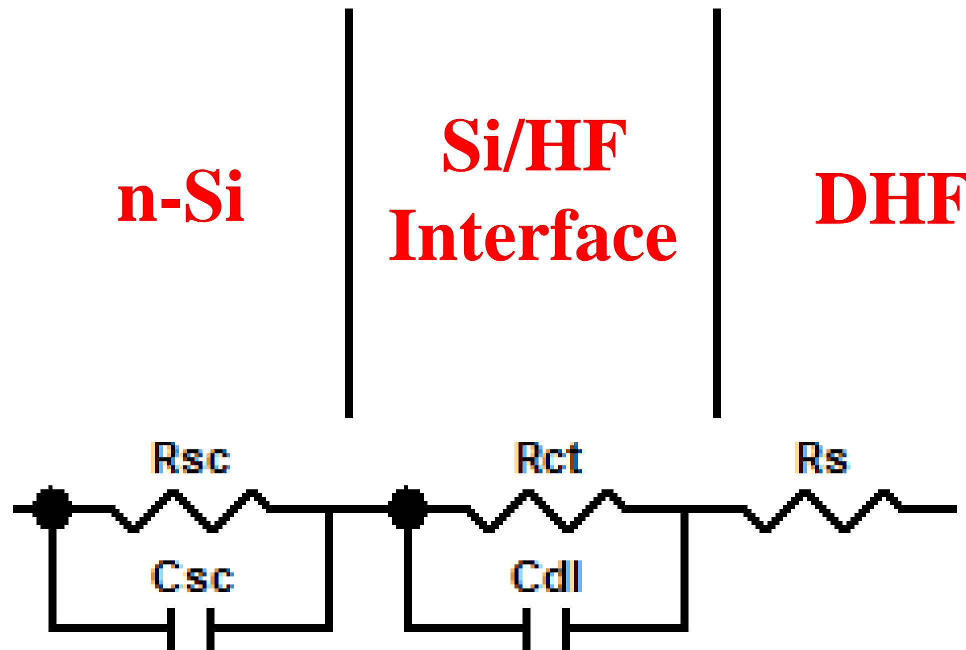
Methods
Electrochemical Impedance Spectroscopy (EIS)(100k Hz to 0.1 Hz)
Single Frequency EIS (1 Hz)

Materials
Phosphorus doped Si (100) 6~10 ohm-cm
HF (metal concentration <50 ppb)
18 Mohm-cm DI water (air-saturated)

Equipment
Gamry Series G potentiostat



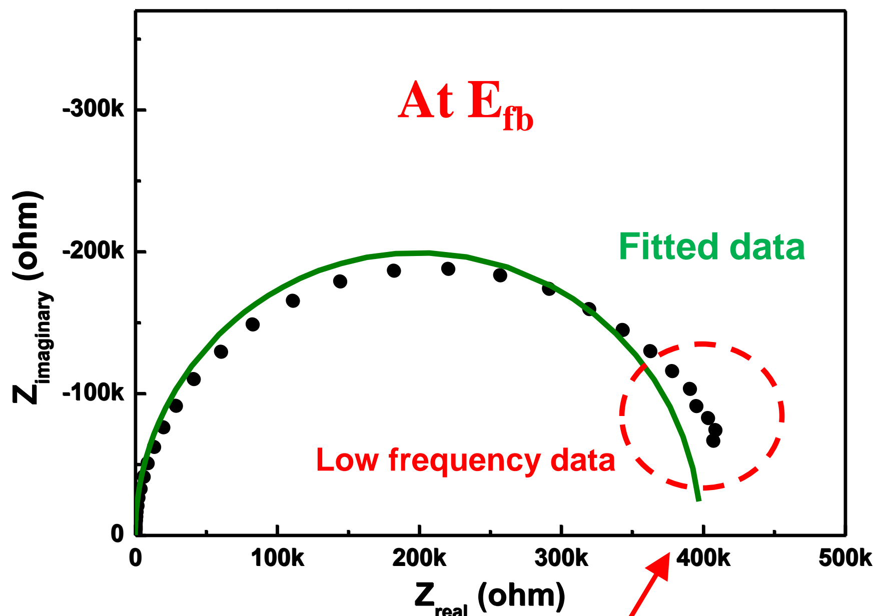
Equivalent Circuit of Silicon Sample Immersed in Dilute HF

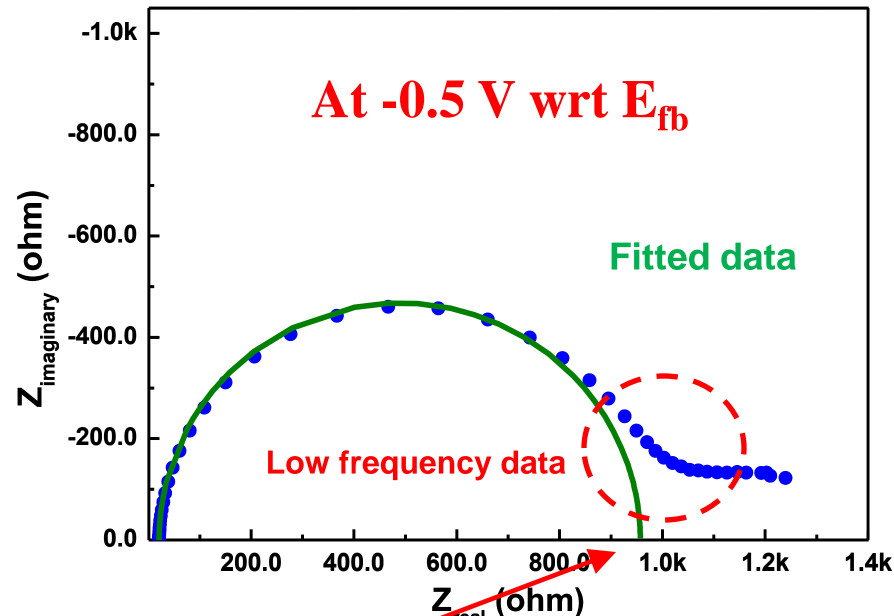


Rsc: Space charge resistance
Csc: Space charge capacitance
Rct : Charge transfer resistance
Cdl : Double layer capacitance
Rs : Solution resistance

EIS measurements were fitted using this equivalent circuit to characterize Si/HF interface.

Electrochemical Impedance Spectroscopy of n-Si Immersed in 2% HF



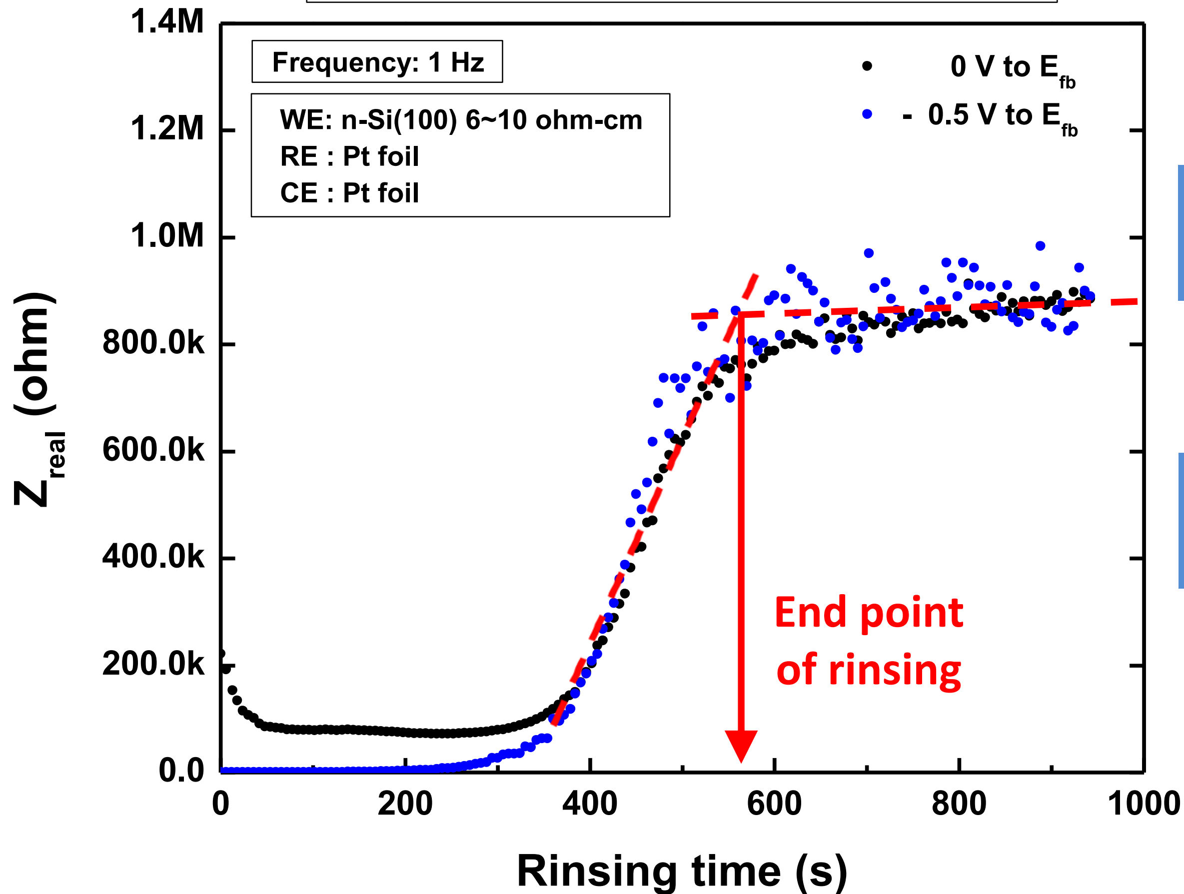


(Fitted data) 2% HF

Potential(V) vs E_{fb}	0	-0.5
Rs (ohm-cm^2)	23	21
Rct (ohm-cm^2)	398370	936
Cdl (μF/cm^2)	0.24	6.86
Rsc (ohm-cm^2)	8.63	267.20
Csc (μF/cm^2)	1.04	946.74

Z_{real} at low frequency of 1 Hz was followed during rinsing process

Rinsing of n-Si(100) Immersed in 2% HF



Z_{real} increased with rinsing time and reached plateau

End point of rinsing can be determined

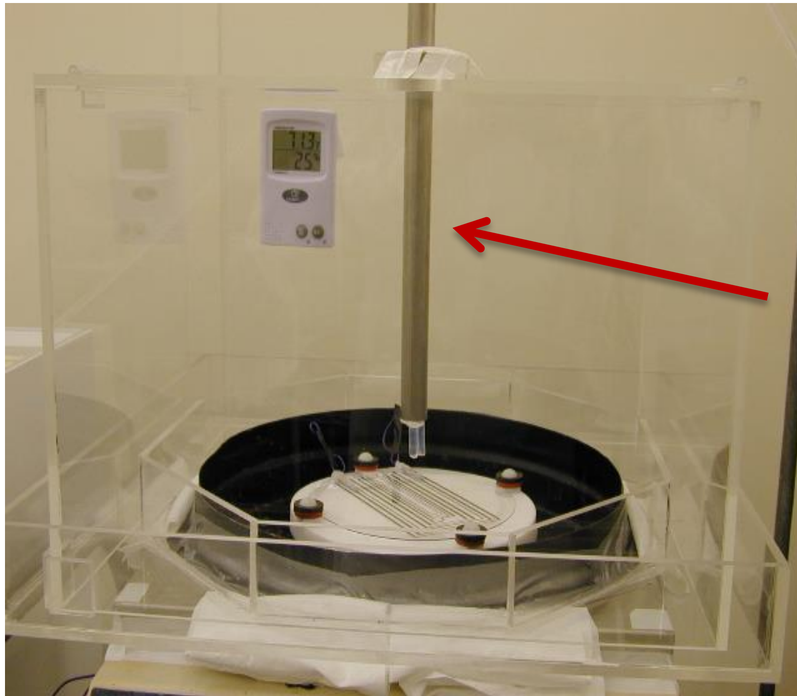
Conclusions and Future Plans

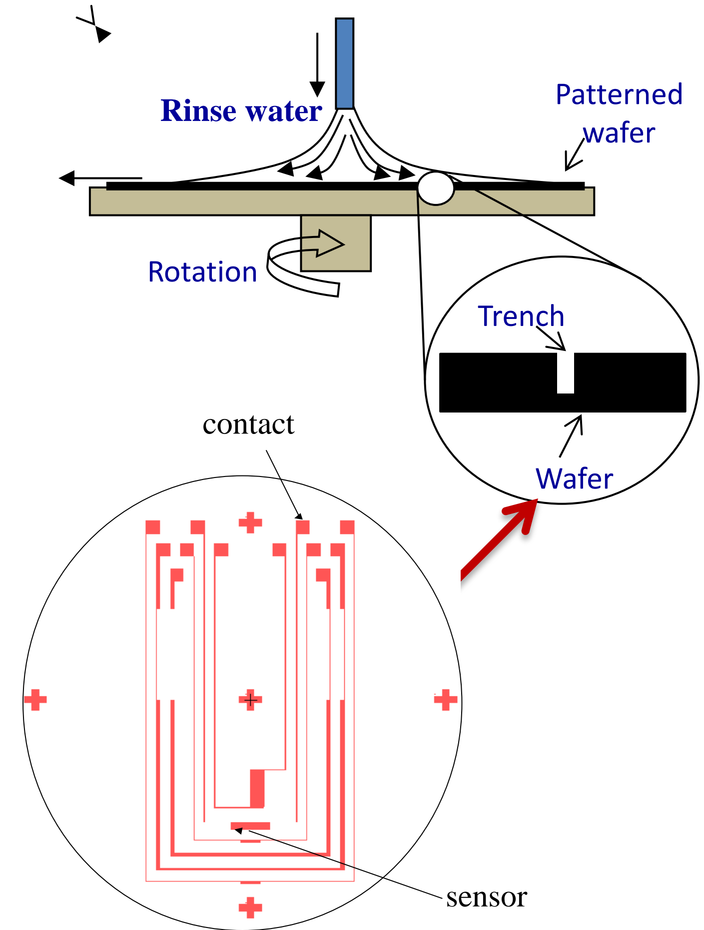
- **Aqueous cleaning of patterned wafers, particularly those with multi-materials, involves significant increase in the usage of resources as well as increase in the processing time.**
- **The primary rinse bottleneck is the surface retention as well as transport of impurities inhibited by surface interactions and charge effects.**
- **A combination of experimental and simulation method is developed to study the bottleneck of the rinse process**
- **Cleaning of small features can be enhanced by decreasing the transport resistance. A key bottleneck is boundary mass transport; it can be potentially enhanced by mild megasonic.**
- **Future Work:**
  - **Experimental validation of simulation results using other substrates and impurities (both ionic and non-ionic).**
  - **Determination of surface interaction parameters using QCM.**

3. Direct Measurement of Surface Interaction Parameters: Input to the Process Simulator

Testbed for Single-Wafer Spin Rinsing

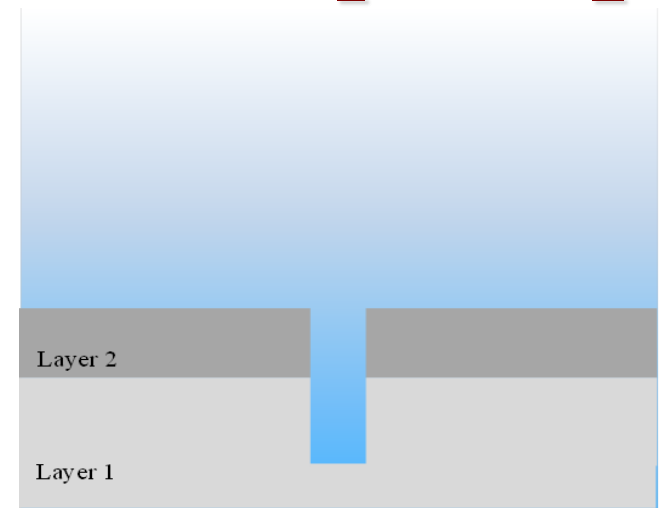
Single-wafer spin rinse tool equipped with Electro-Chemical Residue Sensor (ECRS) for wafer-level rinse studies



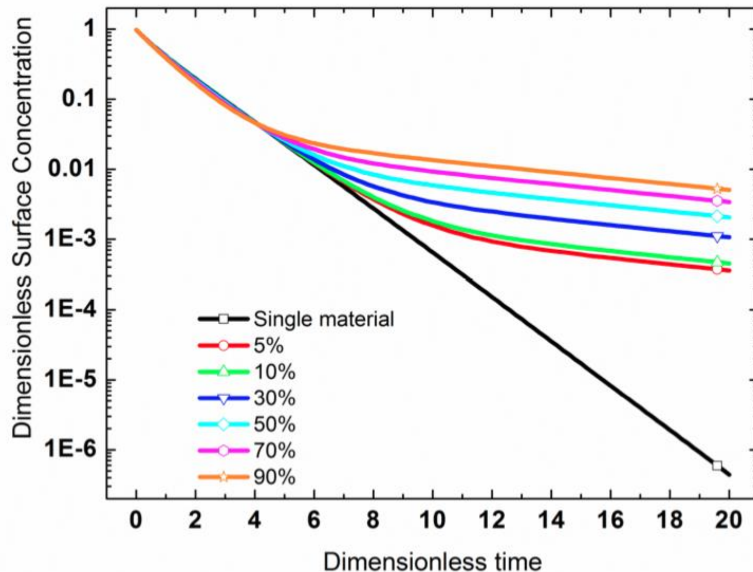


Key Surface Interaction Parameters (k_a and k_d)

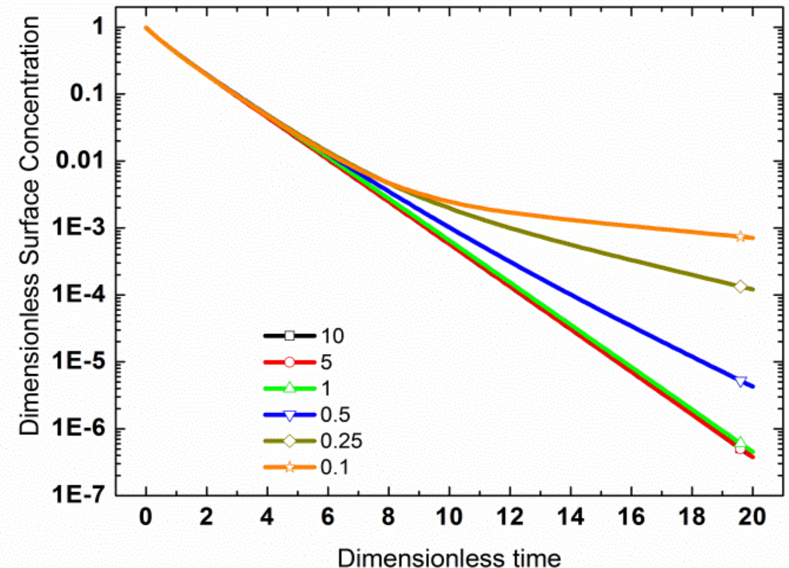
For a two-layer trench the ratio of desorption rate coefficients can have a significant role in contaminant removal from the bottom of the trench.



Effect of layer 2 thickness

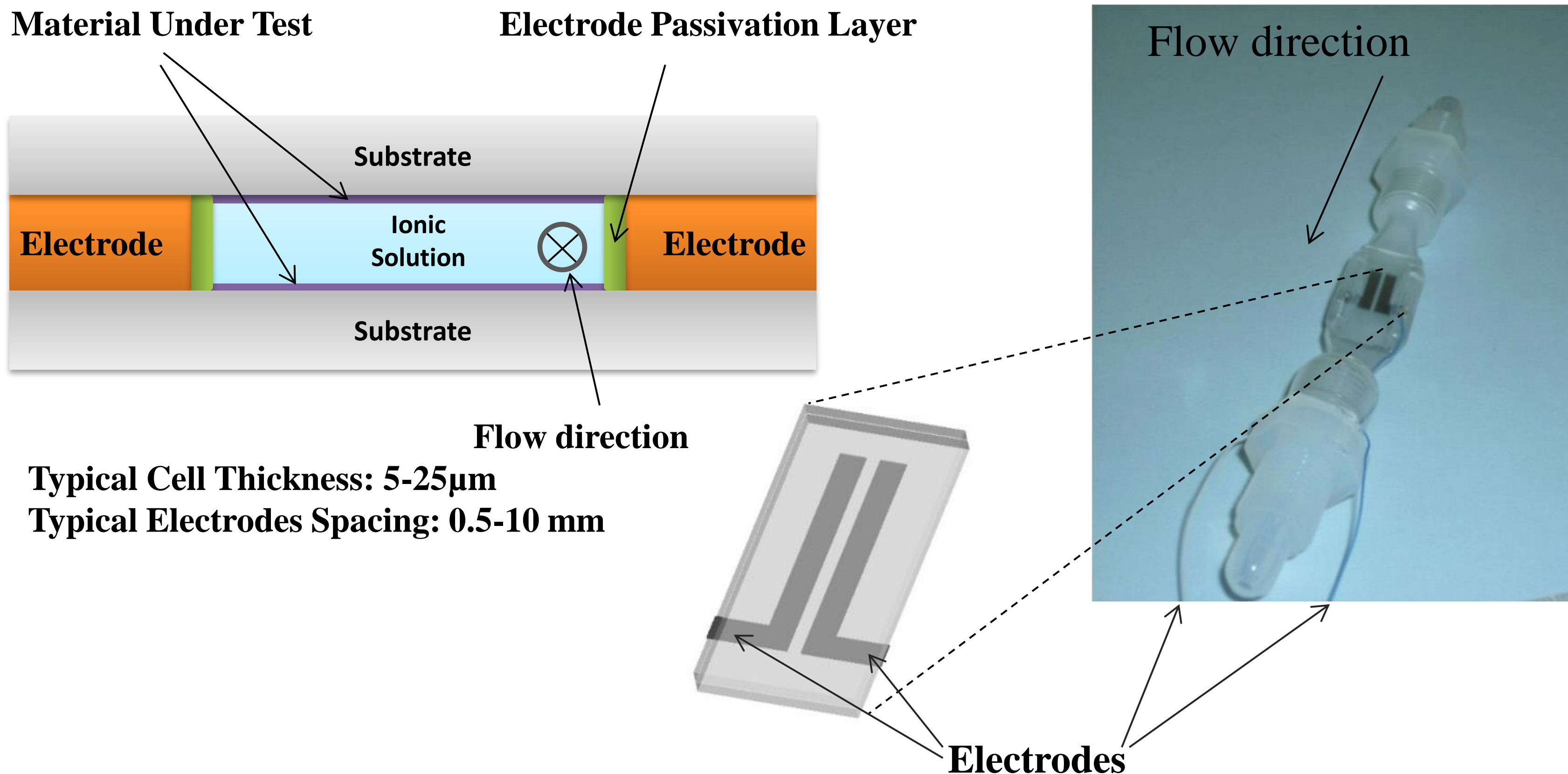


Effect of layer 2 desorption rate coefficient



Adsorption/Desorption Test Cell (AD Test Cell)

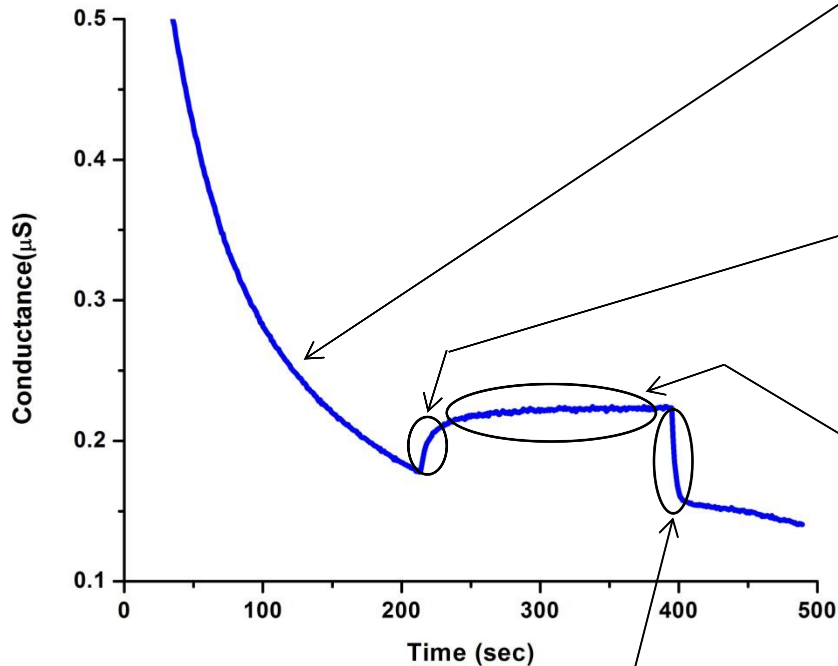
A Novel Device for Direct Measurement of Surface Interactions

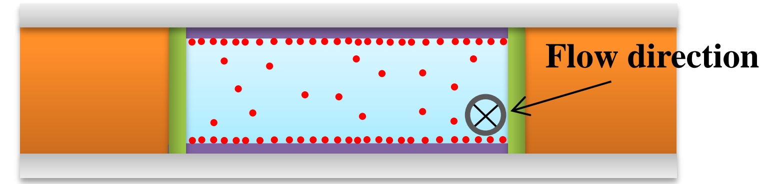


Principle of Operation of AD Test Cell

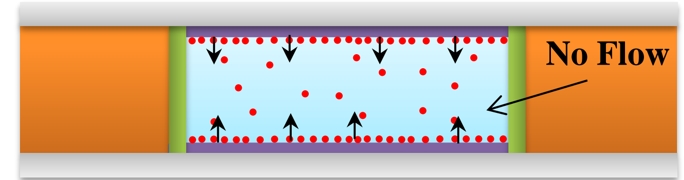
- Dynamics of surface concentration is governed by Langmuir equation: $\frac{\partial C_s}{\partial t} = k_a C\,(S_0 - C_s) - k_d C_s$
- When the bulk concentration is very small, surface concentration exponentially decays as the contaminants are desorbed from the surface.
- The desorption rate coefficient can be extracted from the decay rate.
- If the desorbed contaminants are accumulated in a limited volume, the decay format is deviated from exponential due to adsorption. The adsorption rate coefficient can be calculated from this deviation.

Measurement Method Using AD Test Cell

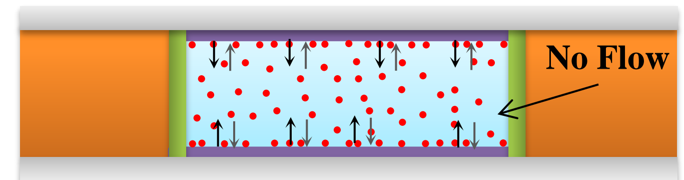




Contaminants desorbing from surface and washed away via flow of water



Flow is stopped; contaminants desorbing from surface, concentration increases in the cell, conductance goes up



As contaminant concentration increases adsorption rate increases too and adsorption-desorption reach equilibrium, conductance flattens

Flow is turned on again, ions are washed away, conductance decreases

Determining the Desorption Coefficient From AD Test Cell Data

- While cell is being rinsed, the bulk concentration may be considered negligible, so the surface concentration decays exponentially:

$$C \cong 0,\ \frac{\partial C_s}{\partial t} = k_a C\,(S_0 - C_s) - k_d C_s \Rightarrow \frac{\partial C_s}{\partial t} \cong -k_d C_s \Rightarrow C_s \cong C_{s0} e^{-k_d (t-t_0)}$$

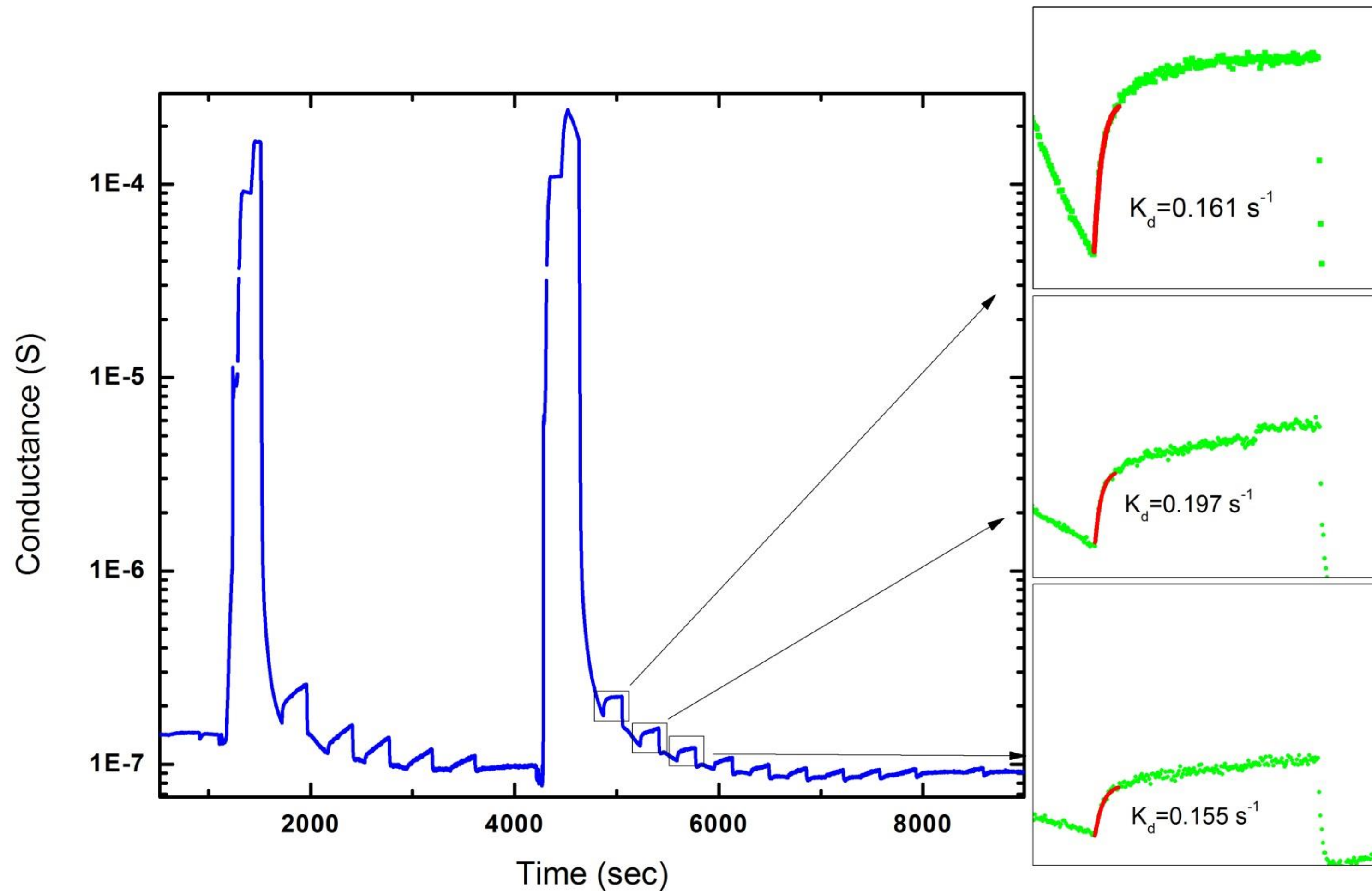
- If we stop the flow of water, the bulk concentration can be written as

$$C \cong C_{in} + \frac{\left(C_{s,in} - C_s\right) A}{V} = C_{in} + \frac{C_{s,in} A}{V}\left(1 - e^{-k_d (t-t_0)}\right)$$

- Conductance is proportional with concentration so it can be written as:

$$Y \cong Y_0 + Y_1\left(1 - e^{-k_d (t-t_0)}\right)$$

Experimental Results
Sulfuric Acid Retention on Silica



Summary and Conclusions

- AD test cells with surface to volume ratio as high as 10^5 m^{-1} can be fabricated and tested.
- Desorption rate coefficient can be extracted from resistance/conductance data using a simple analytical model.
- Adsorption rate coefficient can be obtained using the equilibrium data or application of a process model
- The substrates of cells can be coated with any desired material prior to cell assembly and corresponding adsorption-desorption rate coefficients for various ions can be measured.
- Adsorption-desorption properties can be measured for various fluids and different temperatures.

Industrial Interactions and Acknowledgment

- **Financial and technical support from ProSys**
- **Technical discussions with Ian Brown of TEL.**
- **COMSOL Corp. assistance in software application.**

Publications and Presentations

- **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* (submitted in January 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.**
- **Chiang, C.C., Raghavan, S., Farhang Shadman "Simulation of Rinsing Dynamics of Patterned Structure" SRC-TECHCON 2014 (submitted in February).**