SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Program Overview

Annual ERC Meeting
February 28-29, 2008

Outline of Presentation

- A short background and some statistics on the ERC
- Report on the structure of the program and the on-going projects
- New activities that are started or proposed, according the new strategic plan that was approved last year

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

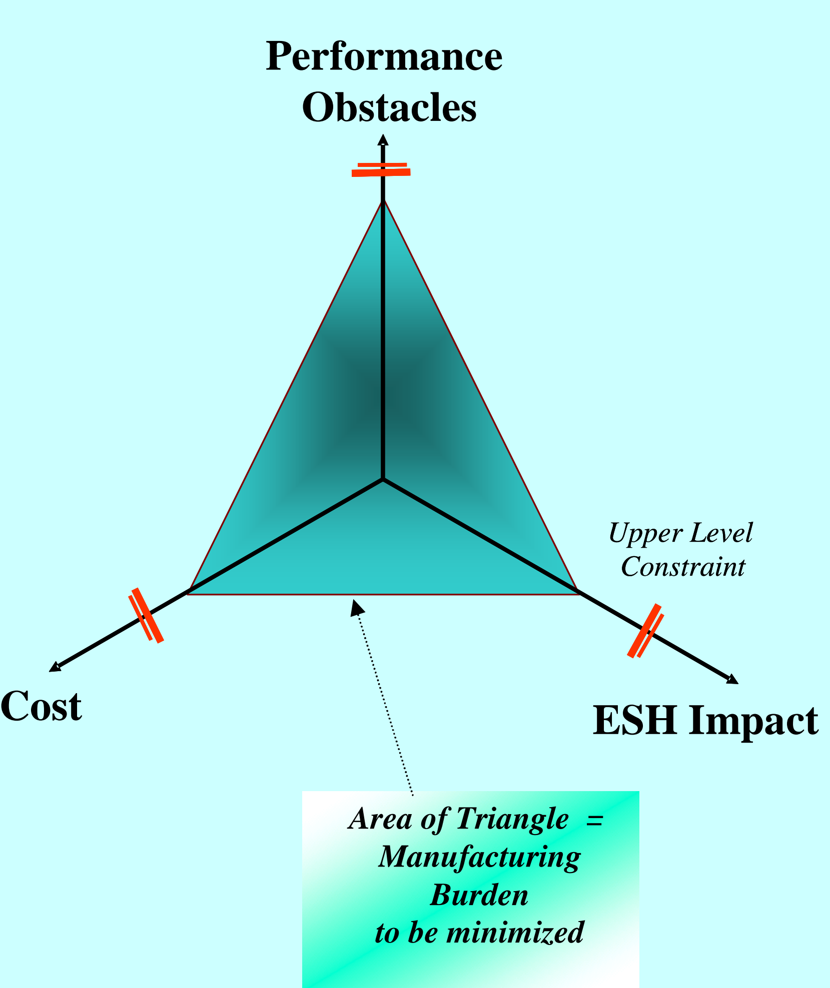
- University of Arizona
- MIT
- Stanford University
- UC Berkeley

Founders 1996

- Cornell University (1998 -)
- University of Maryland (1999-2003)
- Purdue University (2003 - 2006)
- Tufts University (2005 -)
- Columbia University (2006 -)
- University of Massachusetts (2006 -)

ERC Mission and Objectives

1. Research to develop science and technology leading to simultaneous ***performance improvement***, ***cost reduction***, ***and ESH gain***
2. Incorporating ESH principles in engineering and science education
3. Promoting ***Design for Environment and Sustainability as a Technology Driver*** and not a burden



Our Definition of ESH Gain

Four primary factors used as metrics of ESH gain:

1. **Eliminating or reducing the use of hazardous compounds**

2. **Eliminating or reducing emissions of potentially hazardous compounds**

3. **Reducing the "*net*" use of water and energy for manufacturing**

4. **Increasing the "*utilization factor*" of chemicals and materials (minimizing waste per unit product)**

ERC's New Strategic Plan

Focus Areas, Priorities, and Funding Plan

Presented and Approved Last Year

New Research Thrust Areas

Environmentally Sustainable Electronics Manufacturing

Thrust A
Novel Solutions to Existing ESH Problems

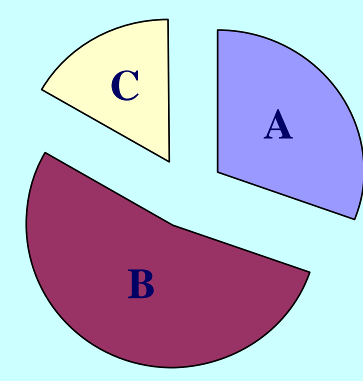
Thrust B
ESH-Friendly Novel Materials and Processes

Thrust C
ESH Aspects of Future Nano-Scale Manufacturing

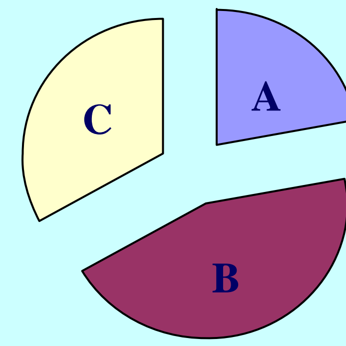
Enabling ESH Fundamentals

Research Thrust Areas

- **Thrust A: Novel Solutions to Existing ESH Problems**
  Examples:
  - Organic (e.g. PFOS) and ionic (F^- and Cu^{++}) removal from wastewater
  - CMP slurry use reduction
  - Water recycling
- **Thrust B: ESH-Friendly Novel Materials and Processes**
  Examples:
  - Novel PAG materials to replace PFOS
  - Low-energy and low-chemical deposition and pattering methods
  - Low-waste planarization beyond CMP
- **Thrust C: ESH Aspects of Future Nano-Manufacturing**
  Examples:
  - New low-energy and low-chemical processes specific to nano-scale fabrication (e.g. mimicking bio-systems for patterning and selective deposition)
  - ESH aspects of nano-particles and other nano-structures
  - Environmentally sustainable processes for cleaning nano-structures



Current Funding Distribution



Funding Distribution Goal Based on Strategic Plan

Long-Term ERC Funding Plan

Approved in 2005

- **Continued core funding from SRC and Sematech**
- **Commitment by ERC to raise supplemental funds as leverage (minimum 50% of core funding).**
- **Sources of supplemental funding:**
  1. **Grants from Federal and State agencies (*major source)**
  2. **Customized projects (*major source)**
  3. **Industrial membership in international level**
  4. **Cost sharing through interactions with other Centers**
  5. **Cost sharing by participating universities**
  6. **Lower ID cost in some cases**

Supplemental funding raised last year was over 100%.
Significant funding leverage for the benefit of S/C industry

Current ERC Research Projects

- Two types of projects:
  - 12 ***core projects*** (funded by the core SRC/Sematech contract and some membership funds)
  - 9 ***customized projects*** (non-core funding)
- Core projects are selected through RFP process, proposals, and review/selection by a committee appointed by SRC and Sematech, coordinated through ERC.
- Customized projects are added throughout the year. Review and selection procedures are set by the ERC and the sponsors.

Core Projects in 2007-2008

1. Reductive Dehalogenation of Perfluoroalkyl Surfactants in Semiconductor Effluents (A)
2. Destruction of Perfluoroalkyl Surfactants in Semiconductor Process Waters Using Boron-Doped Diamond Film Electrodes (A)
3. CMOS Biochip for Rapid Assessment of New Chemicals (A,B)
4. An Integrated, Multi-Scale Framework for Designing Environmentally-Benign Copper, Tantalum, and Ruthenium Planarization Processes (A,B)
5. Environmentally Benign Electrochemically Assisted Chemical Mechanical Planarization (B)
6. EHS Impact of Electrochemical Planarization Technologies (B)
7. Non-PFOS/non-PFAS Photo-Acid Generators: Environmentally Friendly Candidates for Next Generation Lithography (B)
8. Environmentally Benign Vapor-Phase and SC-CO_2 Processes for Patterned Low-k Dielectrics (B)
9. Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro-and Nano-Electronics Manufacturing (B,C)
10. Low-Water and Low-Energy Rinsing and Drying of Nano-Structures and New Materials Surfaces (C)
11. Low Environmental-Impact Processing of sub-50 nm Interconnect Structures (C)
12. ESH Assessment of Materials, Structures, and Processes for Nano-scale MOSFETs with High-Mobility Channel (C)

Focus Areas of Core Projects

- Replacing PFOS
- Lowering net water and energy usage
- Low-impact water and wastewater purification
- Removing F-organics from wastewater
- Lowering waste in CMP and post-CMP processes
- Rapid chemical toxicity assessment
- ESH-friendly processing of low-k dielectrics
- ESH-friendly cleaning and drying of new materials and structures
- Low-waste additive processing alternatives
- ESH aspects of future materials and devices

Customized Projects

- First approved and initiated in 2000
- Meets the special needs of member groups, research interests of PIs, and the educational needs of students
- Most customized projects emphasize applied research and shorter-term technology insertion goals and plans
- IP arrangements are tailor-made and negotiated between the parties on a case-by-case basis.
- Criteria:
  - In line with the mission of the Center
  - Synergy with the core projects (ERC leverage)
  - In line with the SRC and Sematech funding leverage expectations
- Maximizes the use of resources and the multi-disciplinary environment that ERC has established and should be utilized.

Customized Projects in 2007-2008

- **Post-Planarization Waste Minimization; Philipossian,**
  Sponsored by ITW Rippey Corporation

- **Simulation of Pad Stain Formation during Copper CMP; Philipossian,**
  Sponsored by Araca, Inc.

- **Effect of Concentric Slanted Groove Patterns on Slurry Flow during Copper CMP; Philipossian,**
  Sponsored by Toho Engineering

- **Biologically Inspired Nano-Manufacturing; Muscat, McEvoy, Mansuripur**
  Co-sponsored by Science Foundation of Arizona, ASM, SEZ, Arizona TRIF

- **Lowering Material and Energy Usage during Purging Gas Distribution Systems; Shadman, Geisert (Intel)**
  Sponsored by Intel

Customized Projects in 2007-2008

- **Electro-Coagulation Applied to Water Conservation & Wastewater Treatment; Baygents, Farrell, Boyce, Fuerst, Georgousis,**
  Co-sponsored by WSP and Intel

- **Impact of Fluoride and Copper in Wastewater on Publicly-Owned Treatment Works; Sierra,**
  Sponsored by Sematech

- **Low-Energy-Hybrid (LEH) Technology for Water Purification and Recycling; Shadman**
  Sponsored by ERC and Arizona TRIF Initiative

- **A Survey of Water Use, Reuse, and Policies Affecting Semiconductor Industry in Southwest US; Megdal**
  Sponsored by Arizona TRIF initiative

Strategic Plan

New Focus Area

ESH Aspects of Nano-Scale Manufacturing and Nano-Technology in Semiconductor Industry

ESH Aspects of Nano-Manufacturing

1. **Nano-Particles in Manufacturing**
   - **Workers exposure to nano-particles in the fabs**
   - **Emission of nano-particles through fab waste streams**

2. **Impact on Resource Utilization**
   - **Increase is water, energy, and chemical usage**

3. **Introduction of New Materials**
   - **New device materials, new processing fluids, etc.**

4. **Positive Environmental Impact**
   - **Opportunities for major ESH gain**

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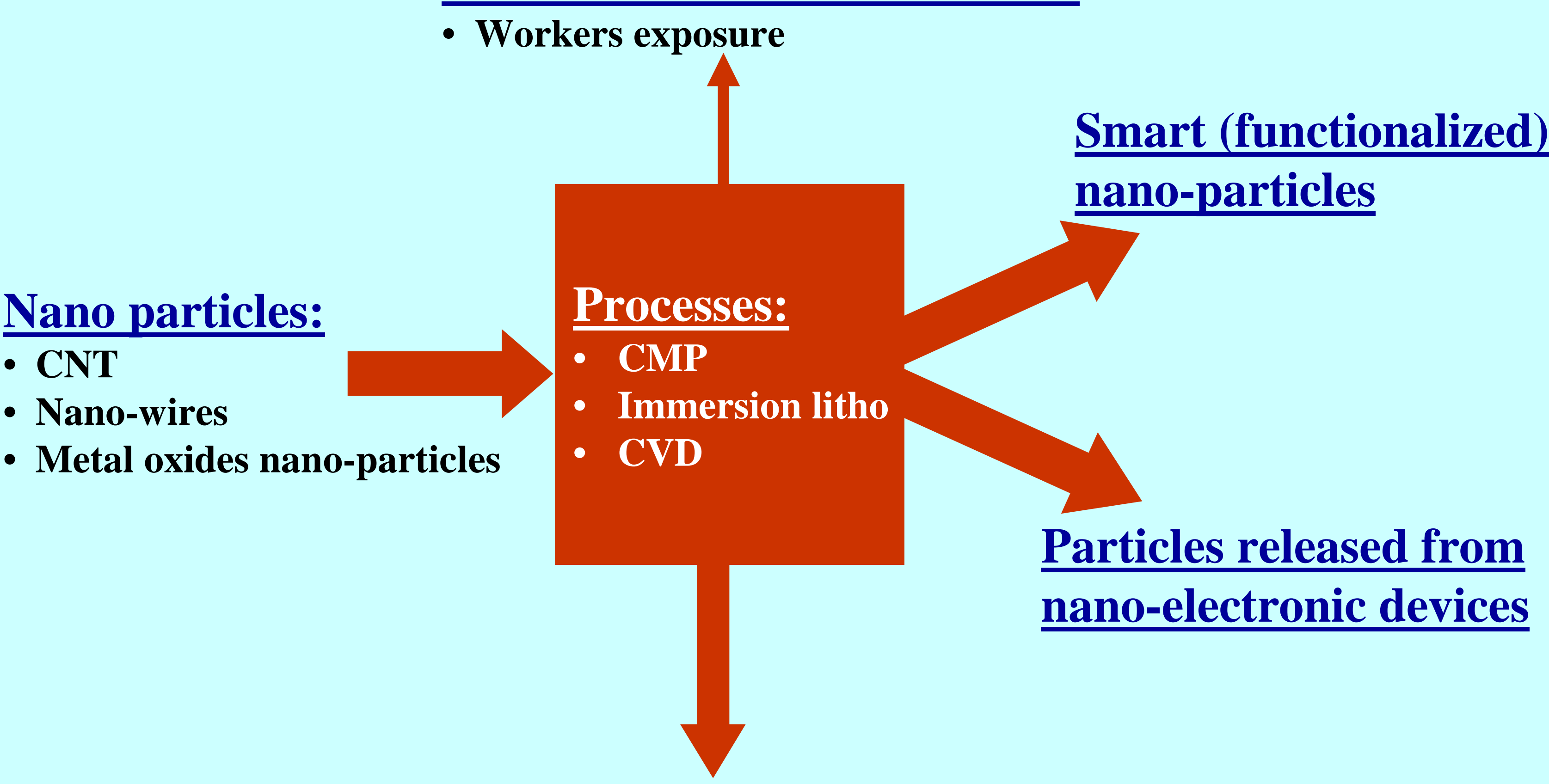
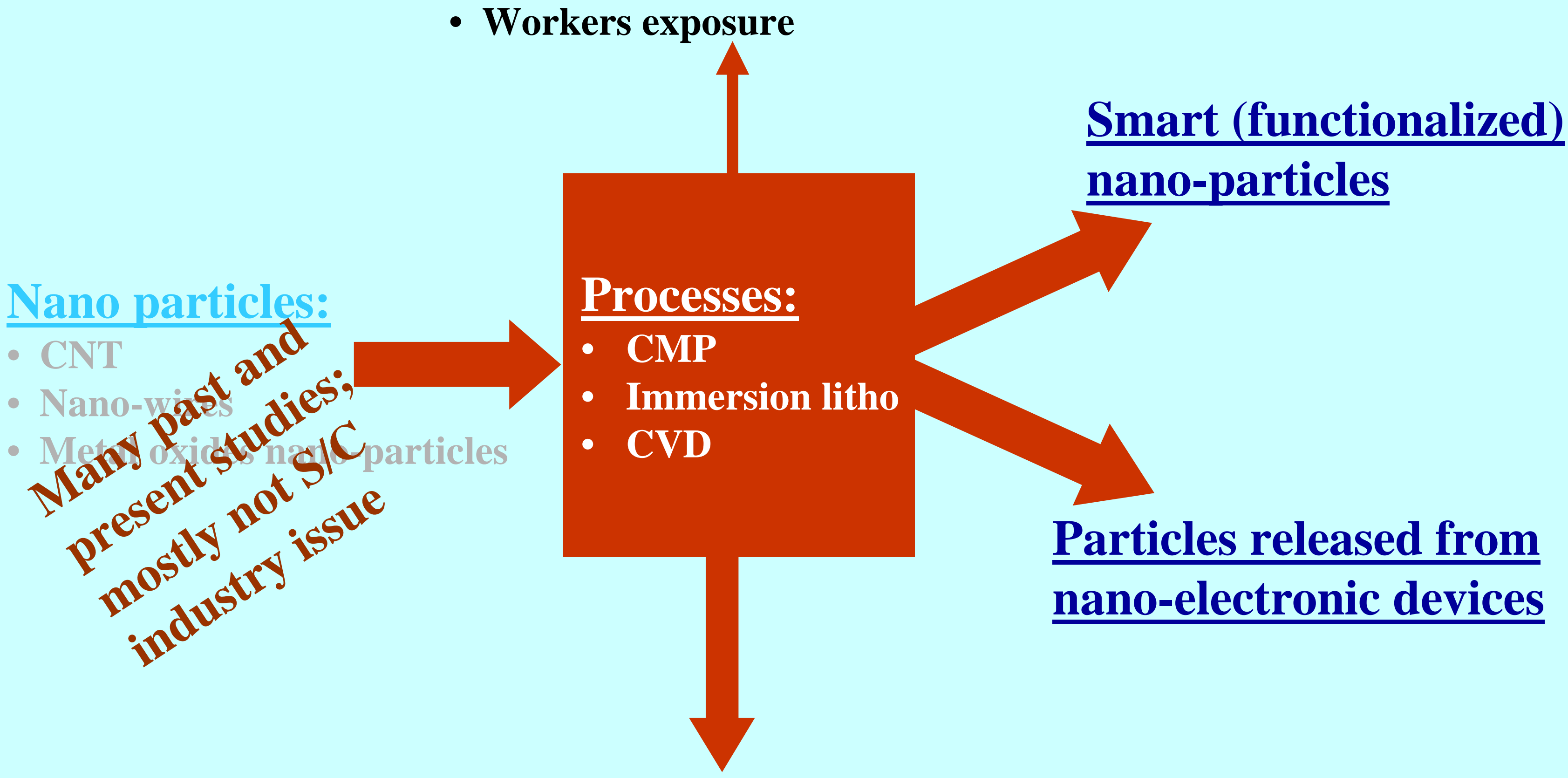
ESH Impact of Nano-Particles



Process-modified or process-generated particles in waste streams:

- High loading of Cu on CMP particles
- High loading of F-organics on carbon nano-particles

ESH Impact of Nano-Particles



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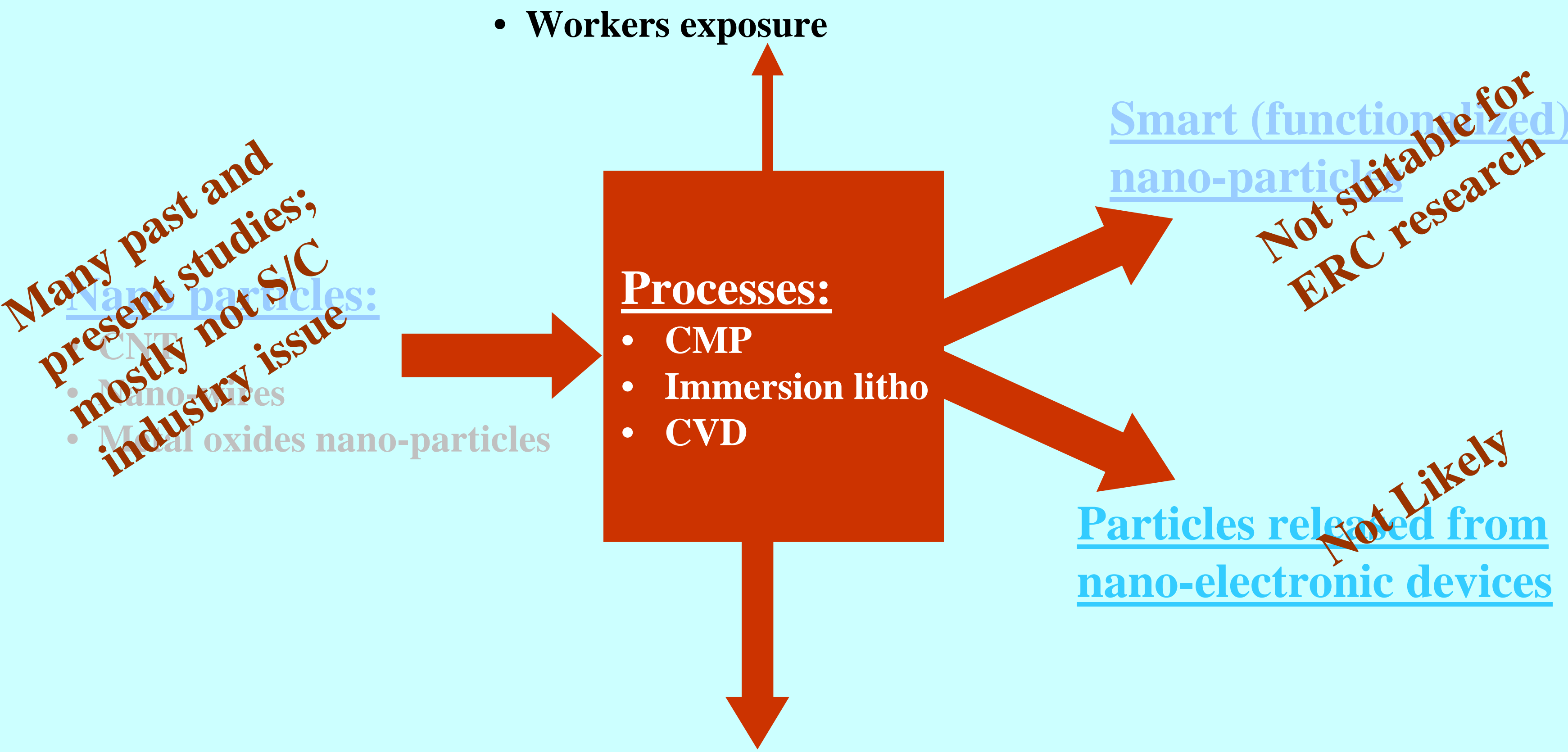

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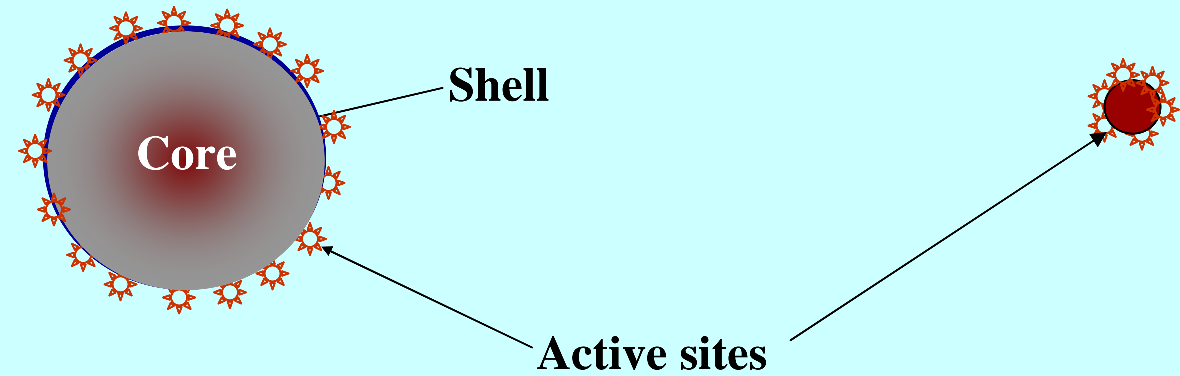
Examples of Nano-Particles in Fabs

CMP Nano-Particles:

Primary particles
(engineered particles; 15-90nm)

Secondary particles
(very active surface; <10nm)



Others:

- Nano-droplets in sprays and aerosols in vents
- Future: nano-tubes and nano-wires, nano-particles as porogens for porous low-k.

What is Unique About Nano-Particles?

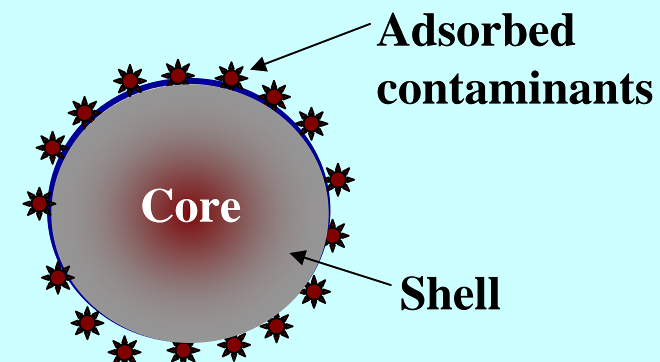
Treatment problem:

- **Nano-particles cannot be effectively removed by *agglomeration, settling, and filtration;* they also clog membranes.**

Synergistic ESH impact of nano-particles:

- ***Active surface***
- ***Selective adsorption***
- ***Pore condensation*** ***(Kelvin Effect)***

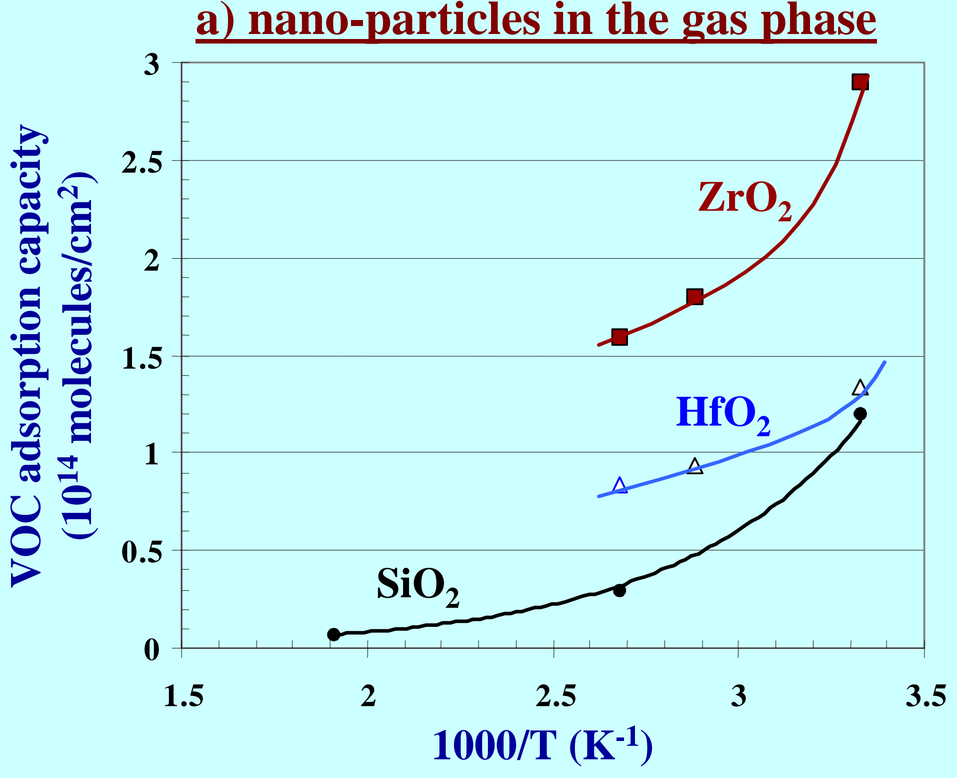
Consequence
- o ***Concentration***
- o ***Facilitated transport***
- o ***Enhanced life-time***



What is Unique About Nano-Particles?

ERC Research: Toxicity and environmental impact of nano-particles in most cases is not due to the particles material, but due to their synergistic interaction with other contaminants.

a) nano-particles in the gas phase



b) nano-particles in the wastewater

- **10 ppb of Cu^{++} in CMP wastewater results in $3x10^6$ ppb of adsorbed copper on 90 nm CeO_2 nano-particles**
- **10 ppb of PFOS in wastewater results in $2.8x10^4$ ppb of contaminated 10 nm carbon nano-particles**

ESH Aspects of Nano-Manufacturing

1. Nano-Particles in Manufacturing
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2. **Impact on Resource Utilization**
   - **Increase is water, energy, and chemical usage**

3. Introduction of New Materials
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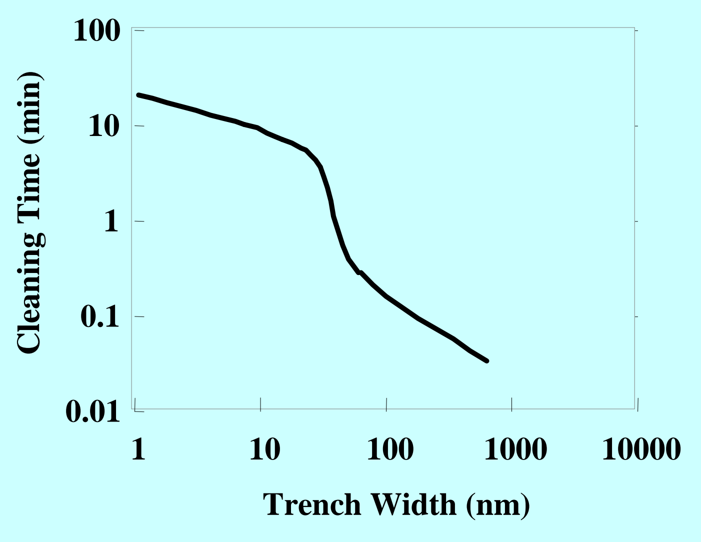
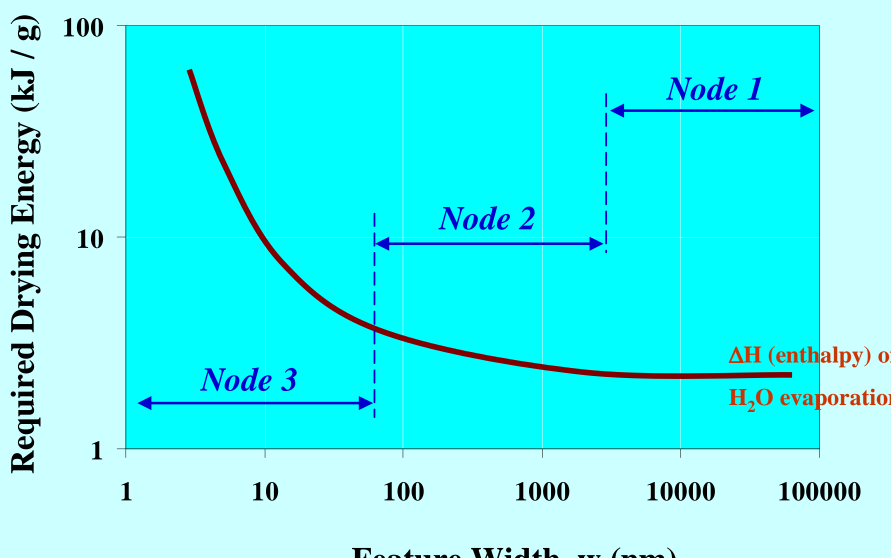
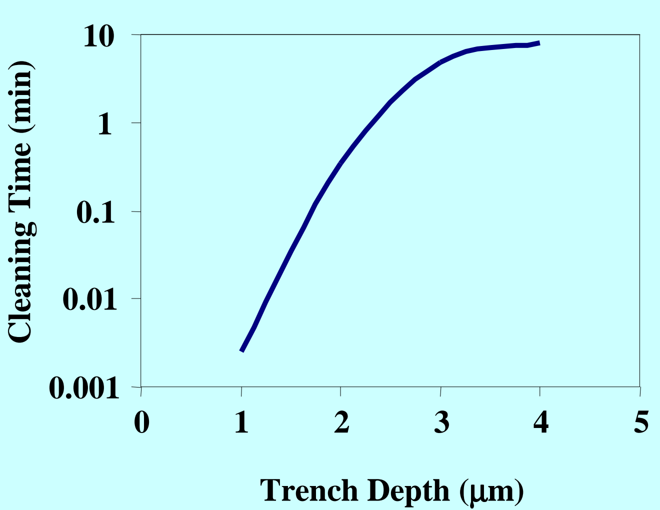
   - Opportunities for major ESH gain

Impact on Use of Natural Resources







ERC Research:

Large increase in *water, chemicals, and energy usage* in various nano-manufacturing processes

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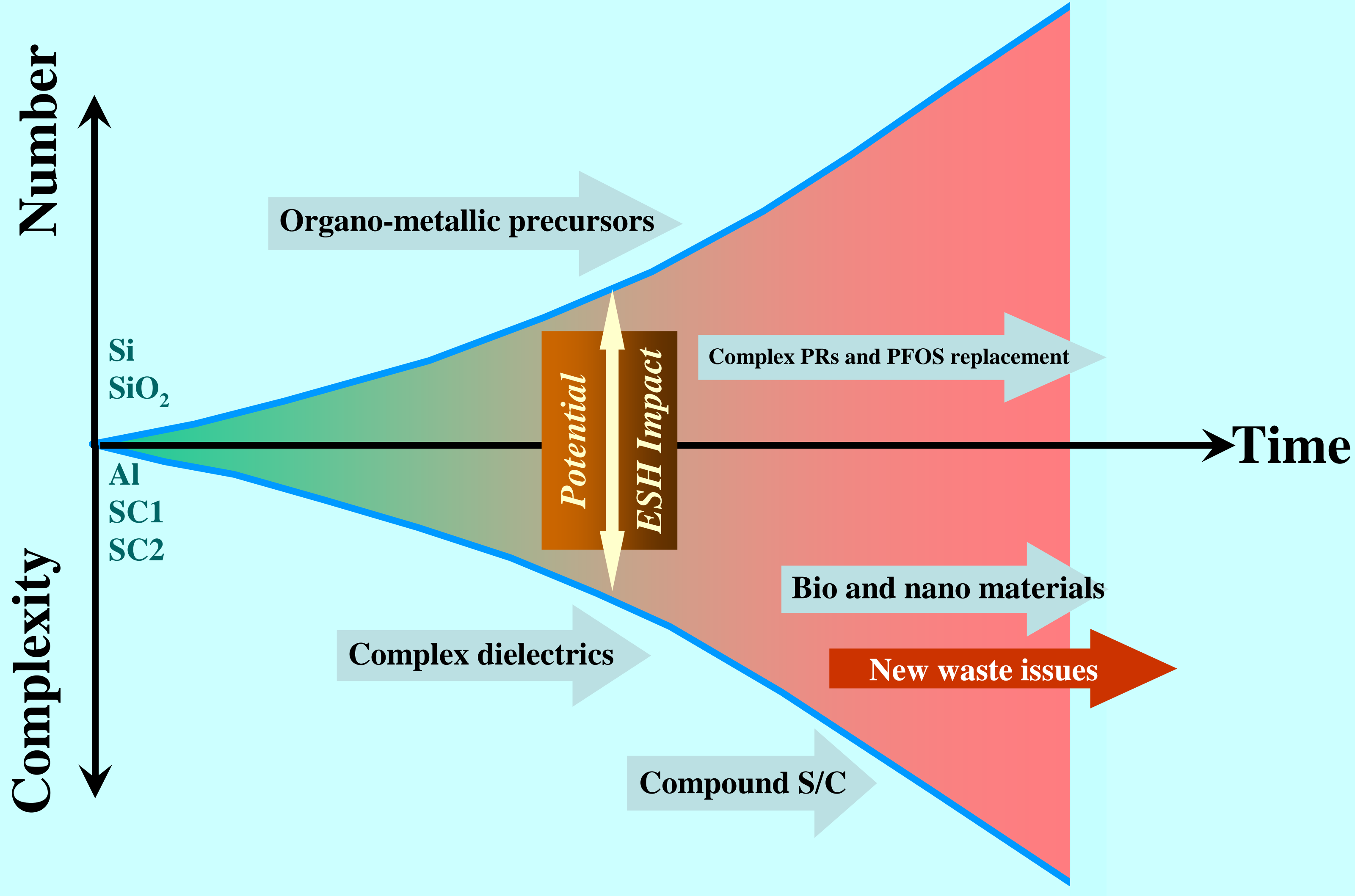
Potential Risks of Introducing New Materials



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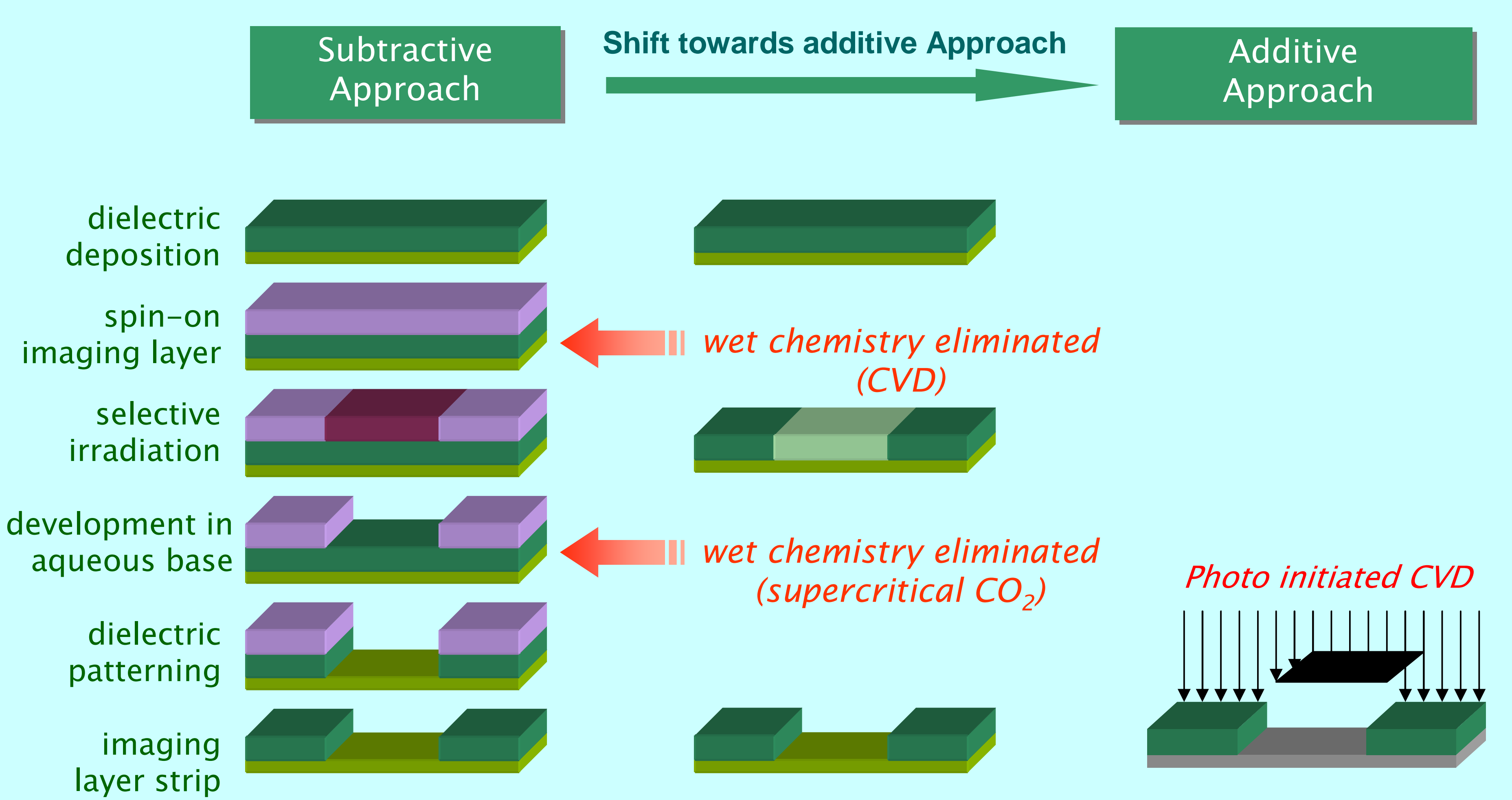
Deposition and Patterning of Dielectrics

Karen Gleason (MIT), Chris Ober (Cornell)



SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Selected Accomplishments

- Research: 74 research projects
- Technology Development: 17 patents
- 22 national/international awards for faculty
- 55 students national/international awards and fellow positions; many institutional fellowships and scholarships
- Simon Karecki Fellowship and Award
- 22 technology transfer projects directly with member companies
- $1 M Fujimi Endowment and Professorship in Planarization
- Five new spin-off companies

Selected Accomplishments

- **Pre-University Outreach**
  - ***Teachers Institute,*** **funded by RET Program; new $500k grant for three years from NSF (directed by Kim Ogden)**
- **University Education:**
  - **Industry internship for students**
  - **REU Program for undergraduates continuing 3 year grant to ERC from NSF (PI: Kim Ogden); participation by women and minorities (60%)**
  - **Course on Environmentally Benign S/C Manufacturing**
- **Post-University Education:**
  - **Short courses and workshops for practicing scientists and engineers; bi-weekly tele-seminars; distance learning courses; internships for industry residents at universities; faculty sabbaticals sponsored by industry**

Partial List of Student Awards in 2006

- **Amber Young, Willis Lamb Scholarship, Optical Sciences, UA, 2007**
- **Kedar Dhane and Jun Yan, Best Session Paper Award, *In-Situ and Real Time Metrology during Cleaning, Rinsing and Drying of Micro- and Nano Structures*, TECHCON, 2007**
- **Rachel Morrish, ARCS Scholarship and Chapman Fellowship, 2007**
- **Valeria Ochoa, Outstanding Graduate Teaching Assistant Award, Chemical and Environ Eng, 2007**
- **Nandini Venkataraman, Applied Materials Graduate Fellowship, 2007**

Congratulatory Notes

- **Hsi-An Kwong (Freescale), *Mahboob Khan Award*, SRC; for outstanding mentorship in several ERC projects, TECHCON 2007.**
- **Krishna Saraswat (Stanford), *Techno-Visionary Award*, Indian Semiconductor Association (ISA); for lifetime achievement in the field of electronics, August 01, 2007.**
- **Belated congratulations to Ara Philipossian for Promotion to *Full Professor (Koshiyama Chair of Planarization)*, 2006.**

AGENDA

Thursday, February 28

7:00 - 8:00	Continental Breakfast and Registration
7:30 - 8:00	*TAB Caucus*
8:00 - 8:40	Introduction and Overview
8:40 - 9:00	Reductive Dehalogenation of PFOS in Semiconductor Effluents
9:00 - 9:30	Destruction of PFOS in S/C Process Waters Using Boron Doped Diamond Film Electrodes
9:30 - 9:50	CMOS Biochip for Rapid Assessment of New Chemicals
9:50- 10:05	Break
10:05-10:20	Invited presentation on NIH Opportunities and Interactions
10:20-11:15	An Integrated, Multi-Scale Framework for Designing Environ-Benign Cu, Ta, Ru Planarization
11:15-11:40	Environmentally Benign Electrochemically-Assisted Chemical-Mechanical Planarization
11:40-12:00	EHS Impact of Electrochemical Planarization Technologies
12:00 - 1:00	Lunch
1:00 - 1:30	Non-PFOS Photoacid Generators: Environ Friendly Candidates for Next Generation Lithography
1:30 - 2:10	Environ Benign Vapor-Phase and Supercritical CO2 Processes for Patterned Low k Dielectrics
2:10 - 2:40	Environ Friendly Cleaning of Materials and Structures for Future Micro- and Nano- Electronics
2:40 - 2:55	Break
2:55 - 3:15	Low Water/Energy Rinsing and Drying of Patterned Wafers, Nano-Structures, and New Materials
3:15 - 3:55	Low Environmental Impact Processing of Sub-50 nrn Interconnect Structures [Gleason, Muscat]
3:55 - 4:25	ESH Assessment of Mat/Struc/Processes for Nano-Scale MOSFETs with High-Mobility Channels
4:25 - 6:30	Poster Session and Social Mixer
5:15 - 6:30	*TAB Caucus*
6:30 - Open	Dinner

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Friday, February 29

6:30 - 7:30 Continental Breakfast and Registration

7:30 - 8:30 **Customized Projects**

- Customized Planarization Projects
  - Post-planarization waste minimization
  - Simulation of pad stain formation during copper CMP
  - Effect of concentric slanted groove patterns on slurry flow during copper CMP
- Biologically Inspired Nano-Manufacturing
- Lowering Material and Energy Usage during Purging Gas Distribution Systems
- Electro-Coagulation Applied to Water Conservation & Wastewater
- Treatment Impact of Fluoride and Copper in Wastewater on Publicly-Owned Treatment Works
- Other Projects and Plans

8:30 - 8:45 Simon Karecki Award Presentation

8:45 - 9:00 Break

9:00 - 10:50 **Seed and Proposed Projects**

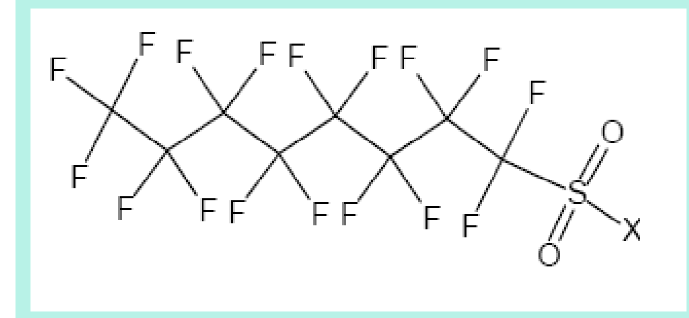
- ESH Assessment of Nano-Materials
  - Introduction and process aspects
  - An experimental method for characterization and toxicity assessment of nano-particles
  - Rapid toxicity assessment for nano-materials
  - Data mining method for predicting the toxicity of nano-materials
- Novel Materials and Device Structures for High-Mobility MOSFETs and Interconnects
- Low Environmental Impact Fabrication of Gate Stack Structures
- New Initiative on High-Volume Nano-Manufacturing
- New Projects on Planarization
- Impact of Chelators and Biocides Utilized in S/C Manufacturing on Municipal Wastewater Treatment
- High-Dose Implant Stripping

10:50 -12:00 Industrial Advisory Board Meeting
12:00 - 1:00 Working Lunch; Feedback to PIs
12:30 - 2:30 Executive Advisory Board Meeting
2:30 PM Program End

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

CORE PROJECTS

425.015 - Reductive Dehalogenation of Perfluoroalkyl Surfactants in Semiconductor Effluents



R Sierra[1], V Ochoa[1], JA Field[1], N Jacobsen[2], V Wysocki[2], A Somogy[2]

[1] Dept. Chemical & Environmental Engineering
[2] Chemistry Department, University of Arizona

Feb 28, 2008

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

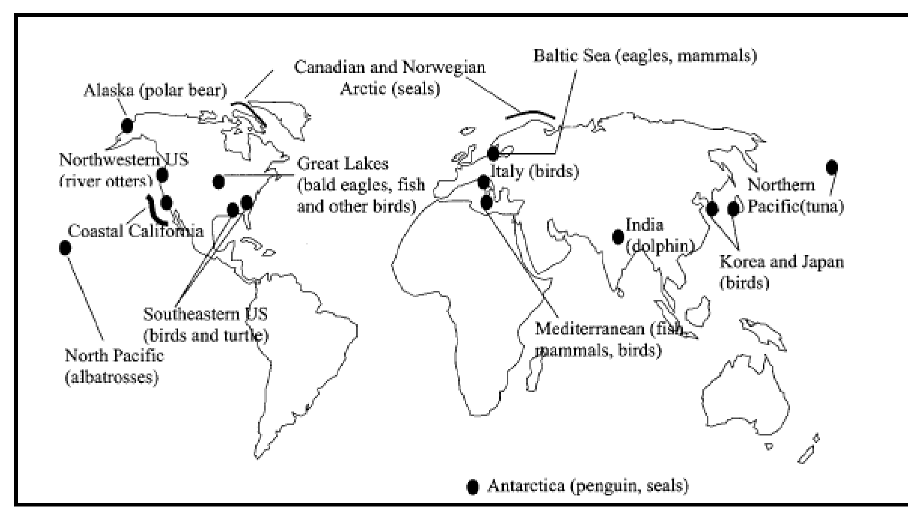
PFOS: Properties and Utilization

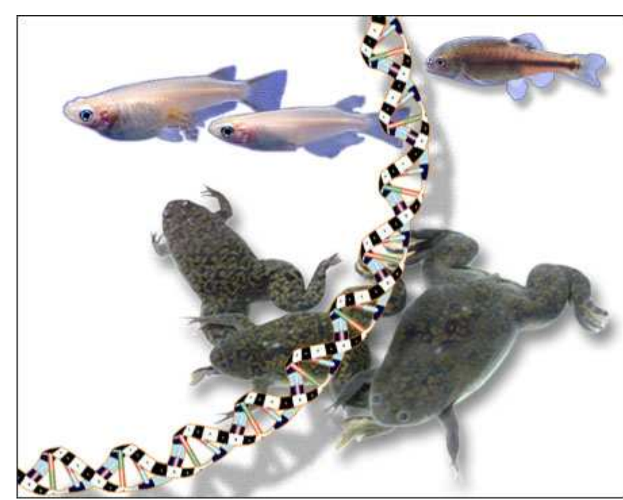
- PFOS important chemical in photolithography.
- The compound is known to bioaccumulate.

- PFOS does not appear to hydrolyze, photolyze or biodegrade under environmental conditions.
  - Stable and chemically inert
  - High strength of **C-F bond (485 KJ/mol)**
  - Rigidity of perfluorinated chain
  - Absence of structures susceptible to electrophilic or nucleophilic attack.

Environmental and Public Health Impact

- Relatively high concentrations of PFOS have been reported in mammals, birds, and fish from locations throughout the world.
- Half-life of PFOS in human body > 8 years.





Giesy et al. (2001) Environ. Sci. Tech. 35:1339

Environmental and Public Health Impact

- Studies in laboratory animals indicate that PFCs may interfere with liver and thyroid function and may cause developmental effects.
- EPA established an **action level of 0.5 µg/l** for PFOA in drinking water (DuPont's Washington Works facility, Washington, W. Va.)
- Health-based limits for PFOA/PFOS in drinking water

PFOS: **0.3 µg/l** (Minnesota)
PFOA: **0.5 µg/l** (Minnesota)
PFOA: **0.04 µg/l** (State of New Jersey)

Need for Effective Treatment Methods

- PFOS use is being regulated and forbidden for many industries by the EPA:
  - 2002: Significant New User Rule (SNUR) forbidding the use of PFOS with exemptions for semiconductor industry.
  - 2006: Reduction of PFOA emissions by 95% (2010) and 100% (2015).
  - 2006: SNUR issued to limit the use of 183 PFOAS.

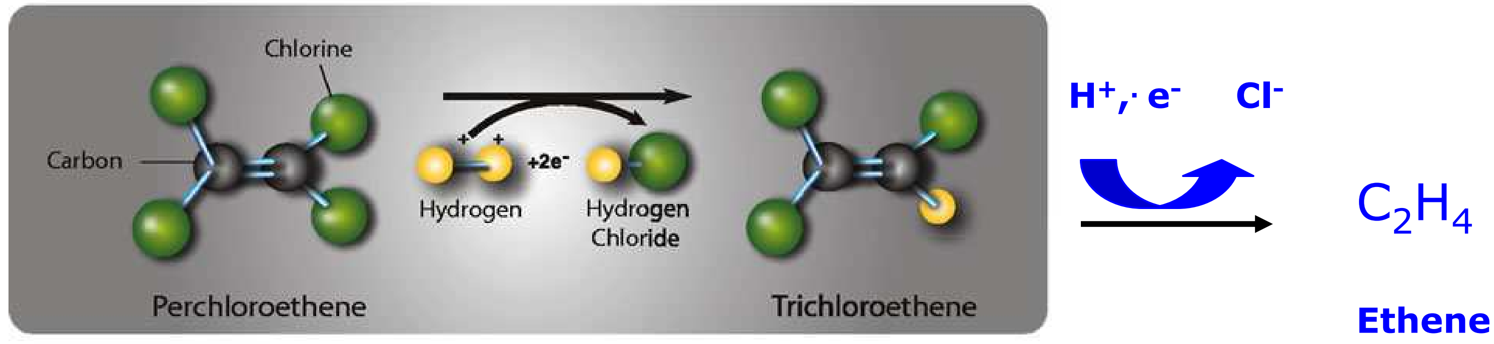
- Need for effective methods to minimize environmental emissions of PFOS and maintain existing regulatory exemptions.

Objective

Investigate the feasibility of novel reductive dehalogenation pretreatment methods to facilitate the removal of PFOS in semiconductor wastewaters.

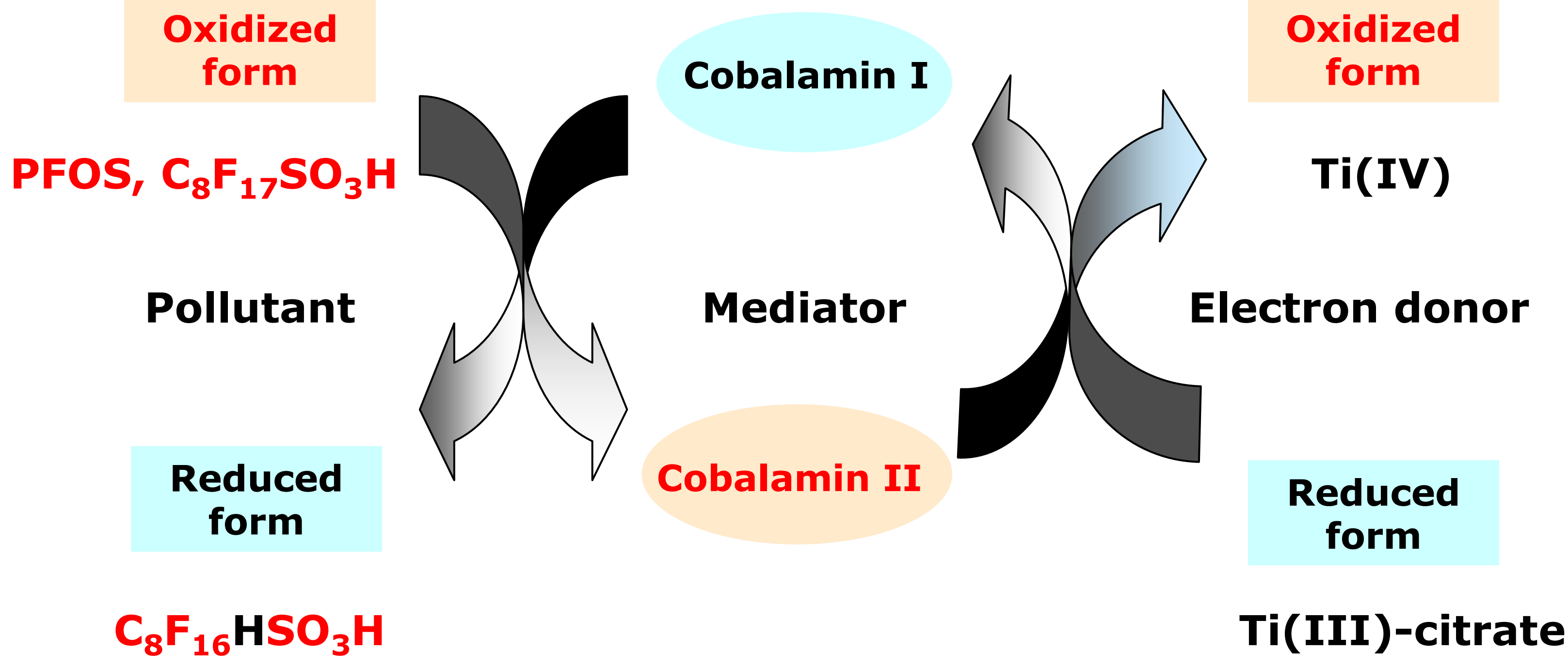
Reductive Dehalogenation

Reductive dehalogenation is the main means of degradation of highly halogenated organics. Eg. PCE, PCBs, PBDEs in the environment.



$$R{-}F + 2e^{-} + 2H^{+} \longrightarrow R{-}H + HF$$

Mechanism of Reductive Dehalogenation



EHS Benefits

- **Reduction in emission of ESH-problematic materials to environment:**

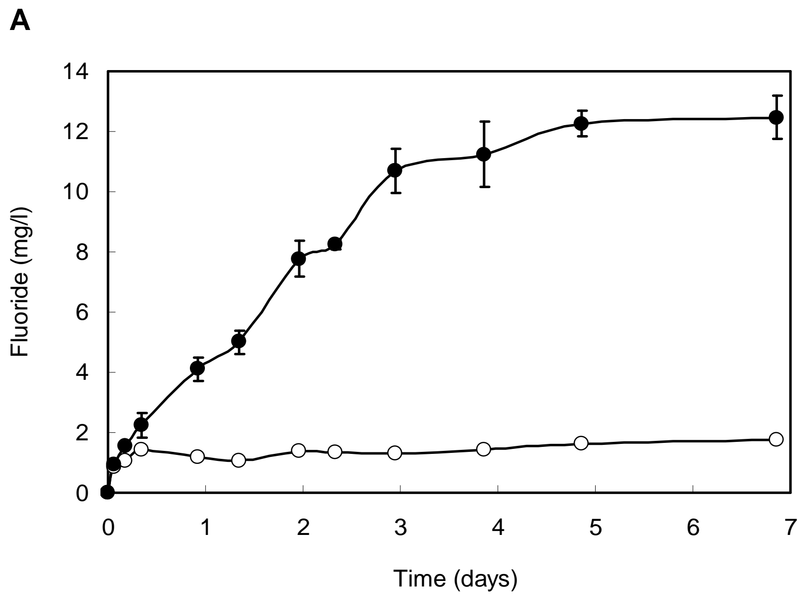
- **Reduction in the use of natural resources involved in alternative treatment methods (energy):**

  Considerable reduction in energy consumption compared to alternative treatment methods such as reverse osmosis, ultrasonic treatment, etc.

- **New strategies to design biodegradable PFAS.**

Results:

Chemical *vs.* Microbial Reductive Dehalogenation



Time course of fluoride release in: (○) PFOS + Ti(III) citrate; (●) PFOS + vit. B12 + Ti(III) citrate) during the chemical reductive defluorination of PFOS by vit. B12 (260 µM) and Ti(III) citrate (36 mM). Samples were incubated at 70ºC and pH 9.0.

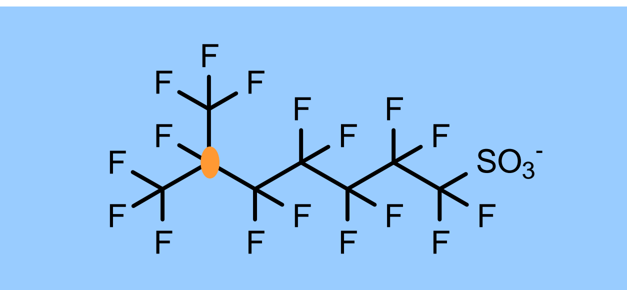
- PFOS is reductively dehalogenated by vitamin B_{12}/Ti(III) citrate.
- PFOS is highly resistant to microbial reductive degradation by natural mixed inocula after long periods of incubation

Results

Chemical Reductive Dehalogenation

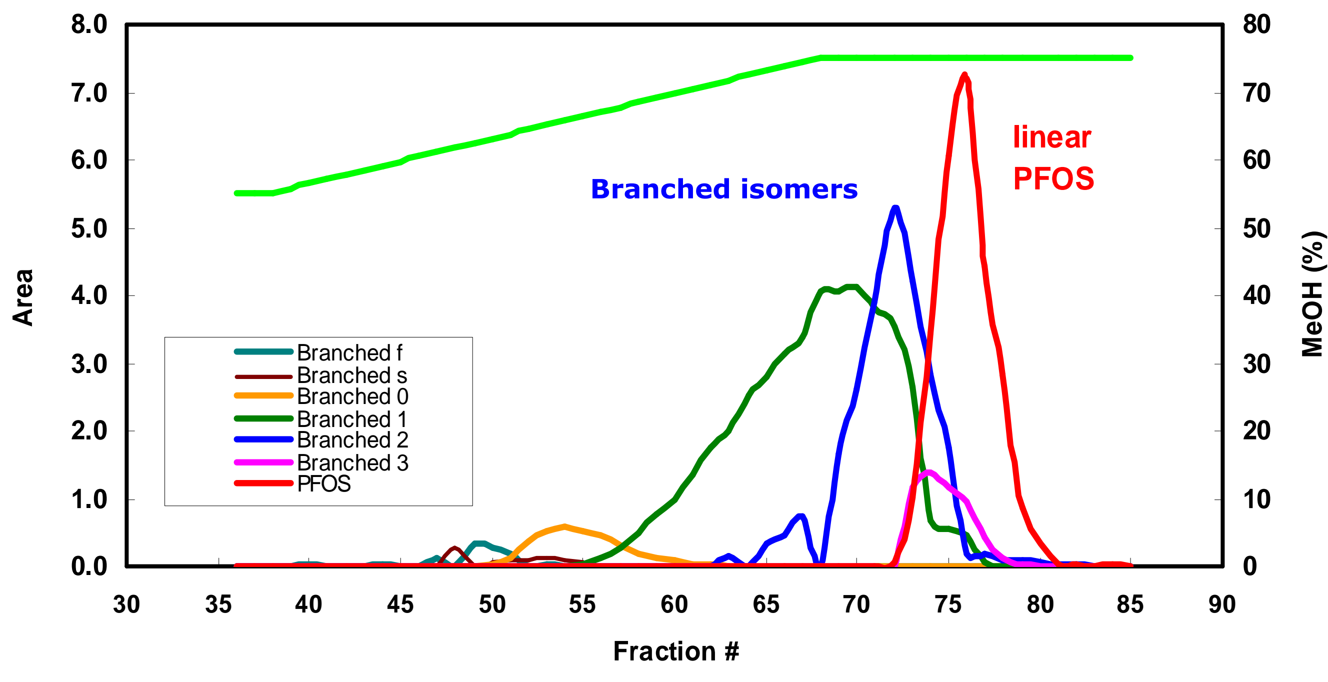
- Technical PFOS contains 20-30% (w/w) branched isomers.
- Branched PFOS isomers are more susceptible to reductive dehalogenation compared to the linear PFOS isomer.

Linear isomer

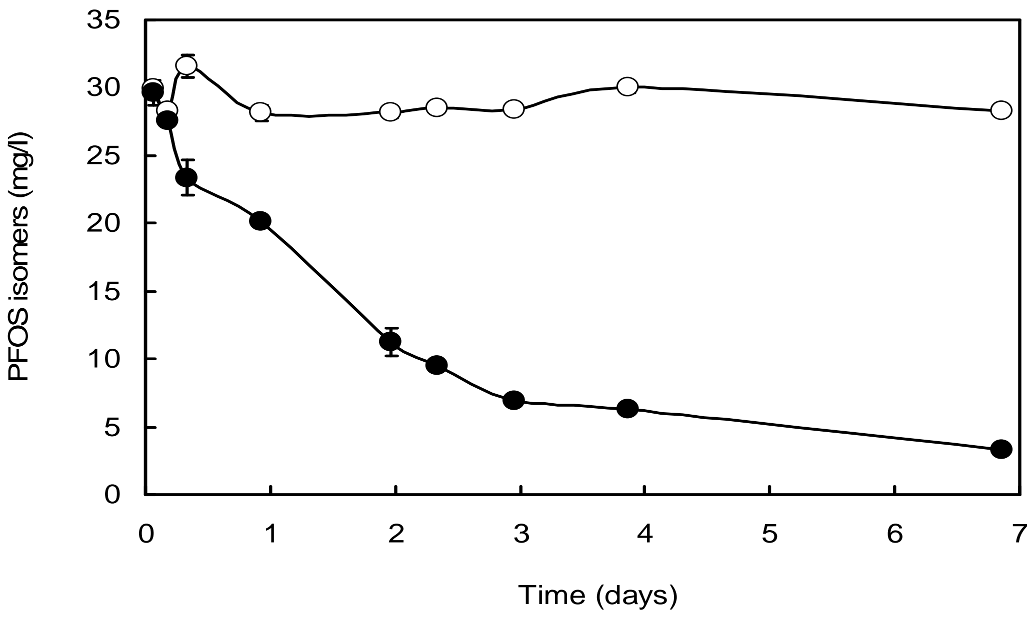


Branched isomer

Fractionation of PFOS isomers by Solid Phase Extraction



Biomimetic Reductive Dehalogenation of Branched PFOS Isomers

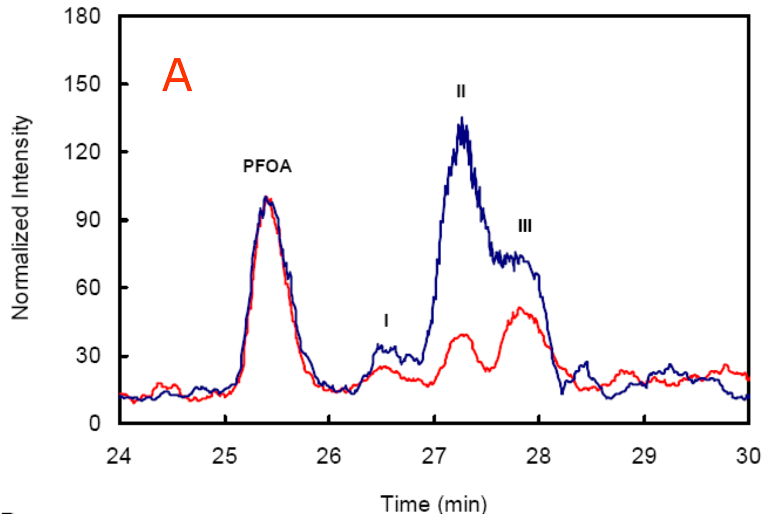


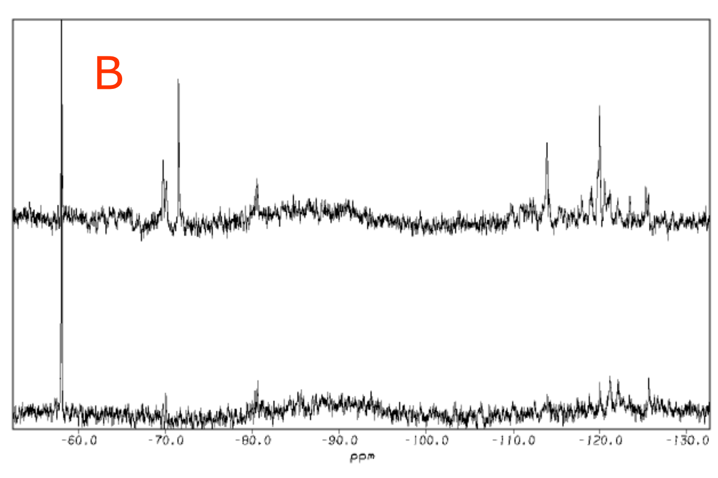
(●) **Treatment samples:** (PFOS + Ti(III)-citrate + Vitamin B_{12})

(o) **Control** (PFOS + Ti(III)-citrate); Samples were incubated at 70ºC and pH 9.0

- Approx. 80% F recovery (12 atoms F-/mol PFOS)

Biomimetic Reductive Dehalogenation of Branched PFOS Isomers





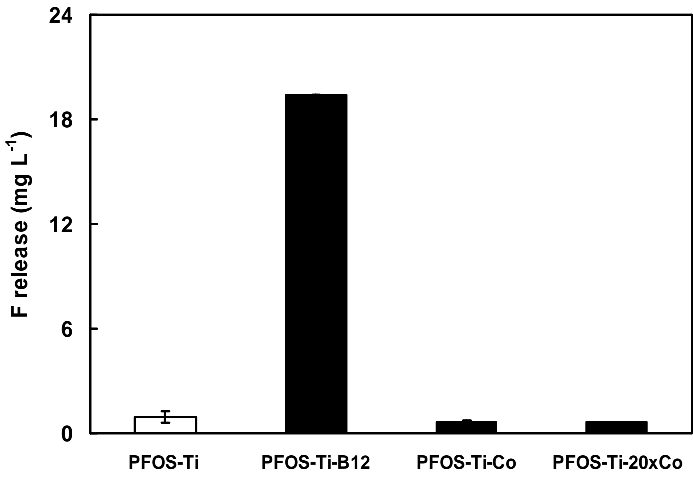
Reductive dehalogenation of branched PFOS isomers at 70ºC and pH 9.0 at day 7.

(A) LC-MS/MS chromatograms of branched PFOS isomers in control samples (PFOS + Ti(III) citrate) (blue) and treatment samples (PFOS + Ti(III) citrate + Vitamin B12) (red).

(B) 19F-NMR spectra of branched PFOS isomers in control (upper panel) and treatment samples (lower panel).

Environ. Sci. Technol. (in press)

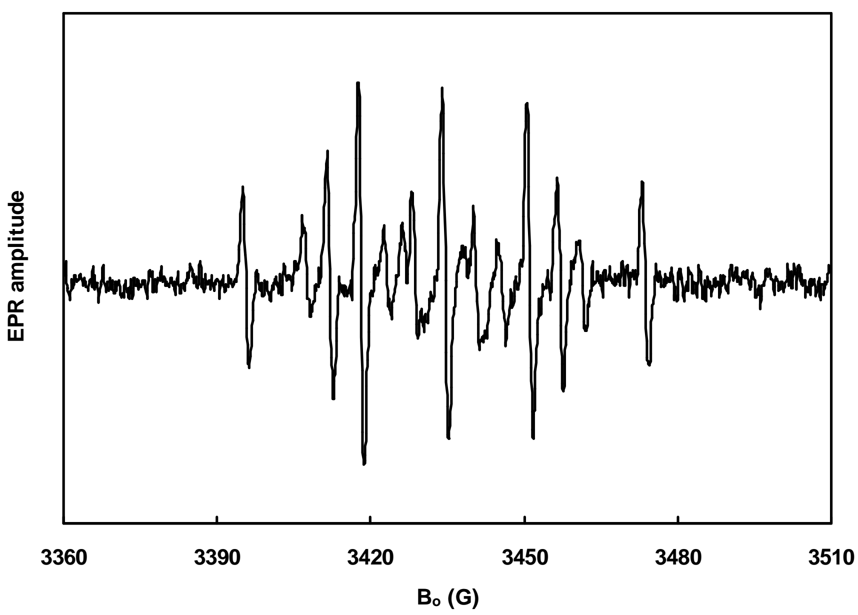
Mechanism of Reductive Dehalogenation of PFOS with Vitamin B_{12}/Ti(III)



Effect of catalyst on the biomimetic reductive dehalogenation of technical PFOS on day 7. Control samples (white bars) and treatment samples (black bars).

- Vitamin B_{12} (cobalamine) is responsible for PFOS dehalogenation.
- PFOS was not degraded when Co(II) was used in lieu of vitamin B12.
- Electron paramagnetic resonance (EPR) results confirmed the involvement of a radical-mediated mechanism.

Mechanism of Reductive Dehalogenation of PFOS with Vitamin B_{12}/Ti(III)



EPR spectrum of treatment sample (PFOS + Ti(III) citrate + B12 + DMPO) in the chemical reductive dehalogenation of technical PFOS at day 7.

- EPR results demonstrated the formation of a vitamin B12 carbon-center radical in the presence of a strong electron donor, Ti(III) citrate.

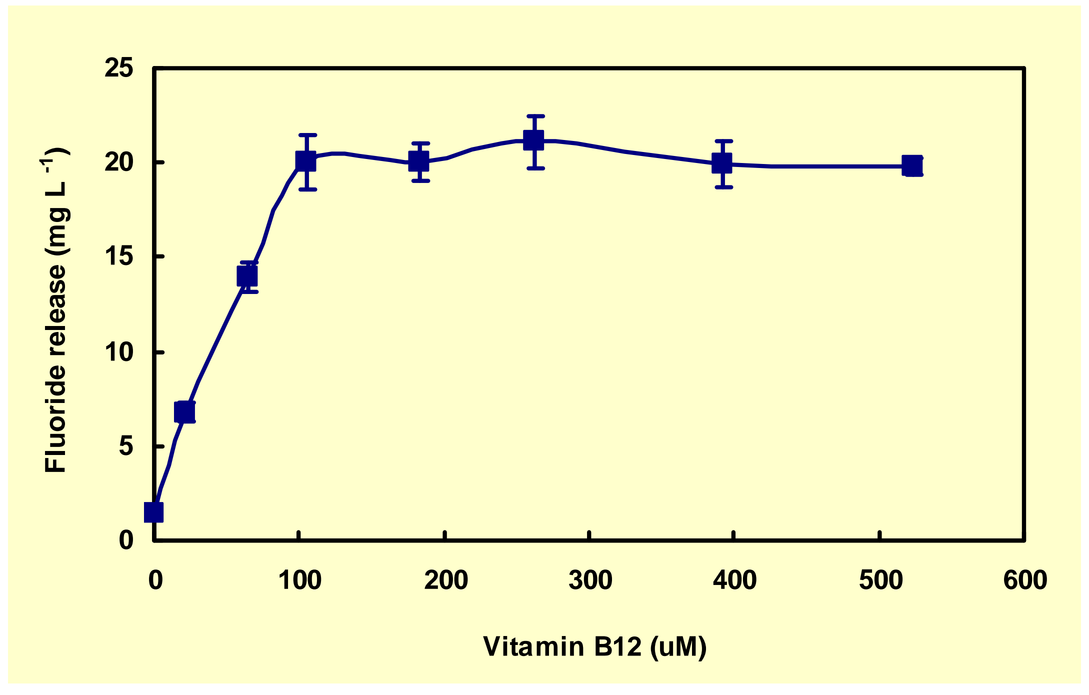
Results

Optimization of Chemical Reductive Dehalogenation

- The impact of temperature and pH, as well as vitamin B_{12} and Ti(III) citrate dosage on the rate of PFOS dehalogenation was assessed:
  - The degradation rate increased 37-fold by raising the temperature from 30º to 70ºC.
  - 5.9-fold rate enhancement by increasing the reaction pH from 7.5 to 9.0.
  - An optimal vitamin B_{12} dosage of 393 μM was determined
  - 21-fold rate increase by raising the molar ratio Ti(III)/PFOS from 27 to 110.
- The impact of adding co-solvents and using reactive surfaces to improve compound availability is being investigated.

Reductive Dehalogenation of PFOS

Effect of Vitamin B12 Dosage

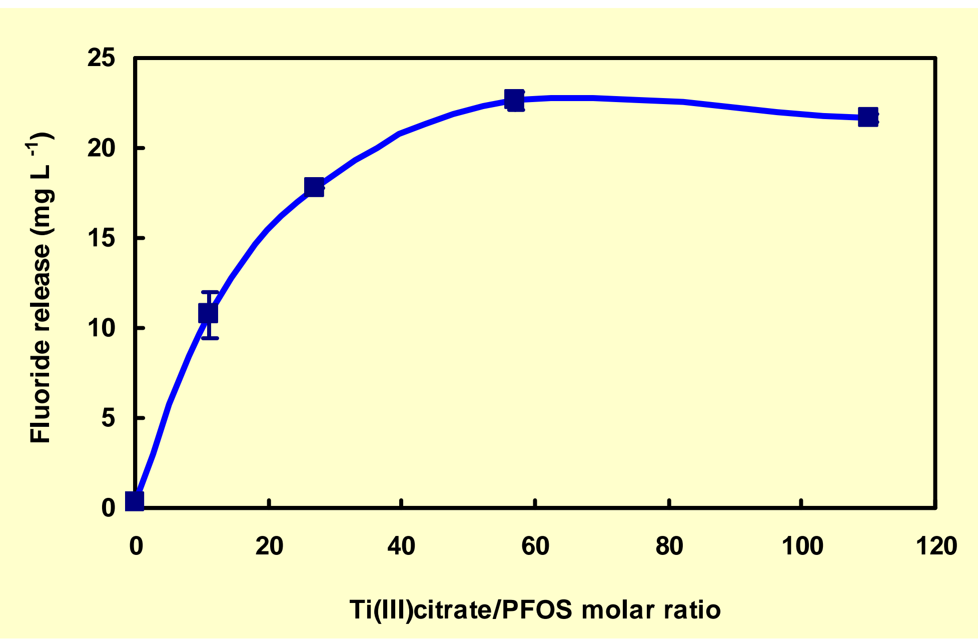


Fluoride release during the chemical reductive dehalogenation of commercial PFOS

by vit B12/Ti at day 7. Samples were incubated at 70°C and solution pH 9.0 [Ti(III)] = 36 mM

Reductive Dehalogenation of PFOS

Effect of Ti(III) Dosage



Fluoride release during the chemical reductive dehalogenation of commercial PFOS

by vit B12/Ti at day 7. Samples were incubated at 70°C and solution pH 9.0 [Vit B12] = 262 uM

Conclusions I

- **PFOS is susceptible to chemical reductive dehalogenation by vitamin B12/Ti(III).**

  Microbial reductive defluorination of PFOS might be possible.

- **Branched PFOS isomers are more susceptible to reductive dehalogenation than the linear PFOS isomer.**

  Branched PFOS better ESH characteristics (more prone to biodegradation in anaerobic sediments).

  Clue for the design of perfluorinated chemicals more prone to biodegradation.

- **Reductive dehalogenation of PFOS involves a radical mechanism.**

Conclusions II

- **Optimized temperature and pH greatly enhances PFOS reductive dehalogenation kinetics.**

  T = 70ºC ; pH = 9

- **PFOS is highly recalcitrant to microbial dehalogenation.**

  No F^- release in 2 years from technical PFOS.

Future Work

- **Improve treatment conditions to promote the chemical reductive dehalogenation of PFOS and reduce treatment costs:**
  - Use of sorbents with reactive surfaces.
  - Use of co-solvents to improve PFOS availability.
  - Replacement of the catalyst and the electron donor:
    Alternatives to vitamin B12: eg. Ni- and Fe-cofactors (F_{430}, hematin, etc.)
    Alternatives to Ti(III) citrate: dithiotreitol, etc.
- **Complete the identification of key products of reductive dehalogenation.**
  - Explore CO_2 and organic acids.
- **Evaluate the reductive dehalogenation of PFOS by microorganisms that biosynthesize high levels of vit. B12** (eg. *Methanosarcina barkerii*).

Industrial Collaboration/ Technology Transfer

Industrial Liaisons:

Walter Worth - Sematech

Tim Yeakley – TI

Disclosures:

UA07-037 (active) - Biomimetic degradation of perfluorinated and highly-fluorinated organic compounds. R. Sierra

SRC students on project *425.015*

- Graduated Students and Current Affiliation
  - Beshoy Latif, May 2007
- Current Students and Anticipated Grad Date
  - Valeria Ochoa, PhD candidate Environ Engr, Dec. 2008.
  - Chandra Kathri, BS Chemical Engr, May 2009.

Destruction of Perfluoroalkyl Surfactants (PFAS) in Semiconductor Process Waters using Boron Doped Diamond Film Electrodes

Task # 425.018 / Thrust C

James Farrell, Kimberly Carter, Valeria Ochoa, Reyes Sierra
Department of Chemical and Environmental Engineering
The University of Arizona

Research Objectives

- Determine the feasibility of oxidative destruction of PFOS and PFBS using BDD electrodes.
- Determine the reaction products.
- Determine the reaction mechanisms and rate limiting steps.
- Develop a multi-step concentration and destruction treatment technology.
- Pilot test treatment technology at a semiconductor facility.

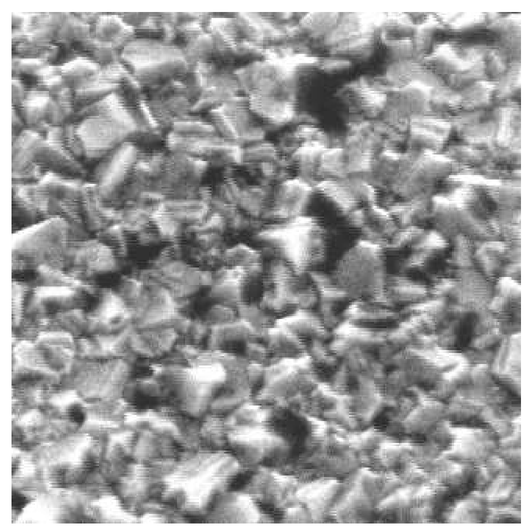
ESH Impact / ESH Metrics

- PFAS are used in photoresist developers and antireflective coatings.
- Most PFAS waste is contained in organic solvents and destroyed by incineration.
- There is a need to treat dilute aqueous waste streams containing PFAS.
- Ion exchange, carbon adsorption, UV/peroxide, sonolysis & biodegradation treatments are impractical or ineffective.
- An effective method for removing PFAS from aqueous waste streams is needed in order to secure a limited use exemption from the U.S. Environmental Protection Agency.

Goal/Possibilities	**Energy**	**PFCs**
Remove PFAS from aqueous waste streams	Elimination of costly reverse osmosis treatments	>99% removal from disposed wastewaters

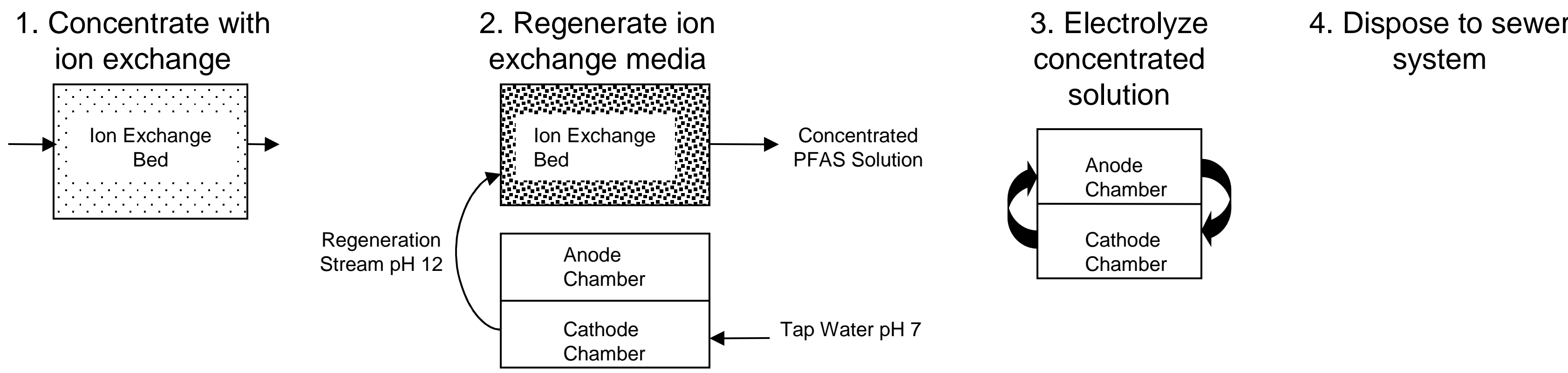
Boron-Doped Diamond Film (BDD) Electrodes

- Diamond film grown on p-silicon substrate using CVD
- Boron doping provides electrical conductivity
- Highly stable under anodic polarization
- No catalyst to foul or leach from electrode
- Emerging technology being adopted for water disinfection



Scanning electron micrograph of BDD electrode. The individual diamond crystals are ~0.5 μm in size.

Proposed Treatment Scheme



Multi-step treatment scheme:

1. Concentrate PFAS from dilute aqueous solutions using ion exchange resin.
2. Regenerate ion exchange resin using cathodically generated high pH solution.
3. Recirculate concentrated PFAS solution through a BDD electrode reactor.
4. Dispose of treated solution containing electrolysis products (CO_2 & F^-) into sanitary sewer system.

Experimental Systems

- No mass transfer limitations
- Electrode surface area = 1 cm^2
- Solution volume = 350 mL
- a_s = 0.00286 cm^2/mL

Parallel plate flow-cell.

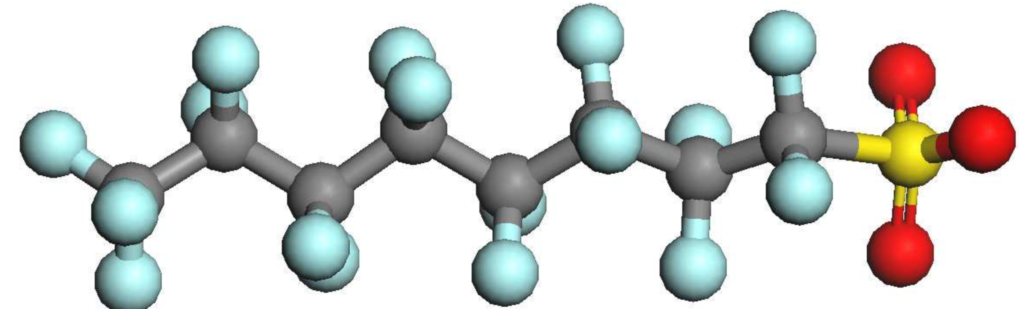
- Rates similar to real treatment process
- Electrode surface area = 25 cm^2
- Solution volume = 15 mL
- a_s = 1.67 cm^2/mL

Quantum Chemistry Calculations

- Density functional theory (DFT) calculations performed using DMOL3 or ADF codes.
- Unrestricted GGA calculations with VWN-BP or BLYP functionals.
- All electron calculations performed with double-numeric with polarization (DNP/DMOL3) or triple-zeta with polarization (TZ2P/ADF) basis sets.
- Solvation effects incorporated using the conductor-like screening model (COSMO).
- Transition state searches employed LST/QST (DMOL3) or LT (ADF) followed by nudged elastic band (NEB) and eigenvector-following optimization.

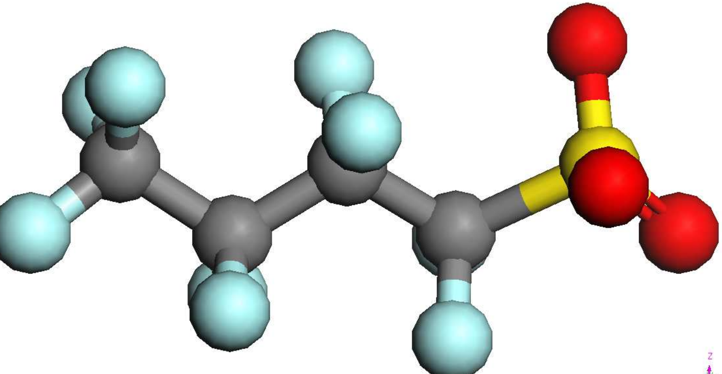
Target Compounds:
Perfluorooctyl sulfonate & Perfluorobutyl sulfonate

Perfluorooctyl sulfonate (PFOS)



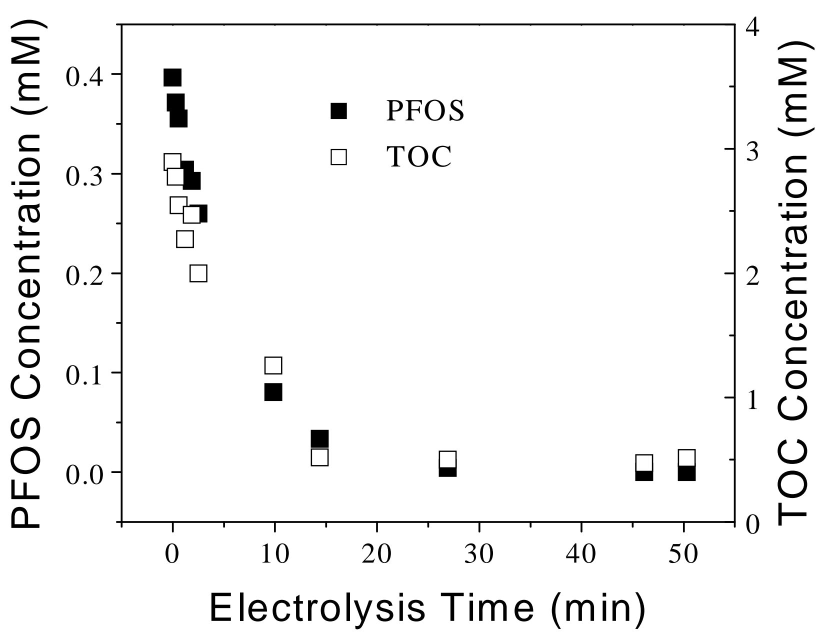
Most widely used PFAS.

Perfluorobutyl sulfonate (PFBS)



Suggested replacement for PFOS.

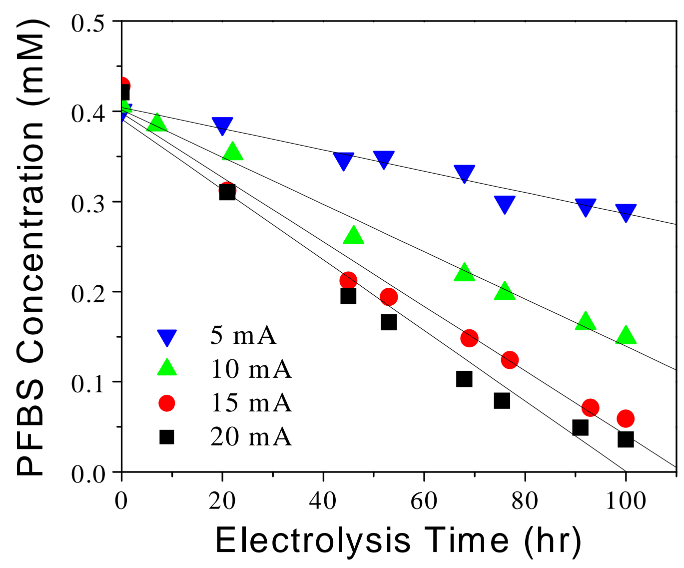
Experimental Results: Flow Through Reactor

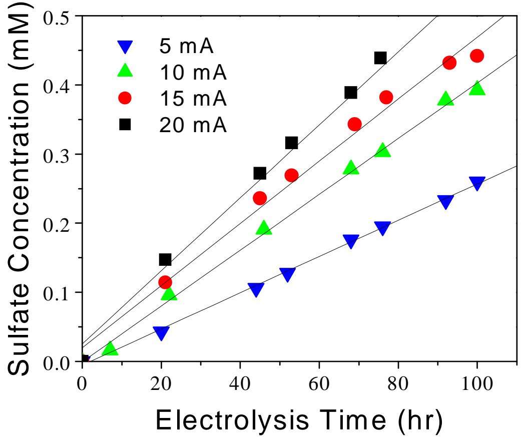


PFOS & total organic carbon (TOC) concentrations as a function of electrolysis time for the flow-cell operated at a current density of 20 mA/cm^2.

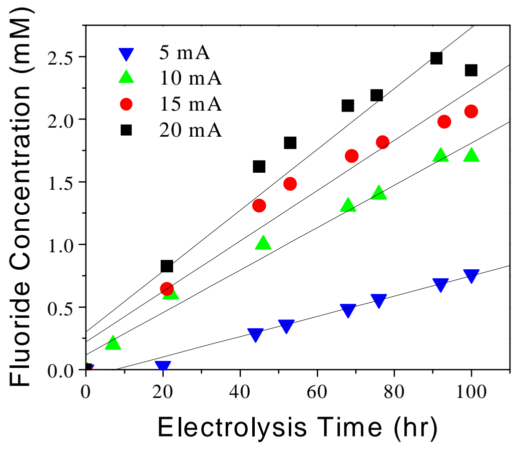
- PFOS can be rapidly removed from water with a half-life ~7 min.
- Reaction rates are first order in PFOS concentration.
- No build-up of fluorinated organic reaction products.
- Similar results observed for PFBS.

Experimental Results: Rotating Disk Reactor





- Reaction rates are 0th order in PFBS concentration.
- 1 sulfate ion produced per PFBS degraded.
- 7.5 out of 9 fluoride ions per PFBS degraded.
- 14 out of 17 fluoride ions per PFOS degraded.
- Some fluoride loss via HOF volatilization.

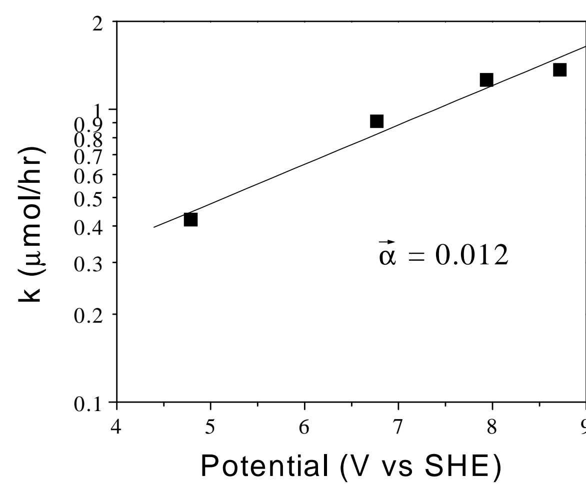


PFAS Oxidation Rate-Limiting Mechanism (RLM)

Use DFT simulations to help distinguish between two possible RLMs.

Direct electron transfer

$$rate = k[e^{\alpha F(E-E_{eq})/RT}]$$



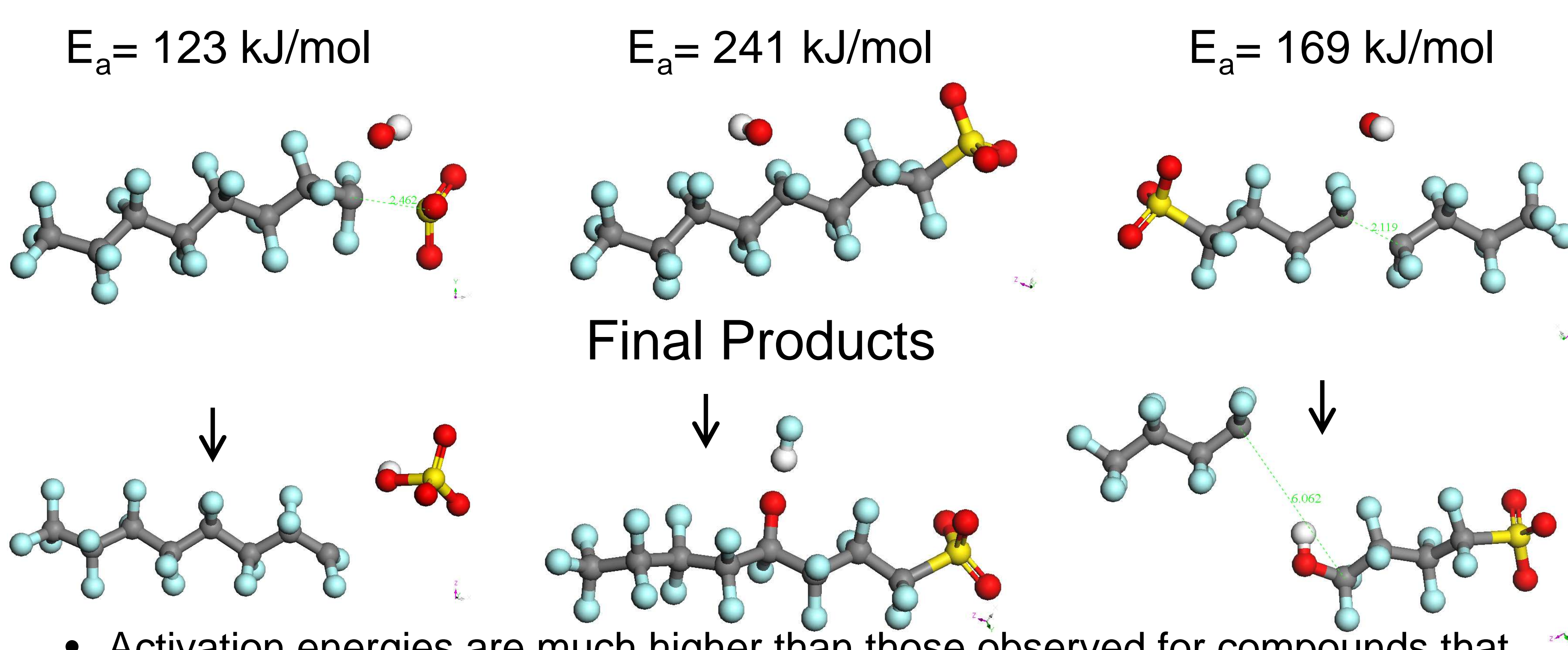
Oxidation by HO•

$$H_2O \rightarrow HO^{\bullet} + H^{+} + e^{-}$$

$$OH^{-} \rightarrow HO^{\bullet} + e^{-}$$

Quantum Chemistry Modeling: Activation Energies for $HO^{\bullet}$ Attack

Transition State Structures



- Activation energies are much higher than those observed for compounds that readily react at room temperature.
- PCBs are unreactive with $HO^{\bullet}$ at room temperature: E_a= 71-93 kJ/mol.
- Phenol readily reacts with $HO^{\bullet}$ at room temperature: E_a=4-25 kJ/mol.

Reaction Mechanisms

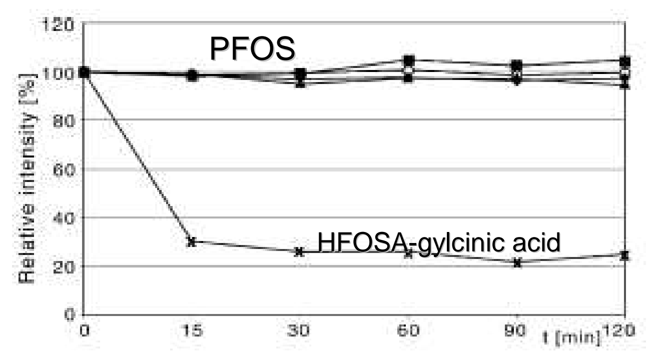


Fig. 1. Graphs of elimination for PFOS and HFOSA-glycinic acid under AOP treatment over a period of 120 min applying different AOP reagents (PFOS treated with: O_3 ▲; O_3/UV ■; O_3/H_2O_2 ♦; Fenton ○; HFOSA-glycinic acid treated with: O_3/UV ×).

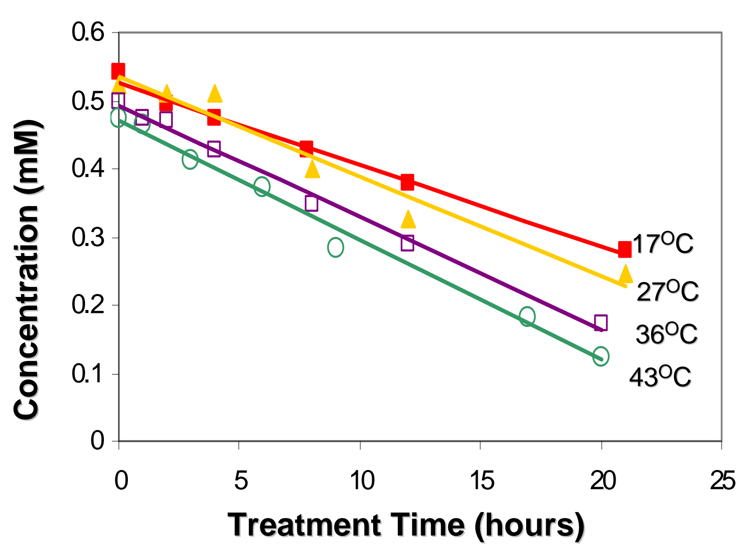
Schroder and Meesters, *J. Chromatog. A.*, 2005.

PFOS unreactive with:

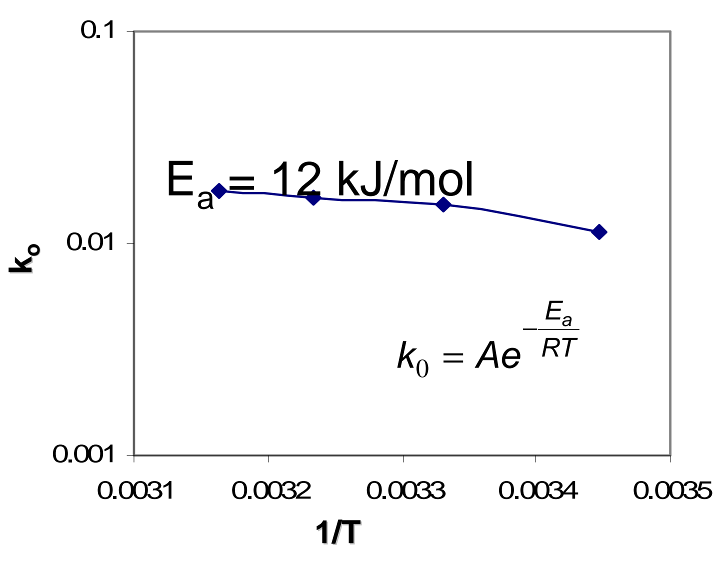
1. O_3
2. O_3/UV
3. H_2O_2/O_3
4. H_2O_2/Fenton (Fe^{2+}/Fe^{3+})

High activation energies for oxidation by $HO^{\bullet}$ is consistent with absence of reactivity with H_2O_2 based AOPs.

Effect of Temperature on PFOS Reaction Rates



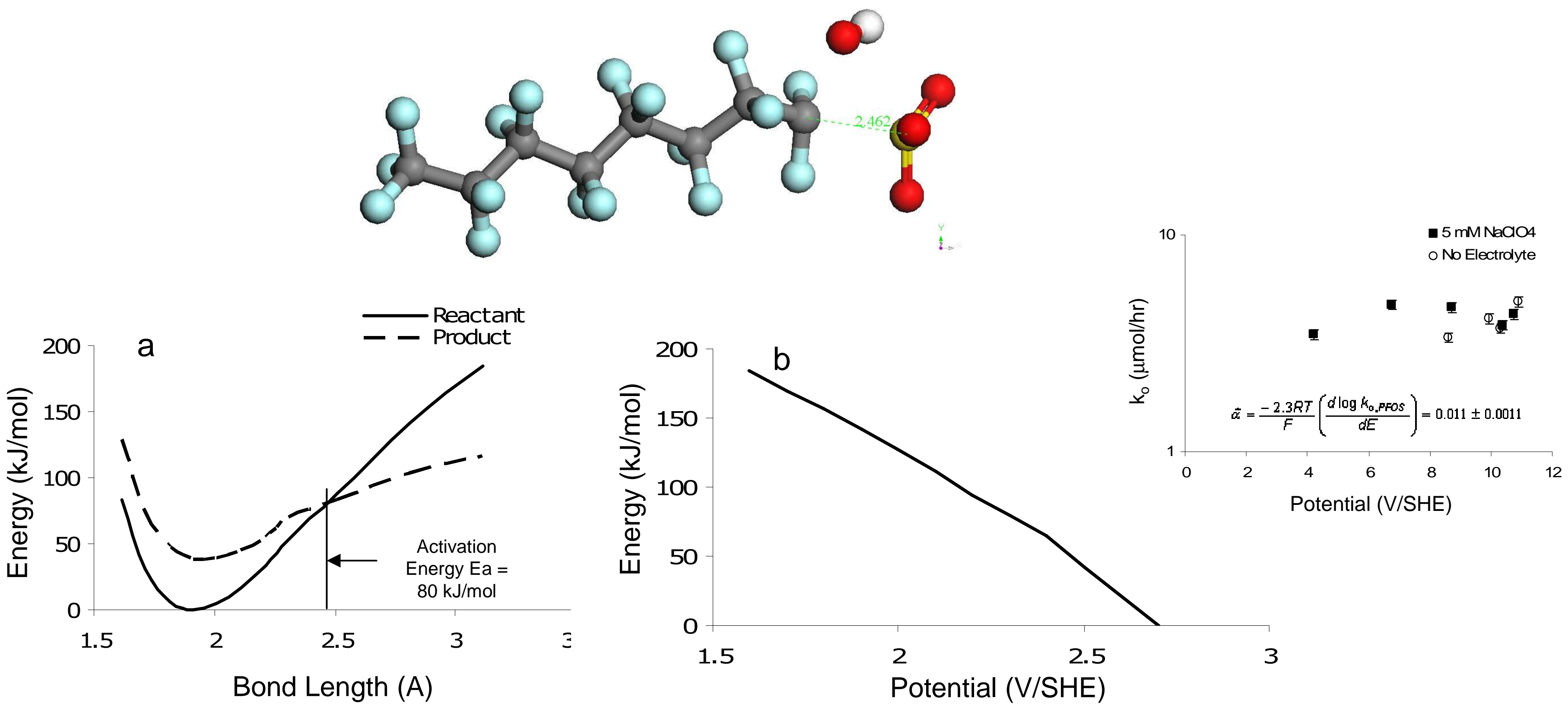
PFOS degradation at different temperatures in RDE reactor at a current density of 10 mA/cm².



Arrhenius plot of k_o used to determine activation energy for degradation of PFOS at 10 mA/cm².

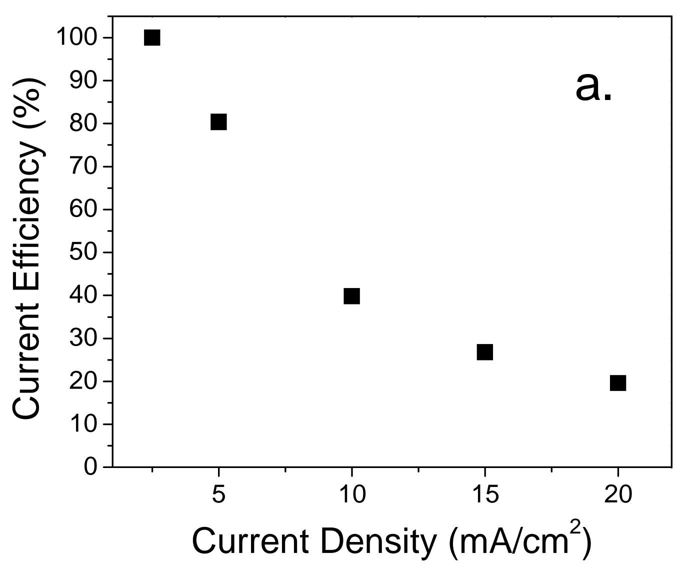
- At 10 mA/cm^2, <10% of the HO$^{\bullet}$ generated react with PFOS.
- Large excess of HO$^{\bullet}$ at each temperature.
- Activation energy for PFOS oxidation by HO$^{\bullet}$ is ≥122 kJ/mol.
- Small apparent E_a suggests that oxidation by HO$^{\bullet}$ is not the RLM.

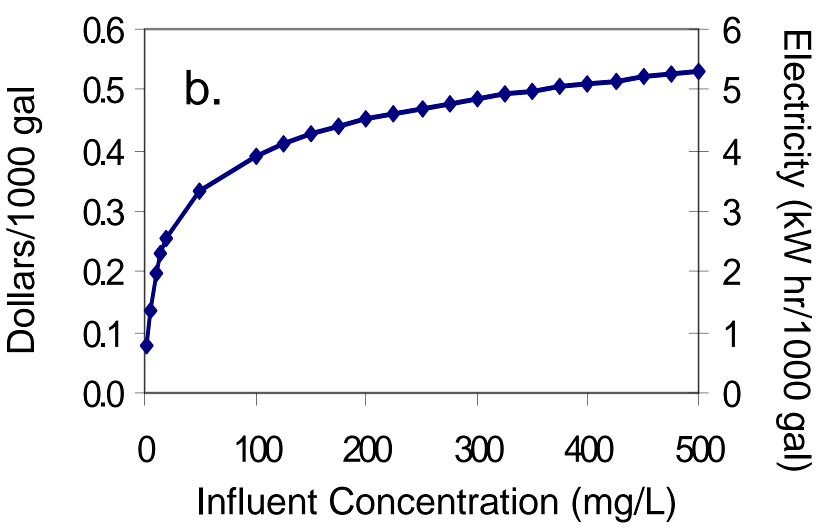
Quantum Chemistry Modeling: E_a for Direct Electron Transfer



a) Energy profiles for reactant ($C_8F_{17}SO_3^-$) and products ($C_8F_{17}SO_3^{\bullet} + e^-$) for vertical electron transfer as a function of the C-S bond length at an electrode potential of 2.5 V/SHE. b) Activation energies as a function of electrode potential for a direct electron transfer reaction.

Current Efficiencies and Treatment Costs



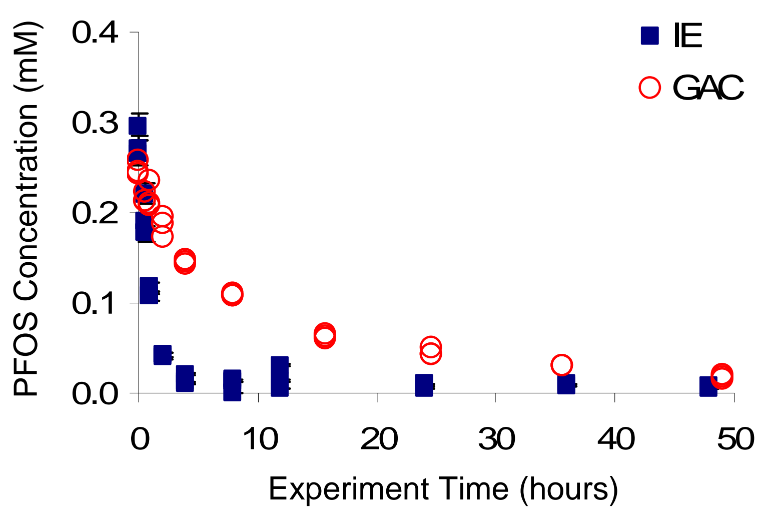


a) Faradic current efficiencies for PFOS oxidation based on 34 mol e^- per mol of PFOS.

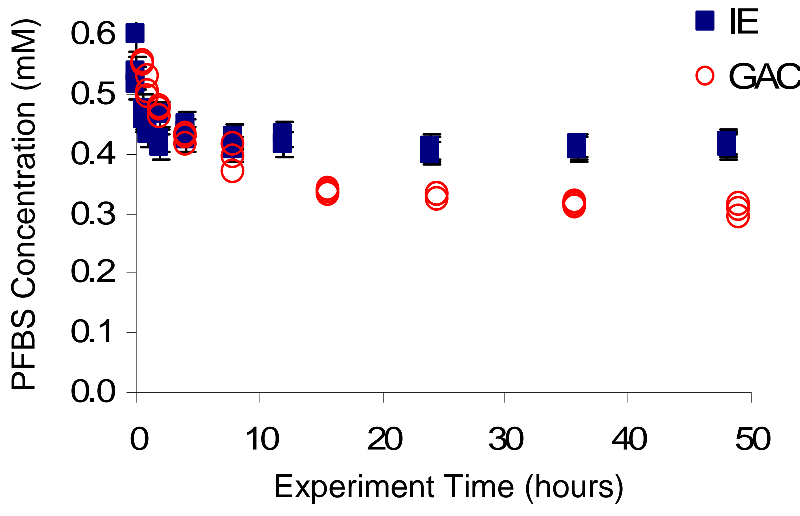
b) Electrical power requirements and costs required to reach a final PFOS concentration of 1 mg/L (2.5 μM) as a function of the influent PFOS concentration. Costs based on flow-cell operated at a current density of 20 mA/cm^2 and an energy cost of $0.10/kWhr.

- Electrical power costs are small compared to other treatment methods.
- Capital costs for a 10 liter per minute flow-cell are ~$2500.

Batch Testing of Ion Exchange (IE) and Granular Activated Carbon (GAC) Equilibrium & Kinetics



10 g of ion exchange resin or 10 g of GAC into 6 L of 0.3 mM PFOS solution



10 g of ion exchange resin or 10 g of GAC into 6 L of 0.6 mM PFBS solution

- 5 hours of equilibrium time is needed for ion exchange
- PFOS more effectively removed than PFBS

Conclusions

- Demonstrated that PFOS and PFBS can be rapidly oxidized to CO_2 and F^- at BDD electrodes.
- Determined the rate-limiting step involves direct electron transfer in the activationless overpotential region.
- Demonstrated that PFOS and PFBS can be removed from aqueous solution using Amberlite® IRA 458 ion exchange resin.

Future Plans

- Perform column tests to optimize the concentration and regeneration steps in the four-step process.
- Pilot test treatment scheme on real process wastewaters.

Acknowledgements

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- NSF Chemical and Transport Systems CTS-0522790
- Petroleum Research Fund 43535-AC5

Industrial Collaboration

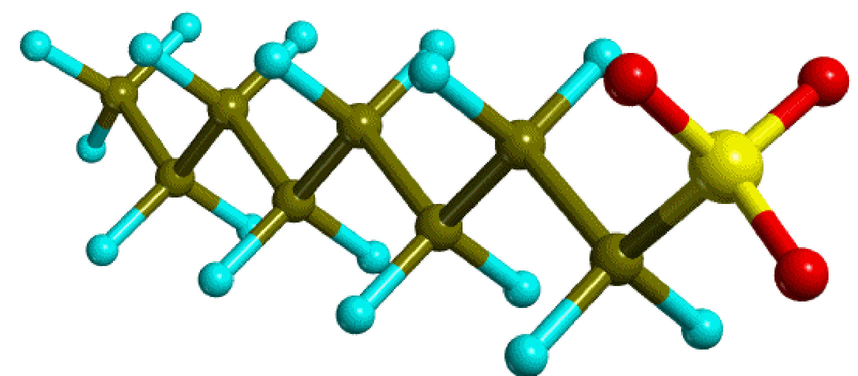
• Tim Yeakley	Texas Instruments
• Thomas P. Diamond	IBM
• Jim Jewett	Intel
• Laura Mendicino	Freescale Semiconductor

Destruction of Perfluoroalkyl Surfactants in Semiconductor Process Waters Using Boron Doped Diamond Film Electrodes (*Task Number: 425.018)*

Valeria Ochoa-Herrera, Reyes Sierra and Jim A Farrell
Chemical and Environmental Engineering Department

University of Arizona, Tucson

February 28, 2008



Objectives

- Determine the degree of electrolysis required for PFOS and PFBS to generate products that are readily biodegraded in municipal wastewater treatment plants.
- Determine the impact of electrolysis on the microbial toxicity of the degradation products from PFOS and PFBS.
- Develop an adsorptive method for concentrating PFAS compounds from dilute aqueous solutions.

ESH Metrics and Impact

Electrolysis of PFAS

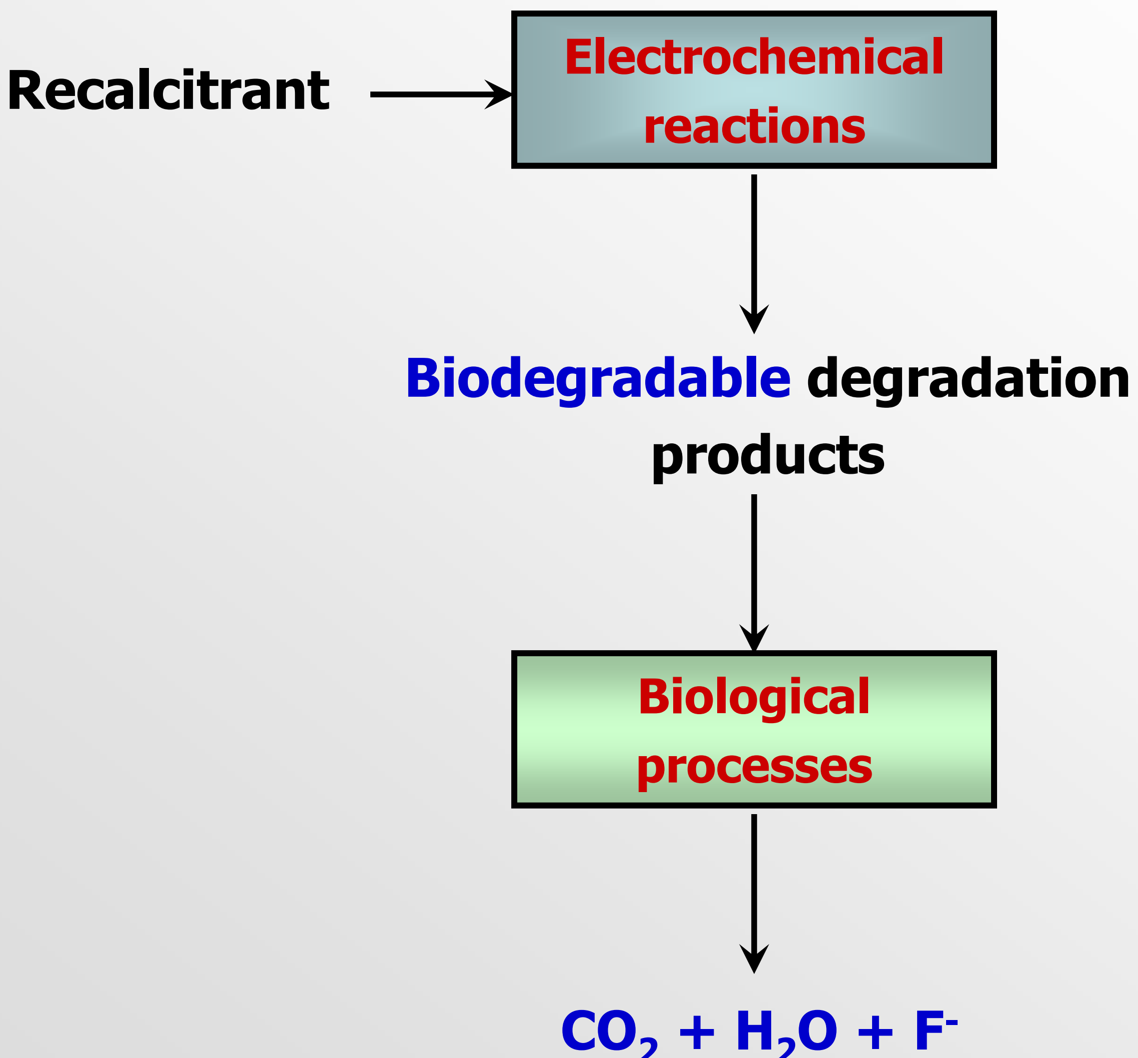
100 % removal of PFOS and other PFAS from waste streams

Use less natural resources

- Low energy consumption
- No addition of chemicals

Secure use exemption for PFAS in Semiconductor Industry

Electrochemical-Biological Processes



Research lines

A) Characterization and microbial degradation of PFOS electrochemical samples.

B) Concentrate PFAS compounds from dilute aqueous solutions by adsorption onto GAC and zeolites.

A) Method of Approach

Electrochemical treatment:

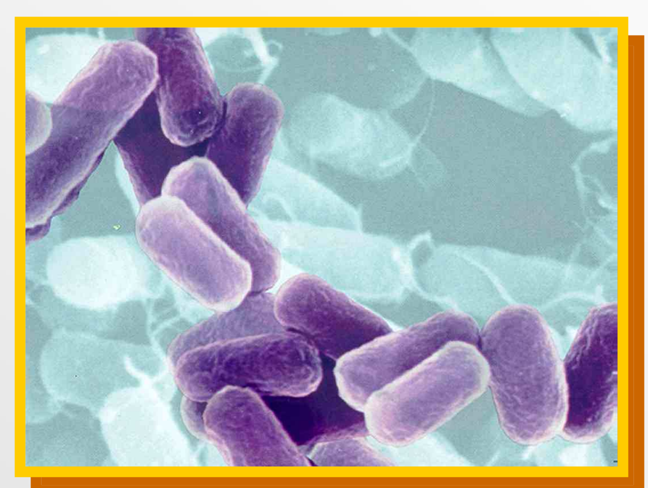
- PFOS (0.4 mM): batch reactor (V= 350 ml, anode surface= 1 cm^2, current= 10 mA) for 0-24 h.
- PFBS (0.4 mM): flow-through reactor (100 ml/min, current density of 2.5 mA/cm^2) for 0, 1, 2, 3, 4 d.
- No electrolyte was added.

Microbial Toxicity:

- Methanogenic microorganisms WWT sludge
- 30ºC utilizing H_2 as substrate

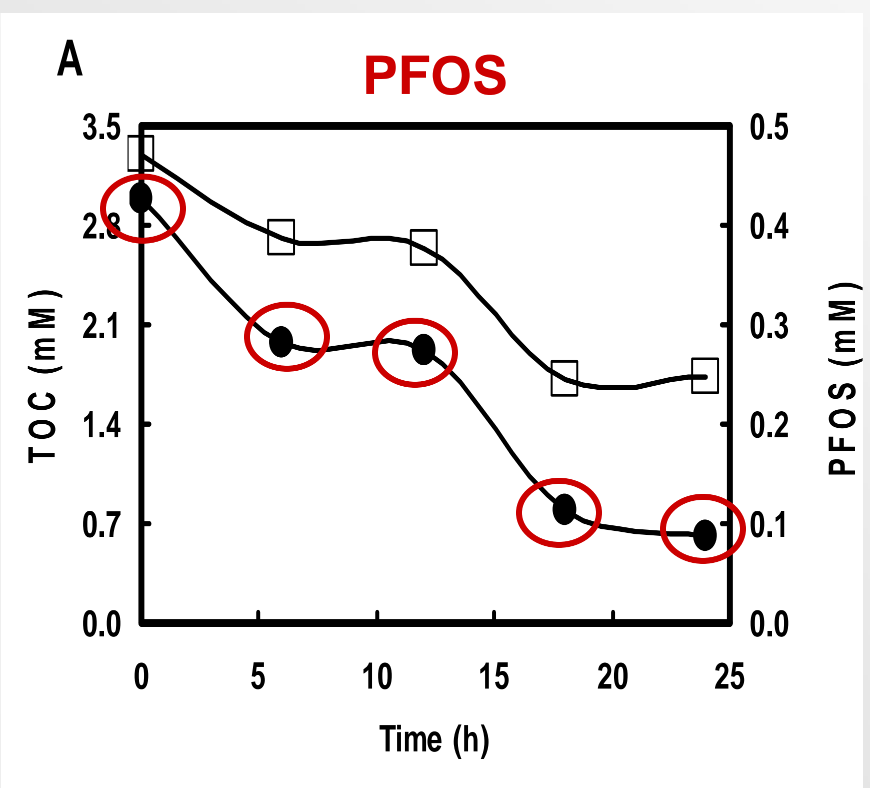
Microbial degradation:

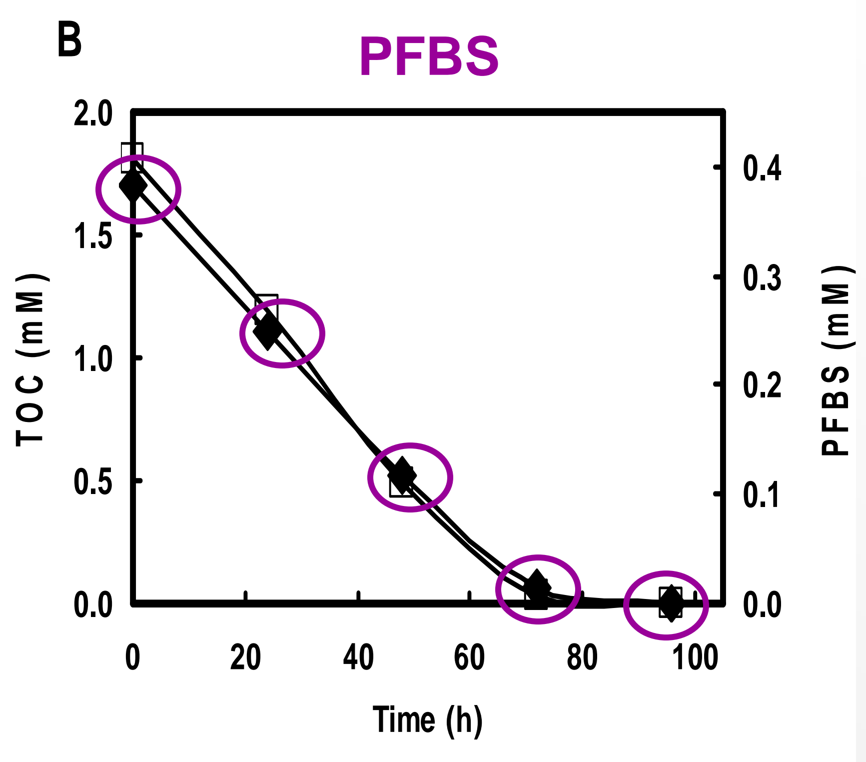
- Batch bioassays.
- 30°C utilizing H_2 as as the electron donor.
- F^- ⟶ ion selective electrode
- Fluorinated compounds ⟶ HPLC-IC



Time course of PFAS electrolysis

PFOS and PFBS are removed by electrochemical treatment





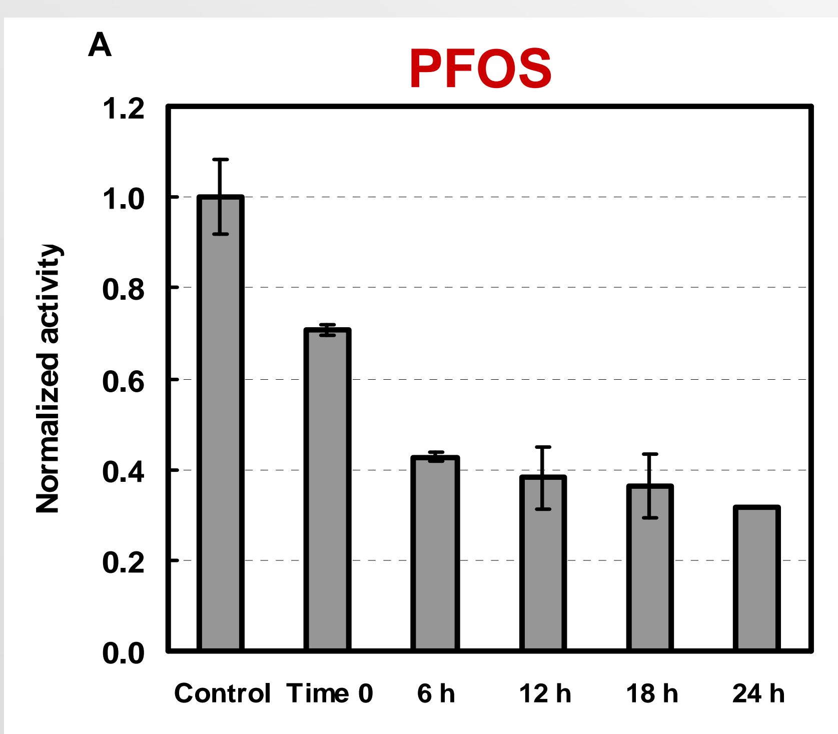
Concentration of PFAS and total organic carbon (TOC) as a function of time in the electrolysis experiments. Legend: A) PFOS (●), B) PFBS (♦) and TOC (□)

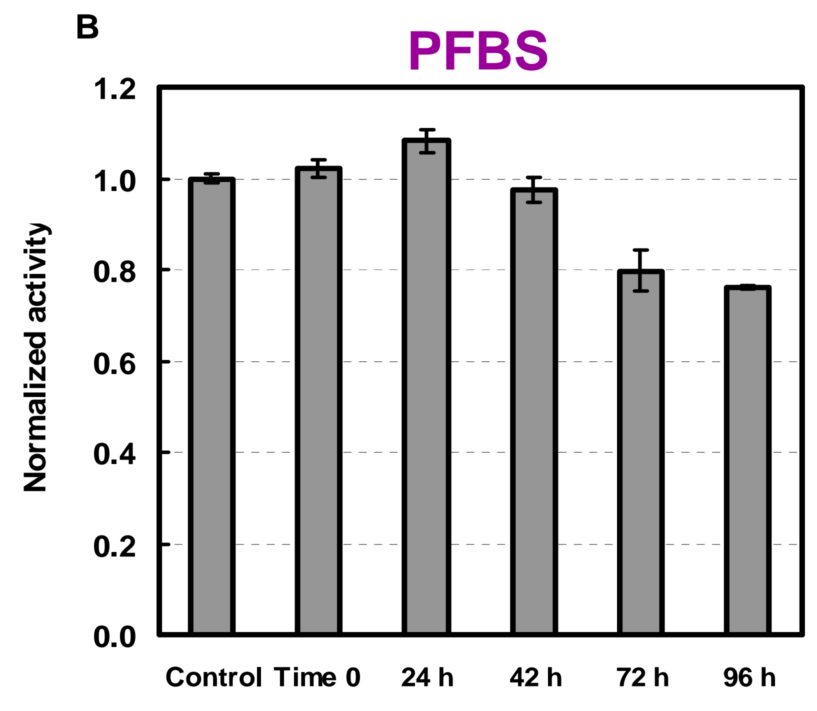
Characterization of PFAS electrolysis samples

^{19}F-NMR spectra

Microbial inhibition by products of PFAS electrolysis

Electrolysis products caused microbial inhibition up to 70% for PFOS and 25% for PFBS samples

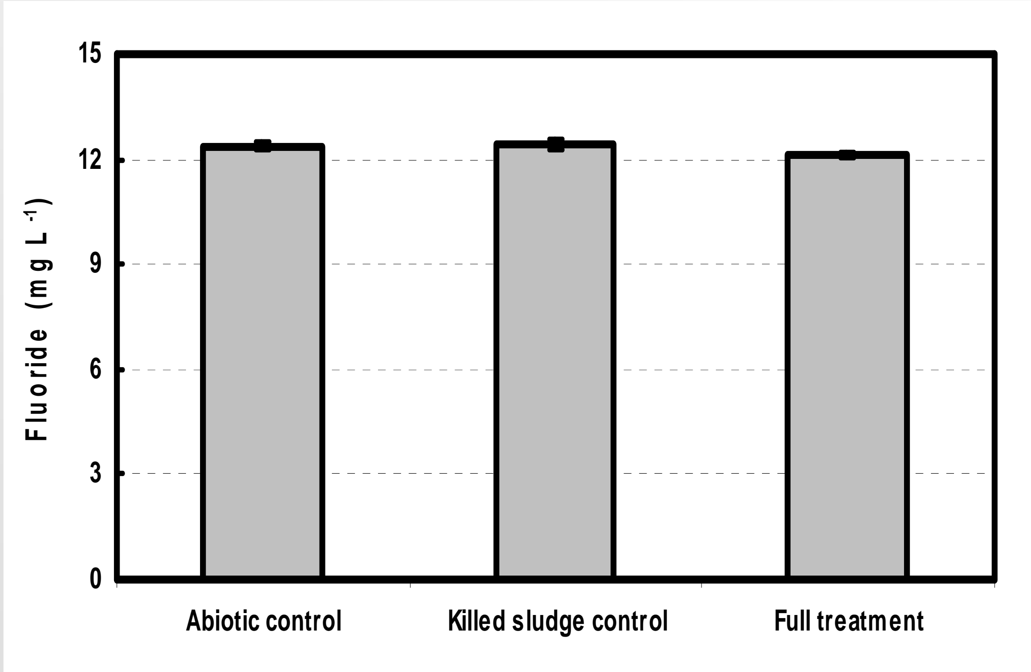




Methanogenic activity of PFAS solutions subjected to electrochemical treatment for different time periods. Initial [PFOS] = 0.4mM and [PFBS] = 0.4mM

Microbial degradation of PFOS electrolysis products

No evidence for the degradation of PFOS electrolysis products based on F- measurements after extended incubation



Fluoride release of the anaerobic degradation of PFOS electrolyzed for 18 h after 165 days of incubation. $[TOC]_o$ = 1.7 mM, $[PFOS]_o$ = 0.1 mM and $[F]_o$ = 15.2 ppm

Conclusions

- Electrolysis increased the microbial toxicity of PFOS, likely due to the release of F^- and possibly other degradation products.

- No evidence for the microbial degradation of PFOS electrolysis products after 165 days of incubation based on fluoride measurements.

B) Method of Approach

Adsorption isotherms with activated carbon and zeolites

- pH 7.2 phosphate buffer
- 30°C for 48 hours.
- Experimental data fitted to Langmuir and Freundlich models

Langmuir isotherm

$$C_s = \frac{a \cdot b \cdot C_e}{1 + b \cdot C_e}$$

Freundlich isotherm

$$C_s = K_F \cdot C_e^{\ n}$$

Structuur van zeoliet Y

Substitution SO_3^- by COO^- group and shorter fluorocarbon chain resulted in weaker adsorption

PFOS
PFOA
PFBS
Cs (mg contaminant/ g GAC)
300
250
200
150
100
50
0
0
25
50
75
100
125
150
Ce (mg contaminant/l)

Adsorption of PFOS by Zeolites

Hydrophobic zeolites (high Si content) adsorb PFOS

Cs (mg PFOS/g zeolite)
120
100
80
60
40
20
0
NaY80 (Si/Al 80)
13X (Si/Al 2.8)
NaY (Si/Al 5.5)
0 25 50 75 100 125 150
Ce (mg PFOS/l)

Conclusions

- PFOS/PFAS can be removed from dilute solutions by adsorption onto activated carbon.
- The affinity of GAC for PFOS is moderate when compared to chemical compounds traditionally suitable to carbon adsorption.
- PFOS is readily adsorbed by hydrophobic zeolites with a high silica content (eg. NaY80, Si/Al = 80).
- Affinity of sorbents for PFOS: GAC > hydrophobic zeolite.

Next Year Plans

- Investigate the microbial degradation of products from the incomplete electrolysis of PFBS.
- Evaluate the microbial degradation of partially fluorinated compounds
- Perform column breakthrough experiments with activated carbon to determine the mass transfer characteristics for the best performing PFAS adsorbents.

Acknowledgments

- Chandra Khatri, University of Arizona
- Sandra Hernandez, Autonomous University of Coahuila, Mexico

- SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing.

Collaborators

- Walter Worth, Sematech,WalterWorth@ismi.sematech.org
- Tim Yeakley, Texas Instruments, t-yeakley@ti.com
- Thomas P. Diamond, IBM, tdiamond@us.ibm.com
- Jim Jewett, Intel, jim.jewett@intel.com
- Laura Mendicino, Freescale Semiconductor, Laura.Mendicino@freescale.com

Students on task 425.018

- Current Students and Anticipated Grad Date
  - Valeria Ochoa-Herrera, December 2008.
  - Sandra Hernandez, exchange PhD student, Autonomous University of Coahuila, Mexico (01/07-05/07).

CMOS Biochips for Rapid Assessment of Chemical Toxicity

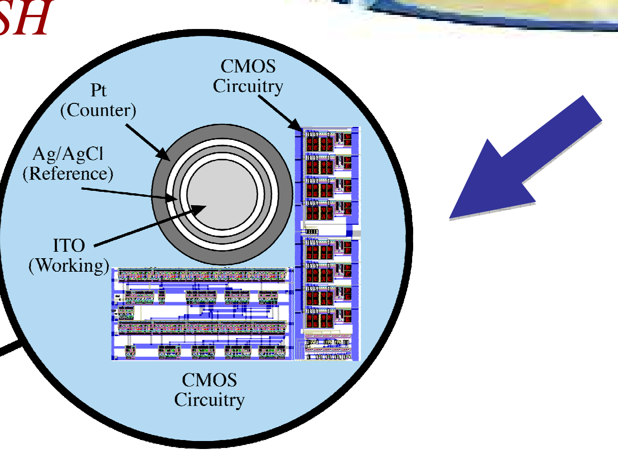
(*Task Number: 425.012)*

By
Jadrian Rusche, Department of Anatomy and Cell Biology, UA
Matt Scholz, Department of Plant Sciences, UA
Raymond B. Runyan, Department of Anatomy and Cell Biology, UA
David L. Mathine, Optical Sciences, UA

Rapid Assessment of Chemicals and Process Chemistries

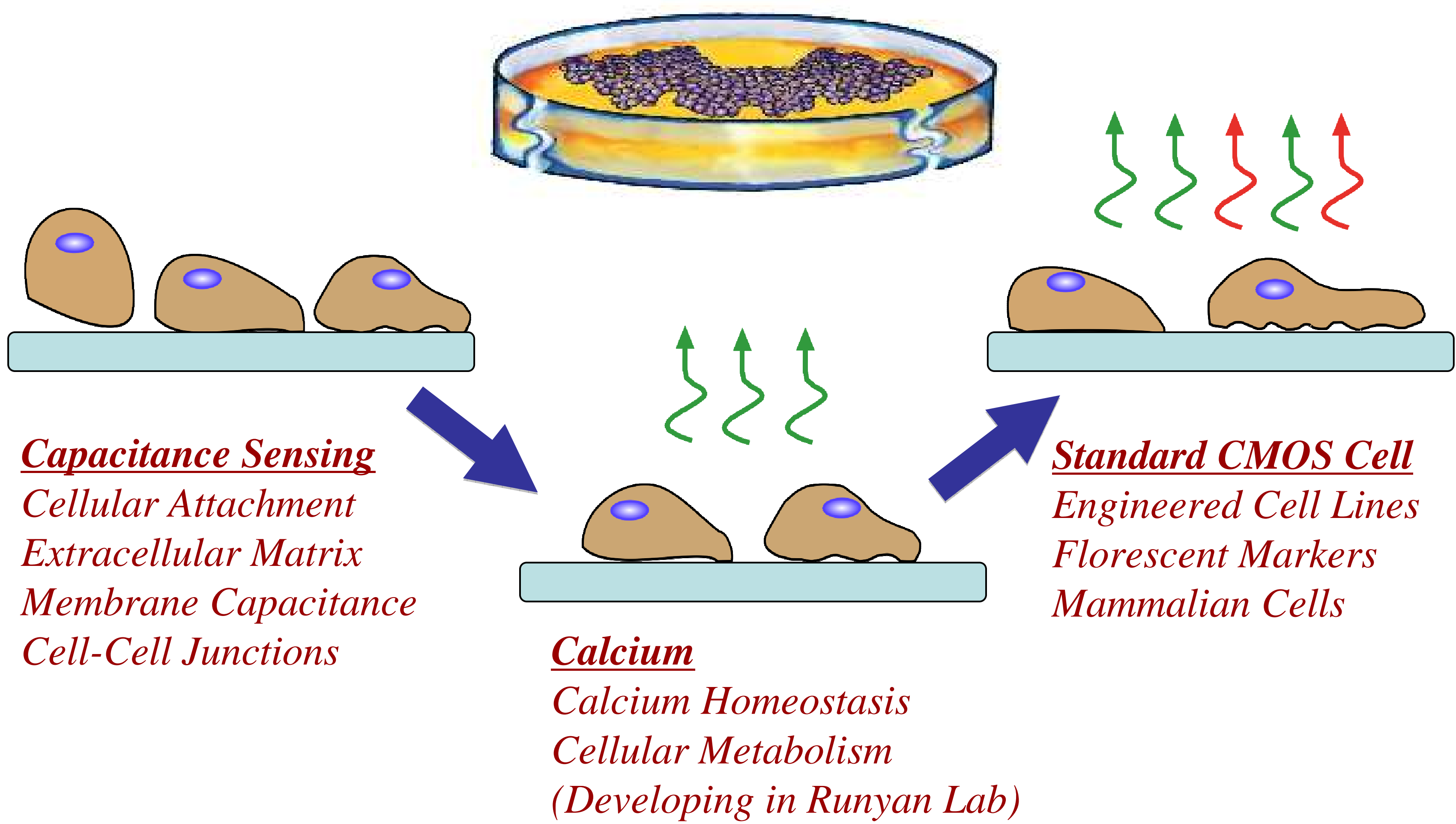
- *Rapid assessment of chemicals and process chemistries*
- *A smart CMOS substrate is used to monitor cell activity*
- *A first step towards an on-line ESH monitor.*

Mammalian Cells

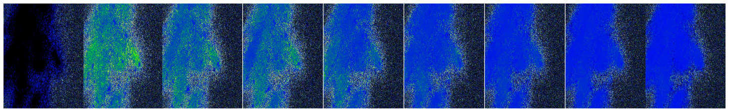


Smart CMOS Sensor

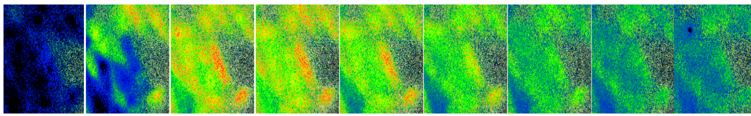
Toxicity Assessment



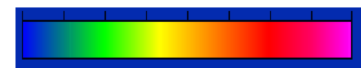
Develop New Techniques for Toxicity Testing



Control for 10ppb/100ppb TCE cells @ 10nM VP



Treated: 10ppb TCE cells @ 10nM VP



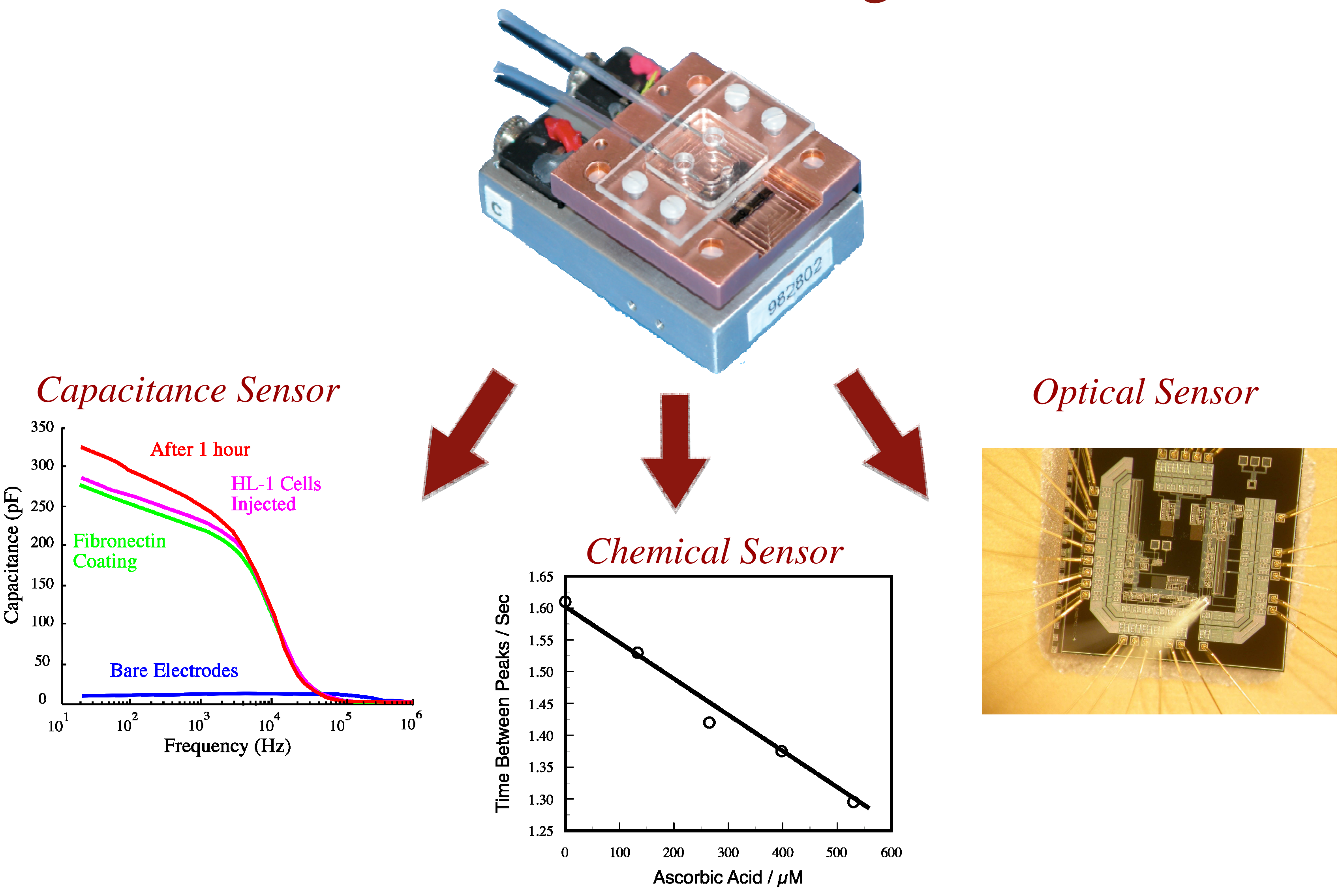
Low Calcium flow High Calcium flow

•Developed novel technique for toxicity determination

• Demonstrated on the known toxic TCE

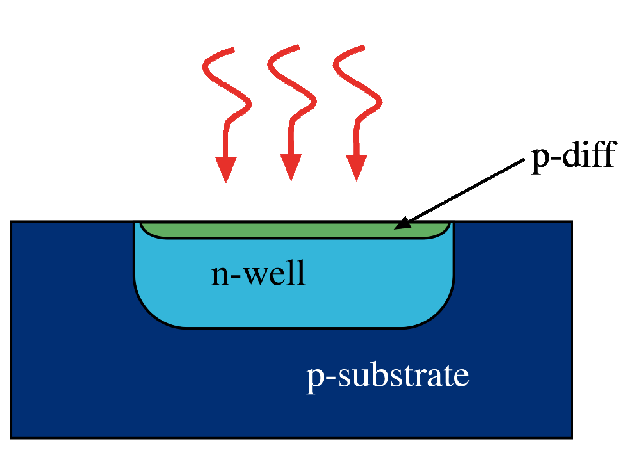
• Next step it to evaluate new chemicals

Sensor for Monitoring Cells

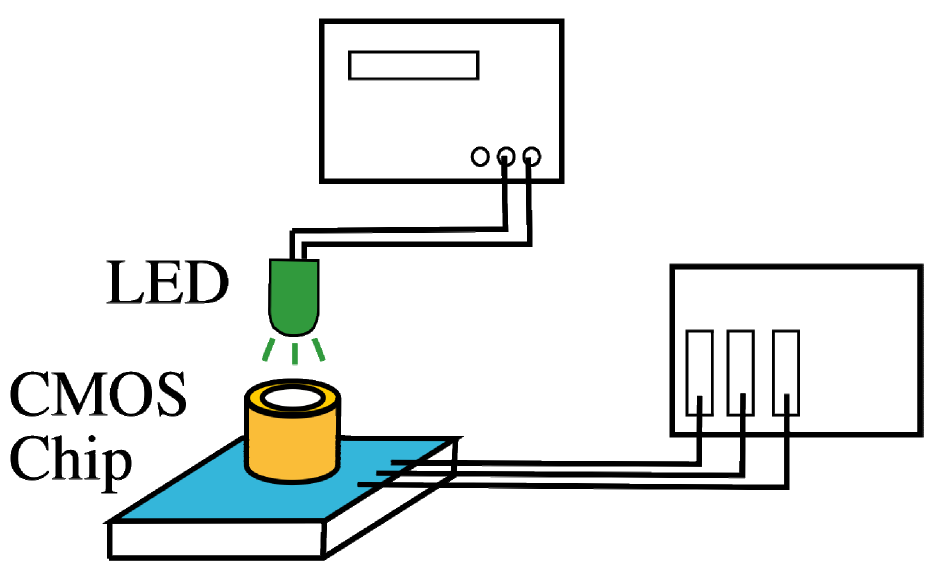


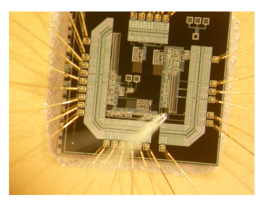
Phenol Red Sensor Development

CMOS Photodetector

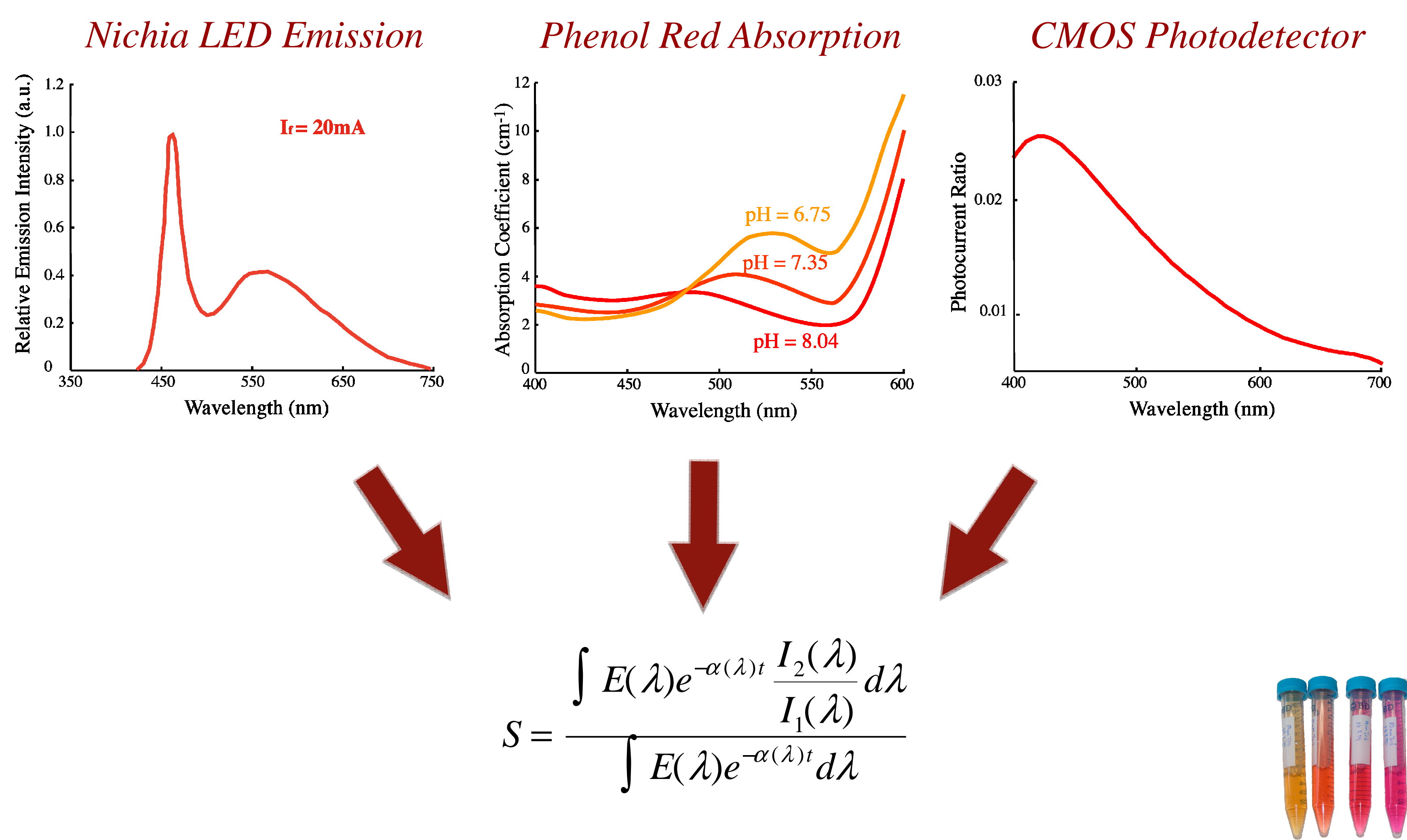


Experimental Validation





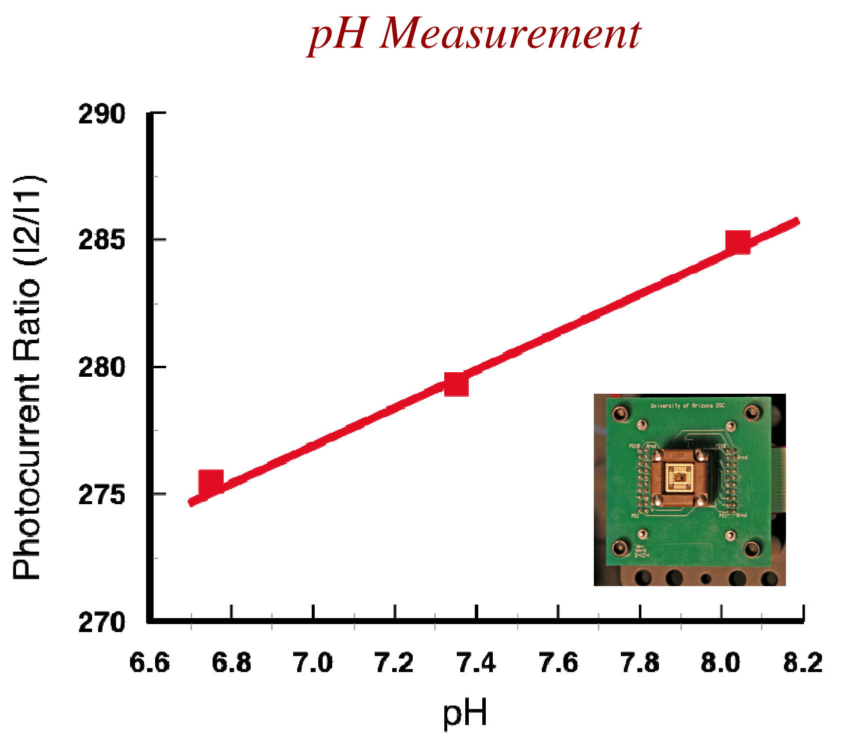
Phenol Red Sensor Development



$$S = \frac{\int E(\lambda) e^{-\alpha(\lambda)t} \frac{I_2(\lambda)}{I_1(\lambda)} d\lambda}{\int E(\lambda) e^{-\alpha(\lambda)t} d\lambda}$$

Phenol Red Sensor Development

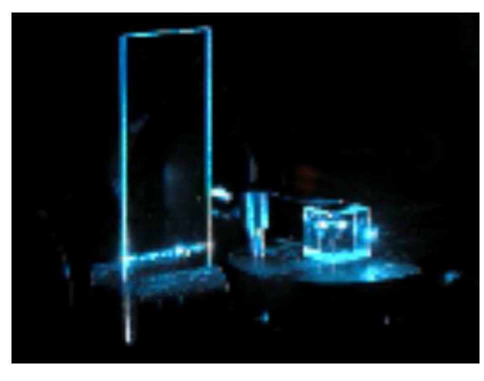
pH Measurement



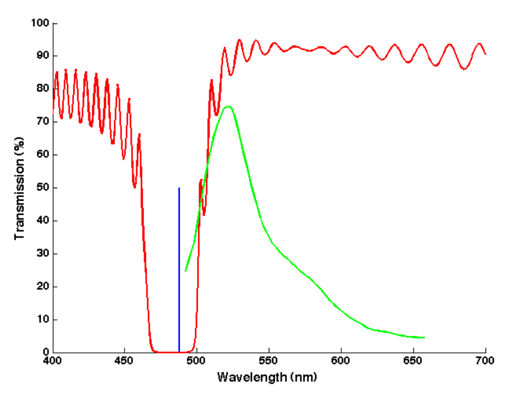
- *Optical determination of pH demonstrated*
- *Shows validity of CMOS photodetectors for use in biological measurements*
- *Readily integratable into biochip sensor*

Measurement of Fluorescence Labeled Yeast

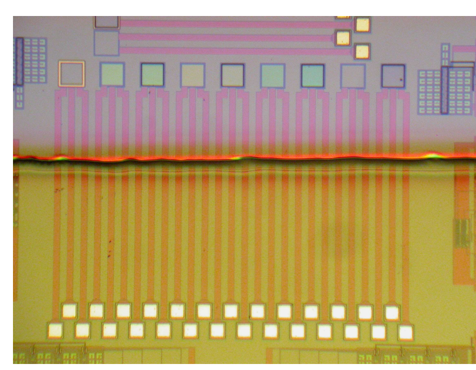
Argon Laser Source

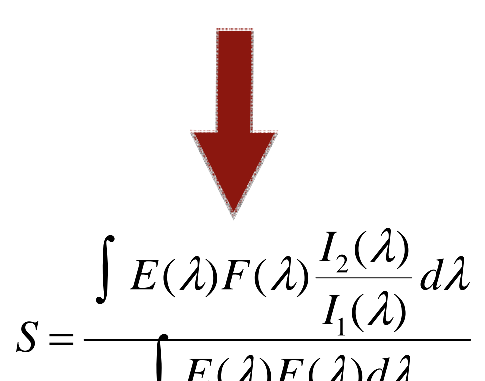


GFP Florescence Spectra

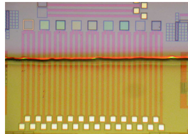


Integrated Optical Filter



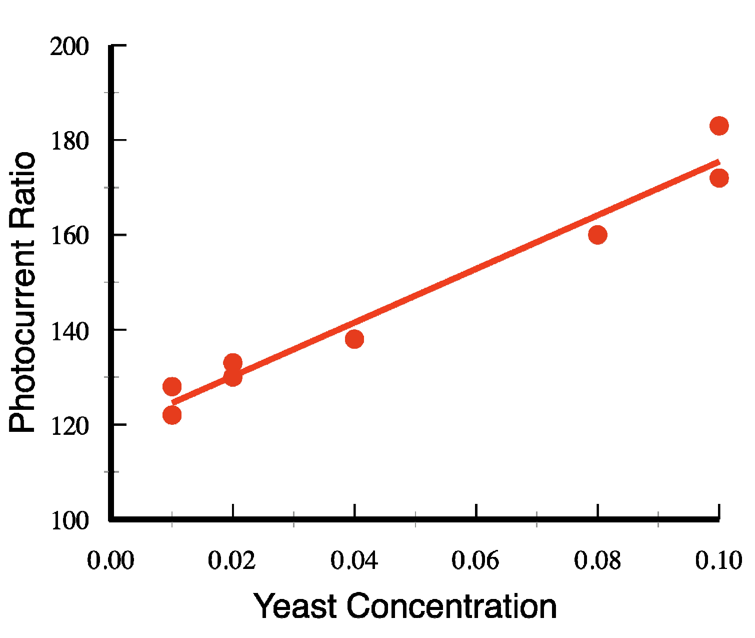


$$S = \frac{\int E(\lambda)F(\lambda)\frac{I_2(\lambda)}{I_1(\lambda)}d\lambda}{\int E(\lambda)F(\lambda)d\lambda}$$

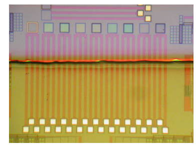


Measurement of Florescence Labeled Yeast

Photodetector Ratio

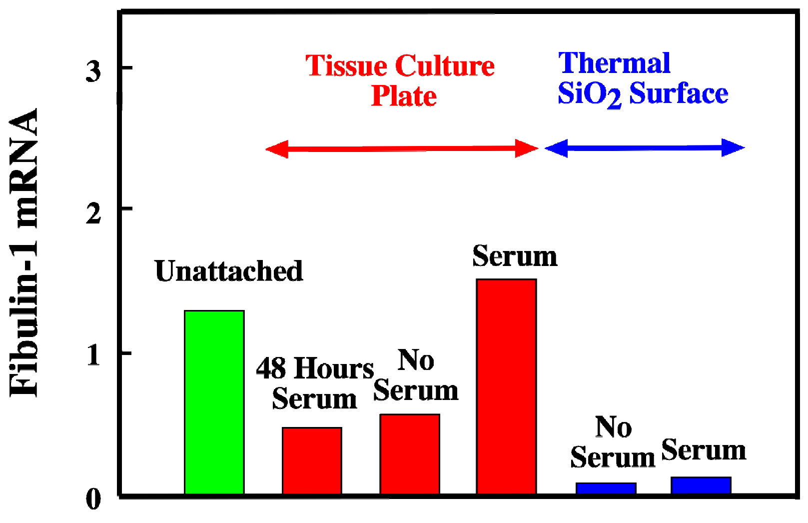


- *Optical determination of pH demonstrated*
- *Shows validity of CMOS photodetectors for use in biological measurements*
- *Sensor is easily integrated into biochip sensor*

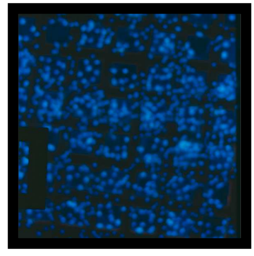


Attachment of Cells to Dielectric Surfaces

Cellular Response



- *The extracellular matrix protein Fibulin-1 was monitored from COS-7 cells.*
- *COS-7 cells attached to SiO_2 surfaces with minimal stimulus.*
- *Mammilian cells show attachment to a variety of common semiconductor manufacturing materials.*

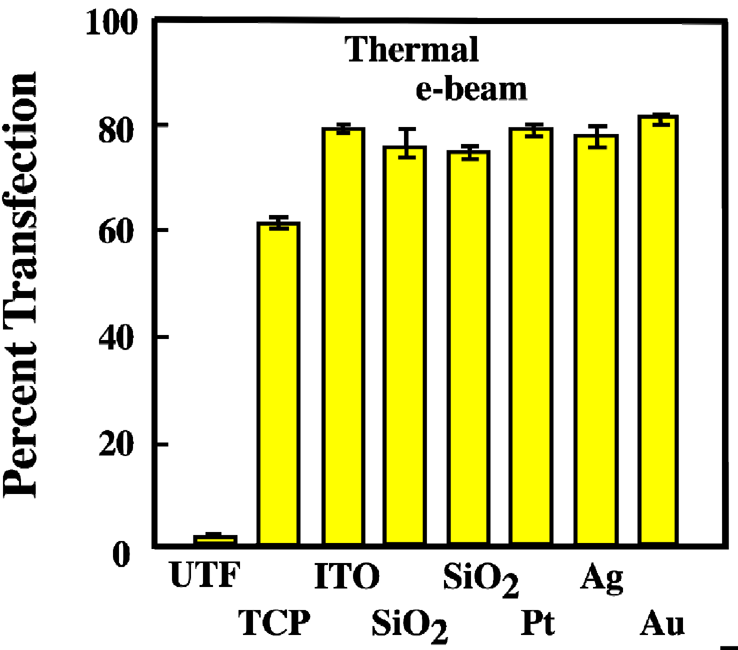


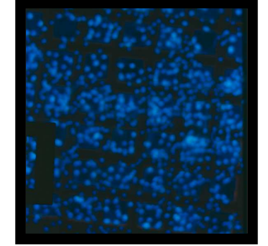
Transfection of Cells on Biosensor Surfaces

•Changes in the expression of a single gene were evaluated

• COS-7 cells transfected with a reporter plasmid that contained coding sequence for EGFP.

• Demonstrates real time measurement of changes in gene expression.





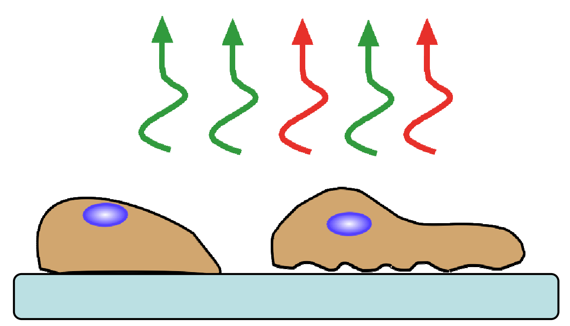
Future Plans

Next Year Plans

- **Determine Toxicity of New Chemicals**
- **Integrate Multiple Sensors on CMOS Chip**
  - **Capacitance**
  - **Photodetectors**
- **Demonstrate Hand Held Sensor**
  - **Like Swimming Pool Testing Kit**
- **Move this Tool Toward Commercialization**

Long-Term Plans

- **Commercialize this Tool**

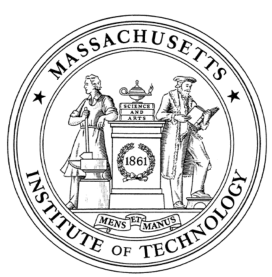


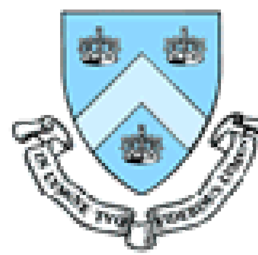
Publications, Presentations, and Recognitions/Awards

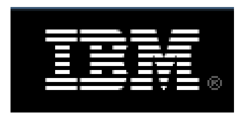
- **D. J. O'Connell, A. J. Molinar, A. Luiz Pasqua Tarares, D. L. Mathine, R. B. Runyan, and J. J. Bahl, "Cell Attachment to Selected Cell Based Biosensor Surfaces," *Life Sciences* 80 (2007) 1395.**
- **P.T. Caldwell, P. A. Thorne, S. Boitano, R. B. Runyan, P. D. Johnson, and O. Selmin," "Tricholoroethylene Disrupts Cardiac Gene Expression and Calcium Homeostasis in Rat Myocytes," *Enviromental Health Perspectives*, Revised December 29, 2007.**
- **D. L. Mathine, T. Hoda, D. J. O'Connell, J. J. Bahl, and R. B. Runyan, "A Colorimetric pH Sensor for Use in a Cell-Based Biosensor," Submitted to *Sensors and Actuators B: Chemical.***
- **D. L. Mathine, J. Rusche, T. Hoda, and R. B. Runyan, "A CMOS Spectroscopic Duel Photodetector for Determination of Green Fluorescent Protein Labeled Yeast," Submitted to *Lab on a Chip***
- **D. L. Mathine, J. J. Bahl, R. B. Runyan, "CMOS Photodetectors for a Cell Based Biosensor," Photonincs North, Ottawa, Ontaria, Canada, June 2007 (Invited Talk)**

Planarization Long Range Plan

February 2008







P. Fischer (Intel) … L. Economikos (IBM) … C. Spiro (Cabot) …
C. Borst (U at Albany) … Y. Moon (AMD)

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Next Five Years

- **Landscape:**
  - Research, fundamental in nature yet industrially relevant, addressing the technological, economic and environmental challenges of planarizing copper, tantalum, ruthenium (also STI and new structures related to memory devices)
- **Gaps to be filled:**
  - Processes & consumables for advanced planarization, ECMP and post-planarization cleaning

ALWAYS KEEP THE BIG PICTURE IN MIND

… YIELD IS EVERYTHING …

environmental and economic losses resulting from lower yields
are far greater than any gains realized through
consumables reduction and incremental process tweaks

Advanced Processes & Consumables for Planarization

- **Focus:**
  - Basic scientific investigations of the controlling processes in planarization of advanced materials over several length scales and levels of complexity
  - Development of validated, science-based descriptions that relate specific planarization process and material attributes (including material micro-structure) to measurable process outcomes
  - Specification and testing of environmentally-conscious process and material alternatives for rapid feedback into the planarization design process

Advanced Processes & Consumables for Planarization

- **Objectives**
  - **Real-time detection and modeling of pattern evolution**
  - **Effect of pad grooving on process performance**
  - **Wear phenomena and their effect on process performance**
  - **Fundamental limits of topography control (new) !**
    - **Development & characterization of consumables to modulate removal rate selectivity, dishing and erosion for ‘n + 1’ and ‘n + 2’ technology nodes**

Advanced Processes & Consumables for Electrochemically Assisted Planarization

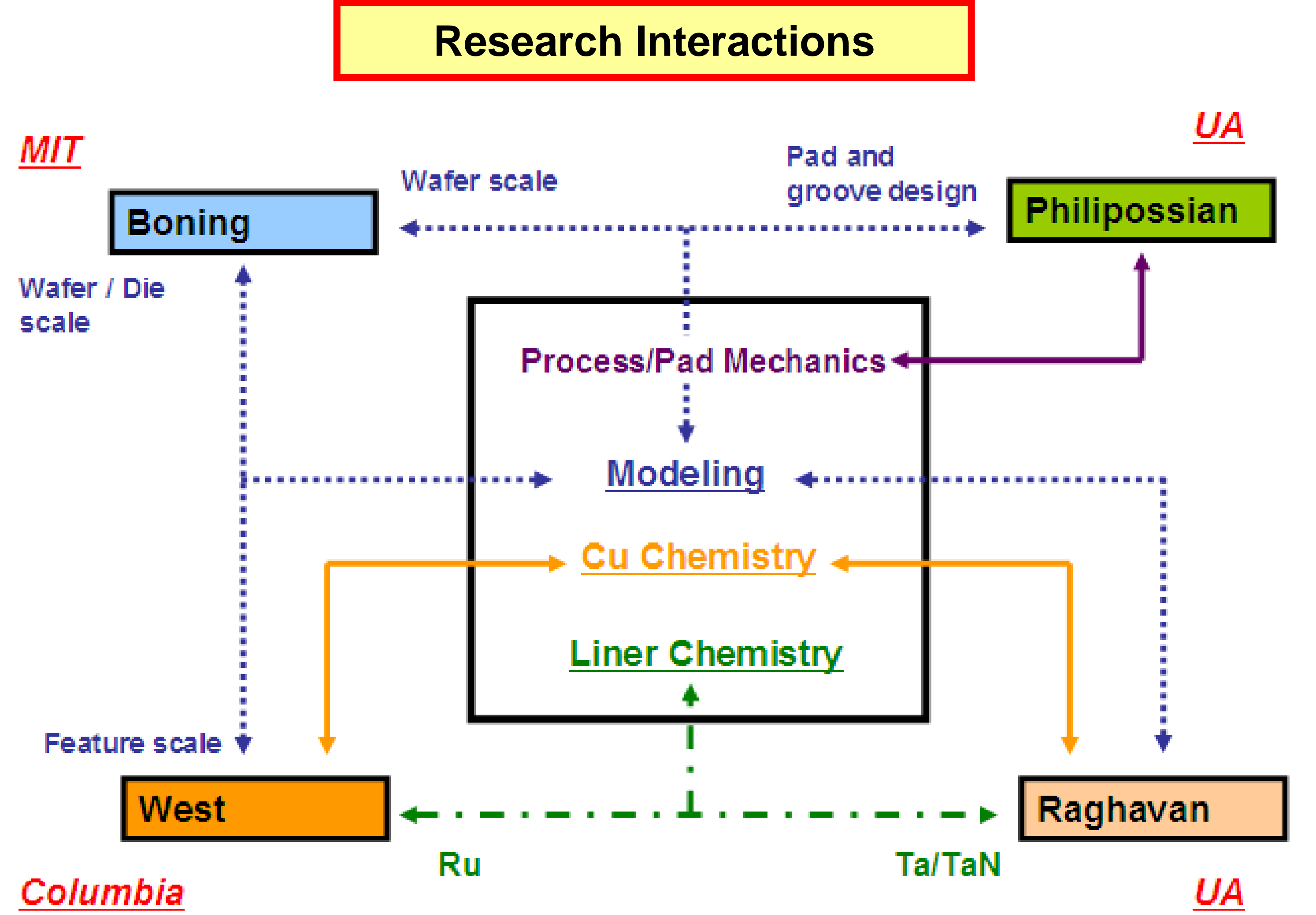
- **Focus and Objectives:**

  - Development and implementation of a 'full' process that includes clearing of copper & planarization of the barrier (i.e. tantalum) layer. 'Full' process may include post-processing steps such as oxide planarization or buff steps.

  - **Novel chemistries** to enhance and control electrochemical removal and passivation of copper, tantalum and ruthenium

  - **Modeling and characterization** of tool, pad and wafer interactions for design and control (particularly endpoint detection) are needed to minimize process cost and environmental impact

Advanced Processes & Consumables for Electrochemically Assisted Planarization



Advanced Post-Planarization Cleaning Processes & Consumables

- **Focus and Objectives:**
  - Fundamental study of the effects of brush (new and used) material and design on shear force, creep, rebound and cleaning efficiency of insulator and metal films
  - **Novel surface mechanical testing methodologies** to perform cyclic and incremental brush deformation measurements before and after extended wear to understand failure mechanisms
  - **Design and use of novel tribometers** to study the frictional forces in post-planarization scrubbing
  - **Modeling and characterization** of brush, cleaning fluid and wafer interactions within the realm of nano-lubrication theories

An Integrated, Multi-Scale Framework for Designing Environmentally Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task Number: 425.020)*

Subtask 1: Wear Phenomena and Their Effect on Process Performance

PI:

- **Ara Philipossian, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Xiaomin Wei: Ph. D. candidate, Chemical and Environmental Engineering, UA**
- **Ting Sun: Ph. D. candidate, Chemical and Environmental Engineering, UA**
- **Anand Meled: Ph. D. candidate, Chemical and Environmental Engineering, UA**

Undergraduate Students:

- **Geoff Steward, Chemical and Environmental Engineering, UA**
- **Roy Dittler, Chemical and Environmental Engineering, UA**

An Integrated, Multi-Scale Framework for Designing Environmentally Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task Number: 425.020)*

Subtask 1: Wear Phenomena and Their Effect on Process Performance

Other Researchers:

- **Yun Zhuang, Research Associate, Chemical and Environmental Engineering, UA**
- **Jiang Cheng, Visiting Scholar, Chemical and Environmental Engineering, UA**

Cost Share (other than core ERC funding):

- **In-kind donation (pads and slurries) from Cabot Microelectronics Corporation**
- **In-kind donation (diamond discs) from Mitsubishi Materials Corporation**
- **In-kind donation (retaining rings) from Entegris, Inc.**
- **In-kind support from Araca, Inc.**

Objectives

- **Investigate diamond & substrate wear during copper CMP.**
- **Investigate effect of conditioning on pad topography & slurry film thickness.**
- **Investigate effect of materials of construction & design on retaining ring wear.**
- **Investigate effect of retaining ring design on slurry flow.**

ESH Metrics and Impact

1. *Reduce diamond disc consumption by 20%*
2. *Reduce pad consumption by 33%*
3. *Reduce slurry consumption by 20%*
4. *Reduce retaining ring consumption by 33%*

Objectives

On a typical conditioner, there may be appx. 50,000 diamonds

Active diamonds are those diamonds that modify a pad surface by cutting furrows

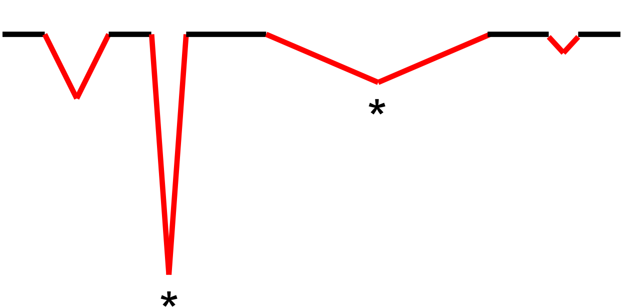
Not all diamonds on a disc are active. If they were, normal load would be 0.0002 lb-f per diamond !

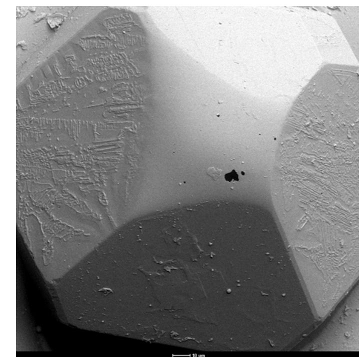
Therefore, the average diamond wear rate would be very small, cut rates would remain high throughout the life of the conditioner and the diamond conditioner would *'Last Forever'*

We know this is NOT the case !

Some of the active diamonds are aggressive. They cut furrows with large areas (*) and do most of the pad cutting work during CMP.

Furrows cut on the pad surface by active diamonds





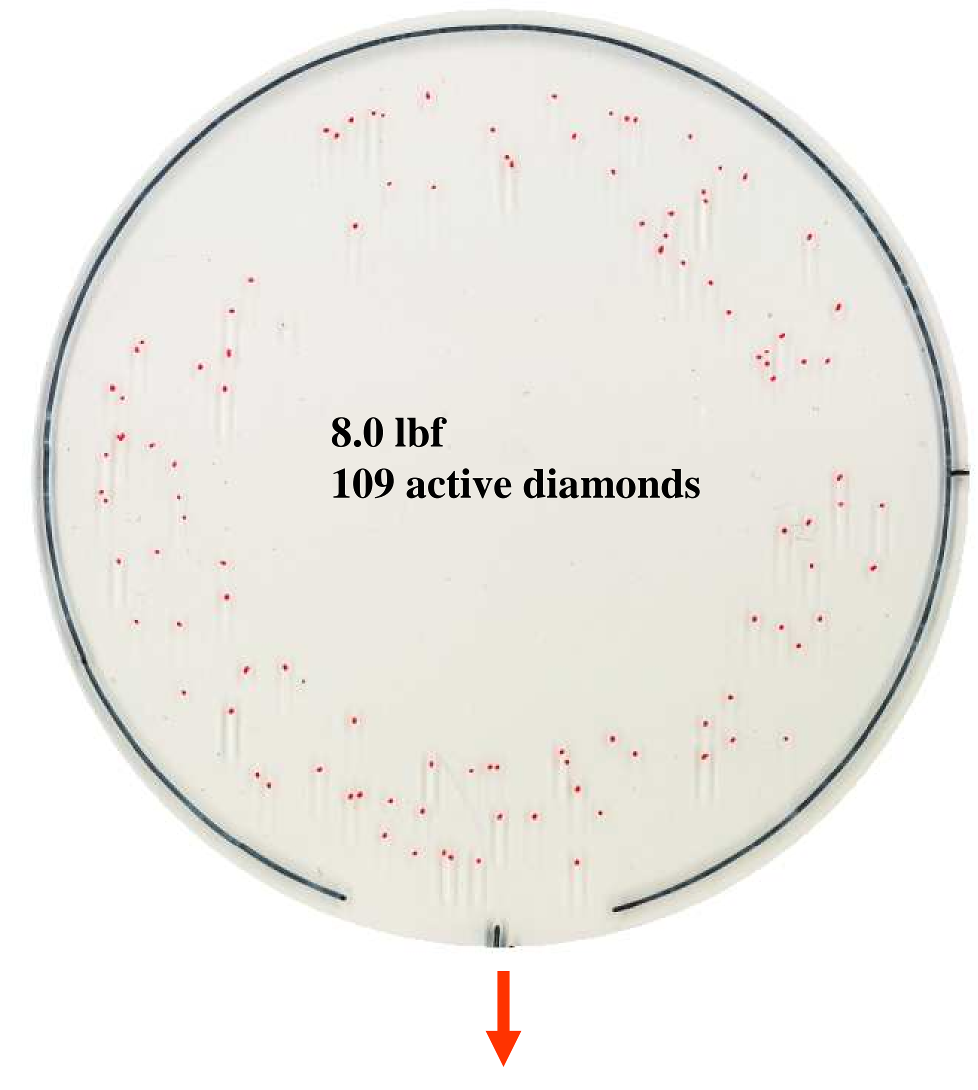
SEM of a very worn diamond

Identify Active Diamond - Short Draw Test

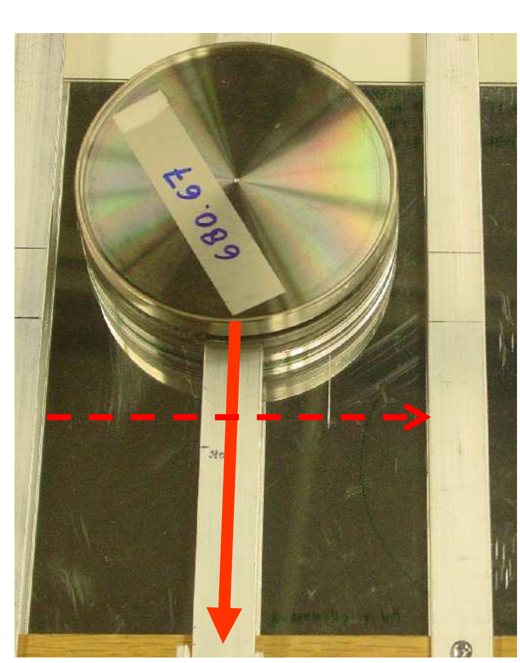
Conditioner is pulled
only about quarter-inch

Scratch origins are marked

- Faint scratches
- Partial scratches



Identify Aggressive Diamond - Long Draw Test



Conditioner is pulled more than one diameter of the disc.

Surface Height (microns)

20 15 10 5 0 -5 -10

0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5

Scan Distance (inches)

Polycarbonate surface is profiled

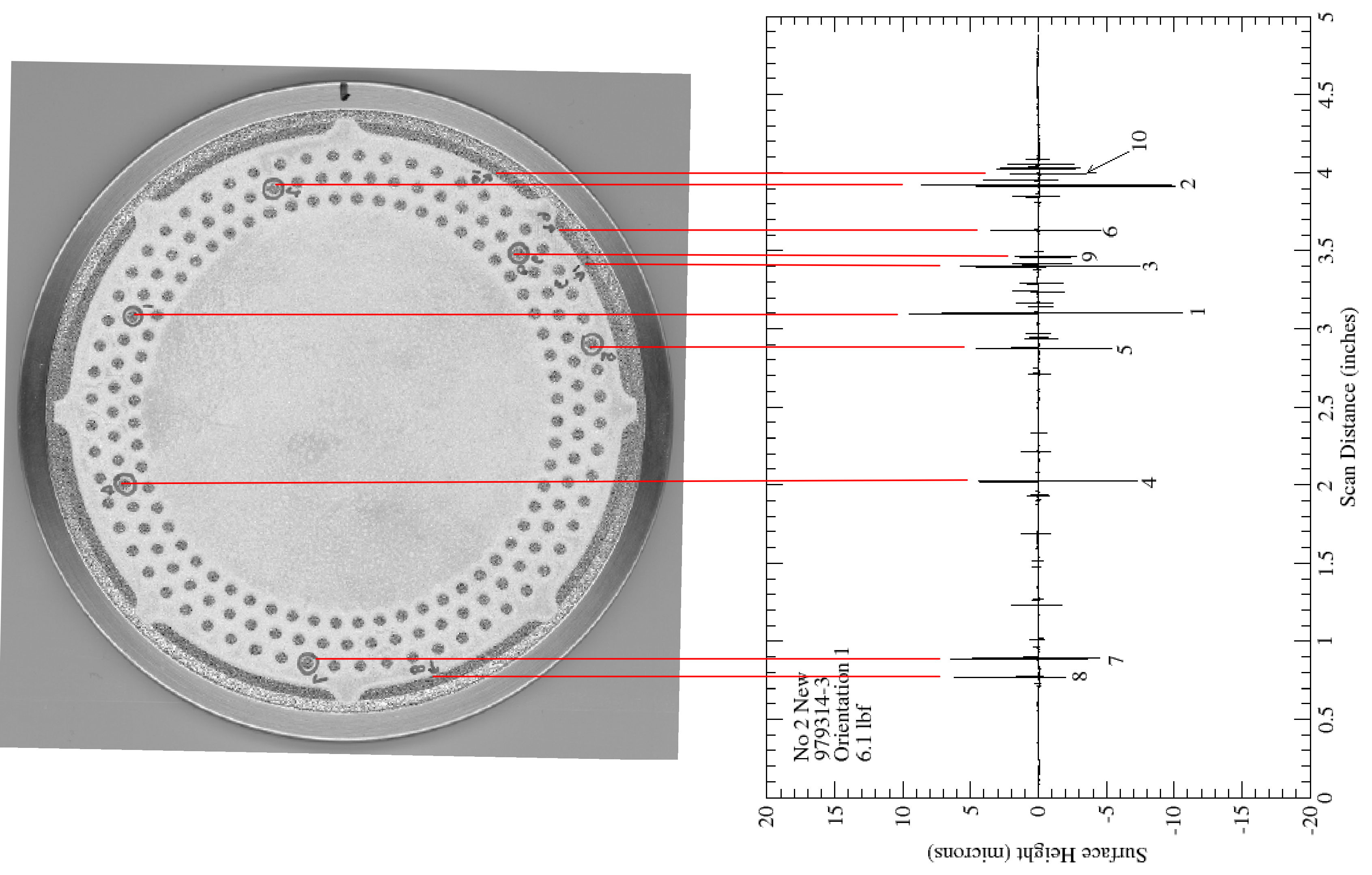
Surface Height (microns)

10 5 0 -5

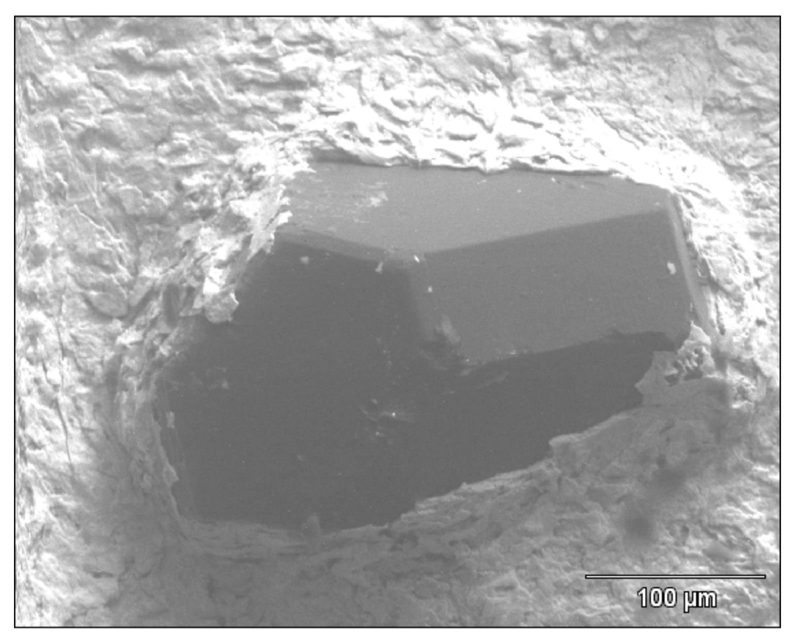
3.7 3.75

Scan Distance (inches)

Locating Aggressive Diamonds



Diamond Wear



New aggressive diamond

Same diamond after wear test

Normally there is no bulk wear on the diamond and micro wear occurs on the cutting edges of the diamond.

Relevance of Pad Surface Abruptness (λ)

Profilometry analysis: surface roughness (top pad asperities to pad valleys), no consistent correlation with material removal rates.

White light interferometry and incremental loading analysis: surface abruptness (top 20 - 30 μm pad asperities), closely correlated with material removal rates.

Two-step modified Langmuir-Hinshelwood removal rate model:

Removal rate $$RR = \frac{M_w}{\rho} \frac{k_2 k_1}{k_2 + k_1}$$

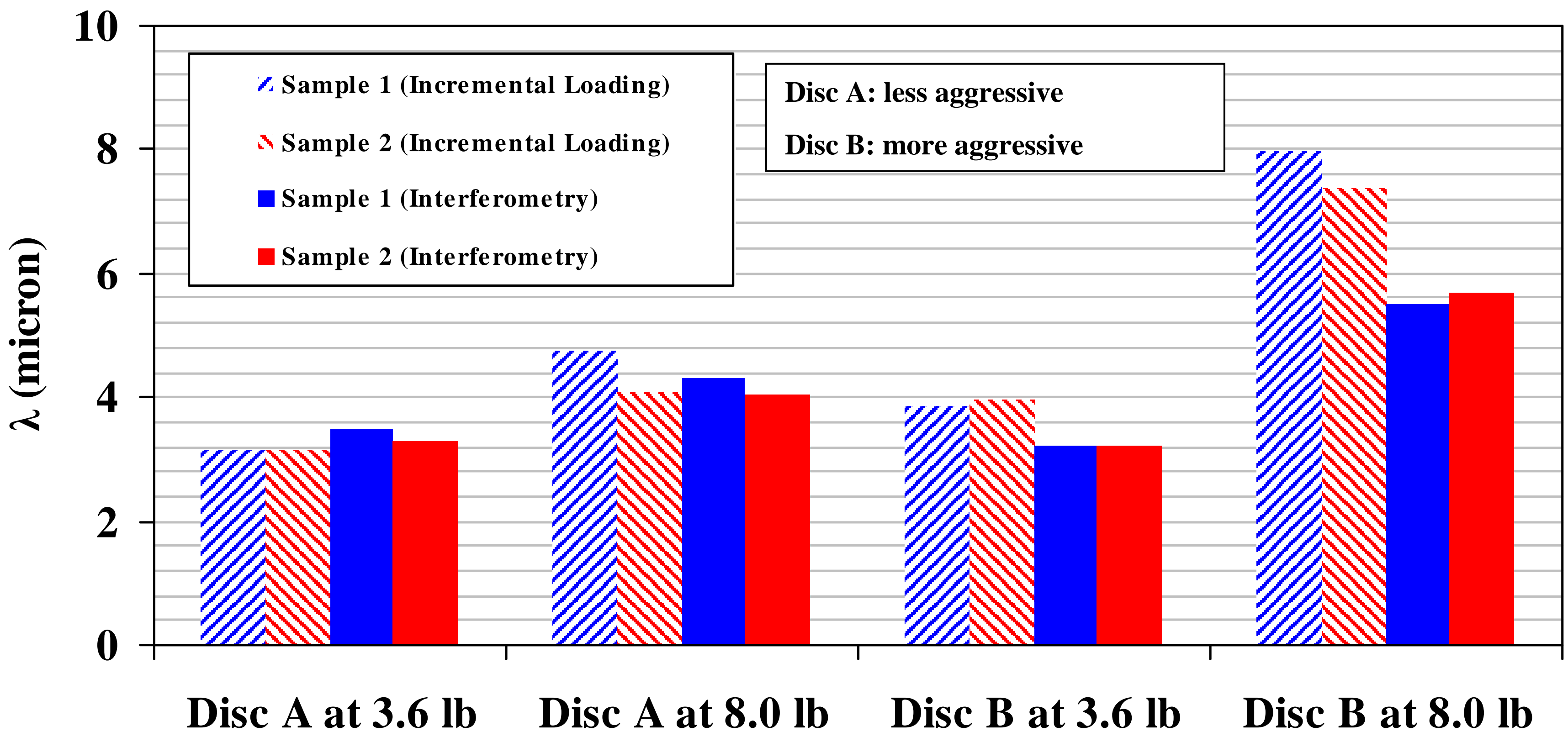
Chemical rate constant $$k_1 = A \cdot e^{-E/k\overline{T}}$$

Mechanical rate constant $$k_2 = c_p \mu_k pV$$

Wafer surface reaction temperature $$\overline{T} = \overline{T}_p + \frac{\beta_1 \kappa_s^{3/4} \lambda^{-1/4} \eta_s^{-1/2}}{V^{1/2+e}} \mu_k pV$$

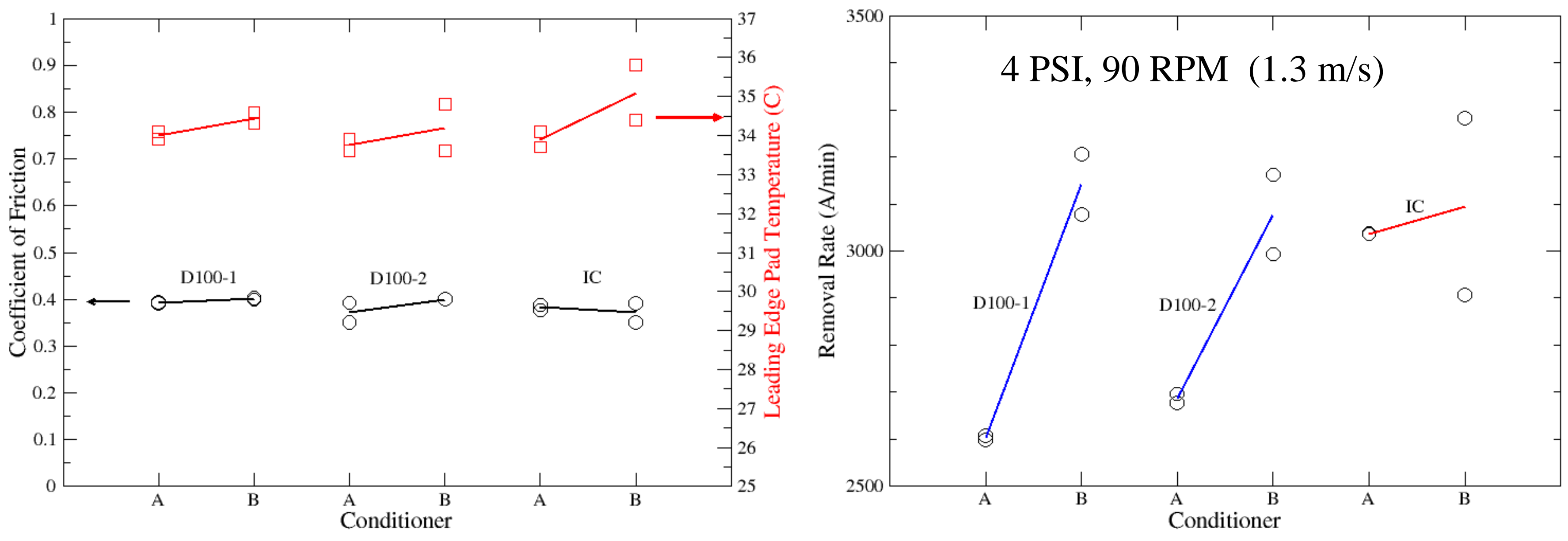
COF $$\mu_k = \mu_{pa} + \mu_{visc}^1 \kappa_s^{0.19} \lambda^{-0.17}$$

Effect of Conditioning on Pad Surface Abruptness



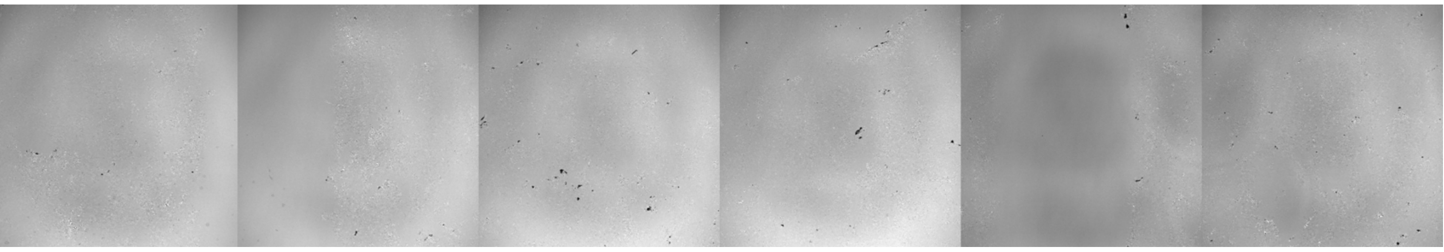
The surface abruptness extracted from the incremental loading analysis and interferometry is consistent. A more aggressive diamond disc generates a more abrupt pad surface under a higher conditioning force.

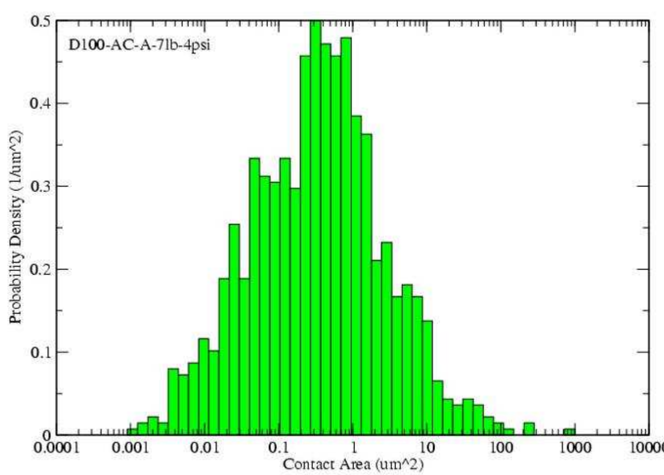
Effect of Conditioning on COF, Pad Temperature, and Oxide Removal Rate



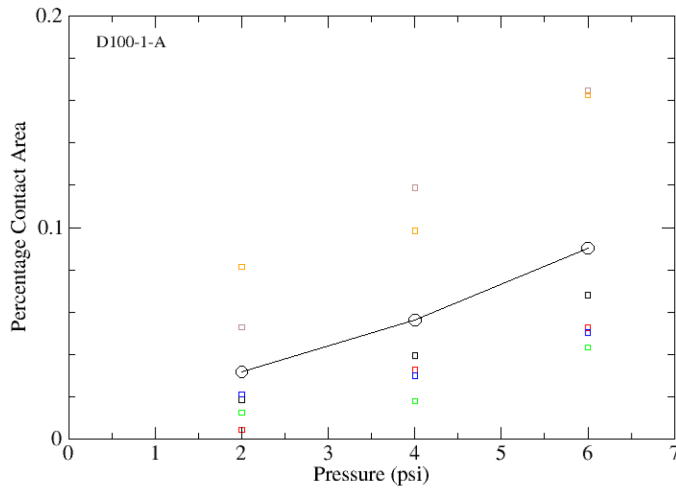
A more aggressive diamond disc generates a higher pad temperature and higher oxide removal rate.

Pad Surface Contact Area Analysis



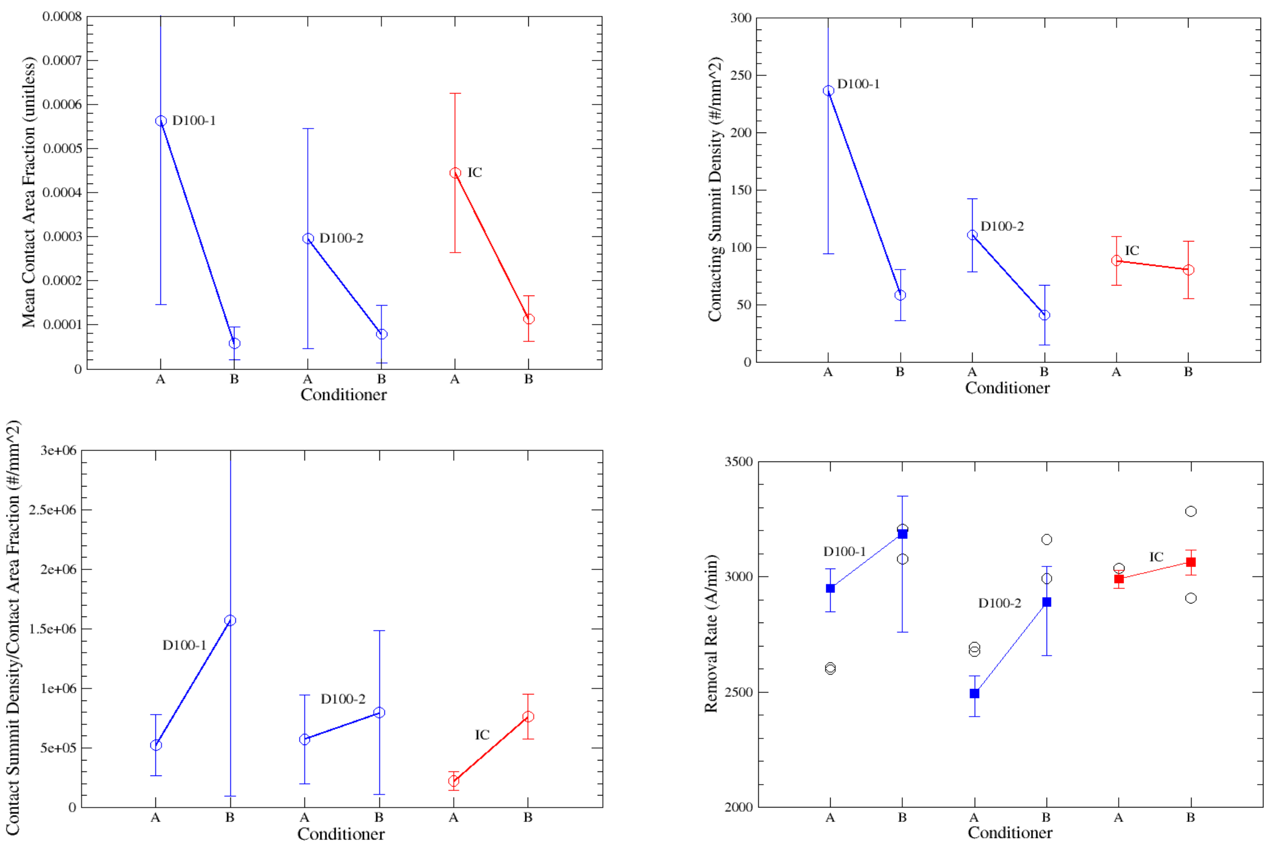


Pad contact area histogram



Pad contact area vs. Pressure

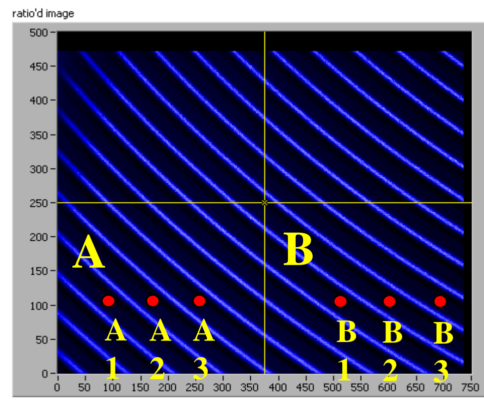
Effect of Conditioning on Contact Area

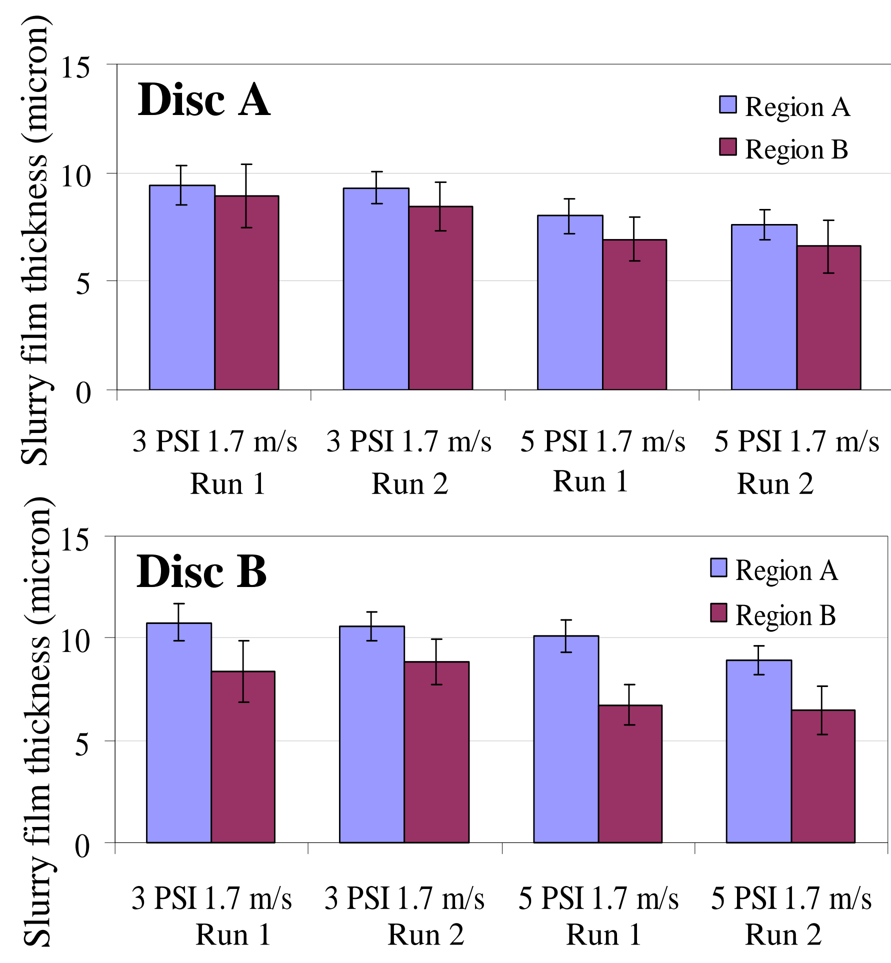


The ratio of the contacting summit density to the contact area fraction is more important than either measured separately since the ratio determines the mean real contact pressure.

Removal rate simulation indicates that the conditioning effect arises from the influence of the mean real contact pressure on the chemical rate of the polishing process.

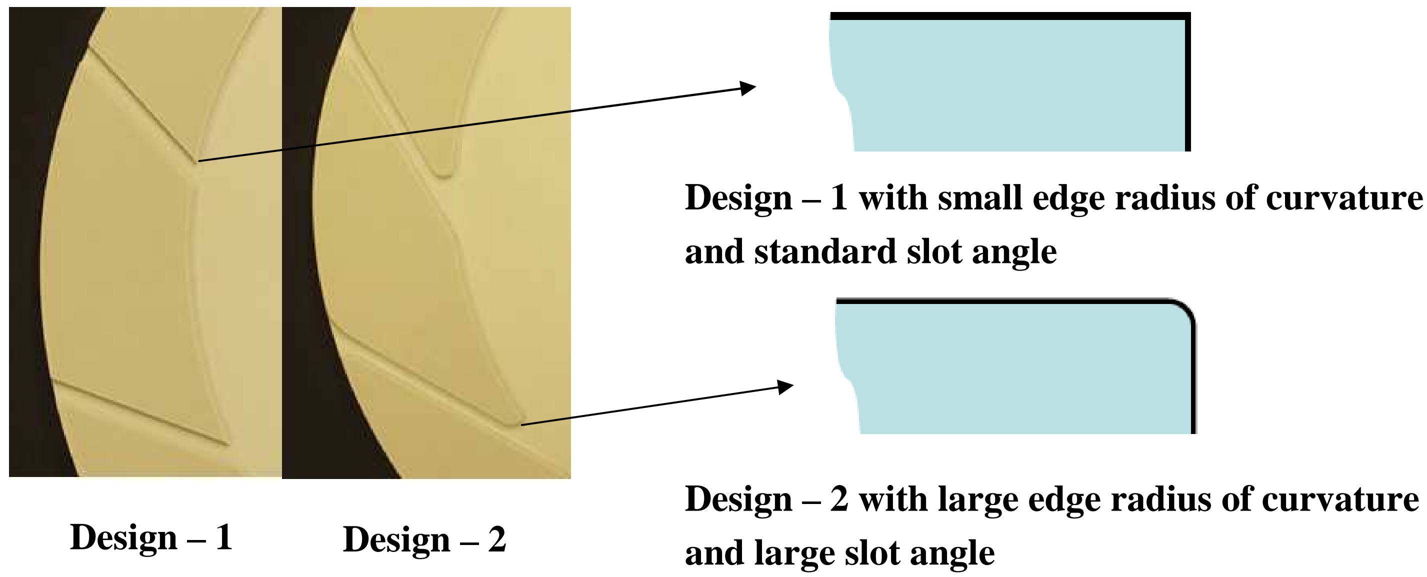
Effect of Conditioning on Slurry Film Thickness





A more aggressive disc generates a more abrupt pad surface, leading to a thicker slurry film in the pad-wafer interface area.

Retaining Ring Material and Design



Three retaining rings were investigated:

- **PPS – 1: made of PPS (polyphenylene sulfide) with Design – 1**
- **PEEK – 1: made of PEEK (polyetherenterketone) with Design – 1**
- **PEEK – 2: made of PEEK (polyetherenterketone) with Design – 2**

Retaining Ring Wear Rate

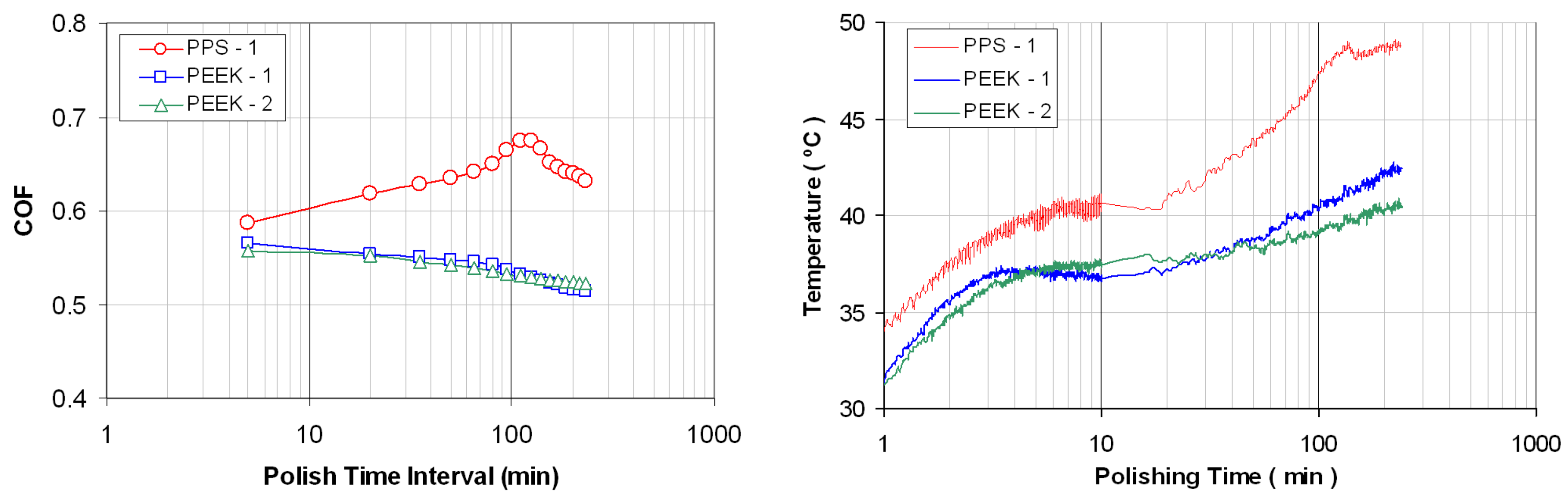
Pre and post interferometry results from the micro-machined trenches indicate the following wear rates:

- **PPS - 1 ring: 28.2 µm/hour**
- **PEEK - 1 ring: 24.0 µm/hour**
- **PEEK - 2 ring: 23.5 µm/hour**

This indicates that the retaining ring material, not design, is the main factor influencing the wear rate.

Micrometry results (taken from areas adjacent to the micro-machined trenches) indicate a difference of ± 13 percent compared to interferometry results.

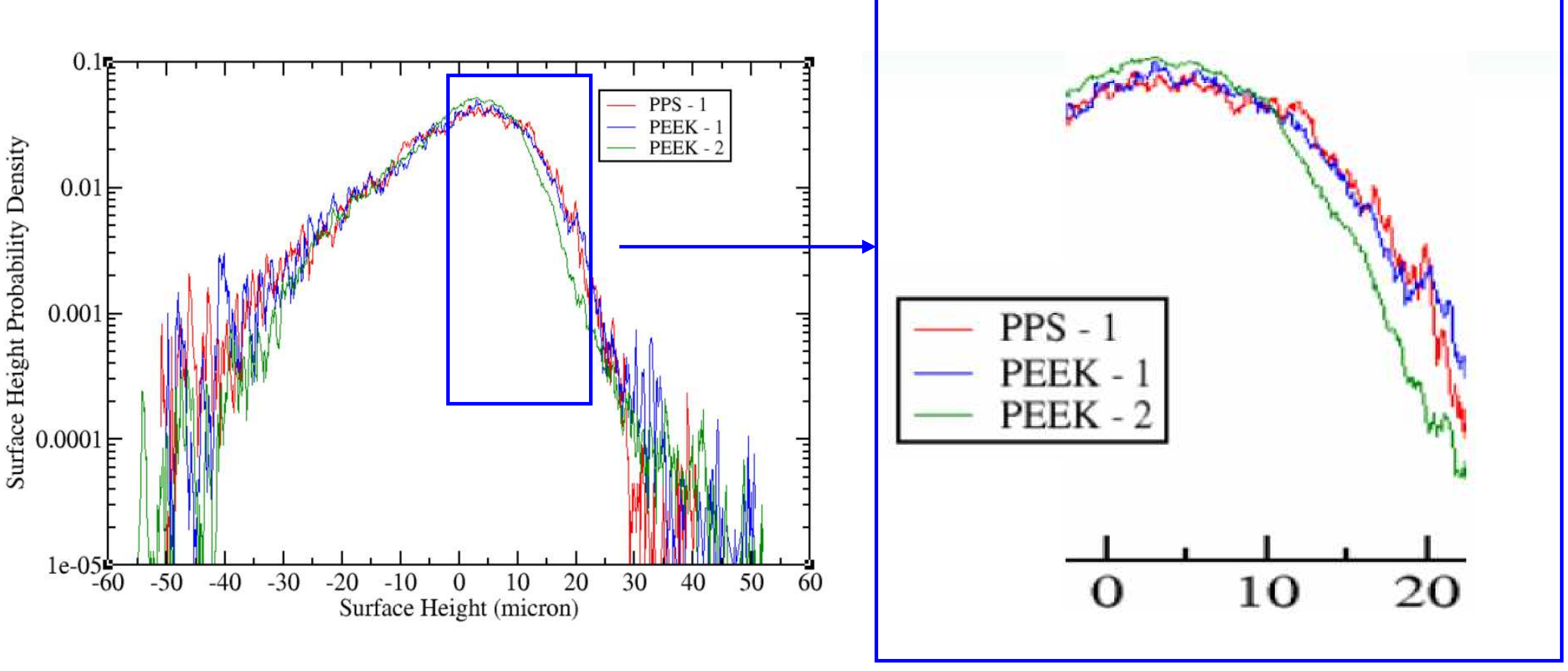
COF and Pad Temperature



The PEEK rings achieve better lubricity and COF stability than the PPS ring.

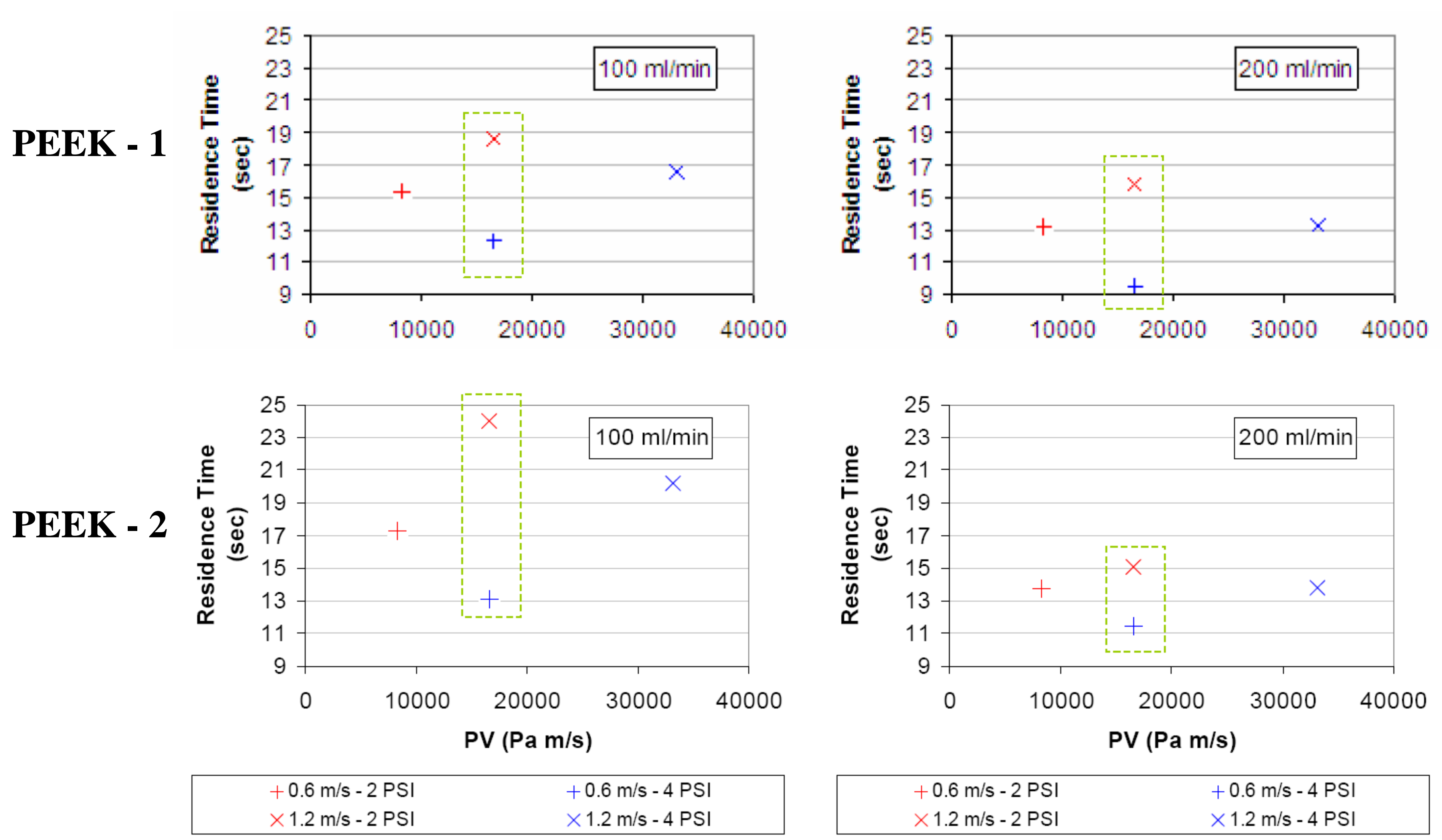
Higher temperatures associated with the PPS ring can cause higher material removal rates, thus indicating that thermal effects need to be taken into account when qualifying rings made of new materials.

Pad Surface Interferometry Analysis



The PEEK – 2 ring achieves a narrower pad surface height distribution than the PPS – 1 and PEEK – 1 rings, suggesting that the slot design and the edge rounding plays significant roles in shaping the pad micro texture.

Slurry Mean Residence Time



Design – 1 is 10 – 20 percent more efficient in getting slurry in and out the wafer-pad interface.

Industrial Interactions and Technology Transfer

Industrial mentors / contacts:

- **Sriram Anjur (Cabot Microelectronics Corporation)**
- **Abaneshwar Prasad (Cabot Microelectronics Corporation)**
- **Ananth Naman (Cabot Microelectronics Corporation)**
- **Cliff Spiro (Cabot Microelectronics Corporation)**
- **Naoki Rikita (Mitsubishi Materials Corporation)**
- **Christopher Wargo (Entegris)**
- **Leonard Borucki (Araca)**

Future Plans

Next Year Plans

- Perform static etch tests and wear tests on diamond discs and quantify the extent of diamond micro-wear and diamond disc substrate wear.
- Investigate the effect of conditioning on pad topography for metal CMP processes.
- Perform DEUVEF (dual emission UV enhanced fluorescence) tests to investigate the effect of retaining ring design on slurry film thickness in the pad-wafer interface.

Long-Term Plans

- Obtain fundamental understanding of diamond and diamond disc substrate wear mechanism and extend diamond disc life.
- Achieve fundamental understanding of the effect of conditioning on pad topography and polishing performance for CMP processes.
- Improve retaining ring design to achieve better slurry utilization efficiency and extend retaining ring life .

An Integrated, Multi-Scale Framework for Designing Environmentally Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task Number: 425.020*)

Subtask 2: Real-Time Detection and Modeling of Pattern Evolution

PIs:

- **Ara Philipossian, Chemical and Environmental Engineering, UA**
- **Duane Boning, Electrical Engineering and Computer Science, MIT**
- **Chris B. Rogers, Mechanical Engineering, Tufts University**
- **Vincent P. Manno, Mechanical Engineering, Tufts University**
- **Robert D. White, Mechanical Engineering, Tufts University**

Graduate Students:

- **Yasa Sampurno, Ph. D. candidate, Chemical and Environmental Engineering, UA**
- **Caprice Gray: Ph. D. candidate, Mechanical Engineering, Tufts University**
- **James Vlahakis: Ph. D. candidate, Mechanical Engineering, Tufts University**

An Integrated, Multi-Scale Framework for Designing Environmentally Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task Number: 425.020)*

Subtask 2: Real-Time Detection and Modeling of Pattern Evolution

Graduate Students (continue):

- **Douglas Gauthier: M.S. candidate, Mechanical Engineering, Tufts University**
- **Nicole Braun: M.S. candidate, Mechanical Engineering, Tufts University**
- **Andrew Mueller: Mechanical Engineering, Tufts University, graduated with M.S. degree in August 2007**
- **Hong Cai, Materials Science, MIT, graduated with Ph. D. degree in June 2007**
- **Xiaolin Xie, Physics, MIT, graduated with Ph. D. degree in June 2007**
- **Wei Fan, Ph. D. candidate, Electrical Engineering and Computer Science, MIT**

Undergraduate Student:

- **Zhipeng Li, Electrical Engineering and Computer Science, MIT**

An Integrated, Multi-Scale Framework for Designing Environmentally Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task Number: 425.020*)

Subtask 2: Real-Time Detection and Modeling of Pattern Evolution

Other Researchers:

- **Yun Zhuang, Research Associate, Chemical and Environmental Engineering, UA**
- **Fransisca Sudargho, Research Technician, Chemical and Environmental Engineering, UA**
- **Siannie Theng, Research Technician, Chemical and Mechanical Engineering, UA**
- **Ed Paul, Visiting Professor, Stockton College**

An Integrated, Multi-Scale Framework for Designing Environmentally Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task Number: 425.020)*

Subtask 2: Real-Time Detection and Modeling of Pattern Evolution

Cost Share (other than core ERC funding):

- **$50,000 from Intel Corporation**
- **$50,000 from Cabot Microelectronics Corporation**
- **In-kind donation (slurries) from Hitachi Chemical Co., Ltd.**
- **In-kind donation (pads) from Neopad Technologies Corporation**
- **In-kind support from JSR Micro, Inc.**
- **In-kind support from Araca, Inc.**

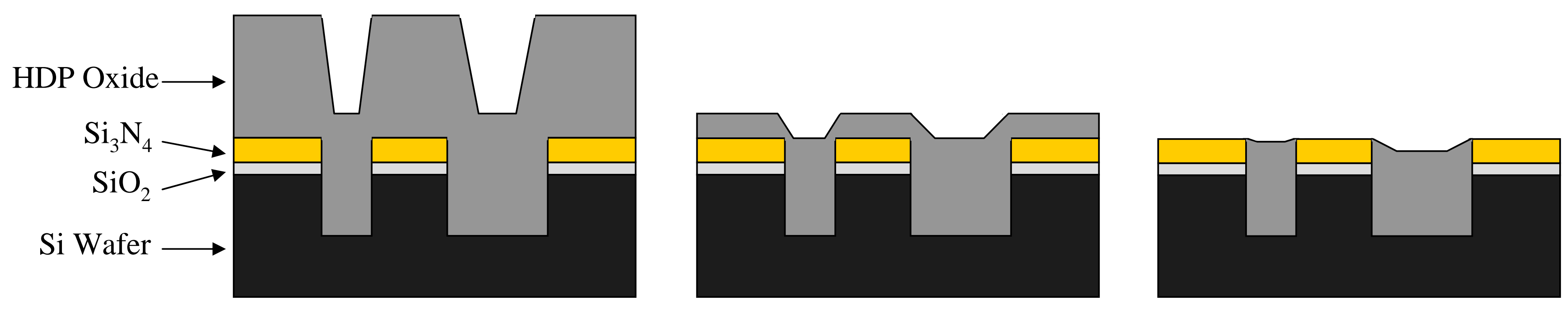
Objectives

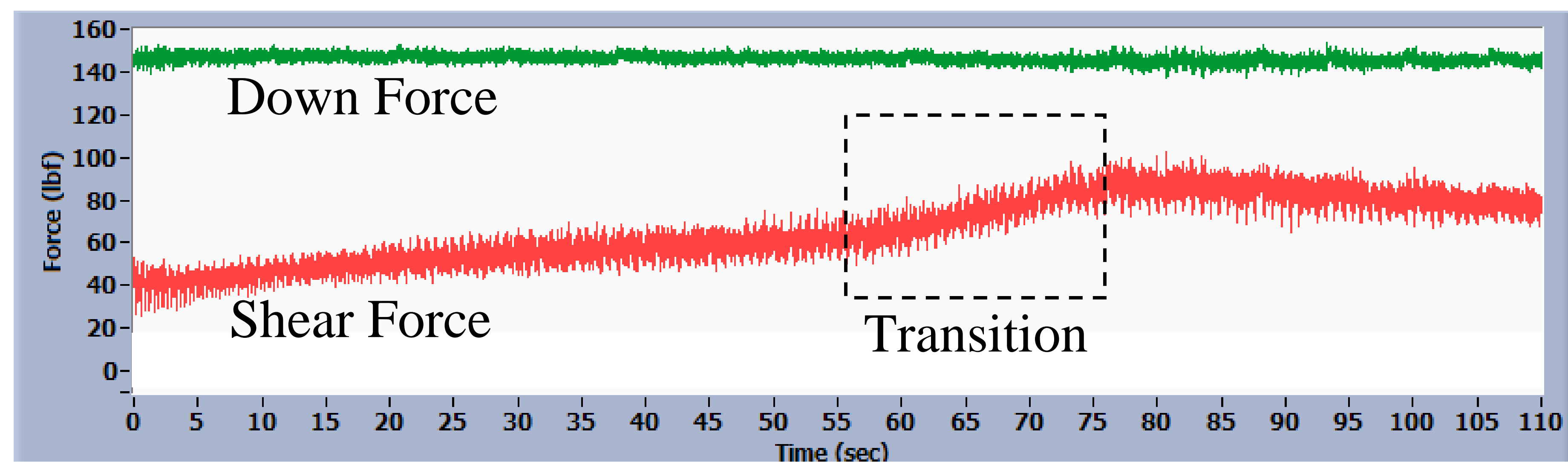
- **Determine whether shear force and down force spectral analysis can generate unique spectral fingerprints before, during, and after transition from oxide to Si_3N_4 layer during STI patterned wafer polishing.**
- **Explore shear force spectral fingerprints to understand the effect of break-in time and in-situ pad conditioning duty cycle during copper CMP.**

ESH Metrics and Impact

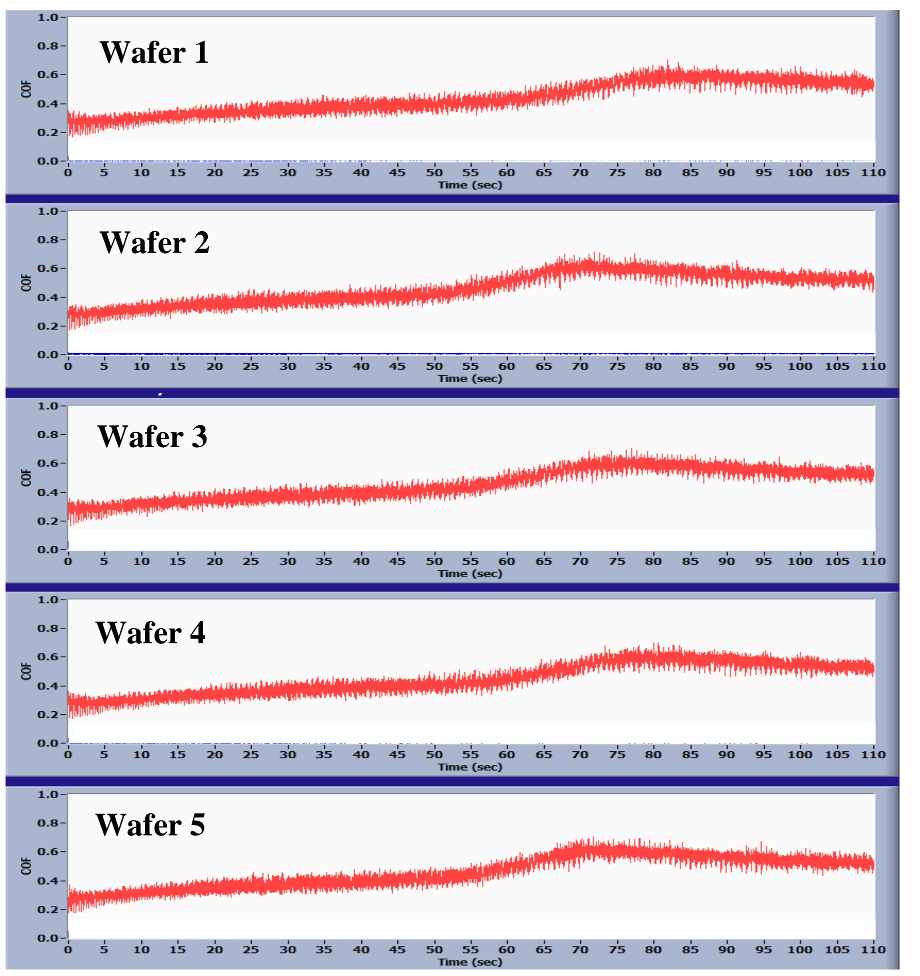
1. *Reduce slurry consumption by 25%*
2. *Reduce pad consumption by 25%*
3. *Reduce diamond disc consumption by 25%*

Shear Force and Down Force Measurement





COF Transients



Polish Time

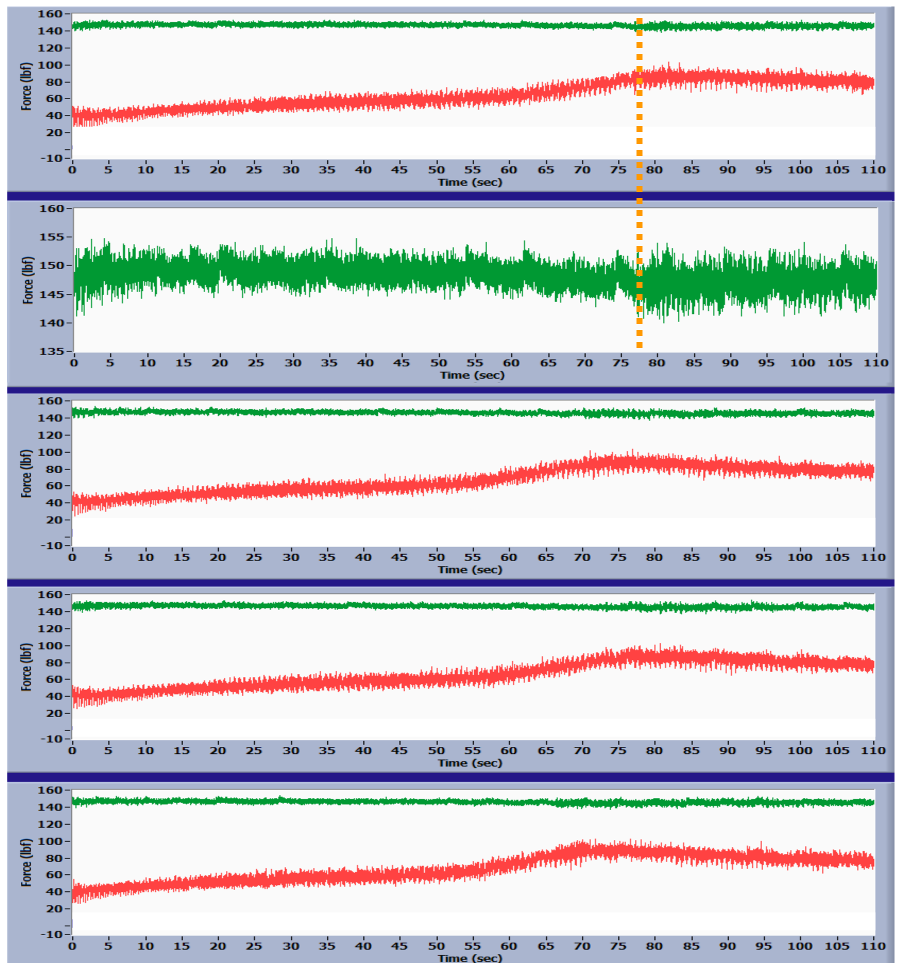
	Transition Start (s)	Transition End (s)
Average	56.4	71.4
SD	3.4	4.5
RSD	6.1%	6.3%

Coefficient of Friction

	Before Transition	During Transition	After Transition
Average	**0.361**	**0.510**	**0.566**
SD	0.004	0.006	0.008
RSD	0.1%	0.3%	0.5%

The COF shows consistent transition during STI patterned wafer polishing.

Force Transients



Polish Time

	Transition Start (s)	Transition End (s)
Average	56.4	71.4
SD	3.4	4.5
RSD	6.1%	6.3%

Variance of Shear Force (σ^2)

	Before Transition (lb_f^2)	During Transition (lb_f^2)	After Transition (lb_f^2)
Average	**58.7**	**57.8**	**33.6**
SD	2.8	7.7	9.2
RSD	4.7%	13.3%	27.4%

Variance of Down Force (σ^2)

	Before Transition (lb_f^2)	During Transition (lb_f^2)	After Transition (lb_f^2)
Average	**2.3**	**2.2**	**3.4**
SD	0.03	0.22	0.19
RSD	1.3%	10%	5.5%

The variances of shear force and down force show consistent transition during STI patterned wafer polishing.

Shear Force Spectral Analysis

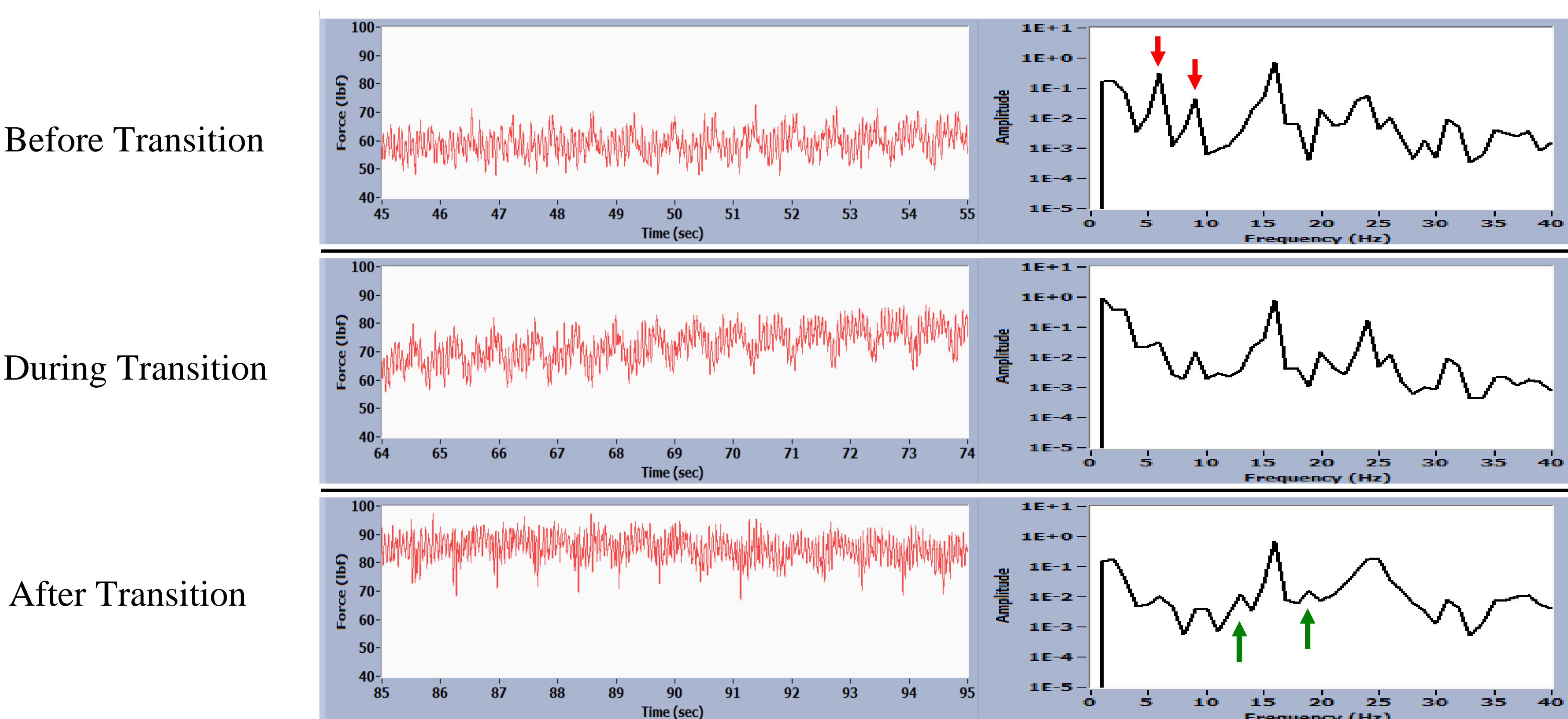
Wafer #1

Raw Shear Force Data **Shear Force Spectral Analysis**

Before Transition

During Transition

After Transition



Down Force Spectral Analysis

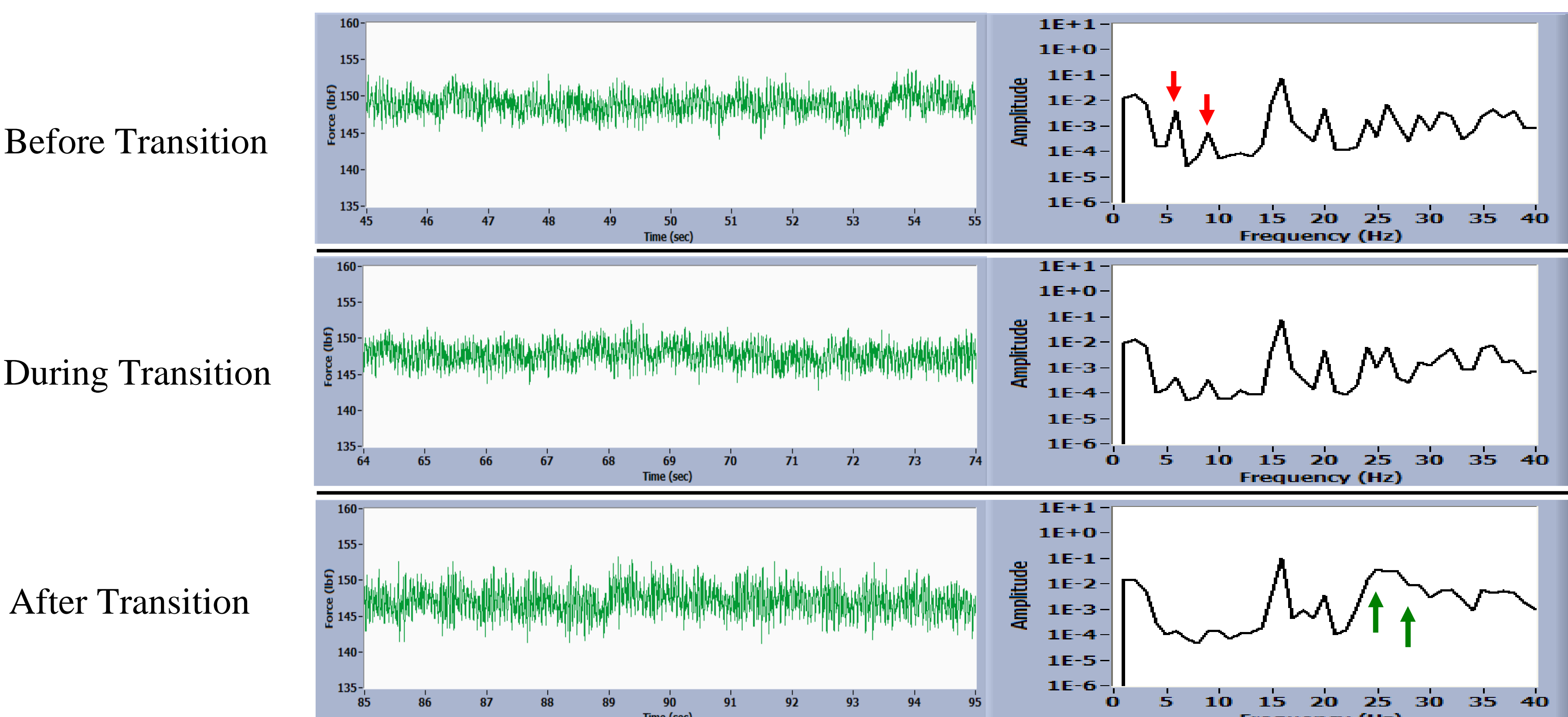
Wafer #1

Raw Down Force Data **Down Force Spectral Analysis**

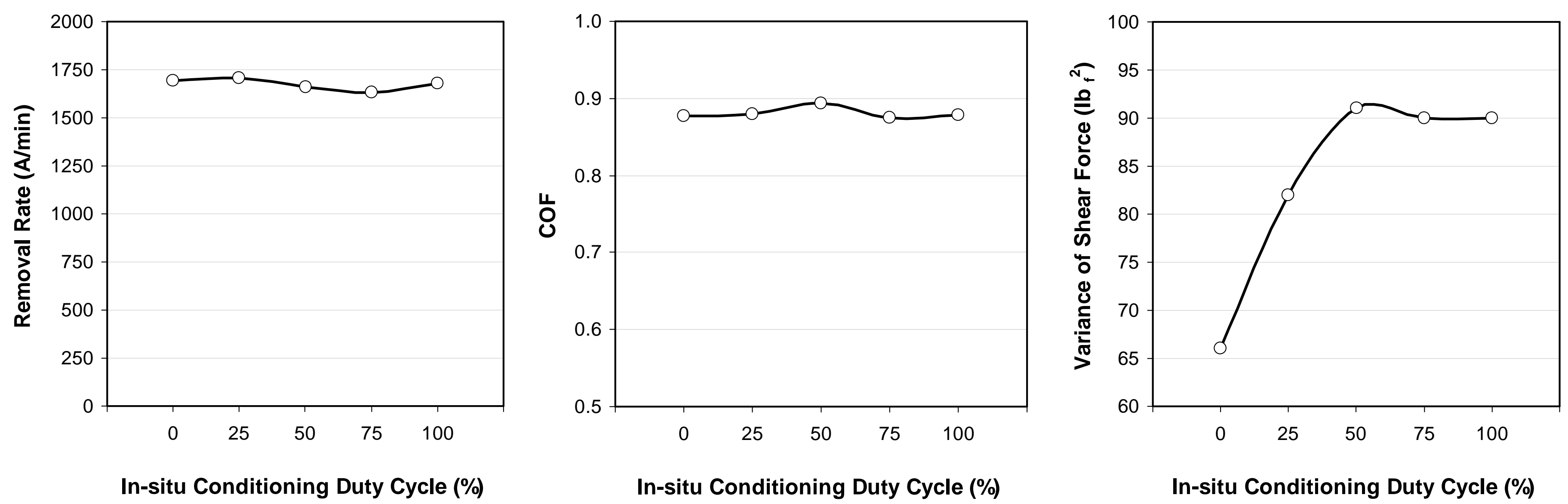
Before Transition

During Transition

After Transition



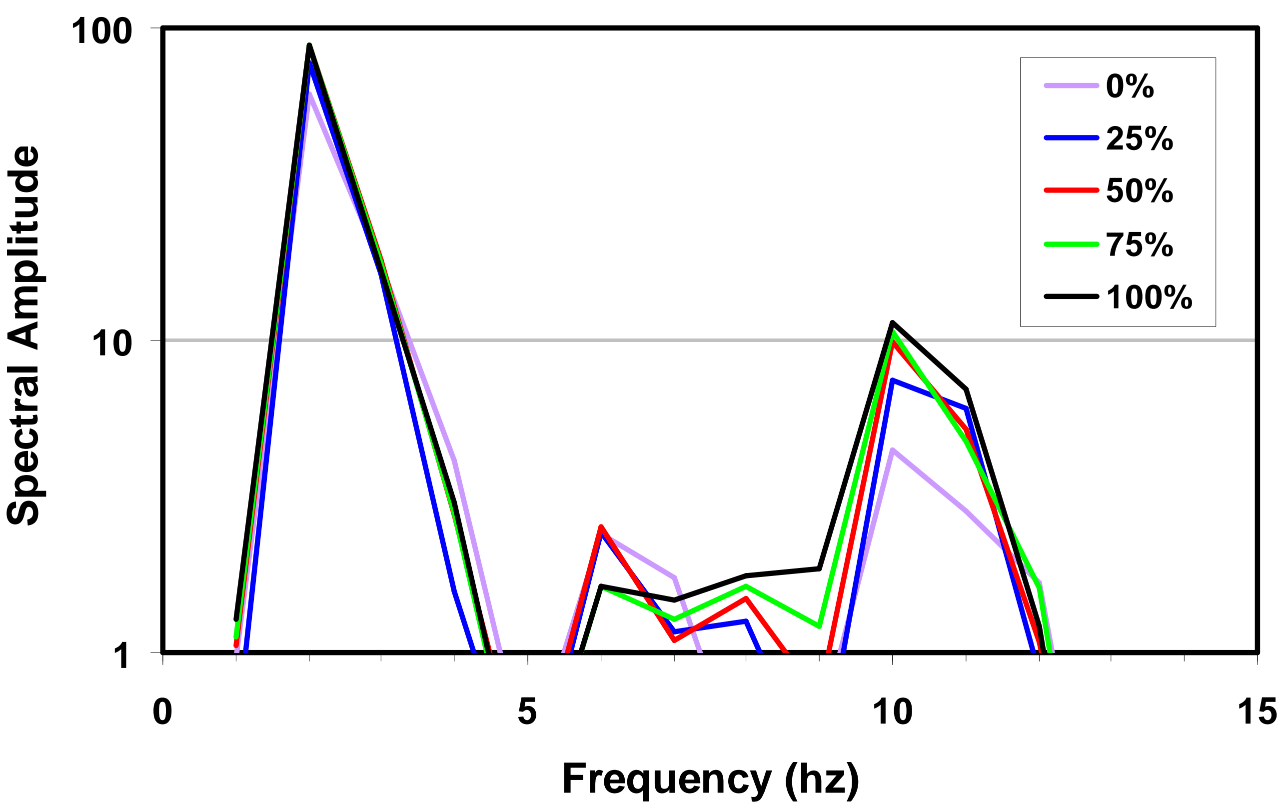
In-Situ Conditioning Duty Cycle Study



Removal rate and COF are not affected by the conditioning duty cycle.

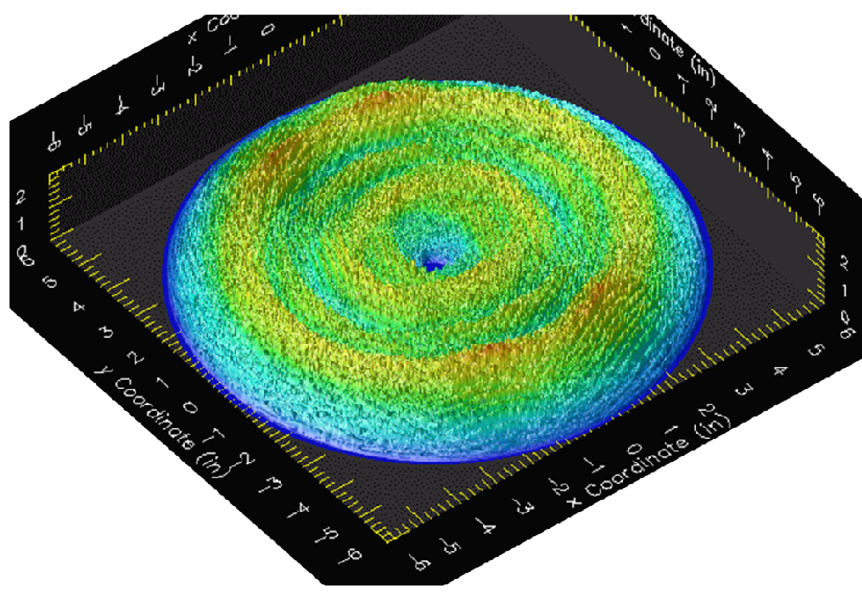
The variance of shear force initially increases with the conditioning duty cycle and then reaches a plateau.

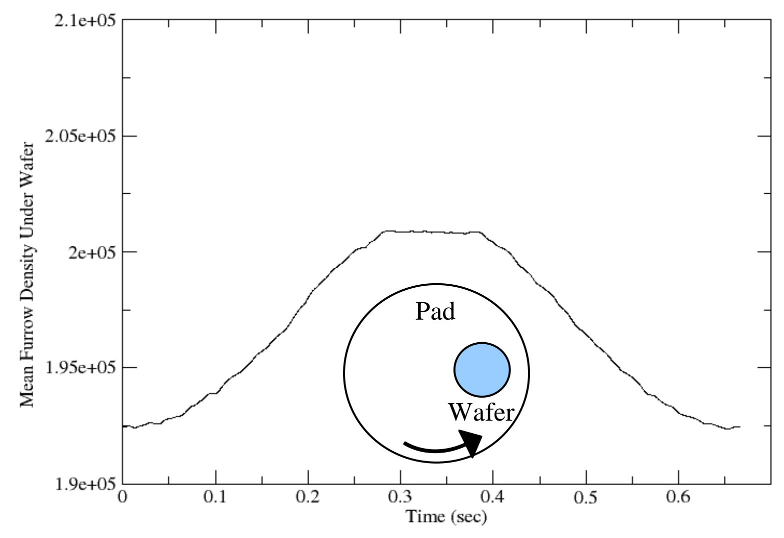
Shear Force Spectral Analysis

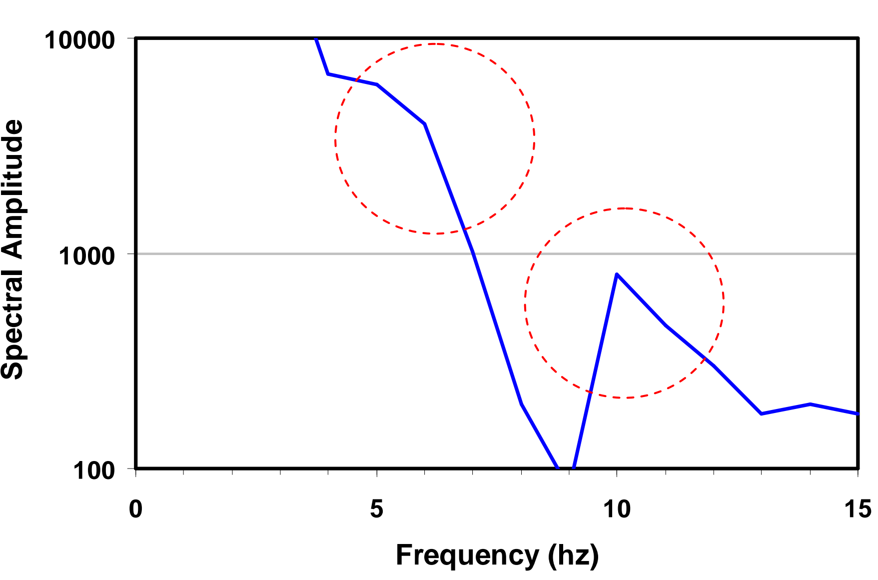


High duty cycles result in similar spectral amplitude distributions.

Mean Furrow Density Under Wafer







Monte Carlo simulation of pad topography with the microscopic furrows generated by the pad conditioner.

Simulated furrow density spectra show similar spectral distributions to the shear force spectra, suggesting some specific peaks are associated with pad conditioning.

Industrial Interactions and Technology Transfer

Industrial mentors / contacts:

- **Morishima-san (Hitachi Chemical)**
- **Habiro-san (Hitachi Chemical America)**
- **Karey Holland (Neopad Technologies)**
- **Naoki Rikita (Mitsubishi Materials Corporation)**
- **Leonard Borucki (Araca)**
- **Peter Ojerholm (Ehwa)**

Future Plans

Next Year Plans

- **Investigate the shear force and down force transition during early evolution of wafer topography for STI CMP.**
- **Prove that shear force spectral signals are indicative of furrow density during CMP for various types of diamonds and conditioning recipes in STI CMP**

Long-Term Plans

- **Investigate the shear force and down force transition during evolution of wafer topography for metal CMP.**
- **Prove that shear force spectral signals are indicative of furrow density during CMP for various types of diamonds and conditioning recipes in metal CMP**
- **Recommend conditioning recipes with optimal duty cycles for STI and metal planarization processes**

Students on Task 425.020

- Graduated Students and Current Affiliation
  - Daniel Rosales-Yeomans (Ph.D.), Intel, 12/2007
- Current Students and Anticipated Grad Date
  - Hyosang Lee (Ph.D.), 3/2008
  - Yasa Sampurno (Ph.D.), 5/2008
  - Ting Sun (Ph.D.), 5/2009
  - Xiaomin Wei (Ph.D.), 5/2010
  - Anand Meled (Ph.D.), 5/2011
- Internships
  - Ting Sun (Ph.D.), Cabot Microelectronics (5/2007 – 8/2007)
  - Yasa Sampurno (Ph.D.), IBM (5/2007 – 10/2007)

An Integrated, Multi-Scale Framework for Designing Environmentally-Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task Number: 425.020*)

Subtask 1: Slurry Thickness and Flow Measurement using *in-situ* Optical Techniques

Caprice Gray: PhD candidate, Tufts Mechanical Engineering, May 2008
Nicole Braun: MS candidate, Tufts Mechanical Engineering, May 2008

Subtask 2: Pad-Wafer Mechanical Characterization using *in-situ* Force and Position Measurements

James Vlahakis: PhD candidate, Mechanical Engineering, August 2008
Douglas Gauthier: MS candidate, Mechanical Engineering, August 2008
Andrew Mueller: MS, Mechanical Engineering, August 2007

Principal Investigators:

- **C. B. Rogers, Mechanical Engineering, Tufts University**
- **V. P. Manno, Mechanical Engineering, Tufts University**
- **R. D. White, Mechanical Engineering, Tufts University**

Objectives

Multi-scale, multi-dimensional *in situ* CMP characterization

Obtain in-situ images of the slurry layer thickness during CMP and quantify wafer-pad contact during polishing – Caprice Gray (PhD Student)

DELIF: Contact/Film thickness

Mechanical: Global forces, motion, MRR

Concurrent measurement of spatially averaged force (3-axis, COF, moments), force spectra, wafer attitude, and material removal rate under a variety of polishing conditions – James Vlahakis (PhD Student)

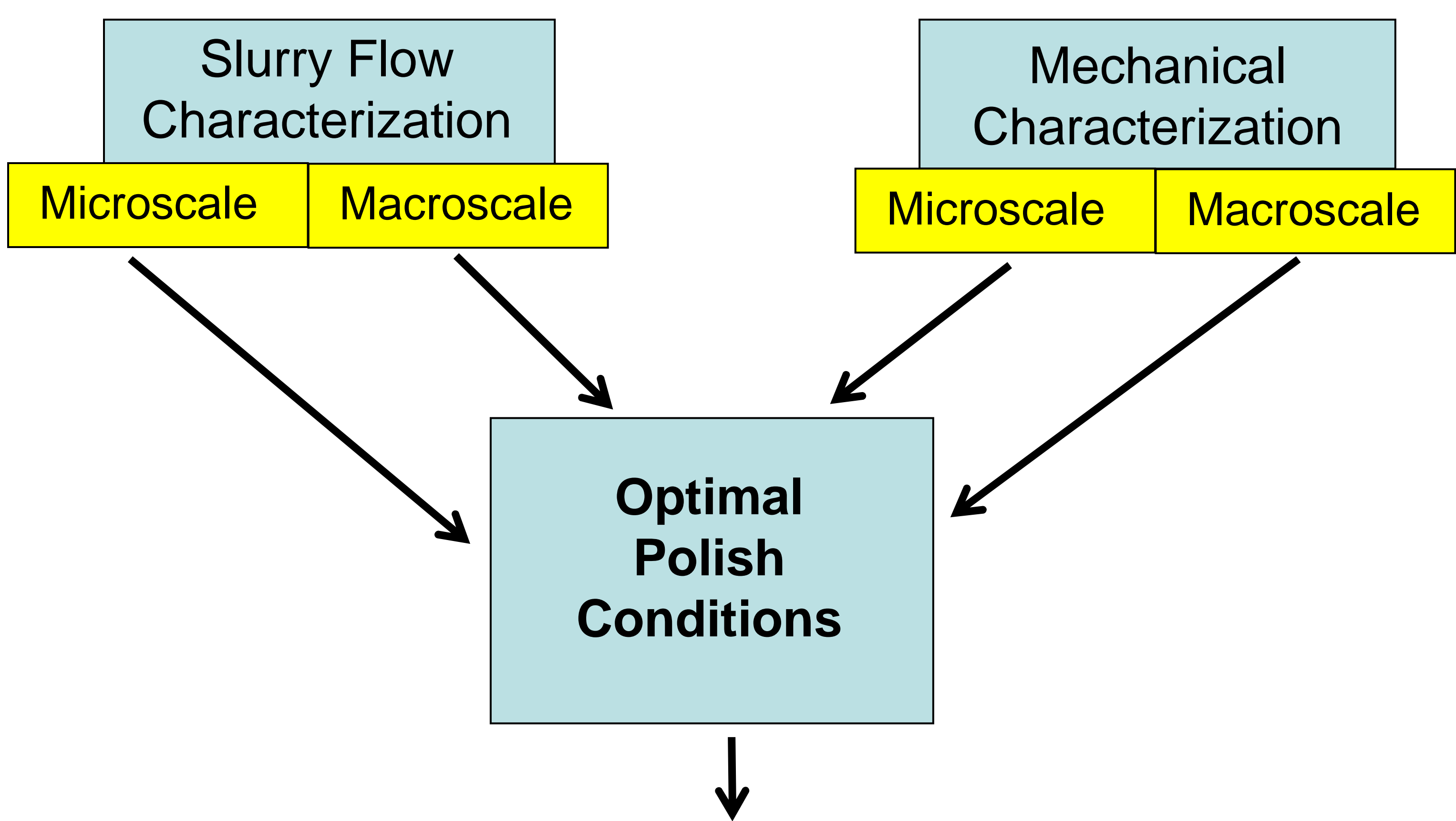
Measure local (100 mm scale), high sample rate (0.1 ms) asperity scale forces at the pad-wafer interface during CMP - Douglas Gauthier (MS Student)

MEMS: Microscale force sensors

PIV/Flow Vis: Visualizing full-pad flows

(Seed Project) Investigate the feasibility of using particle image velocimetry (PIV) to quantitatively measure particle-slurry flow in-situ. – Nicole Braun (MS Student)

ESH Metrics and Impact



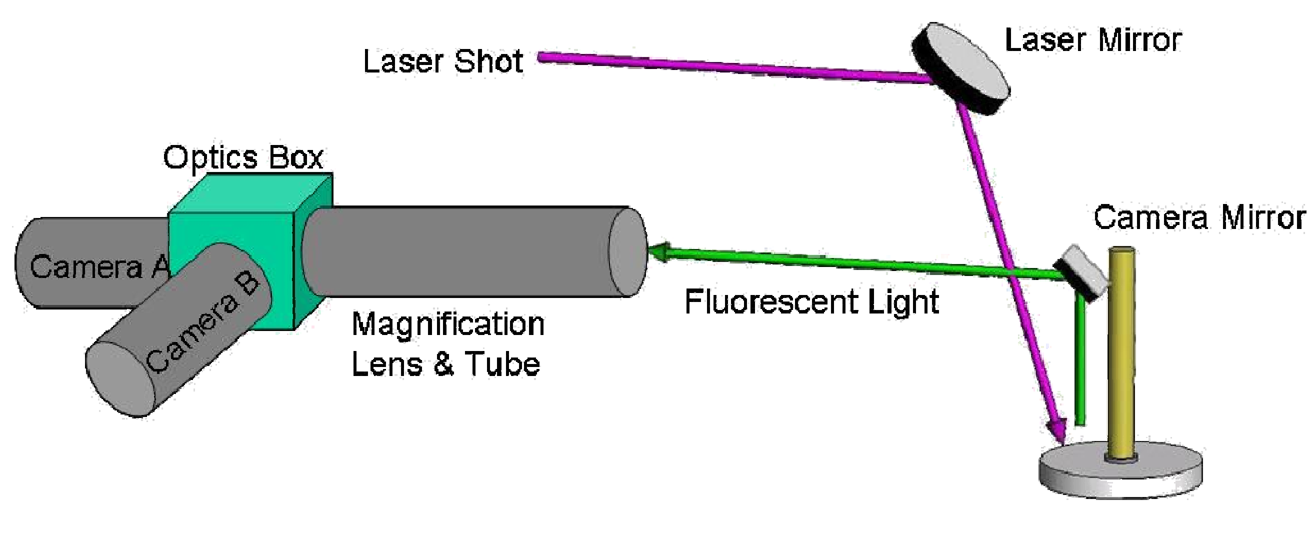
-Reduced time to polish (energy and cost savings)

-Reduced consumables (waste and cost reduction)

Dual Emission Laser Induced Fluorescence

Dual Emission Laser Induced Fluorescence (DELIF)

- In-situ contact images
- 6 ns time integration, 2 images/sec
- ~3 micron/pixel to resolve asperity sized features
- Pads (all polyurethane based): CMC D100, CMC D200, Fruedenburg FX9, IC1000



DELIF: Film Thickness

Slurry Image

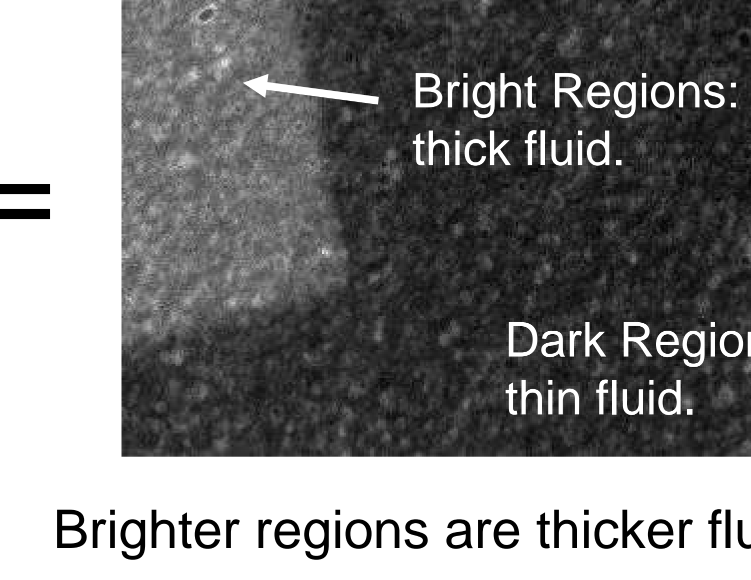
Pad Image

Two cameras:

(1) wavelength of slurry dye

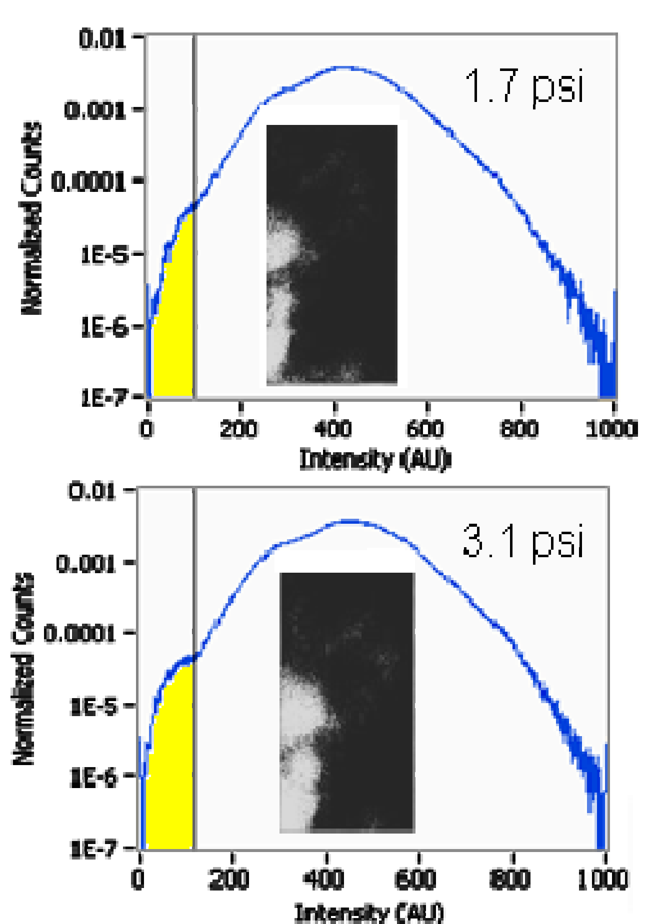
(2) wavelength of pad fluorescence

Image ratio cancels source intensity variation



Brighter regions are thicker fluid layers.

DELIF: Static Contact

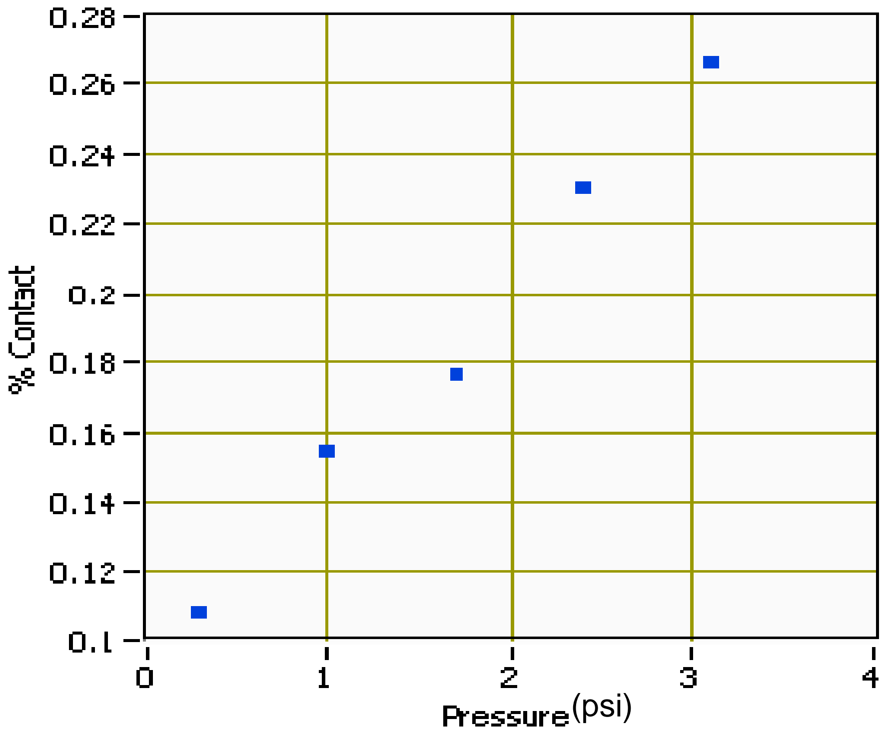


Histogram of height with thresholding gives contact percentage.

Static (no rotation) contact area on flat pads is linearly pressure dependent

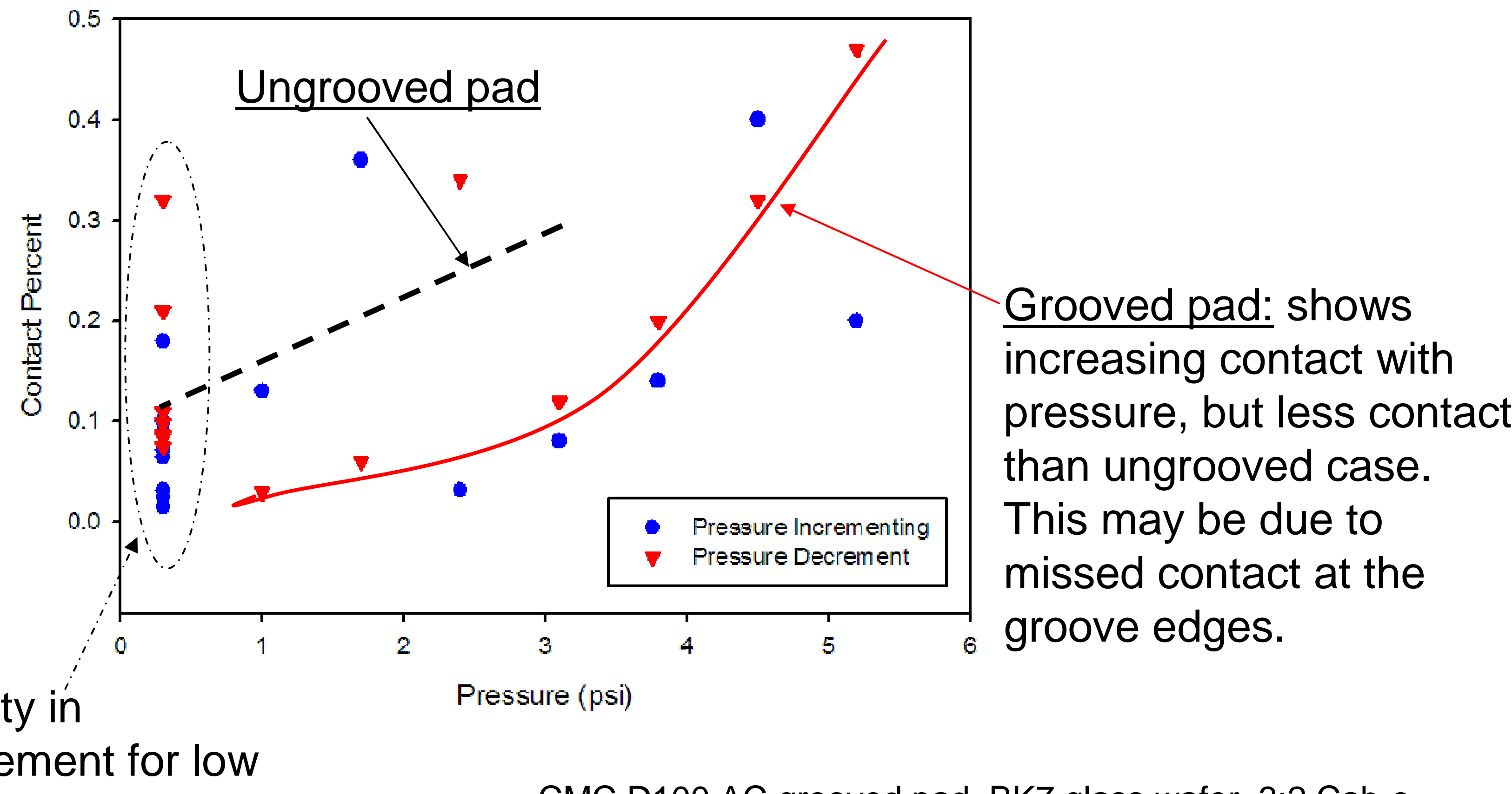
CMC D100 un-grooved pad, BK7 glass wafer

9:1 Cab-o-sperse SC1 slurry (fumed silica, 3 wt% at this dilution)



DELIF: Static Contact

Measured static contact area on grooved pads at low downforce shows more variability; this appears to be a limitation of the optical technique at groove edges.



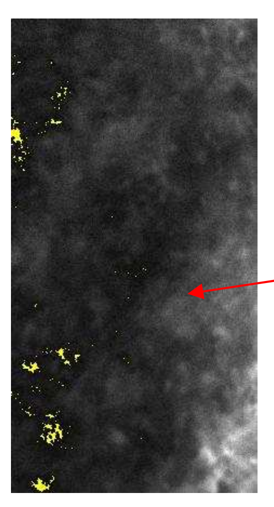
CMC D100 AC grooved pad, BK7 glass wafer, 3:2 Cab-o-sperse SC1 slurry (fumed silica, 22 wt% at this dilution)

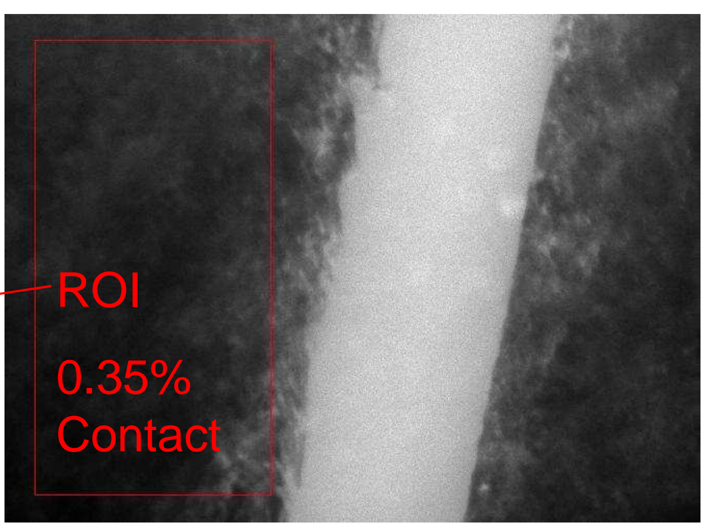
DELIF: Dynamic Contact

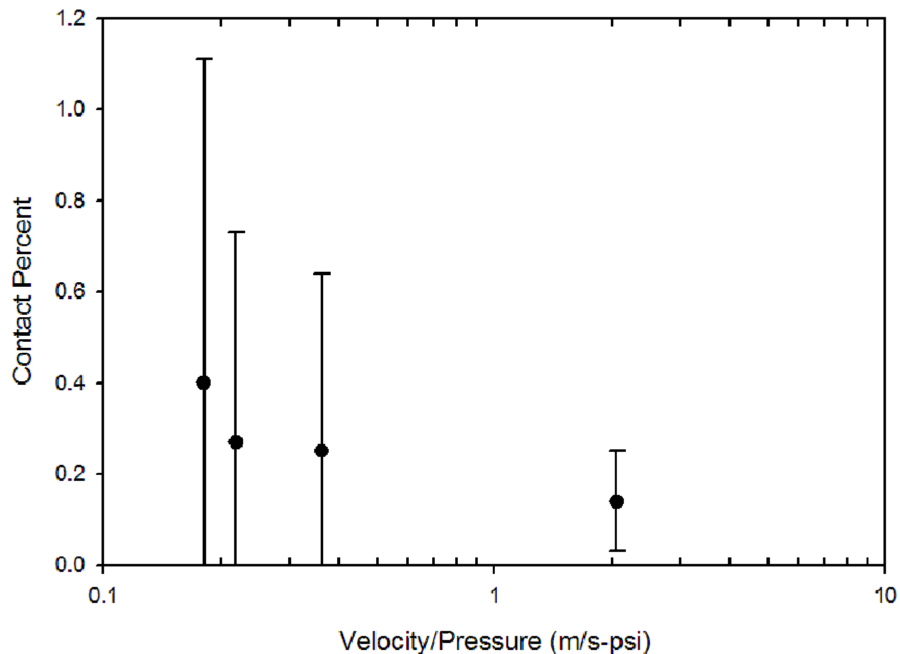
• Contact regions on a soaked pad appear away from the grooves

•Contact percentages in the dynamic case on the same order of magnitude as the static case

• The majority of images show contact < 1%





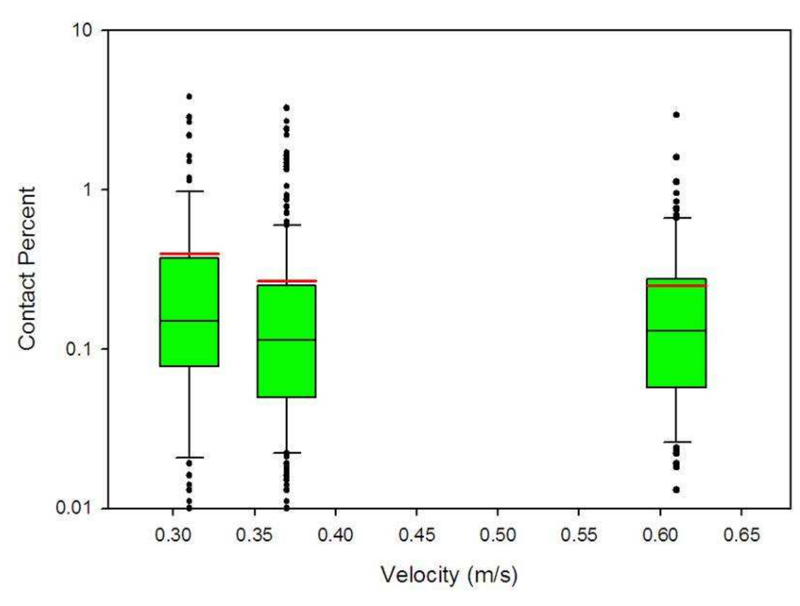


Contact means follows a Stribeck-type curve, suggesting a boundary lubrication regime.

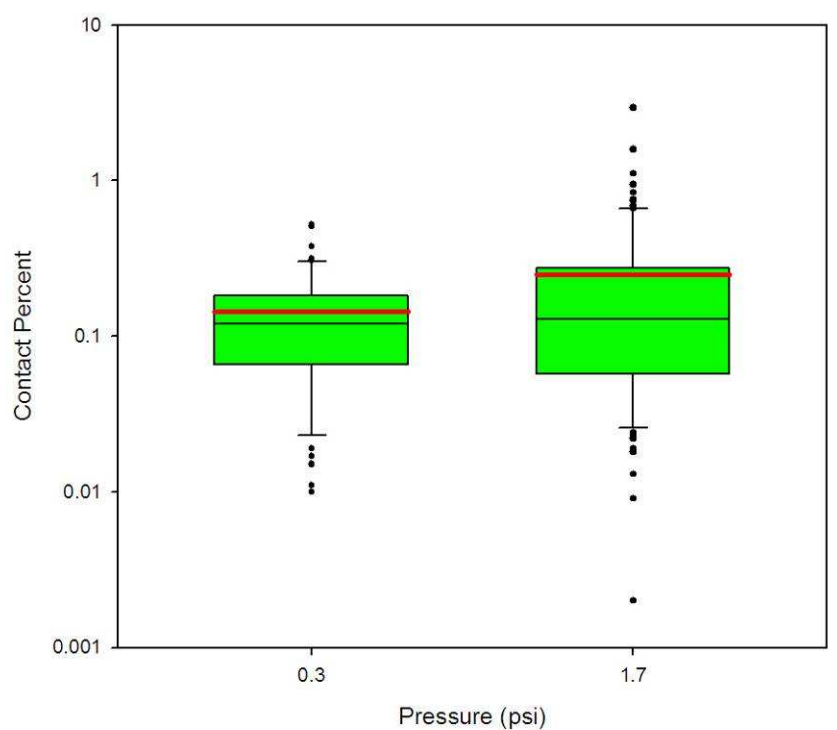
CMC D100 pad, AC grooves,
3:2 Cab-o-sperse SC1 (22 wt%)

DELIF: Dynamic Contact

Contact increases with decreasing velocity



Contact increases with increasing pressure



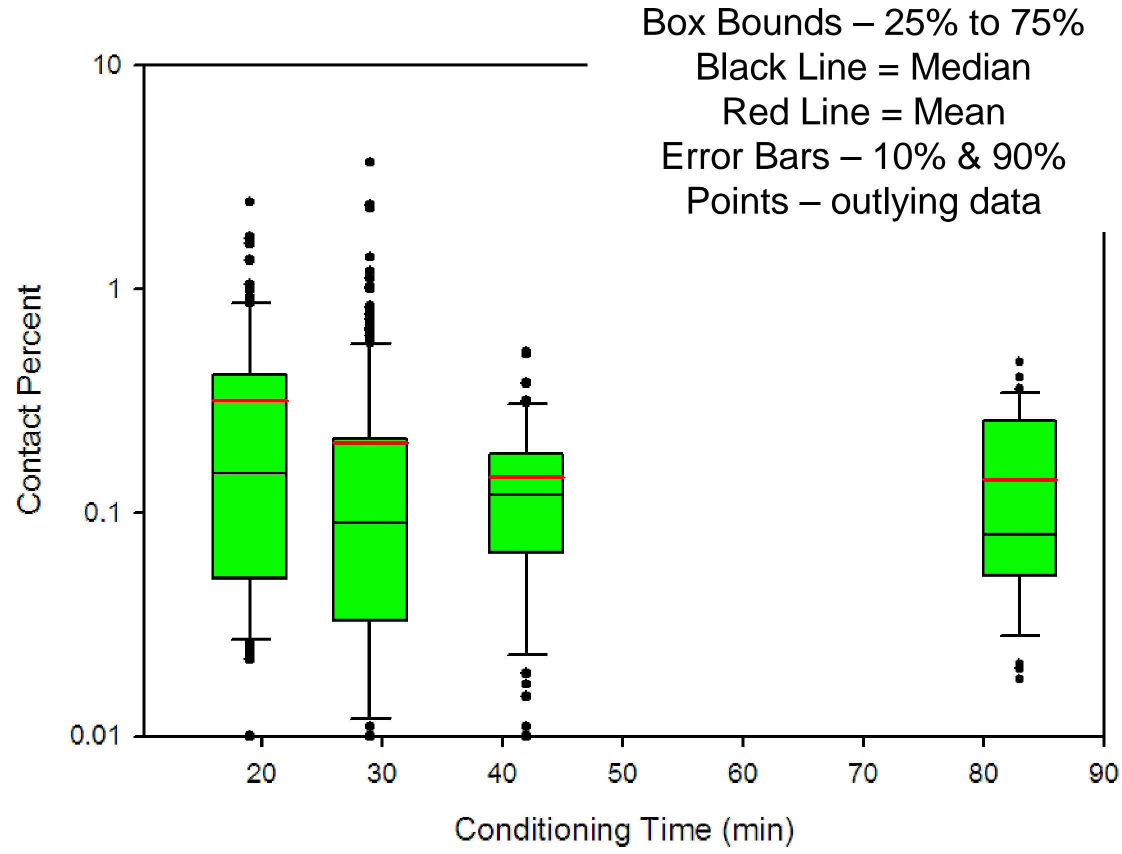
Box Plot

Box Bounds – 25% to 75%
Black Line = Median
Red Line = Mean
Error Bars – 10% & 90%
Points – outlying data

CMC D100 pad, AC grooves, 3:2 Cab-o-sperse SC1 (22 wt%)

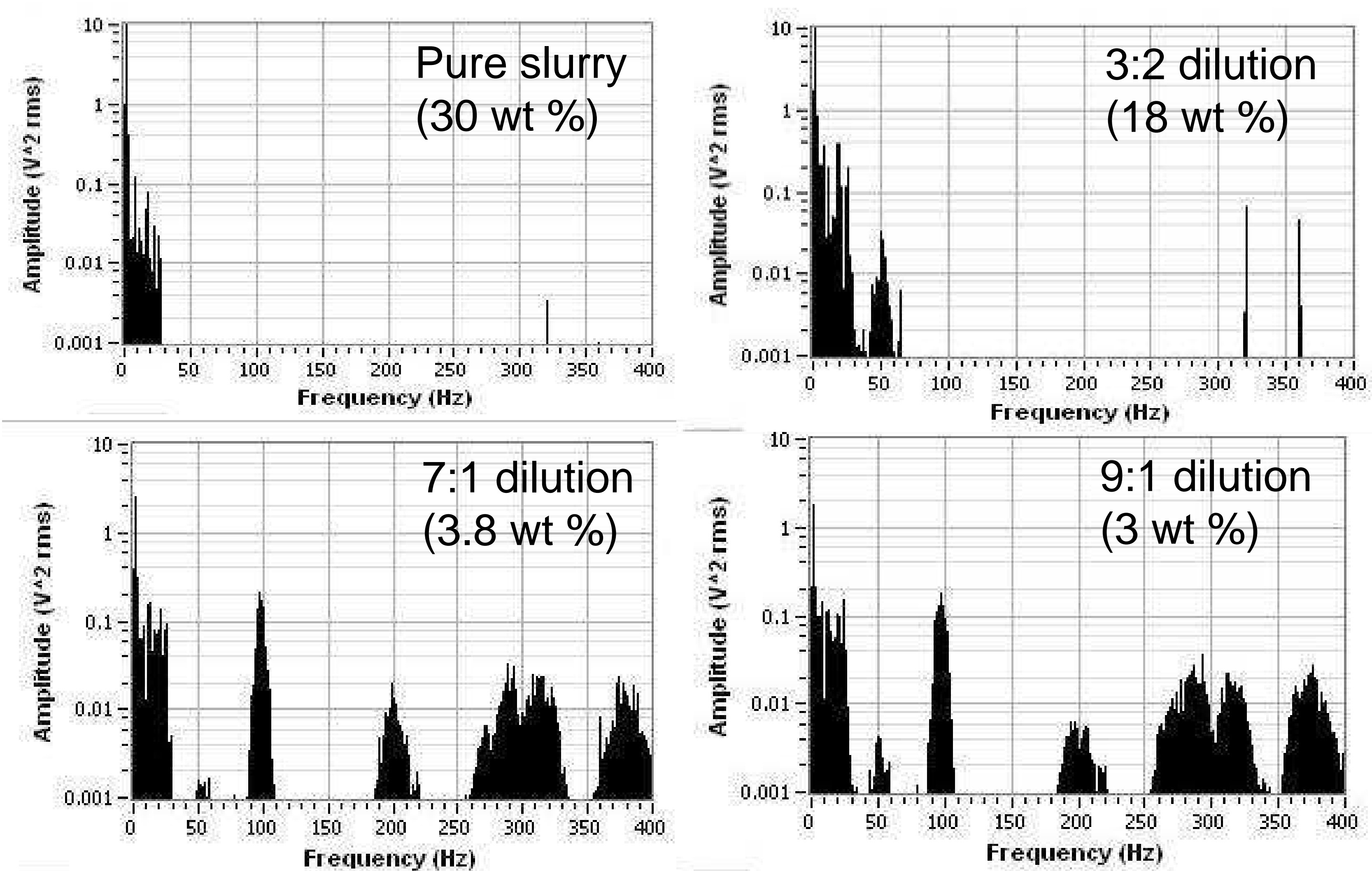
DELIF: Dynamic Contact

- Contact seems to *decrease with conditioning time* for the first 40 minutes of conditioning and break in.
- *Previous studies show the opposite trend*: conditioning increases contact – but also decreases the area for the points of contact.
- It is possible that the regions of contact are becoming smaller with conditioing, and we are losing the ability to detect with DELIF due to spatial resolution limitations of the method.



CMC D100 pad, AC grooves, 3:2
Cab-o-sperse SC1 (22 wt%)

In-Plane Force Spectra



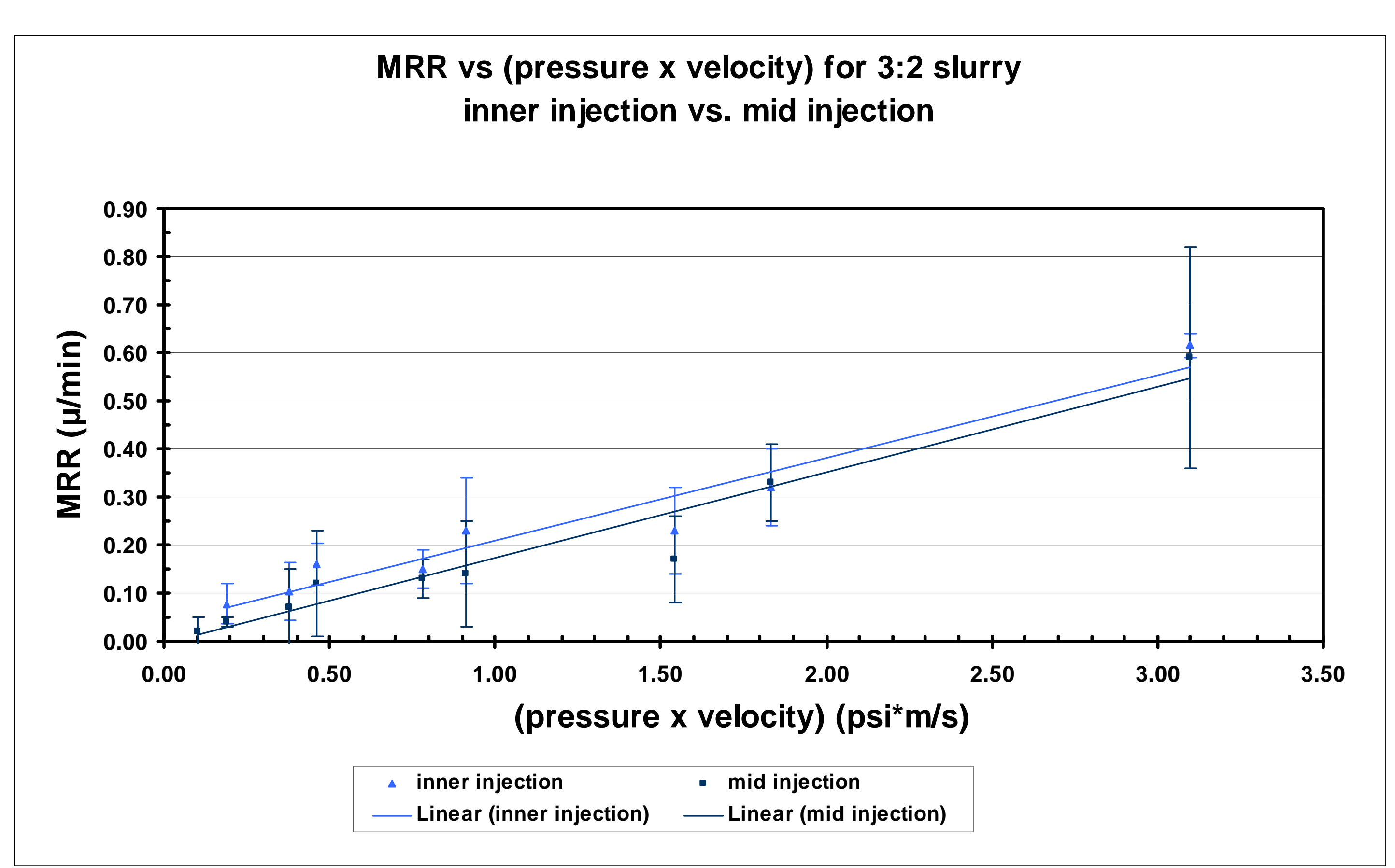
Spectral signatures vary with slurry concentration. 30 wt % slurry (fumed silica slurry) exhibits the least high frequency force content.

Material Removal Rate

• Material removal rate (MRR) is Prestonian for oxide polishing using 22% by weight fumed silica slurry.

• MRR is 50-600 nm/min over the 0.1 to 3.1 psi-m/s range.

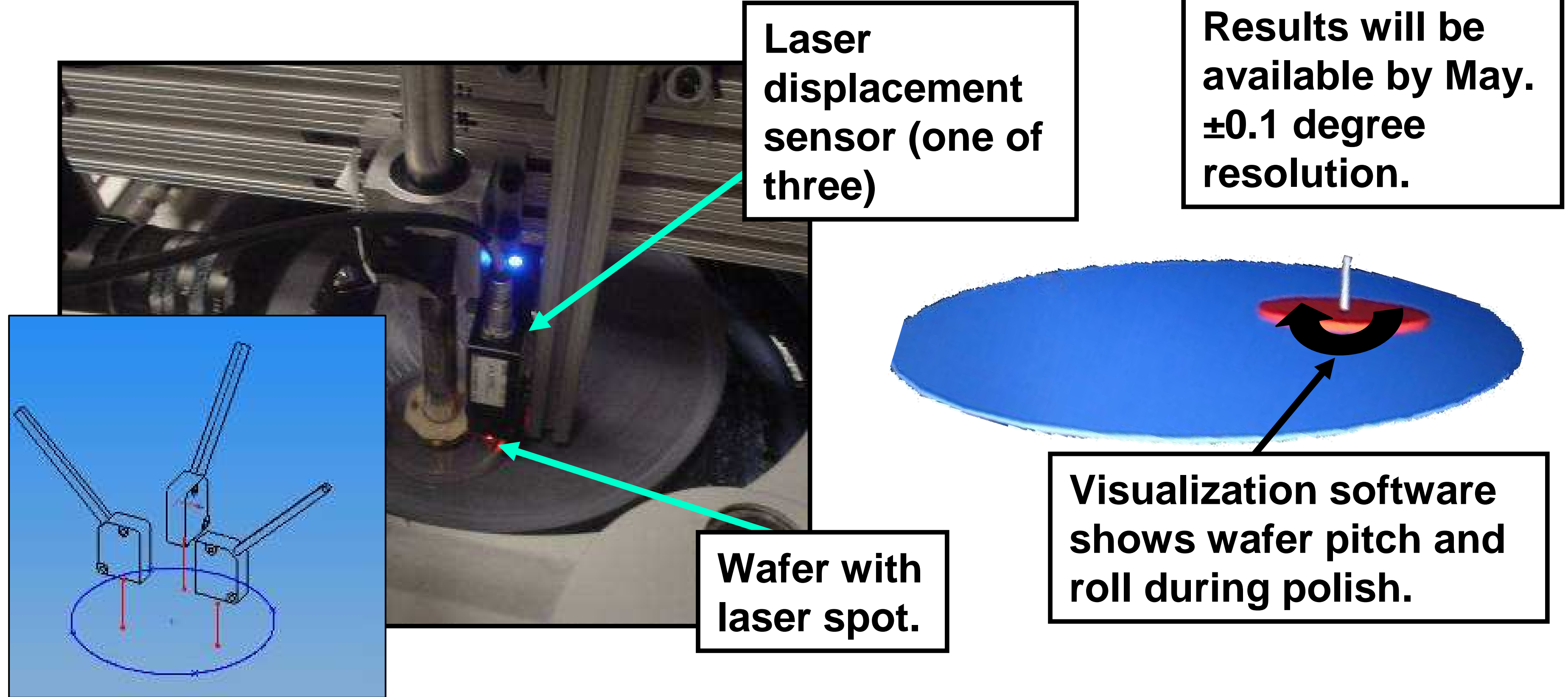
• For the saturated flow rates used, no dependence on slurry injection point is observed.



Wafer Attitude

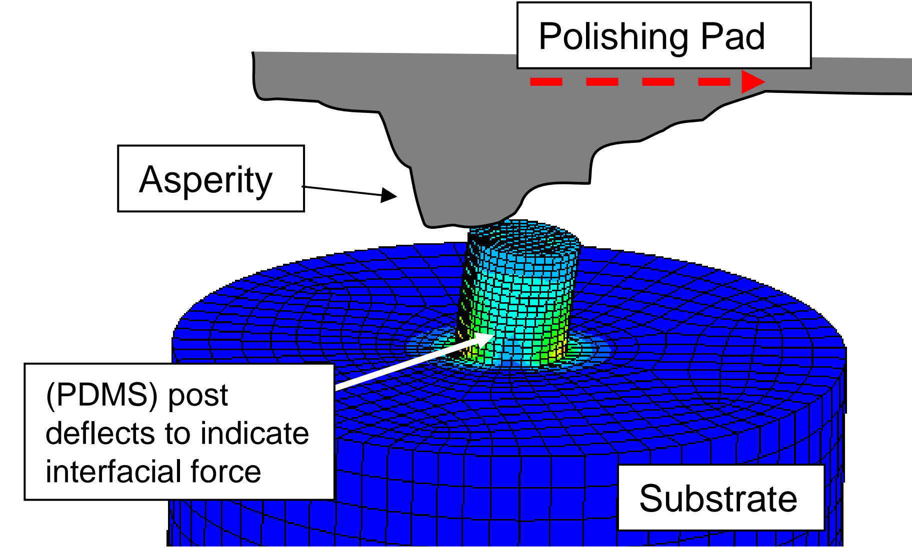
• Three laser displacement sensors are mounted in the rig to measure the wafer pitch, role, and bounce during polishing.

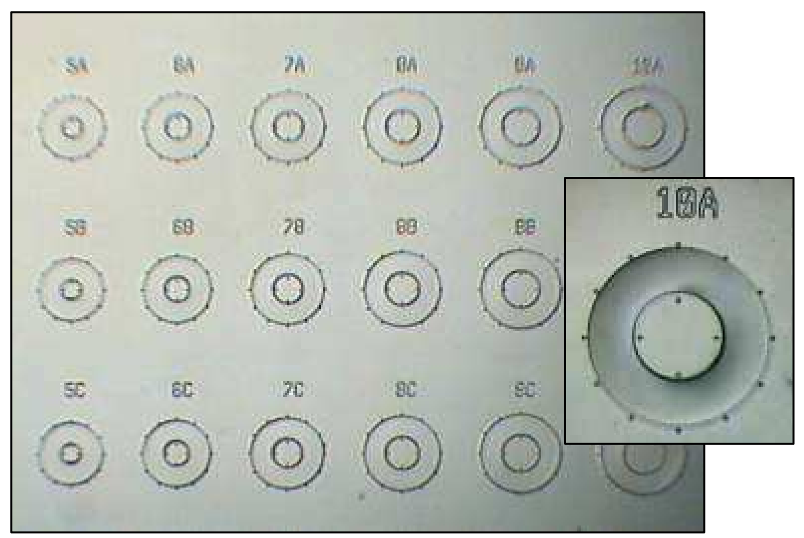
• Wafer displacement is correlated to pad angular position (measured with an encoder).

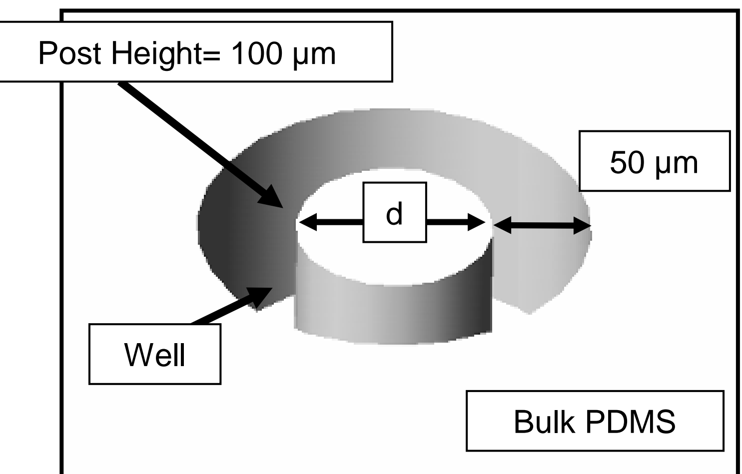


MEMS Force Sensors

- Cylindrical PDMS posts:
  - 100 μm tall, 30-100 μm diameter.
  - Deflect due to shear force.
  - Recessed in wells.
- Calibrated sensitivity is linear:
  - 200 nm/μN for 100 μm diameter

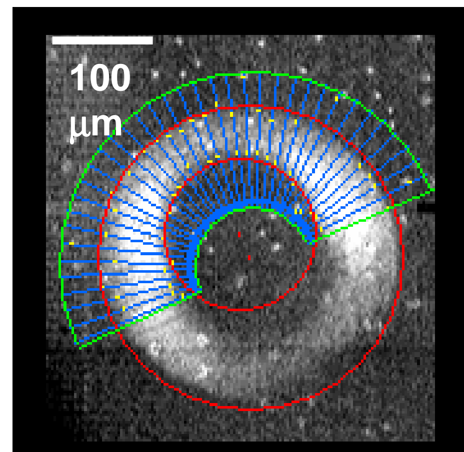




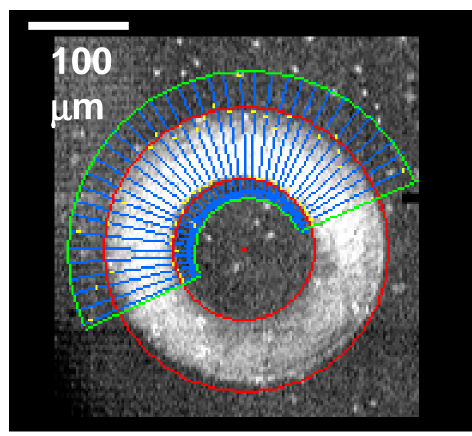


Asperity Level Forces

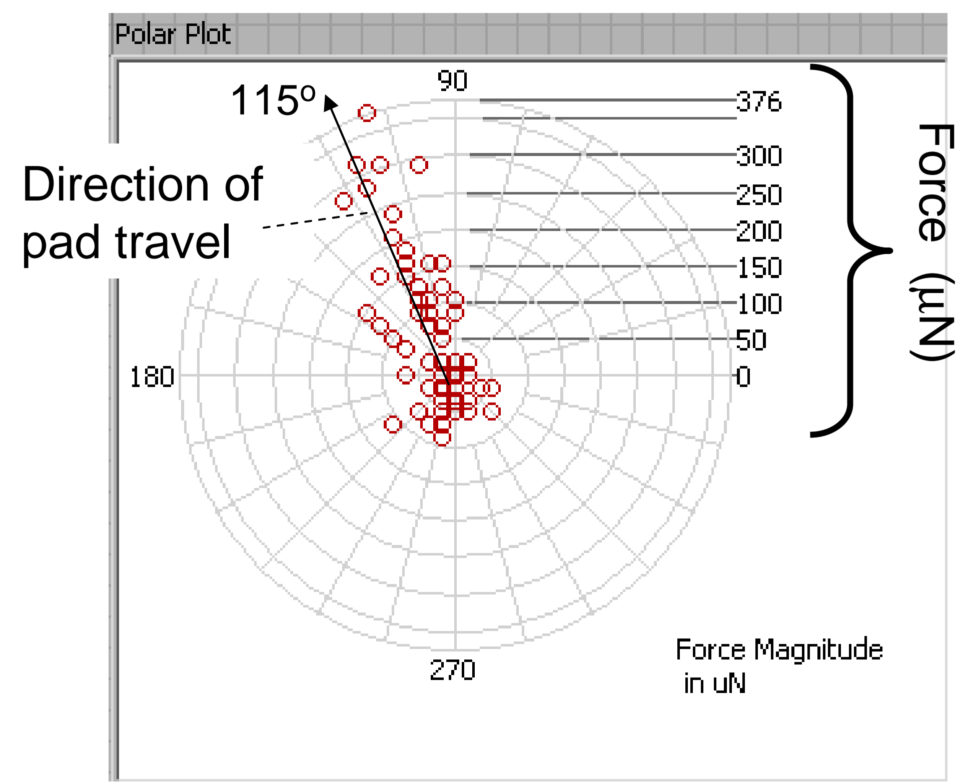
Image processing extracts motion of the post from high-speed (10,000 fps) video.



Deflected

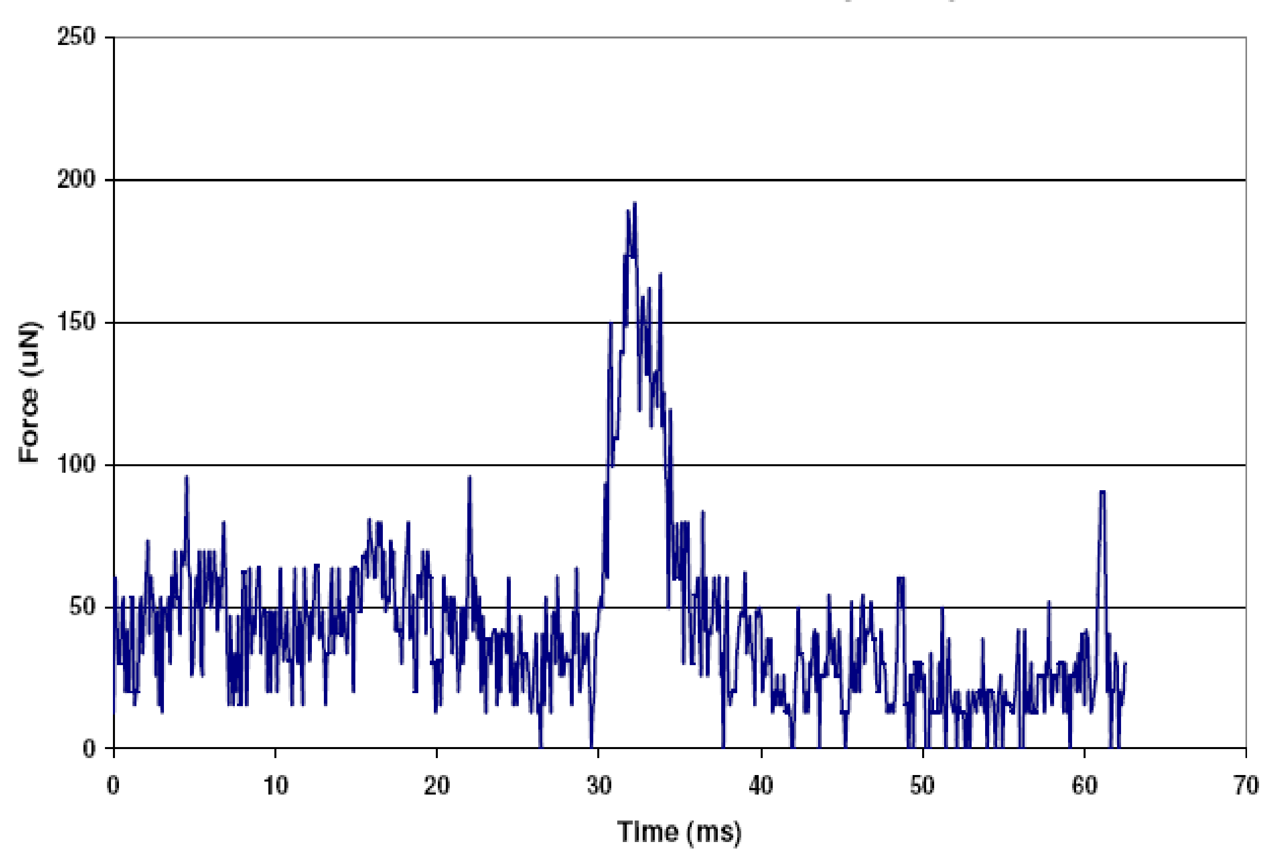


Not deflected



Each point corresponds to the force (direction and magnitude) measured at each 100 microsecond time step. The average force direction aligns with the direction of pad travel.

Asperity Level Forces

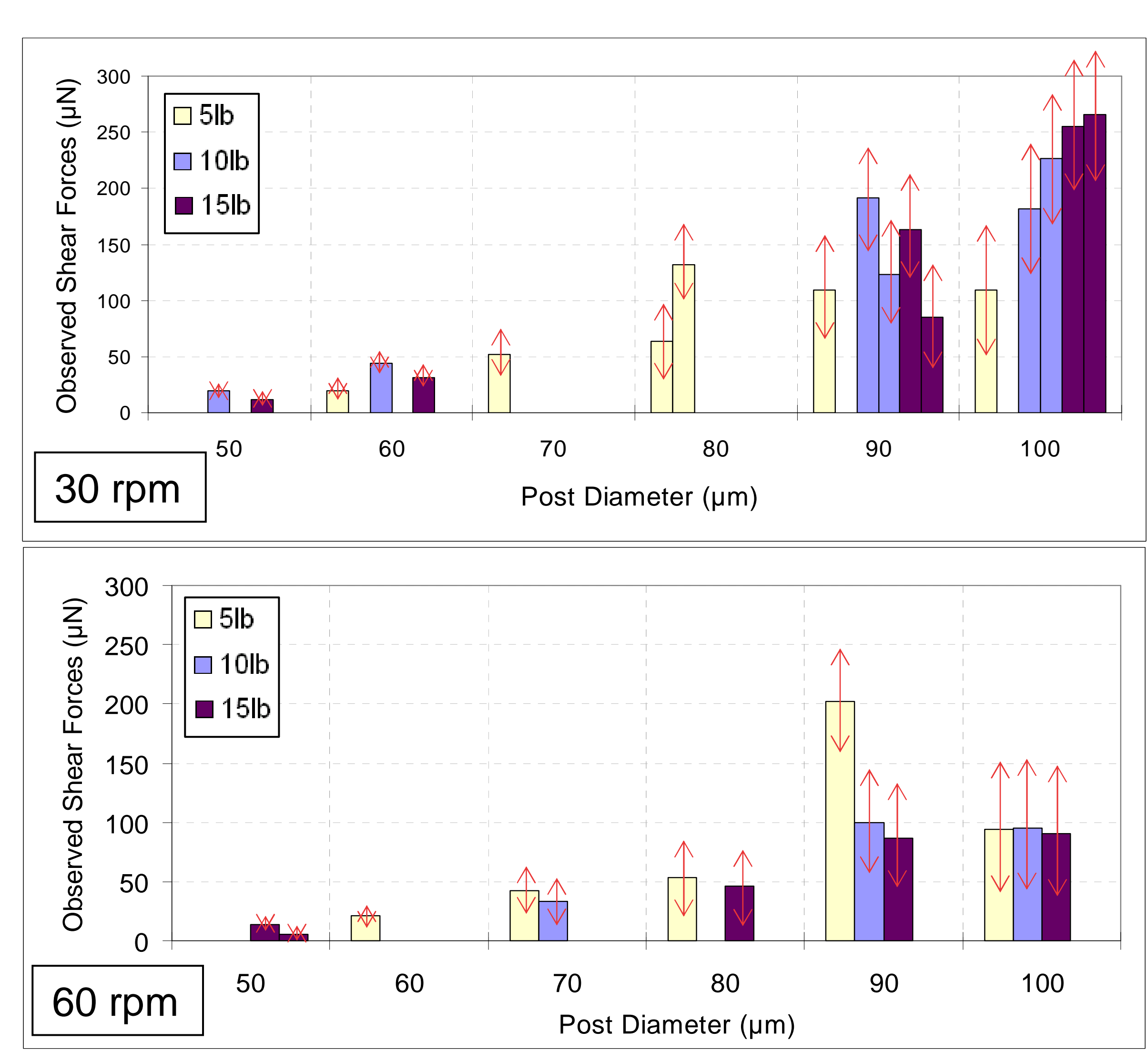


- Example force trace for ***PDMS polishing*** with ***no wafer rotation*** and ***no conditioning***.
- ***Large force events*** (> 100 μN) occur less than 10% of the time and last 0.5-5 ms.

Lateral force vs. time on a 90 μm post. 30 rpm, 1 psi, 9:1 slurry.

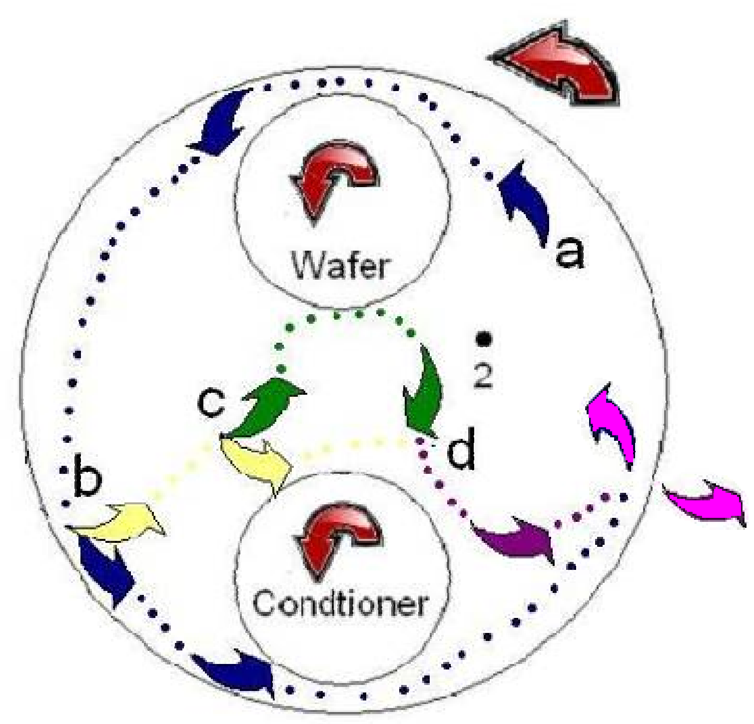
Asperity Level Forces: Trends

- **Increase** in pad rotation leads to a **decrease** in local shear force.
- **Increase** in structure size leads to an **increase** in local shear force.
- Increase in downforce leads to an increase in local shear force only at lower speeds.
- Maximum shear forces for 100 μm structures are approximately 300 μN.



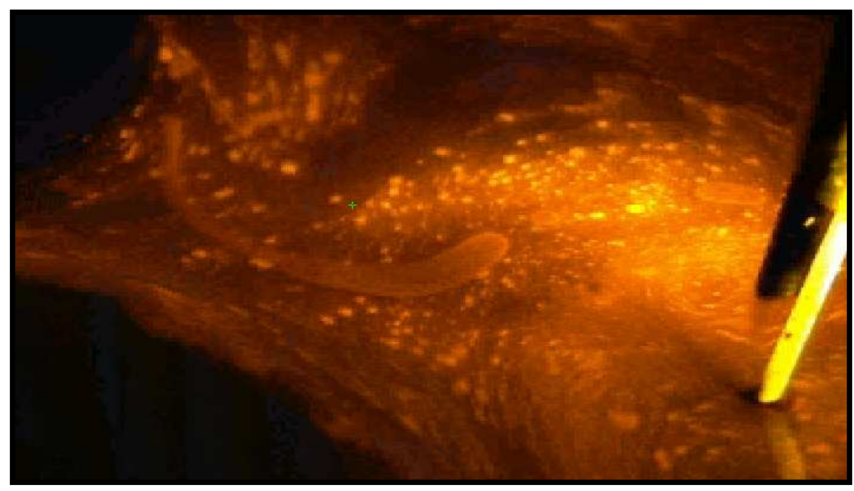
Plots show peak shear forces for maximum force events.

Flow Visualization



Flow visualization using particle tracers allows determination of:

1. Presence of vorticity
2. Presence of bow waves
3. Slurry path
4. Slurry residence.



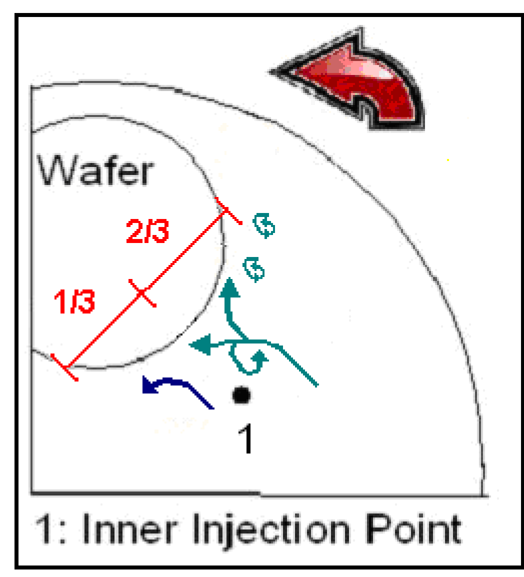
Variables of interest:

1. **Slurry injection point.**
2. **Wafer speed.**
3. **Downforce**

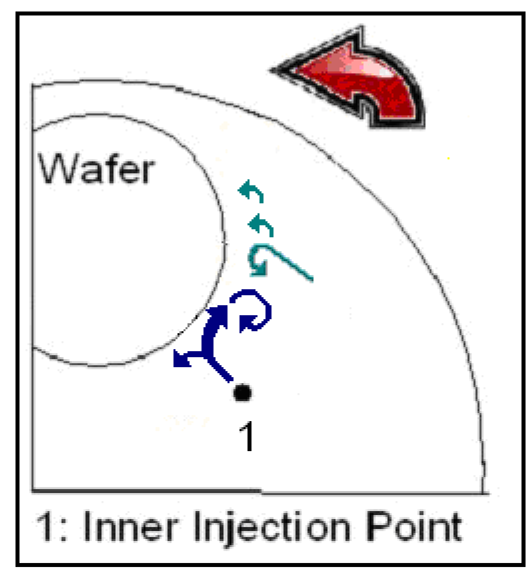
Data is available at:
http://docs.google.com/Doc?id=dc9dhhdb_13fphfz7dp

Example of Flow Visualization

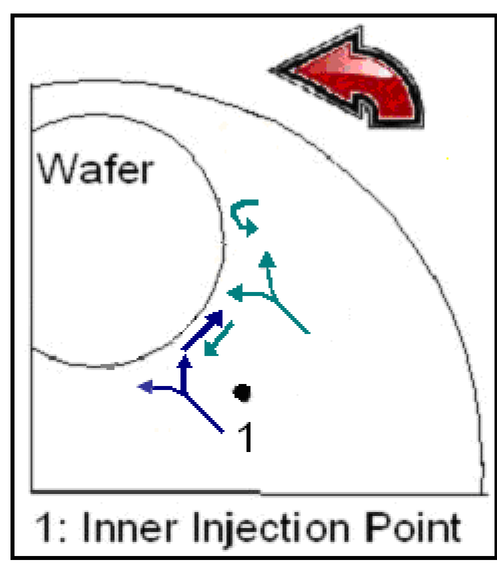
Pad grooving is observed to have a major impact on slurry flow patterns around the wafer.



Ungrooved FX9 pad:
Old slurry dominates wafer bow wave.



XY Grooved FX9 Pad:
New slurry dominates wafer bow wave.



AC Grooved D100 Pad:
Shearing of old and new slurry, mixing at bow wave.

For inner injection point, 35 rpm, conditioning, 22% wt fumed silica slurry.

Industrial Interactions and Technology Transfer

- **Close collaboration with industry partners – Cabot Microelectronics and Intel**
  - **Monthly telecons – secure website for information exchange**
  - **Semi-annual face-to-face meetings**
  - **Thesis committees and joint publication authorship**
  - **Metrology and analysis methodology technology transfer**
  - **In-kind support – specialized supplies and equipment**
  - **Student internships (e.g. D. Gauthier at Draper Labs, summer 2007)**
- **Close coordination with A. Philipossian research group at U of Arizona**
- **Student (J. Thompson) work on Die Thinning for 3D Multi-Chip Module Design at Draper Laboratories via a Draper Fellowship.**
- **Information and results exchange with MIT (D. Boning, G. McKinley), Stockton College (E. Paul), Harvard University (H. Stone).**
  - **Monthly joint meetings of PIs and research students**

Future Plans

Next Year Plans

- All current students complete theses and graduate:
  - C. Gray, PhD : DELIF for pad-wafer contact and slurry thickness
  - J. Vlahakis, PhD : Wafer-scale characterization of CMP mechanics
  - N. Braun, MS : Particle image velocimetry for CMP slurry flow
  - D. Gauthier, MS : MEMS for asperity scale force measurement in CMP

Long-Term Plans

- Deploy the newly demonstrated *in situ* measurement technologies (DELIF, wafer attitude, PIV, MEMS force sensing) to a 200 mm polisher.

- Characterize polishing of patterned tantalum/copper and oxide substrates using the suite of new measurement technologies on the 200 mm platform.

- Apply results of the experimental study to optimize polish conditions, pad geometry/type, conditioner geometry/type for improved polish quality and reduced consumables.

Publications & Presentations

Gray, C., White, R. D., Manno, V. P., and Rogers, C. B. "*Simulated Effects of Measurement Noise on Contact Measurements between Rough and Smooth Surfaces",* **Tribology Letters**, In Press, Accepted Manuscript, December 27, 2007.

N. Braun, C. Gray, A. Mueller, J. Vlahakis, D. Gauthier, V. P. Manno, C. Rogers, R. White, S. Anjur, M. Moinpour. "*In-Situ Investigation of Wafer-Slurry-Pad Interactions during CMP*" in the **Proceedings of the International Conference on Planarization/CMP Technology,** Dresden, Germany, October 25-27, 2007.

Gray, C., Rogers, C. Manno, V., White, R., Moinpour, M., Anjur S.."*Determining Pad-Wafer Contact using Dual Emission Laser Induced Fluorescence*", in the **Proceedings of the Material Research Society**, Vol. 991, Symposium C, Advances and Challenges in Chemical Mechanical Planarization, 2007.

N. Braun, C. Gray, A. Mueller, J. Vlahakis, D. Gauthier, V. P. Manno, C. Rogers, R. White, S. Anjur, M. Moinpour. "*In-Situ Investigation of Wafer-Slurry-Pad Interactions during CMP*" in the **Proceedings of the International Conference on Planarization/CMP Technology,** Dresden, Germany, October 25-27, 2007.

Mueller, A. White, R. D., Manno, V., Rogers, C., Barns, C. E., Anjur, S., and Moinpour, M. "*Micromachined Shear Stress Sensors for Characterization of Surface Forces During Chemical Mechanical Polishing*" in the **Proceedings of the Material Research Society**, Vol. 991, Symposium C, Advances and Challenges in Chemical Mechanical Planarization, 2007.

Students on Task 425.020 – Tufts

- Graduated Students and Current Affiliation
  - Andrew Mueller, Draper Laboratories, May, 2008
- Current Students and Anticipated Grad Date
  - C. Gray, PhD, May 2008
  - J. Vlahakis, PhD, August 2008
  - N. Braun, MS, May 2008
  - D. Gauthier, MS, August 2008
- Internships
  - D. Gauthier, Draper Laboratories, Summer 2007

An Integrated, Multi-Scale Framework for Designing Environmentally Benign Copper, Tantalum and Ruthenium Planarization Processes

(*Task 425.020*)

Subtask 1: Modeling of Planarization Performance

PI:

- **Duane Boning, Electrical Engineering and Computer Science, MIT**

Graduate Students:

- **Hong Cai, Materials Science, MIT, graduate with Ph.D. in June 2007**
- **Xiaolin Xie, Physics, MIT, graduate with Ph.D. in June 2007**
- **Wei Fan, Ph.D. candidate, EECS, MIT, started Sept. 2007**

Undergraduate Student:

- **Zhipeng Li, EECS, MIT**

Other Researcher:

- **Ed Paul, Visiting Professor, Stockton College**

Cost Share (other than core ERC funding):

- **Experimental support, JSR Micro**

Objectives

- **Focus on *chip-* and *feature-scale* performance of CMP processes**
  - **Connect with physical investigations by team members**
  - **Connect with metrology and wafer level for control**
- **Understand how pad properties relate to the *planarization* capability of CMP processes**
  - **Pad bulk: chip-scale uniformity (pattern density)**
  - **Pad surface: step-height removal dependencies (dishing)**
- **Joint optimization of pad properties to achieve processes with reduced time, consumables, and waste, *as well as* reduced dishing, erosion, and within die nonuniformity**

ESH Metrics and Impact

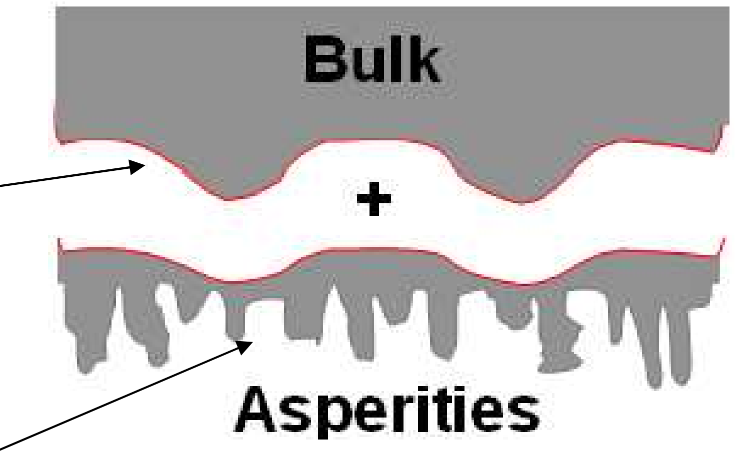
Driving principle: Joint improvement in CMP performance and ESH performance

1. *Reduction in the use or replacement of ESH-problematic materials*
2. *Reduction in emission of ESH-problematic material to environment*
   - **Reduce slurry particle use and Cu solid waste by 20-50%**
3. *Reduction in the use of natural resources (water and energy)*
   - **Shorten CMP polish times (copper, barrier) by 20-50%**
   - **Improve yield (multiplication over all inputs/outputs) by 1-2%**
4. *Reduction in the use of chemicals*
   - **Reduced plated copper thickness by 25%**
   - **reduced slurry usage by 20%**
   - **Improved pad lifetime by 20-50%**

Pad/Planarization Modeling Approach

- **Previous CMP chip-scale model:**
  - **"planarization length" concept for pattern density effect on amount removed uniformity within die**
  - **"critical step height" concept for feature-scale step height removal**
- **New CMP chip-scale model:**
  - **More directly physically based**
  - **Effective pad bulk modulus**
    - Explicit long range pad bending (replaces planarization length)
  - **Asperity height distribution**
    - Probabilities on asperity heights replaces critical step height
- **Application/Verification**
  - **Alternative CMP water-soluble particle (WSP) pad, JSR Micro**

Parameters of Physical CMP Chip-Scale Model

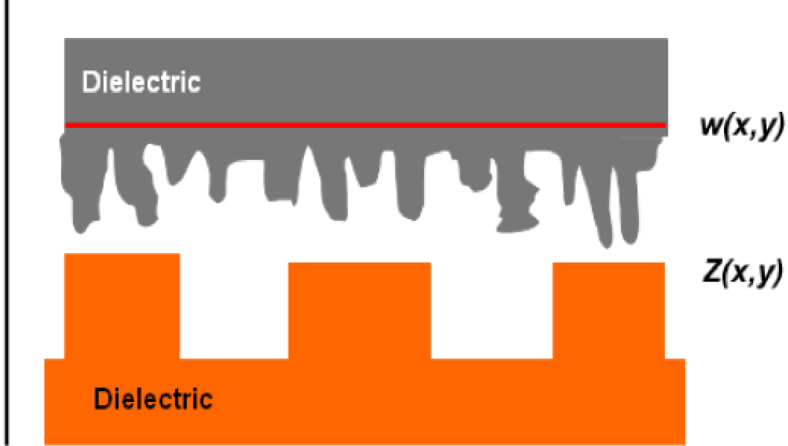


- *E* = Effective Young's Modulus (Property of pad bulk)
- λ = Characteristic Asperity Height (Property of pad asperities)
- *K* = Blanket Removal Rate at reference pressure (Scaling factor of the system)

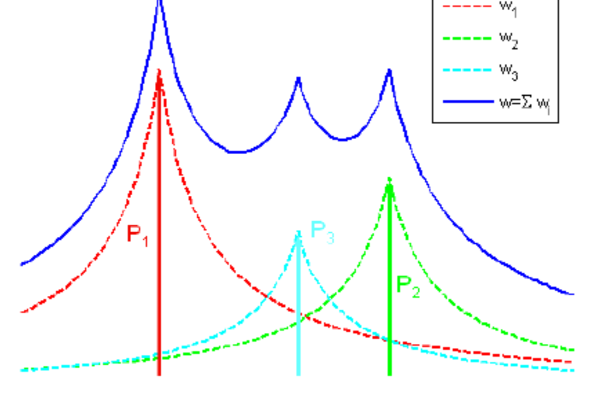
Pad Bulk: Contact Mechanics

Contact Mechanics describes the relationship between pad displacement w(x,y) and pad pressure P(x,y)

- Point pressure, w(r) ~ 1/r
- Linear superposition



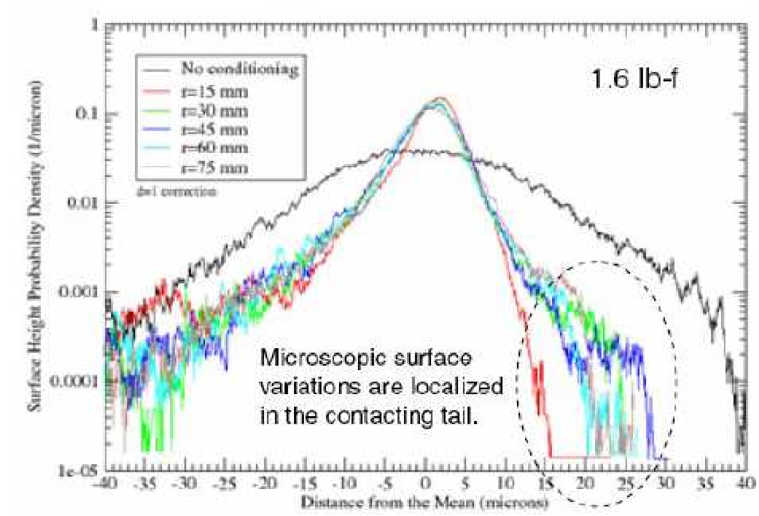
$$w(x,y) - w_0 = \frac{1-\nu^2}{\pi E_p} \int d\xi \int d\eta \frac{P(\xi,\eta)}{\sqrt{(x-\xi)^2 + (y-\eta)^2}}$$



Pad Asperities

Assumptions:

1. **Negligible width**
2. **Exponential distribution of height, mean λ**
3. **Hooke's law: force proportional to compressed amount**



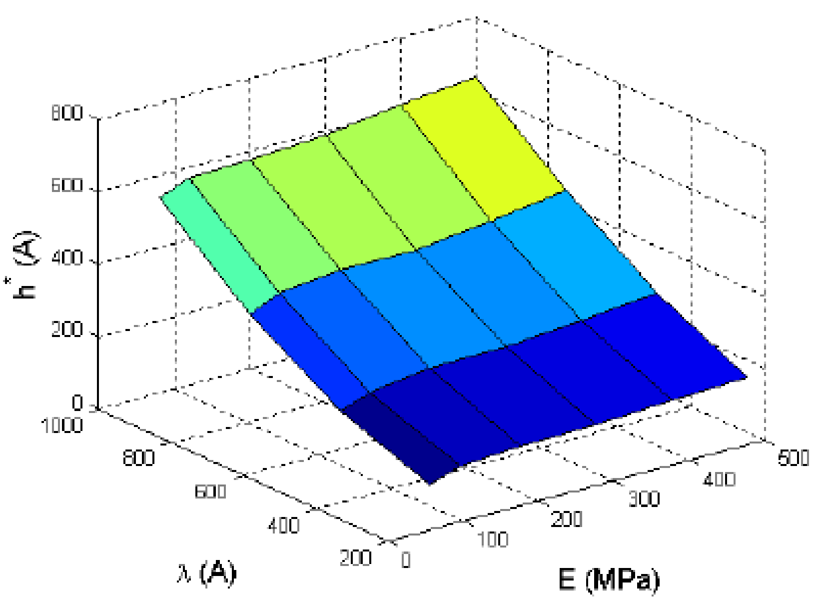
Surface Height Distribution
L. Borucki, 2006, ICPT

$$\begin{cases} P_d = \dfrac{1}{1+\rho(e^{h/\lambda}-1)}P \\ P_u = \dfrac{e^{h/\lambda}}{1+\rho(e^{h/\lambda}-1)}P \end{cases} \Rightarrow \begin{cases} K_d = \dfrac{1}{1+\rho(e^{h/\lambda}-1)}K \\ K_u = \dfrac{e^{h/\lambda}}{1+\rho(e^{h/\lambda}-1)}K \end{cases}$$

Interpreting Pattern-Density/ Step-Height Parameters

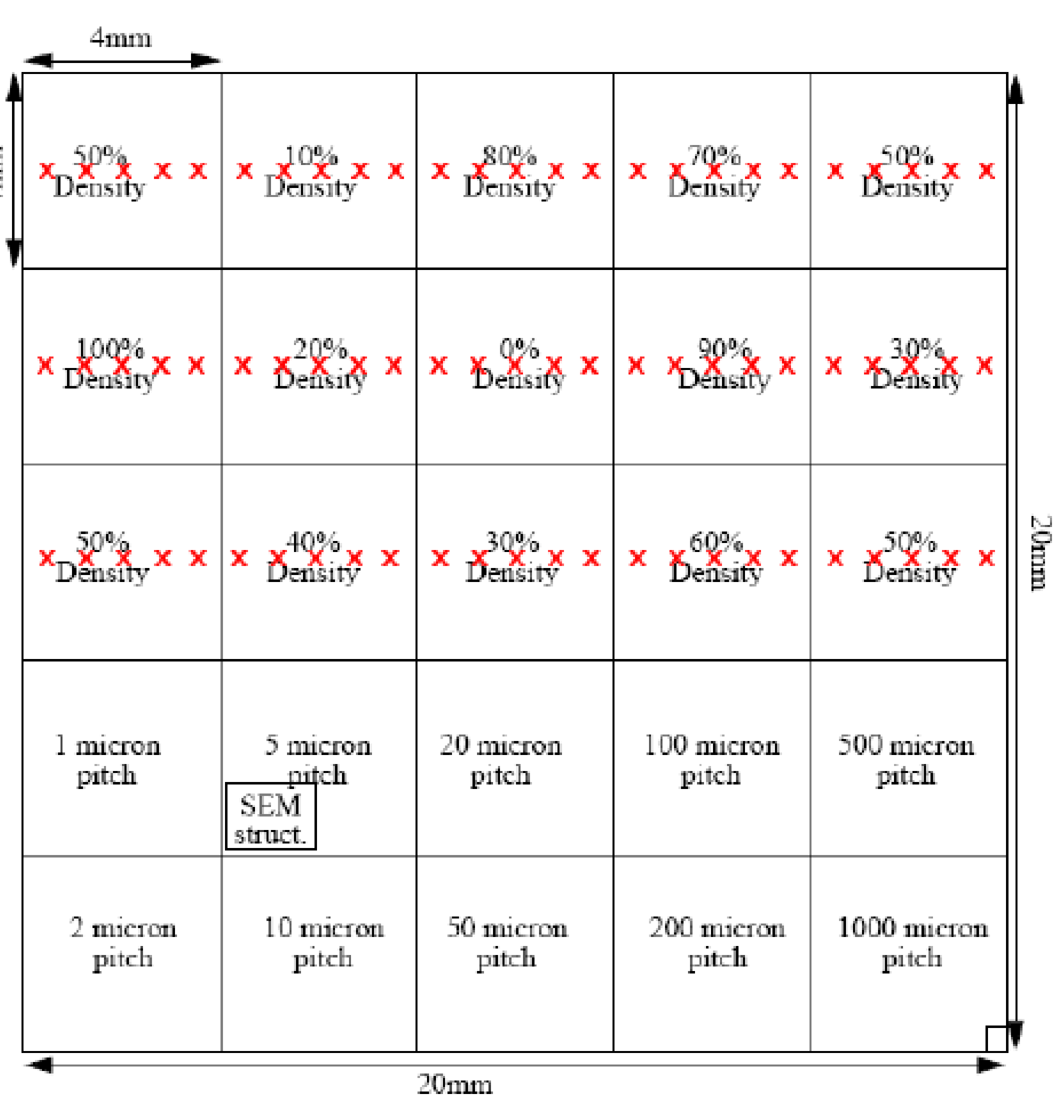
- **Planarization length L_P**
  → z_u (across chip)
  - **increases with E**
  - **insensitive to asperity height distribution**

- **Characteristic step-height h^***
  → step height evolution
  - **Depends strongly on asperity height distribution**
  - **insensitive to E**

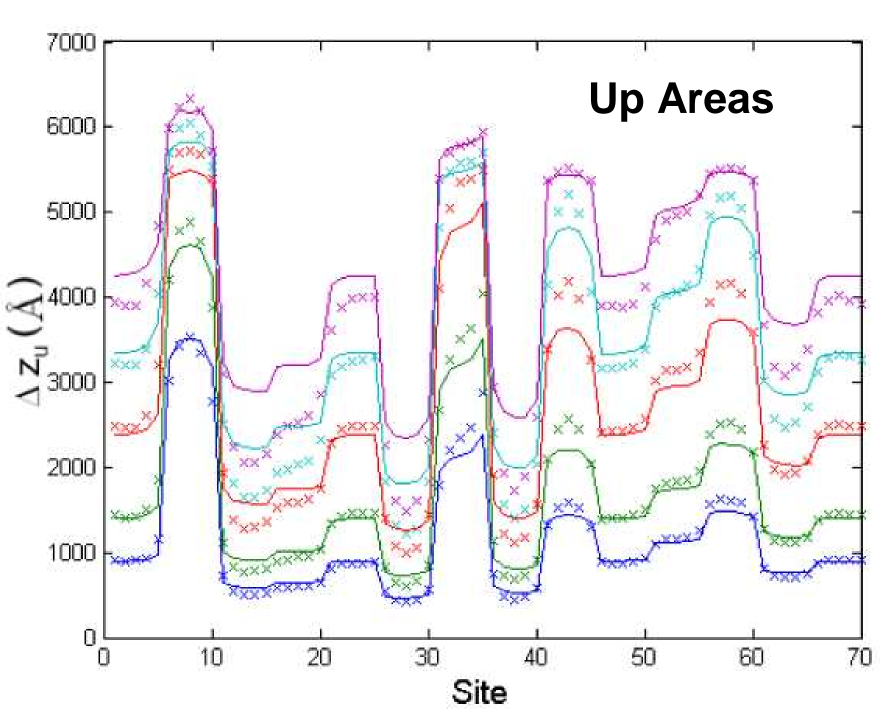


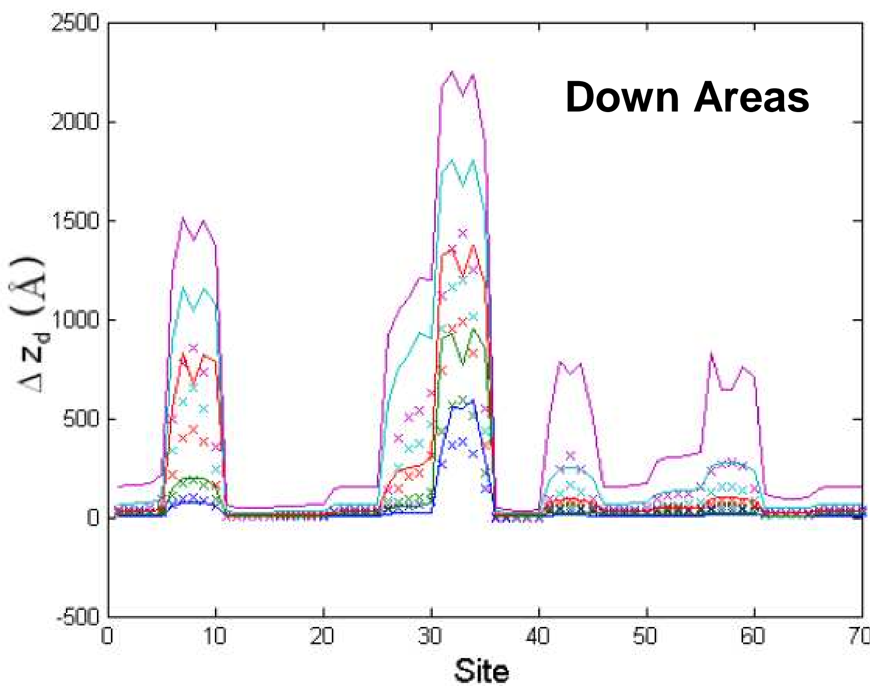
Experimental Verification of Model

- **STI CMP experiment**
- **STI CMP test mask**
- **IC-1400 pad**
- **SS-25 slurry**
- **Polishing time splits:**
  - **5, 10, 15, 30, 40 seconds**
- **Optical thickness measurements**
  - **at "x" marks**
  - **both raised and trench areas**



Physically-Based Model Results

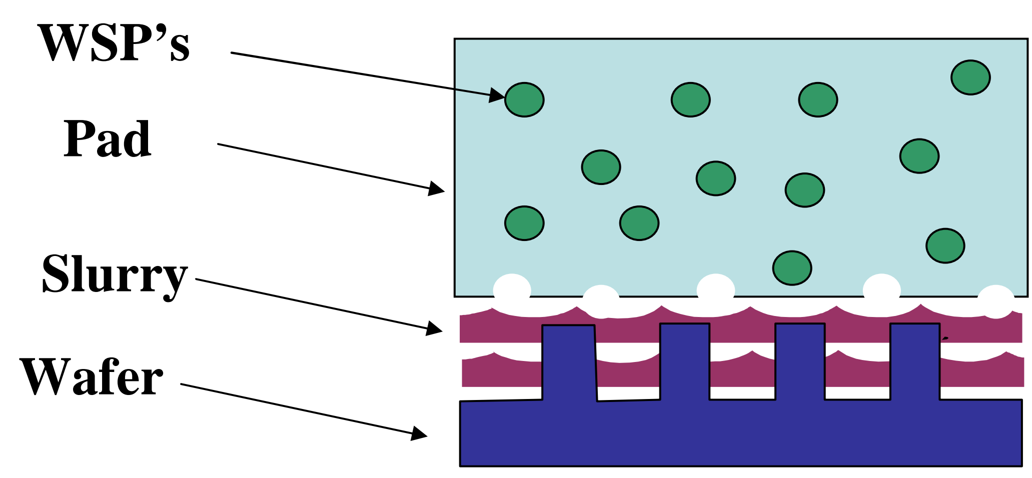




- **Fitting errors:**
  Δz_u is 251 Å
  Δz_d is 262 Å

Model Application: Study of Pad/Planarization Dependencies

- Pad with water soluble particles (WSP's)
  - Keeps pad bulk rigid (increased bulk stiffness)
  - Pores aid in slurry transport
  - Modifies/controls pad surface/asperity structure



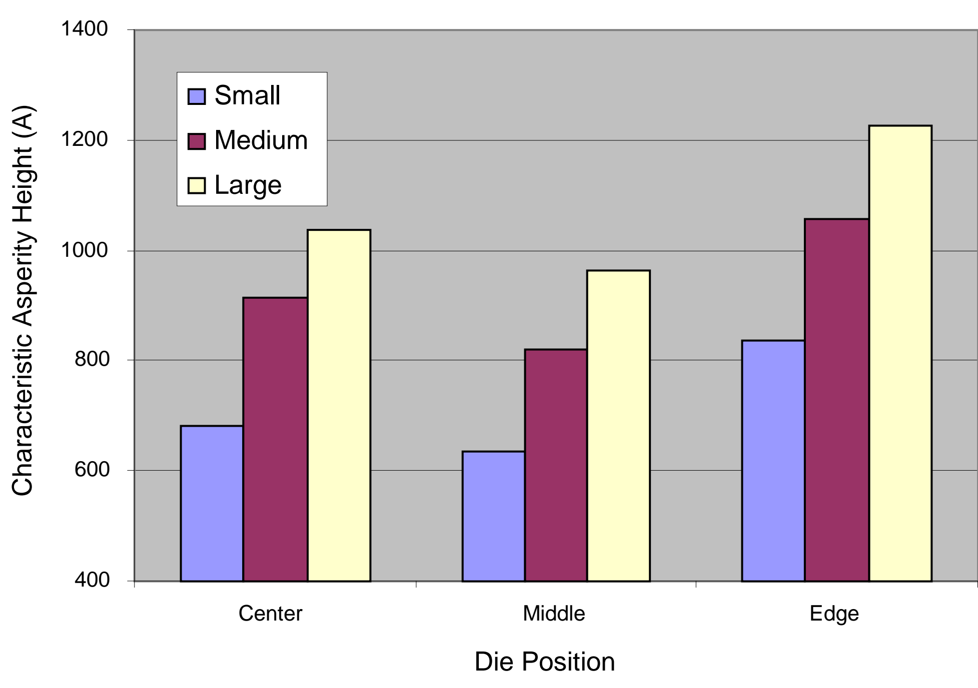
- Goal of study
  - Extract chip-scale model parameters for different WSP pad designs
  - Understand chip-scale performance as function of pad parameters
- Experiments
  1. Vary WSP size (fixed concentration)
  2. Vary WSP concentration (fixed size)

Effect of WSP Concentration

1400
1200
1000
800
600
400
Characteristic Asperity Height (A)
Low
Standard
High
Center
Middle
Edge
Die Position

- Higher concentration → more porous surface when particles dissolve in slurry → a larger mean asperity height
- Asperities longer at wafer edge, effect of different conditioning?

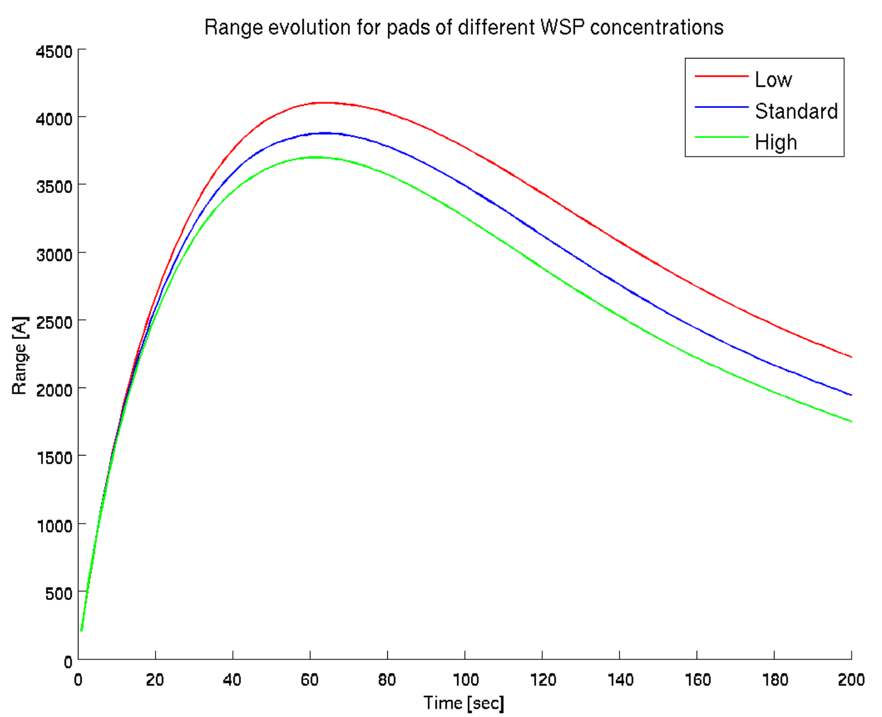
Effect of WSP Size



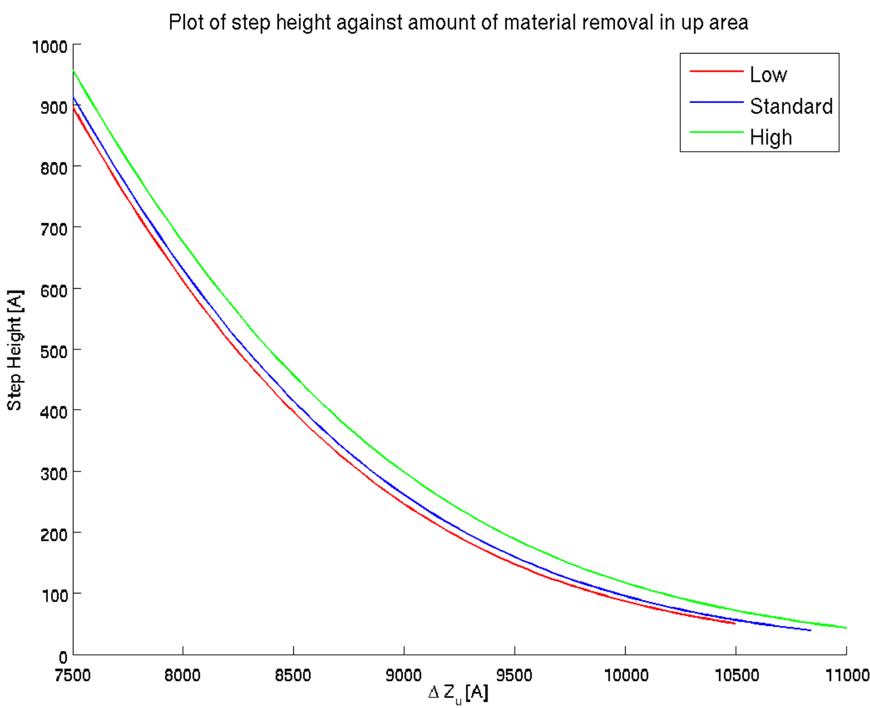
- Large WSP size → bigger pores → extract a larger mean asperity height

Performance Metrics

Up-Area Range (Max-Min) Across Chip

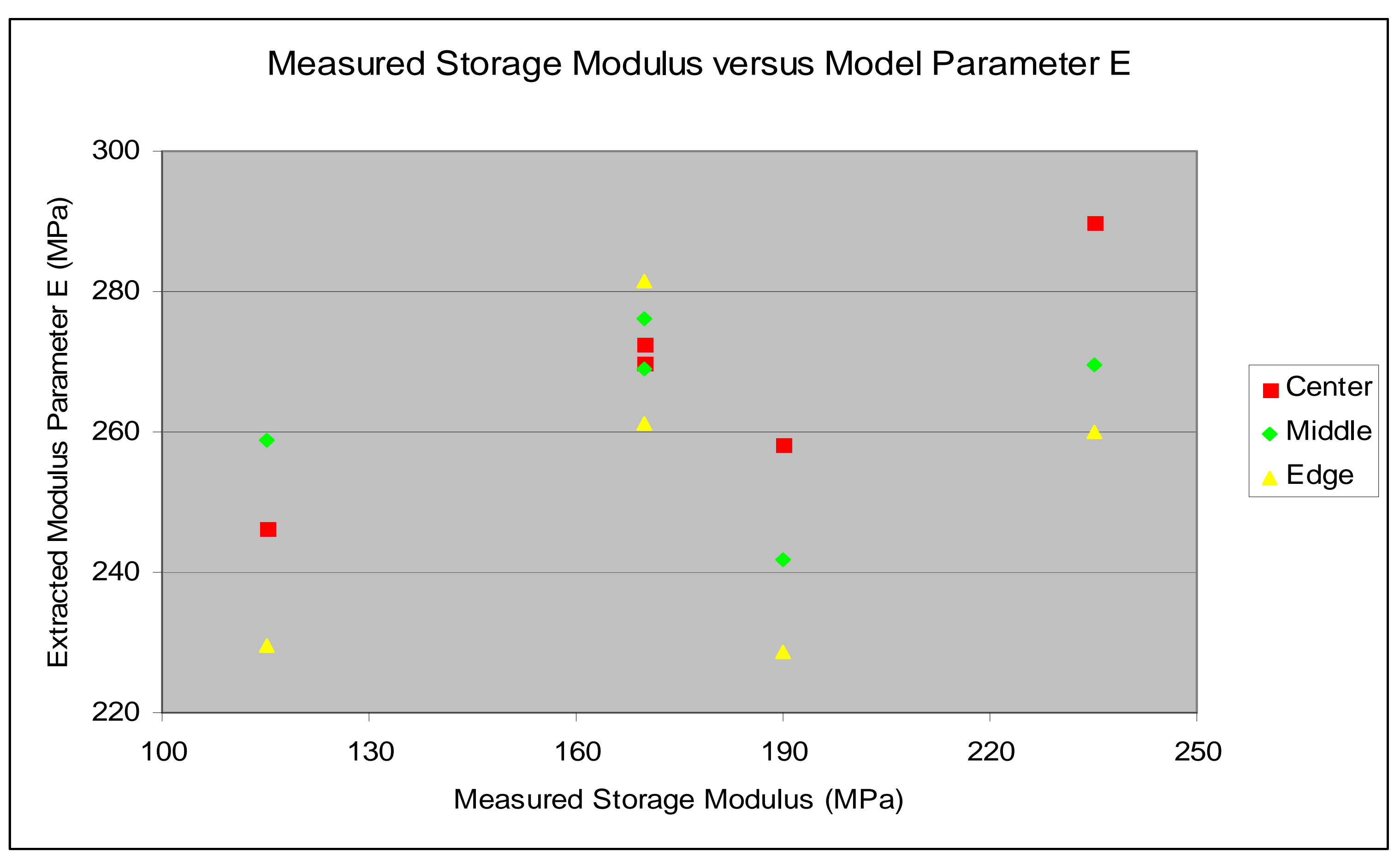


Planarization Efficiency



- **Enables exploration of trade-off or joint optimization between**
  - **Chip-scale (within-die) uniformity**
  - **Feature-scale planarization (dishing)**

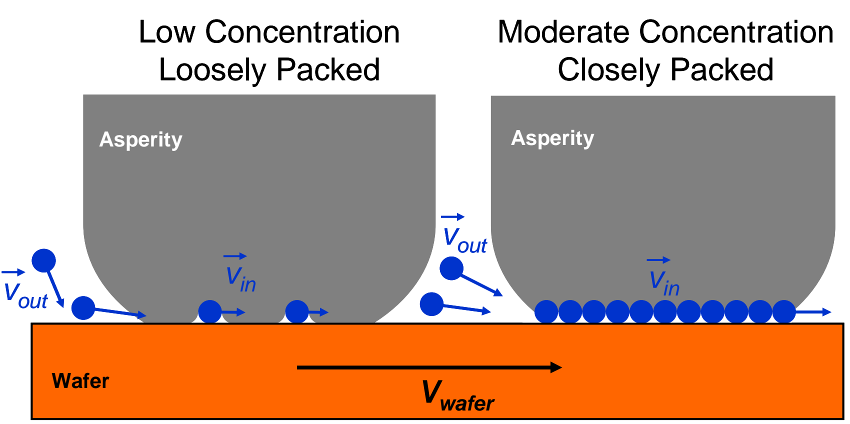
Modulus: Physical Measurement vs. Model



- **Need to understand difference**
  - **"Effective" bulk Young's modulus?**
  - **Experimental measurement of bulk vs. asperity mechanical properties**

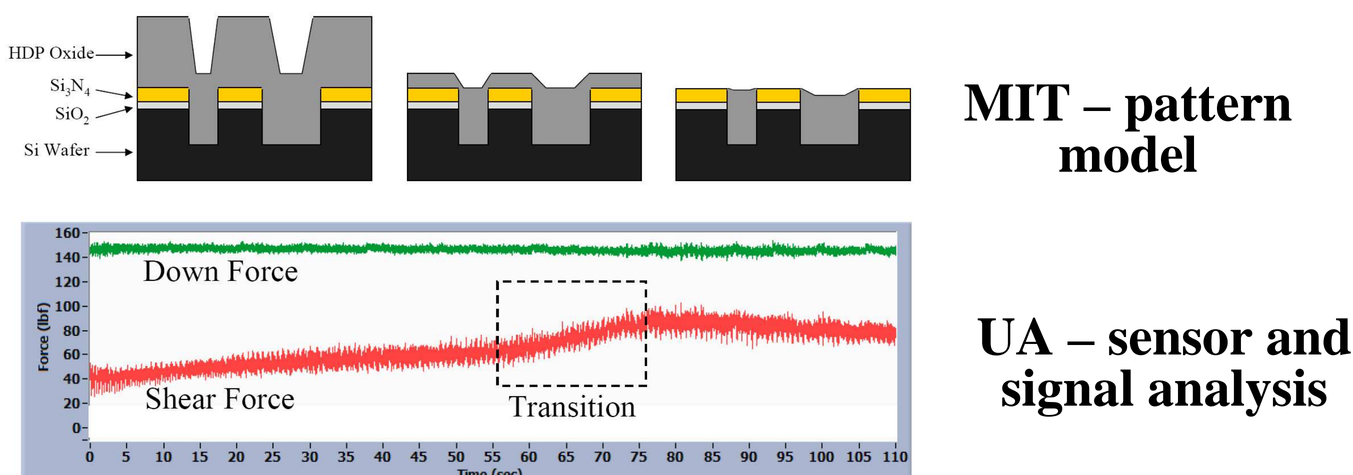
Next Year Plans

- Modeling & verification experiments
  - Pad bulk modulus and surface distribution experiments for improved planarization and step-height reduction (range of polymer stiffness)
  - Measurement of pad asperity vs. bulk mechanical properties using nanoindentation
  - Mechanical model of force distribution: asperities vs. pad bulk
- Experimental exploration of slurry particle density on pad asperities (with Tufts)
  - Establish whether model assumption of dense pack is correct; potential implications for slurry particle concentration (solid waste reduction)



Extension Program Plans

- Integrate feature, chip and wafer-scale CMP models with in-situ sensor models
  - Based on in-situ sensor signals, identify stage of planarization, dishing, erosion, across chip and wafer



MIT – pattern model

UA – sensor and signal analysis

- Develop CMP physical model improvements and interfaces
  - In-situ studies of pad/wafer contact, pad topography, slurry/particle flow (UA, Tufts)
  - Apply to process optimization and waste reduction

Industrial Interactions and Technology Transfer

- **JSR Micro**
  - **CMP experiments: patterned wafer evolution for different WSP pad designs**

Publications, Presentations, and Recognitions/Awards

1. X. Xie and D. Boning, "Physical-based Die-level CMP Model," CMP Symposium, MRS Spring Meeting, April 2007.
2. D. Truque, X. Xie, and D. Boning, "Wafer Level Modeling of Electrochemical-Mechanical Polishing (ECMP)," CMP Symposium, MRS Spring Meeting, April 2007.
3. D. Boning, "Chip-Scale Modeling of CMP and Plating Processes," Fourth International Copper Interconnect Technology Symposium, Fudan University, Shanghai, China, May 2007. Also at Tsinghua University, Beijing, China, May 2007.
4. D. Boning, "Modeling of Chip-Scale Pattern Dependencies in Interconnect Fabrication Processes," Advanced Metallization Conference, Albany, NY, Oct. 2007.
5. D. Boning, "Green Fab and Manufacturing," in Session SE1, Green Electronics: Environmental Impacts, Power, E-Waste, International Solid-State Circuits Conferences, San Francisco, CA, Feb. 2008.

Students on Task 425.020

- Graduated Students and Current Affiliation
  - Xiaolin Xie (Ph.D.), Goldman Sachs, 6/2007
  - Hong Cai (Ph.D.), Goldman Sachs, 6/2007

- Current Students and Anticipated Grad Date
  - Wei Fan (Ph.D.), 6/2011
  - Zhipeng Li (B.S.), 6/2009

- Internships
  - None this year

Environmentally Benign Electrochemically-Assisted Chemical Mechanical Planarization (E-CMP)

(*Task 425.014)*

Subtask 2: Modeling, Optimization and Control of E-CMP Processes

PI:

- **Duane Boning, Electrical Engineering and Computer Science, MIT**

Graduate Students:

- **Daniel Truque, EECS, MIT, graduated with M.S. in June 2007**
- **Wei Fan, EECS, MIT Ph.D. candidate, started Sept. 2007**
- **Joy Johnson, EECS, MIT M.S. candidate, started Sept. 2007**

Undergraduate Students:

- **Zhipeng Li, EECS, MIT**

Other Researchers:

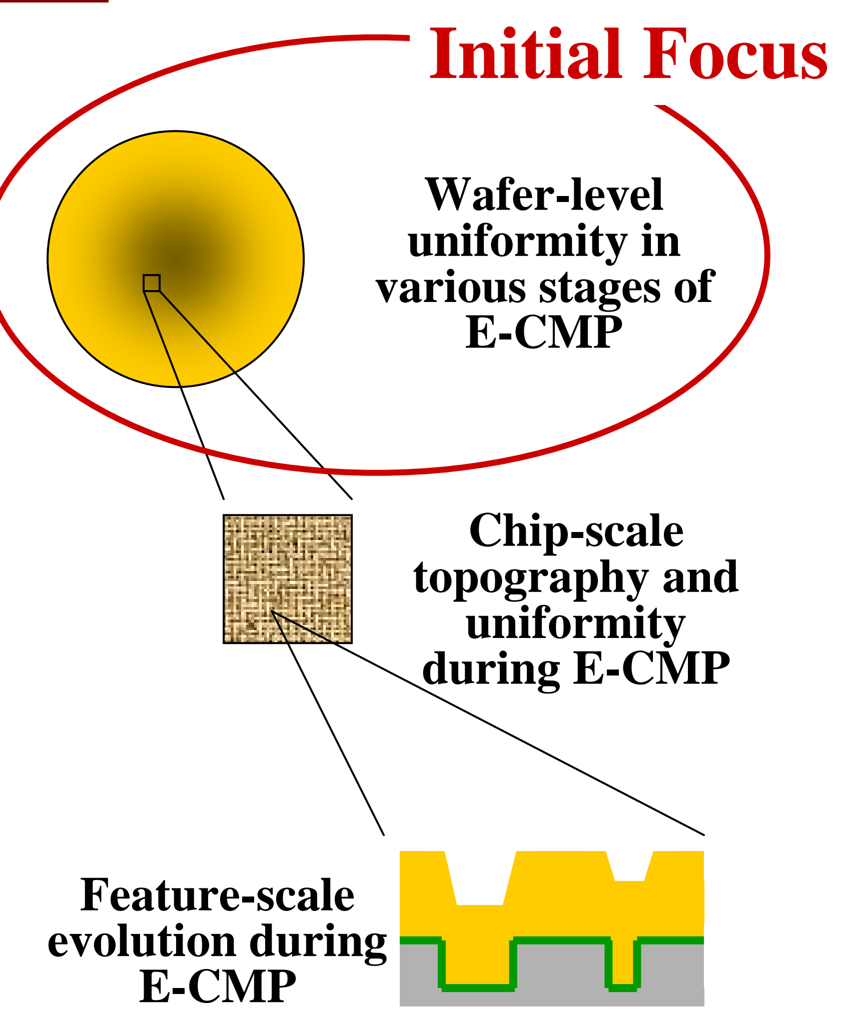
- **Ed Paul, Visiting Professor, Stockton College**

Cost Share (other than core ERC funding):

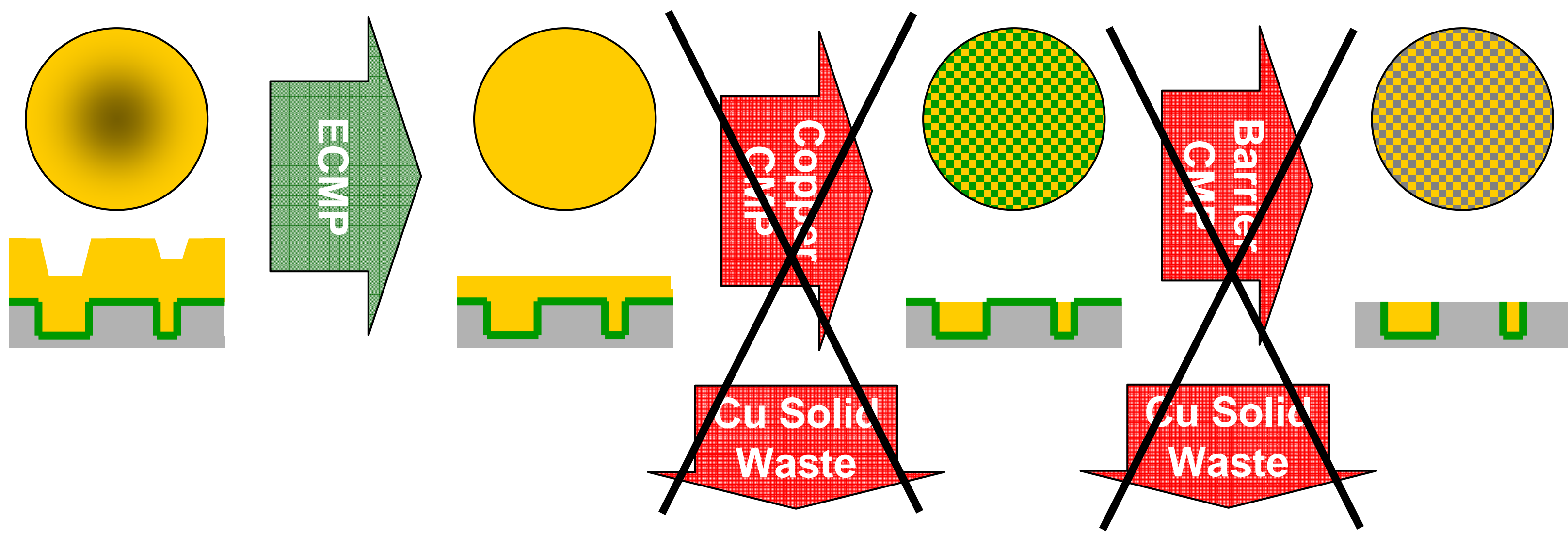
- **Experimental support, Albany Nanotech**

Objectives

- **Develop models for ECMP (bulk copper, full copper, and barrier removal steps) at the:**
  - wafer-scale
  - chip-scale
  - feature-scale
- **Develop control and optimization strategies utilizing integrated models**
  - minimize process time, consumables usage
  - maximize uniformity, yield



ESH Metrics and Impact

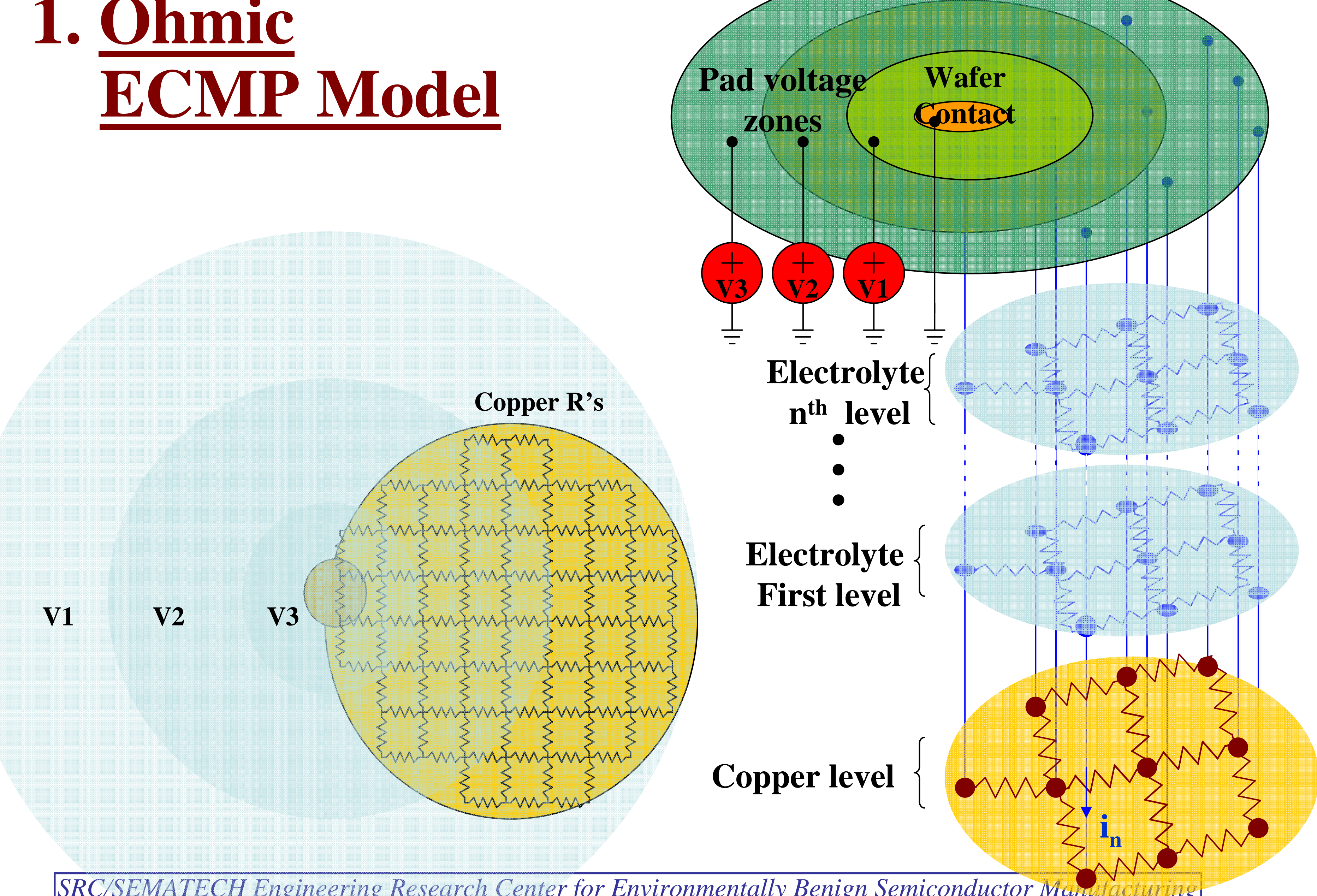


1. ***Reduction in the use or replacement of ESH-problematic materials***
2. ***Reduction in emission of ESH-problematic material to environment***
   - **Reduce or eliminate solid slurry particle waste**
     - Eliminate copper touch-down CMP (eliminate ~20% of planarization cycle)
     - Lower solid content barrier ECMP (~80% solids reduction in this step)
3. ***Reduction in the use of natural resources (water and energy)***
   - **Shorten process cycle time by ~20%**
   - **Increase in pad lifetime (5X)**
4. ***Reduction in the use of chemicals***
   - **Replace CMP slurry with more benign ECMP electrolyte**

ECMP – Wafer Scale Modeling Approach

- **Cu removal rate across wafer as function of:**
  - Initial copper thickness (e.g. nonuniform plating profile)
  - Applied voltages in multiple zones in ECMP tool
  - Tool/process parameters: geometry of electrical contact to wafer, velocity, pressure
- **Semi-physical model**
  - Model structure based on physics of process
  - Fit to experimental characterization data
- **Two models considered:**
  1. Ohmic: voltage drops vertically/laterally in electrolyte
  2. Nonlinear: focus on electrochemical dependence at electrode (ignore lateral voltage drop in electrolyte)

1. Ohmic ECMP Model



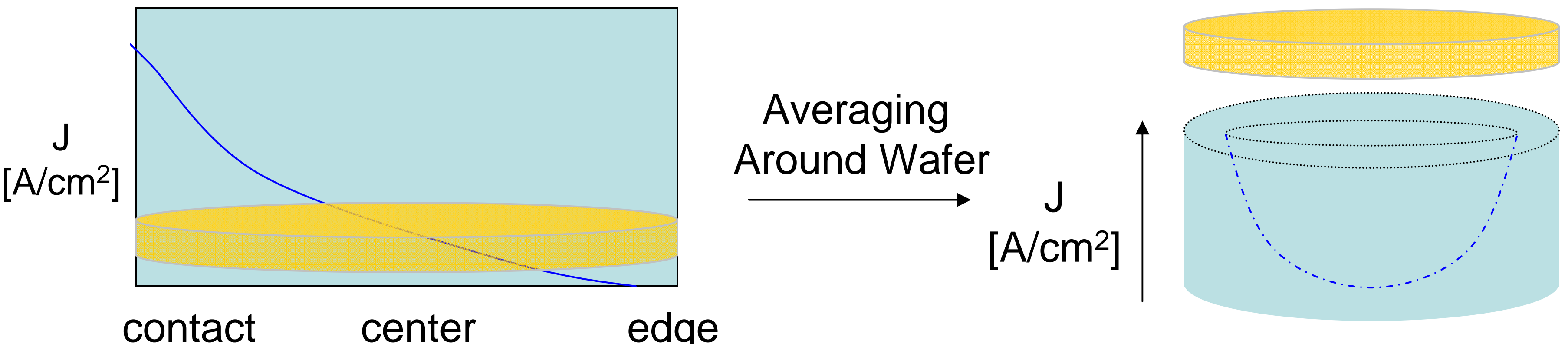
Ohmic ECMP Model Approach

- **Calculate static current density to calculate removal**

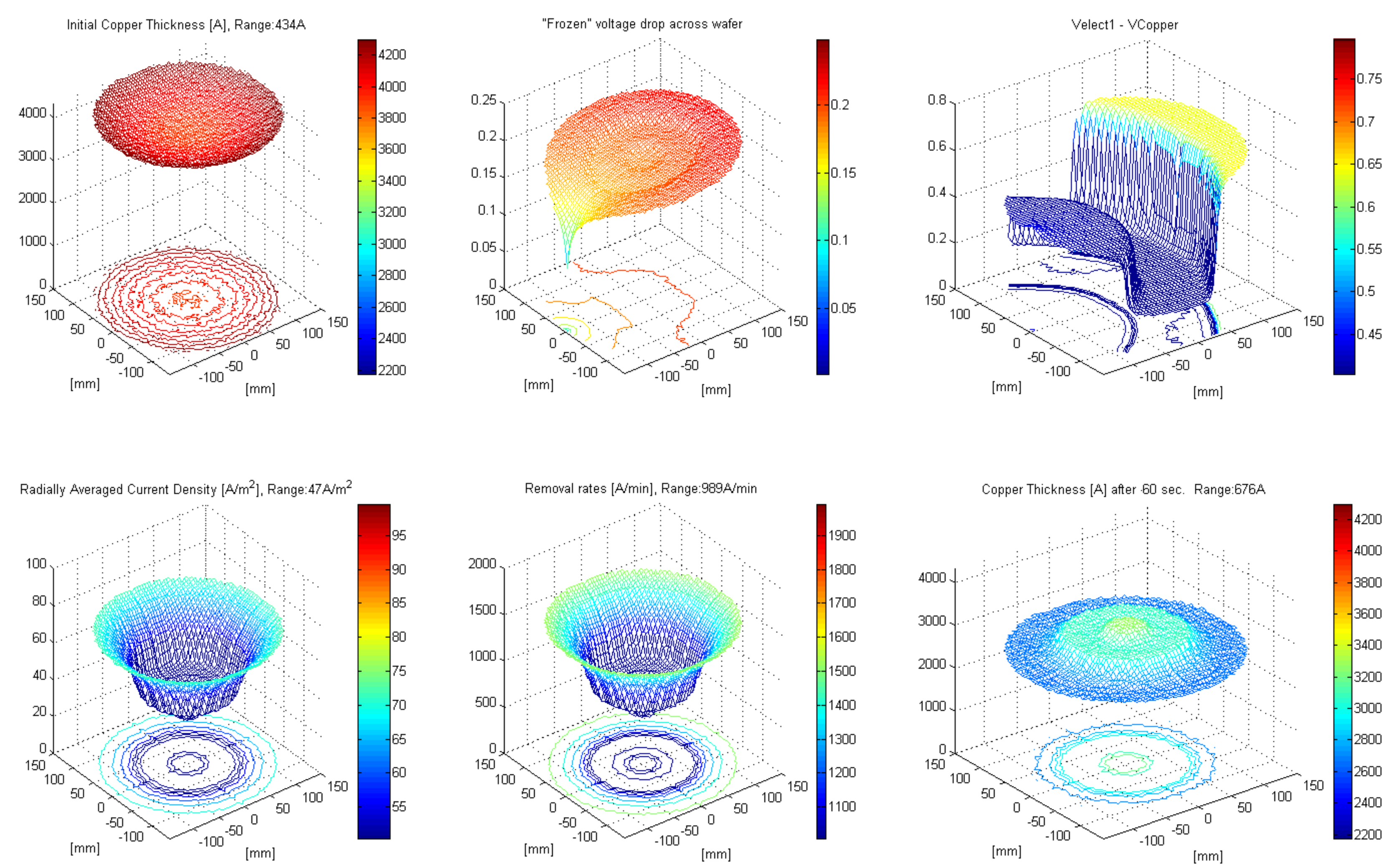
$$I\left[\frac{C}{sec}\right]\cdot\frac{1}{\text{area }[cm^2]}\cdot\frac{1\,atom_{Cu}}{2e^-[C]}\cdot\frac{1\,mole_{Cu}}{N_A\,atoms_{Cu}}\cdot\frac{63.546\,g_{Cu}}{1\,mole_{Cu}}\cdot\frac{1\,cm^3}{8.941\,g_{Cu}}\cdot\frac{10^7\,nm}{1\,cm}\cdot\frac{60\,sec}{1\,min}=RR\left[\frac{nm}{min}\right]$$

$$area_{wafer}=683.4cm^2\rightarrow\frac{RR}{I}=31.02\frac{nm}{A\cdot\min}$$

- **Average radially and calculate removal rate**
- **Add static etch rate and calculate time interval's amount removed**
- **Update thickness and iterate**



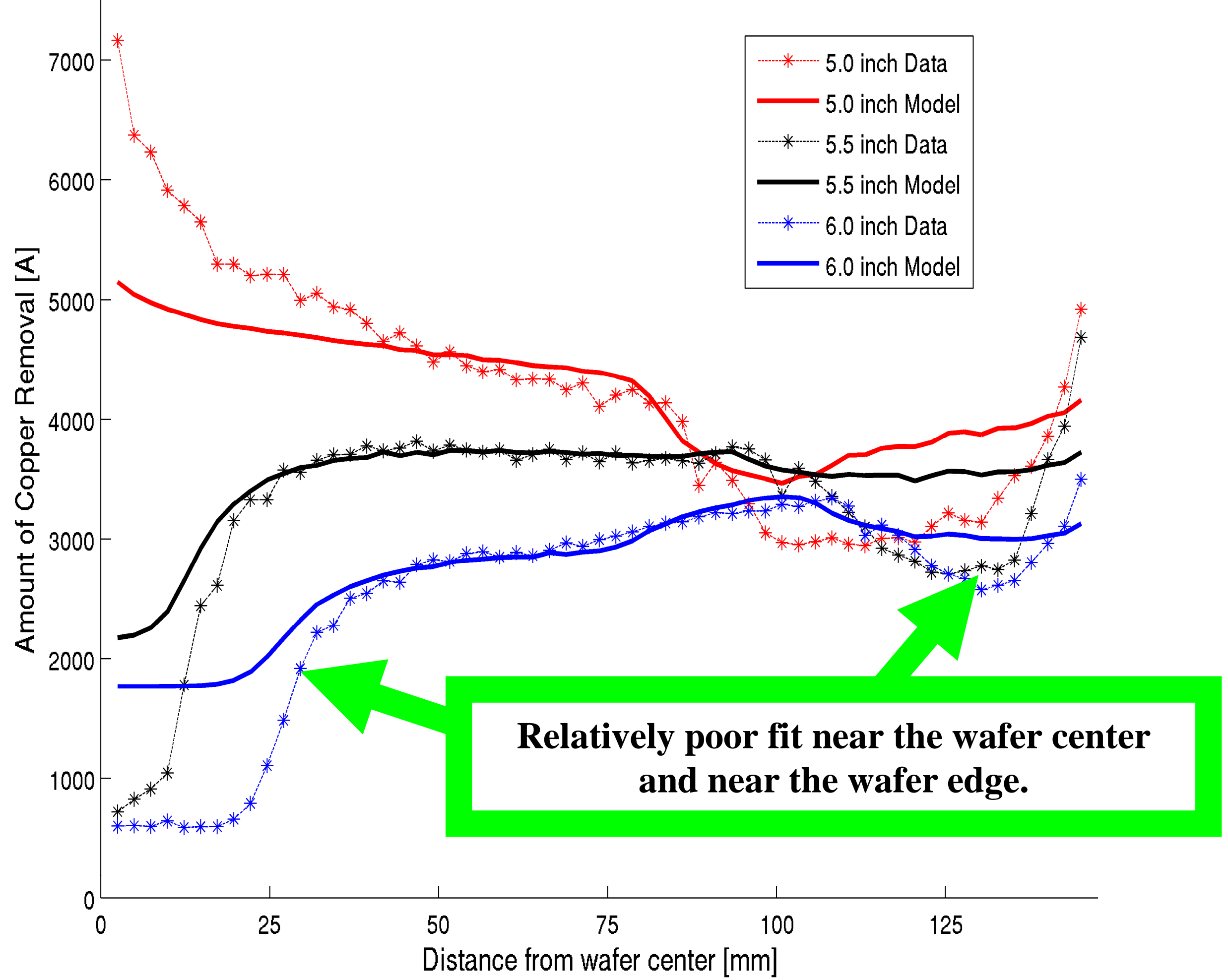
Ohmic ECMP Model Results: t = 10 sec



Ohmic ECMP Model Experiments & Results

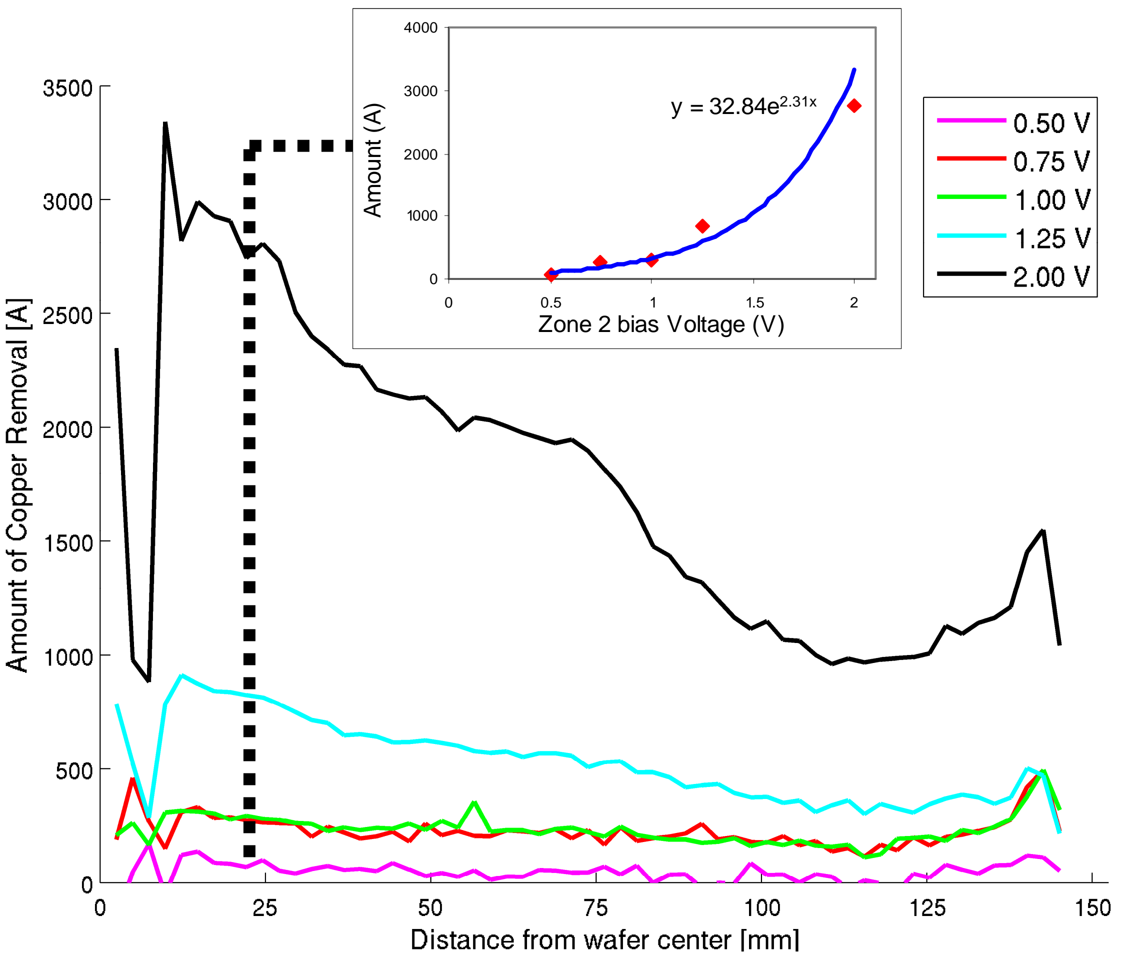
- **Collaboration with Albany Nanotech**
- **Experiment:**
  - **Different voltages on different zones – intentionally introduce nonuniformity to aid in modeling**
  - **Measure Cu thicknesses on blanket films before and after**
  - **With and without head sweep (to better localize kinematics)**
- **Revised numerical implementation of model**
  - **Better handling of zero-current boundary conditions**
- **Results: Model accuracy limitations**
  - **Nonlinear voltage dependence**
  - **Does not fit well near center of wafer**
  - **Edge region – difficult to fit**

Ohmic ECMP Model Results – Different Voltages in Each Zone



Amount of copper removal for head position L of 5.0, 5.5, and 6.0 inches, and voltage zone settings of *V1, V2, V3* = 2, 1, 3 V. Basic ohmic model versus data. The RMS error of this fit is 531 Å.

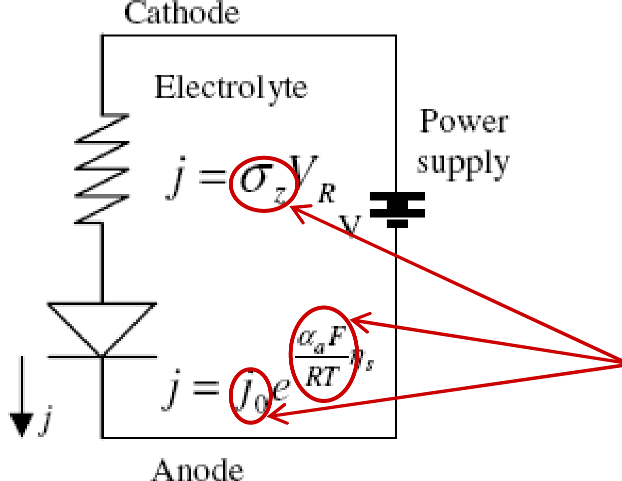
Removal is Nonlinear in Applied Voltage



Experimentally measured copper removal for five different values of *V2* (with *V1* = *V3* = 0V, L = 6.0 inch). Figure inset shows the observed nonlinear relationship between *V2* and the removal amount (current density) for one selected wafer radius.

2. Non-Ohmic ECMP Model

- **Account for nonlinear (exponential) Butler-Volmer electrochemical dependence at the wafer surface using a simple equivalent diode electrical model**
- **1D implementation**
  - **Neglect voltage drop across wafer (highly conductive copper film)**
  - **Neglect lateral coupling and current flow in the electrolyte**



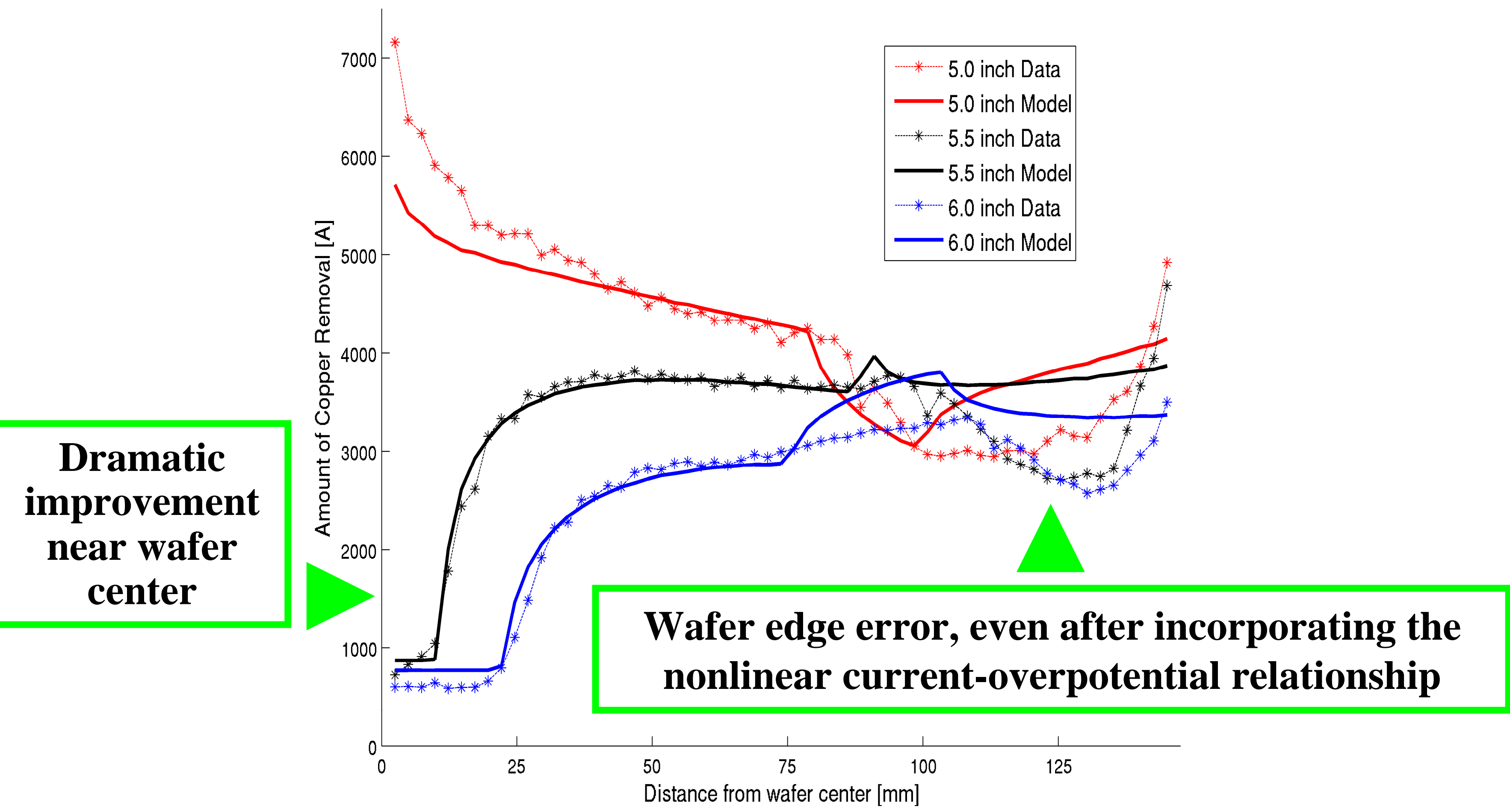
Assumptions:

1. Conduction and Faradaic current are equal
2. Instantaneous /complete removal of surface layer
3. Removal of passivation layer by zone
4. "Best fit" values for V_o, J_o, & σ
5. Only anodic reaction contribution

Removal Rate (J,t))

$$t \cdot \frac{J \cdot C}{s \cdot cm^2} \cdot \frac{1Cu}{2e^-} \cdot \frac{1molCu}{N_A \cdot Cu} \cdot \frac{63.54gCu}{1mols} \cdot \frac{cm^3}{8.96g} \cdot \frac{1e^-}{1.67 \times 10^{-19}C} \cdot \frac{10^7 nm}{1cm} = nm$$

Non-Ohmic Model Results



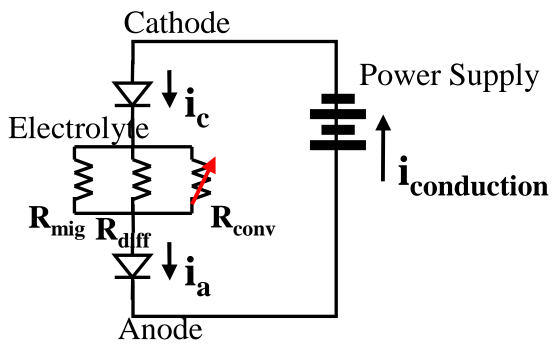
Amount of copper removal for L = 5.0, 5.5, 6.0 inch, and voltage zone settings of *V1, V2, V3* = 2, 1, 3 V. Non-ohmic model versus data. The RMS error of this fit is 412 Å, a 22% improvement.

Next Year Plans

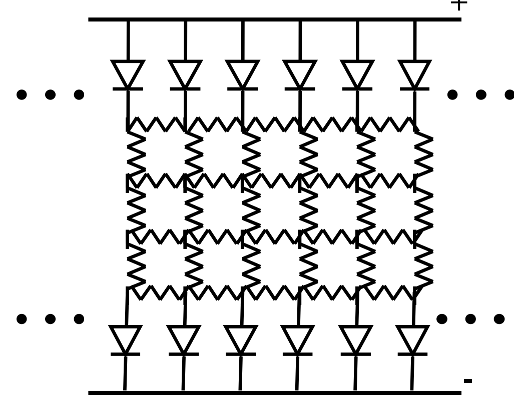
- Improve wafer scale ECMP model physics
  - Two electrode model with electrochemistry
  - Consider dynamics of protective film formation/removal
- Implement 2D/3D version of wafer scale model
  - Cross-coupling in electrolyte; thin film resistance for full copper removal
- Analysis of conductive pad configuration
- Begin feature/chip-scale ECMP model development

3. Full Electrochemical Non-Ohmic ECMP Model

1-D View:
[without lateral coupling current]

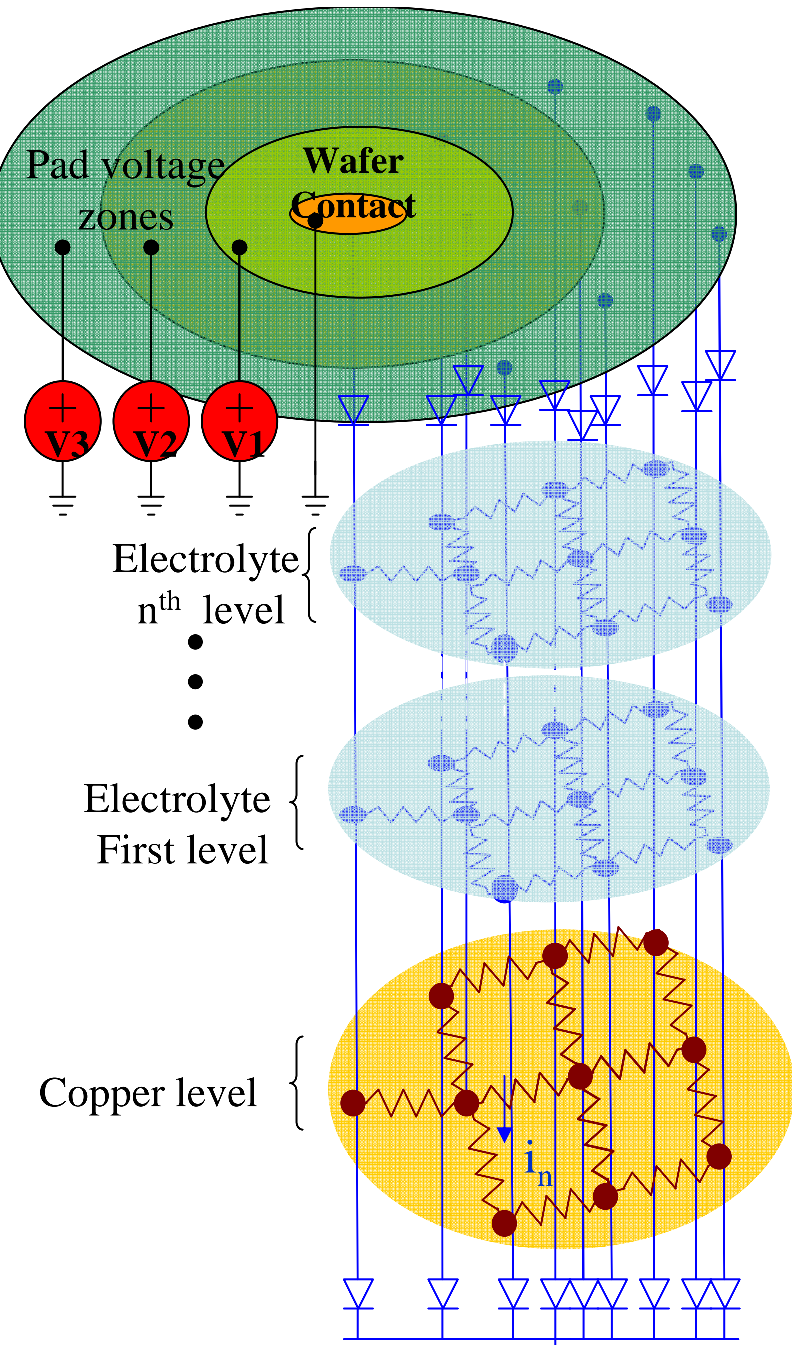


2-D View:
[with lateral coupling current]

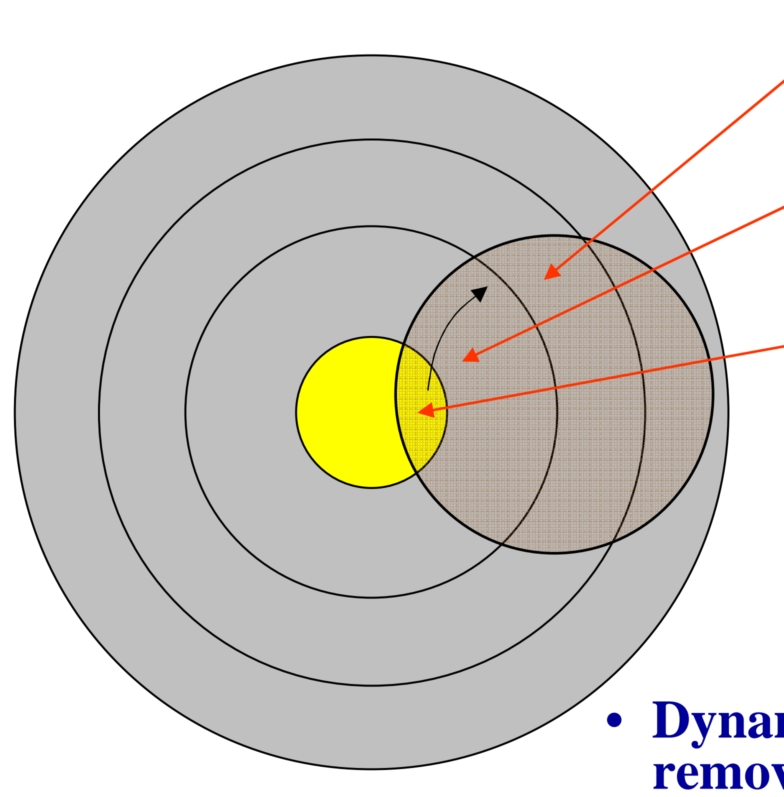


Assumptions:

1. Anodic & cathodic electrochemical current contributions
2. *Lateral coupling current contributions
3. Faradaic current and conduction not always equivalent
4. Instantaneous and complete removal of surface layer
5. Neglect voltage drop across the wafer (highly conductive copper film)
6. *Passivation layer formation and removal effects on the time-averaged voltage



Possible Passivation Kinetics Effects



3. Electropolish of exposed copper (where passivation removed)

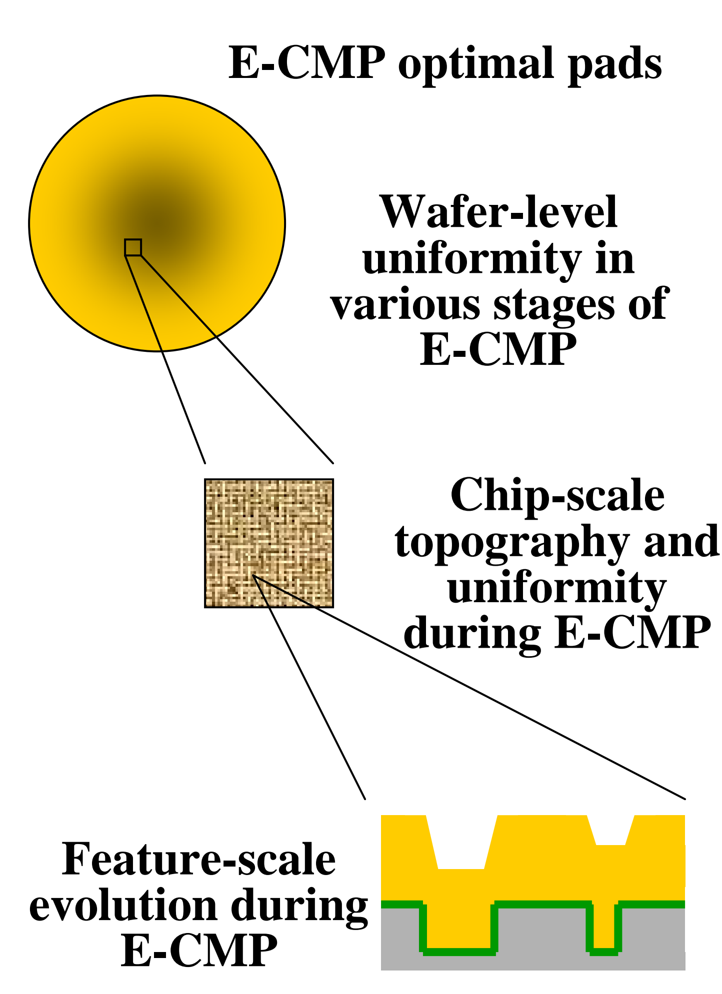
2. Polishing pad begins removal of passivation layer, but not instantaneous

1. While in contact with beads, passivation layer may develop (cannot be instantaneous, else lose electrical contact with wafer)

- **Dynamics of passivation layer formation and removal may affect the time-averaged voltage & current that different regions on the wafer experience**
  - **Explain model prediction errors near wafer edge?**

Extension Program Plans

- Integrated feature, chip and wafer-scale ECMP model
  - Incorporate electrochemical effects for range of chemistries, metals/barriers (developed by Raghavan, West)
- Design of pads for ECMP (with Raghavan, Philipossian)
  - Electrical contact modeling: metal vs. other conductive layers
  - Placement of contacts for controlling electric field distribution, and implication for performance and uniformity
    - Modeling and optimization
  - Pad property optimization
    - For feature, chip, and wafer scale performance and uniformity in ECMP
- Optimization and control strategies for maximized uniformity and minimized process consumption/time



Industrial Interactions and Technology Transfer

- **Albany Nanotech (Chris Borst)**
  - **ECMP experiments on blanket wafer copper removal**
  - **Modeling for wafer-scale ECMP as a function of position, zonal electrical bias**

Publications, Presentations, and Recognitions/Awards

- D. Truque, X. Xie, and D. Boning, "Wafer Level Modeling of Electrochemical-Mechanical Polishing (ECMP)," CMP Symposium, MRS Spring Meeting, April 2007.
- Z. Li, D. Truque, D. Boning, R. Caramto, and C. Borst, "Modeling Wafer Level Uniformity in Electrochemical-Mechanical Polishing (ECMP)," Advanced Metallization Conference, Albany, NY, Oct. 2007.

Students on Task 425.014

- Graduated Students and Current Affiliation
  - Daniel Truque (M.S.), McKinsey, 6/2007
- Current Students and Anticipated Grad Date
  - Joy Johnson (M.S.), 6/2009
  - Wei Fan (Ph.D.), 6/2011
  - Zhipeng Li (B.S.), 6/2009
- Internships
  - None this year

Environmentally Benign Electrochemically-Assisted Chemical-Mechanical Planarization (E-CMP)

(*Task Number: 425.014*)

Experimental Investigation of Cu and Ta E-CMP Processes

PI:

- **Srini Raghavan, Department of Materials Science and Engineering, UA**

Graduate Student:

- **Ashok Muthukumaran: PhD candidate, Department of Materials Science and Engineering, UA**

Undergraduate Student:

- **Raymond Lee, Department of Materials Science and Engineering, UA**

Cost Share (other than core ERC funding):

- **In-kind donation (patterned wafers) from Intel :$10,000**

Objectives

- Optimize dihydroxybenzene sulfonic acid (DBSA) based chemical system for electrochemical mechanical **removal of Ta with a 1:1 selectivity with respect to copper**
- Evaluate DBSA based chemical system for the removal of TaN under ECMP conditions
- Working with an industrial partner (Intel), fabricate a test structure for additional evaluation

ESH Metrics and Impact

- ECMP Electrolyte
  - Requires very low solid content (~ 0.1 wt%) as compared to ~ 10 wt% solids in conventional Ta CMP slurry

- Low toxicity of DBSA

Compound	LD_{50} (rat)	Carcinogenic
DBSA	> 5000 mg/kg	NO
Catechol	260 mg/kg	YES
Benzotriazole	965 mg/kg	NO

- EHS Impact

Goals	Usage Reduction		Waste Reduction	
	Chemicals	Abrasives	Solid	Liquid
Using full sequence ECMP	N/A	> 90%	> 99%	N/A

Current Year Activities

- During the last contract year, Di-hydroxybenzene Sulfonic acid (DBSA) was shown to have promise as a chemical agent suitable for ECMP of Ta

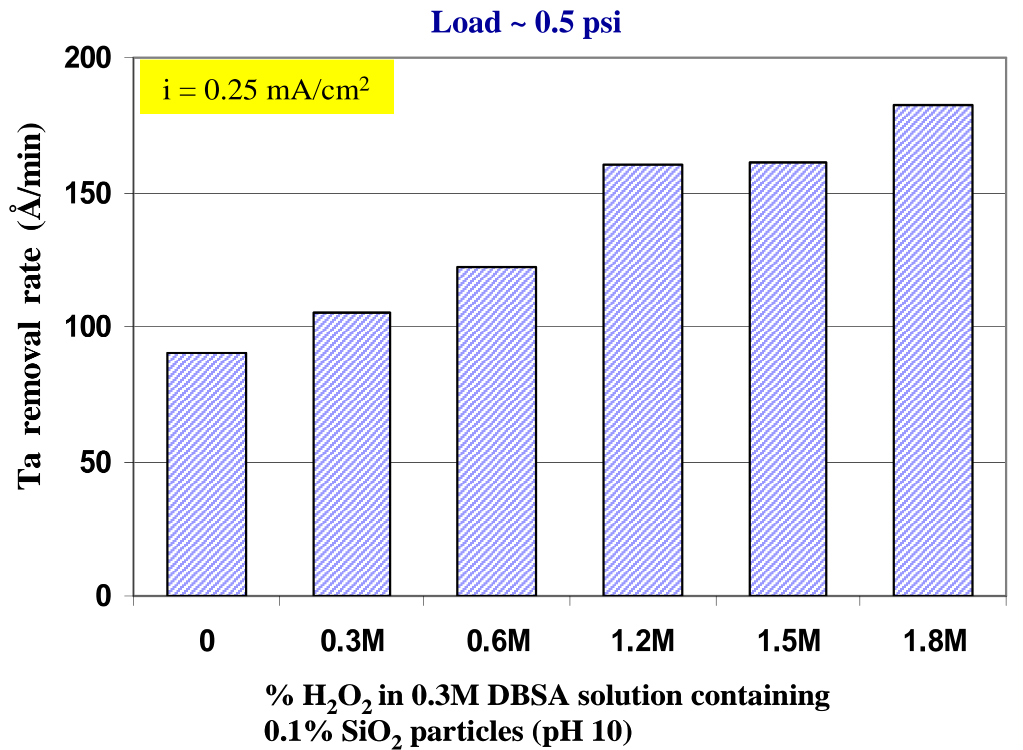
In the current contract year, optimization of DBSA based chemical system has been done to obtain a Ta removal rate of ~ 200 Å/min with a 1:1 selectivity with respect to Cu

  - Variables Optimized: Peroxide Concentration, pH, Current density

- Used optimized formulation for the removal of TaN

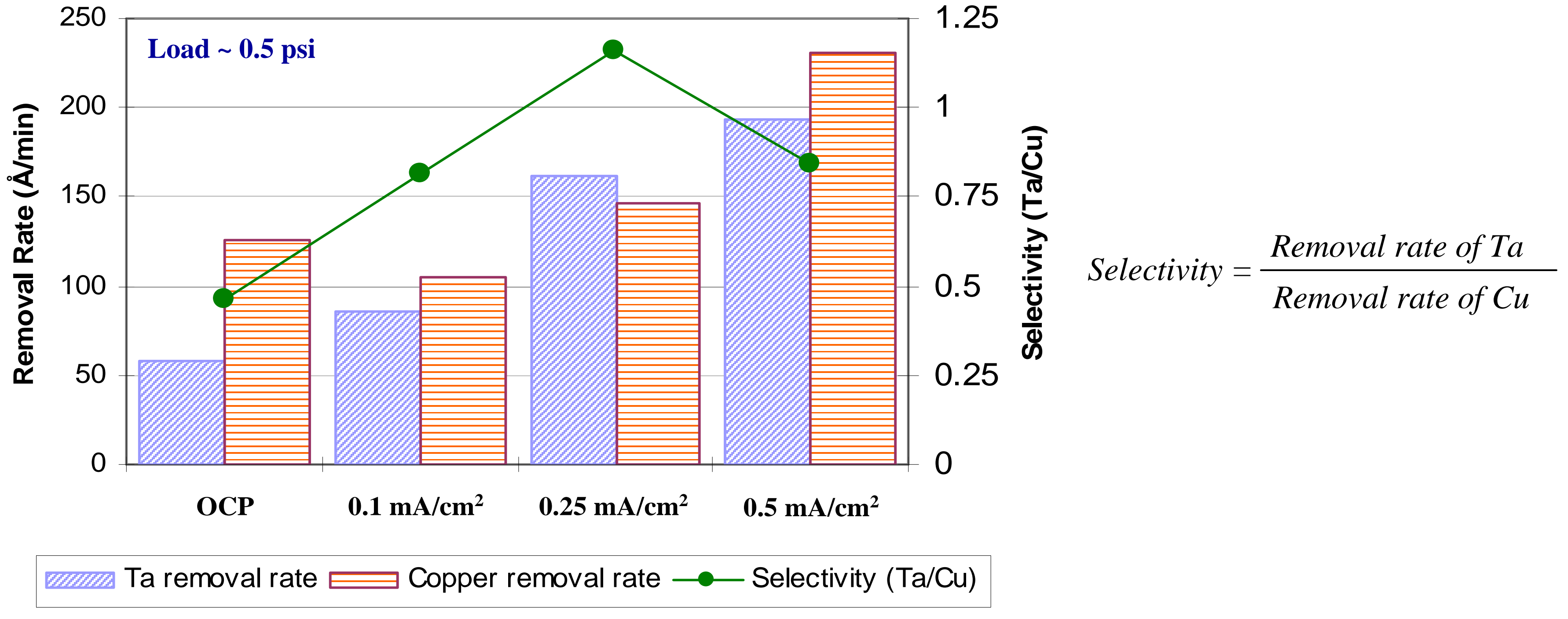
- Fabricated a patterned test structure and conducted experiments to verify blanket wafer results

Effect of Peroxide Concentration on Ta Removal



- 0.3M DBSA solution (pH 10) containing 0.1% of 80 nm SiO_2 particles ; current density = **0.25 mA/cm^2**
- Removal rate of tantalum is 90 Å/min in the absence of peroxide
- **Addition of 1.2M peroxide, increases the removal rate to 160 Å/min**
- Peroxide concentration greater than 1.2M increases the removal rate only marginally

Effect of Current Density on Removal Rate and Selectivity (Ta/Cu)



$$Selectivity = \frac{Removal\ rate\ of\ Ta}{Removal\ rate\ of\ Cu}$$

- 0.3 M DBSA solution + **1.2M H_2O_2** + 0.1 % SiO_2 **(pH 10)**
- Ta removal rate of **~ 200 Å/min** at 0.5 mA/cm^2 (corresponding to 1 V overpotential)
- Selectivity (Ta/Cu) of **1.2:1** and **0.85:1** at 0.25 and 0.5 mA/cm^2, respectively

Proposed Mechanism and Current Efficiency

➢MECHANISM OF Ta REMOVAL

- Ta undergoes an **interfacial 2 e⁻ transfer reaction** forming TaO on the surface

$Ta + H_2O \rightarrow TaO(surface) + 2H^+ + 2e^-$

- TaO is further oxidized and dissolved by H_2O_2 and DBSA in the bulk solution to form complexes of the type,

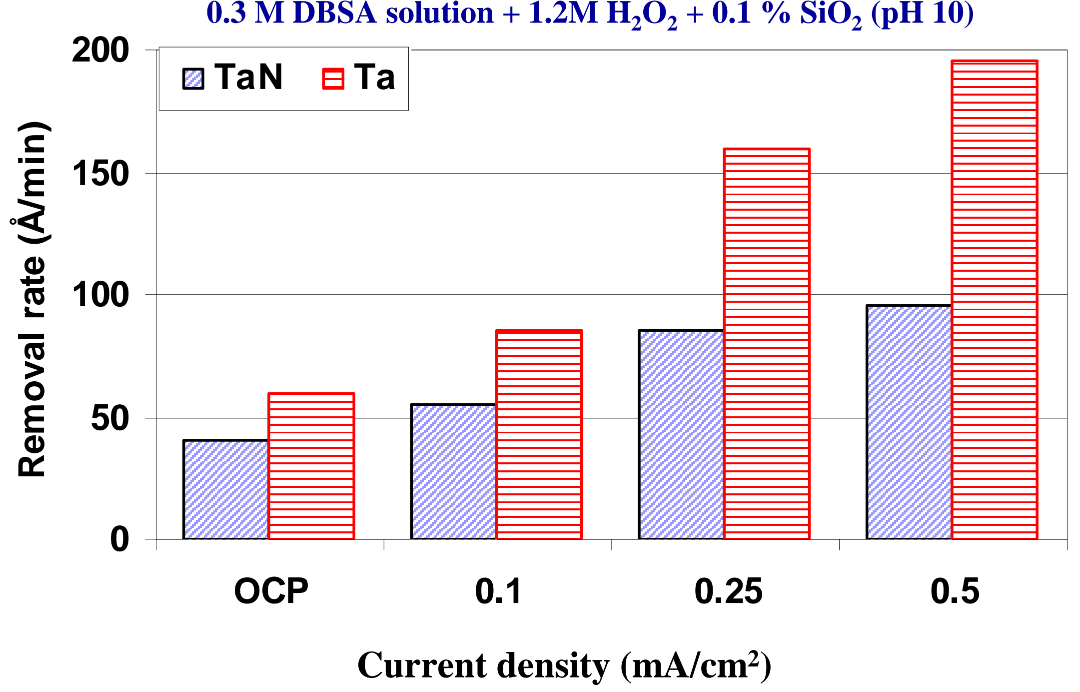
$TaO(s) + x\ H_2O_2\ (bulk) + y\ L \rightarrow [Ta(O_2)_x L_y]^{3-}$

where x = {1,2,3} with corresponding y ={6,4,2} and **L represents one ionized DBSA molecule**

Applied current density (mA/cm^2)	Estimated removal rate (Å/min) of tantalum based on $2e^-$ transfer	Actual removal rate of tantalum (Å/min) in 0.3M DBSA + 1.2M H_2O_2 + 0.1% SiO_2 (pH 10)	Calculating current efficiency (%) after correcting for OCP removal rate
OCP	-	60	-
0.1	34	85	80
0.25	85	160	109*
0.5	169	195	81

Note: * Current efficiency greater than 100% most likely due to analytical error

Evaluation of DBSA for TaN Removal



Schematic representation of barrier stack

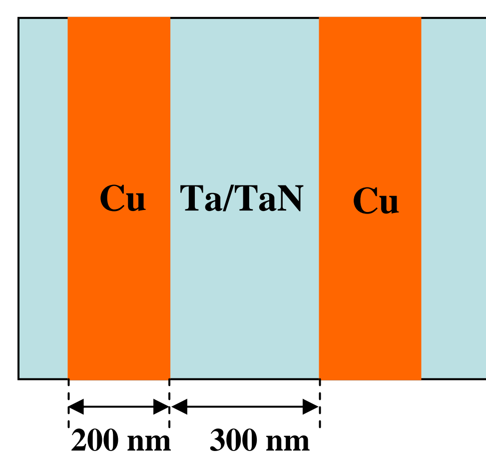
- At i = 0.5 mA/cm^2
  - TaN removal rate ~ 100 Å/min
  - Ta removal rate ~ 200 Å/min

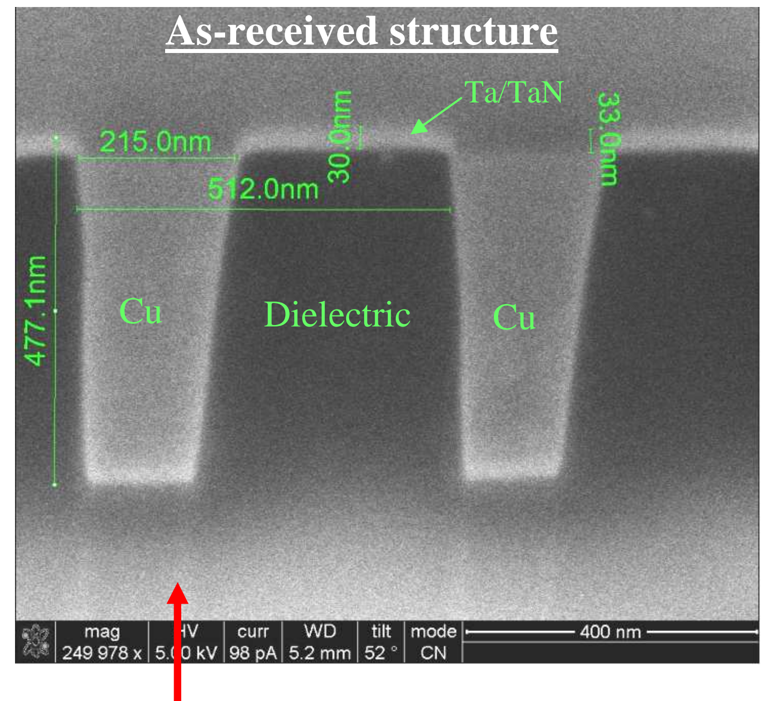
Potassium salt of dihydroxy benzene sulfonic acid

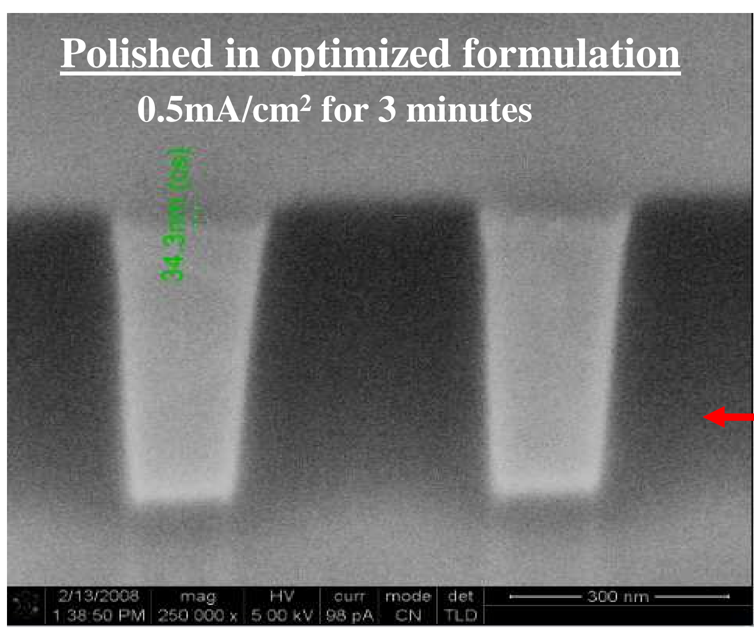
DBSA is not as effective for TaN as it is for Ta

ECMP of Patterned Structure in Optimized Formulation

Schematic of patterned structure

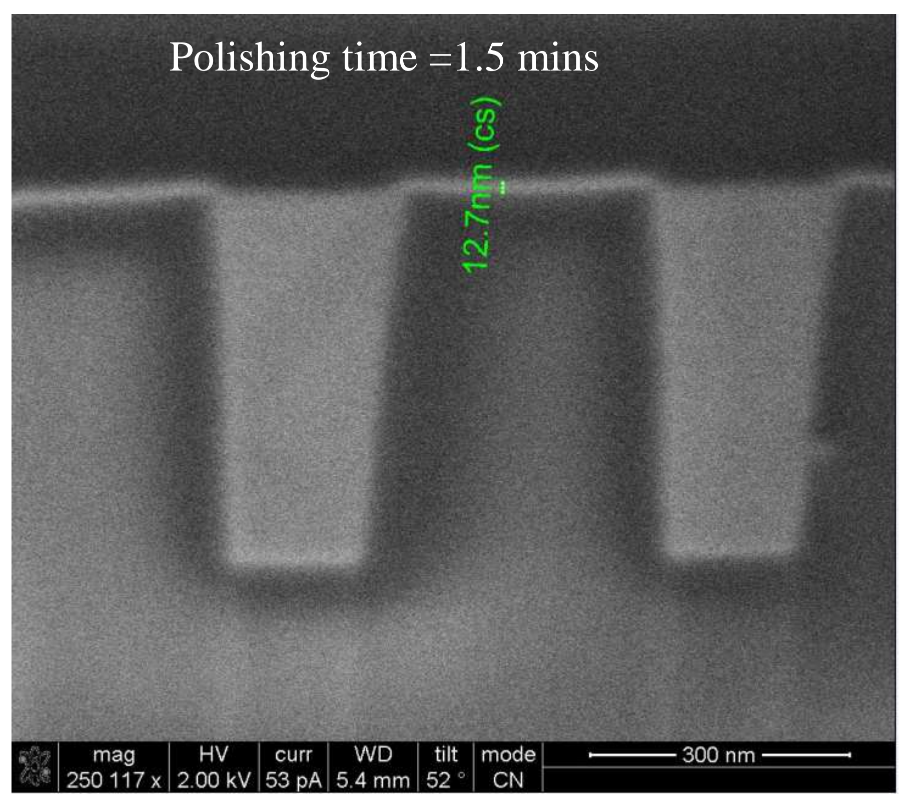


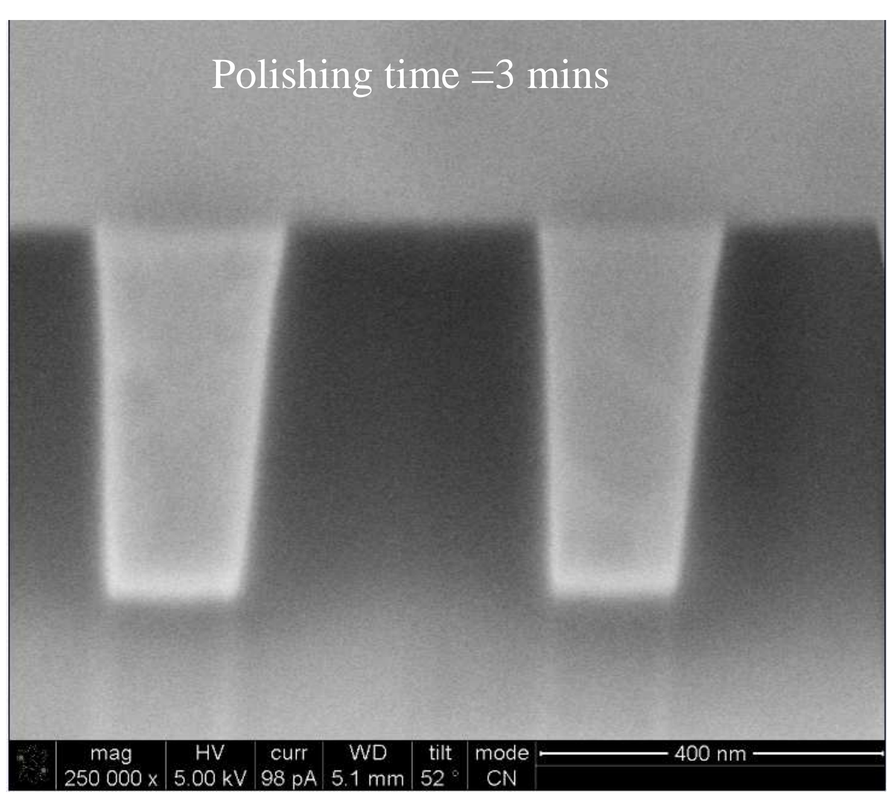




- As received test structure : Cu removed on platen 1 and 2 stopping on Ta.
  Note ~ 30 nm Cu recess
- Barrier layer is removed; however surface planarity NOT achieved (step height between the dielectric and Cu ~ 34nm)

ECMP of Patterned Structure in Optimized Formulation with BTA





- Barrier layer thickness and step height reduced to ~ 13 nm

- Barrier film is completely removed and the surface appears to be ***planar***

Note: Test structure polished in 0.3M DBSA solution containing 1.2M H_2O_2, 0.1% SiO_2 and **0.01M BTA** (pH 10) at 0.5 mA/cm^2

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Summary

- Ta removal rate of ~ 200Å/min obtained in 0.3 M DBSA solution containing 1.2M H_2O_2 and 0.1% SiO_2 (pH 10) at i = 0.5 mA/cm^2
- Ta/Cu selectivity of ~ 1:1 observed at pH 10 at a current density of 0.5 mA/cm^2 (oxide removal rate in the formulation ~ 30 Å/min)
- DBSA is not as effective for TaN as it is for Ta
- Patterned test structure
  - Complete removal of barrier layer and surface planarity achieved by polishing in optimized solution containing **0.01M BTA**

Industrial Interactions and Technology Transfer

- Work on Ta ECMP was presented at **Applied Materials** in August 2007; the seminar was hosted by Dr. Tom Osterheld
- Technical discussions with Dr. Renhe Jia of **Applied Materials**
- Interacted with Dr. Liming Zhang, Dr.Raghu Gorantla, Dr. Michael Ru and Dr. Zhen Guo of **Intel Corporation**, Santa Clara (to design test structures)

Publications/Presentations

- A.Muthukumaran, N. Venkataraman and S. Raghavan, "Evaluation of Sulfonic Acid Based Solutions for Electrochemical Mechanical Removal of Tantalum," ***J. Electrochem. Soc***., 155 (3), pp. H184-87 (2008).
- A.Muthukumaran, N. Venkataraman, S. Tamilmani and S. Raghavan, "Anodic Dissolution of Copper in Hydroxylamine Based Solutions with Special Reference to Electrochemical Planarization (ECMP)," ***Proceedings of The Corrosion Control 007 Conference***, Australia, Paper 105, 8 pp (2007).
- A.Muthukumaran and S. Raghavan, "Sulfonic Acid Based Chemistries for Electrochemical Mechanical Removal of Tantalum," ***TECHCON***, Texas, Sep 10-12 (2007).
- A.Muthukumaran, N. Venkataraman, V. Lowalekar and S. Raghavan, "Sulfonic Acid Based Chemistries for Electrochemical Mechanical Removal of Tantalum," ***Proceedings of the ECS - The 6th International Semiconductor Technology Conference (ISTC)***, China, 273-80 (2007).

Future Plans

Next Year Plans

- Find methods to improve TaN removal rate
  - Use of a different oxidant (ex. KIO_3)
  - Use DBSA with –OH groups in the ortho position

- Extend the studies to tungsten nitride barrier layer

- Preliminary studies on removal of self forming barrier materials such as Cu-Mn alloys

Future Plans

Long-Term Plans

- Develop chemical systems for one step removal of Cu and barrier layer

- Design of pads for ECMP
  - Electrical contacts: metal vs. other conductive layer coatings
  - Placement of contacts for controlling electric field distribution : Modeling effort (with MIT/ Boning)
  - Pad Surface and Mechanical Property Optimization for ECMP (with Philipposian and Boning)

Students on Task 425.014

- Graduated Students and Current Affiliation
  - Viral Lowalekar (2006)
  - Intel Corporation, OR

- Current Students and Anticipated Grad Date
  - Ashok Muthukumaran (graduation date 3/1/08)
  - Will be joining Novellus, San Jose

ESH Impact of Electrochemical Mechanical Planarization Technologies

(*Task Number: 425.016*)

PI:

- Alan West, Chemical Engineering, Columbia University

Graduate Student:

- Kristin Shattuck: PhD candidate, Chemical Engineering, Columbia Univeristy

Undergraduate Student:

- Neha Solanki, Chemical Engineering, Columbia University

Other Researcher:

- Jeng-Yu Lin, PhD candidate, Chemical Engineering, National Tsing-Hua University

Objectives

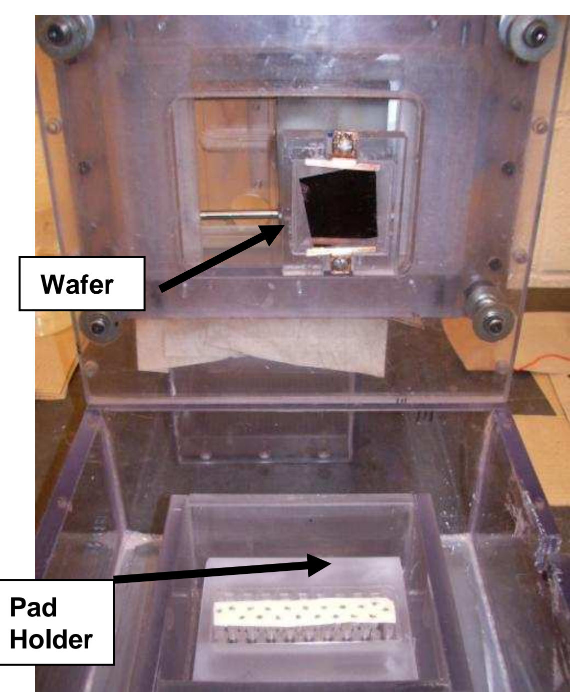
- Develop methods for planarization that optimize the use of electrochemistry and improve aspects of current technologies
- Develop a method to predict feature scale planarization through the use of planarization factors
- Test planarization capabilities of novel ECMP electrolytes using patterned structures
  - Phosphate based electrolytes containing BTA inhibitors
- Develop electrolytes for polishing liner materials
  - Ruthenium
- Study galvanic corrosion between Cu and Ru
  - Potentially utilizing microfluidics

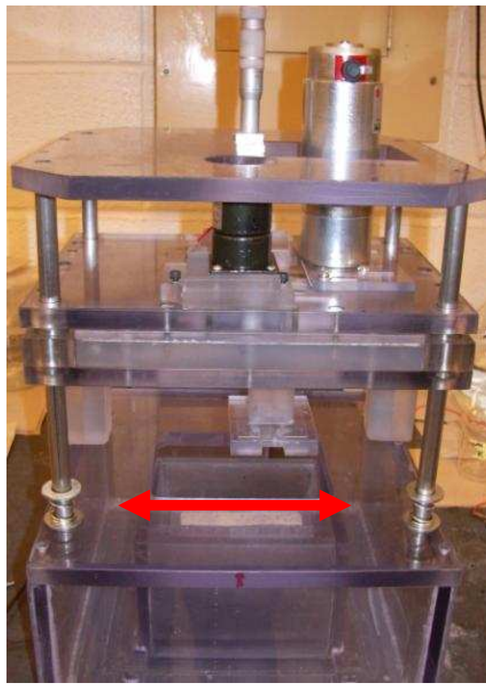
ESH Metrics and Impact

- Development of a more environmentally benign polishing electrolyte
  - Improve process yield
  - Potential elimination of slurry particles
  - Reduction or elimination of complexing agents and oxidizers in solution, facilitating waste treatment
- Potential reduction in electrolyte volume
  - Reduce waste generation
- Extend lifetime of consumables
  - Polishing pads

Method

- Screen ECMP electrolytes using an RDE
  - Potassium phosphate based electrolytes investigated
- Use custom built ECMP tool to evaluate electrolytes for their planarization capabilities
  - Compare results with RDE predictions to develop a potential screening technique and model for planarization



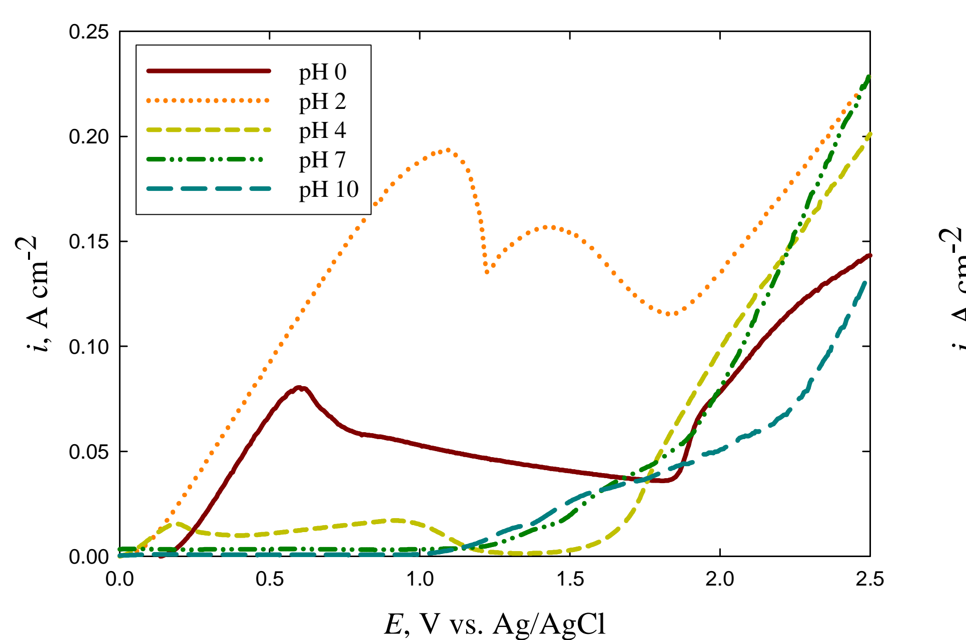


Design features:

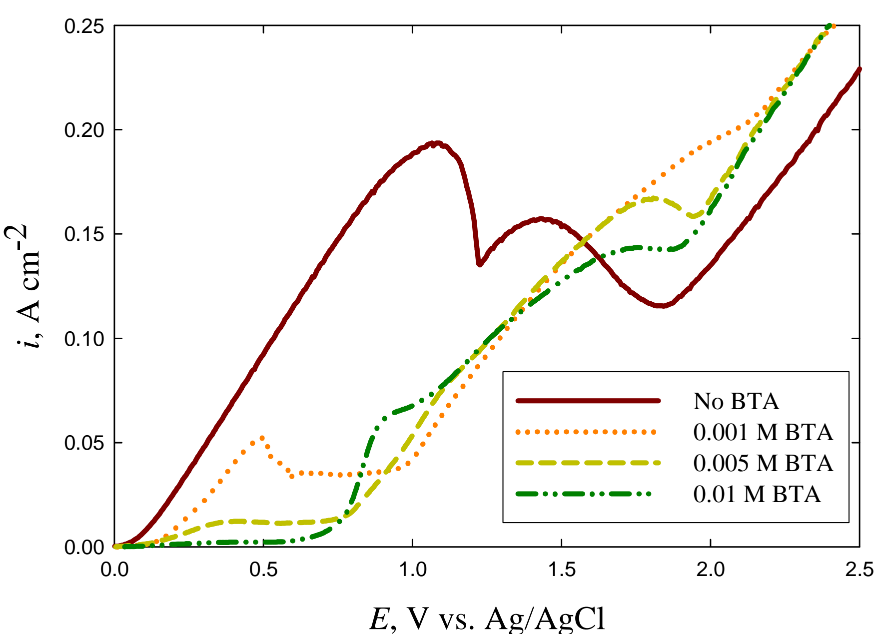
- **2D linear motion**
- **Apply and control low downforces (<1 psi)**
- **Ease of changing between various electrolytes and pads**
- **Operate in contact and non-contact modes**

Results

- pH values 0 to 10
  - No BTA



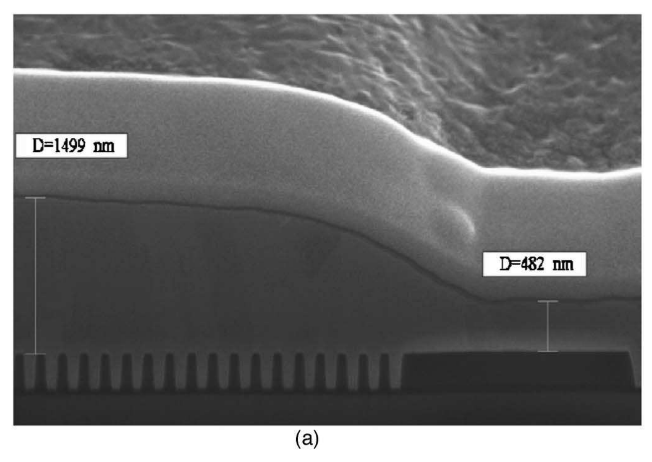
- pH 2
  - 0 to 0.01 M BTA



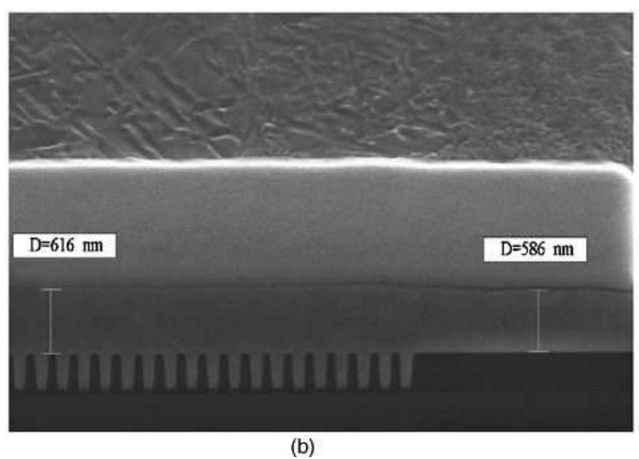
Anodic polarization curves for oxidation of a Cu RDE

Challenges

- Samples plated with 2 different electrochemical plating baths[1]



(a)



(b)

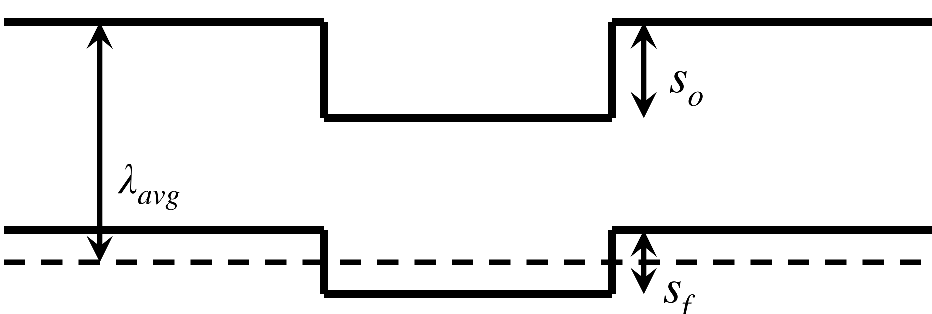
- Challenges:
  - Rates
  - Wafer-scale uniformity
  - Feature-scale planarization

[1] Willey, M. J., J. Reid, A.C. West, Adsorption Kinetics of Polyvinylpyrrolidone during Cu Electrodeposition. *Electrochemical and Solid-State Letters,* **10** 4 D38-D41 2007

Method

- Planarization is most challenging for low-aspect ratios
  - Hills or valleys: ~ 100 μ m wide; ~ 0.2 to 1.0 μ m tall
  - Can be theoretically characterized as:

$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}}$$



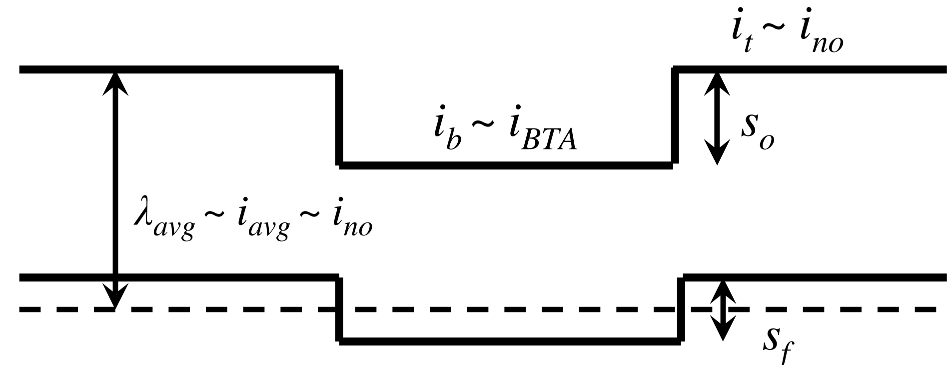
Method

- To screen potential ECMP electrolytes
  - Relate removal rate to current density

$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}} \sim \frac{i_t - i_b}{i_{avg}}$$

For Experiments Using RDE

$$\varepsilon_{RDE} = \frac{i_{no} - i_{BTA}}{i_{no}}$$



For Experiments using Tool with Blanket Wafers

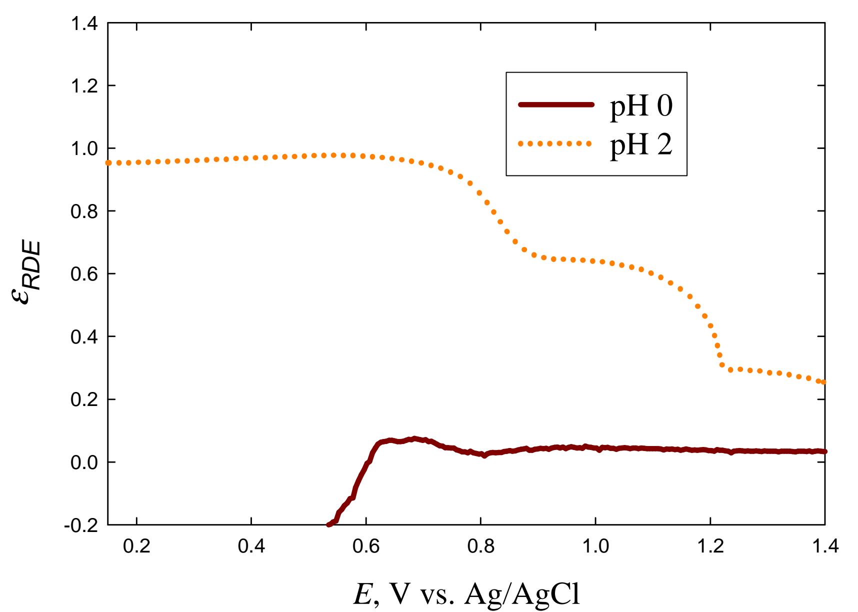
$$\varepsilon_{ECMP} = \frac{i_{pad} - i_{no-pad}}{i_{pad}}$$

Results

- Theoretical Planarization Factors

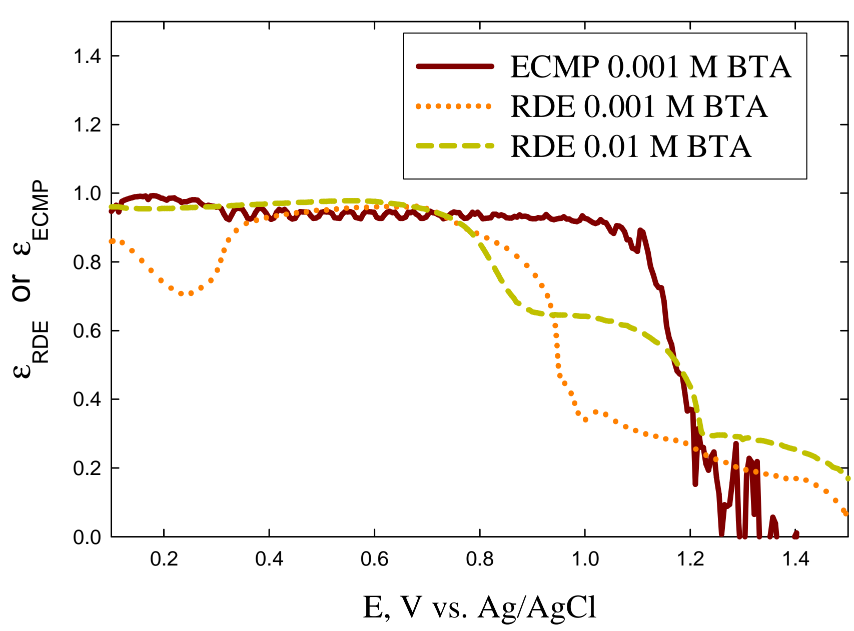
RDE

- pH 0 & pH 2
  - 0.01 M BTA



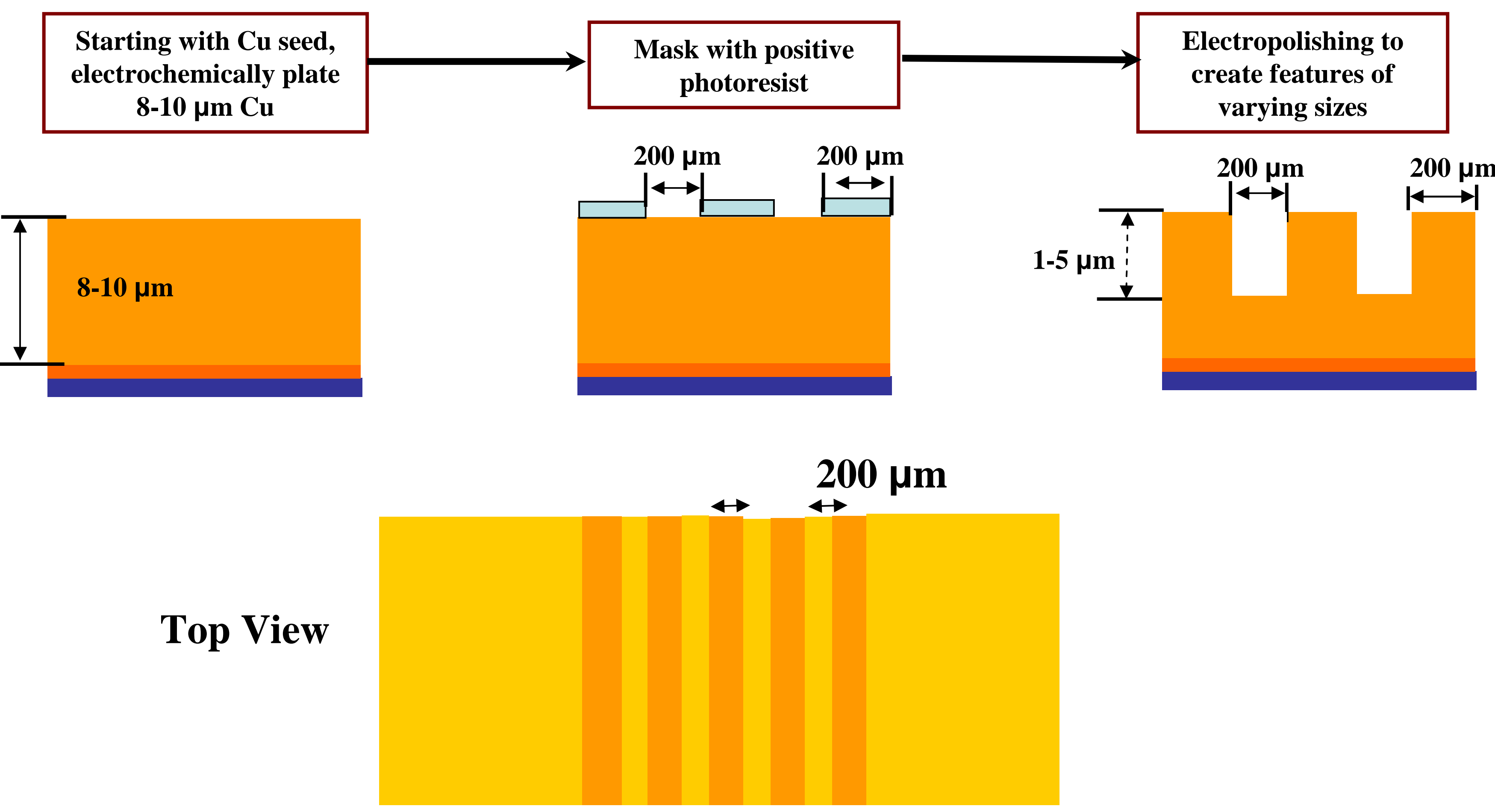
RDE & ECMP

- pH 2
  - 0.001 or 0.01 M BTA



Method

- Fabricating patterned structures



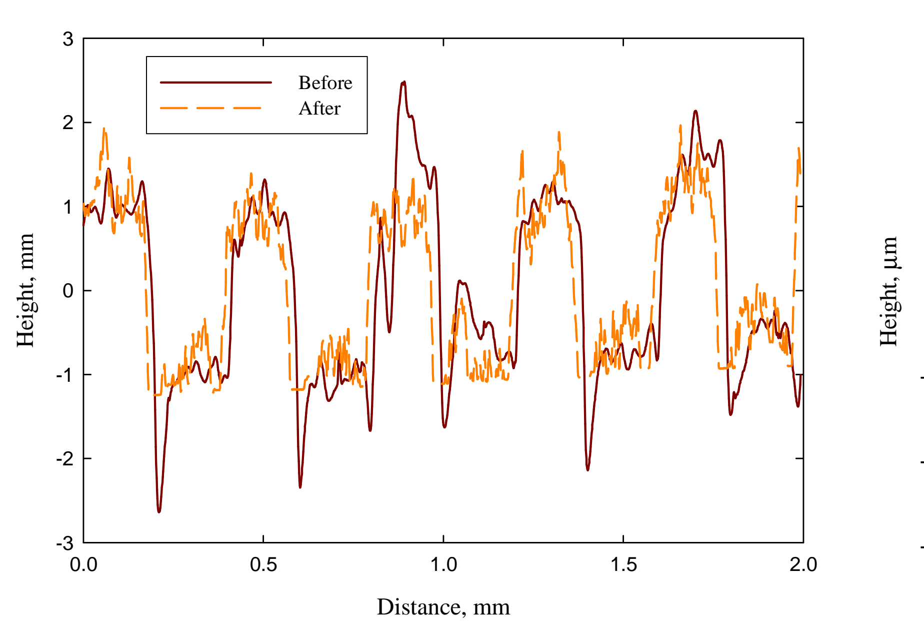
Results

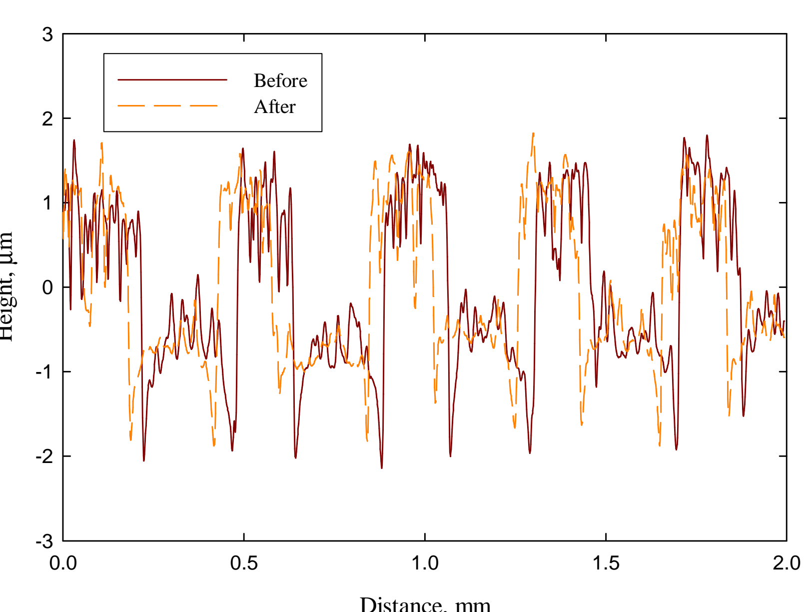
- All planarization experiments were performed at:
  - 0.5 V vs. Ag/AgCl
  - Downforce ~ 1 psi

Planarization Results – *No BTA*

No Contact

Contact





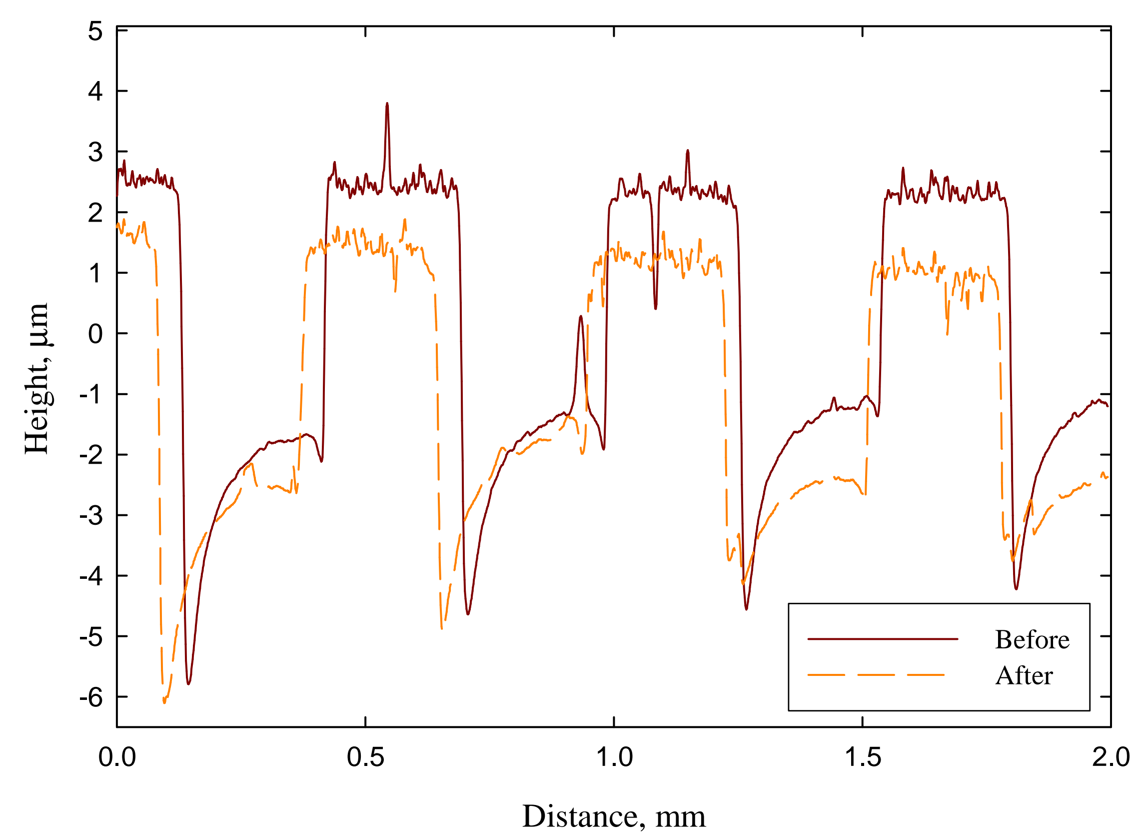
➢ **No BTA – No Planarization Achieved**

Results

- Planarization Results
  - *0.001 M BTA*
  - *D100 Pad*
    - *Grooved*

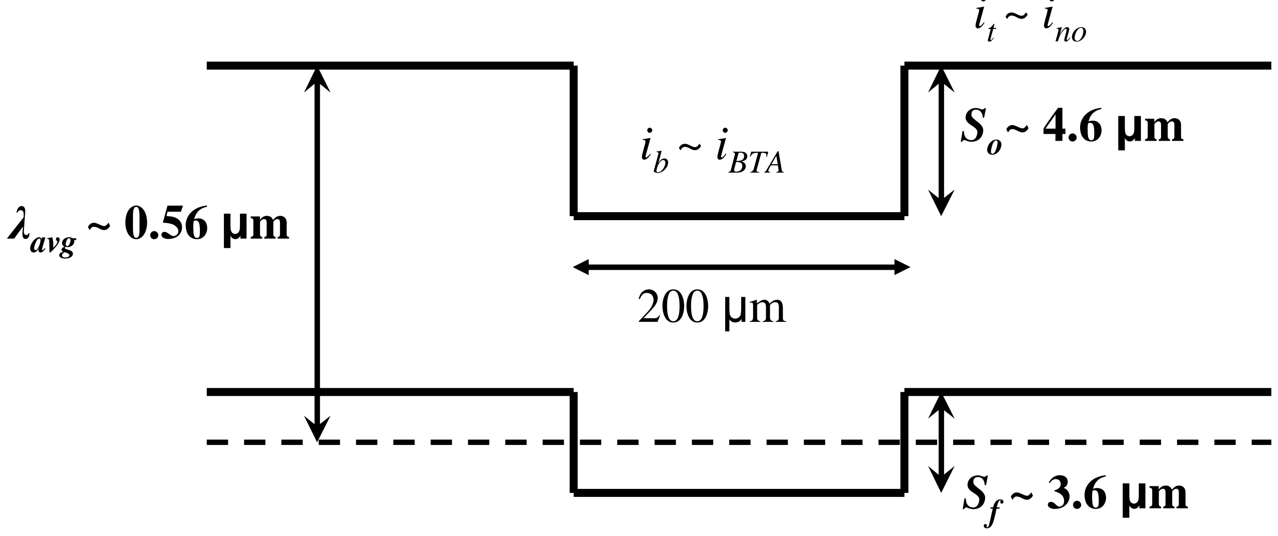
Contact – 30 s

- Step Height Reduction
  - ~ 1.0 μ m



Results

- Calculation of Planarization Factor



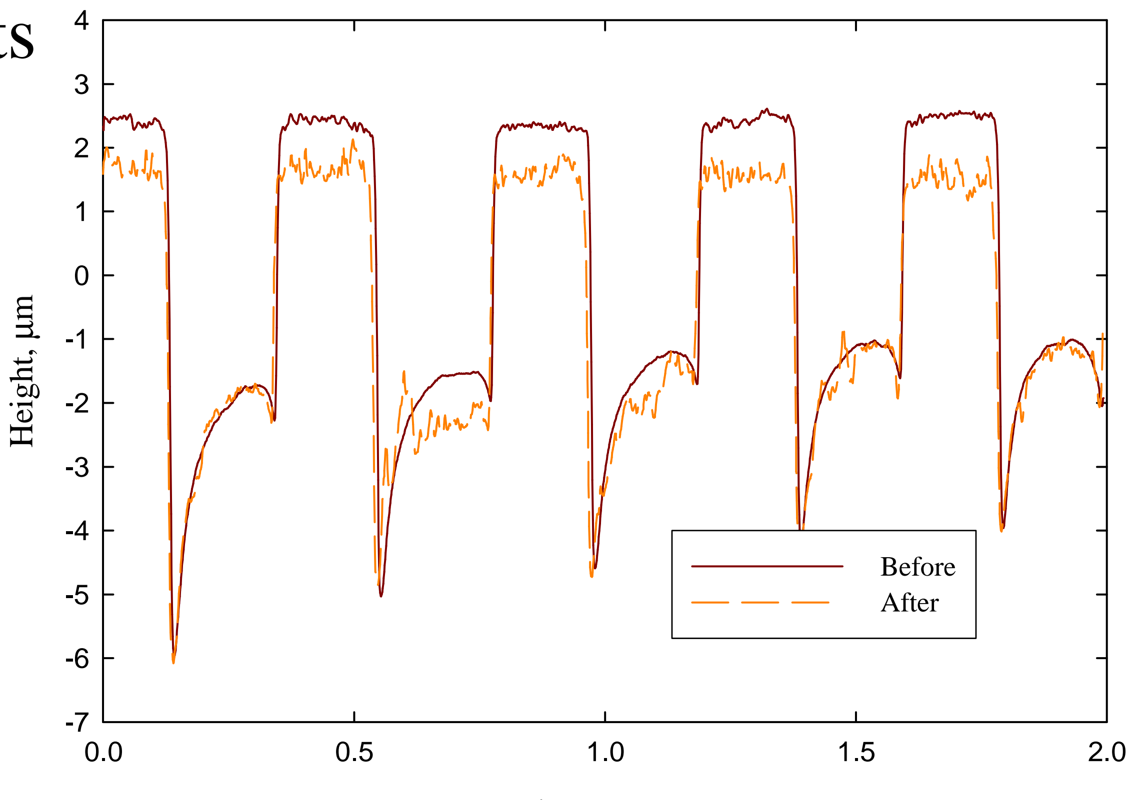
$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}} \sim \frac{4.6 - 3.6}{0.56} \sim 1.8$$

Predicted By RDE:

~ 1.9

Results

- Planarization Results
  - *0.001 M BTA*
  - *Suba Pad*
    - *No grooves*



Contact – 60 s

- Step Height Reduction
  - ~ 0.78 µ m

$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}} \sim \frac{4.1 - 3.3}{0.39} \sim 2.1$$

Predicted By RDE:

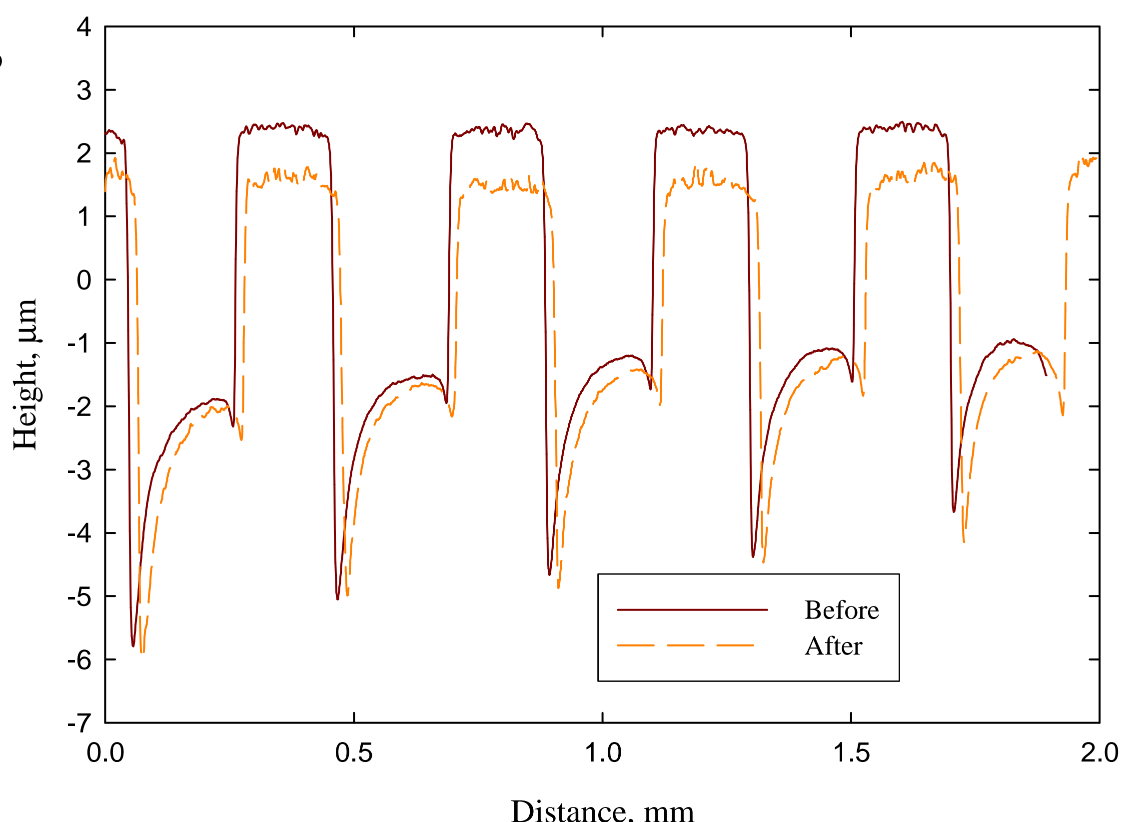
~ 1.9

Results

- Planarization Results
  - *0.001 M BTA*
  - *IC1000 Pad*
    - *No grooves*

Contact – 40 s

- Step Height Reduction
  - ~ 0.74 μ m



$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}} \sim \frac{4.4 - 3.7}{0.34} \sim 2.1$$

Predicted By RDE:

~ 1.9

Planarization Summary

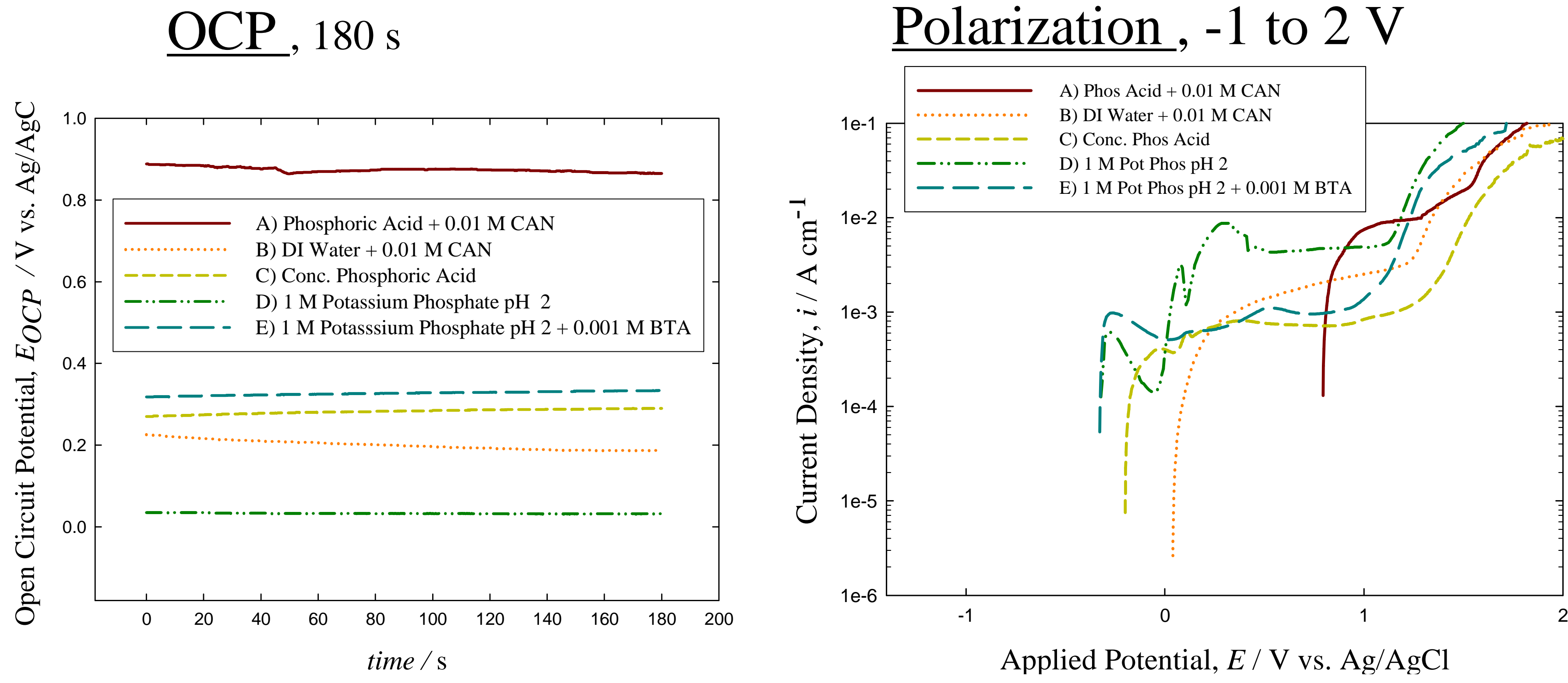
- *Planarization was achieved using 3 pad types:*
  - D100
    - *Decrease in Step Height* ~ 1.0 μm
      - 0.56 μm min^{-1}
      - ε ~ 1.9
  - Suba
    - *Decrease in Step Height* ~ 0.78 μm
      - 0.40 μm min^{-1}
      - ε ~ 2.1
  - IC1000
    - *Decrease in Step Height* ~ 0.74 μm
      - 0.34 μm min^{-1}
      - ε ~ 2.1

✓ *Electrochemical screening of electrolytes is possible*

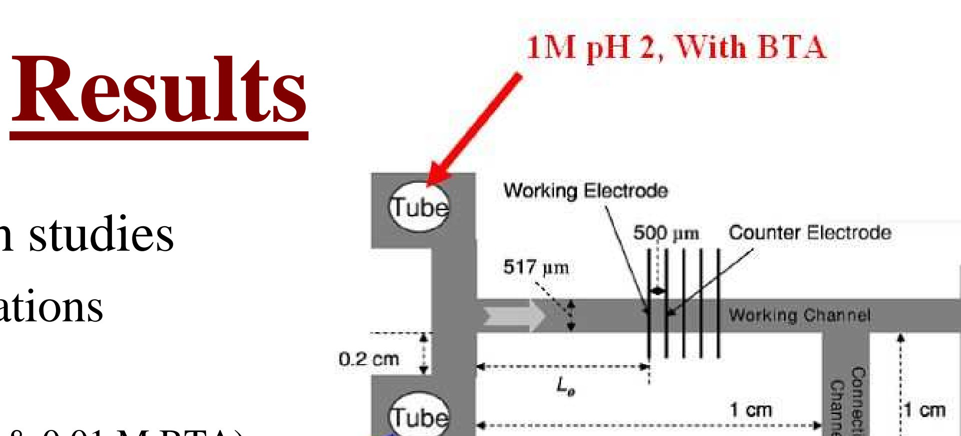
➢ More accurate results could potentially be achieved if using an ECMP tool with an improved mechanical design

Results

- Polishing Liner Materials: Ruthenium
  - Initially investigating:
    - Potassium phosphate based electrolytes
    - Electrolytes containing CAN, ceric ammonium nitrate



Results



Base Soln (1M pH 2)

- BTA adsorption and desorption studies
  - For CMP and cleaning applications

- **0 – 180 s**, BTA electrolyte (1M pH 2, 0.001 & 0.01 M BTA)
- **180 – 300 s**, Base Solution (1M pH 2)

0.001 M BTA, 300 s

Solns Switched

0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
A/cm^2
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
Time (s)
0.1 V
0.3 V
0.5 V
0.6 V
0.7 V
0.8 V

0.01 M BTA, 300 s

Solns Switched

0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
A/cm^2
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
Time (s)
0.1 V
0.3 V
0.5 V
0.6 V
0.7 V
0.8 V

[1] Willey, M. J., A.C. West, A Microfluidic Device to Measure Electrode Response to Changes in Electrolyte Composition. *Electrochemical and Solid-State Letters,* **9** 7 E17-E21 2006

Industrial Interactions and Technology Transfer

- **Industry mentors/contacts**
  - **Intel**
  - **Novellus**
  - **Texas Instruments**

- **Polishing Pads**
  - **Cabot**
  - **Rohm & Haas**

- **Wafers**
  - **IBM**
  - **Novellus**

Future Plans

Next Year Plans

- Finish planarization studies on Cu ECMP
  - Establish appropriate model to predict planarization
- Continue investigation of polishing liner materials
  - Ru
- Begin microfluidic studies to investigate galvanic corrosion between Ru and Cu

Long-Term Plans

- Optimize pad / chemistry
- Demonstrate on Cu/Ru/Ta structures
- Collaborate with industry/university to perform wafer-scale ECMP tool experiments

Publications, Presentations, and Recognitions/Awards

Presentations:

- **ECS May 2008**
- **SRC Teleconference Oct 2007**

Papers:

- **K. G. Shattuck, J. Y. Lin, and A. C. West, Characterization of Phosphate Electrolytes for use in Cu Electrochemical Mechanical Planarization, Electrochimica Acta, (*Submitted*)**

- **K. G. Shattuck, J. Y. Lin, and A. C. West, Planarization Studies of Phosphate Based Electrolytes for use in Cu ECMP, (*Pending*)**

- **J. Y. Lin, A. C. West, and C. C. Wan, Adsorption and Desorption Studies of Glycine and Benzotriazole during Cu Oxidation in a Chemical Mechanical Polishing Bath, Journal of the Electrochemical Society, (*Submitted*)**

- **J. Y. Lin, A. C. West,and C. C. Wan, Evaluation of Post-Cu CMP Cleaning of Organic Residuals Using a Microfluidic Device, Electrochemistry Communication, (*Submitted*)**

Non-PFOS/non-PFAS Photoacid Generators: Environmentally Friendly PAGs for Next Generation Lithography

(*Task Number: 425.013*)

PIs:

- **Christopher K. Ober, Materials Science and Engineering, Cornell University**
- **Reyes Sierra, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Victor Gamez, PhD candidate, Chemical and Environmental Engineering, University of Arizona**

Other Researchers:

- **Yi Yi, Postdoctoral Fellow, Materials Science and Engineering, Cornell University**

Cost Share (other than core ERC funding):

- **$25k from Rohm and Haas Microelectronics**

Objectives

- Develop PFOS free photoacid generators for chemically amplified resist application with superior imaging performance
- Evaluate lithographic performance in selected model 193 nm and EUV resists
- Evaluate the environmental aspects of new PFOS free photoacid generators

ESH Metrics and Impact

1. *Reduction in the use or replacement of ESH-problematic materials*

   Complete replacement of perfluorooctanesulfonate (PFOS) structures including metal salts and photoacid generators in photoresist formulations

2. *Reduction in emission of ESH-problematic material to environment*

   Develop new PAGs that can be readily disposed of in ESH friendly manner

3. *Reduction in the use of natural resources (water and energy)*

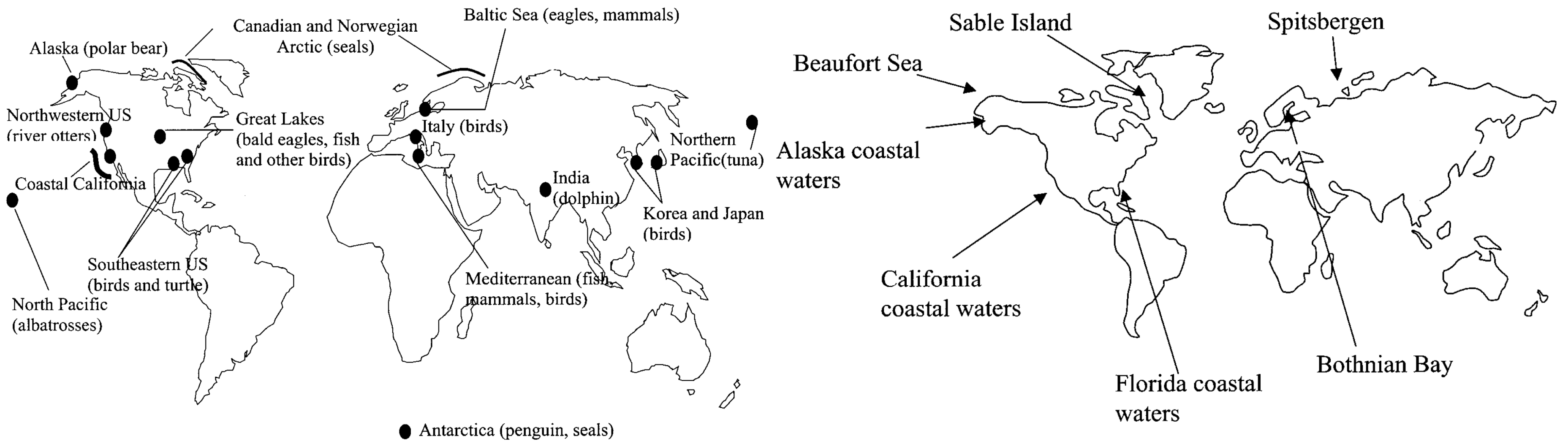
   All of the non-PFOS PAG compounds were prepared using simple, energy reduced chemistry (within 4 steps) in high yields and purity, which reduces water use and the use of organic solvents.

4. *Reduction in the use of chemicals*

   By preparing non-PFOS PAG compounds using simple chemistry (within 4 steps) in high yields and purity, we have reduced the use of fluorinated chemicals.

Bioaccumulation of PFOS

Global Distribution of PFOS in Wildlife | **Accumulation of PFOS in Marine Mammals**



***Environ. Sci. Technol.* 2001, *35*, 1339.**

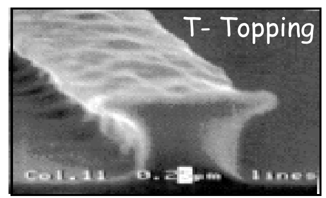
***Environ. Sci. Technol.* 2001, *35*, 1593.**

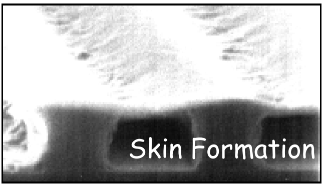
The EPA proposed a significant new use rule (SNUR) for PFOS in 2000.

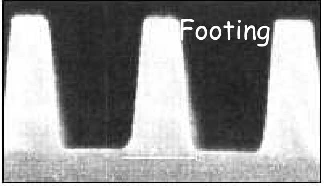
Next Generation PAGs — environmentally friendly, no bioaccumulation

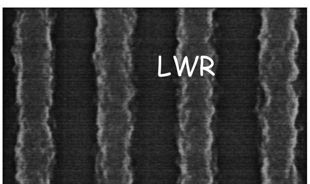
PFOS PAG Performance Issues

"Segregation or non-uniform distribution of PAG"



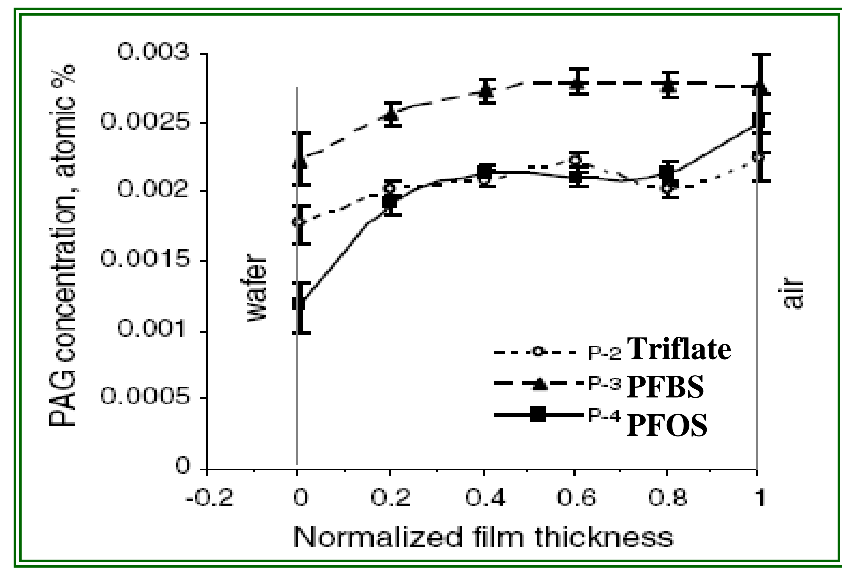




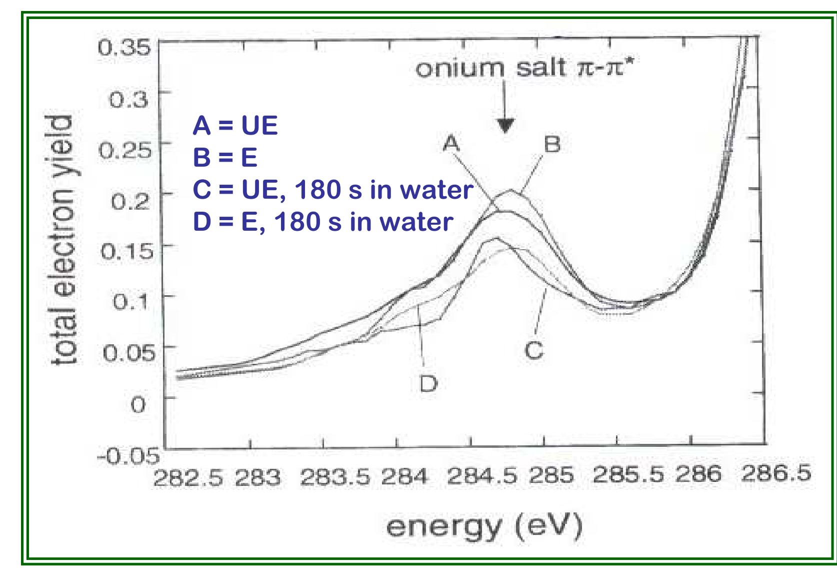


"Surface segregation increases with increase in fluorine content"

"PAG leaching Surface Phenomena"



RBS Depth Profile of polar PAGs in a IBMA-MMA-MAA-t-BMA matrix

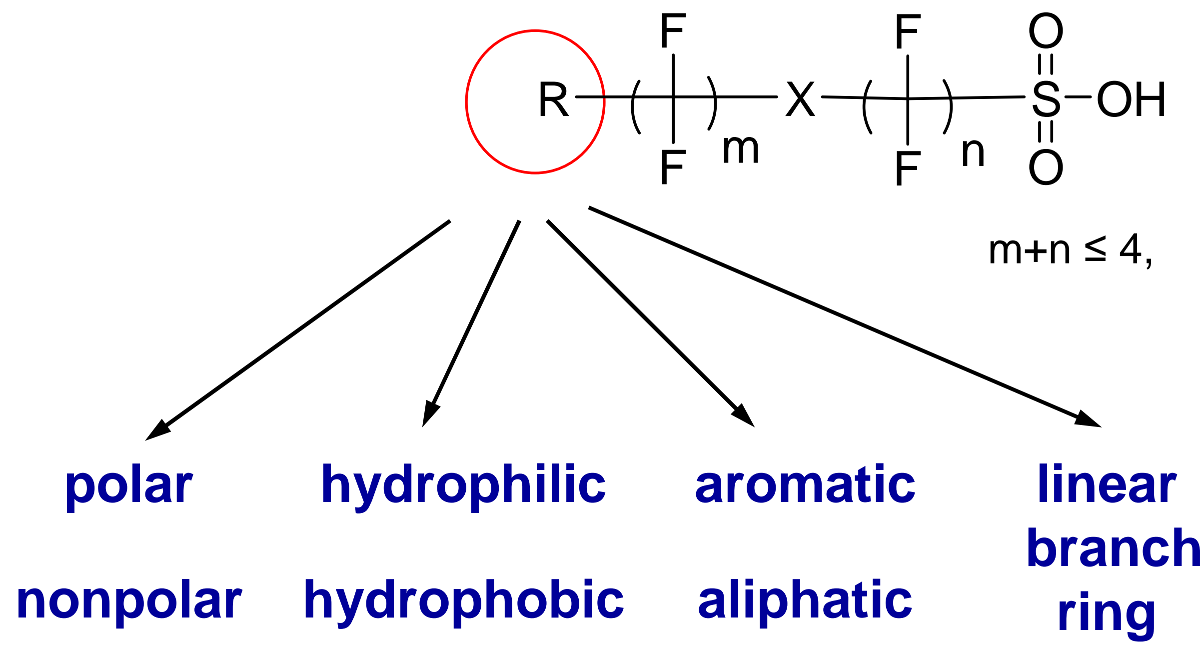


NEXAFS spectra of polar PFOS in a IBMA-MMA-MAA-t-BMA matrix

C.K. Ober et al., *JPST* (1999); J. L. Lenhart et al., Langumir, (2005); W. Hinsberg et al., SPIE, 2004; M. D. Stewart et al., *JVSTB* (2002)

Molecular Design of New Acids:

Environmentally Safe, Better Performance



Practical synthetic chemistry considerations:

- **Simple chemistry — low cost & less time**
- **Efficient reactions — high yield & high purity**

New non-PFOS PAG Anions

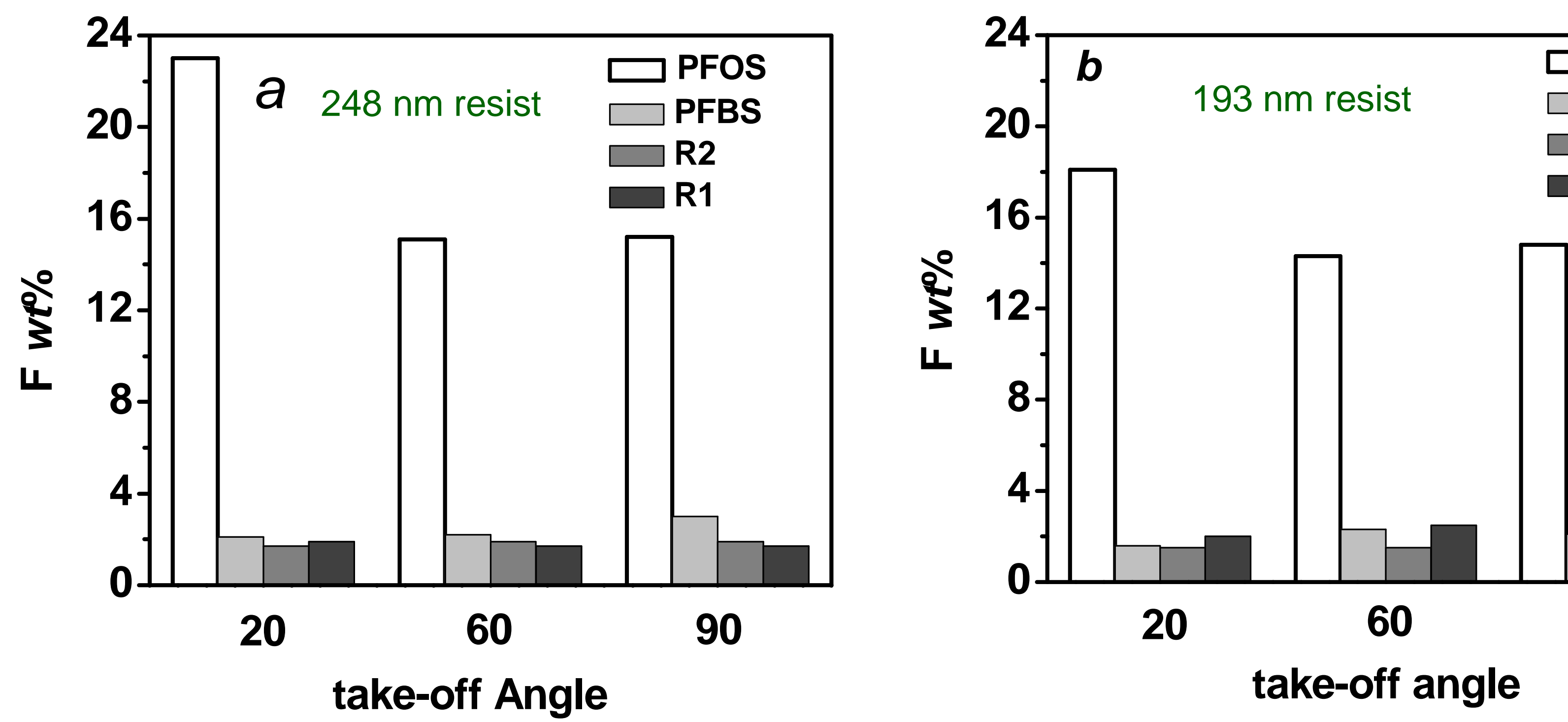
Selected examples:

Synthetic scheme of a PAG anion:

NaOH, H_2O

NaS_2O_4 / $NaHCO_3$, CH_3CN/H_2O

XPS Analysis: New PAGs Mix Better with Resists

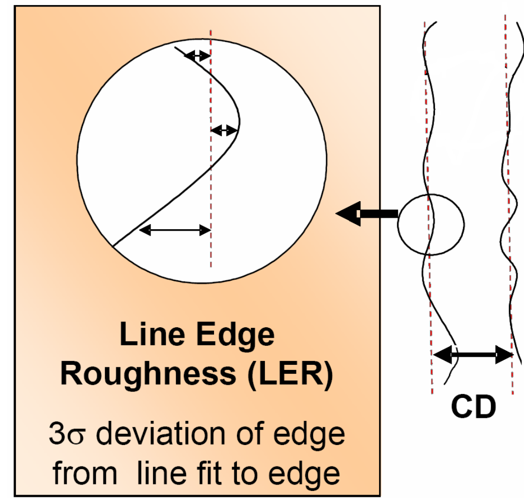


- Heavy surface segregation of TPS PFOS
- Homogeneous distribution and better performance of non-PFOS PAGs (R1 & R2)

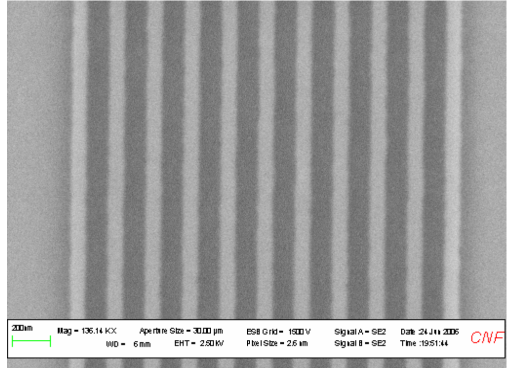
Better Line Edge Roughness @ EUV

Less LER, better performance

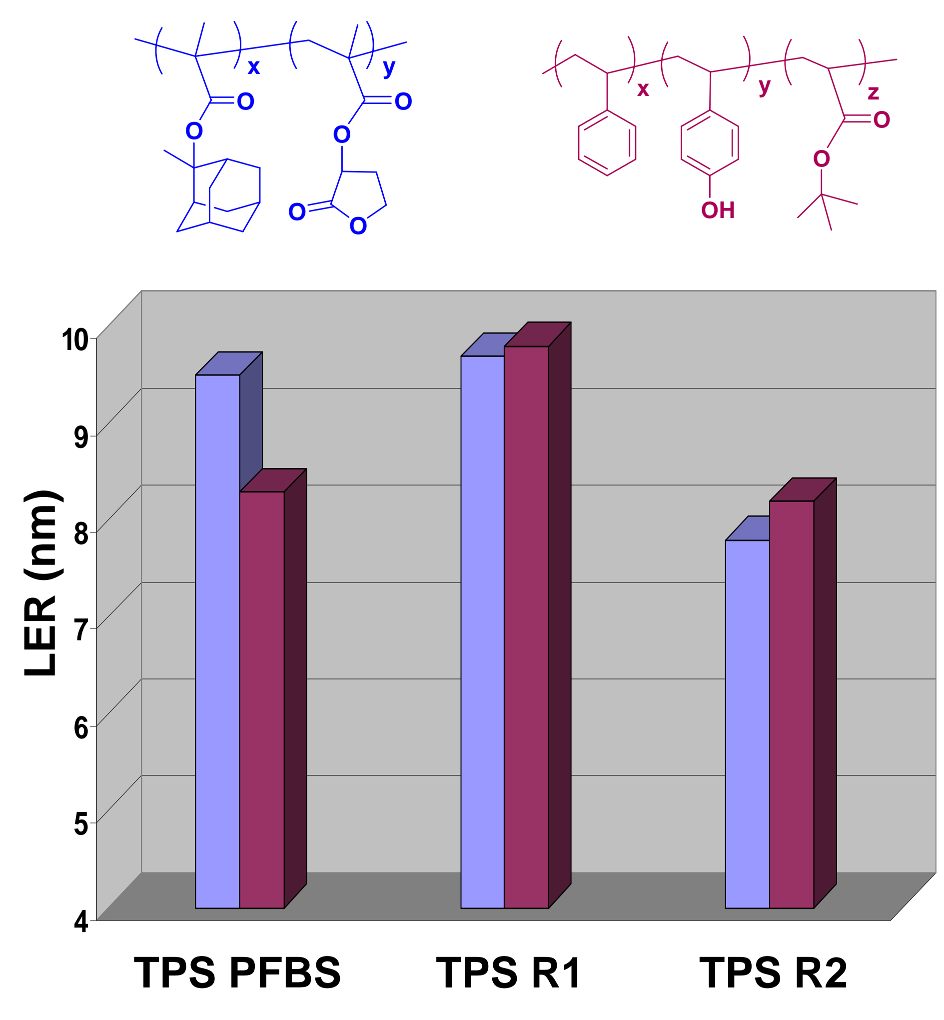
Cao H. et al. *Proc. SPIE* Vol. 5376, p757, 2004.



100 nm (1: 1) lines



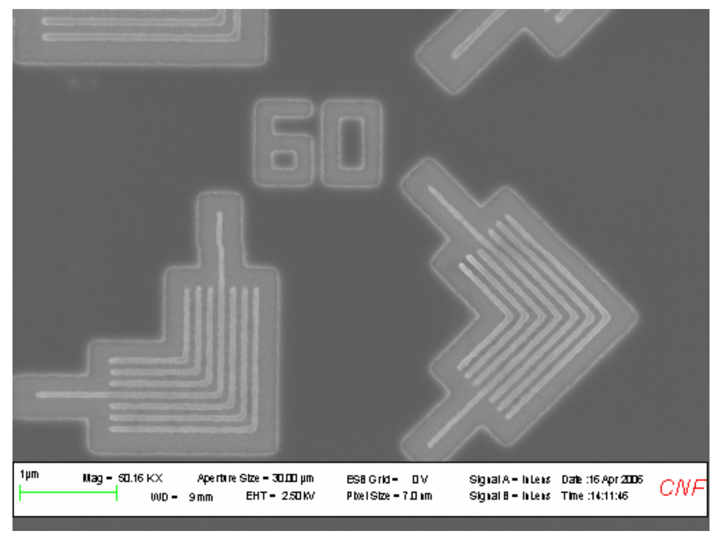
LER calculated by SuMMIT software



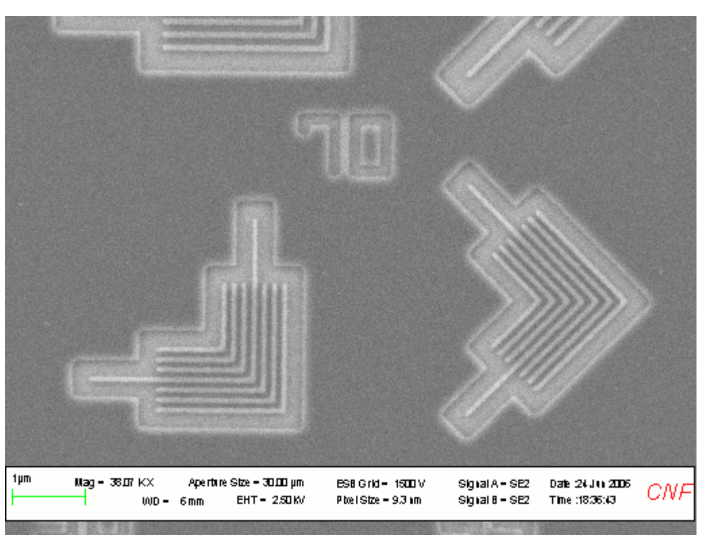
The non-PFOS PAGs (R1 & R2) demonstrate better or similar LER performance as PFBS PAG.

Outstanding Non-PFOS PAG Performance @ EUV

TPS R1



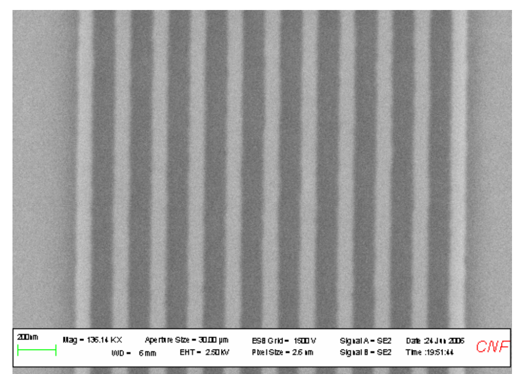
TPS R2



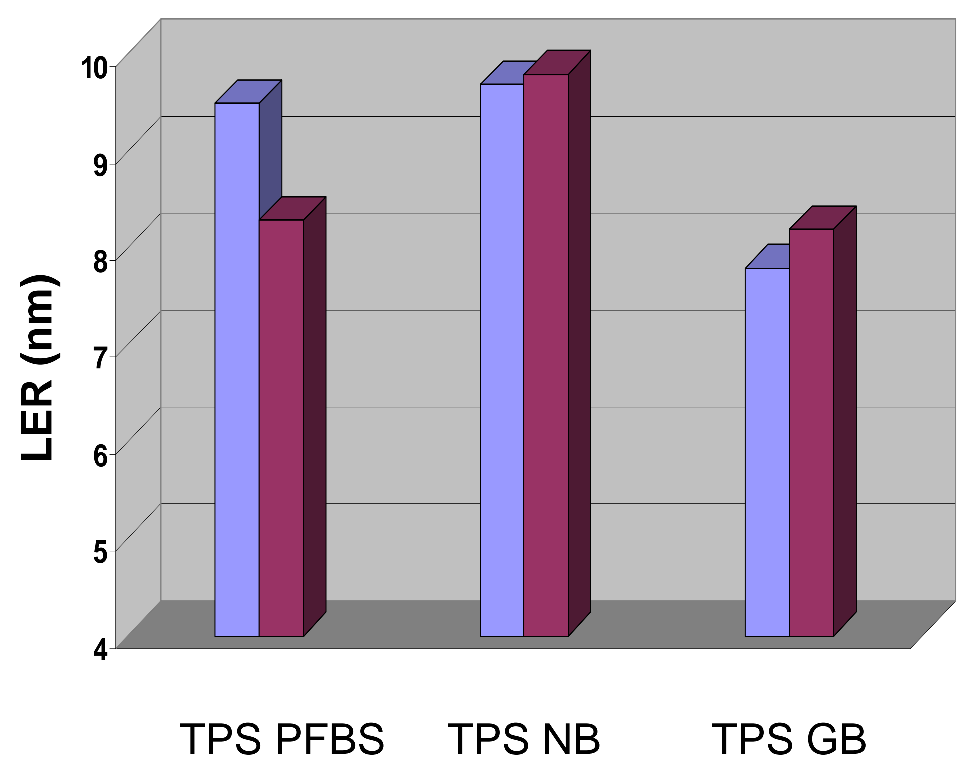
Non-PFOS PAGs easily reach sub-100 nm resolution with ESCAP resist under non-optimized conditions.

Line Edge Roughness @ EUV

100 nm (1: 1) lines



LER calculated by SuMMIT software



LER: (ESCAP) TPS R1 > TPS PFBS ≈ TPS R2

(Methacrylate) TPS R1 ≈ TPS PFBS > TPS R2

Industrial Interactions and Technology Transfer

- Collaboration with Rohm & Haas Electronic Materials for photolithography tests of non-PFOS photoacid generators
- Samples provided to Rohm & Haas Electronic Materials
- Samples provided to TOK
- Samples provided to AZ Microelectronics
- Performance at 193 nm and EUV evaluated with the assistance of International Sematech
- Interactions with Intel on LER issues

Future Plans

Next Year's Plans

- Prepare new generation non-PFOS photoacid generators
- Environmental evaluation of new non-PFOS photoacid generators
- Compare environmental toxicity of different iodonium/sulfonium cations
- Summarize previous studies and submit several manuscripts for transfer of know-how to technical community

Long-Term Plans

- Establish the relationship between photoacid generators' structure and their environmental properties
- Use advanced analytical tools to evaluate photoacid generators' environmental properties

Publications, Presentations, and Recognitions/Awards

Publications

•Ayothi R., Yi Y., Cao H. B., Wang Y., Putna S., Ober C. K. "Arylonium Photoacid Generators Containing Environmentally Compatible Aryloxyperfluoroalkanesulfonate Groups" ***Chem. Mater.*** **2007, 19, 1434.**

•Ober C. K., Yi Y., Ayothi R. "Photoacid generator compounds and compositions" ***PCT Application*** **WO2007124092, April 2007.**

Presentations

•IBM Self-assembly Workshop, Almaden, CA, Jan. 15, 2008. "Photopatternable Block Copolymers: Chemically Active BCP Resists", invited talk.

•International Symposium on Advanced Materials and Nano-materials with Precisely Designed Architectures, October 4th – 6th in Sapporo, Japan. "Studies in the biological-materials interface", invited talk.

•European Polymer Congress, Portorož, Slovenia, 2 – 6 July, 2007. "Building and Patterning the Biology-Materials Interface", invited talk.

•Humboldt University, Berlin, Germany, 17 June, 2007. "Building and Patterning the Biology-Materials Interface", invited talk.

•IUMACRO-07, Brooklyn, NY, June 10 – 13, 2007. "Tailoring Surfaces to Resist Non-Specific Binding"

•BIOS Conference Series, University of Pisa, Pisa, Italy, May 31, 2007. "Tailoring the Material-Biology Interface", invited talk.

•Conference on Nanomaterials for Defense Applications, San Diego, CA, April 24 – 26, 2007. Lithography and Biology: 2D and 3D Patterning for the Biology-Materials Interface, invited talk.

Recognitions/Awards

•2007 Humboldt Research Prize for C.K. Ober

Students on Task 425.013

- Graduated Students and Current Affiliation
  - Nelson Felix, AZ Microelectronics, Dec 2007
  - Victor Pham, JSR Microelectronics, May 2004
- Current Students and Anticipated Grad Date
  - None
- Internships (Task and related students)
  - Katy Bosworth, IBM
  - Evan Schwartz, Intel
  - Anuja de Silva, IBM

Task 425.013

Non-PFOS/non-PFAS Photoacid Generators: Environmentally Friendly Candidates for Next Generation Lithography

Victor M Gamez[1], Ramakrishan Ayothi[2], Yi Yi[2], James A Field[1], Chris K Ober[2], Reyes Sierra[1]

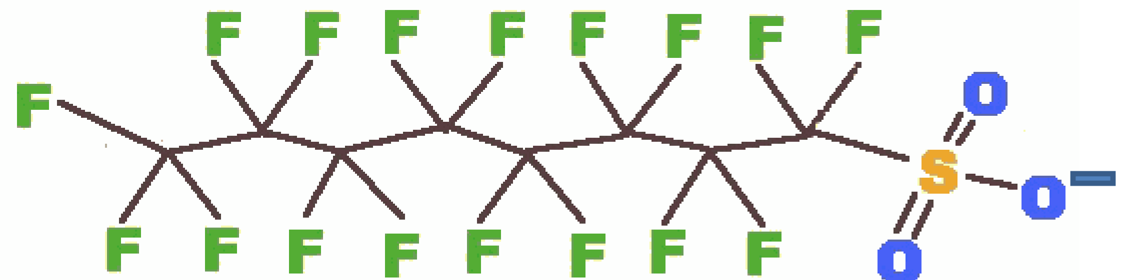
[1] *Department of Chemical & Environmental Engineering, University of Arizona*
[2] *Department of Materials Science and Engineering, Cornell University*

Project Objectives

- To characterize the environmental behavior of novel PFOS-free (and PFAS-free) photoacid generators (PAGs).
- To investigate the treatability of novel PFOS-free (and PFAS-free) PAGs using conventional physico-chemical and biological treatment methods.

Why the development of new PAGs is necessary?

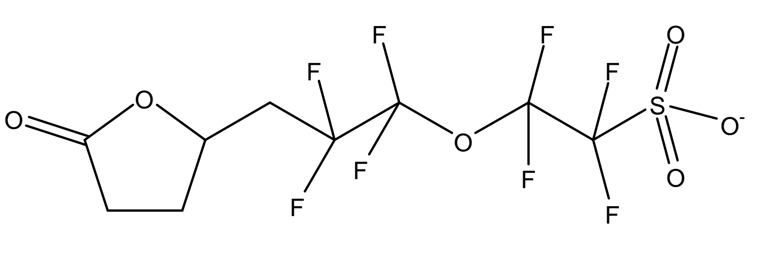
- PFOS is known to bioaccumulate.
- It is recalcitrant.
- Not known to undergo further degradation by any biological means.



ESH Metrics and Impact

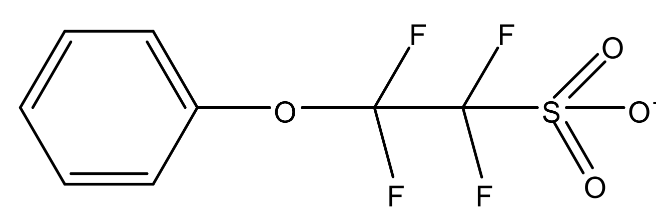
- *Reduction in emission of ESH-problematic materials to environment: 100% removal of PFOS utilized as PAG in photolithography.*

PAGs and Counterions Tested



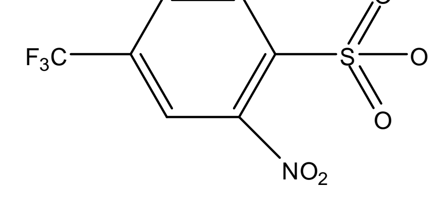
Lactone

SF Sulfonate 1

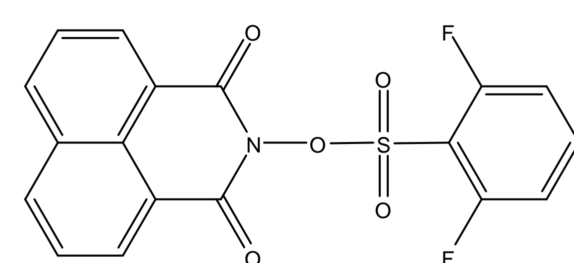


PF Sulfonate 1

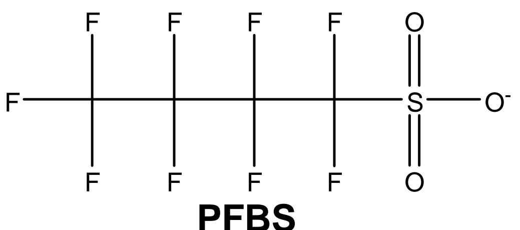
SF 3



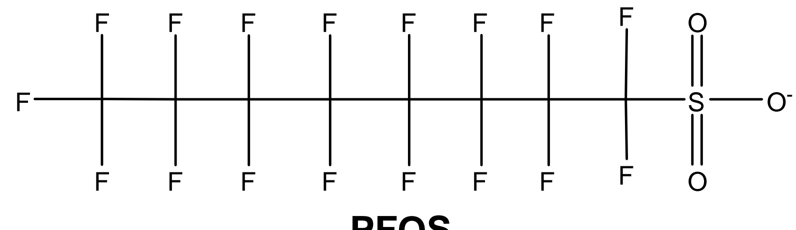
SF Sulfonate 2



SF 4

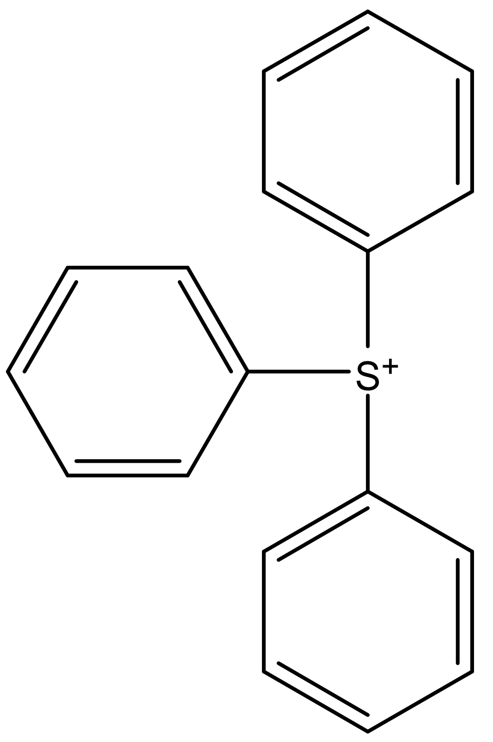


PFBS

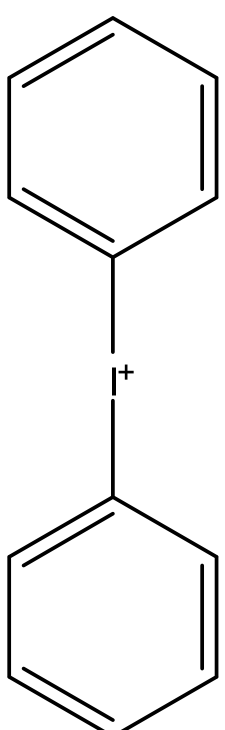


PFOS

PAGs and Counterions Tested

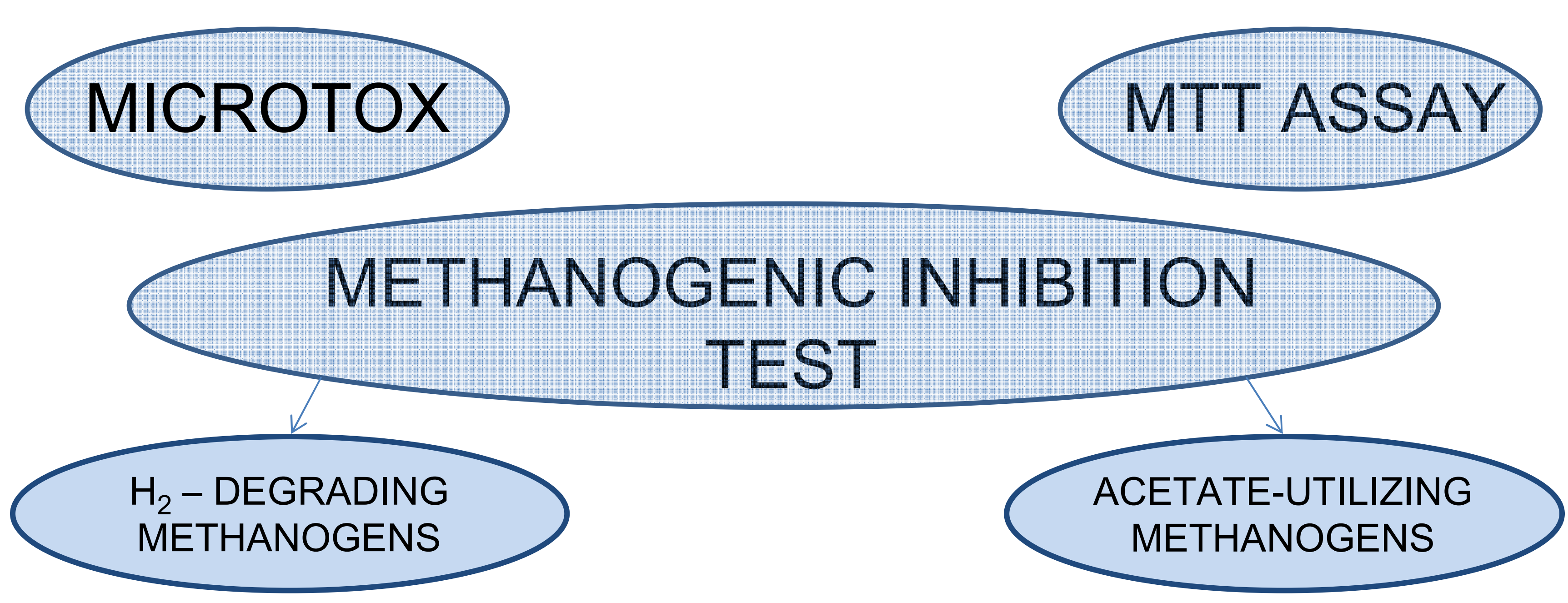


Triphenylsulfonium
(TPS)



Diphenyliodonium
(DPI)

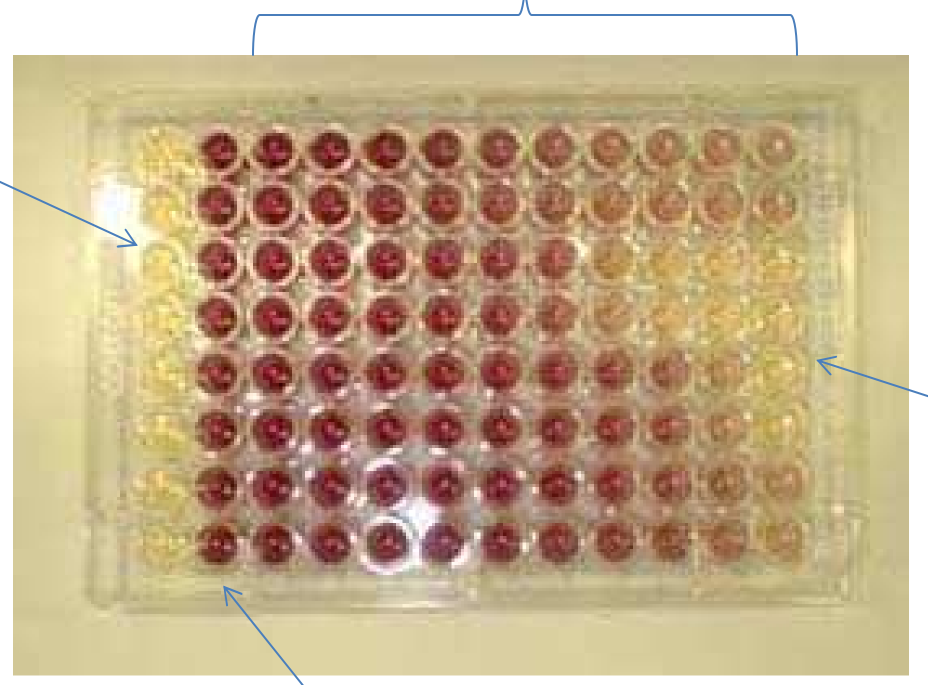
Environmental Toxicity



MTT Assay

Treatment wells

Positive control (a known toxicant is added)

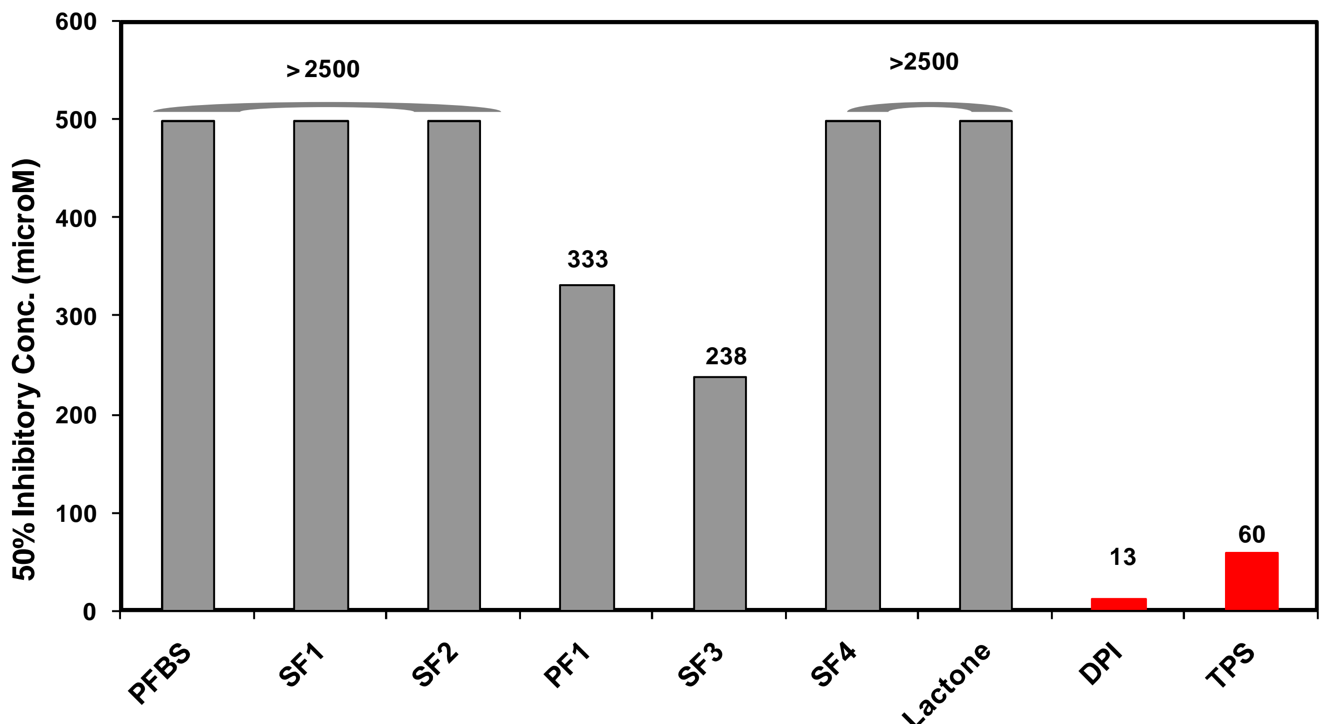


Less color change indicates more toxicity at that concentration.

Negative control (no toxicant)

MTT Assay

- The PAG counter ions, DPI and TPS, showed the highest toxic effects in the MTT assay PF1 was the only PAG displaying toxicity in this bioassay.



Inhibitory effect of the new non-PFOS PAGs and the PAG counter ions in the MTT bioassay.

Microtox Assay

Gamma

10

1

0.1

1 10 100

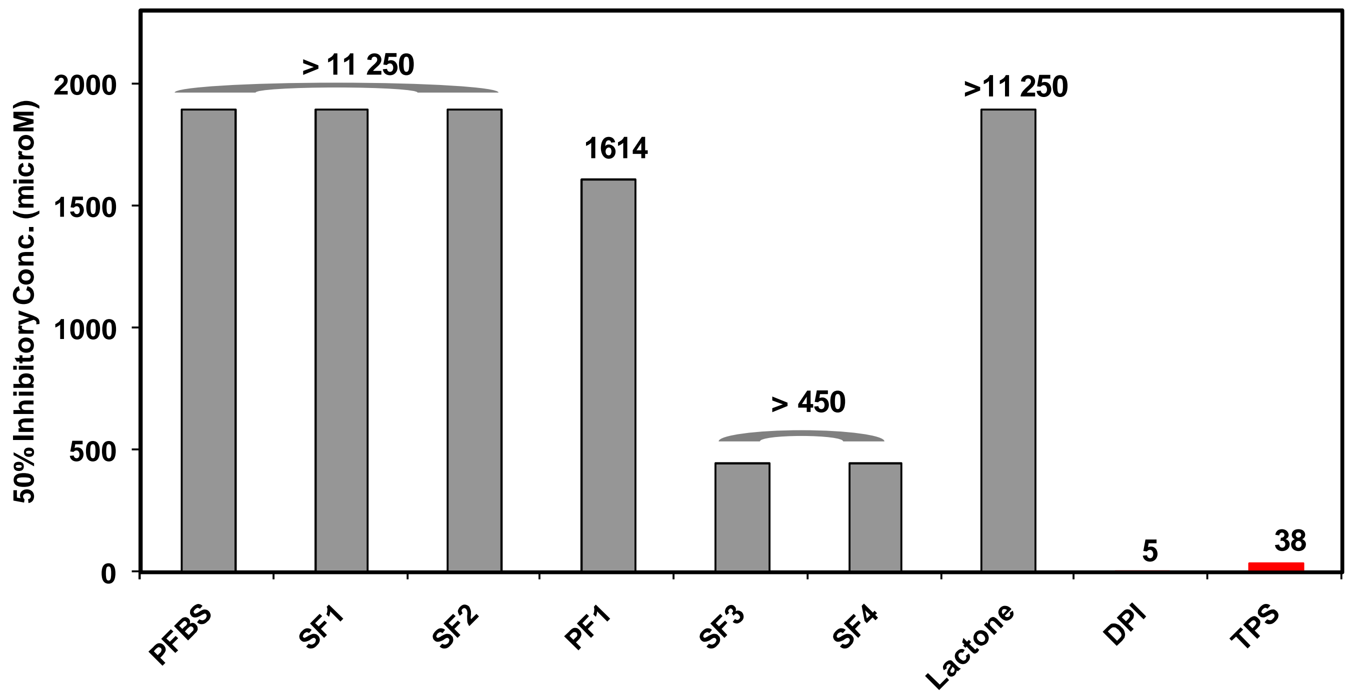
Concentration

1# 2# 3# 4#

5 15 Fit

Microtox Assay

- In agreement with the findings of the MTT assay, the PAG counter ions were also the most inhibitory compounds in the Microtox assay.



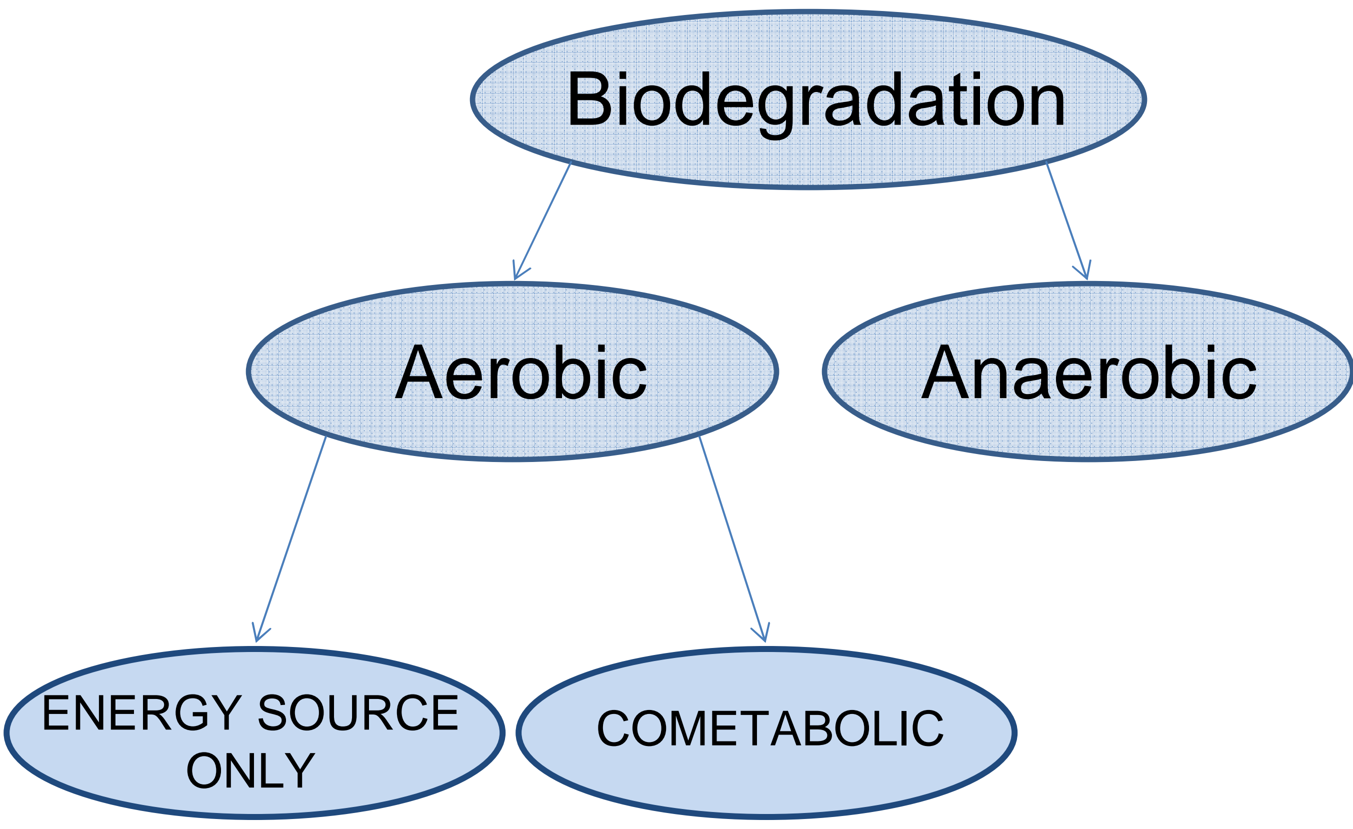
Inhibitory effect of the new PAGs and their counter ions in the Microtox bioassay.

Methanogenic Inhibition

- The counter ions displayed inhibition towards H_2 and acetate-utilizing methanogenic microorganisms. In contrast, the PAGs were generally not toxic.

	Acetatoclastic		Hydrogen-utilizing	
NAME	Concentration (μM)	Inhibition	Concentration (μM)	Inhibition
SF Sulfonate 1	2589	7% ± 1%	2589	3% ± 3%
SF Sulfonate 2	1850	63% ± 3%	1850	4% ± 5%
PF Sulfonate 1	1830	43% ± 4%	1830	-2% ± 1%
Lactone	1600	56% ± 1%	1600	0% ± 2%
Perfluorobutane sulfonate	1672	15% ± 1 %	1672	7% ± 2%
Triphenylsulfonium	1519	31 % ± 3%	1519	51% ± 21%
Diphenyliodonium	1779	56% ± 1%	711	28% ± 5%

Microbial Degradation



Biodegradation

Fluoride Released as a % of total fluoride content of PAG

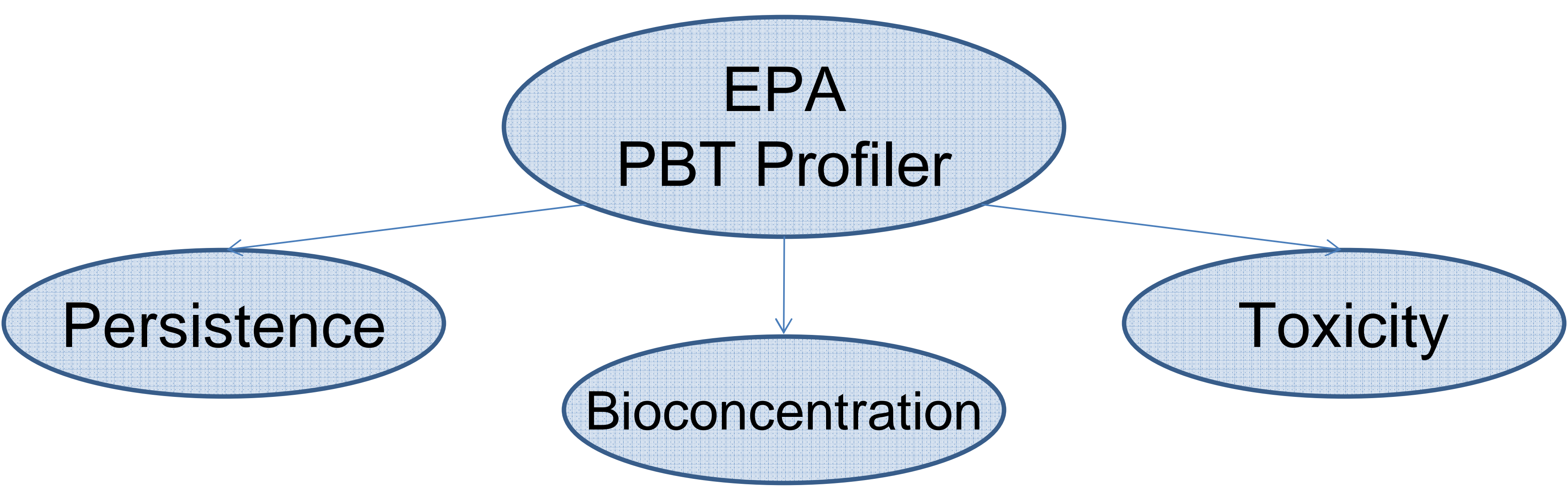
	Aerobic Treatment		Anaerobic Treatment
PAG	Solely Carbon and Energy Source (After 26 days)	Methane Cooxidation (After 75 days)	Hydrogen as Electron Donor (after 158 days)
SF1	0.6 ± 0.1	1.6 ± 0.1	0.5 ± 0.3
SF2	1.6 ± 0.3	1.3 ± 0.1	9.2 ± 0.5
PF1	0.4 ± 0.0	1.3 ± 0.1	0.4 ± 0.1
PFBS	ND	ND	ND

ND= Not Detected (Detection Limit 0.1 ppm Fluoride)

Biodegradation

- With the exception of SF2, PAGs were not biodegraded under any of the redox conditions evaluated.
- SF2 was rapidly degraded under anaerobic conditions. The nitro compound was transformed to the corresponding aromatic amine, which was persistent even after extended incubation.
- Further research will evaluate the cooxidation potential of the new PAGs under nitrifying conditions. Nitrifiers possess ammonia monooxygenases, which are known to attack lower halogenated hydrocarbons.

Environmental Risk Assessment and Environmental Fate Modeling



http://www.pbtprofiler.net/

PBT Criteria

Persistence

Environmental Compartment	Half-Life		
	Not Persistent	Persistent	
Water	< 2 months (< 60 days)	>= 2 months (>= 60 days)	> 6 months (> 180 days)
Soil	< 2 months (< 60 days)	>= 2 months (>= 60 days)	> 6 months (> 180 days)
Air	<= 2 days		> 2 days
Sediment	< 2 months (< 60 days)	>= 2 months (>= 60 days)	> 6 months (> 180 days)

Green: no criteria have been exceeded (no environmental concern)
Orange: EPA criteria have been exceeded (environmental concern)
Red: EPA criteria have been exceeded (High environmental concern)

PBT Criteria

Bioconcentration

Bioconcentration Factor		
Not Bioaccumulative	Bioaccumulative	
< 1,000	> = 1,000	> = 5,000

Toxicity

Fish ChV (mg/l)		
Not Toxic	Toxic	
> 10 mg/l or no effects at saturation	< 10 mg/l	< 0.1 mg/l

Green: no criteria have been exceeded (no environmental concern)
Orange: EPA criteria have been exceeded (environmental concern)
Red: EPA criteria have been exceeded (High environmental concern)

PBT Estimates for PAGs

PAG	PBT Color code[1]	Persistence[2]	Bioaccumulation[3]	Fish- Chronic Toxicity[4]
SF1	PBT	+	—	—
SF2	PBT	+	—	—
PF1	PBT	+	—	—
Lactone	PBT	+	—	—
PFBS	PBT	+	—	—
PFOS	PBT	+	—	—
SF3	PBT	++	—	Not calculated
SF4	PBT	++	—	Not calculated

PBT Estimates for Counterions

Counter Ions	PBT Color code[1]	Persistence[2]	Bioaccumulation[3]	Fish- Chronic Toxicity[4]
Diphenyliodonium (K^+)	PBT	+	--	+
Triphenylsulfonium (K^+)	PBT	+	+	++

Conclusions

- The novel PAGs exert no/low toxicity and are not bioaccumulative. However, they are resistant to microbial degradation.
- Improved PAG substitutes which are more prone to biodegradation still need to be developed.
- Diphenyliodonium and triphenylsulfonium, two common PAG counterions were highly toxic in assays with microbial and human cells.

Future Work

Next Year Plans

- Evaluate the environmental compatibility of new generation PAGs.
- Continue the evaluation of the treatability of the most promising PAGs using conventional physico-chemical and biological methods.
- Evaluate the environmental fate properties of the new PAGs using a commercial prediction engine (CATABOL)* known to be suited for fluorinated compounds. The applicability of the EPA PBT profiler for these compounds is limited.

Long-Term Plans

- Establish the main chemical features for enhancing biodegradation potential of PAG compounds and facilitate design of environmentally compatible chemistries.

* Dimitrov et al. (2004) Predicting the biodegradation products of perfluorinated chemicals using CATABOL. SAR QSAR Environ Res. 15(1):69-82).

Acknowledgements

- SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing. (Funding)
- Dr. Ober's Group at Cornell University. (Samples)

Industrial Liaisons

Industrial liaisons:

Jim Jewett (jim.jewett@intel.com), Intel Corporation

Students on task 425.013

- Former students
  - Matthew West, undergraduate student (Chemical Environ Eng Dept, Tucson, AZ)

- Current Students and Anticipated Grad Date
  - Victor M Gamez, PhD candidate, Dec. 2008.

Environmentally Benign Vapor Phase and Supercritical CO_2 Processes for Patterned Low k Dielectrics *(Task Number: 425.017)*

PIs:

- **Karen K. Gleason, Department of Chemical Engineering, MIT**

Graduate Students:

- **Salaman Baxamusa: PhD Candidate, Department of Chemical Engineering, MIT (NSF Fellow)**
- **Shannan O'Shaughnessy, PhD: Department of Chemical Engineering, MIT (Graduated 5/07)**
- **Nathan J. Trujillo: PhDCEP Candidate, Department of Chemical Engineering, MIT (Started 9/07)**

Cost Share (other than core ERC funding):

- **$70,000 (NSF Fellowship for Sal Baxamusa)**

Objectives

- **Develop new methods to deposit, pattern, and process low k materials**
    1. **Additive polymer patterning using self assembled mask (no traditional lithography)**
    2. **Resistless patterning**

- **Process step reduction results from EHS focused approach**

ESH Metrics and Impact

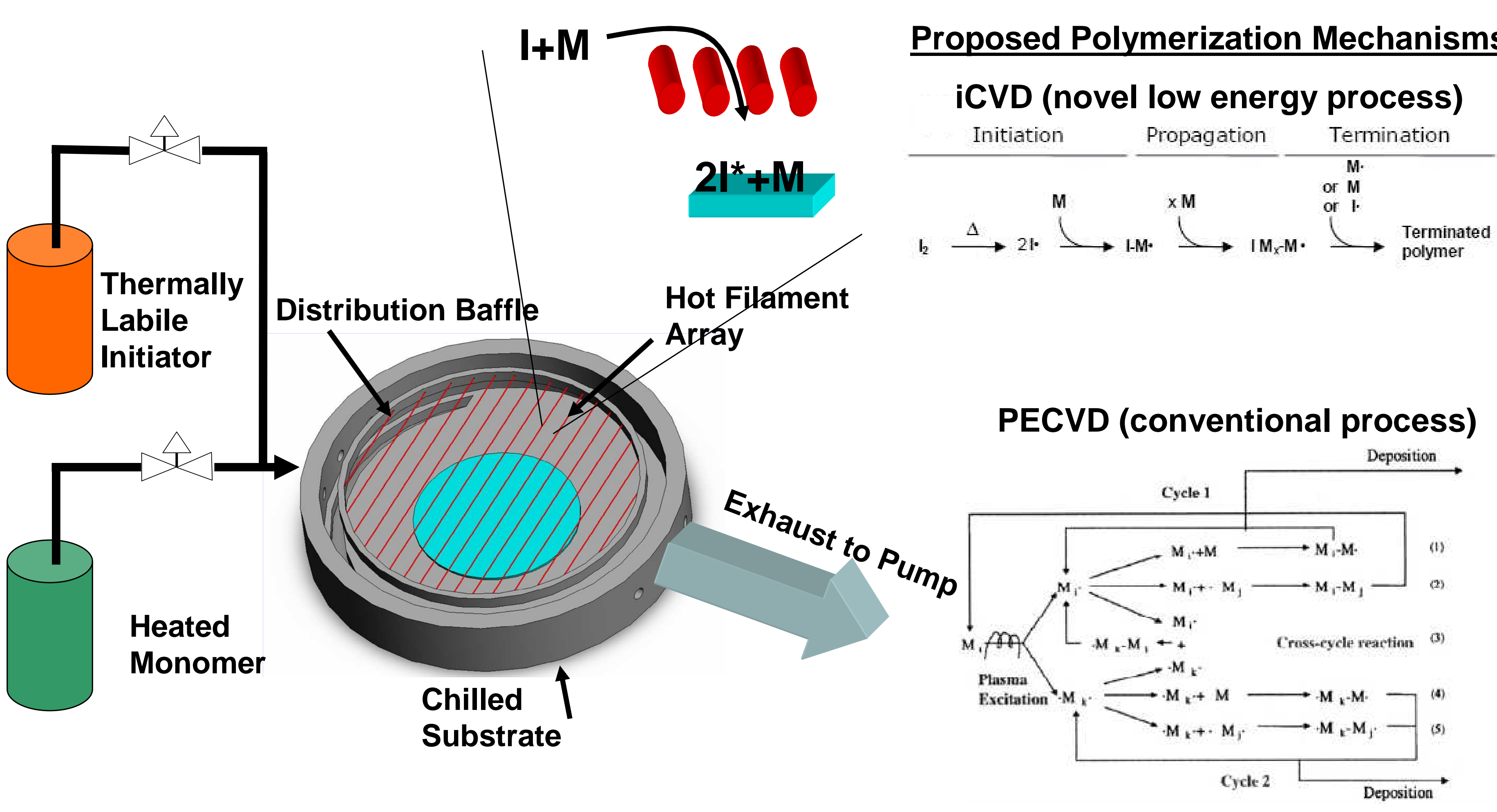
1. ***Resist-free photolithography would eliminate use of photoresist. Approximately 25,000 liters of photoresist materials is used annually in typical semiconductor foundries, at a cost of about $1,600 per liter. Through spin-on process approximately 95% of resist is wasted and disposed as toxic material [1] .***

2. ***Common positive tone resist developer tetramethyl ammonium hydroxide poses health hazards when handled[2] . Acute aquatic toxicity testing of neutralized solution has been shown to be highly toxic to organisms. High resolution features were developed using IPA which is biodegradable, not likely to bioconcentrate, and has low potential to affect organisms.***

3. ***Typical iCVD process requires between .02-.12 W/cm^2 [3] for polymer deposition compared to conventional PECVD which uses 0.4-2.1 W/cm^2[4,5] . No plasma etch eliminates additional >7.1 W/cm^2[6] power requirement.***

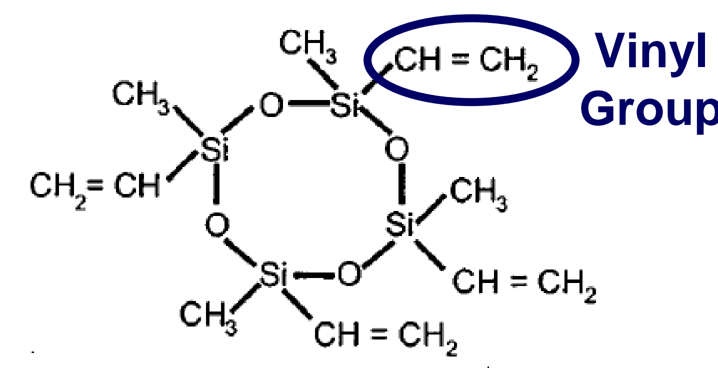
[1] Percin et al., IEEE Transactions on Semiconductor Manufacturing (2003) 16 (3)
[2] Lee et al., J. Micromech. Microeng. (2005) 15
[3] Martin et al.Surf. Coating Tech. (2007) 201
[4]Castex et al. Microelec. Eng. (2005) 82
[5]Wong et al. Thin Sol. Films 462–463 (2004)
[6]Berruyer et al. J. Vac. Sci. Technol. A. 16.3 (1998)

iCVD Process Chemistry

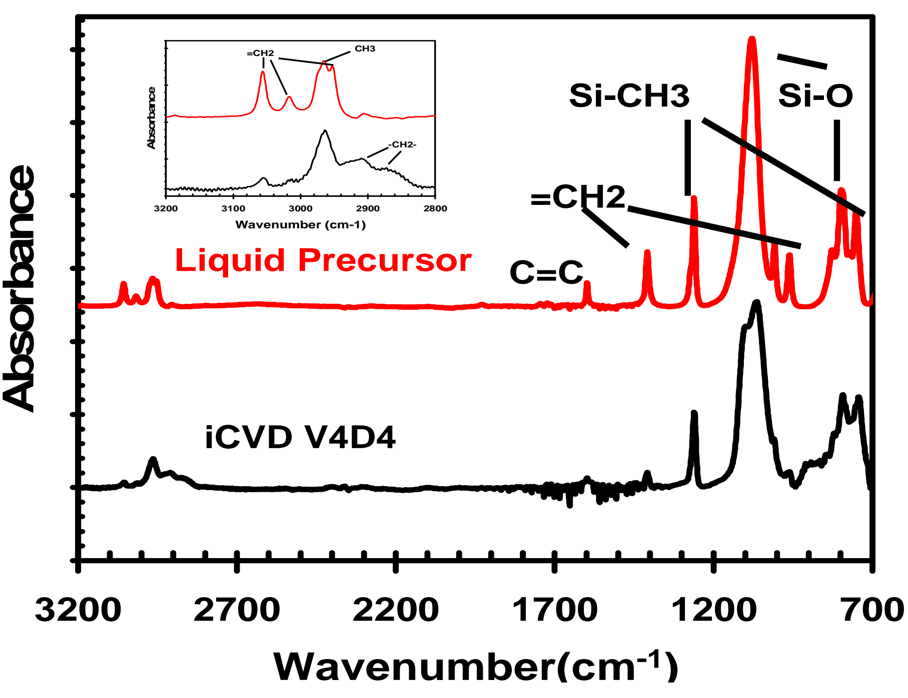


New Low-k iCVD Precursor V4D4

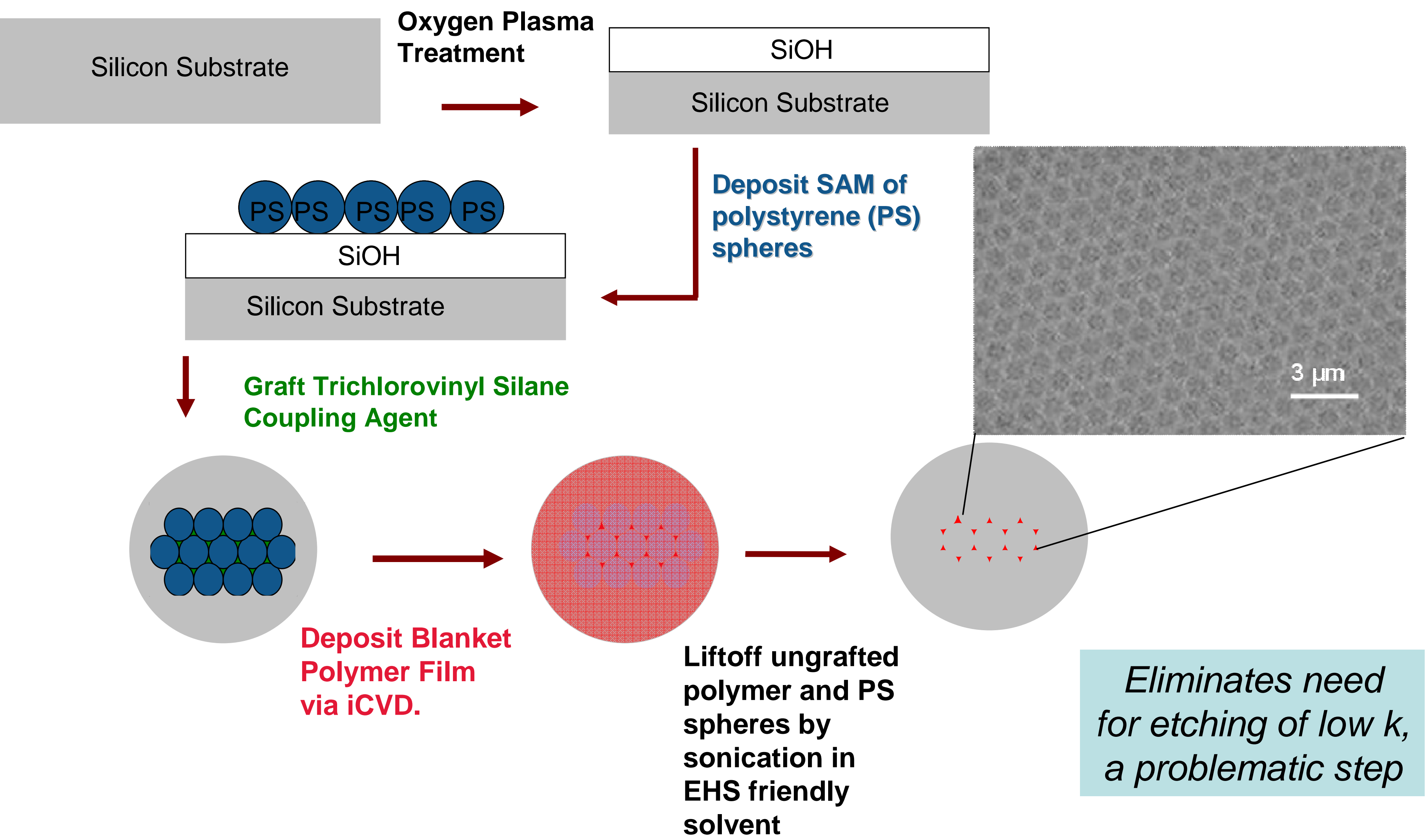
- Free volume of siloxane ring for low-k
- Chemical structure analogous to commercially used low k organosilicate glass (OSG) precursors such as TOMCATS
- Four vinyl groups make ideal for free radical polymerization via iCVD
- No need for cross linker
- 3-D network from "puckered" ring
- k-value of 2.7 measured at Novellus for dense film, typical for OSG. Last year, reduced k of iCVD V3D3 by incorporating novel porogens provided by Cornell



1,3,5,7-TETRAVINYLTETRAMETHYLCYCLOTETRASILOXANE

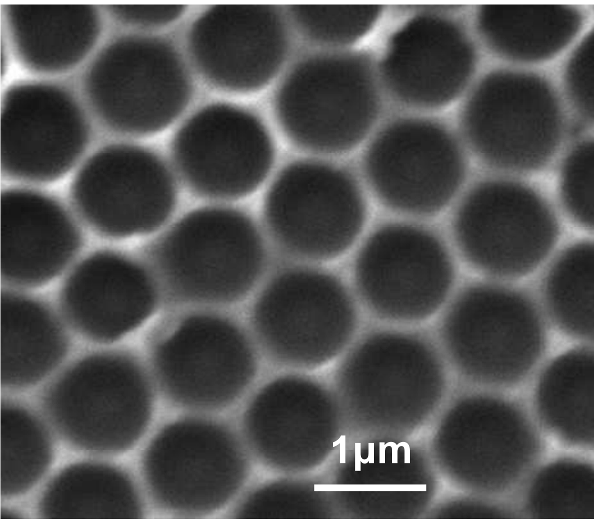


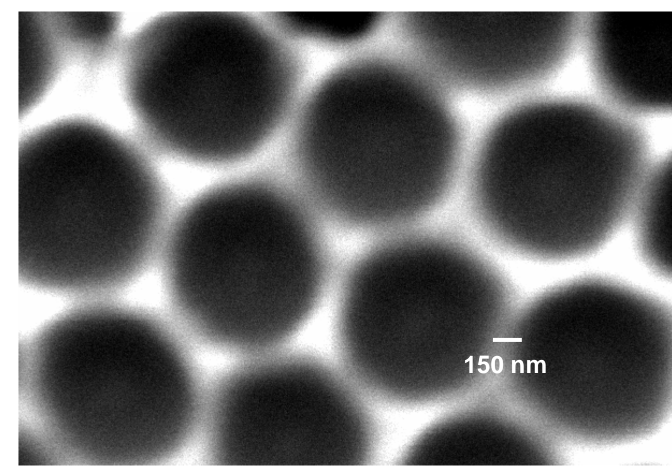
Additive Polymer Patterning Using Self Assembled Mask (no traditional lithography)

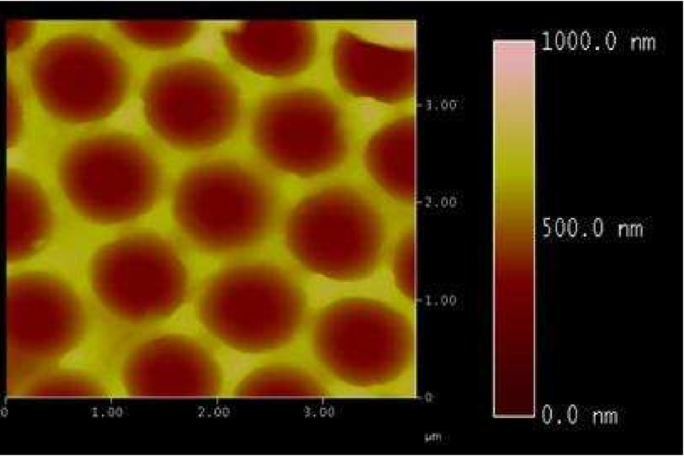


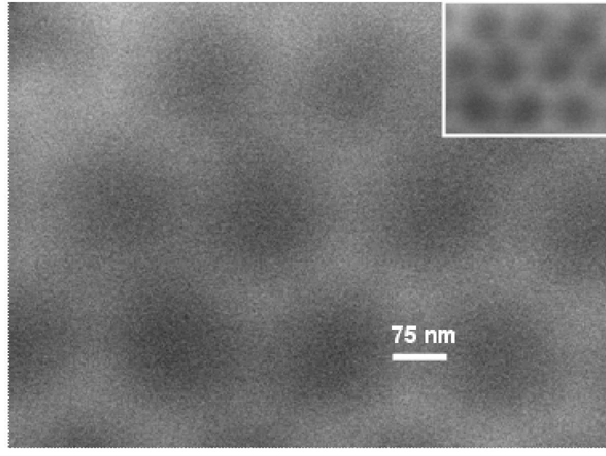
Low-k iCVD V4D4 Patterns: No Traditional Lithography

- Low k templating with 1 µm and 200 nm diameter spheres
- Very well-ordered patterns achieved after sonicating in environmentally friendly IPA for 1 hr
- Large features up to 700 nm in height and smallest about 75 nm wide and about 100 nm in height
- Excellent substrate adhesion: survives >10 minute sonication in THF

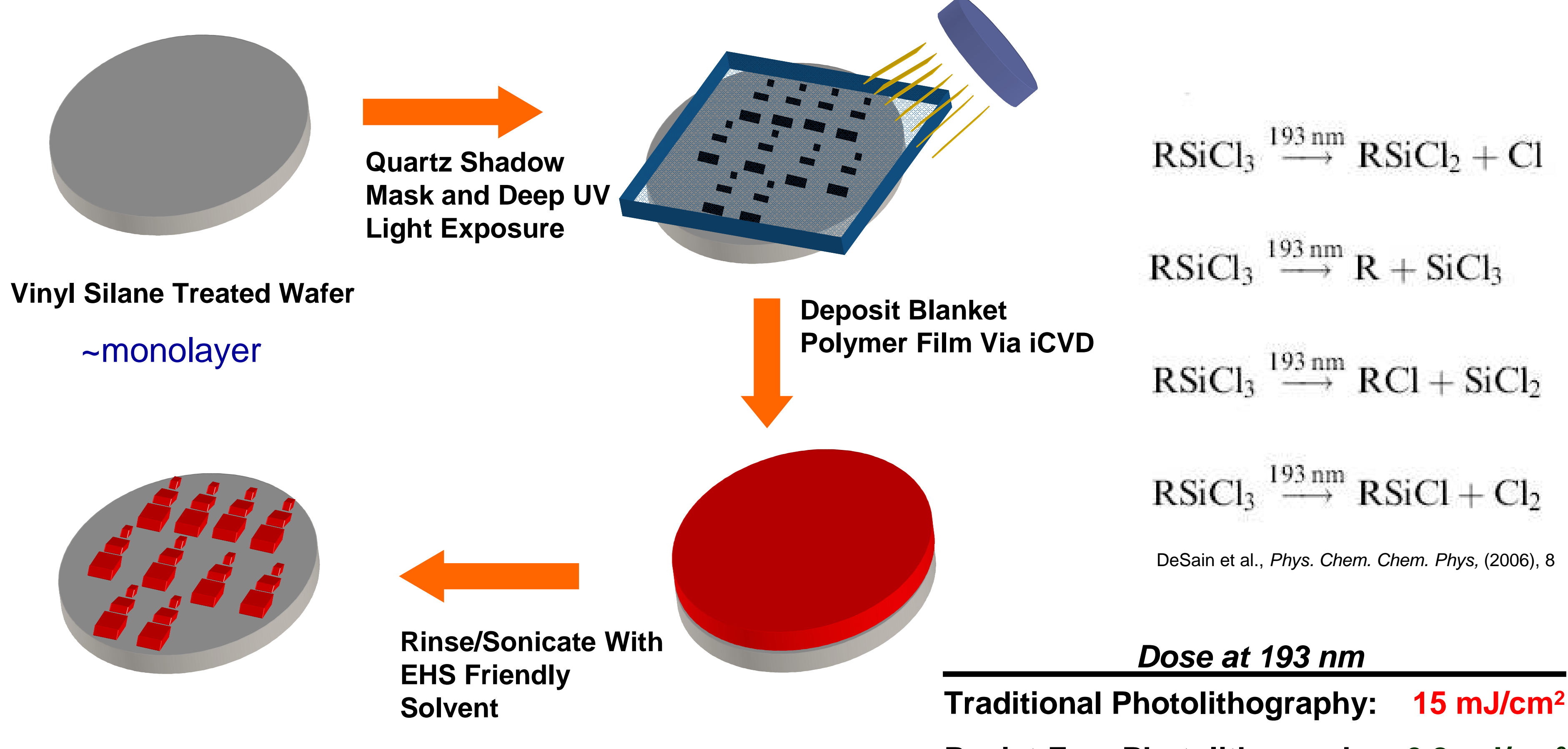








Resist-Free Photolithography



$$RSiCl_3 \xrightarrow{193\text{ nm}} RSiCl_2 + Cl$$

$$RSiCl_3 \xrightarrow{193\text{ nm}} R + SiCl_3$$

$$RSiCl_3 \xrightarrow{193\text{ nm}} RCl + SiCl_2$$

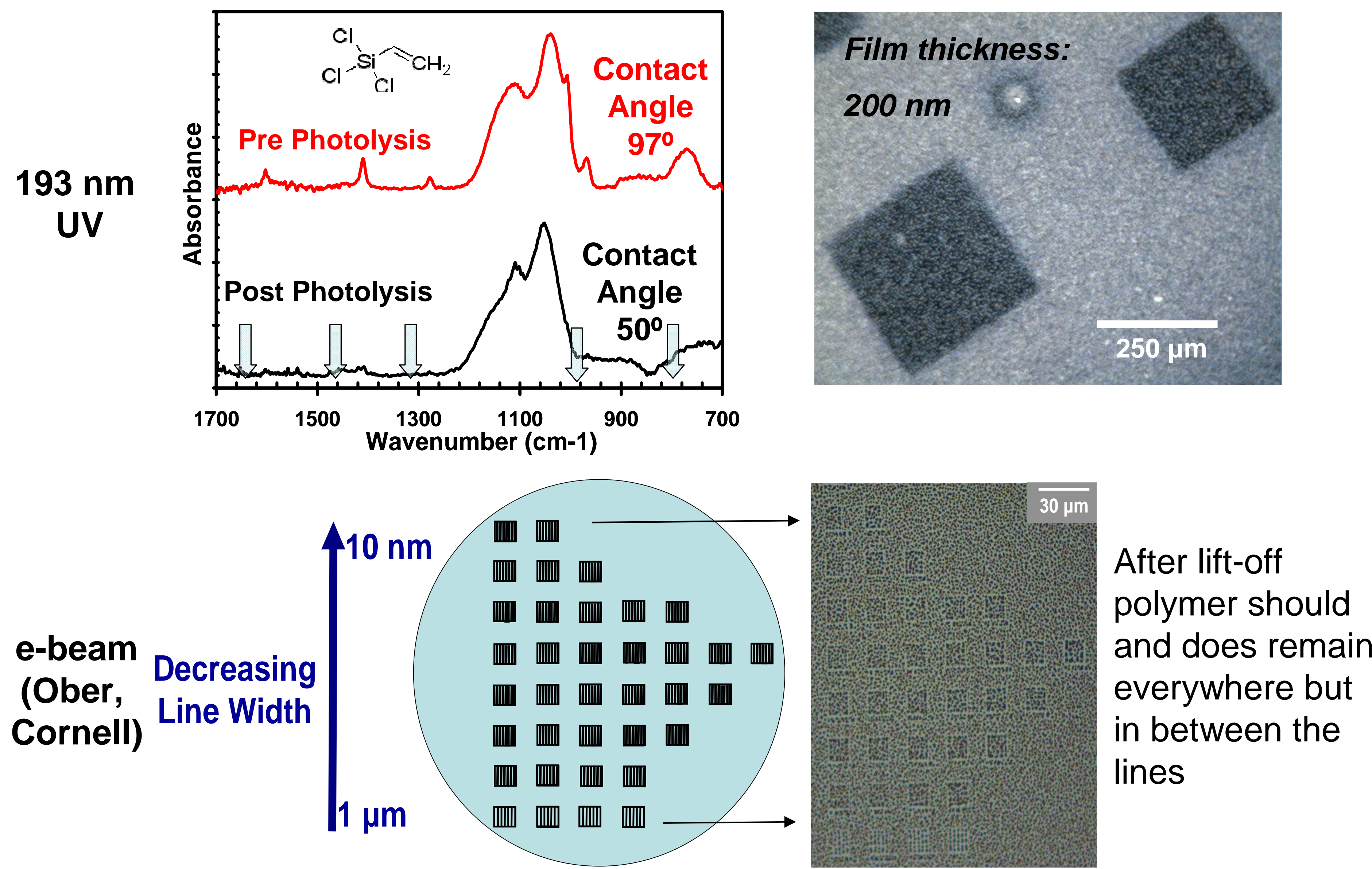
$$RSiCl_3 \xrightarrow{193\text{ nm}} RSiCl + Cl_2$$

DeSain et al., *Phys. Chem. Chem. Phys,* (2006), 8

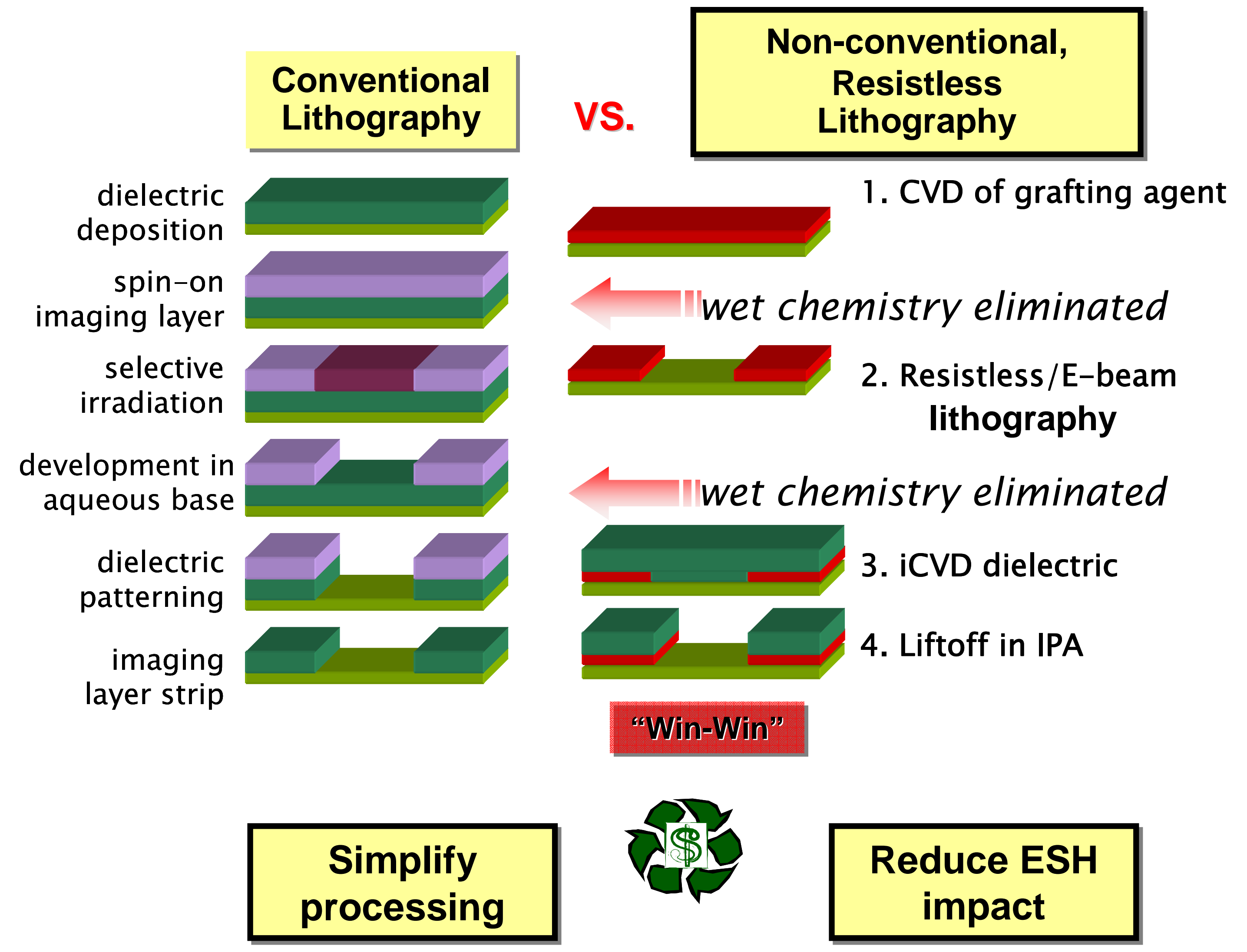
	Dose at 193 nm
Traditional Photolithography:	15 mJ/cm^2
Resist-Free Photolithography:	0.8 mJ/cm^2

- **Exposing grafted vinyl silane monolayer to 193 nm light photolyzes vinyl bonds and removes ability to tether iCVD polymer. Could use commercial steppers for irradiation and lithography masks to define exposure pattern.**

Resist-Free Patterning



Resist-Free Photolithography Reduces Waste



Industrial Interactions and Technology Transfer

- **Harry Levinson, Manager Strategic Lithography Technology and Senior Fellow: AMD**
- **Qingguo Wu, Technologist: Novellus Systems Inc.**
- **Dorel Toma, Director: US Technology Development Center, Tokyo Electron Limited.**
- **Robert Miller, Manager: Advanced Organic Materials Almaden Research Center, IBM**

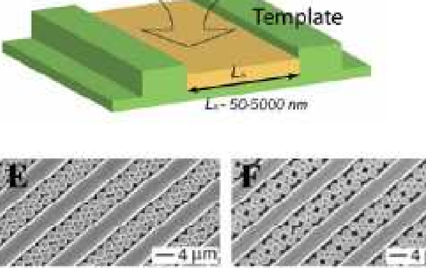
Future Plans

Next Year Plans

- Incorporate porogens into additively patterned low k material to reduce k value.
- Achieve resolution of additively patterned low k to sub 50 nm using smaller self assembled polymeric beads
- Optimize iCVD process for resist free patterning using a trichlorovinyl silane surface treatment, patterned by e-beam lithography at Cornell, to achieve sub 50 nm resolution

Long-Term Plans

Demonstrate the hierarchical use of conventional lithography to define large features which template low defect self assembled iCVD low k



Cheng et al., *Adv. Mater.* (2006), *18*

Publications, Presentations, and Recognitions/Awards

PUBLICATIONS

- W. Shannan O'Shaughnessy, Sal Baxamusa, Karen K. Gleason, "Additively Patterned Polymer Thin Films by Photo-Initiated Chemical Vapor Deposition (piCVD)",Chem. Mater. 19, 5836–5838 (2007).
- W. S. O'Shaughnessy, S. K. Murthy, D. J. Edell, and K. K. Gleason; Stable Insulation Synthesized by Initiated Chemical Vapor Deposition of Poly(1,3,5-trivinyltrimethylcyclotrisiloxane) Biomacromolecules, 8, 2564-2570 (2007).
- O'Shaughnessy, W.S.; Mari-Buye, N.; Borros, S.; and Gleason, K.K.; Initiated Chemical Vapor Deposition (iCVD) of a surface modifiable copolymer for covalent attachment and patterning. Macromol. Rapid Commun. 28, 1877–1882 (2007).
- Tyler P. Martin, Kenneth K.S. Lau, Kelvin Chan, Yu Mao, Malancha Gupta, W. Shannan O'Shaughnessy, Karen K. Gleason, Initiated chemical vapor deposition (iCVD) of polymeric nanocoatings, Surface And Coatings Technology, 201, 9400-9405 (2007).
- O'Shaughnessy, W.S.; Edell, D.J.; Gleason, K.K.; Thin Solid Films, Initiated chemical vapor deposition of biopassivation coatings, Thin Solid Films 516, 684-686 (2008).
- Ph.D. Thesis, W. Shannan O'Shaughnessy, Dept. of Chemical Engineering, MIT

PRESENTATIONS

- K.K. Gleason, Polymeric Nanocoatings by Chemical Vapor Deposition, Pall Corporation, 2/6/2007
- K.K. Gleason, Design of CVD processes for low k dielectrics and air gap formation, 2007 MRS Spring Meeting:Symp. B, San Francisco, CA 4/11/2007 (invited)
- K.K. Gleason, Initiated chemical vapor deposition (iCVD) of polymeric nanocoatings, 16th European Conference on Chemical Vapor Deposition, Den Haag, Netherlands, 9/20/2007 (invited).
- K.K. Gleason, Chemical Vapor Deposition of Polymeric Nanocoatings, U. Calgary, Dept. Chemical Engineering, 10/5/2007 (invited).
- K.K. Gleason, Conformal Polymeric Thin Films via Initiated Chemical Vapor Deposition, AVS Seattle, WA, 10/15/2007 (invited)
- K.K. Gleason, Engineering Polymeric Nanocoatings by Vapor Deposition 31th Annual Symposium of the Macromolecular Science and Engineering Program at the University of Michigan., Ann Arbor, MI, 10/25/2007 (invited).
- Nathan J. Trujillo and Karen K. Gleason, ERC TeleSeminar, "Additive Patterning of Low Dielectric Constant Polymer Using iCVD", December 13, 2007

Students on Task 425.017

- Graduated Students and Current Affiliation
  - Shannan O’Shaughnessy, PhD 5/07, Stericoat

- Current Students and Anticipated Grad Date
  - Salaman Baxamusa: PhD expected 5/09
  - Nathan J. Trujillo: PhDCEP expected 5/11

Environmentally Benign Vapor Phase and Supercritical CO_2 Processes for Patterned Low k Dielectrics

(*Task Number: 425.017; Ober sub-task)*

PIs:

- **Christopher K. Ober, Cornell University**
- **Karen K. Gleason, Massachusetts Institute of Technology**
- **James J. Watkins, University of Massachusetts, Amherst**

Graduate Students:

- **Nelson M. Felix, Cornell University, Chemical Engineering (graduated 1/08)**
- **Jing Sha, Cornell University, Materials Science & Engineering**
- **Katy Bosworth, Cornell University, Chemistry (other support)**

Cost Share (other than core ERC funding):

- **IBM Fellowship ($80k), KB**
- **NSF Support ($80k), JS**

Objectives

- Understand the fundamental solubility characteristics of resist molecules in supercritical (sc) CO_2
  - scCO_2 is an environmentally friendly, non-polar high performance solvent
- Demonstrate the high-resolution patternability and development of non-polar materials in scCO_2
  - scCO_2 has performance attributes that may make it ideal as a high resolution resist developer
- Provide lithography expertise and patterning capabilities to Gleason and Watkins groups
- Provide needed specialty materials to Gleason and Watkins groups

ESH Metrics and Impact

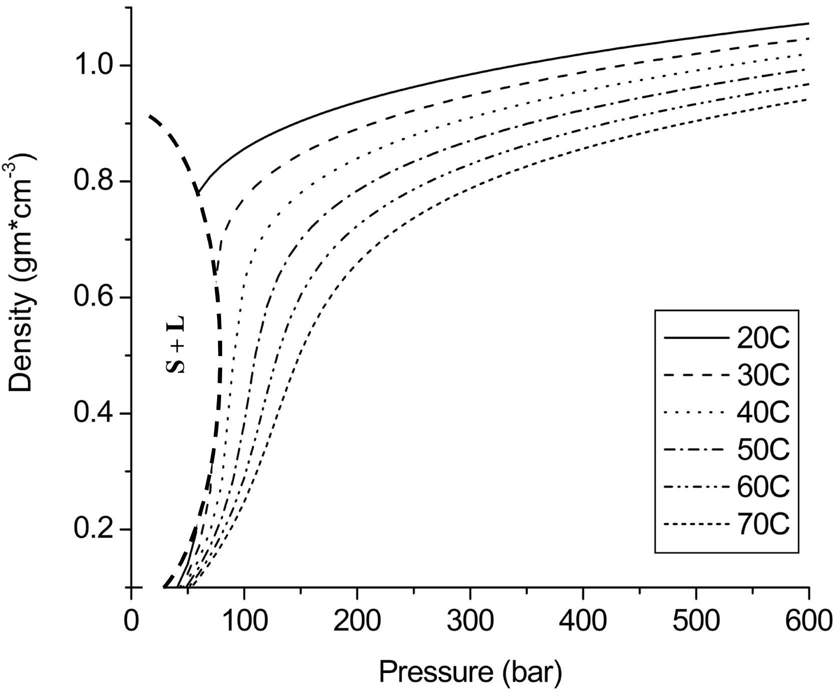
	Usage Reduction			Emmision Reduction			
Goals/Possibilities	Energy	Water	Chemicals	PFCs	VOCs	HAPs	Other
Reduce organic solvents used in processing materials	No energy used to purify and treat water	Eliminate need for water usage	Up to 100% reduction of organic solvents used	N/A	Minimal use of organic solvents	Up to 100% reduction of HAPs	N/A
Reduce processing time / temperature	Reduce anneal process costs	N/A	N/A	N/A	N/A	N/A	N/A
Additive processing	N/A	N/A	Eliminate waste of costly material	N/A	Minimal use of organic solvents	N/A	N/A

- **Eliminates water usage in development**
- **Eliminates need for organic solvents**
- **Recyclable**

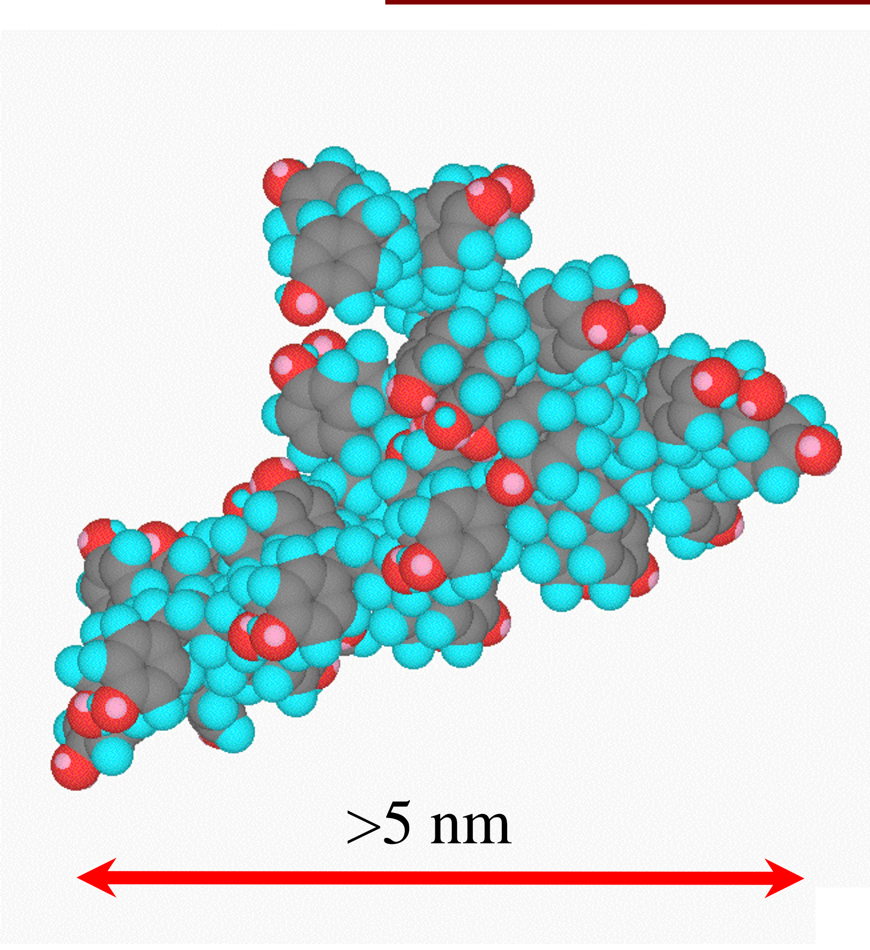
Why a New Developer Solvent?:

Environmental and Performance Advantages of $scCO_2$

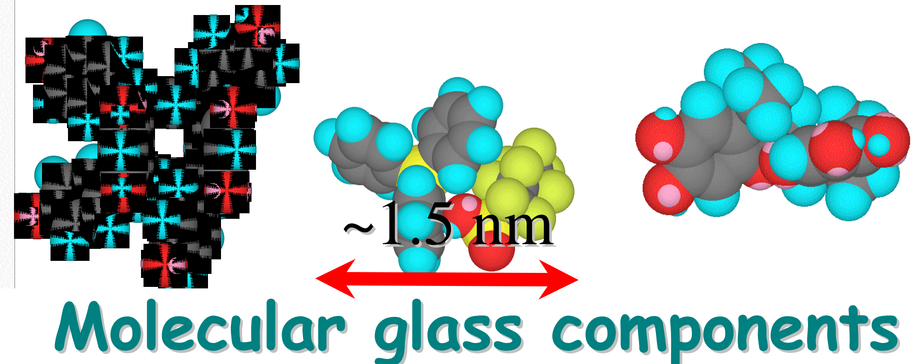
- **Environmentally friendly, zero VOC solvent**
- **Highly tunable solvating power**
  - $\rho(T,P)$
  - **Leaves no residue**
  - **Clean separations**
- **One-phase fluid**
  - **Zero surface tension**
  - **Transport, viscosity between that of liquid and gas**
- **Nonpolar, inert character**
- **Potential to reduce LER and eliminate pattern collapse**



Molecular Glasses as Patternable Materials



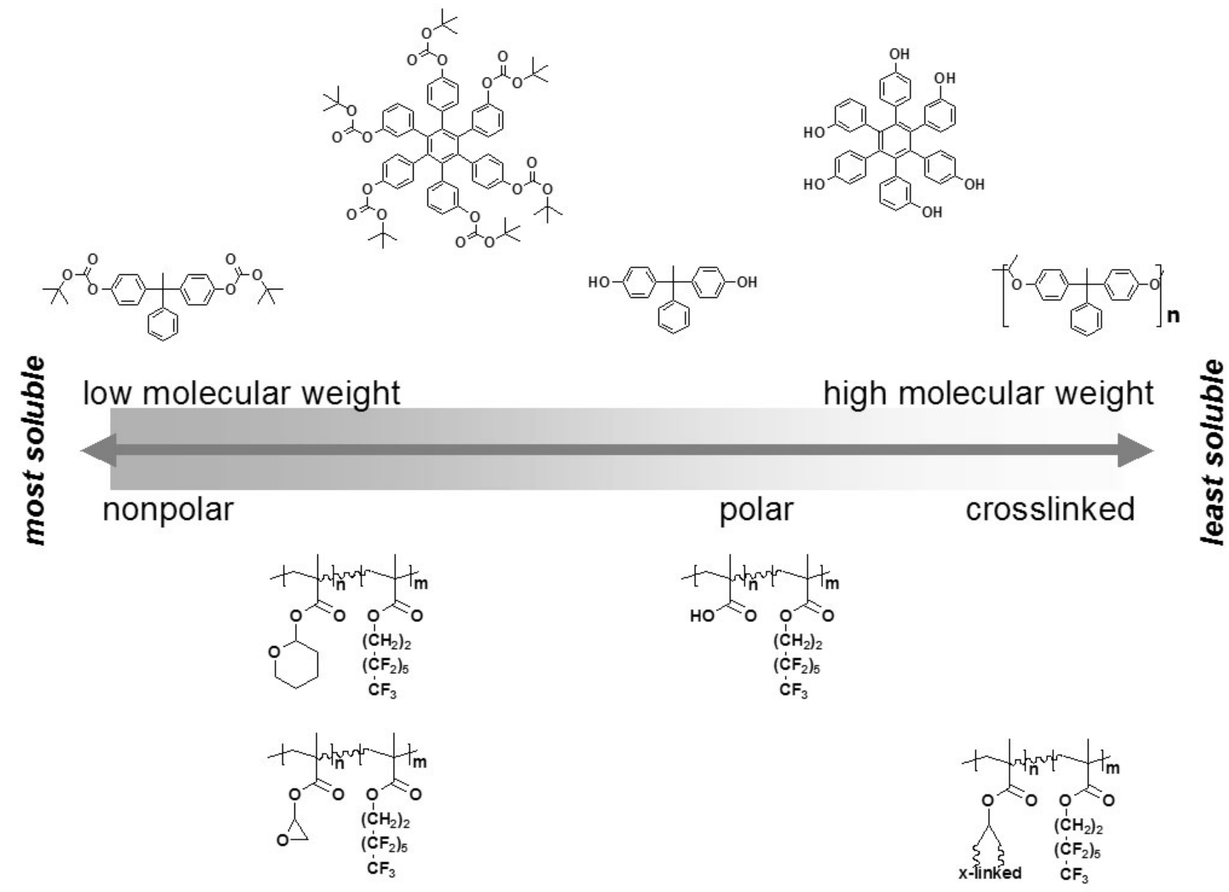
- Molecular glasses uniform, small size
- Potential low k precursors
- Possibility of vapor deposition
- Processing in untraditional solvents



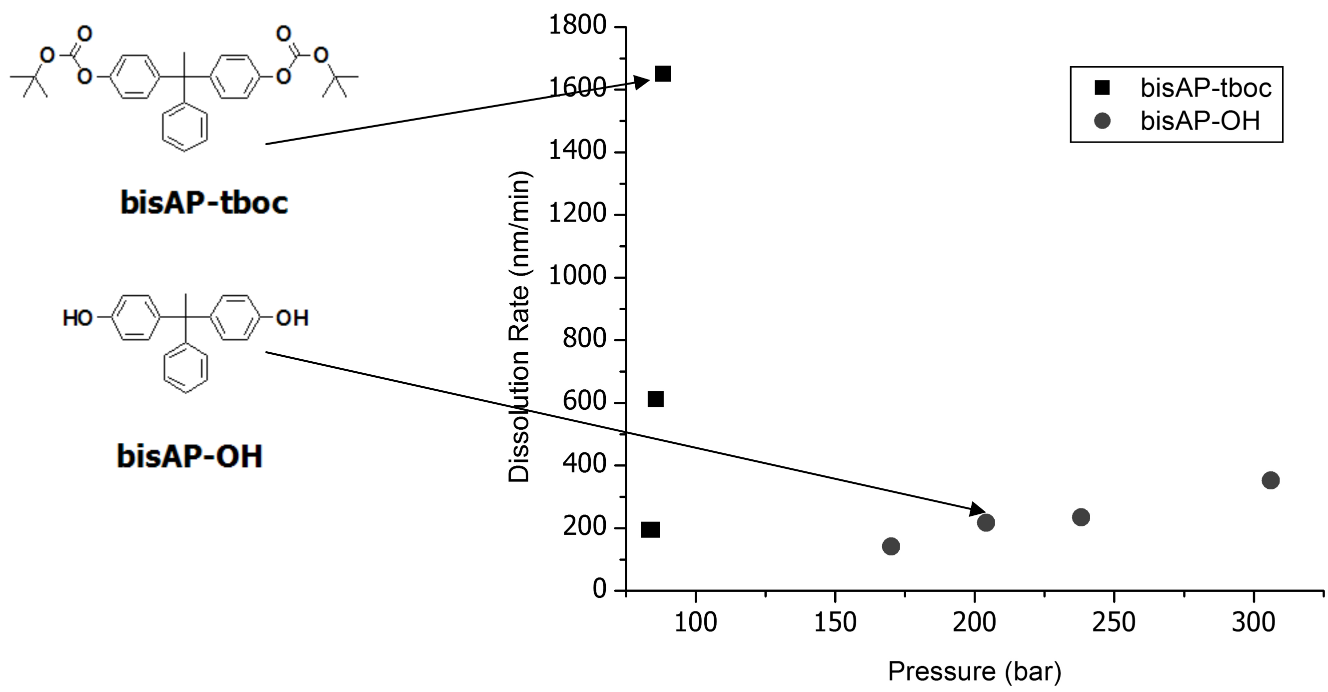
Molecular glass components

Keys to Solubility Control in $scCO_2$

- **Increasing polarity decreases solubility in $scCO_2$**
- **Increasing molecular size decreases solubility**

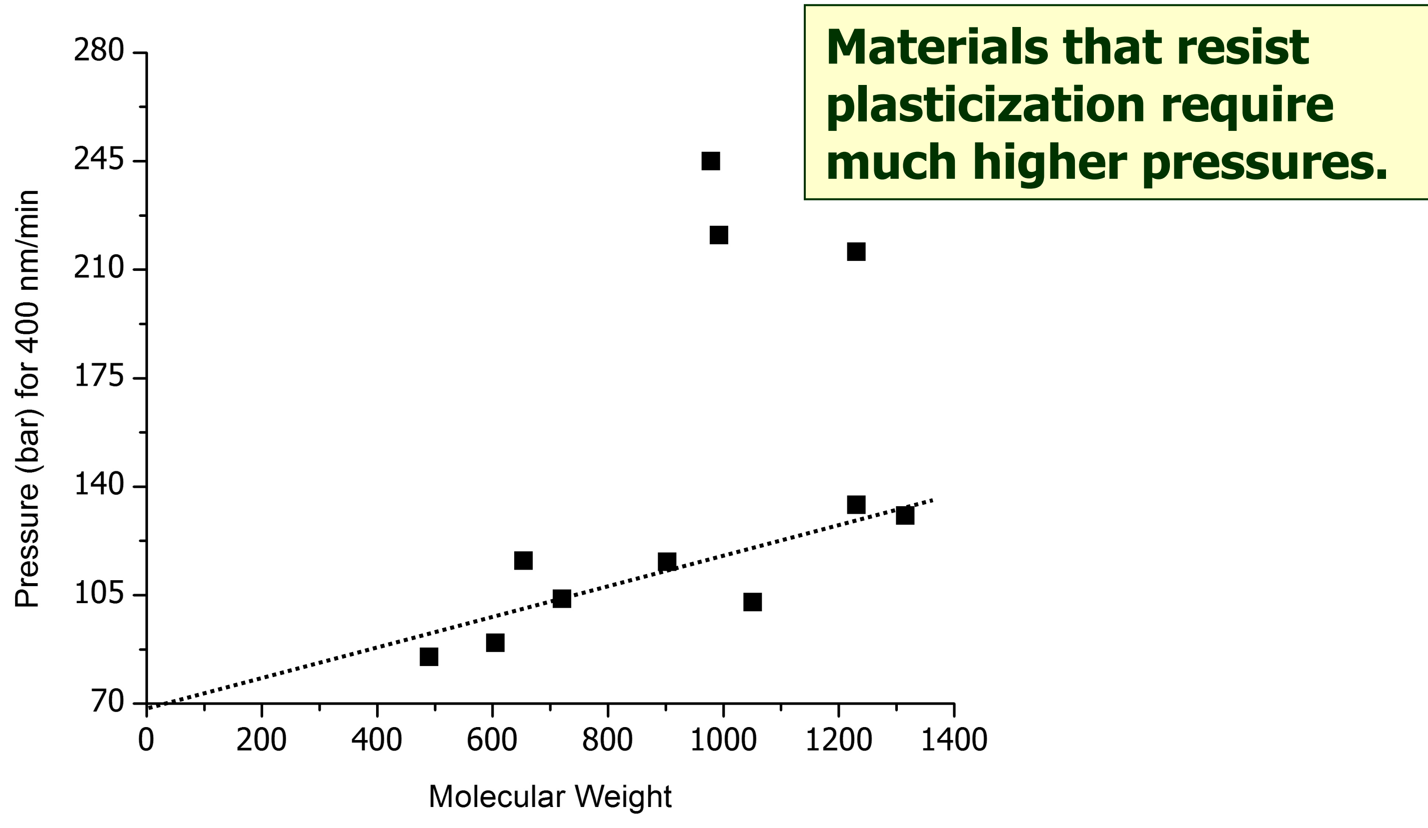


Effects of Polarity: More Polar, Less Soluble



- **Study using Cornell dissolution rate monitor**
- **Molecules with less than 3 –OH groups still significantly soluble.**
- **Effect more pronounced at lower temperatures.**
- **Indicative of contrast between exposed and unexposed regions.**

Effect of Molecular Weight and Tg



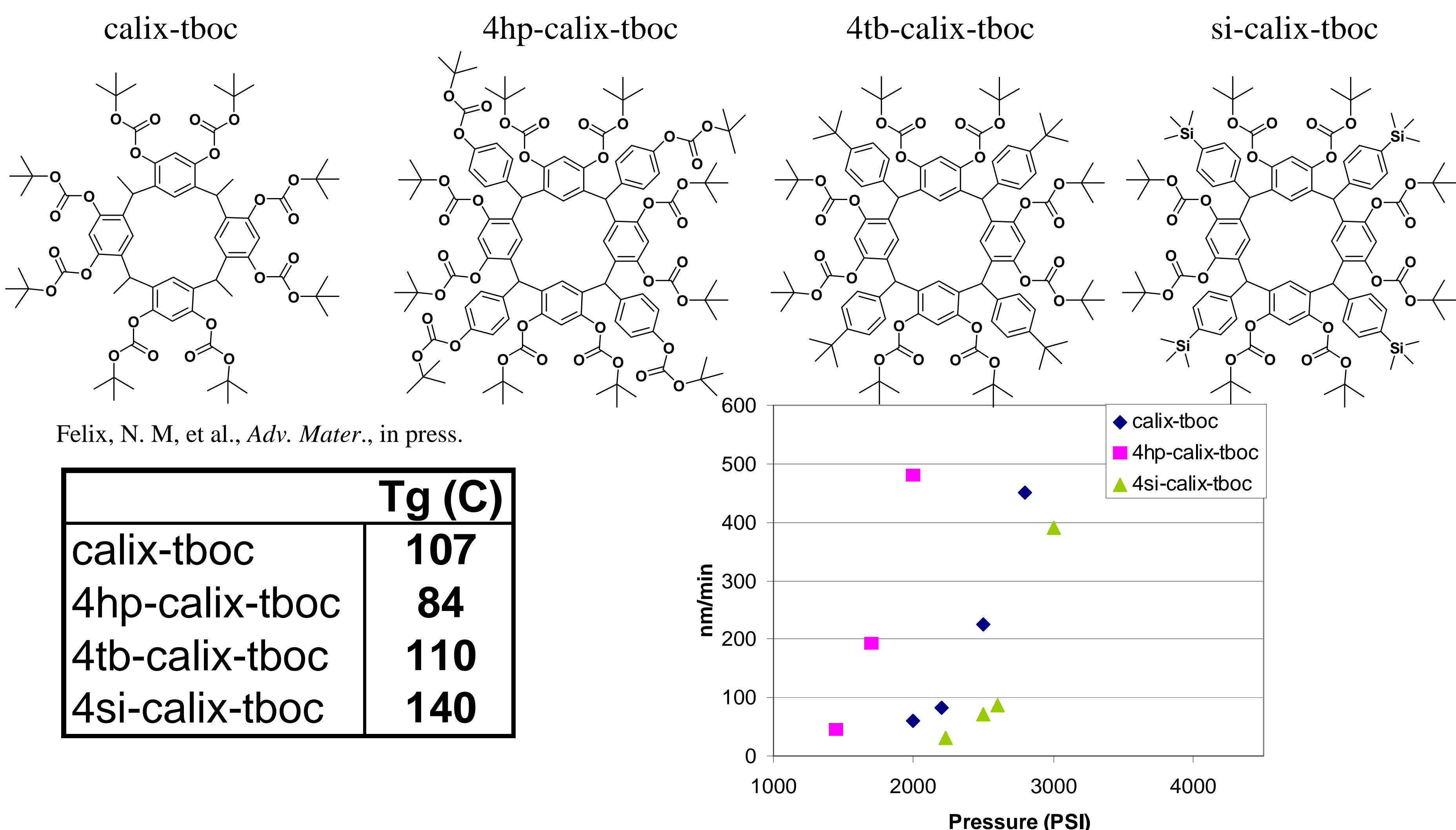
Necessary pressure to achieve dissolution rate increases predictably with larger MW.

However, photoresists approaching 2000 g/mol still soluble in $scCO_2$!

Felix, N. M, et al., *J. Mat. Chem.*, **17**, (2007) 4598-4604.

Calix[4]resorcinarenes:

Tunable Dissolution Rates, Soluble with no fluorine

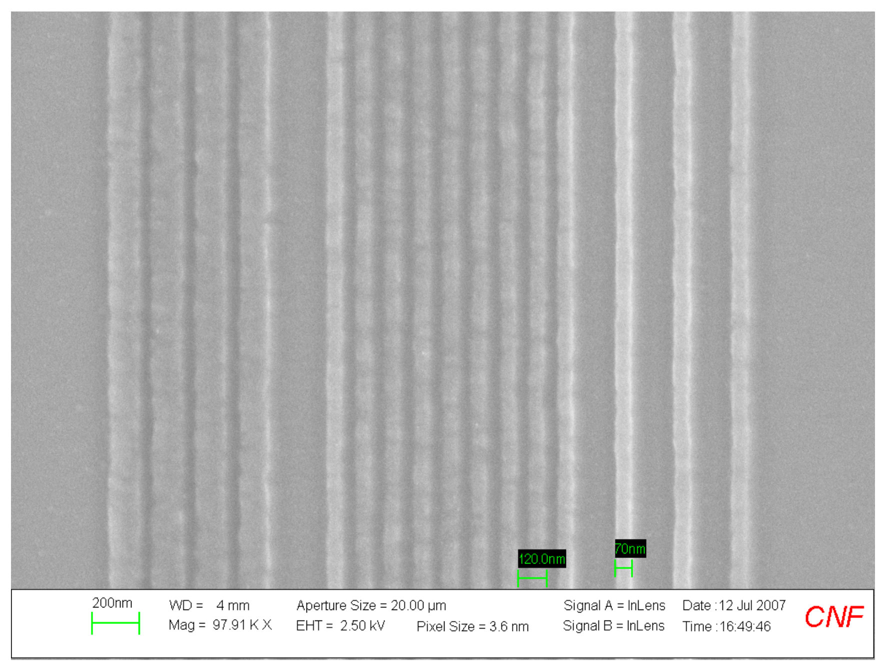


Felix, N. M, et al., *Adv. Mater.*, in press.

	Tg (C)
calix-tboc	107
4hp-calix-tboc	84
4tb-calix-tboc	110
4si-calix-tboc	140

Patterning of Molecular Glasses in $scCO_2$

Developed at 37 °C, 2500psi (e-beam exposure)



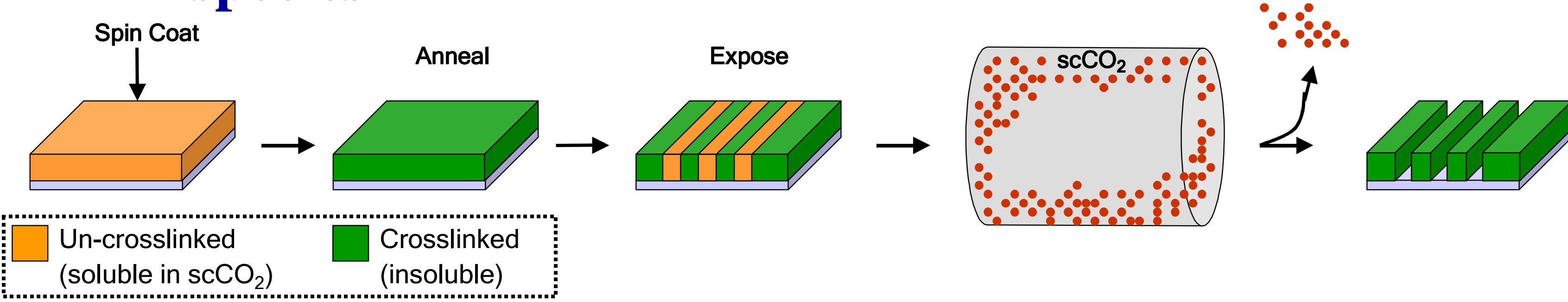
- Calixarenes provide information about patterning non-polar molecular building blocks for a variety of applications

- Sub-100nm performance shown with calix[4]resorcinarenes developed in $scCO_2$
- Model systems for low k glasses

Chain Scission Resists for Positive-tone $scCO_2$ Processing

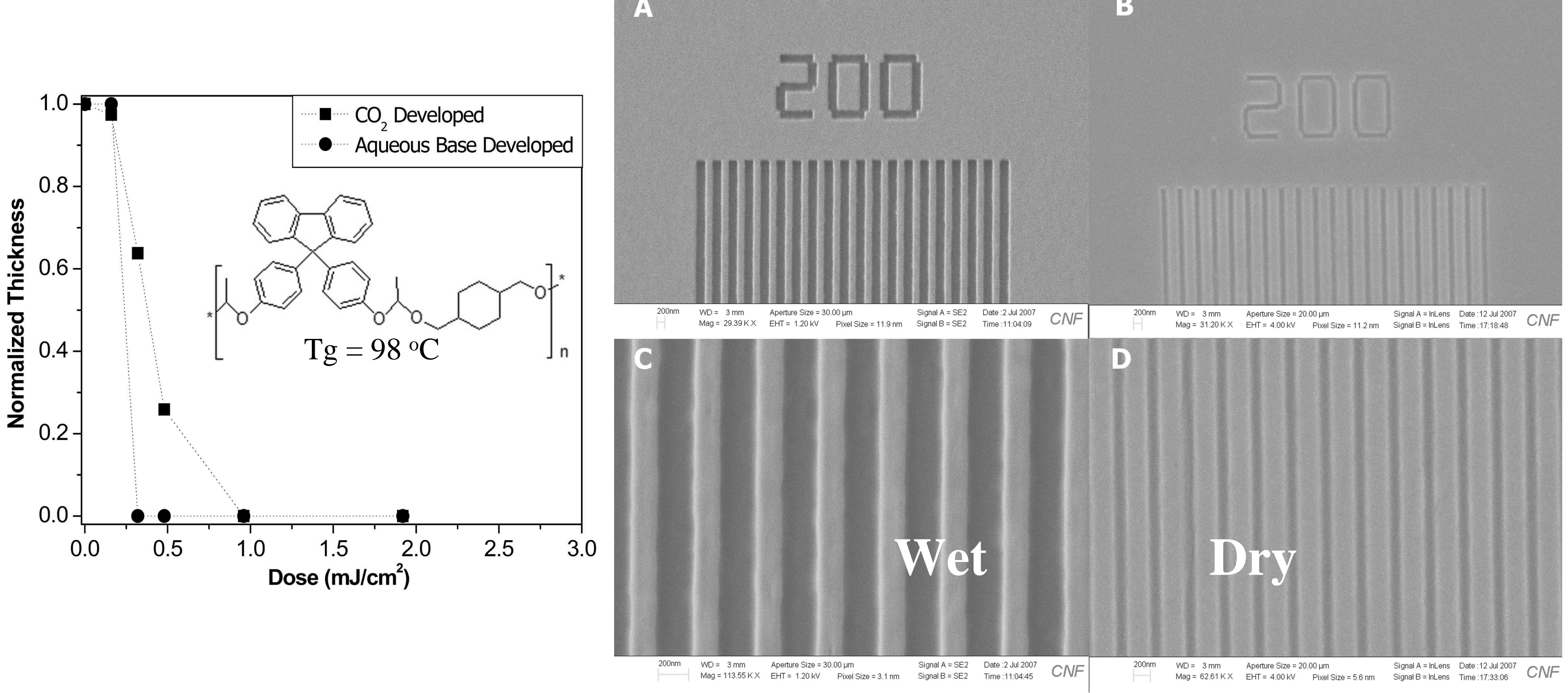
- **PMMA is classical positive tone resist**
  - **High resolution e-beam, EUV resist with low LER**
  - **Problem: low sensitivity**

- **Acid catalyzed chain scission**
  - **Improved sensitivity**
  - **Use acetal bonds to crosslink otherwise $scCO_2$ soluble species**



Positive Tone Patterning:

- **Electron-beam patterning, 100kV, Cornell**
- **Develop in $scCO_2$: 40 °C, 2000 psi (140 bar)**
- **First intrinsic positive-tone system for $scCO_2$ development!**
- **Either aqueous base (wet) or $scCO_2$ (dry) development possible**

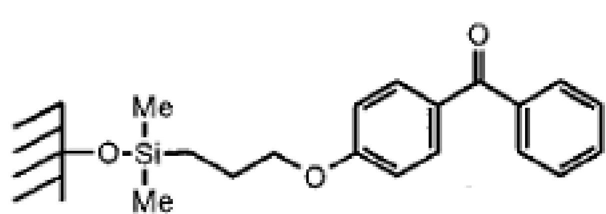


SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Cornell University

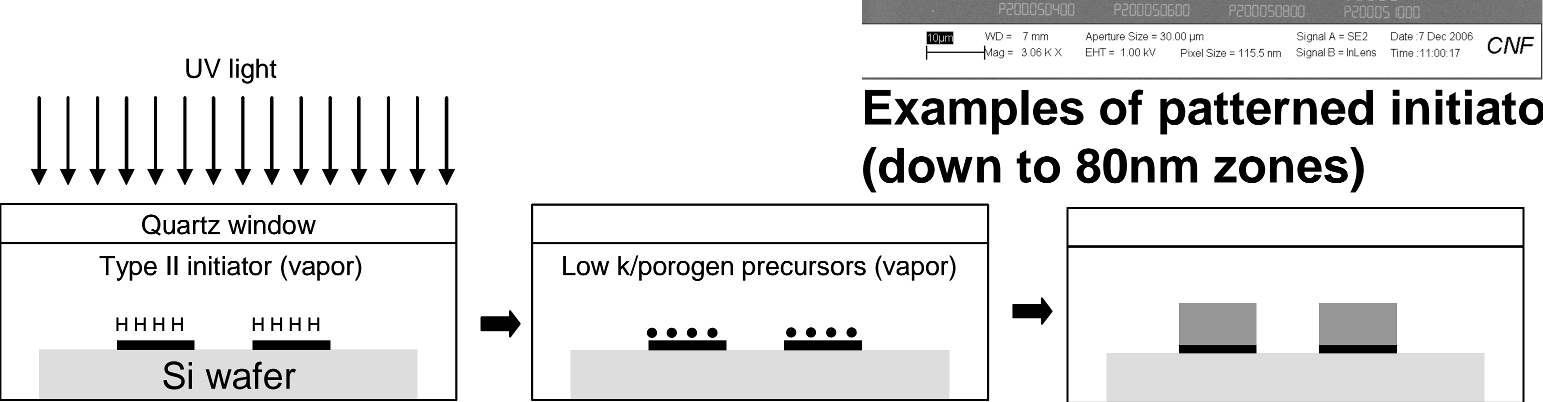
Photoinitiated CVD

- Photoinitiated CVD can grow low k polymer material by initiating free radical chemistry from the patterned surface with potential to directly produce patterned thin films
- Patterned high resolution initiator films supplied to Gleason group

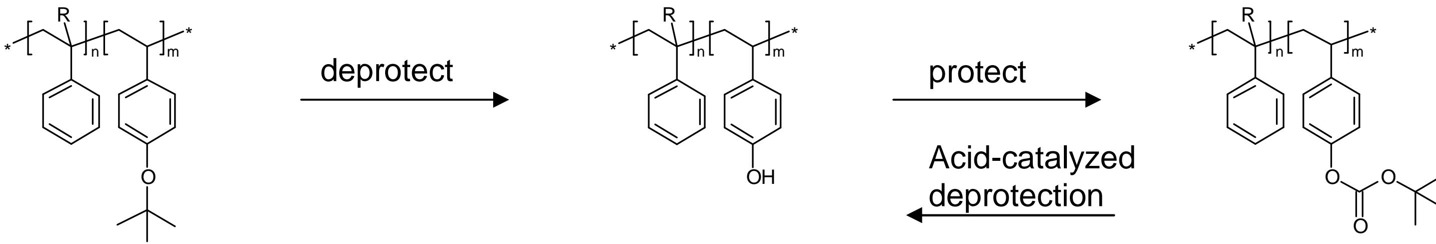


Surface initiator for piCVD

Examples of patterned initiator (down to 80nm zones)



Self-Assembling Polymers



R = -H

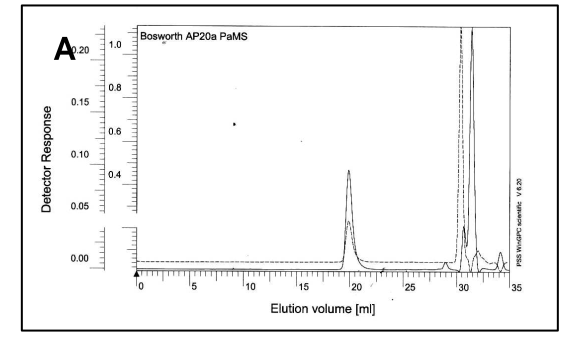
PS-PtBuOS	PS-PHOST	PS-PtBOCOS
34K-29K	**34K-20K**	**34K-36K**

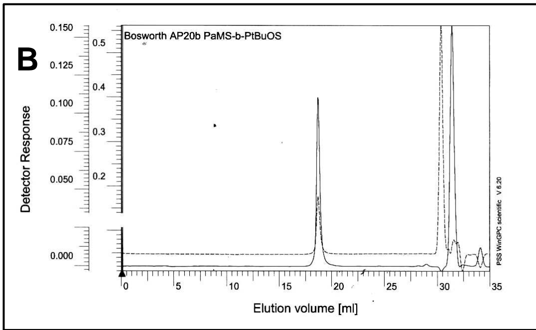
R = $-CH_3$

PαMS-PtBuOS	PαMS-PHOST	PαMS-PtBOCOS
7K-25K	**7K-17K**	
7K-21K	**7K-14K**	
7K-23K	**7K-16K**	**7K-29K**
18K-64K	**18K-35K**	**7K-64K**

Block coolymers used as template by Watkins for patternable low k materials

Black: have been synthesized; Red: polymers provided to Watkins group





GPC traces of synthesized polymer, including UV (solid) and IR (dotted) traces. a) PαMS block, 7.0 kg/mol, D. 1.10; b) PαMS-b-PtBuOS, 28 kg/mol, D 1.10 (from UV traces). This corresponds with PαMS-PHOST 7K-14K

Industrial Interactions and Technology Transfer

- AZ Microelectronics has hired Nelson Felix
- Post-doc (R. Ayothi) and former student (V. Pham) hired by JSR Microelectronics

- Interactions with IBM Almaden Research Center
- Discussions with Rohm and Haas Microelectronics
- Interactions with Intel

- Collaboration with International Sematech for EUV exposures

    - Kim Dean, Sematech
    - Kevin Orvek, Intel / Sematech
    - Will Conley, Freescale / Sematech

Future Plans

Next Year Plans

- Assess use of $scCO_2$-processable inorganic materials as low-k precursors
- Continue synthesis efforts for low-k porogens and self-assembly precursors
- Demonstrate improved vapor deposition of low-k precursors with dry $scCO_2$ processing

Long-Term Plans

- Explore use of $scCO_2$ in ordering / assembly of low-k materials
- Combine molecular glass precursors with self-assembling templates for low k, high resolution patterning materials
- Continue to demonstrate new chemistries for patternability and functionality of small, nonpolar molecules

Publications, Presentations, and Recognitions/Awards

Publications

- Frauke Pfeiffer, Nelson Felix, Christian Neuber, Christopher K. Ober, Hans-Werner Schmidt, "Physical Vapor Deposition of Chemically Amplified Photoresists: A New Route to Patterning Molecular Glass Resists", Adv. Func. Mater., in press.
- Frauke Pfeiffer, Nelson M. Felix, Christian Neuber, Christopher K. Ober, and Hans-Werner Schmidt, "Towards Environmentally Friendly, Dry Deposited, Water Developable Molecular Glass Photoresists", Advanced Materials, in press.
- Nelson M. Felix, Anuja De Silva, Camille Man Yin Luk and Christopher K. Ober, "Dissolution Phenomena of Phenolic Molecular Glass Photoresist Films in Supercritical CO2", J. Mater. Chem., (2007), 17(43), 4598-4604.
- Anuja De Silva, Jin Kyun Lee, Xavier André, Nelson M. Felix, Heidi B. Cao, Hai Deng and Christopher K. Ober, "Study of the Structure-Properties Relationship of Phenolic Molecular Glass Resists for Next Generation Photolithography", Chem. Mater., in press.
- Nelson Felix and Christopher K. Ober, "Acid-Labile, Chain-Scission Polymer Systems Used as Positive-Tone Photoresists Developable in Supercritical CO2", Chem. Mater., in press.
- Nelson M. Felix, Anuja De Silva, and Christopher K. Ober, "Calix[4]resorcinarene Derivatives as High Resolution Photoresist Materials for Supercritical CO2 Processing", Adv. Mater., in press.

Presentations

- IBM Self-assembly Workshop, Almaden, CA, Jan. 15, 2008. "Photopatternable Block Copolymers: Chemically Active BCP Resists", invited talk.
- International Symposium on Advanced Materials and Nano-materials with Precisely Designed Architectures, October 4th – 6th in Sapporo, Japan. "Studies in the biological-materials interface", invited talk.
- Conference on Nanomaterials for Defense Applications, San Diego, CA, April 24 – 26, 2007. Lithography and Biology: 2D and 3D Patterning for the Biology-Materials Interface, invited talk.

Recognitions/Awards

- 2007 Humboldt Research Prize for C.K. Ober
- Nelson Felix, ERC Simon Karecki Award, Feb 2007.

Students on Task 425.017

- Graduated Students and Current Affiliation
  - Nelson Felix, AZ Microelectronics, Dec 2007
  - Victor Pham, JSR Microelectronics, May 2004
- Current Students and Anticipated Grad Date
  - Jing Sha, Sept. 2011
  - Katy Bosworth, May 2009
- Internships (Task and related students)
  - Katy Bosworth, IBM
  - Evan Schwartz, Intel
  - Anuja de Silva, IBM

Environmentally Benign Vapor Phase and Supercritical CO_2 Processes for Patterned Low k Dielectrics

(*Task Number: 425.017; Watkins sub-task)*

PIs:

- **James J. Watkins, University of Massachusetts, Amherst**
- **Christopher K. Ober, Cornell University**
- **Karen K. Gleason, Massachusetts Institute of Technology**

Graduate Students:

- **Alvin Romang, UMass Chemical Engineering**
- **Sivakumar Nagarajan, UMass Polymer Science & Engineering**

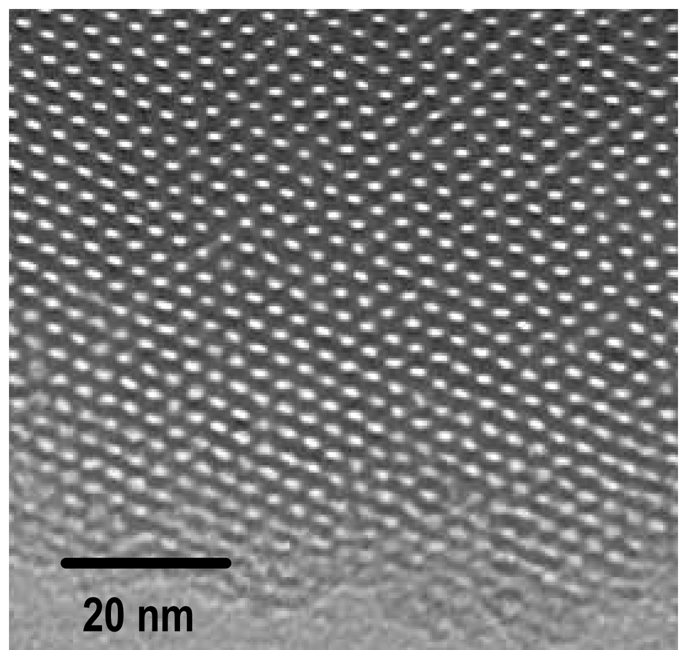
Cost Share (other than core ERC funding):

- **NSF Center for Hierarchical Manufacturing, 40K**
- **NSF NIRT, 25K**

ULK Mesoporous Films Prepared in CO_2

First Generation Films Exhibit Excellent Performance

- k< 2.2 demonstrated
- Rapid process times, 1st generation survives CMP
- Low stress, high crack threshold
- Small pores are accessible via template blends



Program Objectives:

- **Improve Performance, Reduce ESH Burden**

- **Optimize Mechanical Properties**
  inclusion of novel POSS copolymer templates
  (see A. Romang poster)

- **Demonstrate Viable Direct Patterning Approach**
  simultaneous pattern generation of nanopores and device features
  eliminate/reduce traditional litho, etch, clean cycles
  process compression = cost savings + resource reduction
  fat lines now, subsequent entry point for ULK < 2.2

ESH Metrics and Impact of CO_2 as Solvent (Ober Talk)

	Usage Reduction			Emmision Reduction			
Goals/Possibilities	Energy	Water	Chemicals	PFCs	VOCs	HAPs	Other
Reduce organic solvents used in processing materials	No energy used to purify and treat water	Eliminate need for water usage	Up to 100% reduction of organic solvents used	N/A	Minimal use of organic solvents	Up to 100% reduction of HAPs	N/A
Reduce processing time / temperature	Reduce anneal process costs	N/A	N/A	N/A	N/A	N/A	N/A
Additive processing	N/A	N/A	Eliminate waste of costly material	N/A	Minimal use of organic solvents	N/A	N/A

Eliminates water usage in development --- Eliminates organic solvents --- Recyclable

Additional ESH Benefits of Direct Patterning (This Talk)

- Compression/Elimination of Multiple Solvent/Water/Waste Intensive Processes
- Eliminate traditional litho sequence
- Eliminate etch sequence
- Eliminate/reduce clean and repair sequences

Doping Templates with "Nanoparticle" Fillers to Improve Mechanical Properties

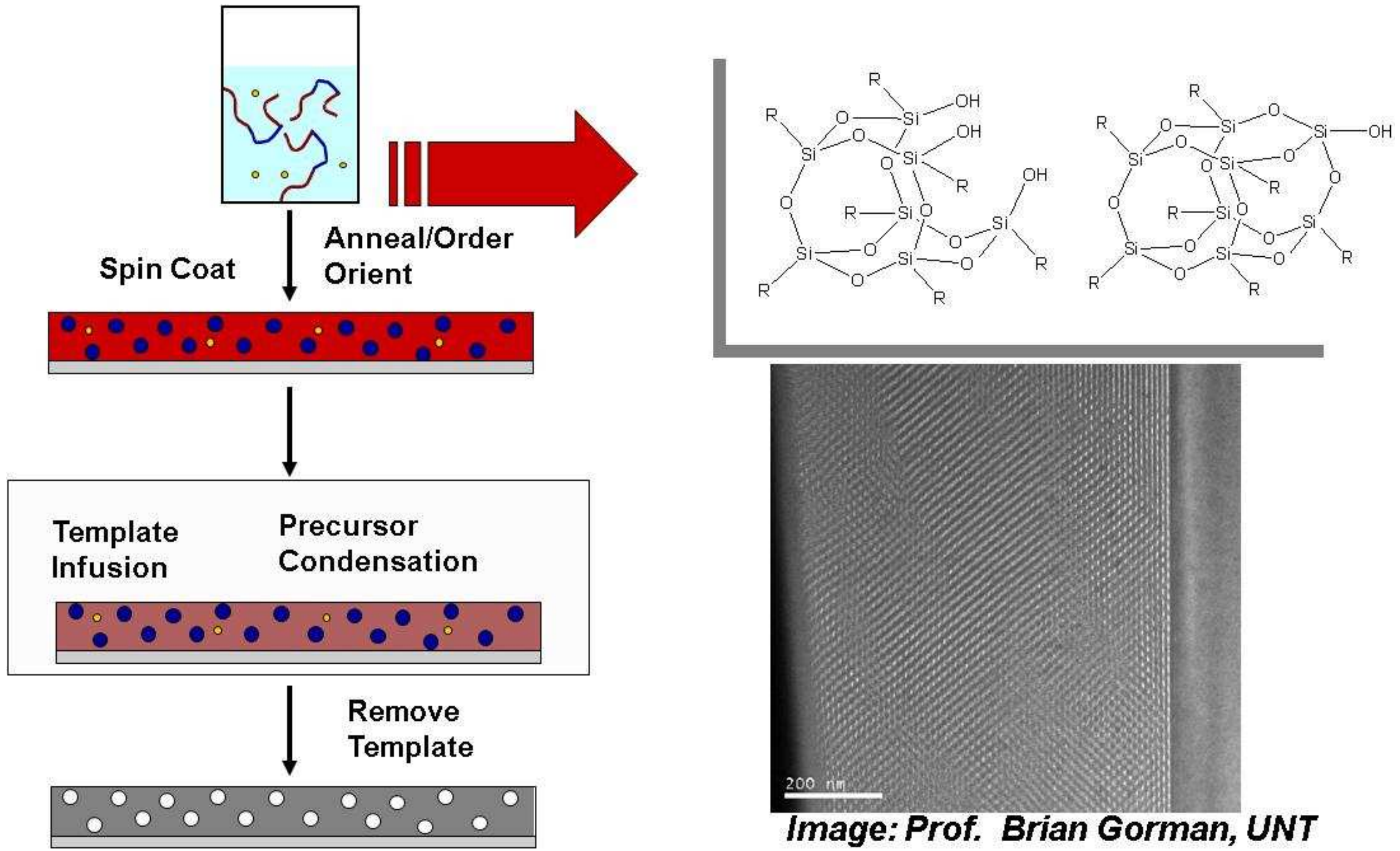


Image: Prof. Brian Gorman, UNT

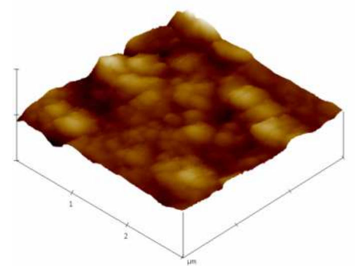
Last year we reported promising feasibility results including improved modulus and hardness but film uniformity at the wafer scale was an issue

Copolymerization of Acryl isobutyl POSS with Acrylic Acid: Uniform template films, No POSS aggregation

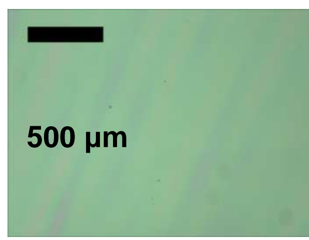
R = *i*-butyl

Free radical polymerization with 2 to 1 weight ratio of POSS to acrylic acid in THF

Smooth Silica/POSS Films upon Template Infusion

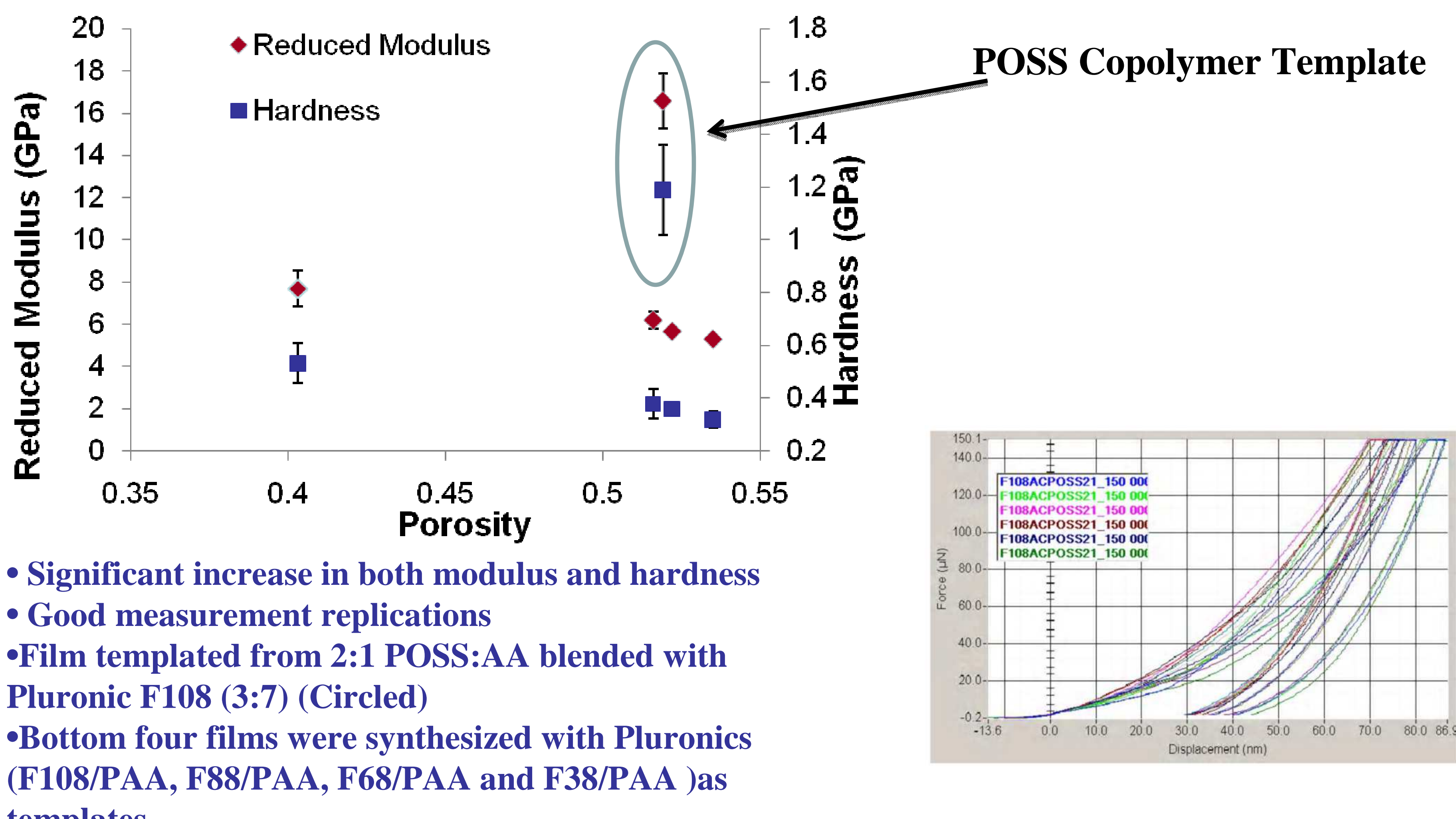


RMS Roughness: 5.7 nm
Z range: 49.7 nm
Z scale: 100 nm



Optical micrograph showing long-range film smoothness

Addition of POSS Improves Mechanicals Significantly

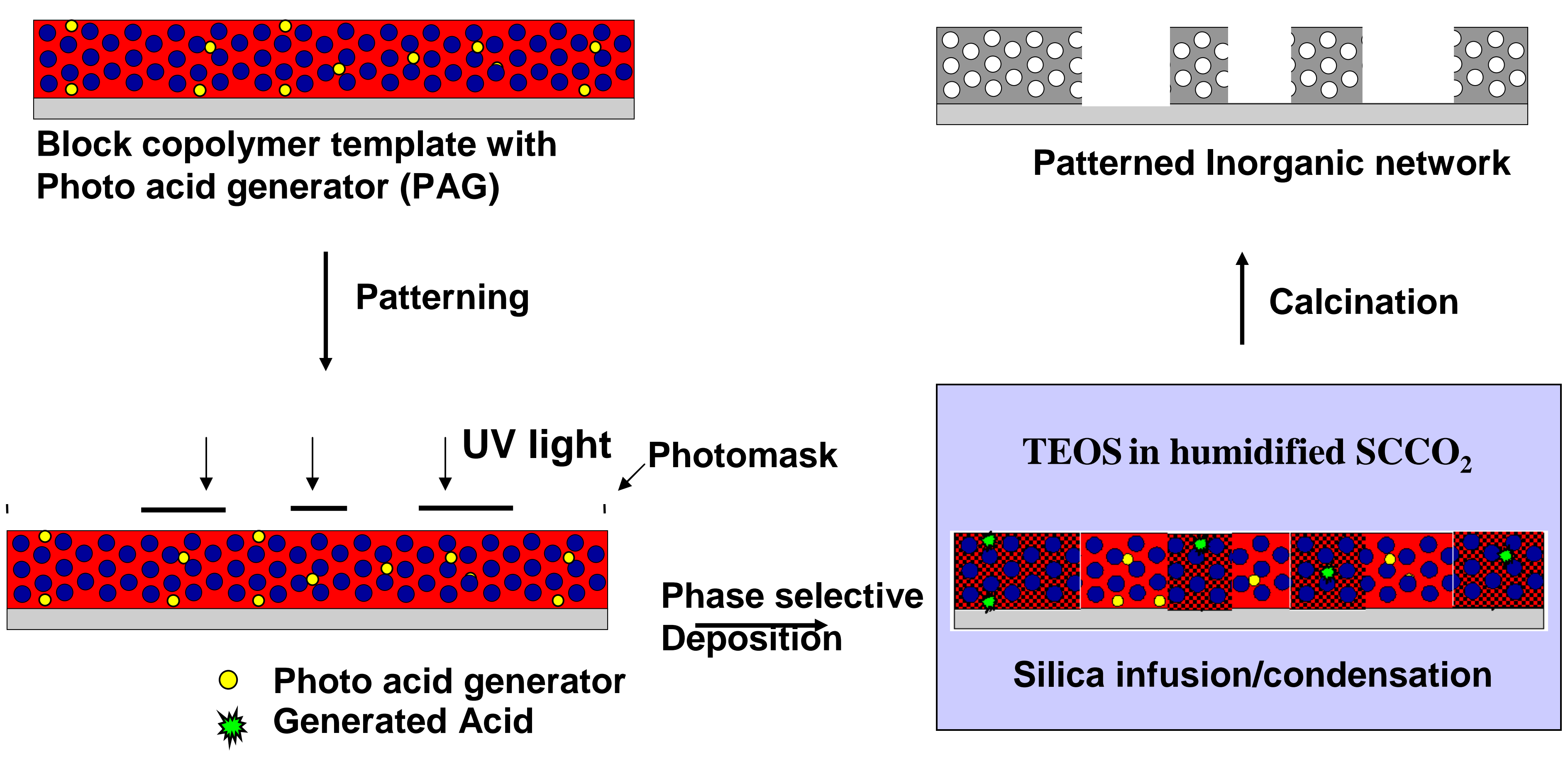


• Significant increase in both modulus and hardness
• Good measurement replications
•Film templated from 2:1 POSS:AA blended with Pluronic F108 (3:7) (Circled)
•Bottom four films were synthesized with Pluronics (F108/PAA, F88/PAA, F68/PAA and F38/PAA)as templates

Fabrication of Micro-patterned Mesoporous Silica Films

Domain (microscopic) and Device (nanoscopic) level control:

Controlling the presence of acid in two different length scales by using a photo acid generator (PAG) instead of normal acid (pTSA).



Summary of Process Steps

1. **Spin Coat Template Containing PAG**
   similar to photoresist spinning

2. **Expose Template Using Stepper**

3. **Infuse Template with CO_2 / Alkoxide Solution**
   infusion is rapid (minutes)
   low CO_2 volumes (2-3 vessel exchanges; purge, infuse, purge)

4. **Detemplate and Cap**
   in plasma using PECVD tool

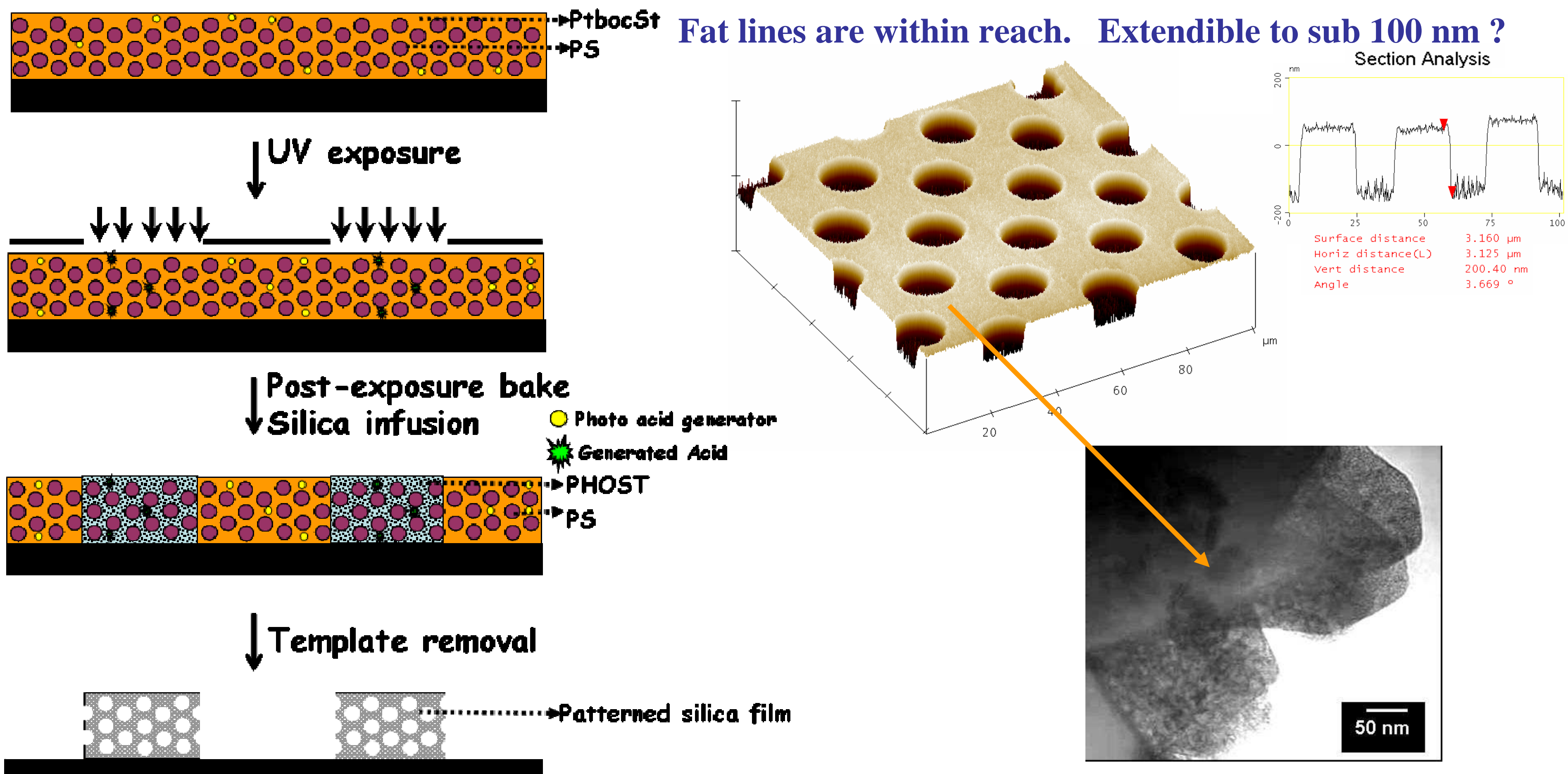
Patterned Mesoporous silica films from PS-b-PtbocSt films

Collaboration with C. Ober

Domain (nanoscale) and Device (micron scale) level control

Feasibility Test – Crude Contact Mask

Fat lines are within reach. Extendible to sub 100 nm ?



Last year we reported feasibility in 248 resists

This Year: Mesoporous silicate films from chemically amplified Poly(tertiary butyl methacrylate) copolymer templates

By using a PtbMA based block copolymers, micro-patterned mesoporous silicate films can be obtained via dual tone replications

Dual Tone Replication

PtbMA

PS

UV exposure; <130°C Baking

UV exposure; >180°C Baking

PMAA

PMAN

Silica deposition; Calcination

Flood exposure

Patterned Mesoporous silica film (Negative tone replication)

Silica deposition; Calcination

Patterned Mesoporous silica film (Positive tone replication)

H^+ Bake <130°C

Bake >180°C

Poly(tertiary butyl methacrylate)(PtbMA) (Hydrophobic)

Poly(methacrylic acid)(PMAA) (Hydrophilic)

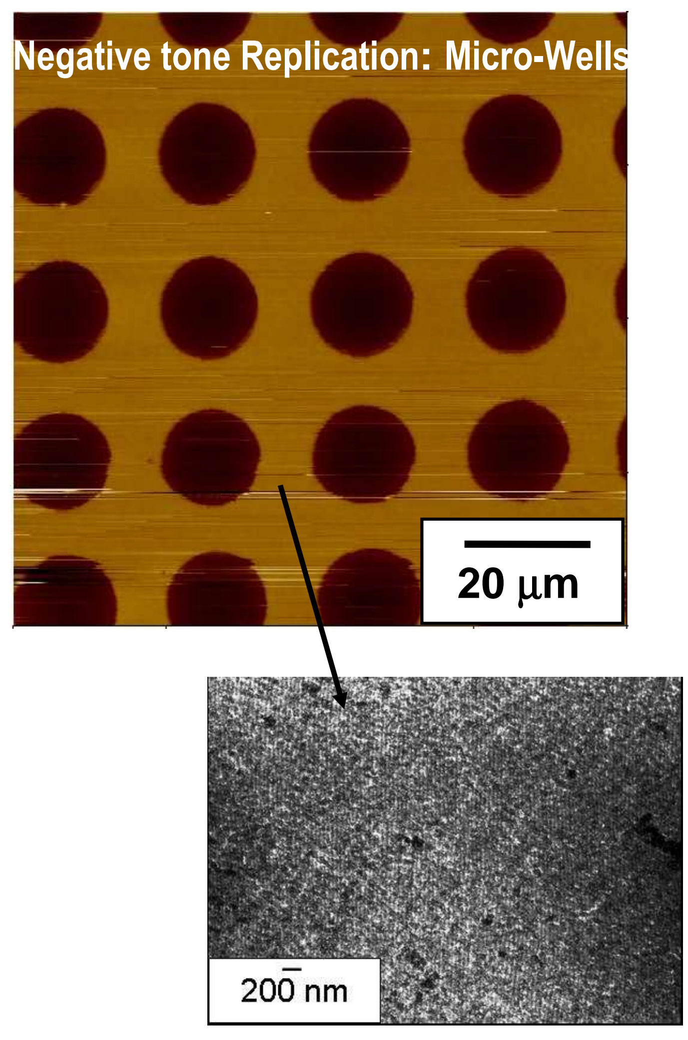
Poly(methacrylic anhydride) (PMAN) (Relatively hydrophobic, crosslinked)

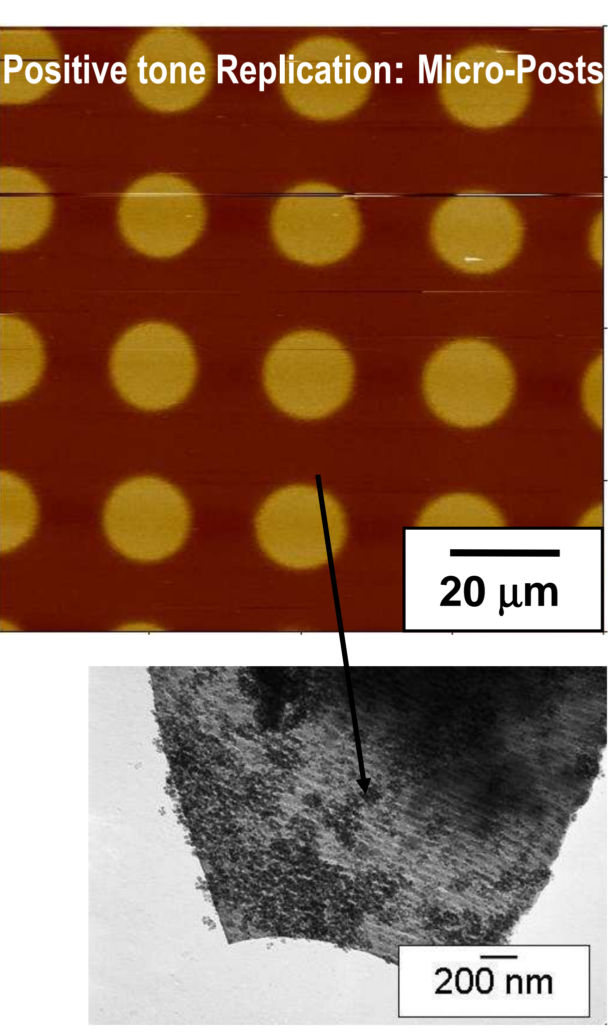
(Ito H et al., Macromolecules 1988)

Dual-tone Patterned Mesoporous Silica Films via SCF Processing:

Combining domain and device level replications

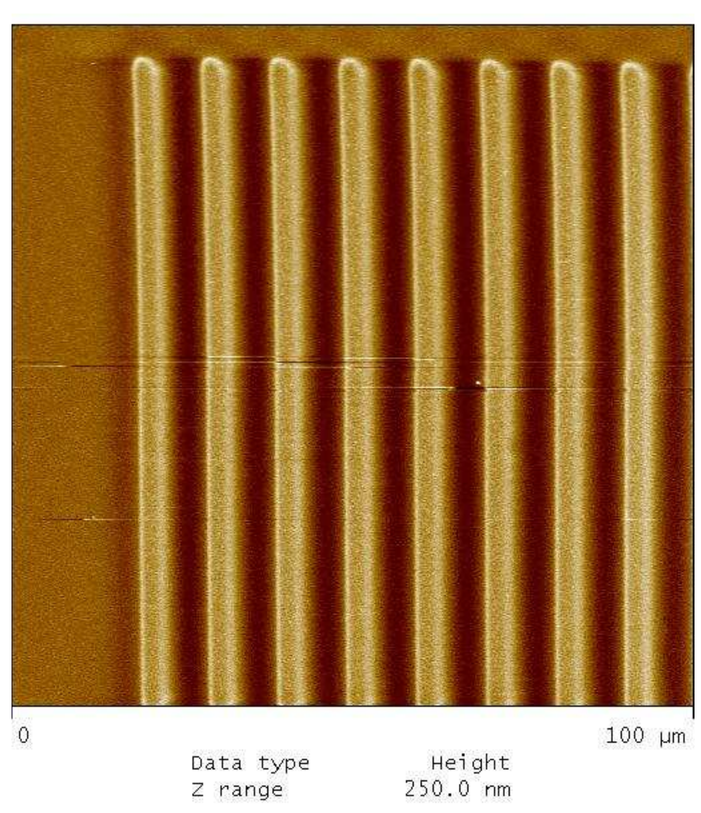
- Photolithography – done with crude contact mask



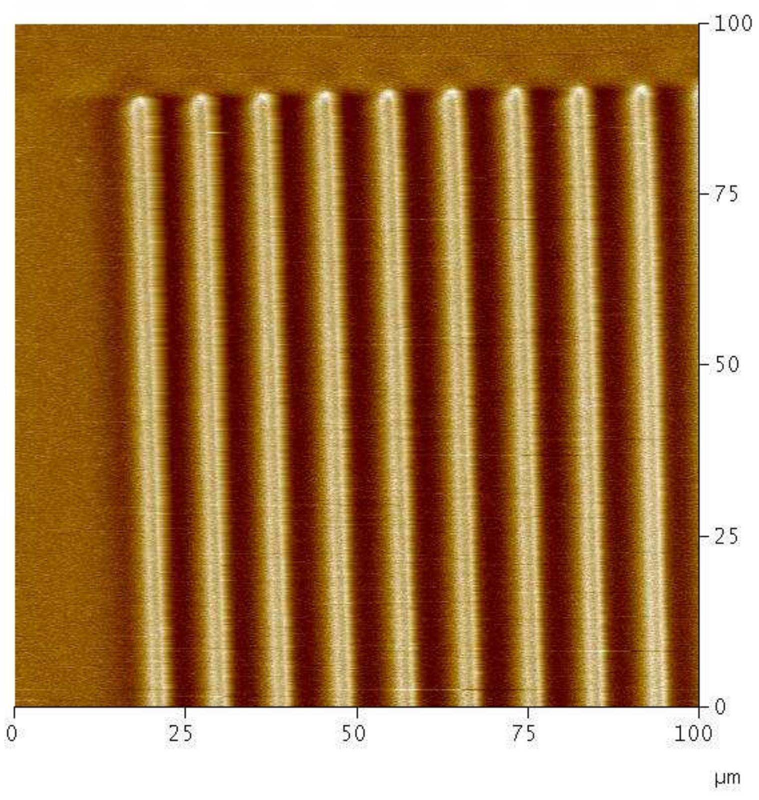


Negative tone replications using a crude contact mask: Patterns with various sizes of lines and spaces

Lines: ~ 4 µm ; Space: ~ 6µm

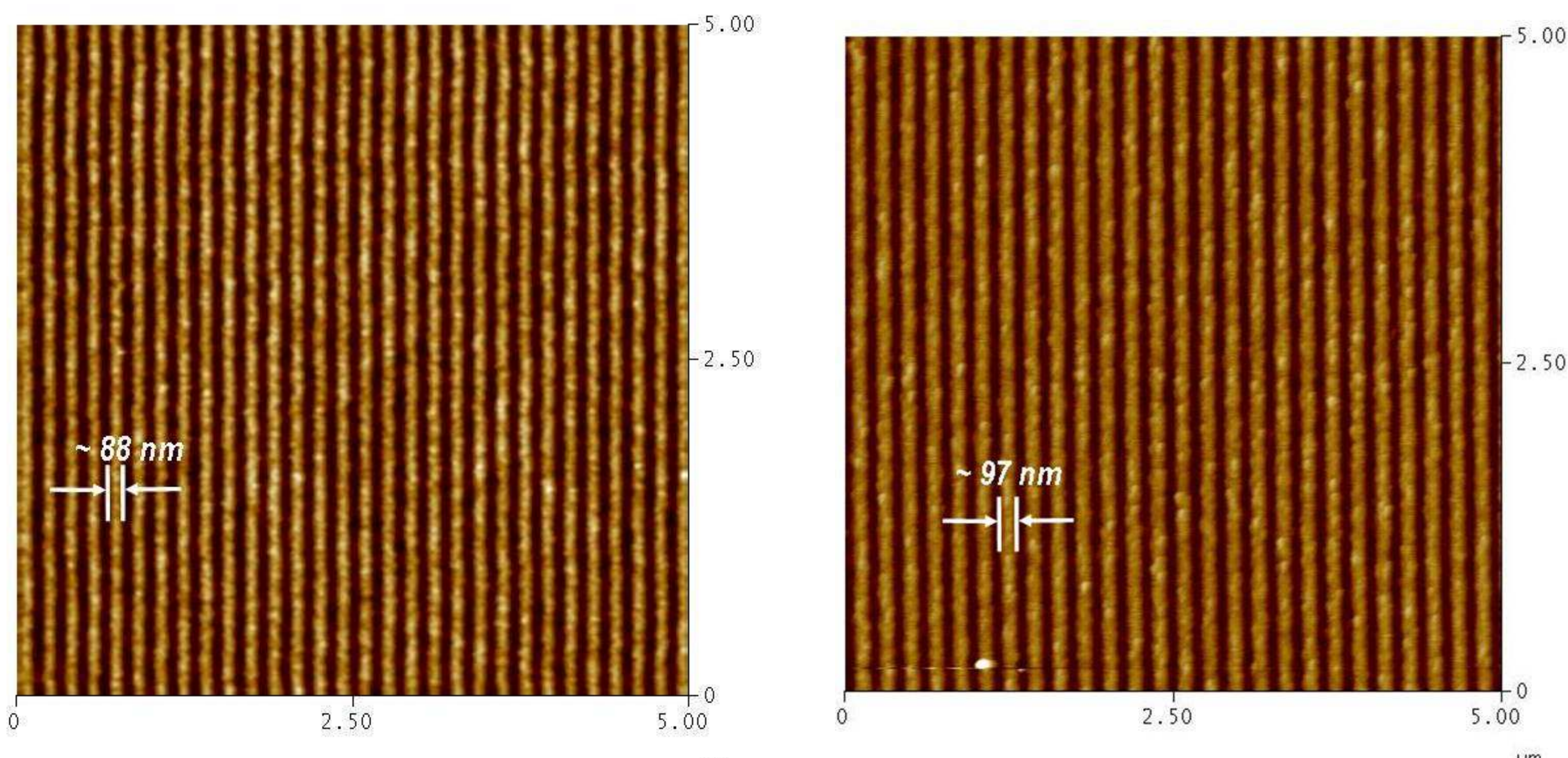


Lines: ~ 2.5 µm ; Space: ~ 6µm



Directly Patterned Dielectric Films: Is High Resolution Possible?

- In collaboration with a partner, feasibility demonstration of direct patterning of sub -100 nm lines.
- First attempt, off-the-shelf resist, no optimization
- No etch!!



Impact: Potential for streamlined integration of ULKs, ESH benefits and, cost savings via process simplification

Conclusions

Use of POSS additives substantially improves mechanicals
- **this year we developed a POSS copolymer template that improves uniformity**
- **k measurements underway with Gleason**

Direct Patterning Shows Promise
- **last year feasibility at 248 using contacts masks demonstrated**
- **this year**
  - **extended to acrylate-based 193 nm resists**
  - **demonstrated domain level and device level replications**
  - **demonstrated feasibility of sub-100 nm resolution using un-optimized resists**

Process compression via direct patterning offers cost and ESH benefits

Recent acquisition of 200 mm tool will permit scale-up

Acknowledgments

Additional funding: UMass Center for Hierarchical Manufacturing and NSF NIRT

BOC Edwards 200 mm Tool Donation

Milestones and Future Work

- **Milestones**
  - **Substantial increase in film hardness**
    - POSS/acrylic acid copolymer blended with Pluronics offer increases in hardness and good uniformity
    - Hardness > 1.9 GPa, exceeds initial goals
  - **Directly patterned dielectrics**
    - Proof of concept achieved in 248 and 193 nm resists
    - Demonstrated good domain and device level replication
    - Demonstrated sub-100 nm patterning without etch
    - Significant co-funding from NSF CHM / NSF NIRT
- **Future Work**
  - **Optimize film and template chemistry**
    - optimize mechanical properties
    - develop families of films, establish k vs. hardness for doped materials
  - **Optimize resists and resolution for directly patterned dielectrics**
  - **Explore NIL of new monomers with Gleason**

Industrial Interactions and Technology Transfer

- Interactions with IBM Almaden Research Center
- Resist formulations from Rohm and Haas Microelectronics
- Interactions / collaboration on exposed resists with AMD
- Interactions with IMEC
- 200 mm tool donation from BOC
- SCF Clean Room Facility Operational at UMass

Publications, Presentations, and Recognitions/Awards

Publications

Nagarajan, S.: Joan K. Bosworth, J. K.; Ober, C.K.; Russell, T.P; Watkins, J. J. "Simple Fabrication of Micropatterned Mesoporous Silica Films Using Photoacid Generators in Block Copolymers" *Chemistry of Materials,* 2008, 20, 604–606.

Tirumala, T. R.; Pai, R.A. Agarwal, S.; Bhatnagar, G. Romang A., Chandler C. Gorman, B. P. Jones, R. L.. Lin E. K. , Watkins, J.J. "Nanoporous Silica Films with Long-ranged Order Prepared from Block Copolymer/ Homopolymer Blend Templates" *Chemistry of Materials* 19(24); 5868-5874, 2007.

Presentations

Advanced Metallization Conference Short Course on Micro and Nano-Scale Interconnect Techniques , October 2007, invited

IUMRS-ICMAT-2007 Bangalore, India (October 2007), "Preparation of Device Nanostructures via Templating Techniques in Supercritical Fluids", invited

Materials Research Society 2007 Fall Meeting, Synthesis and Surface Engineering of 3D Nanostructures Symposium, Boston, MA (Nov 2007), invited.

ACS Division of Polymer Chemistry Workshop "Opportunities for Nanostructured Polymeric Materials for Device Fabrication, Lake Tahoe, NV (Nov. 2007), invited

Materials Research Society, 2007 Spring Meeting, Robust Ultra-Low K and Directly Patterned Interlayer Dielectrics via Templating Processes, San Francisco, (April 2007), invited

TechCon 2007 "Directly Patterned Dielectric Films Templated from Chemically Amplified Block Copolymers", Austin TX, presented by S. Nagarajan

Recognitions/Awards

UMass Chancellors Award for Excellence in Research to Jim Watkins

Students on Task 425.017

Current Students and Anticipated Grad Date

- Siva Nagarajaran, June 2008 (interviewing now)
- Alvin Romang, Summer 2010

Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro- and Nano- Electronics Manufacturing

(Task Number: B,C- 425.022)

- **Subtask A: Ge Surface Clean and Passivation,**
  Presenter: Masaharu Kobayashi

- **Subtask B: Post Etch Residue Removal in Copper Damascene Structures,**
  Presenter: Nandini Venkataraman

- **Subtask C: Cleaning and Drying of Dielectrics and Nano-structures,**
  Presenter: Harpreet Juneja

Environmentally-Friendly Cleaning New Materials and Structures for Future Micro- and Nano- Manufacturing

(Task Number: B,C- 425.022)

Subtask A. Ge surface clean and passivation

PIs:

- **Yoshio Nishi, Electrical Engineering, Stanford University**

Graduate Students:

- **Masaharu Kobayashi: PhD candidate, Electrical Engineering, Stanford University**
- **Jungyup Kim (40%), PhD candidate, Material Science and Engineering, Stanford University**

Other Researchers:

- **Jim McVittie (10%), Senior research associates, Electrical Engineering, Stanford University**

Cost Share (other than core ERC funding):

- **$25k INMP**

Objectives

- **Examine the effectiveness of Ge surface cleaning/passivation to device component, especially metal/Ge contact.**
- **Develop new technique for low contact resistance in metal/Ge Schottky contact for high performance/low power Ge device application.**
- **Validate low Schottky barrier in metal/Ge Schottky junction with novel surface passivation.**

ESH Metrics and Impact

1. *Reduction in the use or replacement of ESH-problematic materials*
2. *Reduction in emission of ESH-problematic material to environment*
3. *Reduction in the use of natural resources (water and energy)*
4. *Reduction in the use of chemicals*

Ge is viewed as the future of high performance MOSFET beyond ITRS 32nm node, as Si based channel will face significant difficulty in performance improvement, and also provide opportunity to deal with power reduction based upon lower operating voltages, and coupled with introduction of optical interconnect with Ge based on-chip detectors.

This research would result in the following ESH impacts:

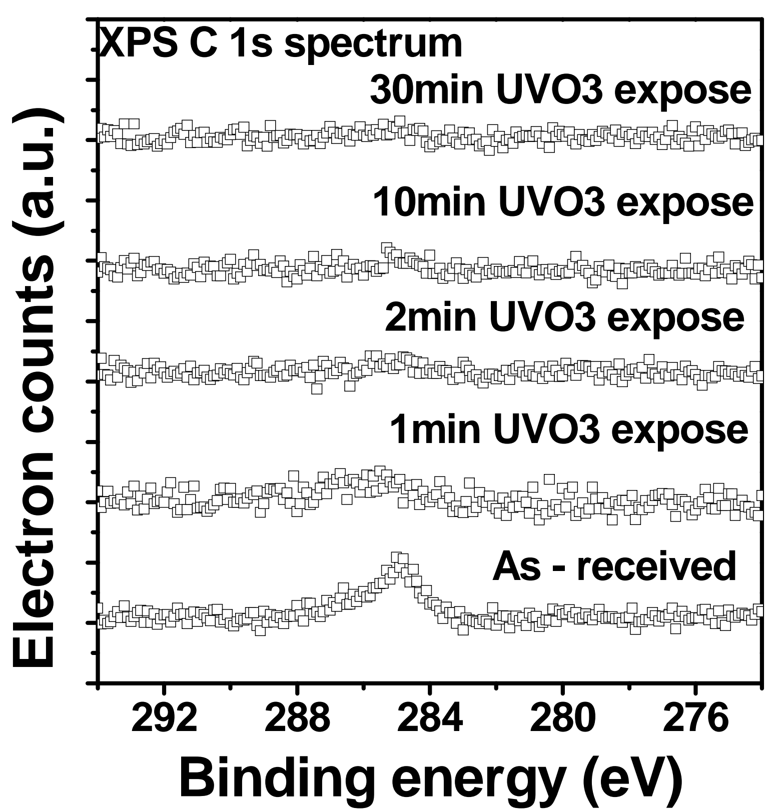
1. **Process simplification as a consequence of metal source and drain technology which eliminate heavy ion implantations of both donor and acceptor impurities which are known as potentially toxic. Metal source/drain will eliminate implanted impurity activation process, and also allow "gate first process" for reduction of thermal and chemical process steps.**
2. **Power reduction due to lower operating voltage which will reduce consumption of natural resources in energy generation.**

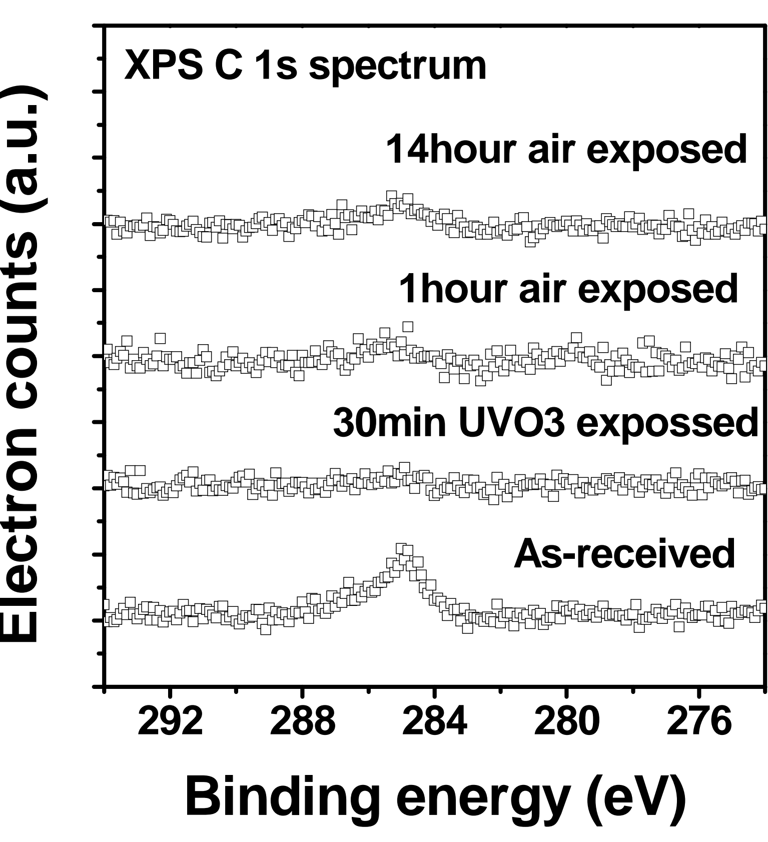
Importance of Ge surface clean/passivation

- Appropriate Ge surface clean is essential for reliable process control.
  - Metal removal (2006-2007 annual report)
  - Carbon contamination removal
  - Native oxide removal
- Ge surface is more sensitive to oxygen so that defective Ge native oxide is easily grown.
- Proper oxide removal and surface passivation is necessary to obtain sharp interface for high performance/low power Ge device fabrication.

Cleaning procedure and effectiveness(1)

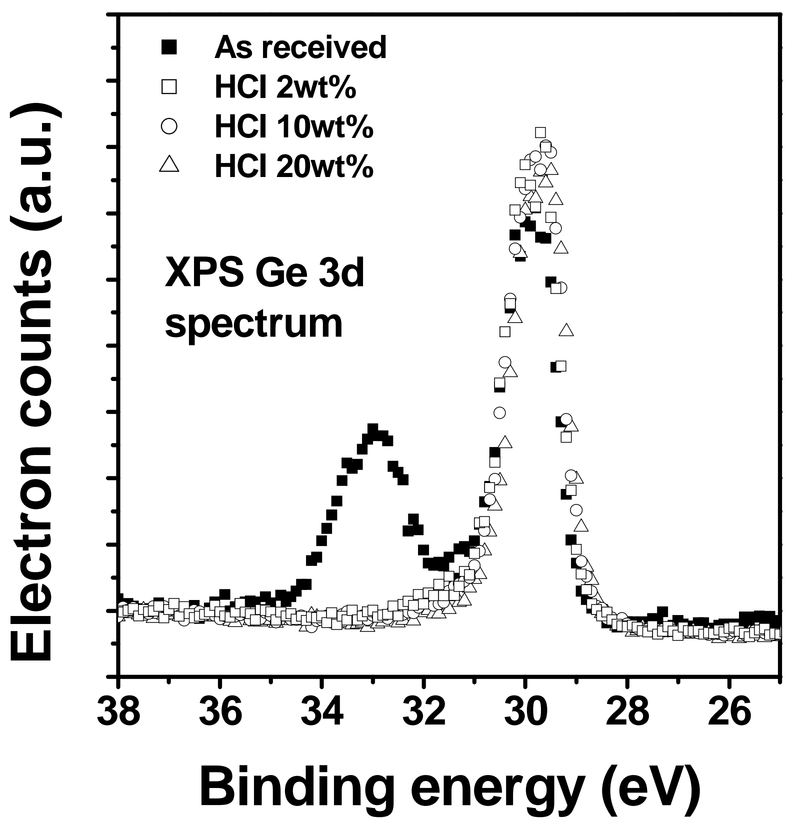
- Carbon removal
  - UVO2 or O2 plasma exposure
  - UVO3 exposure effectively removes carbon contamination

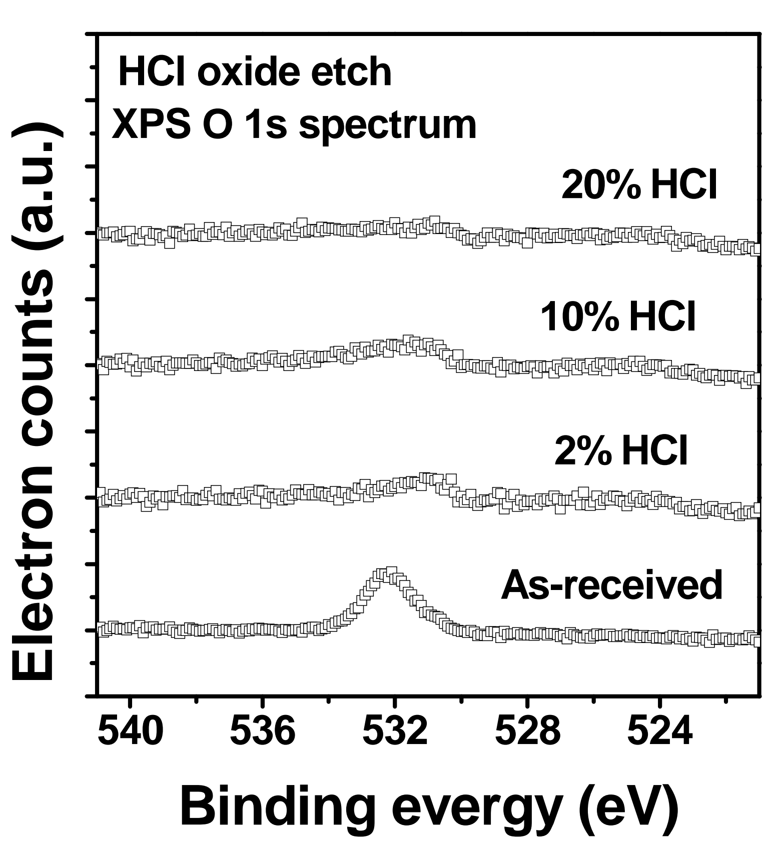




Cleaning procedure and effectiveness(2)

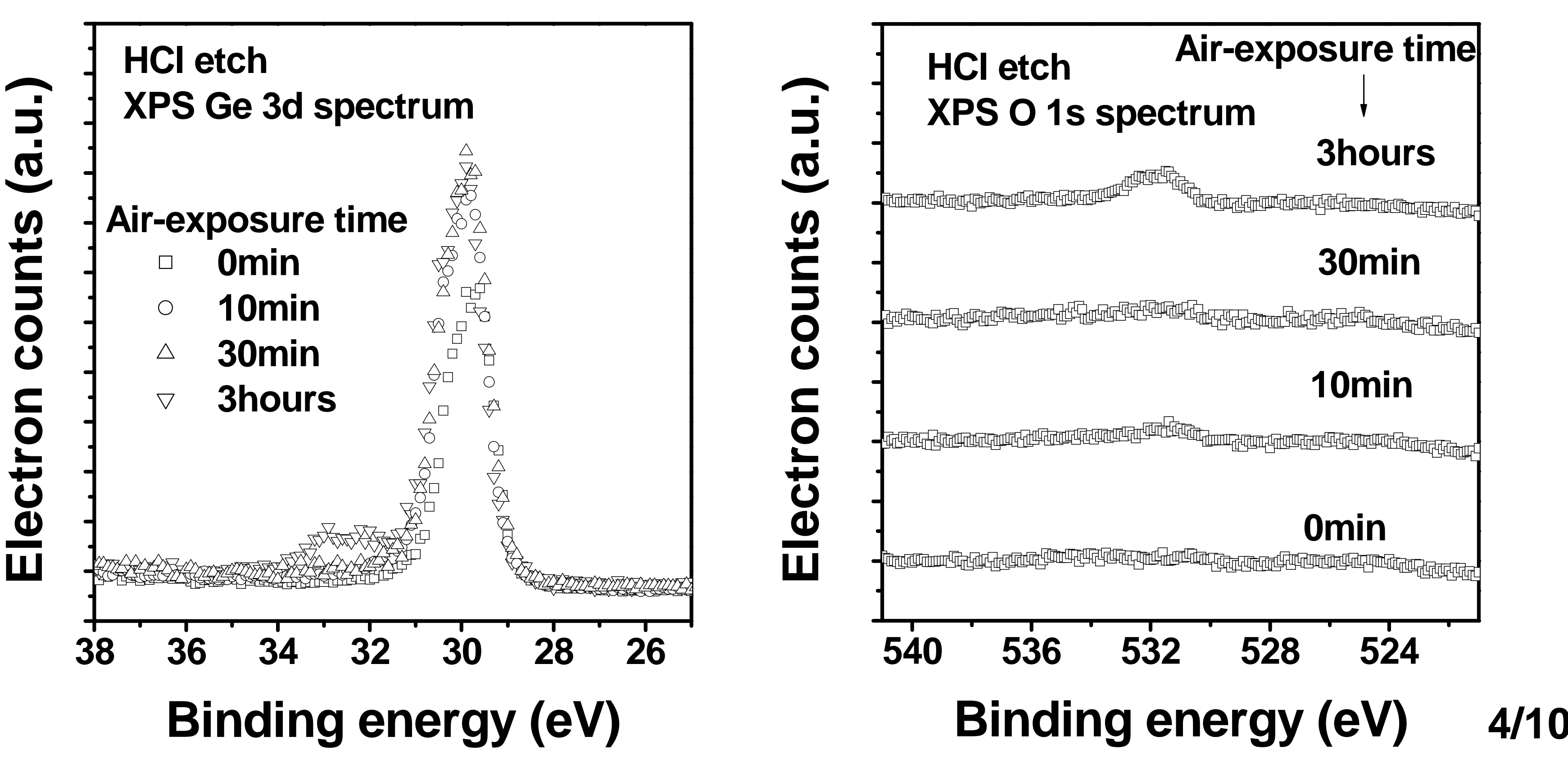
- Oxide removal
  - HCl can effectively remove native oxide at high concentration, while HF cannot





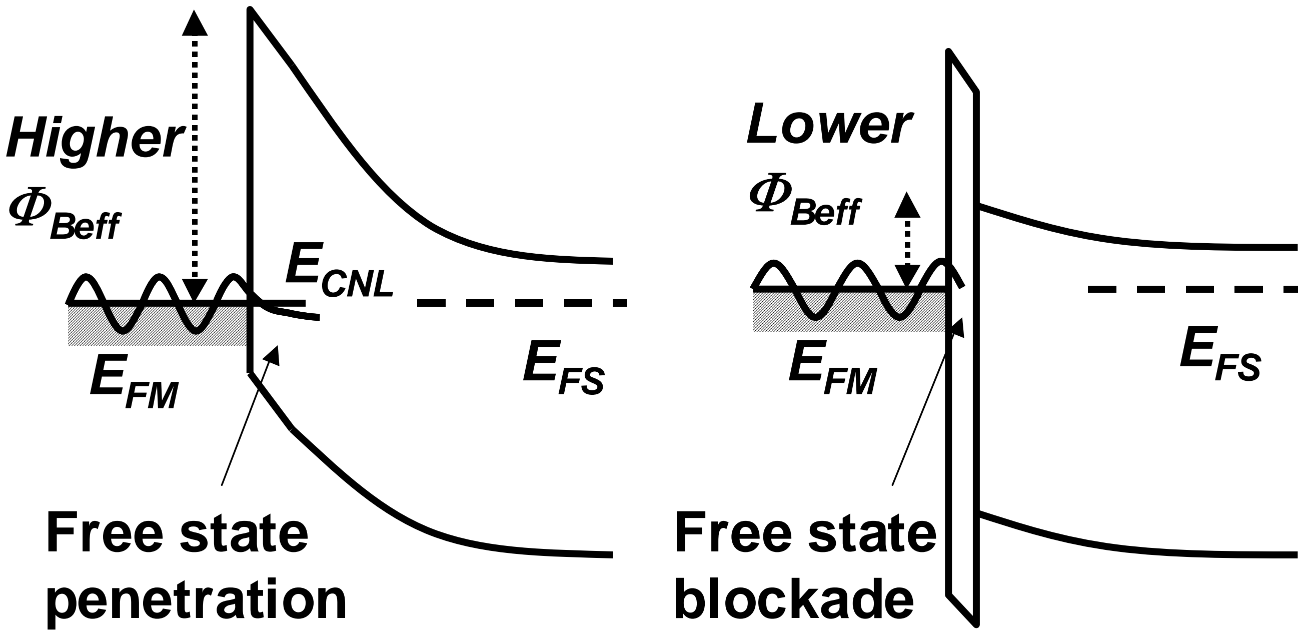
Cleaning procedure and effectiveness(3)

- Surface passivation
  - HCl can not only etch oxide but also passivate Ge surface for at least 30mins
  - Keep oxide free surface until transfer sample into load lock chamber



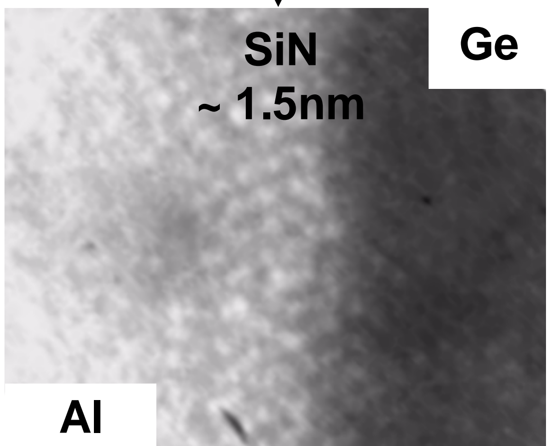
Problems in metal/Ge contact

- Fermi-level is strongly pinned at charge neutrality level (E_{CNL}) close to Ge valence band* based on MIGS theory *A. Dimoulas APL 2006, T. Nishimura SSDM2006
  - Very high Schottky barrier height for electron conduction
- Appropriate passivation layer can block wavefunction pentration and release Fermi-level pinning** *D. Connely IEEE Nanotechnol 2004
  - Leads to low contact resistance in n-type metal/Ge Schottky jucntion



Experiments

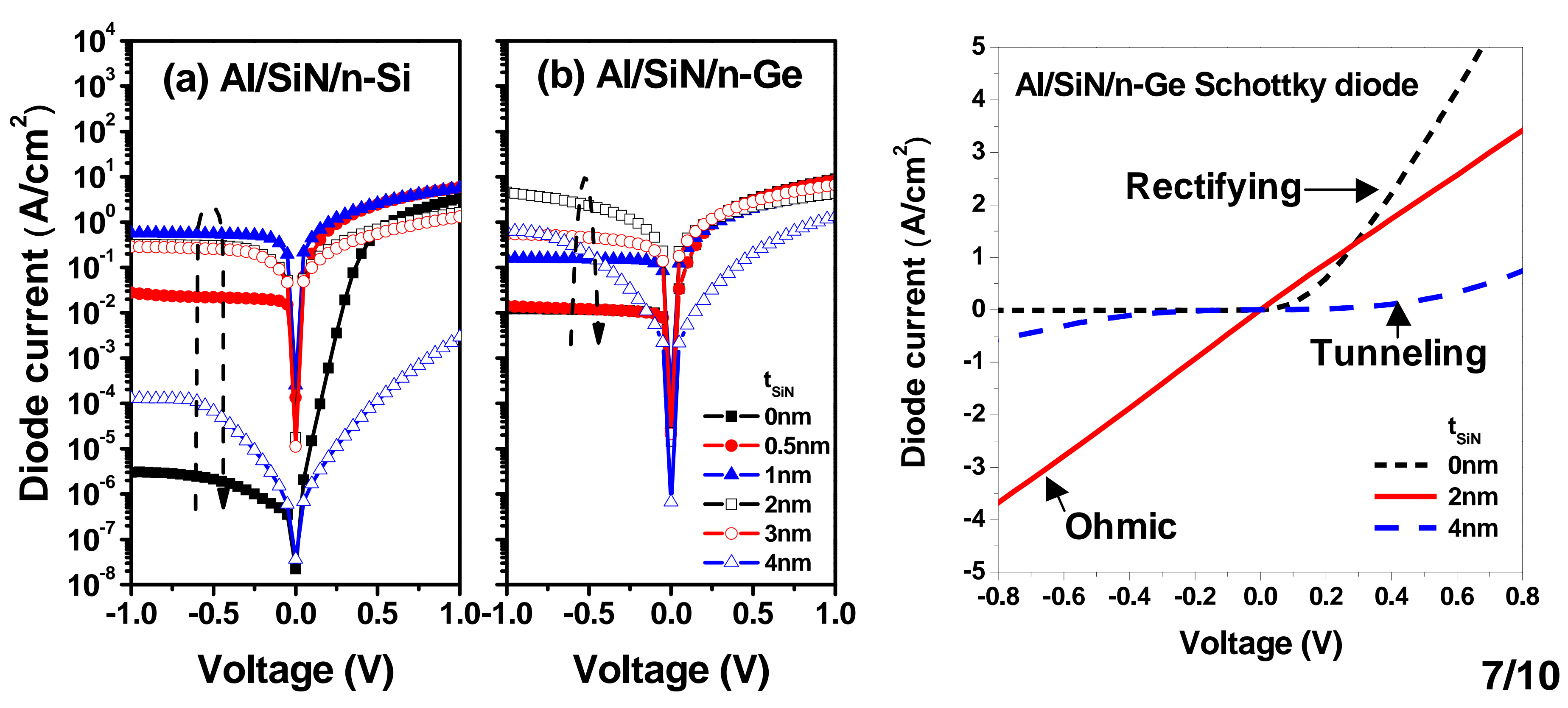
- Metal/SiN/Ge Schottky diode fabrication
  - Ge surface clean/passivation before loading Ge wafer into load-lock chamber of sputter system
    - Cyclic HF and HCl cleaning + final HCl passivation
  - SiN deposition with several thickness (t_{SiN})
    - 300°C heating to depassivate Cl-terminated Ge surface
  - Metal deposition and patterning
    - Metals with wide range of metal workfunction (WF)



- Characterization
  - I-V measurement
  - Four-point probe measurement to extract contact resistance

Al/SiN/n-Ge Schottky diode

- I-V characteristics
  - Reverse current is maximized at optimal t_{SiN}
  - Transport changes from rectifying, ohmic and tunnel



Al/SiN/n-Ge Schottky diode

- Contact resistance (R_c)
  - R_c is minimized at optimal t_{SiN} due to the balance between lowering MIGS density and series tunnel resistance

Al/SiN/n-Si, Ge Schottky diode

Si

Ge

Reduce MIGS density

Increase tunnel resistance

Min. Rc in Si

Min. Rc in Ge

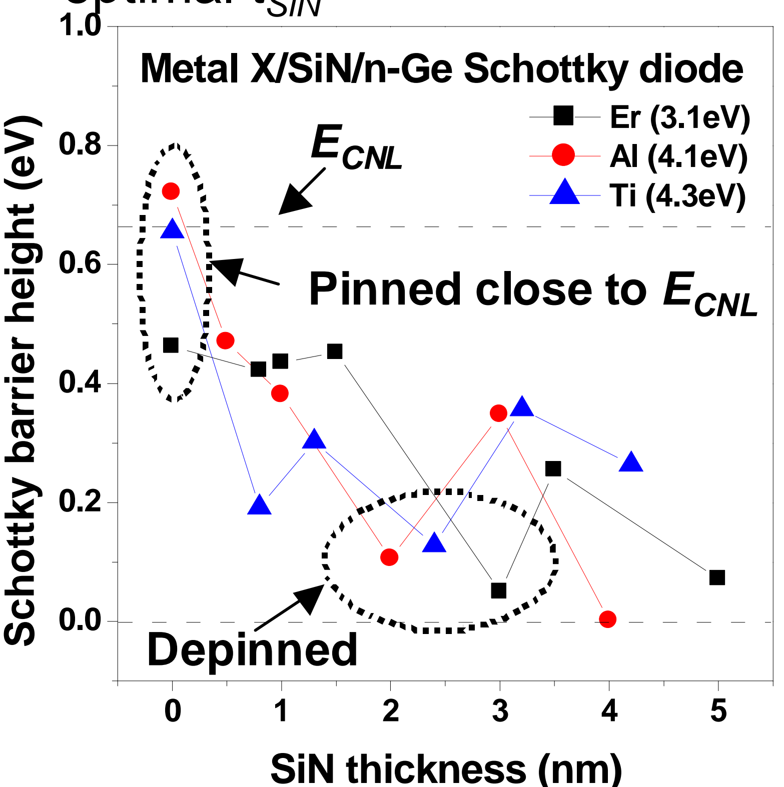
Contact resistance (ohm-cm^2)

10^6 10^5 10^4 10^3 10^2 10^1 10^0 10^{-1} 10^{-2}

0 1 2 3 4

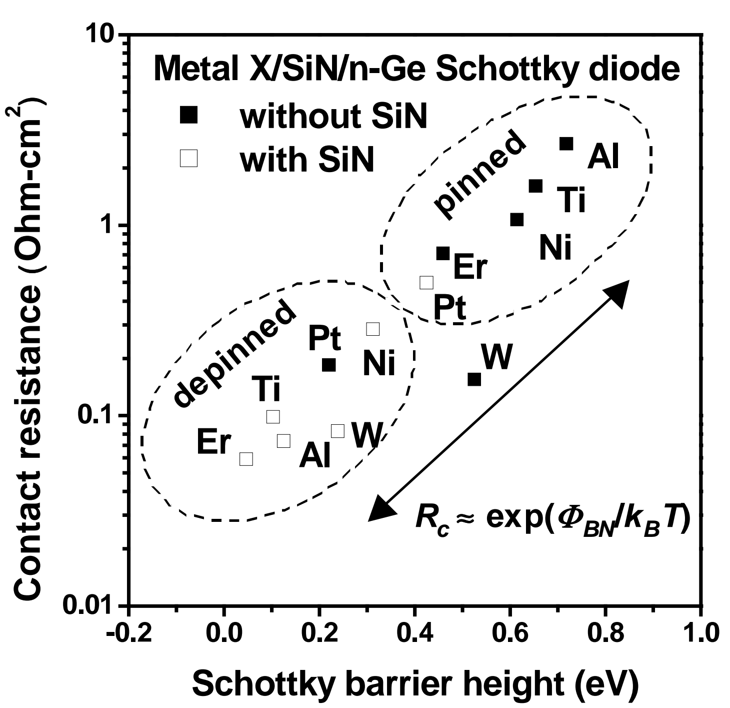
SiN thickness (nm)

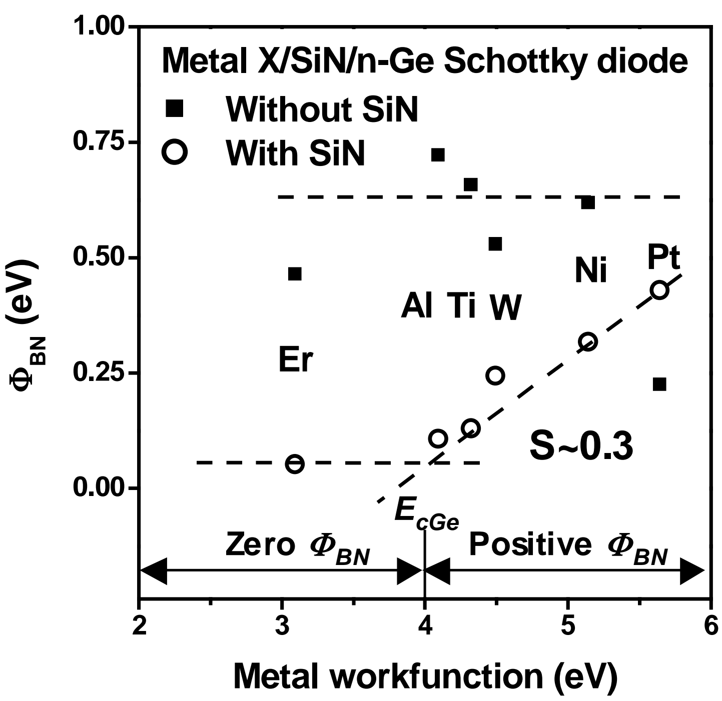
- Schottky barrier height (Φ_{BNeff})
  - Φ_{BNeff} becomes almost ideal *Schottky-limit* barrier height at the optimal t_{SiN}



R_c vs Φ_{BNeff} and Φ_{BNeff} vs WF

- R_c vs Φ_{BNeff}
  - Clear exponential correlation
  - Prove R_c reduction by lowering Φ_{BNeff}
- Φ_{BNeff} vs WF
  - Linear correlation between Φ_{BNeff} and WF
  - Pinning factor (S) is 0.3, close to the analytical value 0.4 for SiN*





*W. Monch "Electronic Properties of Semiconductor Interfaces" Springer 2004

Summary

- Verify the effectiveness of surface cleaning method in terms of organics and native oxide
  - Effective removal of carbon contamination and native oxide and effective surface passivation
- Develop the new passivation technique for low contact resistance in metal/Ge Schottky contact
  - Ultrathin SiN passivation layer successfully releases Fermi level pinning and this results in low contact resistance due to low Schottky barrier height

Industrial Interactions and Technology Transfer

This research has collaborative interactions with Initiative for Nanoscale Materials and Processes, INMP, at Stanford which is supported by 7 semiconductor and semiconductor equipment manufacturing companies.

Future Plans

Next Year Plans

- Fabrication and characterization of metal source/drain Ge MOSFET based on the newly established passivation technique
- Investigation on the effect of surface passivation by plasma oxidation/nitridation on Ge MOS gate stack with high-k dielectrics

Long-Term Plans

- Investigation on the effect of surface passivation on the transport property of Ge MOSFET
- Development of process for high performance/low power Ge CMOS integration

Publications, Presentations, and Recognitions/Awards

Since this is a new project started in 2007, there is no refereed publications available. Some publications made prior to this period are listed below:

J. Kim, J. McVittie, K. Saraswat and Y. Nishi, "Passivation Studies of Germanium Surface", ***8th International Symposium on Ultra Clean Processing of Silicon Surfaces,*** **Antwerp, Belgium, September, 2006**

J. Kim, J. McVittie, K. Saraswat and Y. Nishi, "Passivation Studies of Germanium Surface", ***8th International Symposium on Ultra Clean Processing of Silicon Surfaces***, **Antwerp, Belgium, September, 2006**

Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro and Nano Electronics Manufacturing

(Task Number: B,C- 425.022)

Subtask B: Post Etch Residue Removal in Copper Damascene Structures

PI:

- **Srini Raghavan, Materials Science and Engineering, University of Arizona**

Graduate Student:

- **Nandini Venkataraman, PhD candidate, Materials Science and Engineering, University of Arizona**

Objectives

- **Evaluate and optimize chemical systems having low solvent and fluoride content, for the selective removal of copper oxides (CuO_X) over copper and dielectric**
- **Understand the mechanism of removal of copper oxide films on copper using electrochemical impedance spectroscopy**

ESH Metrics and Impact

- *ESH objective:* Reduction of solvent content in semi aqueous fluoride (SAF) based solutions for removal of post etch residue

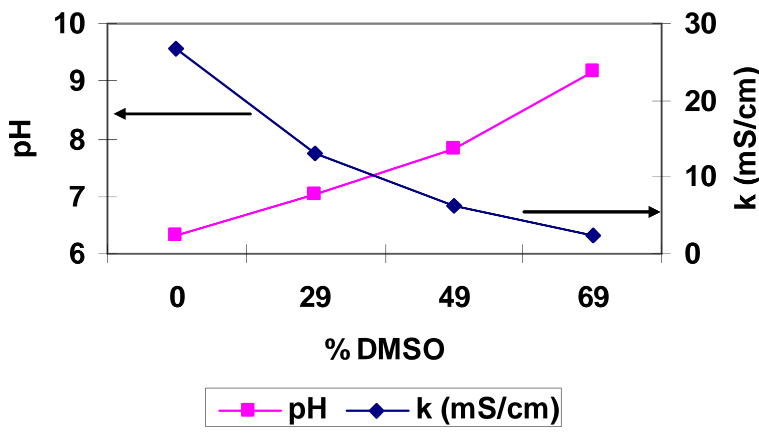
Solution components	Weight % in typical formulations	Weight % in best formulation in this study	% Reduction
Solvent	> 60%	29%	> 50%
Water	< 40%	71%	- 35% (increase)
Fluoride	~ 1-2%	1%	0 – 50%

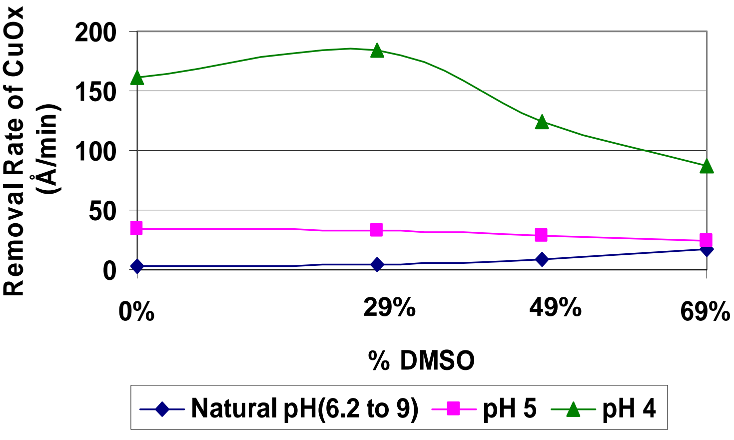
• The project will ultimately lead to the development of all aqueous chemical systems

Experimental Approach

- **Samples**
  - CuO_X films of controlled thicknesses formed by thermal oxidation of copper blanket wafers at 300^0C
- **Selection of Chemical Systems**
  - Semi aqueous solutions containing Dimethyl Sulfoxide (DMSO), NH_4F and water, buffered with oxalic acid in the pH range of 4-6
  - Variables studied for optimization: pH (Natural pH, 5, 6), DMSO content (0% to 69%)
- **Determination of Removal Rates**
  - CuO_X and Cu removal rates determined by solution analysis using Atomic Absorption Spectrophotometry
  - Removal Rate of TEOS determined by Ellipsometry
- **Electrochemical Impedance Spectroscopy**
  - Impedance measurements of CuO_X films and patterned wafer structures in various cleaning formulations performed by multi- sine technique using PARSTAT 2273 potentiostat/impedance analyzer
  - Equivalent circuit fitting performed using ZView software (Version 2.b)

Removal Rates of Copper Oxides





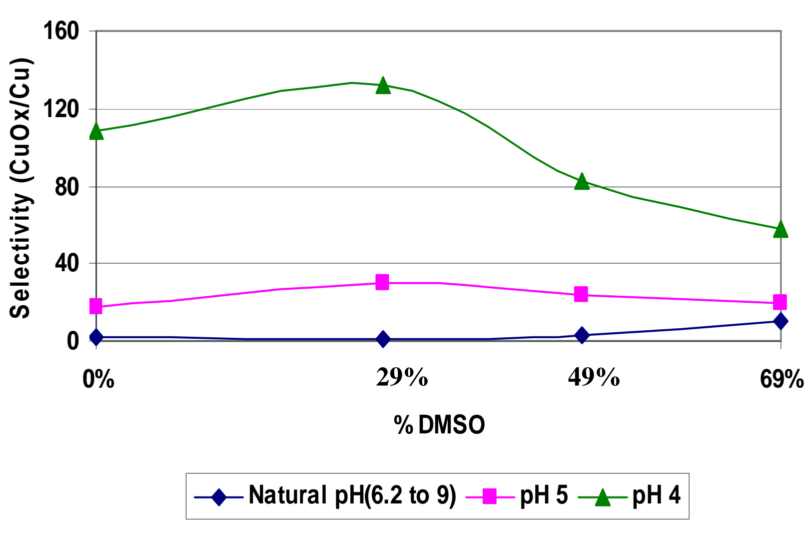
•1 wt% NH_4F in all formulations

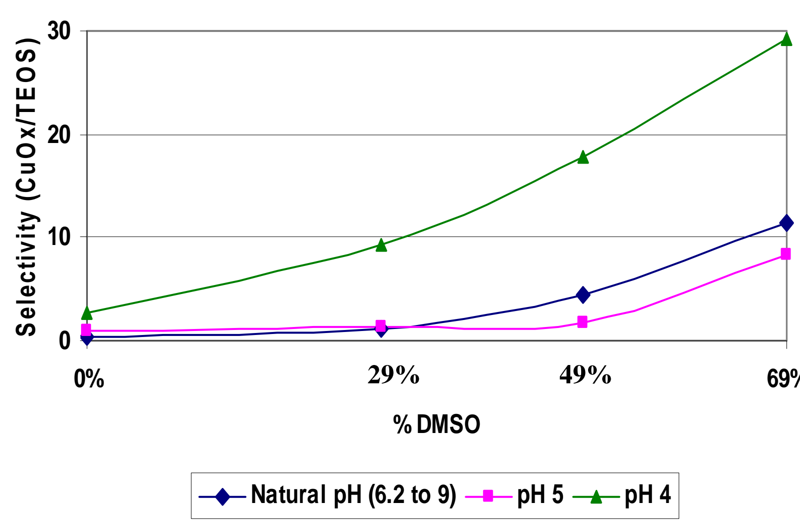
• pH increases and conductivity decreases with increase in DMSO concentration

- **Effect of pH**
  - Removal rate is a strong function of pH
  - Increase in removal rate with decrease in pH
- **Effect of DMSO concentration**
  - Above 29% DMSO, removal rate decreases

•At pH 4, removal rate ~ 160 Å/min for DMSO concentration $\leq$ 29%

Selective Removal of CuO_X over Cu and TEOS





CuO_X/Cu selectivity:

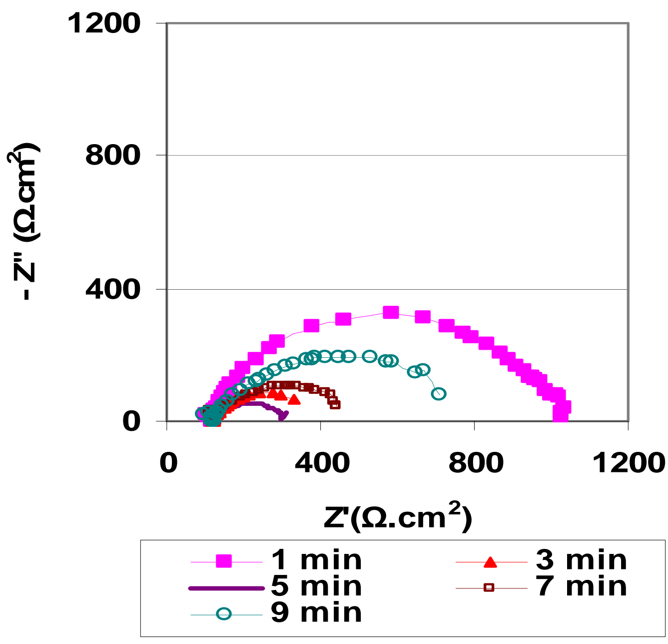
- Removal rate of Cu < 3Å/min in most cases
- **pH:** Decrease in pH increases CuO_X/Cu selectivity
- **DMSO content**: Better selectivity for DMSO concentration ≤ 29%
- Highest selectivity of ~ 130:1 in solutions containing 29% DMSO at pH 4

CuO_X/TEOS selectivity:

- **DMSO:** Decrease in selectivity with increase in DMSO content
- **pH:** Reducing pH increases TEOS and CuO_X removal rate
- CuO_X removal is a stronger function of pH than TEOS removal
- Highest selectivity of ~ 30:1 obtained in solutions containing 69% DMSO at pH 4

Solution containing 29% DMSO and 1% NH_4F at pH 4 provides CuO_X removal rate of 180 Å/min with CuO_X/Cu selectivity of ~ 130:1 and CuO_X/TEOS selectivity of ~ 10:1

Electrochemical Impedance Spectroscopy



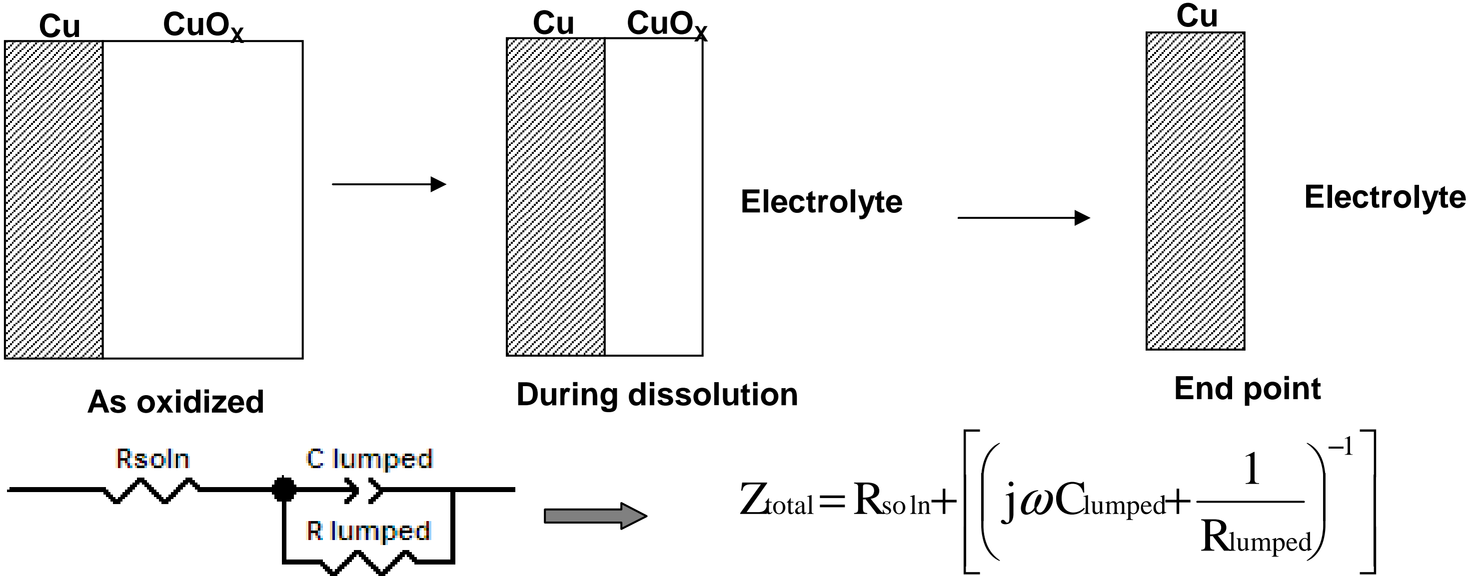
Impedance Spectra of CuO_X film as a function of time in solution containing 49% DMSO, 1% NH_4F and 50% H_2O (pH 4)

Ω

- **Sample:** CuO_X film of thickness ~55 nm
- **Electrochemical Setup**
  - Working Electrode – CuO_X film
  - Reference Electrode – Pt wire (quasi reference)
  - Counter Electrode – Pt foil
- Amplitude of AC signal: 5 mV rms
- Measurement frequency range – 10^5 Hz to 0.1 Hz
- Impedance spectra consists of a single depressed semicircle
- Semicircle diameter decreases first and then increases after a certain duration

Equivalent Circuit Modeling

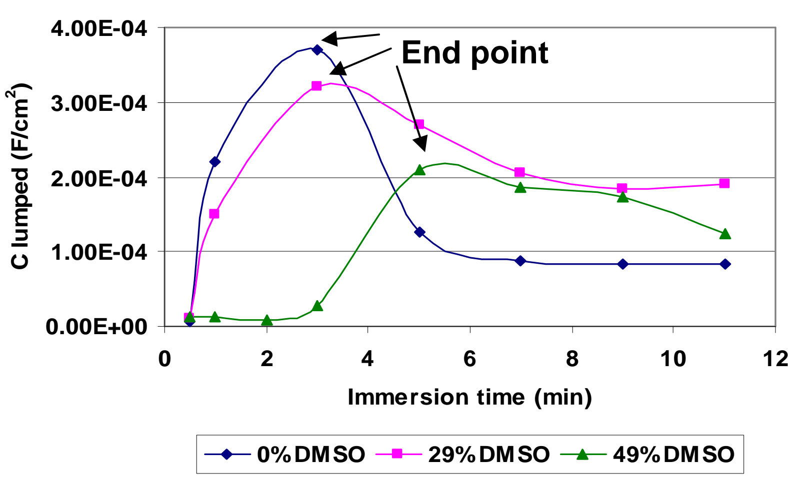
Uniform Dissolution Model

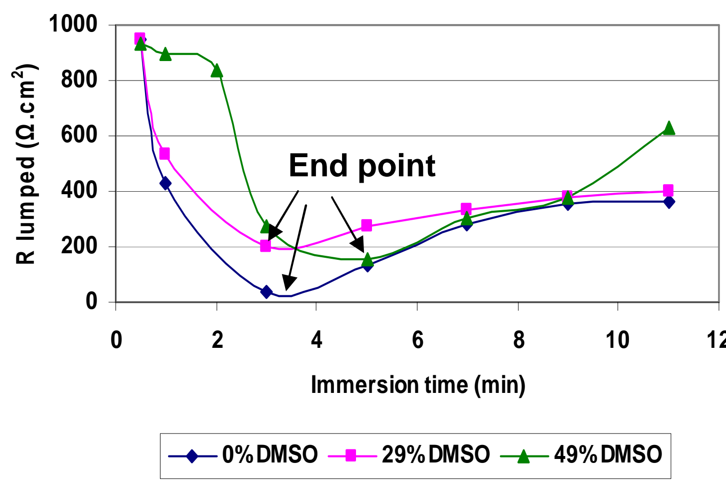


$$Z_{total} = R_{soln} + \left[\left(j\omega C_{lumped} + \frac{1}{R_{lumped}} \right)^{-1} \right]$$

- Lumped parameter model; exhibits excellent fit to the impedance data
- Major contributions to C_{lumped}: Double layer capacitance at CuO_X/electrolyte interface (C_{dl}) and film capacitance (C_{oxide})
- Major contributions to R_{lumped}: Charge transfer resistance at interface (R_{ct}) and film resistance (R_{oxide})
- C_{dl} and R_{ct} expected to be nearly constant during dissolution; Typical values of $C_{dl} \approx$ 10-50 μF/cm^2
- C_{oxide} and R_{oxide} depend on thickness of the film
- $C_{oxide} = \varepsilon\varepsilon_0 A/d$; $R_{oxide} = \rho d/A$

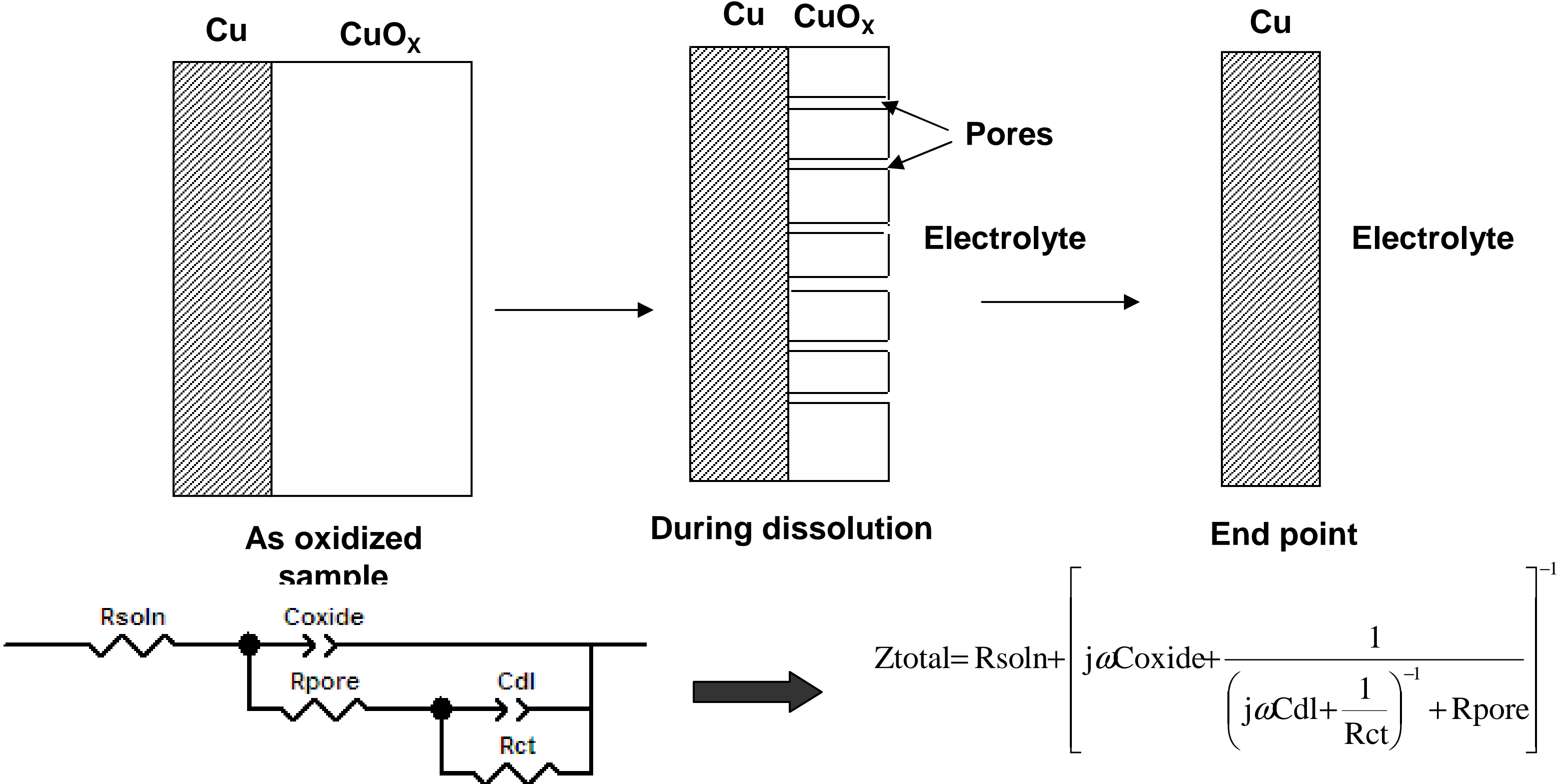
Uniform Dissolution Model





- Formulations contain 1% NH_4F and maintained at pH ~ 4
- During dissolution
  - Increase in C_{lumped} attributed to decrease in film thickness (increase in C_{oxide} contribution)
  - Decrease in R_{lumped} attributed to decrease in R_{oxide}
- At end point
  - C_{lumped} mainly due to C_{dl} at Cu/electrolyte interface
  - R_{lumped} mainly due to R_{ct} at Cu/electrolyte interface
- Beyond end point
  - Decrease in C_{lumped} and increase in R_{lumped} attributed to adsorption/repassivation of the surface (possibly reoxidation)

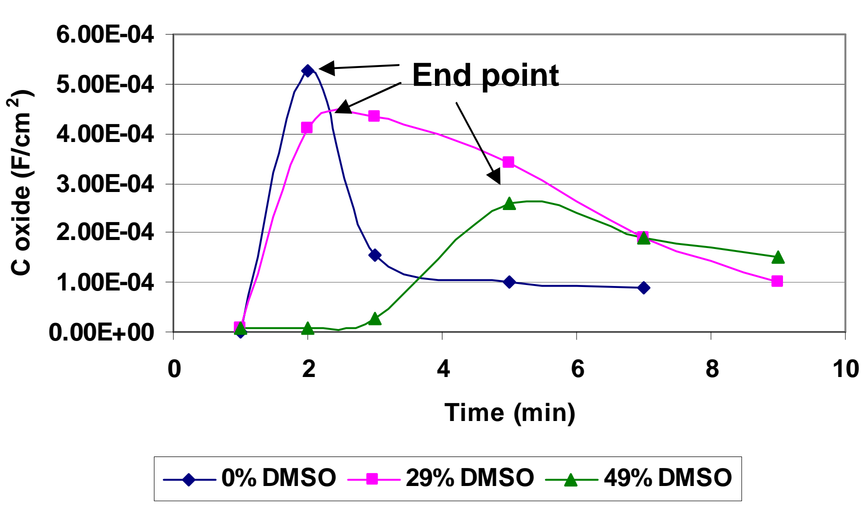
Porous Film Model

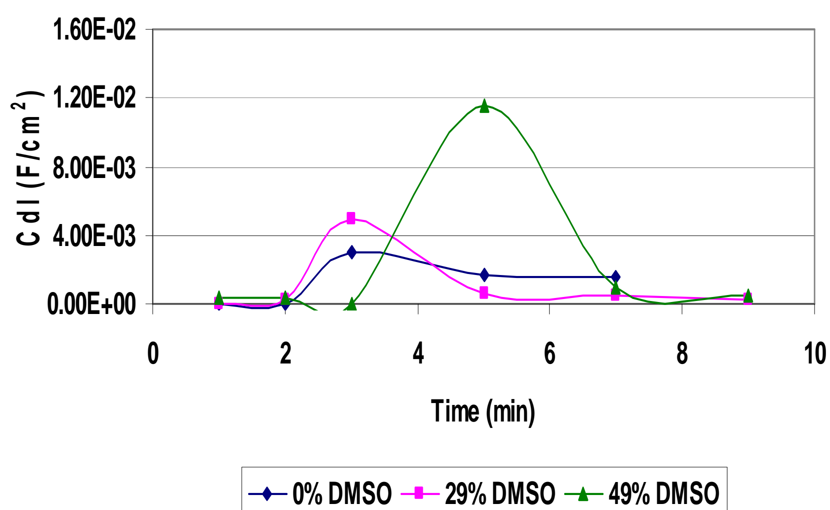


$$Ztotal = Rsoln + \left[j\omega Coxide + \frac{1}{\left(j\omega Cdl + \frac{1}{Rct} \right)^{-1} + Rpore} \right]^{-1}$$

- Also provides excellent fit to acquired data
- **Model Features:**
  - Pores develop in passive CuO_X film during dissolution; underlying copper exposed to solution
  - Charge transfer at Cu/electrolyte interface
  - Porosity of the film increases as dissolution occurs

Porous Film Model

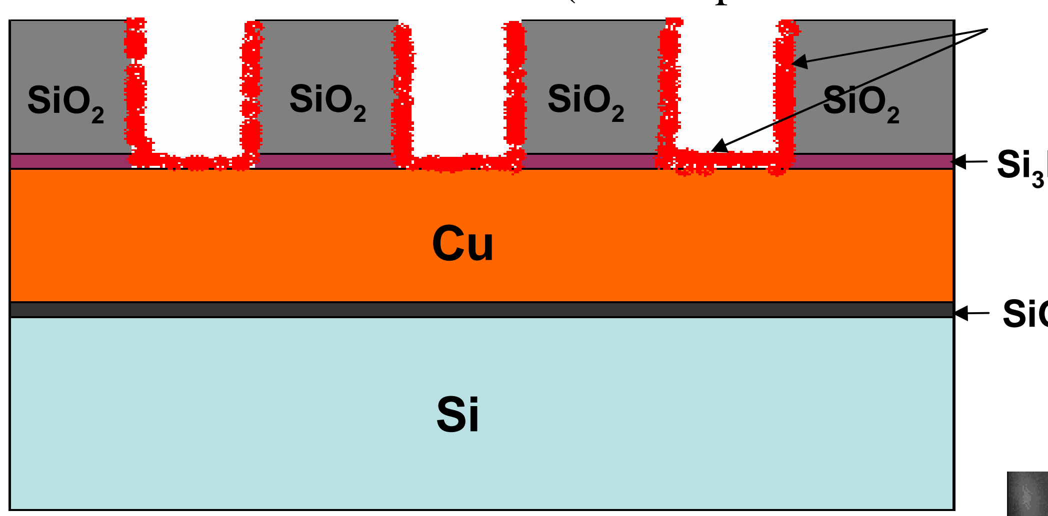




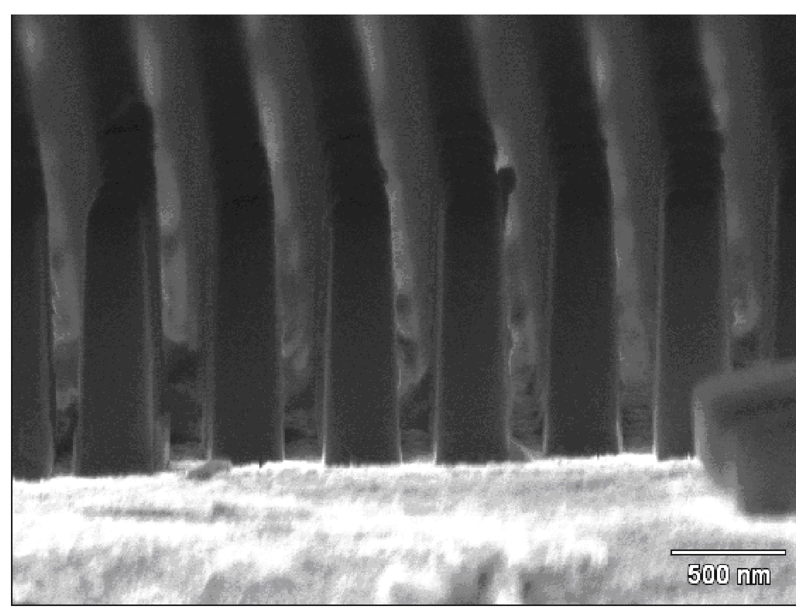
- Increase in C_{oxide} during dissolution due to loss of oxide
- After end point, decrease in C_{oxide} due to repassivation
- Increase in C_{dl} during dissolution, due to increase in exposed Cu area (increase in porosity)
- Values of C_{dl} abnormally high to represent double layer capacitance – reasons are being investigated

Patterned Test Structure

(Developed at Intel D2 fab, Santa Clara)



Cross-sectional SEM of test structure



- Patterned test structures contain vias plasma etched in SiO_2
- Width of vias ~ 180 nm
- Aspect ratio ~ 4:1
- Ongoing work
    - End point detection in patterned structures by Electrochemical Impedance Spectroscopy
    - Impedance data is being acquired and various models are under investigation

Summary

- Selective removal of CuO_X over copper and dielectric in buffered DMSO, NH_4F based chemical systems has been systematically investigated
- CuO_X removal rate of ~180 Å/min with CuO_X/Cu selectivity of ~ 130:1 and CuO_X/TEOS selectivity of ~ 10:1 has been obtained in 1% NH_4F solutions containing 29% solvent at pH 4.
- Reasonable selectivity over TEOS requires some amount of DMSO
- Electrochemical Impedance spectroscopy and equivalent circuit modeling has been used to detect end point of copper oxide removal in DMSO, NH_4F based chemical systems

Industrial Interactions

- Patterned test structures were developed at Intel Corp., Santa Clara with the assistance of Dr. Liming Zhang, Dr. Zhen Guo and Dr. Michael Ru
- Telephone discussions with Dr. Liming Zhang, Dr. Zhen Guo and Dr. Michael Ru, Intel Corp., Santa Clara
- Discussions with Dr. Robert Small, R.S. Associates, Tucson

Future Plans

Next Year Plans

- Improve selectivity towards TEOS in solutions with very low or no solvent content
- Perform detailed Electrochemical Impedance Spectroscopy investigations on the patterned test structures
- Study rinsing processes

Long-Term Plans

- Identify and investigate novel aqueous chemical systems, compatible with low k materials, for post etch residue removal

Publications, Presentations, and Recognitions/Awards

Publications

- N. Venkataraman, A. Muthukumaran, S. Raghavan, "Evaluation of Copper Oxide to Copper Selectivity of Chemical Systems for BEOL Cleaning Through Electrochemical Investigations", **Mater. Res. Soc. Symp. Proc.** Volume 990, Paper # 0990-B08-25, 2007

Awards

- **AMAT Graduate Fellowship** awarded to Nandini Venkataraman by Applied Materials, Santa Clara, for 2007-2008

Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro- and Nano- Electronics Manufacturing

(Task Number: B,C- 425.022)

Subtask C: Cleaning and Drying of Dielectrics and Nano-structures

PI:

- **Farhang Shadman, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Harpreet Juneja: PhD candidate, Chem & Env Eng, UA**
- **Junpin Yao: PhD candidate, Chemical and Environmental Engineering, UA**
- **Asad Iqbal: PhD, Chem Eng, UA, graduated 2007 (currently with Intel)**

Other Researchers:

- **T. Tsui, formerly with TI**
- **Roger Sperline, Chemistry, UA**

Undergraduate Students:

- **Paul Swift: Chemical and Environmental Engineering, UA**

Cost Sharing:

- **Sematech and TI (samples)**

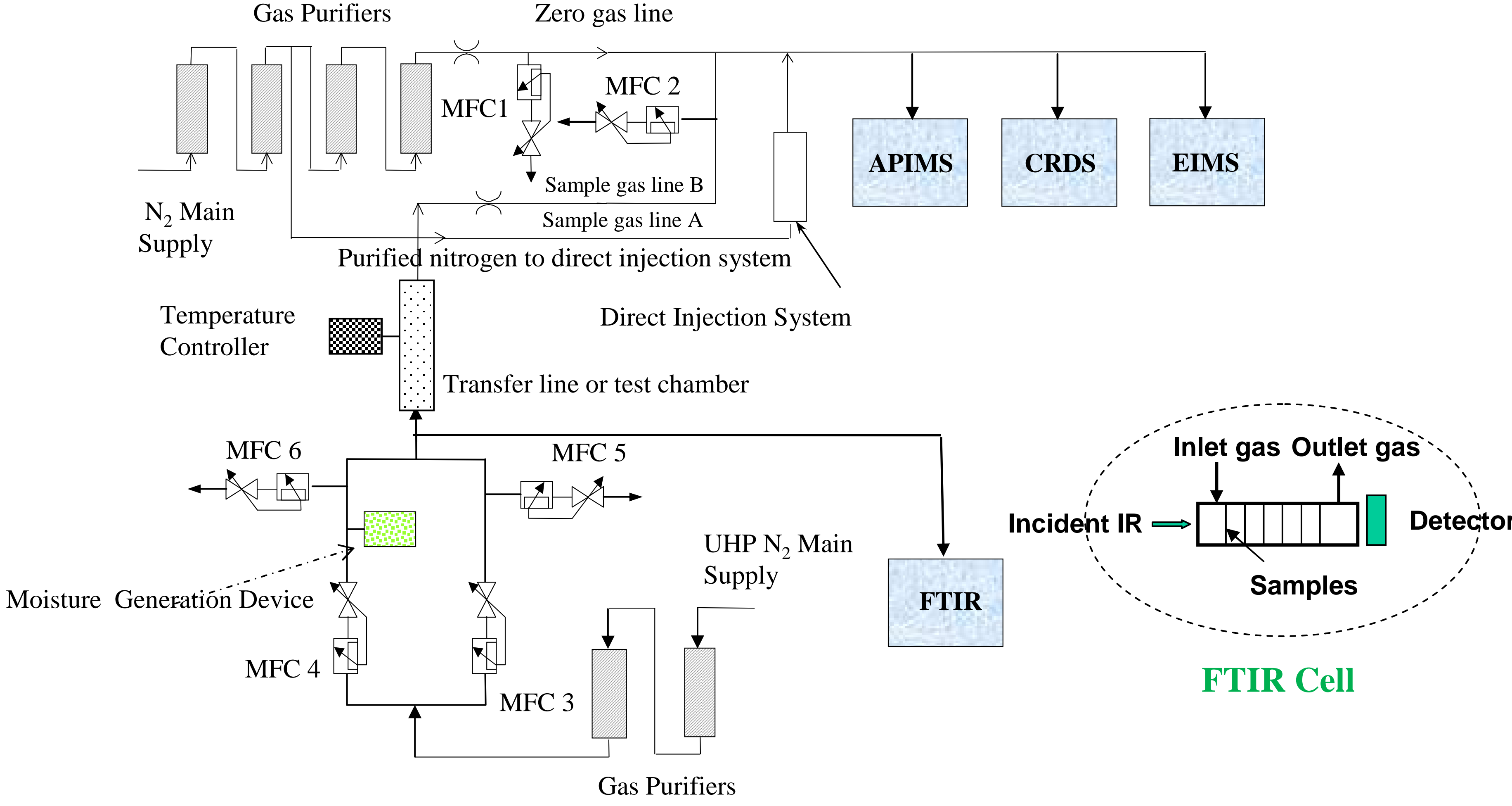
Objectives

- **Determine the fundamentals of moisture and VOC uptake and removal in porous low-k ILD films.**
- **Determine film properties and develop operational conditions for low-chemical and low-energy outgassing and cleaning of porous low-k films.**
- **Extend this approach to determine the fundamentals gaseous contaminants interactions with nano-particles**

ESH Impact

- **Expected large reduction in the use of gas and energy for outgassing of the low-k films; results also help in selection of capping materials for low-k.**
- **Adsorption of contaminants on nano-particles is a primary reason for their potential ESH effect (a focus area for the ERC).**

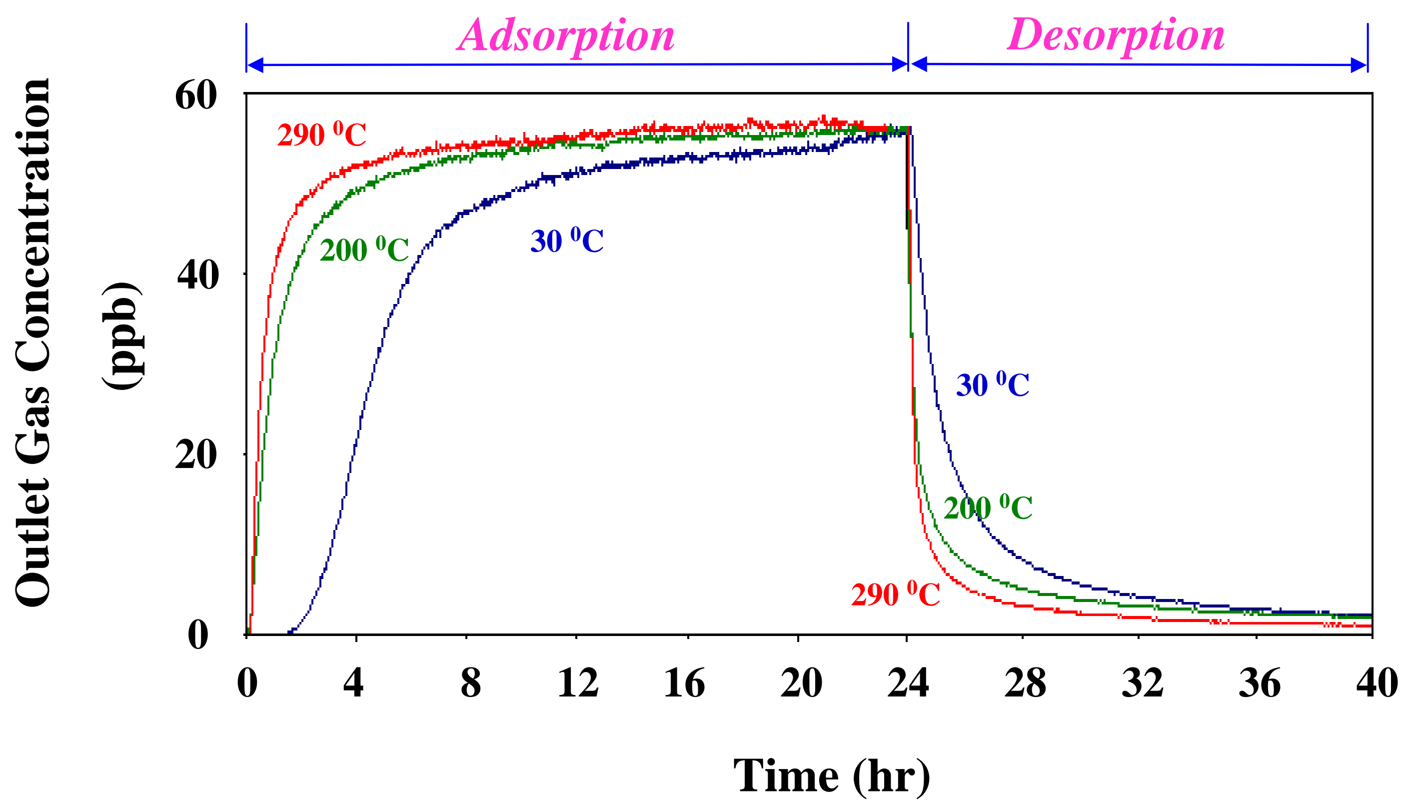
Experimental Setup



Dynamics of Moisture Adsorption and Desorption

Sample: Black Diamond (BD IIx); NH_3 plasma treated;

Moisture challenge concentration: 56 ppb; Purge gas purity: 1 ppb

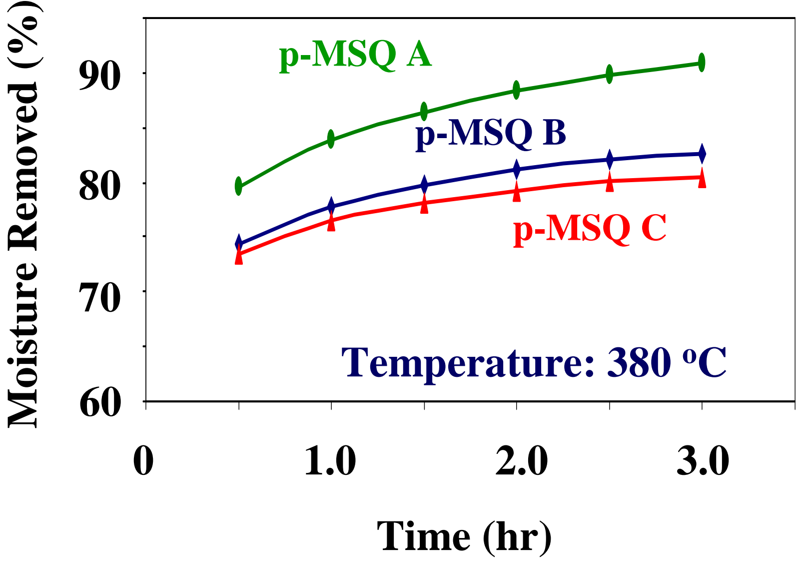


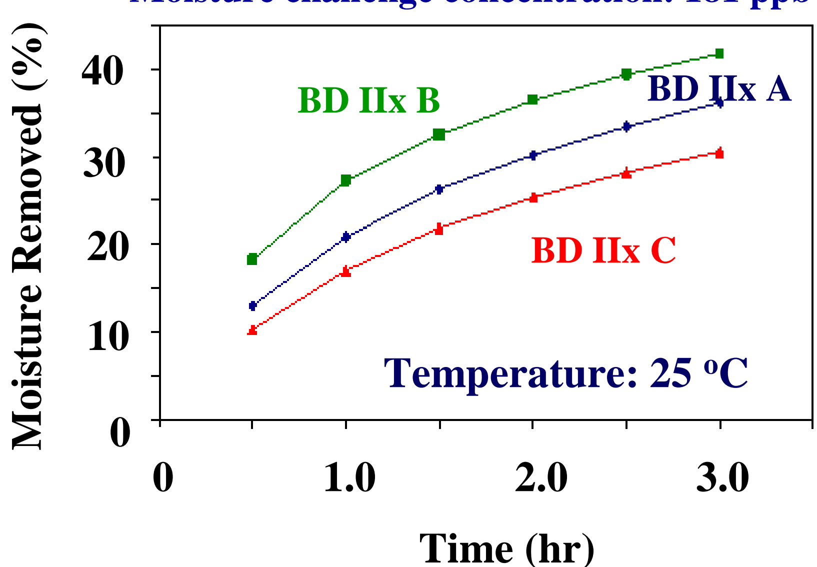
Dynamics of Moisture Removal

Purge gas purity: 1 ppb

p-MSQ samples:
A: 10s etch in N_2H_2, 20s ash;
B: 10s etch in HeO_2, 20s ash;
C: 10s etch in H_2, 20s ash

BD IIx samples:
A: Blanket;
B: NH_3-plasma treated;
C: NH_3He-plasma treated





Moisture removal is a slow and activated process

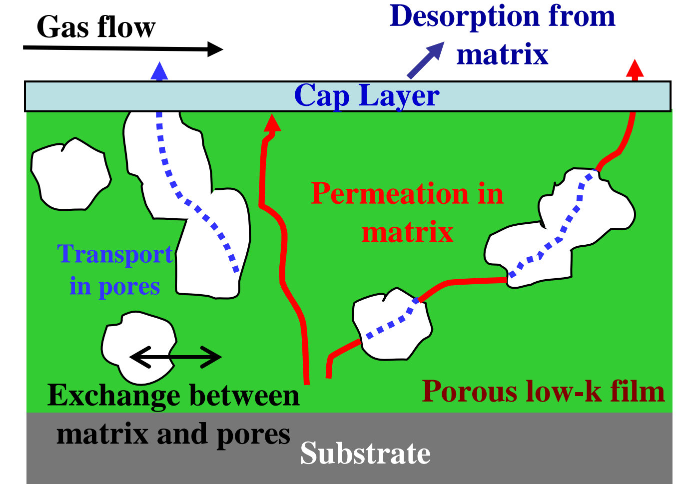
Process Model for Predicting Impurity Concentration in Porous Low-k Film

Transport of moisture in matrix:

$$\frac{\partial C_S}{\partial t} = \frac{1}{1-\varepsilon}\frac{\partial}{\partial z}[(1-\varepsilon)D_S\frac{\partial C_S}{\partial z}] - \frac{\varepsilon}{1-\varepsilon}k_m S_p(\frac{C_S}{S} - C_g)$$

Transport of moisture in pores:

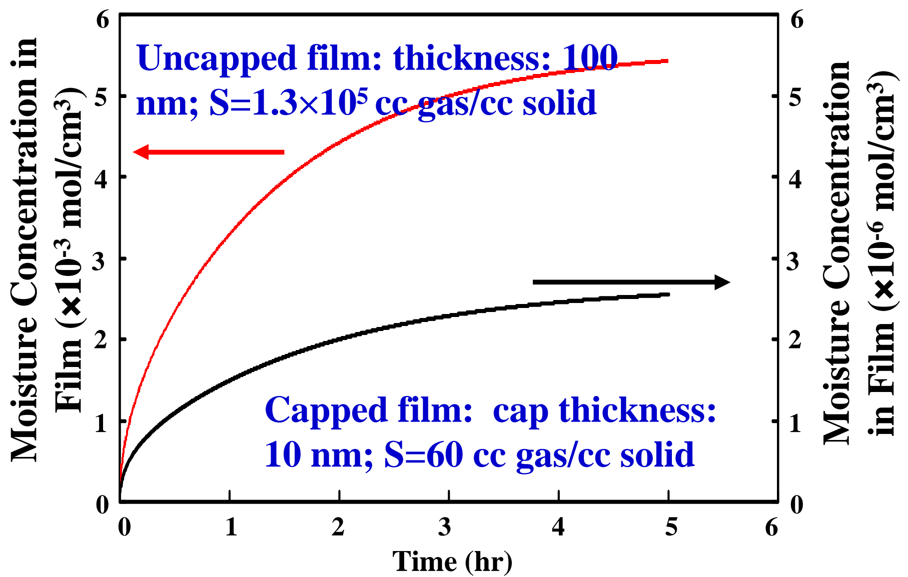
$$\frac{\partial C_g}{\partial t} = \frac{1}{\varepsilon}\frac{\partial}{\partial z}[\varepsilon D_g \frac{\partial C_S}{\partial z}] + k_m S_p(\frac{C_S}{S} - C_g)$$



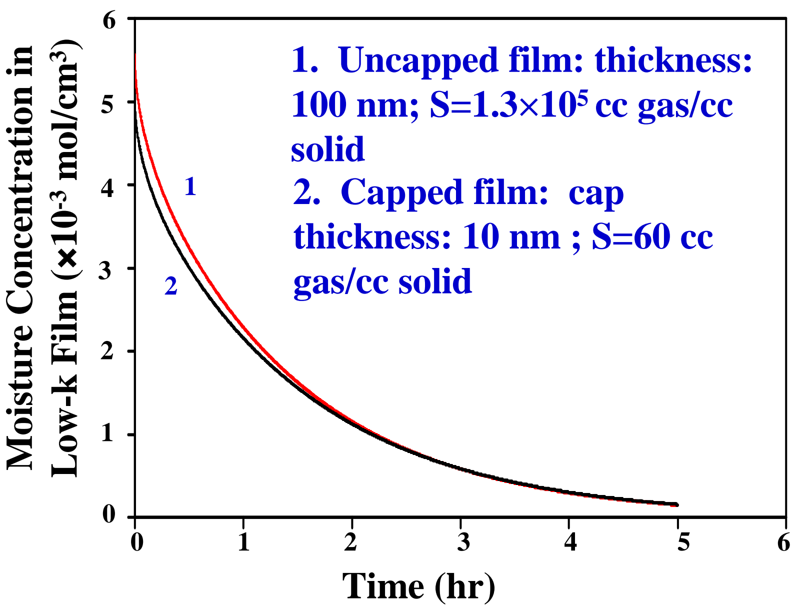
C_S , C_g	Moisture concentration in matrix and pores
D_S , D_g	Moisture diffusivities in matrix and in pores
ε	Film porosity
S_p	Specific surface area
S	Moisture solubility in matrix
k_m	Interphase transport coefficient between pore and matrix

Effect of Capping on Moisture Removal

Initial moisture challenge concentration: 1500 ppm; Temperature: 25 °C
Purge gas concentration: 1 ppb; p-MSQ low-k



Cap layer with low moisture solubility prevents moisture intrusion

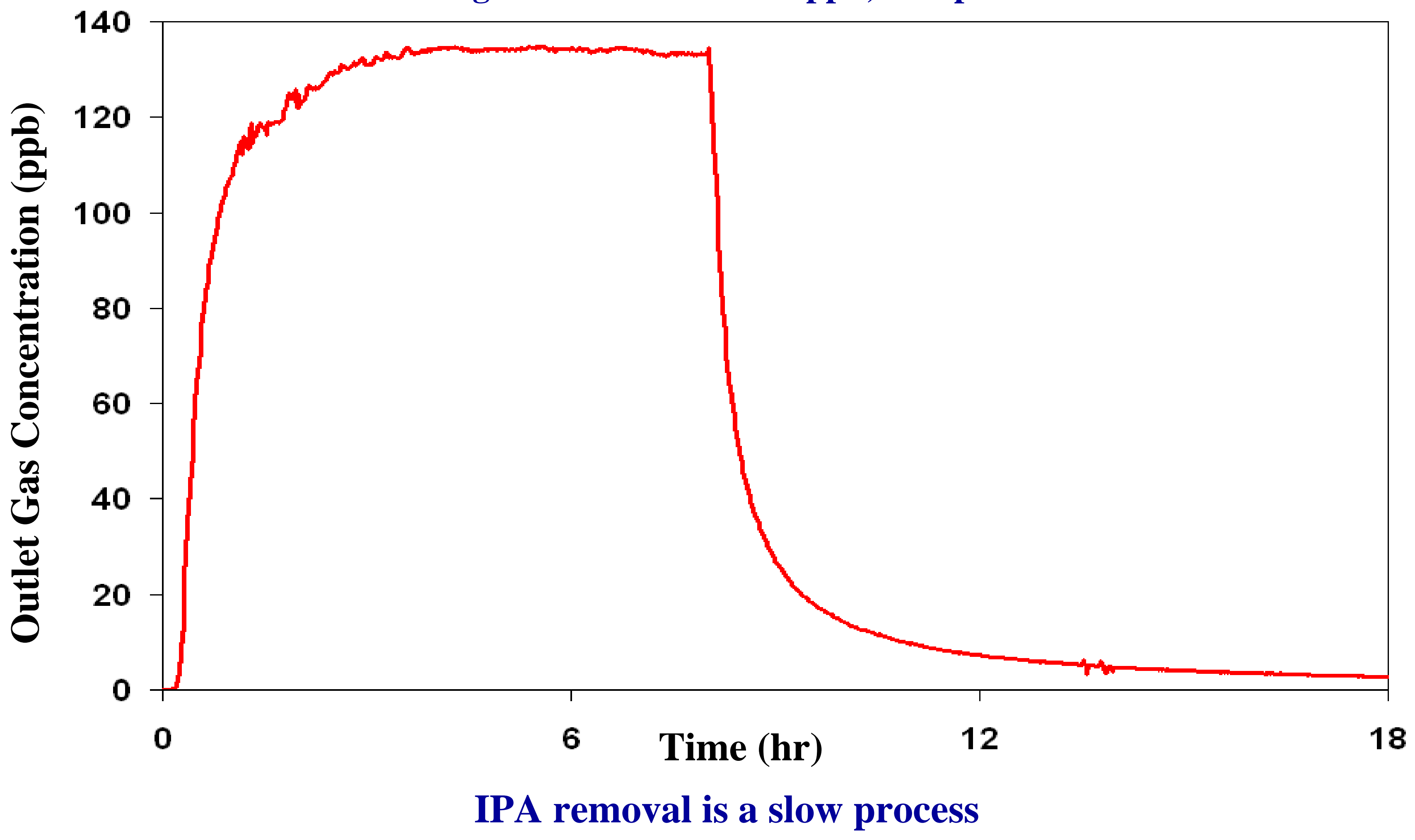


Cap layer with low moisture solubility does not prevent moisture removal

Dynamics of IPA Outgassing

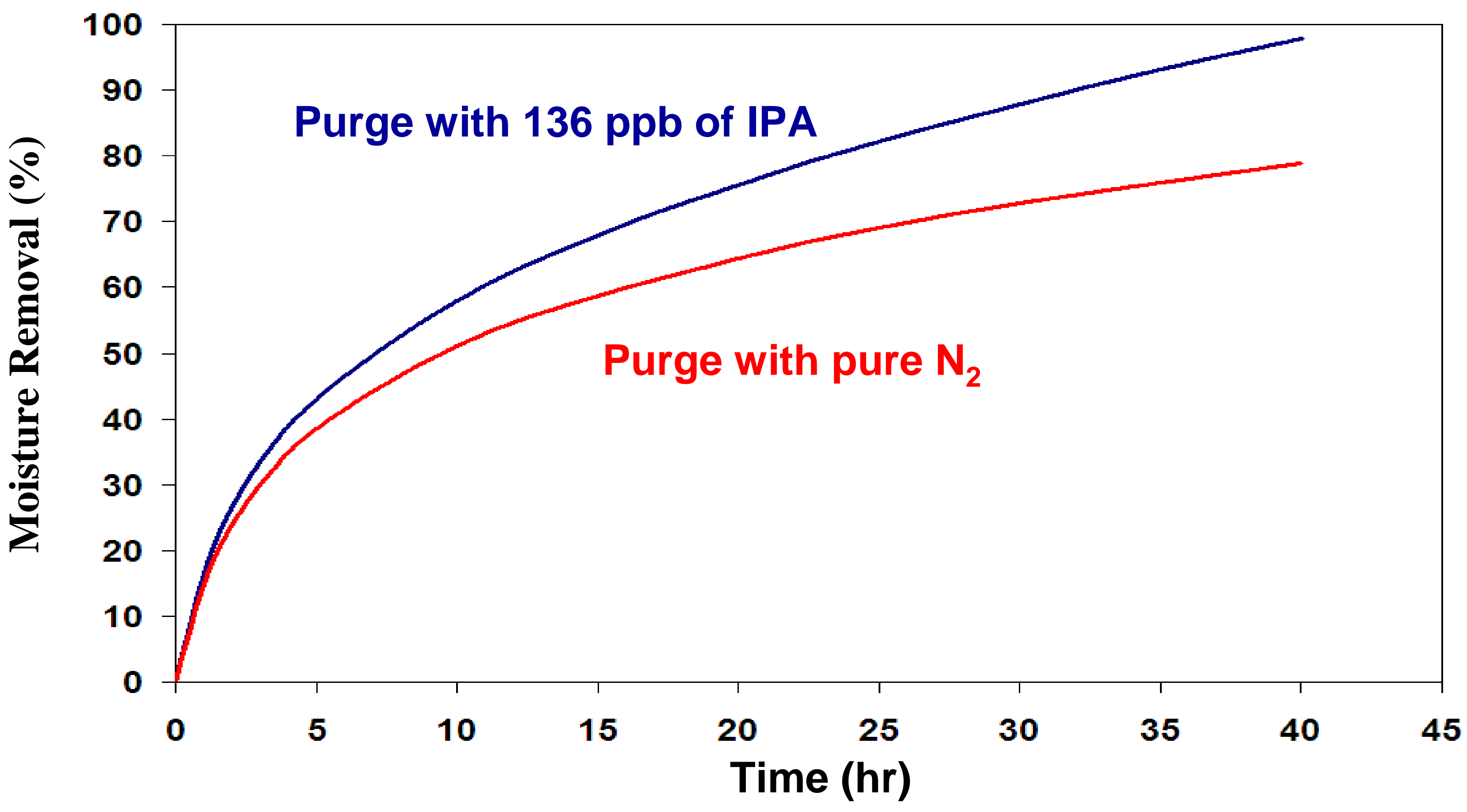
Sample: Black Diamond (BD IIx)

IPA challenge concentration: 134 ppb; Temperature: 25 ^{0}C



Effect of IPA on Moisture Removal

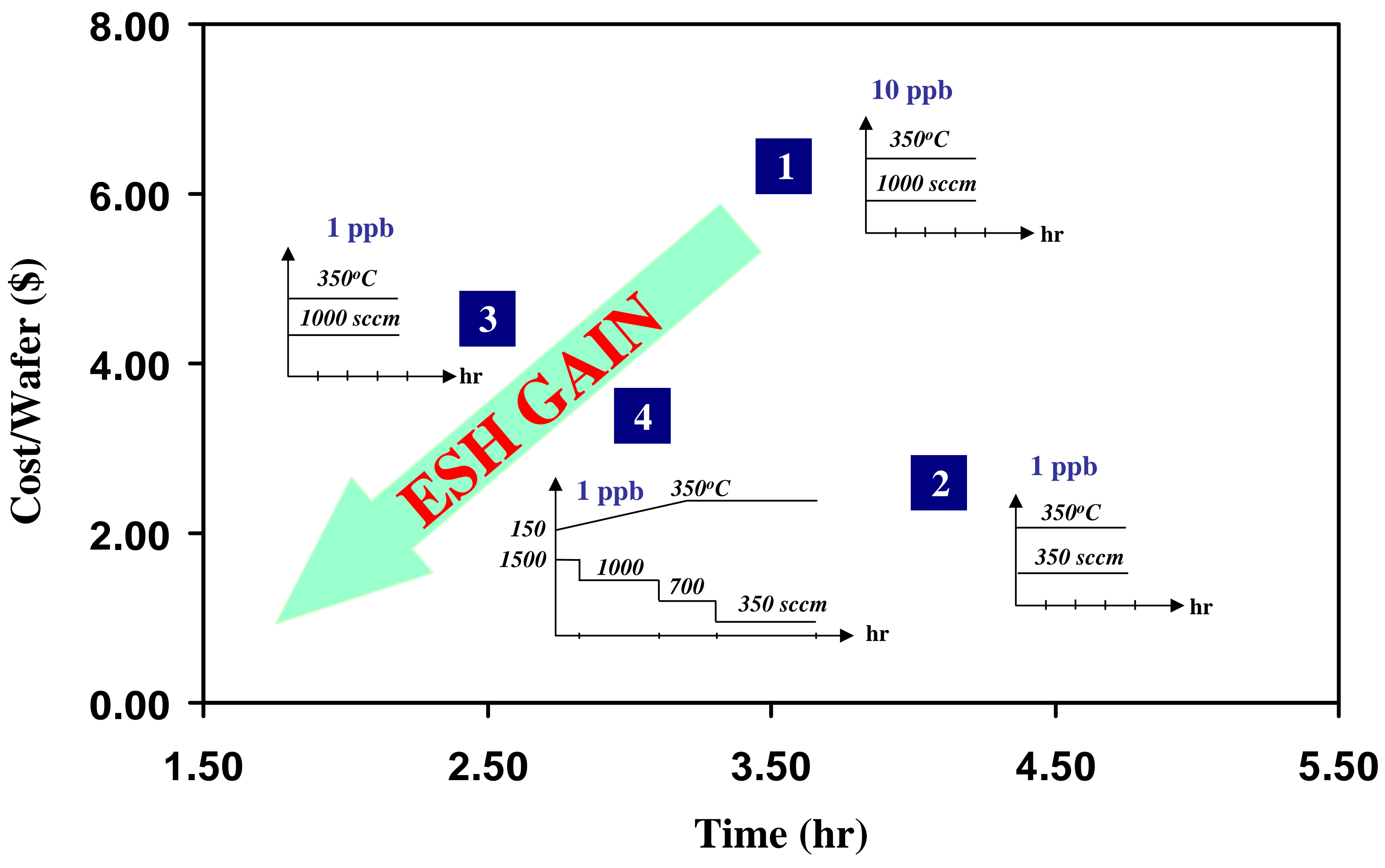
Films initially saturated with 130 ppb of moisture; purge temperature: 25 °C
Low-k: Black Diamond (BD IIx); cured blanket



IPA enhances moisture removal in low-k film

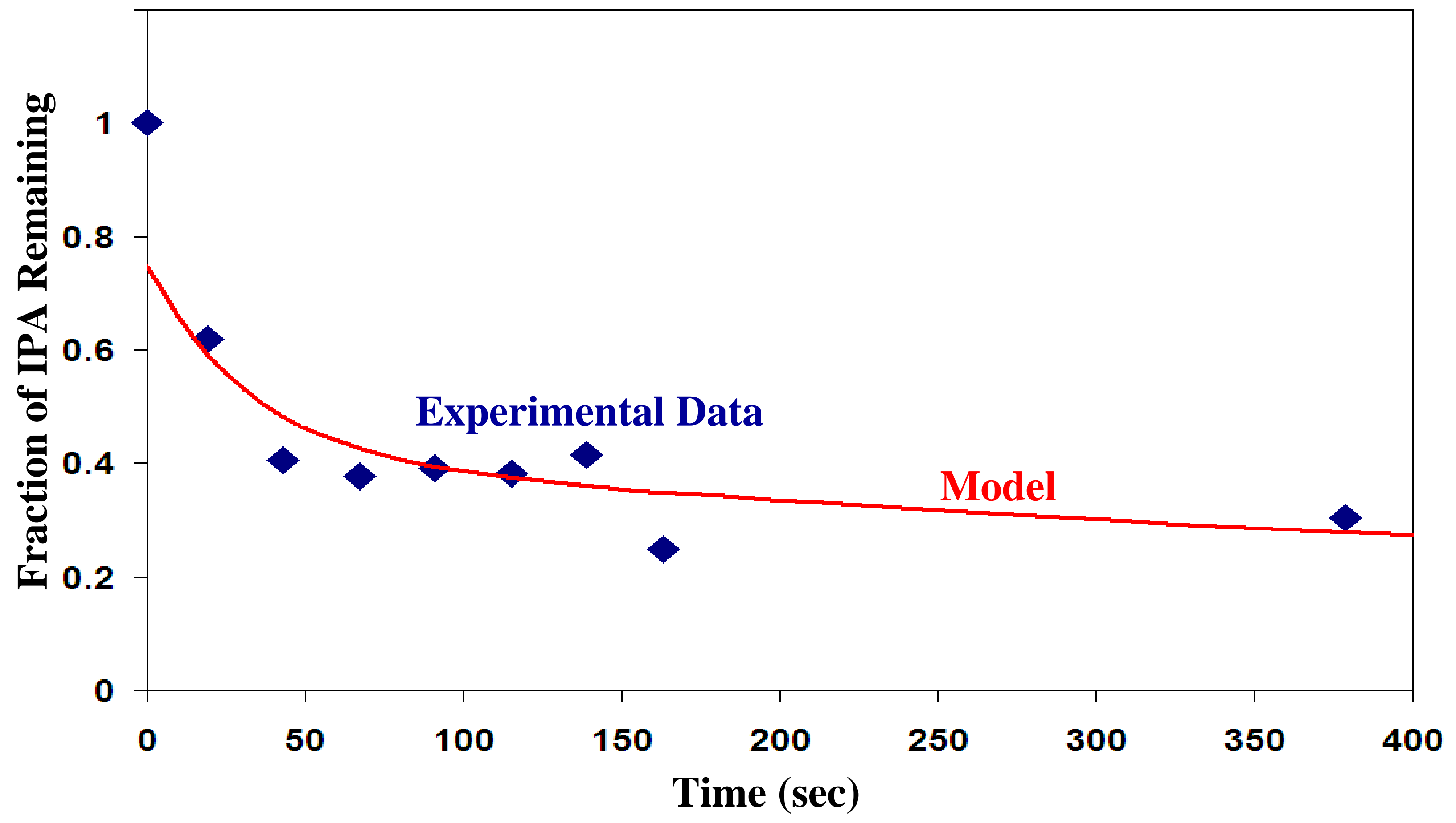
ESH Metrics and Impact

Illustration of significant impact on reducing cost and usage of purge gas, chemicals, and energy by applying the project results



VOC Interaction with SiO_2 Nano-Particles

Model Compound: IPA, IPA concentration: 5113 ppm, Temperature: 25 ^{0}C



Nanoparticles adsorb significant amount of IPA

Industrial Interactions and Future Plans

- **Collaborated with Sematech and Texas Instruments: preparation of samples and consultation on process applications.**
- **Software package for application will be made available to members.**
- **Continue work on the interactions of nano-particles with VOCs**
  - **Use the newly developed FTIR cell and method.**
  - **Study surface interactions and structural adsorption/desorption of contaminants on nano-particles (experiments and fundamental modeling).**

Publications and Presentations

- **H. Juneja, J. Yao, A. Iqbal, Ting Tsui, F. Shadman, "Dynamics of Moisture Uptake and Removal in Porous Low-k Dielectric Films", Poster Presentation, *MRS Spring Meeting*, 2007.**
- **A. Iqbal, J. Yao, H. Juneja, R. Sperline, F. Shadman, "In-Situ Characterization of Dynamics of Impurity Absorption and Outgassing in Porous Low-k Dielectric Thin Films", *AIChE Annual Meeting*, November 2007.**
- **J. Yao, A. Iqbal, H. Juneja, F. Shadman, " Moisture Uptake and Outgassing in Patterned and Capped Porous Low-k Dielectric Films, *Journal of the Electrochemical Society*, 154(10) G199-206 (2007).**
- **J. Yao, A. Iqbal, H. Juneja, F. Shadman, and Ting Y. Tsui, "Moisture Uptake and Removal in Porous MSQ and Black Diamond Low-k Dielectric Films", *Techcon 2007*, September, 2007**

Low-Water and Low-Energy Rinsing and Drying of Patterned Wafers, Nano-Structures, and New Materials Surfaces

(Task Number: 425.021)

PIs:

- Farhang Shadman, Chemical Engineering, UA
- Bert Vermeire, Electrical Engineering, ASU

Other Researchers:

- Jun Yan, Postdoctoral Fellow, Chemical Engineering, UA
- Omid Mahdavi, Micro/Nano Fabrication Center, UA

Graduate Students:

- Kedar Dhane, PhD candidate, Chemical Engineering, UA
- Nijad Anabtawi, PhD candidate, Electrical Engineering, ASU
- Xu Zhang, PhD candidate, Electrical Engineering, ASU

Cost Share (other than core ERC funding):

- Freescale, Samsung, EMC, NSF ($85k)

Objective

- Investigate the fundamentals of the cleaning, rinsing, and drying of micro- and nano-structures
- Develop new technologies (hardware, process models, and process recipes) to reduce water, chemicals, and energy usage during these processes.

ESH Metrics and Impact

- Reduction of water and energy usage in cold and hot rinse
- Decrease in the use of monitor wafers
- Decrease in the usage of chemicals during cleaning
- Decrease in the use of purge gas and energy during drying.

Method of Approach

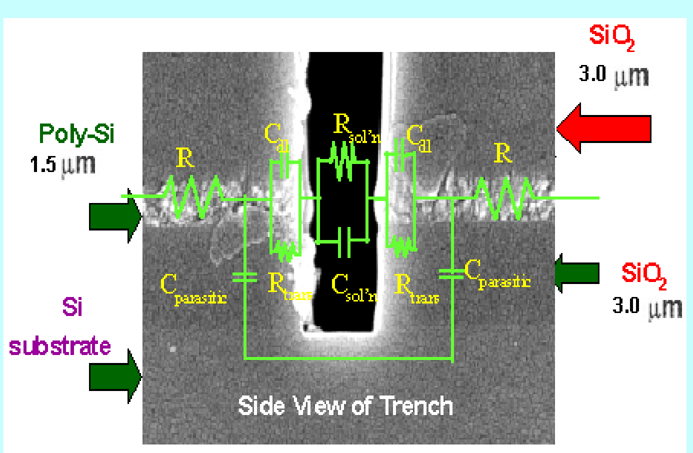
Method of Approach:

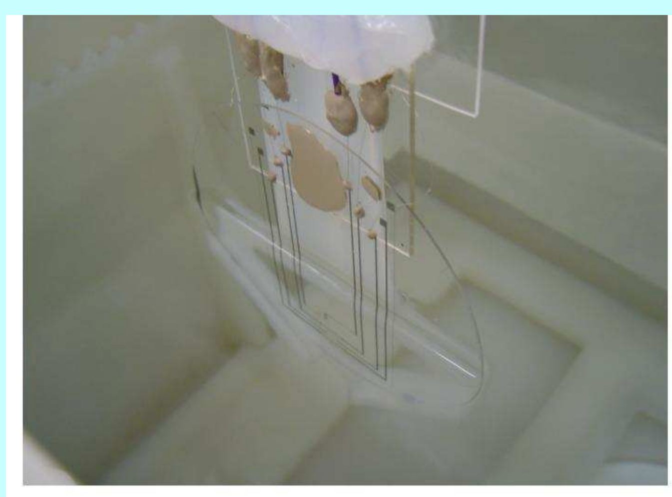
- **Develop a novel metrology method for in-situ and real-time monitoring of the dynamics of impurity transport inside micro- and nano-structures.**
- **Apply the metrology method as well as process modeling to find procedures and operational strategies for lowering resource usage in the cleaning, rinsing, and drying of small structures.**

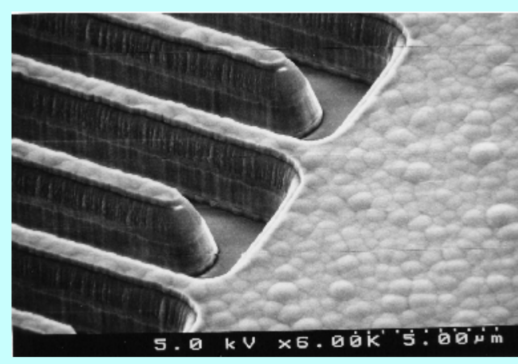
Metrology Requirements:

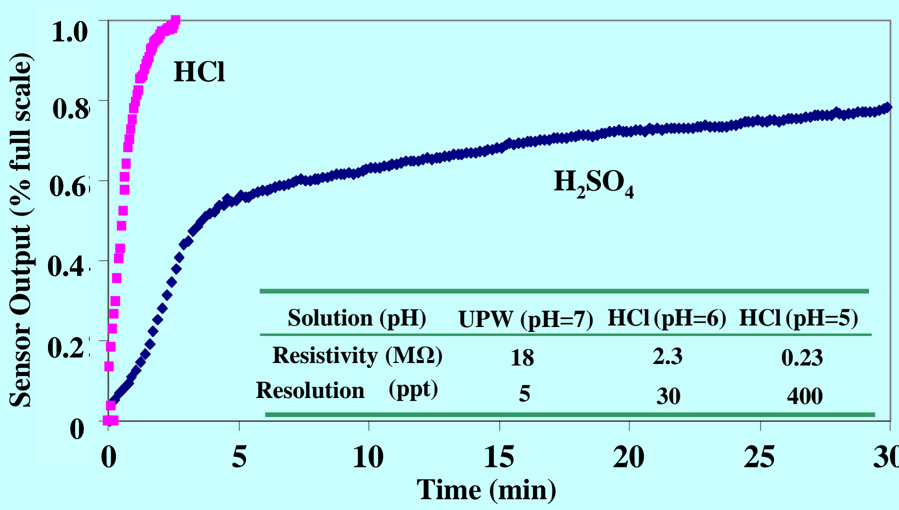
- **Low-ppt sensitivity**
- **On-line, real time, and in-situ**
- **Compatible with cleaning chemicals, and rinse/dry conditions.**

A) Novel Hardware: Electro-Chemical Residue Sensor (ECRS)



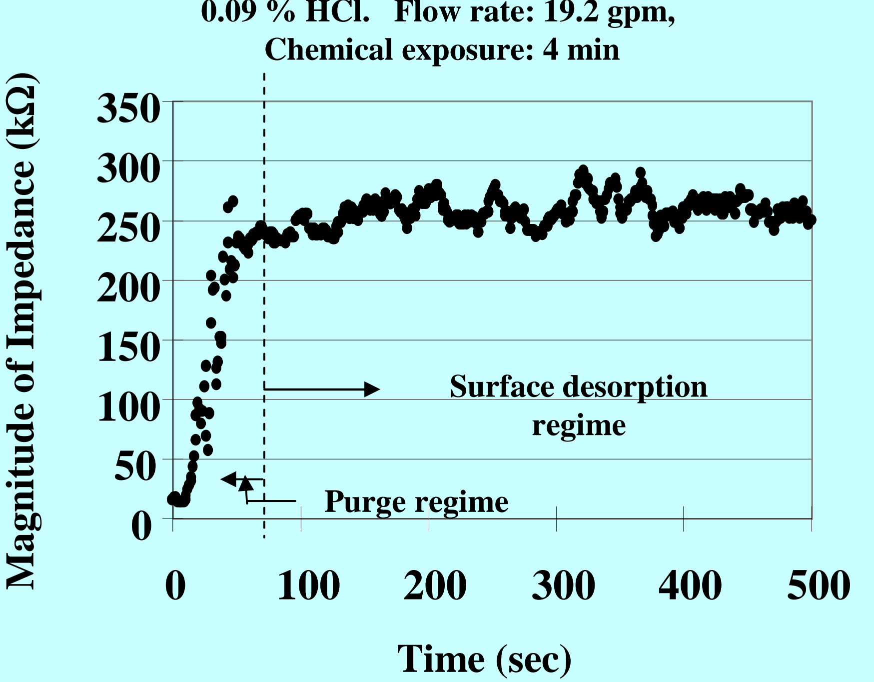


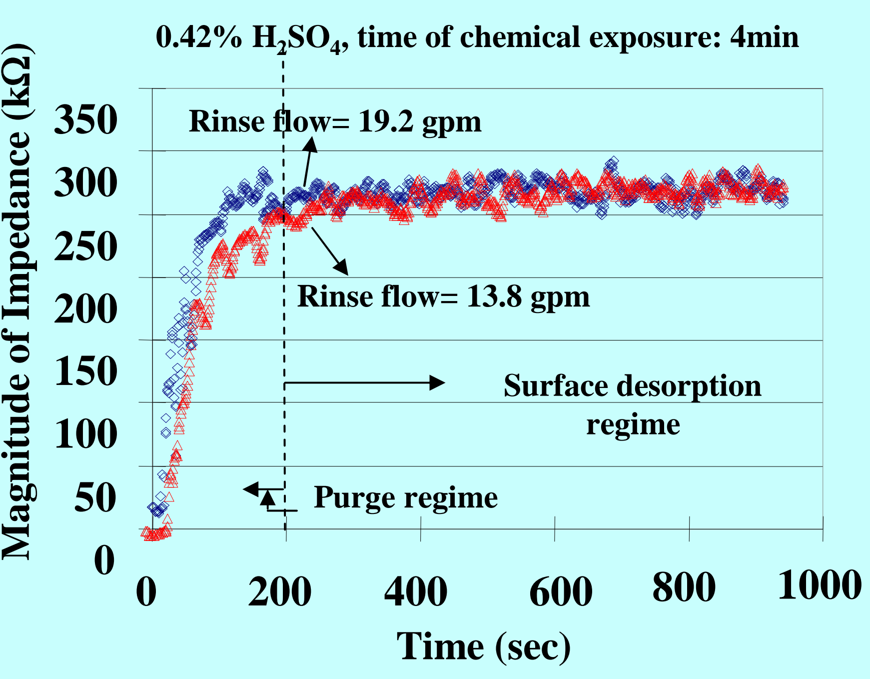




Solution (pH)	UPW (pH=7)	HCl (pH=6)	HCl (pH=5)
Resistivity (MΩ)	18	2.3	0.23
Resolution (ppt)	5	30	400

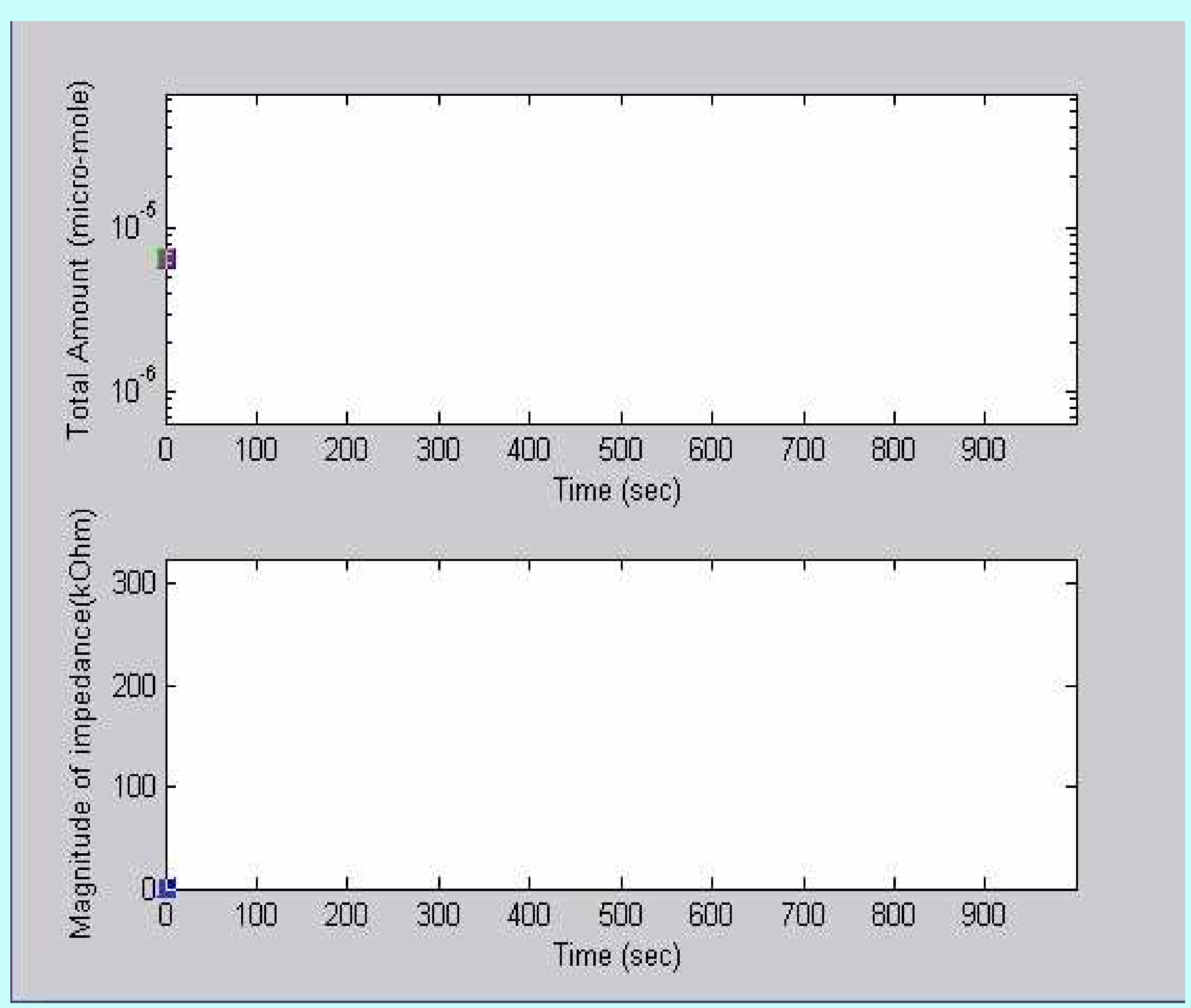
Rinse Optimization Implications





- Transitions from *tank purge regime* to *surface desorption regime* after 2-3 min.
- High flow-rate does not help rinse during the surface desorption regime.

Dynamics of Rinse, Monitored by ECRS



B) Software: Comprehensive Simulation of Rinse Process

Multi-component species transport equations :

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

Change in tank concentration :

$$V \frac{\partial C_b}{\partial t} = Q(C_{in} - C_b) + A \cdot Flux$$

Surface adsorption and desorption:

$$\frac{\partial C_{S2}}{\partial t} = k_{a2} C_2 (S_{02} - C_{S2}) - k_{d2} C_{S2}$$

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

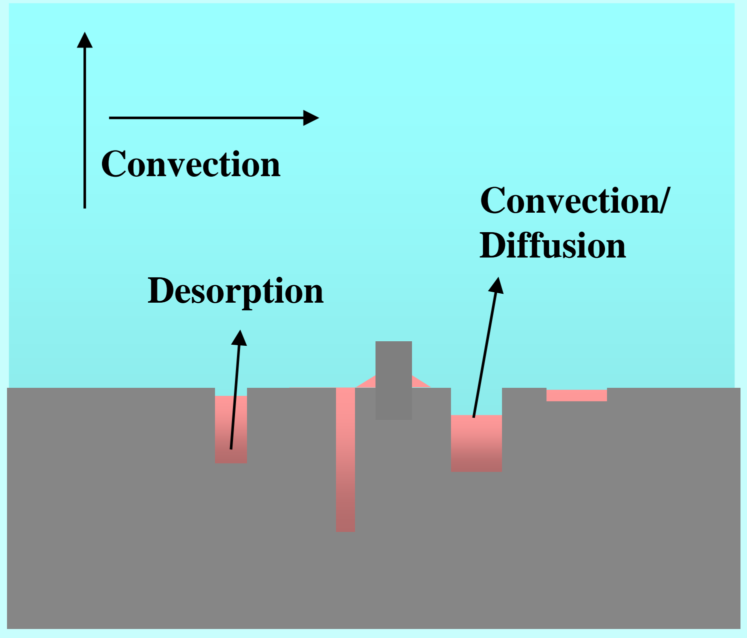
where charge density: $\rho = F \sum_i z_i C_i$

Ohm's law: $\vec{J} = \sigma \vec{E}$ $\qquad \nabla \times \vec{E} = 0$

where electrical conductivity:

$$\sigma = \sum_i \lambda_i C_i$$

- **Surface Charge**
- **Diffusion**
- **Surface reaction**
- **Ionic transport**



Significance of the Proposed Metrology

What is Currently measured and used for process control:

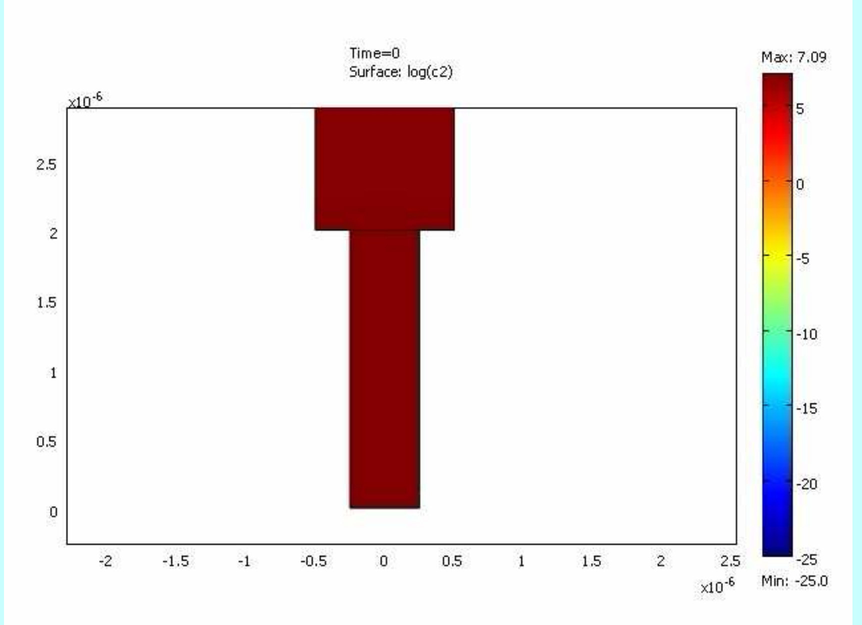
Conventional method

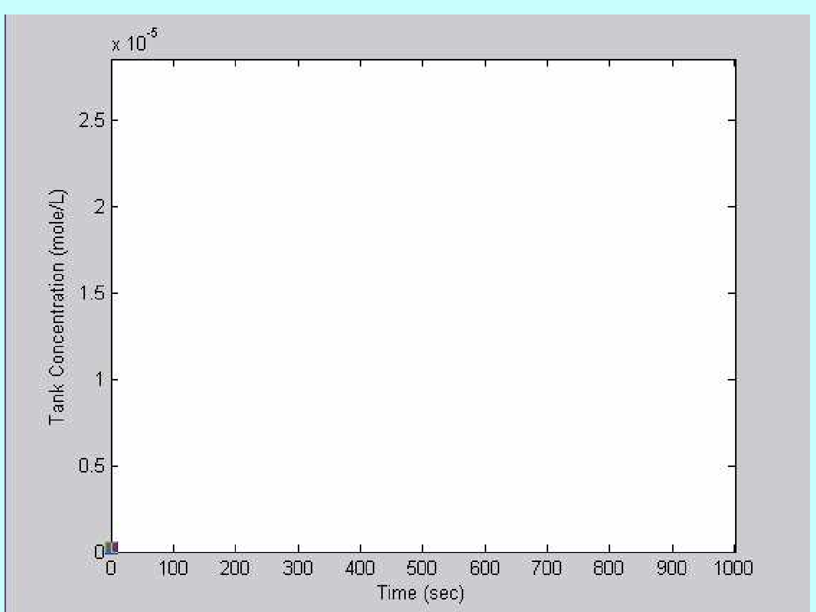
Time and space distribution of impurity during rinsing a sub-micron trench:

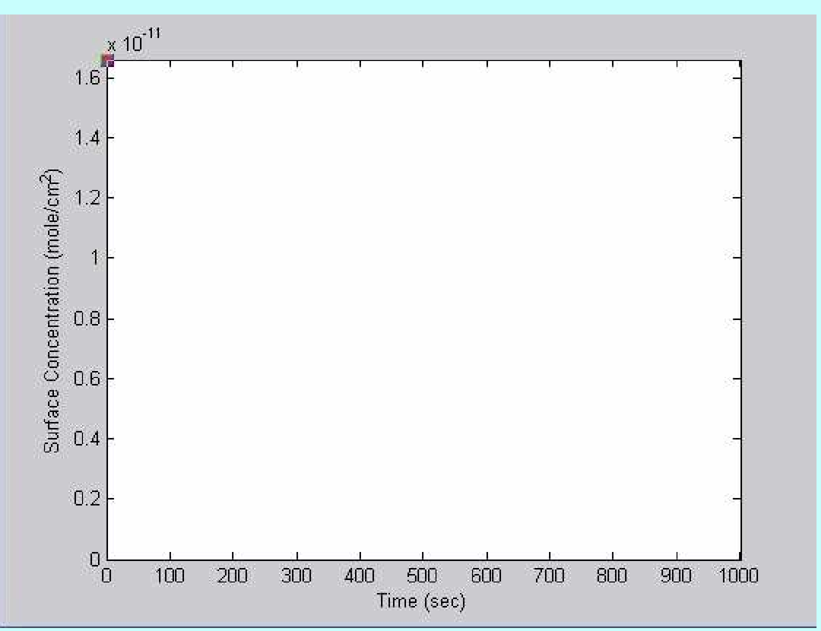
Enabled by proposed metrology

What needs to be measured and used for process control:

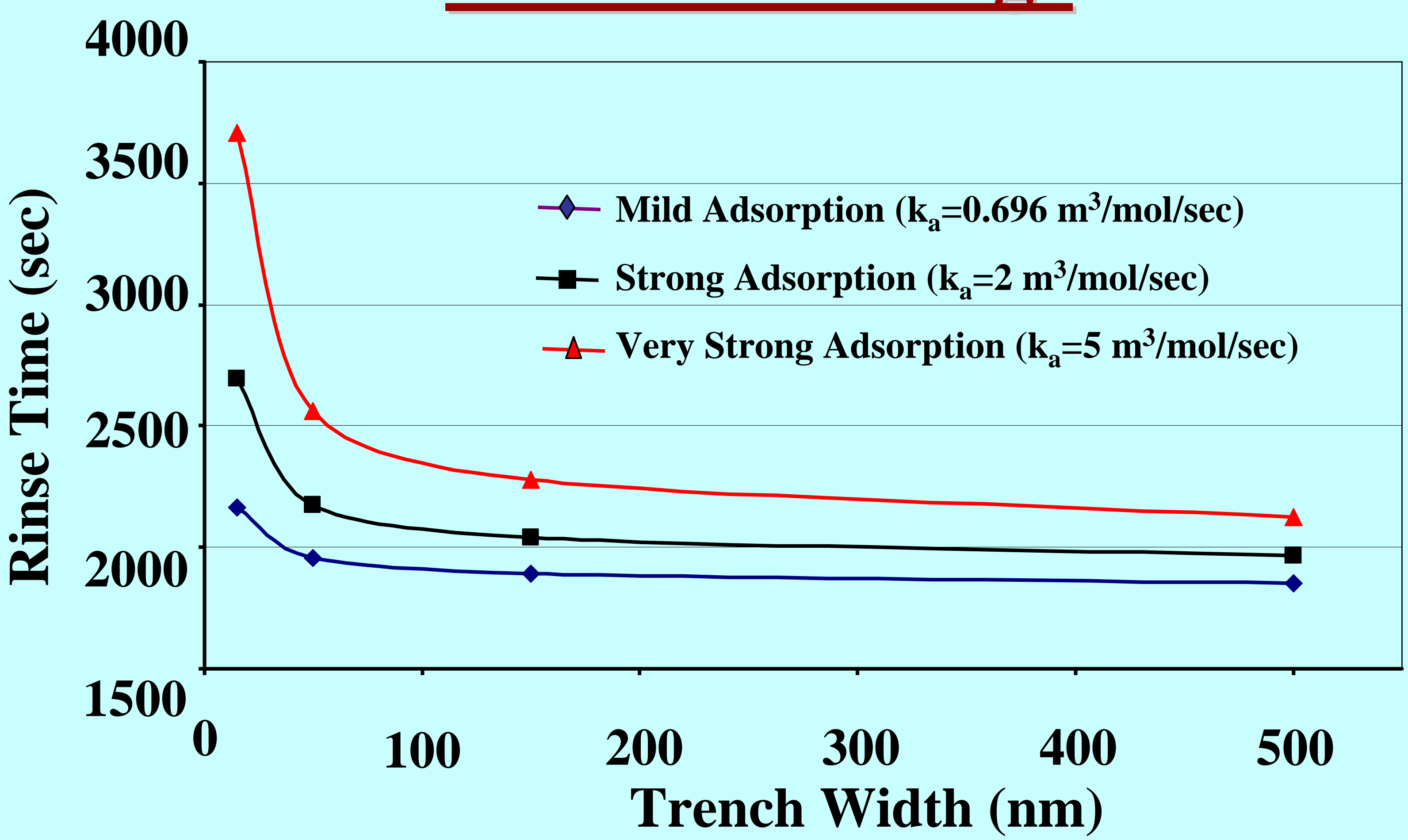
Enabled by ECRS


Time=0
Surface: log(c2)
Max: 7.09
Min: -25.0
x10^-6
2.5
2
1.5
1
0.5
0
-2
-1.5
-1
-0.5
0.5
5
-5
-10
-15
-20
-25


x 10^-5
Tank Concentration (mole/L)
Time (sec)
0
100
200
300
400
500
600
700
800
900
1000
0.5
1
1.5
2
2.5


x 10^-11
Surface Concentration (mole/cm^2)
Time (sec)
0
100
200
300
400
500
600
700
800
900
1000
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6

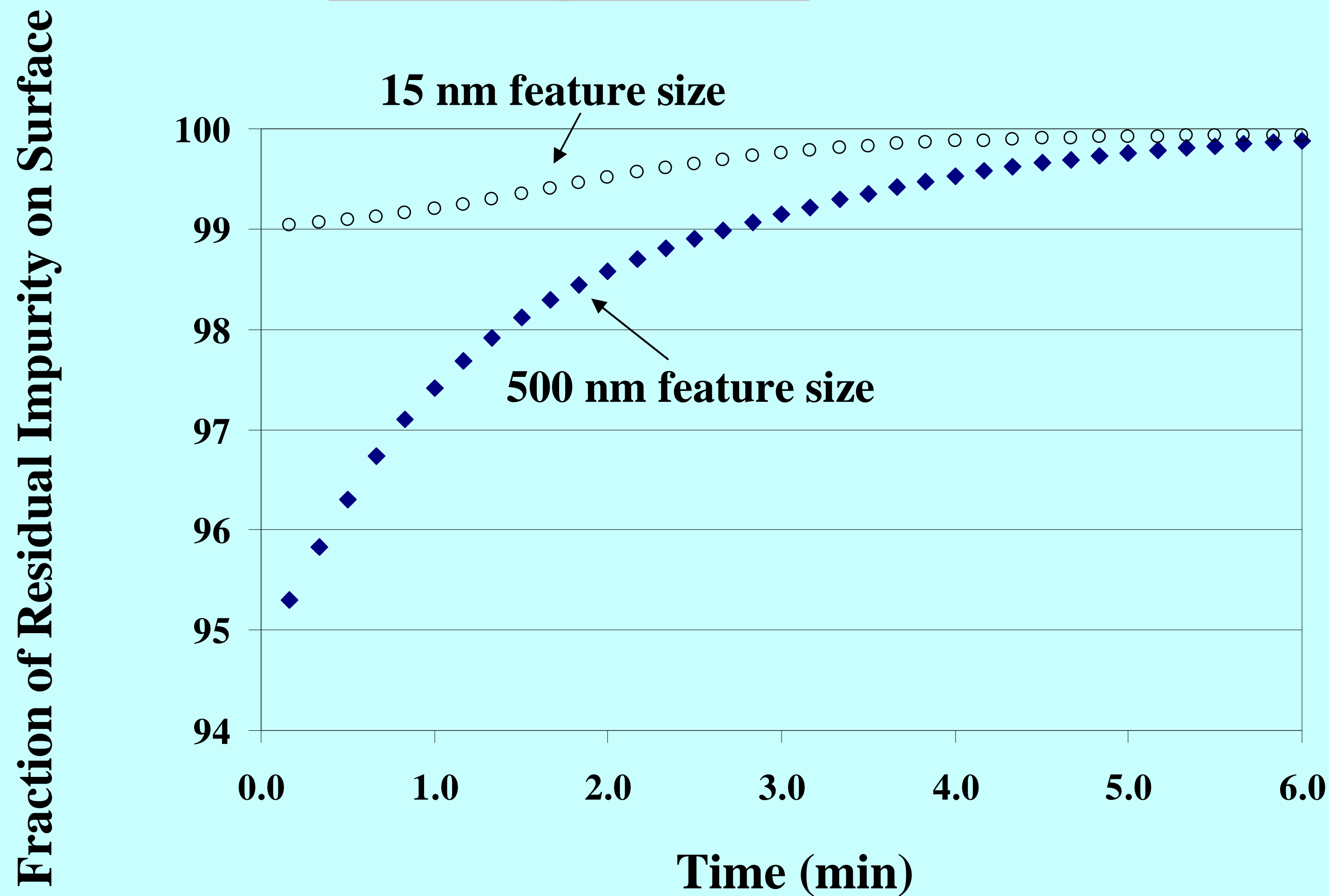
Effect of Feature Size on Rinse Time and Water Usage



Rinse time to reach 10^{12} ions/cm^2 on the surface of the trench.

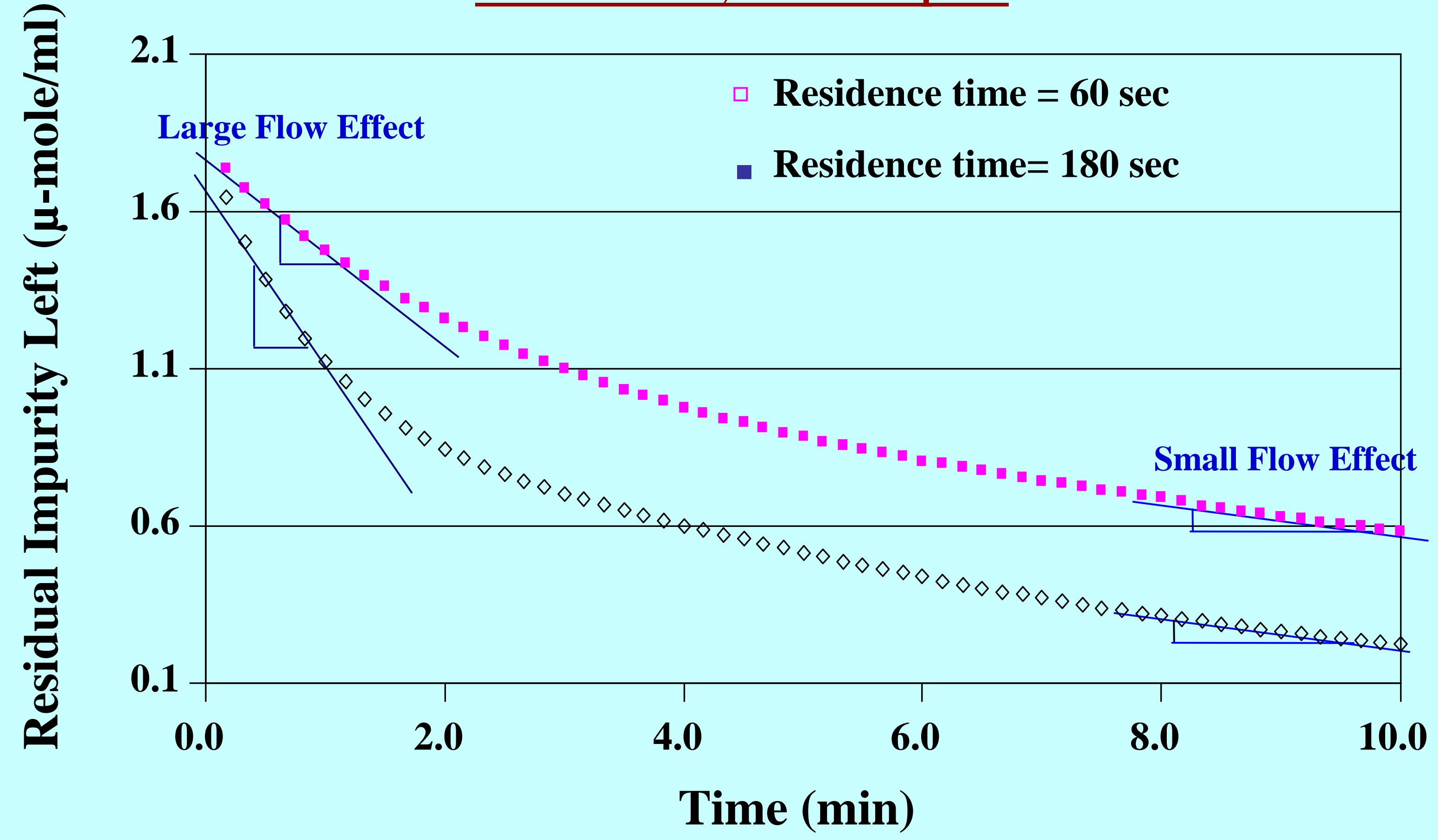
Rinse Mechanism and Dynamics

2 micron deep trench or via, mild adsorption



Effect of Flow on Rinse Dynamics

width- 500 nm, mild adsorption



Large savings and water use reduction are possible with staged flow rate based on the proposed metrology.

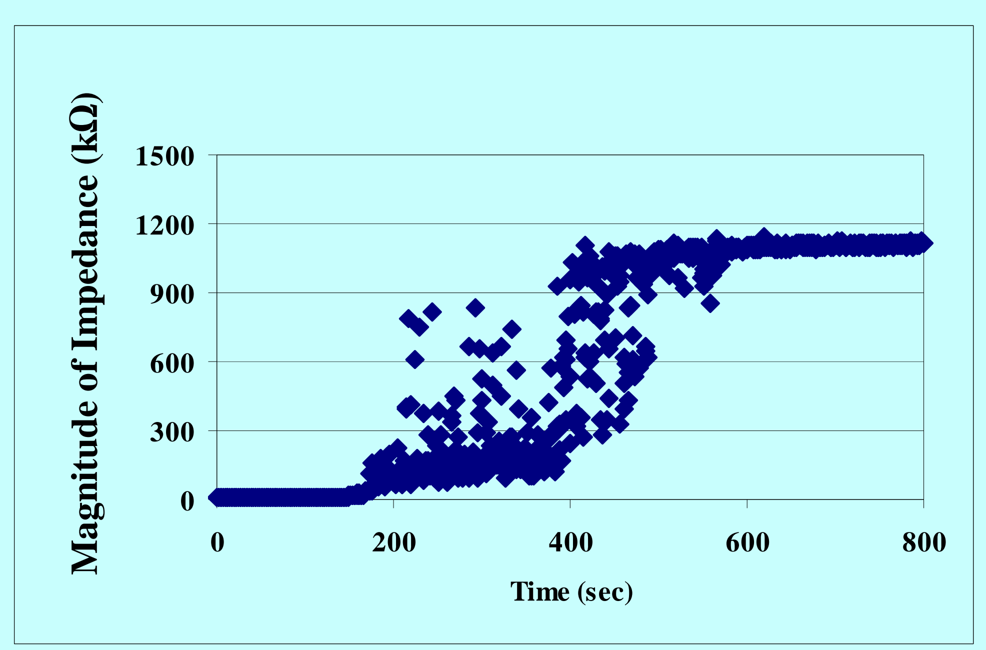
Low-Water and Low-Energy Rinsing and Drying of Patterned Wafers, Nano-Structures, and New Materials Surfaces

(Task Number: 425.021)

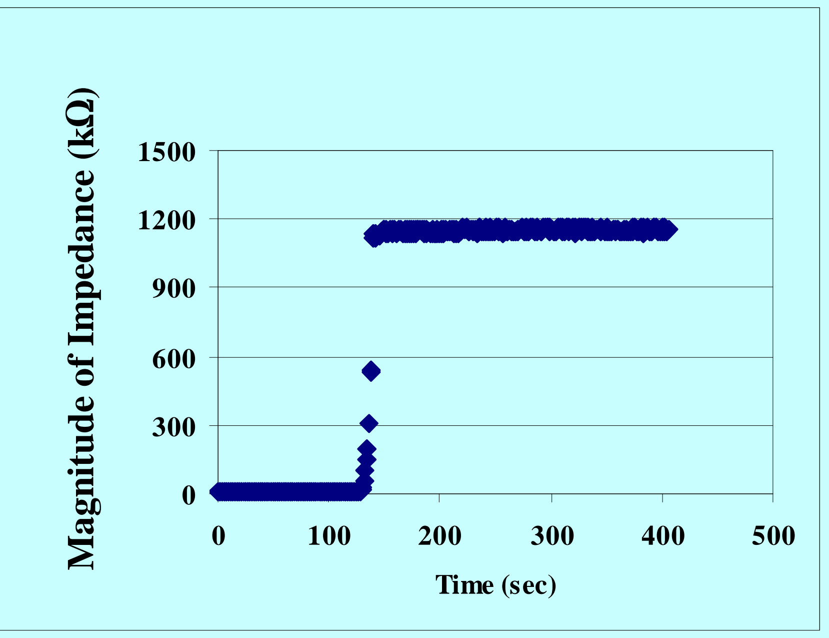
Part 2

Development of Low-Impact Drying

Determining the Bottlenecks Using ECRS



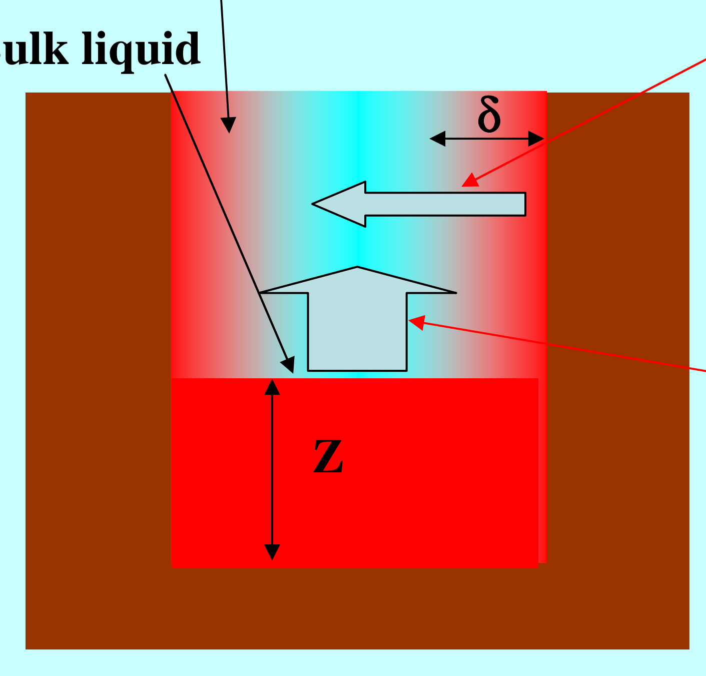
Hydrophilic



Hydrophobic

- **Time required for drying depends on the surface condition.**
- **ECRS detects complex mechanism for drying, particularly for hydrophilic surfaces.**

Mechanism of Drying of Small Structures



Removal rate from adsorbed layer:

$$R_d = k_d C_s - k_a C_g$$

$$k_a = k_{aI} + (k_{aII} - k_{aI})\frac{\theta}{1+\theta}$$

$$k_d = k_{dI} + (k_{dII} - k_{dI})\frac{\theta}{1+\theta}$$

Removal rate from bulk liquid:

$$R_e = k(P_{sat} e^{-\frac{\alpha}{w}} - P_{bulk})$$

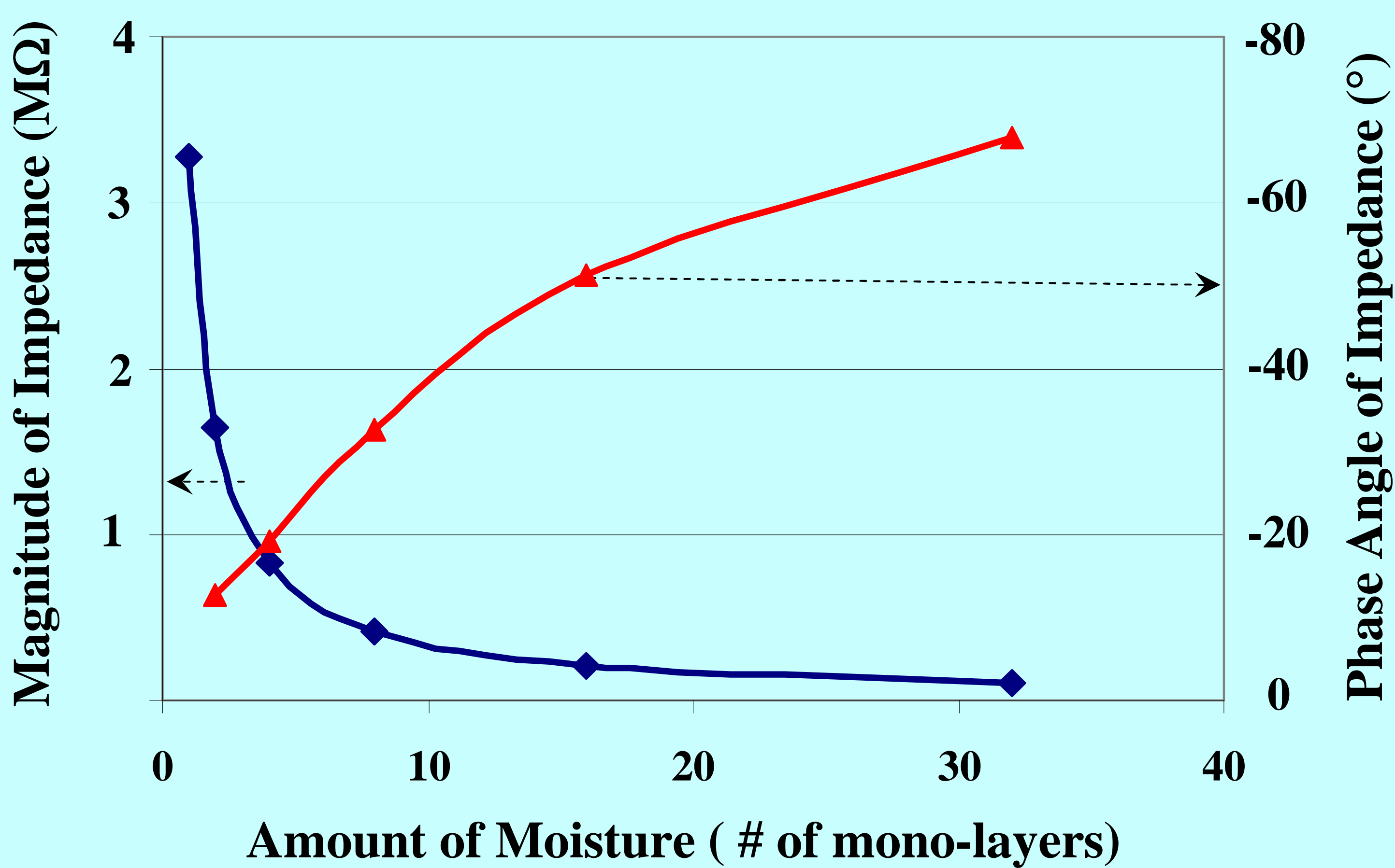
Total removal rate from pore:

$$R = R_e + R_d$$

Two simultaneous processes:

- **Conventional evaporation of liquid-like molecules (mild feature size effect)**
- **Adsorption and desorption in a multi-layer (both chemisorbed and physisorbed; strong feature size dependence)**

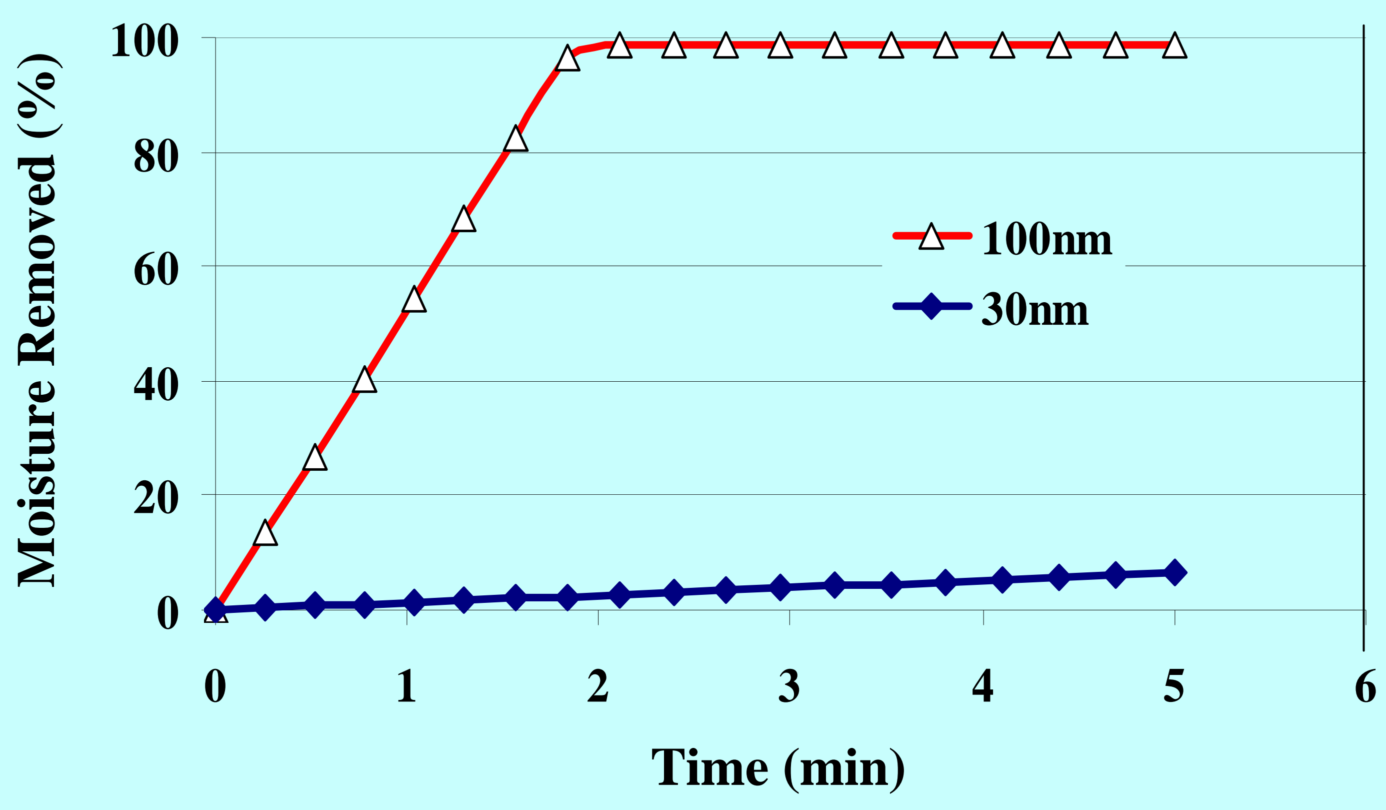
ECRS Calibration for Drying



*** Magnitude was collected at optimum frequencies; Phase angle was collected at 100Hz.**

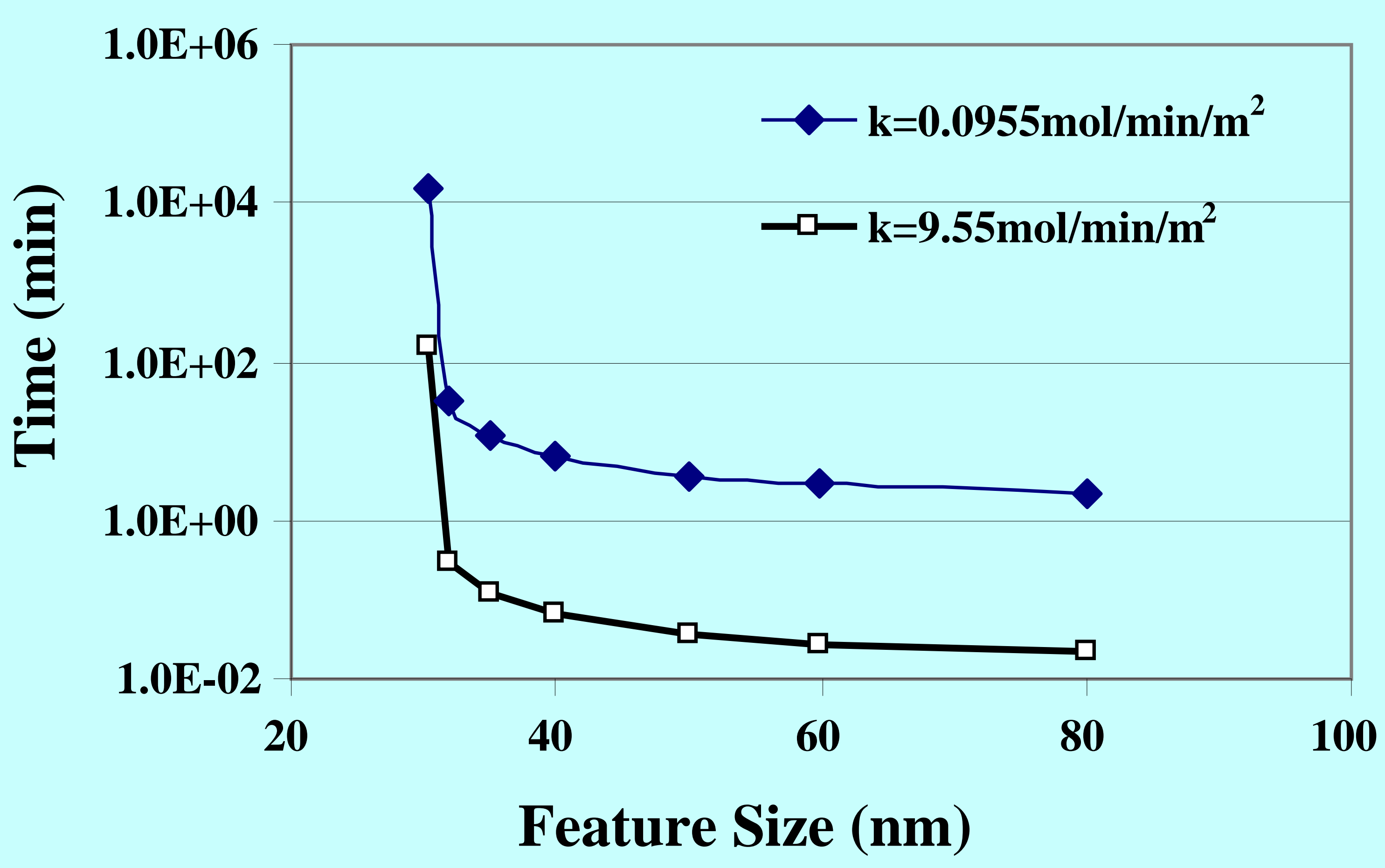
Dynamics of Drying of Nano-Structures

Feature Size Dependence



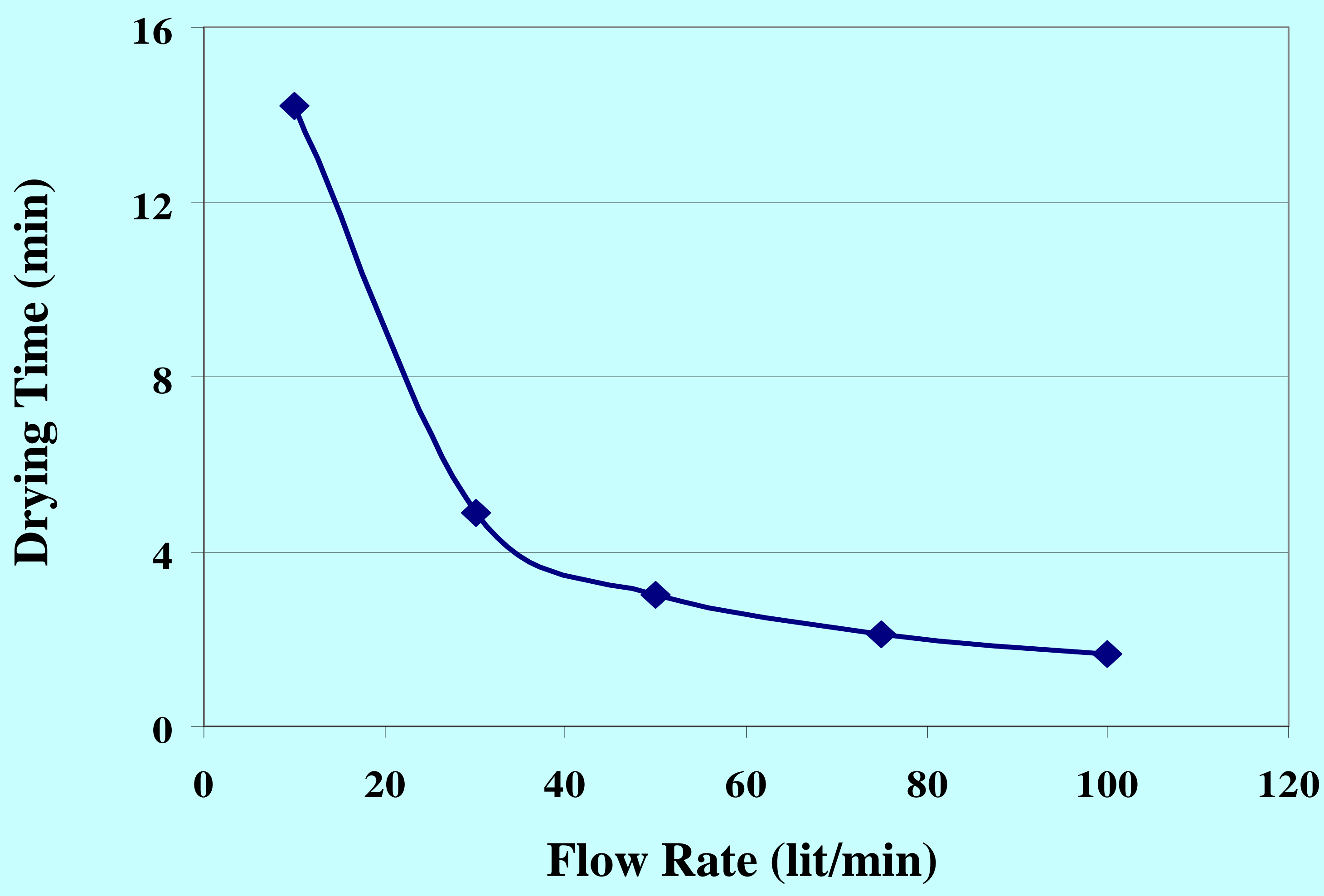
Dynamics of Drying of Nano-Structures

Feature Size Dependence



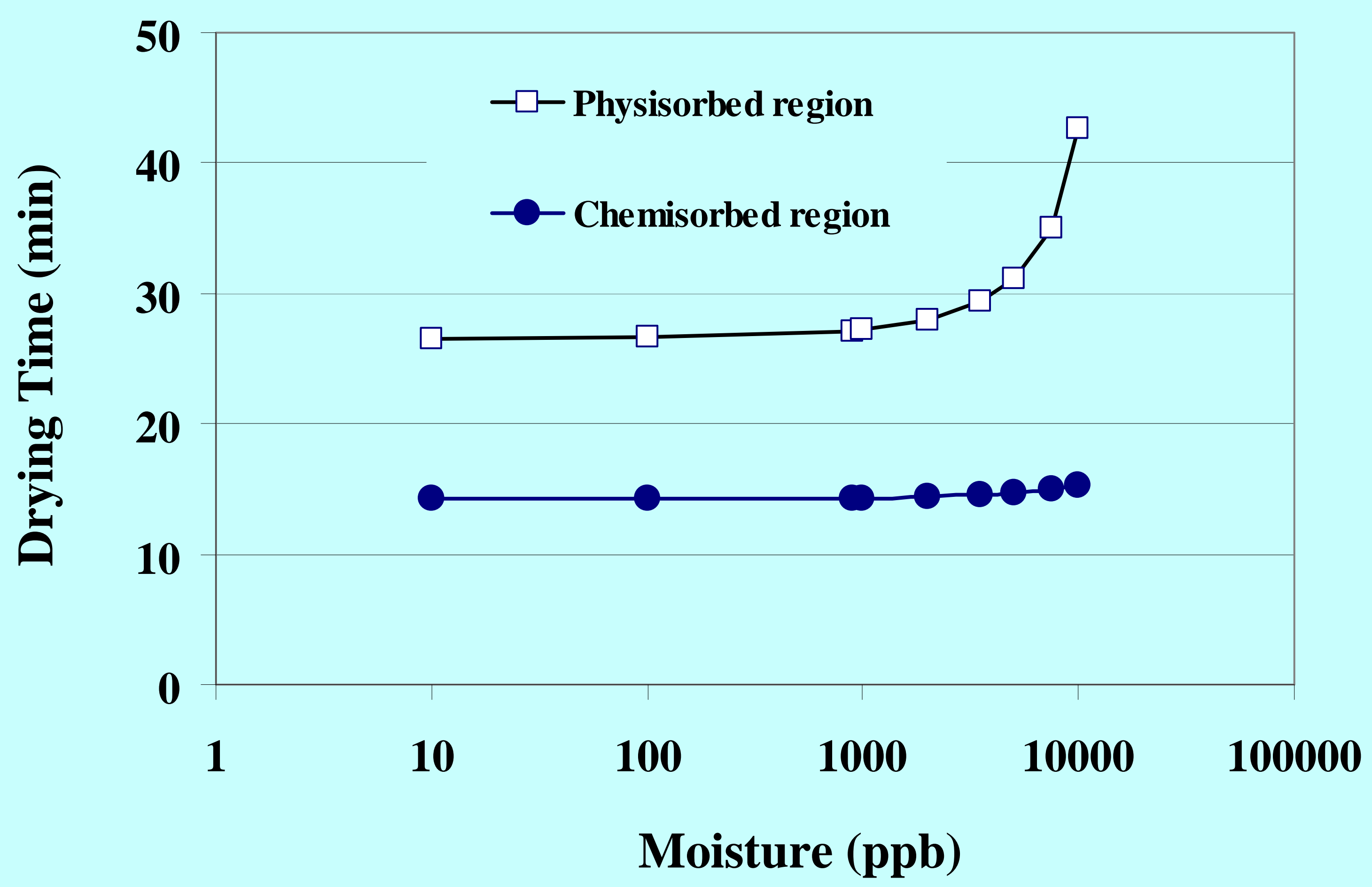
Drying of Nano-Structures

Effect of Purge Gas Flow Rate



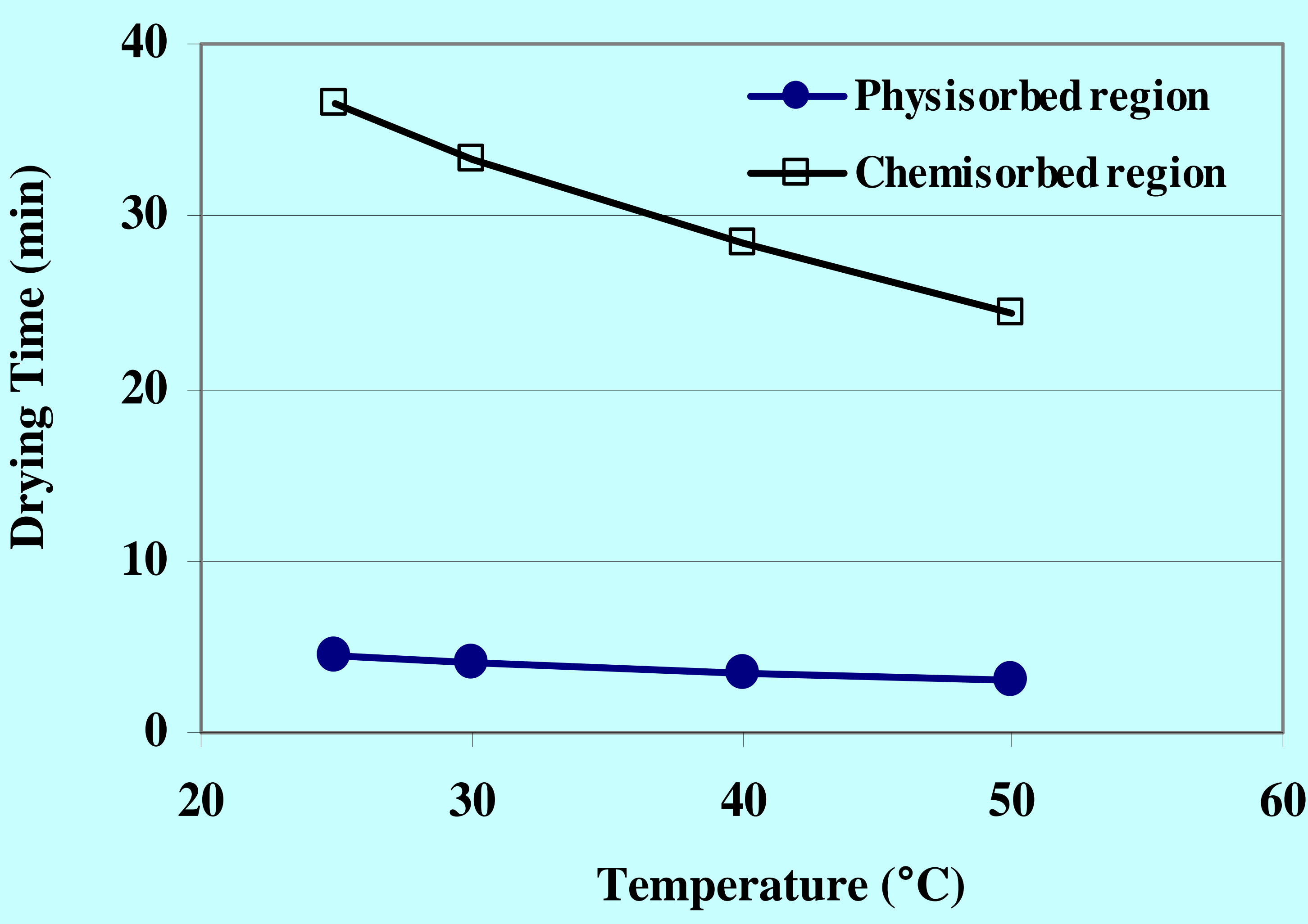
Drying of Nano-Structures

Effect of Purge Gas Purity



Drying of Nano-Structures

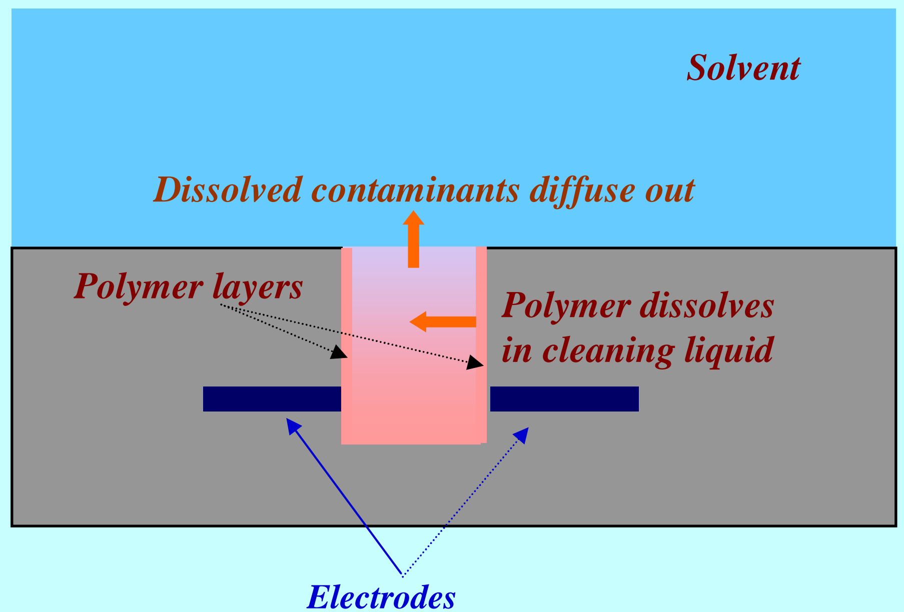
Effect of Temperature



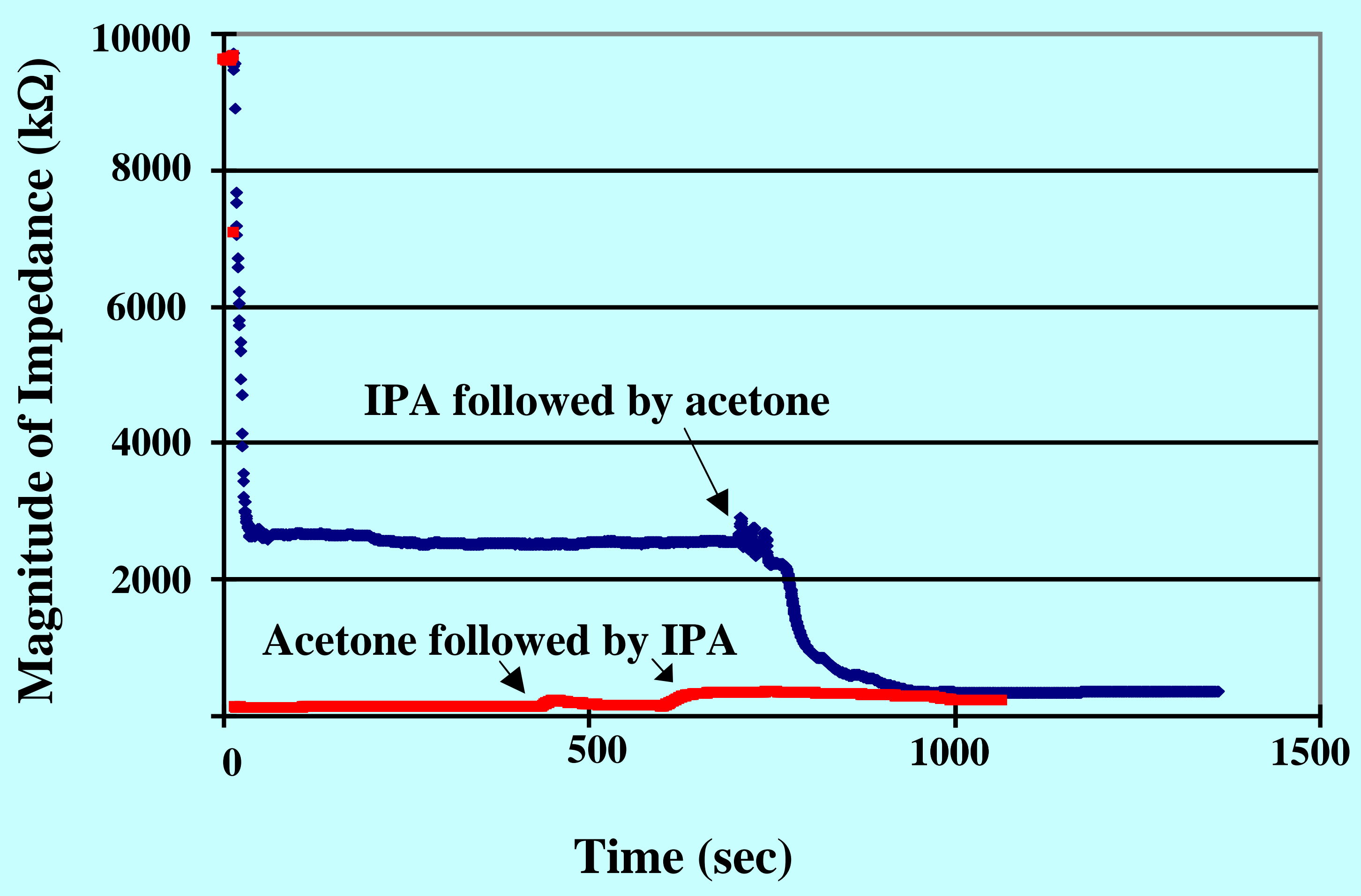
Development of Low-Impact Cleaning

Determining the Bottlenecks Using ECRS

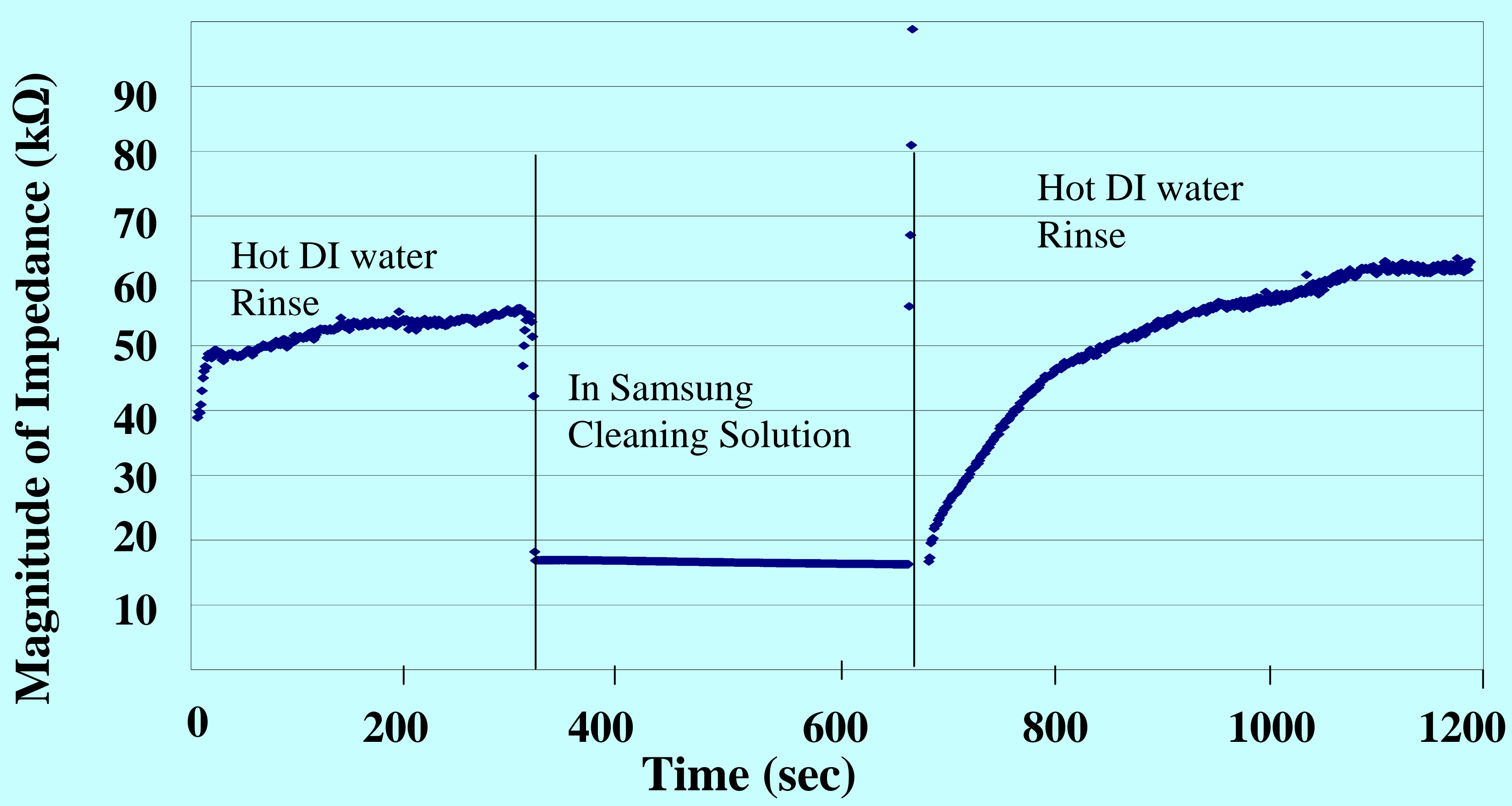
- **Etching creates residues on the sidewalls of the trenches and vias.**
- **Side wall cleaning becomes more complex, more difficult, and more resource intensive as we move further into manufacturing of high-aspect-ratio nano-features**
- **No in-situ sensor is available for on-line monitoring of residues; ECRS would result in significant reduction in use of cleaning chemicals.**



Cleaning of Micro- and Nano-Structures

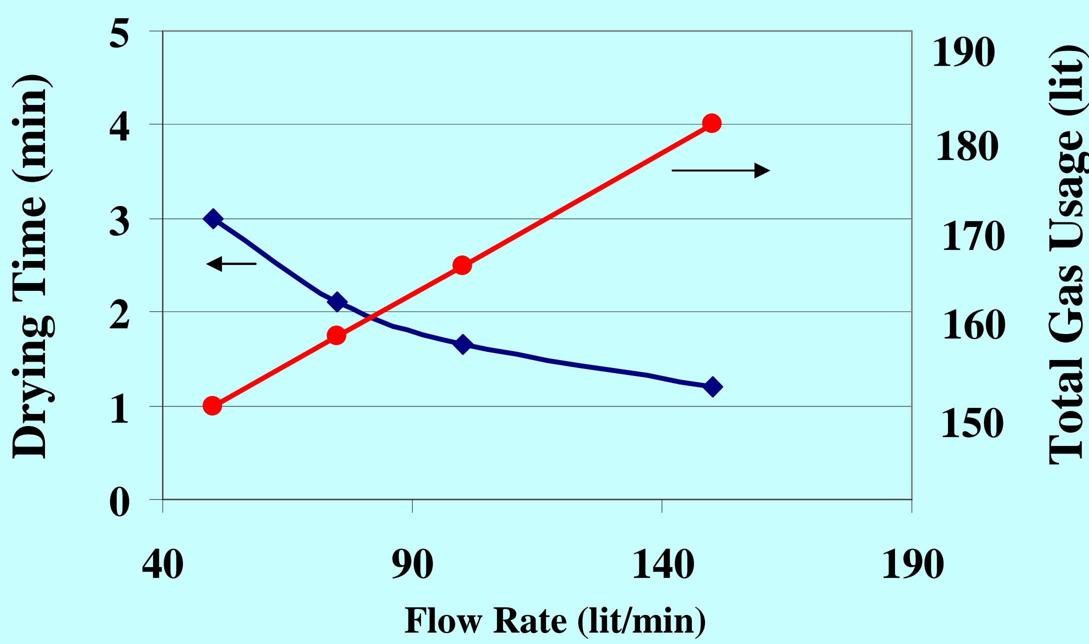


Cleaning of Micro- and Nano-Structures



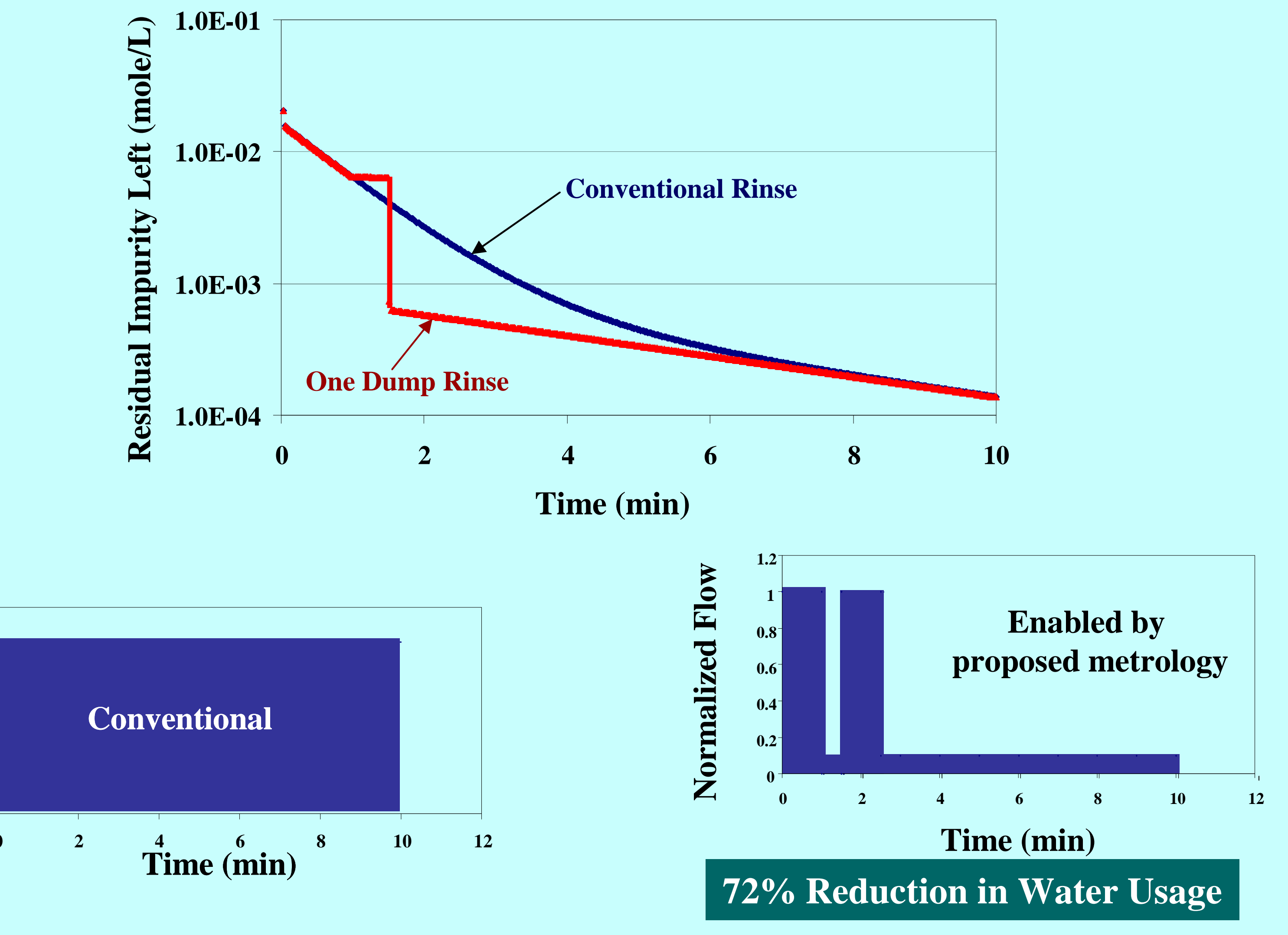
ECRS can monitor cleaning of the polymer residue inside trench

ESH Impact



- Optimum purge is a balance between throughput and gas usage
- ECRS provides in situ and real-time profile of residual moisture
- ESH gain is by developing purge recipes (flow rate, purity, and temperature) to enhance the two modes of drying discovered in this study.

ESH Impact



SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Industrial Interactions and Future Plans

- **Continue work on application and tech transfer:**
  - **Joint work, co-sponsored by Freescale (Hsi-An Kwong, Marie Burnham, Tom Roche, Jack Shively); rinse process**
  - **Joint work, co-sponsored by Samsung (Seung-Ki Chae, Jeong-Nam Han, Pil-Kwon Jun); cleaning and rinse processes**
  - **EMC (Doug Goodman); commercialization**
- **Fundamental work on a novel wireless metrology version of ECRS**

Presentations, Awards

- **Dhane, K., Yan, J., Vermeire, B., Shadman, F., "*In-Situ and Real Time Metrology during Cleaning, Rinsing and Drying of Micro- and Nano Structures*", TECHCON, September 2007**

❖ **Selected as the Best Paper in Session, TECHCON, September 2007**

Low Environmental Impact Processing of Sub-50 nm Interconnect Structures

(*Task Number: 425.019)*

PIs:

- **Karen K. Gleason, Department of Chemical Engineering, MIT**

Graduate Students:

- **Chia-Hua Lee: PhD Candidate, Department of Material Science and Engineering, MIT**
- **Wyatt Tenhaeff, Ph.D Candidate, Department of Chemical Engineering, MIT (NSF Fellow)**

Cost Share (other than core ERC funding):

- **$70k (NSF Fellowship for Wyatt Tenhaeff)**

Objectives

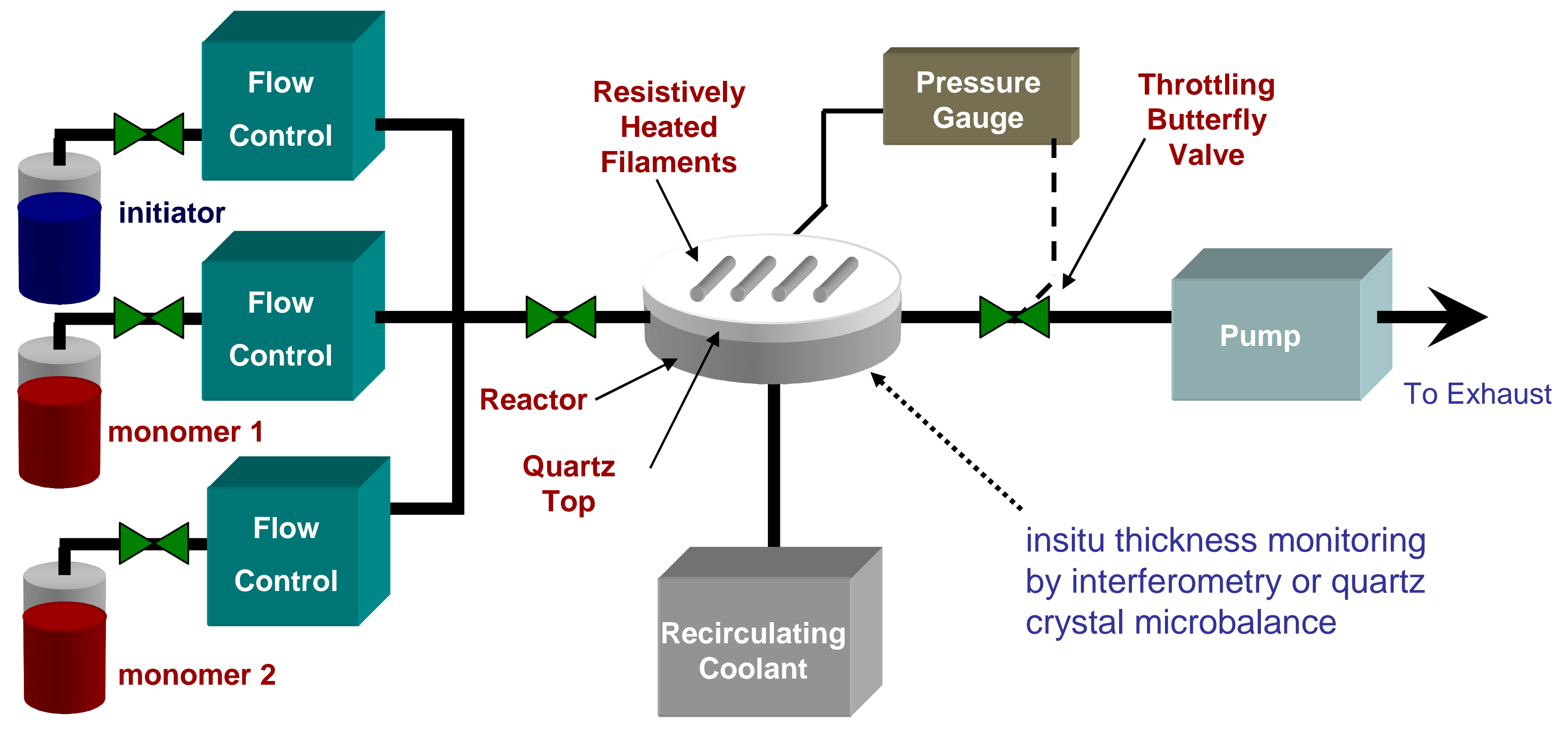
- **Develop new methods to deposit patterns at resolution of 50 nm and below without conventional UV or ebeam lithography**
  - **Using Dip-Pen Nanolithography (DPN) and microcontact stamping to create surface quantum dot patterns on the polymer substrate.**
  - **Using carbon nanotubes (CNTs) as the etching masks to create high resolution functional polymer patterns**
- **Use EHS focused design approach to minimize process steps in the novel patterning processes**
- **Use low energy iCVD method as the process platform technology.**
- **Develop integration methods for quantum dots (QDs), allowing integration of high performance devices onto flexible substrates, relying on the naturally small dimensions of the QDs to achieve high resolution.**

ESH Metrics and Impact

1. *Resist-free lithography would eliminate use of photoresist. Approximately 25,000 liters of photoresist materials is used annually in typical semiconductor foundries, at a cost of about $1,600 per liter. Through spin-on process approximately 95% of resist is wasted and disposed as toxic material [1]. In contrast, the cost of CNTs is about $ 10 per gram. For typical 4 inch wafer,(assuming 50% masking area), only 0.124mg of CNTs are needed. Hence, the cost of CNT needed for obtaining patterns on a 4-inch diameter wafer is about 1 cent.*
2. *Typical iCVD process requires between 0.02-0.12 W/cm^2 [3] for polymer deposition compared to conventional PECVD which uses 0.4-2.1 W/cm^2 [4,5]. No plasma etch eliminates additional >7.1 W/cm^2 [6] power requirement.*

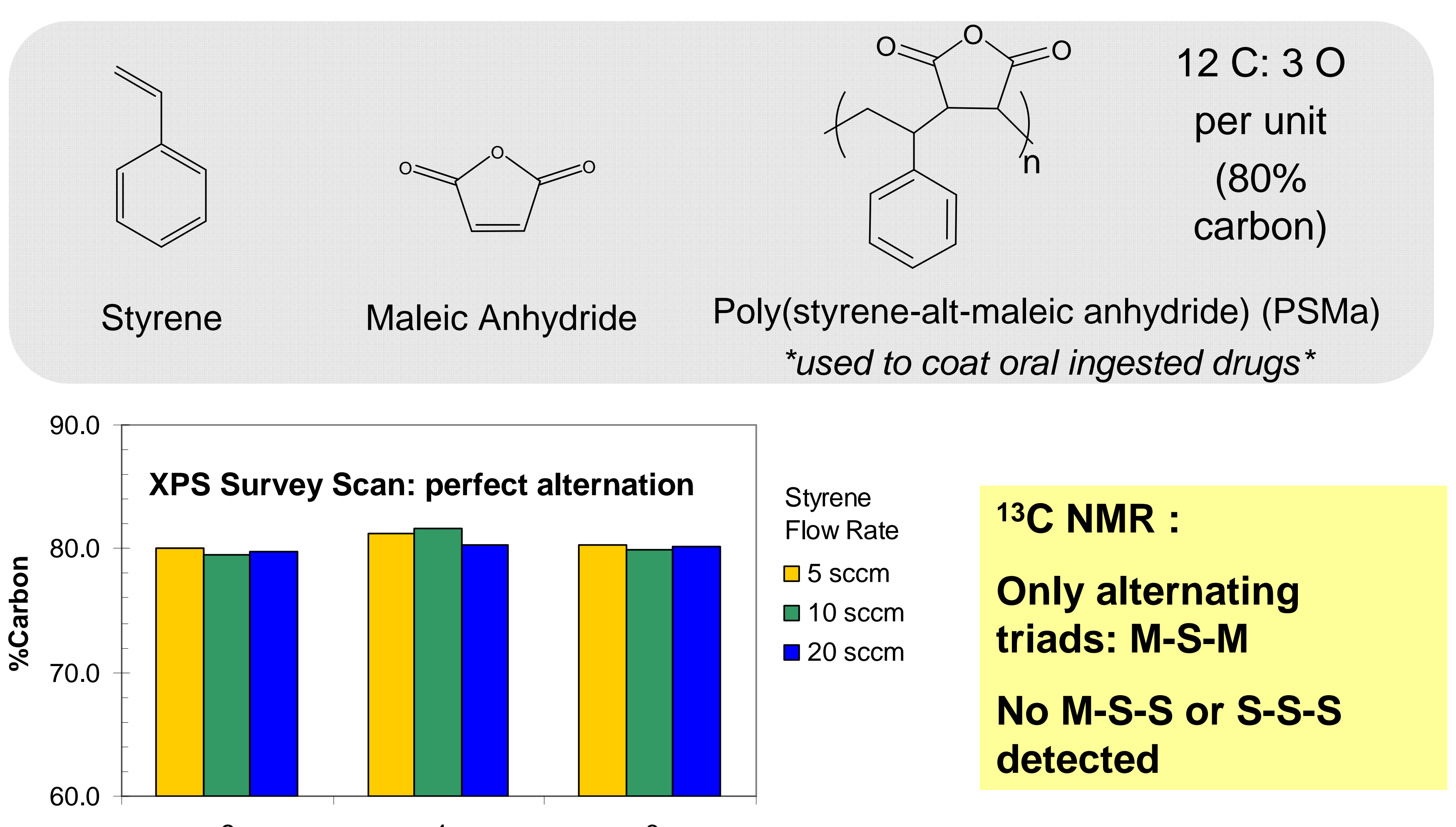
[1] Percin et al., IEEE Transactions on Semiconductor Manufacturing (2003) 16 (3)
[2] Lee et al., J. Micromech. Microeng. (2005) 15
[3] Martin et al.Surf. Coating Tech. (2007) 201
[4]Castex et al. Microelec. Eng. (2005) 82
[5]Wong et al. Thin Sol. Films 462–463 (2004)
[6]Berruyer et al. J. Vac. Sci. Technol. A. 16.3 (1998)

Initiated CVD of Functionalizable Polymers



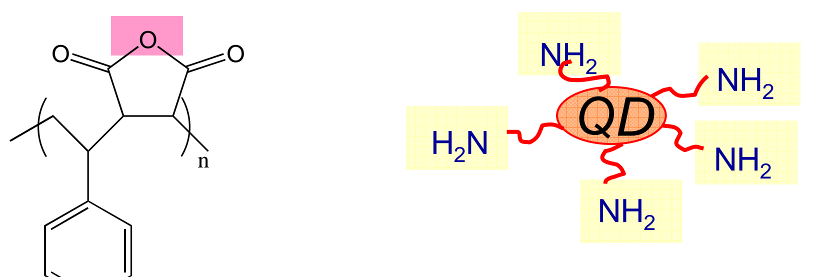
Functional groups in iCVD films can be used to covalently tether nanoparticles

iCVD poly(styrene-alt-maleic anhydride)



W.E. Tenhaeff and K.K. Gleason
Langmuir 23, 6624 (2007).

Covalent attachment of QDs to iCVD PSMa



- **Poly(styrene-alt-maleic anhydride) (PSMa)**
- **CdSe quantum dots (QD)**

  capped bifunctional ligands $-NH_2$

QD Size ~ 5 nm

UV spectrum

Post-ultrasonication
Polymer / QDs

QDs

Polymer

450 500 550 600 650 700 750 800

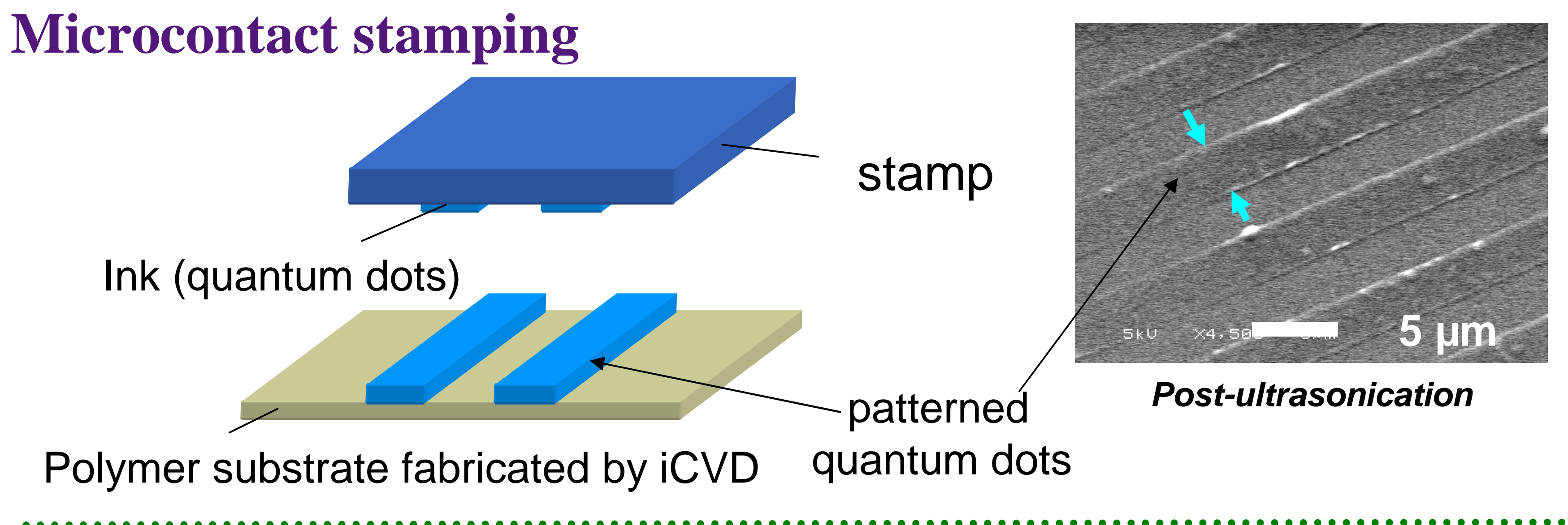
(nm)

NH_2
NH_2
QD
H_2N
NH_2
N
O
O
n

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

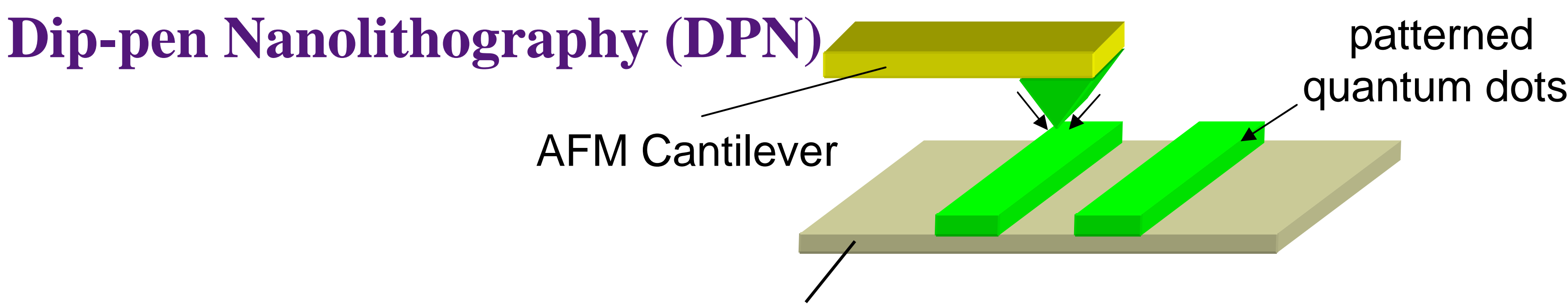
Direct writing with QD ink on iCVD PSMa

Microcontact stamping



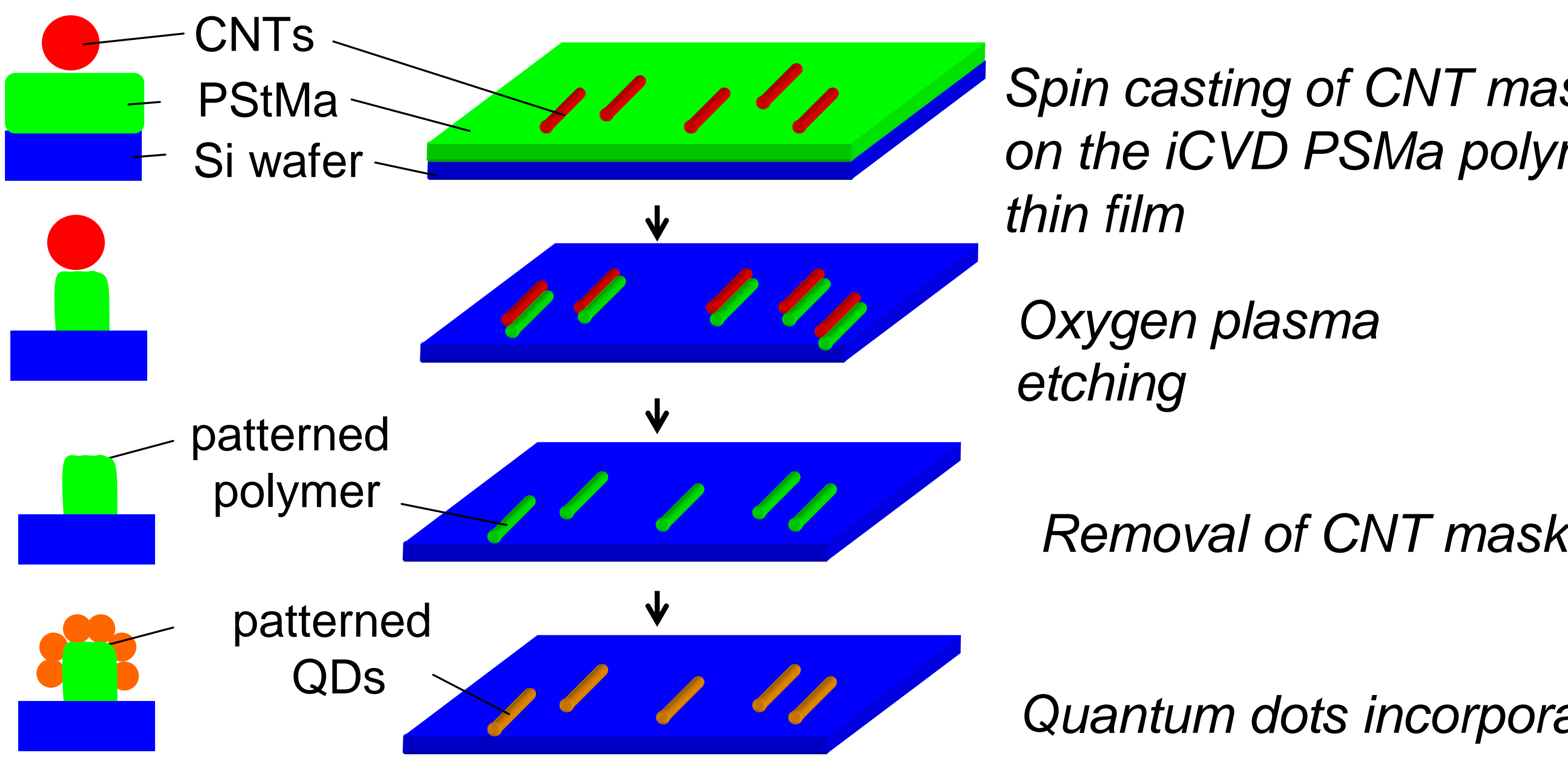
Post-ultrasonication

Dip-pen Nanolithography (DPN)



Writing speed can be increased by using multiple cantilevers in parallel

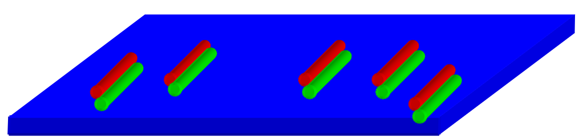
CNT masks for patterning iCVD PSMa



Use of semiconducting QDs removes the need for substrates to be high quality substrates.

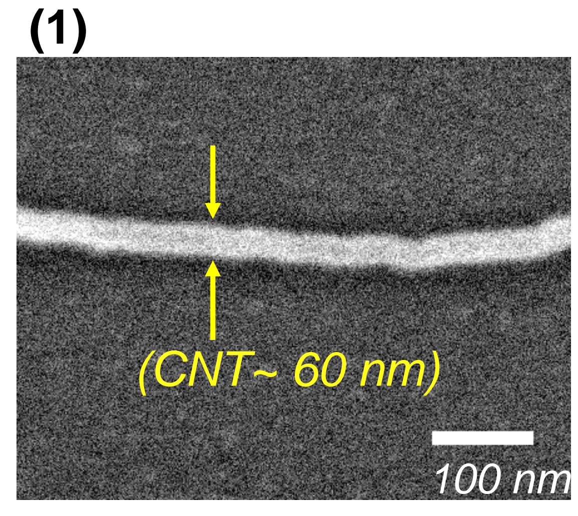
Inexpensive, lightweight flexible substrates possible. Avoids energy intensive fabrication of high purity silicon wafers.

Carbon Nanotube (CNT) masking results



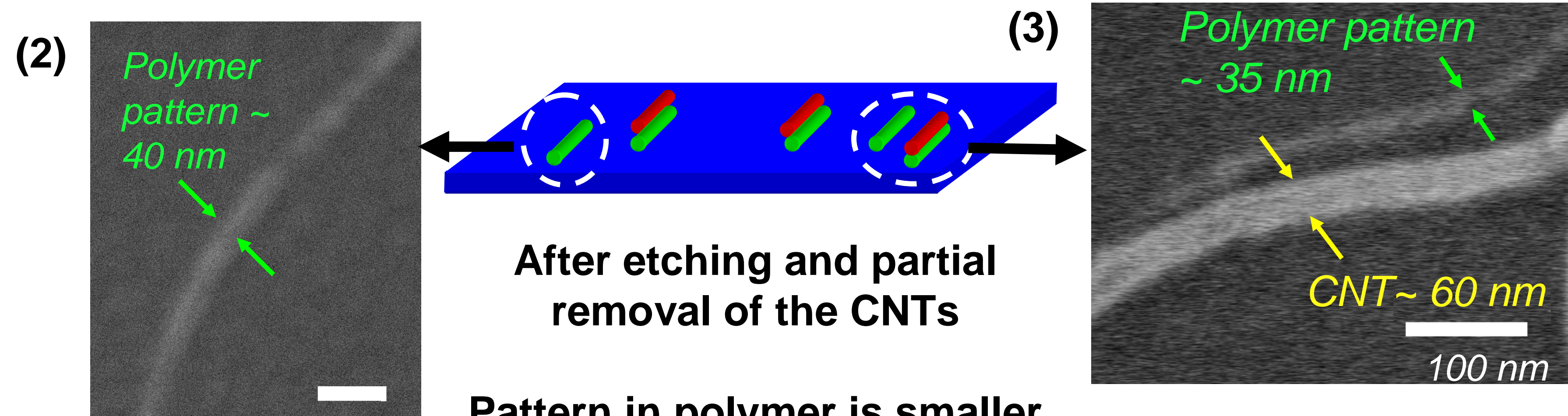
After spin-casting of CNTs

(1)



(2)

(3)

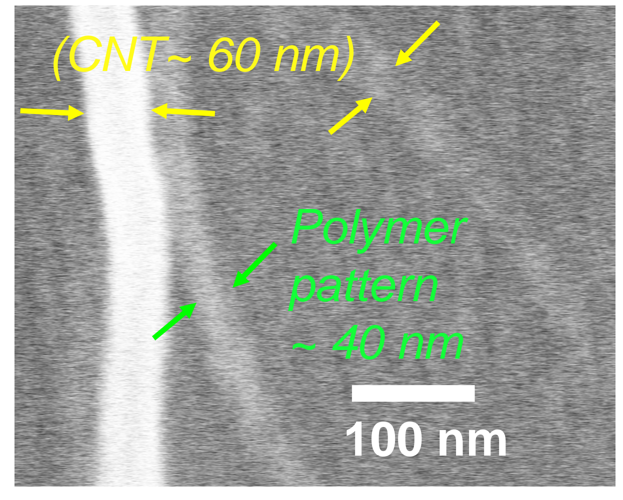


After etching and partial removal of the CNTs

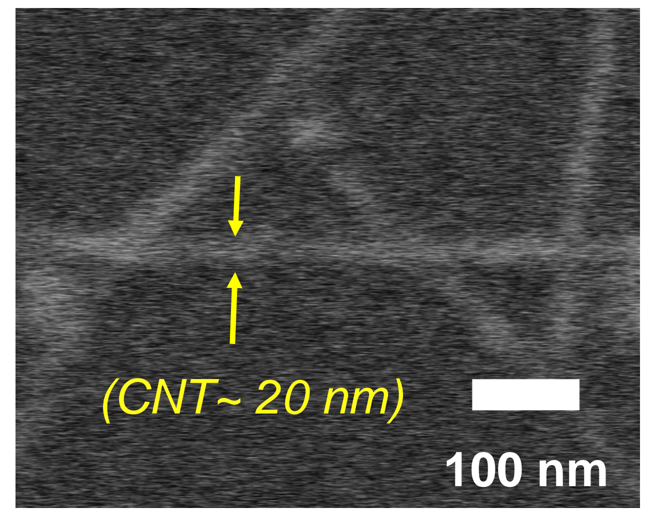
Pattern in polymer is smaller than CNT diameter

(Etching time: 30 s)

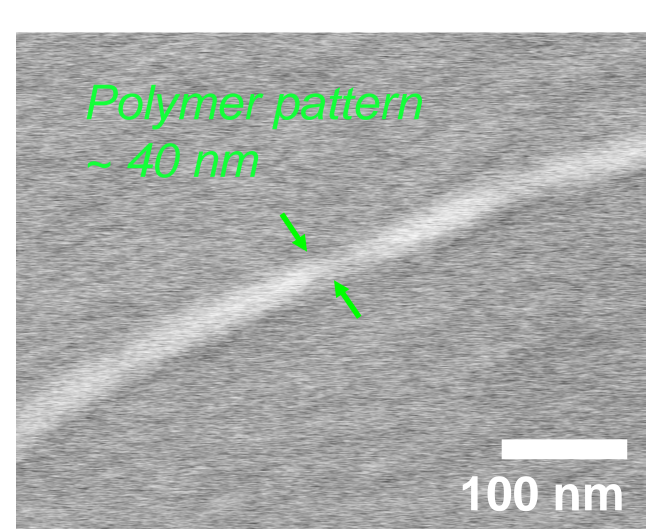
(Etching time: 40 s)



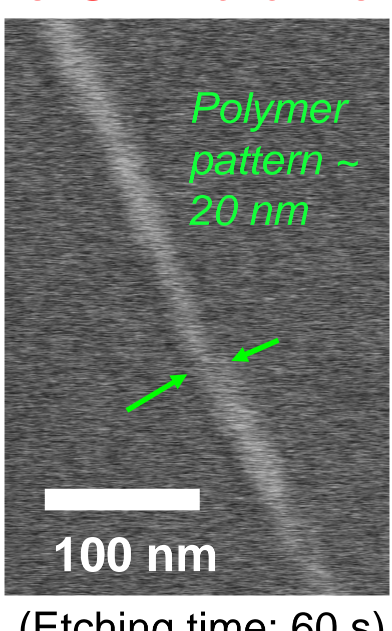
(Etching time: 30 s)



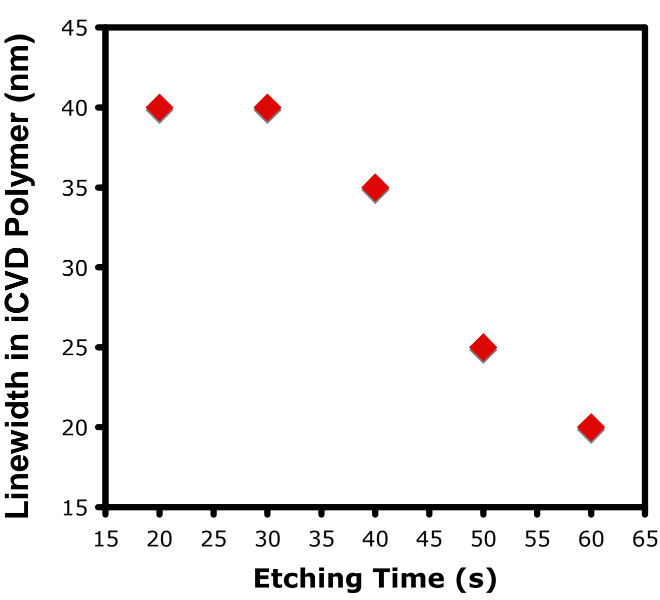
Pattern sizes depend on the CNT diameters and the etching time



(Etching time: 60 s)

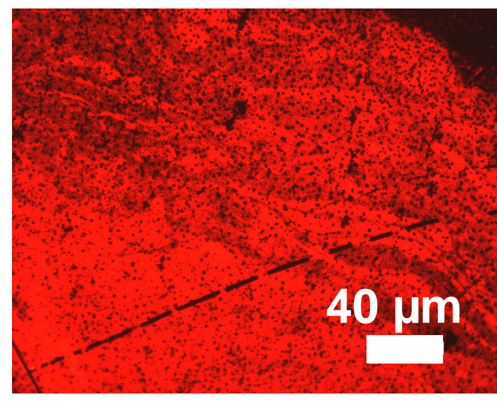


(Etching time: 60 s)

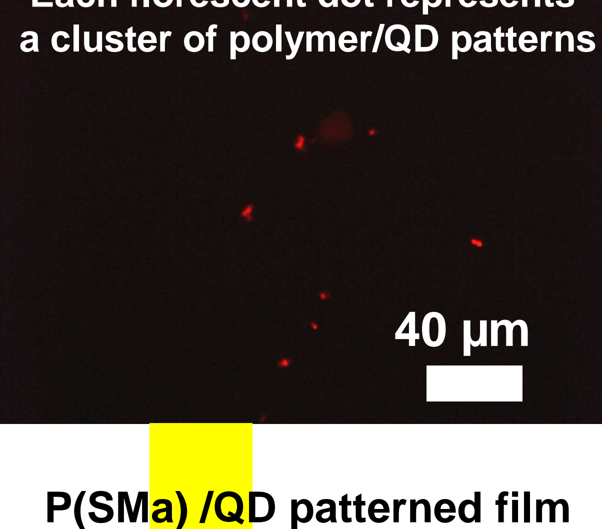


Fluorescence Microscope

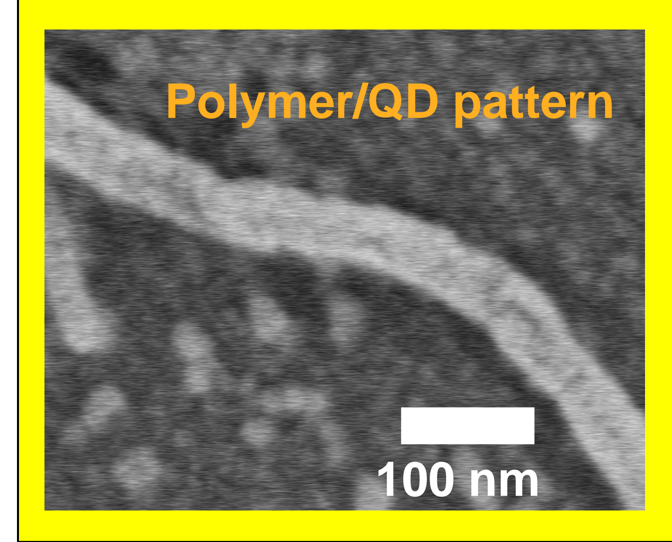
P(SMa) iCVD polymer film



P(SMa) /QD blanket film

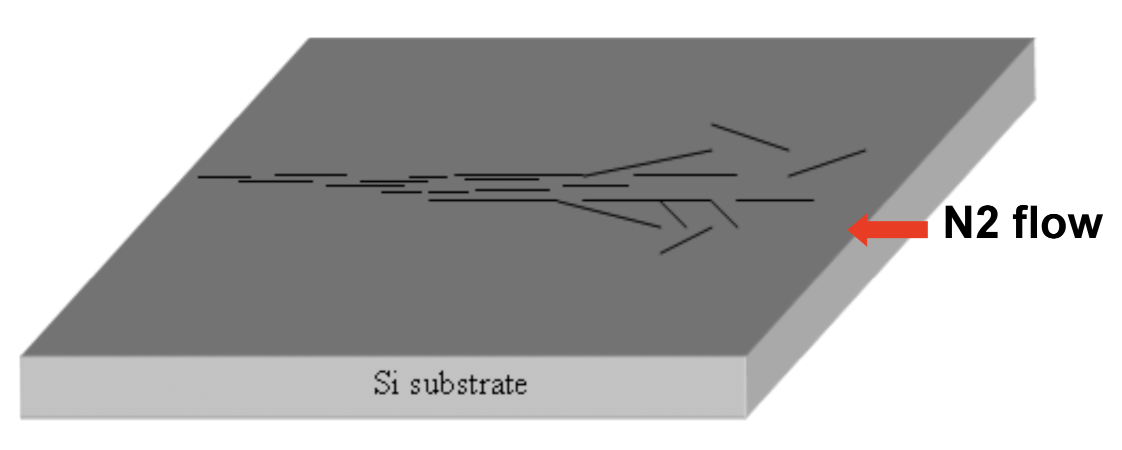


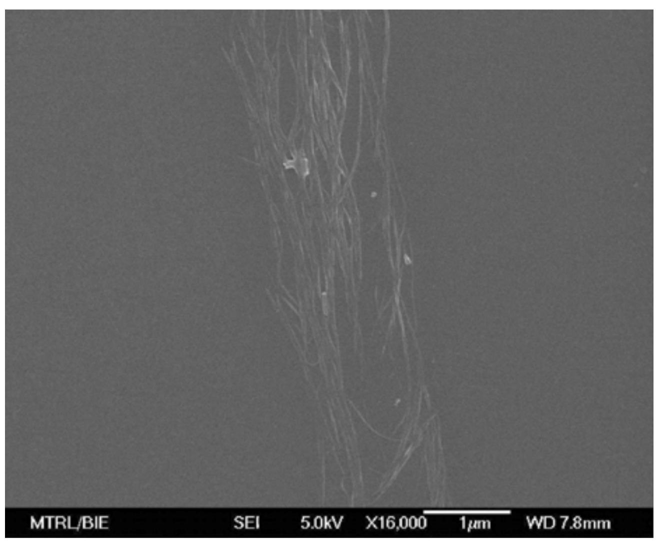
P(SMa) /QD patterned film



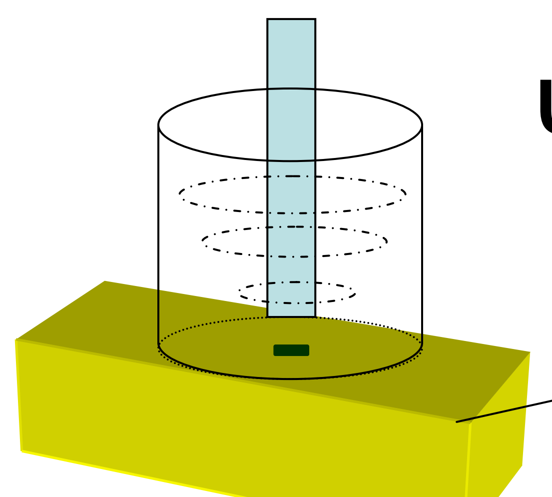
SEM images of polymer/QD pattern

Carbon Nanotube (CNT) Alignment





S Li et al, Nanotechnology 18 (2007) 455302



Using vortex to create flow field to align CNTs

magnetic stirring apparatus

Future Plans

Next Year Plans

- Optimize the incorporation of the monodisperse and functionalized quantum dots in collaboration with Prof. Muscat's group
- Use functional iCVD polymers to align the carbon nanotubes
- Fabricate simple quantum dot devices using the novel patterning strategies

Long-Term Plans

- Demonstrate the performance of high resolution devices on flexible, low cost, light weight substrates.

Publications, Presentations, and Recognitions/Awards

PUBLICATIONS

- W.E. Tenhaeff, K.K. Gleason, Initiated Chemical Vapor Deposition of Alternating Copolymers of Styrene and Maleic Anhydride, Langmuir 23(12), 6624-6630 (2007).
- Wyatt E. Tenhaeff and Karen K. Gleason, Initiated chemical vapor deposition of perfectly alternating poly(styrene-alt-maleic anhydride),Surface And Coatings Technology 201,9417-9421 (2007)

PRESENTATIONS

- K.K. Gleason, Polymeric Nanocoatings by Chemical Vapor Deposition, Pall Corporation, 2/6/2007
- K.K. Gleason, Design of CVD processes for low k dielectrics and air gap formation, 2007 MRS Spring Meeting:Symp. B, San Francisco, CA 4/11/2007 (invited)
- K.K. Gleason, Initiated chemical vapor deposition (iCVD) of polymeric nanocoatings, 16th European Conference on Chemical Vapor Deposition, Den Haag, Netherlands, 9/20/2007 (invited).
- W. Tenhaeff and K.K. Gleason, Initiated chemical vapor deposition of perfectly alternating Poly(styrene-alt-maleic anhydride), 16th European Conference on Chemical Vapor Deposition, Den Haag, Netherlands, 9/20/2007
- K.K. Gleason, Chemical Vapor Deposition of Polymeric Nanocoatings, U. Calgary, Dept. Chemical Engineering, 10/5/2007 (invited).
- K.K. Gleason, Conformal Polymeric Thin Films via Initiated Chemical Vapor Deposition, AVS Seattle, WA, 10/15/2007 (invited)
- K.K. Gleason, Engineering Polymeric Nanocoatings by Vapor Deposition 31th Annual Symposium of the Macromolecular Science and Engineering Program at the University of Michigan., Ann Arbor, MI, 10/25/2007 (invited).
- W.E. Tenhaeff and K.K. Gleason, Initiated Chemical Vapor Deposition of Functional Thin Hydrogel Films to Incorporate Quantum Dots, MRS Fall Conference, Boston, MA, 11/30/2007

Students on Task 425.017

- Current Students and Anticipated Grad Date
  - Chia-Hua Lee, PhD expected 5/11
  - Wyatt Tenhaeff, Ph.D expected 5/09

Low Environmental Impact Processing of sub-50 nm Interconnect Structures

(*Task Number: 425.019)*

PIs:

- **Anthony Muscat, Chemical and Environmental Engineering, UA**
- **Masud Mansuripur, College of Optical Sciences, UA (added 2008)**

Other Researchers:

- **Zhengtao Deng, Postdoctoral Fellow, ChEE & Optical Sciences, UA**

Cost Share (other than core ERC funding):

- **$85k from Arizona TRIF**

Objectives

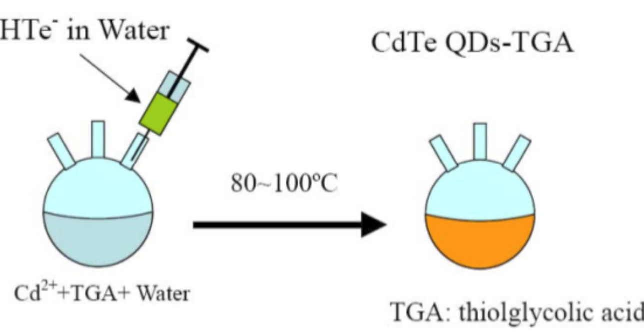
- Reduce the power required for switching and to transmit signals on a chip and between chips by using light
- Reduce the water, energy, and materials required to fabricate interconnect wiring
- Use clusters of crystalline semiconductors (quantum dots) to build interconnect structures
  - Inherently small 1-5 nm q-dots ⇒ scaling
  - Tunable band gap and photosensitivity ⇒ optical switching or signal transmission
- Develop processes to
  - (1) grow crystalline quantum dots in water and in a gas phase
  - (2) pattern quantum dots on surfaces and thin films with alternative lithographic processes
  - (3) use materials that have low ESH impact

ESH Metrics and Impact

Sustainability Metrics		
Attribute	Si wafer	QD on plastic
Cost per cm^2	$50-120	< $100
Energy used per cm^2 in fabrication	>1KWh	<1KWh
Flexible?	No	Yes
Processing	batch Si Si substrate	batch or semi-continuous (roll to roll)
Optical	not directly	yes
Lithography	traditional/e-beam	hierarchical assembly of carbon nanotubes

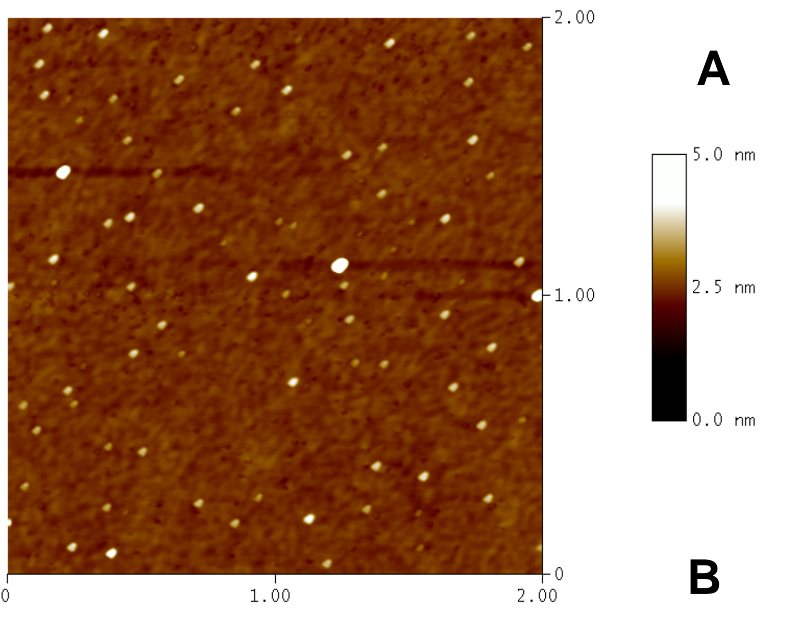
Methods and Approach

- **Develop fast, simple, reproducible, cost-efficient, and environmentally friendly routes to fabricate highly luminescent quantum dots with tunable photoluminescence (PL) peaks**

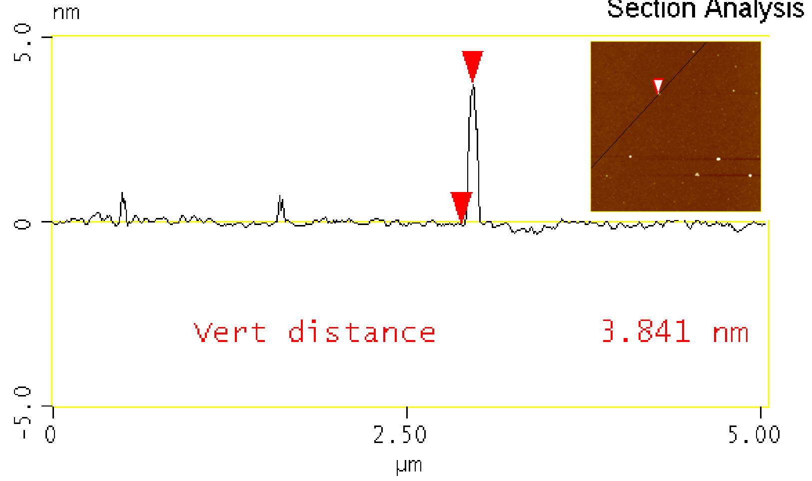


- **Water based and gas phase synthesis routes that are scaleable to commercial applications**
- **Deposit on Si and dielectric surfaces by tuning ligand**
  - **Thiol ligands with different chain lengths and chemistries**
- **Validate properties of quantum dots in solution and on surfaces**
  - **Bleaching**
  - **Fluorescence intensity intermittency (blinking) and frequency shift**

AFM of QDs Deposited on Si Surface

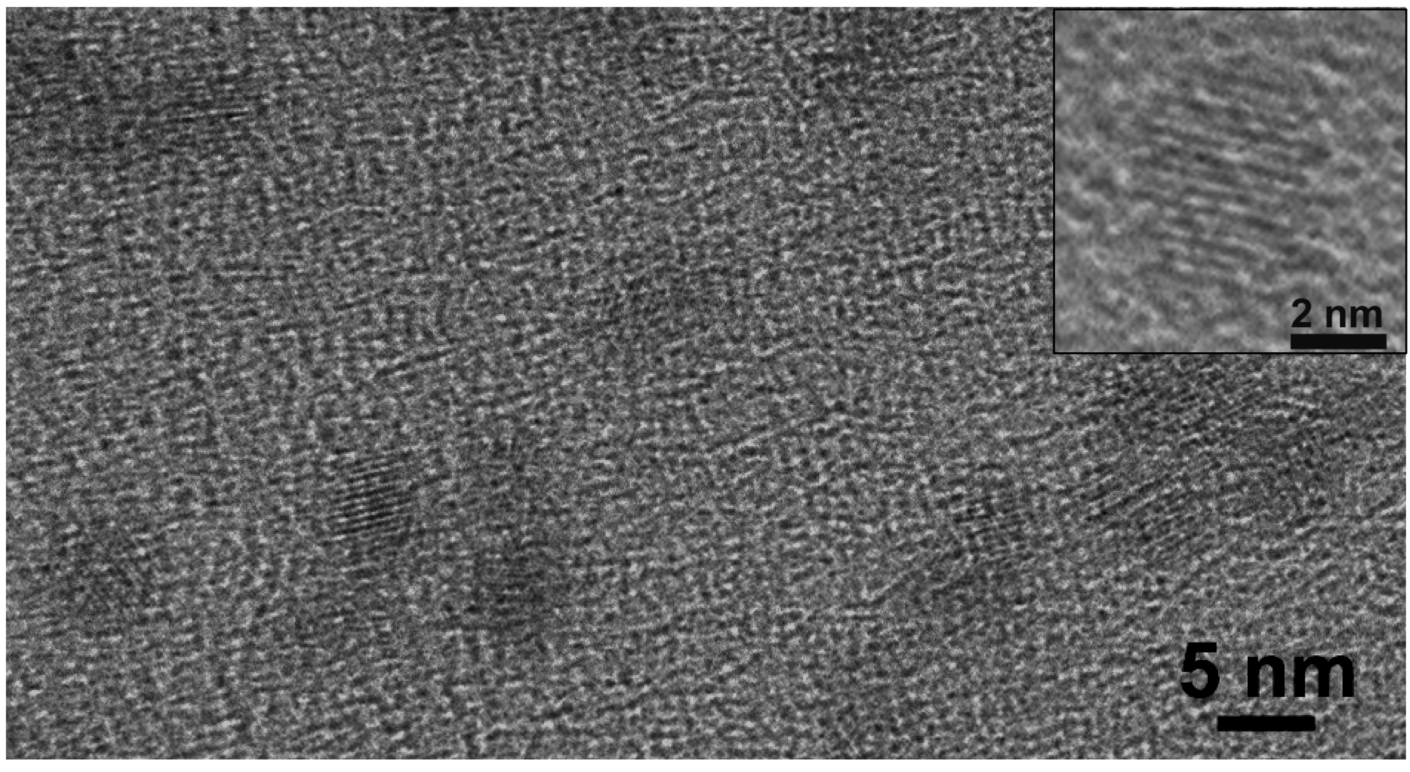


A AFM topography image of TGA-capped quantum dots with maximum emission at 590 nm on hydrophilic silicon wafer substrate



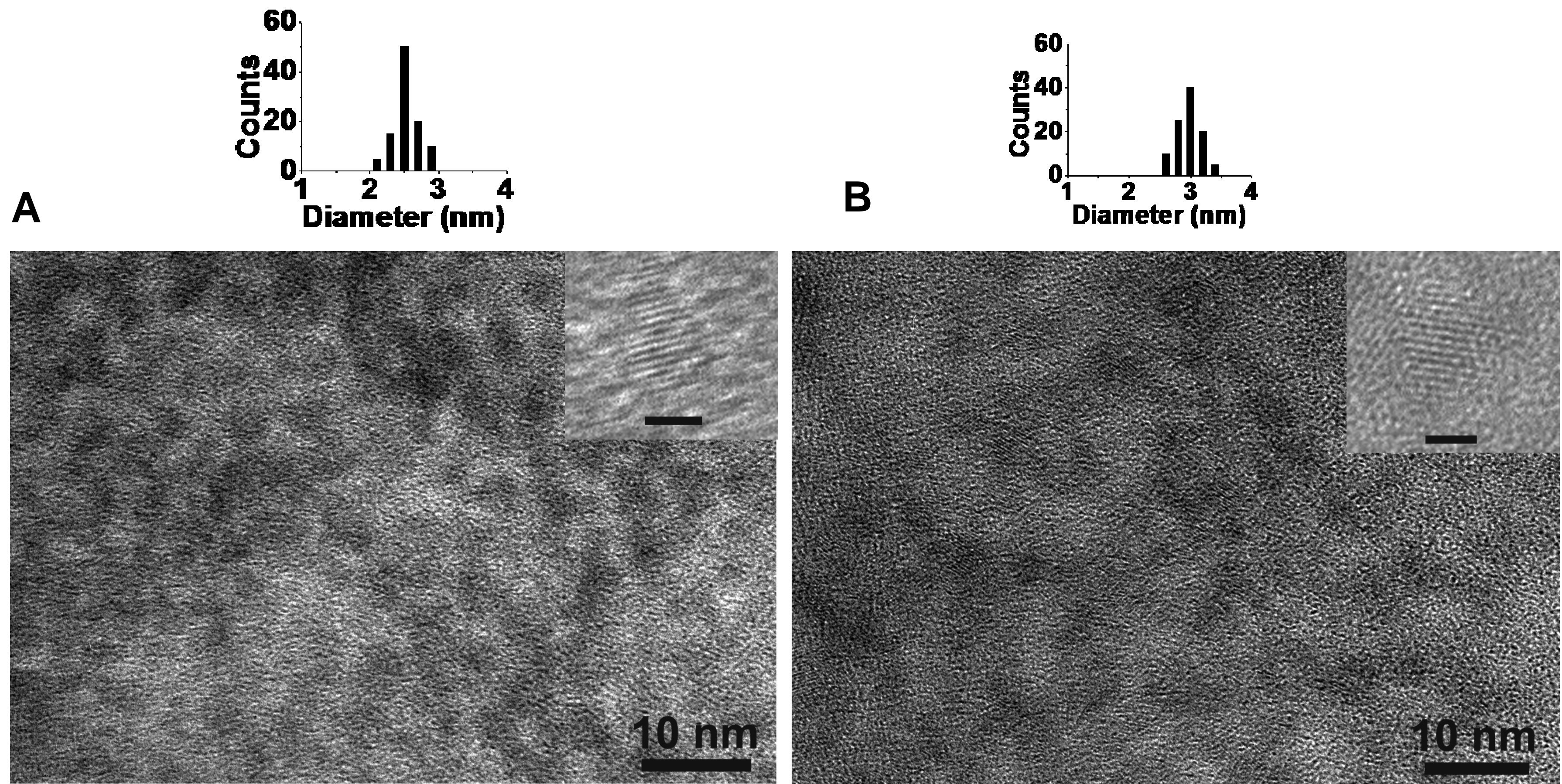
B Height profile of AFM line scan in the image shown in the inset. Red arrows define dimensions of one typical quantum dot with a diameter close to 3.8 nm.

TEM study of CdTe QDs



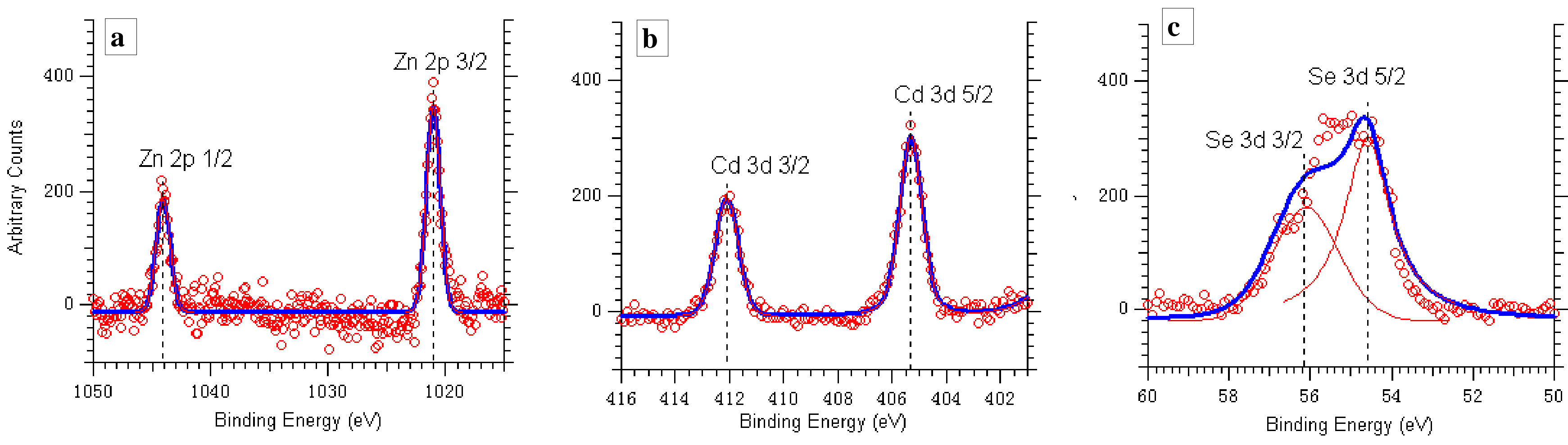
Transmission electron microscopy image of thiolglycolic acid capped CdTe quantum dots deposited on TEM grid

TEM study of ZnSe and $Zn_xCd_{1-x}Se$ QDs



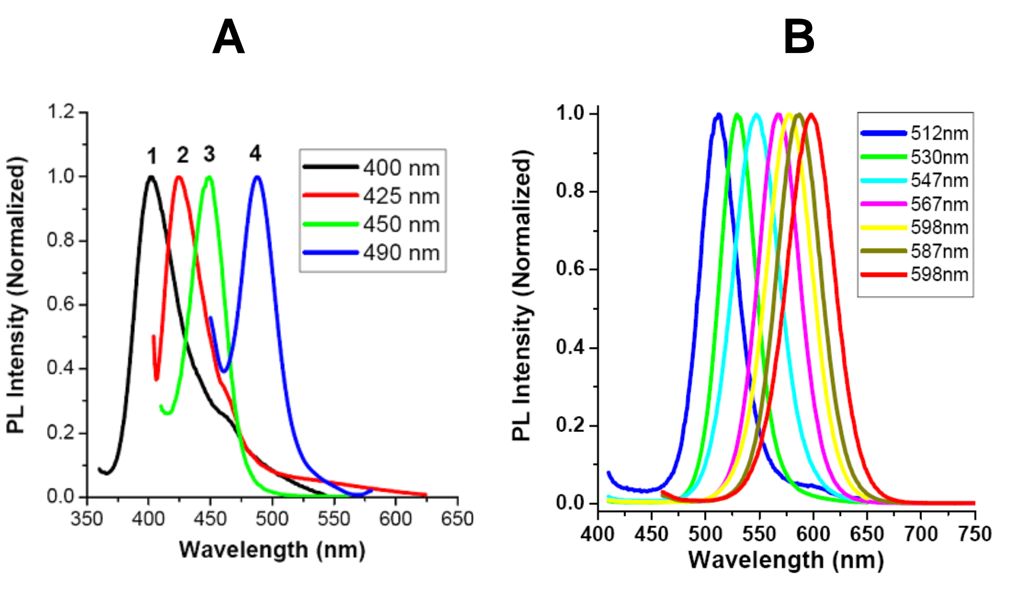
TEM images of TGA-capped ZnSe (A) and $Zn_xCd_{1-x}Se$ QDs samples (B). Inset is the enlarged images of single QDs, scale bar 2 nm.

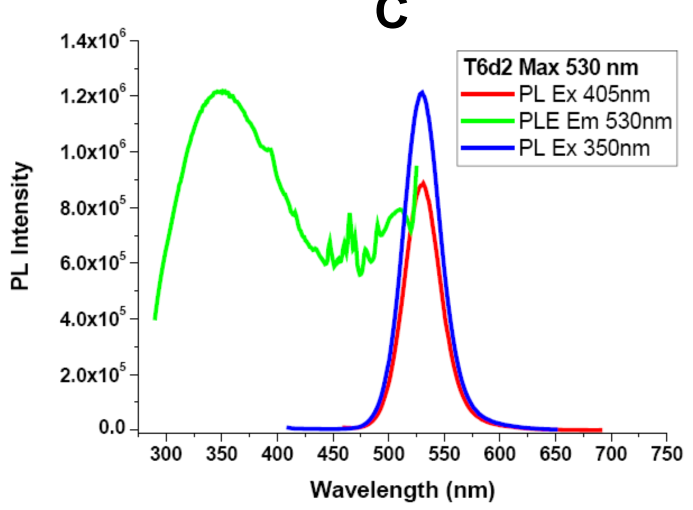
XPS study of $Zn_xCd_{1-x}Se$ QDs



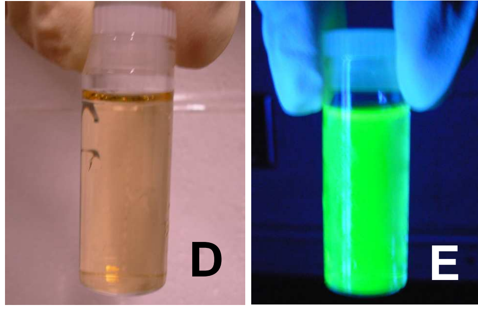
High-resolution x-ray photoelectron spectra of $Zn_xCd_{1-x}Se$ QDs samples with near bandgap emission peak at 490 nm: (a) Zn 2p3/2 and Zn 2p1/2 spectral lines; (b) Cd 3d3/2 and Cd 3d5/2 spectral lines; (c) Se 3d5/2 and Se 3d3/2 spectral lines.

Optical Properties



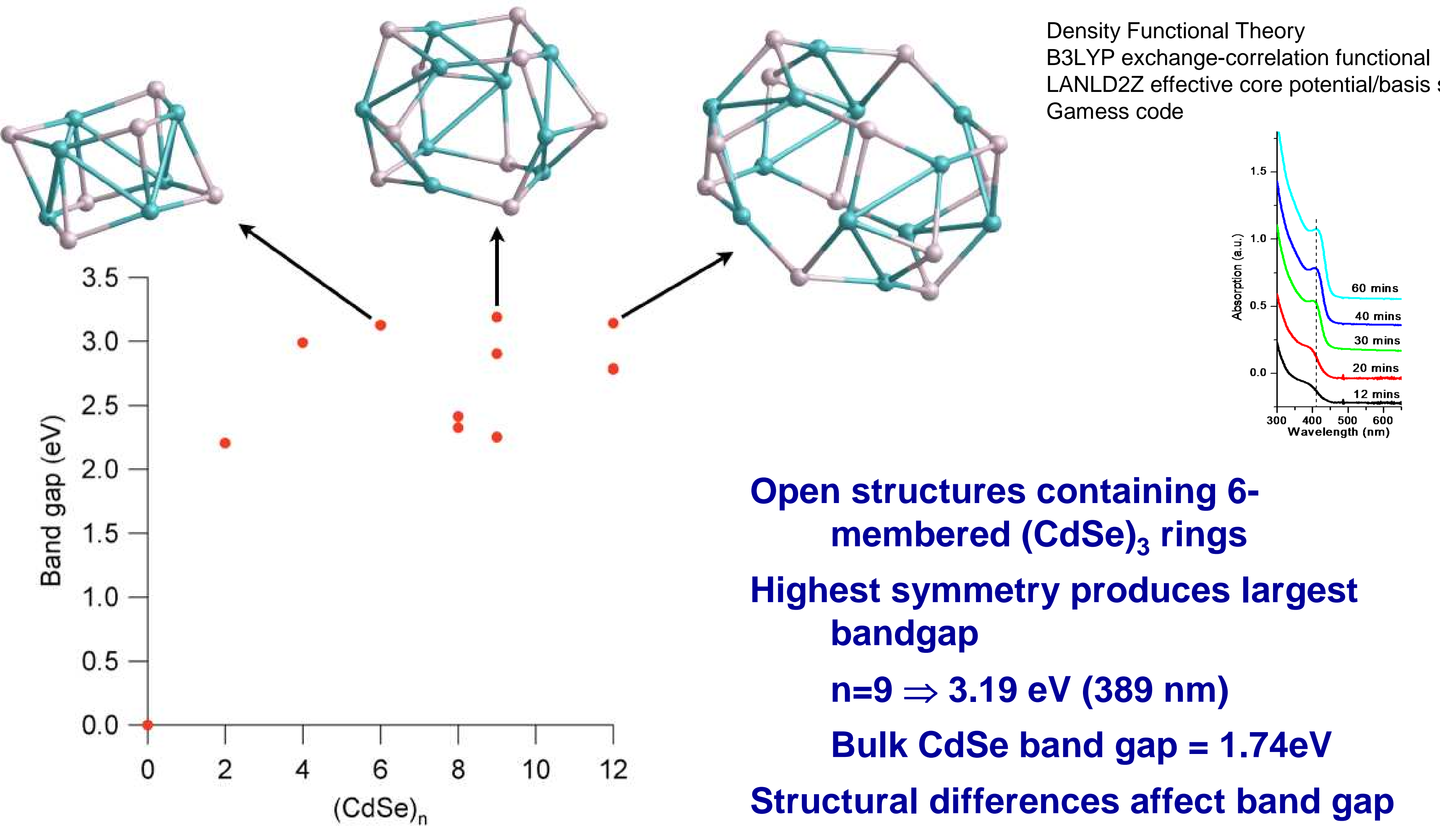


A photoluminescence (PL) spectra of a series of thiolglycolic acid capped $Zn_xCd_{1-x}Se$ QD samples
B PL spectra of a series of thiolglycolic acid capped CdTe QD samples
C PL and PLE spectra of one typical thiolglycolic acid capped CdTe QD samples



Pictures of typical TGA-capped CdTe QDs samples under
D room light
E 365 nm UV light

Band Gap of QD Clusters Computed by Molecular Modeling



Density Functional Theory
B3LYP exchange-correlation functional
LANLD2Z effective core potential/basis set
Gamess code

Open structures containing 6-membered $(CdSe)_3$ rings

Highest symmetry produces largest bandgap

n=9 ⇒ 3.19 eV (389 nm)

Bulk CdSe band gap = 1.74eV

Structural differences affect band gap

Future Plans

Next Year Plans

- Investigate replacing the reproductive toxin Cd with Cu or Mn
- Model q-dot structure and properties with computational chemistry
- Deposit q-dots on semiconductor and dielectric surfaces by varying ligand chemistry
- Define prototype devices
- Assess costs of introducing new processing technology

Long-Term Plans

- Work with Prof. Karen Gleason's group at MIT to selectively deposit q-dots on surfaces patterned using iCVD
- Build a prototype device based on q-dots

Students on Task 425.019

- **Current students and anticipated grad date**
  - **Rachel Morrish, December 2009**

ESH Assessment : Materials, Structures and Processes for Nano-Scale MOSFETs with High-Mobility Channel

(*Task Number: 425.023)*

PIs: Paul C. McIntyre, Krishna C. Saraswat, Yoshio Nishi

Eunji Kim, Joseph P. T. Chen, Byungha Shin

Stanford University

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Objectives

- III-V based MOSFETs are of great interest for their high effective carrier mobilities and low supply voltage.
- Achieving a native oxide-free semiconductor surface prior to high-k dielectric deposition is the key for fabrication of high-performance III-V-based MOSFETs.
- A chemically-stable passivation of the III-V substrate surface allows wafers to be queued during manufacturing and reduces the need for subsequent surface cleans, which holds advantages of reducing As-containing effluents from III-V surface cleans.
- As a way of improving interfacial properties, post-deposition anneals may result in "self-cleaning" of the III-V surface by the high-k film, avoiding cleaning steps prior to high-k deposition. This has the potential to save on water usage and reduce chemical usage and hazardous effluents resulting from wet cleaning of the III-V surface.

ESH Metrics and Impact

Native oxide removal process

HCl-etching

$As_2O_3 + 6HCl \rightarrow 2AsCl_3 + 3H_2O$

$As_2O_5 + 10HCl \rightarrow 2AsCl_5 + 5H_2O$

$Ga_2O_3 + 6HCl \rightarrow 2GaCl_3 + 3H_2O$

Toxic or harmful effluents :

$AsCl_3$, $AsCl_5$, $GaCl_3$

HfO_2 deposition

Atomic layer deposition

TDEAH, water, 150 ^{o}C

- **Low thermal budget**
- **Relatively lower vacuum**

➢ **Lower energy cost compared to other deposition methods (e.g. MBE)**

S-passivation

$(NH_4)_2S$ solution

Hardly produce any As-containing effluents

Disposal as hazardous waste

- **S-passivation reduces emission of As-containing effluents by reducing the need for subsequent surface cleans**

Post-deposition anneal

Rapid thermal anneal

N_2, 650 ^{o}C

- **High temperature process**
- **No need of chemical cleans**

➢ **Reduction in emission of ESH-problematic effluents and in the use of chemicals**

Part I : ESH Assessment : Materials, Structures and Processes for Nano-Scale MOSFETs with High-Mobility Channel I
(*Task Number: 425.023*)

PIs:

- **Paul C. McIntyre, Materials Science and Engineering, Stanford**
- **Krishna C. Saraswat, Electrical Engineering, Stanford**

Graduate Students:

- **Eunji Kim : PhD candidate, Materials Science and Engineering, Stanford**

Undergraduate Students:

Other Researchers:

- **Byungha Shin : Postdoctoral Fellow, Materials Science and Engineering, Stanford**

Cost Share (other than core ERC funding):

- **$ 60K (gift) from Intel Corp.**
- **$ 150K from SRC Non-classical CMOS research center**

ALD-HfO_2/GaAs: Procedures

High Temp. Anneal Study

Epitaxial Be-doped GaAs ($1\sim5*10^{17}cm^{-3}$)

Atomic Layer Deposition of HfO_2

TDEAH, water, 150 ^oC

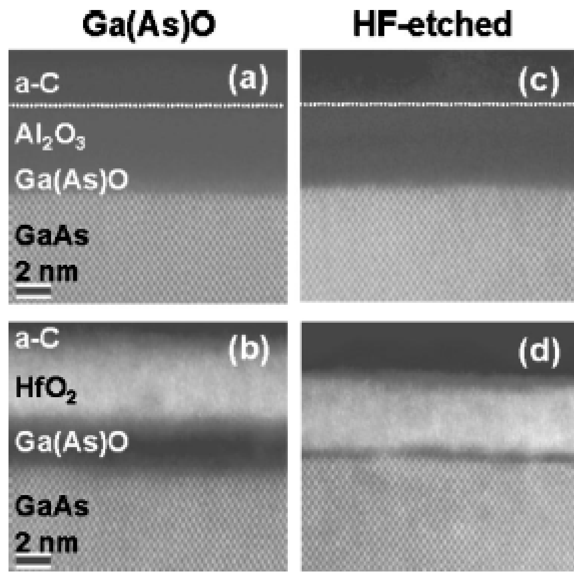
Post Deposition Anneal

N_2, 650 ^oC, 3 min

Pt gate electrode deposited by e-beam evaporation through shadow-mask

SIMS, XPS, MOSCAP Testing

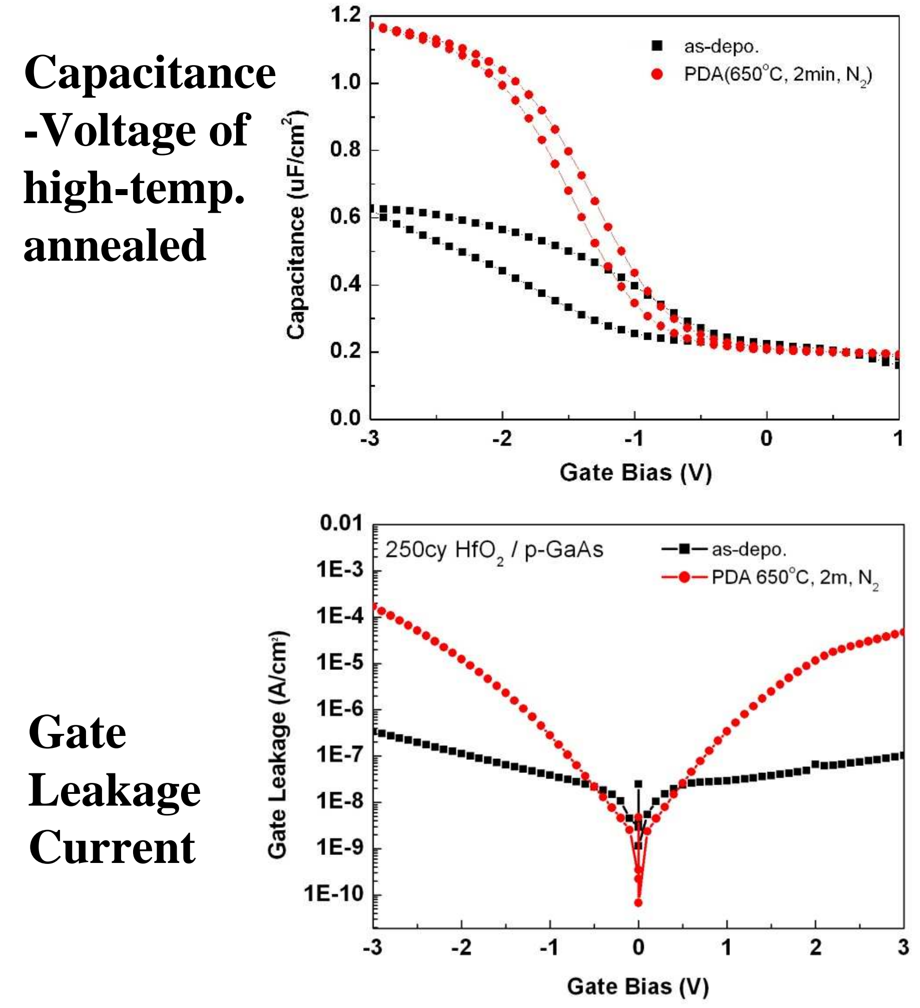
Highlight of Results : High Temp. Anneal



M.M. Frank et al., APL 86, 152904 (2005).

Capacitance -Voltage of high-temp. annealed

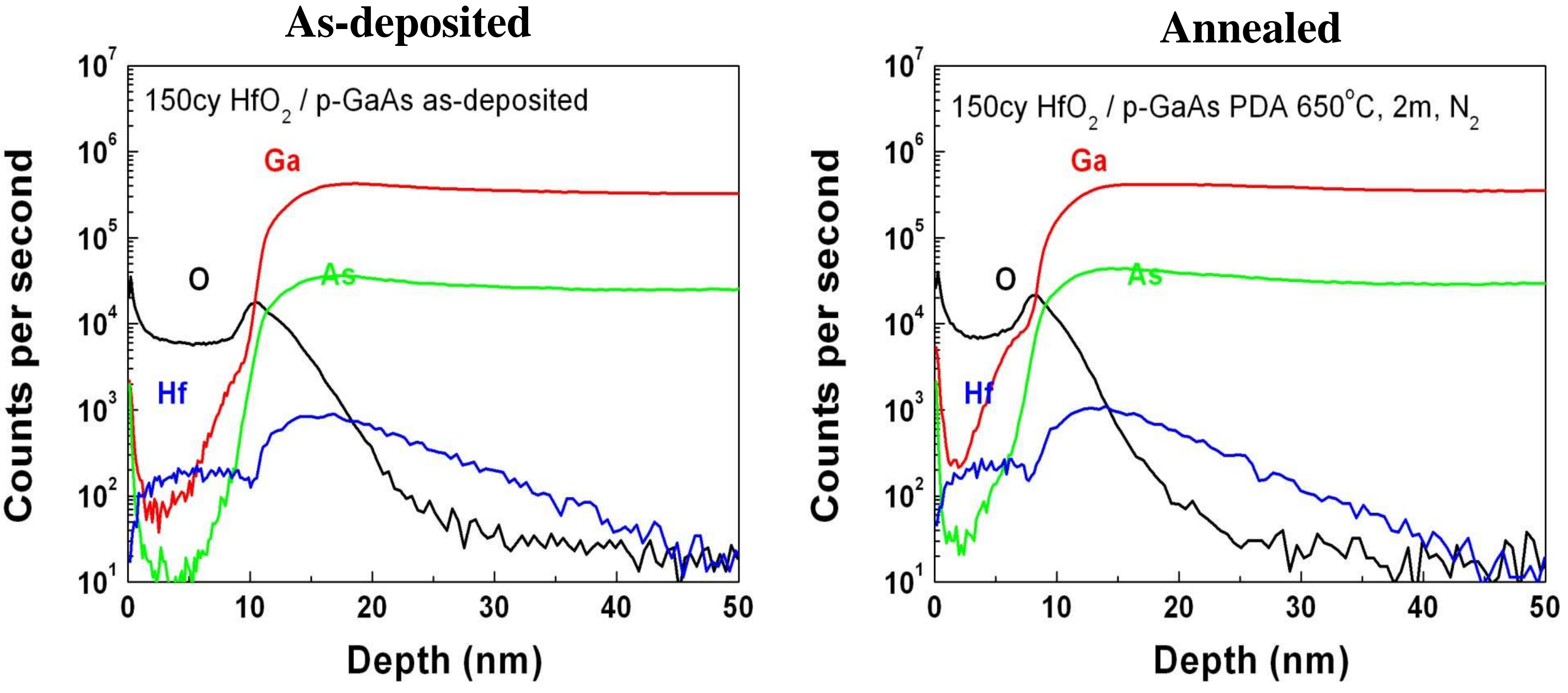
Gate Leakage Current



- Post-ALD anneals at 480 - 650°C were found to produce desorption of arsenic and gallium oxides through the high-k film, improving device performance.

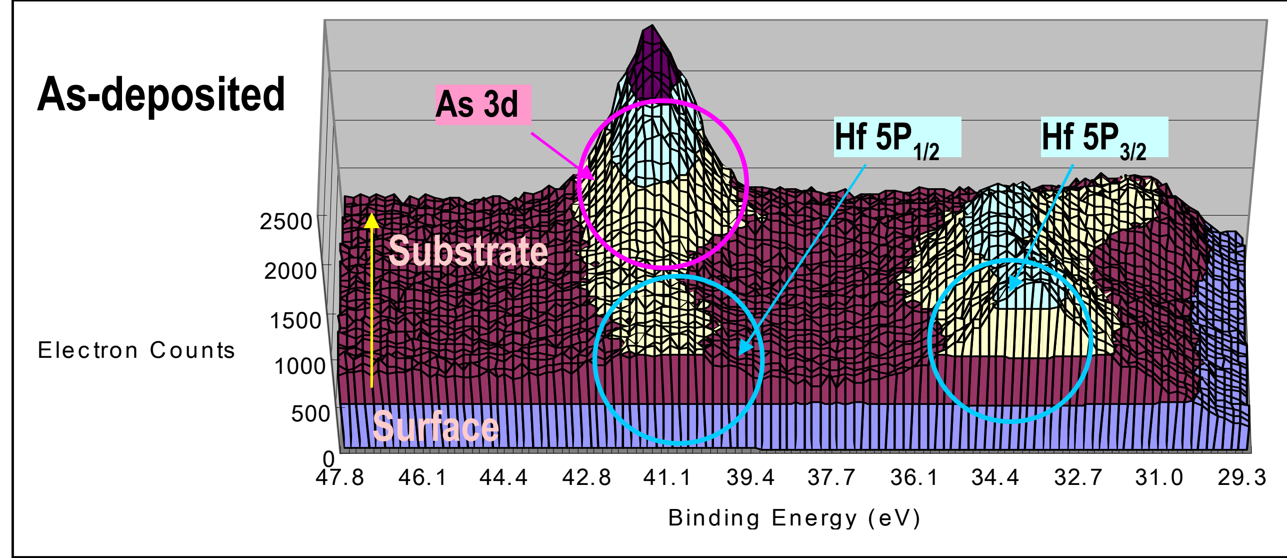
- Improved C-V characteristics, high gate leakage current consistent w/ reduced EOT.

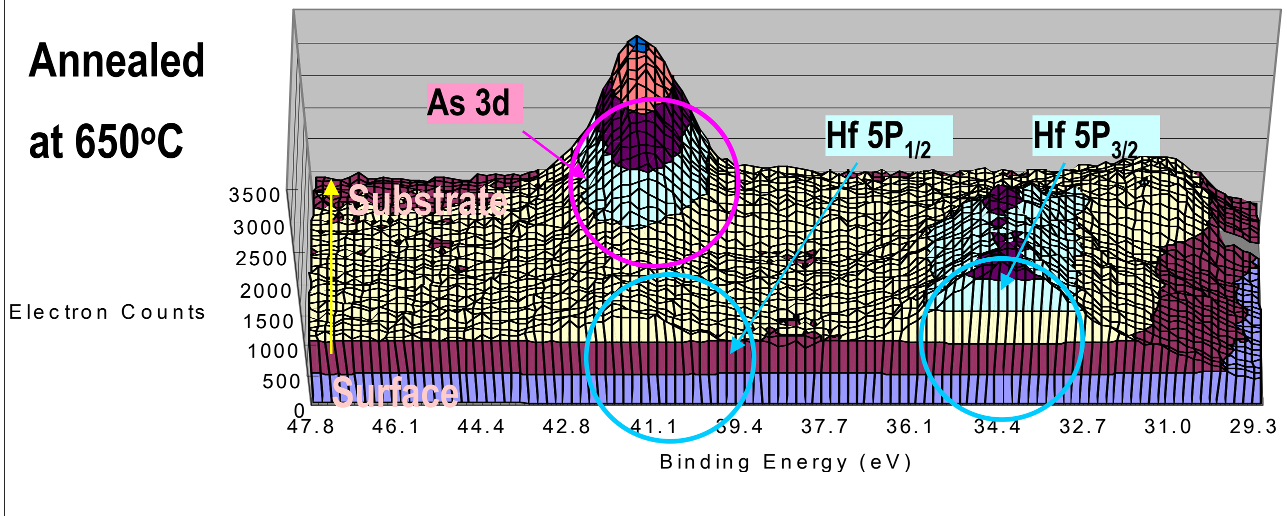
Highlight of Results: High Temp. Anneal



- SIMS data suggest that there may be Ga diffusion into the HfO_2 layer after the 650°C anneal; further work is needed to confirm.
- Evidence for As diffusion is not obvious.
- Apparent concentration tail for Hf in GaAs is likely a SIMS artifact.

Highlight of Results: High Temp. Anneal





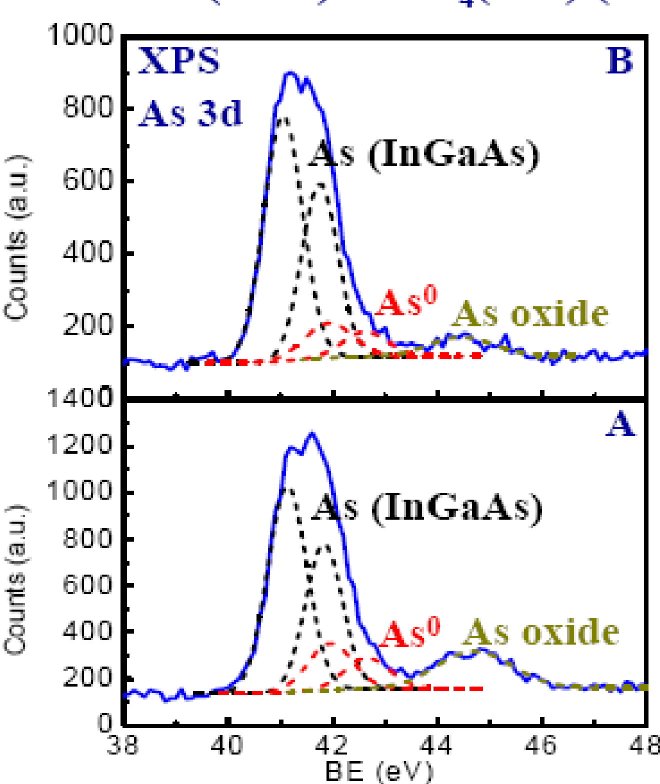
XPS depth profiling

(150cy HfO_2 on p-GaAs)

- **No evidence of oxide features for As within the HfO_2 layer in the expected binding energy range of 44.9~46.2eV (As oxides)**

InGaAs: Native oxide removal, wet-etching

- Preparation of clean native oxide free $In_{0.2}Ga_{0.8}As$ surface for subsequent high *k* film deposition: wet-etching and pre-ALD anneal
- Choice of wet etchant? A: HCl (30%), B: HCl (30%) + $NH_4(OH)$ (4%), C: HCl (30%) + $NH_4(OH)$ (30%), D: $NH_4(OH)$ (30%)



Compositional analysis by XPS

	In oxide*	Ga oxide**	As^0	As oxide
A	1.26	0	5.62	4.96
B	2.39	0	2.66	1.68
C	2.56	0	2.57	3.73
D	2.49	0	2.02	4.91

* Most likely In-hydroxide

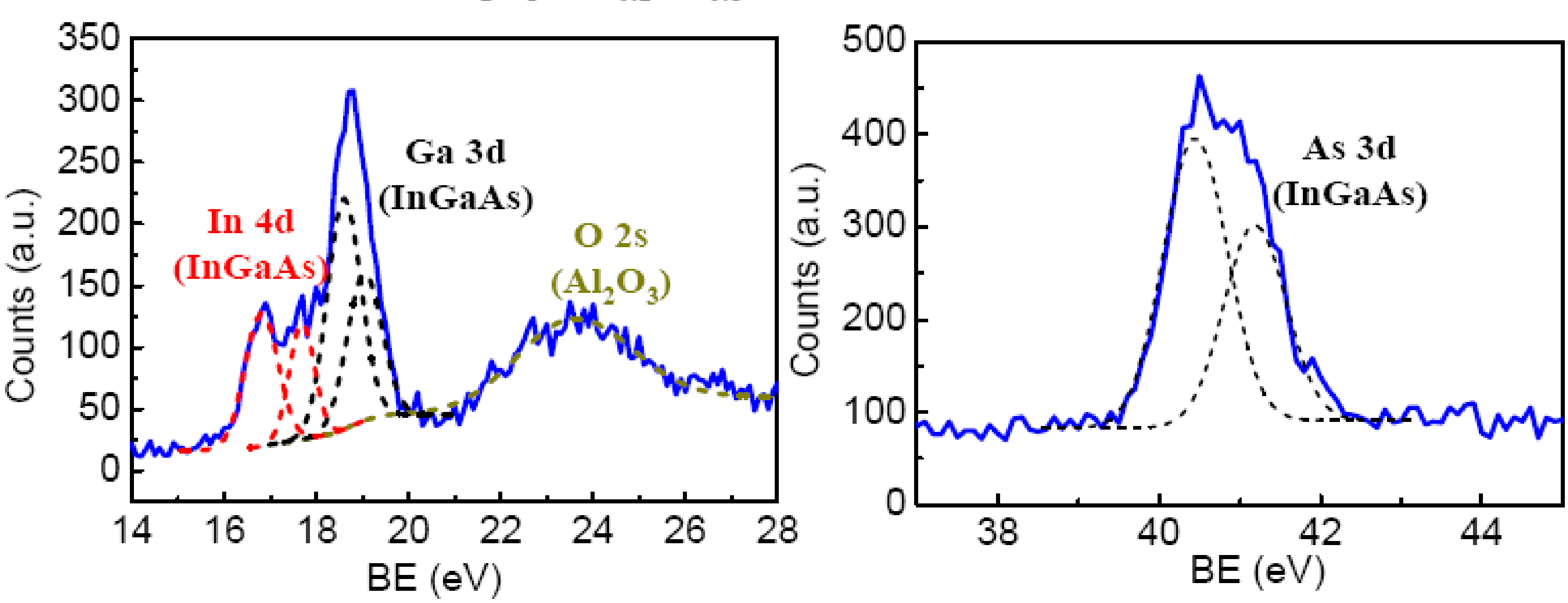
** From Ga 3p spectra (BE ~105eV), Ga oxide seen in Ga 2p spectra (BE ~1167eV)

=> existence of very thin surface Ga oxide layer

Ultrathin Al_2O_3 on wet-etched $In_{0.2}Ga_{0.8}As$

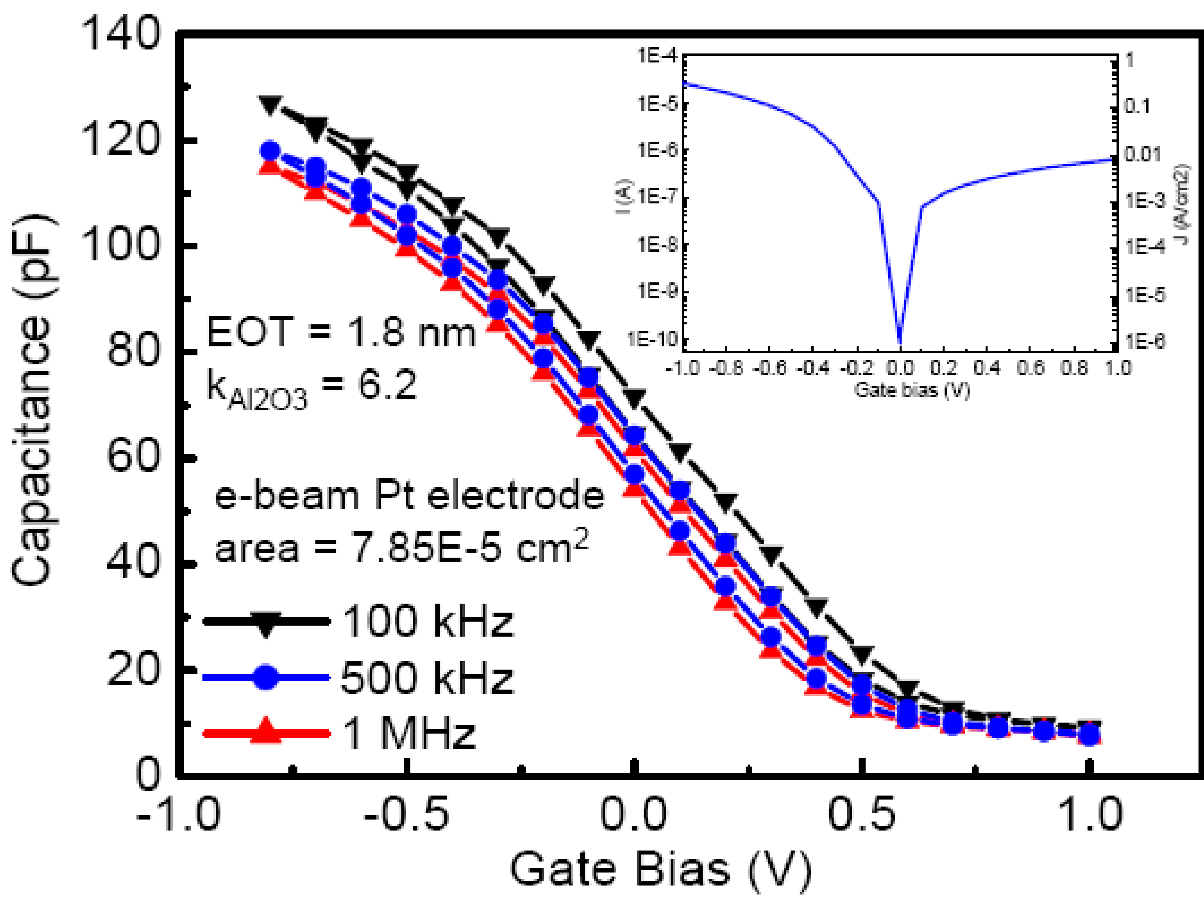
- Chemical removal of native oxides by HCl and $NH_4(OH)$
- Pre-ALD anneal at 360 °C for thermal desorption of remaining oxides
- ALD-Al_2O_3 : 30 cycles (2.8 nm) at 310 °C

XPS on 2.8 nm Al_2O_3 / $In_{0.2}Ga_{0.8}As$: confirmation of no In-, Ga-, As- oxide



Ultrathin Al_2O_3 on wet-etched $In_{0.2}Ga_{0.8}As$

- **Demonstration of scaling down EOT to 1.8 nm**



Part I: Conclusions

- **We have performed an assessment of ESH impact of chemistries used in this research.**

- **As a way of improving interfacial properties, we have demonstrated improved C-V characteristics of W/HfO_2/p-GaAs by post-deposition anneals (PDA).**

  [PDA may result in "self-cleaning" of the III-V surface by the high-k film, avoiding cleaning steps prior to high-k deposition. It could possibly save on water usage and reduce chemical usage and hazardous effluents resulting from wet cleaning of the III-V surface]

- **We have investigated pre-ALD wet cleaning and passivation of (100) InGaAs channels and have demonstrated ultrathin Al_2O_3 MOS capacitors with EOT < 2 nm and low CV hysteresis.**

Industrial Interactions and Technology Transfer

- **ALD-HfO_2 growth mechanism study in collaboration with Dr. Wilman Tsai (Intel) and Dr. David P. Brunco (Intel & IMEC)**
- **ALD-Al_2O_3/III-V interface engineering study in collaboration with Dr. Wilman Tsai (Intel) and Dr. Niti Goel (Intel & SEMATECH)**

Publications, Presentations, and Recognitions/Awards

- E. Kim, P-T. Chen, D. Choi, J. Harris, Y. Nishi, K. Saraswat, and P. McIntyre, "Atomic Layer Deposition of HfO_2 on III-V Semiconductors: Effects of Surface Treatment and Post-Deposition Anneals," TMS Electronic Materials Conference (EMC 2007), University of Notre Dame, IA, June 20-22, 2007. (oral presentation)

- E. Kim, J. Chen, D. Choi, N. Goel, C.O. Chui, W. Tsai, J. Harris, Y. Nishi, K. Saraswat and P.C. McIntyre "Electrical and Physical Characterization of ALD-Grown HfO_2 Gate Dielectrics on GaAs (100) Substates with Sulfur Passivation," Spring MRS Meeting, San Francisco, CA, April 9-13, 2007. (poster)

Future Plans

Next Year Plans

- Optimization of pre-ALD wet clean and vacuum anneal procedures for reduced charge-trapping in Al_2O_3/InGaAs gate stacks
- D_{it} measurements using MOSCAPs (low-T conductance) and MOSFETs (collaboration w/ UCSB)
- Comparison of electrical behavior and ESH trade-offs for wet-cleaned InGaAs channels vs. decapping of protective As layer prior to high-k ALD

Long-Term Plans

- Explore HfO_2/Al_2O_3 and TiO_2/Al_2O_3 bilayer gate insulators for thinner (~ 1 nm EOT) gate stacks on $In_{0.53}Ga_{0.47}As$ channels

Part II : ESH Assessment : Materials, Structures and Processes for Nano-Scale MOSFETs with High-Mobility Channel II

(*Task Number: 425.023)*

PIs:

- **Yoshio Nishi, Electrical Engineering, Stanford**

Graduate Students:

- **Joseph P. T. Chen : PhD candidate, Materials Science and Engineering, Stanford**

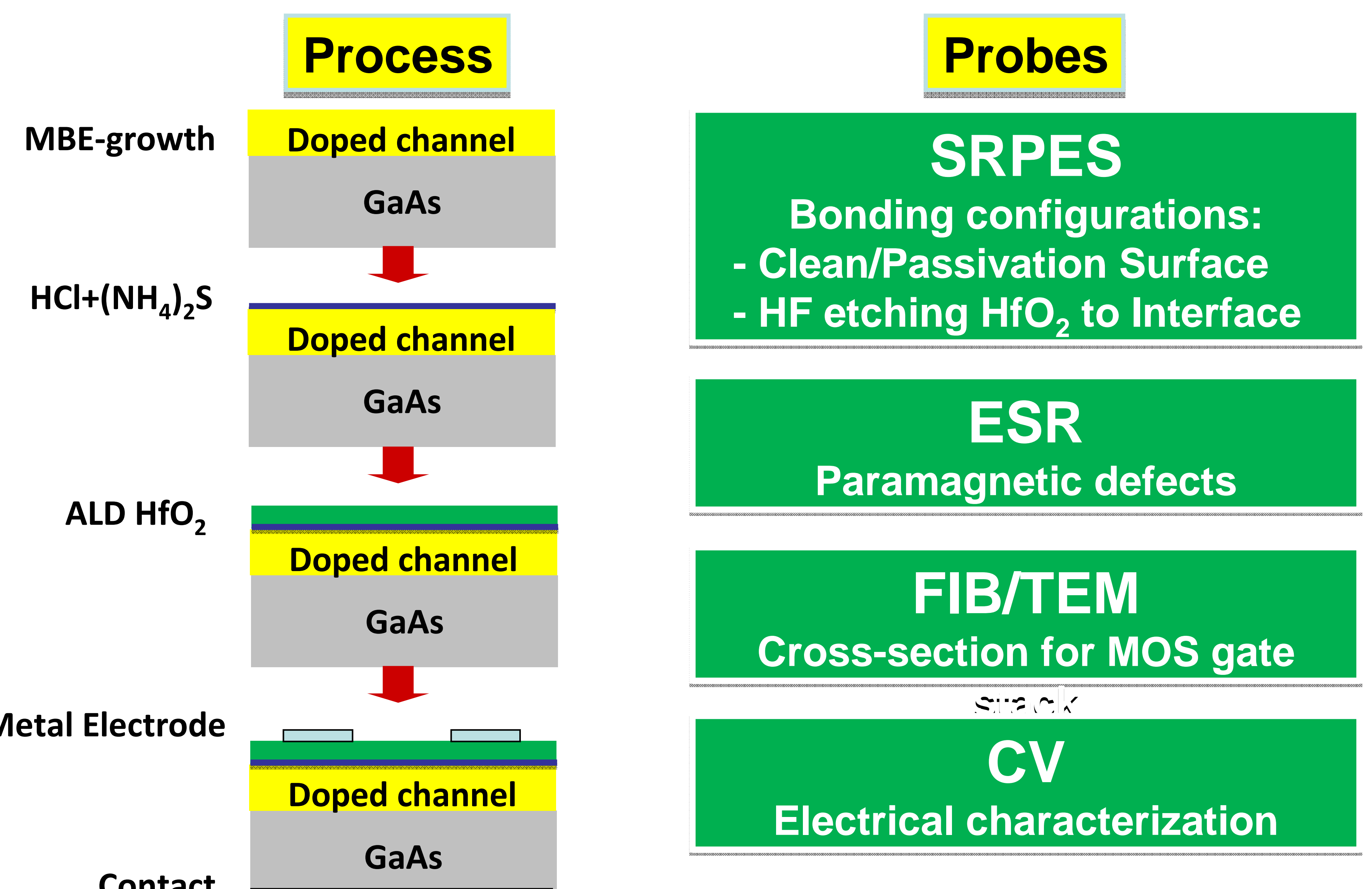
Undergraduate Students:

Other Researchers:

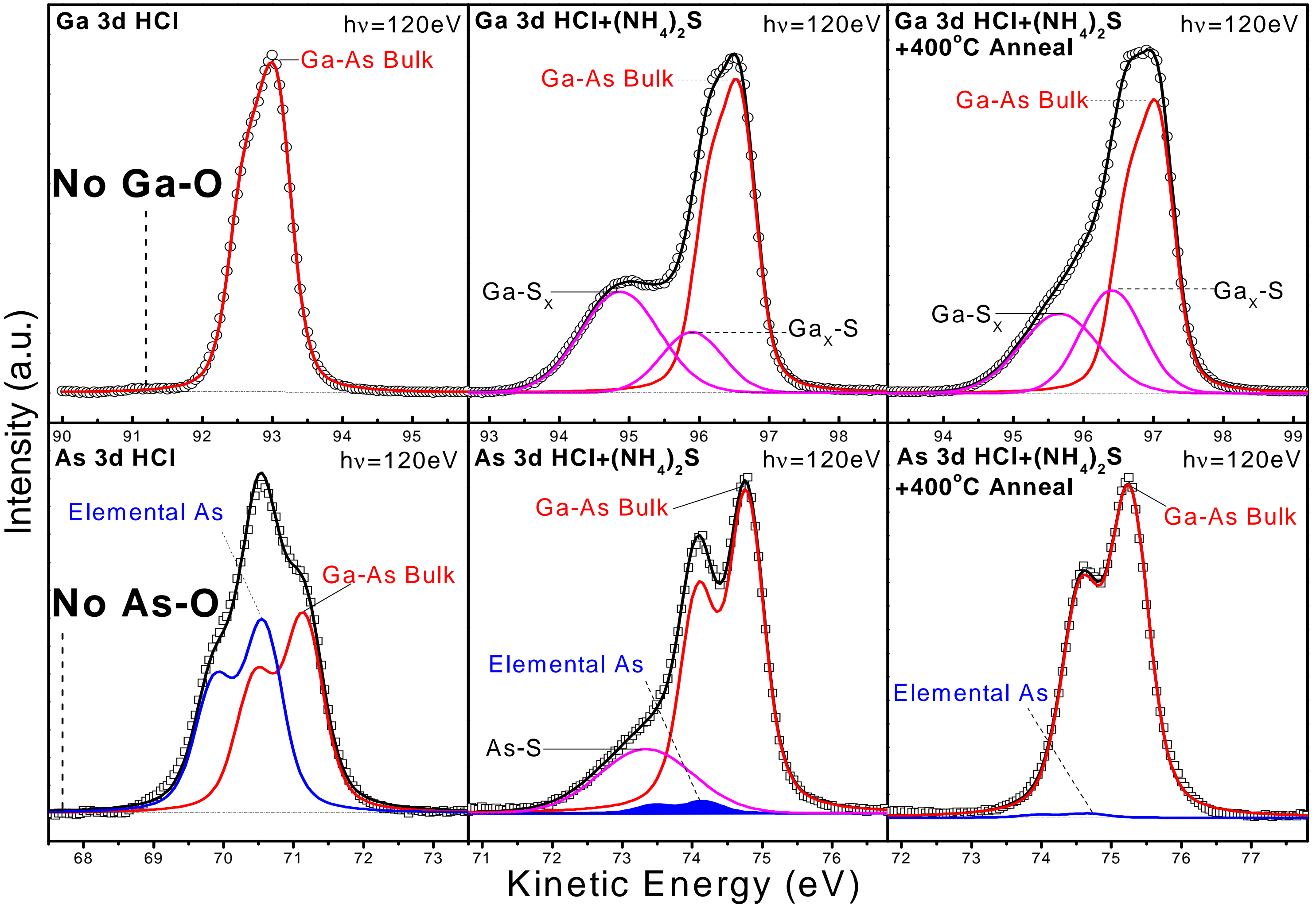
Cost Share (other than core ERC funding):

- **$ 50K (gift) from Intel Corp.**

Experiment

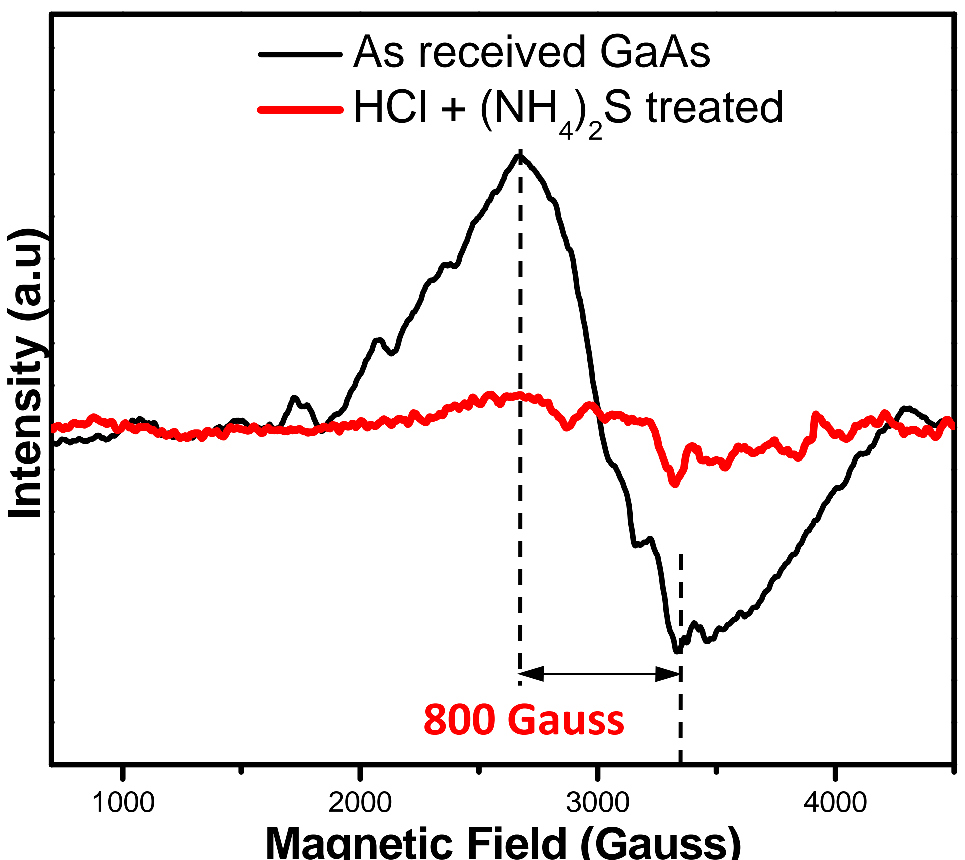


SRPES-GaAs Surface Bonding



HCl+$(NH_4)_2S$ Clean/Passivate GaAs; As-S thermal instability is a problem

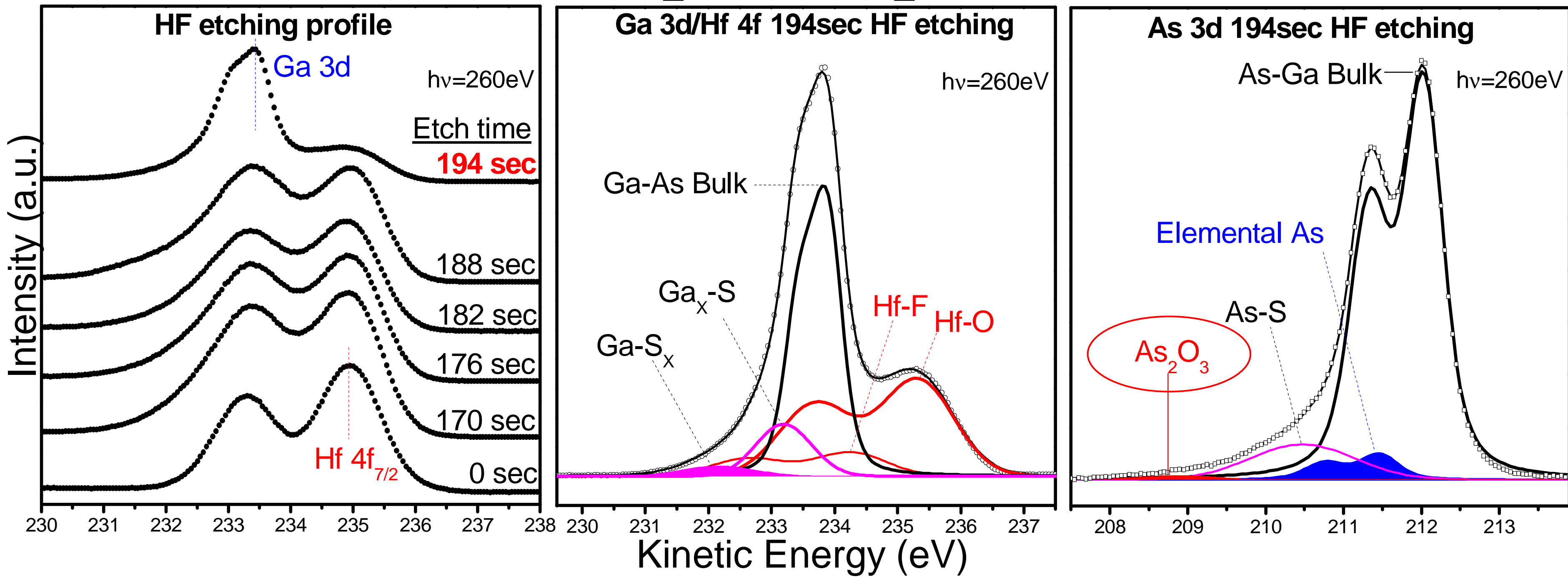
ESR-GaAs Paramagnetic Defects



- **HCl+($(NH_4)_2$S** **removes intrinsic paramagnetic defects on GaAs surface- from native oxides**
- **Very broad spectra**: B_{pp}^{G} **= 800 Gauss:**
  - Multiple signals overlap including isotropic defect signal

SRPES-HfO_2/S/GaAs Interface

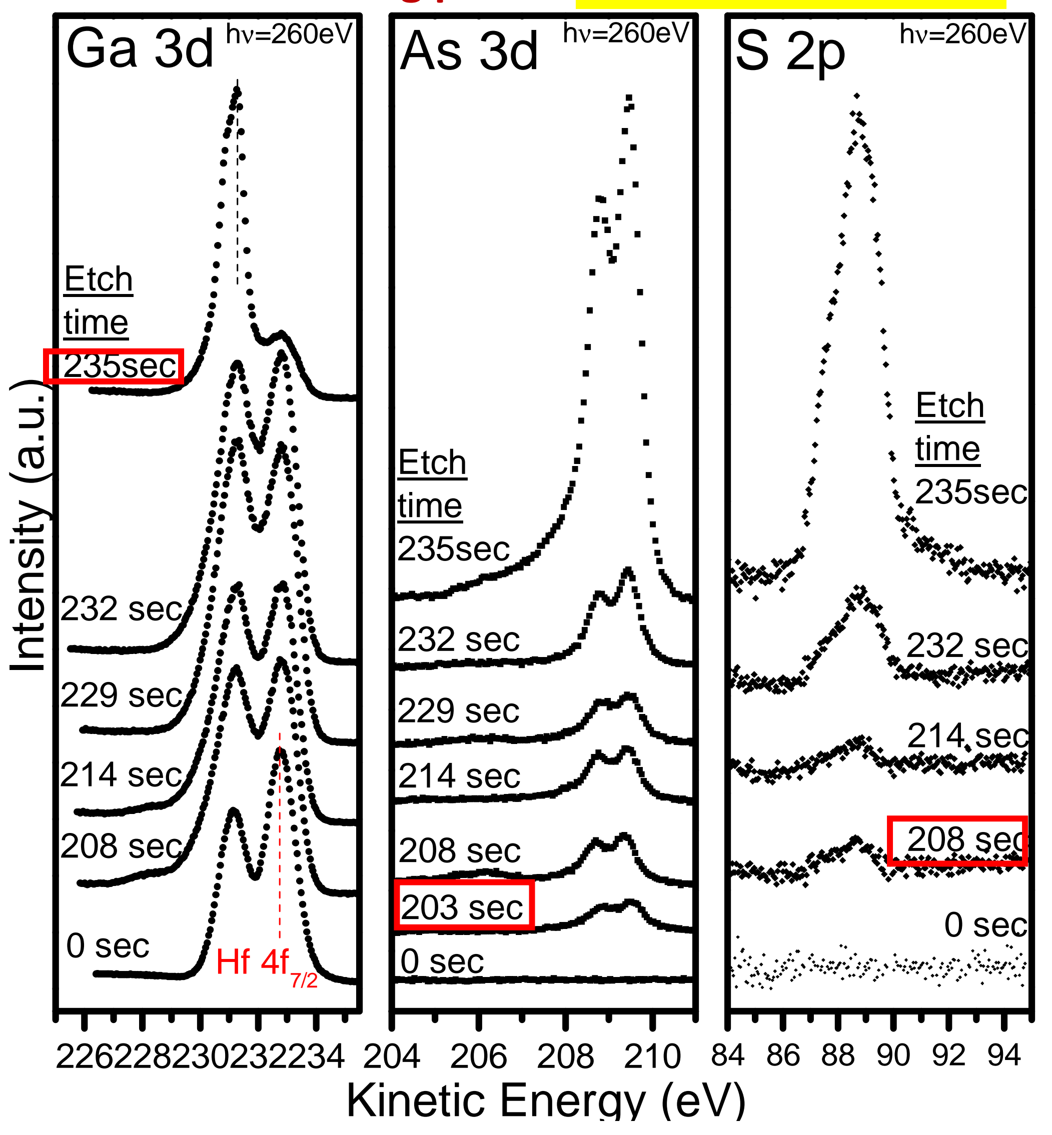
HF etching HfO_2 to HfO_2/S/GaAs interface.



- 194 sec HF etching shows overlapped Ga 3d and Hf 4f
- Gallium is well passivated by sulfide.
- Arsenic is slightly re-oxidized after the ALD HfO_2 deposition.

SRPES- *Annealed* HfO_2/S/GaAs-1

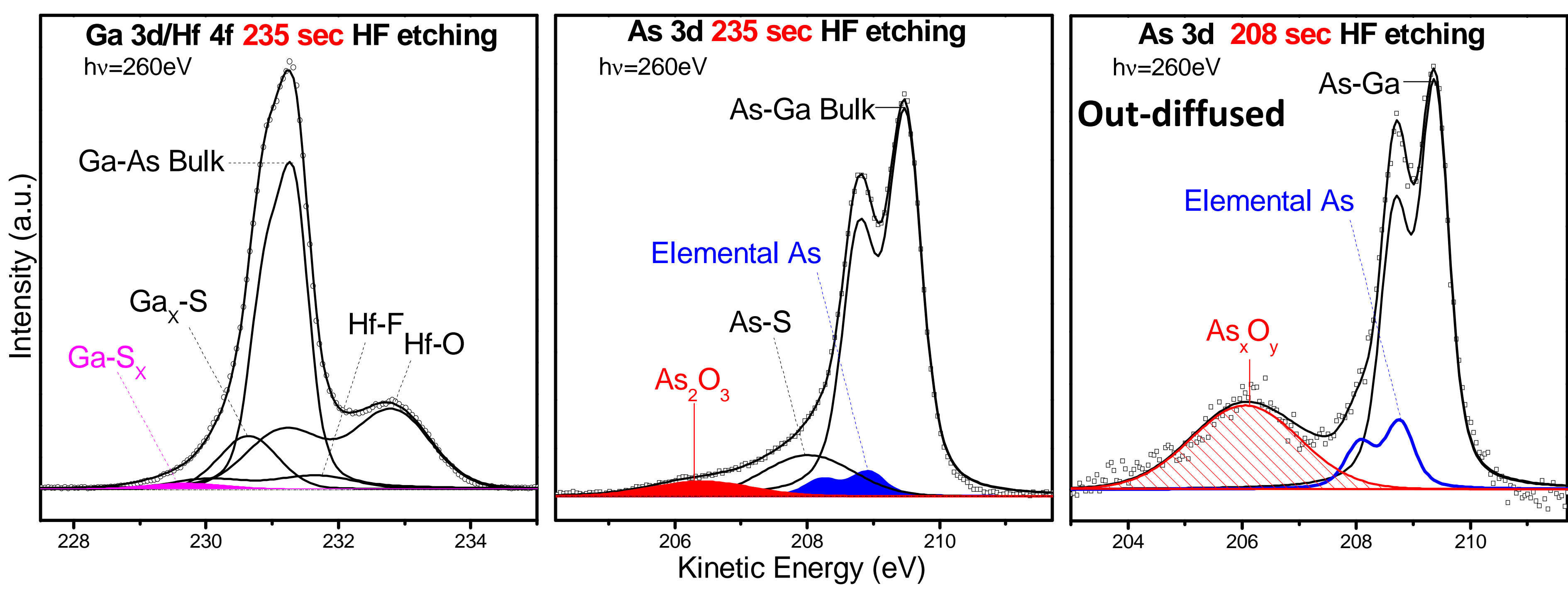
Etching profiles After N_2 PDA @ 450°C



SRC/SEMATI

Arsenic and sulfur out-diffuse into HfO_2 film

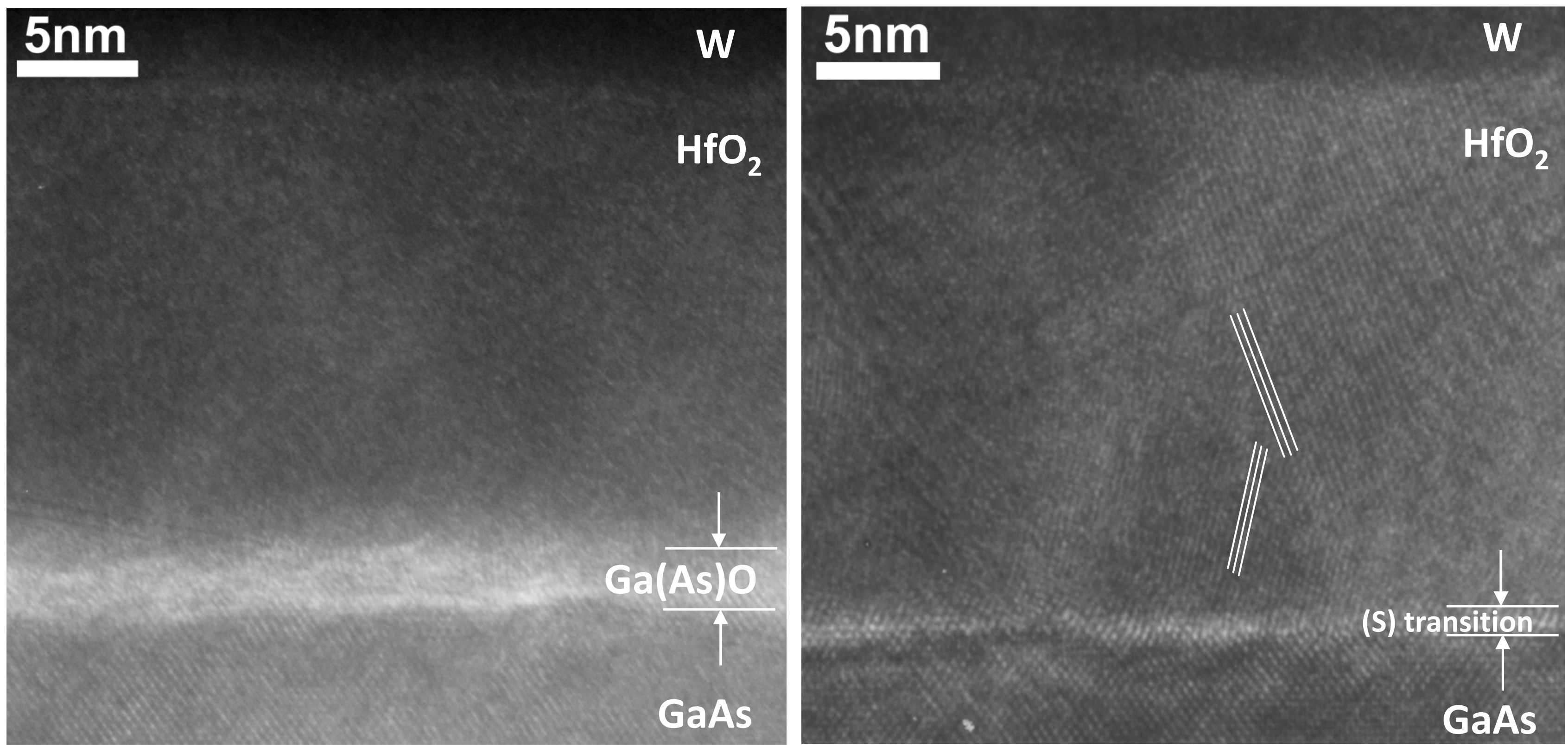
SRPES- *Annealed* HfO_2/S/GaAs-2



HF etching HfO_2 to annealed HfO_2/S/GaAs interface

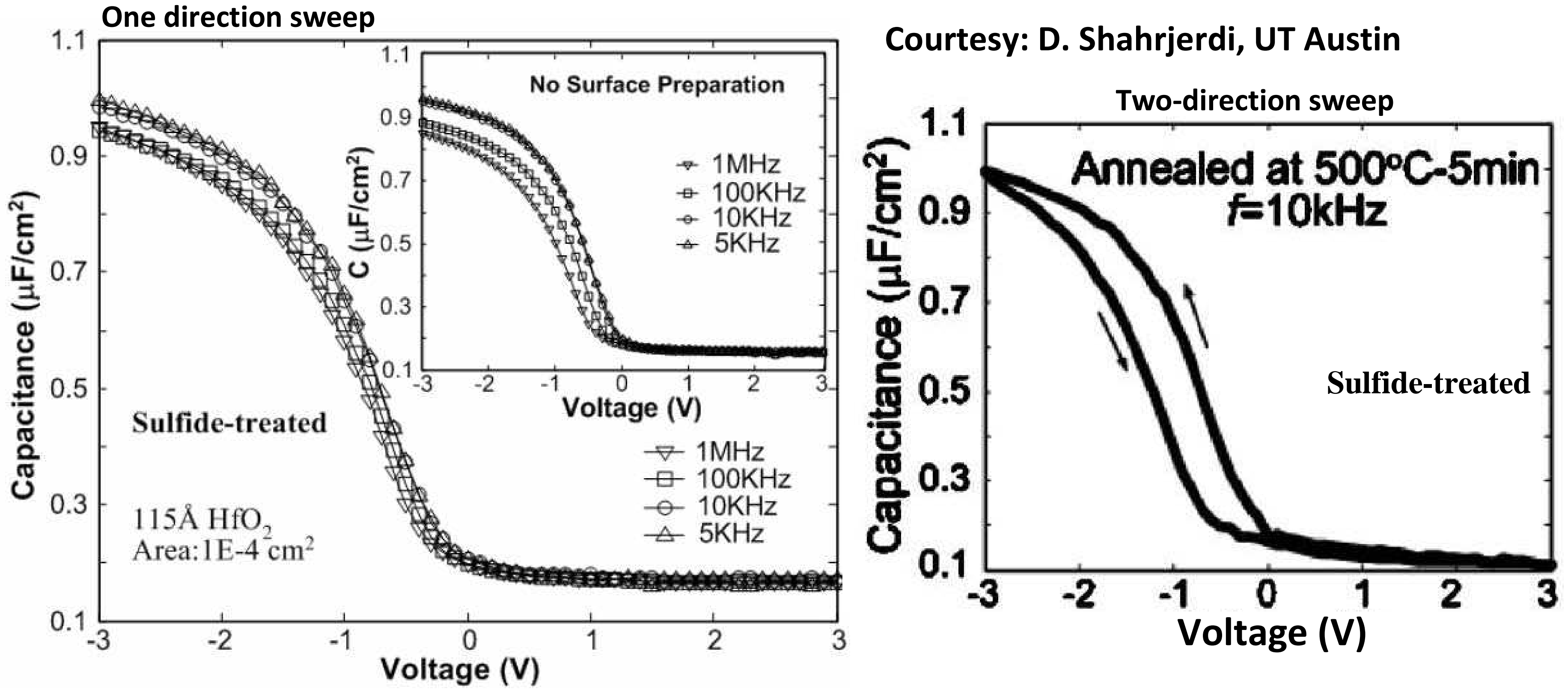
- **Gallium is well passivated by sulfides.**
- **Arsenic is slightly re-oxidized again after PDA @ 450°C.**
- **Arsenic out-diffusion: As_xO_y and elemental As in HfO_2**
  - Potential electrically active defects.

TEM: $W/HfO_2/S/GaAs$ MOS gate stack



450°C PDA W/HfO_2/Native oxide/GaAs		450°C PDA $W/HfO_2/S/GaAs$
Interface	- 2~3 nm Native Oxide	-1~3 monolayers of S-transition region
High-k HfO_2	- near amorphous	- partially poly-crystallized - possible diffusion path

Electrical Characterizations: *C-V*



- **Frequency dispersion is improved on MOS capacitor made on S-treated *p*-GaAs substrate- D_{it} removal (no much improvement on *n*-GaAs (not shown))**
- **PDA does not reduce hysteresis- Charge injection remains**

Part II: Conclusions

- ***$HCl+(NH_4)_2S$*** *surface treatment successfully removes native Ga(As)O, leave passivating sulfides on top of GaAs surface.*
- ***ESR*** *detects reduction of intrinsic paramagnetic surface defects of GaAs after $HCl+(NH_4)_2S$ surface treatment.*
- *150^oC ALD HfO_2 deposition and PDA @450^oC partially* ***re-oxidize*** *interfacial As to form As_2O_3.*
- ***Trace of As and S out-diffusion*** *are observed after 450^oC PDA, could become the potential electrically active defects shown as the hysteresis in CV characterization.*
- ***Frequency dispersion is improved*** *on MOS capacitor made on $HCl+(NH_4)_2S$ treated p-GaAs substrate suggests* ***D_{it} removal*** *in the interface.*

Industrial Interactions and Technology Transfer

- **Pre-ALD III-V surface cleaning/passivation mechanism study in collaboration with Dr. Wilman Tsai (Intel)**

Publications, Presentations, and Recognitions/Awards

- **P. T. Chen, S. Sun, E. Kim, P. C. McIntyre, W. Tsai, M. Garner, P. Pianetta, Y. Nishi, C.O. Chui, " HfO_2 gate dielectric on $(NH_4)_2S$ passivated (100) GaAs grown by atomic layer deposition", Journal of Applied Physics, 103, 034106 (2008).**

- **P. T. Chen, Y. Sun, C.O. Chui, E. Kim, P.C. McIntyre, N. Goel, W. Tsai, M. Garner, P. Pianetta, J. Harris, Y. Nishi, "Interface analysis Between ALD high-k HfO_2 and sulfur passivated GaAs", Mat. Res. Soc. (MRS) Symp., H4.3, Spring, San Francisco, CA, April 9-13, 2007. (Oral presentation)**

Future Plans

Next Year Plans

- **Surface cleaning/passivation study of $In_xGa_{1-x}As$, x=0.13, 0.53 and InAlAs substrates before ALD HfO_2 deposition.**
- **SRPES study of ALD induced III-V native oxide cleaning mechanism. (Collaboration with SLAC)**

Long-Term Plans

- **Identify ESR anisotropic paramagnetic defect signals in high-K/III-V interface.**

CUSTOMIZED PROJECTS

Post-Planarization Waste Minimization

PI:

- **Ara Philipossian, Chemical and Environmental Engineering, UA**

Graduate Student:

- **Ting Sun: Ph. D. candidate, Chemical and Environmental Engineering, UA**

Other Researcher:

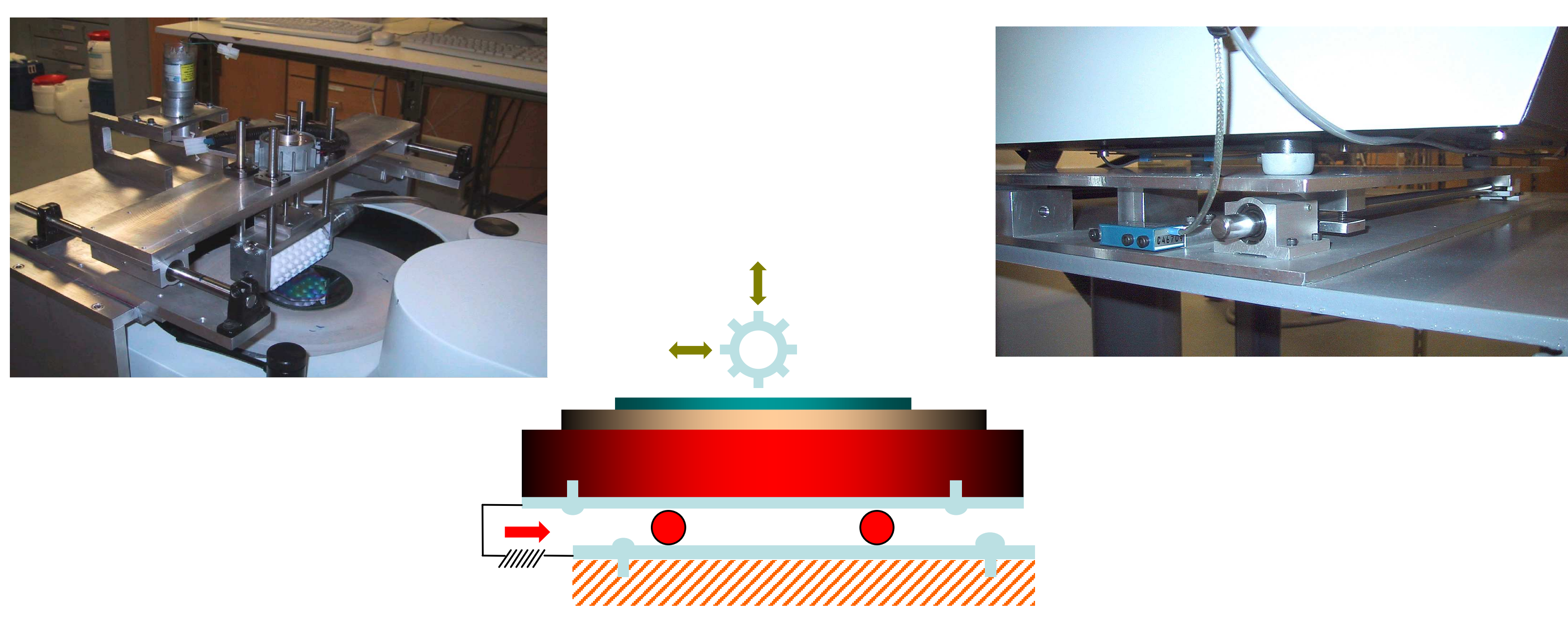
- **Yun Zhuang, Research Associate, Chemical and Environmental Engineering, UA**

Cost Share (other than core ERC funding):

- **In-kind donation (PVA brushes) from ITW Rippey Corporation**

Objective

Develop a functional test (see tester below) to identify performance differences (in terms of brush contact pressure, contact area and variance of shear force) between a good (i.e. perfectly concentric) PVA brush and one that is slightly eccentric during post-CMP cleaning



ESH Metrics and Impact

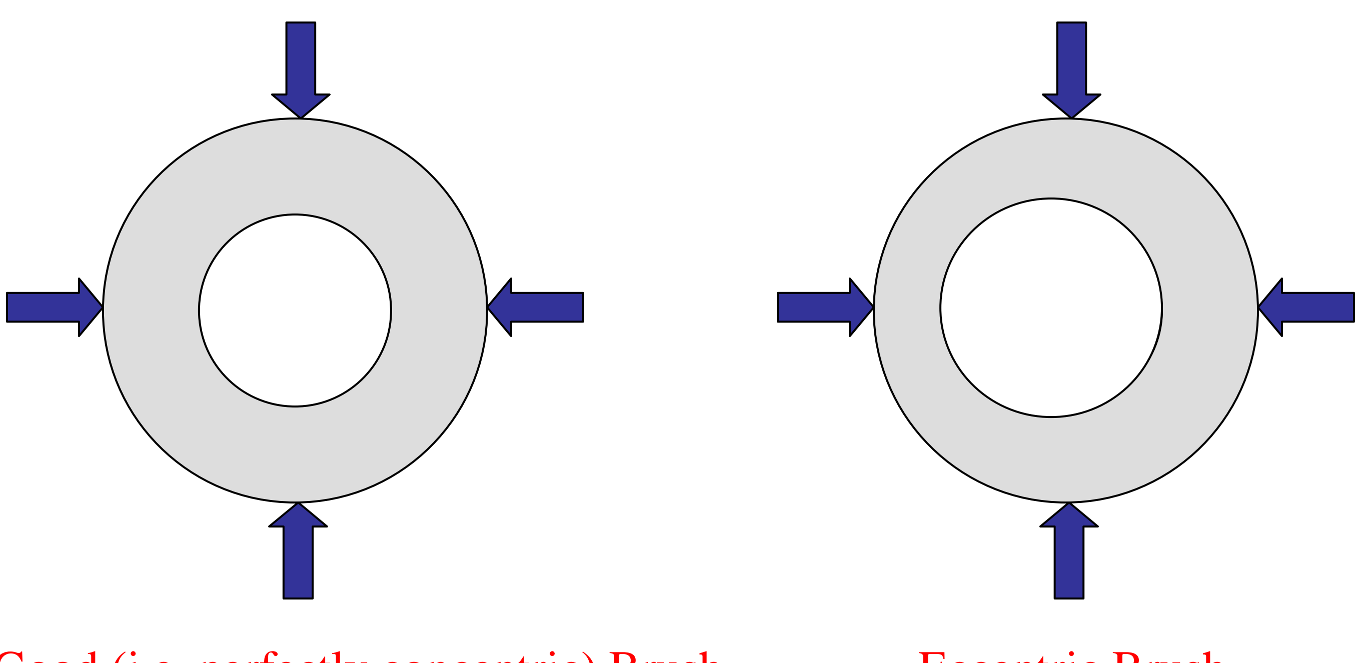
1. *Eliminates chemical, water, and energy consumption associated with qualifying PVA brushes that are eccentric for post-CMP cleaning processes.*

2. *Reduce PVA brush consumption by 20%.*

3. *Reduce post-CMP cleaning solution consumption by 20%.*

4. *Increases module productivity*

Method and Approach

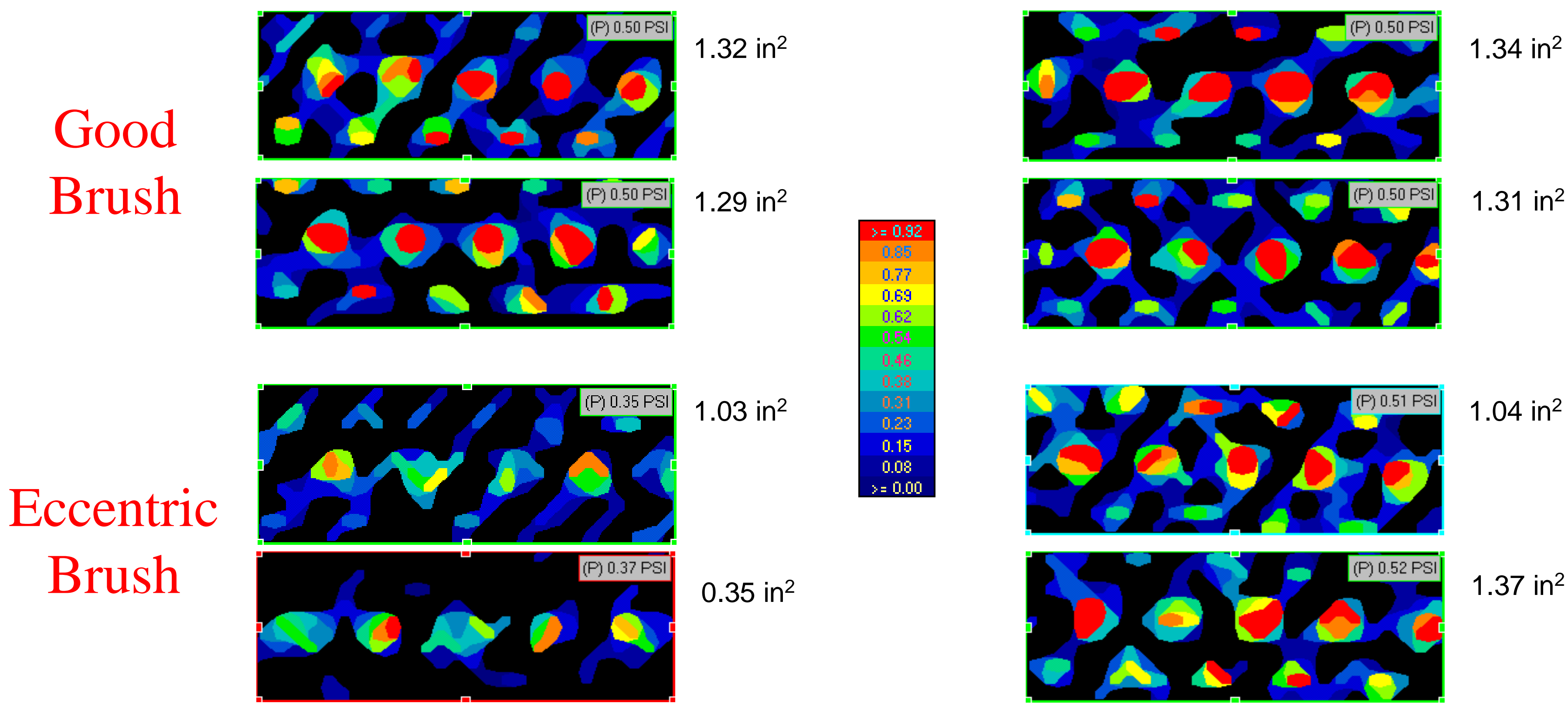


Good (i.e. perfectly concentric) Brush Eccentric Brush

Good brushes were tested and compared with eccentric brushes when scrubbing under the same compression distance, *i.e.*, all brushes were compressed to the same point to generate a pressure of 0.5 PSI for the good brushes.

Multiple contact pressure and area measurements were performed by rotating brushes under four different orientations to investigate the effect of eccentricity.

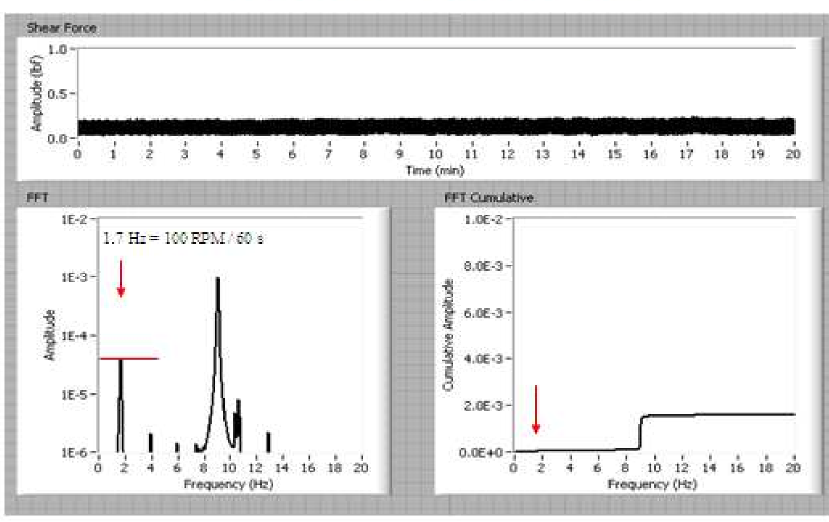
Pressure Contour Map and Contact Area



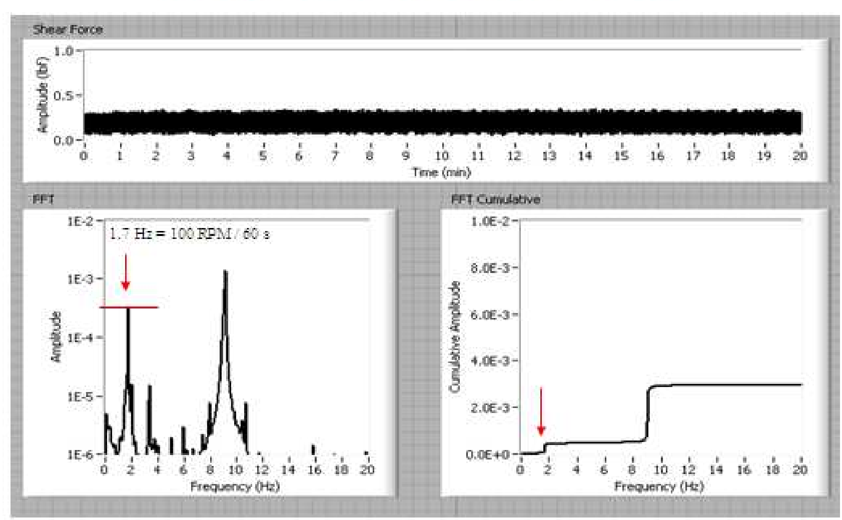
For the good brush, the contact pressure and contact area were consistent when rotating the brush. In comparison, for the eccentric brush, both the contact pressure and contact area varied significantly when rotating the brush.

Shear Force Spectral Analysis

Good Brush, 100 RPM



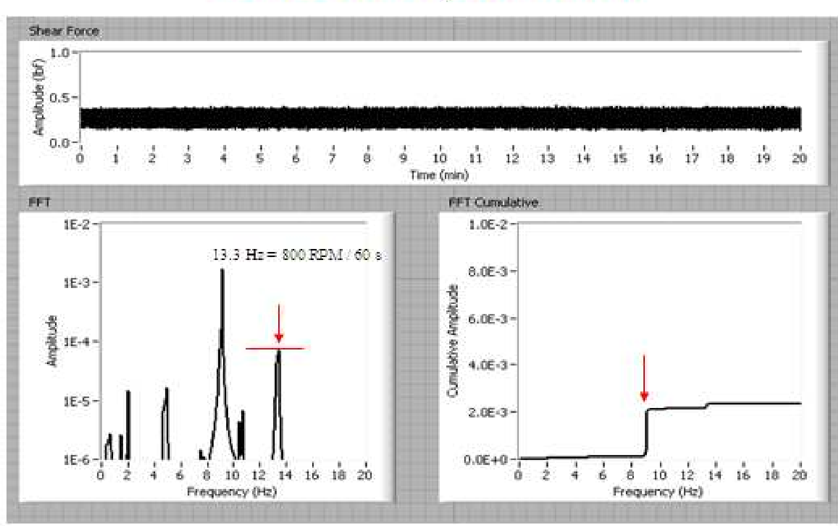
Eccentric Brush, 100 RPM



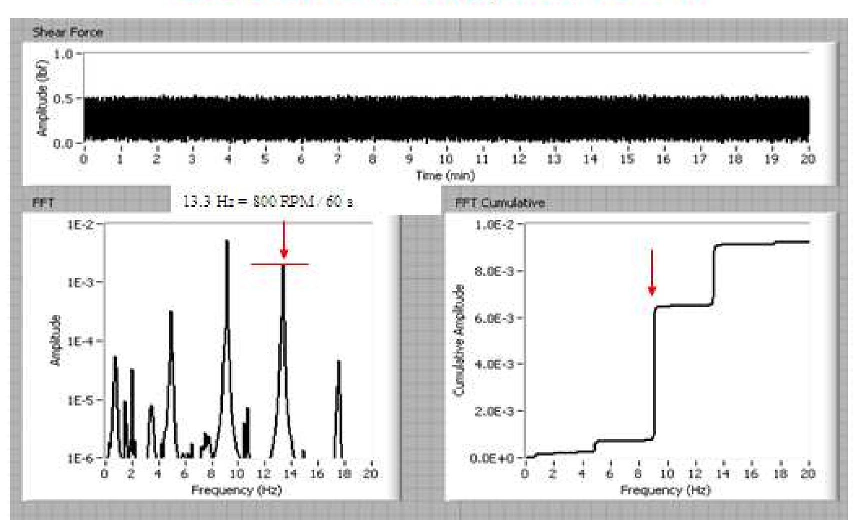
At 100 RPM, the eccentric brush showed higher spectral amplitudes at 1.7 Hz.

Shear Force Spectral Analysis

Good Brush, 800 RPM



Eccentric Brush, 800 RPM



At 800 RPM, the eccentric brush showed higher spectral amplitudes at 13.3 Hz.

Future Plans

Next Year Plans

- Investigate the effect of brush physical properties on the tribological behavior during post-CMP cleaning processes.
- Design, construct and qualify an incremental loading tool to investigate brush nodule deformation as a function of applied load and extended use.

Long-Term Plan

- Extend PVA brush life by better understanding the brush wear mechanism.

Simulation of Pad Stain Formation during Copper CMP

PI:

- Ara Philipossian, Chemical and Environmental Engineering, UA

Graduate Student:

- Hyosang Lee: PhD candidate, Chemical and Environmental Engineering, UA

Other Researcher:

- Yun Zhuang, Research Associate, Chemical and Environmental Engineering, UA

Cost Share (other than core ERC funding):

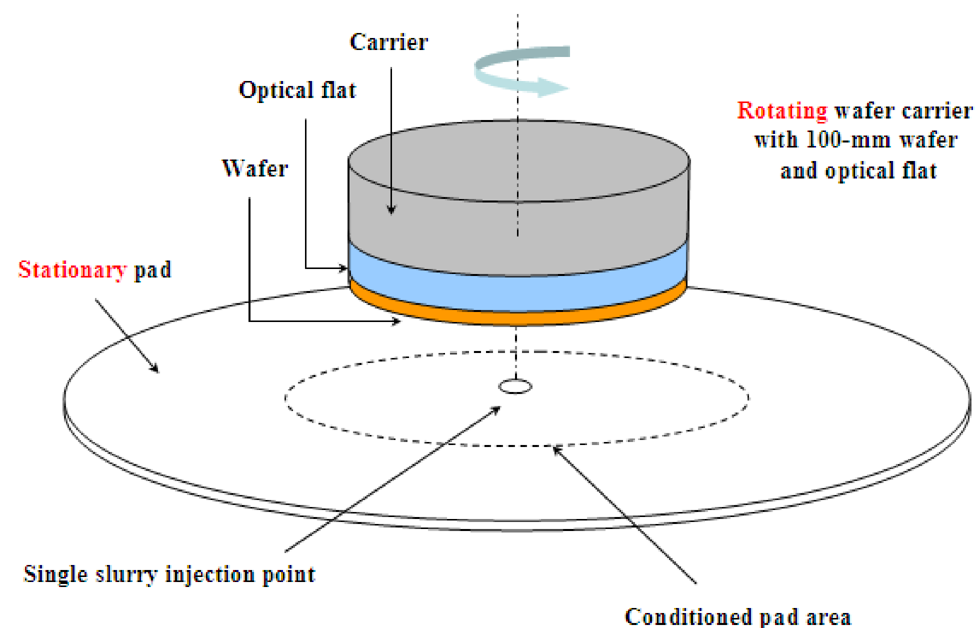
- In-kind support from Araca, Inc.

Objective & EHS Metrics

Develop 3-D fluid transport, thermal and kinetic models to simulate pad stains formed during copper CMP process.

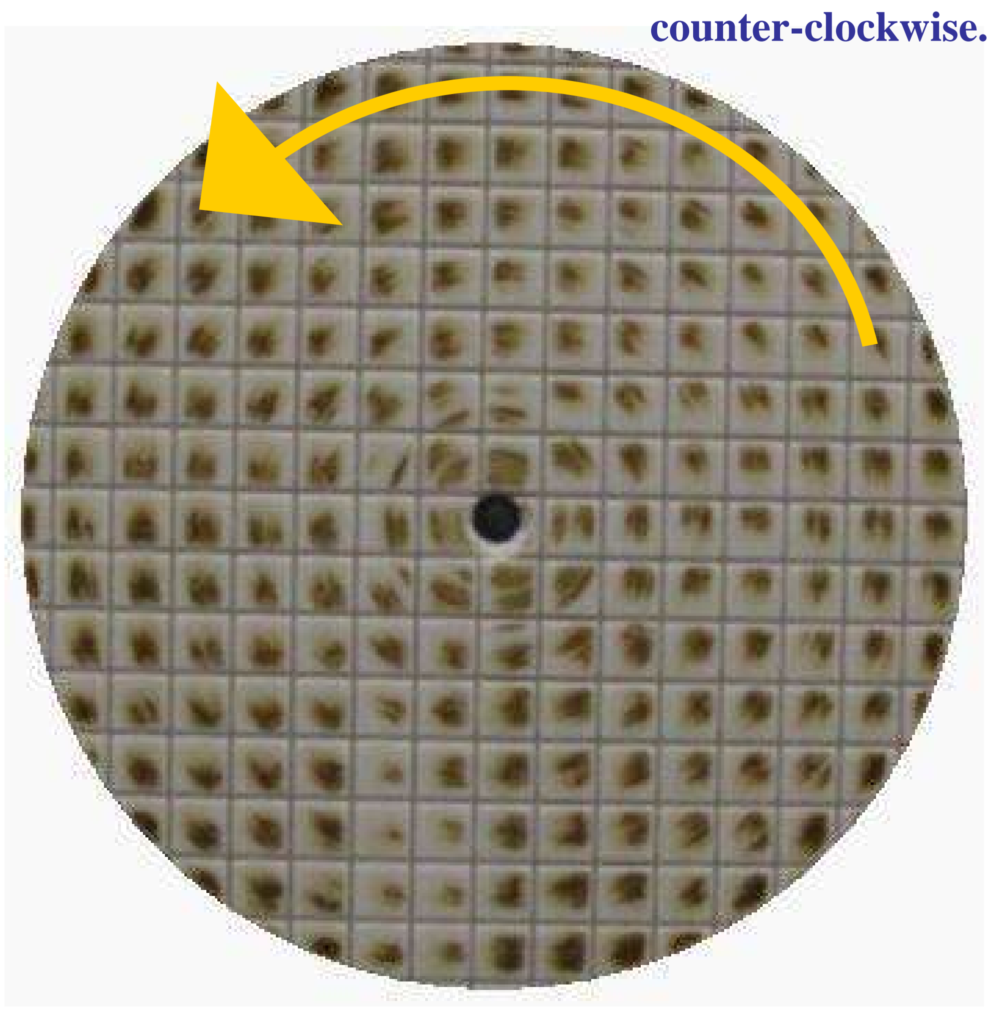
Reduce pad and pad cleaning solution consumption by 25 percent

Axisymmetric Polishing System

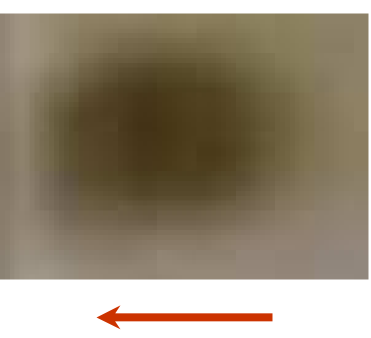


Stain Advection

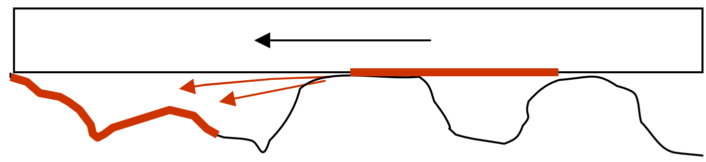
Pad was rotating counter-clockwise.



The generated pad stain on each land area was darker following the direction of wafer rotation, suggesting the stain was affected by slurry advection.



Simulation of By-Product Concentration on Pad Surface



Governing equation:

$$\frac{\partial c_s}{\partial t} + \vec{V} \cdot \vec{\nabla} c_s = \nabla \cdot (D \nabla c_s)$$

Advection by the fluid with a velocity

C_s: Concentration of by-product

B.C. at wafer surface:

$$D \vec{\nabla} C_s \cdot \vec{n} = \frac{k_2 k_1}{k_1 + k_2}$$

$$k_1 = A_1 \cdot \exp\left(\frac{-E_1}{kT}\right)$$

T: extracted from copper surface

$$k_2 = c_p \text{ x } \mu_k \text{ x } p_s \text{ x } V$$

B.C. at pad surface:

$$-D \vec{\nabla} C_s \cdot \vec{n} = k_4 C_s$$

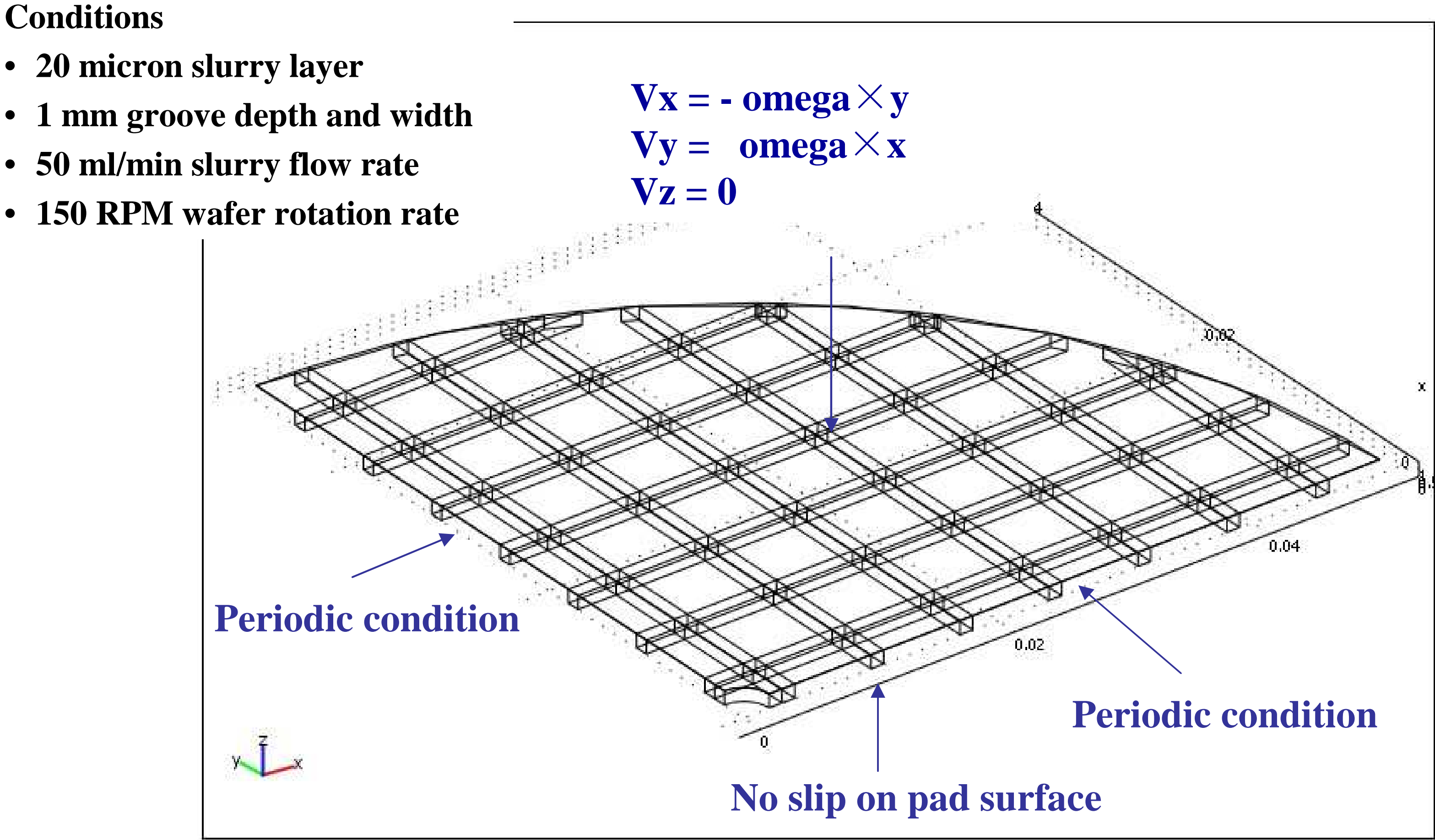
$$k_4 = A_4 \cdot \exp\left(\frac{-E_4}{kT}\right)$$

T: extracted from pad surface

Slurry Velocity Simulation

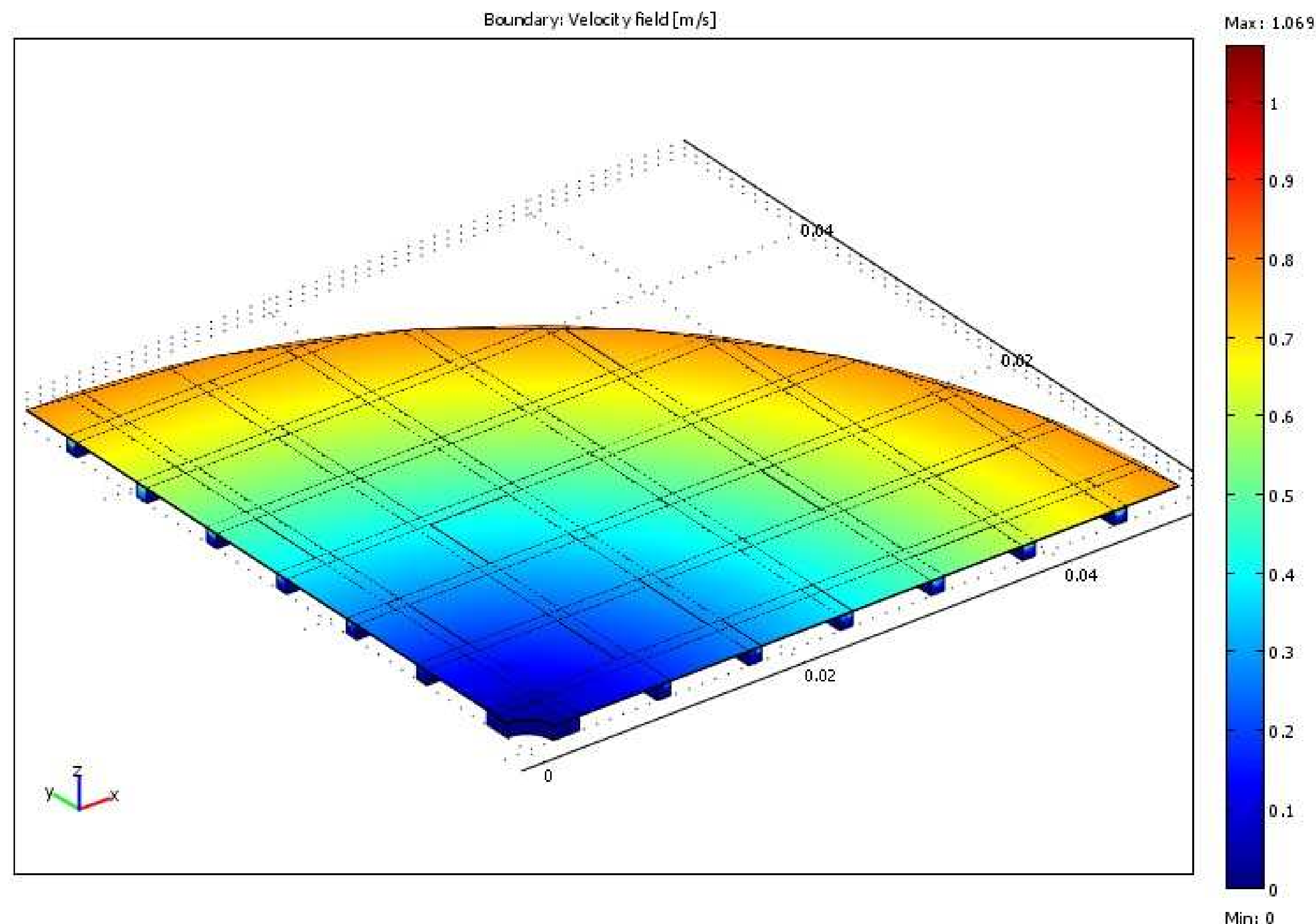
Conditions

- **20 micron slurry layer**
- **1 mm groove depth and width**
- **50 ml/min slurry flow rate**
- **150 RPM wafer rotation rate**



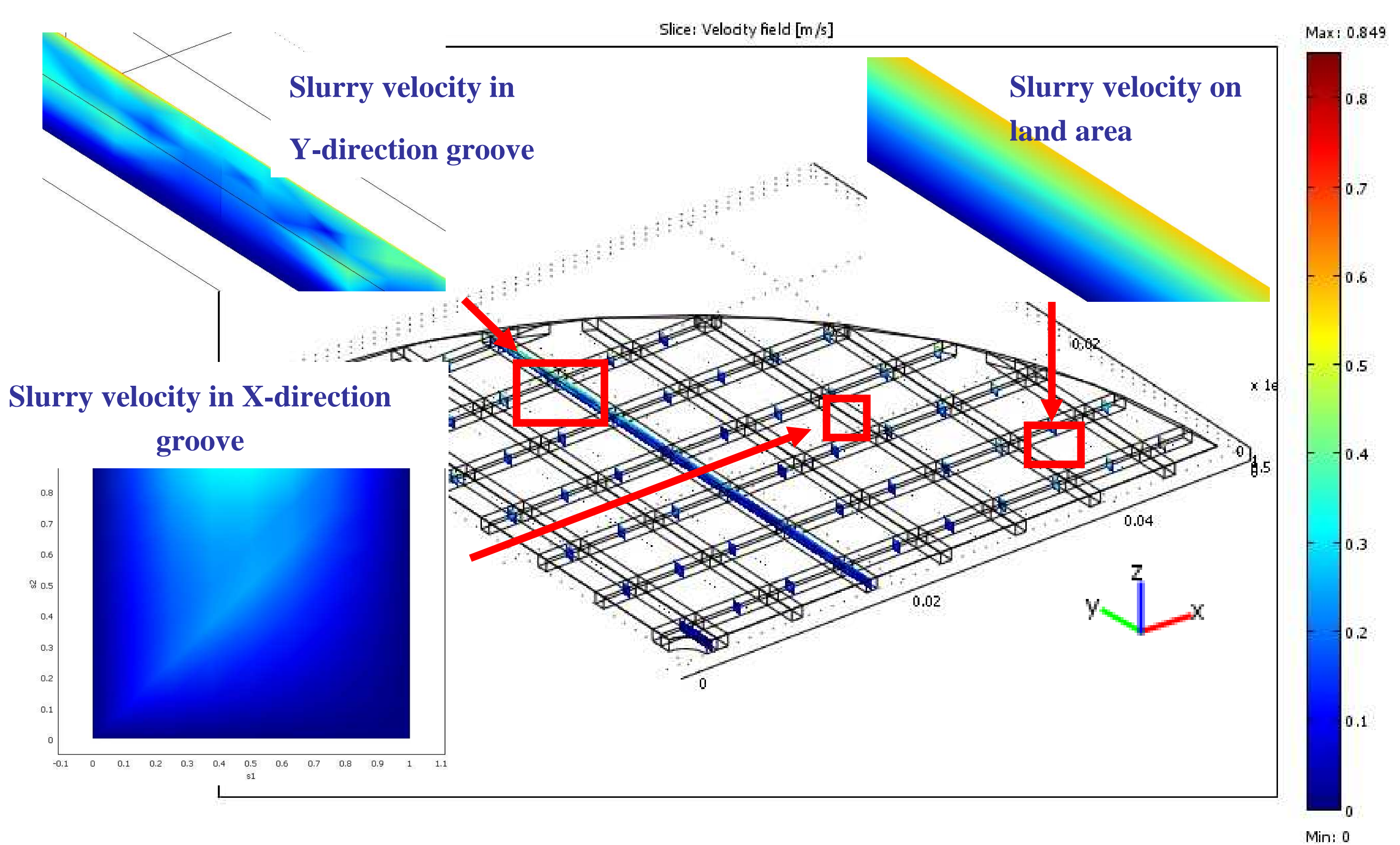
The Navier-Stokes equations for the slurry flow were solved only in the grooves and on the land areas.

Simulated Slurry Velocity on Wafer Surface



Slurry velocity increased gradually on wafer surface in the radial direction due to wafer rotation, thus affecting slurry velocity in the grooves.

Simulated Slurry Velocity in Grooves and on Land Area



Results showed shear flow on the land areas and wafer-driven circulation in the grooves.

Thermal Model

Heat equation

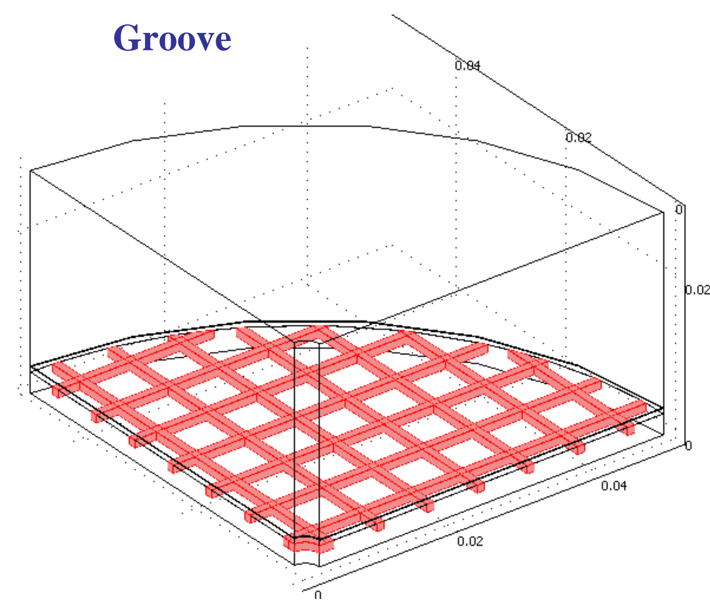
$$\rho C_p \left(\frac{\partial T}{\partial t} + \vec{V} \cdot \vec{\nabla} T \right) = \vec{\nabla} \cdot (\kappa \vec{\nabla} T) + Q$$

$\vec{V}$:
- From Navier-Stokes in slurry layer
- Rigid body in wafer and above
- 0 in pad

Q : $\frac{\mu_k p_s V_s}{h}$ in slurry layer

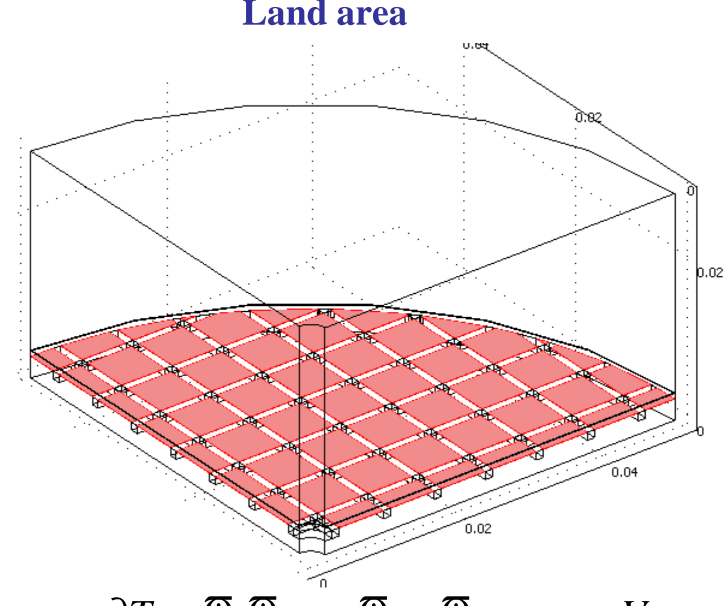
μ_k : COF

Groove



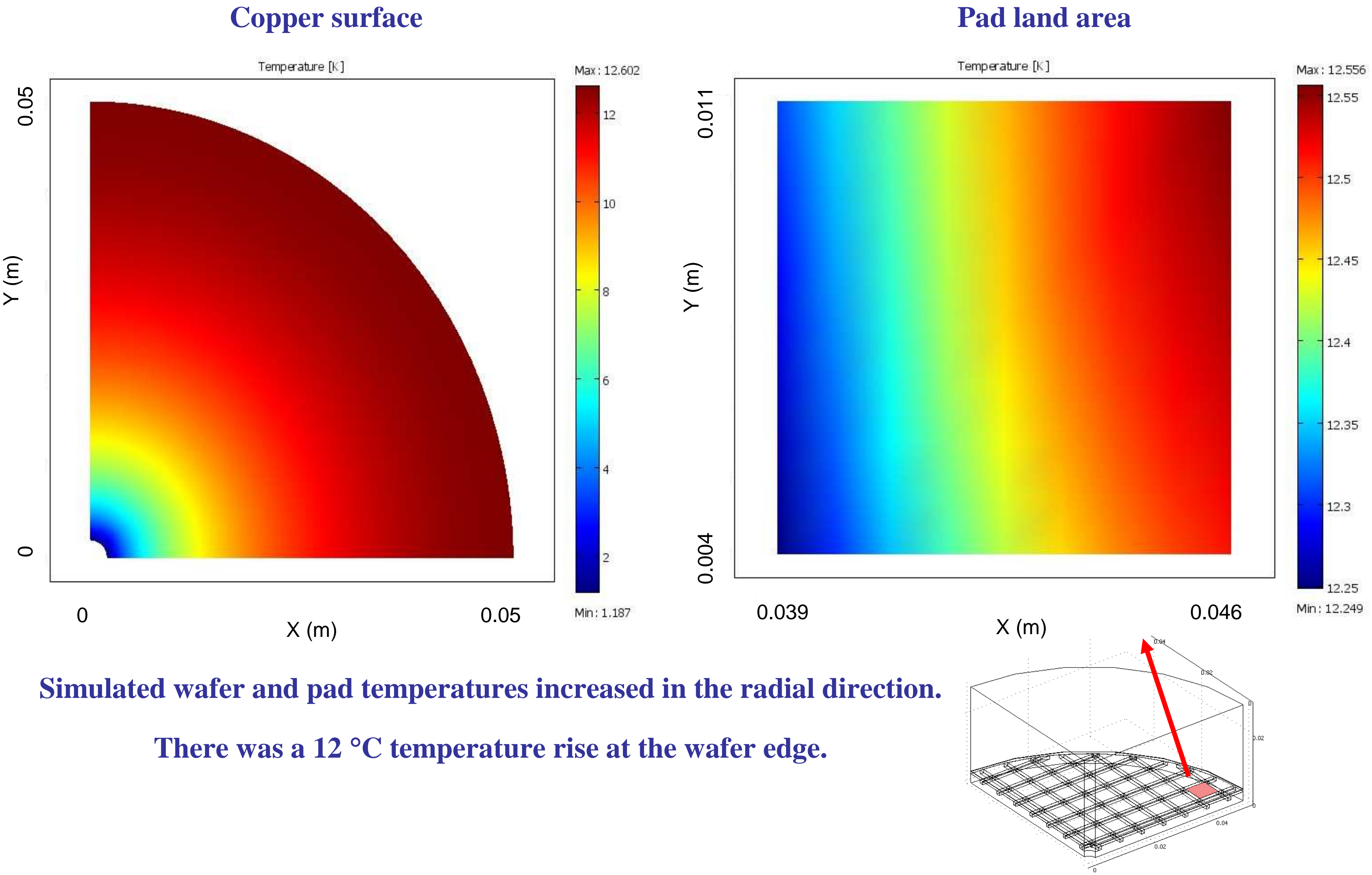
$$\rho C_p \left(\frac{\partial T}{\partial t} + \vec{V} \cdot \vec{\nabla} T \right) = \vec{\nabla} \cdot (\kappa \vec{\nabla} T)$$

Land area



$$\rho C_p \left(\frac{\partial T}{\partial t} + \vec{V} \cdot \vec{\nabla} T \right) = \vec{\nabla} \cdot (\kappa \vec{\nabla} T) + \frac{\mu_k p_s V_s}{h}$$

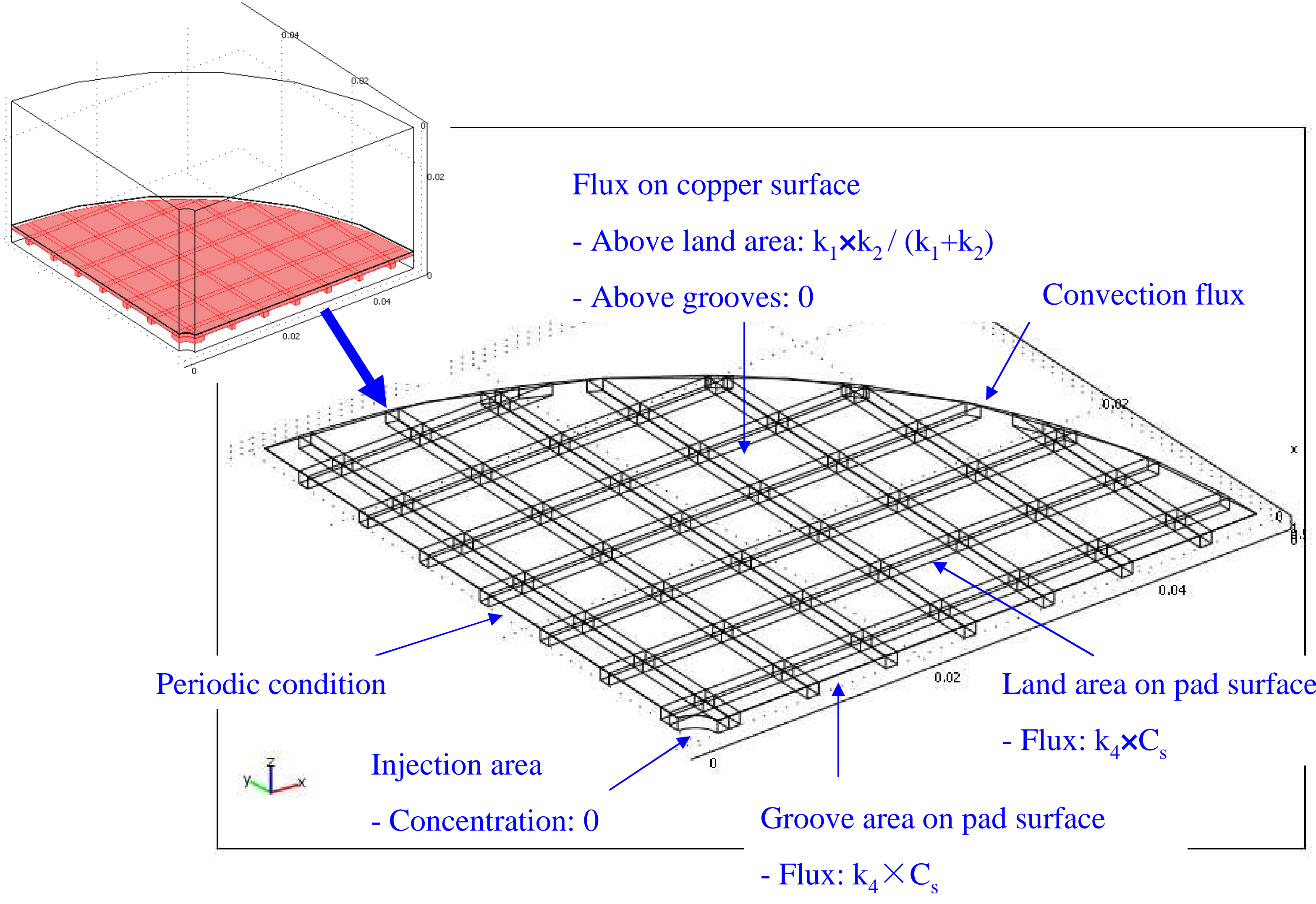
Simulated Temperature Profile



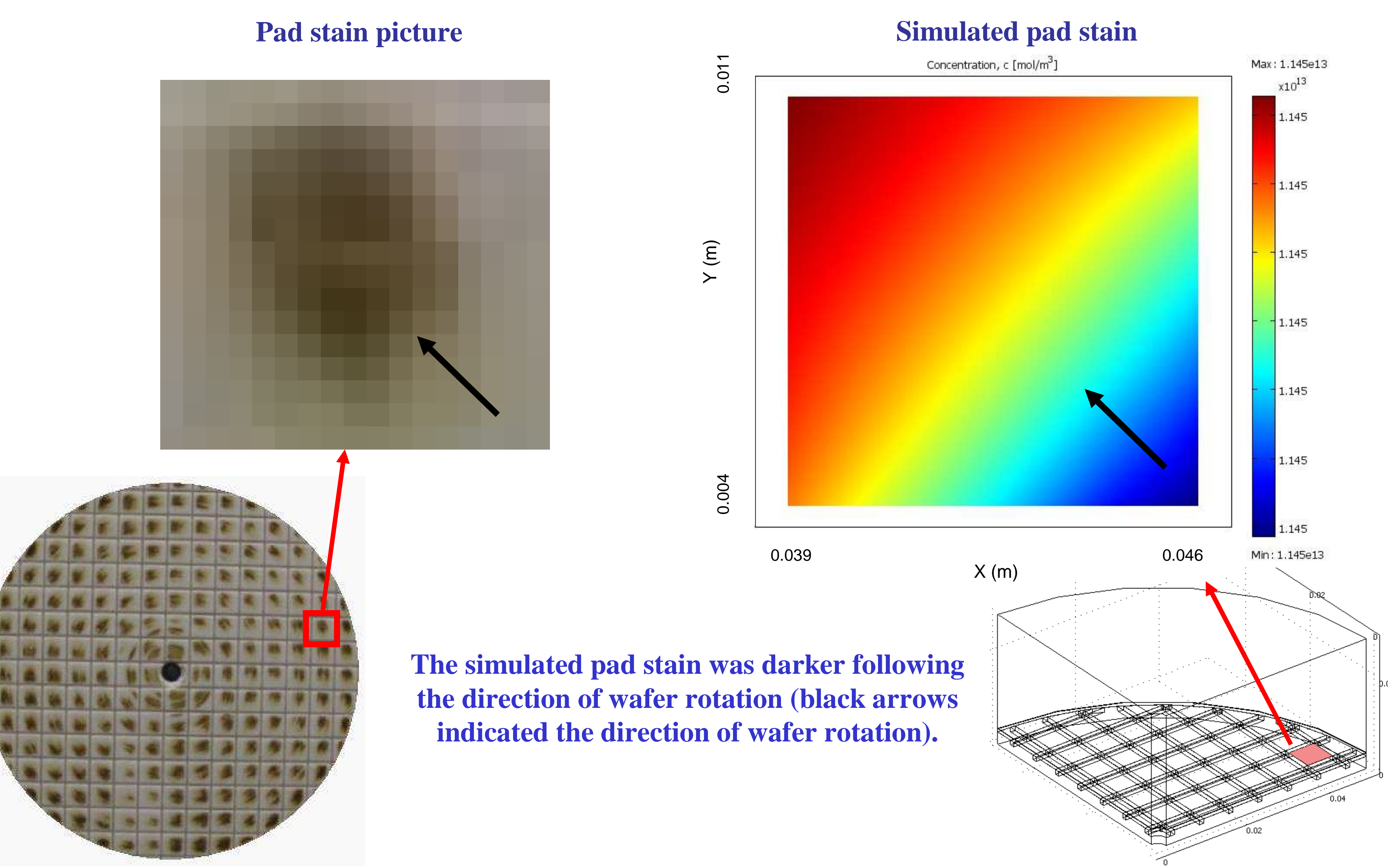
Simulated wafer and pad temperatures increased in the radial direction.

There was a 12 °C temperature rise at the wafer edge.

Boundary Conditions for Stain Formation



Simulated Stain Formation



SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Industrial Interactions and Technology Transfer

Industrial mentors / contacts:

- **Fergal O'Moore (Novellus Systems, Inc.)**
- **Sooyun Joh (Novellus Systems, Inc.)**
- **Brian Brown (Novellus Systems, Inc.)**
- **Leonard Borucki (Araca, Inc.)**

Effect of Concentric Slanted Groove Patterns on Slurry Flow during Cu CMP

PI:

- Ara Philipossian, Chemical and Environmental Engineering, UA

Graduate Students:

- Daniel Rosales-Yeomans: Chemical and Environmental Engineering, UA, graduated with Ph. D. degree in December 2007
- Hyosang Lee: Ph. D. candidate, Chemical and Environmental Engineering, UA

Undergraduate Student:

- Roy Dittler, Chemical and Environmental Engineering, UA

Cost Share (other than core ERC funding):

- In-kind support (pad grooving service) from Toho Engineering

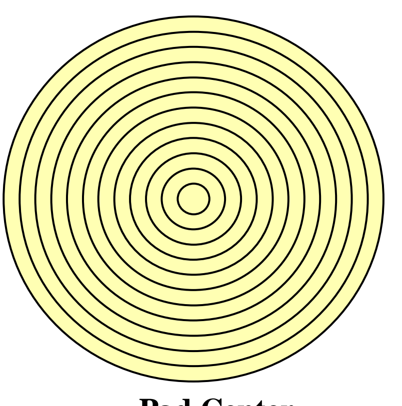
Objective

Determine the effects of concentric slanted groove design, wafer pressure, sliding velocity, and slurry flow rate on slurry film thickness between pad and wafer interface.

ESH Metrics and Impact

1. *Reduce slurry consumption by 33%*
2. *Extend pad life and reduce pad consumption by 33%*

Concentric Slanted Groove Design

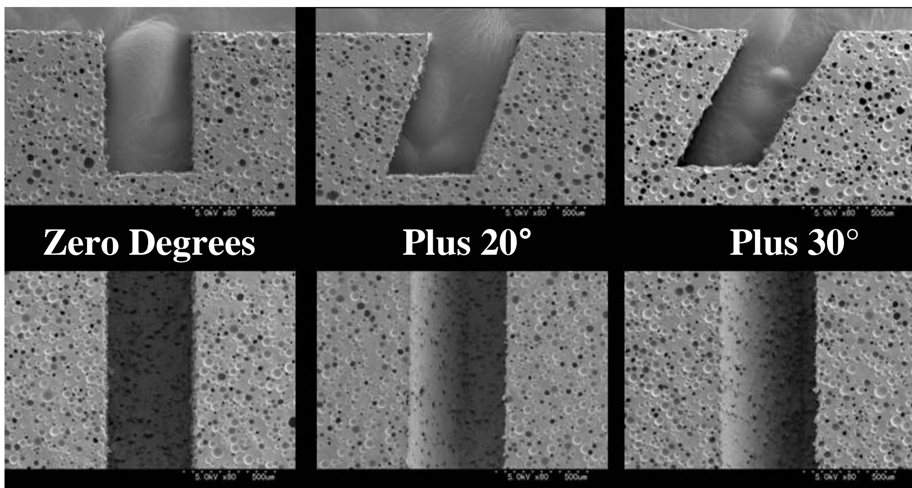


Wafer and pad rotate counter – clockwise.

Pad Center

Positive Direction

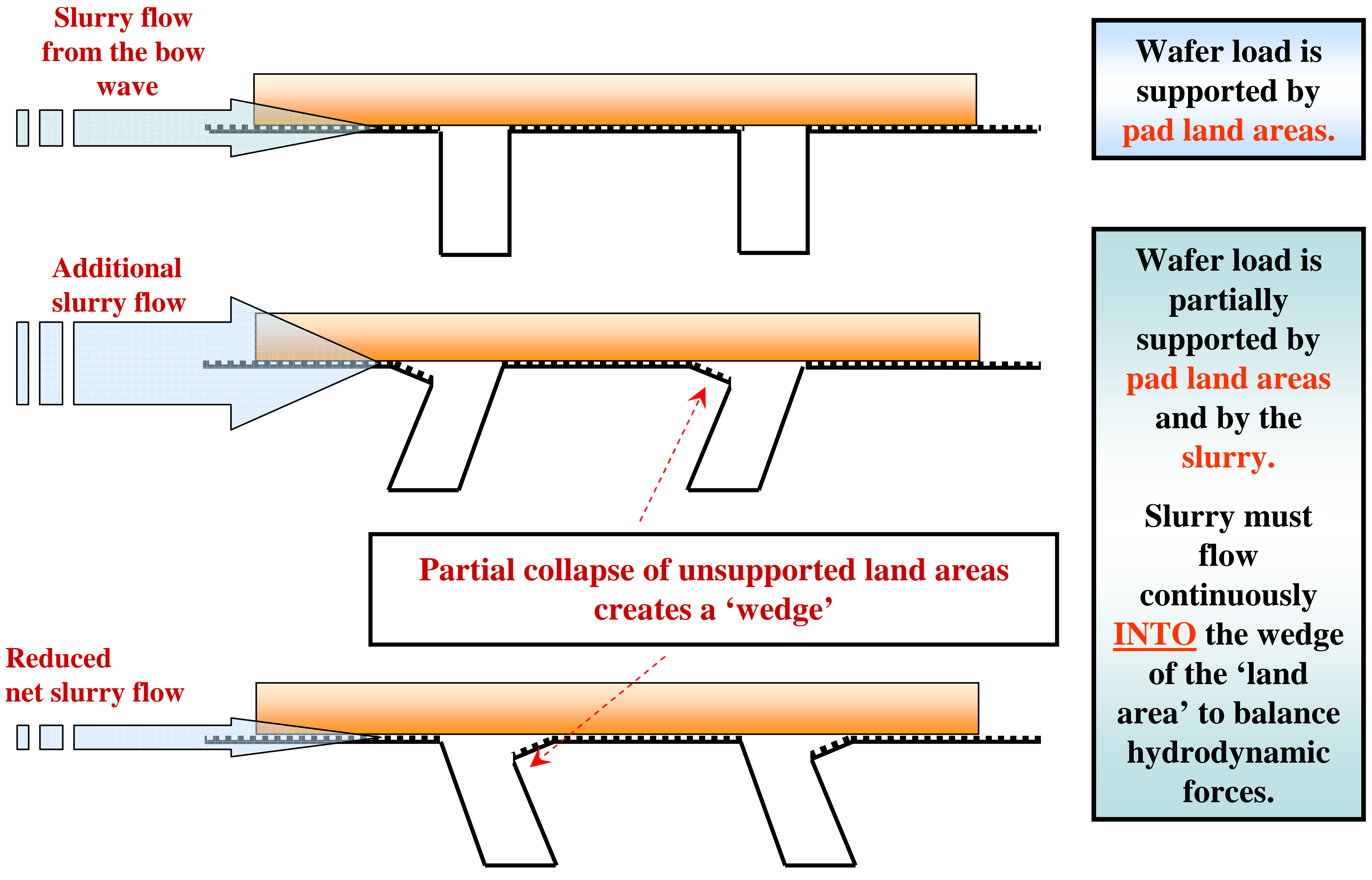
Negative Direction



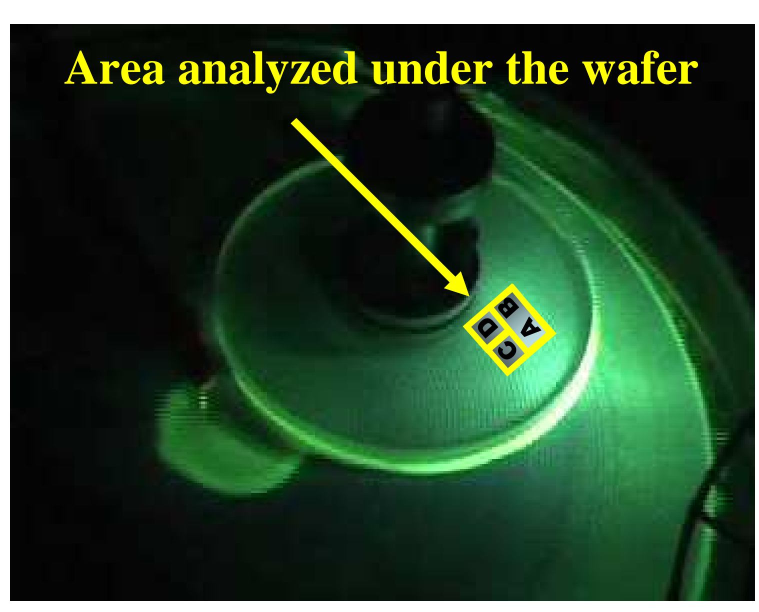
Side View

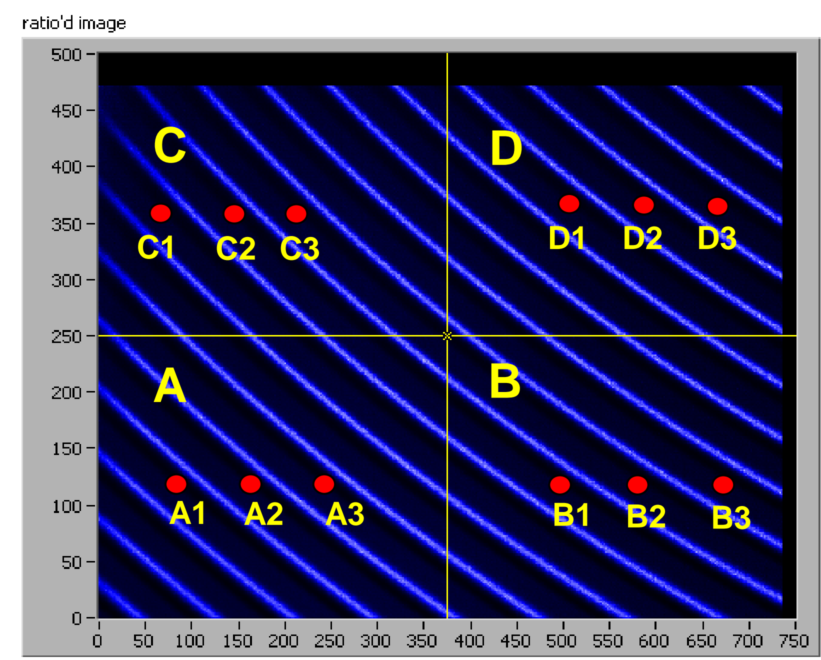
Top View

The Effect of Slanted Grooves on Slurry Flow



Slurry Film Thickness Measurement Area





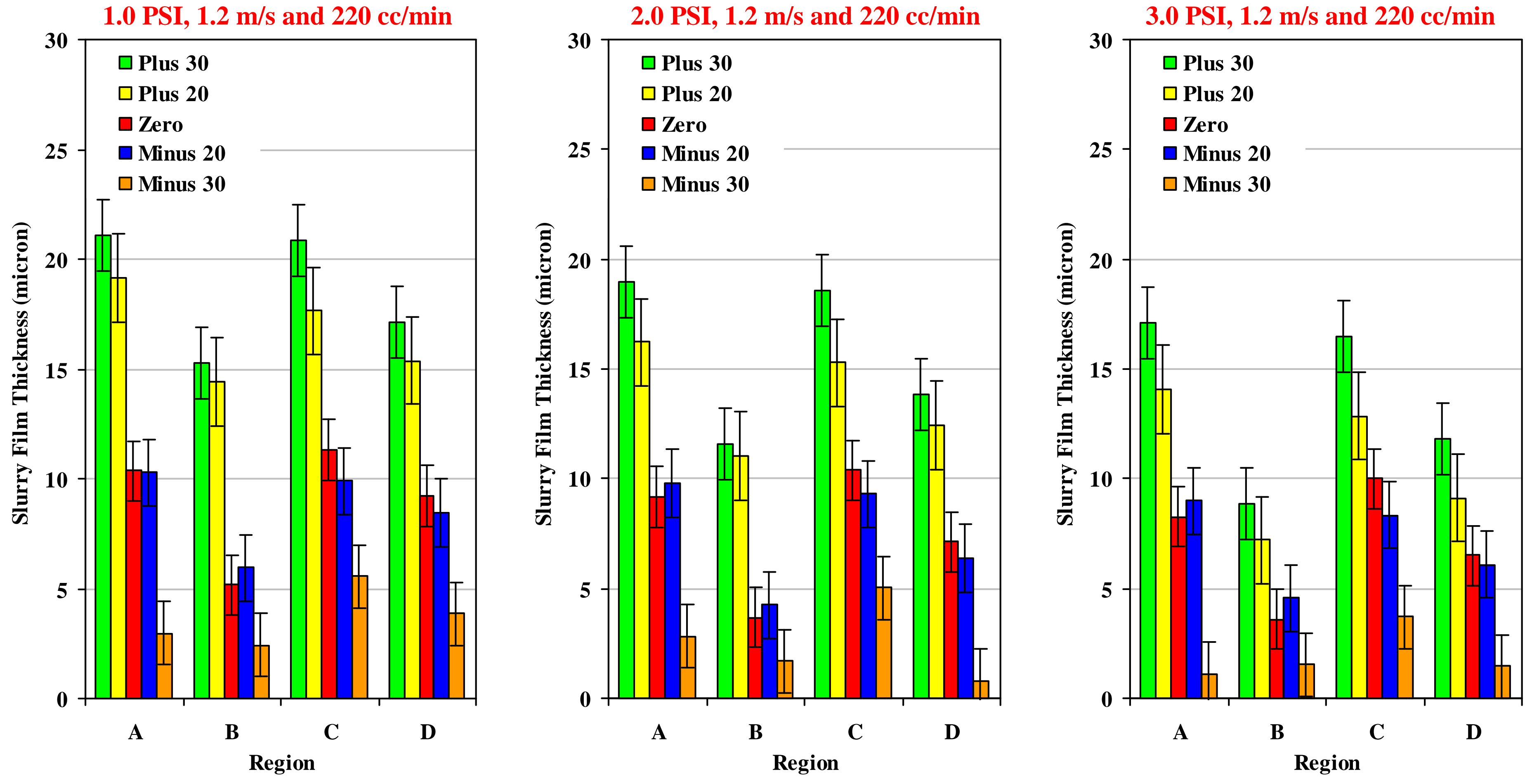
The area analyzed under the wafer is divided into four smaller regions: A, B, C and D.

Regions A & C are close to the wafer edge; Regions B & D are close to the wafer center.

In each region, three sub land areas are analyzed.

Values reported for each region (A, B, C and D) are an average of the three sub land areas.

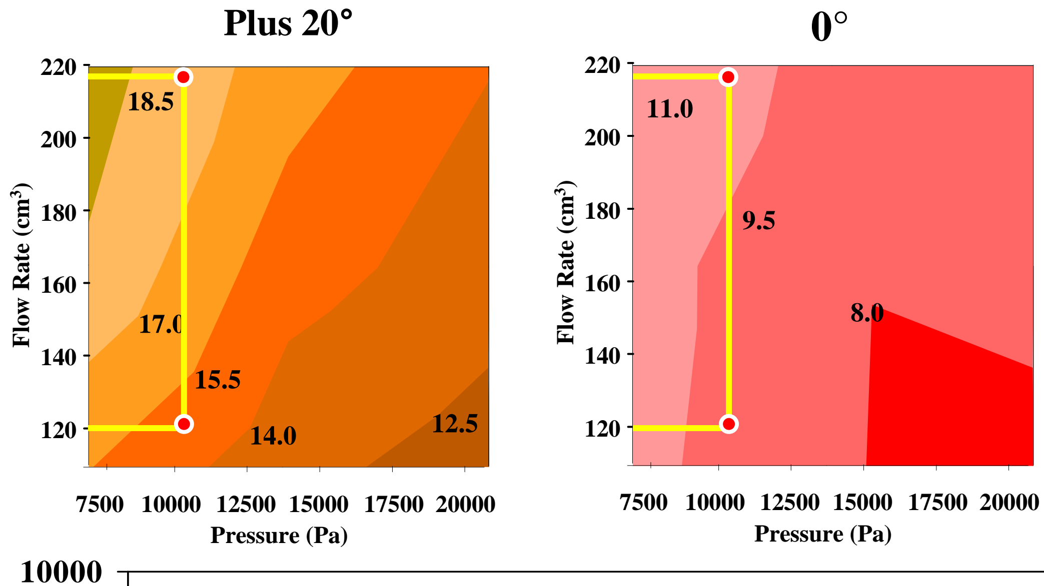
Effect of Groove Slanting on Slurry Film Thickness



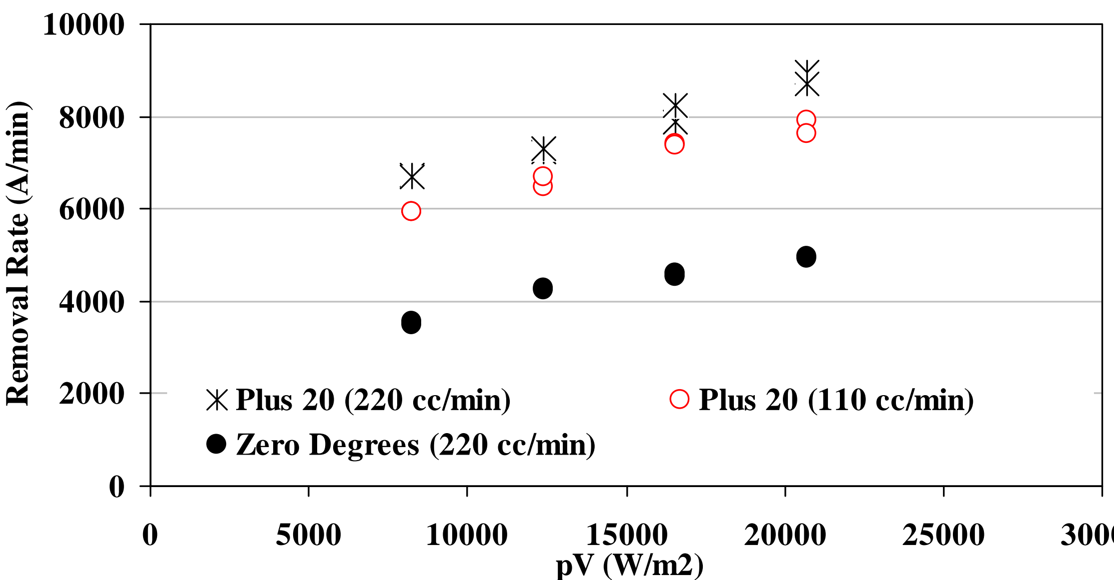
Slanting the grooves towards the edge of the pad (i.e. positive direction) facilitates slurry flow into the pad-wafer interface area.

Slanting the grooves towards the center of the pad (i.e. negative direction) reduces slurry flow into the pad-wafer interface area.

Effect of Groove Slanting on Removal Rate



At any given sliding velocity, pressure, and flow rate, the Plus 20° pad shows a higher slurry film thickness at the pad land area compared to the 0° pad. This can have significant pad-wafer contact area ramifications that affect removal rate and defectivity.



Removal rate slightly decreases as the flow rate is cut by 2X for the Plus 20° pad. However, even at this lower flow rate (110 cc/min), the Plus 20° pad has a significantly higher removal rate than the 0° pad at 220 cc/min.

Future Plans

Next Year Plans

- **Investigate the effect of groove slanting on RR with various copper slurries for copper – 1 and copper – 2 applications on 300-mm wafers.**

- **Determine the optimal slant degree that is a win-win from both EHS and performance points of view**

Long-Term Plan

- **Partner with ERC member pad and IC makers for defectivity testing and possible tech transfer to 300-mm platforms.**

Biologically Inspired Nano-Manufacturing (BIN-M)

PIs:

- Anthony Muscat, Chemical and Environmental Engineering, UA
- Megan McEvoy, Biochemistry and Molecular Biophysics, BIO5 Institute, UA
- Masud Mansuripur, College of Optical Sciences, UA

Graduate Students:

- Amber Young, PhD candidate, College of Optical Sciences, UA
- Sam Jayakanthan, PhD candidate, Biochemistry and Molecular Biophysics, UA
- Shawn Miller, PhD candidate, College of Optical Sciences, UA
- Rahul Jain, PhD candidate, Chemical and Environmental Engineering, UA

Undergraduate Student:

- Ben Mills, Chemical and Environmental Engineering, UA

Other Researchers:

- Zhengtao Deng, Postdoctoral Fellow, ChEE & Optical Sciences, UA
- Babak Imangholi, Postdoctoral Fellow, ChEE & Optical Sciences, UA
- Gary Fleming, Postdoctoral Fellow, Chemical and Environmental Engineering, UA

Cost Share (other than core ERC funding):

- $825k Science Foundation Arizona, ASM, SEZ, Arizona TRIF

Objectives

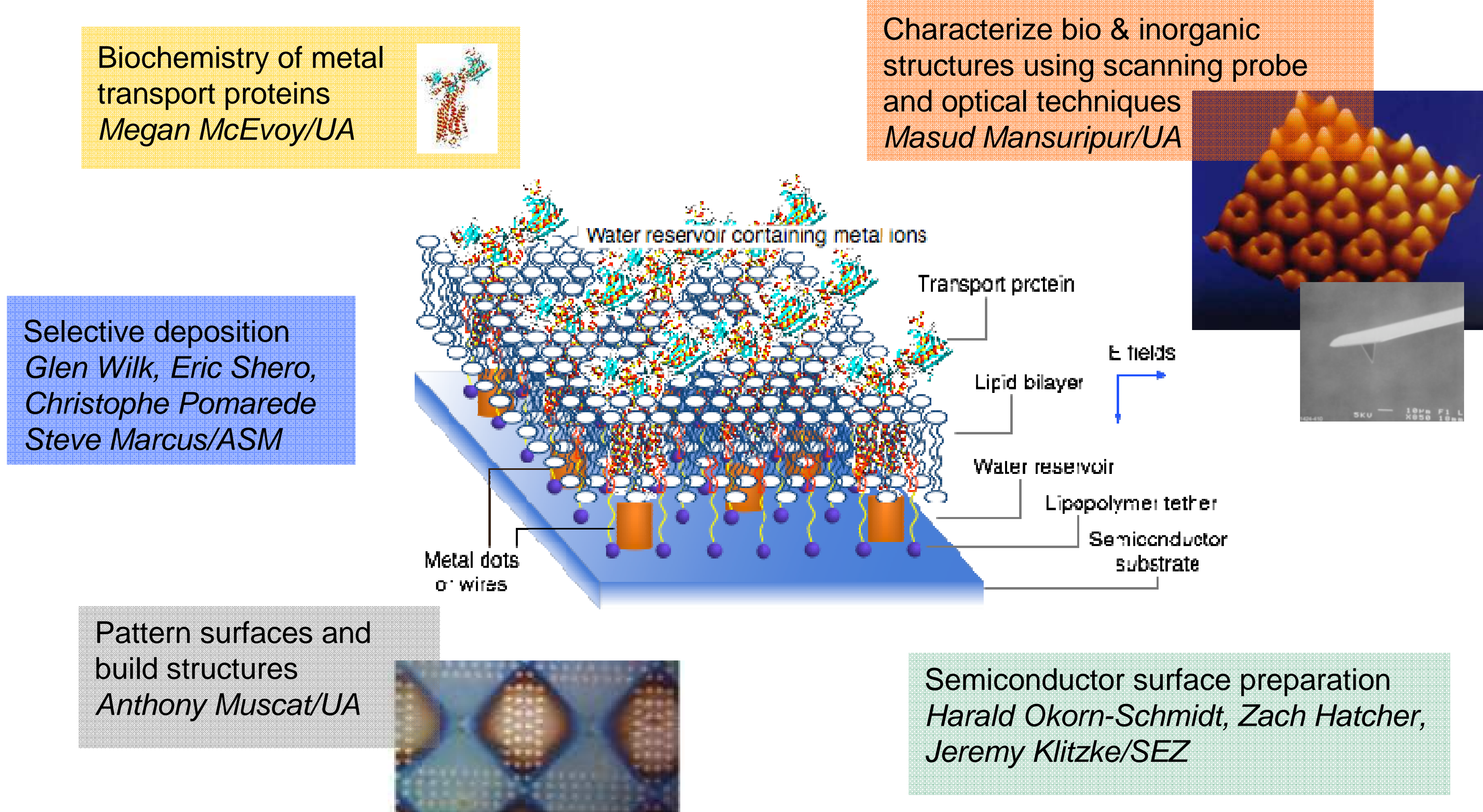
- **Minimize costs of materials, energy, and water to fabricate nanoscale devices using bio-based strategy**
- **Exploit homogeneity, mild reaction conditions, and specificity of active biological molecules**
- **Grow 3D structures to achieve scalable architecture**
- **Employ additive, bottom up patterning methods**

ESH Metrics and Impact

Sustainability metrics			
Process	Water l/bit/masking layer	Energy J/bit/masking layer	Materials g/bit/masking layer
Subtractive 32 nm*	$3.3x10^{-10}$	$1.5x10^{-12}$ EUV	$2.9x10^{-16}$
Additive	$3.6x10^{-13}$	$9.2x10^{-17}$	$1.8x10^{-19}$

*D. Herr, Extending Charge-based Technology to its Ultimate Limits: Selected Research Challenges for Novel Materials and Assembly Methods. Presentation at the NSF/SRC EBSM Engineering Research Center Review Meeting: February 24, 2006.

Process Goal: Deposit Array of Metal Dots

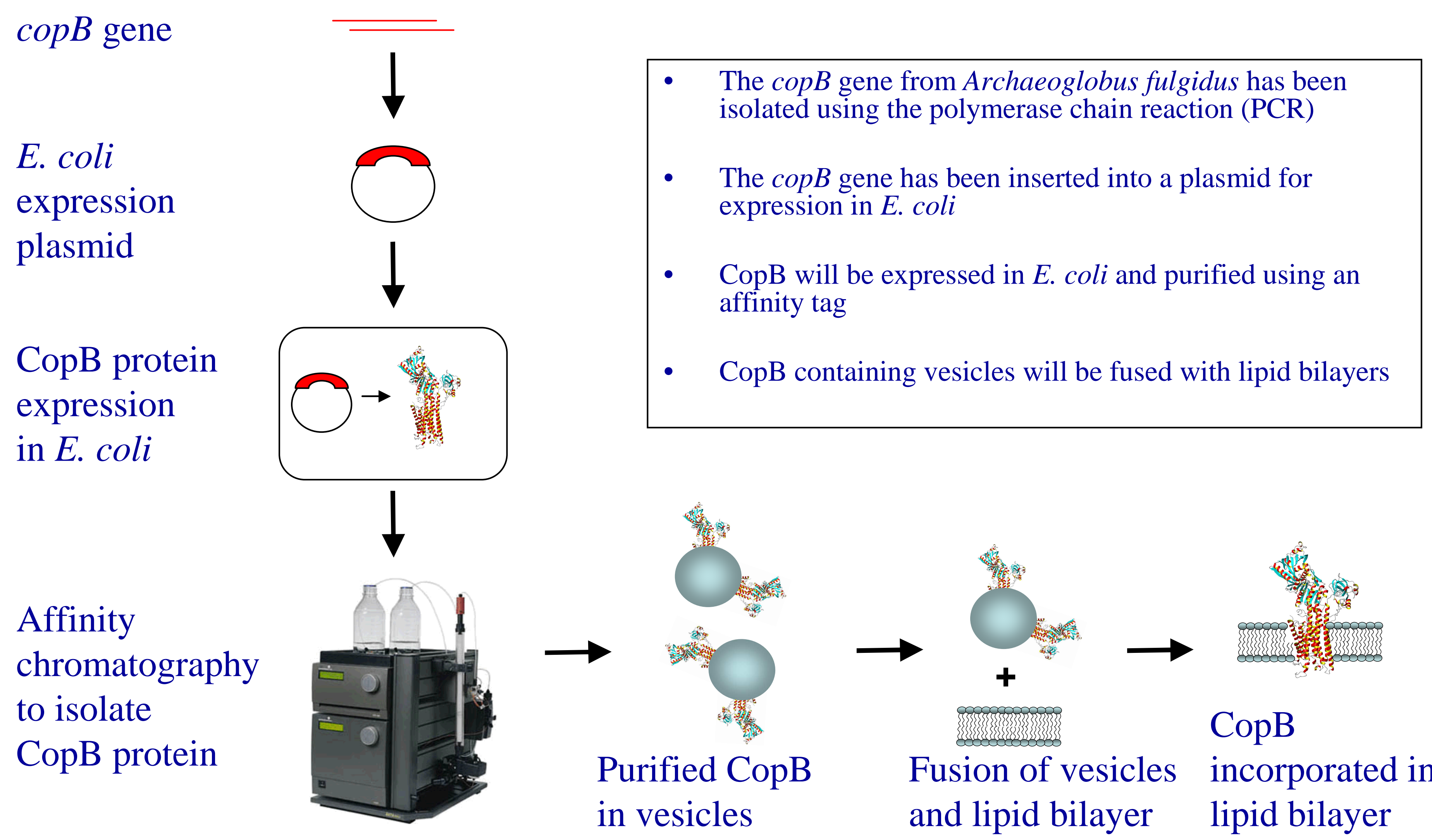


Methods and Approach

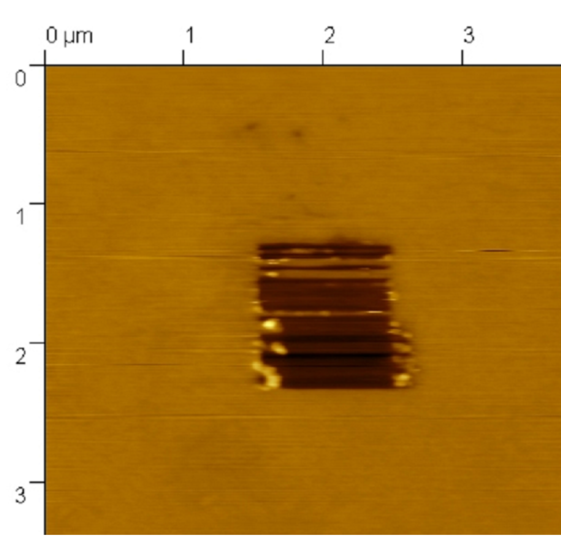
Metal Transport Proteins:
CopB from *Archaeoglobus fulgidus*

- Recombinant protein purified from *E. coli*
- Cu(II) transport activity in artificial membranes
- Energy source: Adenosine triphosphate (ATP)
- Enhanced stability at room temperature

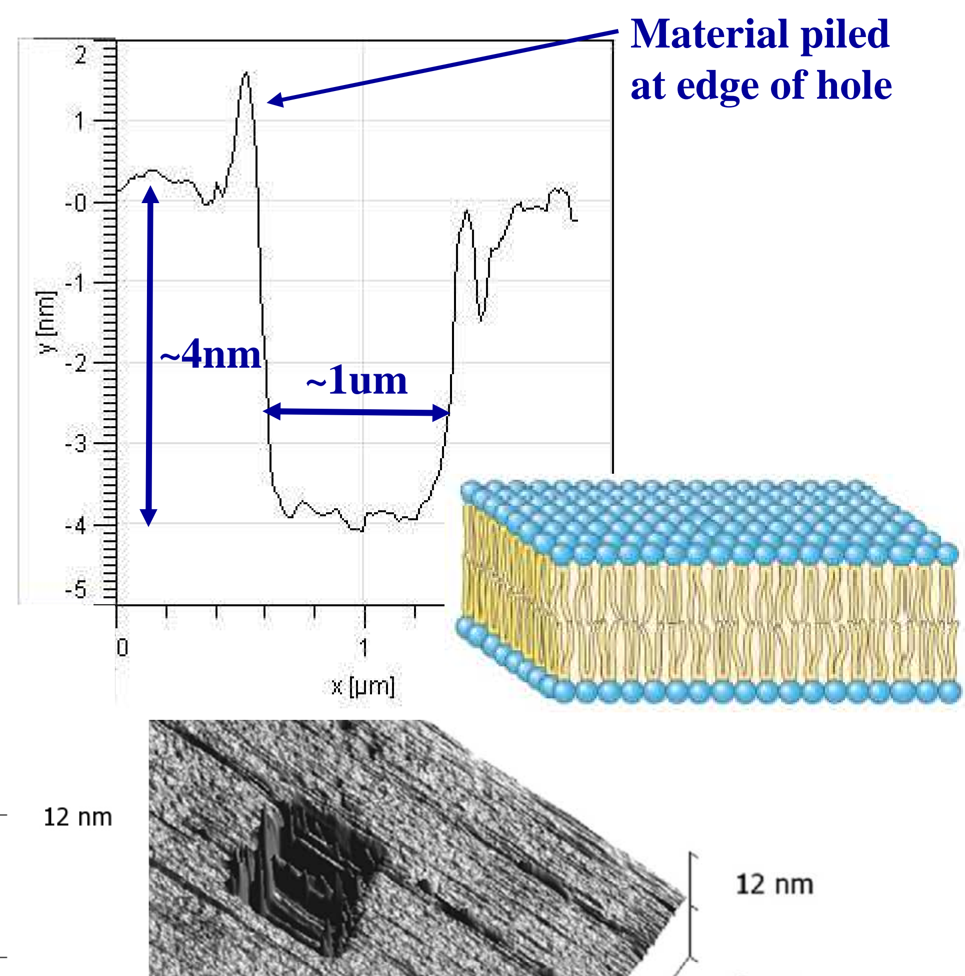
Preparation of CopB

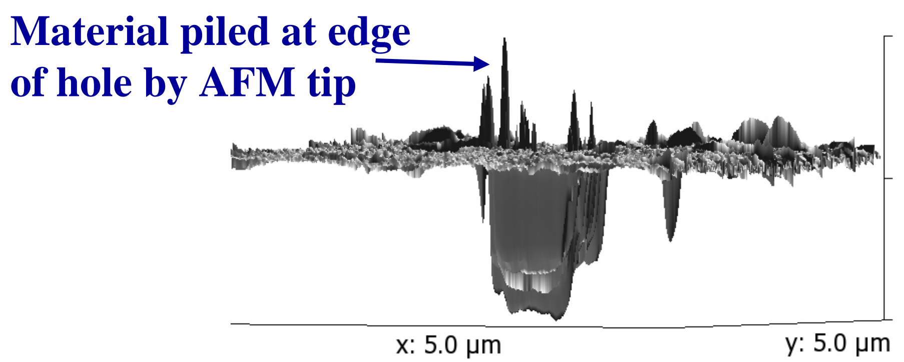


Bilayer Deposition



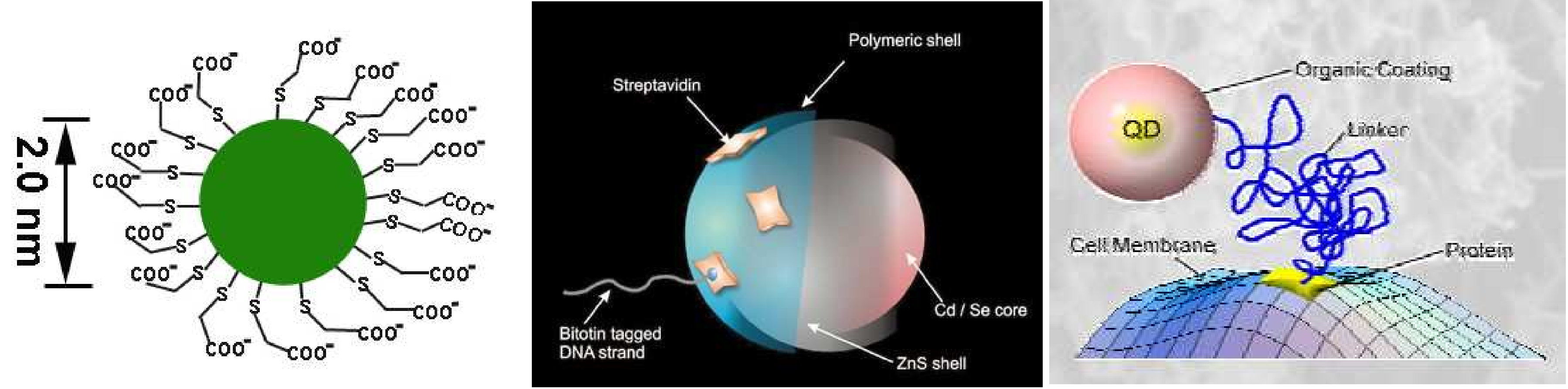
1um square hole dug in lipid membrane. Observe smooth bilayer surface. Note excess material piled at edge of hole.





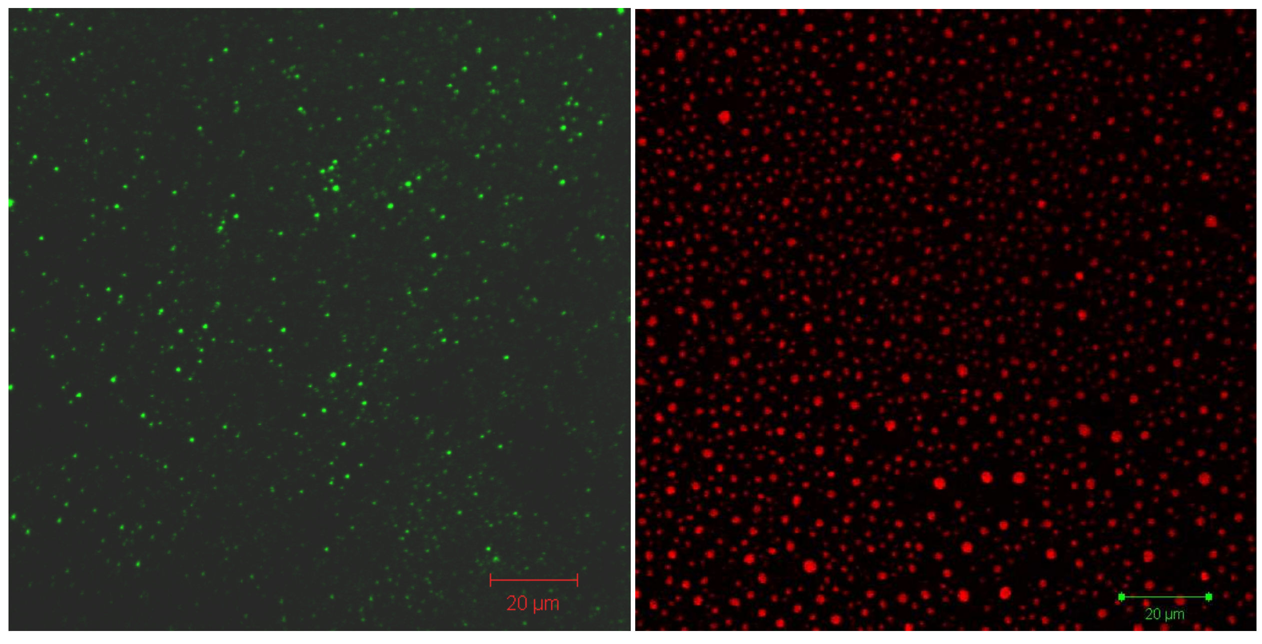
3D representations of hole dug in bilayer.

Link Quantum dots to proteins



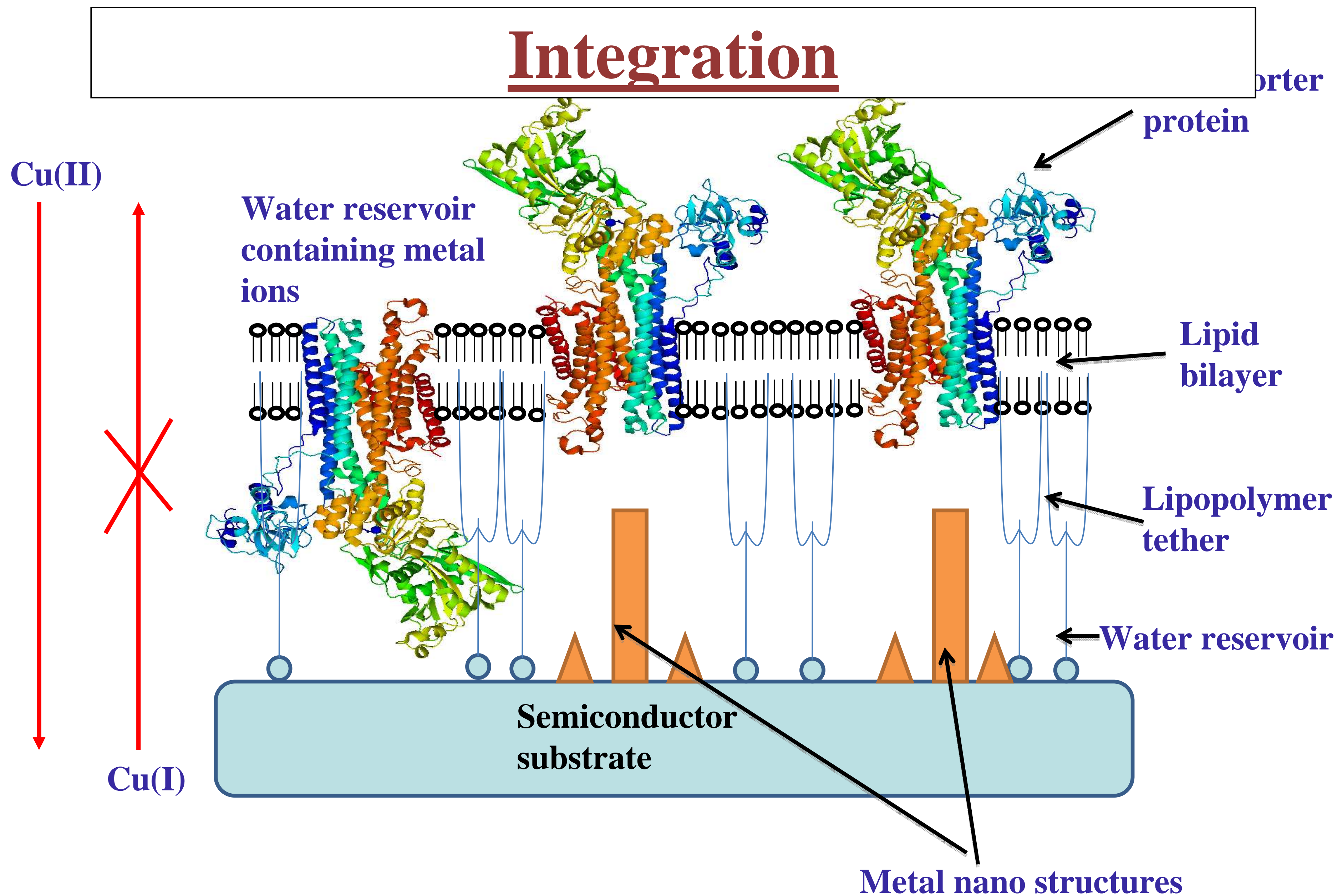
(Left) Single quantum dot terminated with COOH groups
(Middle) Functionalized quantum dot
(Right) Quantum dot attached to protein with linker

Image Q-dots with Confocal Fluorescent Microscope



(Left) Confocal fluorescent microscopy image of the green emission from CdSe quantum dots.
(Right) Confocal fluorescent microscopy image of the red emission from CdTe quantum dots.

Integration



Surface Patterning

(ii) Surface Functionalisation

(iii) Lipid Bilayer Addition

Attachment of lipid bilayer to surface.

(i) Surface Preparation

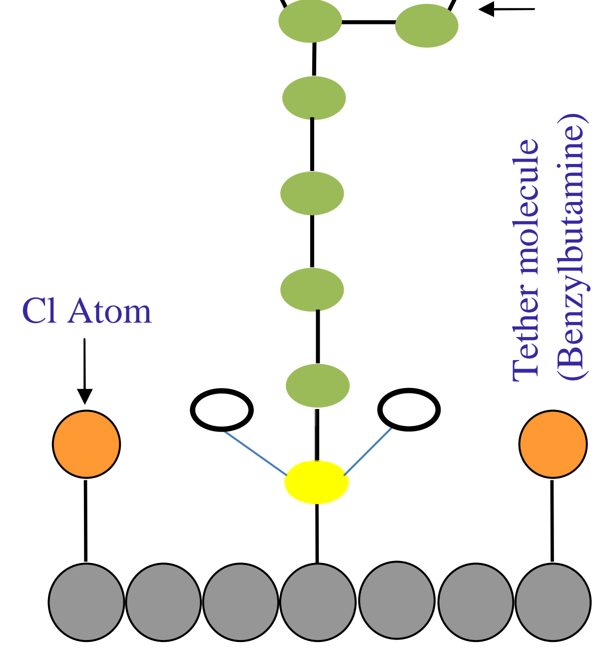
Cleaning performed by chemical etching.

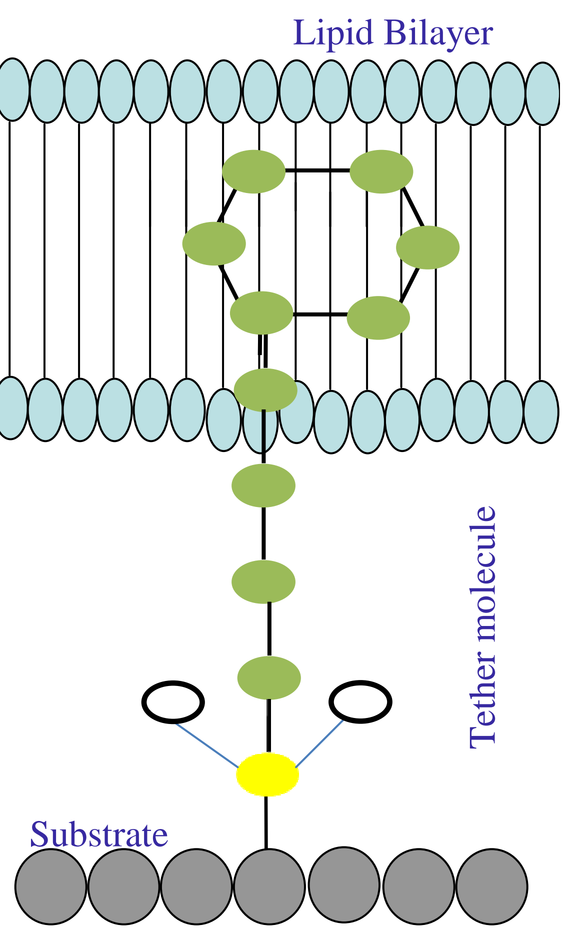
Characterised via XPS, AFM,TPD.

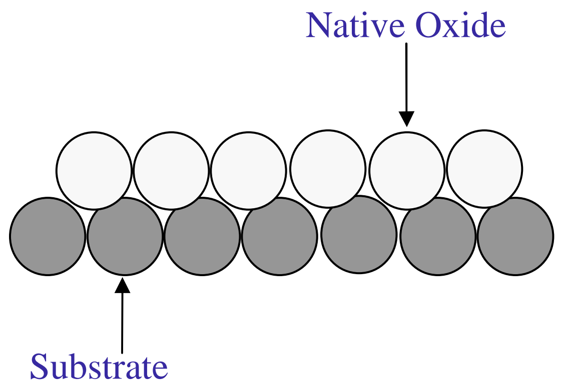
Possible Substrates for Use

Si, Ge, GaAs, InAs, InP, InSb

Tertiary Materials.







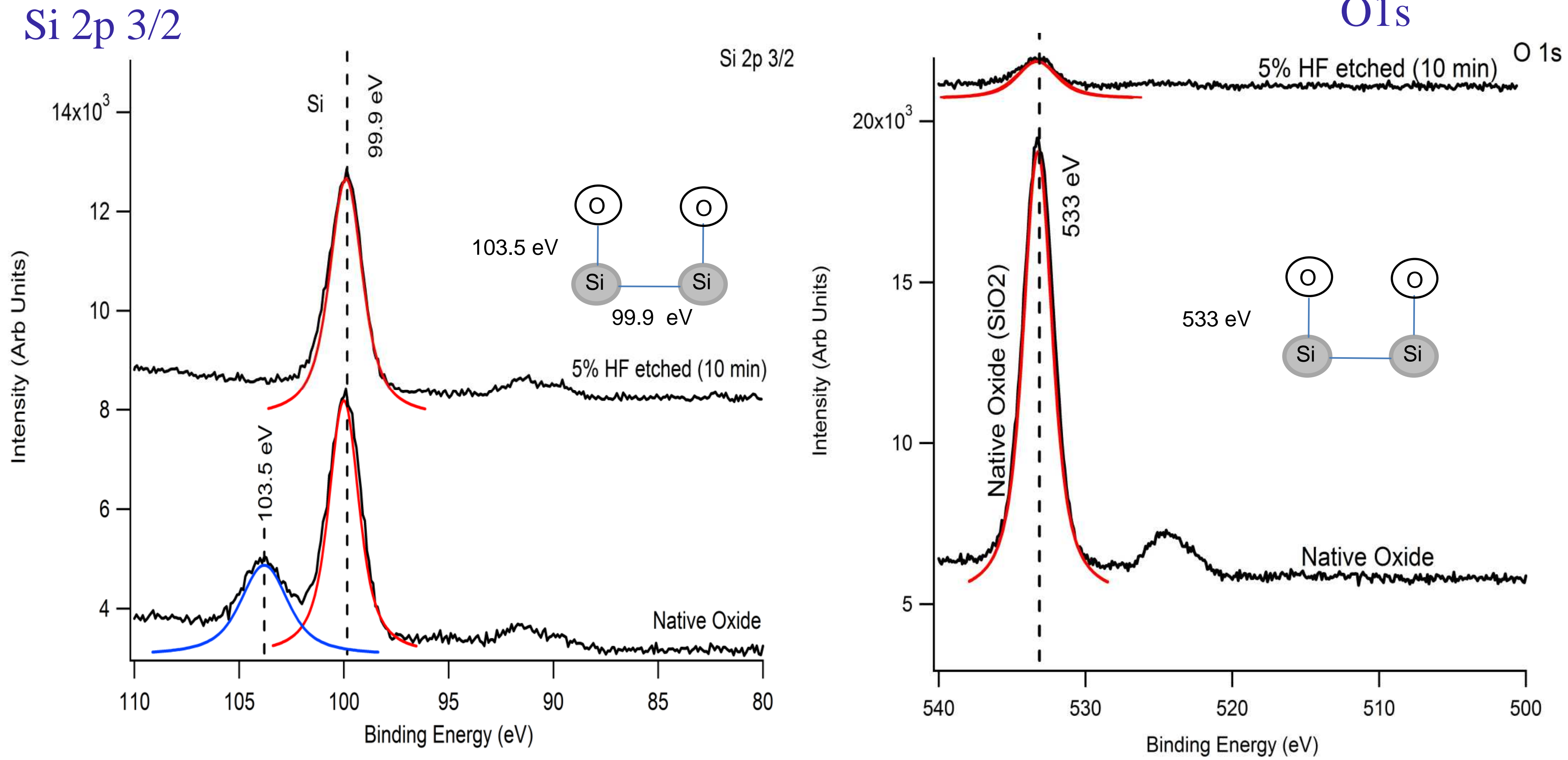
Surface chemistry used to modify surface and to introduce patterning and tether molecules to attach lipid bilayer

Types of Chemistry

Patterning Step: UV/Cl_2, NH_3

Tethers = Amines (dibutylamine, ethylamine), Benzene, Pyridine.

Si (100) Surface Characterization

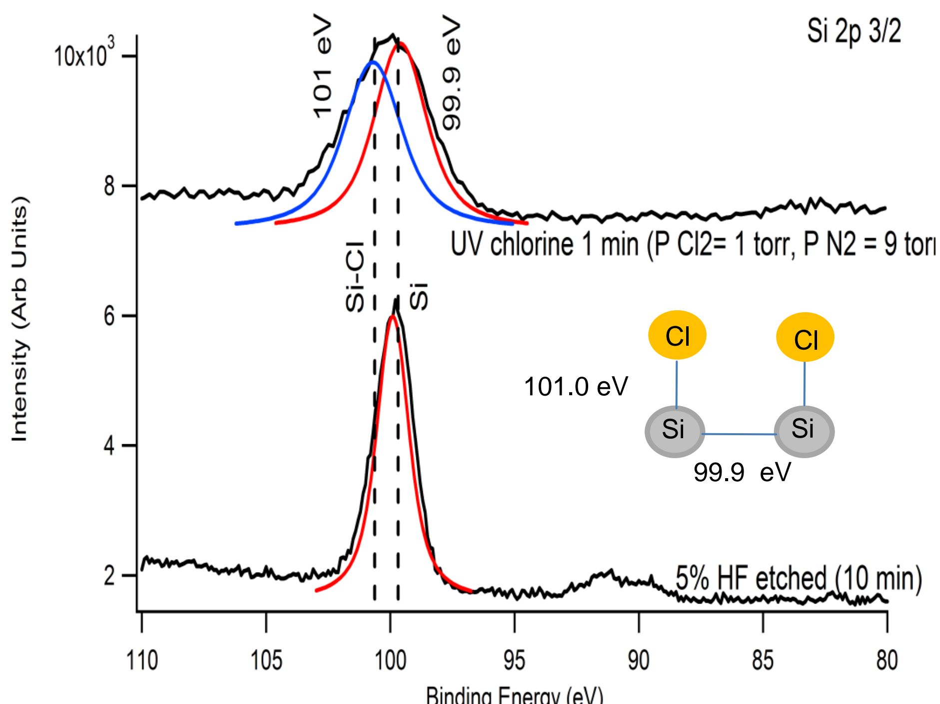


Si 2p 3/2 = 2 main features
103.5 eV = Native oxide (SiO_2)
99.9 eV = Si
After etching 103.5 eV peak removed = Native oxide removed

O 1s = Strong oxide signal present before HF etching (533 eV).
After HF etching oxide peak dramatically reduced
Applied Surface Science (2007), 253(18), 7387-7392

UV/Cl_2 on Si(100) Surfaces

Si 2p 3/2



UV/Cl_2 conditions:
p_{Cl} = 1 torr, p_N = 9 torr
Exposed HF etched sample to mixture with350 nm UV light for 1 min

Cl 2p spectrum shows presence of Cl on the HF etched Si substrate after exposure to UV/Cl_2
200 eV = Cl 2p 3/2, 201.8 eV = Cl 2p 1/2.

Post Cl exposure 2 features are noticeable in Si 2p 3/2 spectrum
99.9 eV = Si, 101 eV = SI-Cl

Cl 2p

Cl 2p
Intensity (Arb Units)
8000
7000
6000
5000
4000
201.8 eV
200 eV
2p 1/2
2p 3/2
210
205
200
195
190
Binding Energy (eV)

Industrial Interactions and Technology Transfer

- Presentation on liquid and gas phase cleaning of high mobility substrates to SEZ
- Jeremy Klitzke from SEZ visiting scientist at UA
- ALD film growth development with ASM

Future Plans

Next Year Plans

- Liquid and gas phase cleaning of high mobility substrates
- ALD film nucleation on high mobility substrates
- Express CopB protein
- Demonstrate chemically patterned surface
- Attach membrane to patterned surface and build structures
- Characterize proteins and structures using q-dots

Long-Term Plans

- Develop characterization techniques for nanostructures
- Demonstrate patterned nanostructures over cm length scale

Novel Approach for Building Patterned Copper Nano-interconnects by Self-Assembly, Selective Photoactivation and Deposition *(Proposed project)*

PI:

- **Roberto Guzman, Chemical and Environmental Engineering, UA**

Graduate Students:

- **2, PhD candidates, Chemical and Environmental Engineering**

Undergraduate Students:

- **2, Chemical and Environmental Engineering**

Other Researchers:

- **1, Postdoctoral Fellow, Chemical and Environmental Engineering**

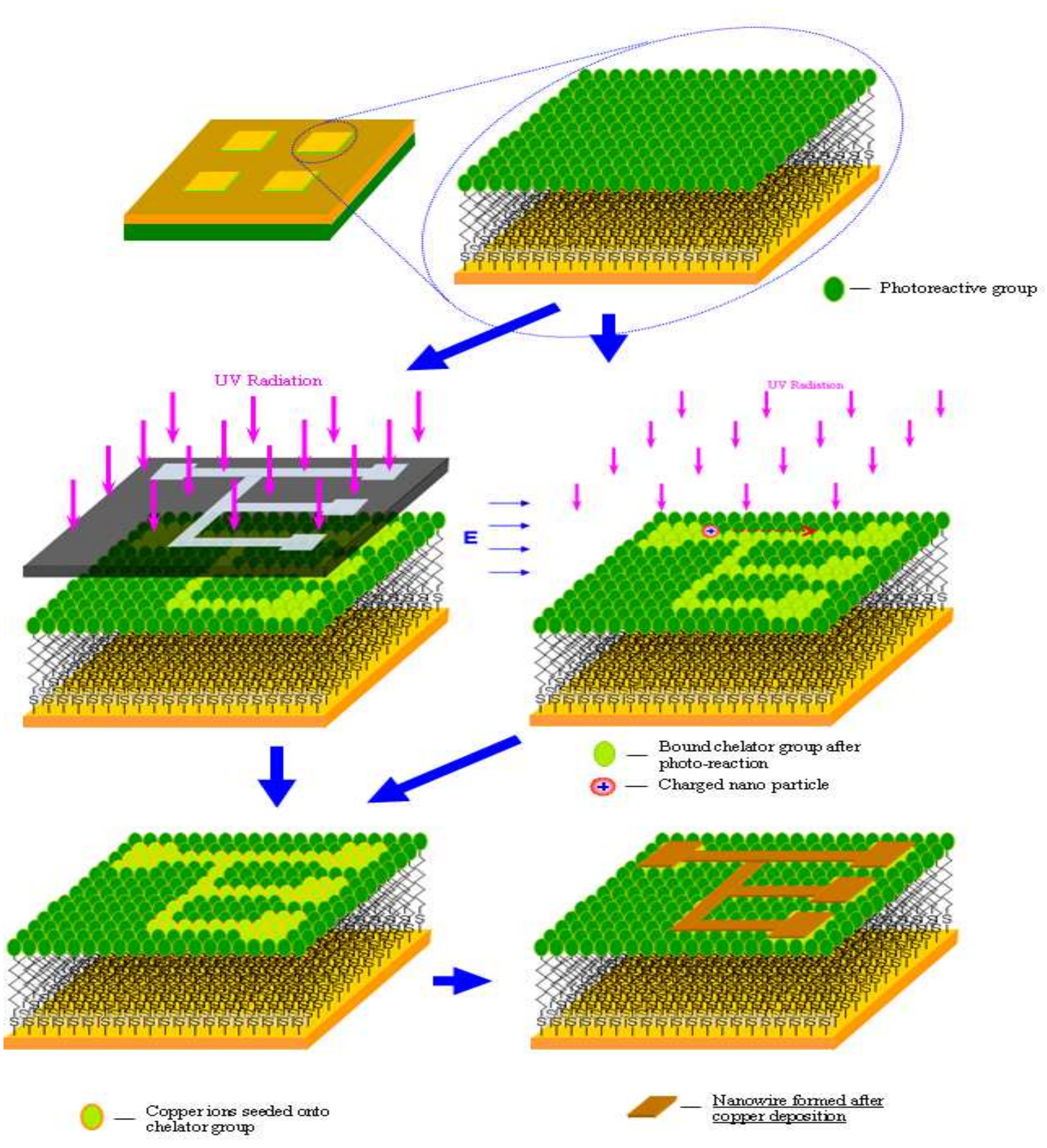
Objectives

- Development of patterned silicon oxide surfaces at the nanoscale for the formation of copper nanointerconnects (from 5-20 nanometers width)

•To accomplish such objective the following tasks will be performed

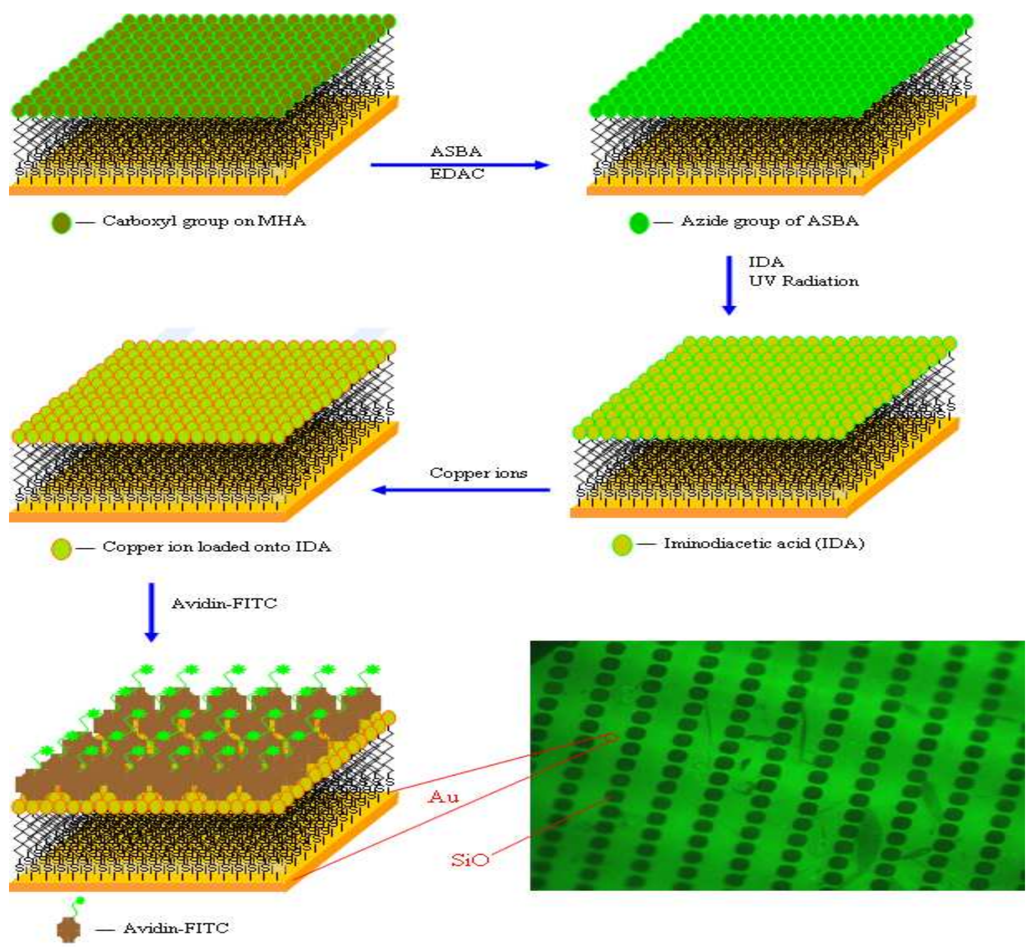
- **Activation of silicon oxide surfaces**
  - **Self-assembly and self-assembled monolayers in micro/nanoscale**
  - **Activation with photoreactive species (azide derivatives)**
- **Patterning/Positioning of reactive species:**
  - **By using quantum dots or carbon nanotubes as templates or guides**
  - **Using UV light to selectively photocatalyze activation of nano patterned structures to obtain amine or carboxylic acid species**
- **Incorporation of binding agents (e.g. chelating agents)**
  - **Attachment of specific chelating agents including imino diacetate derivatives (e.g. IDA, TREN, TED).**
- **Copper nanowire formation**
  - **Deposition/binding of metallic ions**
  - **Reduction of metal ions for a continuous layer metal line deposition**
- **Passivation of remaining photoreactive species on surface**
  - **Reactivation of remaining photoreative species**
  - **Passivation of surface with insulating ionic species**

Schematic Process for Patterned Copper Nano-interconnects by Self-Assembly, Selective Photoactivation and Deposition

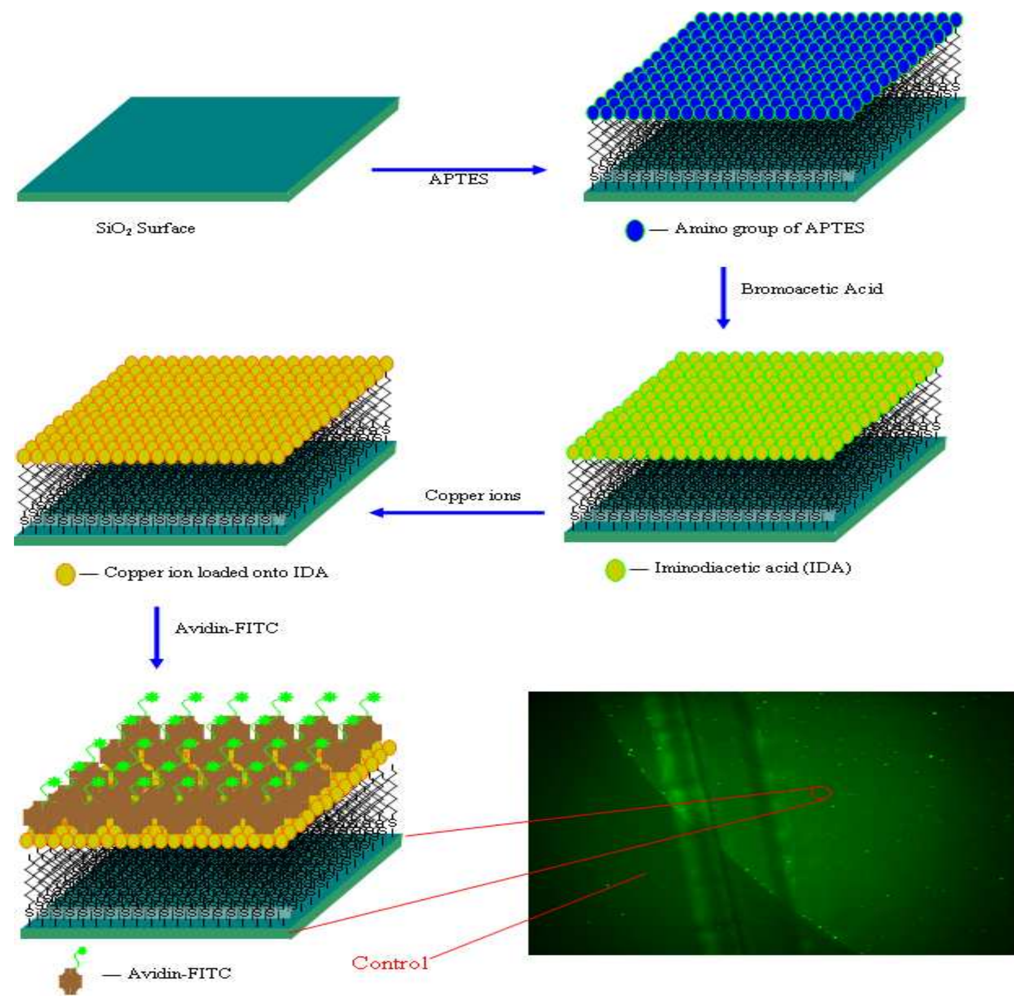


Preliminary Results

1) Deposition of copper on Au surface as evidenced by copper binding to fluorescent derivatized proteins



2) Deposition of copper on silicon oxide surface as evidenced by copper binding to fluorescent derivatized proteins



Lowering Material and Energy Usage during Purging of Gas Distribution Systems

Customized Project; Sponsored by Intel Corporation

Co-PIs

Farhang Shadman, Chemical and Environmental Engineering, UA
Carl Geisert, Intel Corporation

Graduate Students

Junpin Yao, Chemical and Environmental Engineering, UA
Harpreet Juneja, Chemical and Environmental Engineering, UA
Asad Iqbal, Chemical and Environ Eng, UA; graduated (PhD 2008); joined Intel

Cost Share:

Intel Corporation, Arizona

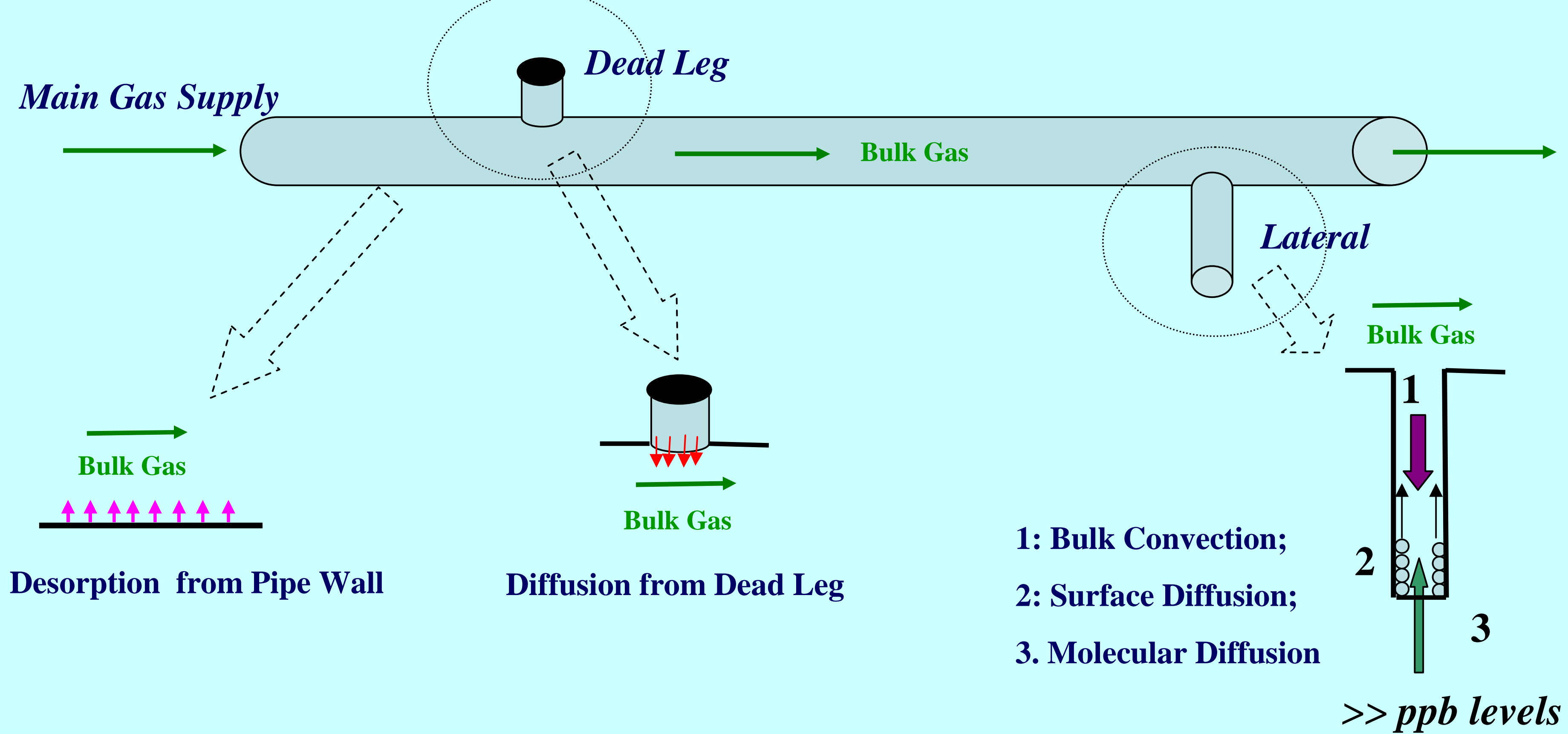
Objectives

- Develop methods to analyze contamination ***introduction*** and ***removal*** in ultra-pure gas distribution systems

ESH Impact

- Contamination of gas distribution systems during operation or at start-up is a major source of wasted time, materials, and energy.
- Significant reduction in purge time and gas usage can be accomplished by optimizing purge and cleaning processes, based on the project results.

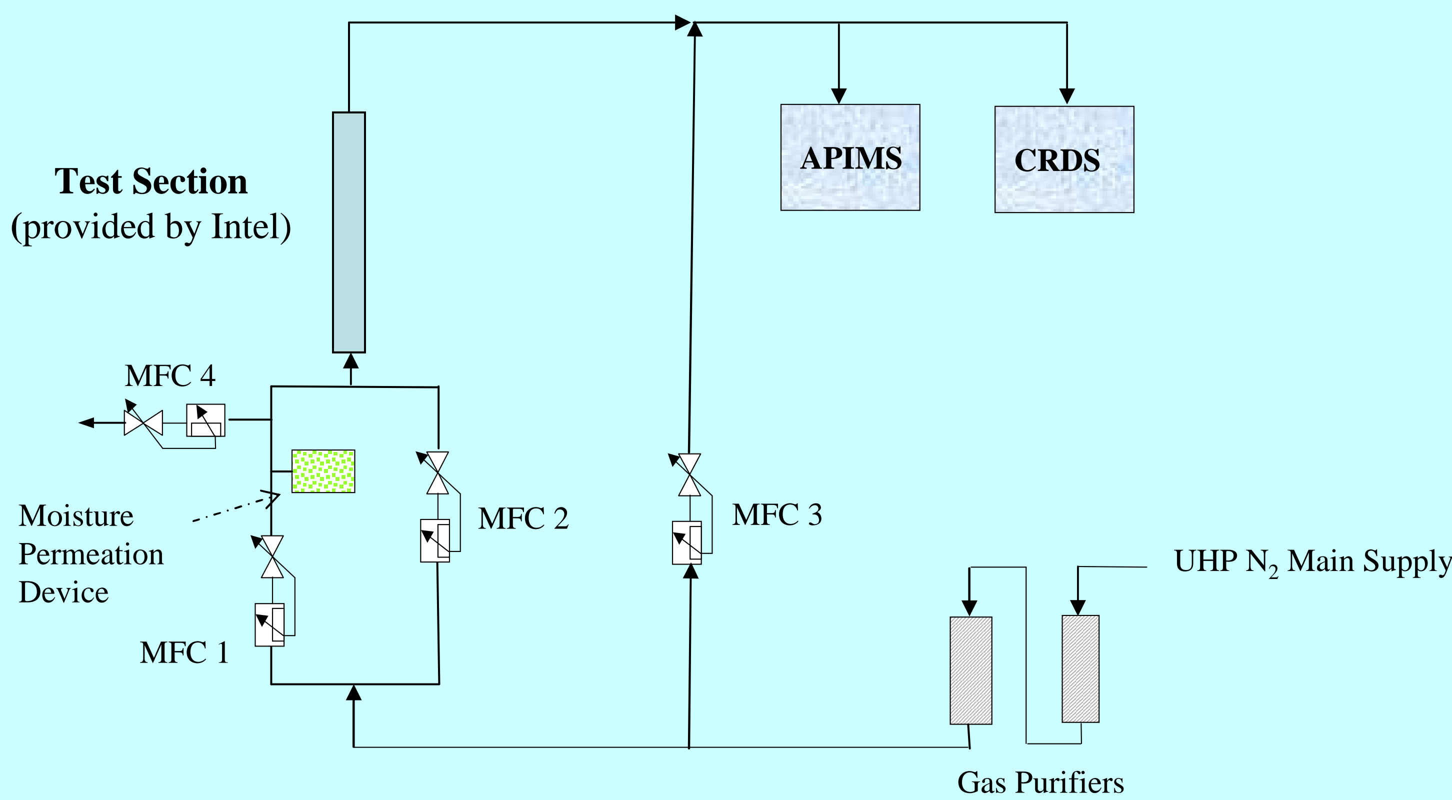
Potential Major Sources of Contamination in Gas Distribution Systems



>> ppb levels

Diffusion from dead legs, desorption from pipe wall and back diffusion from ambient can cause contamination to the whole gas delivery system.

Experimental Setup

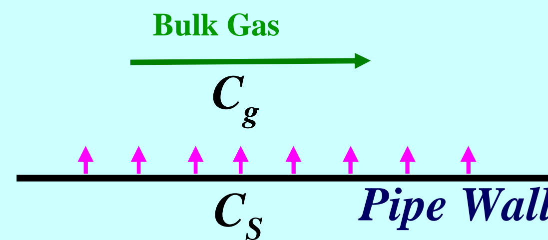


- **Atmospheric Pressure Ionization Mass Spectrometer (APIMS)**
- **Cavity Ring Down Spectroscope (CRDS)**

Adsorption and Desorption on Pipe Surfaces

Change of moisture concentration on pipe wall:

$$\frac{\partial C_S}{\partial t} = k_{ads} C_g (S_0 - C_S) - k_{des} C_S$$



- **Surface adsorption/desorption**
- **Bulk convection**

Change of moisture concentration in gas phase:

$$\frac{\partial C_g}{\partial t} = D_L \frac{\partial^2 C_g}{\partial z^2} - u \frac{\partial C_g}{\partial z} + \frac{A_S}{V} (k_{des} C_S - k_{ads} C_g (S_0 - C_S))$$

C_S: moisture concentration on pipe wall, mol/cm^2; C_g: moisture concentration in gas, mol/cm^3;

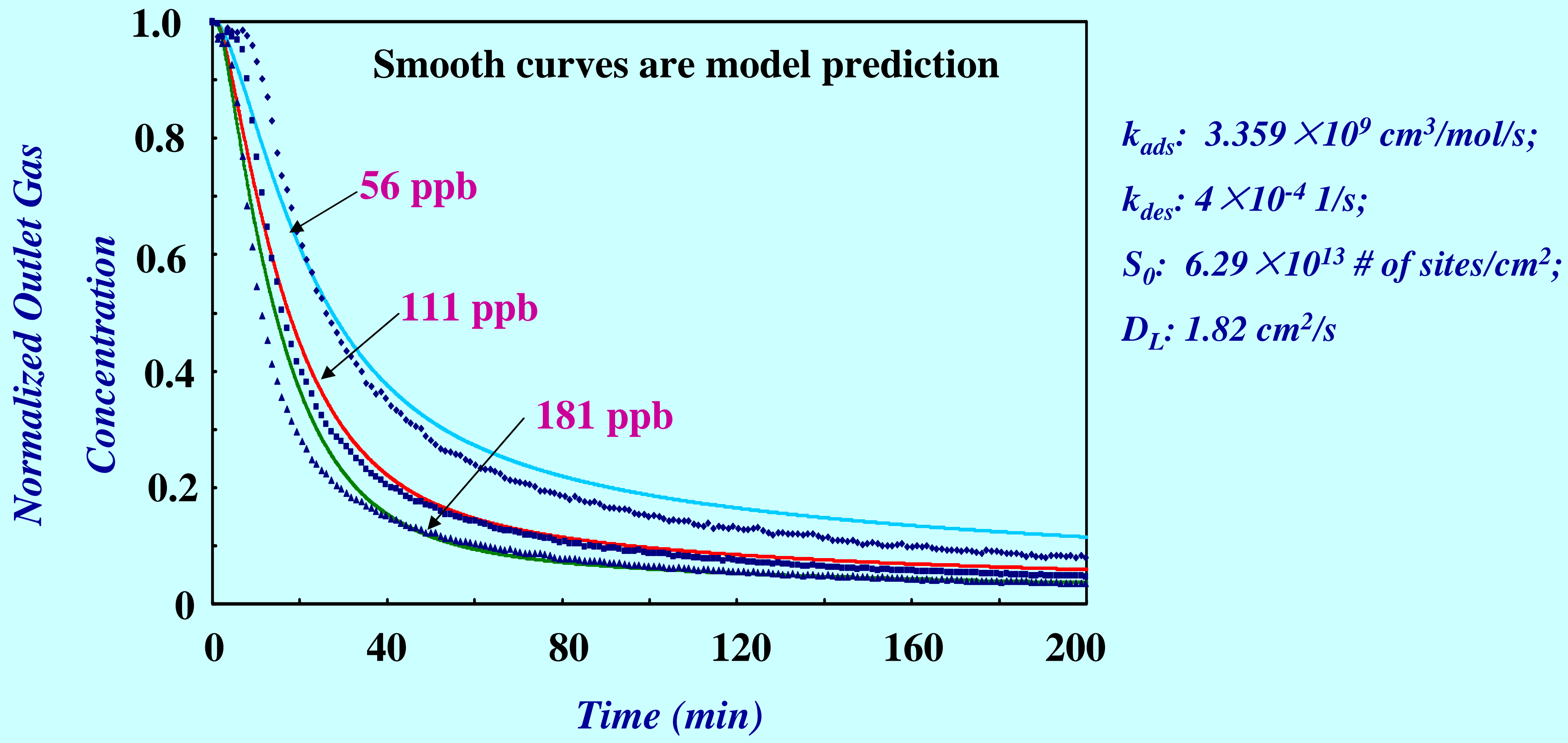
k_{ads}: adsorption rate constant, cm^3/mol/s; k_{des}: desorption rate constant, 1/s

S_0: site density of surface adsorption, mol/cm^2; D_L: dispersion coefficient, cm^2/s;

u: velocity, cm/s; A_S: surface area of pipe wall, cm^2; V: volume of pipe, cm^3

Model Validation and Parametric Estimation

Test Section: EPSS pipe with 1.5 inch OD and 14 inch length. Initially the whole system was equilibrated with different concentrations of moisture at 25 ^{0}C. Isothermal purge with 1 ppb purge gas; purge gas flow rate: 350 sccm



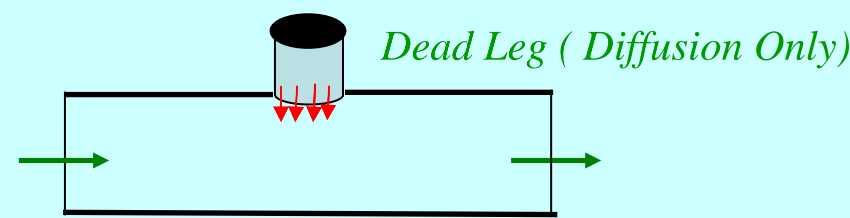
k_{ads}: 3.359×10^9 $cm^3/mol/s$;

k_{des}: 4×10^{-4} $1/s$;

S_0: 6.29×10^{13} # of sites/cm^2;

D_L: 1.82 cm^2/s

Contamination from Stagnant Regions



Moisture concentration in bulk gas:

$$\frac{\partial C_g}{\partial t} = D_L \frac{\partial^2 C_g}{\partial z^2} - u\frac{\partial C_g}{\partial z} + \frac{A_S}{V}(k_{des} C_S - k_{ads} C_g (S_0 - C_S))$$

Moisture concentration in dead leg:

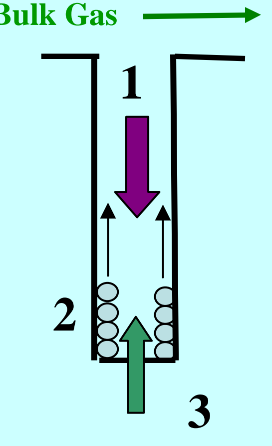
$$\frac{\partial C_{gD}}{\partial t} = D_0 \frac{\partial^2 C_{gD}}{\partial z^2} + \frac{A_{SD}}{V_D}(k_{des} C_{SD} - k_{ads} C_{gD} (S_0 - C_{SD}))$$

Boundary condition at the intersection of dead leg and main pipe:

$$(-D_L \frac{\partial C_{g\mathrm{I}}}{\partial x} + u_{\mathrm{I}} \cdot C_{g\mathrm{I}}) + \frac{A_{cD}}{A_{cm}}(-D_0 \frac{\partial C_{gD}}{\partial z}) = -D_L \frac{\partial C_{g\mathrm{II}}}{\partial x} + u_{\mathrm{II}} \cdot C_{g\mathrm{II}}$$

Moisture removal in dead leg is much slower than that in main pipe since only diffusion is involved in mass transport mechanism.

Contamination from Back Diffusion



$C_{g0} >> ppb$ *levels*

1: Bulk Convection;

2: Surface Diffusion;

3. Molecular Diffusion

Bulk gas:

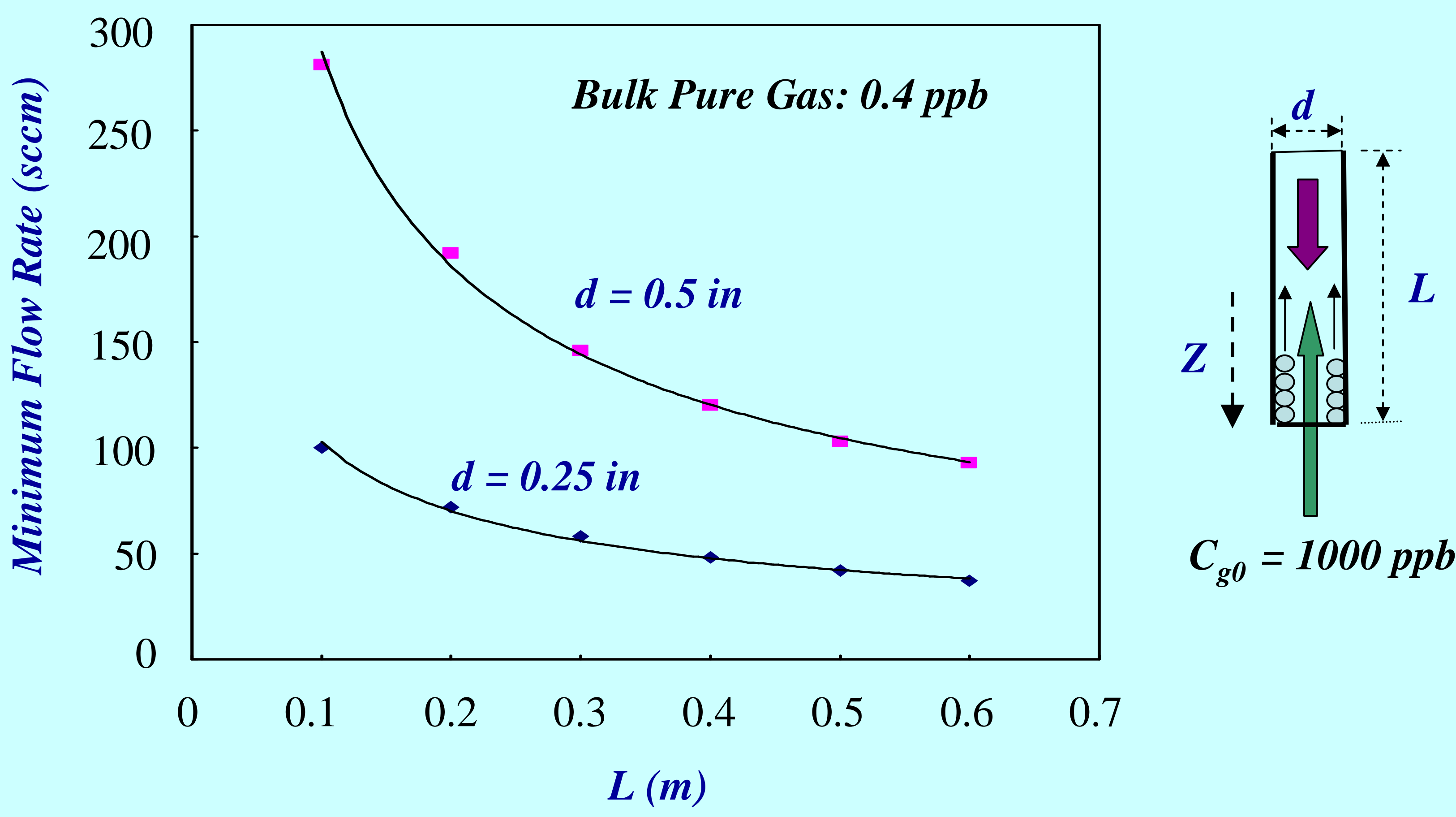
$$D_L \frac{\partial^2 C_g}{\partial z^2} - u \frac{\partial C_g}{\partial z} + \frac{A_S}{V}(k_{des} C_S - k_{ads} C_g (S_0 - C_S)) = 0$$

Surface reaction and surface diffusion:

$$D_S \frac{\partial^2 C_S}{\partial z^2} + k_{ads} C_g (S_0 - C_S) - k_{des} C_S = 0$$

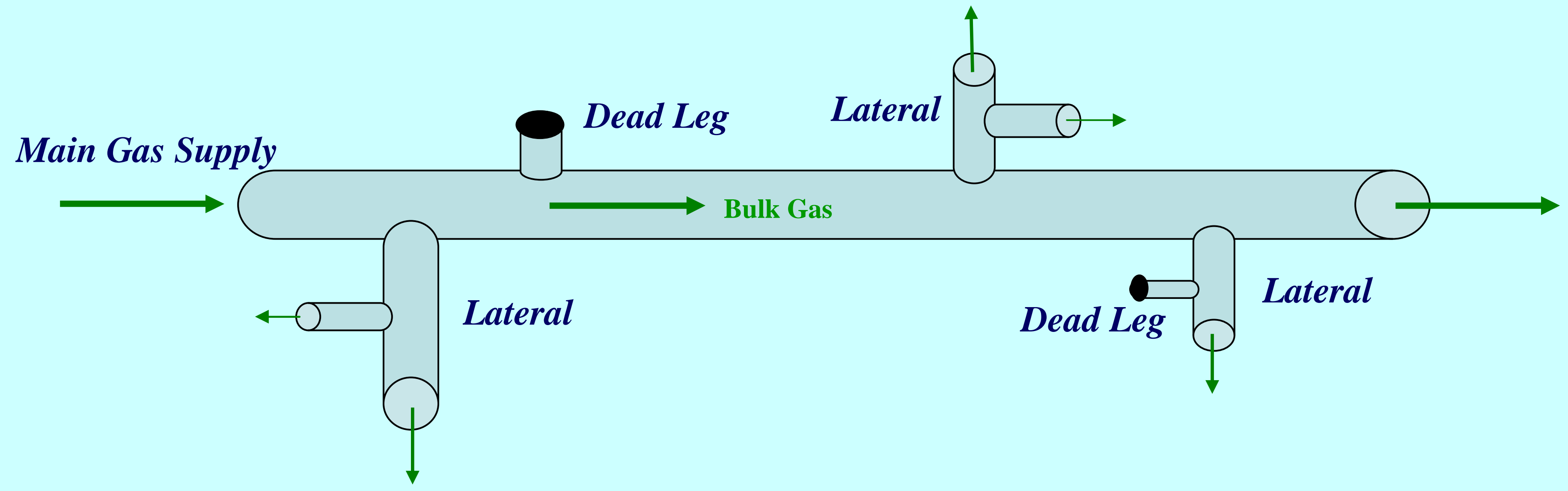
D_S: Surface diffusion coefficient, cm^2/s; C_{g0}: ambient moisture concentration , >> 1 ppb;

Minimum Flow to Block Back Diffusion



1. The required minimum flow decreases as the length of open lateral increases.
2. Large size lateral needs higher critical flow rate than small size lateral.

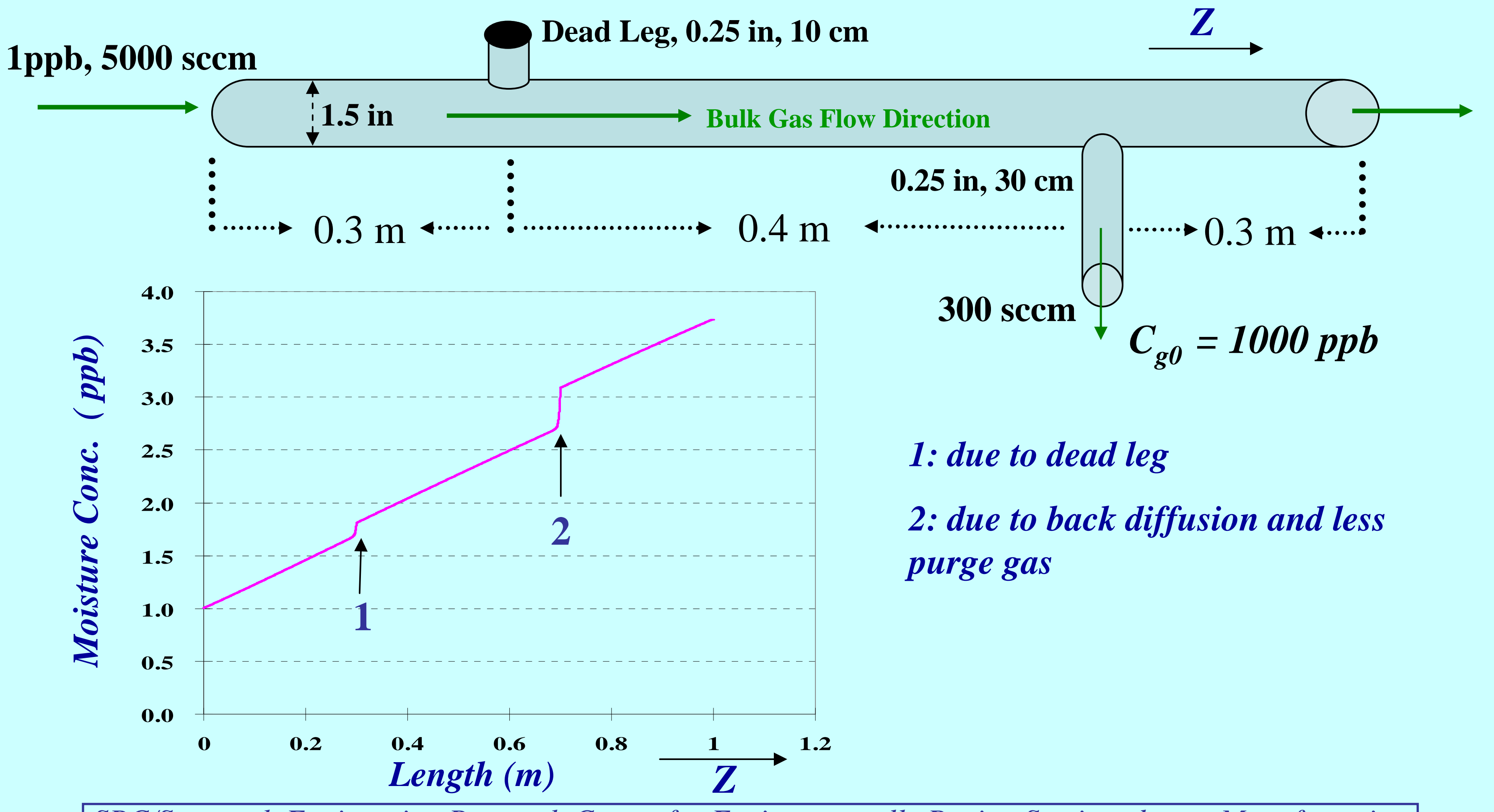
Comprehensive Model for Predicting Moisture Distribution in Gas Delivery Networks



1. The distribution profiles and removal of moisture in main pipe and laterals
2. The effects of dead legs and back diffusion on moisture concentration in main stream

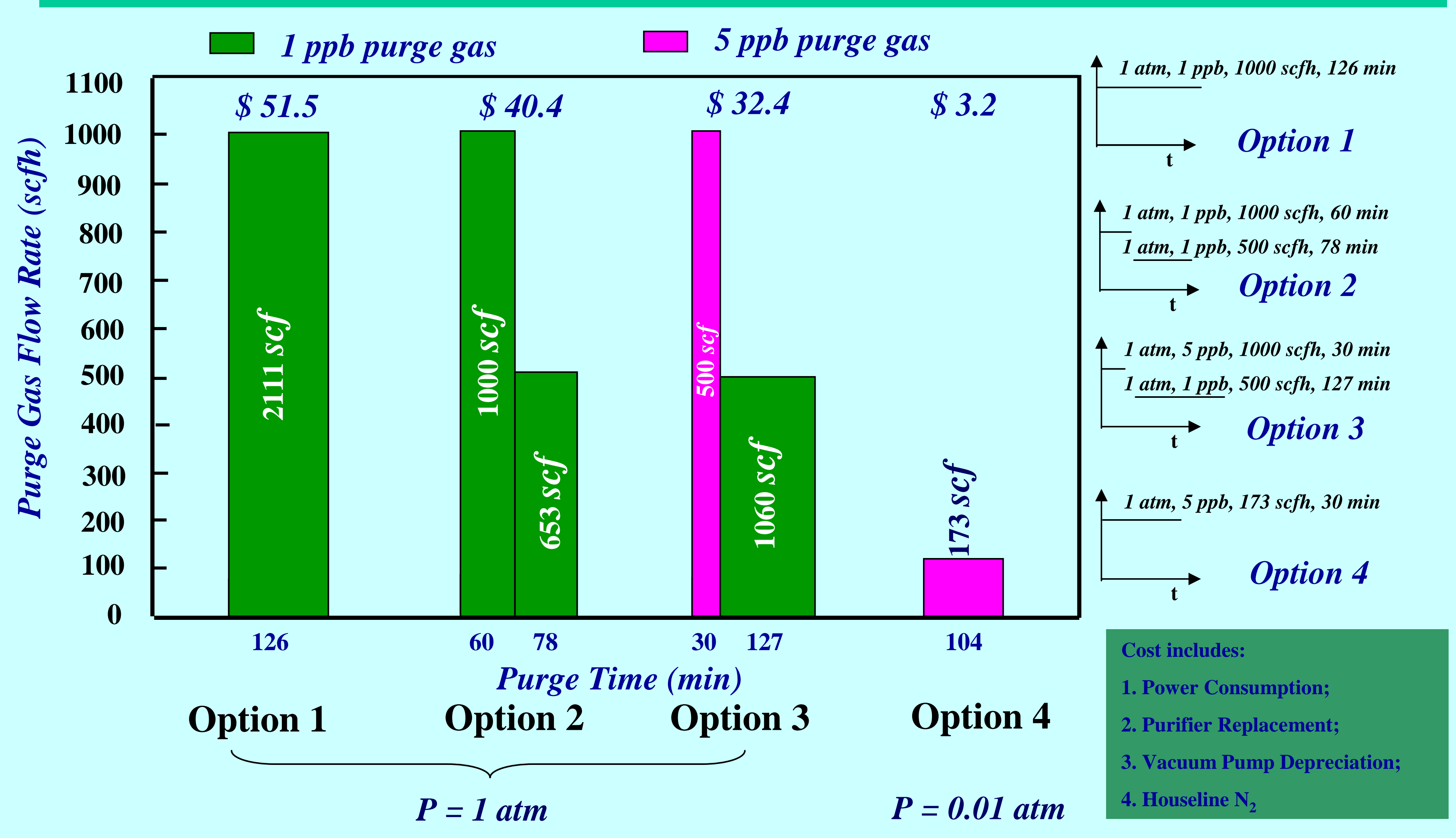
An Example of Model Application

Sample: One main pipe with one dead leg and one open lateral. Initially the whole system was equilibrated with 200 ppb of moisture at 25 ^{O}C. Isothermal purge for 1 hr with 1 ppb purge gas, and total purge gas flow rate: 5000 sccm



Low-Impact Purge Strategies

Sample: 10 meter, 1.5 in OD; Initially was equilibrated with 200 ppb of moisture at 25 ^{O}C. Isothermal purge with different purge options



SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Interactions and Future Plans

- **Continue working with Intel on this customized joint project; initiate similar applications and studies for other members.**
- **Complete the development of a comprehensive model.**
- **Prepare a software package for use in industry.**

Electro-Coagulation Applied to Water Conservation and Wastewater Treatment

(*Customized Project)*

PIs:

- **James C. Baygents & James Farrell, Chemical and Environmental Engineering (ChEE), UA**

Graduate Students:

- **Matthew Schulz, M.S. Student, ChEE, UA**

Undergraduate Students:

- **Jake Davis, Ritika Mohan, Aaron Solt, Bryan Weaver & Devin Whipple, ChEE, UA**

Other Researchers:

- **Brian P. Chaplin, Zheng Gu & Zhaohui Liao, Postdoctoral Fellows, ChEE, UA**

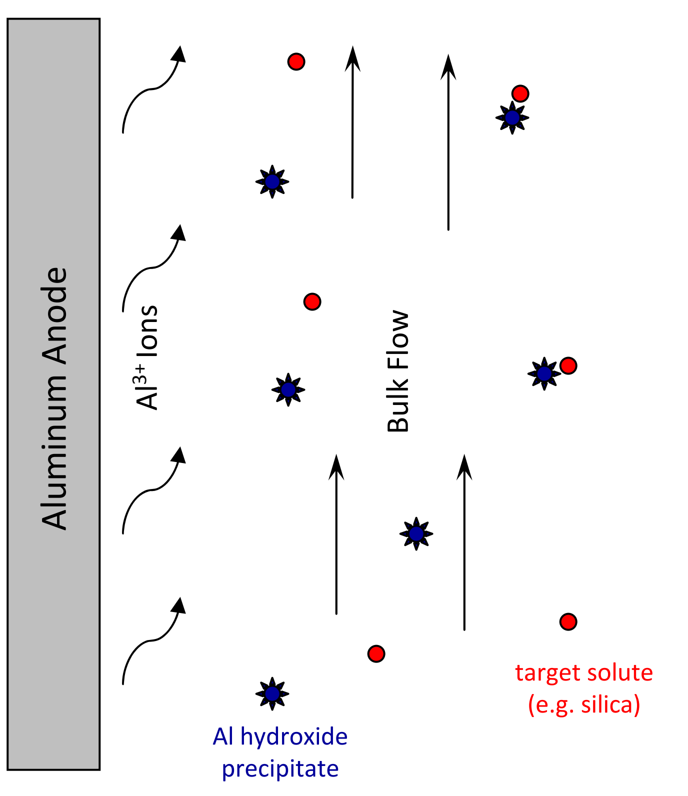
Industrial Collaborators:

- **Allen R. Boyce, Avi Fuerst & Zoe Georgousis, Intel Corporation**

Cost Share (other than core ERC funding):

- **July 06–June 09: $150k from Intel Corporation; $225k from UA TRIF/WSP**
- **Feb 07–Jan 08: $50k from Arizona Water Institute**
- **3 summer internships ($12 to $15k ea.) from Intel**
- **$20k electrocoagulation (EC) bench units from Intel; use of $200k EC pilot unit at Intel**

Objectives



Metal anode dissolution is coupled to a complementary cathodic reaction that generates OH^-

EC is thus a **salt-free** process that avoids the added counterions of standard coagulating agents, such as $Fe(Cl)_3$ and $Al_2(SO_4)_3$

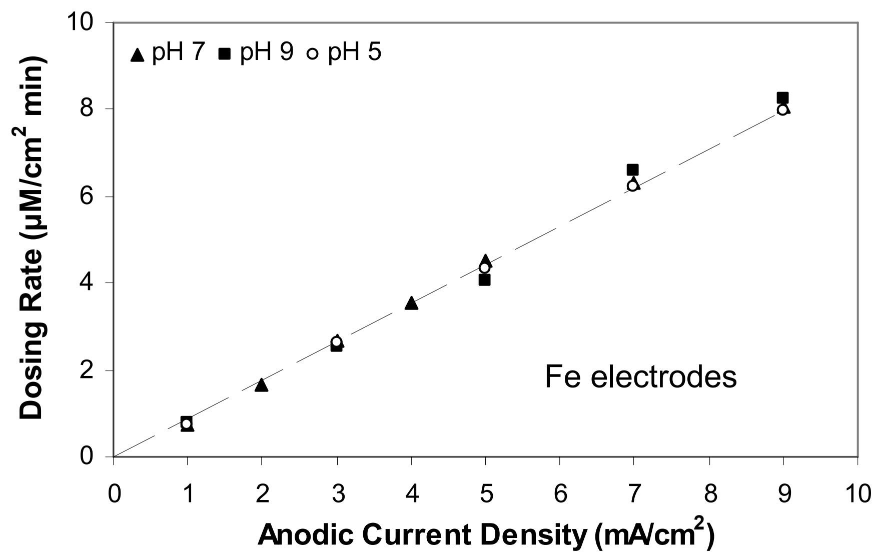
- **Assess electrocoagulation (EC) as a robust water treatment technology compatible with water re-use and recycle, especially as it pertains to semiconductor process waters**
- **EC assessment to include:**
  - **coagulant dose delivered as function of anodic current, etc.**
  - **contaminant removal as function of coagulant dose and post-EC separation method**
  - **energy and material costs to deliver coagulant dose**

ESH Metrics and Impact

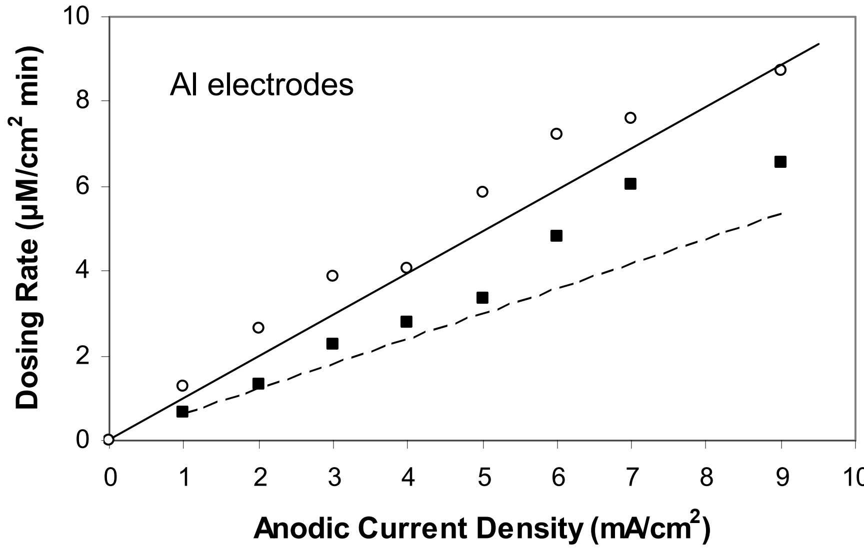
Application	Objective	Process	Projected[†] Water Recovery %
1. Cooling tower blowdown	< hardness, < silica biocontrol	EC, Clarifier	50%
2. RO Reject	< hardness, < silica, etc.	EC, UF, RO	50 %
3. Dilute Fluoride	< F^-, water discharge or reuse	EC, UF, RO	70%
4. Concentrated Fluoride	< F^-, < TDS, water discharge or reuse, solids biproduct to industrial use	EC, Clarifier, filter press, or EC, UF, RO	70%
5. CMP wastes: Cu^{2+}, CuO, W	discharge or water recycle	EC, Clarifier EC, UF	70%
6. Cu electrolytic wastes	discharge or water recycle	EC, Clarifier EC, UF	70%
7. Wafer thinning	< SiO_2 for recycle	EC, UF	95%
8. POTW Effluent	biotreatment, < organics and inorganics	EC, UF, RO	75%
9. Raw Water: well or surface	< hardness, < silica, < boron, < organics, < urea	EC, Clarifier EC, UF	90%
10. Ultrapure water recycle, FAB rinse waters	< organics, <silica, <F^-, < NH_3OH	EC, UF, RO	80%

[†] Intel projections at the outset of the project based on potential utility of EC as a water treatment technology.

Coagulant Dose as Function Anodic Current



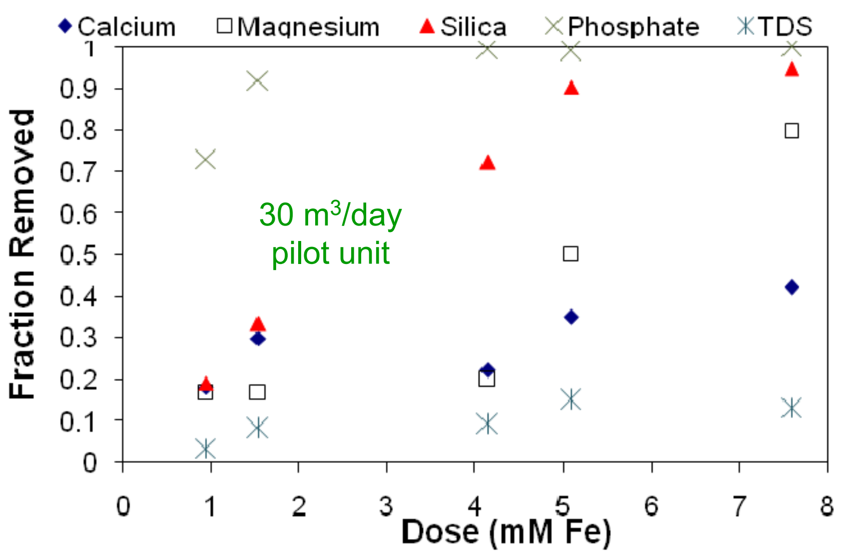
Dissolution rate of iron as a function of anodic current density using weight loss measurement under pH values of 5, 7 and 9.

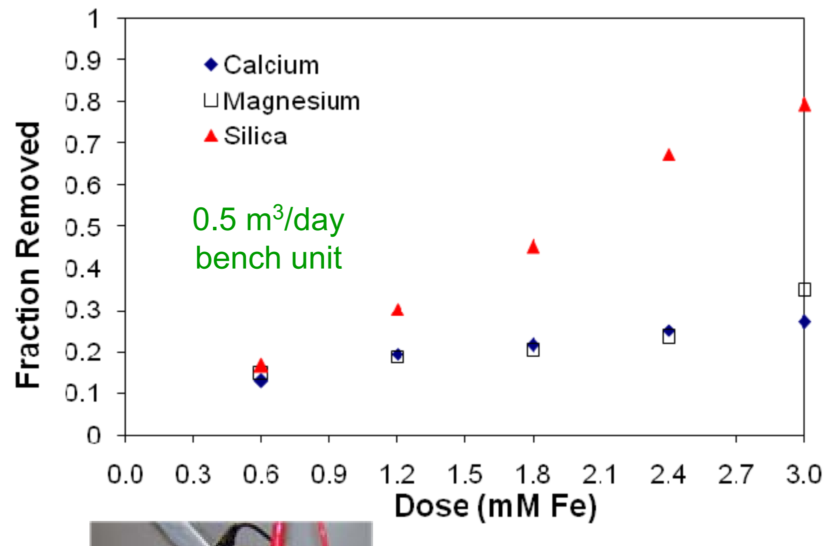


Dissolution rate of aluminum (square: anode; circle: anode + cathode) as a function of anodic current density using weight loss measurement.

Contaminant Removal: Pilot vs. Bench†

cooling tower blowdown from Intel Fab 20 in Hillsboro, OR





View of pilot skid with clarifier in the foreground, influent tank in left background and reactor in right background.

Overhead view of 30 m^3/day pilot EC reactor, showing iron electrodes, the overflow catch and drain.

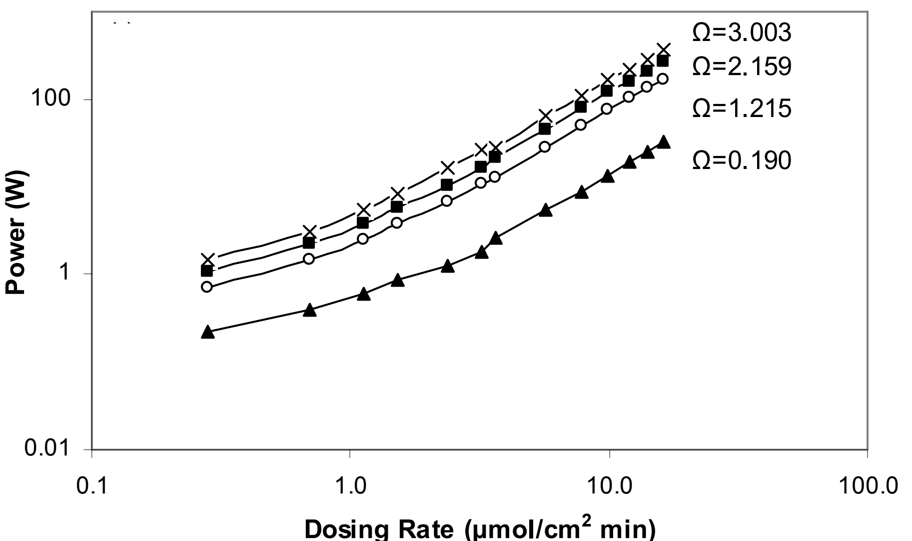
One-half m^3/day bench-scale EC reactor with aluminum electrodes attached to a power source.

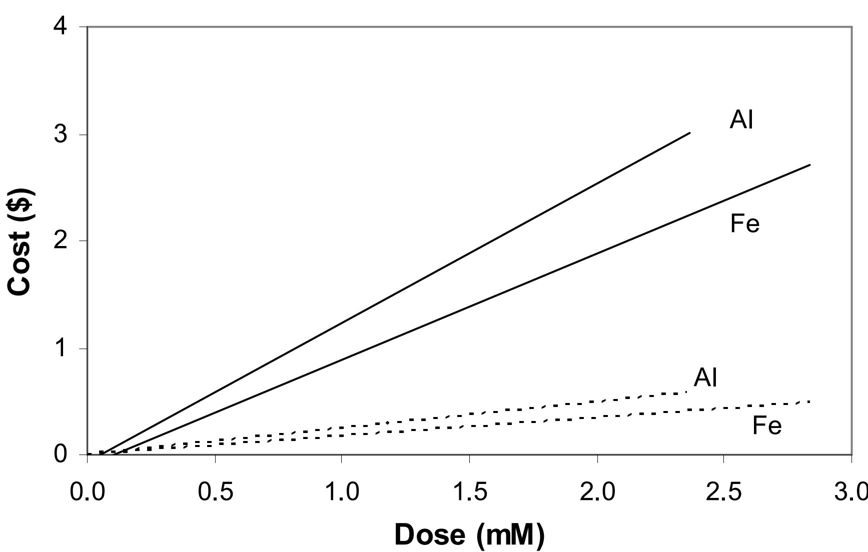
†Pilot and bench units give similar removals; coagulant dose is the key variable; have performed analogous studies on RO reject streams, obtaining similar results.

Power and Cost per Unit Dose of Coagulant

Power consumption (logarithmic) as a function of dosing rate (logarithmic) at different Ω for iron electrodes.

$$\Omega = \frac{\text{electrode spacing (cm)}}{\text{solution conductivity (mS/cm)}}\left[\frac{\text{V cm}^2}{\text{mA}}\right]$$





Electrode cost (dashed line) and total operation cost to treat 1000 gallon of water using electrocoagulation as a function of dose using aluminum or iron electrodes (energy: \$0.1/kWh; aluminum: \$2.40/kg; iron: \$0.80/kg).

Industrial Interactions and Technology Transfer

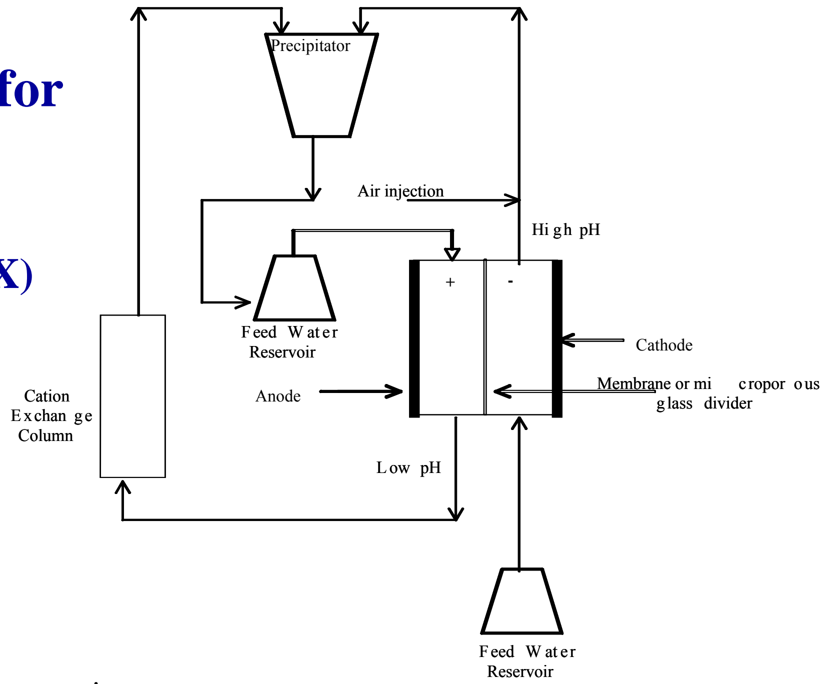
Electro-Coagulation Pilot Study

- **Sponsored by Intel ($250k) and the Arizona Water Institute ($50k)**
- **Pilot study during summer 2007 at Intel site in Ronler Acres, OR**
- **Treated RO reject and cooling tower blowdown**
- **Performance of pilot unit (30m^3/day) versus bench unit (0.5m^3/day)**

Future Plans

Next Year Plans

- Begin development of ERIX technology for control of hardness minerals
  - Ca^{2+}, Mg^{2+}, Ba^{2+} removal by ion-exchange (IX)
  - on-site acid/base production with small electrochemical cell that uses novel (and stable) electrode materials (e.g. Ebonex)
  - economical and environmentally-sustainable regeneration of IX media
  - Partners: Intel Corporation, Lanxess, UA WSP



ERIX† process for regeneration of weak-acid IX media

†ERiX = Electrochemical Regeneration of Ion Exchange

- Initiate line of research on EC treatment of CMP waste for water re-use
  - Potential Partners: Intel Corporation, PARC
- Incorporate "economic value of water" in assessment of technology/process alternatives (S. Megdal, UA WRRC)

Future Plans (continued)

Long-Term Plans

- **Extend and develop ERIX into a general technology for electrochemical acid/base production to regenerate broad classes of sorbents and IX media**
  - **novel cation- and anion-exchange materials (e.g. fibrous materials vs. resins/beads)**
  - **activated carbon**
  - **high-affinity, high-specificity sorbents (e.g. for Cu^{2+} removal)**
  - **Potential Partners: Intel Corporation, WateReuse Foundation, NSF**

- **Miniaturization of ERIX technology**
  - **portable or home use**
  - **lab-on-a-chip (μTAS) applications**

- **Re-use of EC-treated CMP wastewaters**
  - **evaluate for use in industrial waters (e.g. cooling towers)**
  - **evaluate for use in IC manufacturing (e.g. recycle to CMP tools)**
  - **Potential Partners: Intel Corporation, PARC, NSF, SEMATECH**

Publications, Presentations, and Recognitions/Awards

Presentations

- Boyce, A., Georgousis, Z., Schulz, M. Farrell, J. & Baygents, J.C. Electrocoagulation (EC) application to semiconductor industry. UPW Water Executive Forum, Philadelphia, PA, April 2007.
- Whipple, D., Farrell, J. & Baygents, J.C. Electrocoagulation: A technology for water recycle and wastewater treatment in semiconductor manufacturing. Oral communication, University of Arizona Technology and Research Initiative Fund 2006/2007, Water Sustainability Undergraduate Student Fellowship Program, Tucson, AZ, May 2007
- Baygents, J.C. Post-membrane approaches: processes, technologies and research gaps. Oral communication, Arizona Water Institute Workshop on Salinity and Desalination, Tempe, AZ, August 2007.
- Farrell, J. & Baygents, J.C. Electrocoagulation as a water treatment technology. Intel Corporation, Ocotillo, AZ, August 2007.
- Schulz, M., Whipple, D., Davis, J., Solt, A., Liao, L., Gu, Z., Whitten, S. Crittenden, J.C., Goergousis, Z., Boyce, A., Farrell, J. & Baygents, J.C. Electrocoagulation and water sustainability: a pilot study on salt-free removal of silica and hardness minerals. Poster presentation, UA WSP research symposium, Tucson, AZ, October 2007
- Liao, L., Gu, Z., Baygents, J.C. & Farrell, J. EC at the water/energy nexus: treatment of cooling tower blowdown and RO reject. Poster presentation, UA WSP research symposium, Tucson, AZ, October 2007
- Boyce, A., Georgousis, Z., Farrell, J. & Baygents, J.C. Electrocoagulation (EC) application to semiconductor industry—an update. UPW Water Executive Forum, Austin, TX, November 2007.

Awards

- Whipple, D., UA TRIF/WSP Undergraduate Student Fellowship
- Davis, J. UA/NASA Space Grant Undergraduate Research Fellowship

Impact of Fluoride and Copper in Wastewater on Publicly-Owned Treatment Works (POTWs)

(Project #: ESHI004M)

G. Leon, Q. Banihani, V. Ochoa and R. Sierra-Alvarez

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Toxic Impact of Fluoride on Biological Wastewater Treatment

- Growing concern about potential toxic effects of fluoride towards microorganisms in wastewater treatment plants (WWTP) and higher aquatic organisms.
- Fluoride toxic to some oral bacteria.
- Virtually no one has studied the toxicity of fluoride to WWTP bioprocesses before, only nitrification was looked at previously

Objectives

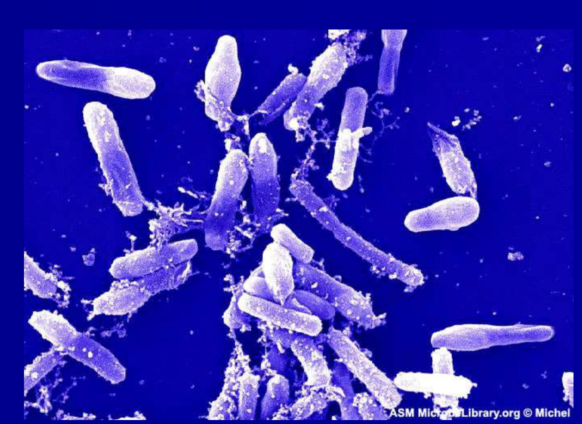
Determine the inhibitory effect of fluoride towards:

- Main microbial populations in wastewater treatment systems.
- Common effluent monitoring species
  (water fleas and fathead minnows)

Daphnia spp

Fathead minnow

Assessment of Fluoride Inhibition



Methodology:

- Microbial toxicity (UofA)
  a) Standardized batch bioassays
  b) Short-term continuous bioreactor studies *(most sensitive microbial population)*

- Acute toxicity to fathead minnows & daphnids (ecotoxicology lab)

  EPA standard methods #2002.0 and #2000.0

Task II

Microbial Inhibition Assays

Set Up

- Medium with nutrients/minerals and substrate
- Inoculum
- Headspace N_2/CO_2 (80/20) or Air

Controls

Medium lacking fluoride

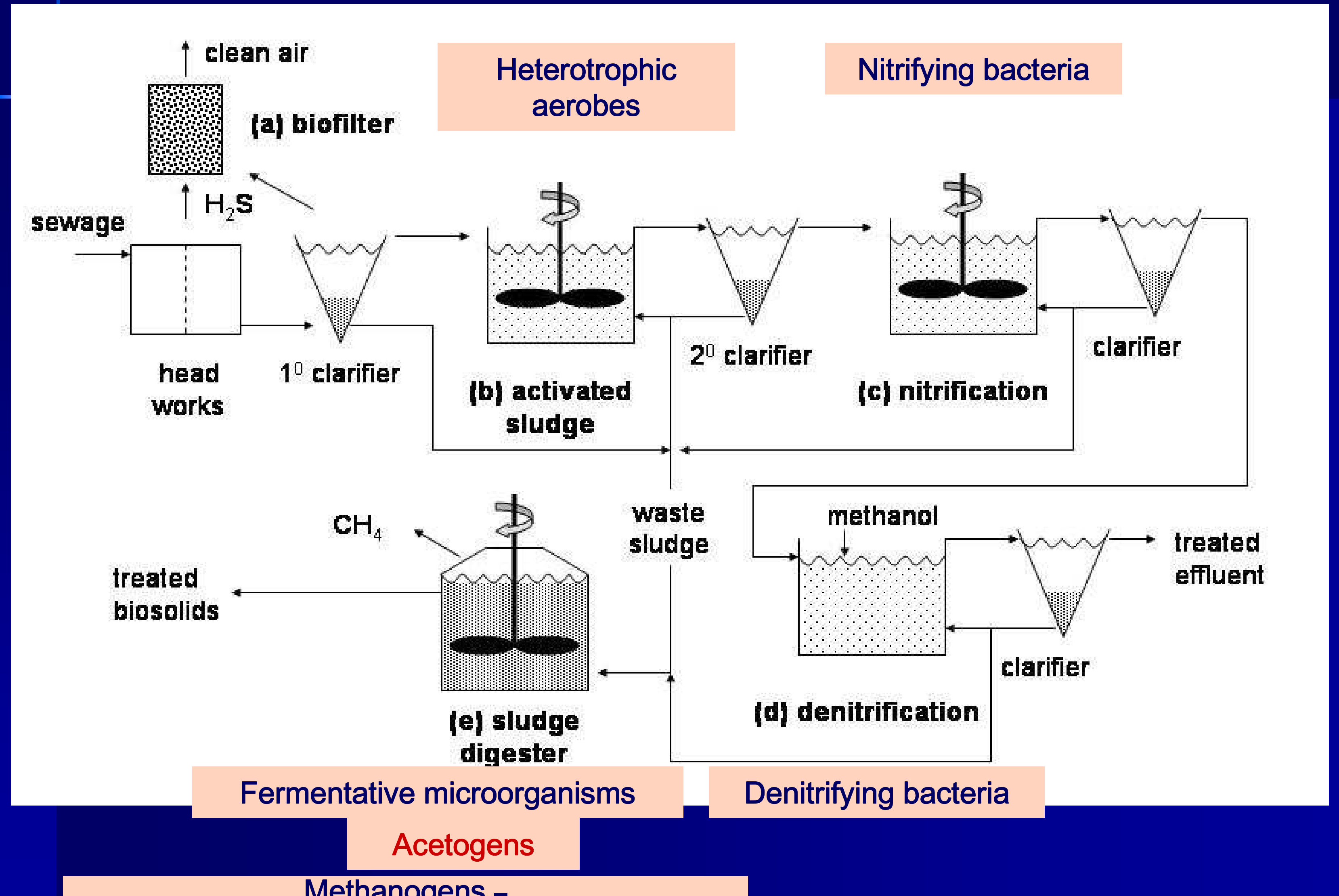
Treatments

Medium with increasing concentrations of fluoride

Controls (− F)

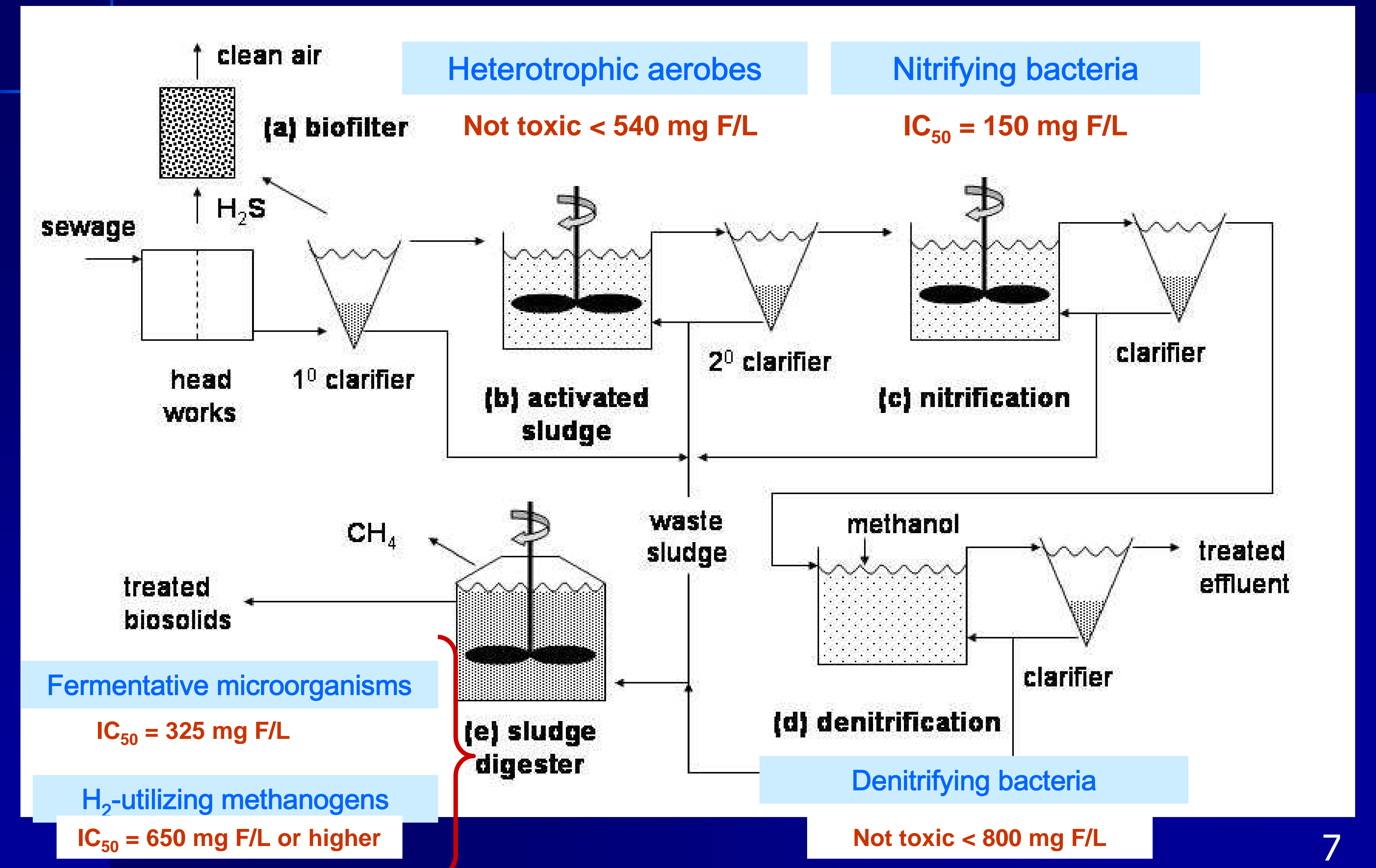
Treatments (+ F)

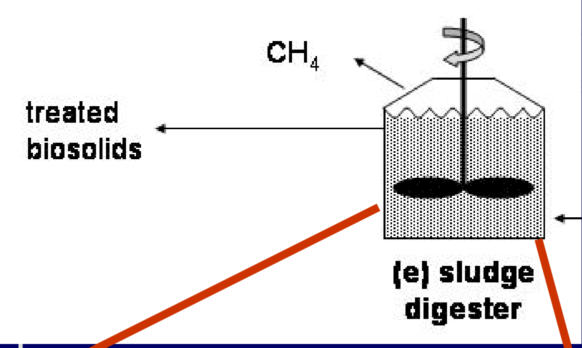
Unit processes and key microbial populations in a typical municipal wastewater treatment plant



Microbial Populations in Municipal Wastewater Treatment Plants

Showing HIGH TOLERANCE to FLUORIDE





Microbial Populations in Anaerobic Processes showing LOW TOLERANCE to FLUORIDE

Organic Matter (OM)

*Fermentation***

Volatile Fatty Acids

Acetogenesis

acetate $H_2 + CO_2$

Methanogenesis

$CH_4 + CO_2$

Butyrate-utilizing microorganisms

IC_{50} = 29 mg F/L

Propionate-utilizing microorganisms

IC_{50} = 35 mg F/L

Acetate-utilizing methanogens - mesophilic

IC_{50} = 26-54 mg F/L

Acetate-utilizing methanogens - thermophilic

IC_{50} = 42 mg F/L

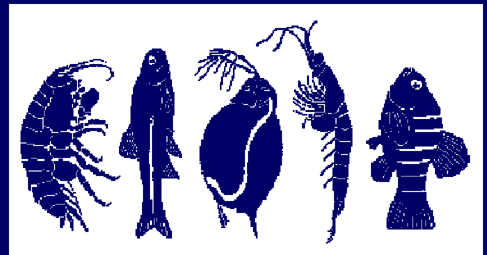
Toxicity of Fluoride to Methanogens: Significance

Anaerobic sludge digesters

Anaerobic bioreactors
(wastewater treatment)

- Acetate (C2), propionate (C3) and butyrate (C4)-utilizing microorganisms appear to be inhibited at concentrations close to those in semiconductor effluents
- These microorganisms are important in anaerobic sludge digesters.

Acute Effects on Biomonitoring Species



	96-hours LC_{50}
FLUORIDE	
Fathead minnows *(Pimephales promelas)*	200 mg/L F^-
Water fleas *(Ceriodaphnia dubia)*	85 mg/L F^-

Conclusions

- Inhibitory effect of fluoride varies considerably depending on the microbial population.

- Only acetate, propionate and butyrate-utilizing methanogens appear to be inhibited at concentrations in the range of those found in semiconductor effluents. Anaerobic sludge digestion, only process which may be impacted, needs to be studied in more detail.

  = IC50: 26 - 54 mg/l

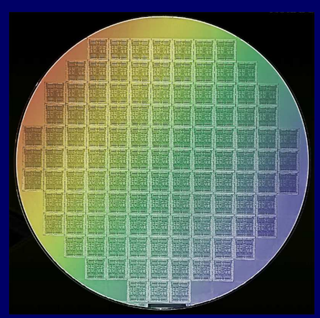
  = Fluoride in semiconductor effluents* (Data from 9 Manufacturing Sites, Sematech)

  Max. Conc: 4.7 - 72.0 mg/L / Avg. Conc: 4.3 - 26.8 mg/L

- The composition of municipal wastewater can affect the inhibitory effect of fluoride (Concn of toxic species (soluble form) can decrease by precipitation /complexation).

$$2\,F^{-} + Ca^{2+} \rightarrow CaF_2$$

Future Plans



- Detailed investigation of the inhibitory effect of fluoride on acetate-, propionate- and butyrate-utilizing anaerobic microorganisms.
- Continuous bioreactor studies to assess the effect of long-term exposure to fluoride.
  - Possible adaptation of microorganism to fluoride.
  - Interaction of fluoride with municipal wastewater components.

Acknowledgments

Walter Worth / Sematech

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing (ERC)

SRC students on non-core project

- Current Students and Anticipated Grad Date
  - Glendy Leon, Expected graduation date: May 2008

Other Customized Projects

- **Low-Energy Hybrid (LEH) Technology for Water and Wastewater Purification and Recycling; Shadman**
  Co-sponsored by ITRI (Taiwan) and TRIF*

- **A Survey of Water Use, Reuse, and Policies Affecting S/C Industry in Southwest; Sharon Megdal (Director of Water Resources Research Center).**
  Sponsored by TRIF*

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* ***Technology Research Initiative Fund (TRIF) is an Arizona initiative. One of its focus areas is water (Waste Sustainability Program). This program is managed by 4 major UA Centers. ERC is one of those Centers and benefits from the TRIF co-sponsorship in water related activities.***

Customized Project 6b
Sponsored by: Technology and Research Initiative Fund, UA

A Survey of Water Use, Reuse, and Policies Affecting S/C Industry in Southwest

Part 1. Water for Manufacturing in Arizona: Focus on the Future

Sharon B. Megdal, Ph.D.
Water Resources Research Center
University of Arizona

Introduction

Water availability for manufacturing depends on a number of factors. In Arizona, surface water or river supplies are essentially fully allocated or over-allocated, and groundwater supplies are often used faster than they are replenished. Reclaimed water, which varies in quality depending on the type of treatment, is being recognized as a critically important water source for meeting municipal water needs. Many areas in Arizona are working on identifying supplies to serve projected population growth. Simultaneously, most communities are looking to diversify their economic bases. Companies with higher-than-average paying jobs, such as many manufacturing facilities, might be expected to be welcome additions to communities. A manufacturing facility often offers a community a sizable number of stable, well-paying positions. When faced with the pressures of finding water for more people, however, will communities in fact welcome manufacturing facilities? What water supplies will be available for manufacturing? In particular, what are the regulatory and policy issues most likely to affect the availability and use of water for manufacturing?

This brief paper provides information on the complex regulatory and policy issues affecting water availability for manufacturing in Arizona. It provides the backdrop or context for discussions of potential large-scale, water-consuming manufacturing facilities. Without an understanding of the manner in which water can be made available to manufacturing, as well of how manufacturing use of water is regulated, it will difficult for corporations to navigate successfully the relevant water supply issues. The information on these policy issues should be considered introductory rather than exhaustive. Because water availability considerations vary by location, additional information for a particular locale must be obtained prior to considering location of a manufacturing facility. In addition, revisions to regulations are frequent.

This paper is to be read with the companion paper, "Background Paper on Manufacturing Water Use in Arizona," (Background Paper) by Richard Rushforth.

An Overview of Water Use in Arizona[1]

Water regulations in Arizona emanate from different sources – statutes, rules, management plans, and case law. The Colorado River, an important water source for Western and Central Arizona, is governed by the Law of the River, which is an amalgam of laws, court determinations and other regulations. Water regulation in Arizona varies by water source, type of water use, and location of use. In particular, Active Management Areas were established by the 1980 Groundwater Management Act. Based on hydrologic considerations, AMAs are areas subject to groundwater regulation. Figure 1 shows the five AMAs in Arizona. The Phoenix and Tucson metropolitan areas are located in AMAs. Many rapidly growing parts of Arizona are not.

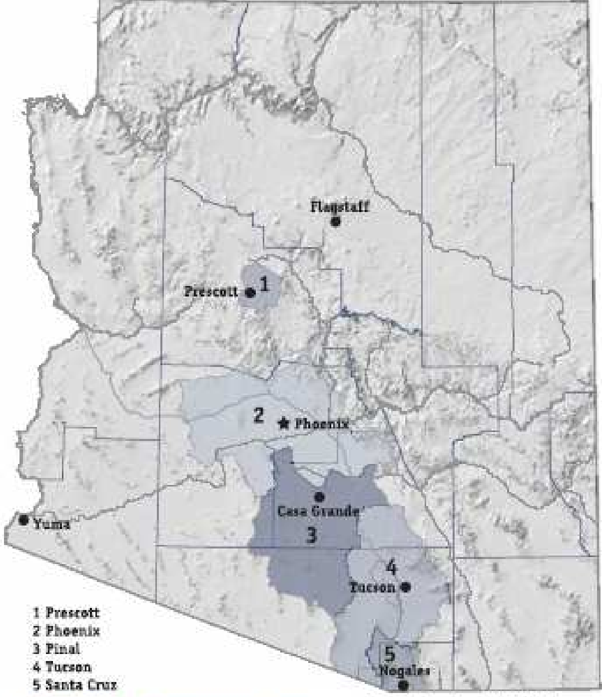

Fig. 1 Active Management Areas

Water management goals are established for AMAs as a whole rather than sub-basins within an AMA. The boundaries of the AMAs are based largely on hydrologic considerations rather than by political jurisdiction. AMAs may and do contain parts of counties and cross multiple county lines. As is evident from Figure 1, most AMAs cover large geographic areas. There may be significant variation in depth to water and natural recharge rates within an AMA. Therefore, physical availability of groundwater may vary within an AMA as well as across AMAs.

The main categories of water use are agricultural, municipal and industrial. Agricultural water use includes water used for irrigated agriculture. It does not include water used for stock watering and dairies. Those uses are included in the industrial category, as are mining, sand and

[1] See *Arizona' Water Future: Challenges and Opportunities*, Background Report for the 85th Arizona Town Hall, 2004, for a summary of water regulation in Arizona, available at www.cals.arizona.edu/azwater/.

gravel, and electrical generation. Also included in the industrial category are some golf course and commercial uses, such as manufacturing. However, commercial and golf course use that is served by a municipal water provider is included in the municipal category. The Arizona Department of Water Resources (ADWR) calls community water companies, whether publicly or privately owned, municipal water providers. These companies provide water to both residential and non-residential customers.

Water use numbers involve estimation. In non-AMA areas of Arizona, much groundwater use is not measured. Even in AMAs, some wells are not metered. Also complicating measurement is the definition of water use itself.[2] Does water use consist of withdrawals of groundwater or diversions of surface water? Or is water use the actual consumptive use of water by the user? There may be different sources of data, depending on the type or location of water use. Estimates of data for 2003 are provided in Table 1. They are reported in acre feet (af), where an acre foot of water is 325,851 gallons or 1.2335 thousand cubic meters.

Table 1: Source of Supply and Amount of Water Used in 2003 (acre-feet)

Water Use Sector	Groundwater	In-state Surface Water	Colorado River Water	Reclaimed Water	Total
Agriculture	2,594,500	898,000	2,275,000	74,000	5,822,100
Municipal	662,600	418,200	421,900	94,000	1,596,700
Industrial	317,500	66,700	1,800	21,200	407,200
Total	3,574,600	1,382,900	2,698,700	189,800	7,826,000

Source: Karl Kohloff and David Roberts, "Beyond the Colorado River: Is an International Water Augmentation Consortium inArizona's Future," *Arizona Law Review*, Vol 49, No 1, Summer 2007, p. 264.

The Background Paper discusses the difficulty associated with identifying and therefore quantifying water use by manufacturers in Arizona. Depending on the circumstance, manufacturing use of water may be classified as "industrial" or it may be a component of "municipal" water use. If a municipal water provider serves a manufacturing facility, there is no requirement that manufacturing water use be separated from other water uses for reporting purposes. Privacy of customer records may interfere with obtaining information on water use by manufacturing facilities. Considerable effort to obtain information on manufacturing use of water was made the primary author of the Background Paper, Richard Rushforth. Unfortunately, significant effort was required to prove a negative, that is, information on water use by manufacturing facilities is not readily available.

Water Regulation in Arizona

The regulation of water use in Arizona depends on the water source and the type and location of use. Within an Active Management Area (AMA), most groundwater use is regulated. Although there are no property rights to the groundwater itself, there is a complex set of rights to use water. Except for domestic wells below a certain size, water use is metered and reported. Conservation programs are required of all large water users who report water use to ADWR. Whereas a manufacturing facility that is pumping water pursuant to an industrial use permit will report water use and be subject to ADWR-enforced conservation programs, water use by a manufacturing facility that is served by a municipal water provider's will usually not be individually monitored by ADWR. New residential growth is subject to Assured Water Supply

[2] See S. Megdal, "Obtaining, Interpreting Water Use Data is Complex Task," *Arizona Water Resource*, March-April 2004, available at www.cals.arizona.edu/azwater/.

(AWS) Rules, and agriculture can not expand its acreage beyond what was irrigated during the 1975 to 1979 period. Outside of an AMA, groundwater use is not regulated. Drilling a well involves only filing a notice of intent to drill. Although AMAs were formed where there were problems of aquifer overdraft, there is the potential for groundwater use to increase within an AMA, as will be discussed below.

Surface water is governed by its own set of laws and procedures, primarily based on first in time, first in right. Surface water has to be used beneficially. Colorado River water use is regulated differently than other surface water. Over half of Arizona 2.8 acre foot allotment of CAP water is delivered to Central Arizona through the Central Arizona Project. Although most of the CAP's 1.5 million acre foot allotment is allocated to users, including Indian Nations, not all of it is being used by the subcontractors. Some is considered excess and is purchased on an annual basis by the Arizona Water Banking Authority, the Central Arizona Groundwater Replenishment District and others. Surface water is essentially over-allocated in Arizona. There are adjudications involving surface water rights. Essentially, there are more claims to surface water than surface water in various river systems. Also, there are several outstanding Indian Water Rights claims. Settlement of the claims is usually preferred to litigation. Because Indian Nations are sovereign, Indian water use is not subject to state regulation. The allocations of Colorado River water across the seven Colorado River basin states and Mexico exceed estimates of the average annual flow. Although groundwater and surface water are connected hydrologically, they are not conjunctively managed in Arizona.

The quantity of treated wastewater used, whether treated to secondary or tertiary standards, is not regulated in the manner groundwater or surface water is regulated. Unless other agreements dominate, wastewater is considered the property of the entity that produces it. Therefore, most wastewater is under the control of the wastewater treatment entity. Tucson is an exception to this. Pima County is the wastewater treatment entity for much of the metropolitan area, yet an intergovernmental agreement has the City of Tucson controlling the majority of the effluent generated. In addition, the Secretary of the Interior manages the use of 28,200 af of effluent for the benefit of the Tohono O'odham Indian Nation. In Maricopa County, Palo Verde Nuclear Generating Plant has a contract to use a significant amount of that metropolitan area's effluent.

The Arizona Department of Water Resources is responsible for groundwater regulation and surface water oversight. The Arizona Department of Environmental Quality regulates water quality. This division of water quantity and water quality oversight is not unique to Arizona. What is unique to Arizona is the manner in which groundwater is regulated in the AMAs.

Arizona requires new residential growth in AMAs to establish it has a 100-year supply of water physically, legally and continuously available. That water use must be consistent with the management goal of the AMA. Four of the five AMAs aspire to reach and maintain safe-yield, where withdrawals of groundwater do not exceed natural and artificial recharge. Through the Assured Water Supply Rules, this consistency requirement means that new growth cannot depend substantially on groundwater. Renewable supplies must be used directly via a treatment plant or indirectly, through recharge and recovery.[3] A municipal water provider can opt for a designation of assured water supply. The larger water providers in the Phoenix and Tucson

[3] See "Artificial Recharge: A Multi-Purpose Water Management Tool," *Arroyo*, Winter 2007, available at www.cals.arizona.edu/azwater/.

AMAs have opted for designations. This means that the entire service area, not just the part growing, must use water in a manner that is consistent with the management goal. The alternative, which is employed by developments outside of the service areas of designated water providers, is for the development to get a certificate of assured water supply.

An in depth discussion of water regulation is beyond the scope of this paper. Title 45 of Arizona Revised Statutes (A.R.S.) contains the laws governing groundwater management in Arizona.

Supplying Manufacturing with Water

If a manufacturing facility located near or within the service areas of a municipal water provider, it is expected that the water provider will serve water to the facility. However, if the facility is located more than three miles from an existing service area or if the municipal water provider refuses service, under certain conditions the Director of the Arizona Department of Water Resources shall issue a General Industrial Use (GIU) permit. A GIU permit entitles the user to pump groundwater. A.R.S. § 45- 515 is summarized in Appendix B of the Background Paper. It could be expected that if a manufacturing facility is located near a populated area, then it will be located within three miles of an existing service area. Nevertheless, in Arizona there is the potential for a major user of water to be issued a permit to drill a well even if the facility is located in an AMA, where groundwater overdraft is a concern.

This situation points to the necessity of thorough exploration of the water supply situation. It cannot be presumed water is not available, even in areas where extensive water management is practiced. Water availability may be particular to a local water provider or jurisdiction, not just a state (or even national) jurisdiction.

In Arizona, water may be supplied by privately or publicly operated water providers. Examples of communities in Arizona served by privately owned water systems are Casa Grande, Sierra Vista and Sun City. Regardless of ownership, large providers located in AMAs are subject to conservation programs, as established in the Management Plan for the respective AMA. Historically, the benchmark for conservation was in terms of the service area's gallons per capita per day (GPCD) utilization of water. Water use, with the exception of effluent or reclaimed water use, would be totaled and then divided by the service area population to arrive at a total GPCD. That would then be compared to a target GPCD, which varied by water provider, to determine regulatory compliance. This program has provided particular challenges to communities where the "profile" of water use changed over time, specifically when large non-residential water users located in a community.

In the mid-1990s, these challenges and others led to authorization of a non-per-capita program, which was based on reasonable conservation measures. Chandler, where Intel is located, enrolled in the non-per-capita program. In the Casa Grande area, where some manufacturing facilities located, Arizona Water Company also faced compliance difficulties under the total GPCD program.[4] Most recently, during the 2007 legislative session, the Arizona Legislature

[4] The details of the conservation programs are included in the Management Plans and will be summarized and discussed in a forthcoming report by the author, which is being prepared for the Arizona Water Institute and the Arizona Department of Water Resources. Arizona Water Company challenged the GPCD program in court. Although the company did not prevail at the Arizona Supreme Court, the judicial decisions led to an ADWR-

authorized a new Best Management Practices (BMP) program for municipal providers.[5] The new BMP program, which must be formally adopted by ADWR as a modification to the existing AMA Management Plans, will be considered the default or base program beginning in 2010. Some water providers will have the option of remaining in the total GPCD program. The importance of the shift is that instead of focusing on the total water use in acre feet, the BMP municipal conservation program will focus on the adoption and implementation of approved best management practices. This change in the regulatory approach to conservation *may* make it more feasible for communities to consider serving manufacturing facilities.

Significant land area in the state of Arizona is Indian Nation land. Water may be available for manufacturing on Indian lands. As noted above, state regulations do not apply to Indian Nations. Some Indian Nations have rights to significant amounts of Colorado River water, either along the Colorado River or via the Central Arizona Project.

Concluding Comments

In Arizona, where water scarcity is a concern, water is in fact available for expanded economic activity and additional people. The type of water and its cost may vary by community. Over time, it is expected that use of reclaimed water will increase substantially. Better or more cost effective treatment technologies may make more water usable. Because new residential growth in the Active Management Areas of Arizona must be based on a 100-year assured water supply, communities are continuously engaged in long-range water planning. Recent statutory changes are likely to change the nature of water management in some non-AMA areas of the state, where there is expected to be more focused attention on adequacy of water supplies over the long term.

The intense focus on future water supplies could be viewed as a signal of a problem. On the other hand, it could be viewed as indication of good planning, something important to businesses considering locating in Arizona.[6]

Water regulation is complex. A company considering locating in Arizona would do well to fully explore and understand the water supply situation. A front-end investment in understanding the water picture could have huge payback not only to the company itself but also the community in which it locates.

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stakeholder process that resulted in agreement to move away from the GPCD program as the base conservation program.

[5] Senate Bill 1557.

[6] Arizona has significant amounts of water in storage. This is not known to the general population and is another indication of the extensive approach to water management in Arizona. See "Artificial Recharge: A Multi-Purpose Water Management Tool," *Arroyo*, Winter 2007, available at www.cals.arizona.edu/azwater/.

SEED/PROPOSED PROJECTS

New Collaborative Initiative

ESH Assessment of Nano-Materials

***Nano-Materials* [=] nano particles as well as new special materials for future nano-electronics**

ESH Impact of Nano-Particles

- Workers exposure

Smart (functionalized) nano-particles

Nano particles:
- CNT
- Nano-wires
- Metal oxides nano-particles

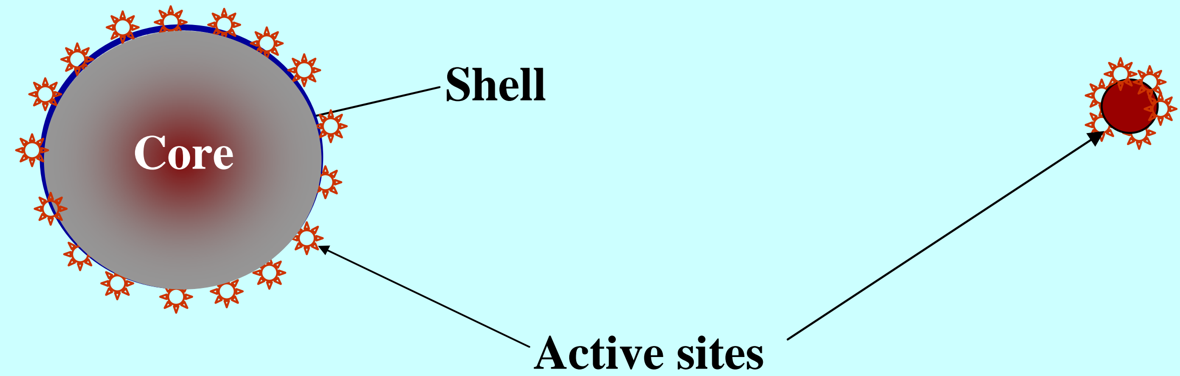
Processes:
- CMP
- Immersion litho
- CVD

Particles released from nano-electronic devices

Process-modified or process-generated particles in waste streams:
- High loading of Cu on CMP particles
- High loading of F-organics on carbon nano-particles

Examples of Nano-Particles in Fabs

CMP Nano-Particles:



Others:

- Nano-particles in immersion lithography
- Nano-droplets in sprays and aerosols in vents
- Nano-tubes and nano-wires, nano-particles as porogens for porous low-k.

What is Unique About Nano-Particles?

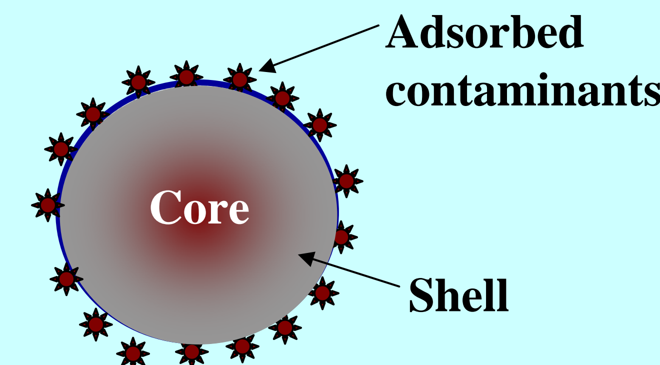
Treatment problem:

- **Nano-particles cannot be effectively removed by *agglomeration, settling, and filtration;* they also clog membranes.**

Synergistic ESH impact of nano-particles:

- ***Active surface***
- ***Selective adsorption***
- ***Pore condensation*** ***(Kelvin Effect)***

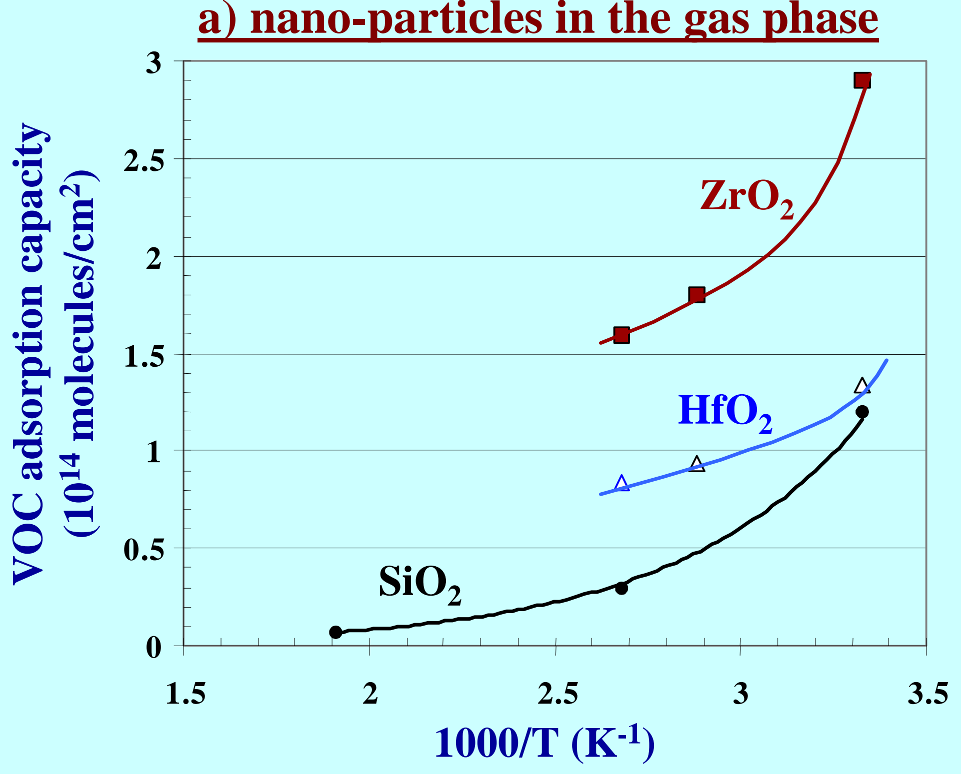
Consequence
- o ***Concentration***
- o ***Facilitated transport***
- o ***Enhanced life-time***



What is Unique About Nano-Particles?

ERC Research: Toxicity and environmental impact of nano-particles in most cases is not due to the particles material, but due to their synergistic interaction with other contaminants.

a) nano-particles in the gas phase



b) nano-particles in the wastewater

- **10 ppb of Cu^{++} in CMP wastewater results in $3x10^6$ ppb of adsorbed copper on 90 nm CeO_2 nano-particles**
- **10 ppb of PFOS in wastewater results in $2.8x10^4$ ppb of contaminated 10 nm carbon nano-particles**

Proposed Collaborative Initiative

Characterization of Nano-Particles
- Physical (focus on size, effective-area, aspect-ratio)
- Chemical (focus: active sites characterization)

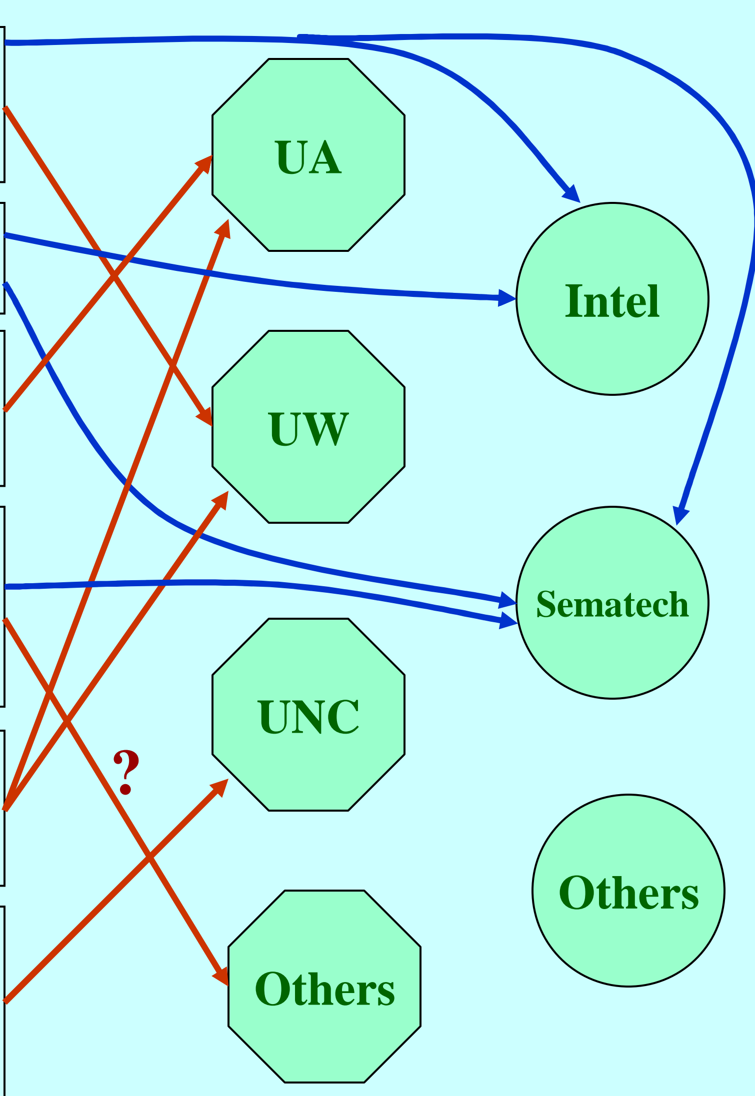
Process Environment and History
- Identification of adsorbing bulk contaminants

Process Modification of Nano-Particles
- Surface activation
- Multi-component adsorption (dynamics; capacity)

Transport and Fluid Mechanics
- Tool and fab environment; workers exposure
- Emission in air and water
- Agglomeration

***Cell-Based* and *Biomimic* Toxicity Assessment**
- Blank nano-particles
- Nano-particles modified by process environment

Predictive Toxicity Assessment
- Structural modeling
- Relating bulk data to nano-particles effect
- Dosage effect (surface vs bulk concentration)



SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Tentative Plan and Method of Approach

Phase 1: Seed Project in 2008

- *Task 1:* **Select two relevant examples of nano particles (CMP and nano-particles in immersion litho) as the initial model compounds.**
- *Task 2:* **Identify and characterize key surface properties that are important in the interactions of nano-particles with process environment (other contaminants).**
- *Task 3:* **Develop an integrated method for assessing the potential safety of nano-particles selected in** ***Tasks 1 and 2*****. This consists of** ***cell-based, biomimic, and predictive*** **methods.**
- *Task 4:* **Develop a proposal for large comprehensive multi-year program for 2009 and beyond (funded by core plus additional sponsors; deadline is December 2008).**

Phase 2: Comprehensive Program, Starting in 2009

- **Expand the project scope to cover other nano-materials; add new partners and new sponsors.**

Reactive oxygen species (ROS) generation and stress reactions as a tool for rapid toxicity assessment of nanomaterials from semiconductor manufacturing

Jim A. Field, Reyes Sierra and Scott Boitano

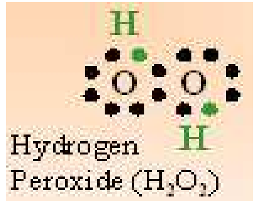
Chemical and Environmental Engineering, Physiology and Arizona Respiratory Center
University of Arizona

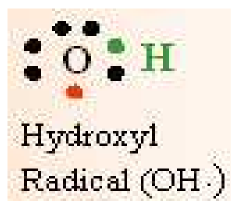
Objectives

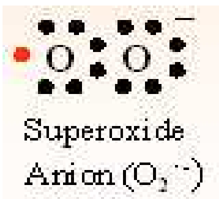
I) Develop and validate simple/rapid testing methods to assess the potential toxicity of nanomaterials and their manufacturing intermediates.

II) Evaluate the impact of transition metals and other contaminants on the toxicity of nanomaterials by selective removal and addition of the contaminants.

Focus of Studies



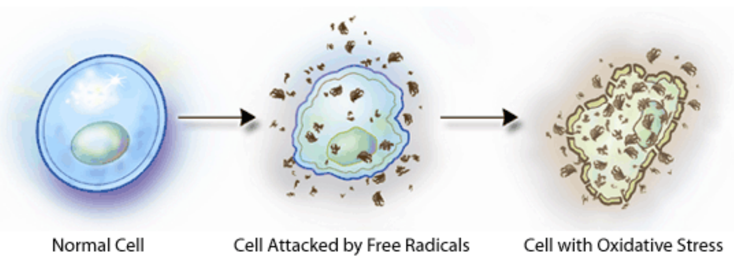




In this project we chose the lung epithelium as a target for nanomaterial toxicity because:

- The lung naturally produces ROS (*i.e.*, OH·, $O_2^{\cdot}$, H_2O_2) in response to injury and insult.
- ROS molecules in the lung can be damaging when over-expressed, or when introduced from an outside source.
- Toxic nanoparticles from semiconductor manufacturing can generate excessive ROS in the lung via:
  - Chemical reactions with bio-fluids
  - Stress response of cells

Hypothesis



In this project we hypothesize that:

ROS production in bio-fluids and cellular stress response via ROS can be used as markers for rapid assessment of potential toxicants from semiconductor manufacturing.

To test this hypothesis we will:

1) Develop rapid screening methodologies to test ROS production.
2) Follow through with longer term studies on compounds that significantly alter ROS in biofluids and in cell production.

Research Tasks for Developing Testing Methods

I. Rapid *in vitro* Screen in Cell-Free Systems

1) **Surrogate Lung Fluid.**

   Airway surface liquid (ASL) mimic medium (Omsland *et al*. 2008).

2) **Measure ROS production of ASL exposed to nanoparticles.**

   HPLC – formation hydroxybenzoic acids after reaction with benzoic acids.

   Fluorescence – 96 well plate assays with fluorescent dyes and plate reader.

   Enzymatic - kinetic colorimetric assays with peroxides and superoxide dismutase.

   EPR – spin trapping of hydroxyl radicals.

3) **Oxidative damage to proteins** (MS-MS method described in task II)**.**

4) **Develop microsensors of ROS.**

Research Tasks for Developing Testing Methods

II: Assessment of ROS Effects on Lung Proteins

- Unlike the skin, the airway epithelium is covered in a thin layer of fluid.
- This fluid can include a variety of signaling proteins that are regularly produced by epithelial and other lung cells (e.g., cytokines, chemokines).
- Recent studies have shown that such signaling proteins can be altered by ROS or RNS.

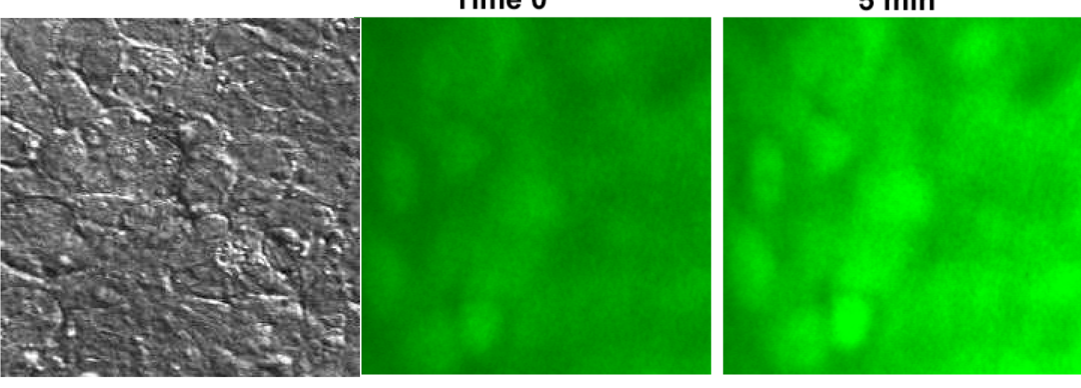
We propose to assay whether representative lung signaling proteins are altered by nanoparticulates produced during nanomaterial manufacturing by:

1) Plating proteins suspended in an airway liquid mimic environment into a 96 well plate.
2) Introduce nanomaterial intermediates and end products into individual wells.
3) Assay proteins for oxidation using proteomic analysis (e.g., MS-MS).
4) Evaluate changes in signaling ability of modified proteins using a receptor binding assay.
5) Evaluate changes in signaling ability of modified proteins using a cellular response pathway.

Research Tasks for Developing Testing Methods

III: Cellular screening methods

Lung epithelial cells can amplify ROS response by enzymatic reactions



Use in rapid screening:

1) Grow cells in 96-well plate format and load with ROS detecting dye.
2) Add nanomaterials.
3) Measure ROS production using microplate reader.
4) Mark Compounds that up-regulate ROS in airway epithelial cells as potential toxicants for further studies (cell signaling, injury, death, or loss of barrier function).

- **Lung cells are our cells of choice, but, for rapid screening, we propose to develop yeast or bacterial readouts that better translate to industrial use.**

- **Long-term we would like to merge to biochip technology.**

Research Tasks for Developing Testing Methods

IV. Nanochemistry versus toxicity

1) Nanoparticles versus manufacturing stage

Nanoparticles end products versus intermediates of manufacturing processing.

2) Heavy metals and metalloids on nanoparticle surfaces

Selective removal – chelating agents; oxidative or reductive treatments to selectively remove metals and metalloids.

Concentration – enable sorption of selected metals and metalloids on nanoparticle surfaces.

3) Organics

Selective removal – solvent, oxidation, incineration to selectively remove organics.

Concentration – enable sorption of organic micro-contaminants on nanoparticle surfaces.

ESH Metrics and Impact

1. Identification of potentially problematic materials in advance of regulatory concern.

2. Considerable reduction in time/costs/regulatory burden with rapid toxicity tests.

3. Reduction in emission of ESH-problematic material to environment by replacement with benign materials.

Proposed Project 7

Task 3. TOXICO-CHEMINFORMATICS AND PREDICTIVE NANOTOXICOLOGY

Alexander Tropsha

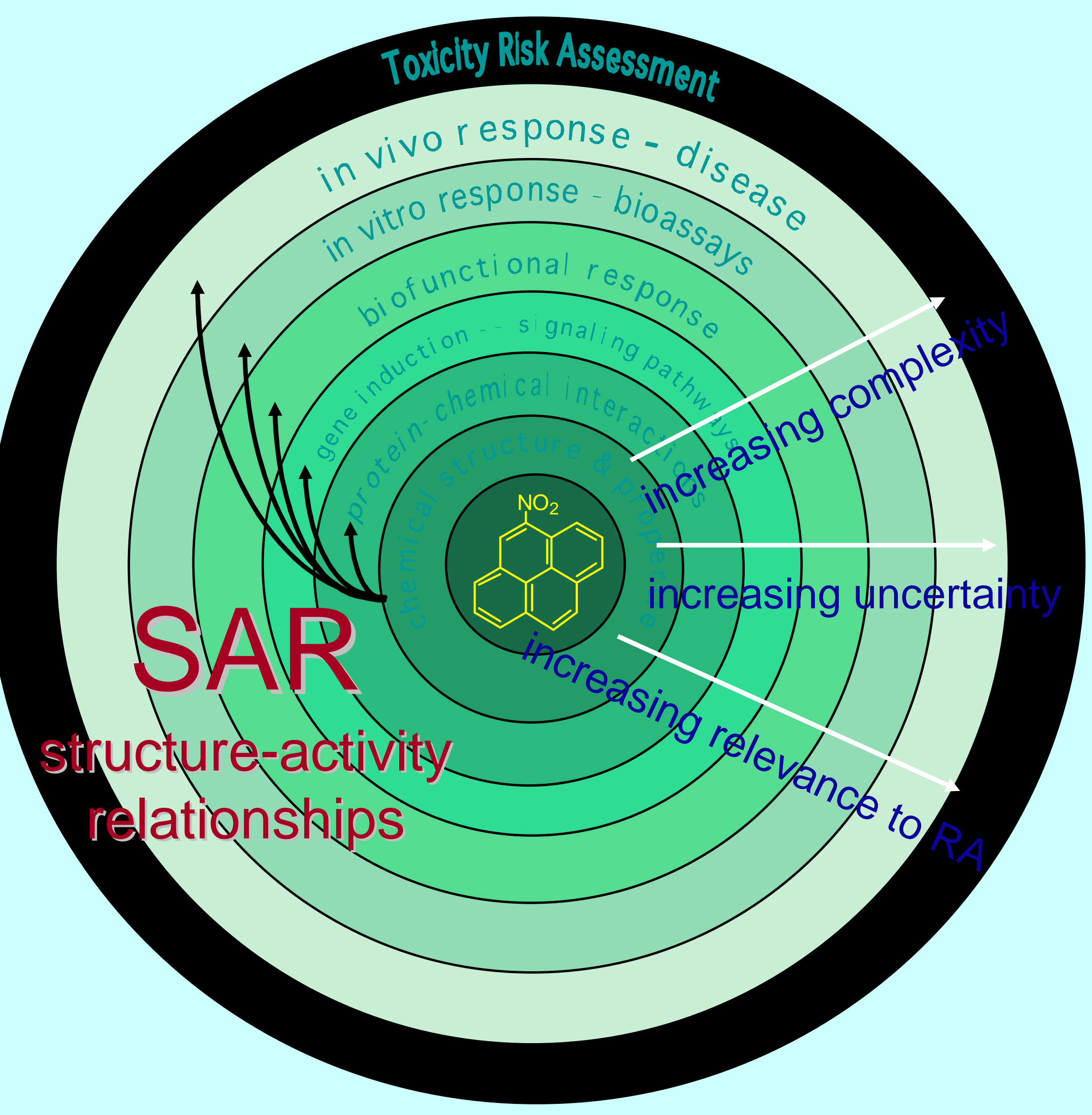
Carolina Center for Exploratory Cheminformatics Research (CECCR) and Carolina Environmental Bioinformatics Research Center (CEBRC)

University of North Carolina at Chapel Hill

OUTLINE

- Key modeling concepts
- Previous toxicity models (predictors)
  - Ames genotoxicity
  - Rodent carcinogenicity and mutagenicity
- Aquatic toxicity
  - Hybrid structure-cytotoxicity-in vivo toxicity modeling
- Future studies: computational nanotoxicology
  - Risk assessment for adsorbents
  - Iterative design of safe nanoparticles

Chemocentric view of biological data and risk assessment



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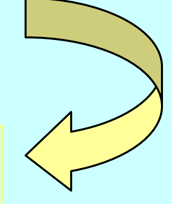
EU-WHITE PAPER on the Strategy for a Future Chemicals Policy (2001)*

Art. 3.2 ...."to keep animal testing to a minimum" "in the interest of time- and cost-effectiveness"...

"particular research efforts are needed for development and validation of modelling (e.g. QSAR) and screening methods for assessing the potential adverse effects of chemicals"

- "Regulatory acceptance of QSAR models":

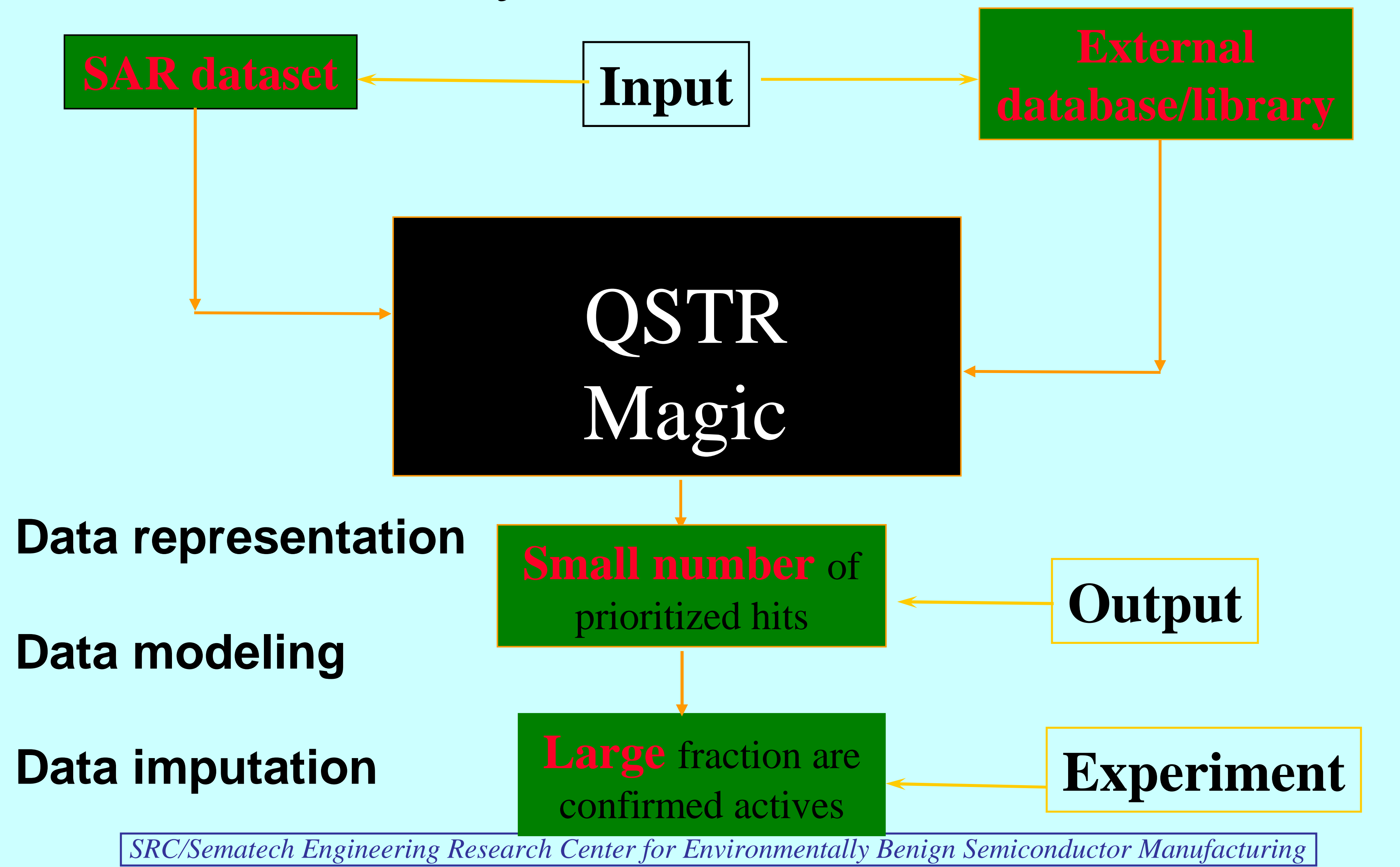
• Workshop ICCA/CEFIC (2002):



Setubal Principles

*Slide is a courtesy of Prof. Paola Gramatica - QSAR Research Unit - DBSF - University of Insubria - Varese (Italy)

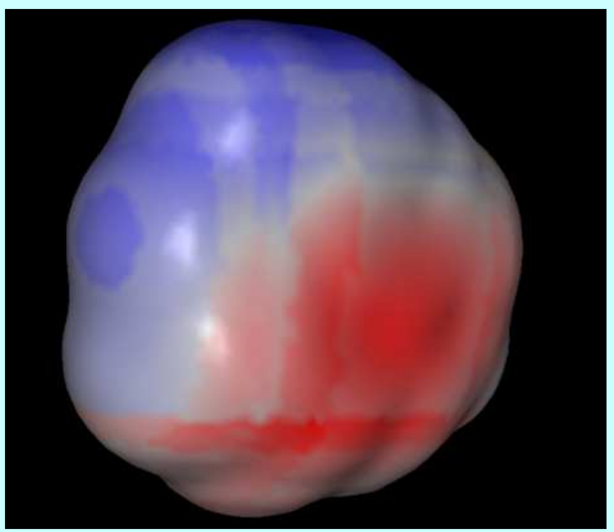
Major research paradigm: Focus on Externally Validated Predictions



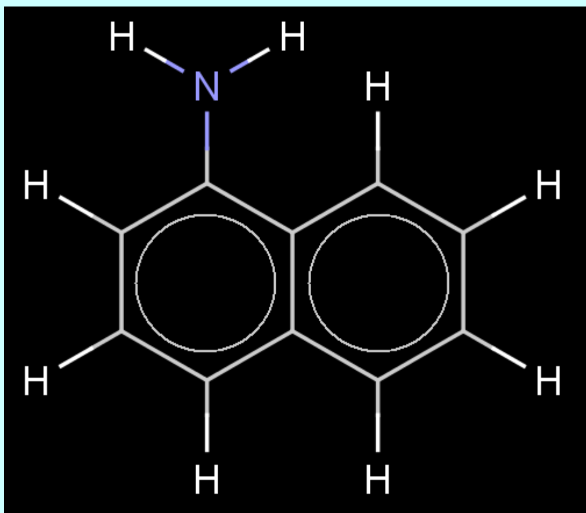
Data Representation

A molecule

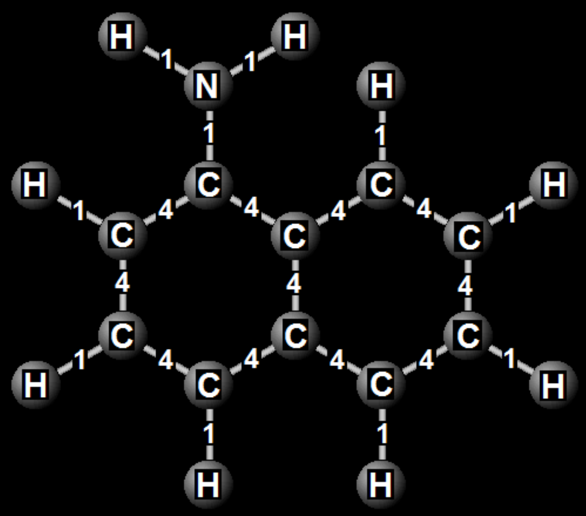
Viewed by another molecule



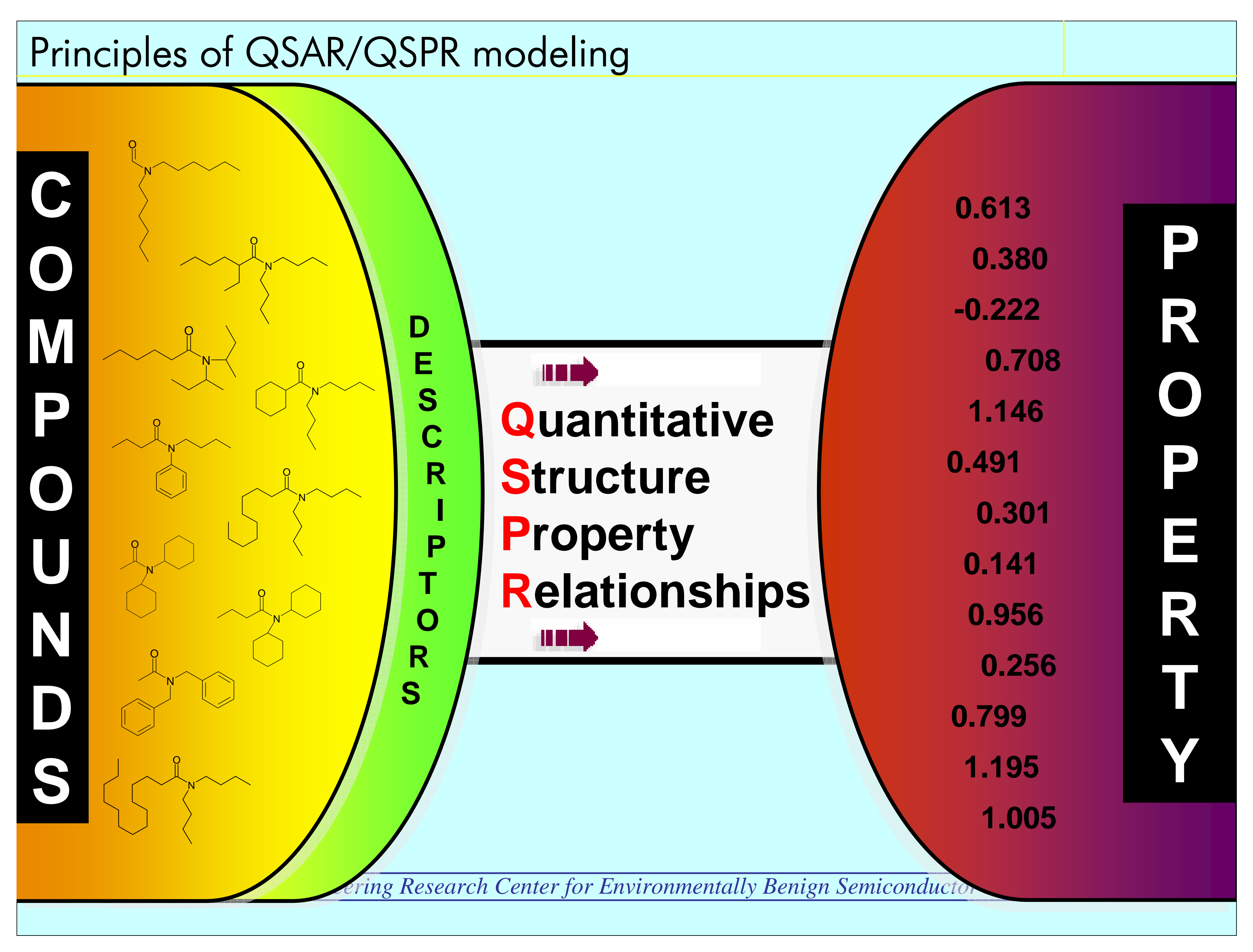
Viewed by chemists



Viewed by cheminformaticians



Graphs are used to represent individual molecules and compute hundreds of descriptors.


Principles of QSAR/QSPR modeling
COMPOUNDS
DESCRIPTORS
Quantitative
Structure
Property
Relationships
PROPERTY
0.613
0.380
-0.222
0.708
1.146
0.491
0.301
0.141
0.956
0.256
0.799
1.195
1.005
ering Research Center for Environmentally Benign Semiconductor

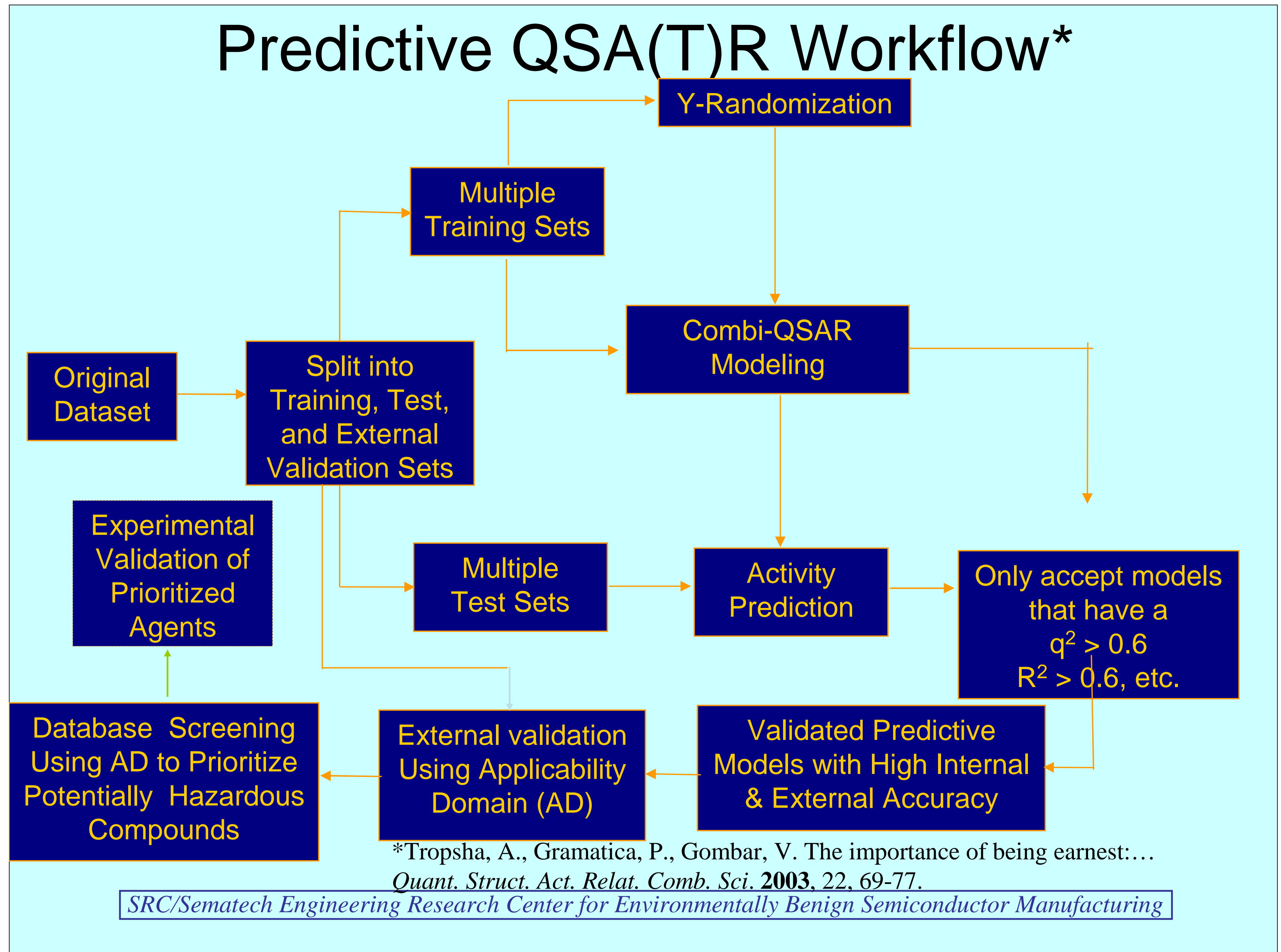
Data Matrix for QSAR Modeling

Goal: Establish correlations between descriptors and the target property capable of predicting activities of novel compounds

Chemistry	Biology (IC50, Kd...)	Cheminformatics (Molecular Descriptors)				
Comp.1	Value1	D_1	D_2	D_3	|	D_n
Comp.2	Value2	"	"	"	|	"
Comp.3	Value3	"	"	"	|	"
- -	- - -	- - -	- -	- - -	- -	- - -
Comp.N	ValueN	"	"	"	|	"

BA = F(D) {e.g., …}

(e.g., $-\mathrm{LogIC50} = k_1D_1+k_2D_2+\ldots+k_nD_n$)


Predictive QSA(T)R Workflow*
Y-Randomization
Multiple Training Sets
Combi-QSAR Modeling
Original Dataset
Split into Training, Test, and External Validation Sets
Experimental Validation of Prioritized Agents
Multiple Test Sets
Activity Prediction
Only accept models that have a
q2 > 0.6
R2 > 0.6, etc.
Database Screening Using AD to Prioritize Potentially Hazardous Compounds
External validation Using Applicability Domain (AD)
Validated Predictive Models with High Internal & External Accuracy
*Tropsha, A., Gramatica, P., Gombar, V. The importance of being earnest:…
Quant. Struct. Act. Relat. Comb. Sci. 2003, 22, 69-77.
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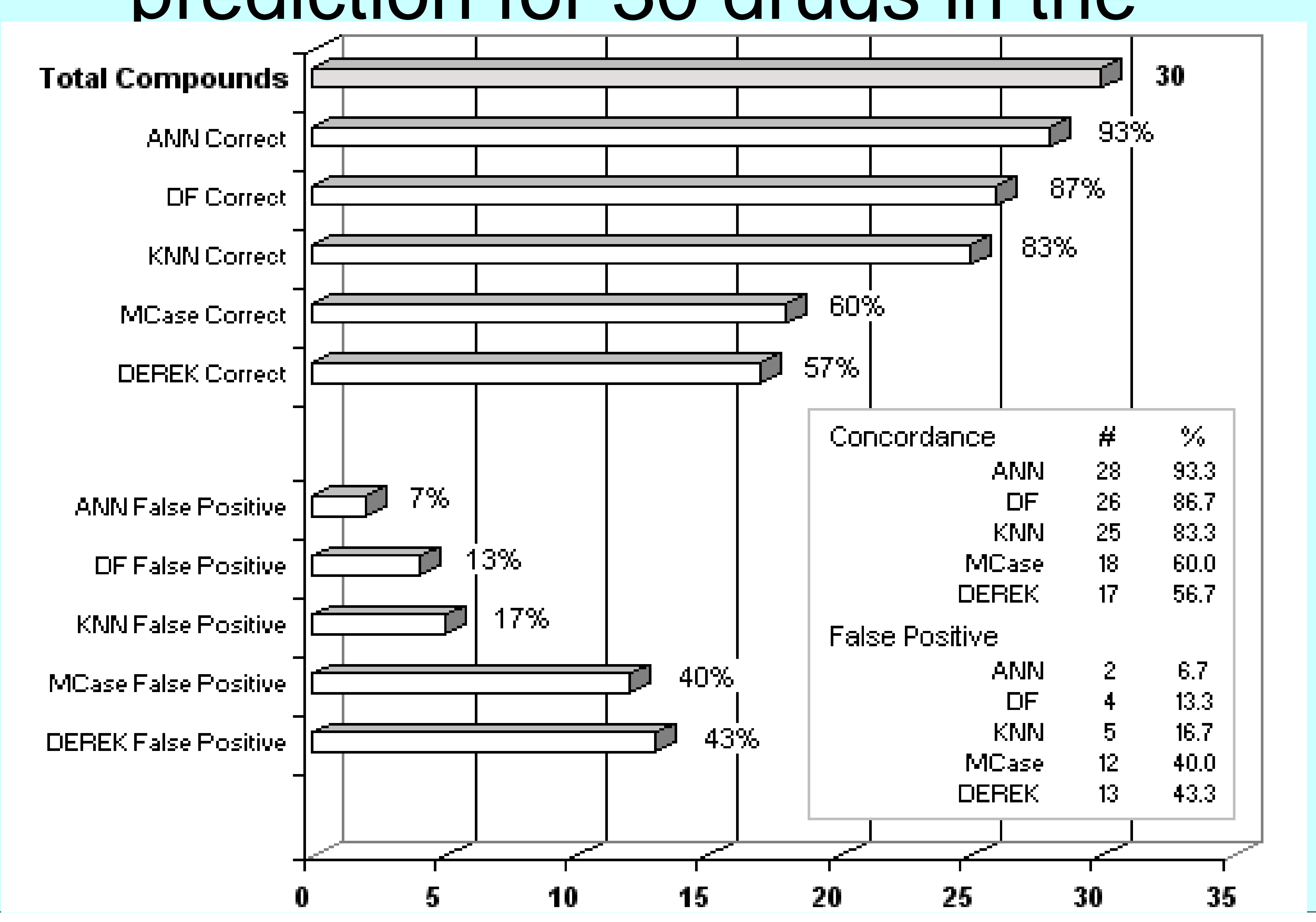
Compound prioritization using QSAR models

Consensus QSPR models for the prediction of Ames genotoxicity*

- 3,363 diverse compounds (including >300 drugs) tested for their Ames genotoxicity
  - 60% mutagens, 40% non mutagens
  - 148 initial topological descriptors
  - ANN, kNN, Decision Forest (DF) methods
- 2963 compounds in the training set, 400 compounds (39 drugs) in randomly selected validation set

*Votano JR, Parham M, Hall LH, Kier LB, Oloff S, Tropsha A, Xie Q, Tong W. *Mutagenesis*, **2004**, 19, 365-77.

Comparison of GenTox prediction for 30 drugs in the

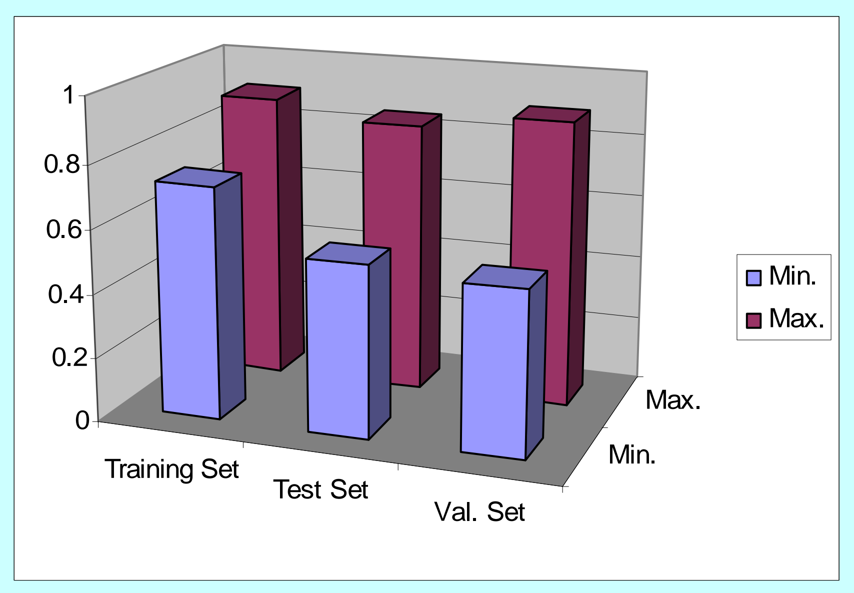


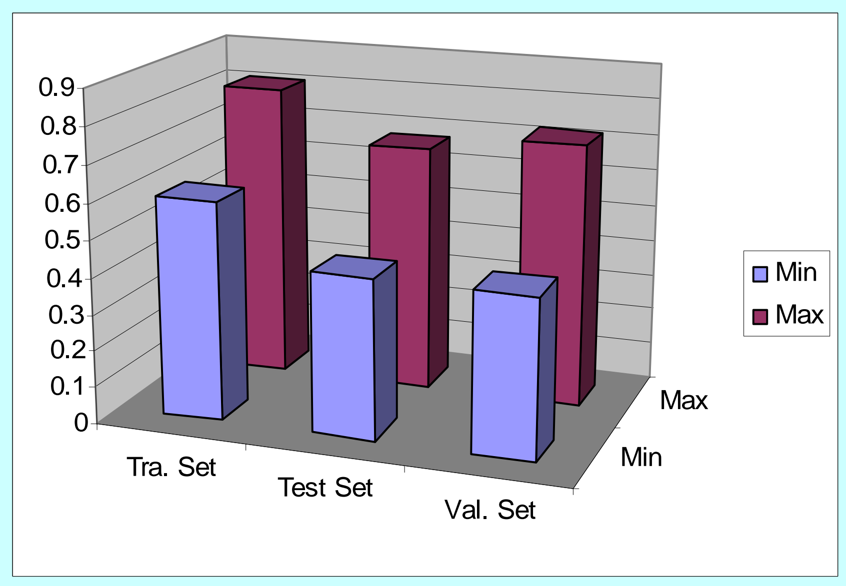
Rodent Carcinogenicity and Mutagenicity data (CPDB Dataset)

	Mut(+) (Mutagenic)	Mut(-) (Not Mutagenic)	Total
Car(+) (Carcinogenic)	252	172	424
Car(-) (Non Carcinogenic)	85	184	269
Total	337	356	693

Mut(+)Car(-): mutagenic and carcinogenic
Mut(+)Car(-): mutagenic but not carcinogenic
Mut(-)Car(+): not mutagenic but carcinogenic
Mut(-)Car(-): neither carcinogenic nor mutagenic

Predictive kNN QSAR models





Mutagenicity

Carcinogenicity

The *T. pyriformis* toxicity dataset

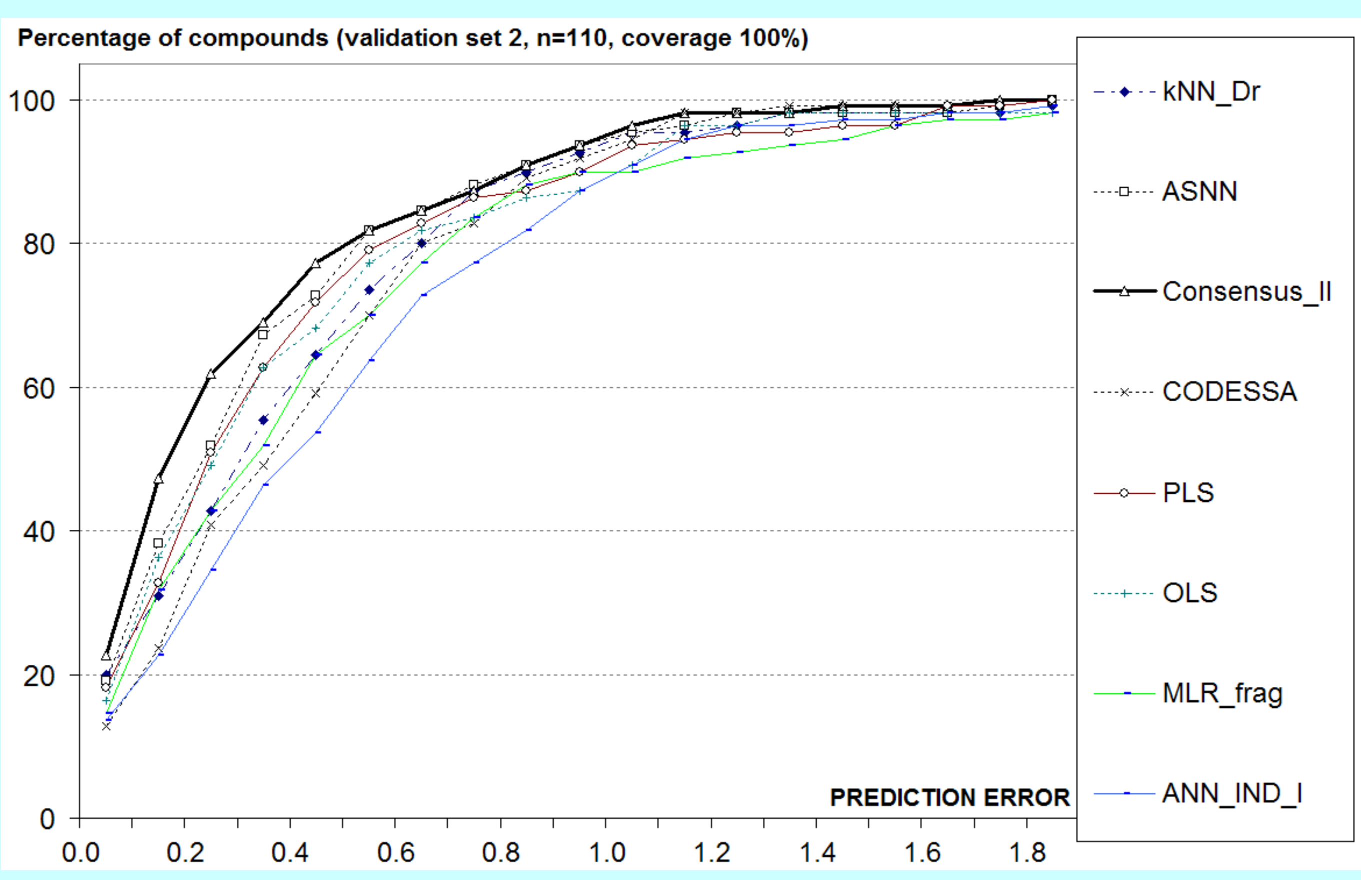
- Compiled from several publications of T. Schultz's group (2001-2005) and the Tetratox website (http://www.vet.utk.edu/TETRATOX/)
- Corrected over 100 errors (chemical structures, chemical name and CAS ids).
- 983 unique compounds: 644 compound in modeling set; 339 compound in the external validation set I.
- 110 new compounds from a recent publication (Schultz et al, 2007) and used as the external validation set II.

International Virtual Collaboratory* of Computational Chemical Toxicology

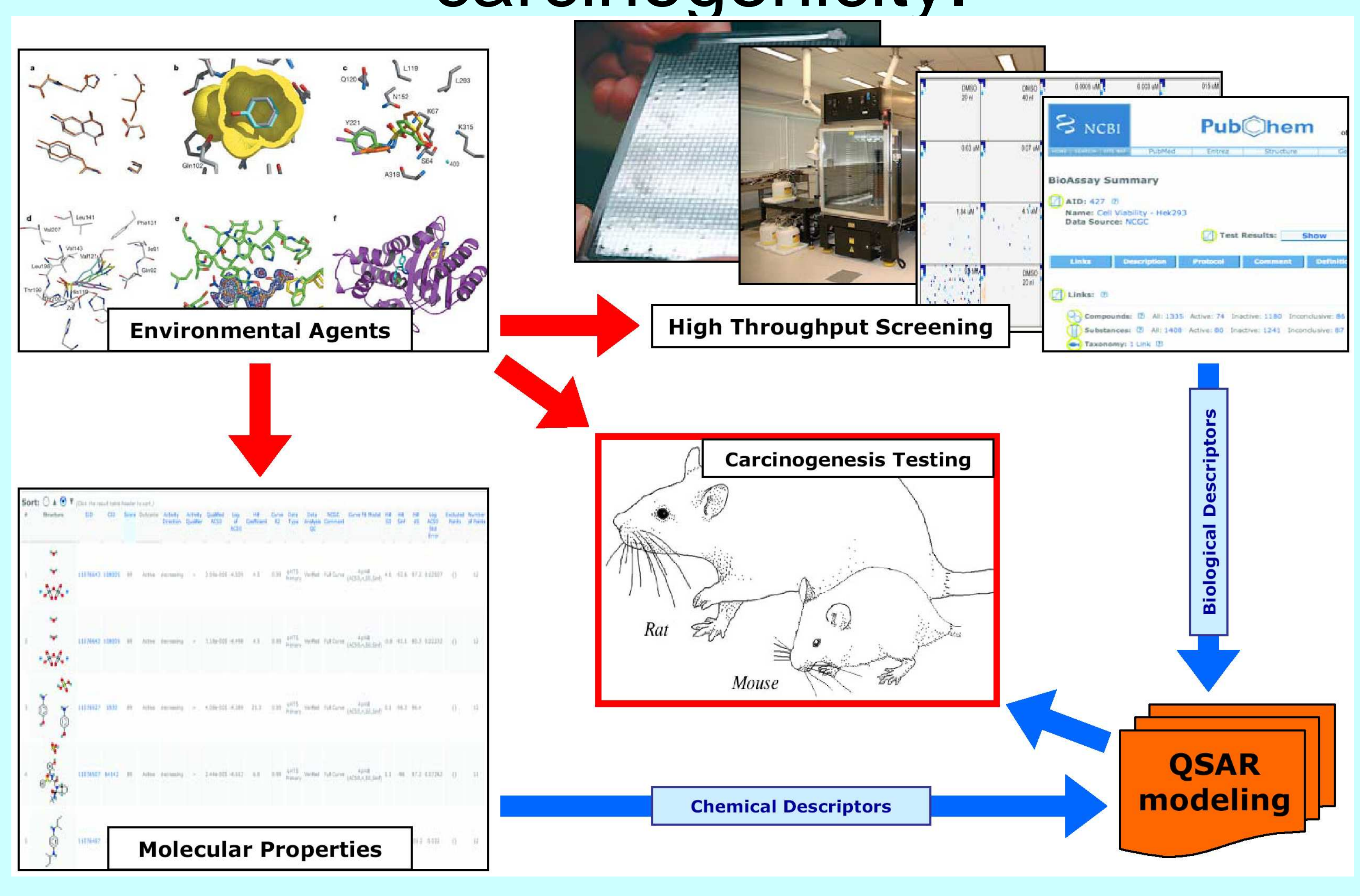
- USA: UNC-Chapel Hill (UNC) - H. Zhu and A. Tropsha
- France: University of Louis Pasteur (ULP) – D. FOURCHES and A. VARNEK
- Italy: University of Insubria (UI) – E. PAPA and P. GRAMATICA
- Sweden: University of Kalmar (UK) – T. ÖBERG
- Germany: Munich Information Center for Protein Sequences/Virtual Computational Chemistry Laboratory (VCCLAB)– I. TETKO
- Canada: University of British Columbia (UBC) – A. CHERKASOV

*a new networked organizational form that also includes social processes; collaboration techniques; formal and informal communication; and agreement on norms, principles, values, and rules

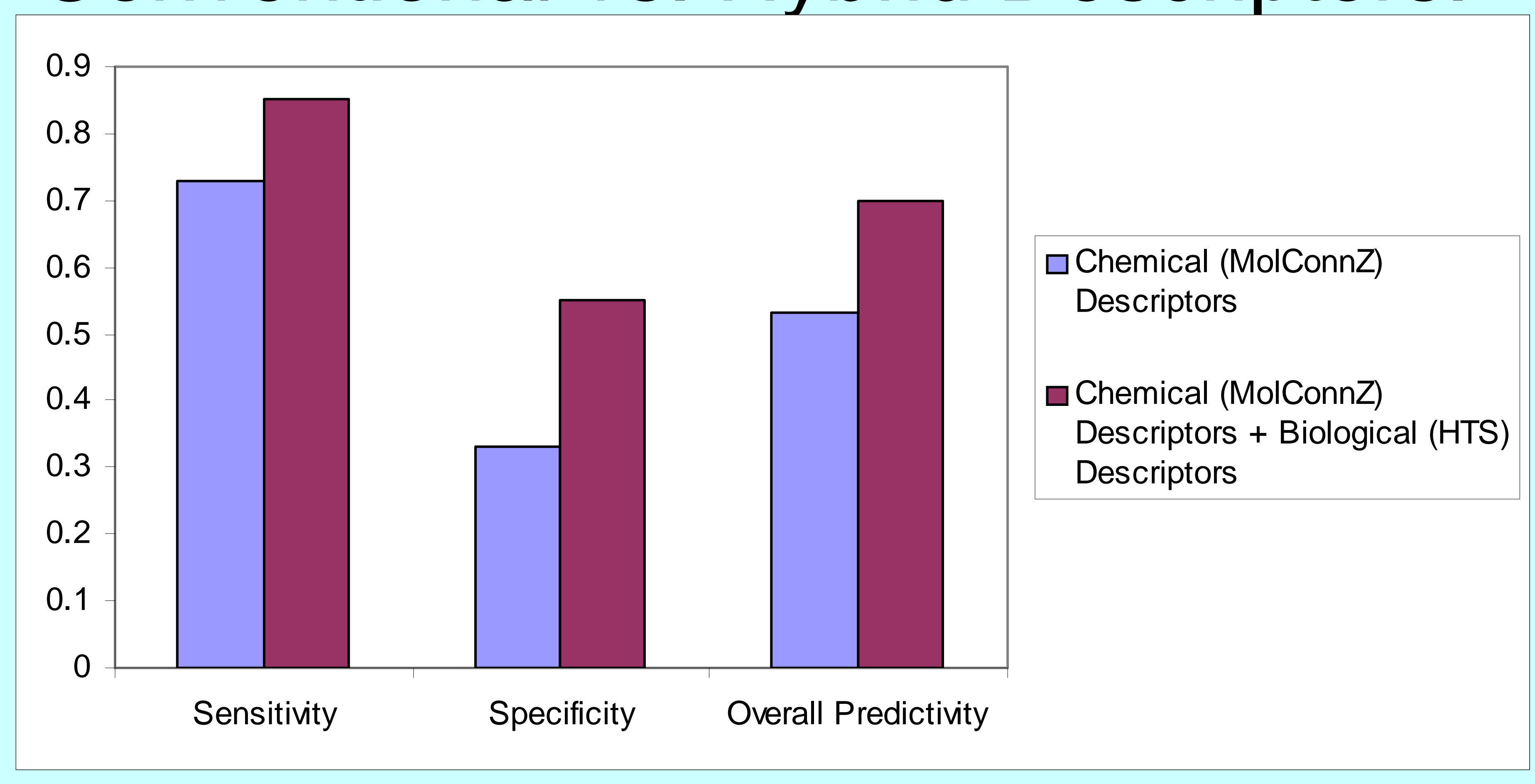
Consensus Model gives the lowest MAE of prediction (Validation Set II)



Combining chemical and biological descriptors in QSAR modeling of chemical carcinogenicity.



Comparison between Predictive Power of QSAR Models using Conventional vs. Hybrid Descriptors.



Computational nanotoxicology and predictive QSTR modeling

- Data on possible toxicity of nanoparticles (including impurities) are emerging (e.g., toxicogenomics studies of Dr. F. Chen, LNL)
- Research Hypotheses
  1. Current toxicity predictors for organic molecules (carcinogenicity, mutagenicty, aquatic and genotoxicity, etc.) could be used to assess potential hazardous effects of impurities or releasable (into bulk phase) components of nanomaterials.
  2. The nature of the interaction of NPs with cells and the body will depend on the physical-chemical properties of the NPs (such as composition, size, shape, surface chemistry/morphology and zeta potential).
  3. The physical-chemical properties of the NPs will determine their acute and chronic Distribution, Metabolism, Elimination, and Effects (DMEE) patterns.
  4. The above physico-chemical parameters can be regarded as descriptors of nanoparticles and used (either by themselves or in combination with conventional chemical descriptors of nanomaterials) in developing Quantitative Nanoparticle Structure – DMEE models (QNPS-DMEE) (e.g., in collaboration with the S. Boitano HTS project).

Generalization of the QSAR matrix: Combined use of chemical descriptors (D) and NP properties (P) as predictors of NP toxicity (e.g., LD_{50})

Chem. descriptors NP descriptors

Nanomaterials	Chem1	Chem2	NP1	…	NPn	Tox.
NP_1	D_{11}	D_{12}	P_{13}	…	P_{1n}	LD_1
NP_2	D_{21}	D_{22}	P_{23}	…	P_{2n}	LD_2
NP_3	D_{31}	D_{32}	P_{33}	…	P_{3n}	LD_3
…		…		…		…
NP_m	D_{n1}	D_{n2}	P_{n3}	…	P_{mn}	LD_m

Novel Materials and Device Structures for High Mobility MOSFETs and Interconnects

Krishna Saraswat
Paul McIntyre
Yoshio Nishi

Department of Electrical Engineering
Department of Materials Science & Engineering
Stanford University, CA, USA

High Mobility Channels

Historic CMOS Performance vs. Scaling: the $1/L_G$ "law"

Carrier velocity increase is paramount for performance scaling

intrinsic delay (ps)
100
10
1
0.1
10
100
L_G (nm)
Bulk Si
str-Si

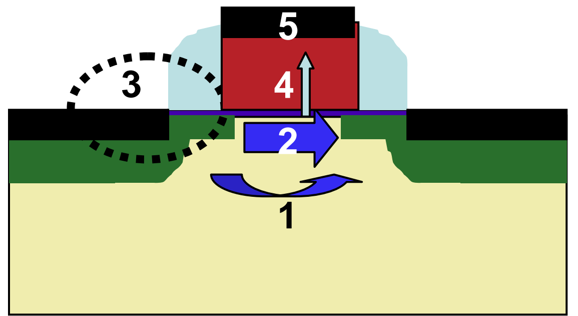
v_{inj} ($\times 10^7$ cms^{-1})
2.0
1.5
1.0
0.5
0.0
10
100
L_G (nm)
e-
h+
str-Si
Bulk Si

High mobility channel: Getting there (L_G=10nm) and proceeding beyond …

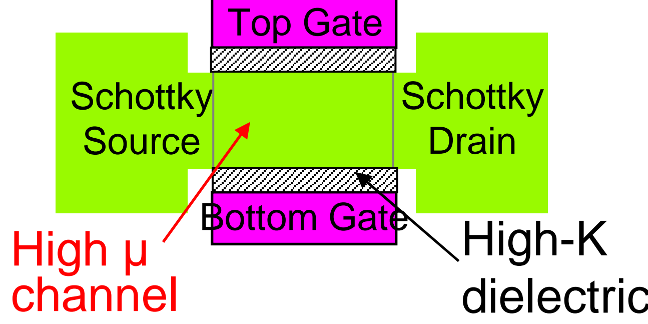
Courtesy: D. Antoniadis (MIT)

New Structures and Materials for Nanoscale MOSFETs

CURRENT BULK MOSFET



FUTURE MOSFET



Problem 1: Poor Electrostatics ⇒ increased I_{off}
Solution: Double Gate
- Retain gate control over channel
- Minimize OFF-state drain-source leakage

Problem 2: Poor Channel Transport ⇒ decreased I_{on}
Solution - High Mobility Channel
- High mobility/injection velocity
- High drive current and low intrinsic delay

Problem 3: S/D Parasitic resistance ⇒ decreased I_{on}
Solution - Metal Schottky S/D
- Reduced extrinsic resistance

Problem 4. Gate leakage increased
Solution - High-K dielectrics
- Reduced gate leakage

Problem 5. Gate depletion ⇒ increased EOT
Solution - Metal gate
- High drive current

Interconnect Power, Latency & Bandwidth

On-chip Global Wires

Increase wire pitch (0.07~0.8um) for Cu and CNTs

Increase # of channels (1~10) for optical interconnects

Power Density
Latency

1cm long wire
10Gb/s global fclk

Cu, CNTs (SA=100%)

Cu

CNTs

Cu, CNTs (SA=20%)

Optics

limited by minimum wire pitch

Optics

Power Density [mW/μm]

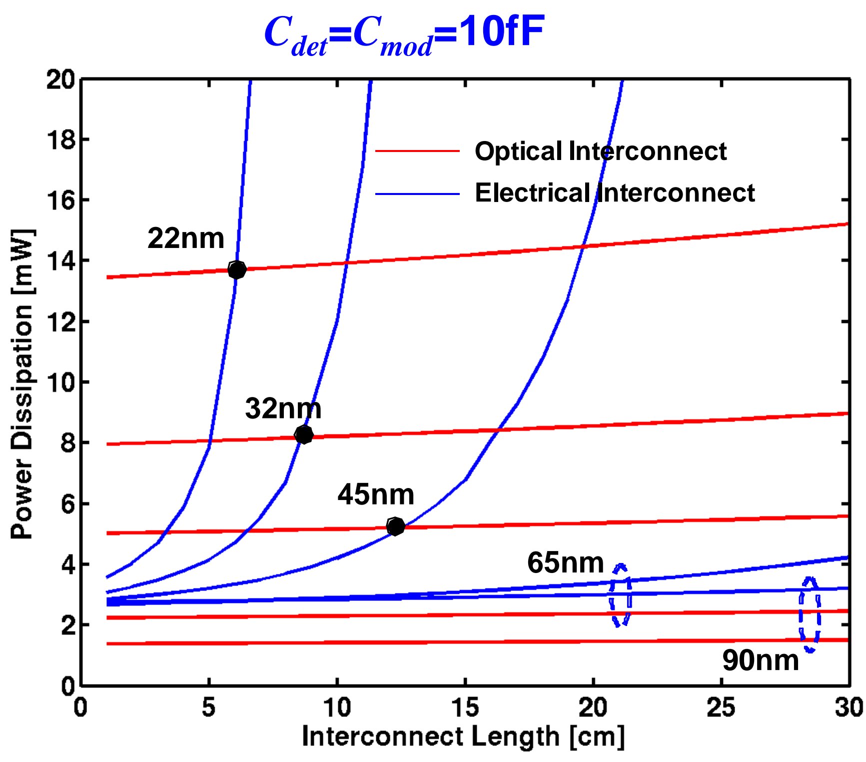
latency [ns]

Bandwidth Density [Gbps/μm]

Koo, Cho, Kapur and Saraswat, IEEE TED, Dec 2007

Off-chip I/O Wires

$C_{det}=C_{mod}=10fF$



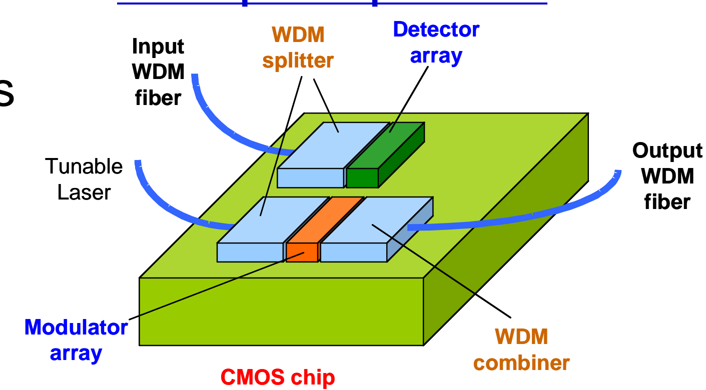
Cho, Kapur and Saraswat, IEEE IITC 2005

- An ideal wire technology should provide a large *BW density*, at the lowest possible latency and power density.
- Optics favorable for longer global and off-chip wires
- Need CMOS compatible technology for monolithically integrated optical components

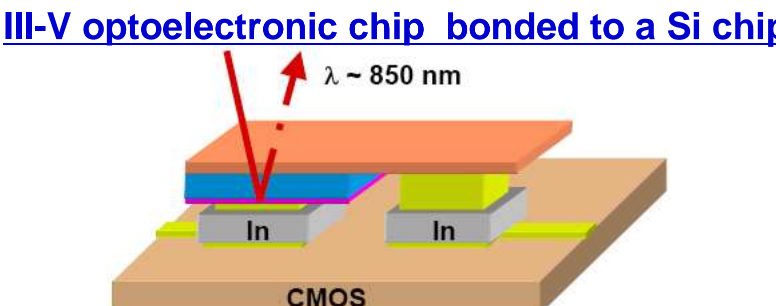
Enabling Optical Technology: Devices

- What are the right optical devices to use?
  - Need to be cheap, available in large numbers
  - Compatible with CMOS
- Silicon devices are a long shot
  - Need 3D heterogeneous integration
- Flip bond III-V to Si CMOS
  - Current 3D process
  - Cost, resources, yield?
- How about germanium?
  - Bandgap ideal for $\lambda = 1.5$ μm
  - Can be monolithically integrated on Si

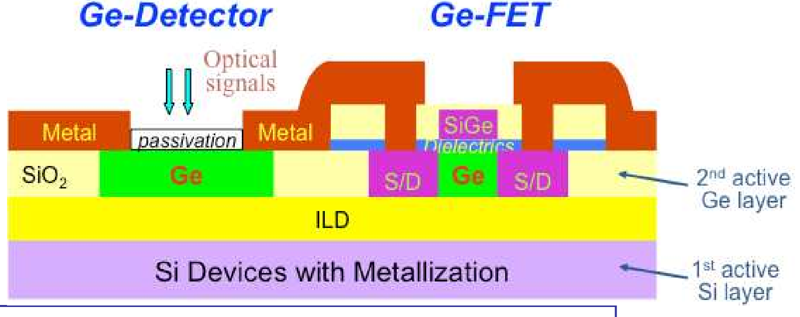
Si compatible photonics



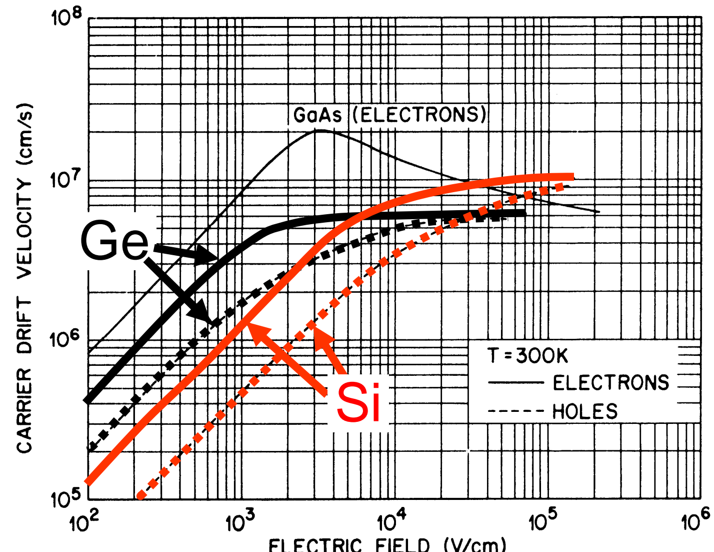
III-V optoelectronic chip bonded to a Si chip



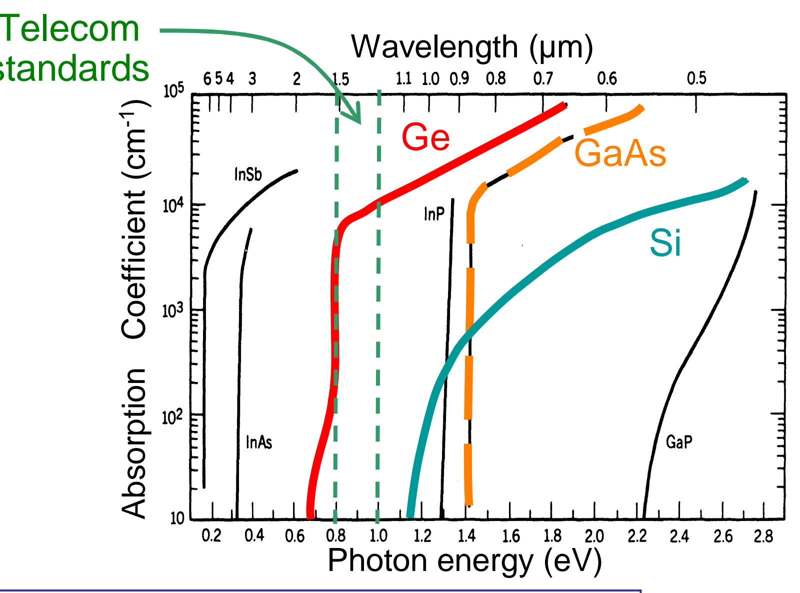
Monolithic Integration of a Ge optical receiver



Ge: Ideal for Nanoscale CMOS and Optoelectronics



- More symmetric and higher carrier mobilities
  - More efficient source injection
  - Higher CMOS speed
- Smaller optical bandgap ideal for 1.3-1.5 μm wavelength optical communications
  - Optical detectors
  - Modulators
  - Lasers (by quantum confinement)?
- Need technology for Heterogeneous integration of Ge on Si



Proposed Projects

- Selective deposition of Ge on Si for MOSFETs and optical interconnects
  - Saraswat, McIntyre and a PhD student (Stanford)
- Near zero Schottky barrier contacts to Ge for metal source/drain MOSFETs, optical MSM detectors and optical modulators
  - Nishi, Saraswat and a PhD student (Stanford)
- Surface passivation of high mobility Ge and III-V substrates
  - McIntyre, Saraswat and a PhD student (Stanford)
- Requested funding for 3 PhD students $400k/year

Ge Integration on Si

Ge Bonding Process	vs.	Selective Ge Growth Process
Oxidation (Oxide / Si)		Oxidation (Oxide / Si)
Ge wafer (Ge)	←	*Ge wafer eliminated*
Anodize Ge (Porous Ge)	←	*Anodization eliminated*
Epi Ge growth (Epitaxial Ge)		Photo-lithography
Bond (Ge / Si)	←	*Bonding Eliminated*
Water Jet (Si)	←	*Water Jet Eliminated*
		Etching
Etching (Ge / Si)		Epi Ge growth (Ge / Si)

Reduce processing steps & materials. Minimize ESH impact

Germanium CVD Selectivity

Deposition Temperature (°C)

Start to deposit on SiO_2

Good Selectivity

GeH_4 Partial Pressure (Pa)

Ge islanding on SiO_2

Growth Model

Ge

dislocations

SiO_2

(100)Si

Selective CVD of Ge on SiO_2

SiO_2

Ge

Si(100)

1um

Before Coalescence

Ge

Ge

SiO_2

Si(100)

After Coalescence

Ge

SiO_2

Si(100)

- Ge can be deposited selectively on Si through SiO_2
- GOI technology is possible through lateral overgrowth

Vertical Ge wires: Enabling 3D ICs

Y Liu, MD Deal, JD Plummer – J. ECS, 2005

Goldberger *et al.*, Nanoletters, 6, 2006
Ng *et al.*, Nanoletters, 4, 2004

Transfer of Epitaxy

Single crystalline Ge seed

Ge CVD homoepitaxy

Liquid phase epitaxy of GOI

SiO_2

Ge NW, possibly doped (local via)

Ge(111)

500 nm

Vertical FETs

Drain

GeNW

Surface passivation

Gate metal

High-k dielectric

Insulating oxide

Substrate (Source)

Active layer technology: Ge NW seeding

Au
Au
Ge Nanowires
Local connection
Gate
PECVD SiO_2
~1 μ m
n+/p+
n+/p+
Si(111) substrate

1.Coat thick plasma oxide

Ge Nanowires
Local connection
Gate
PECVD SiO_2
~1 μ m
n+/p+
n+/p+
Si(111) substrate

2. CMP planarizing process to prepare 2nd active layer substrate

amorphous Ge
Ge seed in SiO_2
Ge Nanowires
Local connection
Gate
PECVD SiO_2
n+/p+
n+/p+
Si(111) substrate

3. Deposit a-Ge on oxide

solid phase lateral epitaxy
Ge Nanowires
Local connection
Gate
PECVD SiO_2
n+/p+
n+/p+
Si(111) substrate

4. Annealing to start SPE

Ge (111) thin film
Local connection
Gate
PECVD SiO_2
n+/p+
n+/p+
Si(111) substrate

5. Single crystal Ge epitaxial layer

Source/Drain formation

Conventional doped S/D vs. Novel metal S/D formation

Conventional doped S/D	Novel metal S/D formation
Gate stack deposition	Gate stack deposition
Gate patterning	Gate patterning
Extension implant	*Extension implant eliminated*
Sidewall formation	Thin sidewall formation
Deep S/D implant	SiN liner depoisition Selective S/D metal deposition
Dopant activation	*Deep S/D implant eliminated* *Dopant activation eliminated*

Fermi Level Pinning in Metal Semiconductor Junctions

Fermi level pinning

Higher Φ_{Beff}

E_{CNL}

E_{FM}

E_{FS}

Free state penetration → Pinning

Ni contacts to Ge

0.01
1E-3
1E-4
1E-5
1E-6
1E-7
I_D (A)
Ohmic
p-Ge
Schottky
n-Ge
NiGe
T=400°C
-0.6 -0.3 0.0 0.3 0.6
V_D (V)

Pethe and Saraswat, IEEE DRC, 2007

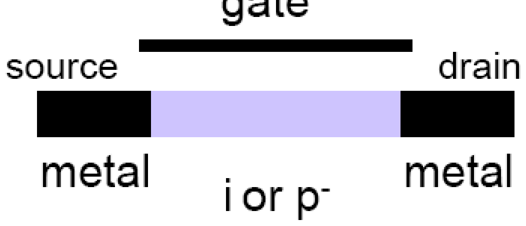
Φ_{bn} vs. Φ_m

Electron Barrier Height $\Phi_{b,e}$ (eV)
0.8
0.6
0.4
0.2
0.0
E_g (Ge)
(b)
Ce Gd La Hf Ti Ta Ni Pt
M S
Vacuum
Φ_m Φ_{CNL} χ_S
E_C
$\Phi_{b,e}$
E_{Fm}
CNL
E_V
Φ_0
(a)
2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
Metal Work Function Φ_m(eV)

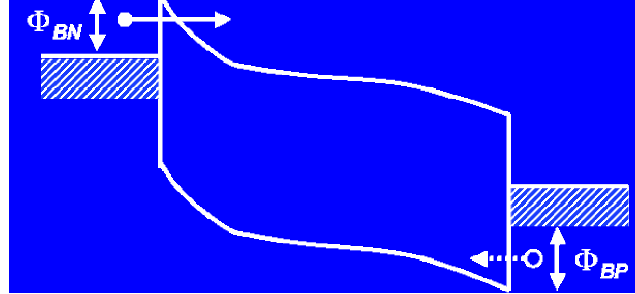
Dimoulas, APL 89, 252110 (2006)

- Various metals show Schottky behavior with n-Ge and ohmic with p-Ge indicating that the Fermi level is pinned close to E_V
- The wave functions of electrons in the metal decay into the semiconductor band gap. This results in states in the forbidden gap known as metal-induced gap states (MIGS)
- MIGS cause pinning of the Fermi level

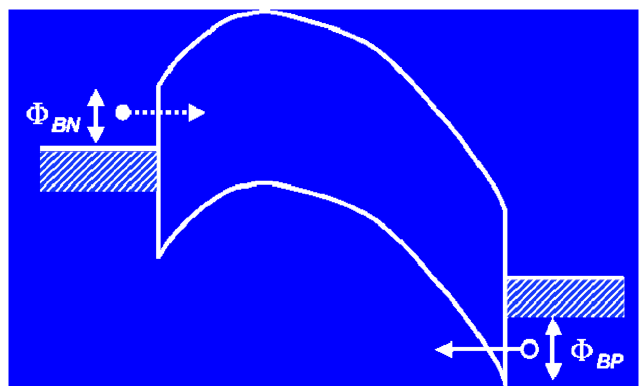
Metal Source/Drain MOS Performance Issue



On state

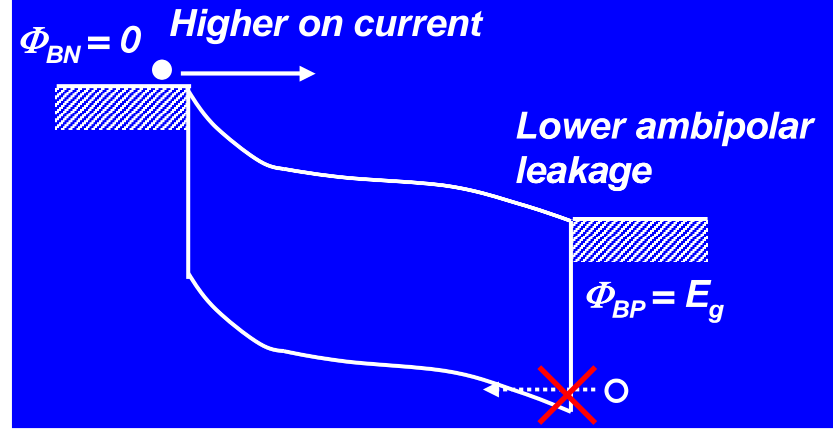


Off state

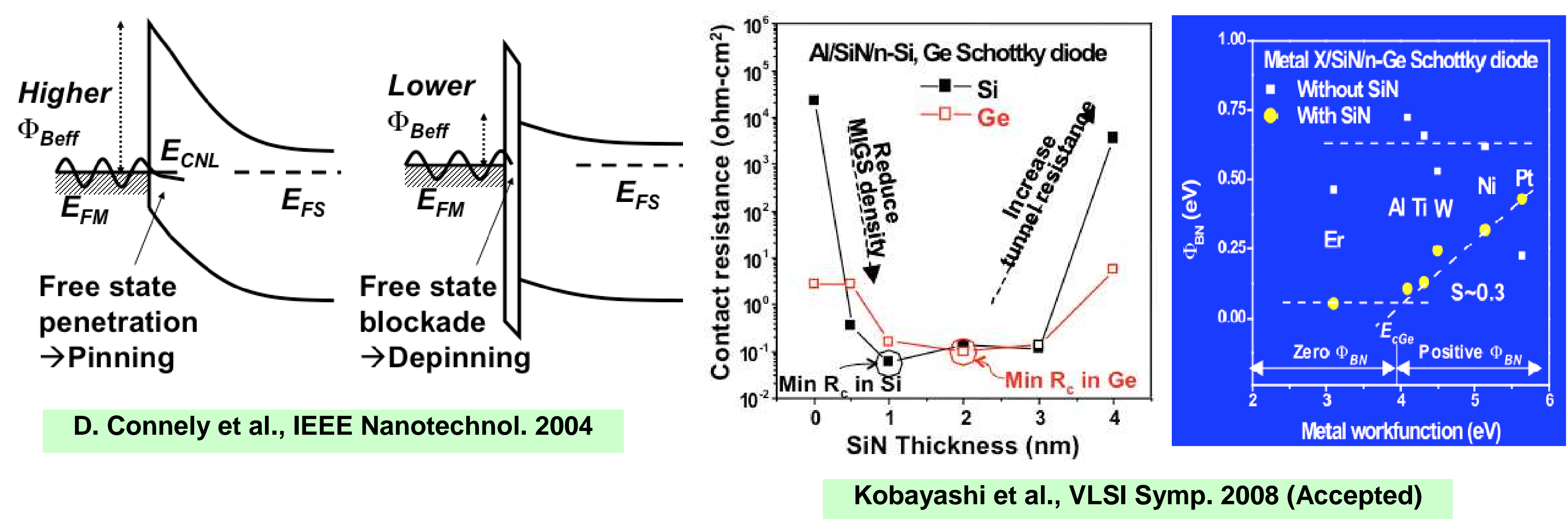


- For NMOS need Φ_{Bn}= 0 to increase I_{on} and reduces drain leakage
- Similarly need Φ_{Bp}= 0 for PMOS
- For Ge Φ_{Bp}= 0.1 eV, excellent for PMOS, Φ_{Bn}= 0.56 eV, really bad for NMOS
- For Si $\Phi_{Bn} \approx 0.67\ E_G$ and $\Phi_{Bp} = 0.33\ E_G$ bad for both NMOS and PMOS

Ideal Schottky Contact for NMOS



Fermi-Level Depinning in Metal/Ge Schottky Junction



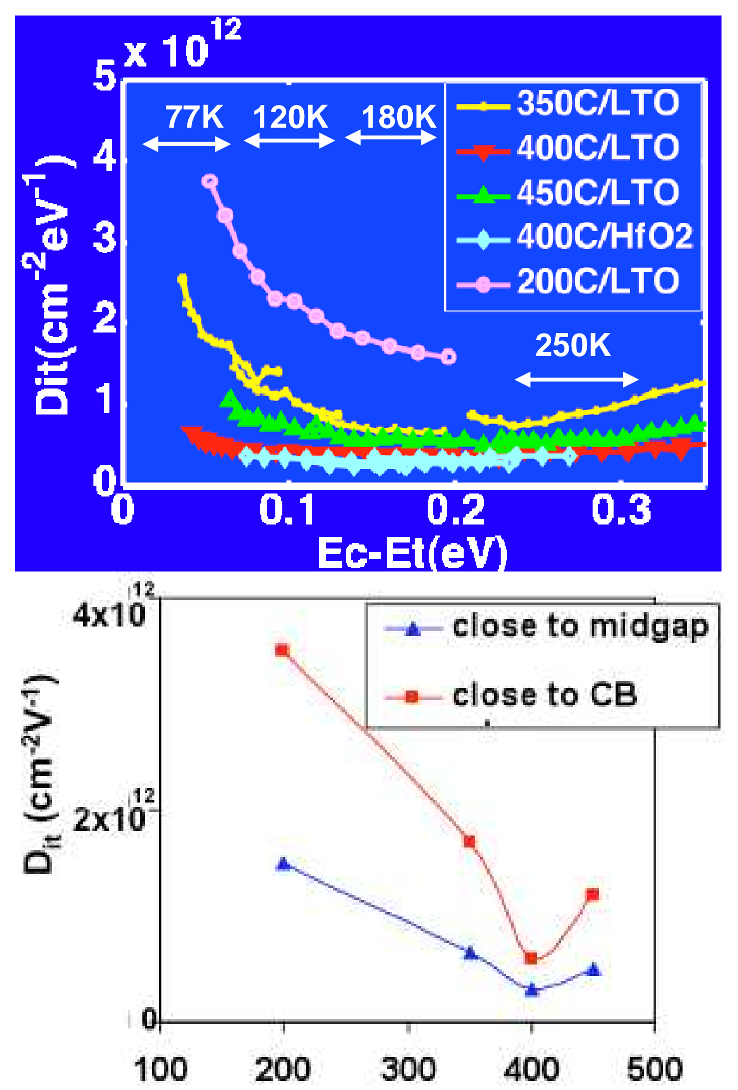
- Small E_g Ge suffers from high MIGS density
  - Pin metal Fermi-level near charge neutrality level
- Ultrathin interfacial layer can prevent free electron wavefunction penetration
  - Eliminate MIGS
- It is possible to get 0 or even negative Schottky barrier height

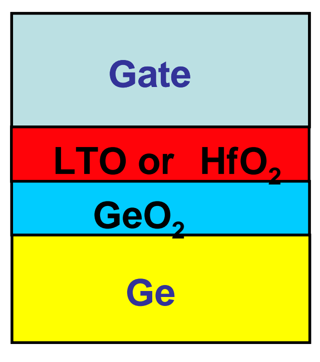
Thermally-stable Ge interface layer

Conventional process		Proposed process
Dummy gate and high-k stack deposition		Gate stack deposition
Dummy gate patterning		Gate patterning
Sidewall formation, implants and dopant activation		Sidewall formation, implants and dopant activation
Pre-metal dielectric deposition and CMP	⇐	***Dummy gate CMP eliminated***
Dummy gate etch	⇐	***Dummy gate etch eliminated***
pMOS or nMOS metal deposition, metal fill and CMP	⇐	***2nd set of metal depositions eliminated***

Reduce processing steps & minimize ESH impact

D_{it} of Ozone Oxidized Ge Surface





D. Kuzum, et al., (Stanford)
IEEE IEDM, Dec., 2007

- Ge oxidation in ozone at 200 - 450ºC
- Minimum D_{it} of $3x10^{11}cm^{-2}V^{-1}$ is obtained for samples grown at 400°C.
  - ➢Interface quality is comparable with state-of-art high-K on Si.
- At lower temperatures sub-oxides form at the interface and at higher temperatures GeO_2 dissociates into Geo resulting in higher D_{it}
- Need technology to stabilize oxidized Ge surface for gate first high temperature processing

Deliverables of Proposed Work

- GOI technology by selective deposition of Ge on Si
- Zero Schottky barrier contacts to Ge and Si
- High temperature compatible passivation of Ge surface
- Demonstrate fabrication of Ge MOSFETs on selectively grown Ge on Si with GeO_2 based high-k gate dielectric and metal S/D contacts (under funding from other sources)
- Demonstrate fabrication of MSM optical detectors on selectively grown Ge on Si with tunable Schottky barrier contacts (under funding from other sources)
- Demonstrate efficacy on ESH impact

Low Environmental Impact Fabrication of Gate Stack Structures

(*Task Number: Proposed Project*)

PI:

- Anthony Muscat, Chemical and Environmental Engineering, UA

Graduate Students:

- Shariq Siddiqui, MS candidate, Chemical and Environmental Engineering, UA
- Fee Li Lie, PhD candidate, Chemical and Environmental Engineering, UA

Undergraduate Students:

- Genevieve Max, Chemistry and Computer Science, UA

Other Researchers:

- Gary Fleming, Postdoctoral Fellow, Chemical and Environmental Engineering, UA

Cost Share (other than core ERC funding):

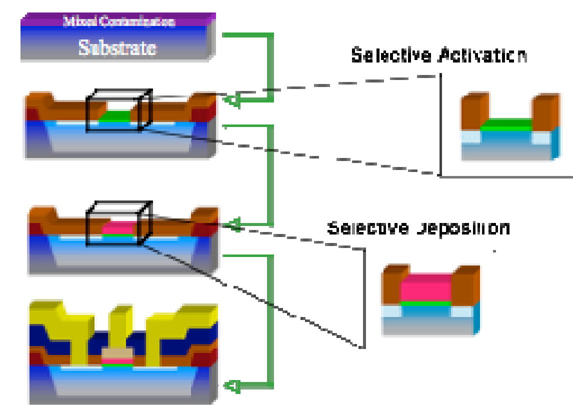
- $25k from SEZ

Objectives

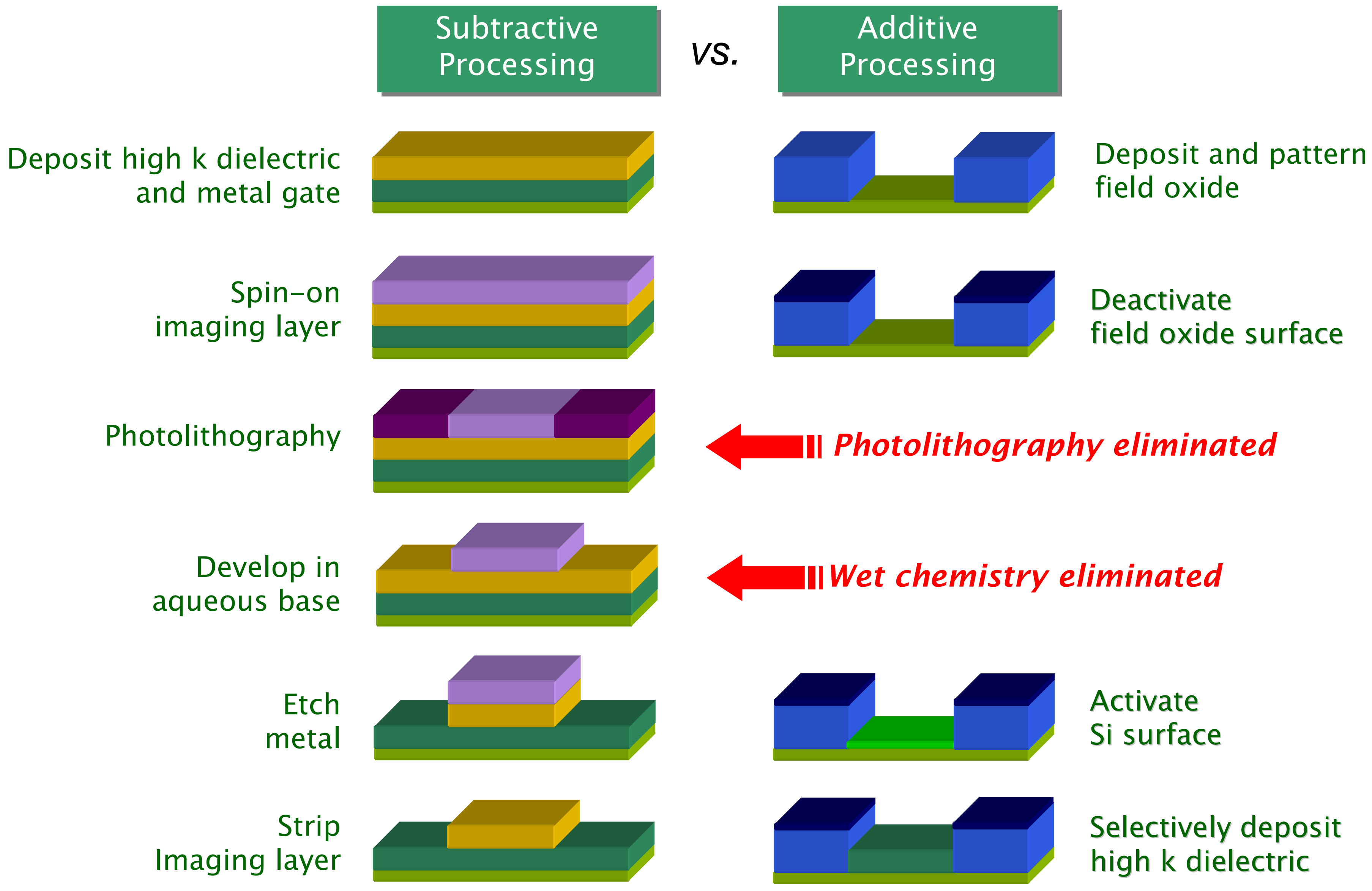
- Develop low cost of ownership surface passivation and activation processes
  - Minimize water, energy, and materials use
  - Introduce cost effective processes into high-volume manufacturing

- Compare chemistries to clean and passivate advanced gate stack materials with minimal impact to high mobility substrates
  - Liquids leverage existing technology base
  - Gases provide ideal surface terminations

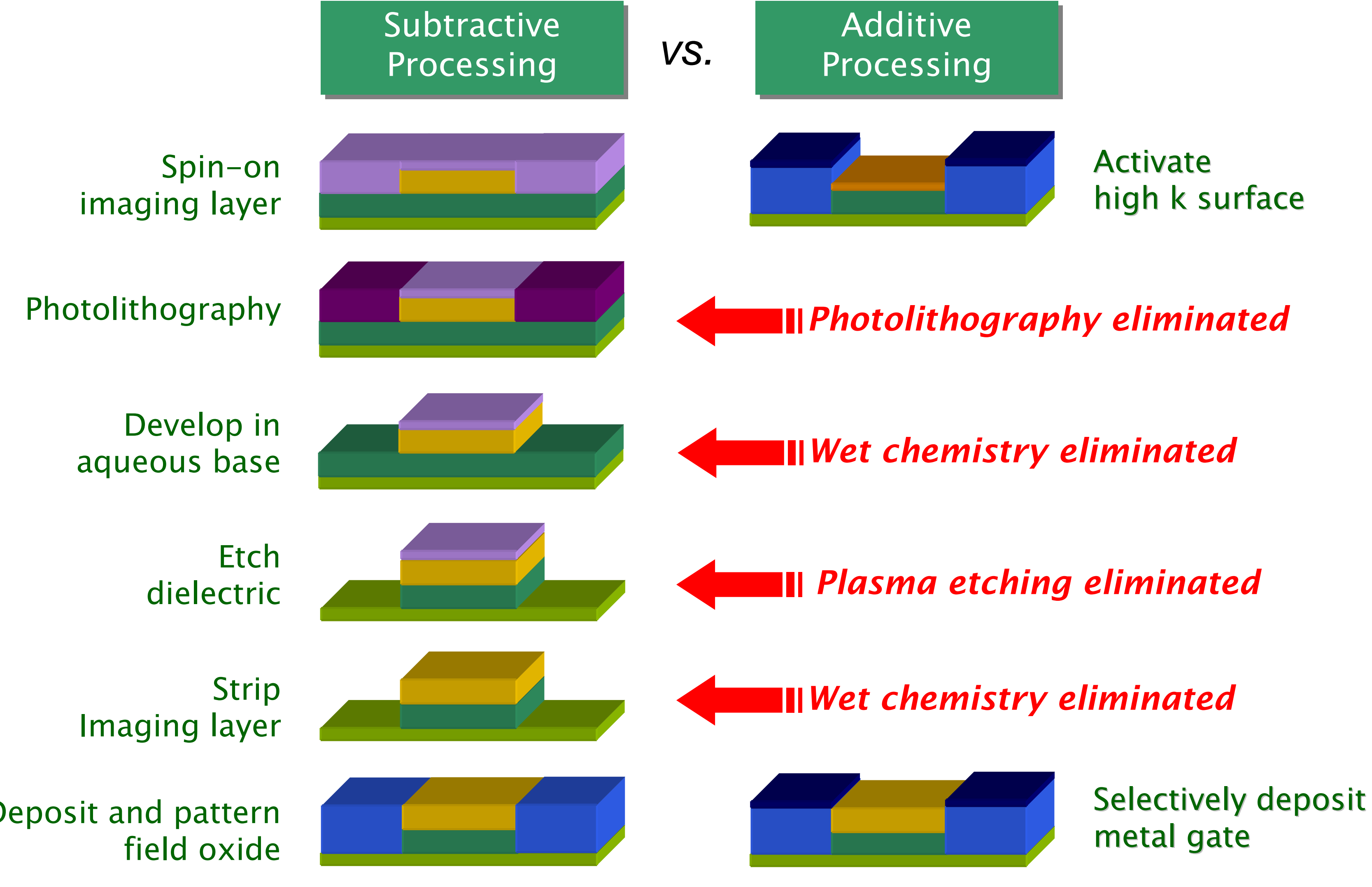
- Enable gate first process by selectively depositing high-k directly on Ge and III-V binary and ternary substrates



ESH Metrics and Impact: Self-aligned High k Gate Stack



ESH Metrics and Impact: Self-aligned High k Gate Stack



SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Methods and Approach

1. Use gas phase chemistries to create ideal surface terminations
2. Generate fundamental data sets containing adsorption, desorption, and reaction rate parameters to compare liquid and gas phase processes
3. Build process models to transfer to tool and device companies in order to assess the viability of integrating new steps into existing manufacturing processes

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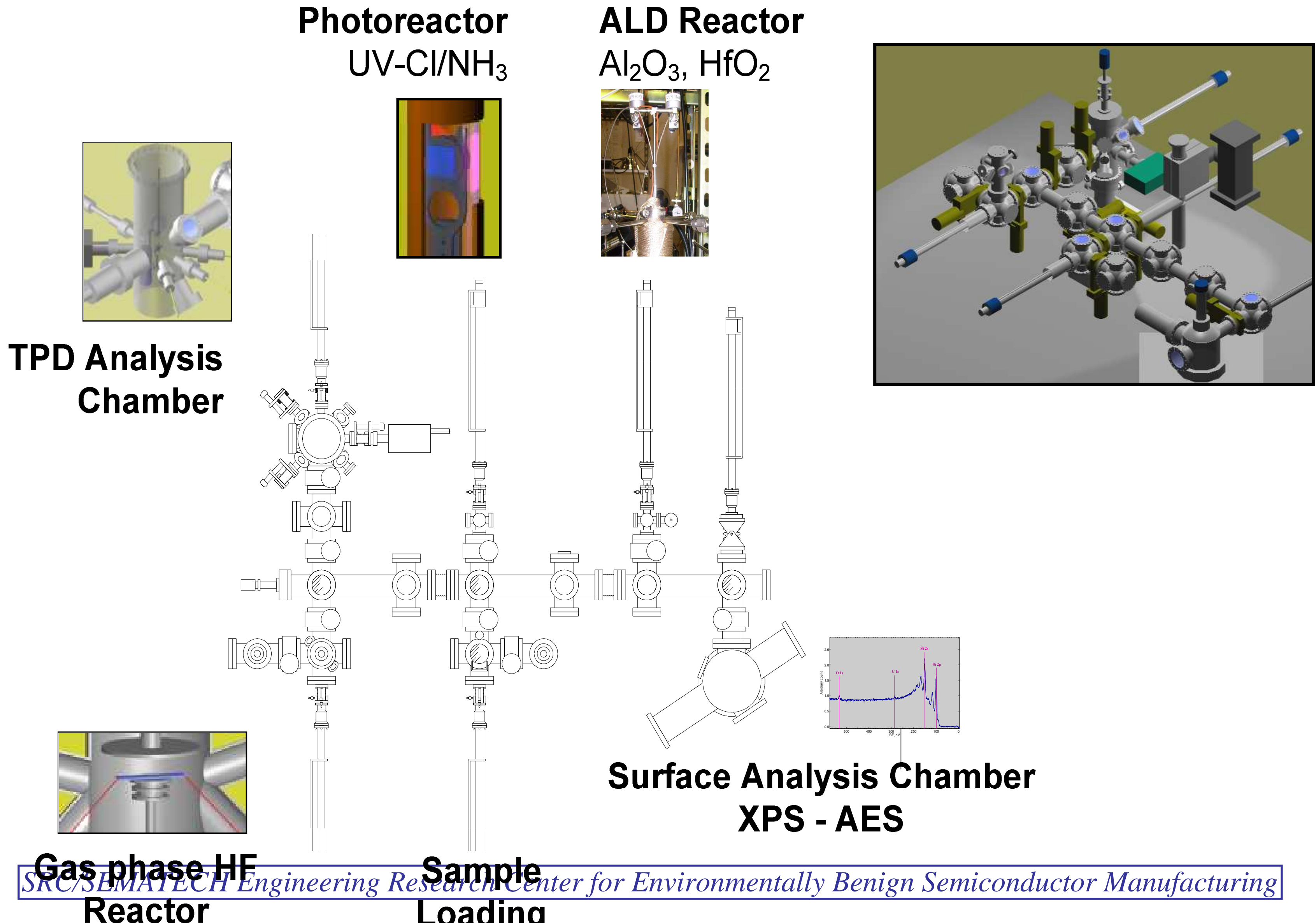
Current Projects

Ge(100) surface prep and high-k deposition

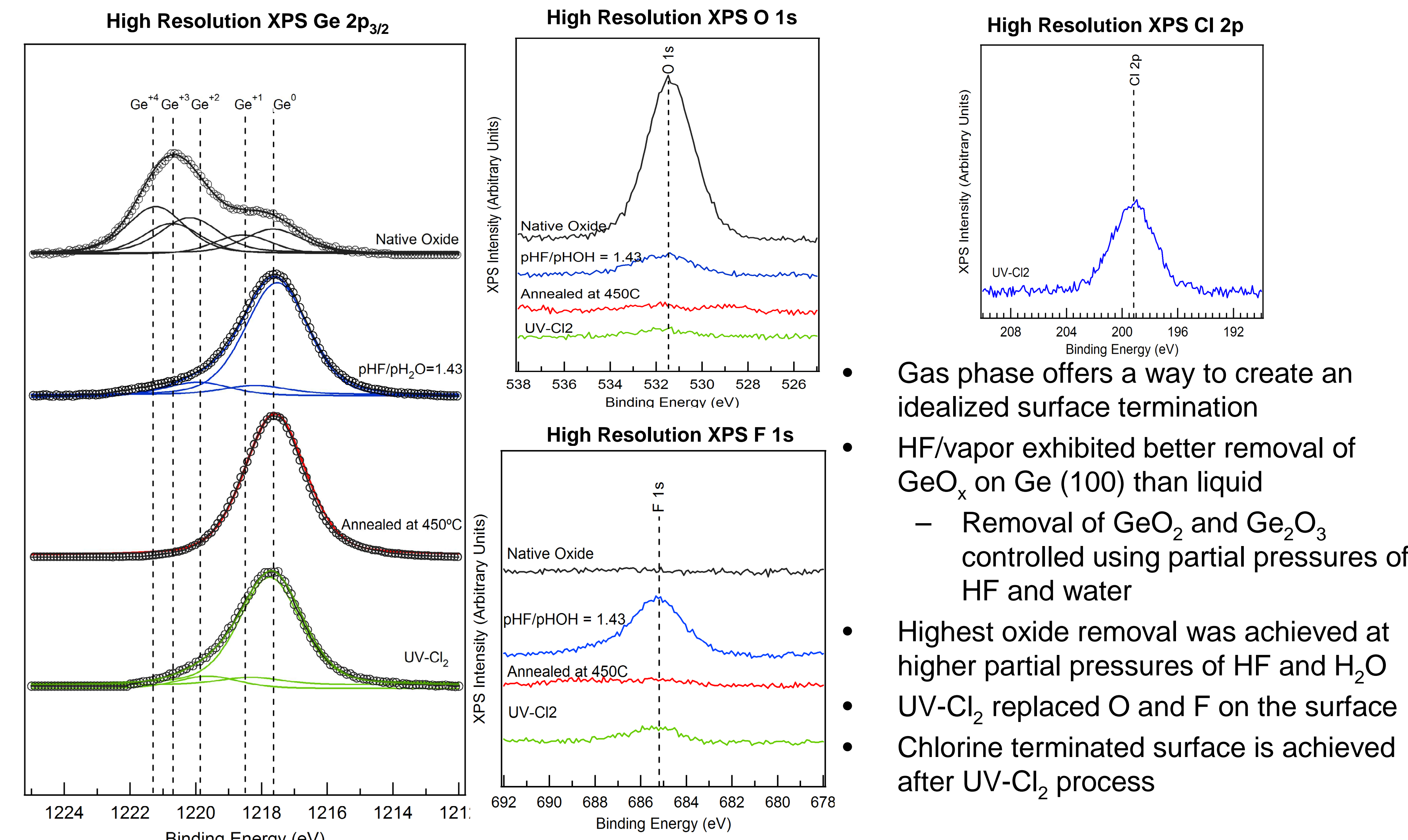
InAs(100) surface prep and high-k deposition

GaAs(100) surface prep

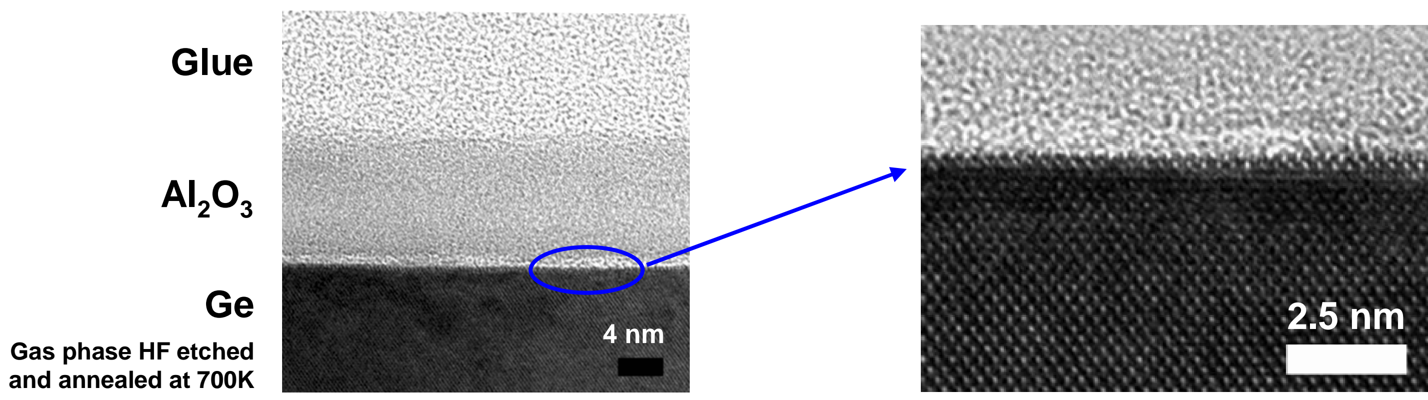
Clustered Reactor Apparatus



Ge Oxide Removal: Gas Phase HF & UV-Cl_2

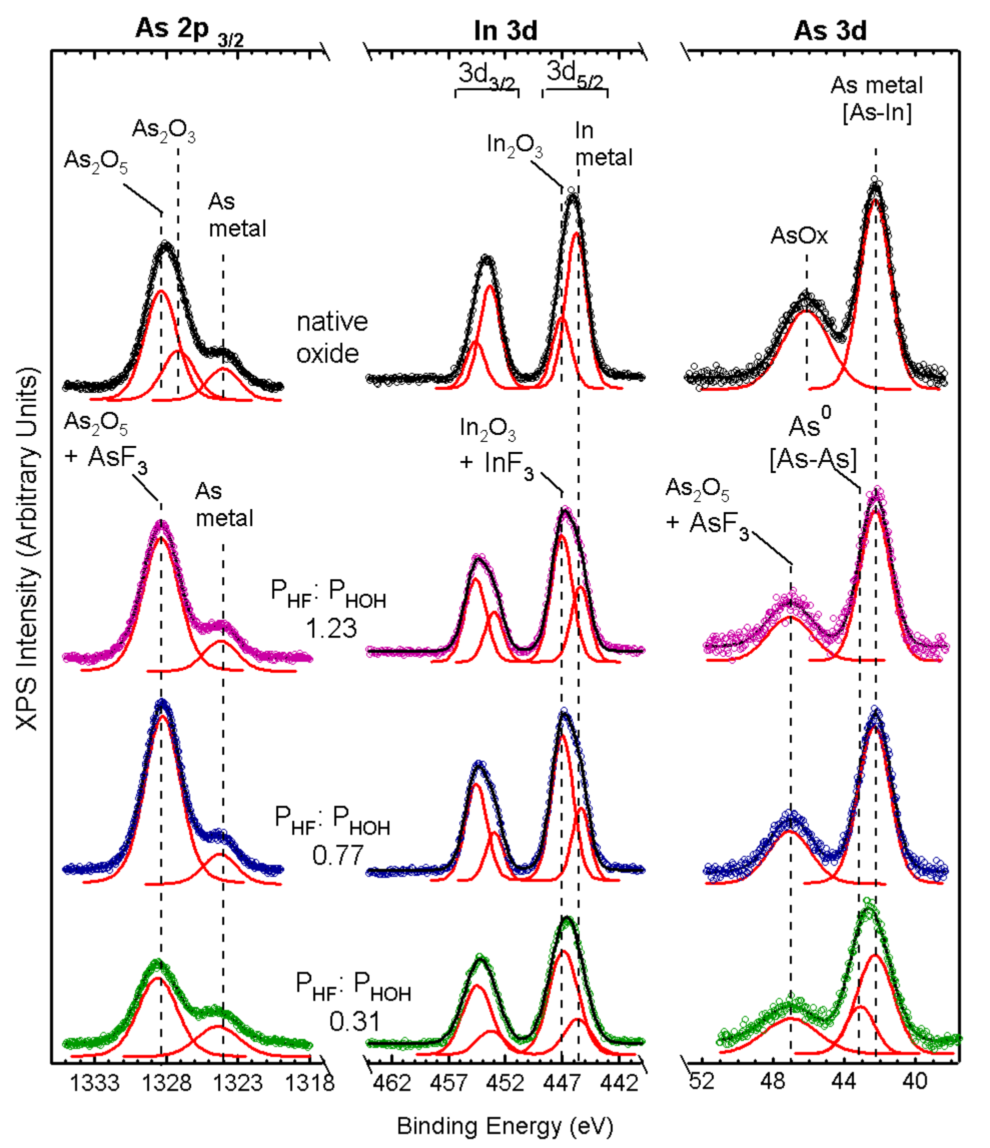


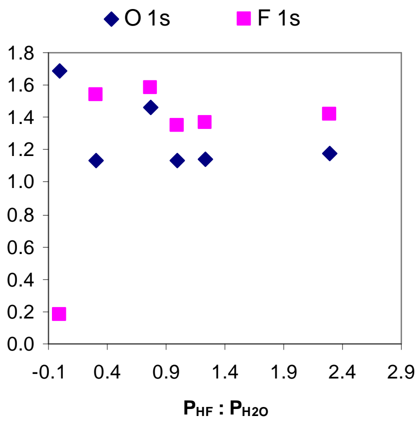
Direct Deposition of Al_2O_3 on Ge(100)



- H_2O pulse followed by TMA pulse
- Obtain controlled growth of Al_2O_3 on Ge using atomic layer deposition
- A 0.8 nm interfacial layer observed between Ge substrate and uniform a- Al_2O_3

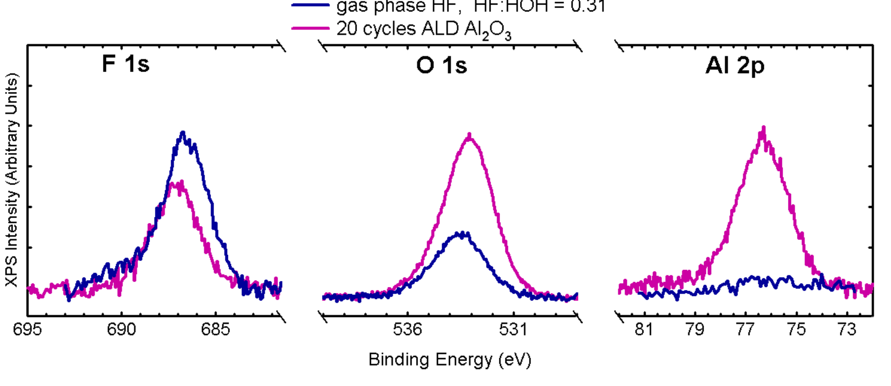
InAs Oxide Removal: Gas Phase HF

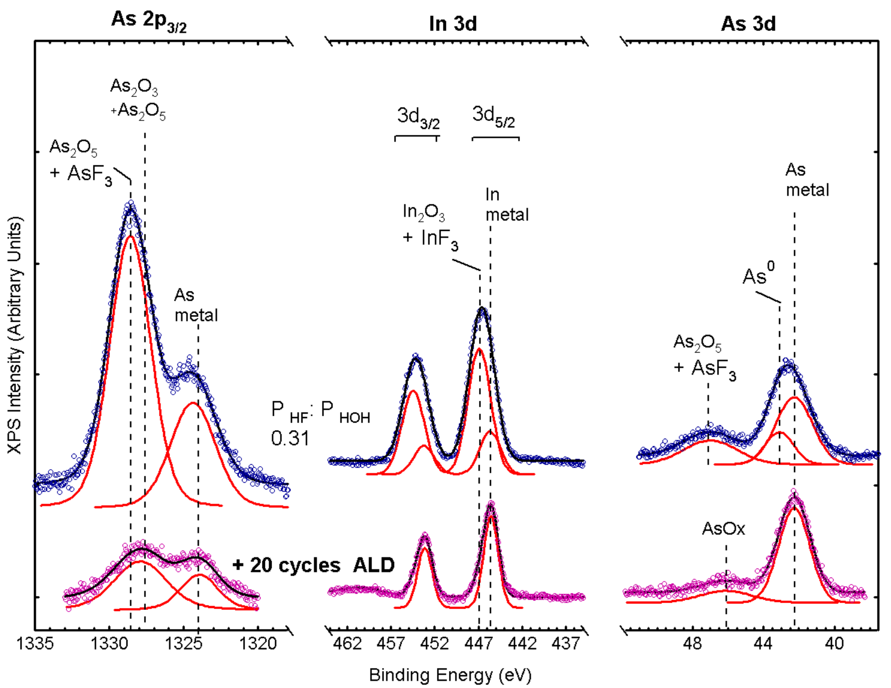




- Complete removal of As_2O_3
- Etching product consists of AsF_3 and InF_3
- Lower HF concentration results in higher oxide removal and lower F residue
- Highest oxide removal achieved at P_{HF}:P_{H2O} 0.31 with elemental As observed

InAs Atomic Layer Deposition of Al_2O_3





- Demonstrate atomic layer deposition (ALD) of Al_2O_3 on gas phase etched InAs(100)
  - Precursors : $Al(CH_3)_3$ and H_2O
  - Growth rate 1.08 Å/cycle
- HR-XPS of Al_2O_3 film shows interfacial reaction between surface species and ALD precursors
  - Removal of In_2O_3 and InF_3
  - Removal/conversion of elemental As and AsF_3 to As_2O_5 and As_2O_3
  - Preferential bonding of O to Al

Industrial Interactions and Technology Transfer

- **Project updates to IMEC**
  - **Marc Meuris**
  - **Valentina Terzieva**

- **Project updates to SEZ**
  - **Harald Okorn-Schmidt**
  - **Jeremy Klitzke**

Future Plans

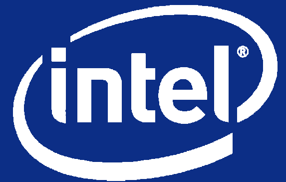
Next Year Plans

- Compare native oxide removal from Ge and III-V using conventional and nonconventional liquid and gas phase processes
- Demonstrate atomic layer deposition of high k material on Ge and III-V materials
- Characterize high-k/substrate interface properties

Long-Term Plans

- Correlate surface preparation method and interfacial properties of high k material/substrate to device electrical performance

ERC – Intel
A Customized Pilot Joint Research Initiative



Expected Outcome: An Update to ERC on the Pilot Initiative with Intel & UA to Explore Additional Capabilities to the Existing ERC Scope via Customized Research Initiatives

Gopal Rao, Intel

Farhang Shadman, ERC

Executive Summary

- A customized pilot initiative/process is underway within the framework of the ERC:
  - Focus on joint research with potential insertion into HVM
  - Integrate research transfer into the plans up front
  - Develop a new Management Philosophy to enable a *pilot initiative on HVM to explore additional capabilities to the existing ERC scope via customized research initiatives*
- Initial Coordination Team structure has been defined under joint ERC/Intel management
  - Facilitate research selection and initiation
- The Coordination Team is currently chaired by Farhang Shadman (ERC) and Gopal Rao (Intel)
- In 2008 we will have at least 3 multi year customized projects jointly funded by Intel with matching funds from non-core ERC budget. The level of total funding ~ $100K/year/project.

Potential benefits: Provides additional capabilities for members within the ERC scope

Goal of the Customized Initiative

Leverage Existing ERC Structure/Strengths/Talent to Enhance ERC/Industry partnership for directed research & transfer to HVM

Engineering Research Center
Director: Farhang Shadman

A multi-university research center leading the way to environmentally friendly semiconductor manufacturing

ERC – Intel
Customized Focused Initiative

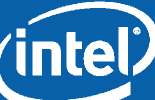
Chairs: Farhang Shadman & Gopal Rao

Enabling Joint Collaborative Research For HVM Implementation

Intel User Groups

A Customized Research Initiative

Operates as an ERC Sub Team



ERC/Intel Initiative Scope

Research Roadmap

(e.g. ITRS)

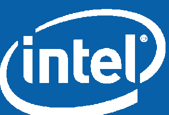
Joint Research

Student & PI Development

Manufacturing Readiness

HVM Insertion Management

Research Capability Management



Joint Collaborative Research Model Resource Weighting

"Focusing on Research With HVM Implementation is Critical to Effectively Managing the Research/Student Supply Chain"

Research

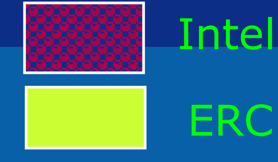
Research Transfer & Pilot

Research Implementation in HVM

Relative Resource Weighting

Minimum Continuous Baseline Interaction Required:
Student Mentorship, E-Scan, Research Roadmap, HVM Feedback/Feed Forward etc..

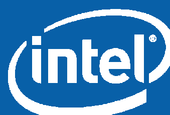
Time



Sustainable High-Volume nano-Manufacturing (HVnM) Research

General Areas of Interest

1. Natural Resources
   - Water Conservation
   - Energy Conservation
2. Bulk Chemicals, gases and Materials
   - Availability – Quality and Quantity
3. Equipment & Process
   - Productivity/Predictability/PCS Enhancement
   - EHS footprint and Assessment
   - Interactions
   - Green Alternatives

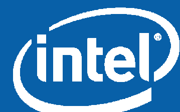


Summary

1. This is a great win-win initiative that links Academia and Industry on HVM centric research projects.

2. Call for Research Proposals with key dates (Open to ERC member Universities) to be posted on the ERC website by early March.

3. The expectation is to initiate approved research projects by June 1, 2008.

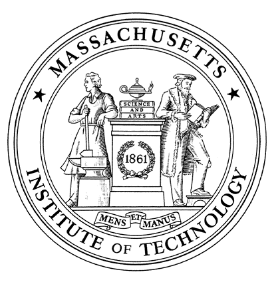


New Planarization Proposal

Effect of Retaining Ring Geometry on Slurry Flow and Pad Micro- and Macro-Texture

Prof. Philipossian … 1 Ph.D. student for Year – 1, Year – 2 and Year – 3 at UA

Prof. Boning … 1 Ph.D. student for Year – 2 and Year – 3 at MIT (Year – 1 activities at MIT will leverage resources from already-funded ERC projects)

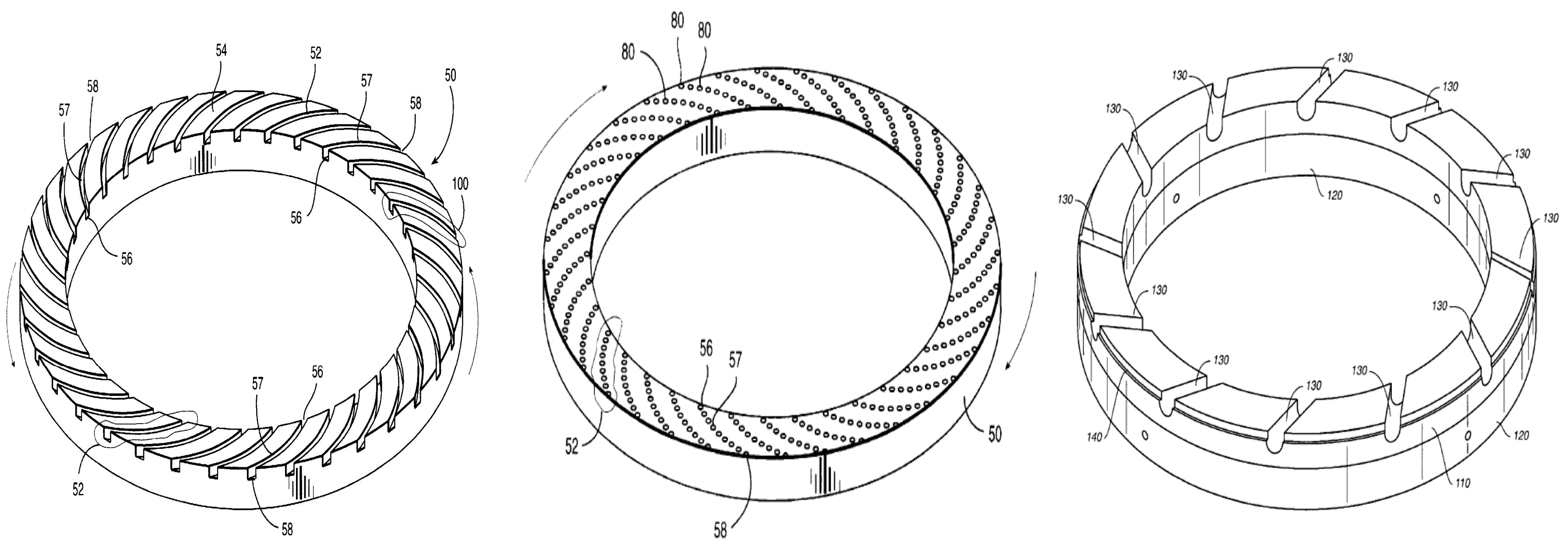


February 2008

Problem Statement

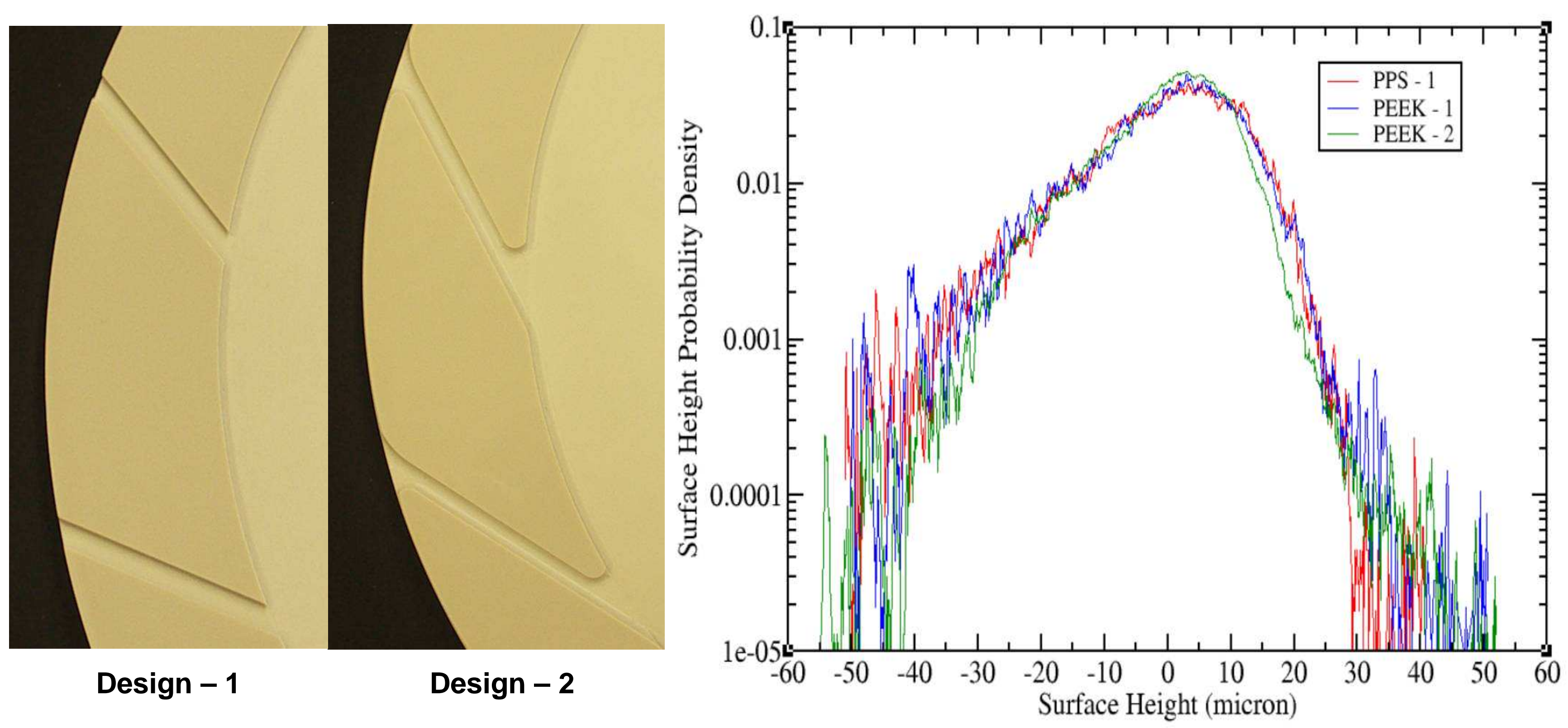
- Slurry consumption continues to be one of the main drivers in **CMP EHS and COO**

- Patent literature claims that retaining rings with different geometric designs (like those shown below) can affect slurry transport in the pad-wafer region, however a systematic study of their slurry transport characteristics has not yet been undertaken

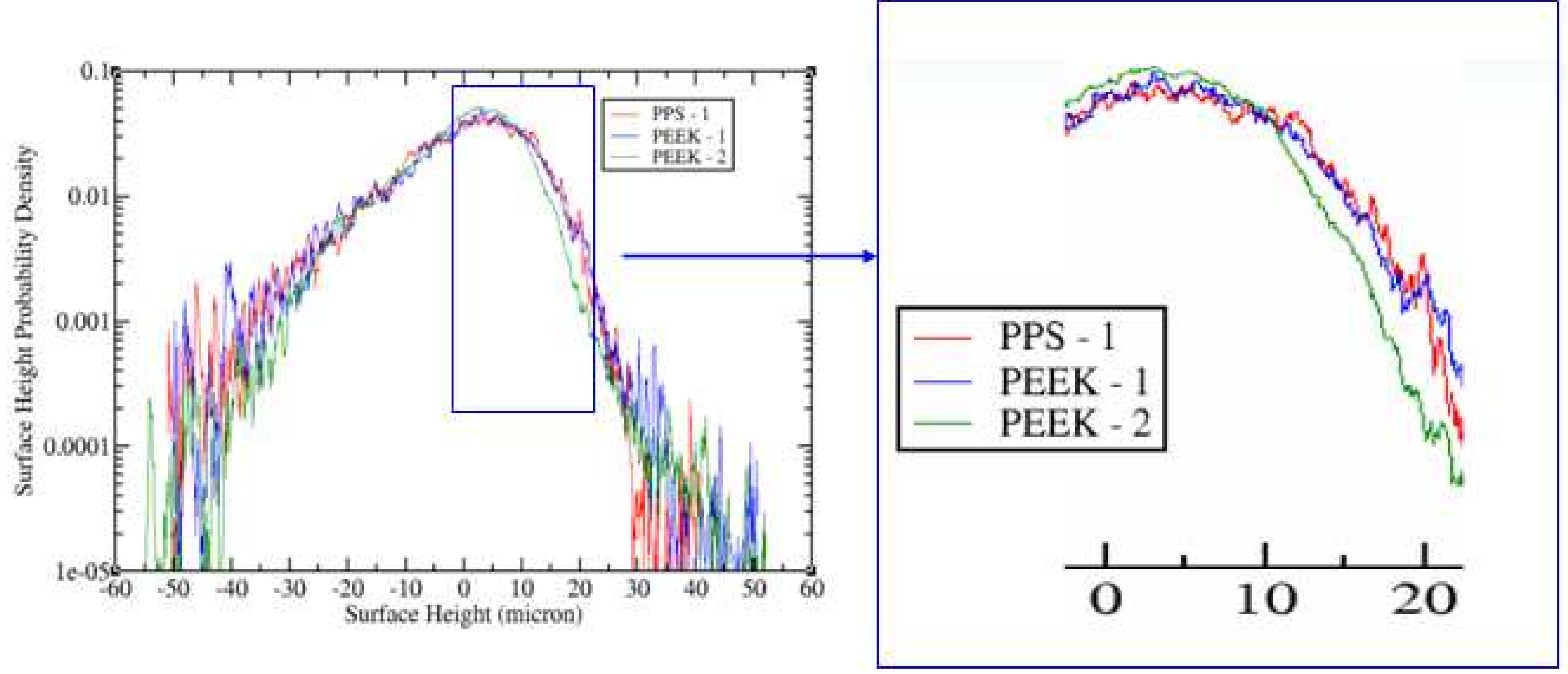


Problem Statement (continued)

- There is evidence that retaining rings with different designs affect pad micro-texture differently
  - ✓ PEEK and PPS rings with Design – 1 result in wider pad asperity height distributions compared to a PEEK ring with Design – 2
  - ✓ This may suggest that planarity can be affected by ring geometry



Problem Statement (continued)



The PEEK – 2 ring achieves a narrower pad surface height distribution than the PPS – 1 and PEEK – 1 rings, suggesting that the slot design and the edge rounding plays significant roles in shaping the pad micro texture.

Objective

- **Objective:**

  - ✓ **Determine how slurry transport in the pad-wafer region is affected by various retaining ring slot angles, concentric pad groove designs, slurry flow rates and polisher kinematics**

  - ✓ **Determine how above ring geometric parameters affect pad asperity height distributions (i.e. micro-texture) and pad profile (i.e. macro-texture)**

  - ✓ **Relate (experimentally and numerically) pad micro-texture and macro-texture to planarity**

  - ✓ **Define novel retaining ring geometries that minimize slurry use yet provide superior polish performance**

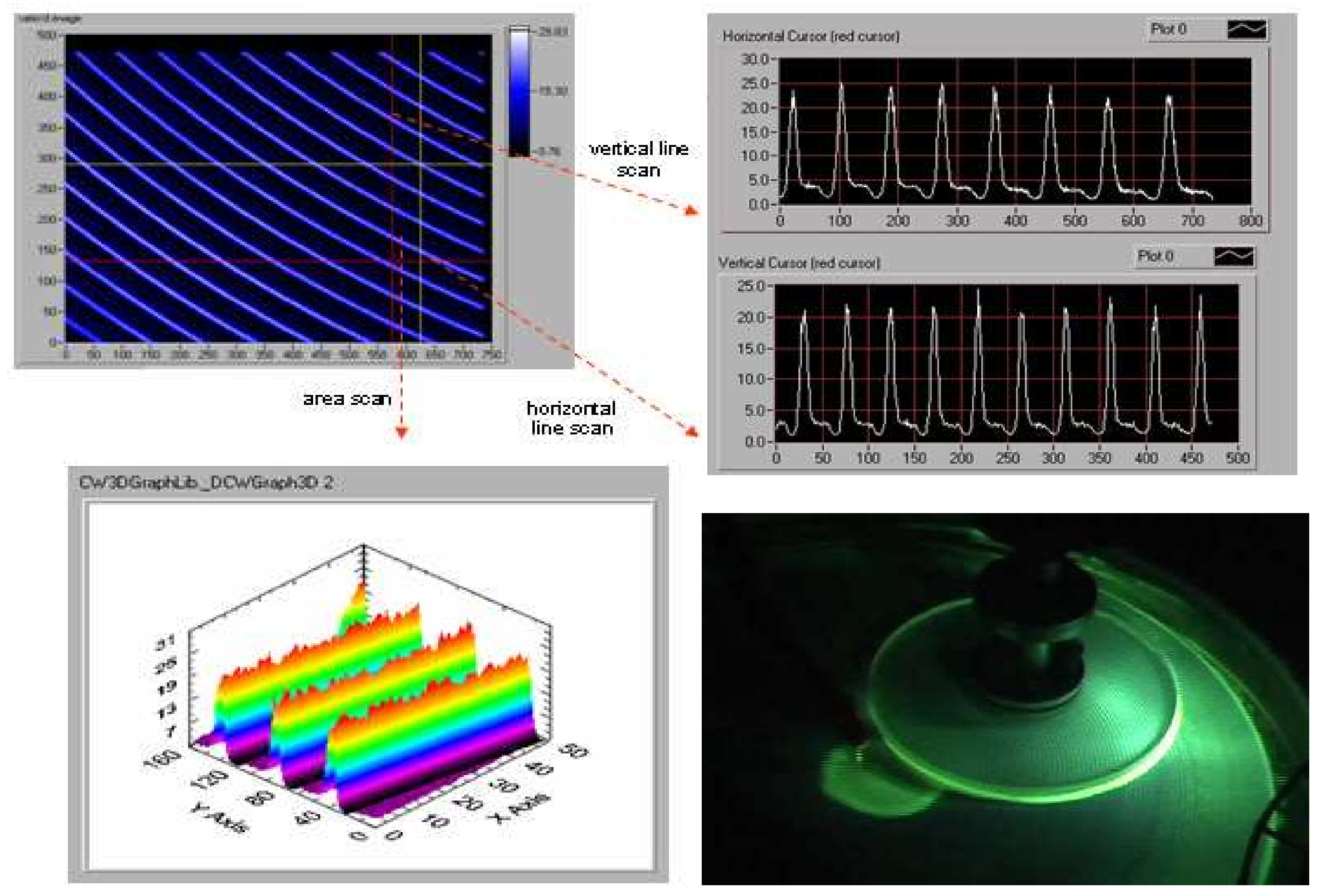
Approach

- **General Approach:**

  ✓ **Work with a retaining ring manufacturer and a pad grooving outfit and make PEEK rings and pads with various designs**

  ✓ **Use dual emission UV-enhanced fluorescence (DEUVEF) on a 200-mm platform fitted with a special quartz wafer and retaining ring assembly to quantify slurry mean residence time and film thickness in the land areas as a function of ring, pad and process (see next page)**

Approach (continued)



Approach (continued)

- Perform land-area slurry film thickness tests and residence time distribution (RTD) tests (using slurry spiked with fluorescent dyes) with multiple types of pads and retaining rings at various:
  - ✓ Velocities
  - ✓ Flow rates
  - ✓ Pressures
- Analyze results using traditional RTD reactor design methodologies to determine mean residence time and dispersion number for each combination of parameters

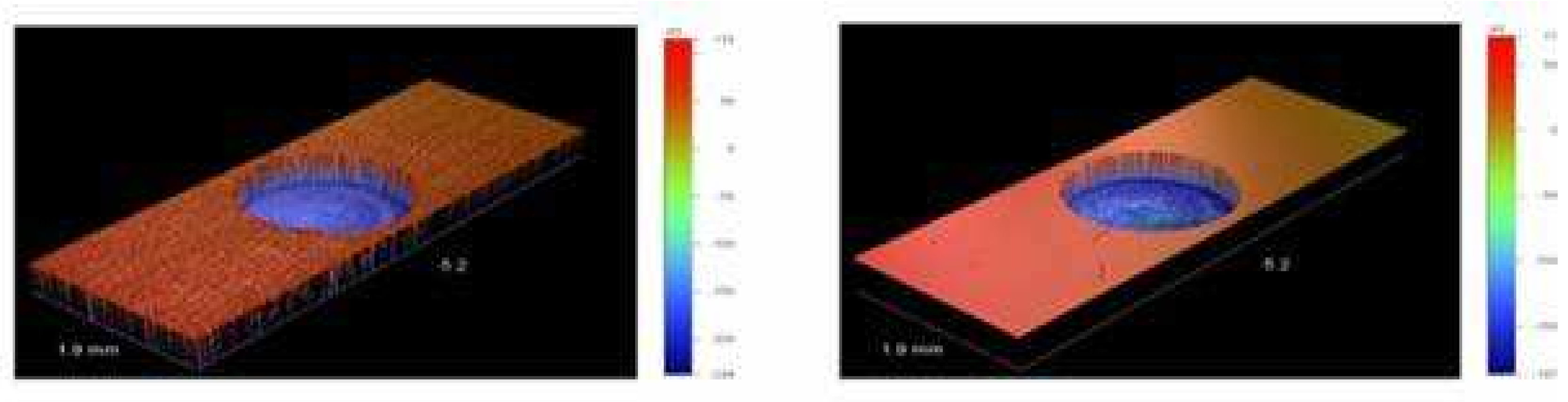
Approach (continued)

- Perform extended wear tests on each retaining ring (on 300-mm STI and copper processes)

  ✓ Determine pad temperature, COF & variance of shear force as a function of wear time

  ✓ Accurately determine wear rate using white light interferometry before (left) and after (right) the 6-hour wear test on shallow trenches machined on the land areas of the ring

  ✓ Determine pad asperity height distribution using white light interferometry, and determine pad wear profile using micrometry



Perceived Technical & EHS Benefits

- **Understanding how retaining ring design can influence slurry transport in the wafer-pad region can aid IC makers in optimizing rings that can:**

  ✓ **Significantly reduce overall slurry consumption**

  ✓ **Facilitate slurry transport into the wafer-pad region and by-product transport out of the wafer-pad region**

- **Micro-scale and macro-scale pad-ring interactions in CMP are not well understood**

- **For a given down force, the ring-slurry-pad shear force is 2 – 3X that of the wafer-slurry-pad shear force (i.e. pads are more prone to wear as a result of contacting the ring than contacting the wafer), hence pad life can be enhanced through novel ring design as well**

Perceived Technical & EHS Benefits

- **For 300 – mm processes, polyurethane pads and retaining rings are similarly priced and tend to get replaced during the same pit stops thus exacerbating COO and EHS issues**

- **Early evidence suggesting an effect on pad micro-texture by differently designed rings may be properly exploited to yield optimum pad micro-textures (critical for achieving die-level topography module target specs) through improved ring design**

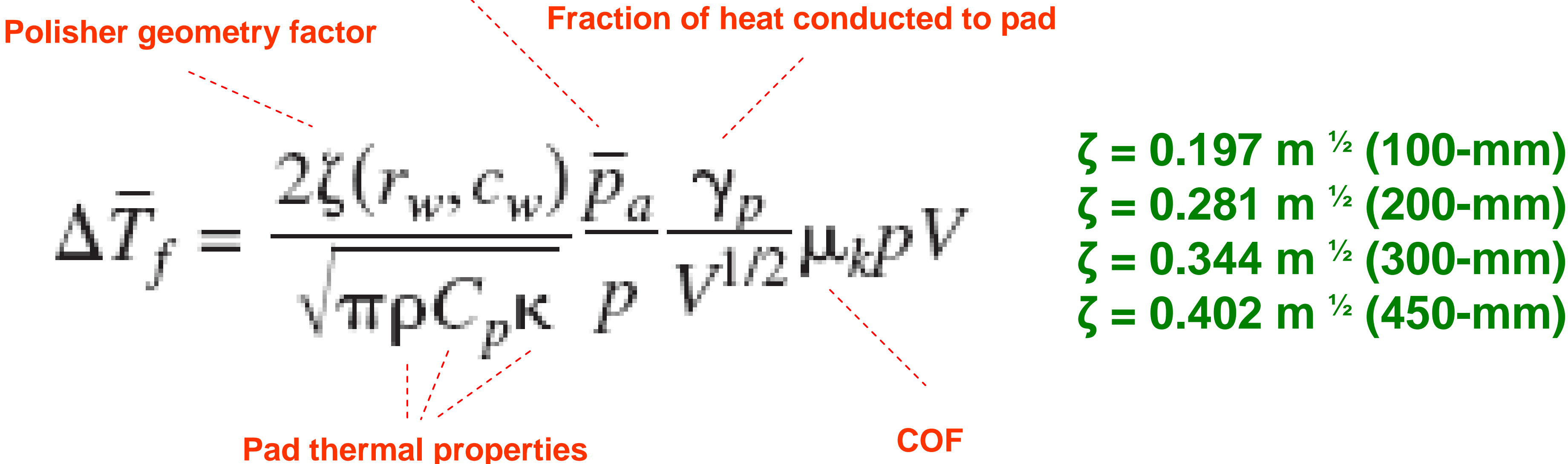
- **For 450 – mm process (*circa* 2015), holding the wafer in place during planarization will be a formidable task thus placing tremendous mechanical (in the shear and normal directions), thermal and slurry fluid dynamics responsibilities on the retaining ring**

$$\bar{T} = \bar{T}_p + \Delta\bar{T}_f$$

Perceived Technical & EHS Benefits

- ‘Bracing’ for 450 – mm processes … reaction temperature (i.e. true wafer surface temperature) increases significantly as wafer size is increased … surface temperature of the retaining ring will increase even more due to higher COF

Mean asperity contact tip pressure (next page)



$$\Delta \bar{T}_f = \frac{2\zeta(r_w, c_w)}{\sqrt{\pi \rho C_p \kappa}} \frac{\bar{p}_a}{p} \frac{\gamma_p}{V^{1/2}} \mu_k p V$$

$$\zeta(r_w, c_w) = \frac{2c_w^{1/2}}{3\pi r_w^2} \int_{c_w - r_w}^{c_w + r_w} R\{2\cos^{-1}[(R^2 + c_w^2 - r_w^2)/(2Rc_w)]\}^{3/2} dR$$

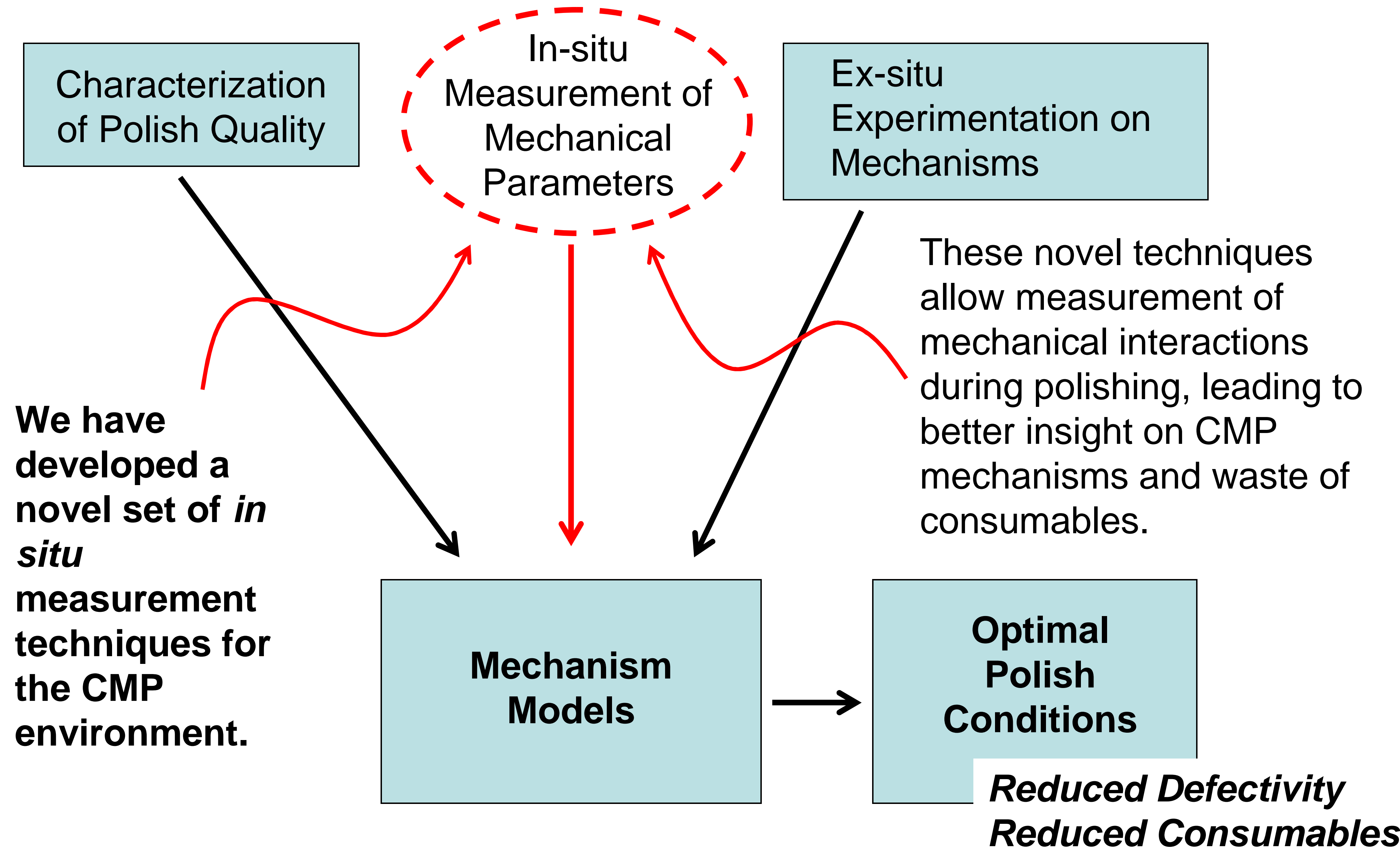
New Planarization Proposal

Investigation of the Impact of Microscale Forces and Global Fluid Mechanics on Polish Defectivity and Consumable Use

Prof. Robert White, Prof. Chris Rogers,
Prof. Vincent Manno

February 2008

Concept



Goals: Planarity

Goal #1: Reduce polish damage to ***fragile structures*** such as porous low-k dielectrics.

Question #1: Does reducing the ***microscale lateral forces*** by optimal choice of polish conditions, pad type, and conditioning reduce damage to fragile structures such as low-k dielectrics?

Goal #2: ***Reduce damage to patterned substrates .***

Question #2: Point defects, scratches, dishing and erosion may be caused by mechanical expansion of the pad around nanoscale features. Thus, does ***increasing pad-wafer contact*** percentage by optimal conditioning and pad design reduce local normal forces, thereby reducing pad expansion around nanoscale features and reducing damage?

Goals: Consumables

Goal #3: ***Reduce pad maintenance time and pad usage*** while maintaining polish quality.

Question #3: In production, pads may be changed early and often to avoid any possibility of loss of polish quality. Will ***in-process monitoring*** of microscale and macroscale forces, wafer attitude, and pad-wafer contact allow improved detection of pad end-of-life condition, resulting in reduced pad usage and tool down-time?

Goal #4: ***Reduce slurry consumption*** while maintaining polish quality.

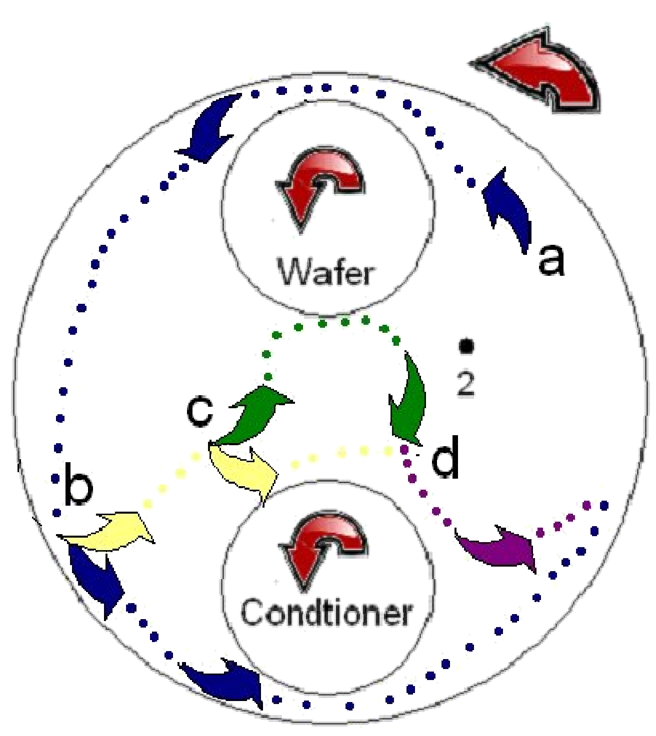
Question #4: Much of the ***slurry introduced to the pad may never interact with the wafer***, and may be wasted. Can optimization of slurry introduction point, pad grooving, and rotation rate increase slurry usage, and therefore reduce the required slurry flow rate?

Technical Approach: Platform

- **Deploy experimental techniques in a relevant system.**
  - Experimental techniques thus far have been developed and demonstrated on a small scale (75 mm substrate) polisher.
  - Deploy the techniques to a 200 mm polisher.
  - Move to dilute, colloidal silica slurries.
- **Use patterned substrates.**
  - Development work at Tufts thus far has focused on unpatterned substrates.
  - Move to patterned substrates to investigate mechanical and fluid effects near patterned structures:
    - Micron-scale patterns fabricated at Tufts.
    - Nano-scale patterns from industrial partners.

Technical Approach: Global Flow

– Fluid visualization and particle tracking velocimetry (PTV).



Example of flow visualization analysis showing observed full-wafer slurry flow on the 75 mm polisher.

Questions to be investigated:

-How does pad grooving affect slurry flow over the entire polishing pad?

-How does asperity distribution on the pad due to pad design and conditioner geometry affect local and global slurry flow patterns?

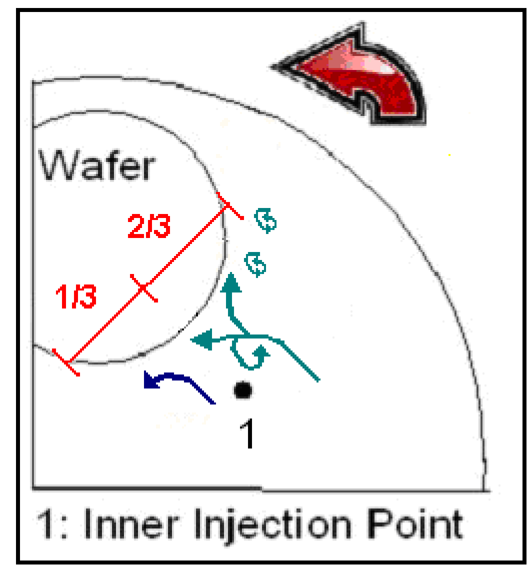
-Is there a correlation between age of the active slurry and defectivity?

-Is there a correlation between local flow patterns at the wafer and defectivity?

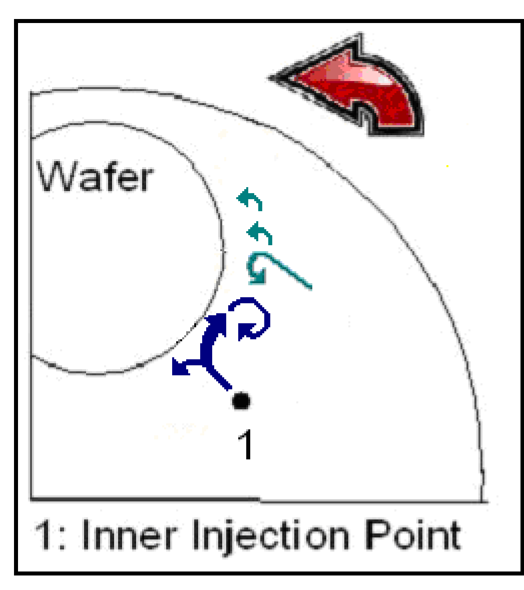
-Can we change the process to reduce slurry waste while maintaining a high quality polish?

Technical Approach: Global Flow

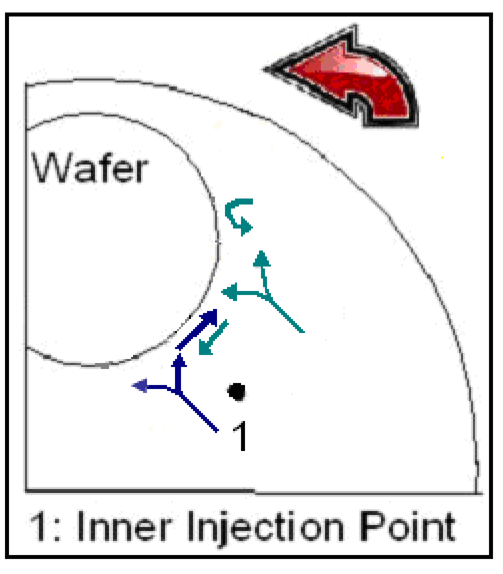
– Initial results using flow visualization show the impact of grooving on global slurry flow patterns.



Ungrooved FX9 pad:
Old slurry dominates wafer bow wave.



XY Grooved FX9 Pad:
New slurry dominates wafer bow wave.



AC Grooved D100 Pad:
Shearing of old and new slurry, mixing at bow wave.

1) Proposed: Flow visualization studies over the whole pad surface.
2) Proposed: Add particle tracking velocimetry (PTV) to quantify the velocity field.

Technical Approach : MEMS Sensors

– MEMS lateral force sensors for asperity-level and feature-level forces.

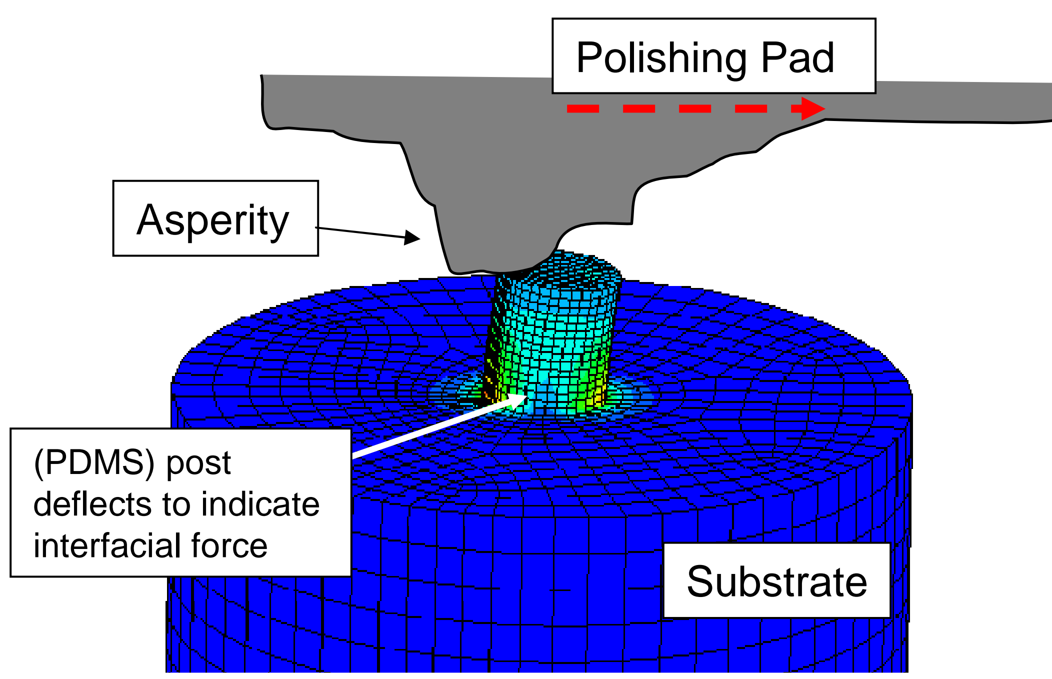


Diagram of a MEMS shear stress sensor, already demonstrated at Tufts on the 75 mm polisher, and capable of resolving forces in the 10-1000 μN range at 30-100 μm scale.

<u>Questions to be investigated:</u>

-How does the geometry of patterns at the wafer surface influence microscale shear forces at the pad-wafer interface?

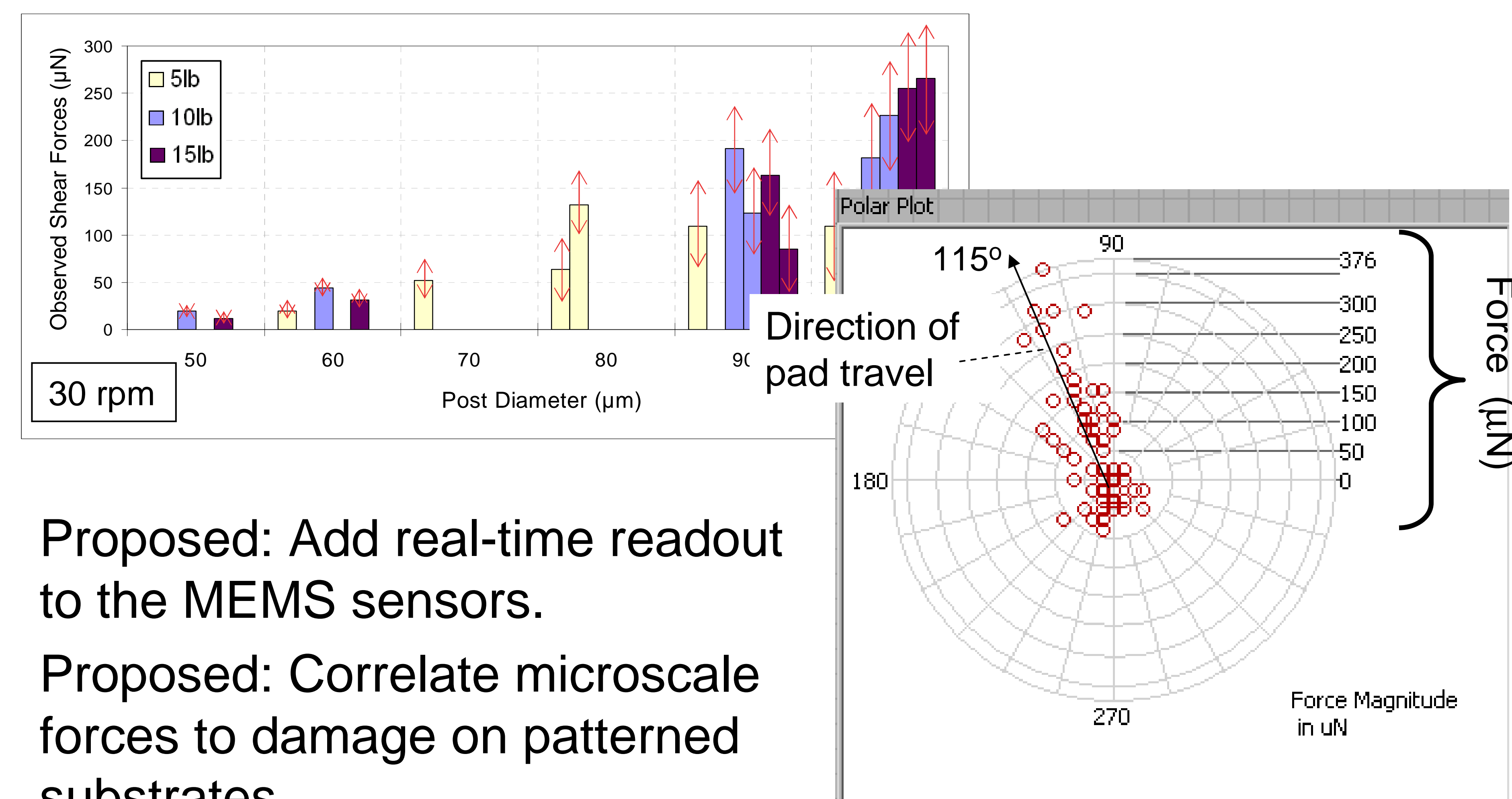
-How do changes in pad and conditioner geometry and material (including grooving) affect microscale shear forces?

-Is there a correlation between microscale shear forces and defectivity of patterned surfaces?

-Can we change the pad and/or conditioner to reduce pad waste while maintaining a high quality polish?

Technical Approach : MEMS Sensors

– Initial results show the ability to measure microNewton forces on micron-scale structures.



1) Proposed: Add real-time readout to the MEMS sensors.
2) Proposed: Correlate microscale forces to damage on patterned substrates.

Technical Approach: DELIF

– Nanosecond dual enhanced laser induced fluorescence (DELIF) for fluid film thickness and pad-wafer contact.

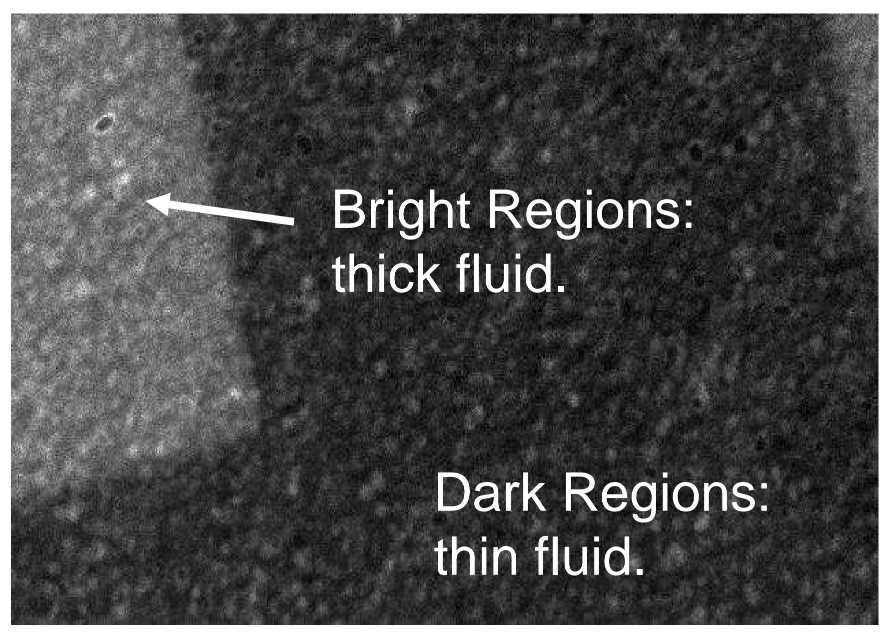


Image showing current DELIF capabilities on the 75 mm polisher. This is an image of a square well in a glass wafer during polish.

Questions to be investigated:

-How does pad-wafer contact/film thickness vary near the edges of a patterned structure on the surface?

-Is there a correlation between contact/film thickness and pad asperity distribution/pad grooving?

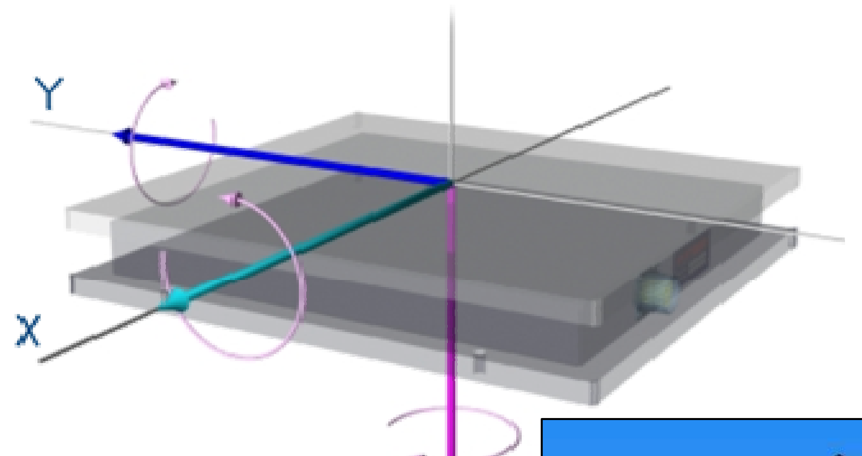
-Is there a correlation between contact/film thickness and conditioner geometry?

-Do these mechanisms correlate to observed polish defectivity?

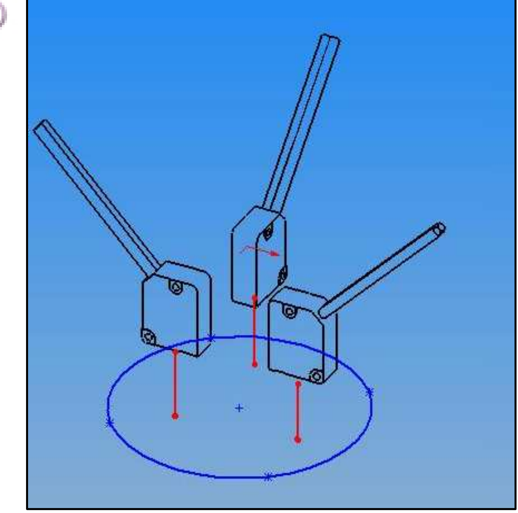
-Can we change the process to maintain quality by reduced consumables?

Technical Approach: Global Force

– Global wafer attitude (laser displacement sensors) and wafer-level forces.



Force and moment plates are used to measure global forces. Three laser displacement sensors measure wafer attitude (pitch & roll) during processing.



Questions to be investigated:

-How do the coefficient of friction (COF) and the force spectra change with pad type, conditioning, and slurry flow?

-How does the wafer attitude change with pad type, conditioning, and slurry flow?

-Is there a correlation between defectivity and force spectra and/or wafer pitch & roll?

-Can we change the pad, conditioner, and/or slurry flow pattern to reduce waste while maintaining a high quality polish?

Leverage

- **Collaborations:**
  - Philipossian: retaining ring fluid mechanics, pad-wafer contact, conditioner activity
  - Boning: modeling of polish of patterned substrates, model validation and providing model parameters
  - Stone (Harvard) and McKinley (MIT): thin film fluid modeling and experimental techniques
  - Paul (Stockton): chemi-mechanical process modeling
- **Experimental Techniques:**
  - DELIF, MEMS sensors, flow visualization, wafer attitude and global force measurement have already been demonstrated on a 75 mm scale model polisher
  - Techniques will be scaled up to a 200 mm polisher.
- **Industry Advisors:**
  - Cabot Microelectronics and Intel served as advisors on our previous project
  - Advanced Diamond is considering partnering by providing experimental conditioner geometries
  - Draper Laboratories has sponsored MS students with projects related to planarization
- **Patterned Substrates**:
  - Patterned substrates will be microfabricated at the Tufts Microfab
  - Tufts Microfab metrology tools will be used for evaluation of planarity on patterned substrates.

Impact of chelators and biocides utilized in semiconductor manufacturing on municipal wastewater treatment

Reyes Sierra

Department of Chemical and Environmental Engineering
The University of Arizona
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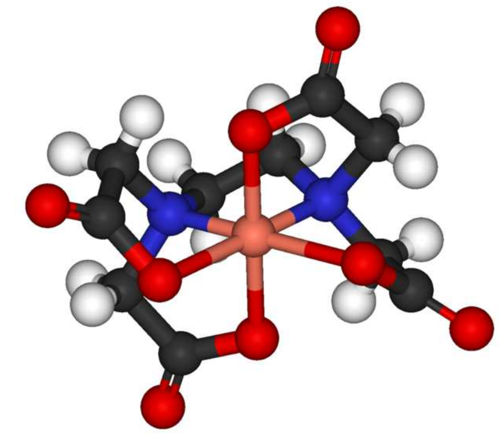
Chelators and Biocides in Semiconductor Manufacturing

- Chelating agents and biocides (C/Bs) are important components in chemistries used in semiconductor manufacturing (eg. CMP).
- Some C/Bs are persistent and inhibitory to microorganisms.
- Little is known about the behavior of these compounds in wastewater treatment systems.



Cu(II)-EDTA complex

Examples of Chelators and Biocides

BIOCIDES

R2
O
N
R1
S

O
NH
S

Isothiazolone derivatives

CHELATORS

NTA

$^{-}OOCH_2C - \overset{+}{N}H - CH_2COOH$

EDTA

$^{-}OOCH_2C$, $HOOCH_2C$ $\overset{+}{N}H - CH_2 - CH_2 - \overset{+}{N}H$ CH_2COOH, CH_2COO^{-}

Aminopolycarboxylates

Objectives

Review trends in the use of biocides and chelators and perform EHS evaluation focusing on wastewater concerns.

I) Inventory of main biocides and chelators used in wet cleans and CMP.

II) Literature review - Impact of main biocide and chelators on:

- Biological wastewater treatment processes.
- Species used in effluent ecotoxicology monitoring.

III) Evaluation toxicity - biodegradability of selected biocides/chelators:

- Selected microbial populations in activated sludge and anaerobic sludge digestion processes.

Method of Approach

- **Inventory of biocides and chelators (ligands) in wet cleans and CMP:**
  Consultation with industry, suppliers, experts
- **Biocide and chelator desk study:**
  Review of literature databases
- **Preliminary evaluation: microbial toxicity – biodegradability of selected ligands:**
  Standardized batch bioassays to evaluate impact on:
  a) BOD removal in activated sludge treatment.
  b) BOD removal in anaerobic sludge digestion (methanogenesis).

ESH Metrics and Impact

1. Strategies to enhance/maintain the effectiveness of biological treatment plants receiving semiconductor manufacturing effluents.

2. Identification of potentially problematic materials in advance of regulatory concern.

Project Funding

- **Matching funding** (Sematech, approx $20K):

  Task 1 – Inventory of B/Cs

  Task 2- Literature review

- **ERC funding request**:

  Task 3 – Toxicity and biodegradability testing
  of B/Cs compounds.

Industrial Interactions and Technology Transfer

Industrial liaisons:

- Walter Worth - Sematech
- Reed Content - AMD
- Brian Raley - AMD

HIGH-DOSE IMPLANT RESIST STRIPPING (HDIS) : ALTERNATIVES TO SUPER- HOT SPM SOLUTIONS

Srini Raghavan

Materials Science and Engineering

University of Arizona

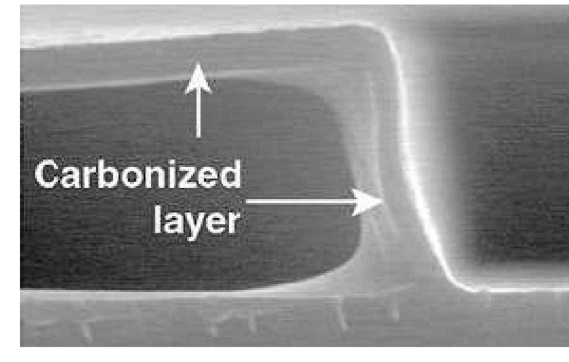
High Dose, Low Energy Implants Used for Formation of Shallow Junctions

ION IMPLANTATION

($> 10^{15}/cm^2$)

CREATES A CRUST

LAYER ON RESISTS



Courtesy: FSI Intl

- Crust is *dehydrogenated* resist in the form of amorphous carbon/graphite

➢ An efficient HDIS process needs to clean all resist (carbonized crust as well as underlying resist) and remove residues without causing substrate damage

HDIS TECHNIQUES USING SPM

- **These techniques rely on making SPM as “hot” as possible (≥ 180^{0}C) without losing oxidizing power**

- Enhanced Sulfuric Acid (ESA) (SEZ)
  - Hot SPM with proprietary additive

- **VIPR Process (FSI-International)**
  - **‘*Freshly’ mixed* SPM with catalyst**

- Modified SPM (high temperature, ***freshly mixed***) with Thermal Pretreatment (DNS)
  . Oxidation power drops off dramatically with time

ARE WE STUCK WITH SUPER-HOT SPM TO BREAK C-C BONDS IN THE CRUST LAYER?

HOW DOES SPM WORK?

. Oxidation by HSO_5^- (peroxy monosulfate)?

$H_3O_2^+$ (hydroperoxonium ion or hydroxyl cation) ?

. Introduction of sulfonic acid groups on the surface amorphous/graphitic carbon crust ? (Note: one strategy for the breakdown/solubilization of carbon nanotubes (CNT) is the introduction of active sulfonic acid groups on the surface)

ARE THERE SAFER ALTERNATIVES TO VERY HOT SPM?

TWO REAGENTS HAVE BEEN FOUND USEFUL IN BREAKING DOWN ORGANIC COMPOUNDS IN SOLUTION

I: ***FENTON'S REAGENT***

. H_2O_2 plus certain metal ions which can exist in multiple oxidation rates (ex. iron, cobalt, manganese, tin) in bare or chelated form

$$H_2O_2 + Fe^{2+} \longrightarrow OH^{*} + OH^{-} + Fe^{3+}$$

OH^{*} is a strong oxidant

. Typically ambient temperature; pH ~ 4 to 6

.

II. *CATALYZED HYDROGEN PEROXIDE (CHP) or MODIFIED FENTON'S REAGENT*

- uses much higher concentration (2 to 25%) hydrogen peroxide
- Contains OH* (oxidant), HO_2 * (weak oxidant), O_2 *- (weak reductant and nucleophile), HO_2 - (strong nucleophile)
- Higher peroxide content provides a solvent effect

Drawback: Rate of oxidation of C-C bonds by Fenton's reagent and CHP is lower than that of hot SPM

PROPOSED WORK

Overall Objective

- **Investigate the feasibility of *disrupting* carbonized crust on deep UV resist layers exposed to high dose (> $10^{15}/cm^2$) arsenic ions using *CHP reagents***

Specific Tasks and Deliverables

- ***Investigate suitable metal ion- hydrogen peroxide combinations and ratios for "attacking" the crust***
- ***Obtain kinetic data with model amorphous carbon and graphite materials***
- ***Evaluate the removal of disrupted layer and the underlying resist using conventional SPM***

INDUSTRIAL MENTORS

- Joel Barnett, Sematech
- John Marsella, Air Products and Chemicals
- Jeff Butterbaugh, FSI-International

PERSONNEL NEEDED

. One graduate (master's) student for two years