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

(*Task Number: : 425.043*)

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Cost Sharing: $40k/year, WSP - Arizona TRIF

Challenges in Cleaning and Rinsing of Multi-Material Surfaces and Structures

- **Fabrication of current state-of-the-art devices requires cleaning and rinsing of sub-micron size structures**

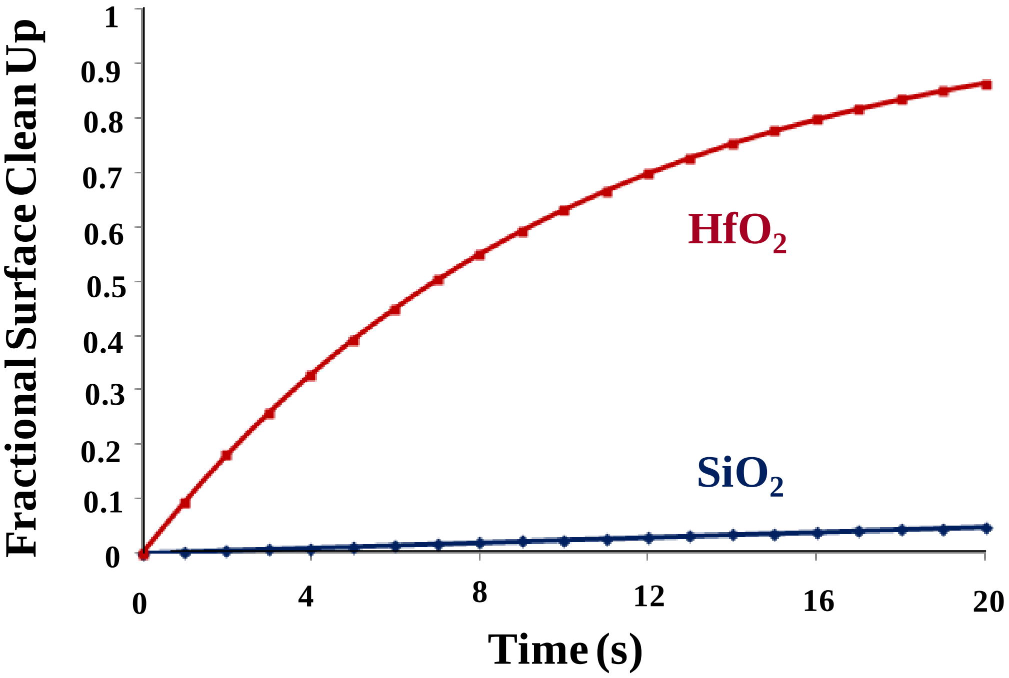
- **The complexities in rinsing of these structures arise from:**

  - **Differences in wettability of various surfaces**
  - **Inhibited rinsing in regions with lower wettability and contributions to watermark and post rinse residues**
  - **Slow transport of cleaning chemicals and rinsing water in and out of the structures**
  - **Impurity retention due to surface interactions and surface charge effects**

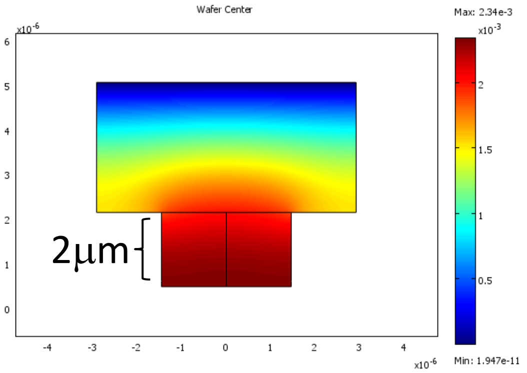
- **The conventional rinsing processes have not been designed based on the rinse process bottlenecks and lack in-situ and real-time monitoring**

Effect of Surface Characteristics on Rinsing Effectiveness

Example showing rinse efficiency of HfO_2 and SiO_2 Surfaces



Typical Profile of Impurity Concentration during Rinse



Wafer Size: 450 mm,

Rinsing of Sulfuric Acid

Flow Rate: 2 lit/min,

Wafer Rotation: 800 rpm

Different dielectric materials have significantly different impurity retention, rinsing dynamics, and cleaning efficiency

Objectives and Method of Approach

Objective:

- **Understand the bottleneck of the rinse process involving small structures that consist of different materials**
- **Develop innovative rinse methods for both performance and ESH gain**

Method of Approach:

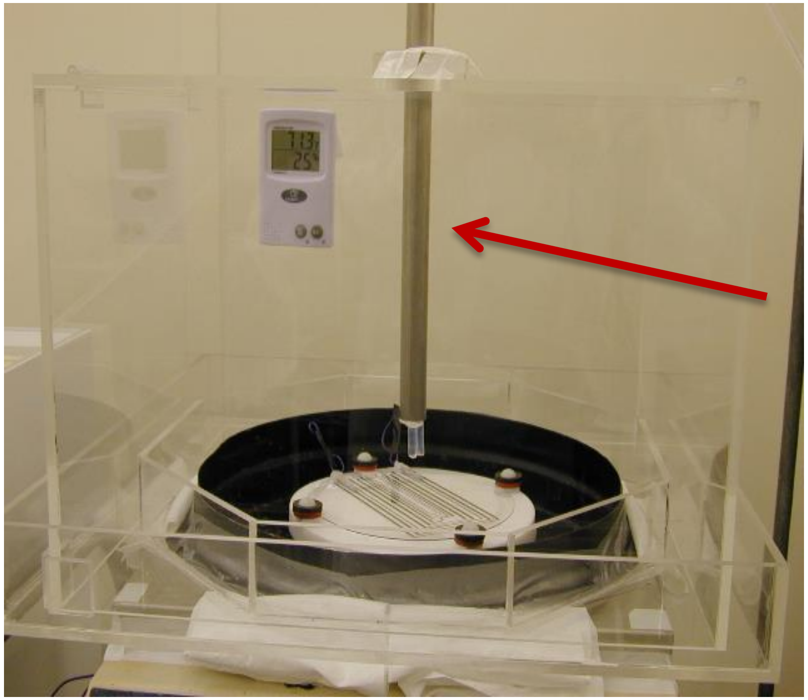
- ***Subtask 1*: In-Situ and Real-Time Investigation of Rinsing of Multi-Material Structures**
- ***Subtask 2*: Megasonic Enhancement of the Rinsing Process**
- ***Subtask 3*: Process Simulation to Develop Optimized Low-Water Rinse Recipes**

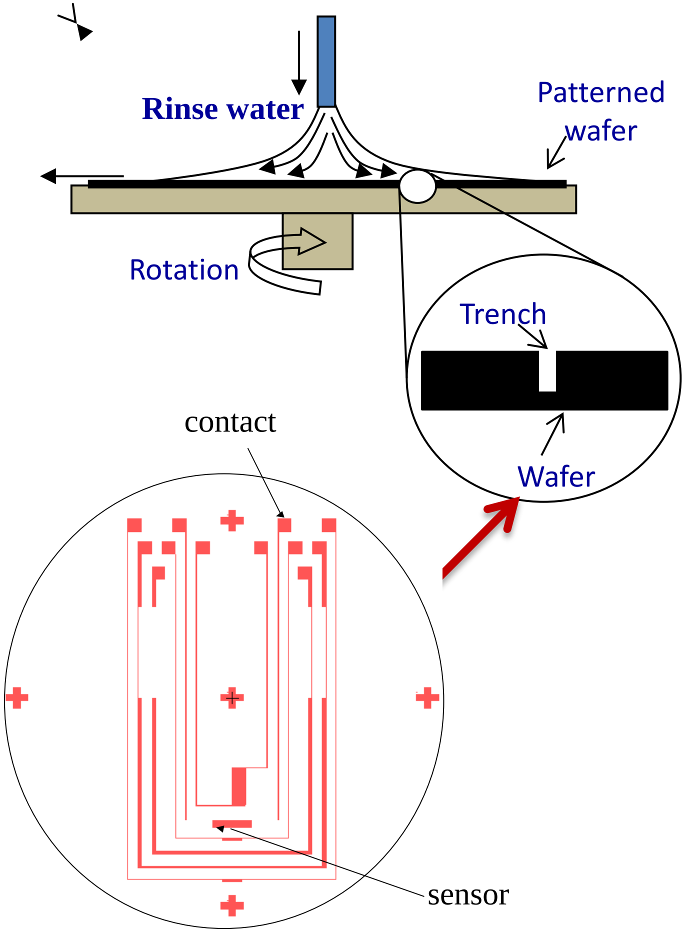
ESH Impact

Robust and efficient rinse processes would have a major ESH impact by reducing the usage of water and energy

Subtask 1:Testbed for Single-Wafer Spin Rinsing

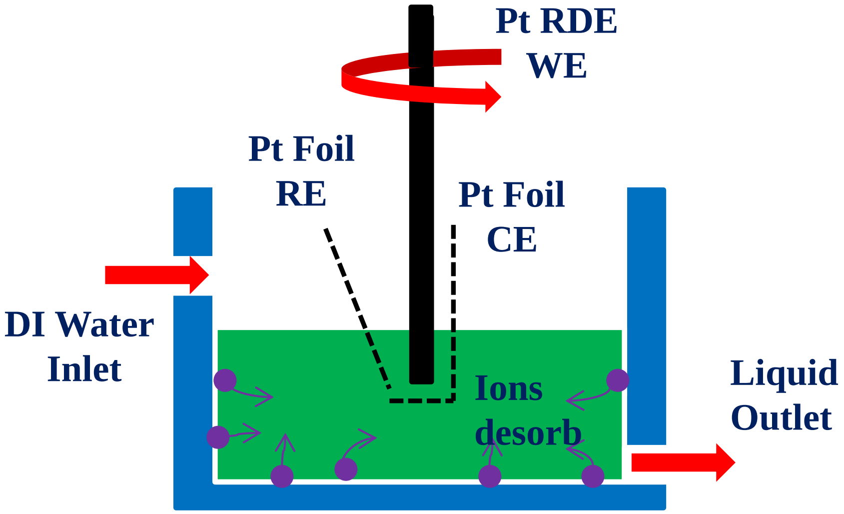
Single-wafer spin rinse tool equipped with Electro-Chemical Residue Sensor (ECRS) is designed and set up.

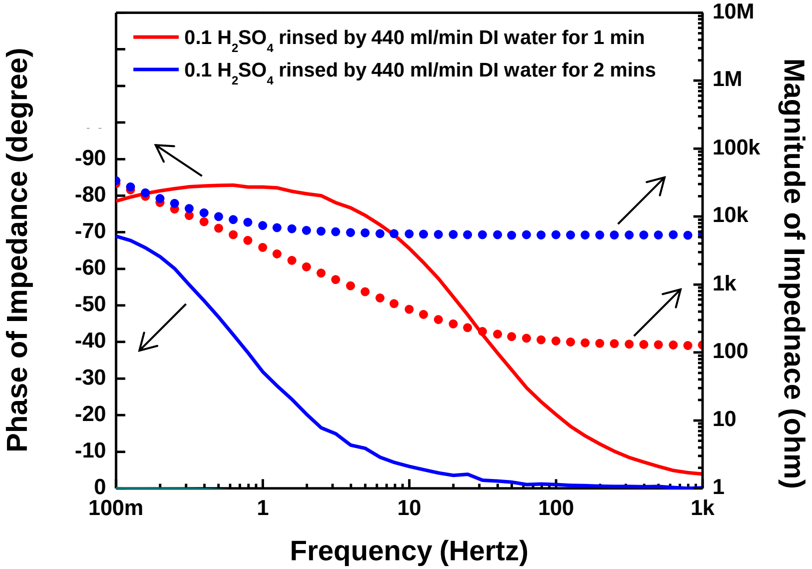




Determining the Desorption Kinetics

- ➢ H_2SO_4 contained in a glass vessel is rinsed by DI water.
- ➢ Impedance of the liquid in the cell is monitored using a rotating disc Pt electrode.
- ➢ Frequency (1000 Hz) was selected based on impedance phase angle.



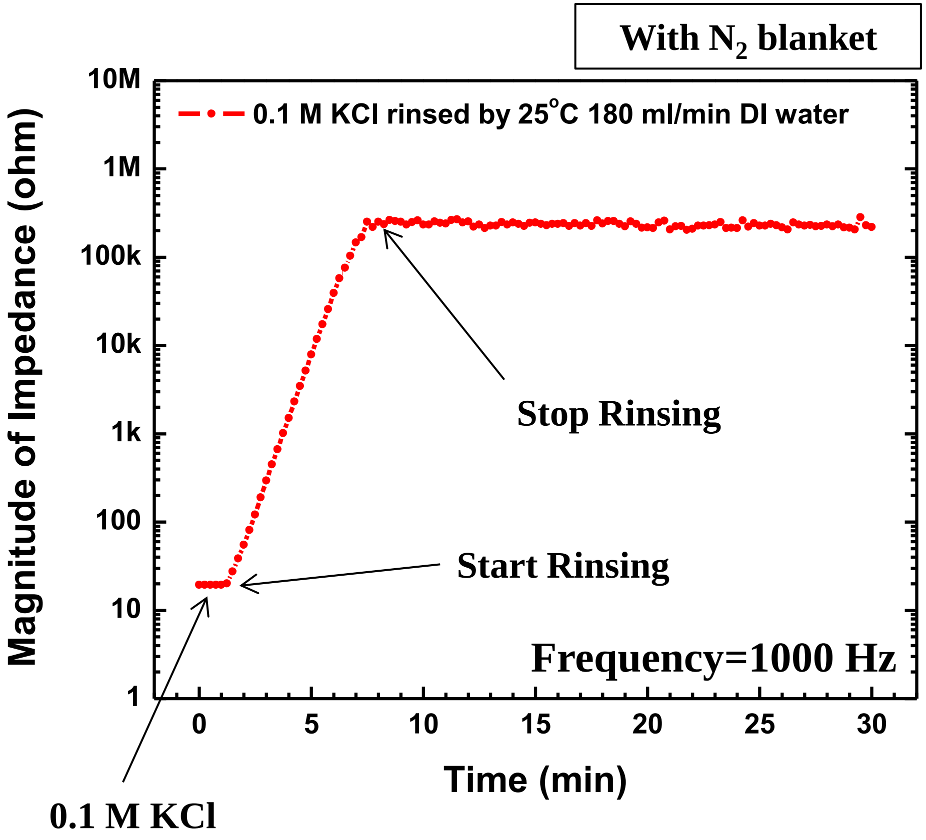


Determining the Desorption Kinetics

- ➢ **Impedance increases as bulk liquid is replaced with DI water.**

- ➢ **No measurable change in impedance when rinsing is stopped . Frequency lower than 1000 Hz may be required.**

- ➢ **Currently conducting measurements at lower frequencies (0.01Hz to 10 Hz) that seem to be more suitable to follow desorption.**

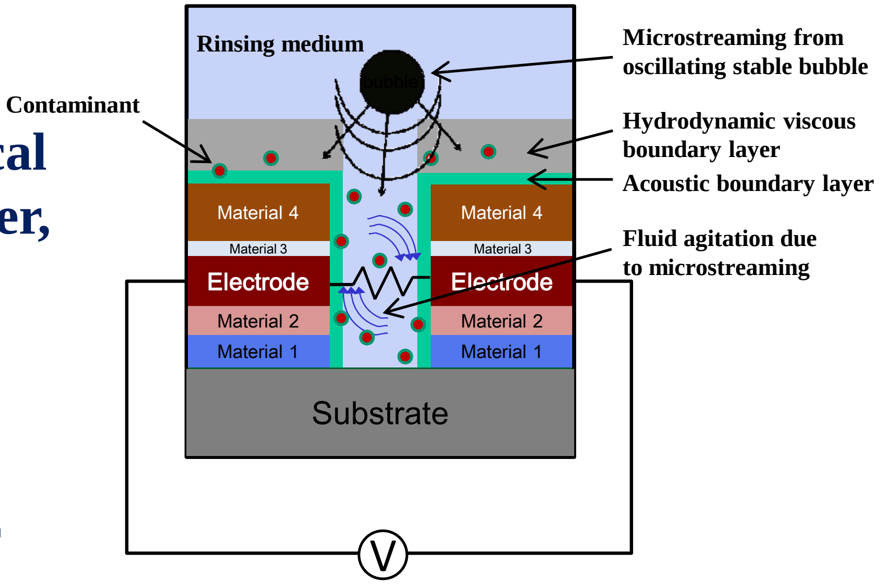


Subtask 2: Megasonic Enhancement of Rinsing Process

- ➢ Potential for significant enhancement of the transport and removal of contaminants (process bottleneck, particularly for high aspect-ratio features and materials with limited wettability)
  - Enhance the diffusion of ionic contaminants out of micro/nano structure.
  - Increase the desorption process through direct interaction of acoustic waves with surface.

- ➢ Advantage of megasonic effect over addition of chemical additives: Chemical additives in cleaning solutions and water, make rinse water recycling difficult or costly (ESH & cost impacts)

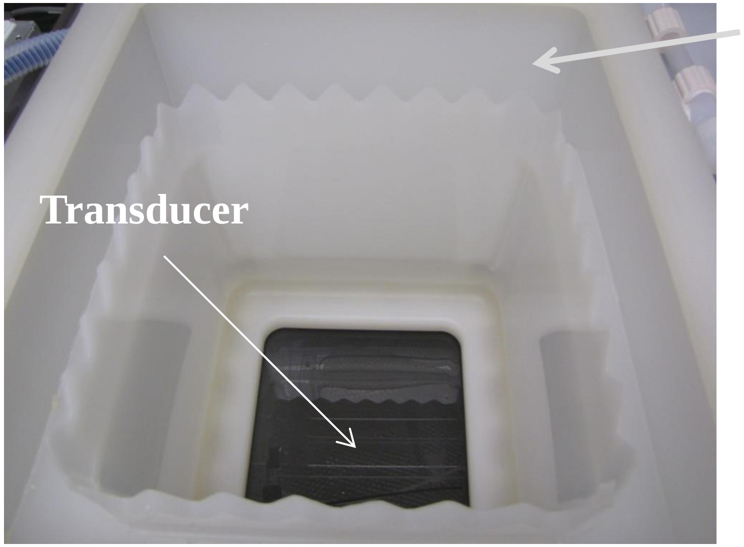
- ➢ Prevent damage to fine structures by using low-power megasonic and proper selection of temperature and dissolved gases.



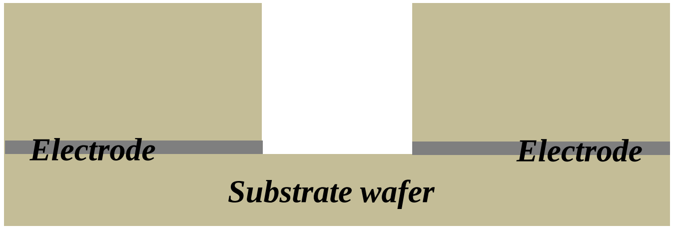
Experimental Setup and Procedure

- **ECR sensor was contaminated with 0.86 M sulfuric acid solution and immersed in megasonic tank with constant DI water overflow (under N2 blanket)**
- **Impedance measurements taken during entire rinsing process**

f=0.93MHz
Power density: 0.6-1.2W/cm^2



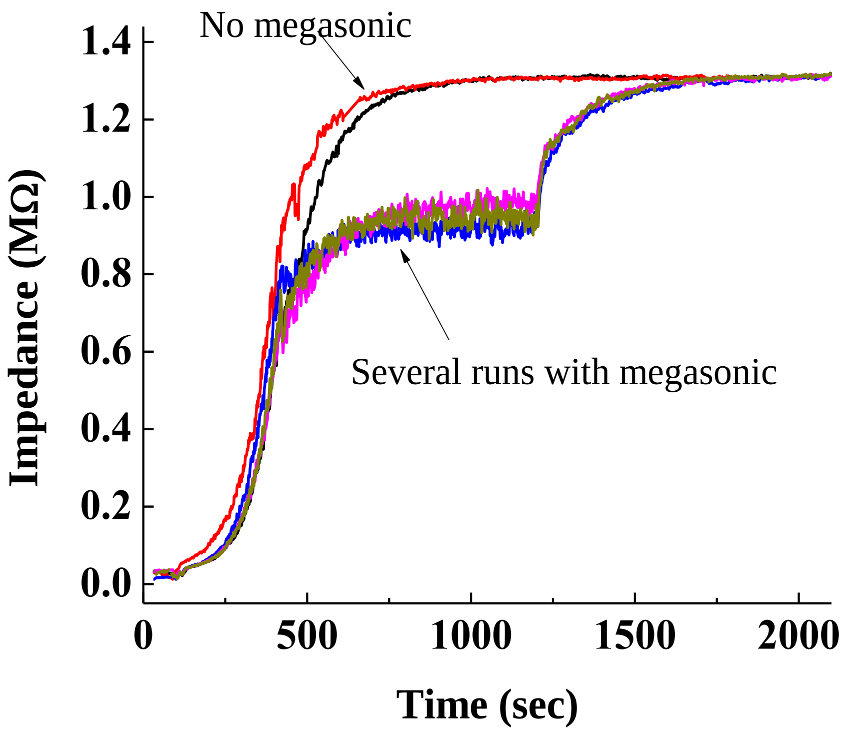
ProSys Megasonic Tank top down view



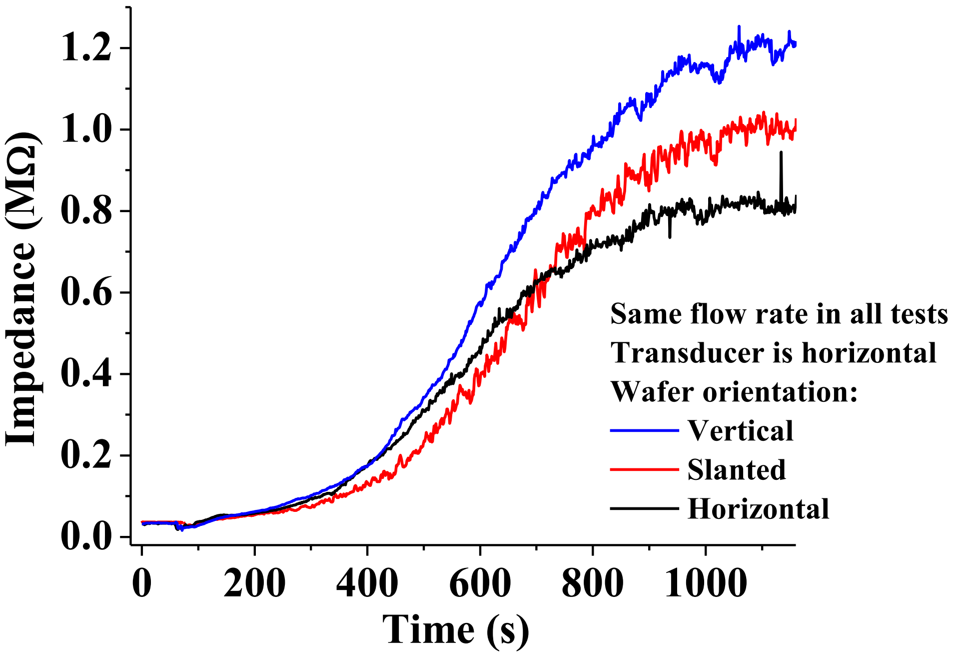
Schematic of electrochemical residue sensor (ECRS)

Megasonic Cleaning: Experimental Data

Rinsing sulfuric acid in a patterned wafer



Experimental data shows a clear and significant penetration of megasonic field inside the channel, as detected by the ECRS.



Subtask 3: Process Simulation to Develop Optimized Low-Water Rinse Recipes

Rinse Model (including impurity removal by convection, diffusion, acoustic field, and surface adsorption/desorption)

To analyze the rinse data

To facilitate the development of new and efficient rinse process

New model development includes:

- **Effects of surface charge, surface adsorption and desorption characteristics, and surface wettabilities of different materials**
- **Enhancement effects of megasonic on rinse process**
- **Model validation using direct measurements**
- **Parametric study for low-water recipe development**

Process Simulator: Concept and Formulation

Multi-component species transport equations:

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

Surface adsorption and desorption:

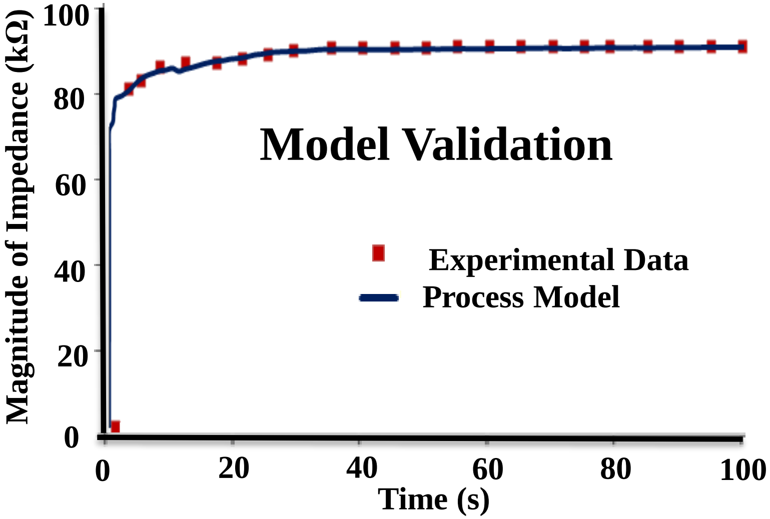
$$\frac{\partial c_s}{\partial t} = k_a c_i (S_0 - c_s) - k_d c_s$$

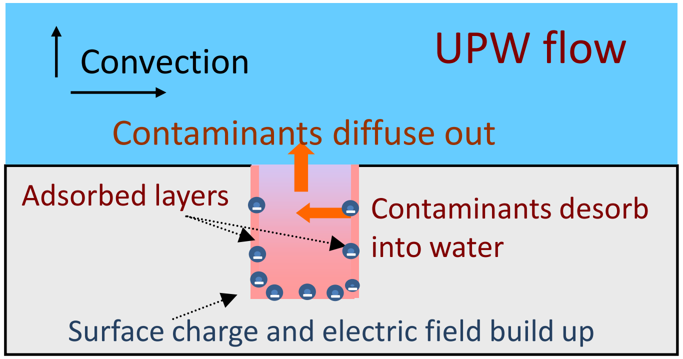
Poisson equation: $\nabla^2 \varphi = -\frac{\rho}{\epsilon}$

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

Ohm's law: $\boldsymbol{J} = \sigma \boldsymbol{E}$

Electrical conductivity: $\sigma = \sum_i \lambda_i c_i$





Convection

UPW flow

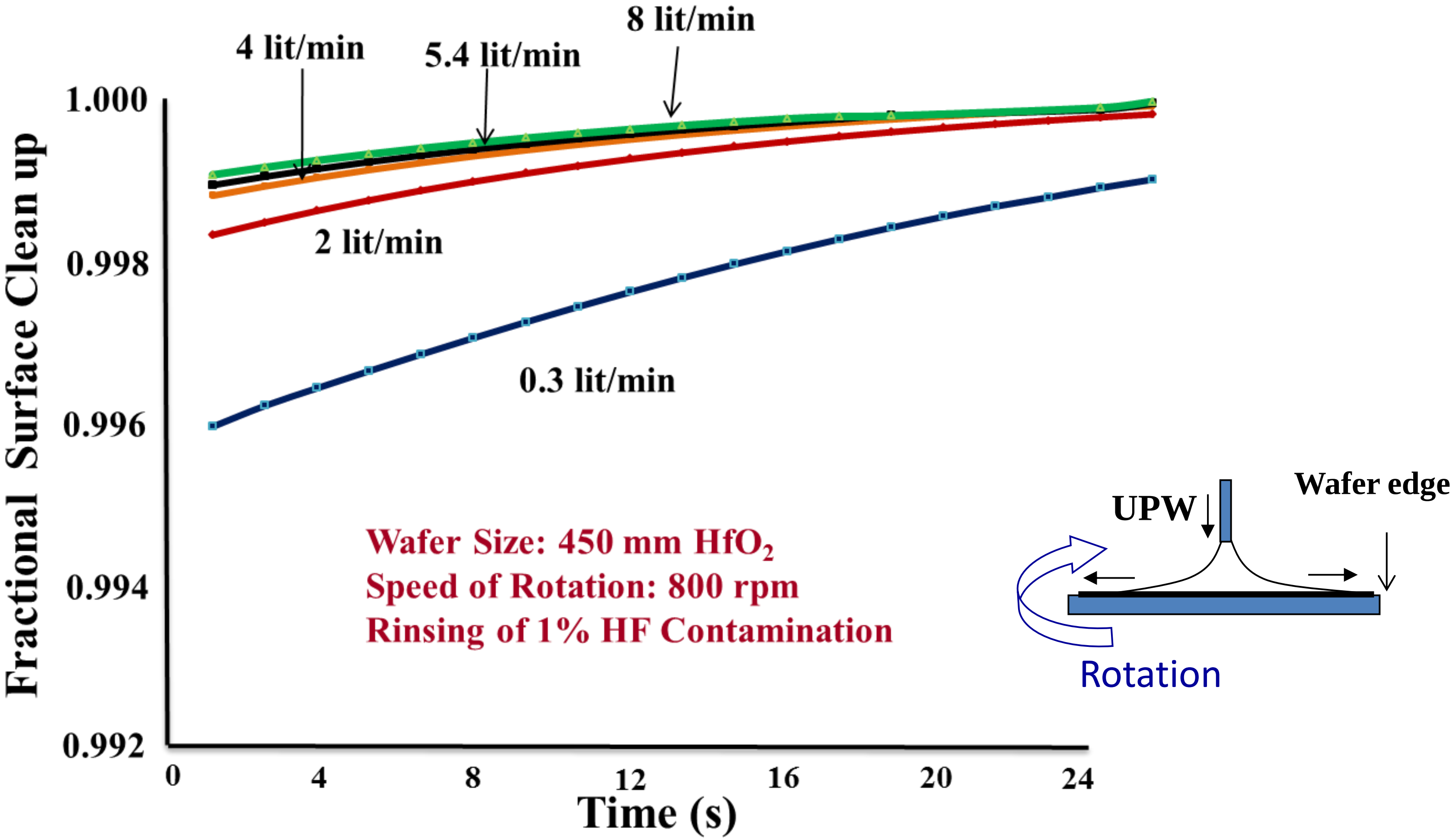
Contaminants diffuse out

Adsorbed layers

Contaminants desorb into water

Surface charge and electric field build up

Effect of Flow Rate in Single-Wafer Tools



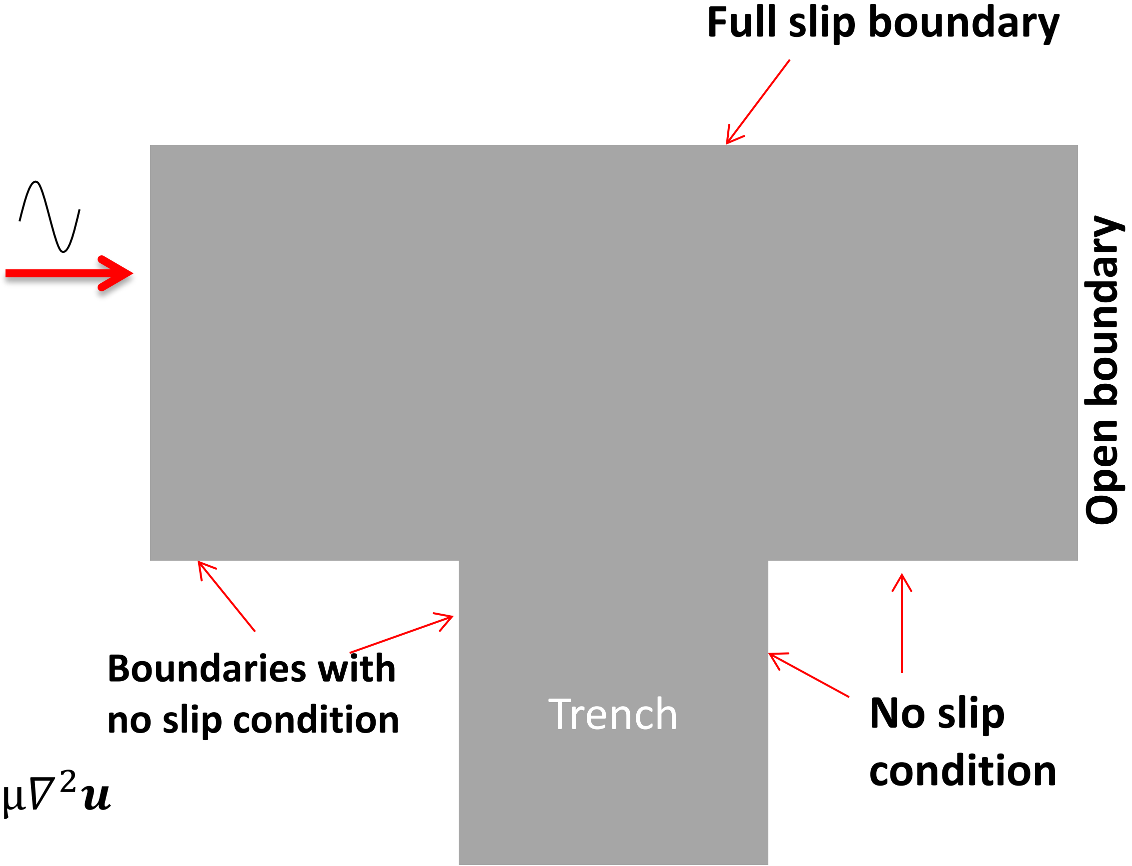
Wafer Size: 450 mm HfO_2
Speed of Rotation: 800 rpm
Rinsing of 1% HF Contamination

The results indicate an increase in rinsing efficiency as the flow rate increases. Increasing the flow rate beyond 4 lit/min has lower impact on the rinse efficiency.

Process Simulator: Megasonic Formulation

Oscillating flow field
$u^*(1+\sin 2\pi f t)$

u is the maximum velocity
of the oscillating flow field


Full slip boundary

Open boundary

Boundaries with
no slip condition

Trench

No slip
condition

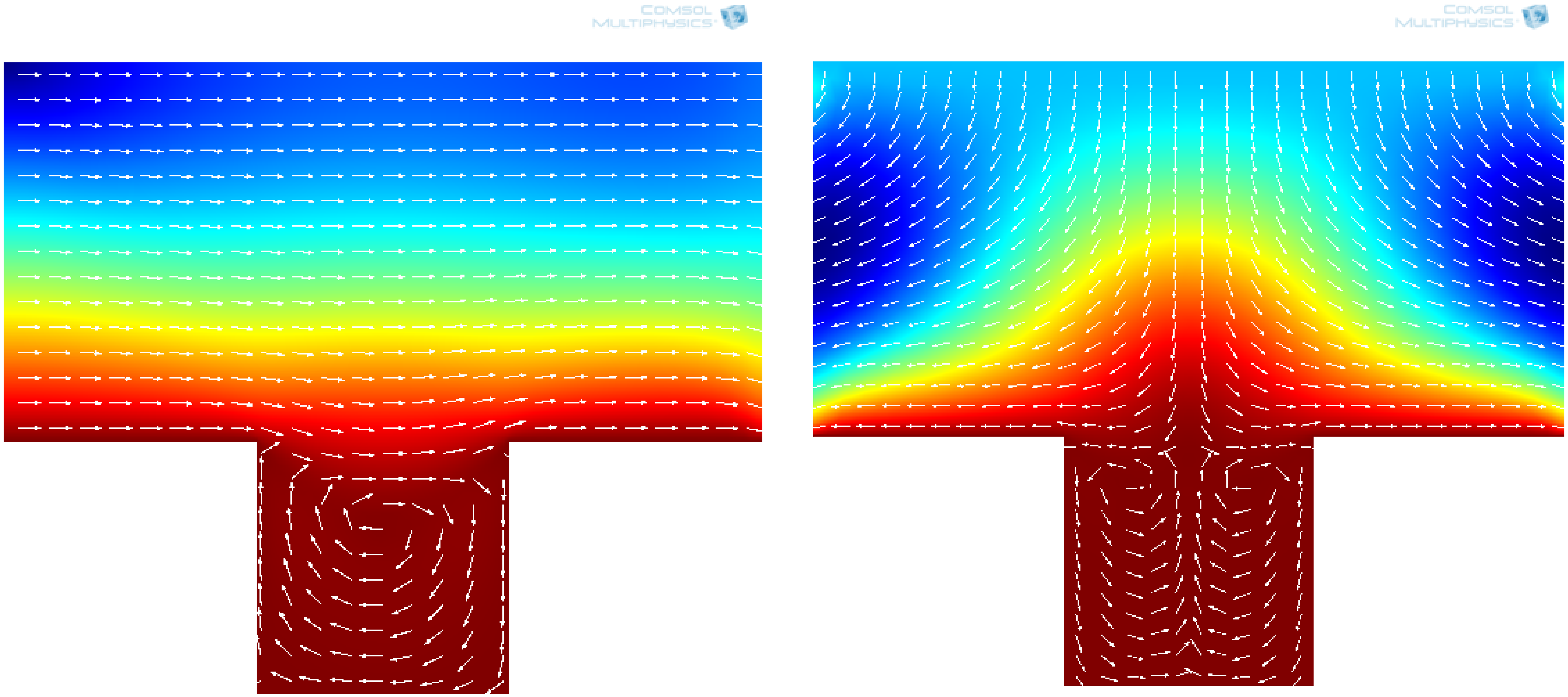
Navier-Stokes equation:

$$\rho\frac{\partial \boldsymbol{u}}{\partial t}+\rho(\boldsymbol{u}\cdot\nabla)\boldsymbol{u}=-\nabla \mathrm{p}+\mu\nabla^2\boldsymbol{u}$$

Conservation of mass: $\frac{\partial \rho}{\partial t}+\nabla\cdot(\rho\boldsymbol{u})=0$

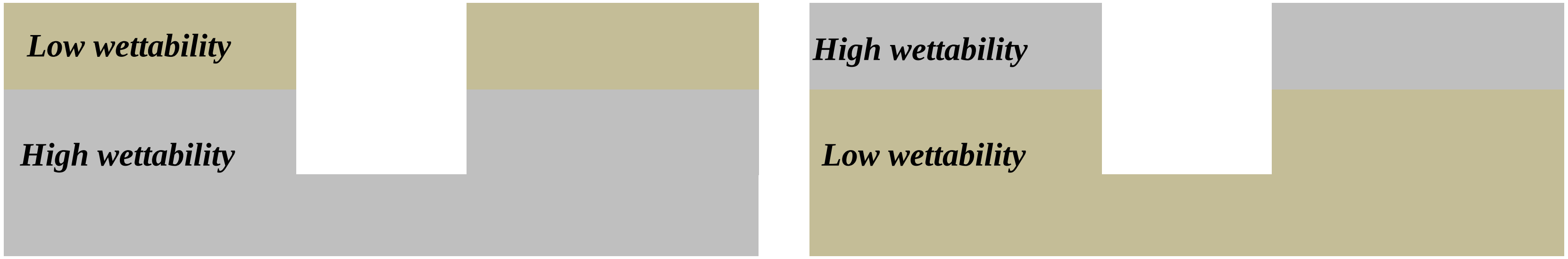
Flow Velocity Patterns in Test Structures

- **Introduction of megasonic changes vortex structure in the trench**



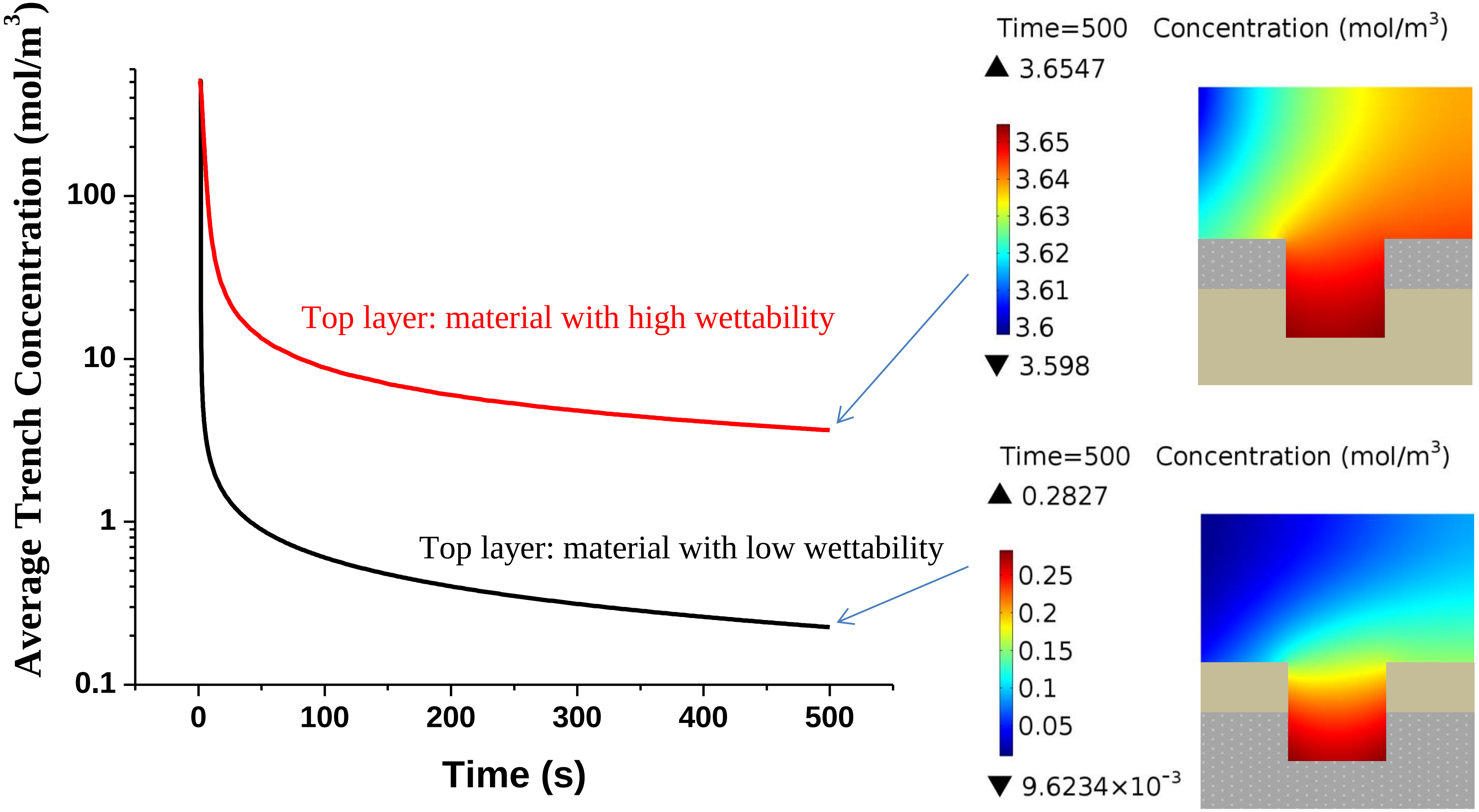
Simulation of the Rinsing of a Two-Layer Multi-Material Structure

- The geometry in the simulation consists of two layers with the same thickness and different wettability.
- The current simulation can be used to study the effect of stack configuration on the fluid dynamics in the vicinity of the surfaces.



Test Structures in the simulation

Rinsing of a Two-Layer Multi-Material Structure



Multi-Material ECRS Structures

- **Two structures, with two different hydrophobic and hydrophilic layer stack configurations, are being pursued.**
- **The fabrication parameters are being fine-tuned.**

Multi-material electrochemical residue sensor

Summary and Conclusions

- **Aqueous cleaning of patterned wafers with high aspect-ratio structures and multi-materials surfaces involves significant increase in usage of resources as well as increase in processing time.**
- **A combination of experimental and simulation method is developed to study the bottleneck of the rinse process**
- **The primary rinse bottleneck is surface desorption followed by migration of impurities. The fundamentals are poorly understood due to surface charge and the electric field effects in the narrow and deep structures.**
- **Addition of low-power megasonic to rinse is an ESH-friendly approach; it does not require chemical additives with potential negative environmental impact.**
- **The megasonic application needs to be optimized for desired process and environmental gain. This is a goal of the proposed future work in this project.**

Industrial Interactions and Technology Transfer

- **Megasonic equipment support by ProSys Inc.**
- **Technical discussions with Ian Brown of TEL**
- **Interactions with Kedar Dhane (Intel) and Jun Yan (Lam Research) on rinse model development**
- **COMSOL Corp. for assistance in software application for modeling.**

Publications and Presentations

- **Zamani, D., Mahdavi, O., Mcbride, M., Dhane, K, Yan. J., Shadman, F., "Cleaning and Rinsing of Hafnium based High-K Micro and Nano Structures in Single-Wafer Cleaning Tools" accepted for publication in Microelectronic engineering Journal.**
- **Zamani, D., Keswani, M., Mahdavi, O., Yan, J., Raghavan, S., Shadman, F., "Dynamics of Interactions between HF and Hafnium Oxide during Surface Preparation of High-K Dielectrics" IEEE Transactions and Semiconductor Manufacturing Vol. 25, No. 3, August 2012.**
- **Zamani, D., Yan, J., Keswani, M., Mahdavi, O., Raghavan, S., Shadman, F., "Reduction of Water Usage during Rinsing of Patterned High-*k* Surfaces in Single-Wafer Cleaning Tools " SRC-TECCHON, Presentation-Poster, September 2012.**
- **Chiang, C.C., Raghavan, S., "Improving rinsing efficiency by studying desorption kinetics of multivalent ion on SiO_2 surface using electrochemical impedance spectroscopy (EIS)" SRC-TECCHON, Abstract submitted (2013)**