SRC/SEMATECH Engineering Research Center
for Environmentally Benign Semiconductor Manufacturing

2009 Annual Review Meeting

Core Projects
Customized Projects
New Projects (Starting 2009)

February 19-20, 2009

AGENDA

2009 SRC/SEMATECH ERC REVIEW MEETING

February 19-20, 2009
Marriott University Park Hotel, Tucson, AZ

Wednesday, February 18

4:00 PM - Open	Poster Set-Up ***[Madera Room]***

Thursday, February 19

7:00 - 7:45 AM	Continental Breakfast and Registration ***[Pima/Sabino Foyer]***
7:30 - 7:45 AM	TAB/PAG Caucus ***[Ventana Room]***
7:45 - 7:50 AM	Welcome by Engineering Dean [Goldberg]
7:50 - 8:30 AM	Introduction and Overview [Shadman]
8:30 - 9:10 AM	An Integrated, Multi-Scale Framework for Designing Environmentally-Benign Copper, Tantalum and Ruthenium Planarization Processes ***425.020*** [Philipossian, White, Boning]
9:10 - 9:35 AM	Environmentally Benign Electrochemically-Assisted Chemical-Mechanical Planarization (E-CMP) ***425.014*** [Boning, Raghavan, Philipossian]
9:35 - 9:50 AM	Break ***[Pima/Sabino Foyer]***
9:50 - 10:05 AM	EHS Impact of Electrochemical Planarization Technologies ***425.016*** [West]
10:05 -10:40 AM	Environmentally Benign Vapor Phase and Supercritical CO2 Processes for Patterned Low k Dielectrics ***425.017*** [Gleason, Ober, Watkins]
10:40 - 11:00 PM	Low-Water and Low-Energy Rinsing and Drying of Patterned Wafers, Nano-Structures, and New Materials Surfaces ***425.021*** [Shadman, Vermeire]
11:00 - 11:30 AM	<u>Keynote</u>: High-Volume IC Manufacturing [Kelleher (Intel)]
11:30 - 12:40 PM	Lunch ***[Canyon Rooms]***
12:40 - 1:05 PM	Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro- and Nano- Electronics Manufacturing ***425.022*** [Nishi, Raghavan]
1:05 - 1:35 PM	<u>Invited Presentation</u>: Role of SC Industry in Development of Future Solar Energy Technology [Ohmi (Tohoku University)]
1:35 - 1:50 PM	Break ***[Pima/Sabino Foyer]***
1:50 - 2:05 PM	Reductive Dehalogenation of Perfluoroalkyl Surfactants in Semiconductor Effluents ***425.015*** [Sierra, Jacobsen, Wysocki]
2:05 - 2:20 PM	Destruction of Perfluoroalkyl Surfactants in Semiconductor Process Waters Using Boron Doped Diamond Film Electrodes ***425.018*** [Farrell, Sierra]
2:20 - 2:40 PM	Non-PFOS Photoacid Generators: Environmentally Friendly Candidates for Next Generation Lithography ***425.013*** [Ober, Sierra]

2:40 - 2:55 PM	Preliminary Investigation of the Toxicity of HfO2 Nano-particles [Boitano, Ratner, Field, Sierra, Shadman]
2:55 - 3:05 PM	Bio-Nano-manufacturing [Muscat, Mansuripur, McEvoy]
3:05 - 3:25 PM	Awards Presentation ***[Pima/Sabino]*** o Simon Karecki Award o Ella Philipossian Memorial Scholarship Award
3:25 - 3:40 PM	SRC Student Information Session (Wiggins)
3:40 - 6:30 PM	Poster Session ***[Madera]***
5:00 - 5:15 PM	SRC Tech-Connect Meeting w/ ERC students ***[Madera/Pima]***
5:00 - 6:30 PM	TAB/PAG Caucus ***[Sabino]***
6:30 - Open	Dinner ***[Canyon Rooms]***
6:30 - Open	PIs group planning meetings

Friday, February 20

6:30 - 7:30 AM Continental Breakfast ***[Pima/Sabino Foyer]***

7:30 - 9:00 AM Customized Projects ***[Pima/Sabino]***

A) New ERC/Intel Initiative on High-Volume Manufacturing

- Introduction of Projects [Rao (Intel)]
- Retaining Ring and Conditioner Interactions [Philipossian, Moinpour, Hooper]
- Relationship Between Planarization and Pad Surface Micro-Topography [Philipossian, Moinpour, Hooper]
- Contamination Control in Gas Distribution Systems [Shadman, Geisert]
- Electrochemical Technology for CMP Wastewater Reclaim [Baygents, Farrell, Megdal, Boyce, Fuerst, Georgousis, Hodges, Wong]
- AFM-Based Methodology for Optimizing APM Composition [Raghavan, Zhang]

B) IMEC/ERC Planned Interactions [Marc Heyns)

9:00 - 9:15 AM Break ***[Pima/Sabino Foyer]***

9:15 - 11:30 AM Special Session on New Projects Starting in 2009 ***[Pima/Sabino]***

- Development of Quantitative Structure-Activity Relationship for Prediction of Biological Effects of Nanoparticles Associated with Semiconductor Industries ***P10365*** [Chen, Thornton, Posner]
- ESH Impacts of Emerging Nanoparticles and Byproducts from Semiconductor Manufacturing ***P10367*** [Field, Sierra, Boitano, Ratner, Shadman]
- Low-ESH-impact Gate Stack Fabrication by Selective Surface Chemistry ***P10370*** [Muscat]
- Predicting, Testing, and Neutralizing Nanoparticle Toxicity ***P10372*** [Nielsen, Draper, Pantano, Musselman, Dierkmann, Philipossian]
- Lowering the ESH Impact of High-k and Metal Gate-Stack Surface Preparation Processes ***P10373*** [Nishi, Raghavan, Vermeire, Shadman]
- Sugar-Based Photoacid Generators (Sweet PAGs): Environmentally Friendly Materials for Next Generation Photolithography ***P10375*** [Ober, Sierra]
- Supercritical Carbon Dioxide Compatible Additives: Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography ***P10376*** [Ober, de Pablo]

- Fundamentals of Advanced Planarization: Pad Micro-Texture, Pad Conditioning, Slurry Flow, and Retaining Ring Geometry ***P10377*** [Philipossian, Boning]
- High-dose Implant Resist Stripping (HDIS): Alternatives to ASH/Strip Method ***P10378*** [Raghavan]
- Improvement of ESH Impact of Back End of Line (BEOL) Cleaning Formulations Using Ionic Liquids to Replace Traditional Solvents ***P10379*** [Raghavan]
- Computational Models and High-Throughput Cellular-Based Toxicity Assays for Predictive Nanotoxicology ***P10381*** [Tropsha, Mumpert]

11:30 -12:30 PM	Lunch ***[Pima/Sabino Foyer and Canyon Rooms]***
11:30 -12:30 PM	Industrial Advisory Board Meeting - working lunch ***[Pima/Sabino]***
12:30 - 1:00 PM	Feedback to PIs ***[Pima/Sabino]***
1:00 - 2:30 PM	Executive Advisory Board Meeting ***[Board Room]***
2:30 PM	Program End

NOTES:

Welcome to the 13th Annual Meeting of the *SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing*

February 19-20, 2009

Program Overview

Annual ERC Meeting

February 19-20, 2009

Outline of Presentation

- Background and some statistics on the ERC
- ERC's program structure and focus; long-term vision regarding the role of ESH in semiconductor industry
- Overview of the existing activities and plans for the new projects and new partnerships

Participating Universities

- U Arizona
- MIT
- Stanford
- U California - Berkeley

ERC was Founded in 1996 by SRC and NSF

- Arizona State U (1998 -)
- Cornell (1998 -)
- U Maryland (1999-2003)
- Purdue (2003 - 2008)
- Tufts (2005 -)
- Columbia (2006 -)
- U Massachusetts (2006 -)
- U Washington (2008-)

New Members

- U North Carolina (2009 -)
- U Wisconsin (2009-)
- U Texas - Dallas (2009 -)

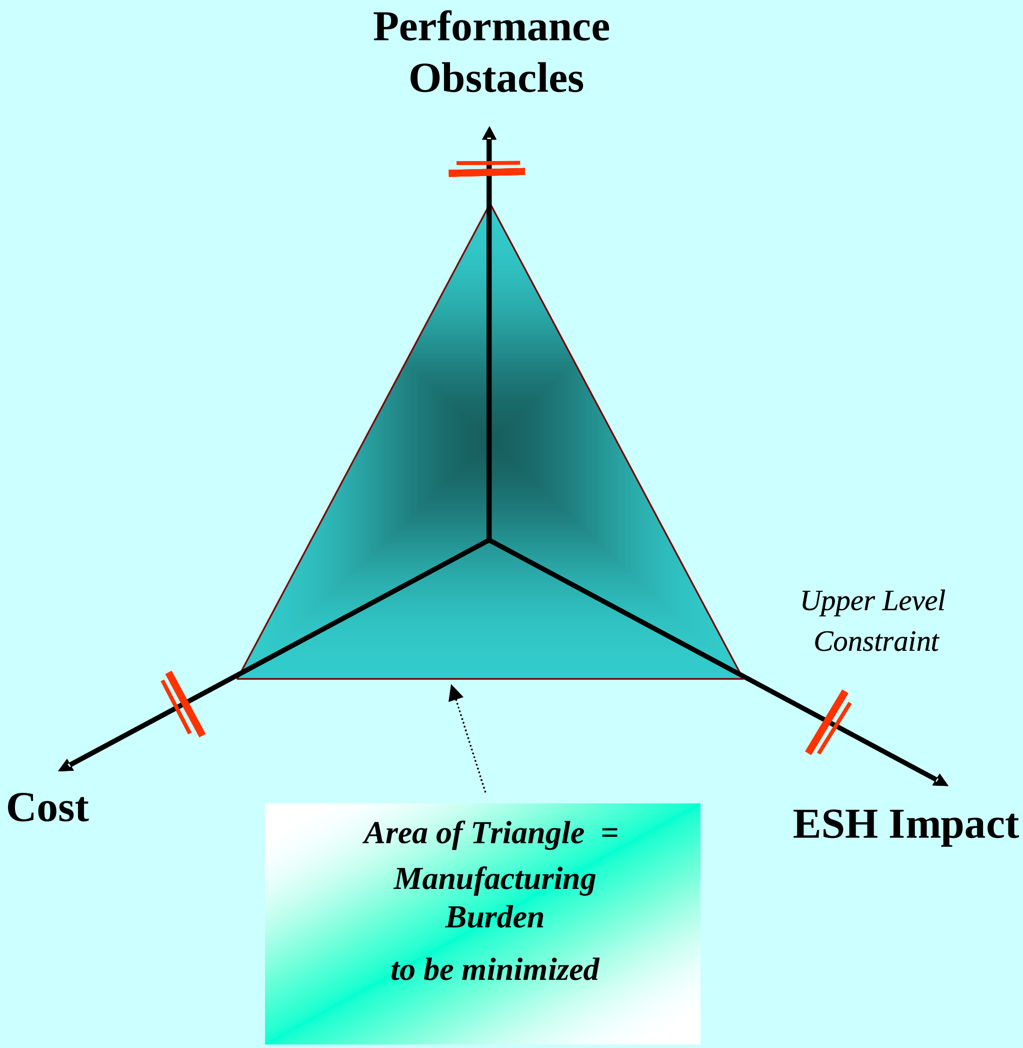
Mission of the ERC

Science and Technology in IC Manufacturing that would:

1. **Eliminate or reduce the *use* of potentially hazardous compounds**
2. **Eliminate or reduce *emissions* of potentially hazardous compounds**
3. **Reduce the *"net" use of water and energy* for manufacturing**
4. **Increase the *"utilization factor"* of chemicals and materials (minimize waste per unit product).**

The same four factors are used as primary *metrics of ESH gain* for evaluating the success/impact of a project.

ERC's Pioneering Vision for Sustainability



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

Sources of Funding

- **SRC (core)**
- **Sematech (core)**
- **Industrial members (membership)**
- **Customized projects (including Intel/ERC new HVnM initiative, Sematech and SRC customized projects, etc)**
- **Cost sharing by participating universities**
- **Grants from Federal and State agencies (NSF, SFAz, WSP, etc.)**
- **Donations (Koshiyama Planarization Chair by Fujimi; Simon Karecki memorial Endowment; Ella Philipossian memorial endowment, etc.)**

Success in creating research leverage for S/C industry

ERC Thrust Areas

Environmentally Sustainable IC 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

Examples of Projects in Thrust Areas

- **Thrust A: Novel Solutions to Existing ESH Problems**
  - Organic (e.g. PFOS) and ionic (F^- and Cu^{++}) removal from wastewater.
  - Reducing the usage of slurry and other consumables in conventional CMP process.
  - ESH-friendly technology for waste reclaim and recycle (e.g. water recycling).

- **Thrust B: ESH-Friendly Novel Materials and Processes**
  - Environmentally sustainable processes for surface preparation of new materials.
  - Replacing problematic materials (e.g. novel PAGs to replace PFOS).
  - Low-energy and low-chemical deposition and pattering methods.
  - ESH-friendly planarization beyond CMP.

- **Thrust C: ESH Aspects of Future Nano-Manufacturing**
  - New low-energy and low-chemical processes specific to nano-scale fabrication (e.g. application of bio-systems for patterning, selective disposition, and self assembly).
  - ESH aspects of nano-particles and other nano-structures.

Current ERC Research Projects

- **Two types of projects:**
  - **9 *core projects* (funded by the core SRC/Sematech contract and some membership funds)**
  - **15 *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 2008-2009

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. **An Integrated, Multi-Scale Framework for Designing Environmentally-Benign Copper, Tantalum, and Ruthenium Planarization Processes (A,B)**
4. **Environmentally Benign Electrochemically Assisted Chemical Mechanical Planarization (B)**
5. **EHS Impact of Electrochemical Planarization Technologies (B)**
6. **Non-PFOS/non-PFAS Photo-Acid Generators: Environmentally Friendly Candidates for Next Generation Lithography (B)**
7. **Environmentally Benign Vapor-Phase and SC-CO_2 Processes for Patterned Low-k Dielectrics (B)**
8. **Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro-and Nano-Electronics Manufacturing (B,C)**
9. **Low-Water and Low-Energy Rinsing and Drying of Nano-Structures and New Materials Surfaces (C)**

Customized Projects in 2008-2009

- **Effect of Various Cleaning Solutions and Brush Scrubber Kinematics on the Frictional Attributes of Post Copper CMP Cleaning Process; Philipossian**
  Sponsored by Hitachi Chemicals

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

- **Slurry Flow Optimization During Copper CMP; Philipossian**
  Sponsored by Toho Engineering

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

- **Effect of Polisher Kinematics in Reducing Average and Variance of Shear Force and Increasing Removal Rate in Copper CMP; Philipossian**
  Sponsored by Hitachi Chemical

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

Customized Projects in 2008-2009

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

- **EHS Assessment of Chelators and Biocides Utilized in Semiconductor Manufacturing; Sierra**
  Sponsored by Sematech

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

- **Assessment of the Fate of CMP Nano-Particles in Typical Wastewater Treatment Systems; Sierra, Shadman**
  Proposed and being planned jointly with ISMI

- **ERC-Intel joint initiative on High-Volume Nano-Manufacturing (HVnM), currently consisting of 5 projects**
  (special session on this on Friday).

Selection of New Core Projects

- SRC/SEMATECH developed an *ESH Research Needs* document (March 2008)
- SRC/Sematech sent call for white papers based on the *Research Needs* document (April 2008)
- Review Board selected 21 out of 70 white papers received (May-July 2008)
- Invitation sent PIs of the selected white papers to submit full proposals (June 2008)
- Review Board selected, and ranked proposals (August- November 2008)
- Carried out budget and contract planning and approval (November 2008 – Feb 2009)
- Finally, eleven projects were selected for the new contract cycle (Start in April 2009).

New Project Starting in 2009

- **Development of Quantitative Structure-Activity Relationship for Prediction of Biological Effects of Nanoparticles Associated with Semiconductor Industries (P10365)**
  PIs: Yongsheng Chen, Trevor Thornton, Jonathan Posner (Arizona State U)

- **Environmental Safety and Health (ESH) Impacts of Emerging Nanoparticles and Byproducts from Semiconductor Manufacturing (P10367)**
  PIs: Jim Field, Reyes Sierra, Scott Boitano, Farhang Shadman (U of Arizona); Buddy Ratner (U of Washington)

- **Low-ESH-impact Gate Stack Fabrication by Selective Surface Chemistry (P10370)**
  PI: Anthony Muscat (U of Arizona)

- **Predicting, Testing, and Neutralizing Nanoparticle Toxicity (P10372)**
  PIs: Steven Nielsen, Rockford Draper, Paul Pantano, Inga Musselman, Gregg Dierkmann, (U of Texas- Dallas); Ara Philipossian (U of Arizona)

New Project Starting in 2009

- **Lowering the Environmental Impact of High-k and Metal Gate-Stack Surface Preparation Processes (P10373)**
  PIs: Yoshio Nishi (Stanford); Srini Raghavan, Farhang Shadman (U of Arizona); Bert Vermeire (Arizona State U)

- **Sugar-Based Photoacid Generators (Sweet PAGs): Environmentally Friendly Materials for Next Generation Photolithography (P10375)**
  PIs: Christopher Ober (Cornell); Reyes Sierra (U of Arizona)

- **Carbon Dioxide Compatible Additives: Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography (P10376)**
  PIs: Christopher Ober (Cornell); Juan de Pablo (U of Wisconsin)

- **Fundamentals of Advanced Planarization: Pad Micro-Texture, Pad Conditioning, Slurry Flow, and Retaining Ring Geometry (P10377)**
  PIs: Ara Philipossian (U of Arizona); Duane Boning (MIT)

New Project Starting in 2009

- **High-Dose Implant Resist Stripping (HDIS): Alternatives to ASH/Strip Method (P10378)**
  PI: Srini Raghavan (U of Arizona)

- **Improvement of ESH Impact of Back-End-of-Line (BEOL) Cleaning Formulations Using Ionic Liquids to Replace Traditional Solvents (P10379)**
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- **Computational Models and High-Throughput Cellular-Based Toxicity Assays for Predictive Nanotoxicology (P10381)**
  PIs: Alex Tropsha, Russell Mumper (U of North Carolina)

New PIs and New Universities Joining the ERC

- **University of Washington**
  - **Buddy Ratner *(Bioengineering/Chemical Engineering)***

- **Arizona State University**
  - **Yongsheng Chen (*Civil and Environmental Engineering*)**
  - **Trevor Thornton *(Electrical Engineering)***
  - **Jonathan Posner *(Mechanical Engineering/Chemical Engineering)***

- **University of North Carolina, Chapel Hill**
  - **Alex Tropsha *(Pharmacy)***
  - **Russell Mumper *(Pharmacy)***
  - ***Denis Fourches (Pharmacy)***

New PIs and New Universities Joining the ERC

- **University of Wisconsin**
  - **Juan de Pablo *(Chemical Engineering)***
- **University of Arizona**
  - **Scott Boitano *(Physiology/ AZ Respiratory Center)***
- **University of Texas in Dallas**
  - **Steven Nielsen *(Chemistry)***
  - **Rockford Draper *(Biology)***
  - **Paul Pantano *(Chemistry)***
  - **Inga Musselman *(Chemistry)***
  - **Gregg Dierkmann *(Chemistry)***

New ERC Focus Area
ESH Aspects of Nano-Manufacturing

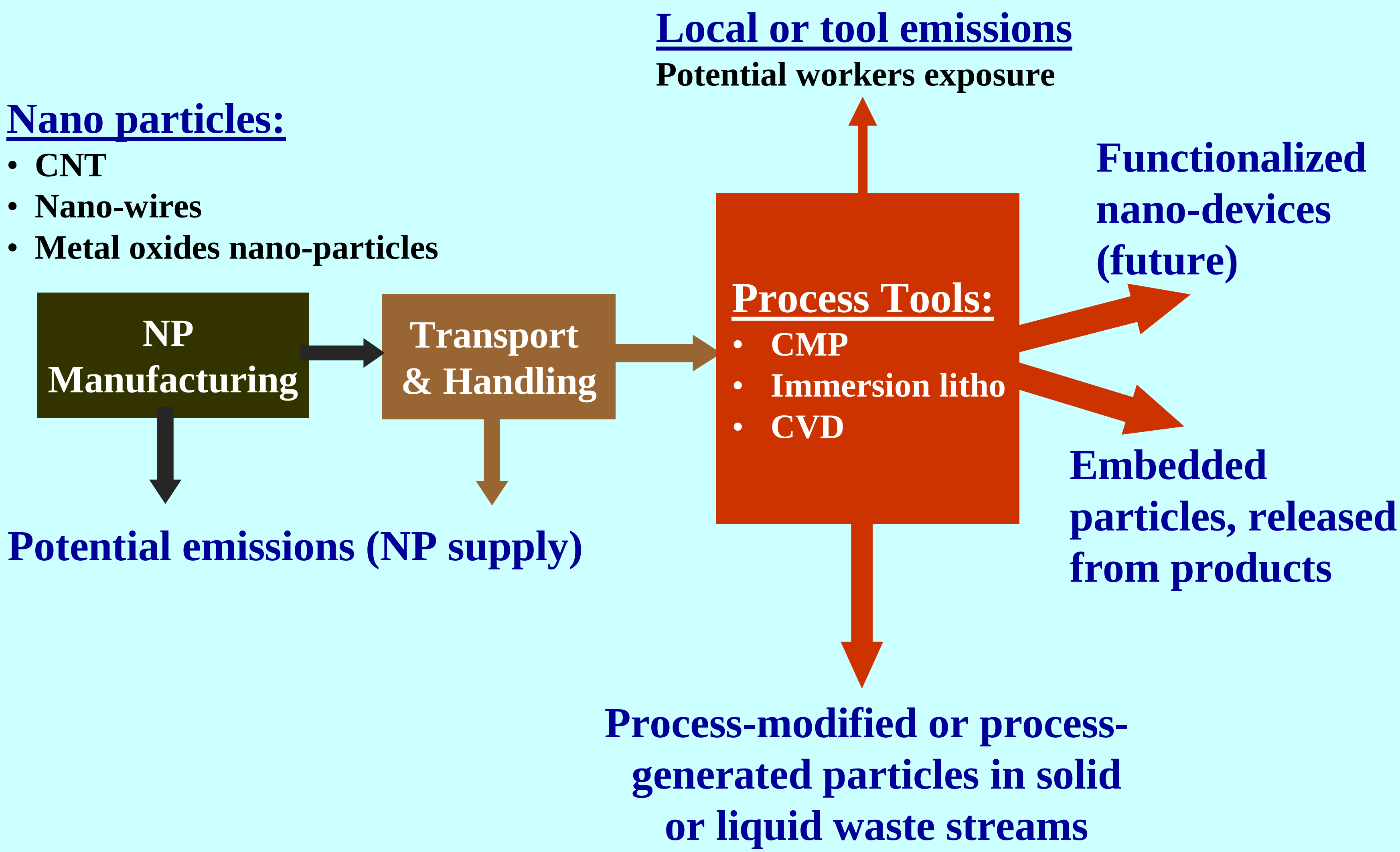
1. **Nano-Particles in Manufacturing**
   - **Workers exposure to nano-particles in the fabs**
   - **Emission of nano-particles through fab waste streams**

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

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

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

Nano-Particles in S/C Manufacturing

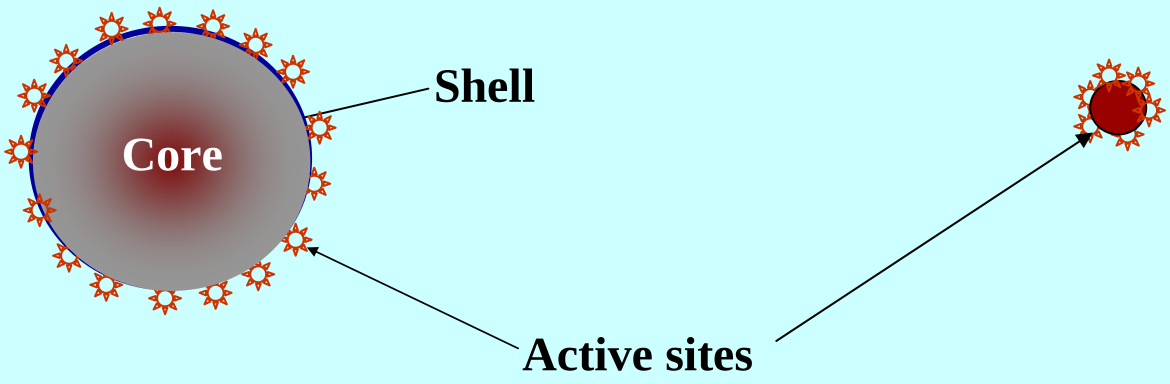


Examples of Nano-Particles in Fabs

CMP Nano-Particles:

Primary particles
(engineered particles; 15-90nm)

Secondary particles
(very active surface; <10nm)



Others:

- **Nano-particles in immersion lithography (< 10mm)**
- **Nano-droplets in sprays and aerosols in vents**
- **Future: nano-tubes, nano-wires, porogen nano-particles for porous low-k, etc.**

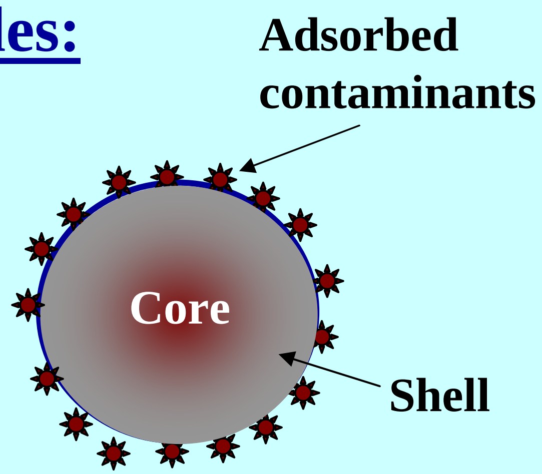
What is Unique About Nano-Particles?

Treatment problem:

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

Synergistic ESH impact of nano-particles:

- **Surface activation** (high-energy sites)
- **Selective adsorption**
- **Pore condensation** (Kelvin Effect)
- **<u>Consequence</u>**
  - ***Concentrating effect (delivery dosage)***
  - ***Facilitated transport (range of activity)***
  - ***Enhanced life-time (duration of activity)***



Collaborative Initiative

Characterization of Nano-Materials
- Physical (focus on size, effective-area, aspect-ratio)
- Chemical (focus: active sites and surface charge)

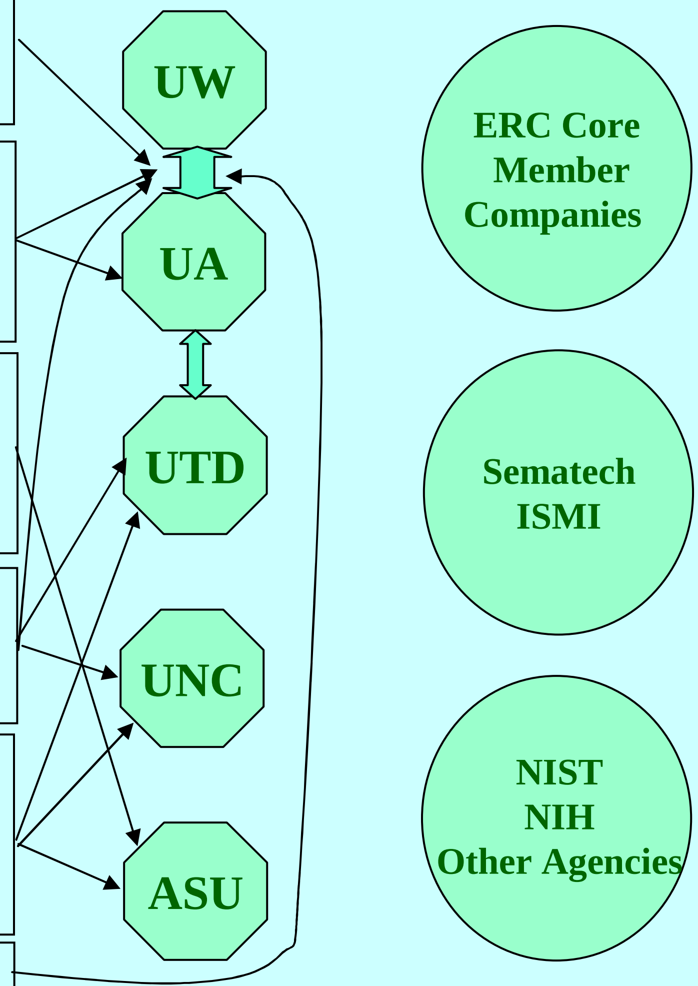
Process Modification of Nano-Materials
- Surface activation
- Multi-component adsorption (dynamics; capacity)
- Identification of adsorbing bulk contaminants

Transport and Fluid Mechanics
- Tool and fab environment; workers exposure
- Emission in air and water
- Interactions with particles/surfaces; 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)

Process Treatment and Emission Abatement



New ERC Focus Area
ESH Aspects of Nano-Manufacturing

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    - Workers exposure to nano-particles in the fabs
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2. **Introduction of New Materials**
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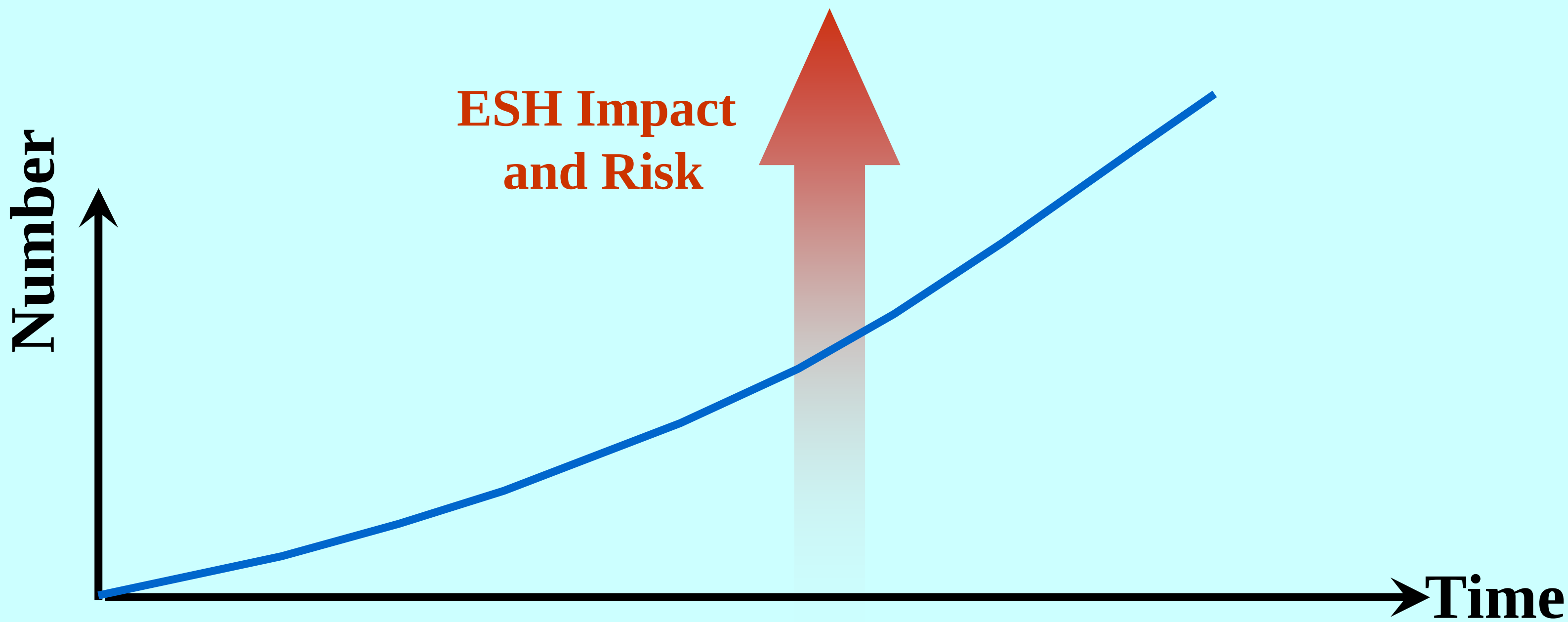
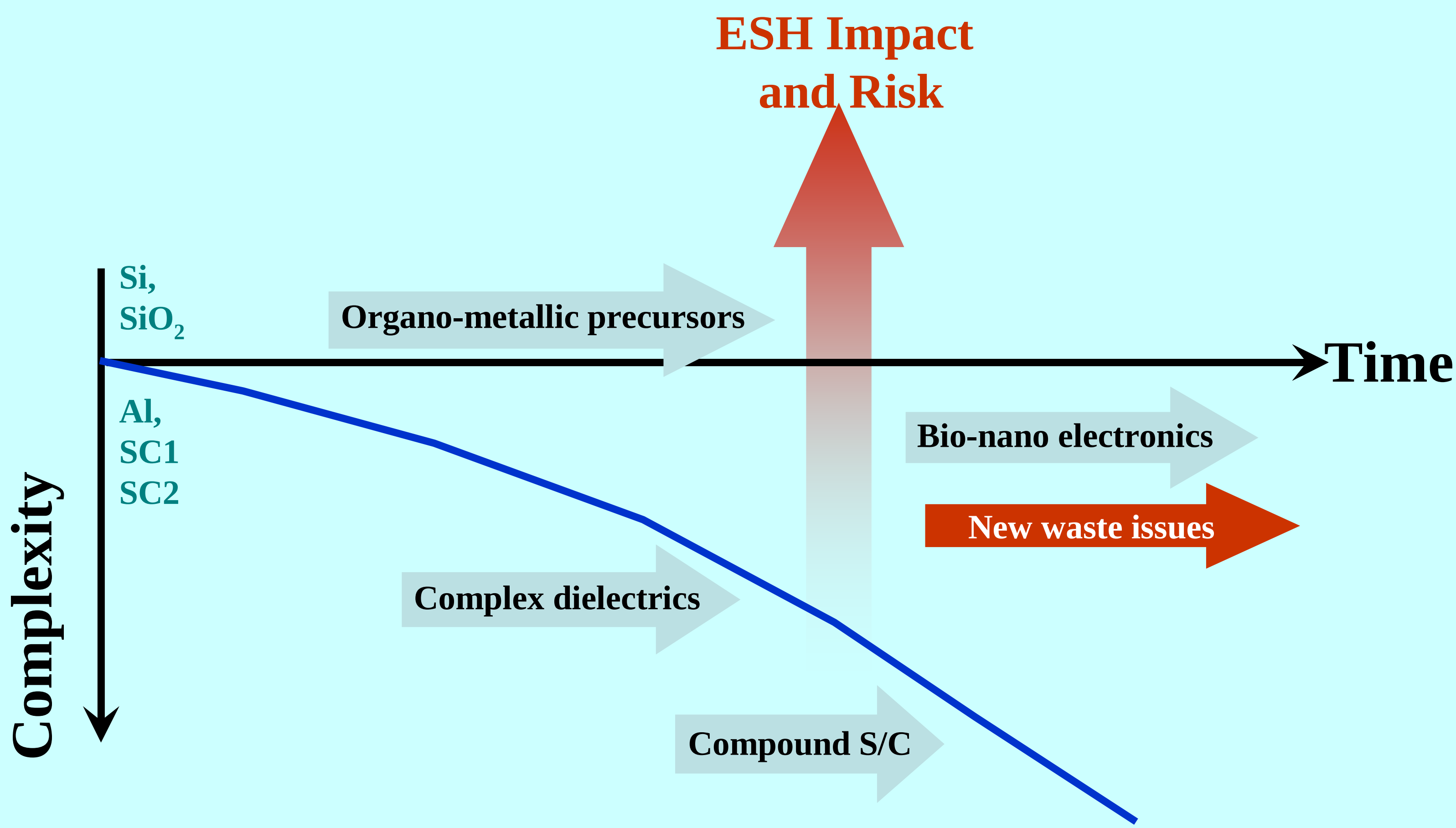
4. Positive Environmental Impact
    - Opportunities for major ESH gain

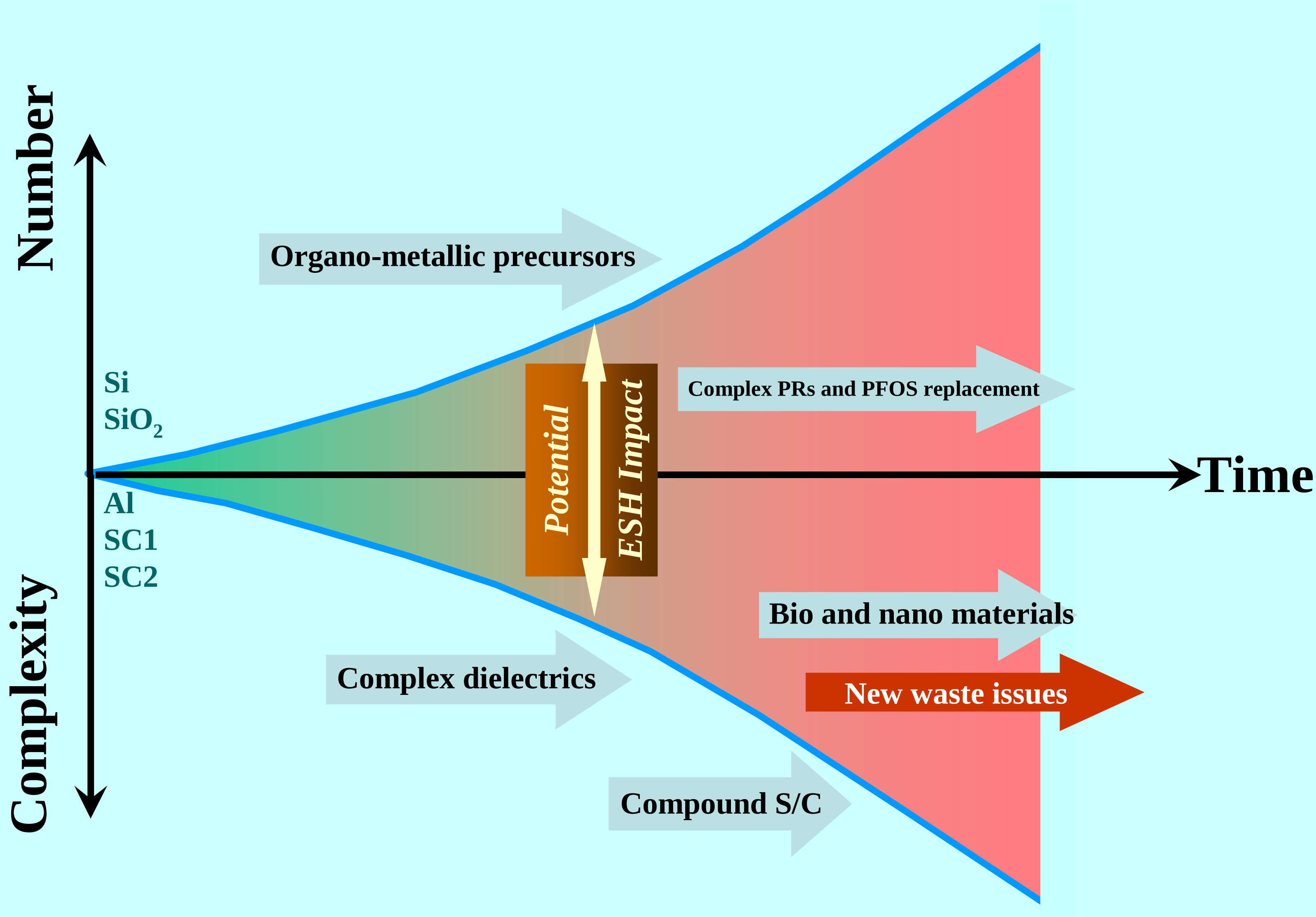
Introduction of New Materials



Introduction of New Materials



Potential Risks of Introducing New Materials



Outlook: Role of ESH is SC Industry

1. **ESH will play an increasingly more important role in the technical and business decision making.**

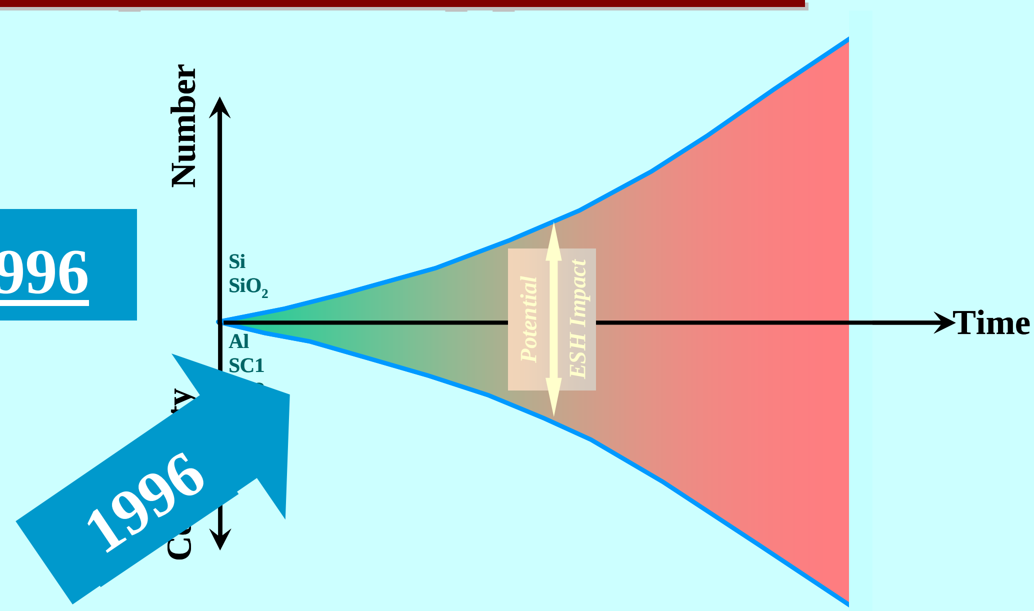
2. **ESH will be more in the heart of process innovation and technology development:**

   New Technology ⇄ New ESH Developments

3. **Companies will invest more in the ESH area: not because they have to, but because they will find it profitable and good for competition.**

4. **ESH application and impact will change: ….**

Evolution of ESH Scope and Application

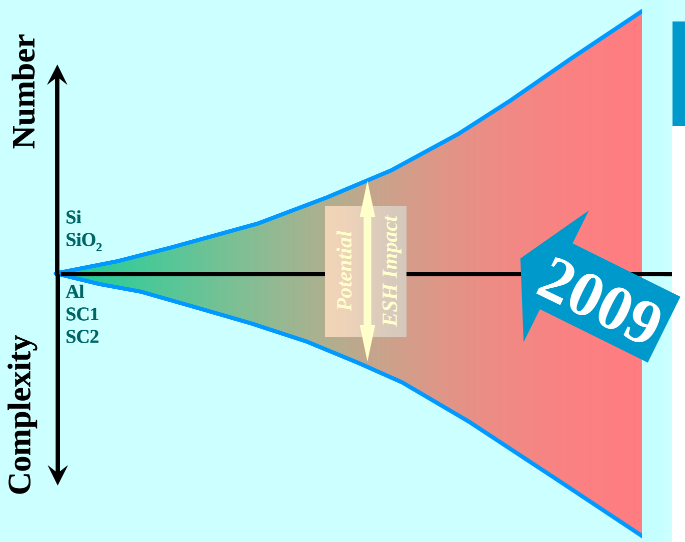


ESH Frontiers and Scope in 1996

- Reduced PFC usage and emission
- Dilute chemistry
- Wastewater treatment and reuse
- Water use reduction (batch tools)
- Abatement of potential VOCs and HAPs
- Lowering energy use in facilities (pumping and ventilation)
- Concern about lead and a few other compounds

Ownership: Facilities Group in a Fab

Evolution of ESH Scope and Application

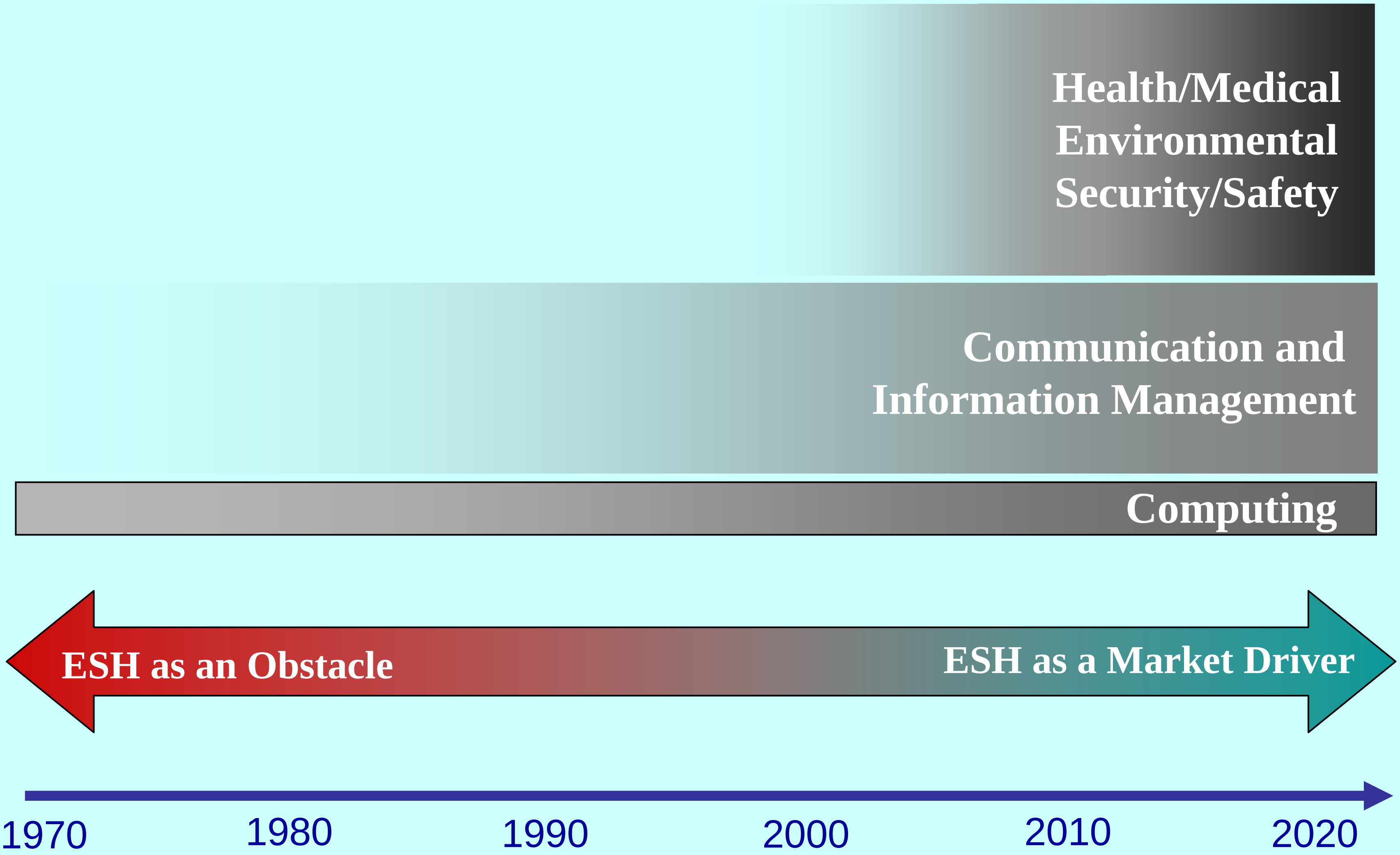


ESH frontiers and scope in 2009

- New litho compounds, PFOS
- New etch, and cleaning materials
- Low-energy processes
- ESH aspect of nano particles and new materials
- Green single-wafer tools
- Planarization of new material
- Surface prep of new materials/nano-structures
- Additive processing and selective deposition
- ESH in high-volume nano-manufacturing
- CMP waste reduction

Ownership: Shared and Integrated in Process

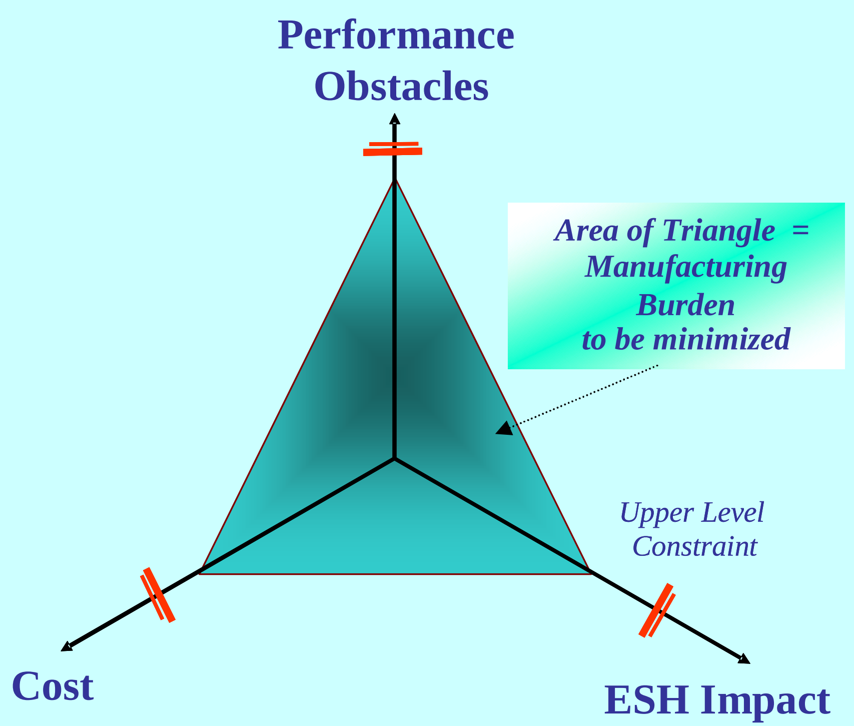
Evolution of ESH Scope and Application



Selected Statistics

The Only Center Dedicated to Research on Sustainability Aspects of Electronics and Photonics Manufacturing

ERC's Model for Sustainability



15 Universities
13 Academic disciplines
39 Faculty members (14 New)

Students Cumulative:

238 PhD and MS
198 Undergraduates (reported)

Employment of graduates:

> 80% joining SC industry & suppliers; mostly by ERC members

Selected Accomplishments

- **Funding Leverage:**
  - **Currently $2M/year from SRC/Sematech core funding**
  - **13-year average: over $3M/year (cash) from other sources**
- **Research: 91 research projects; 19 new projects since 2008**
- **Recognitions: 43 national/international awards and fellow positions for students; 22 national and international awards for faculty**
- **Technology Transfer:**
  - **Joint ventures with member companies; industrial assignees; ERC-Industry co-investigators, etc**
  - **5 spin-off companies**

Industrial Assignees Resident at the ERC

- **Jeongnam Han, Samsung Corporation;**
  One-year assignment
  Joint work with Farhang Shadman (UA) and
  Bert Vermeire (ASU)

- **Jeremy Klitzke from SEZ**
  Anthony Muscat's group (UA)

- **Eisuke Murotani, Asahi Glass Co.**
  Yosuke Hoshi, Hitachi Chemical Company
  Chris Ober's group (Cornell)

Education and Outreach Activities

- **Pre-University Outreach**
  - *Teachers Institute*, funded by RET Program; $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; tele-seminars (running for 13 years without interruption!); distance learning courses; internships for industry residents at universities; faculty sabbaticals sponsored by industry

Congratulatory Notes

- **Yoshio Nishi (Stanford) 2008 SEMI North America Lifetime Achievement Award.**
- **Sharon Megdal (UA): 2008 CW and Modene Neely Endowed Professorship; elected to the Board of Directors of Central Ariz Water Conservation District**
- **Karen Gleason (MIT): Associate Dean of Engineering for Research, MIT**
- **Chris Ober (Cornell): Interim Dean of Engineering**
- **Jim Baygents (UA): Interim Associate Dean of Engineering**
- **Buddy Ratner (U Washington): 2008 BMES Pritzker Distinguished Lecturer Award; 2008 Frontiers of Science Award, Society of Cosmetic Chemists; 2009 Chandra P. Sharma Award, Society for Biomaterials & Artificial Organs (India)**
- **Juan de Pablo (U Wisconsin): 2008 Stanley Corrsin Memorial Lecture in Fluid Mechanics , Johns Hopkins University**
- **Tom Peterson (founding PI and former UA Dean of Engineering): Assistant Director for Engineering at National Science Foundation, DC**

Planarization Long Range Plan

February 2009

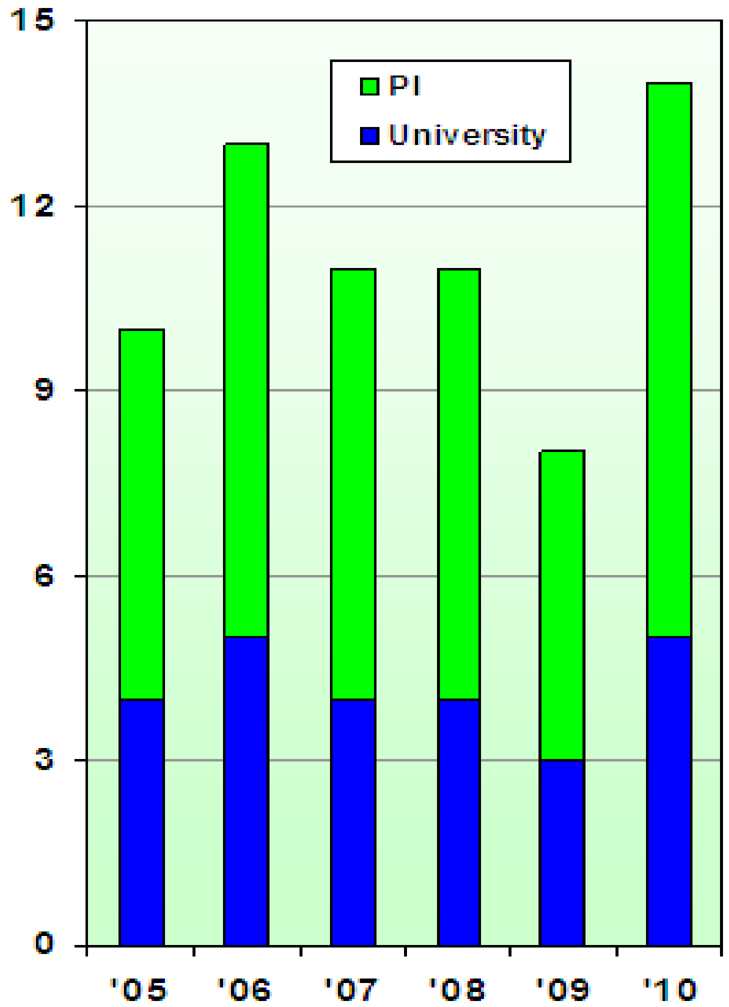
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

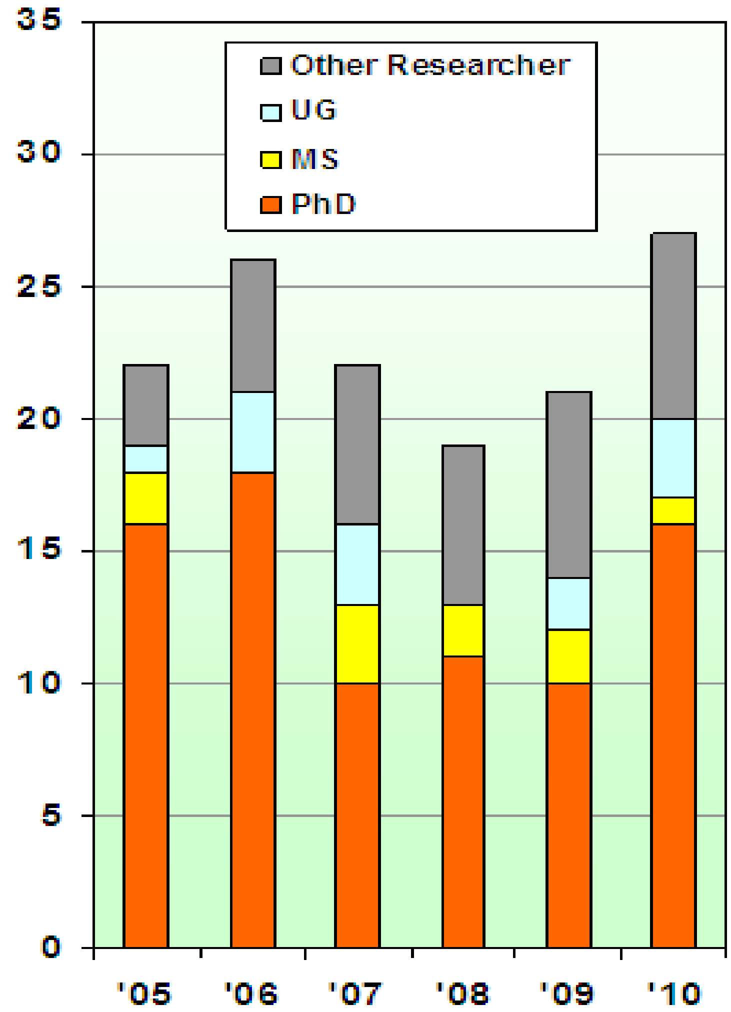
Major Changes Since Last PLRP

- Extend applied research on wear phenomena to include retaining rings and pad micro-texture evolution (EHS metric: improved performance and consumables use reduction)
- Extend scope of post-CMP cleaning to include chemical effects as well as fundamental aspects of cleaning of emerging new FE and BE materials (EHS metric: improved performance and consumables use reduction)
- Identify and quantify factors affecting ULK delamination (EHS metric: improved performance)
- Assuming scaling of classical hardware configurations, lay the initial groundwork for 450 mm CMP by identifying and numerically demonstrating potential process, equipment and material showstoppers (EHS metric: consumables use reduction)

- Discontinue work on E – CMP
- Seek and integrate new research institutions and PIs for continued cutting-edge research and graduates (discussions and planning are underway with are IMEC, Clarkson and Tohoku Univ.)

Trends in the Planarization Thrust Team





Next Five Years

- **Landscape:**

  – **Research, fundamental yet industrially relevant, addressing the technological, economic and environmental challenges of planarization and post-planarization cleaning**

    - **Copper**
    - **Barrier**
    - **Dielectrics (only as it relates to barrier touch-up polish)**

ALWAYS KEEP THE BIG PICTURE IN MIND

! ··· YIELD IS EVERYTHING ··· !

Environmental and Economic Losses Resulting from Lower Yields are Orders of Magnitude Greater than any Gains Realized through Consumables Reduction and Incremental Process Tweaks

Advanced Processes and Consumables for Planarization

- **Objectives**

  - **Wear phenomena and their effect on process performance**
    - **Isolate and quantify interactions among nanoparticles, pads, diamond discs and retaining rings in representative systems (i.e. 200 and 300 mm processes with mainstream consumables)**
    - **Understand how these interactions evolve with extended use**

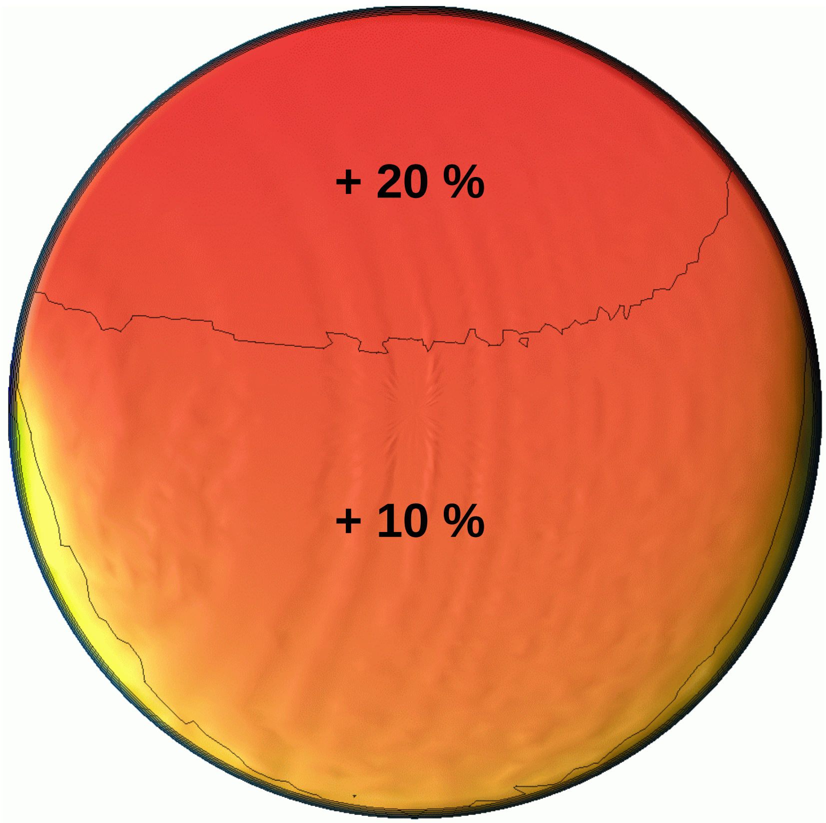
  - **Metrology**
    - **Deploy and develop tools for measuring pad asperity-level forces (considered to be more relevant to defectivity and in-situ process monitoring than global forces)**
    - **Develop methods to visualize slurry flow and measure local wafer-pad-slurry mechanical interactions (i.e. contact area, near-contact area, summit density and wafer topography) using UV-enhanced fluorescence and laser confocal microscopy**

Advanced Processes and Consumables for Planarization

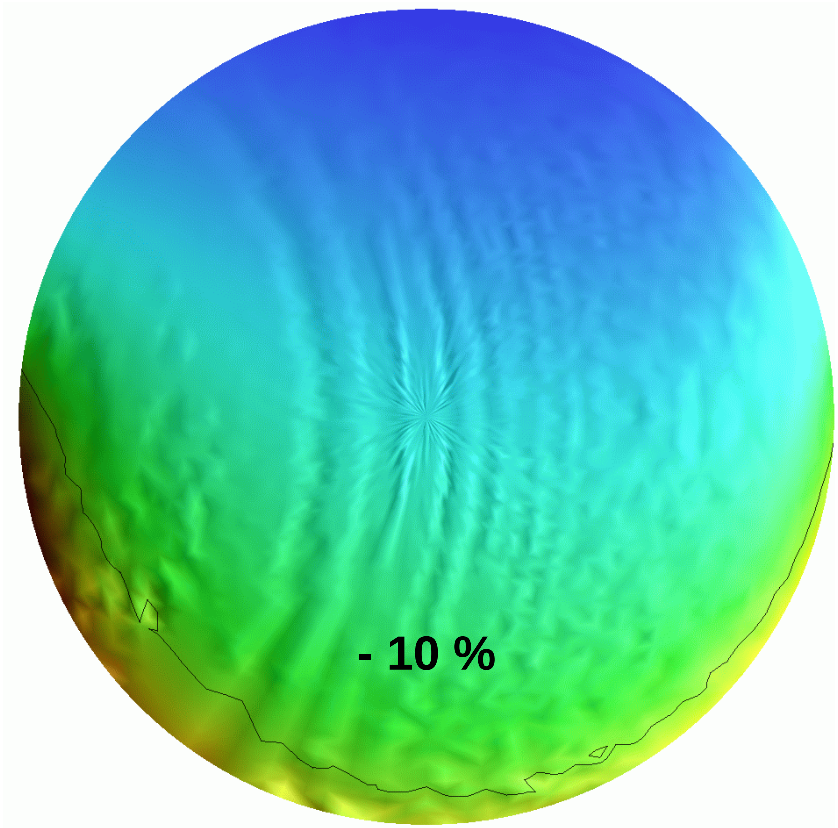
- **Objectives (continued)**
  - Wafer-level and die-level CMP modeling
    - Develop new models of pad macro-texture, micro-texture and slurry flow to study interactions between wafer-level effects, retaining ring design and chip-scale planarization performance
    - Extend die-level models to include key pad micro-texture dependencies to better predict dishing and erosion
    - Integrate die-level and wafer-level models to enable overall uniformity and performance optimization
  - ULK delamination
    - Determine and quantify main factors affecting advanced ULK delamination and develop novel process & consumable solutions
  - Understand the 300 : 450 mm classical rotary platform polisher scaling implications relating to slurry transport, kinematics, pad conditioning, wafer retention, wafer body and flash temperatures and removal rate uniformities

Flash Temperature Differences Among 200, 300 and 450 mm Wafers During CMP

Flash Temperature Increment Ratio – 450 : 300 mm



Flash Temperature Increment Ratio – 200 : 300 mm



Source: L. Borucki (2009)

Advanced Processes and Consumables for Post-Planarization Cleaning

- **Objectives**

  - **Metrology**
    - Extend laser confocal microscopy to quantify brush-wafer mechanical interactions (i.e. contact area, near-contact area and summit density)
    - Develop high-speed imaging methods to validate observed brush-wafer stick-slip effects

  - **Wear phenomena and their effect on process performance**
    - Isolate and quantify chemical and mechanical interactions among brush rollers, cleaning chemicals and wafers in representative systems (i.e. 200 and 300 mm processes with mainstream consumables including various ULK candidates)
    - Understand how these interactions evolve with extended use

  - **Understand mechanisms of residue adsorption and desorption (with focus on emerging new FE and BE surfaces) and correlate wafer-level cleaning outcomes with device-level performance**

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 Student:

- **Anand Meled, Ph. D. candidate, ChEE, UA**
- **Xiaomin Wei, Ph. D. candidate, ChEE, UA**
- **Yasa Adi Sampurno, ChEE, UA (graduated with Ph. D. in December 2008)**

Other Researchers:

- **Yasa Sampurno, Research Associate, ChEE, UA**
- **Yun Zhuang, Research Associate, ChEE, UA**
- **Len Borucki, Araca**
- **Jiang Cheng, Visiting Scholar, ChEE, UA**
- **Takenao Nemoto, Visiting Researcher, Tohoku University**
- **Siannie Theng, Research Technician, ChEE, 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

Cost Share (other than core ERC funding) in Terms of In-Kind Donations:

- **Intel (wafers)**
- **Hitachi Chemical (slurry)**
- **CMC (slurry and pads)**
- **Fujimi (slurry)**
- **Rohm and Haas (pads)**
- **Entegris (retaining rings)**
- **Shinhan (diamond discs)**
- **3M (diamond discs)**
- **Kinik (diamond discs)**
- **Araca (simulation services)**

Objectives & ESH Metrics and Impact

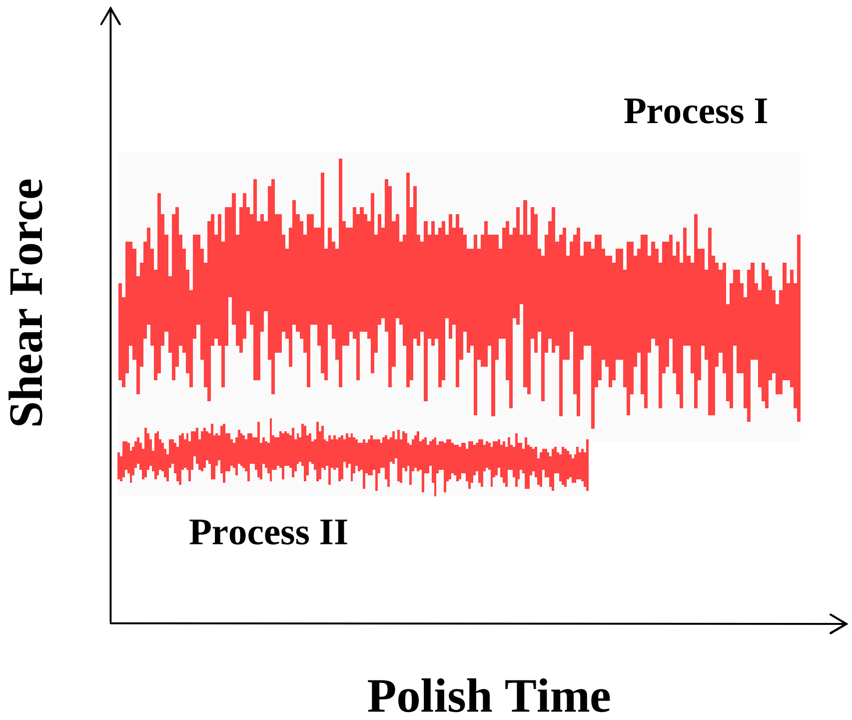
Objectives

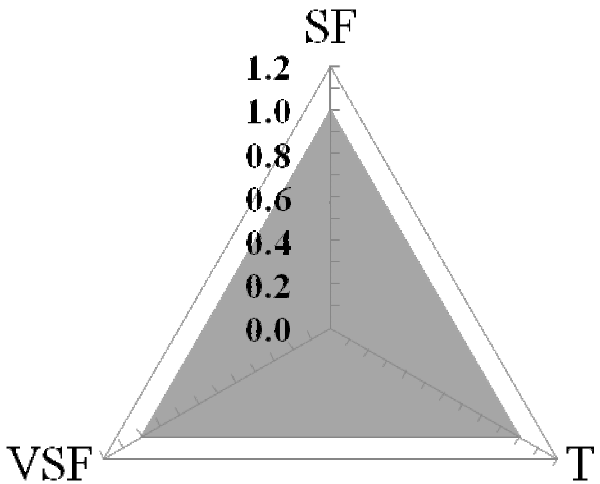
- **Propose and validate a new CMP metric coined as the 'Delamination Triangle'**
- **Understand the effect polishing parameters (i.e. slurry flow rate, pad and wafer rotational rate and polishing pressure) for damage-free CMP**
- **Quantify diamond and diamond disc substrate micro-wear in Cu CMP**
- **Develop methods to quantitatively assess slurry film thickness in various regions within the pad-wafer interface as well as slurry flow patterns in the bow wave and elsewhere on the pad**

ESH Metrics and Impact

- **Reduce CMP consumables and energy consumption by 30 – 40%**
- **Reduce energy consumption by 20 – 30 %**
- **Increase yield by reducing defect formed by delamination, dislodged diamonds and uncontrolled evolution of pad micro- and macro-texture**

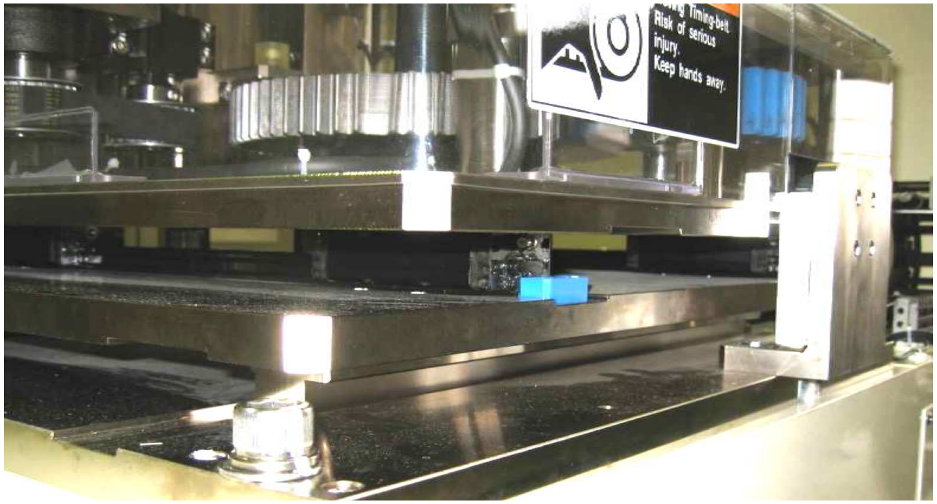
Delamination Triangle

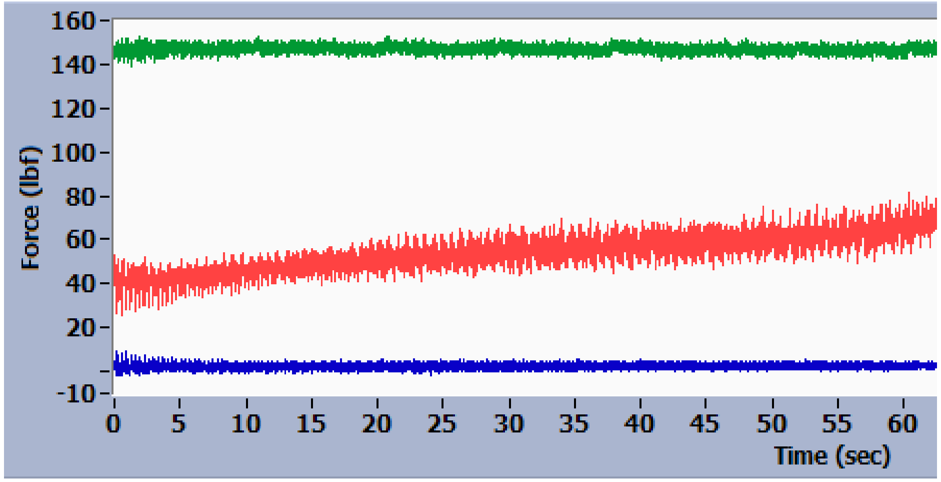




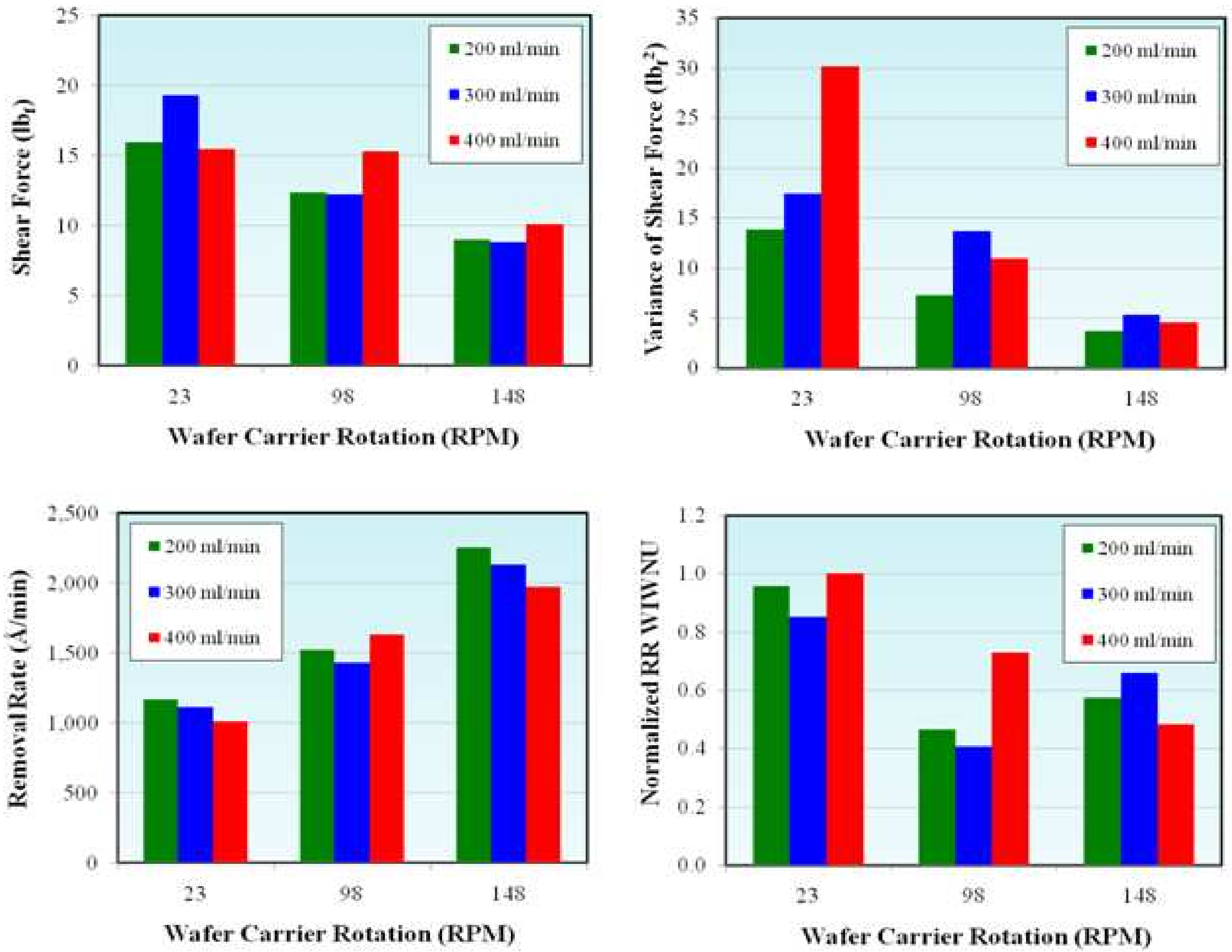
$$Delta = \tau.\varphi.\sigma^2$$

APD – 800 Polisher and Tribometer



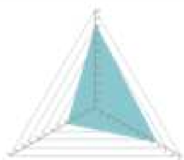
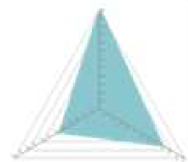
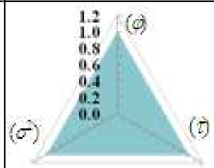
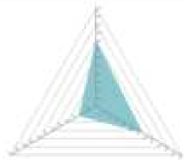
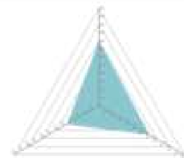
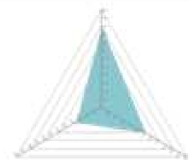
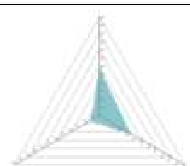
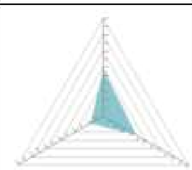
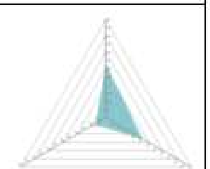


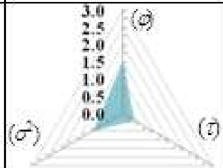
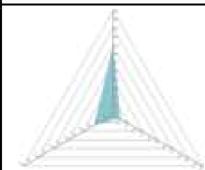
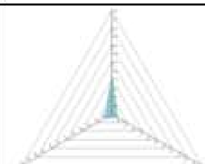
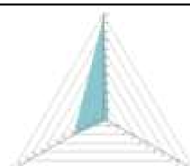
Shear Force, Variance, RR & WIWRRNU



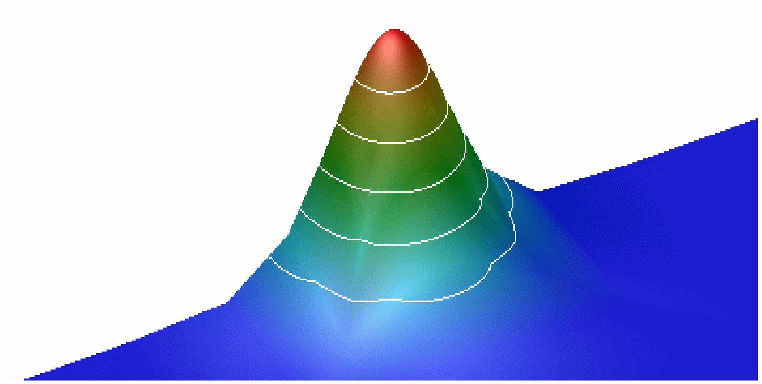
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

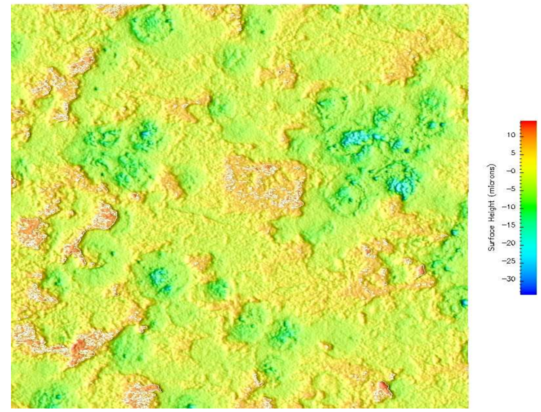
Delamination Triangle

	Slurry Flow Rate (ml/min)		
Wafer Rotational Rate (RPM)	200	300	400
23			
98			
148			

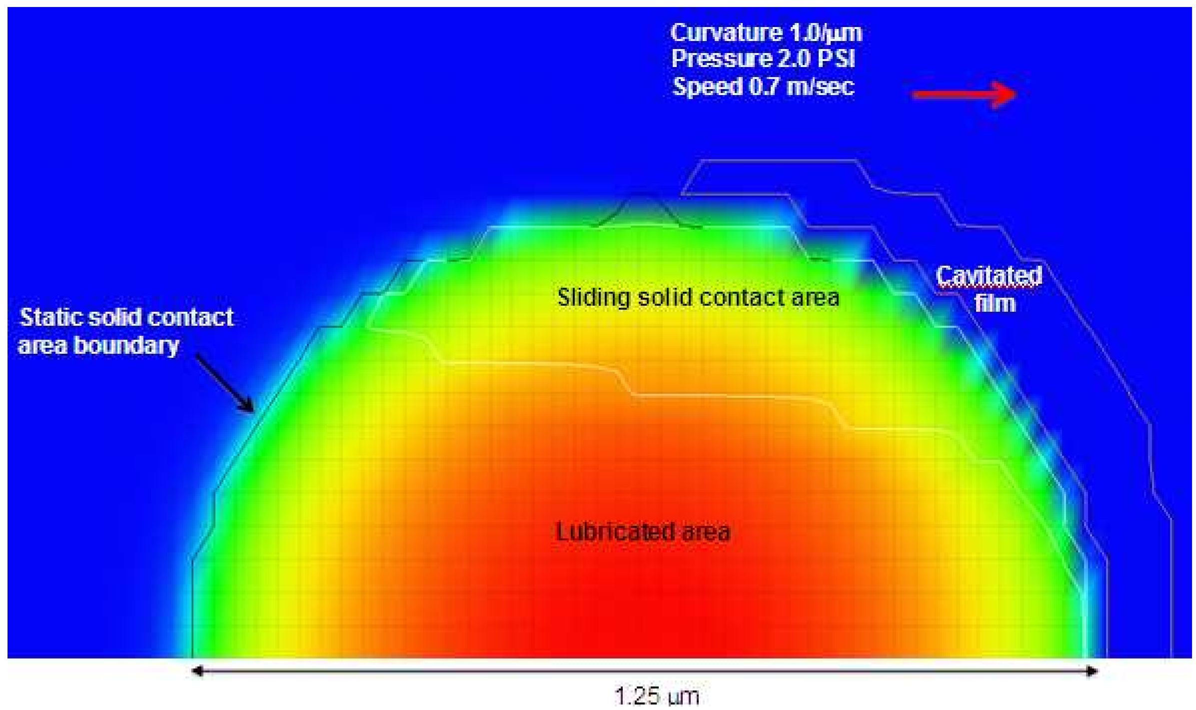
	Platen Rotational Rate (RPM)		
Polishing Pressure (RPM)	25	40	55
1.5			
2.0			
2.5			

Modeling Contacting Solid Lubrication

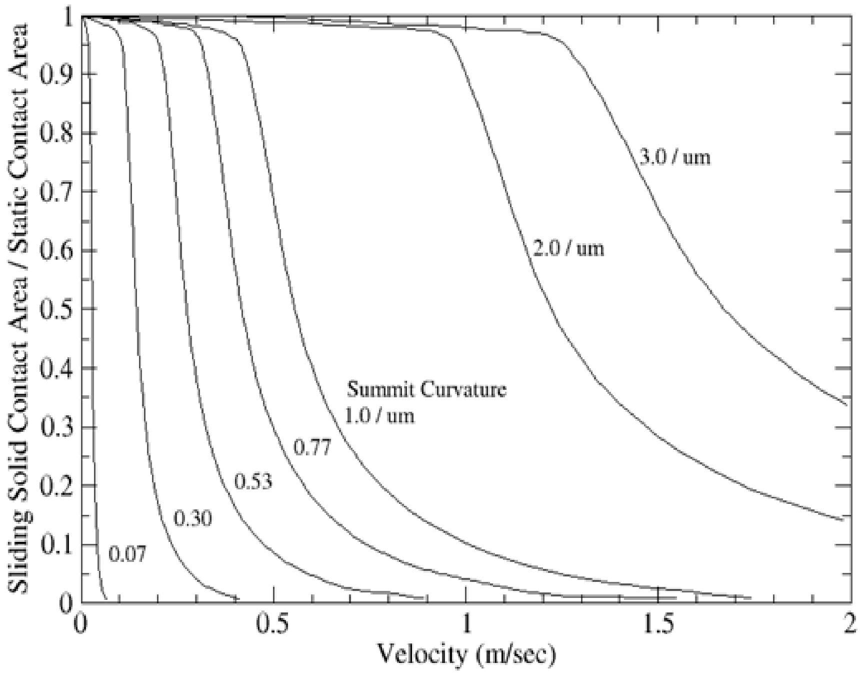




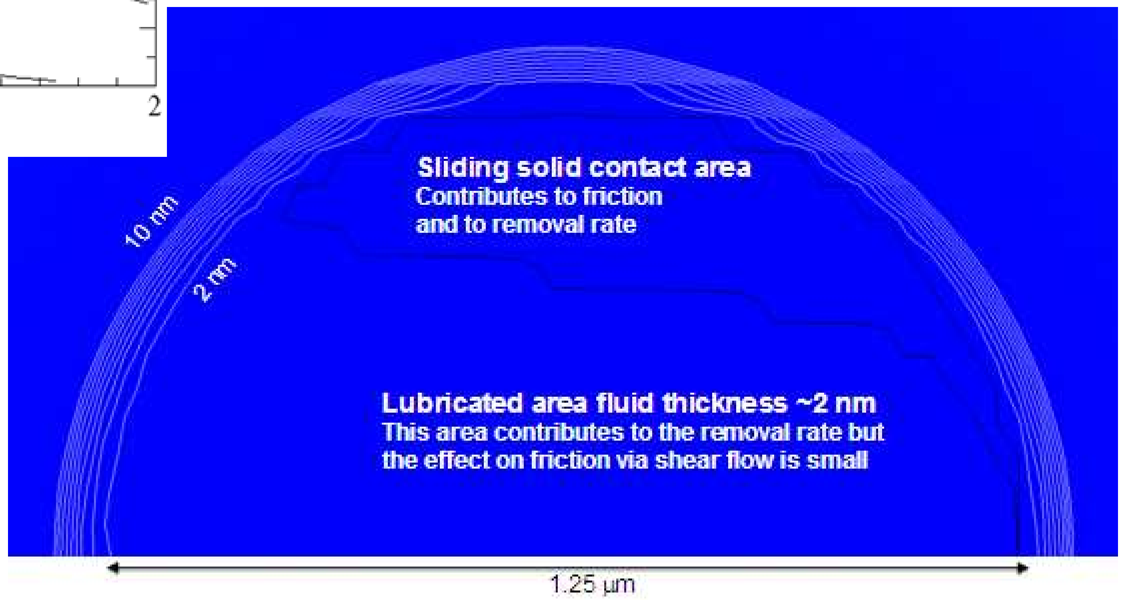
Source: L. Borucki (2009)



Modeling Contacting Solid Lubrication



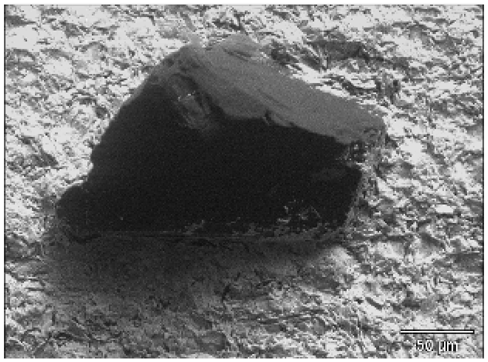
Source: L. Borucki (2009)

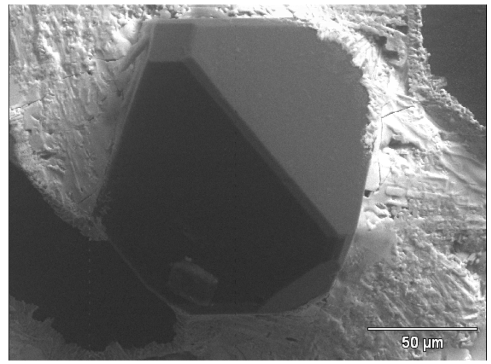


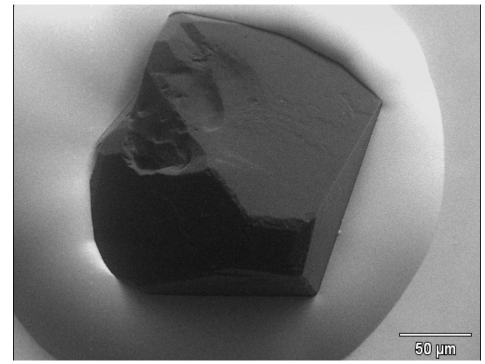
SEM Analysis Example – Static Etch Test

Fujimi PL-7103 Slurry at 50 ºC

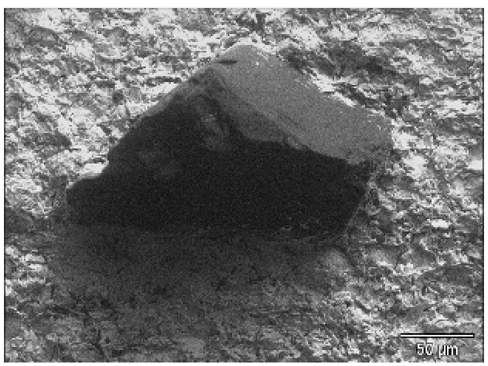
Before Static Etch Test

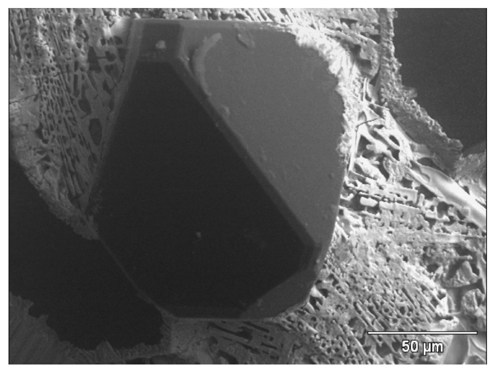


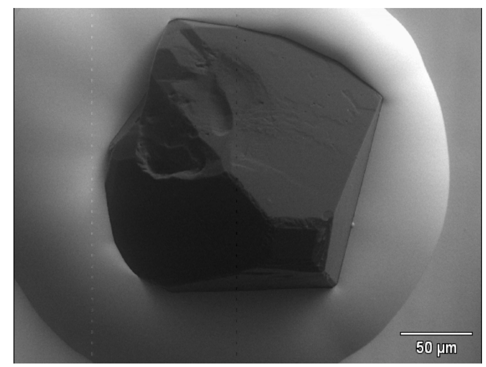




After Static Etch Test







D1 **D2** **D3**

There was no appreciable wear on the diamond disc substrate and diamonds for D1 and D3. In comparison, there was apparent surface corrosion on the diamond disc substrate for D2.

SEM Analysis Summary – Static Etch Test

		D1		D2		D3	
		Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75
25 ºC	Diamond	No appreciable wear					
	Diamond Disc Substrate	No appreciable wear		Apparent surface corrosion	No appreciable wear	No appreciable wear	
50 ºC	Diamond	No appreciable wear					
	Diamond Disc Substrate	No appreciable wear		Apparent surface corrosion		No appreciable wear	

ICPMS Analysis Summary – Static Etch Test

Temperature	Metal	D1 (mg/L)		D2 (mg/L)		D3 (mg/L)	
		Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75
25 °C	Ni	1.35	1.33	13.26	1.89	0	0
	Fe	0.03	0	0.44	0.22	0	0
	Cr	0.10	0.07	0.40	0.45	0.02	0.06
50 °C	Ni	2.28	4.25	54.81	42.85	0.06	0.05
	Fe	0	0.07	0.62	1.72	0	0.04
	Cr	0.04	0.13	2.35	2.33	0.02	0.10

With Fujimi slurry, ICPMS analysis indicated that Ni concentration in slurry increased appreciably at 25 and 50 °C for D1; Ni concentration in slurry increased significantly at 25 °C and increased dramatically at 50 °C for D2.

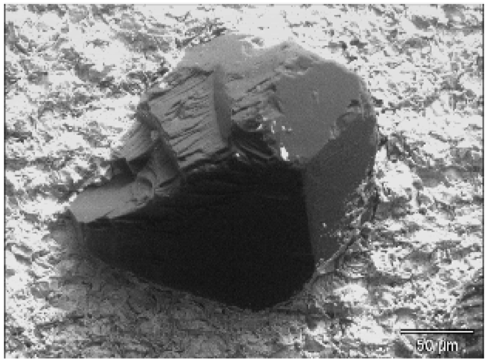
With CMC slurry, ICPMS analysis indicated that Ni concentration in slurry increased appreciably at 25 and 50 °C for D1; Ni concentration in slurry increased appreciably at 25 °C and increased dramatically at 50 °C for D2.

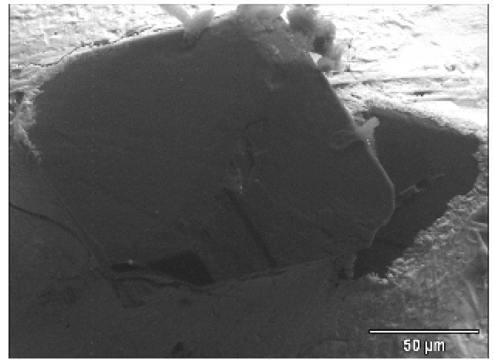
ICPMS analysis indicated that for both Fujimi and CMC slurries, there was barely any increase in Ni, Fe, and Cr concentrations in slurry at 25 and 50 °C for D3.

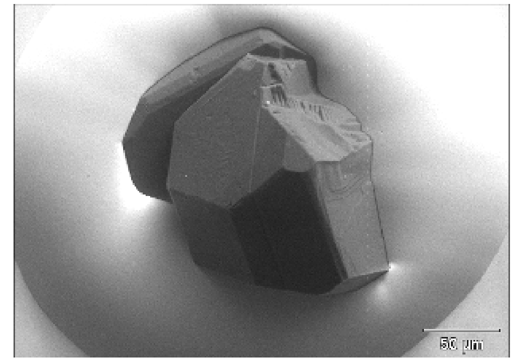
SEM Analysis Example – Wear Test

Aggressive Diamonds – Fujimi PL-7103 Slurry at 50 ºC

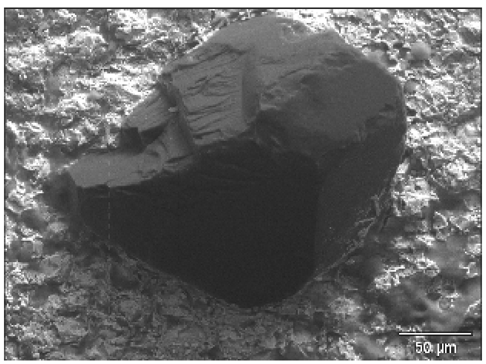
Before Wear Test

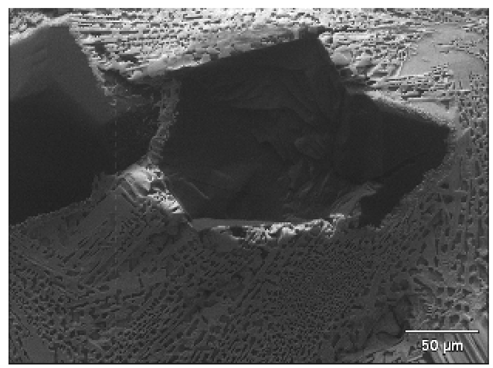


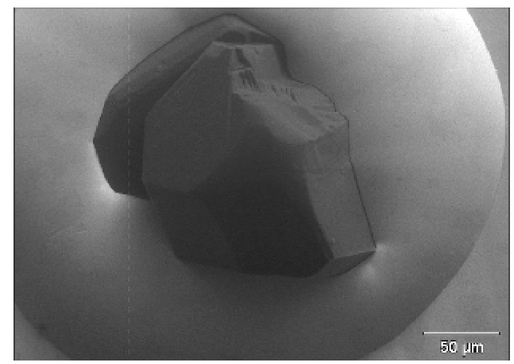




After Wear Test







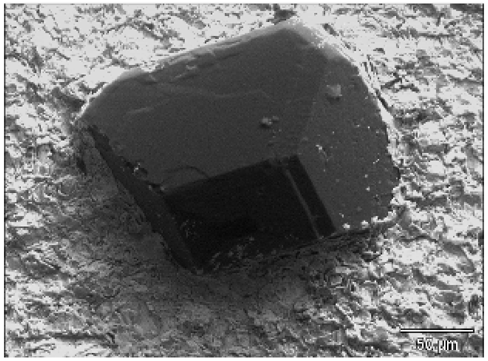
D1 **D2** **D3**

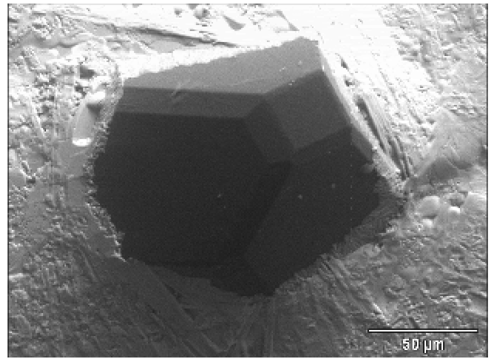
There was micro wear on the cutting edges of aggressive diamonds for D1 and D3. In comparison, the aggressive diamond broke off from the diamond disc substrate and there was apparent surface corrosion on the diamond disc substrate for D2.

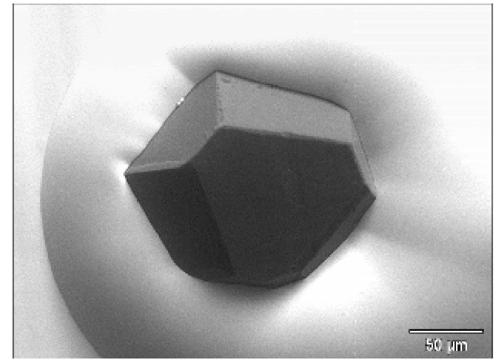
SEM Analysis Example – Wear Test

Inactive Diamonds – Fujimi PL-7103 Slurry at 50 ºC

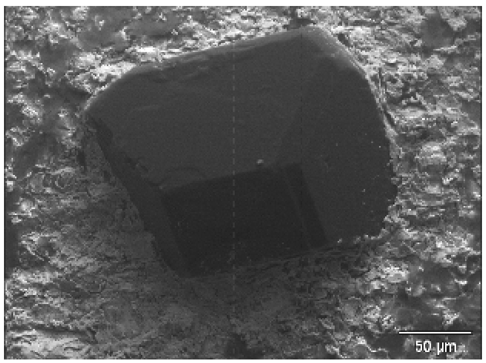
Before Wear Test

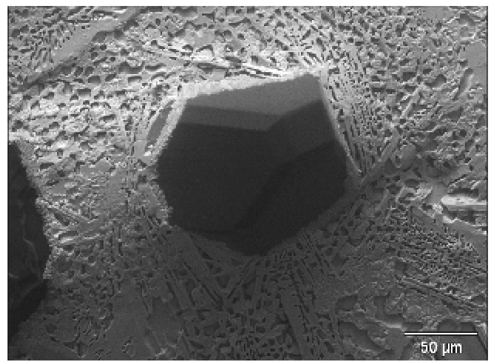


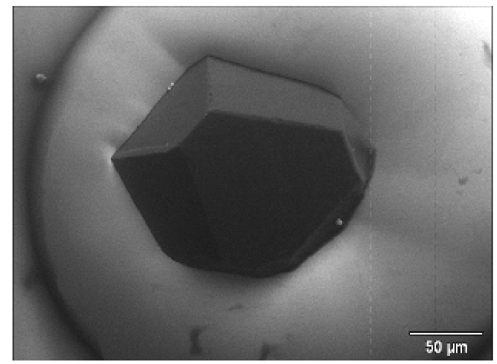




After Wear Test







D1 **D2** **D3**

There was no appreciable wear on the inactive diamond for all three discs. There was no appreciable wear on the diamond disc substrate for D1 and 3. In comparison, there was apparent surface corrosion on the diamond disc substrate for D2.

SEM Analysis Summary – Wear Test

		D1		D2		D3	
		Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75
25 °C	Aggressive Diamond	Micro wear on cutting edges					
	Inactive Diamond	No appreciable wear					
	Diamond Disc Substrate	No appreciable wear		Apparent surface corrosion		No appreciable wear	
50 °C	Aggressive Diamond	Micro wear on cutting edges		Micro wear on cutting edges / broken diamond		Micro wear on cutting edges	
	Inactive Diamond	No appreciable wear					
	Diamond Disc Substrate	No appreciable wear		Apparent surface corrosion		No appreciable wear	

Average Pad Cut Rate

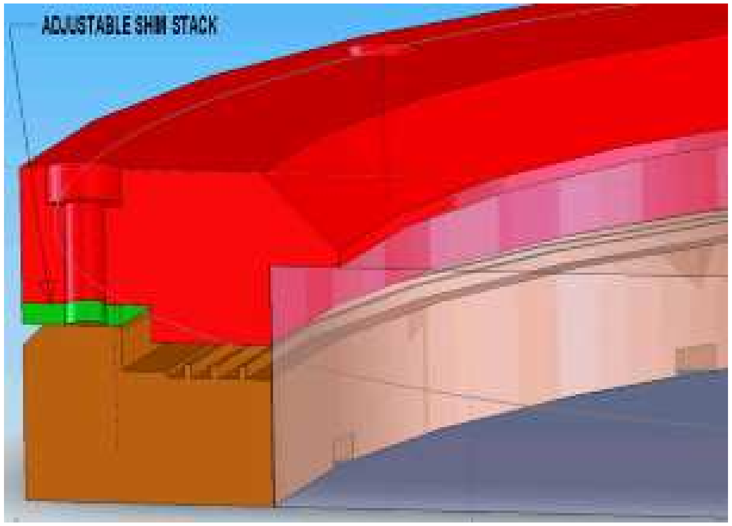
Temp.	D1 (μm/hour)		D2 (μm/hour)		D3 (μm/hour)	
	Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75	Fujimi PL-7103	CMC iCue 600Y75
25 °C	14.33	3.03	7.87	2.32	6.05	0.93
50 °C	10.84	2.05	11.09	2.90	4.98	0.88

For both slurries at 25 °C, D1 generated the highest pad wear rate while D3 generated the lowest pad wear rate. D2 generated the highest pad wear rate while D3 generated the lowest pad wear rate for both slurries at 50 °C.

For both slurries, pad wear rate decreased with the increase of the platen temperature for D1 and D3. Pad wear rate increased with platen temperature for D2 for both slurries.

For all three discs, pad wear rate for Fujmi slurry was significantly higher than CMC slurry, indicating slurry abrasives and abrasive concentration significantly impact pad wear rate.

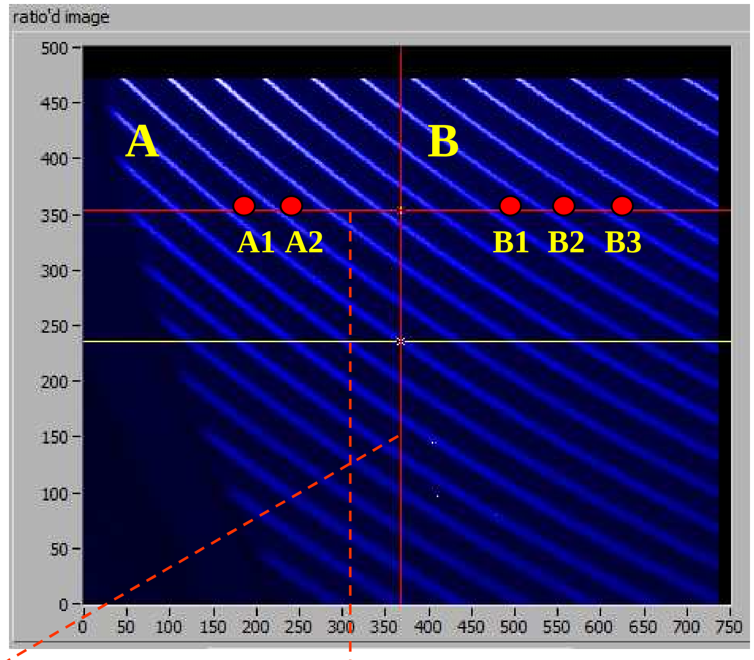
Quartz Wafer and Retaining Ring Assembly



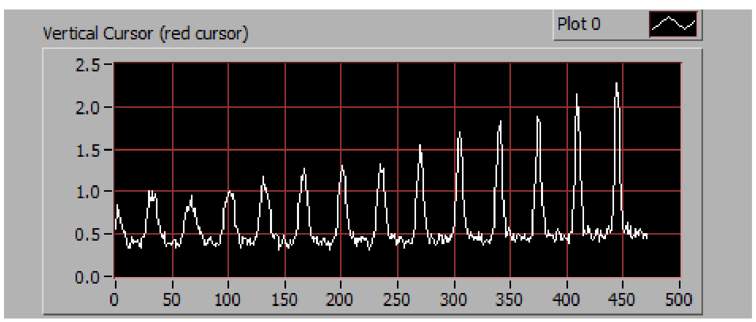
STD Ring - Ratio of 'land area' to total area of this ring is appx. 0.93

ALTRERNATE Ring – Ratio of 'land area' to total area of this ring is appx. 0.52

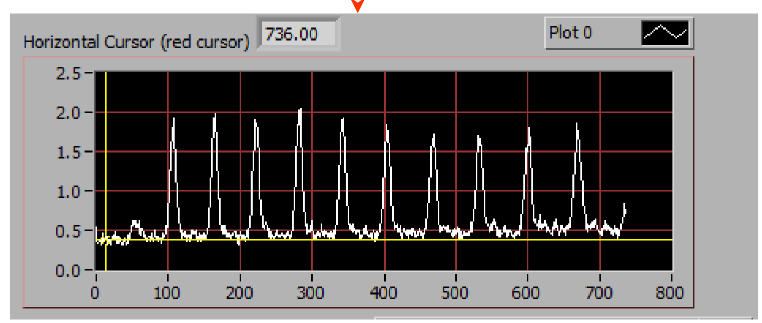
Ratio Analysis for Slurry Film Thickness



vertical line scan

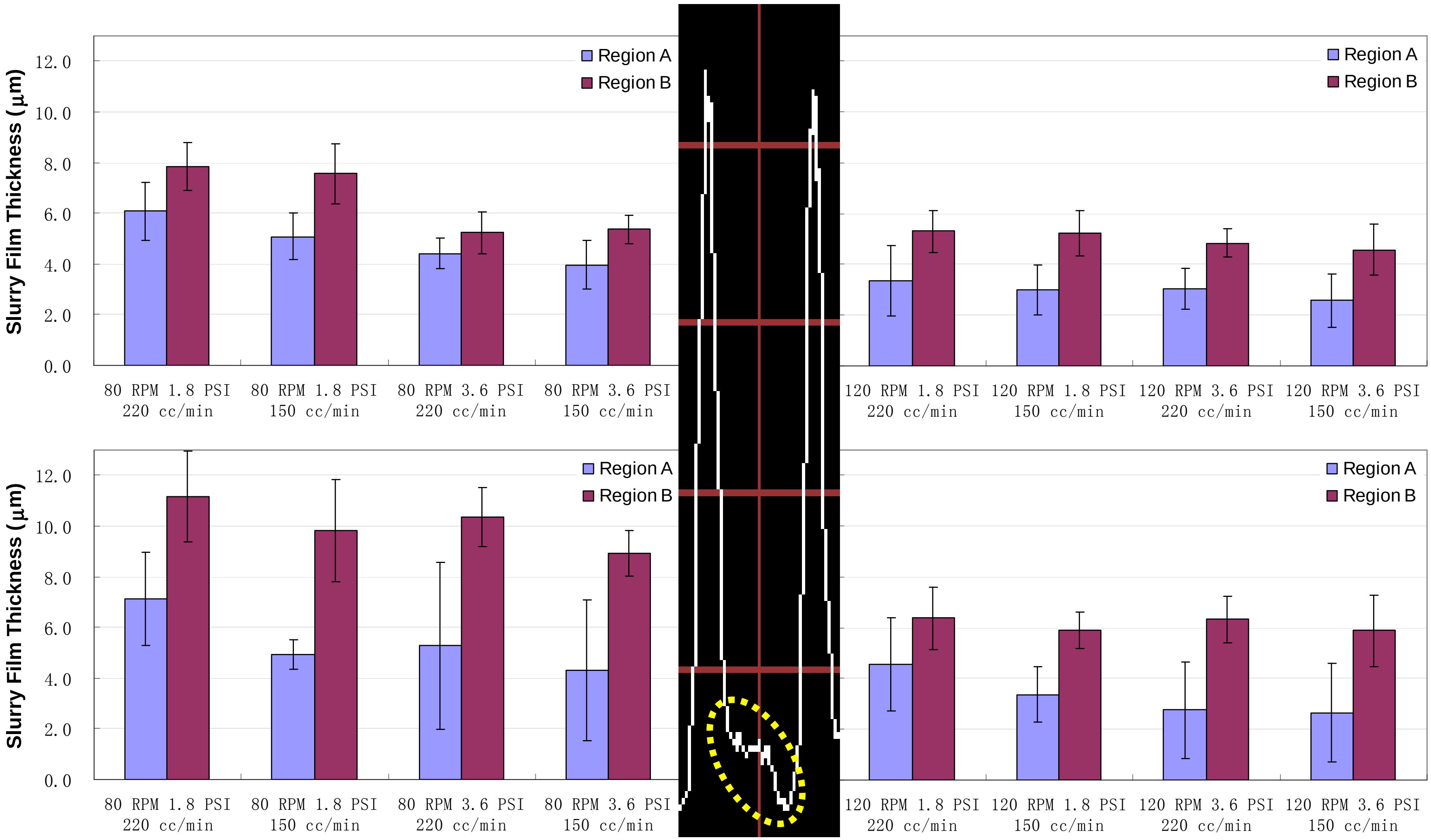


horizontal line scan

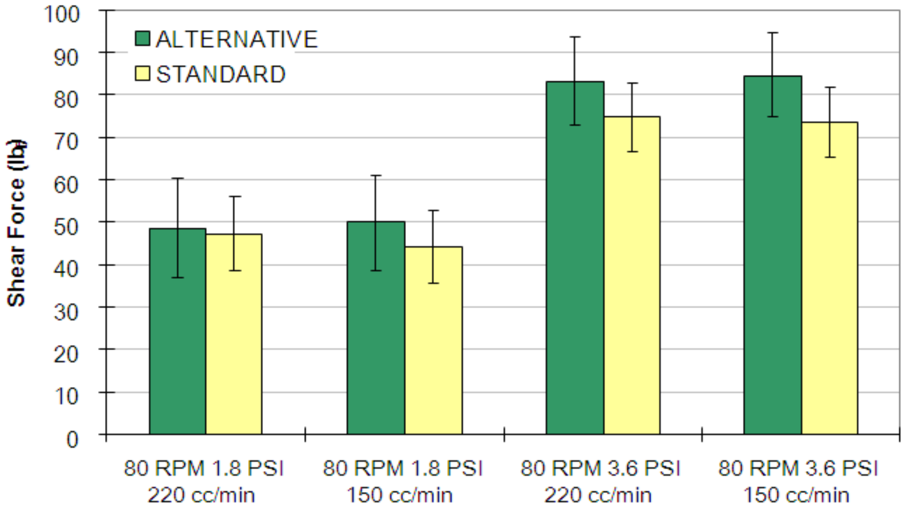


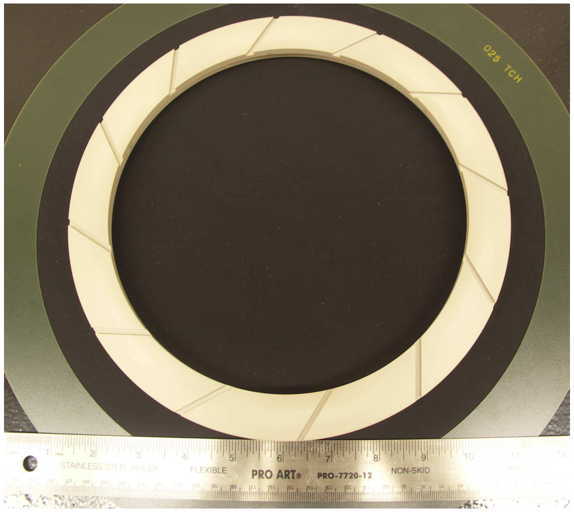
Slurry Film Thickness Measurement

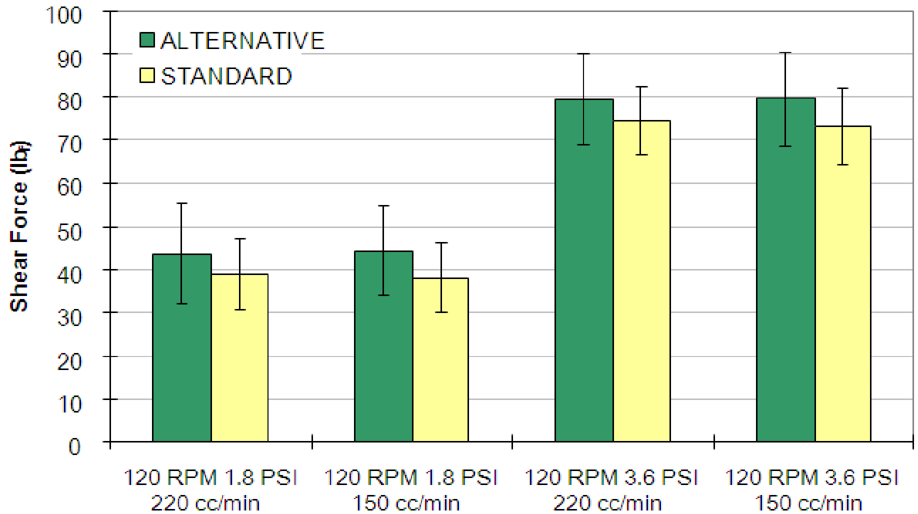
STANDARD (Top) and ALTERNATIVE (Bottom)

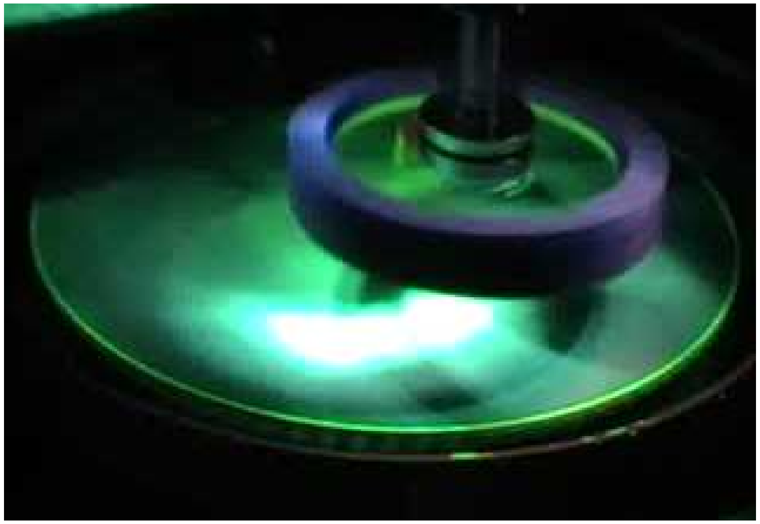


Shear Force Measurement and Video Clip









Industrial Interactions and Plans

Industrial mentors and contacts:

- Tadahiro Ohmi (Tohoku University)
- Akinobu Teramoto (Tohoku University)
- Takee Nemoto (Tohoku University)
- Toranosuke Ashizawa (Hitachi Chemical)
- Hiroyuki Morishima (Hitachi Chemical)
- Mansour Moinpour (Intel)
- Don Hooper (Intel)
- Chris Wargo (Entegris)
- Ralph Stankowski (Entegris)
- Cliff Spiro (CMC)
- Ananth Naman (CMC)

Industrial Interactions and Completion Plans

Completion Plans (until 3/09):

- **Investigate effect of pad groove design in reducing ‘DELTA’**
- **Validate importance of ‘DELTA’ on various Cu – ULK structures**
- **Explain trends via modeling contacting solid lubrication behavior**
- **Develop method and perform accelerated diamond wear tests to investigate pullout for various types of diamond discs**

Summary of Major Accomplishments of the Past 3 Years

- **Developed and qualified contact method to analyze mechanical pad surface properties in dry and moist conditions as well as CMP-relevant temperatures. Validated results with optical interferometry**
- **Modeled slurry flow under the wafer in the land areas with the Reynolds equation with roughness correction and calculated shear flow factors from PDF data using the method of homogenization. Demonstrated that certain pads had 5X the fluid carrying capacity compared to others.**
- **Experimentally and theoretically demonstrated the effect of conditioner force and kinematics on copper RR**
- **Parameters independently calculated from pad surface data are consistent with extracted values from the Langmuir-Hinshelwood model**
- **Provided first experimental and theoretical evidence that a strong correlation existed between pad surface profile and kinetic rate constants**
- **Developed and qualified 200 and 300 mm polishers at UA for real-time XYZ force analysis**

Summary of Major Accomplishments of the Past 3 Years

- **Demonstrated feasibility of 'force spectroscopy' for the detection of STI pattern evolution, silica and ceria-based ILD and STI slurry abnormalities, pad and diamond end-of-life and insufficient diamond conditioning**
- **Demonstrate feasibility of 'force spectroscopy' for Step – 2 and Step – 3 copper and barrier polish**
- **Integrate and validate results with MIT's pattern evolution and nano-topography models**
- **Quantified diamond and diamond disc substrate micro-wear in Cu CMP**
- **Investigated effect of conditioning on pad topography and slurry film thickness and developed and validated a removal rate model consistent with above finding**
- **Developed methods to quantitatively assess slurry film thickness in various regions within the pad-wafer interface as well as slurry flow patterns in the bow wave and elsewhere on the pad**

Summary of Major Accomplishments of the Past 3 Years

- **Developed confocal microscopy method for quantifying pad-wafer contact area, near-contact area, summit density and summit curvature under CMP relevant conditions**
- **Proposed a new CMP metric coined as the 'Delamination Triangle' and developed methodology to understand the effect polishing parameters (i.e. slurry flow rate, pad and wafer rotational rate and polishing pressure) for damage-free CMP**
- **Investigated shear force and down force signal transition during early evolution of wafer topography for STI and metal CMP and correlated the results with polish outcomes**
- **Proved that shear force spectral signals are indicative of furrow density for various types of diamonds and conditioning recipes in STI CMP**

WE WISH TO EXPRESS OUR SINCERE GRATITIDE TO SRC, SEMATECH AND 'IN-KIND' DONOR ORGANIZATIONS FOR THEIR GENEROUS SUPPORT

An Integrated, Multi-Scale Framework for Designing Environmentally-Benign Copper, Tantalum and Ruthenium Planarization Processes (*Task Number: 425.020)*
In-situ Metrology Coupled with Modeling to Improve Control and Operation of CMP Processes – February 2009

PIs:

- C. B. Rogers, Tufts University
- V. P. Manno, Tufts University (Presenter)
- R. D. White, Tufts University

Graduate Students:

- Caprice Gray: PhD, Mechanical Engineering, May 2008
- James Vlahakis: PhD, Mechanical Engineering, August 2008
- Nicole Braun: MS, Mechanical Engineering, May 2008
- Douglas Gauthier: MS, Mechanical Engineering, February 2009
- Minchul Shin: PhD candidate, Mechanical Engineering

Cost Share – ended 2008 (other than core ERC funding):

- $50k/year from Intel Corporation (special project 2008-9)
- $50k/year from Cabot Microelectronics

Three Year Deliverables & Objectives

- **Subtask 1:** Use Dual Emission Laser Induced Fluorescence (DELIF) to obtain in-situ images of the slurry layer thickness during CMP and quantify wafer-pad contact during polishing – **Caprice Gray (PhD, May 2008)**

- **Subtask 2:** 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, August 2008)**

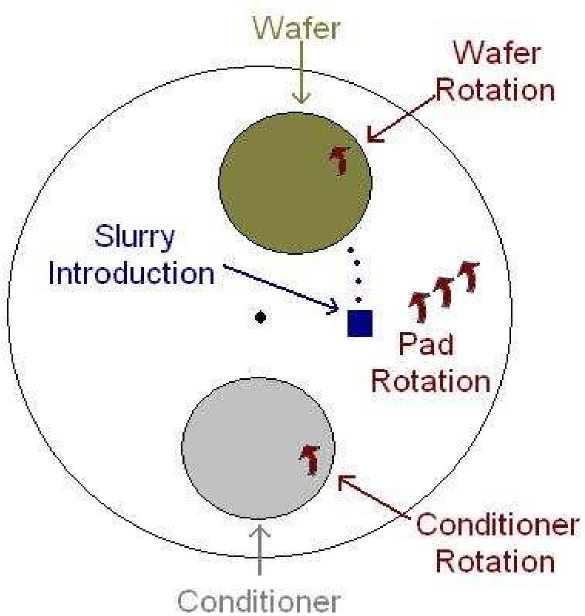
- **Subtask 3:** Use custom micromachined sensors to measure local (100 μm scale), high sample rate (0.1 ms) asperity scale forces at the pad-wafer interface during CMP **- Douglas Gauthier (MS, February 2009)**

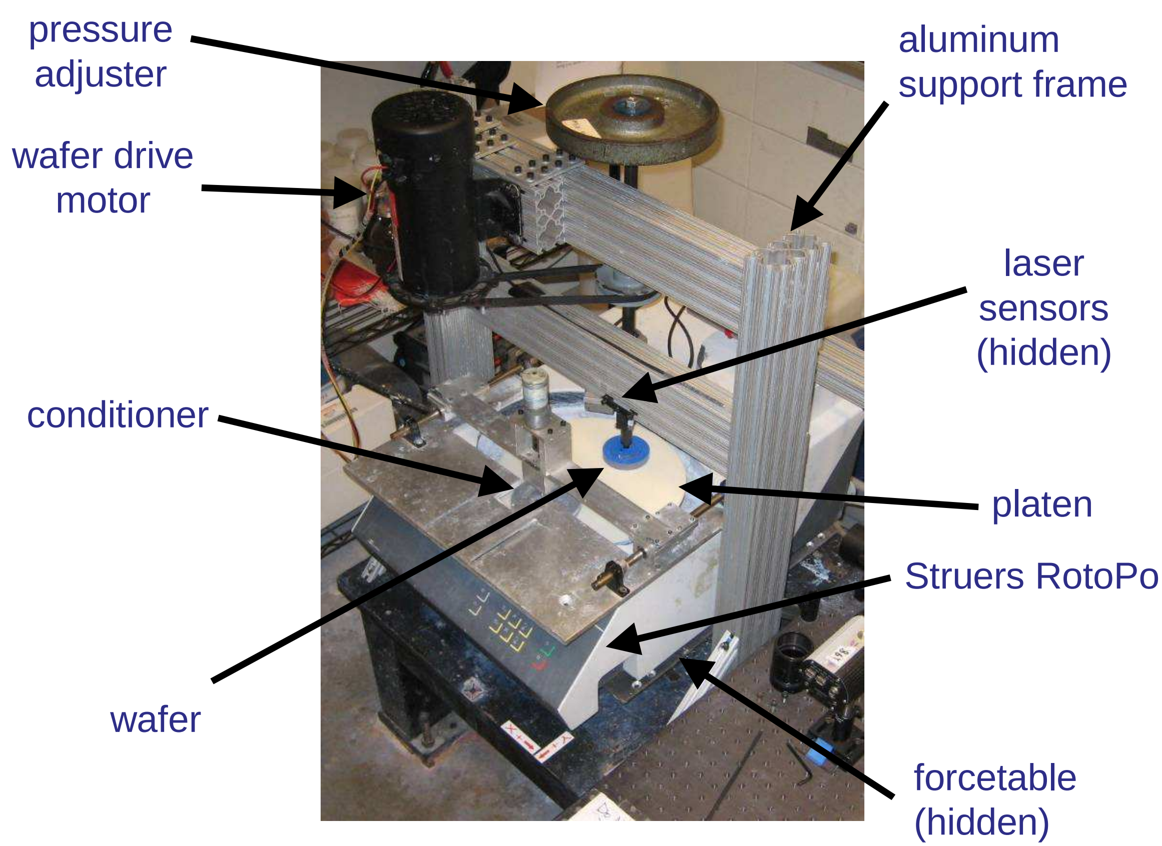
- **Subtask 4:** (Seed Project) Investigate the feasibility of using particle image velocimetry (PIV) to quantitatively measure particle-slurry flow in-situ. – **Nicole Braun (MS, May 2008)**

ESH Metrics and Impact

Metric	Impact
Reduction in the use of natural resources (water and energy)	Understanding wafer-pad interactions during polish leads to reduced time to polish and tool energy consumption
Reduction in emission of ESH-problematic material to environment *Reduction in the use or replacement of ESH-problematic materials*	Optimized process parameters based on in-situ characterization of contact and forces leads to reduced time to polish and slurry consumption.

Experimental Platform





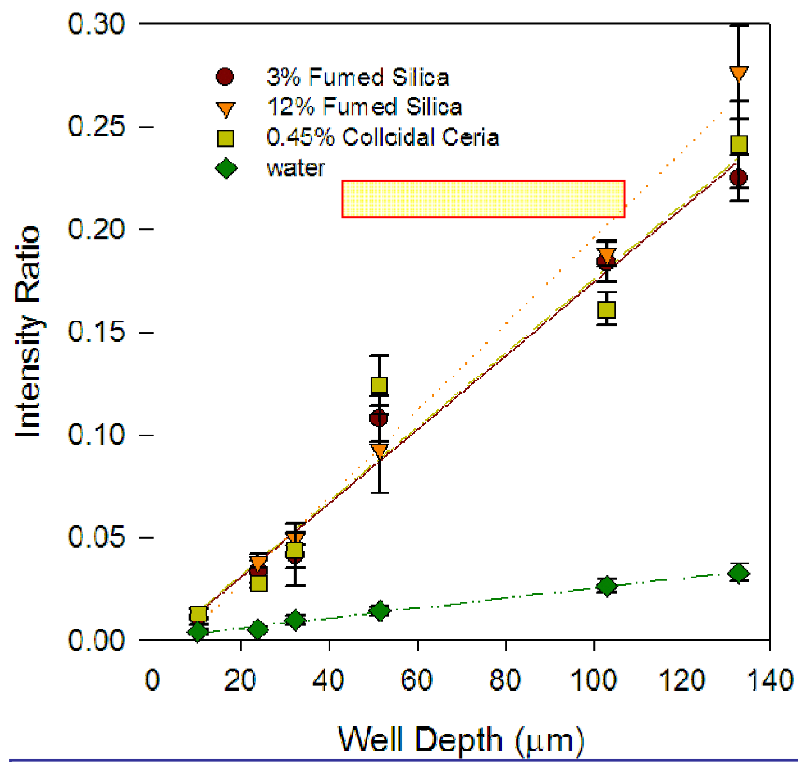
Glass polishing on a Struers Rotopol-31 benchtop polisher

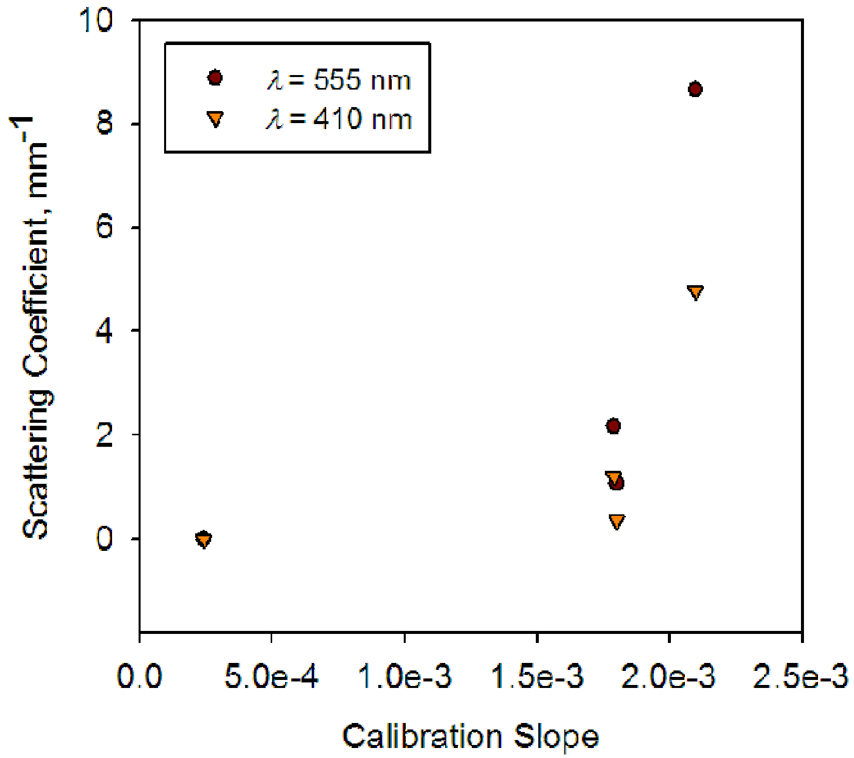
Subtask 1: **Detecting Pad-Wafer Contact In CMP Using Dual Emission Laser Induced Fluorescence**

- Project Goals:
  - Develop an *in-situ* optical technique to observe the slurry layer
  - Provide experimental evidence for model predictions by making *in-situ* measurements varying process parameters (Load, Velocity, Conditioning Time)
    - slurry layer thickness
    - pad-wafer contact area
  - Correlate results to existing modeling and experimental results

Depth Calibration – Smooth Pad

- For the calibration well depths tested (10.3 – 133mm) we have a linear calibration!
- Tested water & 3 slurry types for effects of particle scattering
  - Particles do not effect calibration linearity in this depth regime
  - Scattering increases intensity → better image contrast



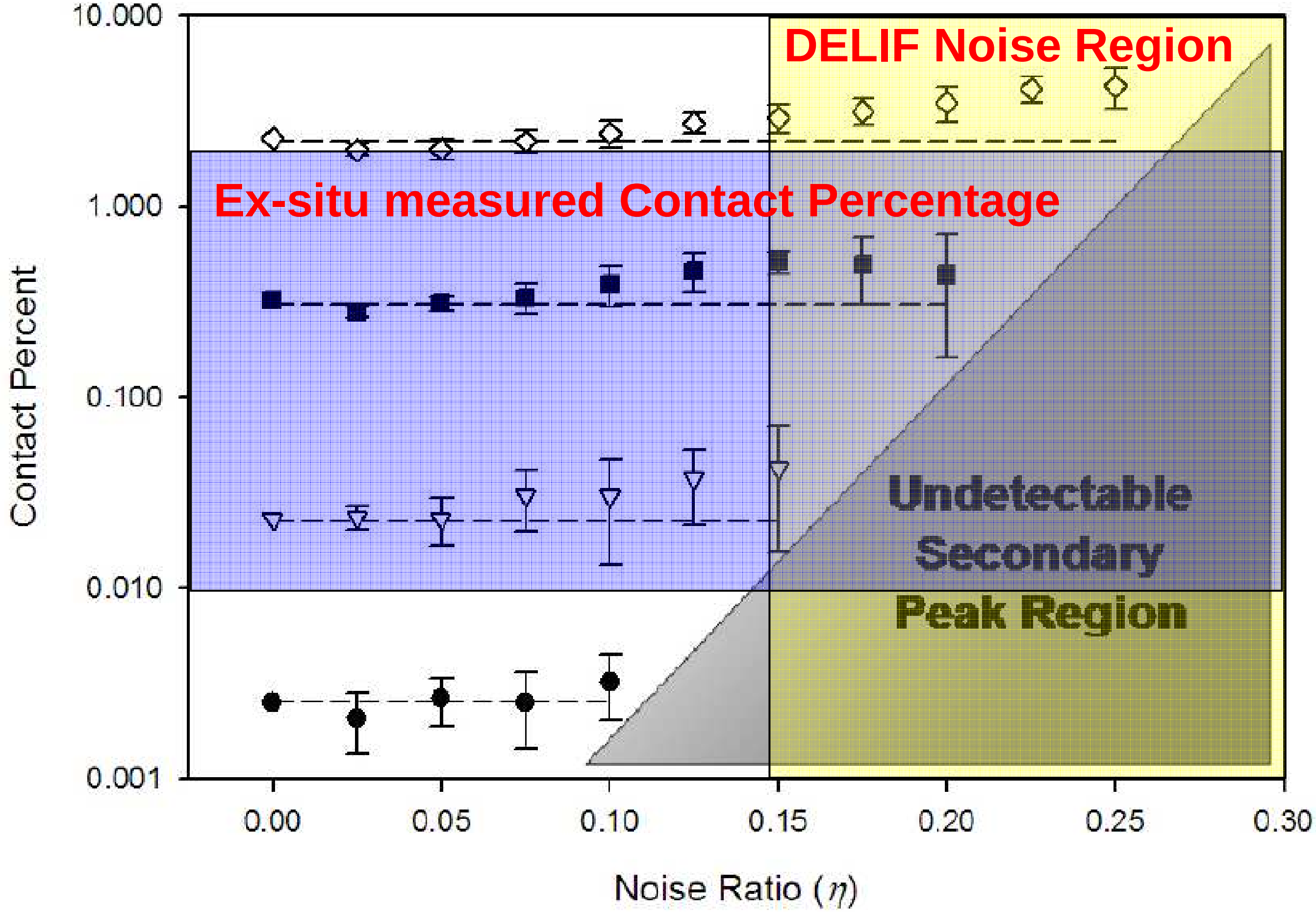


SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Measurement Noise in DELIF

Noise sources: White noise from cameras, misalignment, focus, depth of field.

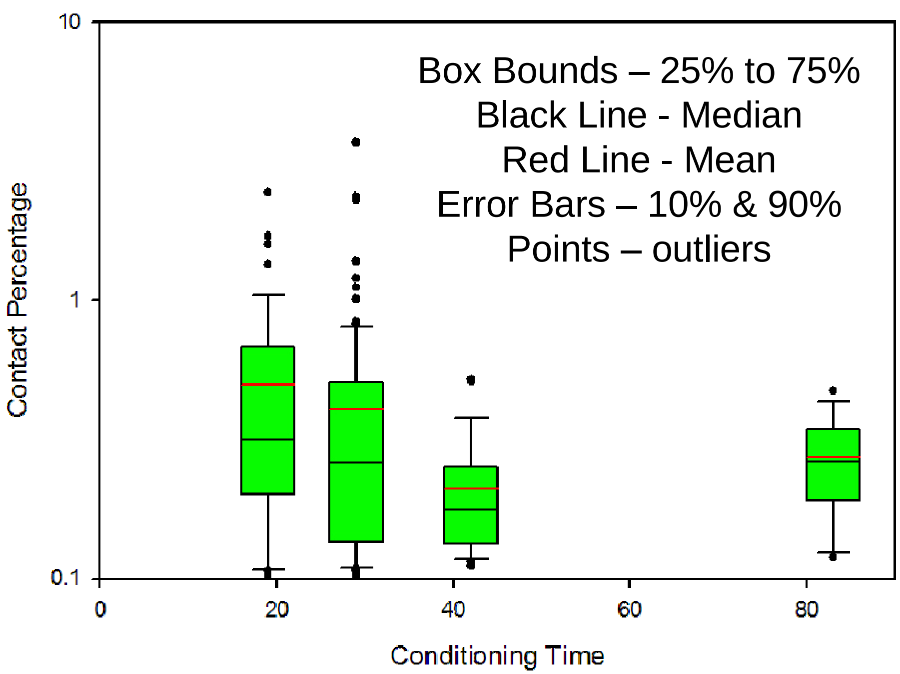
Noise is propagated by the division of the 2 signals



Contact with Conditioning Time

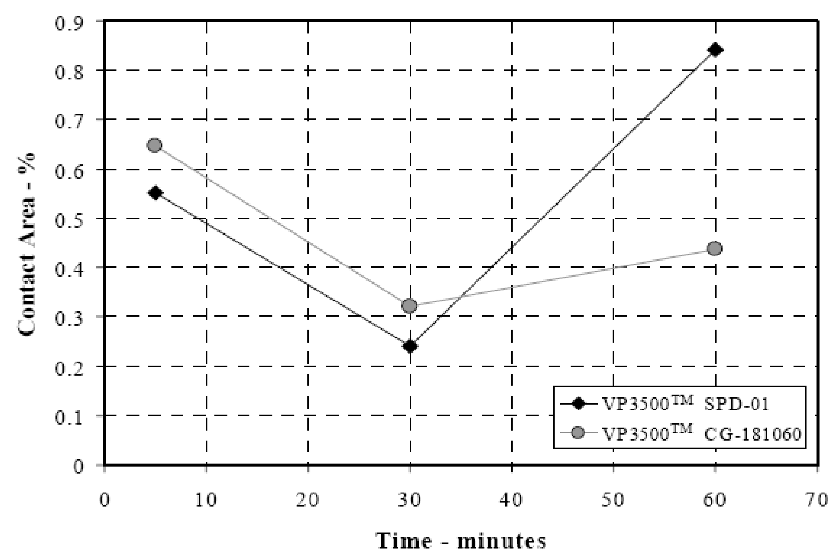
- Contact *appears* to decrease with conditioning time
  - Asperity tips are getting smaller in size = less detectable due to image resolution OR
  - Pad surface modification is changing the lubrication regime = actually have less contact

In-situ experiment



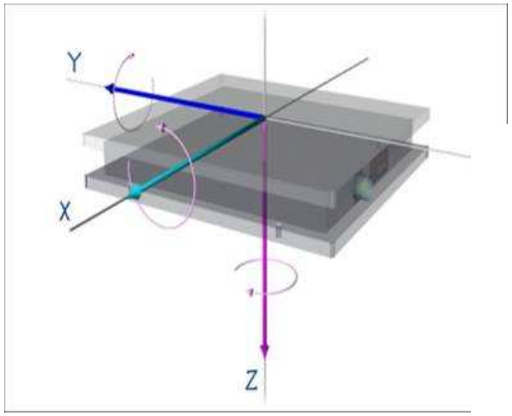
Ex-situ experiment

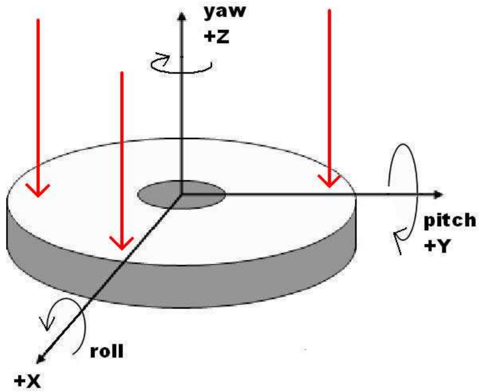
C L Elmufdi and G P Muldowney. *Materials Research Society Proceedings*, **991**:15–26, April 9-13 2007.



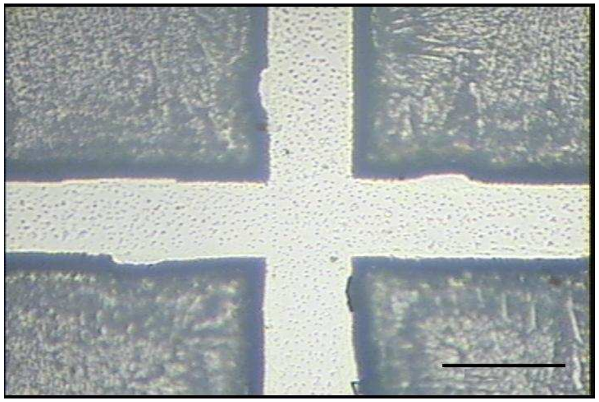
Subtask 2: Synchronous, In Situ Measurements of Coefficient of Friction, Wafer Orientation and Material Removal Rate During Chemical Mechanical Planarization

$$CoF = \frac{\sqrt{F_x^{\ 2} + F_y^{\ 2}}}{F_z}$$





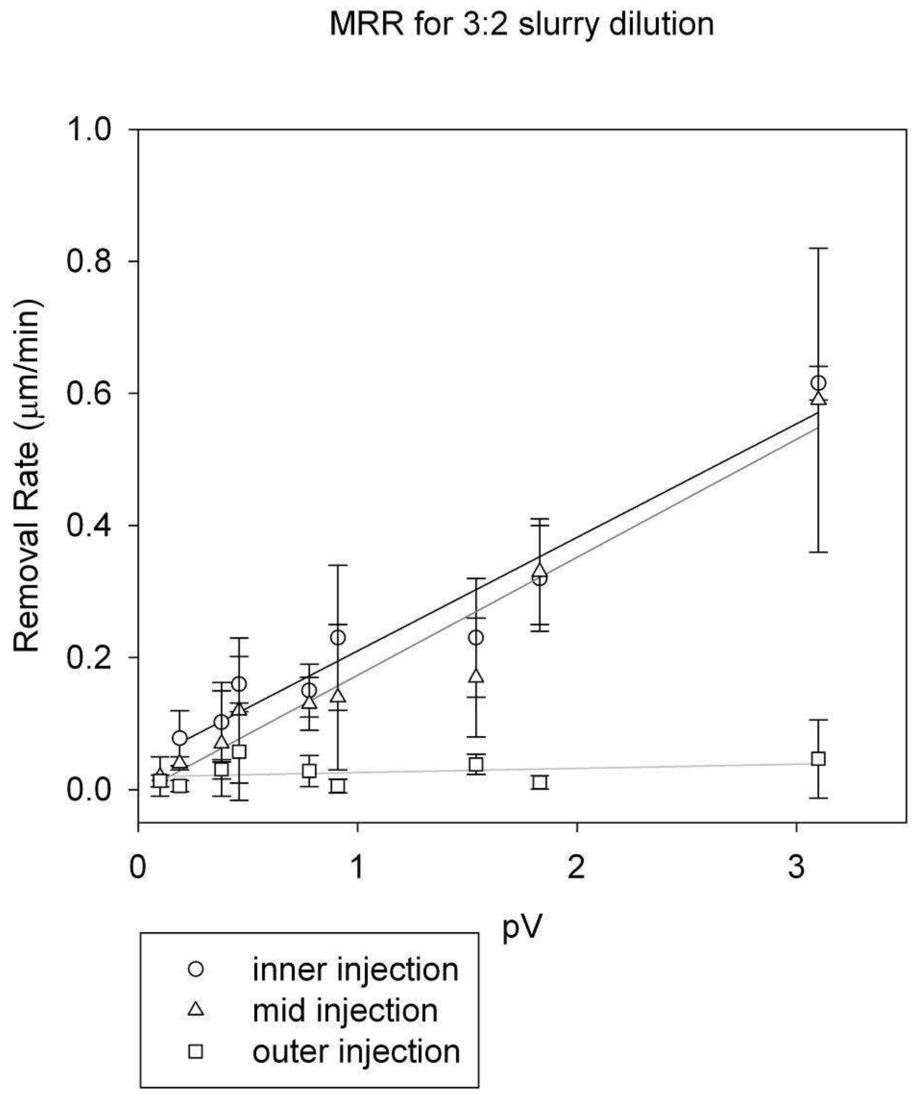
- In–situ Wafer Position



- Ex-situ MRR - Trench depth is measured at three locations before and after experiments

Experimental Results – MRR

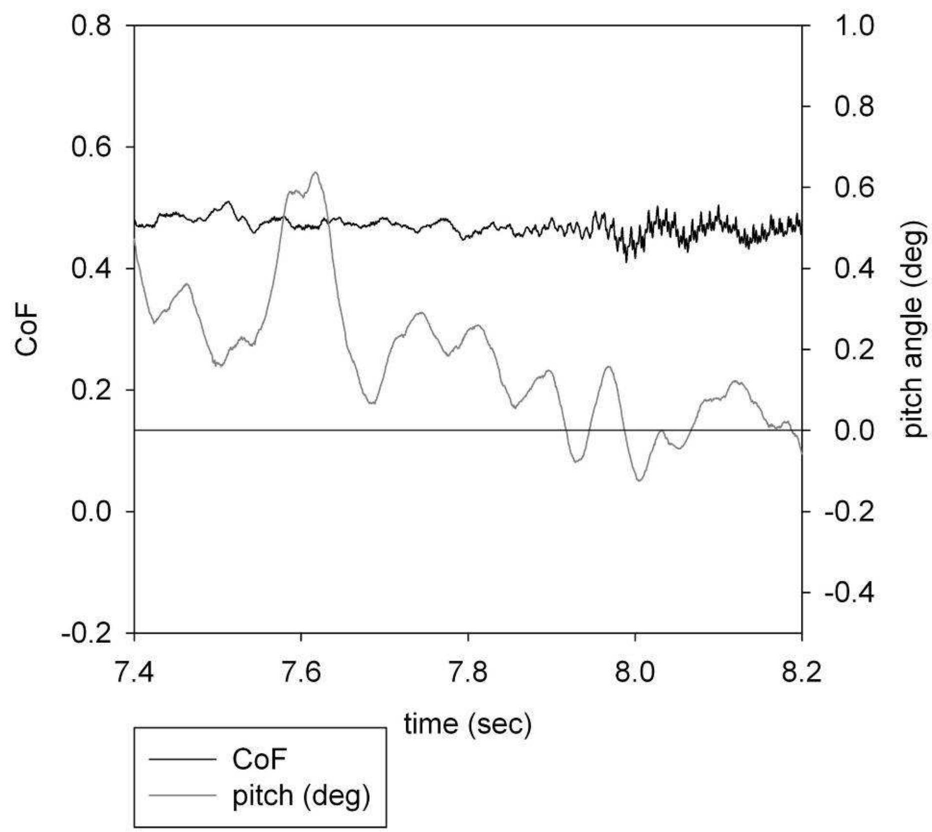
- 12% particle loading
- Difference in slurry transport due to injection point
- Injection point strongly influences MRR in some regimes.



Experimental Results – Stick-Slip

- Transition seems to precede the pitch minimum
- Stick-Slip associated with all minima or with none

Synchronous Data
3:2 slurry – mid injection – 2.4psi - 0.3m/s



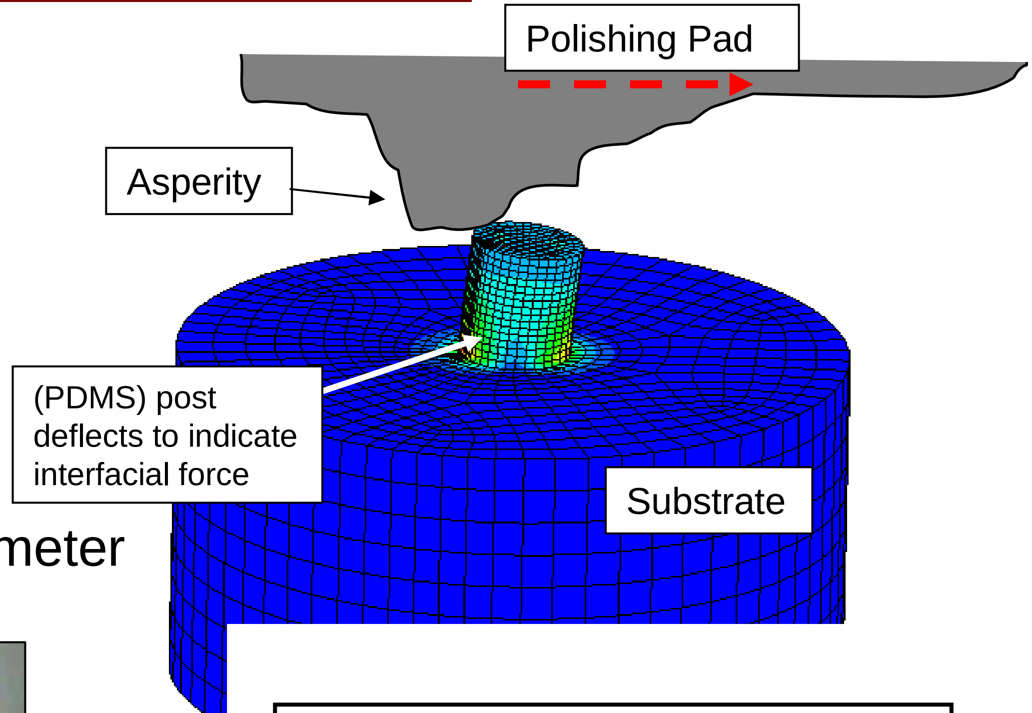
Subtask 3: **Asperity Level Pad-Wafer Force Measurement using Micromachined Structures**

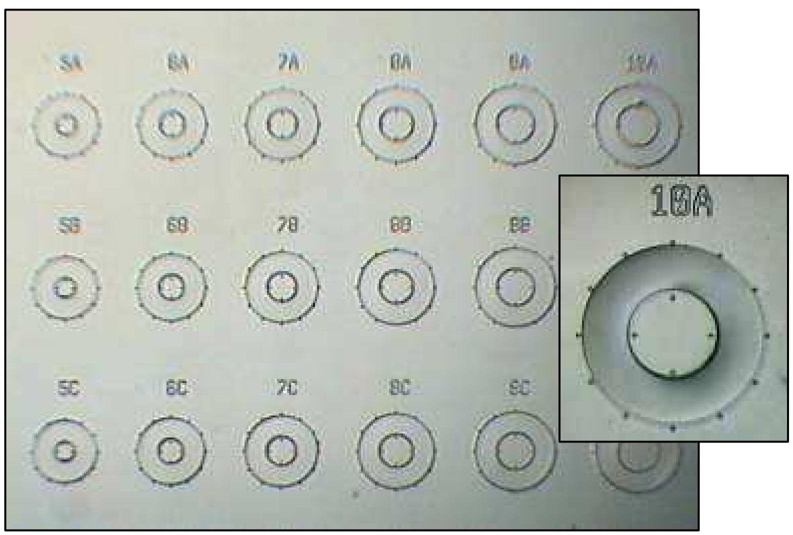
- Project Goals:

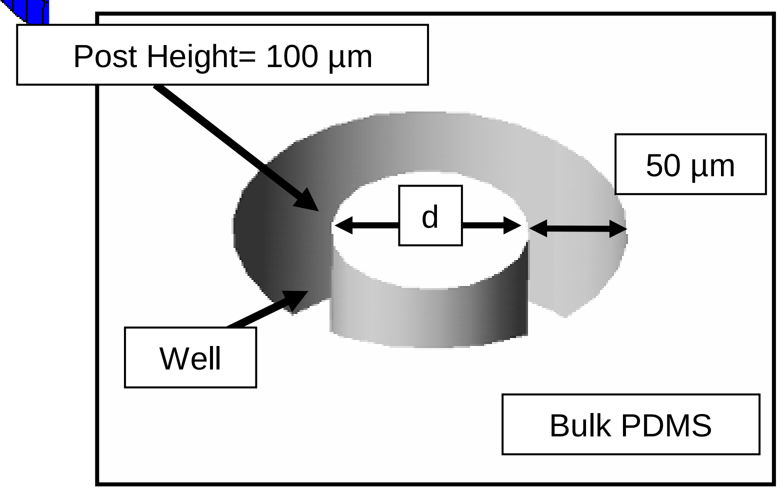
  Use custom micromachined sensors to measure local (100 mm scale), high sample rate (10 kHz) asperity scale forces (1 mN- 10 mN) at the pad-wafer interface during CMP.

PDMS Force Sensor

- 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

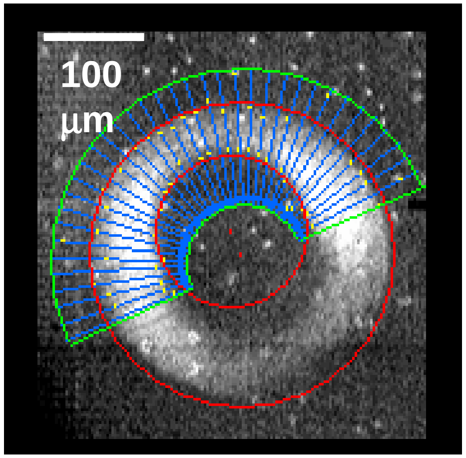




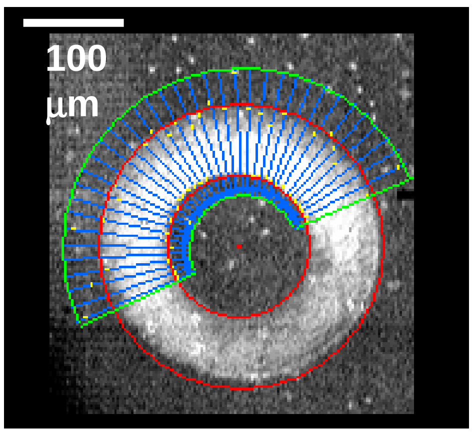


Asperity Level Forces

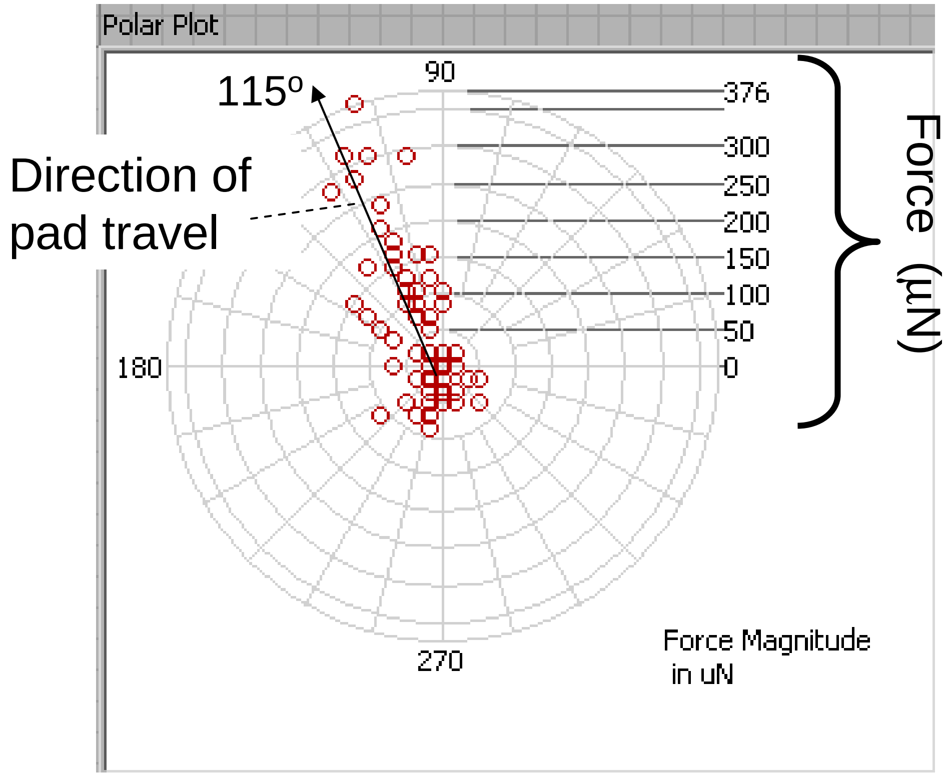
Image processing extracts motion of the post from high-speed (10,000 fps) video.



Deflected

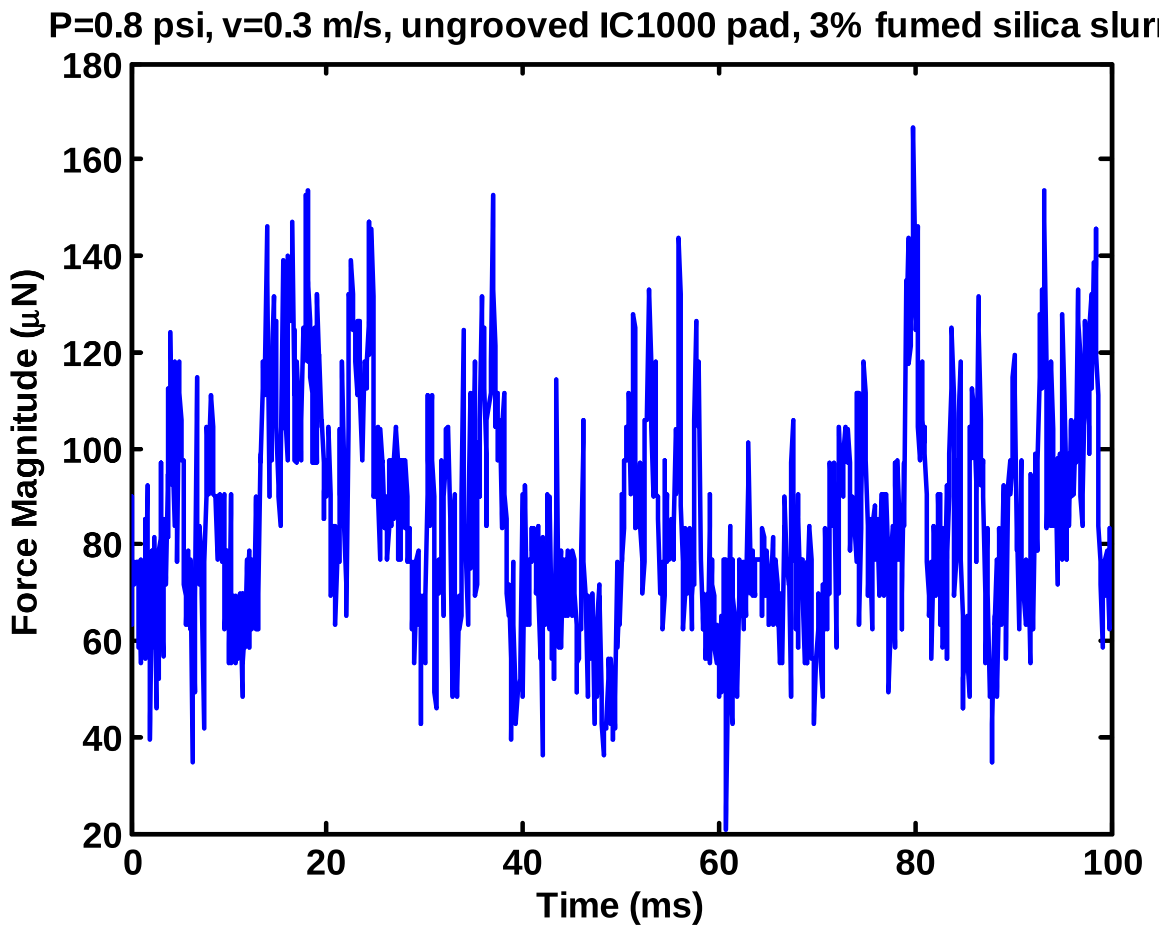


Not deflected



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***.
- ***Force is highly variable in time.*** *Large force events have durations on the order of 0.1-1 ms, which is the time for a point on the pad to pass a post.*

Lateral force vs. time on a 80 μm post. 30 rpm (0.3 m/s), 0.8 psi, 9:1 slurry (3% by wt fumed silica slurry), ungrooved IC1000 pad.

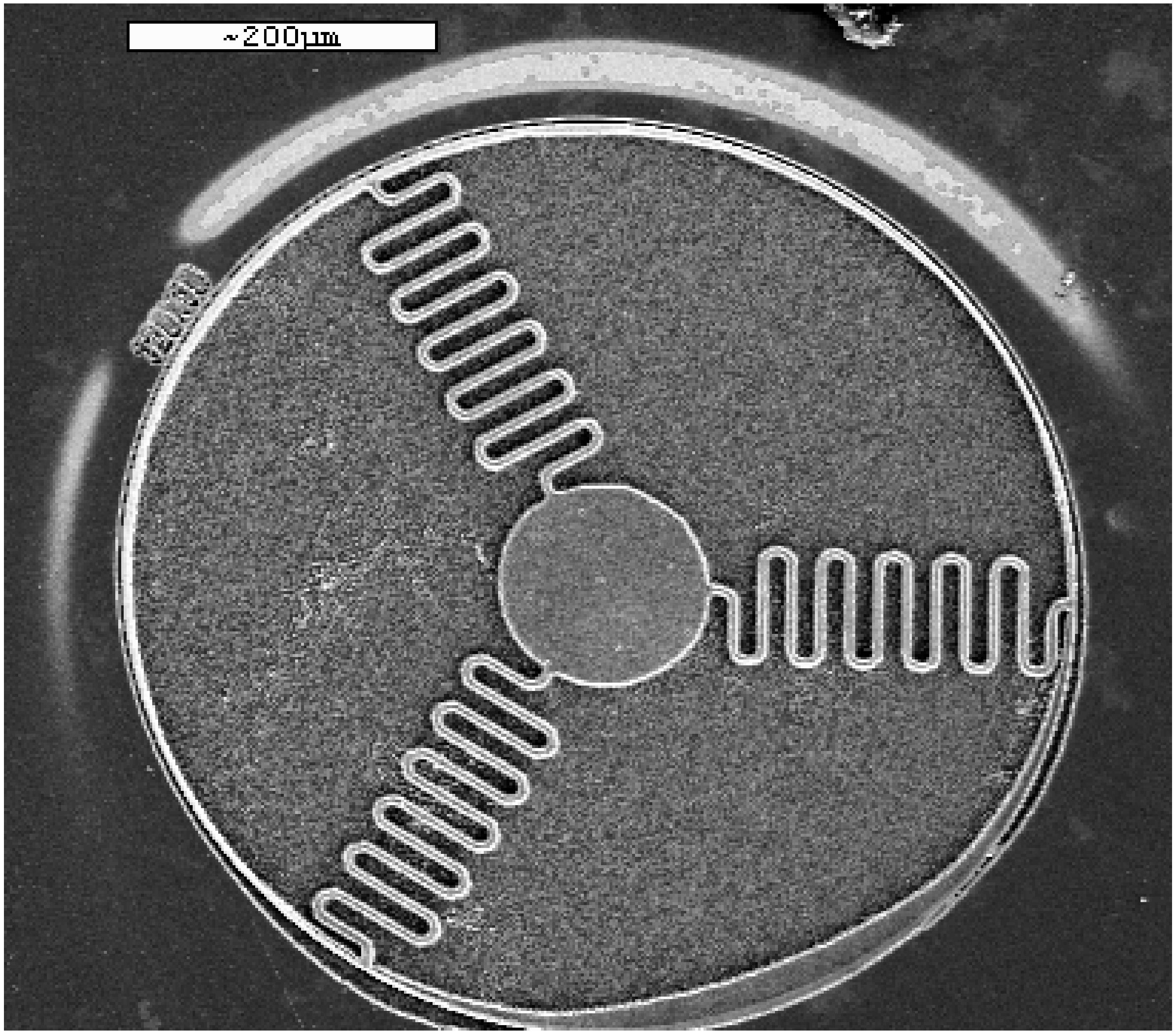
Copper or Silicon Force Sensors

Floating element-style force sensors are under development:

- Silicon or copper elements

- Withstand polishing environment

- Measure asperity level forces with wafer rotation and with a more relevant surface than PDMS.



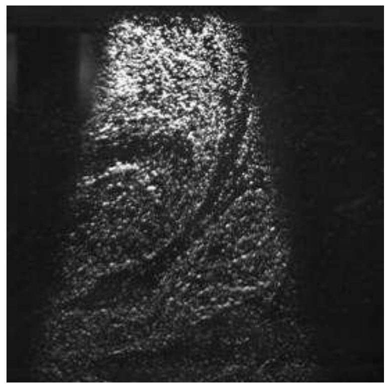
Subtask 4: **In-Situ Flow Visualization during Chemical Mechanical Planarization (Seed Project)**

- Project Goals:

  Investigate the feasibility of using particle image velocimetry (PIV) to quantitatively measure particle-slurry flow in-situ.

- Qualitative flow visualization

- Low rotational speed PIV



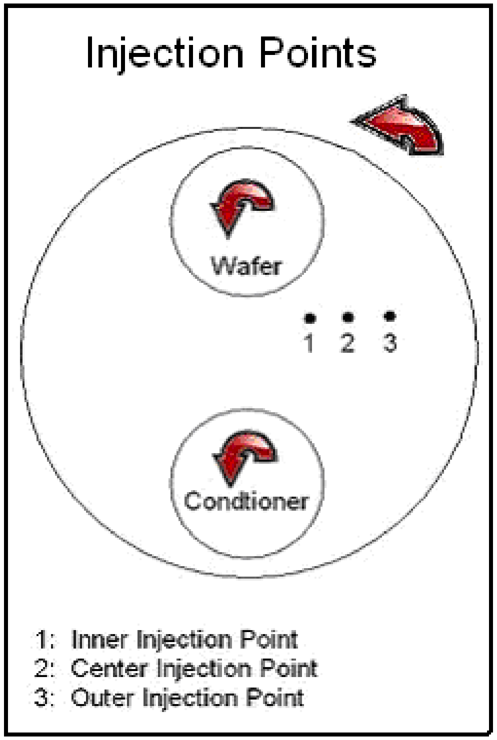
Basic Visualization Parameters

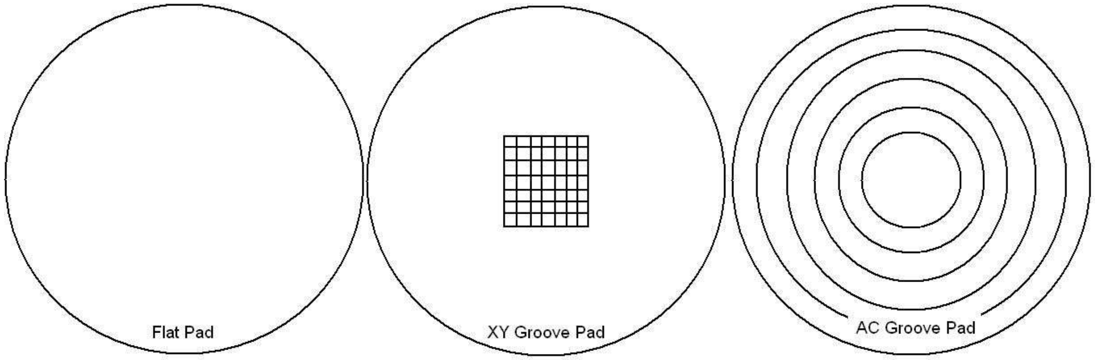
Constants throughout experiments:

- **Platen rotation: 30 rpm**
- **Slurry dilution: 3 to 2**
- **Flow rate: 150 cc/min**

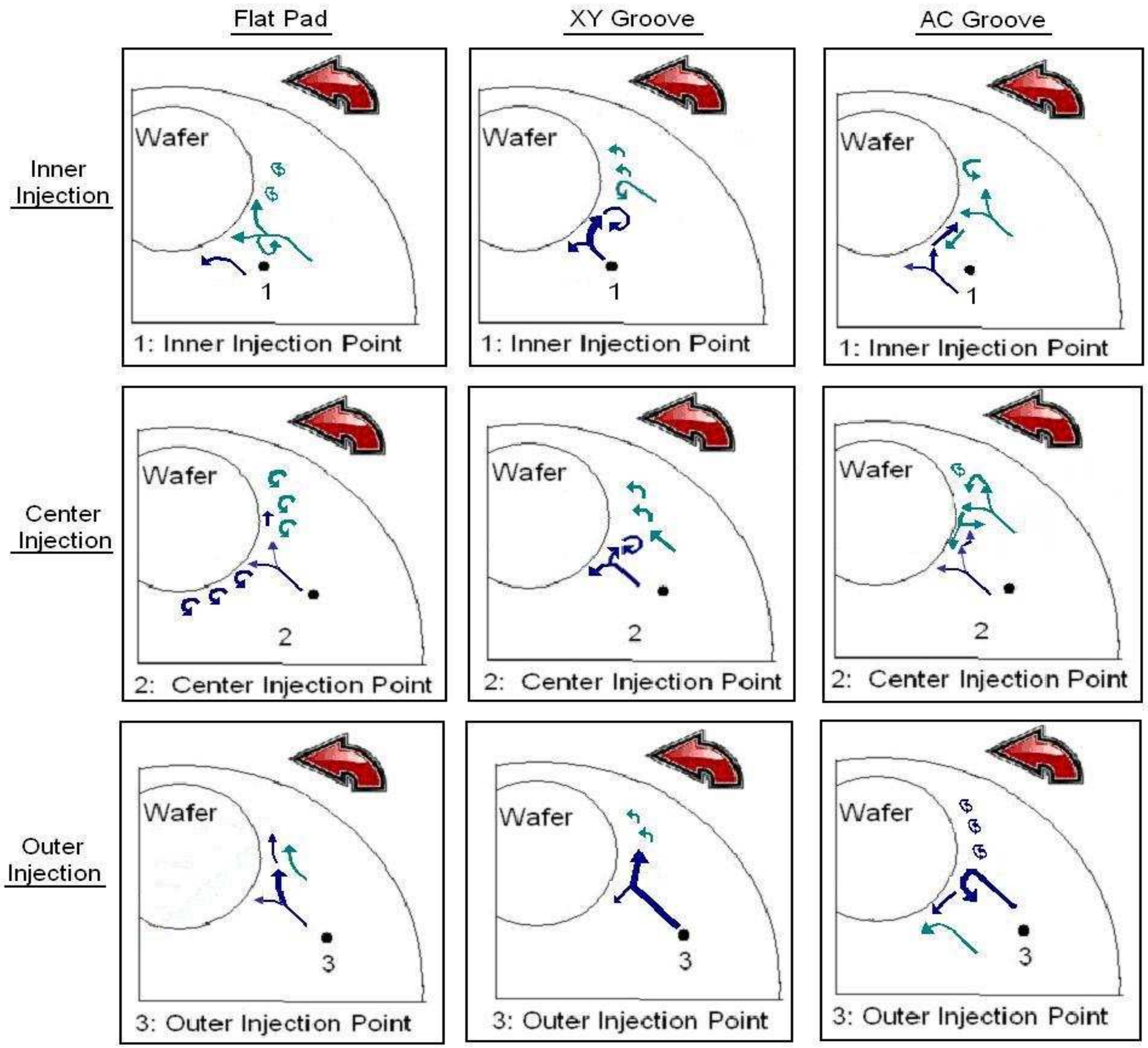
Experimental variables:

- **3 Pad Types**
- **3 Injection Points**
- **Conditioner Presence**
  - **No conditioner and in-situ**
- **Wafer speed was varied:**
  - **0 and 35 rpm**
- **Down force was increased**
  - **0.3 psi, 1.0 psi, and 2.5 psi**





Basic Visualization Results



Dark blue arrows indicate newly injected slurry.

Green arrows indicate old slurry.

Large red arrow indicates direction of pad rotation.

Grooving and injection point both significantly affect bulk slurry flow patterns, slurry mixing, and slurry residence time.

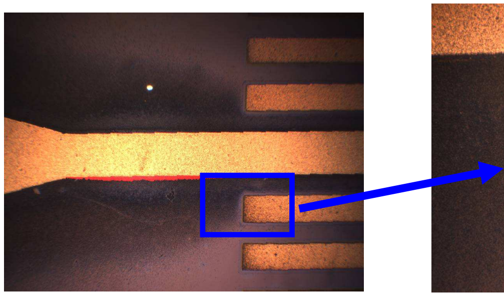
Correlating Polishing Quality on Patterned Copper to Mechanical Forces

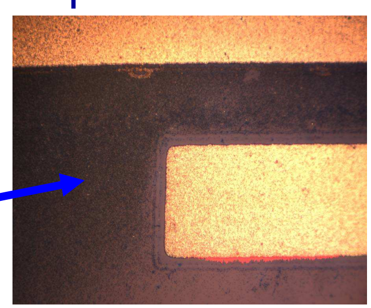
Goal: Measure in situ forces and polish defectivity on patterned Cu substrates. Continue MEMS polish force sensor development.

Objectives:

* Develop wafer plating and patterning capability
* Measure microscale friction forces during Cu CMP.
* Correlate measurements to damage & polish quality on patterned Cu

Cu Plating: Ti/Cu seed layer is sputter coated and wet etched to produce the pattern. Plating occurs in 0.5M $CuSO_4$ + 1.5M H_2SO_4 at 25°C and 5mA/cm^2, resulting in a deposition rate of 200 nm/min.





Industrial Interactions and Technology Transfer

- Close collaboration with sponsors – Cabot Microelectronics & 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 (Intel)

- Close coordination with A. Philipossian group at U of Arizona

- 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 – Final Report of Subtask

- **All current students complete theses and graduate:**
- **Submit patent application on MEMS shear sensors.**
- **Write up thesis results as journal papers.**
- **Execute goals for customized project with Intel**

Follow-on

*** Deploy the newly developed *in situ* measurement technologies (e.g.MEMS force sensing) to a 200 mm polisher.**

*** Characterize polish of patterned Ta/Cu and oxide substrates using new measurement technologies on 200 mm platform.**

*** Apply results to optimize CMP conditions for improved polish quality and reduced consumables.**

Publications, Presentations, and Recognitions/Awards (2008)

- R. White, A. Mueller, C. Rogers, V. Manno, and D. Gauthier, U.S. Provisional Patent: "Shear Sensors and the Uses Thereof", Serial Number 61/042,132 filed 4/3/08.

- Gray, C., White, R. D., Manno, V. P., and Rogers, C. B. "Contact Measurements between Rough and Smooth Surfaces", Tribology Letters, 29 (3), pp. 185-192, 2008.

- White, R., Vlahakis, J., Gray, C., Manno, V., Braun, N., Gauthier, D., Mueller, A., Rogers, C. and Moinpour, M. "In Situ Characterization of the Mechanical Aspects of CMP" in the Proceedings of the International Conference on Planarization/CMP Technology 2008, Hsinchu, Taiwan, November 10-12, 2008.

- D. Gauthier, A. Mueller, R. White, V. Manno, C. Rogers, S. Anjur and M. Moinpour, "Micromachined Force Sensors for Characterization of Chemical Mechanical Polishing" in Proceedings of Nanotech 2008, Boston, MA, June 1-6, 2008.

- D. Gauthier, A. Mueller, R. D. White, V. Manno, C. Rogers, D. Hooper, S. Anjur, M. Moinpour, "Micromachined Lateral Force Sensors for Characterization of Microscale Surface Forces During Chemical Mechanical Polishing." in the Proceedings of the Materials Research Society, MRS Spring Meeting, March 24-28, 2008.

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:

- **Joy Johnson, S.M./Ph.D. candidate, EECS, MIT**
- **Wei Fan, Ph.D. candidate, EECS, MIT**

Cost Share (other than core ERC funding):

- **Experimental support, JSR Micro**
- **Experimental data, National Semiconductor**

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 and goals: Joint improvement in CMP performance and ESH performance

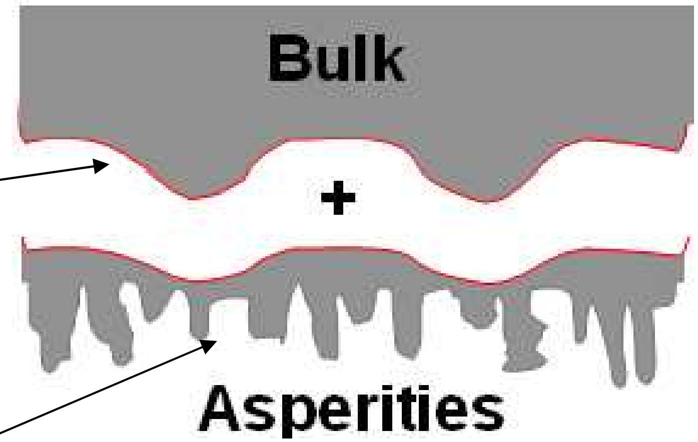
1. ***Reduction in the use or replacement of ESH-problematic materials***
2. ***Reduction in emission of ESH-problematic material to environment***
   - **Reduce slurry particle use and Cu solid waste by 20-50%**
3. ***Reduction in the use of natural resources (water and energy)***
   - **Shorten CMP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

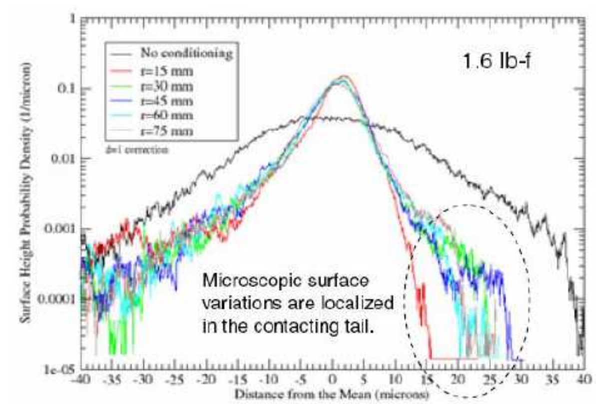
Focus This Year

- **CMP chip-scale model improvements:**
  - **Verify model for chip pattern density & step height effects:**
    - Effective pad bulk modulus: Explicit long range pad bending (replaces planarization length in model)
    - Asperity height distribution: Probabilities on asperity heights (replaces critical step height in model)
  - **Non-conventional (ceria) slurry model (in progress)**
  - **Time evolution of *pattern density* as well as topography (in progress)**
- **CMP chip-scale model application**
  - **Studies of planarization as a function of pad properties**
    - Pads with different *bulk stiffness*
    - Pads with different *surface asperities*, through conditioning with different diamond shapes
- **CMP model/experimental investigations:**
  - **Nanoindentation pad study (in progress)**

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)**





Surface Height Distribution
L. Borucki, 2006, ICPT

Experiments: Pad Properties, Planarization Results, and Model Verification

- **Experiment:**
  - **Four pads with different engineered polymer pad stiffness**
  - **Three different conditioner diamond shapes**
  - **Polish patterned wafers; measure film thickness & step heights**
  - **Fit to CMP physical model**

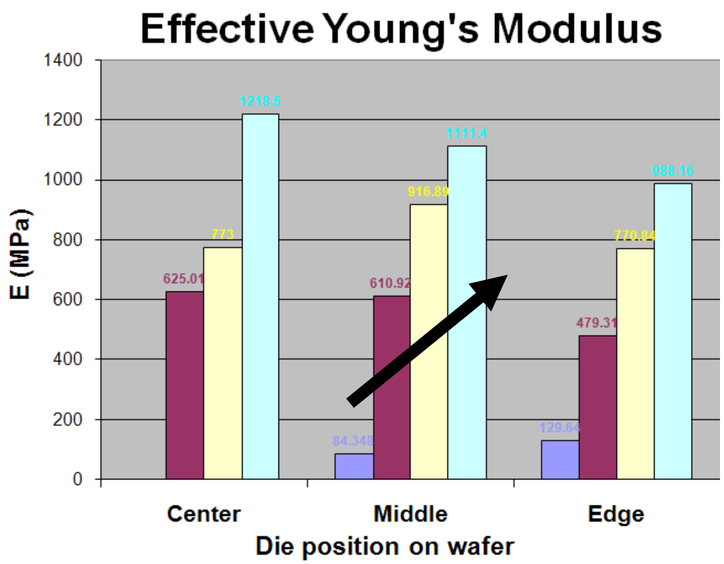
- **Extracted Parameters**
  - **Effective Young's Modulus E**
  - **Blanket removal rate K_0**
  - **Characteristic asperity height λ**

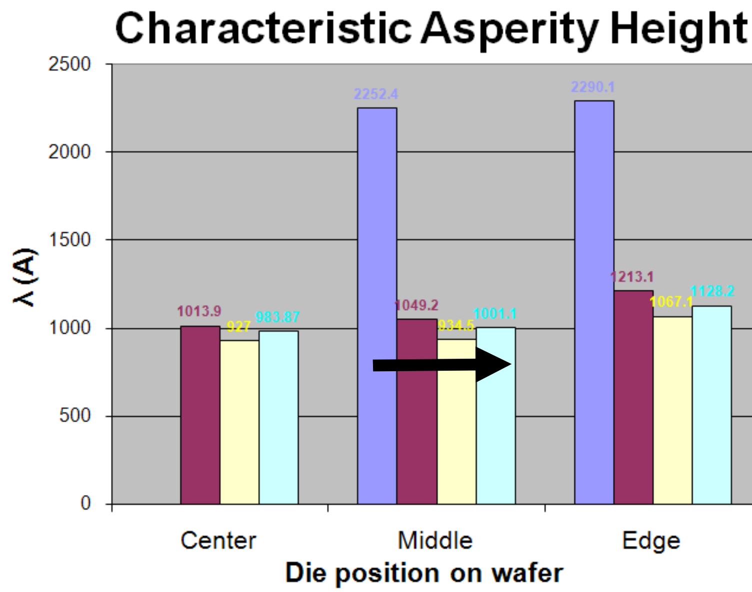
- **Results: Within-Chip Thickness Range**
  - **Difference between the up area oxide thickness of the 90% pattern-density area and that of the 10% area**

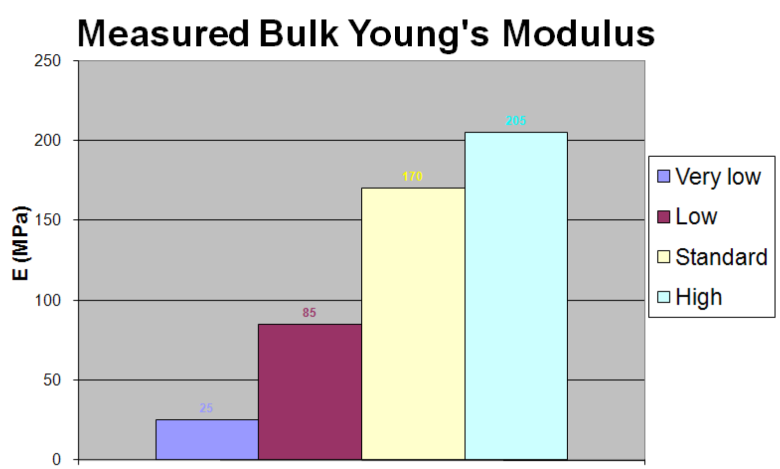
- **Results: Step-height vs Time**

- **Performance Evaluation Tables – Polish Time Comparison/Savings**
  - **Step height target strategy**
  - **Up area thickness target strategy**

Pad Hardness Results

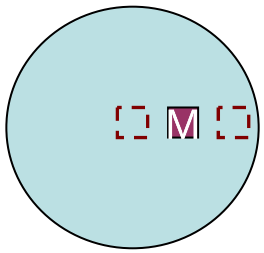


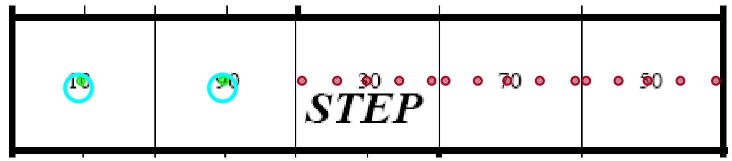




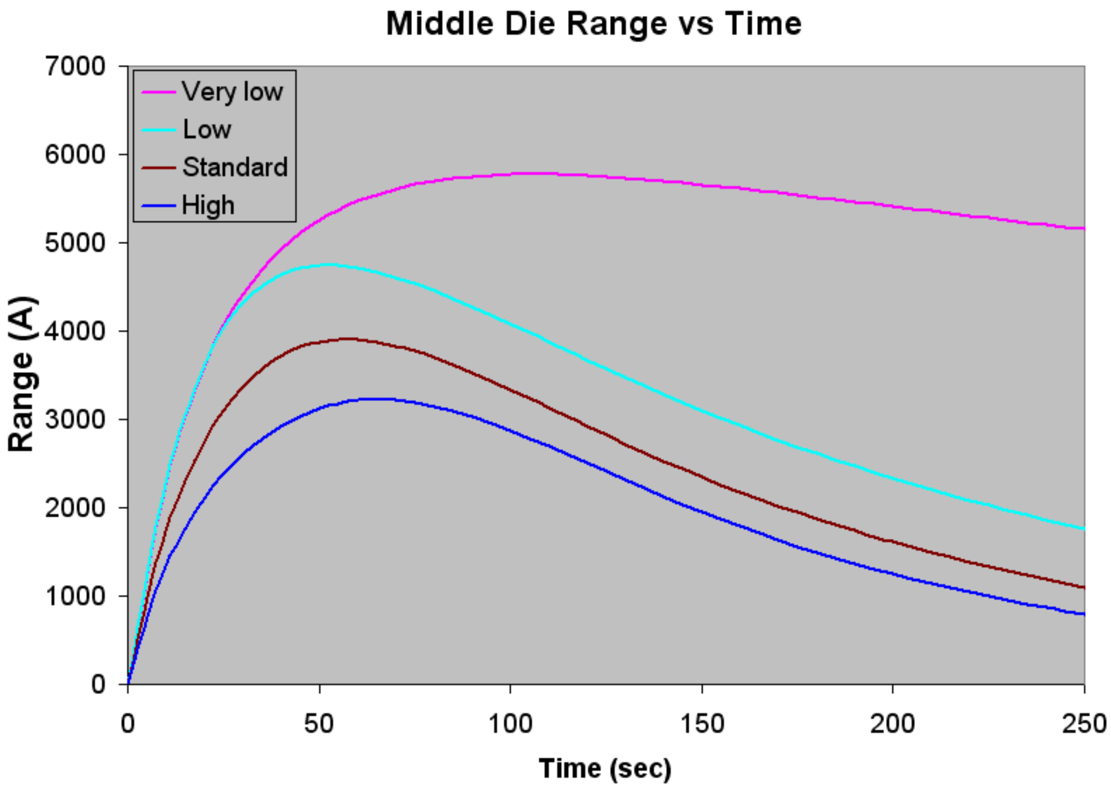
- High hardness pad gives high Young's modulus
- Higher effective modulus → Better planarization
- Relatively small effect on asperity heights

Pad Hardness Results: Fixed Range Evolution





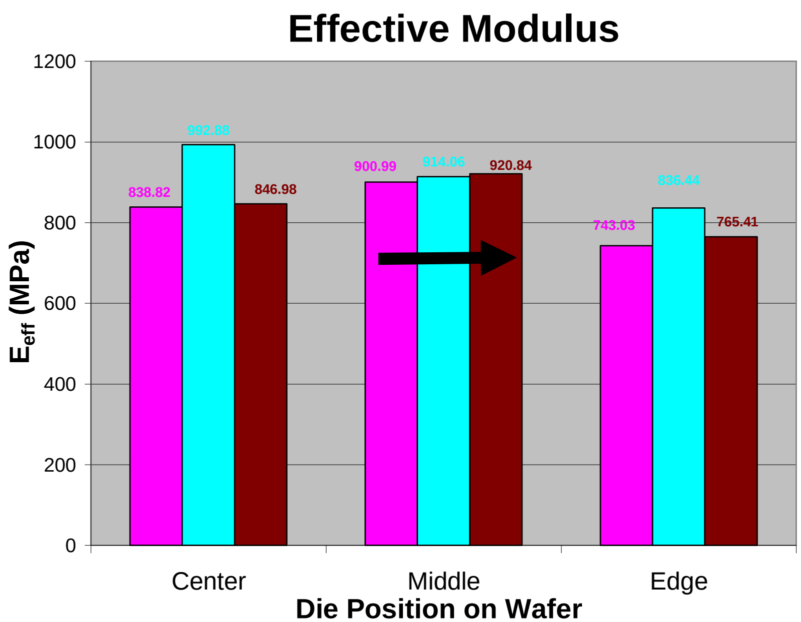
Range is thickness difference between 90% local pattern density region & 10% local pattern density region.

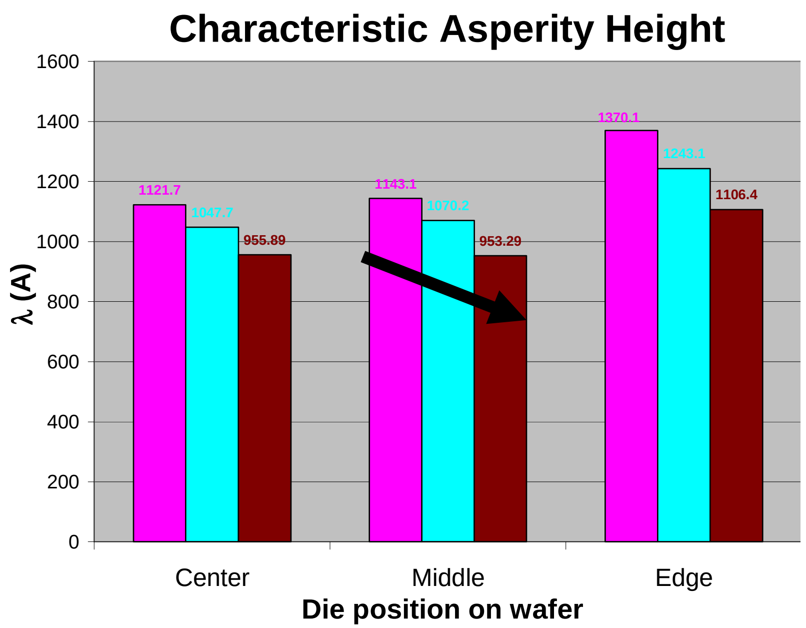


- Higher hardness gives smaller final range: better within-die uniformity due to more uniform effective pattern density

Effect of Conditioner Diamond Shape

Hypothesis: conditioner affects *asperity height* but not pad bulk





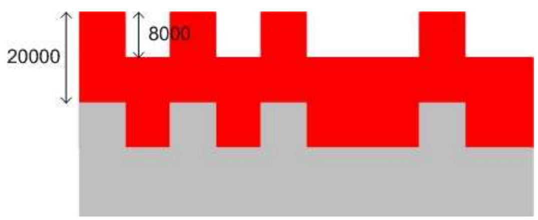
- **Similar effective modulus because of the same pad hardness**
- **Characteristic asperity height varies corresponding to conditioning disk diamond shape**

CMP Endpoint Strategies

- **Step Height Target Strategy**

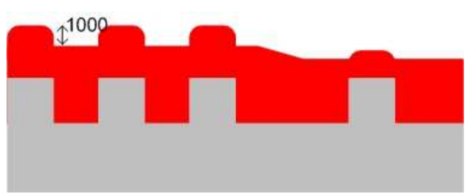
PD=50% PD=10%

Start



PD=50% PD=10%

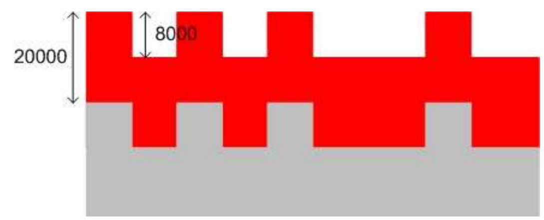
Endpoint



- **Up Area Thickness Target Strategy**

PD=50% PD=10%

Start



PD=50% PD=10%

Endpoint

Pad Performance Evaluation Table

- **Up Area Thickness Target Endpoint (Middle Die)**

Conditioning Disk Diamond Shape		Sharp	Standard	Blocky
Initial Step Height (Å)		8000		
Initial Up Area Thickness (Å)		20000		
Endpoint Time (s)		170	163	165
Remaining Step Height (Å)	Pattern Density = 10%	81	65	44
	Pattern Density = 50%	180	150	109
	Pattern Density = 90%	359	292	232
	Max	653	597	530
	Min	64	50	33
Fixed Range (Å)		1766	1720	1684
Real Range (Å)		2954	2917	2897
Up Area Thickness (Å)	Pattern Density = 10%	9030	9052	9103
	Pattern Density = 50%	10000		
	Pattern Density = 90%	10796	10772	10787
	Max	11711	11695	11724
	Min	8757	8778	8827

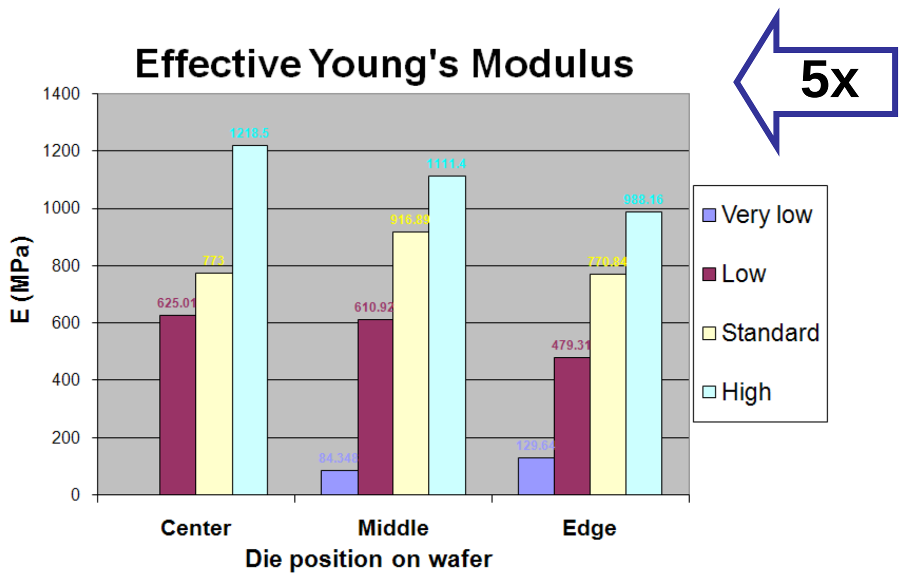
~ 20% Reduction

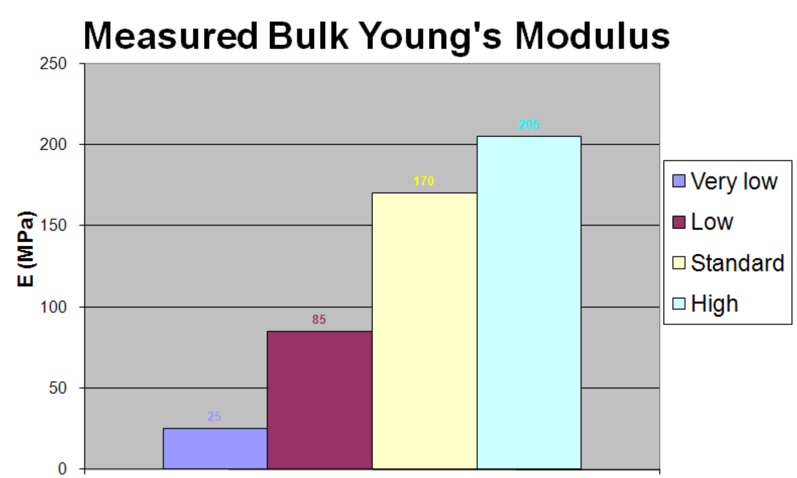
~ Same

❖ Fixed Range = PD90% Up Area Thickness – PD10% Up Area Thickness
❖ Real Range = Max Up Area Thickness – Min Up Area Thickness

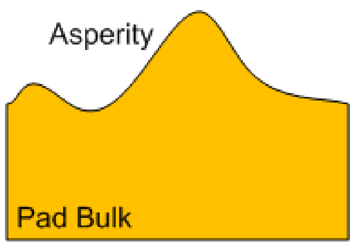
Physical Verification of CMP Chip-Scale Model

- **Reassess Previous Assumptions**
  - **Pad surface has the same modulus as bulk**
  - **Asperities have negligible width and an exponential height distribution**
  - **Asperity spring constant is fixed**
- **Model vs. Direct Measurement of Pad Properties:**
  - **Extracted bulk modulus is higher than measured result**
    - possibilities: high surface modulus or high bulk Poisson's ratio

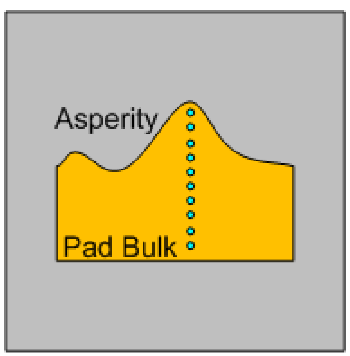


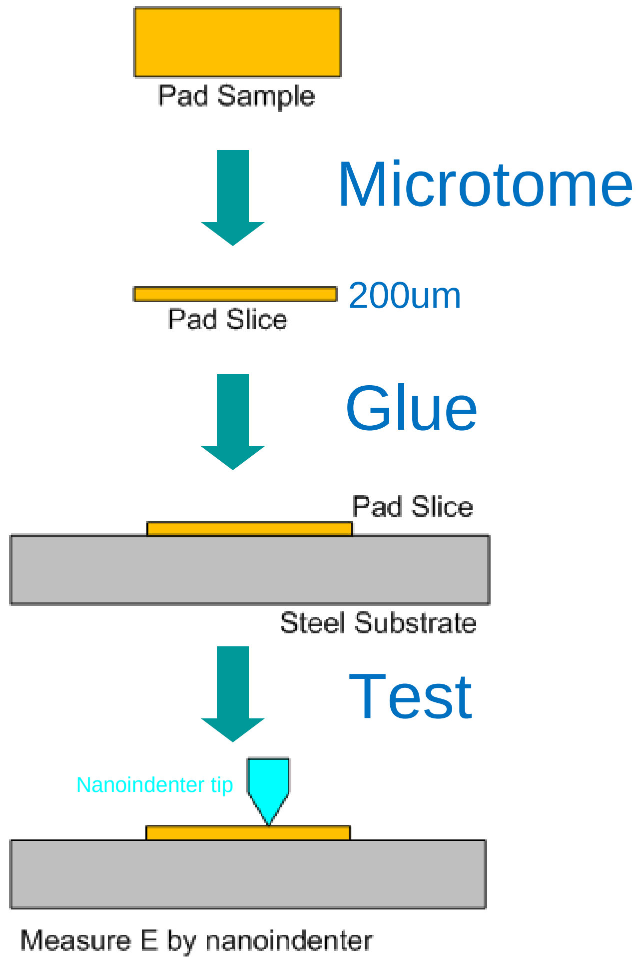


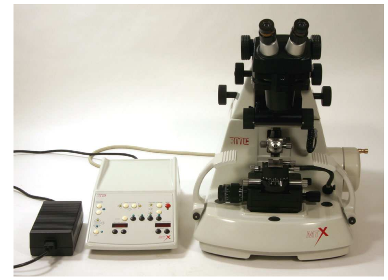
Nanoindentation Measurement Approach



Pad Sample





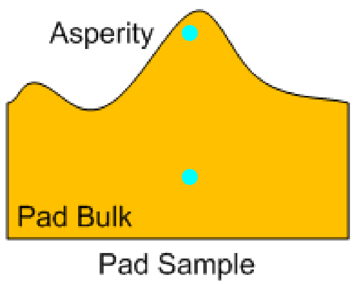

RMC Microtome

Permabond 910


Hystron TriboIndenter

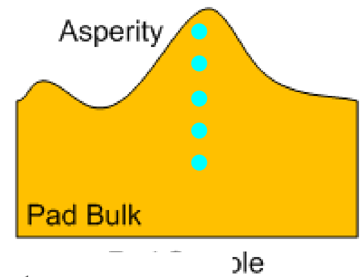
Preliminary Nanoindentation Measurement Results

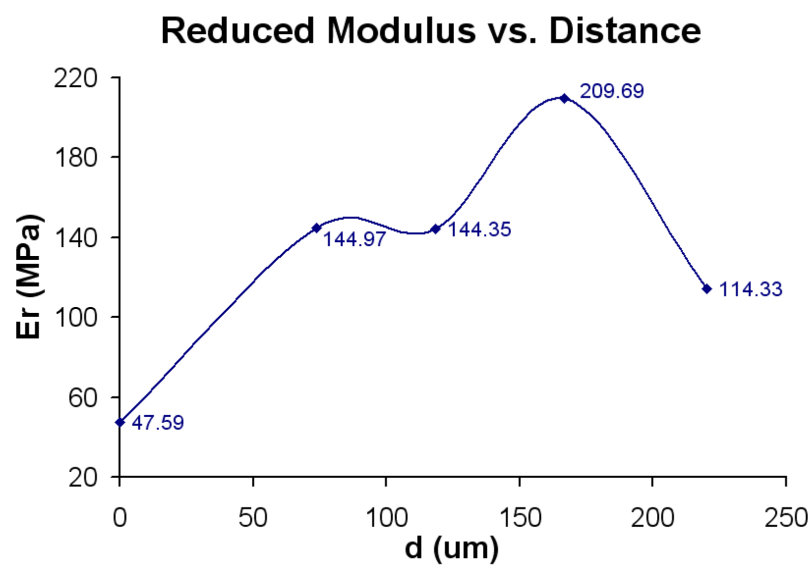
- **Method Demonstration Completed**
  - **It works on JSR soft pad sample (JMT-007)**
  - **The trend is correct**
    - Asperity modulus is lower than bulk



Group # (JMT-007)	Asperity Er (MPa)	Neighboring Bulk Er (MPa)
1	83.3	175.0
2	89.8	251.7
3	139.7	179.5

- **First Successful Scan**
  - **Manual control**
  - **5 points**





$$\frac{1}{E_r} = \frac{1-\nu_{pad}^2}{E_{pad}} + \frac{1-\nu_{tip}^2}{E_{tip}}$$

$$E_{tip} >> E_{pad}$$

Measured Result

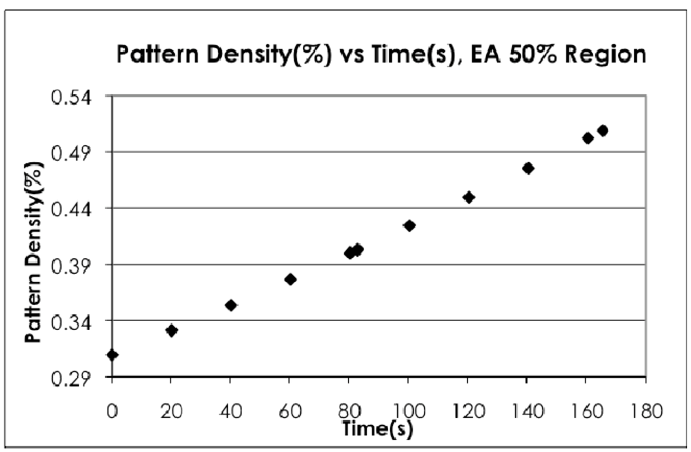
$$E_r \approx \frac{E_{pad}}{1-\nu_{pad}^2} = E_{eff}$$

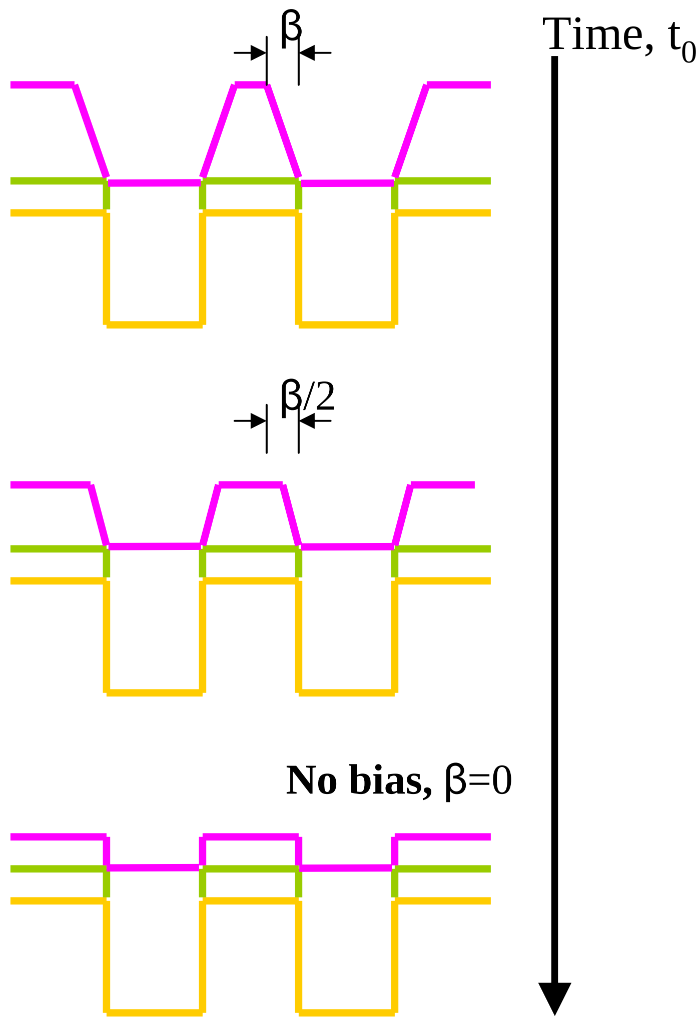
Model Parameter

Current Work on Model Enhancement: Time Evolving Pattern Density

- In STI and other deposited topographies, over *time* the local pattern density of the oxide changes
  - At early stage: small contact area with pad low pattern density
  - At later stages: as topography polishes, the contact area increases and thus local pattern density increases
- Approach: Use "biased" (shrunken) extracted layout maps with a *time-evolving pattern density calculation*.

Simulate region EA of test die with ~50% pattern density and (5-10)x5 µm structures





Time-Evolving Profiles

Project Deliverables & Completion Plans

- Report on the integration of force-frequency sensing with wafer/chip/feature scale modeling for physically based interpretation of signals (Completed: 10/08)
- Report on the demonstration of improved endpoint detection/process control and corresponding reduced CMP consumables usage and waste production (Planned: 2/09)
- Report on the improved dishing/erosion feature and chip-scale modeling, integrating pad asperity and particle/wafer interactions (Planned: 5/09)
- Final report summarizing research accomplishments and future direction (Planned: 5/09)
- Will request no-cost extension to 5/09

Industrial Interactions and Technology Transfer

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

- **National Semiconductor**
  - **Patterned STI wafer experiments, with oxide and ceria slurries**

Publications, Presentations, and Recognitions/Awards

1. D. Boning and J. Johnson, "The Evolution of Pattern-Density in CMP Modeling," to be presented, CMP Symposium, MRS Spring Meeting, April 2009.
2. D. Boning, K. Balakrishnan, A. Chang, N. Drego, W. Fan, J. Johnson, and H. Taylor, "Measuring and Modeling IC Variability at the Process, Device, and Circuit Levels," ICCAD Workshop on Test Structure Design for Variability Characterization (TSD), San Jose, CA, Nov. 2008.
3. A. Philipossian, Y. Sampurno, L. Borucki, Y. Zhuang, S. Misra, K. Holland, and D. Boning, "Characterization of Thermoset and Thermoplastic Polyurethane Pads, and Molded and Non-optimized Machined Grooving Methods for Oxide CMP Applications," Clarkson Workshop on Chemical-Mechanical Polishing, Lake Placid, NY, Aug., 2008.

Students on Task 425.020

- Graduated Students and Current Affiliation

- Current Students and Anticipated Grad Date
  - Wei Fan (Ph.D.), June 2011
  - Joy Johnson (S.M./Ph.D.), June 2009 / June 2012

- Internships
  - Joy Johnson, summer 2008, National Semiconductor (South Portland, Maine)

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:

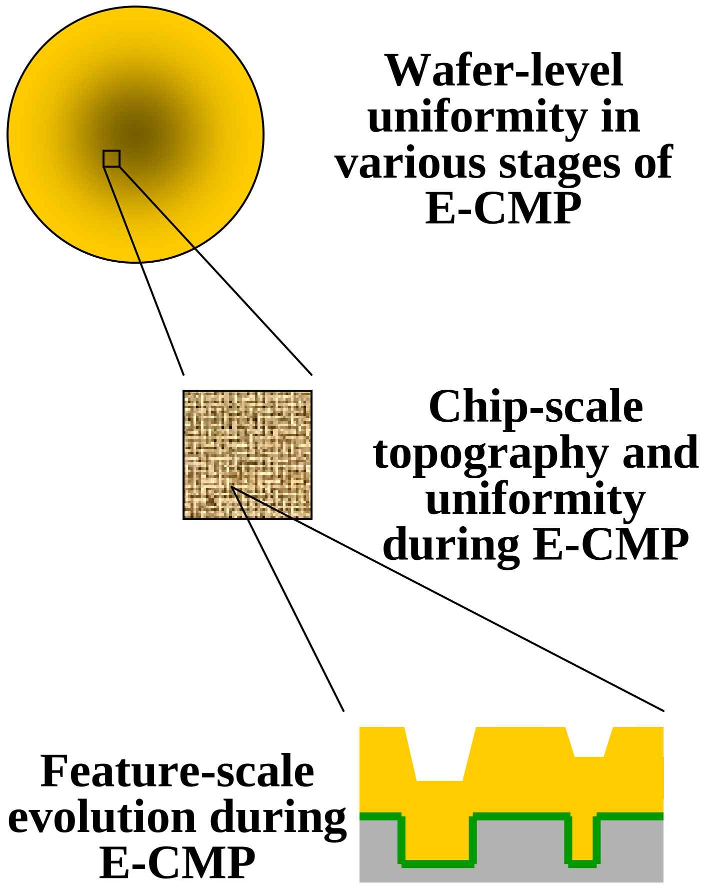
- **Wei Fan, EECS, MIT Ph.D. candidate**
- **Joy Johnson, EECS, MIT S.M./Ph.D. candidate**

Cost Share (other than core ERC funding):

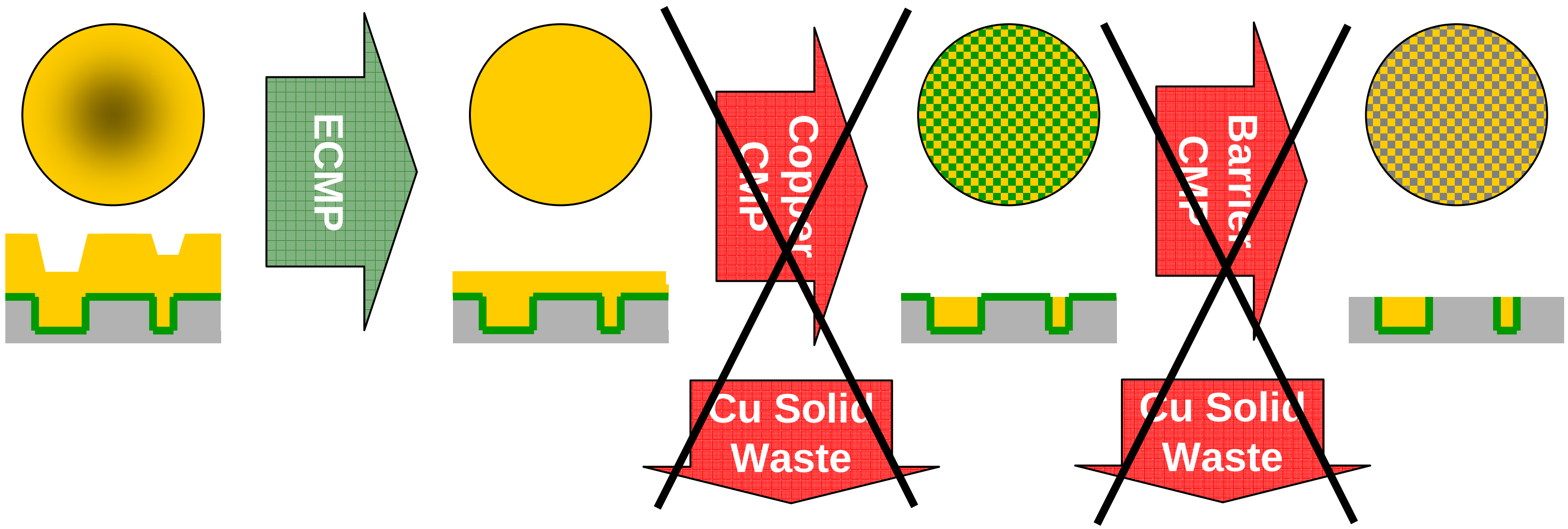
- **Experimental support, Albany Nanotech**

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



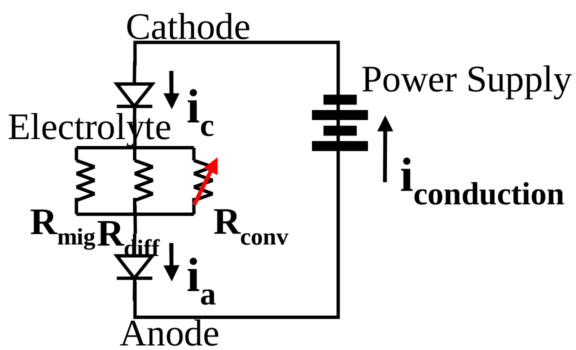
1. ***Reduction in the use or replacement of ESH-problematic materials***
2. ***Reduction in emission of ESH-problematic material to environment***
   - **Reduce or eliminate solid slurry particle waste**
     - Eliminate copper touch-down CMP (eliminate ~20% of planarization cycle)
     - Lower solid 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

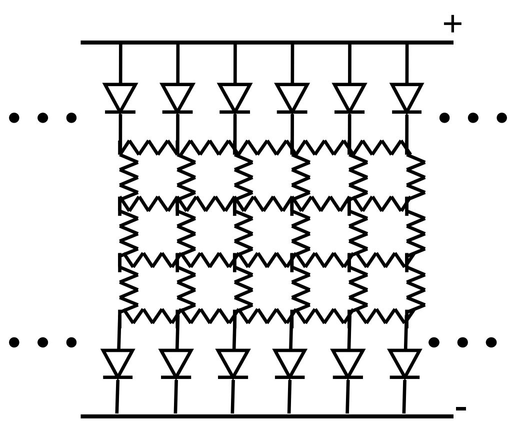
- **Cu removal rate across wafer as function of:**
  - **Initial copper thickness (e.g. nonuniform plating profile)**
  - **Applied voltages in multiple zones in ECMP tool**
  - **Tool/process parameters: geometry of electrical contact to wafer, velocity, pressure**
- **Semi-physical model**
  - **Model structure based on physics of process**
  - **Fit to experimental characterization data**
  - **Nonlinear model: focus on electrochemical dependence at electrodes**
- **2D/3D implementation**
  - **Account for non-axisymmetric bias/geometry, but use time-averaged wafer rotation and assume wafer axisymmetry**

Electrochemical Non-Ohmic ECMP Model

1-D View:
[without lateral coupling current]

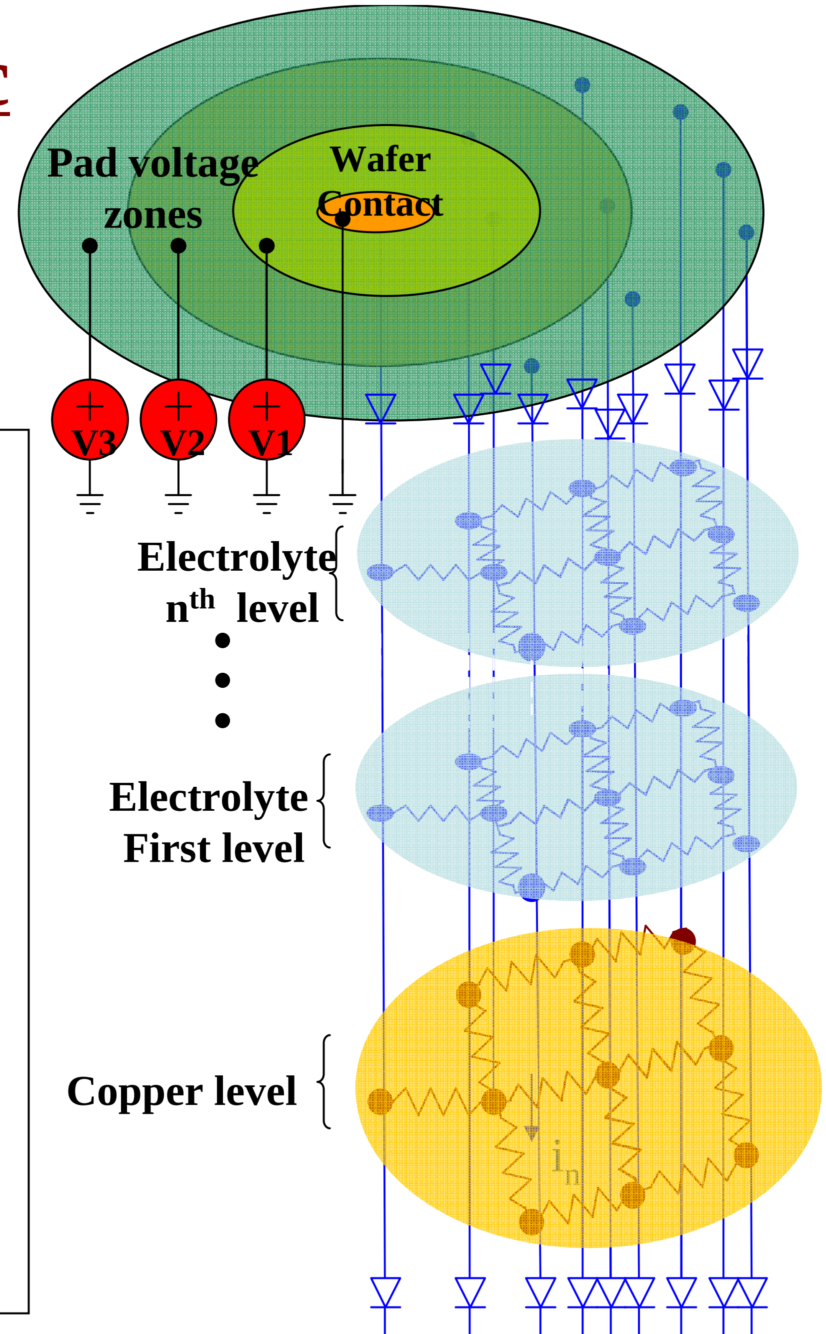


2-D View:
[with lateral coupling current]

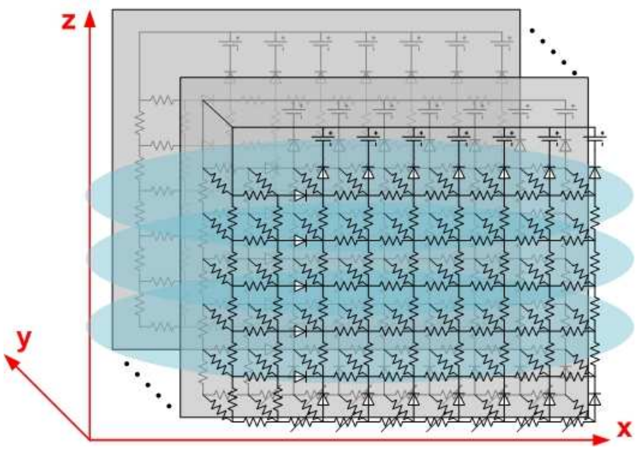


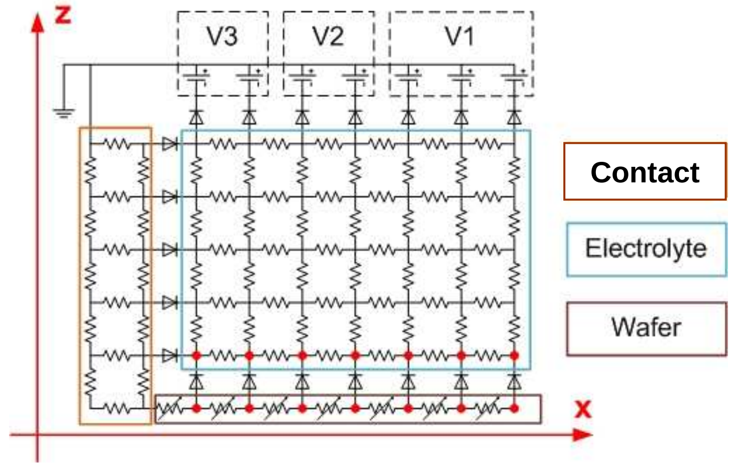
Assumptions:

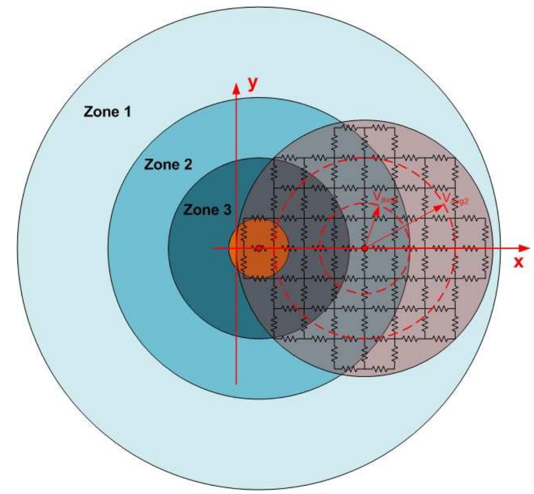
1. Anodic & cathodic electrochemical current contributions
2. *Lateral coupling current contributions
3. Faradaic current and conduction not always equivalent
4. Instantaneous and complete removal of surface layer
5. Neglect voltage drop across the wafer (highly conductive copper film)
6. *Passivation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



Electrochemical Non-Ohmic ECMP Model

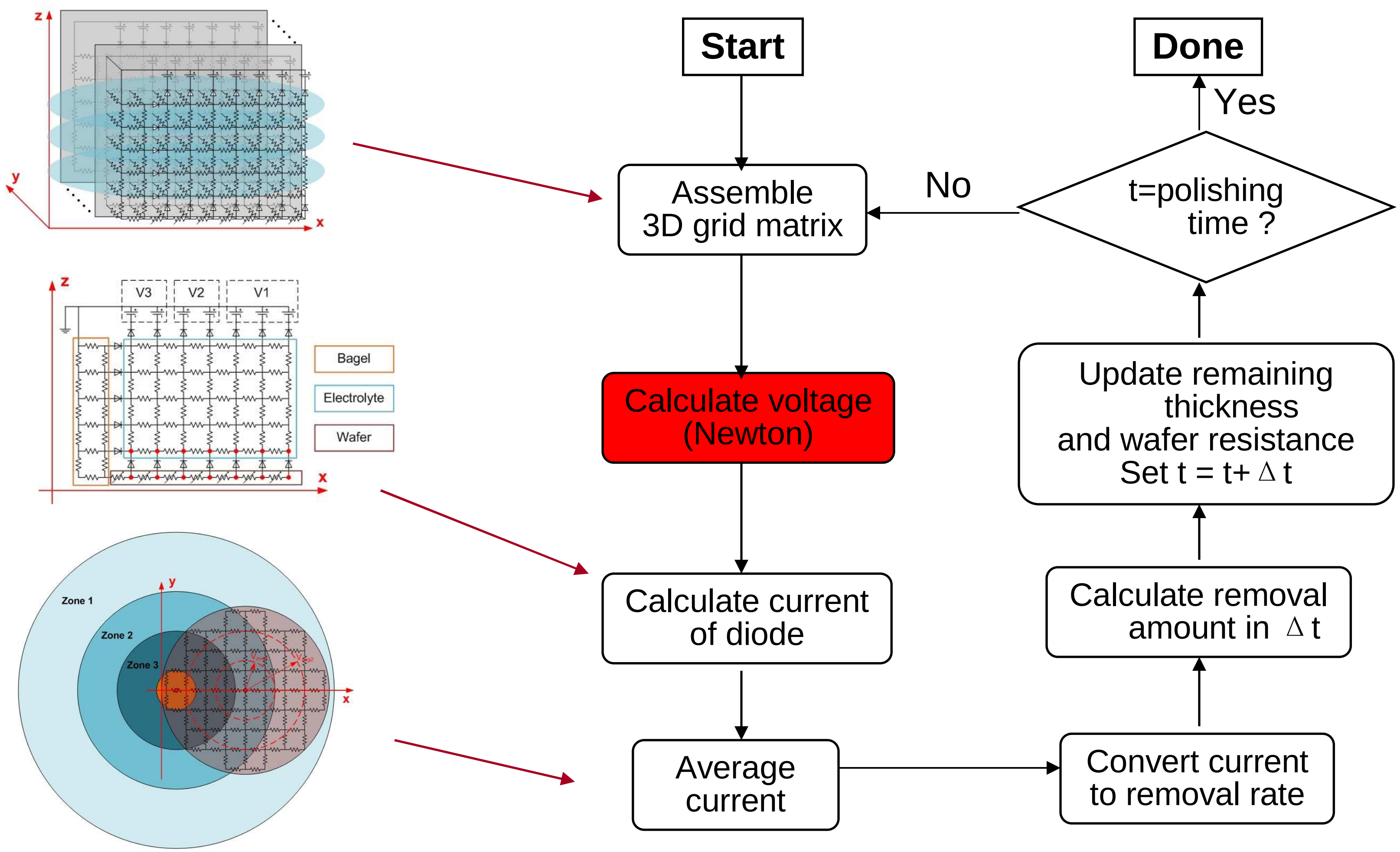






- **3D resistor and diode grid for voltage calculation (instantaneous)**
  - **- Voltage at each node**
  - **- Current across each component**
- **2D radial time-average current calculation for wafer surface**
  - **- Time for one rotation is short**
- **Time step: calculate remaining Cu thickness and wafer resistance (in progress)**

ECMP Semi-3D Program (Current Work)



ECMP Model – Current Work & Plans

- Complete 2D/3D wafer scale model with ECMP kinetics
  - "Two-diode" electrochemical model (Joy)
  - 2D/3D numerical model – wafer scale
    - Numerical methods to deal with the inclusion of the nonlinear diode-like elements, for 2D/3D situations (Wei)
- Integrate with feature/chip-scale ECMP version of existing CMP model
  - Passivation/protective film removal with possibly non-Prestonian pressure dependence
  - Exposed copper dissolution based on wafer scale model
- Analysis of conductive pad configuration
  - Apply the 2D/3D numerical model to alternative conductive pad and local electrochemical cell geometries

Project Deliverables & Completion Plans

- Report on the conducting pad designs capable of E-CMP removal of copper and barrier films on patterned wafers (Completed: 5/08)
- Report on the wafer-level and chip-level models of E-CMP pattern evolution for process design and optimization (Planned: 5/09)
- Final report summarizing research accomplishments and future direction (Planned: 5/09)
- Will request no-cost extension to 5/09

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

1. D. Boning, K. Balakrishnan, A. Chang, N. Drego, W. Fan, J. Johnson, and H. Taylor, "Measuring and Modeling IC Variability at the Process, Device, and Circuit Levels," ICCAD Workshop on Test Structure Design for Variability Characterization (TSD), San Jose, CA, Nov. 2008.

Students on Task 425.014

- Graduated Students and Current Affiliation
- Current Students and Anticipated Grad Date
  - Wei Fan (Ph.D.), 6/2011
  - Joy Johnson (S.M./Ph.D.), 6/2012
- Internships
  - Joy Johnson, summer 2008, National Semiconductor (South Portland, Maine)

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 Students:

- **R. Govindarajan: PhD candidate, Department of Materials Science and Engineering, UA**

Cost Share (other than core ERC funding):

- **In-kind donation (wafers) from Intel / Numonyx (~ $ 5,000)**

Objectives

- **Investigate the use of KIO_3 as an oxidant for the removal of Ta and TaN under ECMP conditions**

- **Optimize conditions to obtain a Ta to Cu selectivity close to 1**

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
KIO_3	136 mg/kg (mouse)	NO
Peroxide	2000 mg/kg (mouse)	NO

- **ESH Impact**

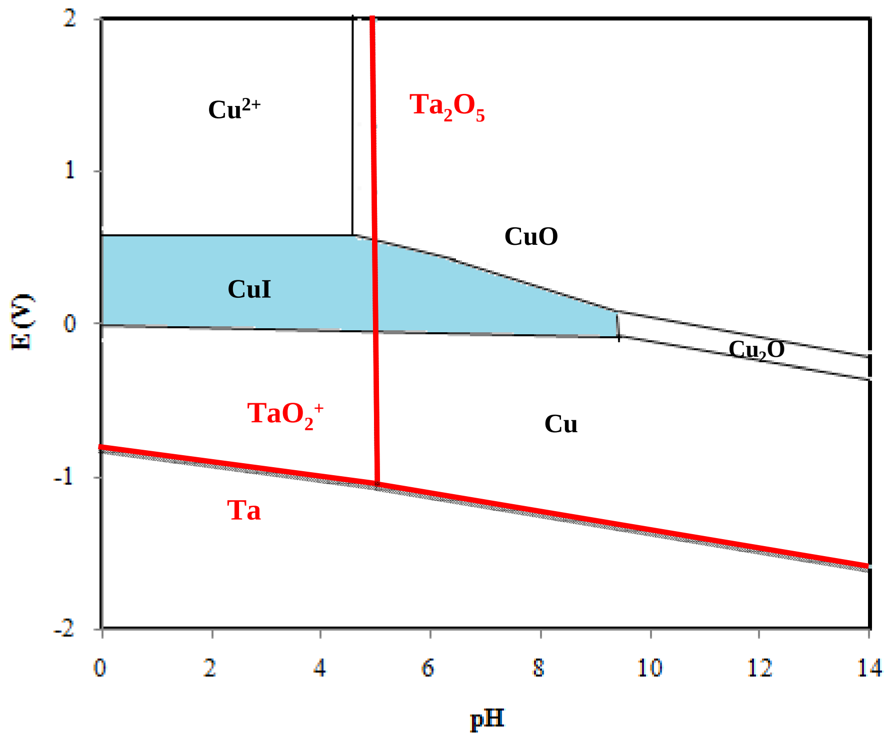
Goals	Usage Reduction		Waste Reduction	
	Chemicals	Abrasives	Solid	Liquid
Using full sequence ECMP	N/A	> 90%	> 99%	N/A

Current Year Activities

➢ **During the last contract year, optimization of peroxide in DBSA based chemical system was done to obtain a Ta removal rate of ~ 200 Å/min with 1:1 selectivity with respect to Cu at a pH of 10. However, the system provided a removal rate of only ~100 Å/min for TaN.**

➢**In an effort to increase the TaN removal rate, the use of KIO_3 as an oxidant in DBSA based chemical system was studied. Additionally, to reduce oxide removal rate, efforts were focused on a slightly acidic system.**

Advantages of KIO_3



Activity of dissolved species:

I : 0.05 ; Cu : 10^{-4} ; Ta : 10^{-4}

Standard potential (E^0):

H_2O_2/H_2O : 1.77 V

IO_3^- / I^- : 1.085 V

KIO_3

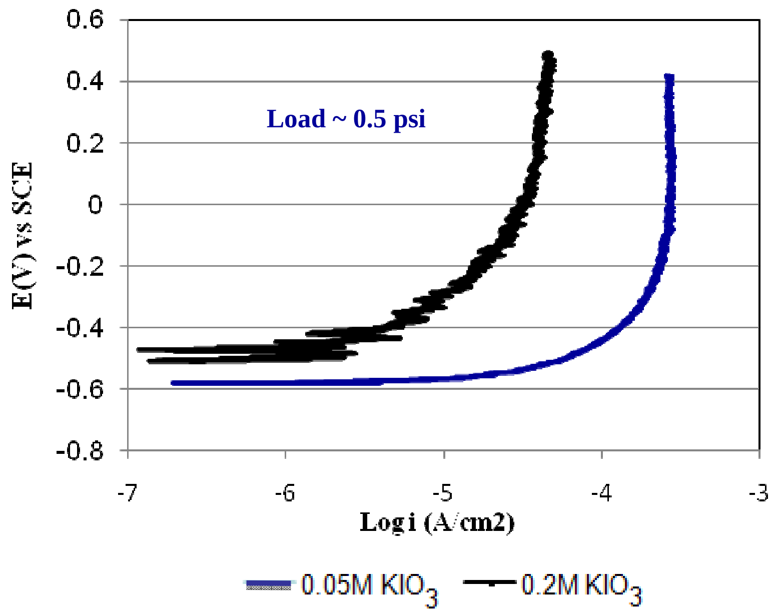
- **More stable than peroxide**
- **Strong oxidizing agent**
- **As shown in the Pourbaix diagram, formation of *solid CuI* is thermodynamically favorable during the oxidation of copper by iodate. By adjusting the potential at a pH in the vicinity of 4.0, Ta can be dissolved and copper can be passivated by CuI (s) layer. This, theoretically would offer a higher selectivity.**

OPTIMIZATION OF IODATE – DBSA FORMULATION

- Studied the effect of iodate concentration, DBSA concentration, pH and current density on removal rate of Ta and TaN at 0.5 psi; Maximum solubility of KIO_3 is 0.2 M

- For initial experiments current density was fixed at 0.1 mA/cm^2 (observed for 0.2M KIO_3) based on polarization data collected under abrasion using a *three electrode set up* and a PARSTAT 2273 potentiostat with a voltage limitation of 10 V

0.1 M DBSA + 0.1 % SiO_2 ;pH 4; 0.5 psi



Limiting current during anodic polarization:

0.05M KIO_3 : 0.25 mA/cm^2
0.2M KIO_3 : 0.1 mA/cm^2

Ta removal rate for 0.1 mA/cm^2 :

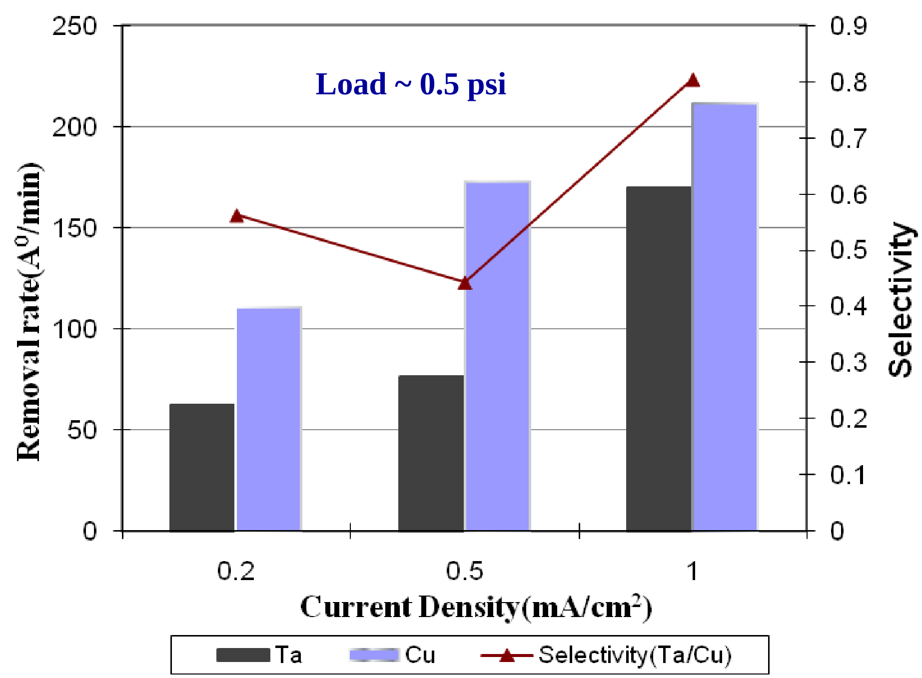
0.05M KIO_3 : ~ 90 A^0/min
0.2M KIO_3 : ~ 35 A^0/min
(Removal rate calculated using ICP-MS)

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

- To increase current density, switched to a 100 V- 1 A HP-DC Power supply and a *two electrode set-up*

- Added BTA to the formulation to reduce copper removal rate and improve selectivity

0.1 M DBSA solution + 0.05M KIO_3 + 0.1 % SiO_2 + 0.01M BTA (pH 4)

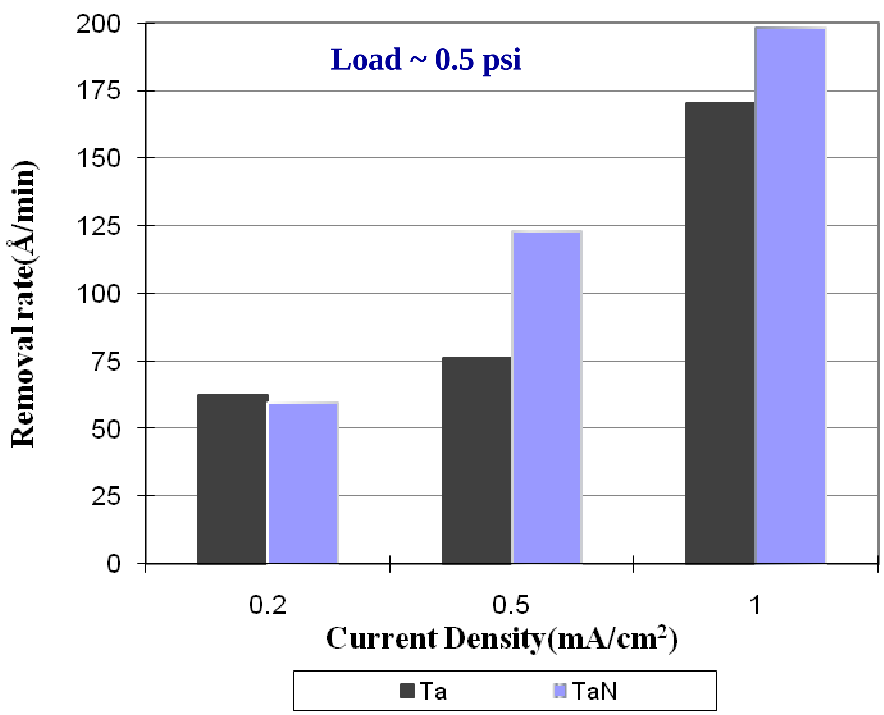


Removal rate (using Four Point Probe) : ~170A^0 /min (1mA/cm^2)

Best obtainable selectivity with BTA inhibitor : 0.8:1 (1mA/cm^2)

Evaluation of Potassium Iodate for TaN Removal

0.1 M DBSA solution +0.05M KIO_3 + 0.1 % SiO_2 (pH 4)



•**Removal rate calculated using Four point probe**

- **At a current density of 1 mA/cm^2**
  - **TaN removal rate ~ 200 Å/min**
  - **Ta removal rate ~ 170 Å/min**

For optimized formulation the difference in removal rate between Ta and TaN:

•Peroxide system : 50%

•KIO_3 system : 15%

Summary

- **Ta and TaN removal rate of ~ 170Å/min and ~ 200Å/min obtained in 0.1 M DBSA solution (pH =4) containing 0.05M KIO_3 and 0.1% SiO_2 at a pressure of 0.5 psi and a current density of 1 mA/cm^2**

- **Ta/Cu selectivity of ~ 0.8:1 attainable by adding 0.01M BTA to the formulation**

- ***Based on the results, switching from peroxide to iodate based system for Ta/TaN ECMP may be beneficial***

Highlights of Work Done During the 3-Year Contract Period

- **Designed a tool for conducting ECMP experiments**
- **Successfully formulated and tested a sulfonic acid-hydrogen peroxide system for Ta ECMP**
- **Established KIO_3 as an alternate oxidant for improving the removal rate of TaN**

Accomplishments

- **One doctoral dissertation (A. Muthukumaran: 2008 – now working for Intel)**
- **One peer reviewed paper in J. Electrochemical Society (2008)**
- **Two conference proceedings (ECS-ISTC 2007 and 2008)**

THANK YOU FOR YOUR SUPPORT!

ESH Impact of Electrochemical Mechanical Planarization Technologies

(*Task Number: 425.016*)

PI:

- **Alan C. West, Chemical Engineering, Columbia University**

Graduate Student:

- **Kristin G. Shattuck: PhD candidate, Chemical Engineering, Columbia University**

Undergraduate Students:

- **Neha Solanki, Chemical Engineering, Columbia University**

Objectives

- **Combine Ru and Cu electrochemical removal studies**
  - **Passivate Cu while removing Ru**
  - **Target Ru removal rate of at least ~ 200 Ǻ min^{-1}**
- **Gain information about long term Ru/Cu interactions**
  - **Corrosion**
- **Reduce any adverse polishing effects on plated Cu during Ru removal process**
  - **At edges of trenches, Cu/Ru interface**
- **Determine appropriate polishing chemistry for Ru**
  - **Preferably controlled mainly by electrochemistry**
  - **Keeping chemistry as simple as possible**

ESH Metrics and Impact

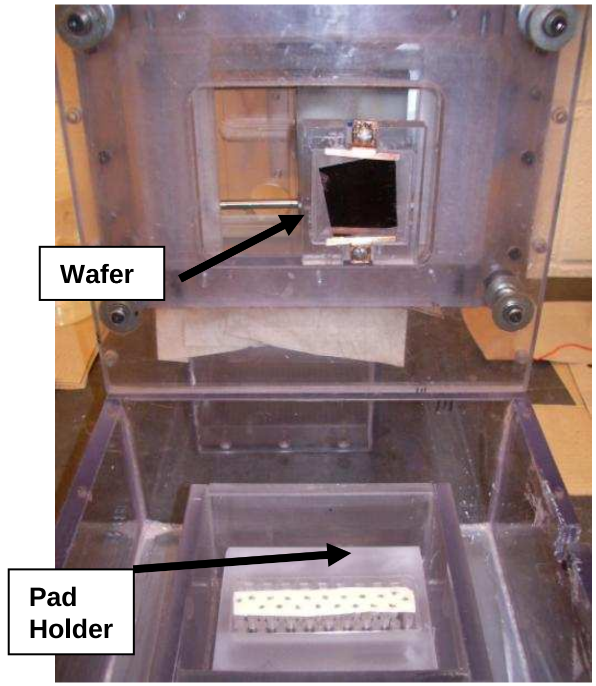
- **Development of an more environmentally benign polishing electrolyte for Ru**
  - **Potential elimination of slurry particles**
  - **Reduction or elimination of complexing agents and oxidizers in solution, facilitating waste treatment**

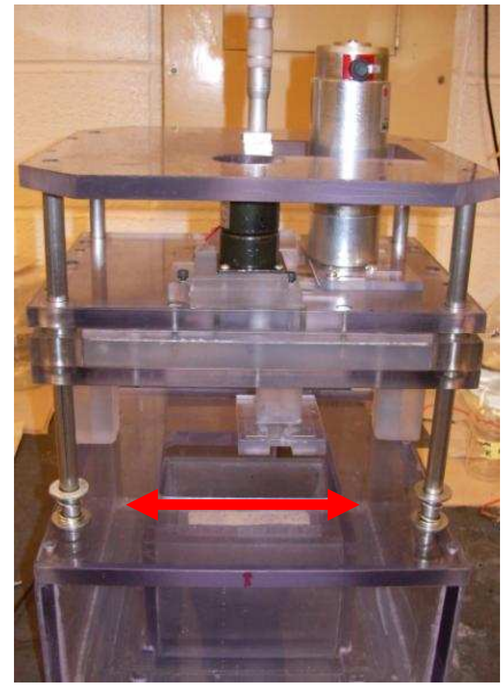
Cu ECMP Summary

- Screening process for Cu ECMP electrolytes

- Parameters Examined (using RDE)
    - pH
    - Salt concentration
    - Inhibitor concentration
    - Mass transfer

- Key Characteristics
    - Metal-removal rates
    - Planarization efficiency





- Phosphate based electrolytes
- Benzotriazole (BTA) inhibitor

Cu ECMP Summary

RDE

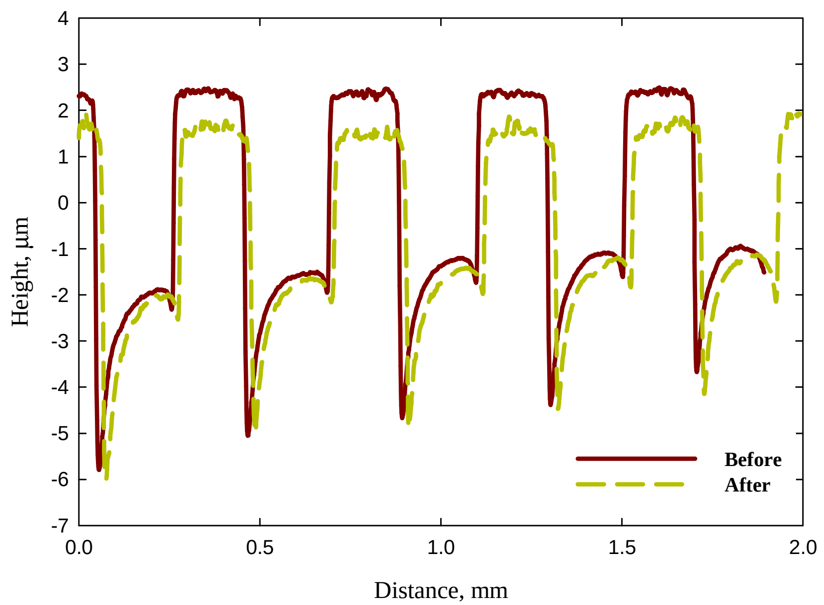
- **Summary Electrolyte Screening**

> - **Operating Conditions**
>   - ***pH* ~ 2.0**
>   - ***Operating Potential* → 0.5 V**
>   - ***BTA concentration* → from 0.001 M**
>   - ***Salt Concentration* → 1 M**

- **Patterned structures tested to support screening process**

ECMP Tool

Pad Type: IC1000



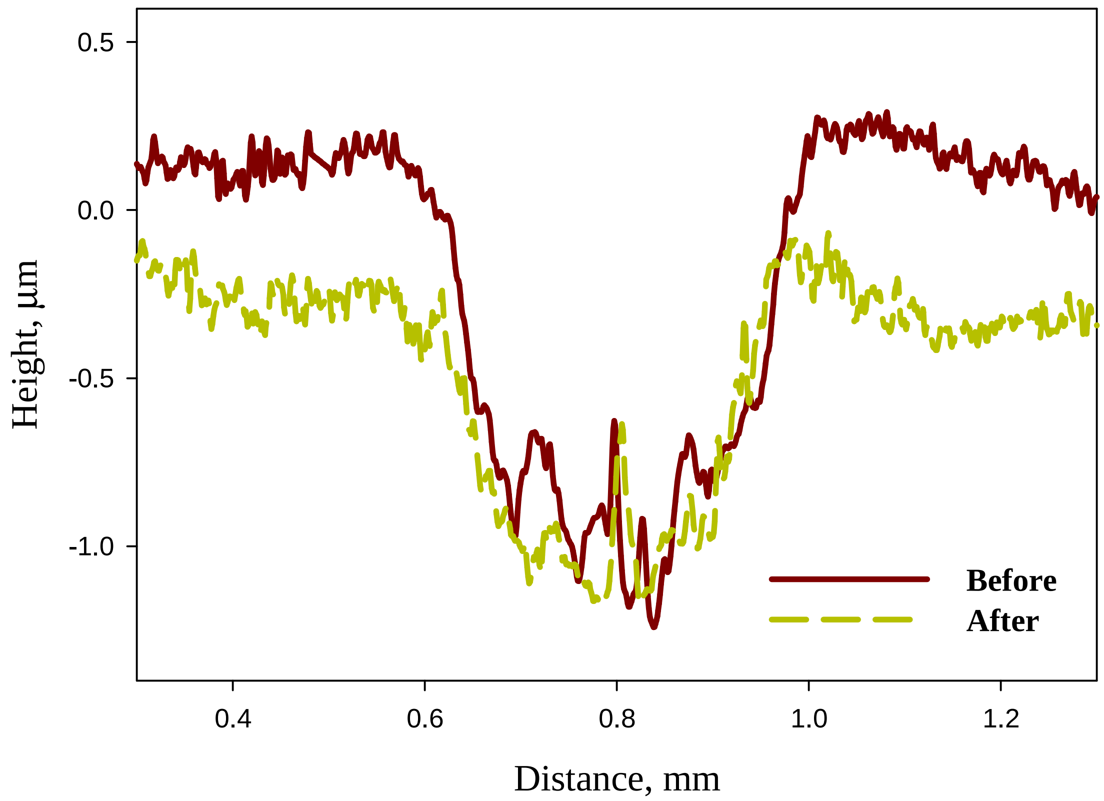
340 nm of Material Removed

- **Step Height Reduction**
  - **~ 740 nm**

Cu ECMP Summary

Pad Type: D100

✓ **Low aspect ratio polishing achieved**



320 nm of Material Removed

- **Step Height Reduction**
    - **~ 400 nm**

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Current Studies on Ru Liners

- **Alloying Ru to generate an amorphous film**
  - **Operate as single entity barrier material**

- **Combine Ru and Ta/TaN as barriers to achieve good adhesion and complete blockage of Cu migration**
    - **Might not solve scaling issues**

- **Direct Cu deposition on Ru**

- **Polishing Ru Particularly Challenging**
  - **Little known about Cu/Ru interactions**
  - **Chemistries currently used are complex and very abrasive**
    - **Could jeopardize Cu in trenches**

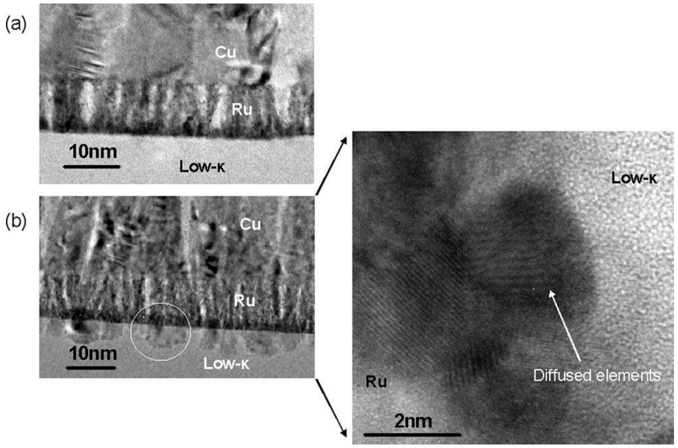
Challenges

- **Combined seed/liner material thickness is projected to be:**
  - **~ 3.3 nm for the 45-nm generation**

- **Ru cannot prevent Cu migration alone due to thickness required**
  - **Forms polycrystalline thin film with a columnar character**
  - **May not address all necessary scaling needs**

- **Oxidizes readily in air and aerated water**
  - **Disrupts proper Cu electroplating/additive interactions**

- **Due to stability, polishing Ru is challenging**
  - **Few studies on Ru CMP**



Ru ECMP: Experimental Approach

- Test various electrolytes for their electrochemical properties
  - On both Ru and Cu
  - Key experimental parameters
    - Oxide type, concentration
    - Acid type, concentration
    - pH
    - Effect of inhibitor

- Ru wafer samples
  - Establish Ru removal rate
  - Ru/Cu selectivity
  - Study Ru/Cu interface

- Current electrolytes
  - Acetates
  - Citrates
  - Phosphates
    - Additives (oxidizers/inhibitors)
      - CAN, ceric ammonium nitrate
      - Sodium periodate ($NaIO_4$)
      - Cu (form: copper sulfate)
      - BTA, benzotriazole

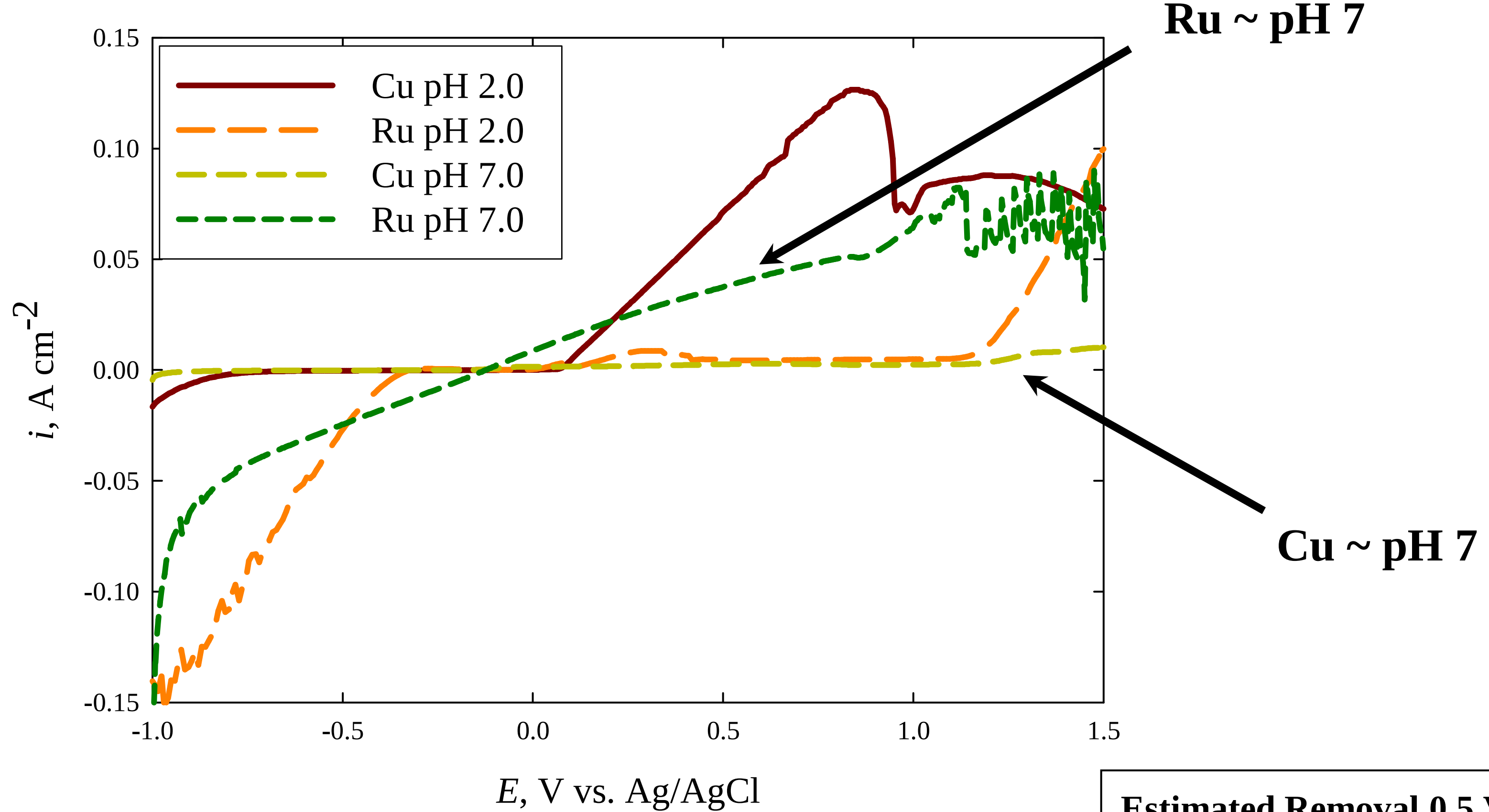
**select results shown*

•**AIM: Passivate Cu (via Cu oxide or inhibitor) while etching Ru**

Ruthenium Results

Potassium Phosphate

Low and Neutral pH's



Estimated Removal 0.5 V pH 7

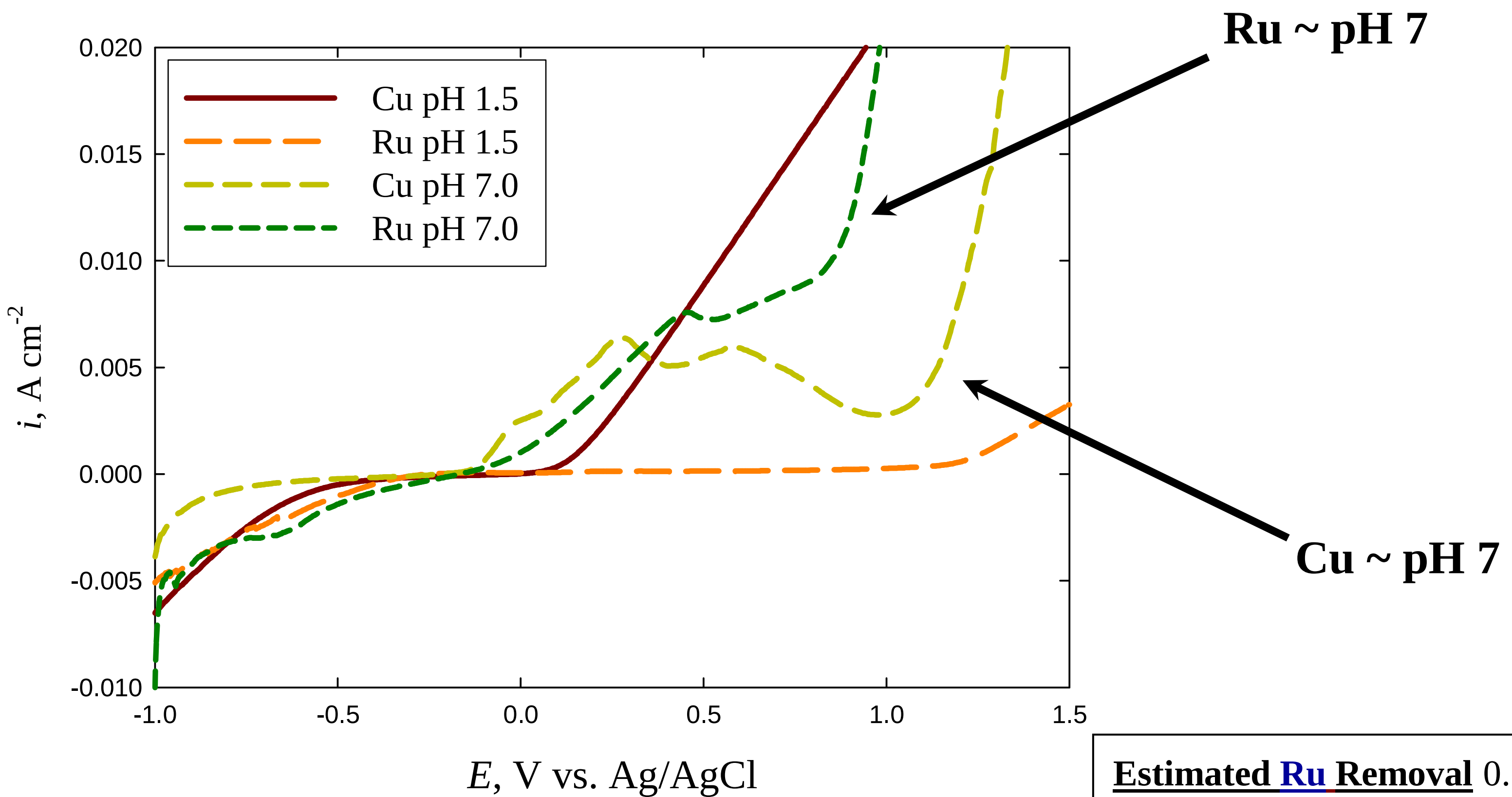
Cu ~ 570 Å min^{-1}

Ru ~ 2300 Å min^{-1}

- **Preferential Ru removal at a neutral pH**
  - **Formation of RuO_4 observed with no additives at ~ pH 7**
  - **Addition of oxidizer not necessary for Ru removal**

Ruthenium Results

Low and Neutral pH's **Citrate**



Estimated Ru Removal 0.5 V

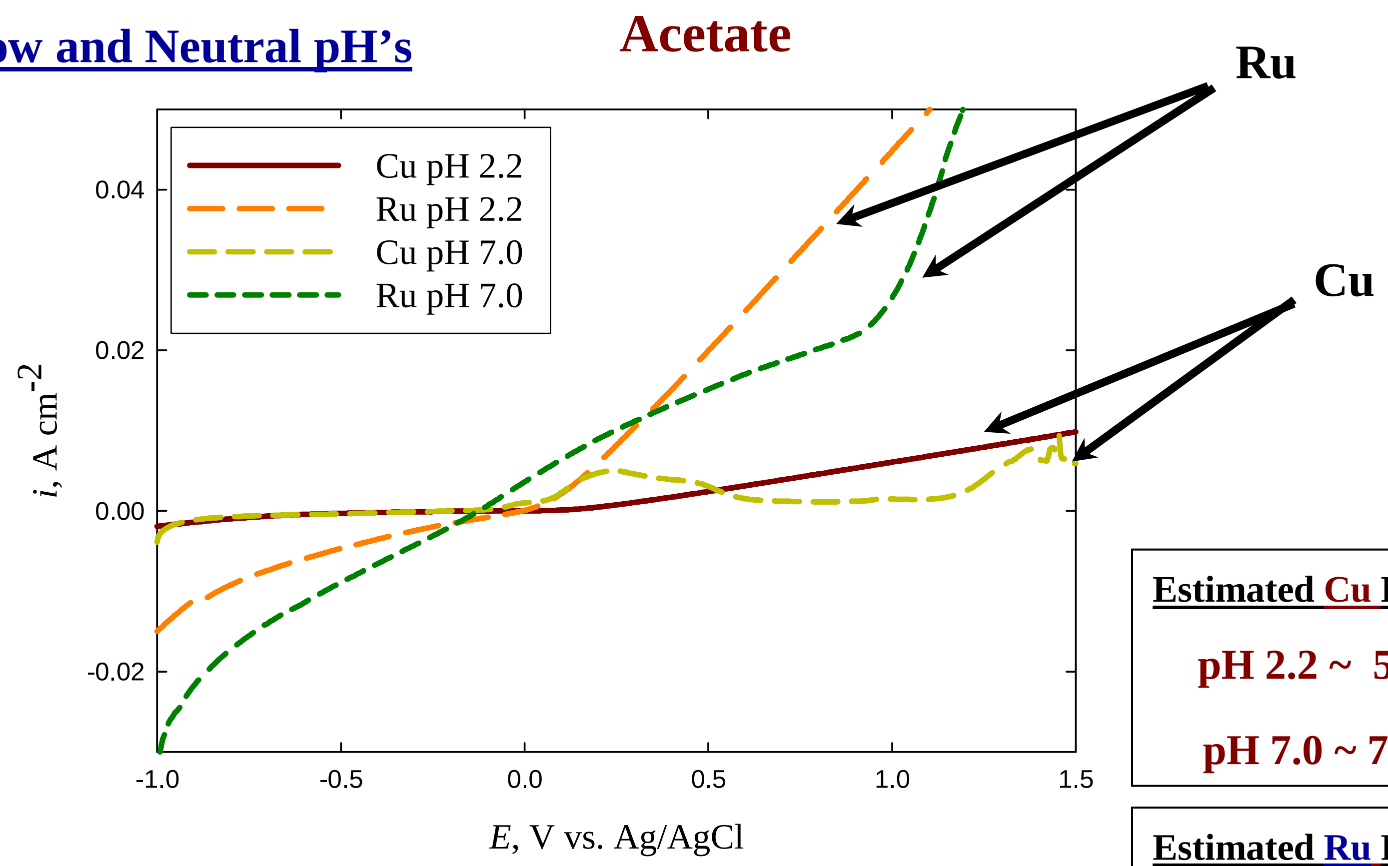
pH 1.5 ~ 20 Å min^{-1}

pH 7.0 ~ 470 Å min^{-1}

- **Preferential Cu removal at both pH levels**
  - **Formation of RuO_4 also observed with no additives at ~ pH 7**
  - **Use of inhibitor could prevent Cu dissolution, while still forming RuO_4**

Ruthenium Results

Low and Neutral pH's



Estimated Cu Removal 0.5 V
pH 2.2 ~ 530 Å min^{-1}
pH 7.0 ~ 700 Å min^{-1}

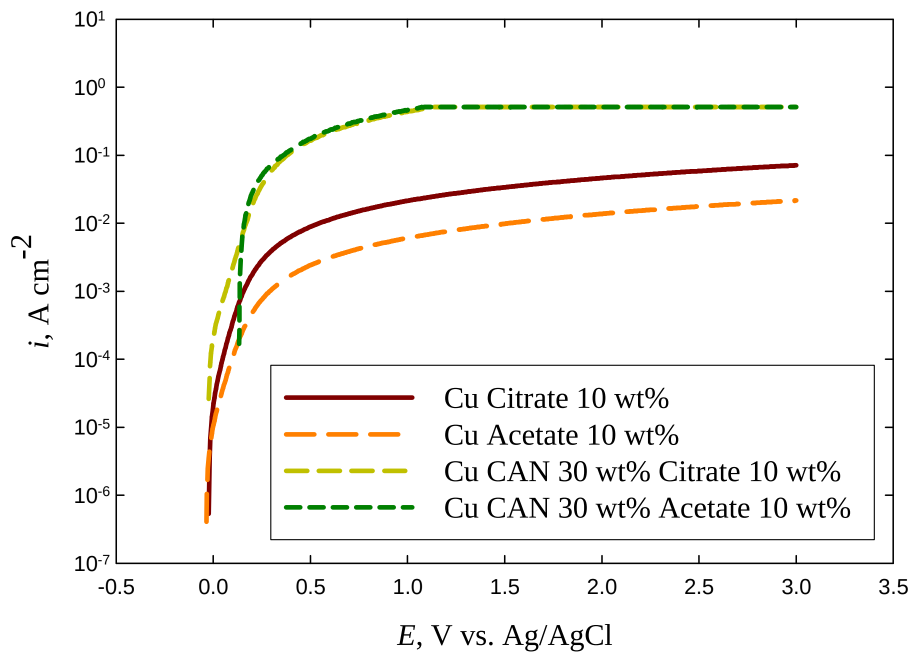
Estimated Ru Removal 0.5 V
pH 2.2 ~ 3100 Å min^{-1}
pH 7.0 ~ 2000 Å min^{-1}

- **Preferential Ru removal at both pH values**
  - **Formation of a Ru oxide**

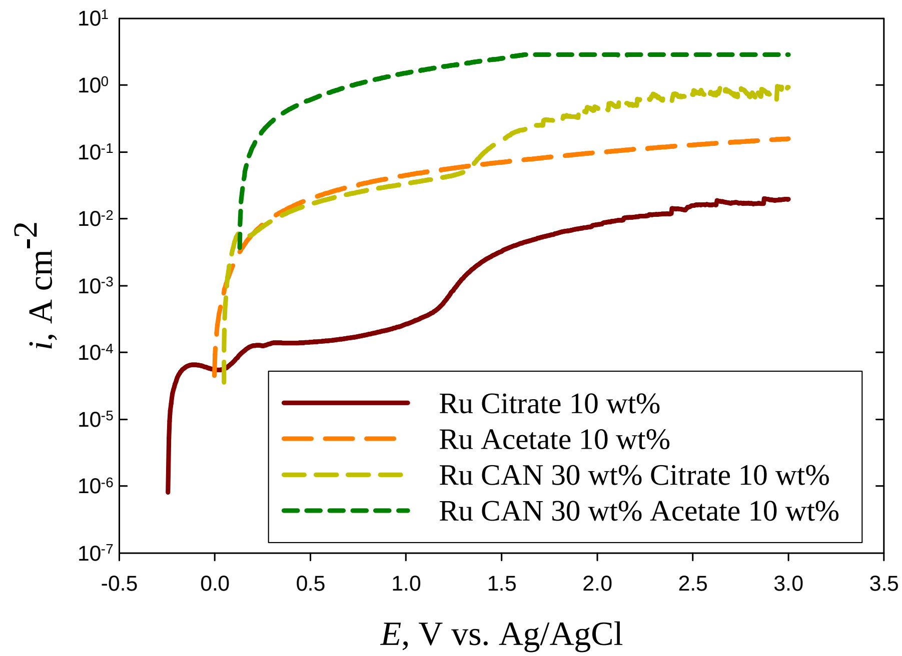
Ruthenium Results

10 wt% Citrate or Acetate + 30 wt% CAN

Cu



Ru



- **CAN increased current density for both Cu and Ru in both Acetate and Citrate buffer solutions at low pH values**
  - **May be used to facilitate combined electrochemical and pad RuO_2 removal at lower pH values in acetate buffer solutions**

Ruthenium Results Summary

- **Acetate Buffer**
    - **Ru has higher removal rate than Cu in both pH ranges**
    - **Forms a Ru oxide, could potentially be removed via oxidizer (CAN, or other)**
    - **Pursuing studies on wafer samples**

- **Potassium Phosphate pH 7 & Citrate Buffer pH 7**
  - **Produced RuO_4, soluble form of Ru oxide**
    - **Literature only published studies using strong oxidizers to form compound**
    - **May be able to passivate Cu using inhibitor while attaining high enough Ru removal rate**

Industrial Interactions and Technology Transfer

Industry mentors/contacts

- Intel
- Novellus
- Texas Instruments

Polishing Pads

- Cabot
- Rohm & Haas

Wafers

- IBM
- Novellus

Future Plans

No-Cost Extension Requested

- **Identify optimal Ru ECMP electrolyte**
  - **Confirm etch rates/selectivity (Atomic Absorption)**
- **Focus on effect of oxides on Ru removal in the presence of an applied potential**
  - **No current studies focusing solely on role of oxides in Ru removal**
- **Study Ru/Cu interface**
  - **Use wafer samples to study galvanic corrosion**
- **Test optimize electrolyte using ECMP tool on Ru wafers**

Summary of Main Deliverables

- **ECMP device design and RDE results of effect of pH on BTA inhibition characteristics (Oct 2006)**
- **Cu – ECMP: Influence of BTA concentration on planarization efficiency (Dec 2006)**
- **Report summary of the influence of bath composition on Cu-ECMP results (Sept 2007)**
- **Identification of bath chemistries for Ru: electrochemical characterization results (Jan 2008)**
- **Report on the identification of potential ECMP baths for Ru and Ta: Initial estimates of barrier/Cu selectivity (July 2008)**
- **Report on the characterization of Cu/Barrier Selectivity on a Benchtop Tool: Effect of Cu Corrosion Inhibitors (Jan 2009)**

Publications, Presentations, and Recognitions/Awards

Presentations:

- **Electrochemical Society, Phoenix, AZ, May 2008**
- **CAMP Seminar, Lake Placid, NY, August 2008**
- **SRC Teleconference, October 2008**
- **SRC Metrology Webinar, February 2009**

Papers:

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

- **K. G. Shattuck, J. Y. Lin, and A. C. West, Characterization of Phosphate Electrolytes for use in Cu Electrochemical Mechanical Planarization, Electrochimica Acta, Volume 53, Issue 28, 30 November 2008, Pages 8211-8216**

- **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, Volume 155, Issue 6,** H396-H400, 2008

- **J. Y. Lin, A. C. West,and C. C. Wan, Evaluation of Post-Cu CMP Cleaning of Organic Residuals Using a Microfluidic Device, Electrochemistry Communications, Volume 10, Issue 5, May 2008, Pages 677-680**

Environmentally Benign Processing of Photoresists with Supercritical CO_2

(*Task Number: 425.017*)

PI:

- **Christopher K. Ober, Materials Science and Engineering, Cornell University**

Collaborators:

- **Karen Gleason, MIT; James Watkins, UMASS Amherst**

Graduate Student:

- **Jing Sha: PhD candidate, Materials Science and Engineering, Cornell University**
- **Christine Ouyang: PhD candidate, Materials Science and Engineering, Cornell University**

Other Researchers:

- **Jin-Kyun Lee, Postdoctoral Fellow, Materials Science and Engineering, Cornell University**

Cost Share (other than core ERC funding):

- **Intel Support ($80k), JS**
- **NSF Support ($80k), JKL**

Objectives

- **Demonstrate the high-resolution patternability and scCO_2 development of molecular glass resists with environmentally benign alicyclic cores for 193-nm lithography**
- **Synthesize and characterize fluorinated quaternary ammonium salts (QAS) as CO_2 compatible additives to develop conventional photoresists in supercritical (sc) CO_2**

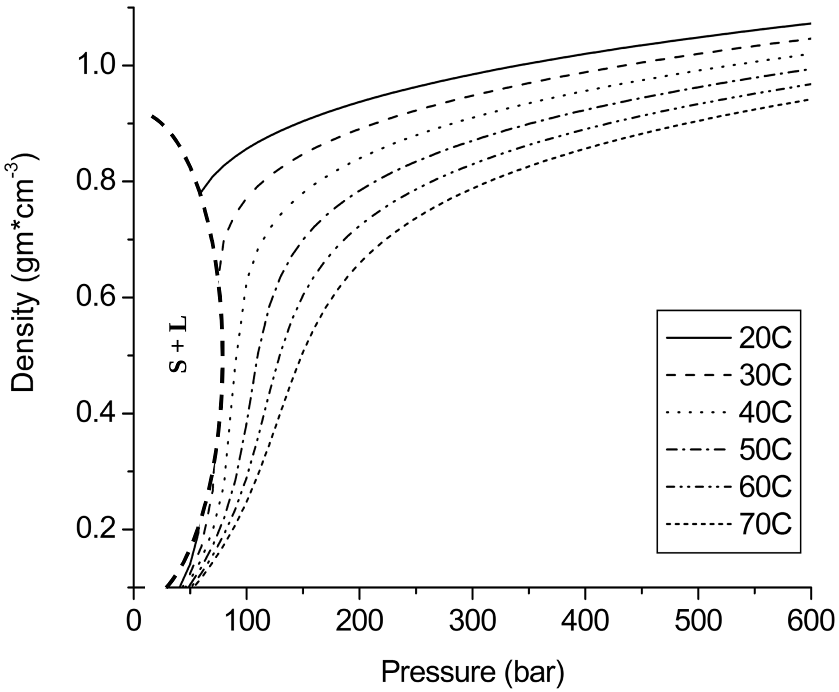
ESH Metrics and Impact

	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

Why a Non-Aqueous Developer Solvent?

Environmental and Performance Advantages of $scCO_2$

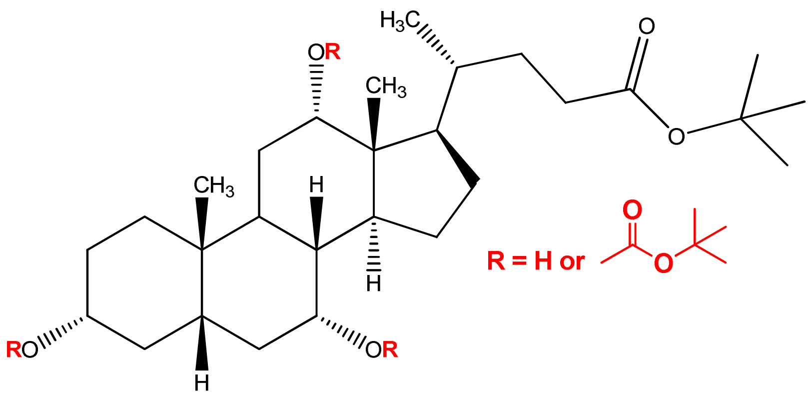
- **Environmentally friendly, zero VOC solvent**
- **Highly tunable solvating power**
  - $\rho(T,P)$
  - **Leaves no residue**
  - **Clean separations**
- **One-phase fluid**
  - **Zero surface tension**
  - **Transport, viscosity between that of liquid and gas**



- **Nonpolar, inert character**
- **Potential to reduce LER and eliminate pattern collapse**

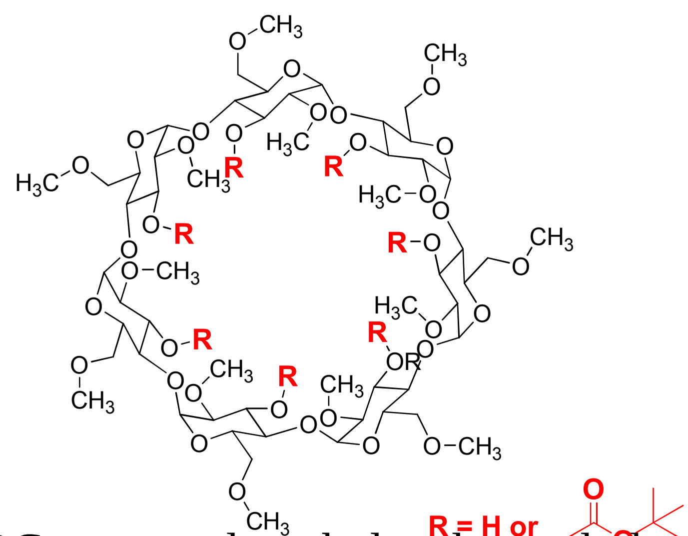
Molecular Glass Resists with Alicyclic Cores

193 nm transparency and $scCO_2$ solubility



tBOC-protected tert-butyl cholate

Tg = ~ 100 °C



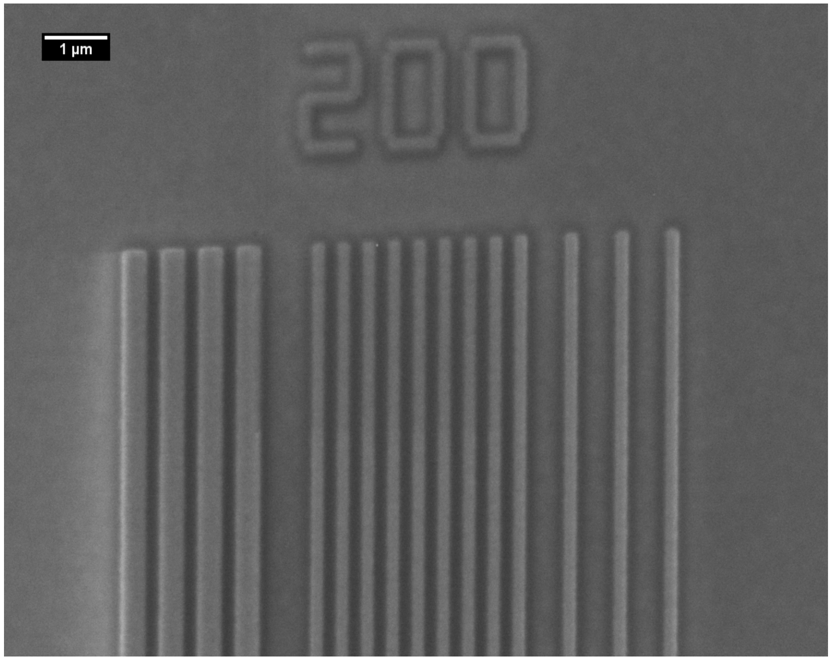
tBOC-protected methylated β-cyclodextrin

Tg = ~ 125 °C

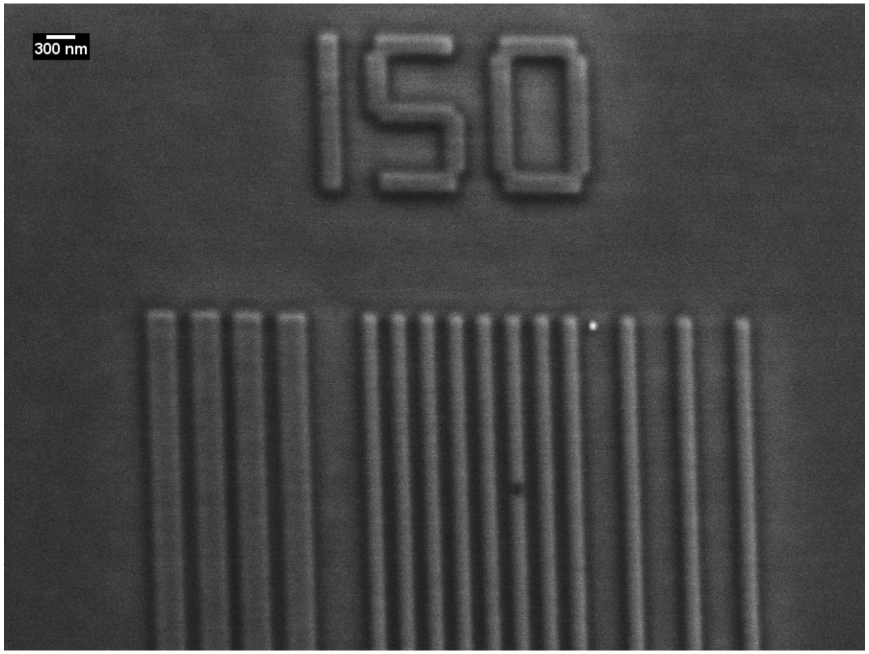
- **Cholic acid cores are etch-resistant and have strong intermolecular interactions which can contribute to the relatively high glass transition temperatures of cholates.**

- **Cyclodextrins are good hosts for inclusion complexes and have potential as molecular glass resists to hold functional moieties in their cavities.**

Electron Beam Patterning and $scCO_2$ Development of tBOC-Protected Alicyclic Resist Molecules

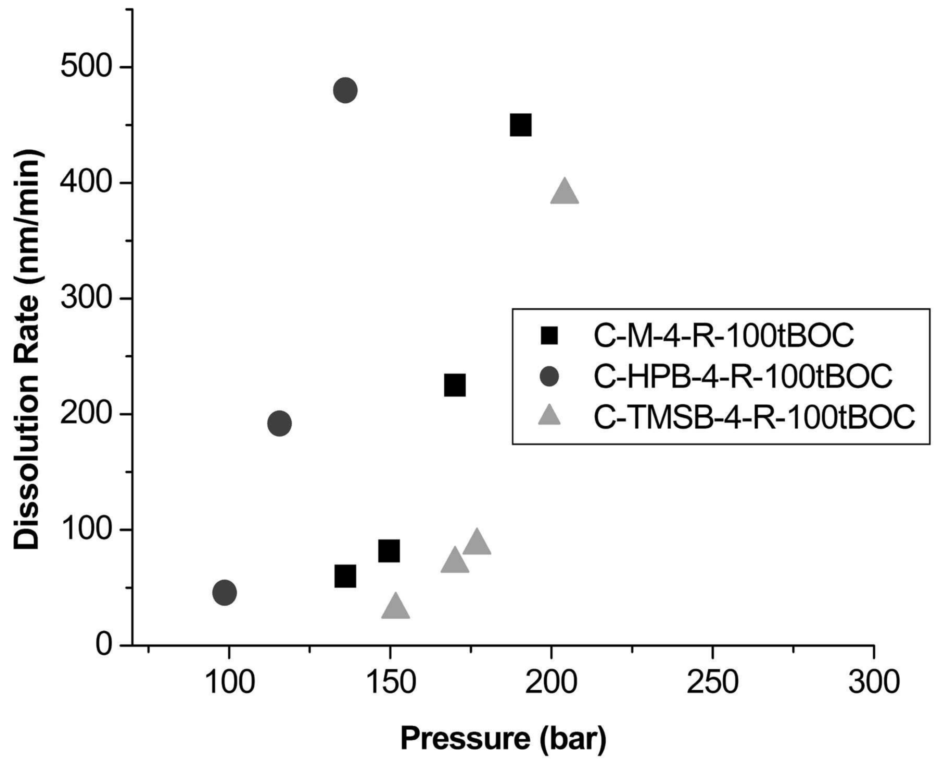


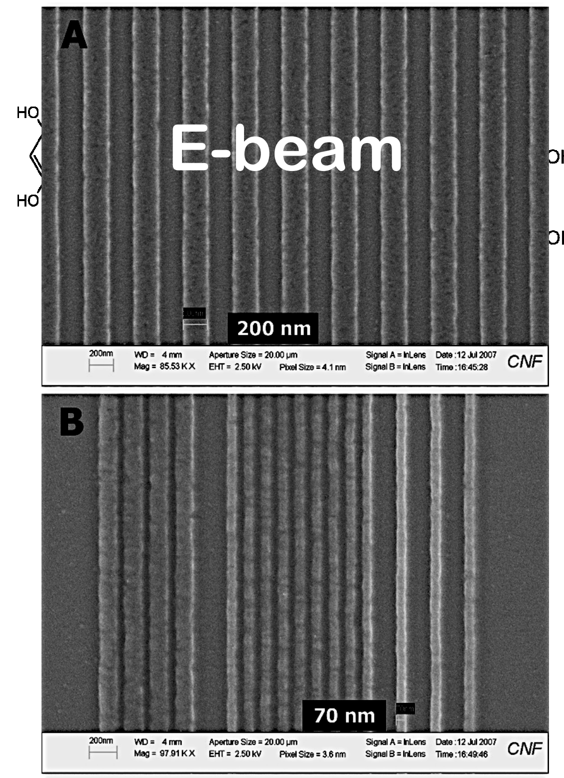
tBOC-protected tert-butyl cholate
PAB: 90°C, 60sec
E-beam dose = 44 µC/cm^2
PEB: 90°C, 60sec
$scCO_2$: 5000psi, 40°C, 5min



tBOC-protected methylated β-cyclodextrin
PAB: 115°C, 60sec
E-beam dose = 163 µC/cm^2
PEB: 90°C, 60sec
$scCO_2$: 5000psi, 40°C, 5min

Development in $scCO_2$

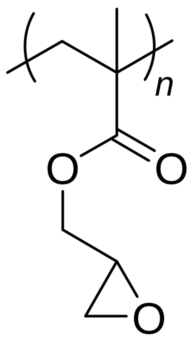




- **t-BOC groups aid solubility in $scCO_2$**
- **Leads to fluorine free development**

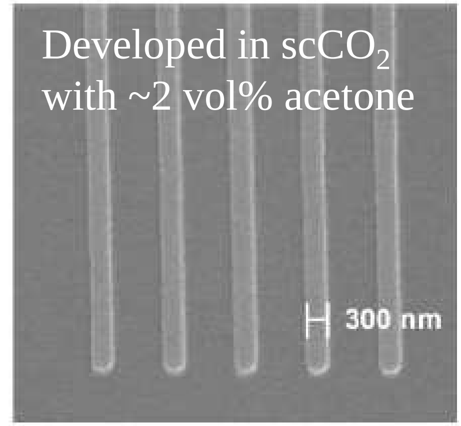
Additives for $scCO_2$ to Develop Conventional Resists

- **Co-solvents**



Addition of **acetone** as a co-solvent

Non-fluorine polymer was dissolved in $scCO_2$.
- Increase solvent density
- Tune polarity of fluid



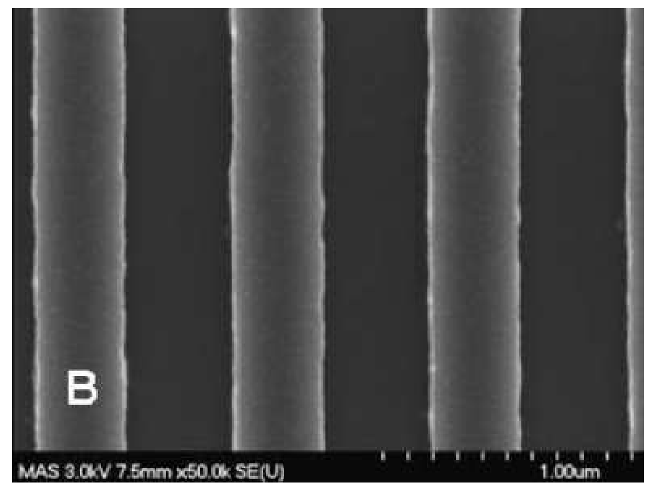
C. K. Ober, K. K. Gleason, et al., *JVST B.* **2004**, 22, 2473-8.

- **$scCO_2$ Compatible Salts**

Micell Integrated Systems developed a new additive for $scCO_2$.

$$(R)_a(R')_bN^+X^-$$

where a + b = 4, and R' is a partially fluorinated alkyl or aryl group, and X- is the counter anion

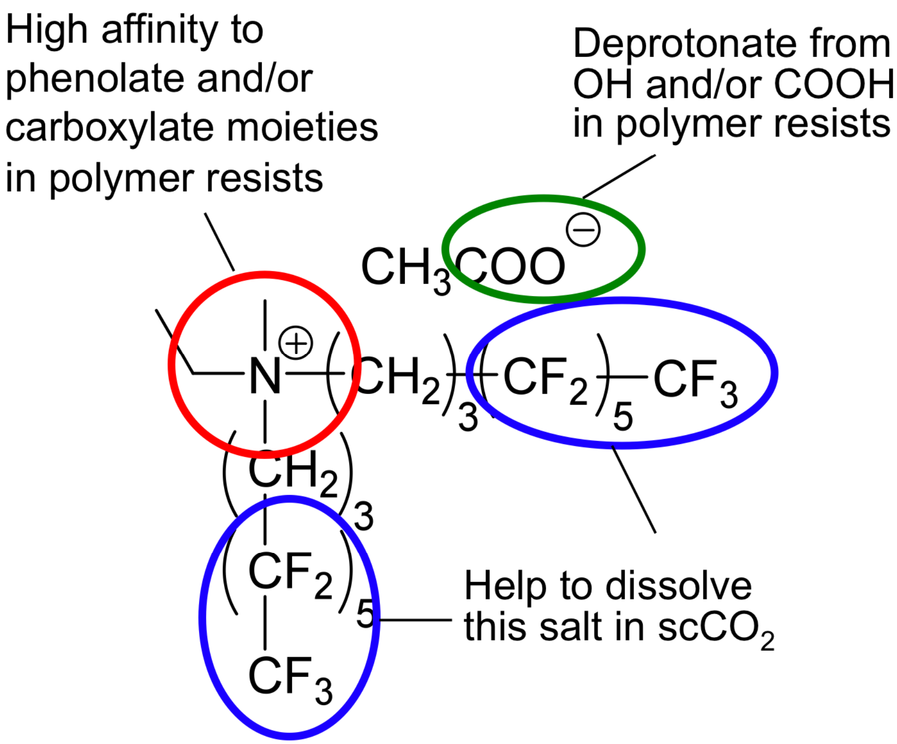


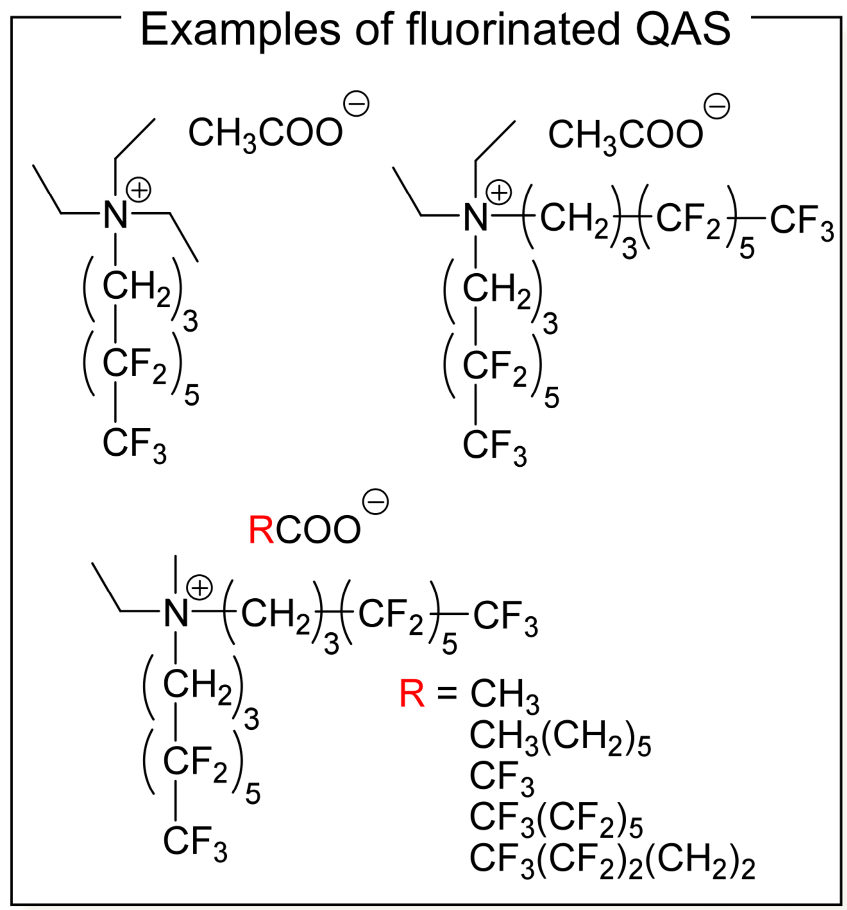
M. Wagner, et al., *Proc. of SPIE* **2006**, 6153, 61531I, *Proc. of SPIE* **2006**, 6153, 615345, *Proc. of SPIE* **2006**, 6153, 615346, *Proc. of SPIE* **2006**, 6153, 61533W, *Proc. of SPIE* **2007**, 6519, 651948.

Quaternary Ammonium Salts (QAS)

$scCO_2$ Compatible Additives:

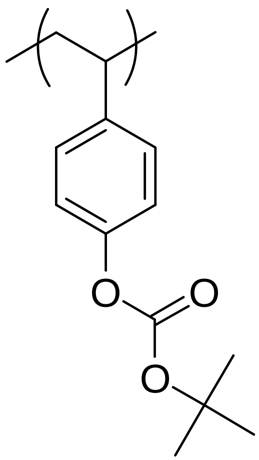
Fluorinated Quaternary Ammonium Salts (QAS)

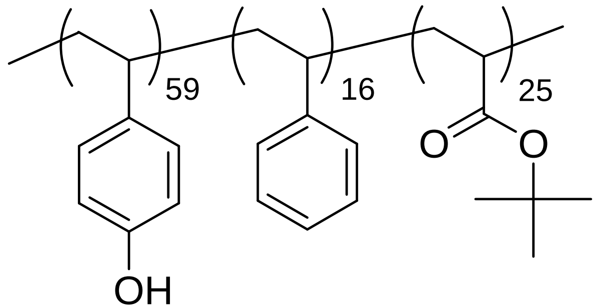




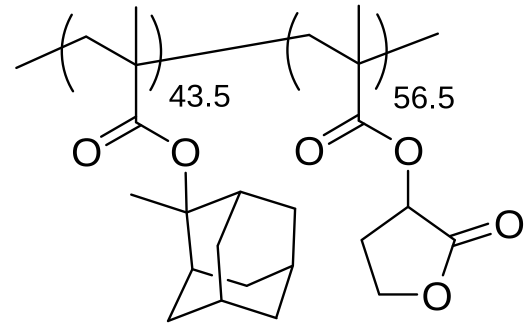
Some of the fluorinated ammonium salts form ***Micelle*** in $scCO_2$.

Test bed EUV/DUV Resists





'GIJ' from DuPont Electronic Polymers
(**ESCAP**)



PMAMA-co-GBLMA from Mitsubishi Rayon America (**PMAMA-co-GBLMA**)

PBOCST

From TOK

EUV-P568 : Old EUV resist made from PHOST based polymer with t-Boc

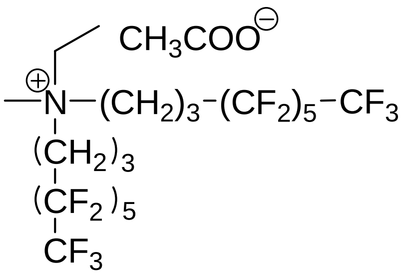
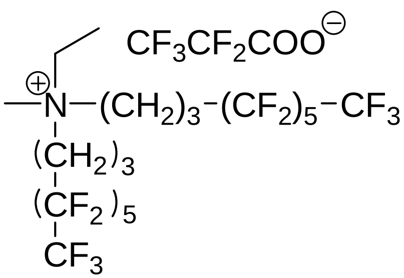
EUVR-P3015 : Molecular glass resist

EUVR-P1123 : One of the latest EUV resist made from PHOST based polymer with bulky protecting group

TARF-P6111 : ArF (193 nm) resist made from poly(methacrylate) backbones.

All of these resists are insoluble in $scCO_2$ at any temperatures and pressures.

Initial Dissolution Results of Resists with QAS

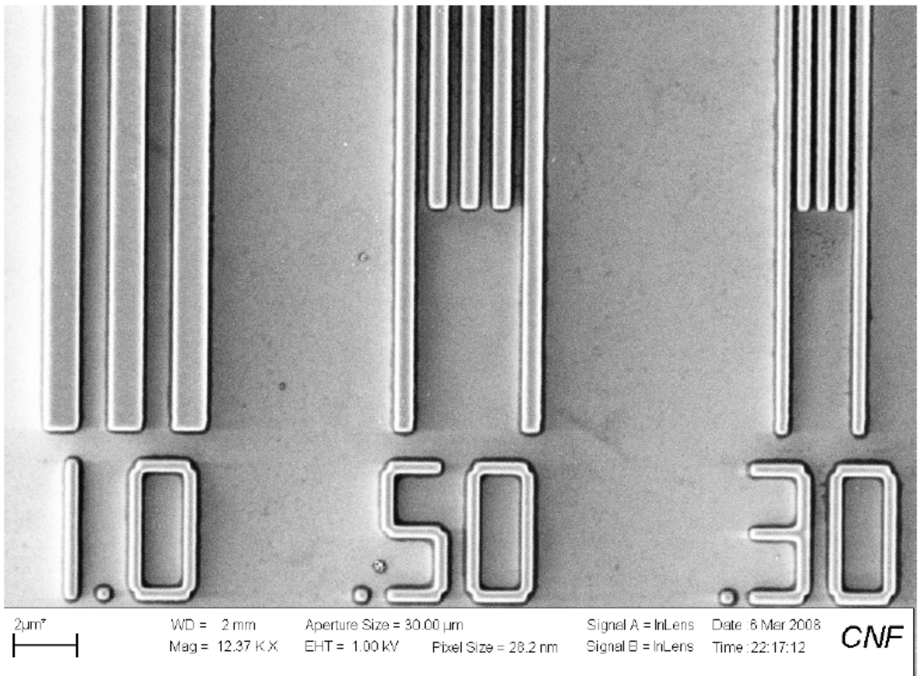
QAS	Resist	Unexposed	Exposed	note
 **QAS-4** (1.25 mM)	PBOCST	**Dissolution** (40 nm/min)	**Slow dissolution** (1-4 nm/min)	*Negative tone resist*
	ESCAP (Du Pont)	**Dissolution** (25 nm/min)	**No dissolution**	*Negative tone resist*
	PMAMA-co-GBLMA (Mitsubishi Rayon)	No dissolution	No dissolution	
	EUV-P568 (TOK)	**Dissolution** (15 nm/min)	**Slow dissolution** (1-2 nm/min)	*Negative tone resist*
 **QAS-7** (1.25 mM)	PBOCST	No dissolution	No dissolution	
	ESCAP (Du Pont)	No dissolution	No dissolution	
	PMAMA-co-GBLMA (Mitsubishi Rayon)	No dissolution	No dissolution	
	EUV-P568 (TOK)	**Dissolution** (45 nm/min)	**Slow dissolution** (<1 nm/min)	*Negative tone resist*

Exposed by UV lamp (254 nm, 24 mC/cm^2), developed in $scCO_2$ at 50° C and 5000 psi.

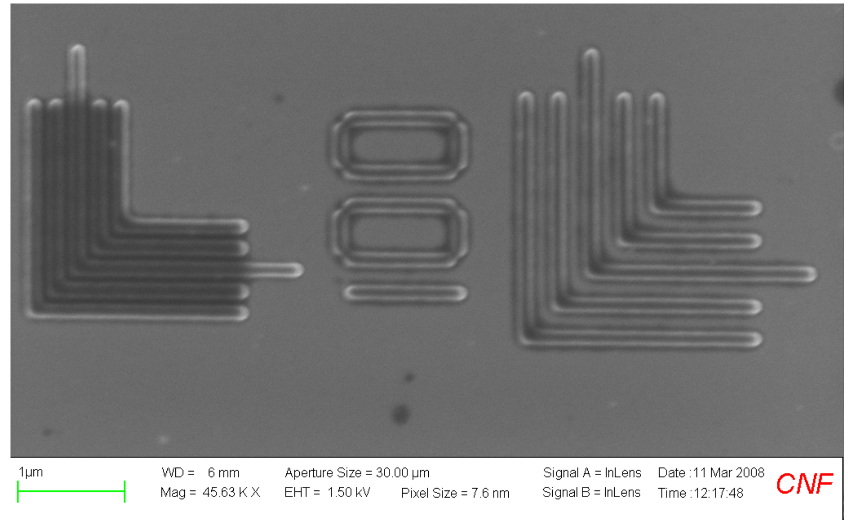
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

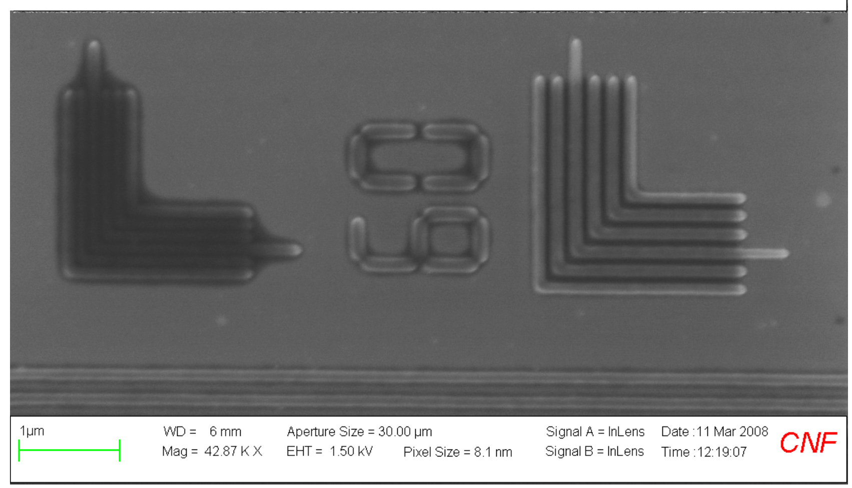
Electron Beam Patterning

Development test of EB-patterned TOK resist (EUV-P568) with QAS-4 or QAS-7



Dose: 107 um/cm^2, QAS-4 (1.25 mM),
dev. for 60 min at 50^{o}C, 5000 psi, flow 30 min





Negative tone patterns with sub-100 nm feature sizes were obtained.

Dose: 20 um/cm^2, QAS-7 (1.25 mM),
dev. for 60 min at 50^{o}C, 5000 psi, flow 30 min

Industrial Interactions and Technology Transfer

- **Former student (N. Felix) hired by IBM Fishkill Research Center**
- **Jing Sha moved to Intel grant and will intern at NIST**
- **Interactions with Intel on this topic have been successful**
- **Collaboration with Albany Nanotech for EUV exposures**

Task Deliverables

- **Report the synthesis and evaluation of molecular glass precursors for low k materials (Q1 2007)**
  - ***completed***
- **Prepare and assess new porogens for ULK materials compatible with $scCO_2$ processing (Q1 2008)**
  - ***completed***
- **Demonstration of high resolution patterning of molecular glass low k materials with SCF development (Q1 2009)**
  - ***completed***

Future Plans

Next Year Plans (seed effort)

- **Design new quaternary ammonium salts (QAS) for faster dissolution of resist molecules in scCO_2 based on computer simulation results from Prof. Juan J de Pablo Group in Univ. of Wisconsin, Madison**
- **Continue synthesis efforts for scCO_2 developable molecular glass resists with naturally occurring and environmentally benign cores for high-resolution patterning**

Publications, Presentations, and Recognitions/Awards

Publications

- M. Tanaka, A. Rastogi, N. M. Felix, C. K. Ober, "Supercritical Carbon Dioxide Compatible Salts: Synthesis and Application to Next Generation Lithography", *Journal of Photopolymer Science and Technology* (2008), 21(3), 393-396.
- J. Sha and C. K. Ober, "Fluorine- and Siloxane-Containing Polymers for Supercritical Carbon Dioxide Lithography", *Polymer International*, in press.
- A. Rastogi, M. Tanaka, G. N. Toepperwein, R. A. Riggleman, J. J. dePablo, C. K. Ober, "Environmentally Benign Development of Photoresists In Supercritical Carbon Dioxide Using CO_2 Compatible Additives", in preparation
- J. Sha, J-K Lee, C. K. Ober, "Molecular Glass Resists Developable in Supercritical CO_2 for 193-nm Lithography", in preparation

Presentations

- 25th International Conference of Photopolymer Science & Technology (June 2008). "Supercritical Carbon Dioxide Compatible Salts: Synthesis and Application to Next Generation Lithography"
- US-Japan Polymat 2008 Symposium (Aug 2008). "Environmentally Benign Development of Polymer Photoresists Using Supercritical Carbon Dioxide"
- ERC Teleseminar (Oct 2008). "Environmentally Benign Development of Standard Resists in Supercritical Carbon Dioxide Using CO_2 Compatible Salts"
- Advances in Resist Materials and Processing Technology XXVI conference (part of the SPIE Symposium on Advanced Lithography) (Feb 2009). "Environmentally Benign Development of Photoresists in Supercritical Carbon Dioxide Using CO_2 Compatible Additives"

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:

- **Nathan J. Trujillo: Ph.D.CEP Candidate, Department of Chemical Engineering, MIT**
- **Salmaan Baxamusa: PhD Candidate, Department of Chemical Engineering, MIT (Funded until 9/07)**
- **Shannan O'Shaughnessy, PhD: Department of Chemical Engineering, MIT (Graduated 5/07)**

Cost Share (other than core ERC funding):

- **~$25,000 (GEM Fellowship for Nathan Trujillo)**
- **$70,000 (NSF Fellowship for Sal Baxamusa)**

Objectives

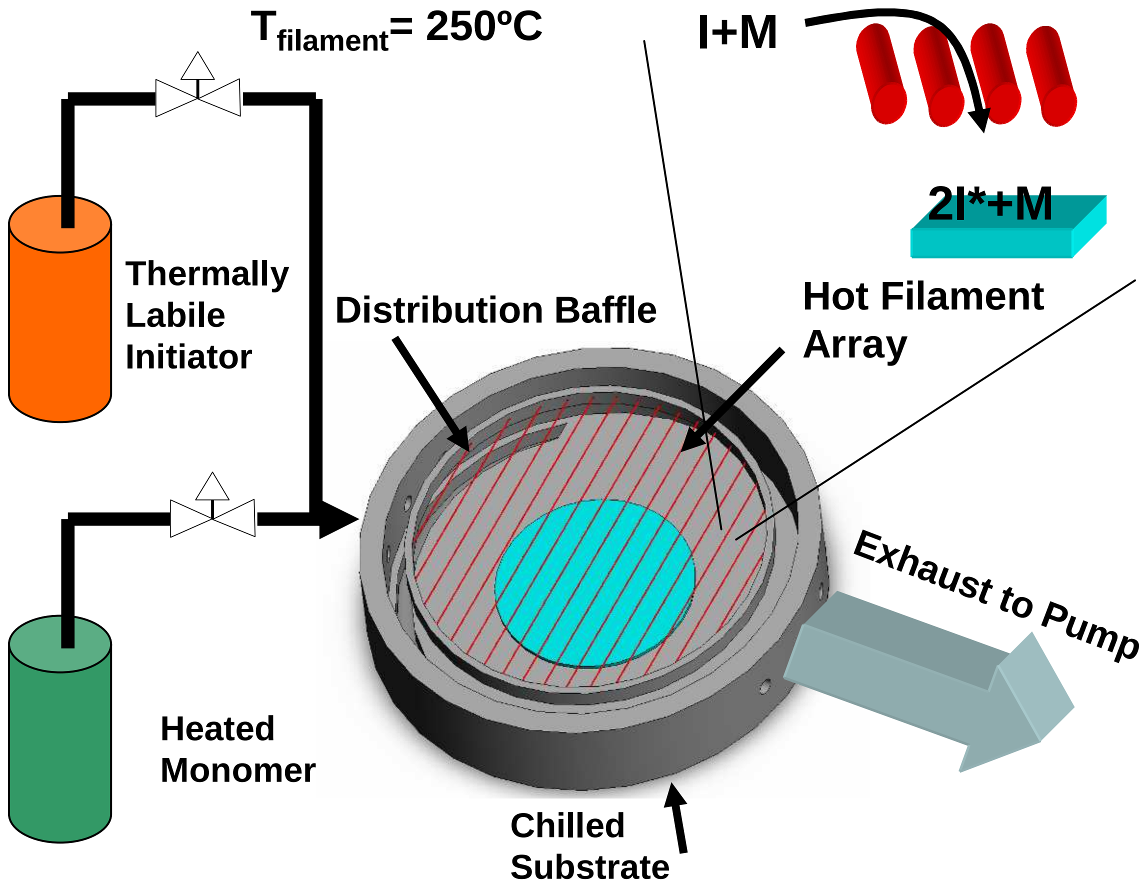
- **Develop new methods to deposit, pattern, and process low-*k* materials**
  - **Multi-scale polymer patterning using self-assembled mask and capillary force lithography (no traditional lithography)**
  - **Low-energy and solvent-free deposition of robust low-*k* films from a novel precursor with "built in" porogen**
- **Process step reduction results from EHS focused approach**

ESH Metrics and Impact

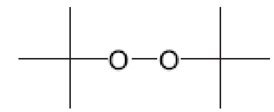
1. ***Resist-free photolithography would eliminate use of photoresist. Approximately 25,000 liters of photoresist materials is used annually in typical semiconductor foundries, at a cost of about $1,600 per liter. Through spin-on process approximately 95% of resist is wasted and disposed as toxic material [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 hierarchical 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 0.13-2.1 W/cm^2[4,5] . No plasma etch eliminates additional >7.1 W/cm^2[6] power requirement.***
4. ***A typical microelectronic fabrication facility processing 5000 wafers per day will generate 5 million liters of organic and aqueous solvent waste per year [7]. The all vapor phase iCVD process reduces solvents and waste associated with spin-on processing.***

[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]Tenhaeff et al. Adv. Funct. Mater. 18 (2008)
[6]Berruyer et al. J. Vac. Sci. Technol. A. 16.3 (1998)
[7] DeSain, Science, 279 (2002)

iCVD Process chemistry preserves functionality



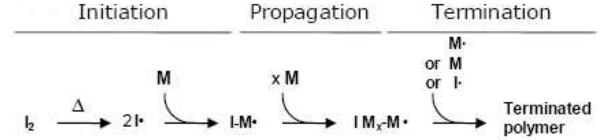
Initiator



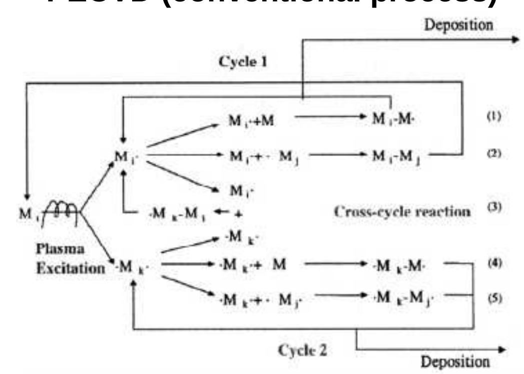
tert-butyl peroxide

Proposed Polymerization Mechanisms

iCVD (novel low energy process)



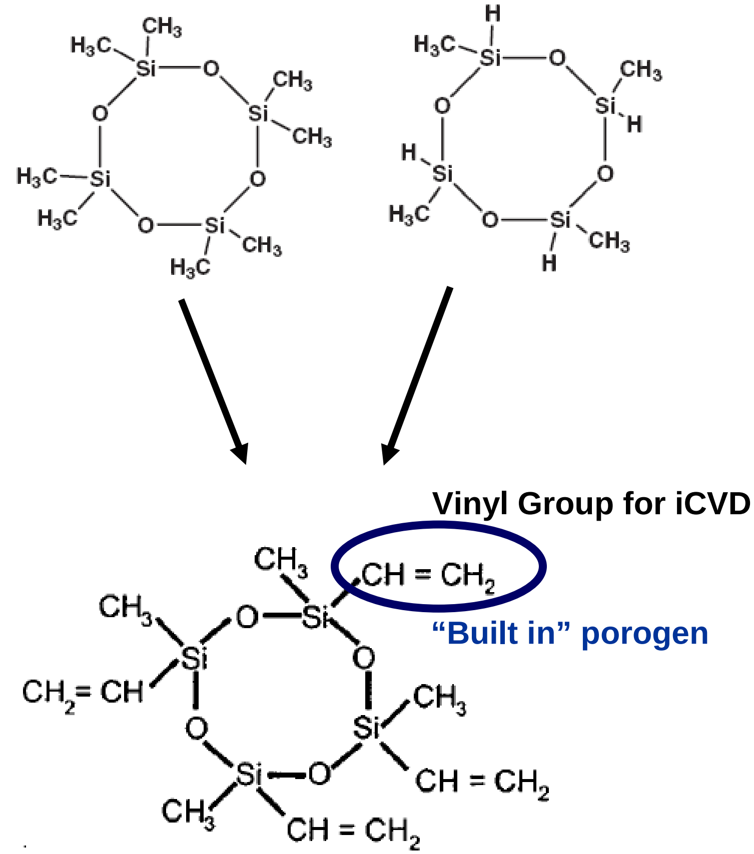
PECVD (conventional process)



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**
- **Unreacted vinyl groups act as “built in” porogens**

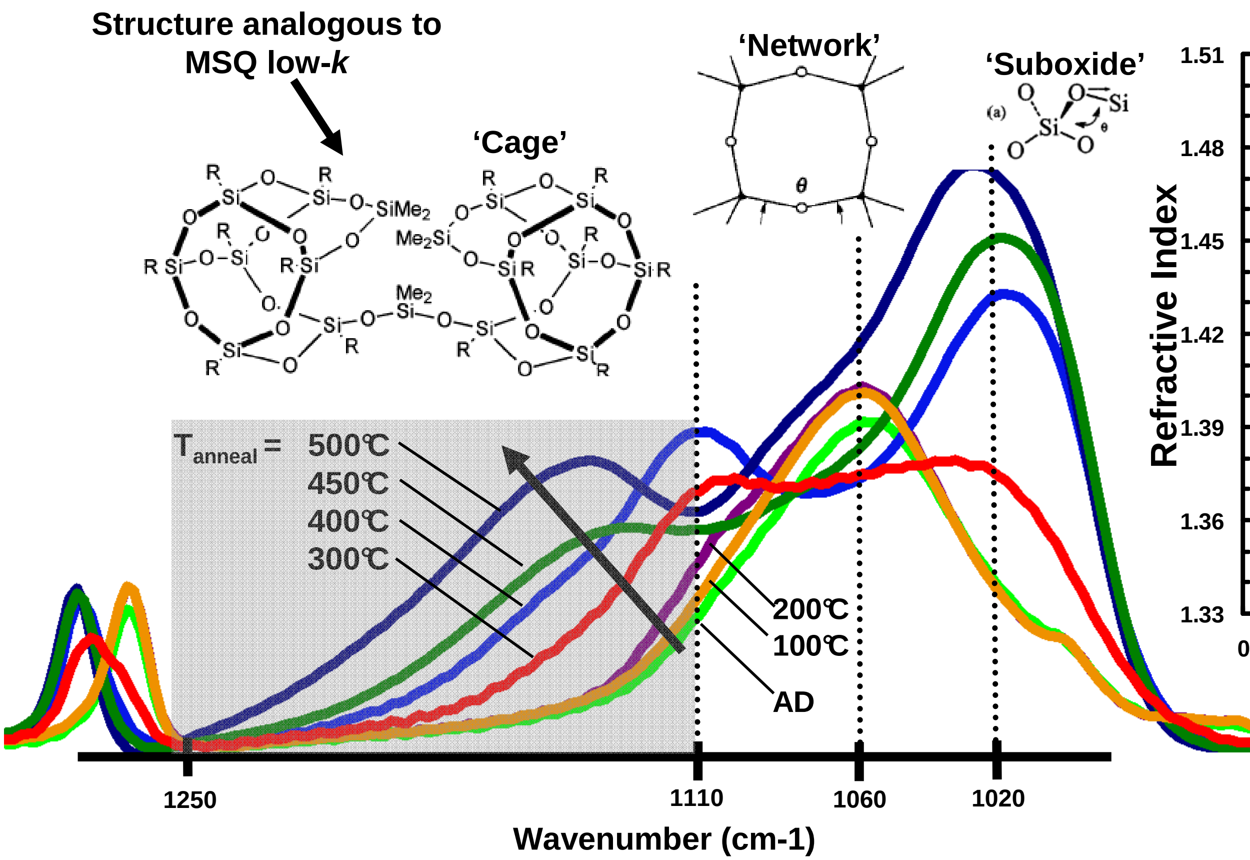
Commercial PECVD Precursors for Low-*k*

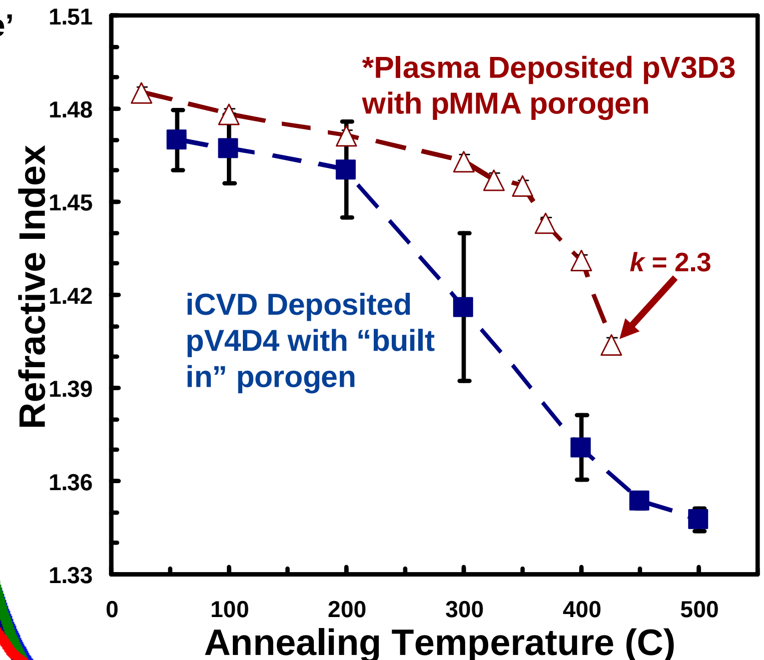


1,3,5,7-TETRAVINYLTETRAMETHYLCYCLOTETRASILOXANE

Novel iCVD Precursor

Cage-like structure from iCVD films annealed in air

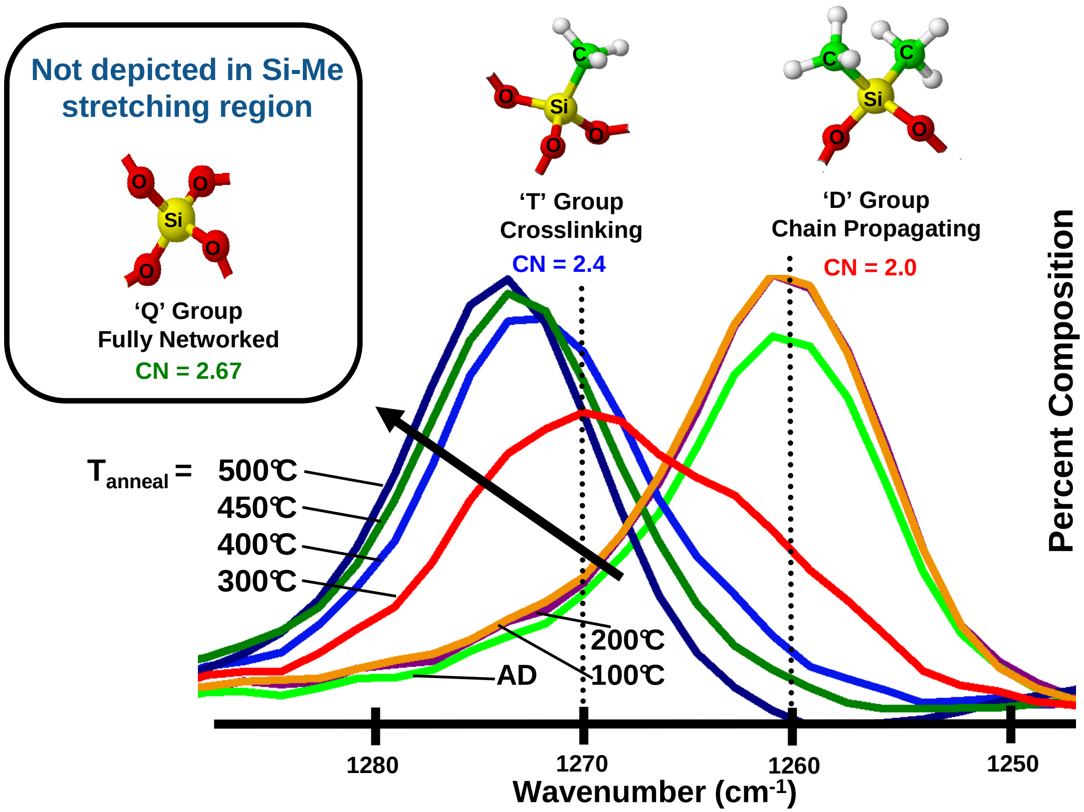


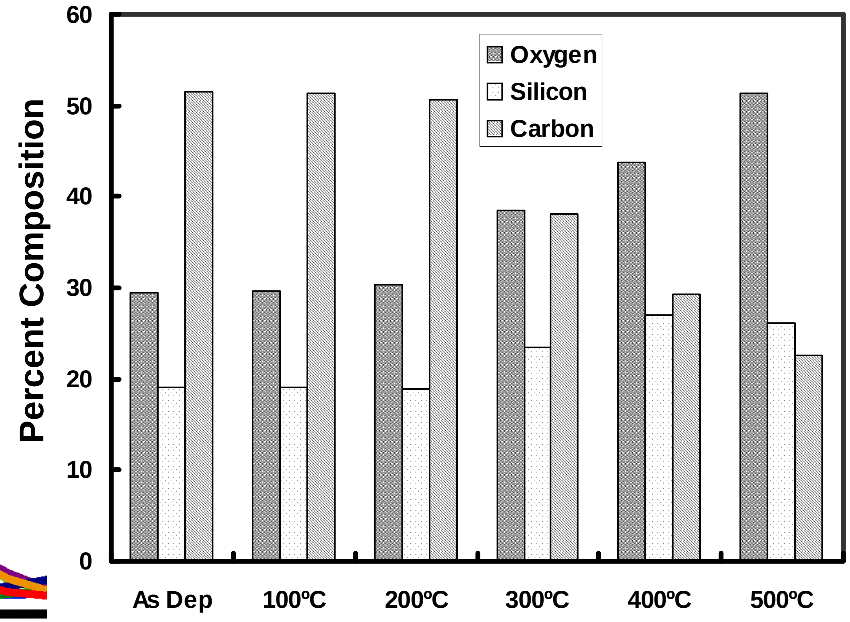


△ *D.D. Burkey , K.K. Gleason, *J. Vac. Sci. Technol. A,* (2004) 22 (1)

Increasing 'Cage' structure (left) results in a less dense film (right)

Increased crosslinking with –CH3 removal

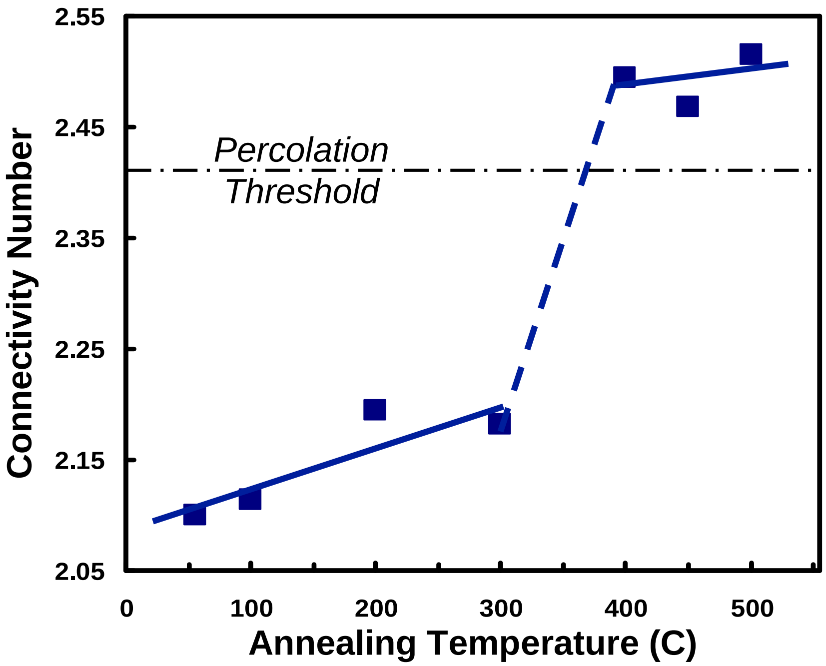


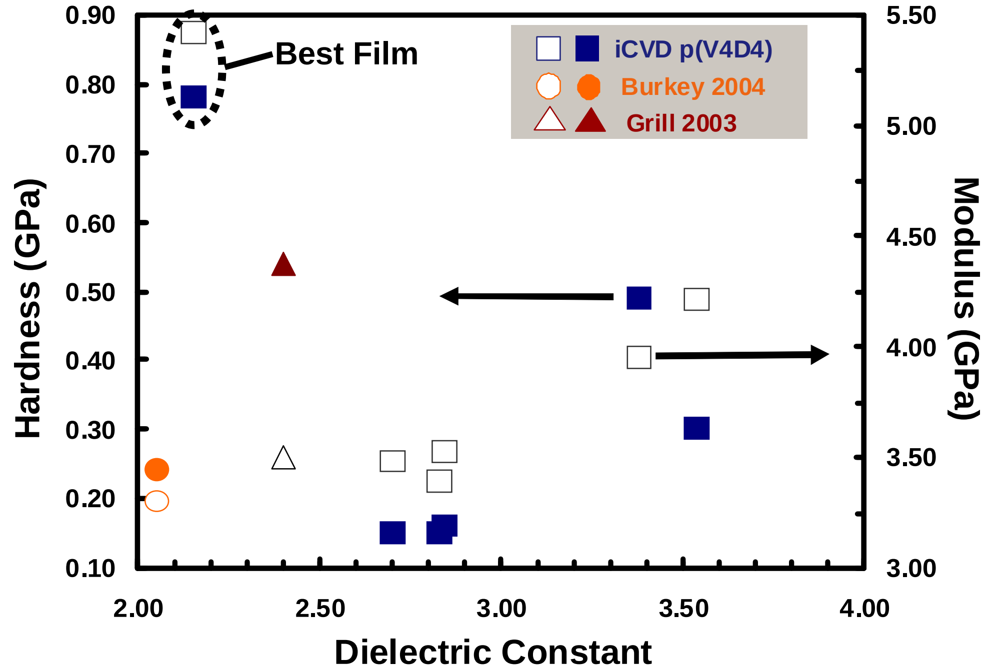


Loss of –CH3 improves mechanical properties, yet sufficient groups remain to help keep k low

•XPS implies increased 'Q' groups from oxygen injection at high temperatures, which is responsible for improved H and M

Mechanical enhancement results from increased connectivity





Percolation threshold at CN = 2.4. Above threshold, film is amorphous and rigid!

•Greater than 0.5 GPa hardness above percolation threshold

•Hardest film associated with lowest dielectric constant. No trade-off between *k* and H !

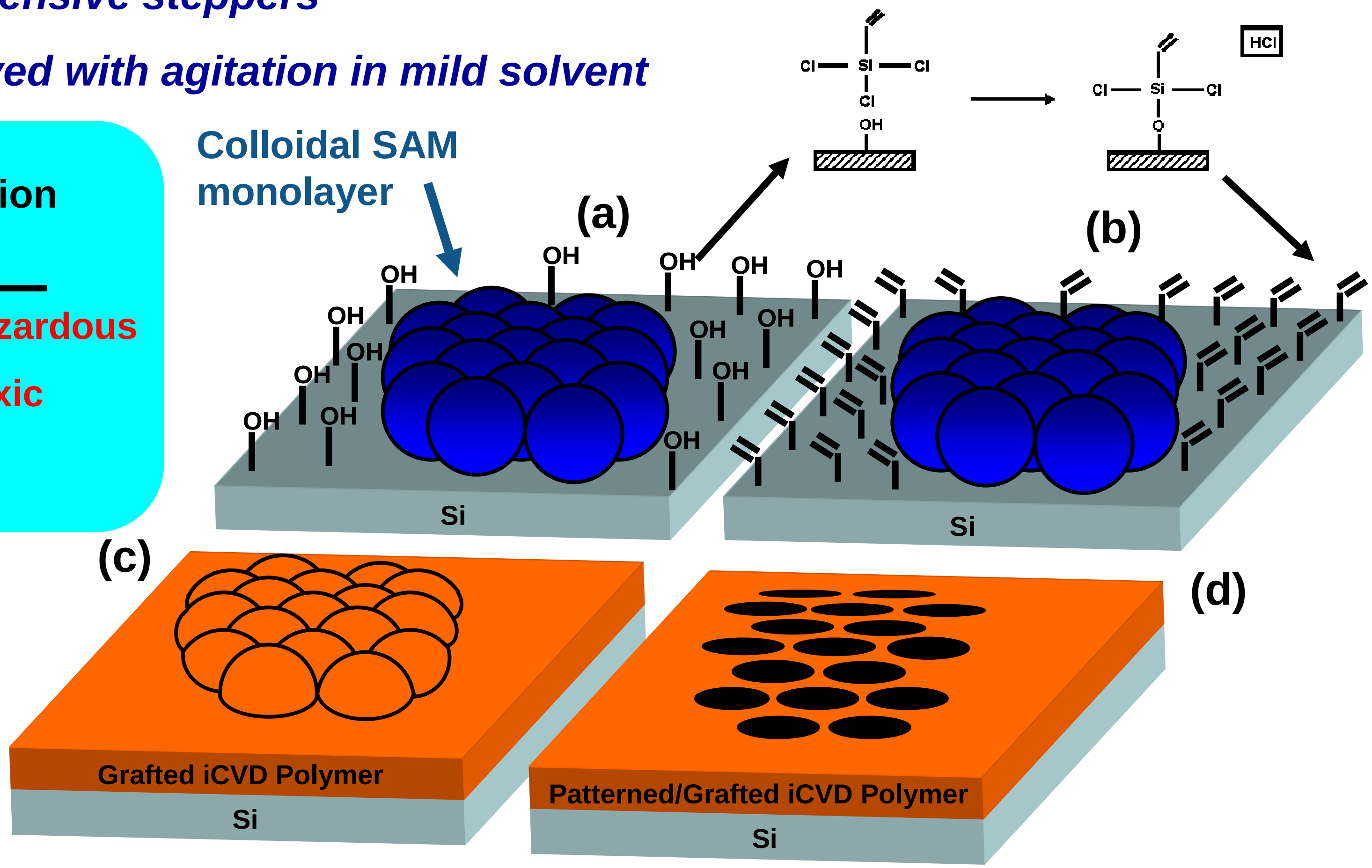
•Combined UV/thermal cure can reduce optimal temperature

Additive polymer patterning using self-assembled mask (no traditional lithography)

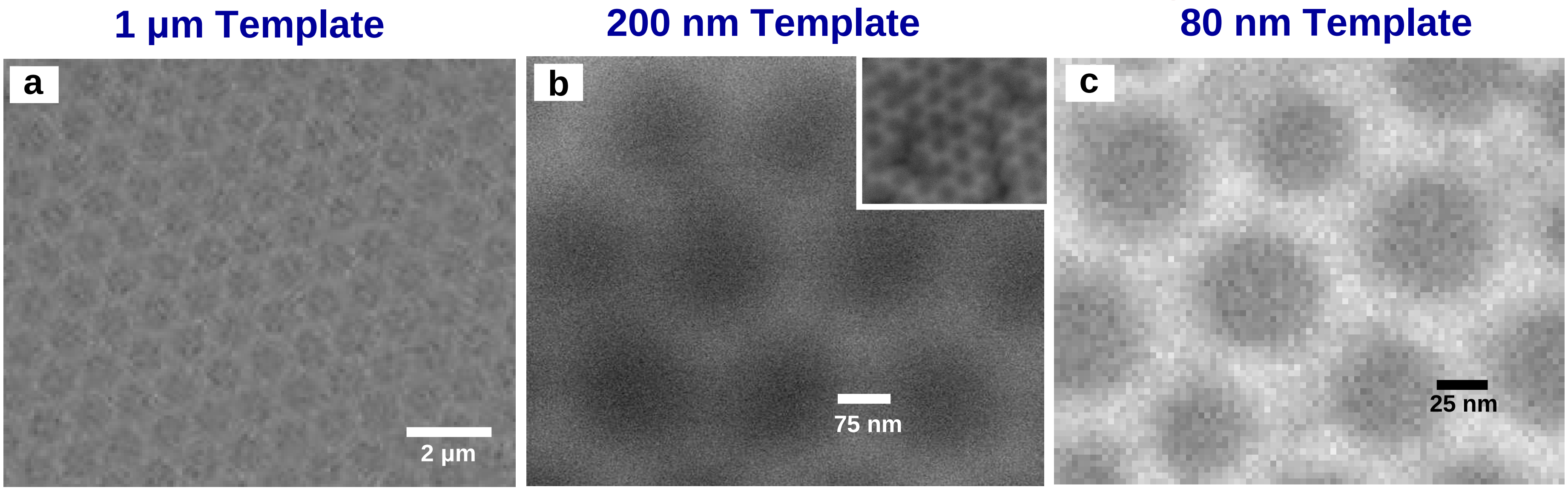
- *Non-Conventional lithography is a cost-saving alternative to conventional photolithography.*
- *No need for expensive steppers*
- *Template removed with agitation in mild solvent*

Solvent Substitution

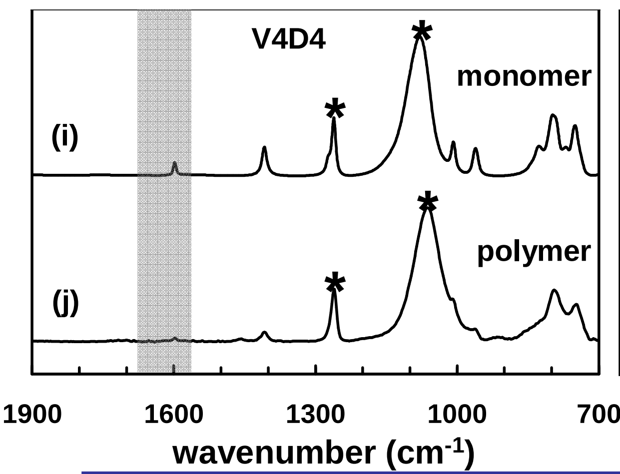
IPA vs.	TMAH
•Non-hazardous	•Hazardous
•Biodegradable	•Toxic
•Non-toxic	



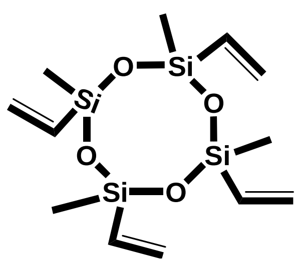
Low-k iCVD p(V4D4) Patterns: 25 nm features & no traditional lithography



Decreasing Template Diameter



Utility: Low dielectric constant polymer for integrated circuits



k ~ 2.7

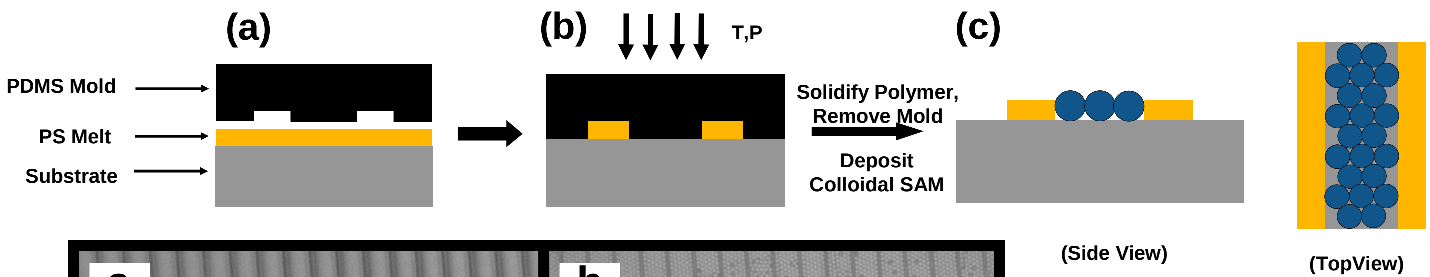
Eliminates need for etching of low-k, a problematic step

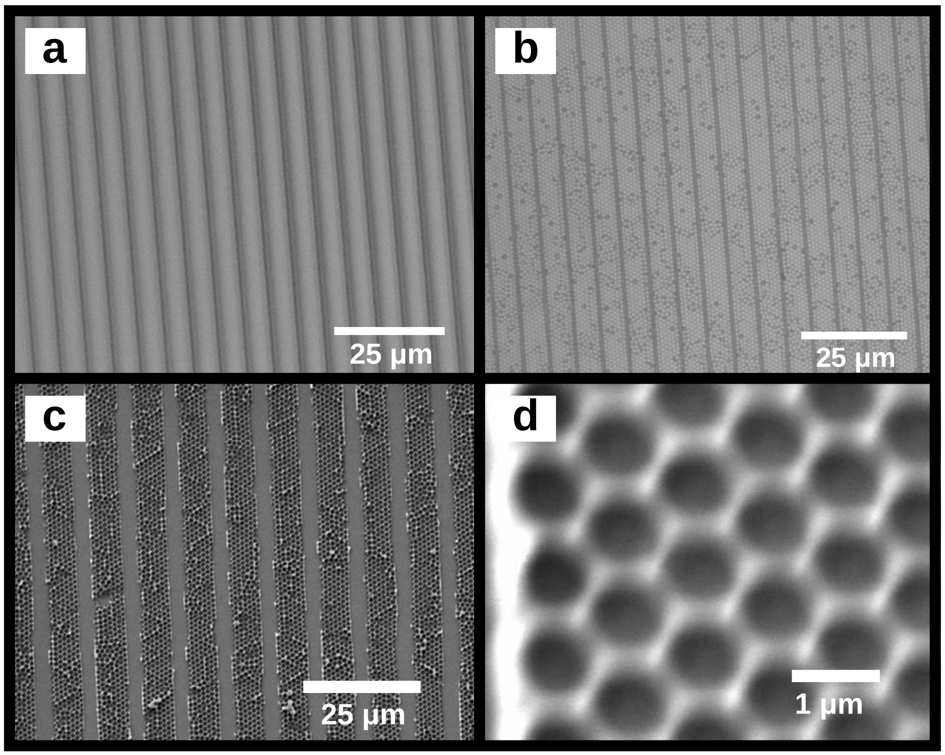
Low k patterns developed in IPA!

Trujillo, Baxamusa, Gleason, *Chem. Mater.* (2009)

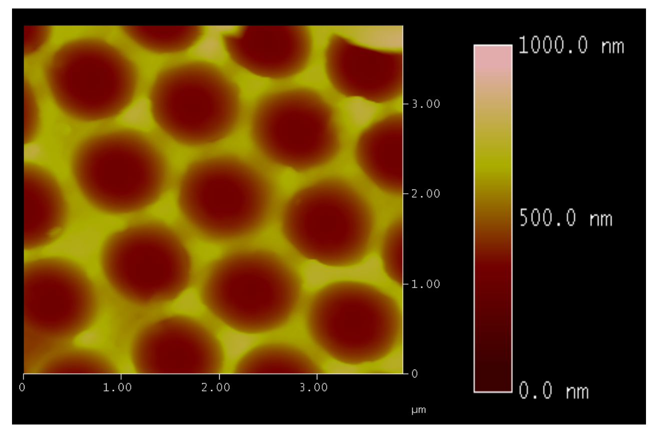
Multi-scale patterned low-k by template assisted assembly

“Top Down” helps “bottom-up”: Capillary Force Lithography Template





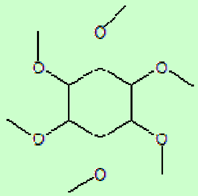
- *Multi-scale low-k features that are spatially addressable.*
- *No Conventional Lithography!*



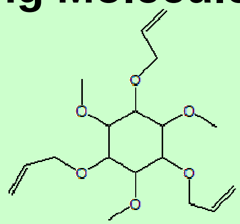
Deliverables from previous two years

✓ **Prepared (Ober) and assessed new porogens for ULK materials compatible with scCO2 processing**

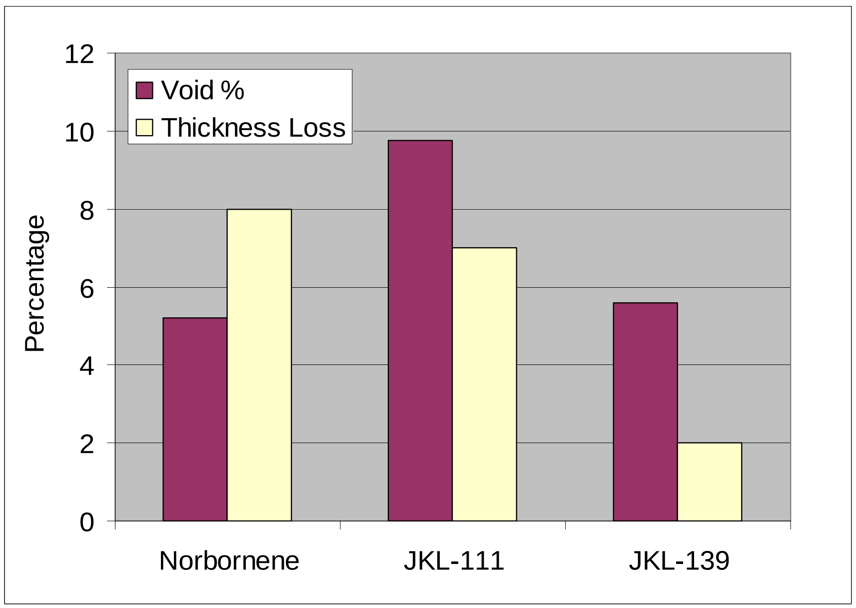
Novel Pore Generating Molecules



Hexamethyl ether of *myo*-inositol
JKL-111

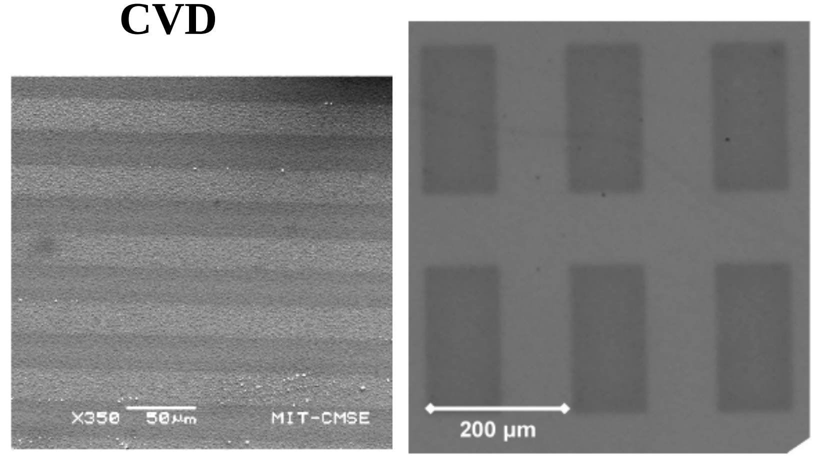


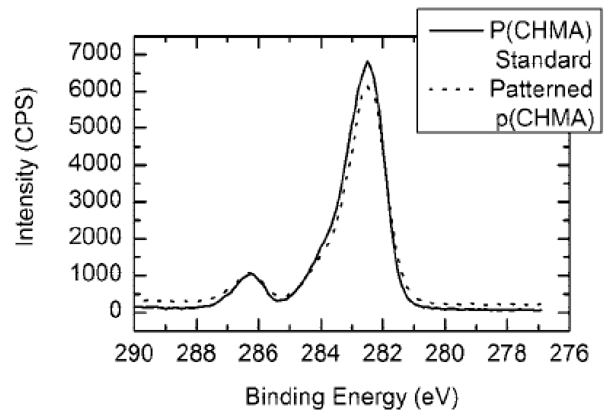
JKL-139



Porogens assessed within iCVD V3D3 matrix

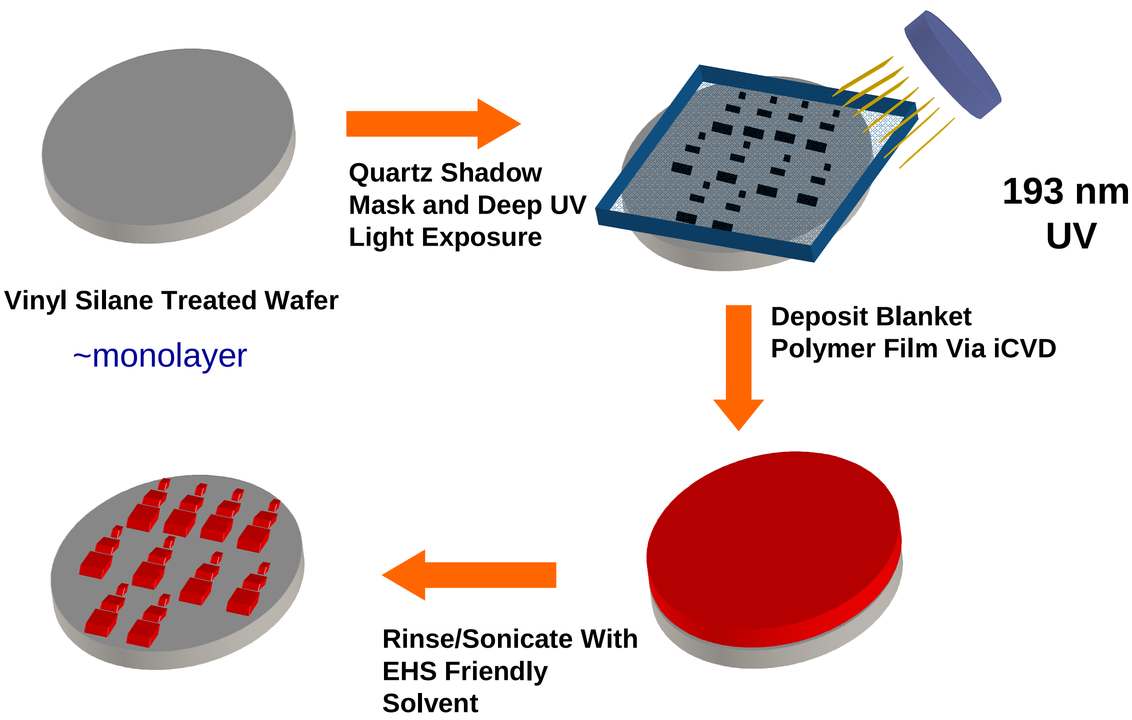
✓ **Demonstrated additively patterned films by photo initiated CVD**

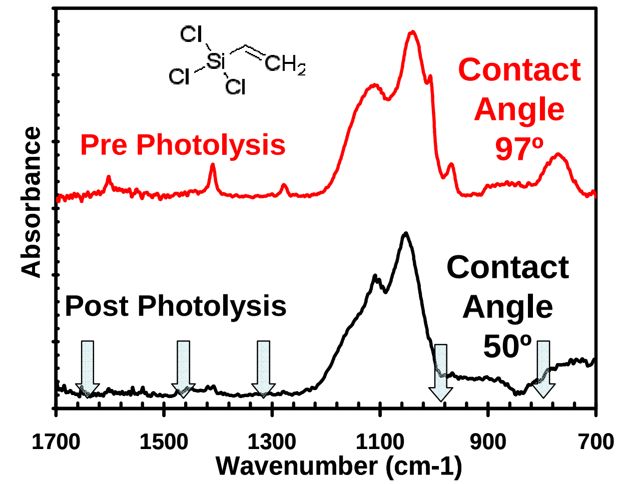


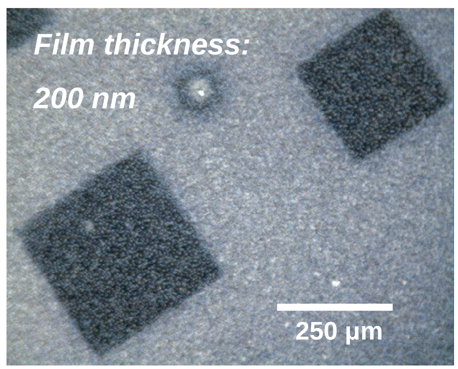


O'Shaughnessy, Baxamusa, Gleason, *Chem. Mater.*, (2007)

Deliverables: Resist-Free Photolithography







✓ **Developed a patterned template by non conventional lithography and demonstrated structure retention in the patterned film**

Dose at 193 nm	
Traditional Photolithography:	**15 mJ/cm²**
Resist-Free Photolithography:	**0.8 mJ/cm²**

Industrial Interactions and Technology Transfer

- **Qingguo Wu, Technologist: Novellus Systems Inc. Obtained hardness and k data.**
- **Dorel Toma, Director, US Technology Development Center, Tokyo Electron Limited.**
- **Junjun Liu, Research Scientist, US Technology Development Center, Tokyo Electron Limited.**
- **Pravin Narwankar, CTO & Investment Manager, Applied Materials in India New Business and New Products Group, Applied Materials**

Tokyo Electron Ltd. (TEL) has developed a prototype iCVD tool for back end of the line processes on 300 mm diameter wafers. More details will be announced at the invited talk by TEL at the International Interconnect Technology Conference (IITC) in Hokkaido, Japan, June 1 to 3.

Future Plans

✓ **Multi-scale colloidal patterning of V4D4 demonstrated incorporation of "built in" porogen during selective deposition**

✓ **Have demonstrated organo-silicon glass (OSG) with robust electronic and mechanical properties**

For project expiration in April we are:

•incorporating molecular porogen (CHMA) into patterned low *k* material to reduce *k* value further

•having pore size/distribution measured for cured V4D4 films with and without molecular porogen (TEL)

Long-Term Plans

- **Modify deposition/curing conditions for optimal thermal stability of V4D4 films**

Publications, Presentations, and Recognitions/Awards

PUBLICATIONS

- S 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
- Nathan J. Trujillo, Salmaan Baxamusa, Karen K. Gleason, “Grafted Polymeric Nanostructures patterned Bottom-Up by Colloidal Lithography and Initiated Chemical Vapor Deposition” Chem. Mater.(2009).
- Nathan J. Trujillo, Salmaan Baxamusa, Karen K. Gleason, “Multi-Scale Grafted Polymeric Nanostructures patterned Bottom-Up by Colloidal Lithography and Initiated Chemical Vapor Deposition Mat. Res. Soc. Symp. Proc. Boston, MA, (2008).
- Nathan J. Trujillo, Salmaan Baxamusa, Karen K. Gleason, ” Grafted Polymeric Nanostructures Patterned Bottom-Up by Colloidal Lithography and Initiated Chemical Vapor Deposition (iCVD) . Thin Solid Films: Special Edition- HWCVD5 Proceedings, 2009

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
- Nathan J. Trujillo, Resist-Free Patterning of Low Dielectric Constant and Functional Polymers by Initiated Chemical Vapor Deposition (iCVD) “Hot Wire CVD conference, 2008, Boston MA
- Nathan J. Trujillo, Multi-Scale Grafted Polymeric Nanostructures patterned Bottom-Up by Colloidal Lithography and Initiated Chemical Vapor Deposition, Poster Session BB Materials Research Society Fall Meeting 2008, Boston MA
- Nathan J. Trujillo and Karen K. Gleason, ERC TeleSeminar, "Depositing and Patterning a Robust and ‘Dense’ Low-*k* Polymer by iCVD ", December 11, 2008

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**
- **Jeongnam Han, Visiting Scholar, Samsung Electronics Co. Ltd.**
- **Omid Mahdavi, Micro/Nano Fabrication Center, UA**
- **Junseok Chae, Electrical Engineering, ASU**

Graduate Students:

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

Cost Share (other than core ERC funding):

- **NSF, Freescale, Samsung, Pall, EMC**

Objective and Approach

Objective:

- **Investigate the fundamentals of 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.**

Method of Approach:

- **Develop and apply a metrology method for in-situ and real-time monitoring of the dynamics of impurity transport inside micro- and nano-structures.**
- **Combine metrology with process modeling to identify the controlling steps (bottlenecks) in the cleaning, rinsing, and drying of small structures.**

ESH Metrics and Impact

I) Basis of Comparison:

Current Best Technology: Current rinse monitoring is primary through conductivity measurements in the rinse tool (tank) and the outlet of the tank; the fundamentals of rinse and chemical removal from micro-structures are poorly understood; there is currently no technology available for direct real-time monitoring of rinse process.

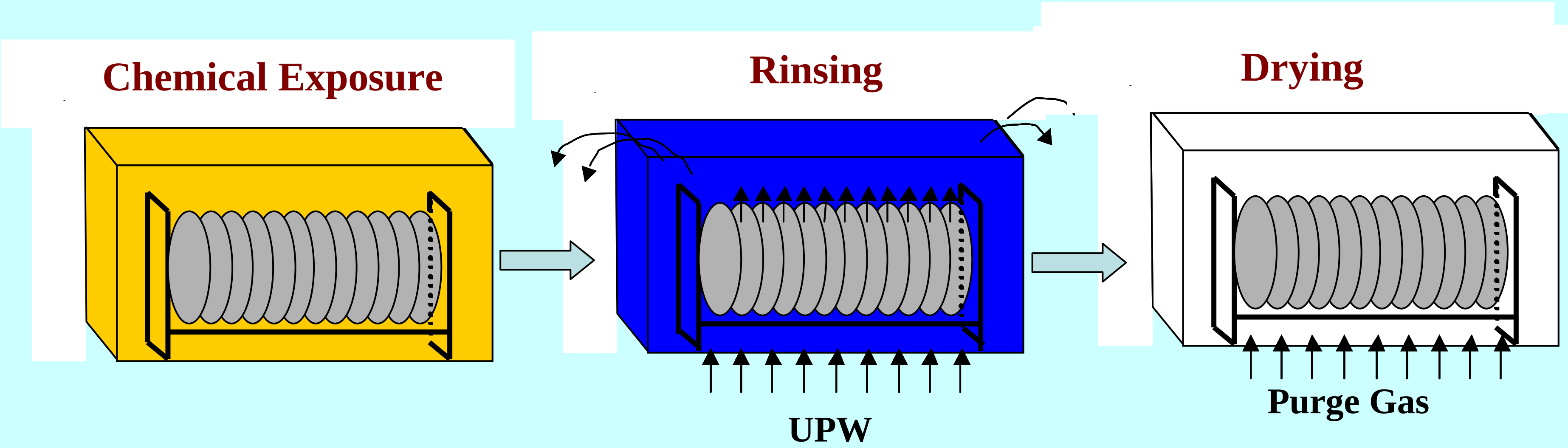
II) Manufacturing Metrics

Over 80% of the ultra pure water in the fab is used for wafer rising. Improvement in the rinse process and technology to monitor and control the rinse effectiveness will have significant impact on saving water, reducing cost, and improving performance through contamination control and defect reduction. Understanding the rinse fundamentals will also enable development of new rinse and wafer cleaning technologies.

III) ESH Metrics

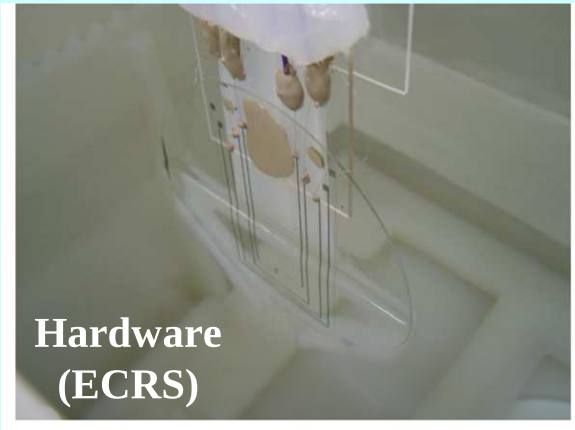
	Usage Reduction			Emission Reduction			
Goals / Possibilities	**Energy**	**Water**	**Chemicals**	**PFCs**	**VOCs**	**HAPs**	**Other Hazardous Wastes**
Optimized rinse enabled by in-situ rinse monitoring	50%	70%	At least 20% reduction in regeneration chemicals	N/A	N/A	Some reduction in acid vapors	20% reduction in regeneration waste/ and wastewater

Conventional Surface Preparation



- No real time and in-situ metrology is available to monitor the extent of cleaning drying.
- The in-situ metrology is key to development of ESH-friendly surface preparation processes, particularly for patterned wafers.

Novel In-situ Metrology (ECRS)



+

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 :

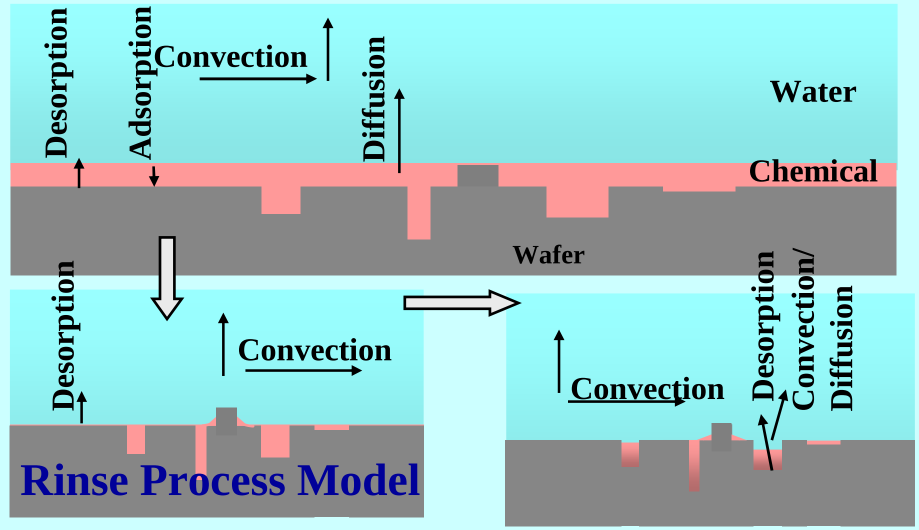
$$V \frac{\partial C_b}{\partial t} = Q(C_{in} - C_b) + A \cdot Flux$$

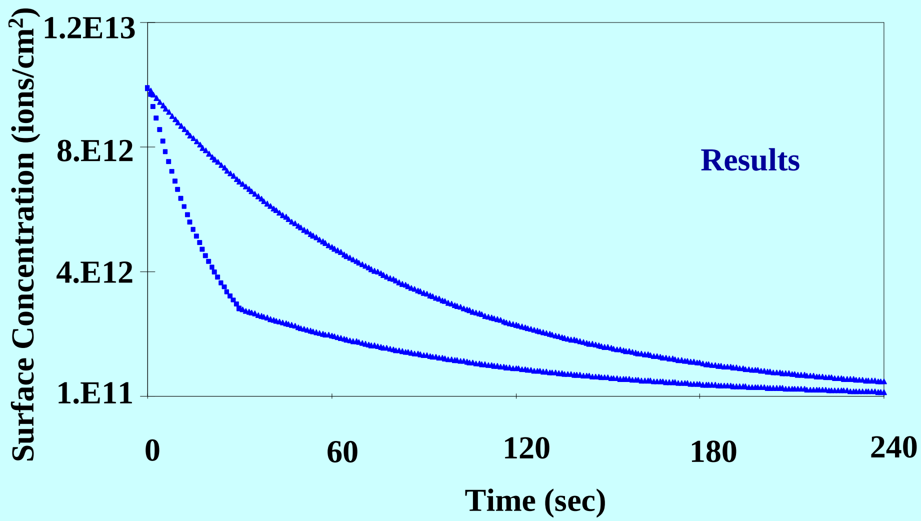
Surface adsorption and desorption:

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

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

Software

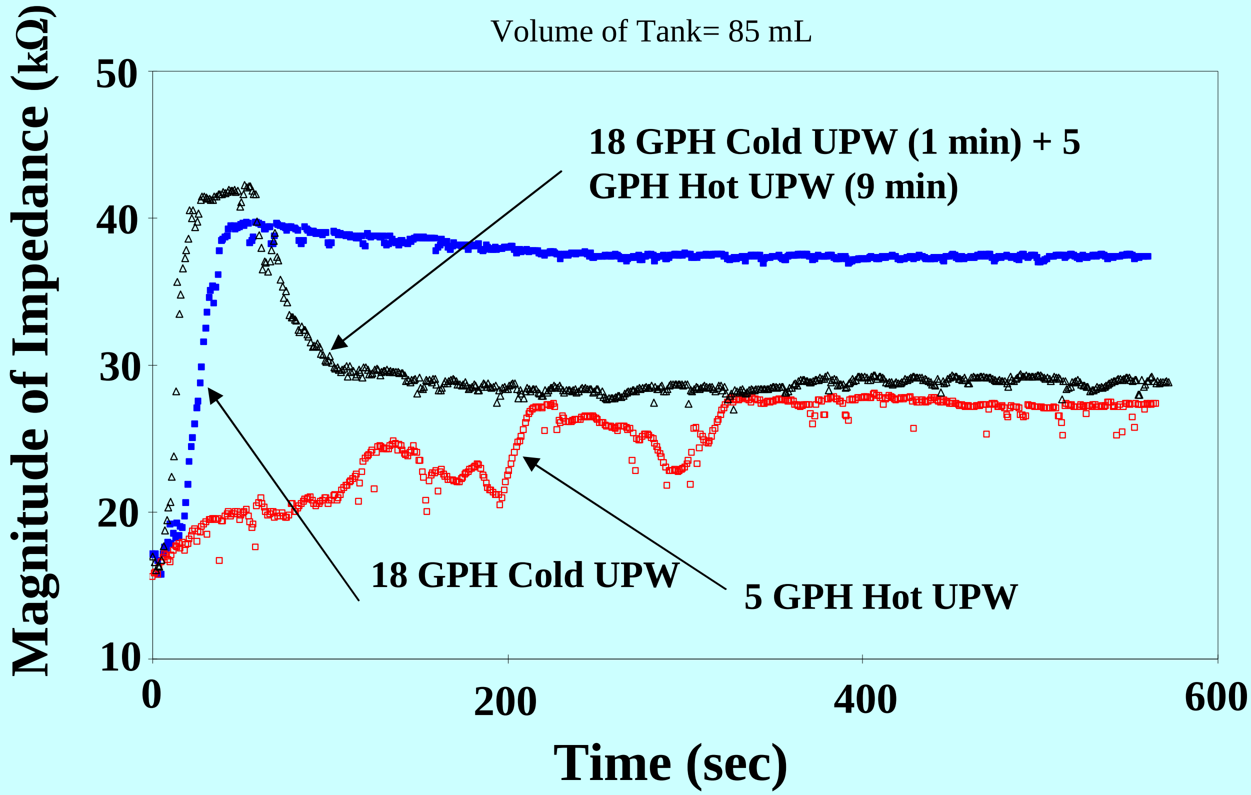


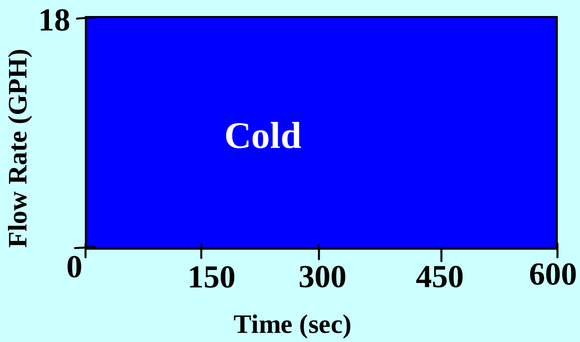


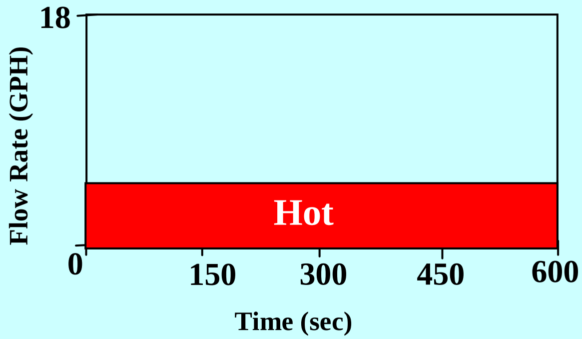
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

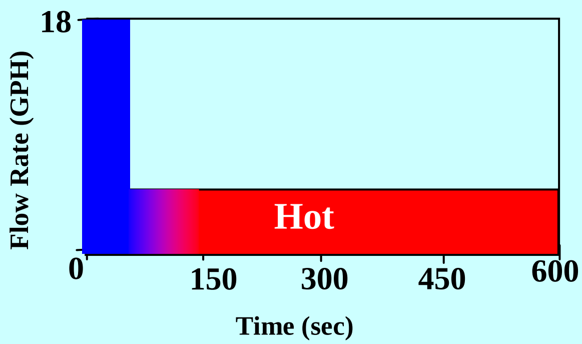
Effect of Flow and Temperature

Post SC-1 Rinsing



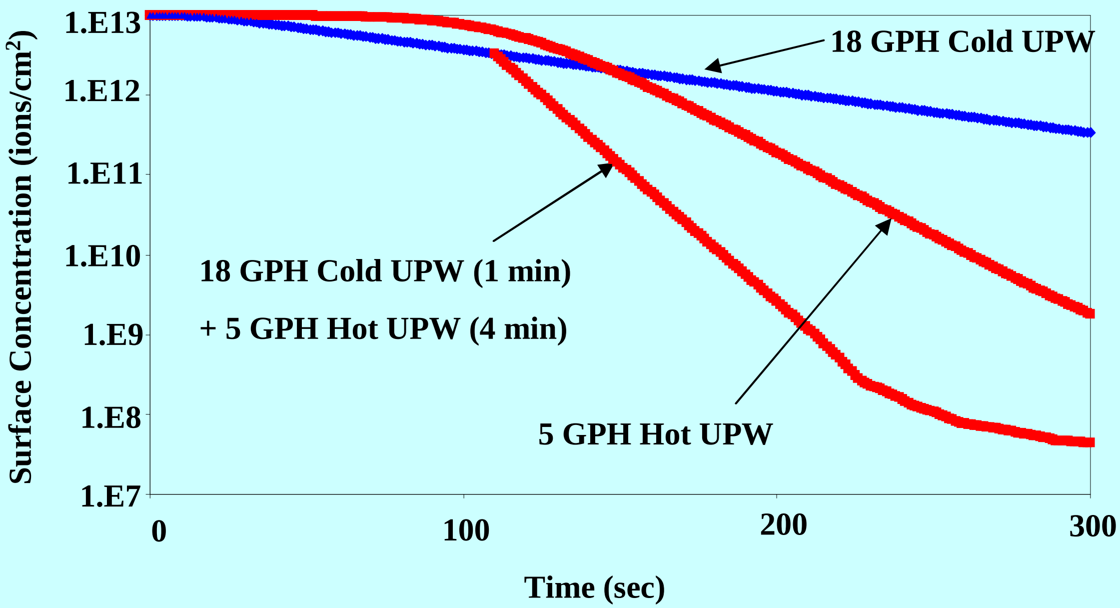


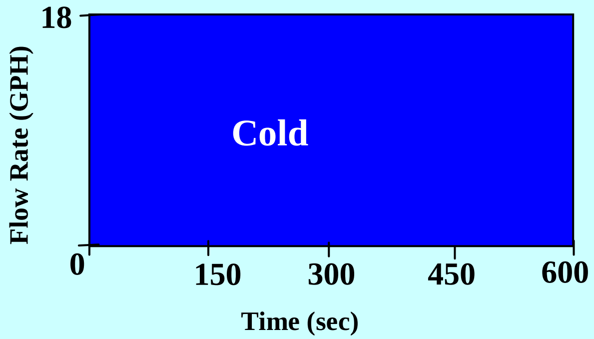


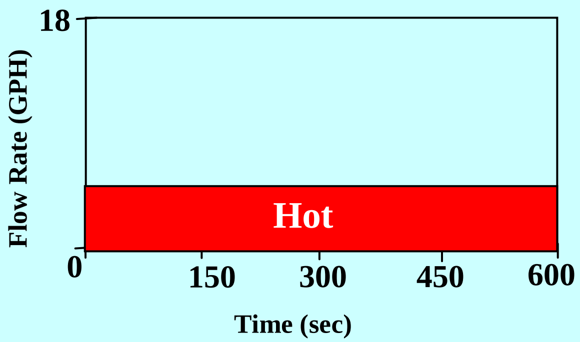


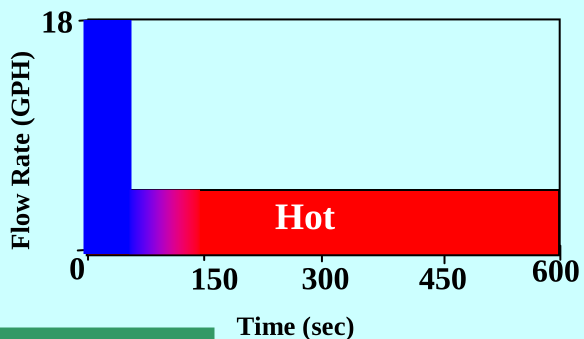
New Staged Rinse Process

Post SC-1 Rinsing







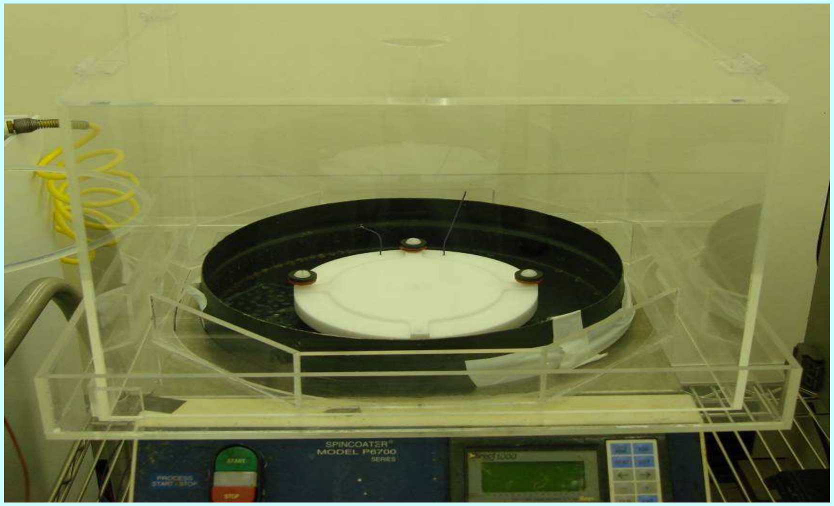


Recipe	Cold UPW	Hot UPW	Staged Flow
Surface Contamination	1	< 0.01	< 0.0001

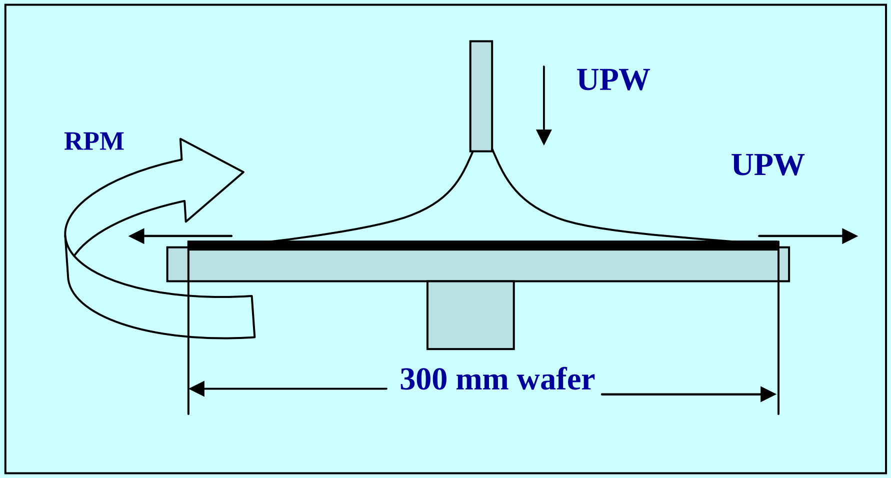
Less water and higher throughput by staged hot/cold rinsing process

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Application of ECRS to Single Wafer Spin Rinsing and Drying



Experimental Setup



Process Model Schematic

- A single wafer tool equipped with ECRS is designed and set up.
- Combination of experiments and process model is used to study the effect of various process parameters.

Mathematical Analysis of Spin Rinsing

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 film concentration :

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

Where film volume:

$$V = A{*}h = A{*}\,0.909 \cdot \left(\frac{2 \cdot \mathrm{Re} \cdot \nu^2}{D \cdot w^2} \right)^{0.33}$$

Surface adsorption and desorption:

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

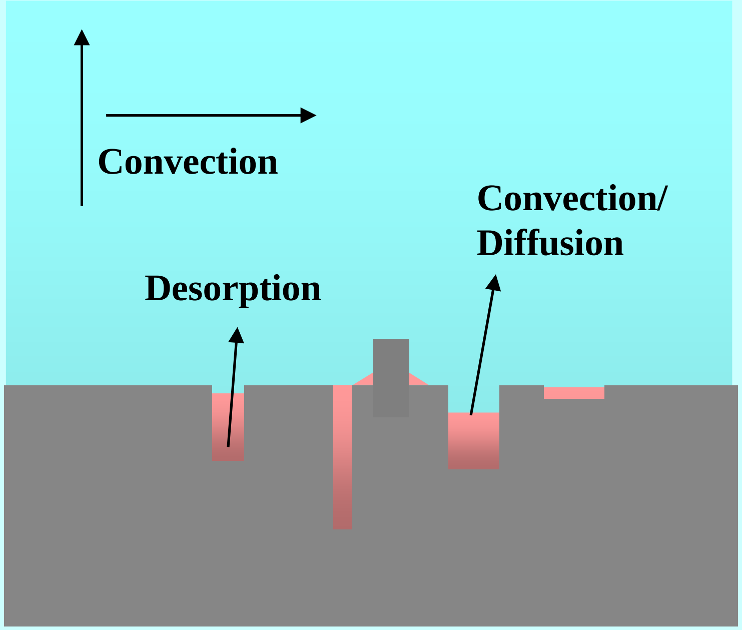
Poisson equation: $\nabla^2 \varphi = -\frac{\rho}{\varepsilon}$

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

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

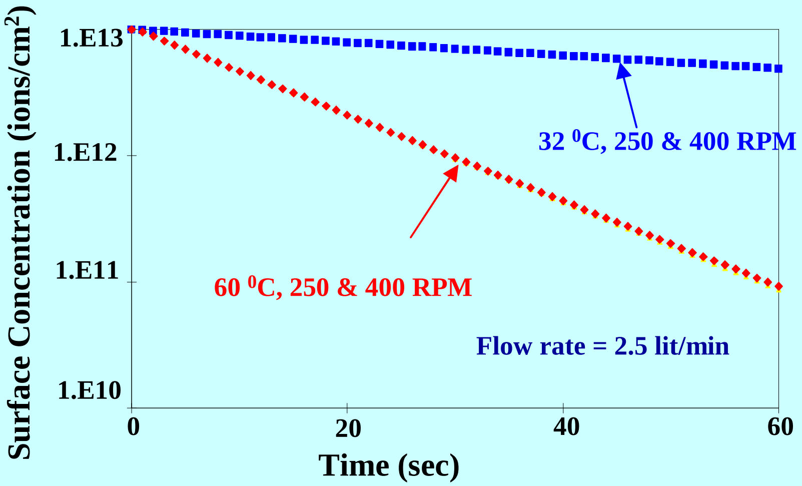
where electrical conductivity: $\sigma = \sum_i \lambda_i C_i$

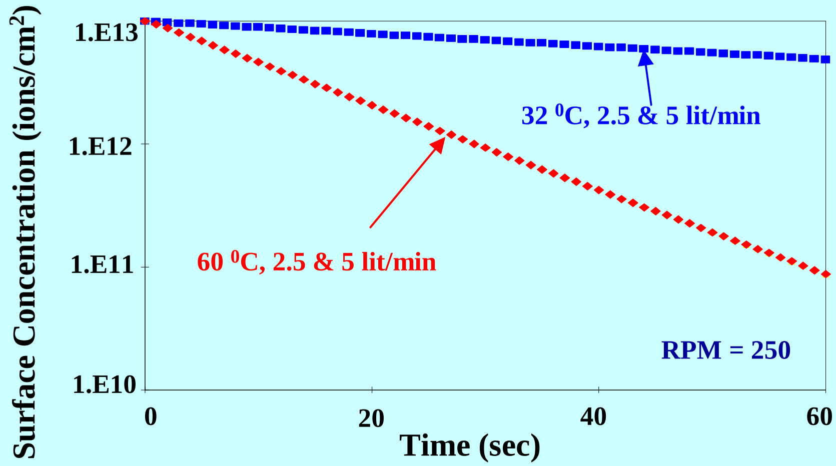
- **Surface Charge**
- **Diffusion**
- **Surface reaction**
- **Ionic transport**

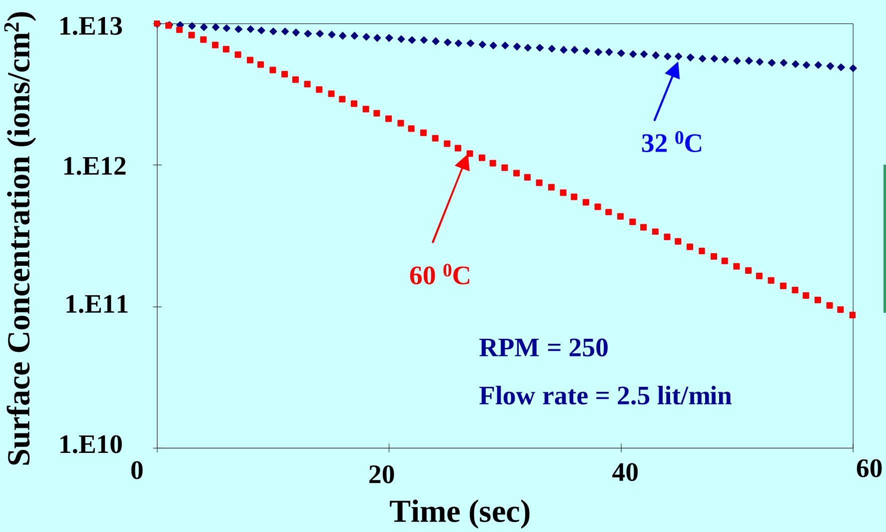


Spin Rinse Process Parameters

Post SC-1 Rinse



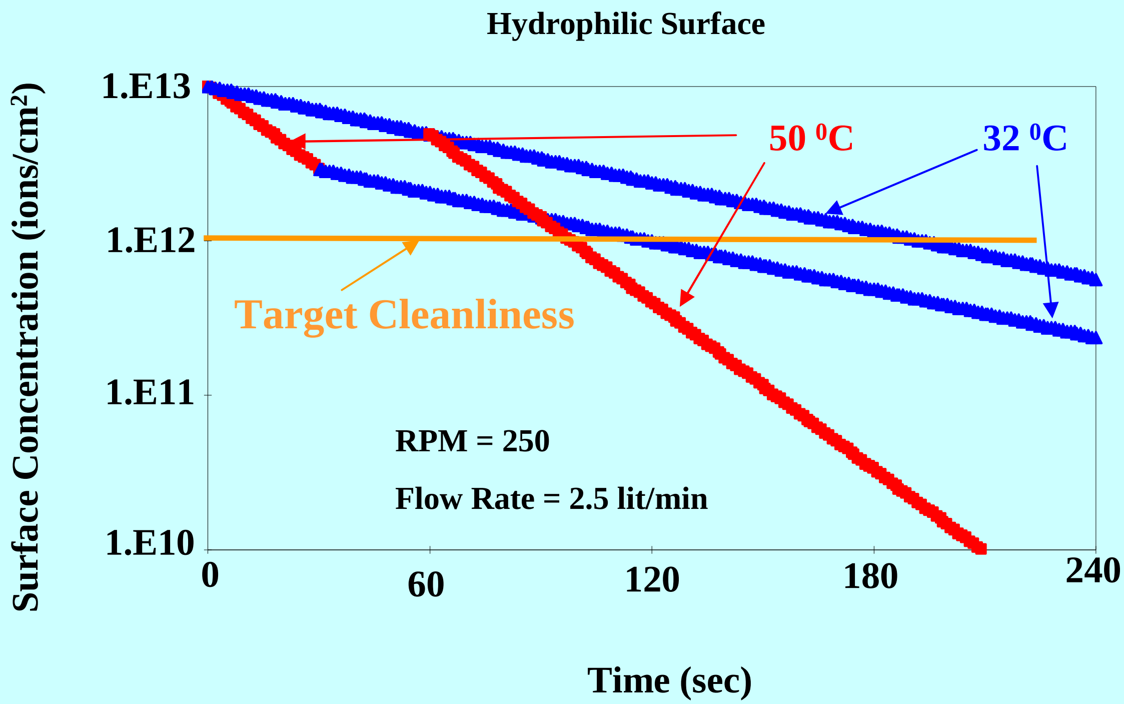


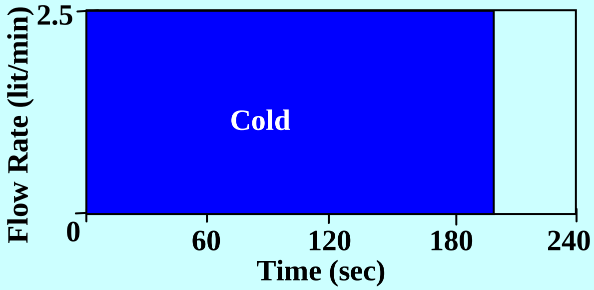


- Temperature has significant impact on cleaning
- RPM and flow rate has less impact on cleaning

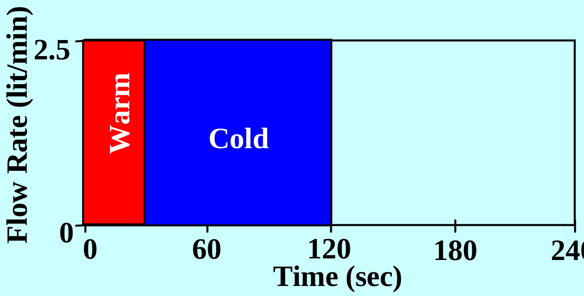
Benefits of Staged Rinsing

Post SC-1 Rinsing





1



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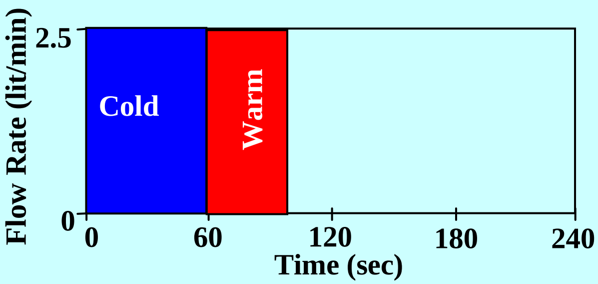
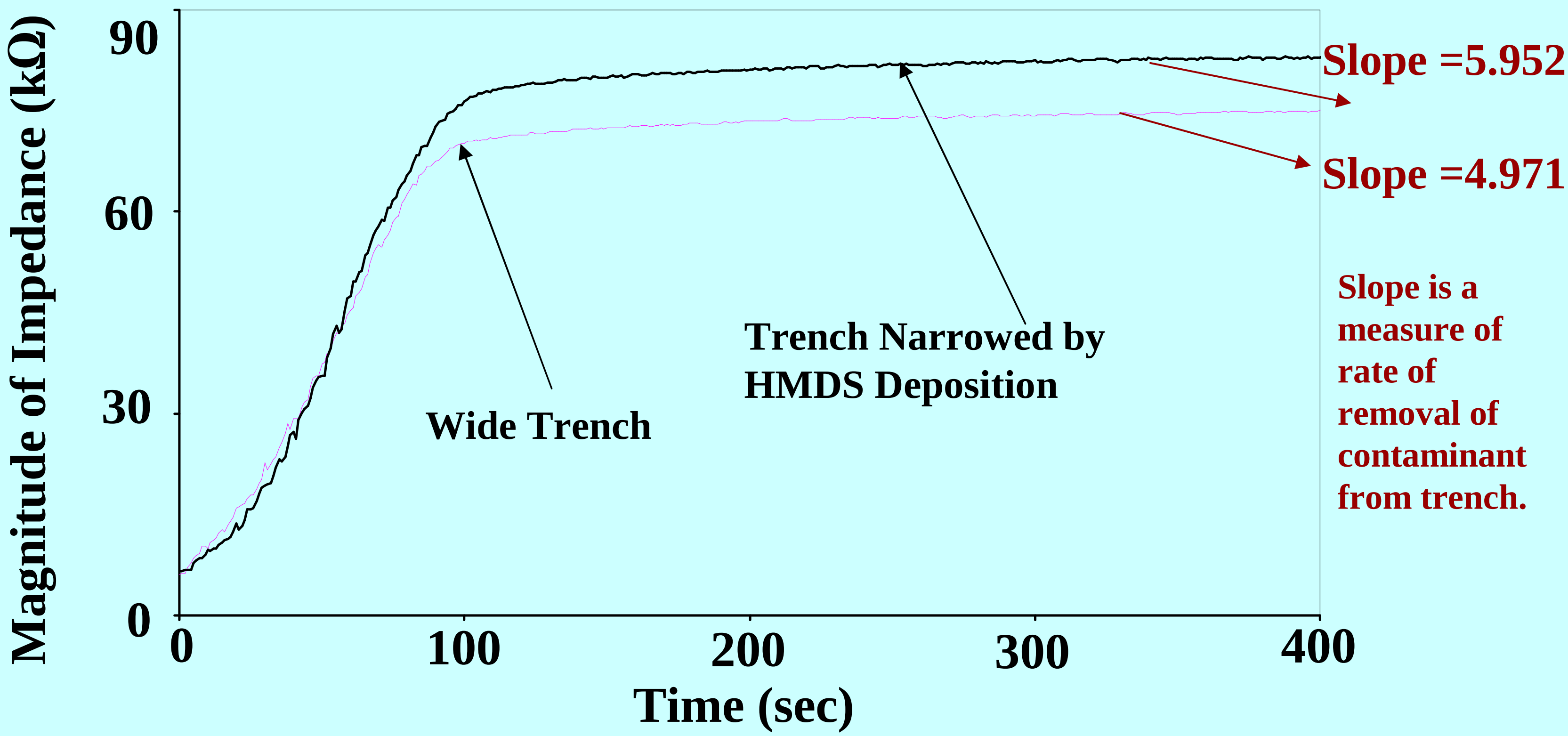


- Staging temperature of UPW decreases rinse time without sacrificing cleanliness
- To reach 1.E12 ions/cm^2, staged rinsing leads to water savings of 40% for staged rinse “1” and 50% for staged rinse “2”.

Effect of Trench Width on Rinsing

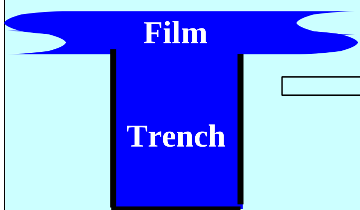
Post SC-1 Rinsing using Cold UPW

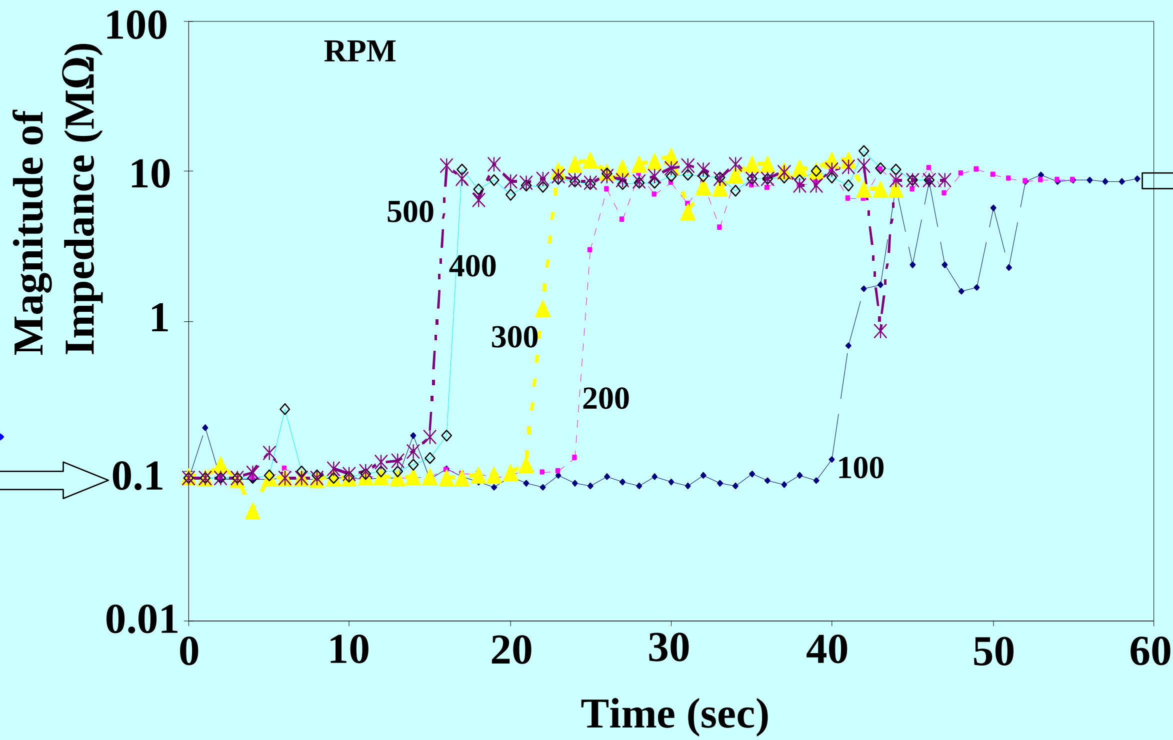


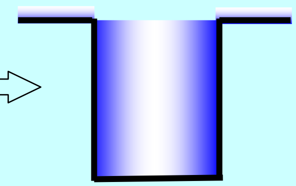
- The rinse process becomes slow as feature size decreases
- ECRS can be used to determine the size effect.

Effect of Spin Rate on Drying

Filled Trench





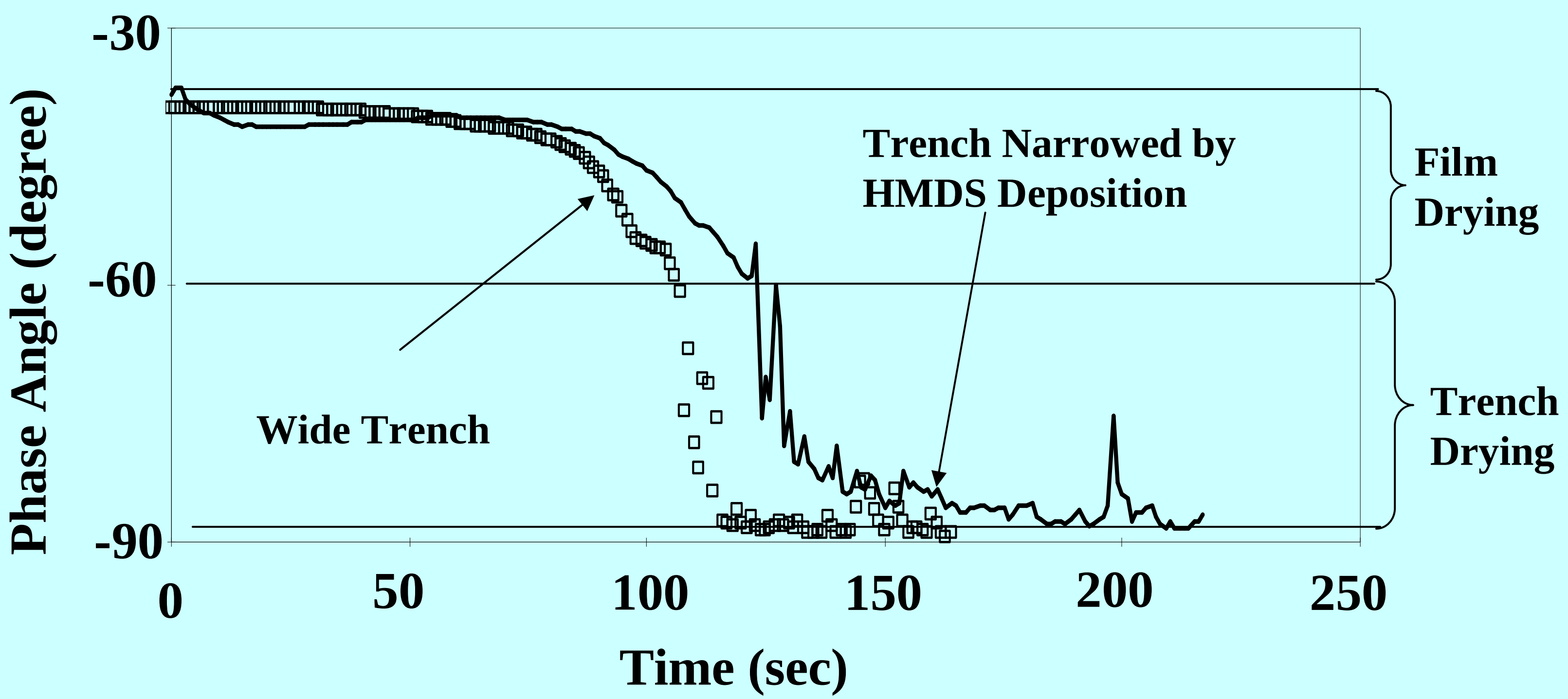


Empty Trench with adsorbed water molecules

- ECRS can be used to monitor spin drying.
- The effect of spin rate on drying is more pronounced in the low RPM range.

Effect of Trench Width on Drying

Drying after SC-1 Rinsing

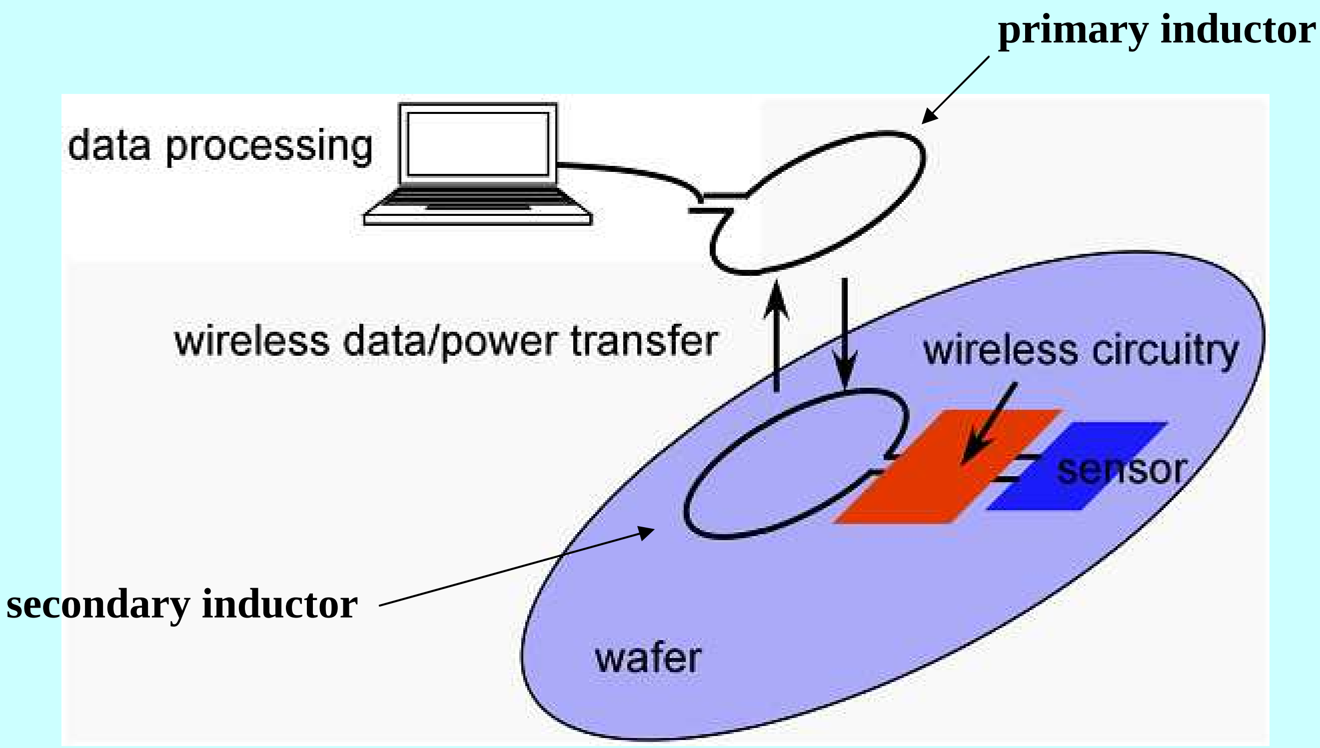


- **Time required for phase angle to go from -60 degree to -90 degree is 90 sec for narrow trench and 20 sec for wide trench.**
- **Drying time increases as feature size decreases**

Future Plans for the ECRS Technology and Technology Transfer

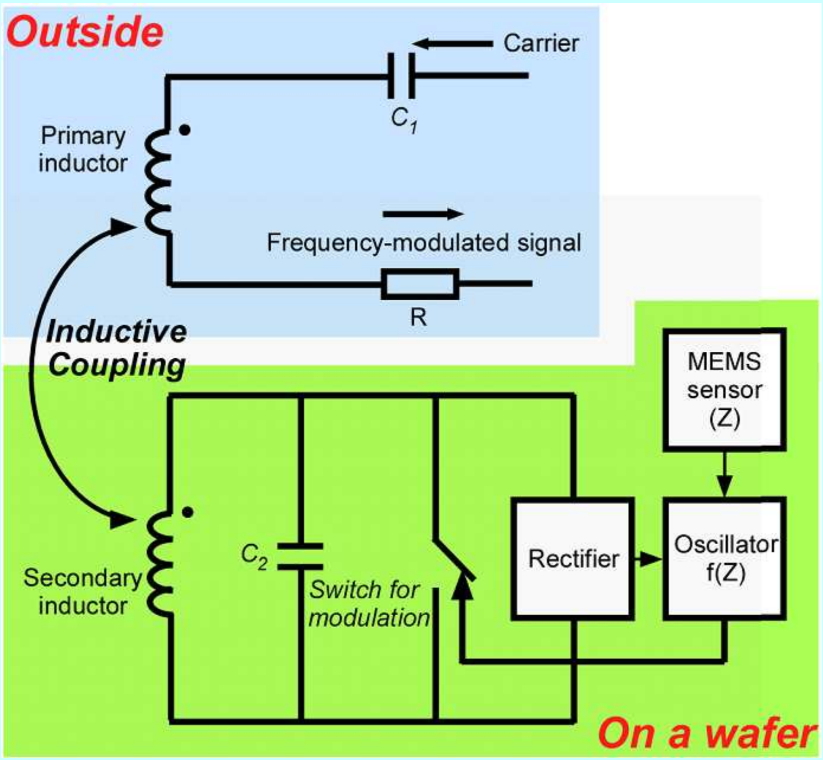
Remote Measurement of ECRS Impedance

- **Wireless passive telemetry using inductive coupling**
- **ECRS and wireless circuitry are on the same wafer to maintain the form factor**



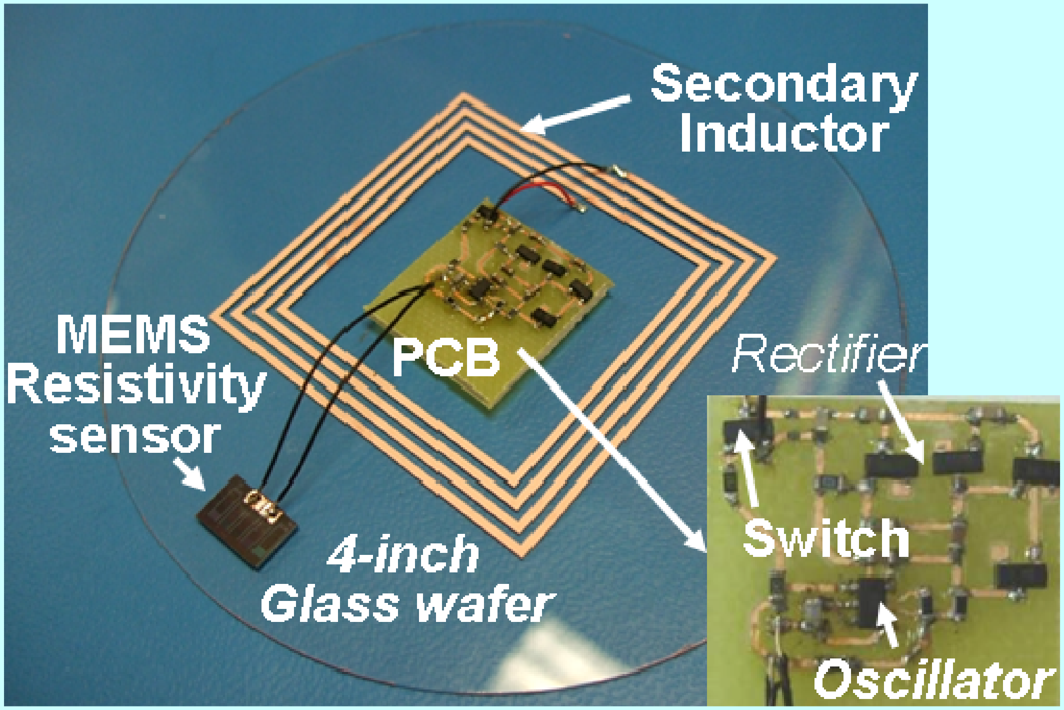
System Overview

- Carrier supplied by external primary coil (13.56 MHz)
- Rectifier converts some RF power to DC
- Residual impurity concentration is measured by ECRS impedance
- Impedance is converted to frequency by local oscillator (kHz range)
- Local oscillator modulates carrier
- Modulation frequency is measured in the primary

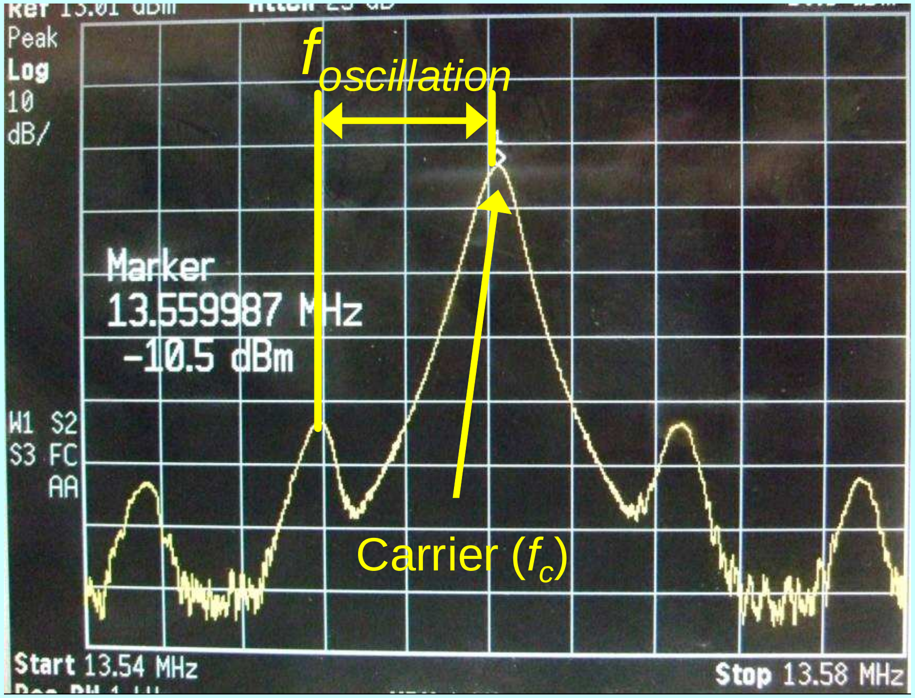


Prototype Fabrication and Assembly

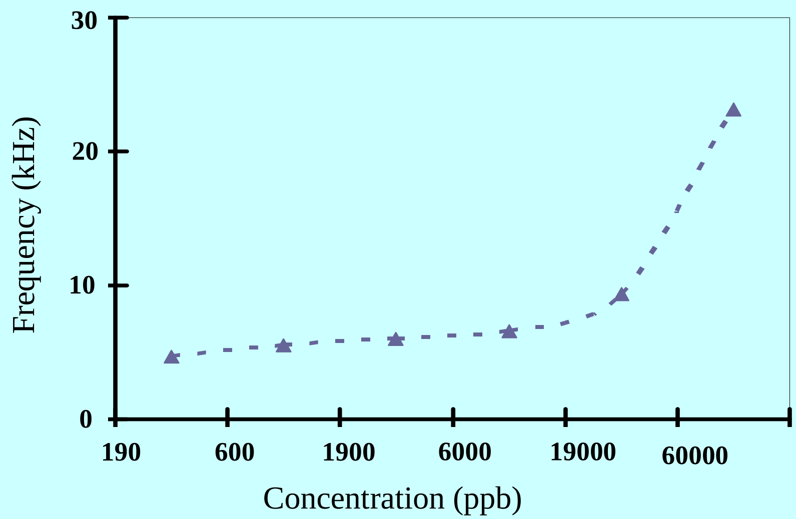
- **Substrate: 4 inch fused silica wafer**
- **Sensor: poly-silicon and SiO_2 on insulated substrate**
- **Inductor: electroplating**
- **Circuitry: PCB**



Remote Measurement of ECRS Impedance



Measured Spectrum of primary signal for 600 ppb solution



Remotely measured response

A fully passive wireless ECRS prototype has been demonstrated

Industrial Interactions and Tech Transfer

- **EMC spin-off company is formed for tech transfer and commercialization of ECRS technology**
- **Joint work with Freescale and EMC on implementation of new low-water rinse processes using ECRS and process modeling developed in this project (Hsi-An Kwong, Marie Burnham, Tom Roche, Amy Belger, Stuart Searing and Georges Robert)**
- **Joint work with Samsung on application of ECRS and process modeling for optimizing rinsing and drying of high-aspect ratio features for both hydrophilic and hydrophobic surfaces (Jeongnam Han).**
- **Other planned tech transfer: Pall and SEZ**
- ***Next Phase: Development of a fully integrated wireless ECRS***

Publications and Presentations

- Yan J., Dhane, K., Vermeire, B., Shadman, F., "In Situ and Real Time Metrology during Cleaning, Rinsing, and Drying of Micro- and Nano Structures", *SEMATECH Surface Preparation and Cleaning Conference*, April-2008
- Yan, J., Dhane, K., Vermeire, B., Shadman, F., "In Situ and Real Time Metrology during Rinsing, Micro- and Nano Structures" *Microelectronics Engineering*, Vol. 86, Issue 2, February 2009, 199-205.
- Dhane, K., Han, J., Yan, J., Vermeire, B., Shadman, F., "Novel Metrology for Application in Wet Surface Preparation of Patterned Wafers", *SEMATECH Surface Preparation and Cleaning Conference*, March-2009- accepted for oral presentation.
- Han, J., Dhane, K., Yan, J., Vermeire, B., Shadman, F., "Rinse Behavior on Hydrophilic, Hydrophobic, and Mixed Patterned Surfaces", *SEMATECH Surface Preparation and Cleaning Conference*, March-2009- accepted for oral presentation.
- Dhane, K., Han, J., Yan, J., Vermeire, B., Shadman, F., "New Metrology for Process Optimization and Water and Energy Savings During Surface Preparation of Patterned wafers" *SESHA's 31st Annual Symposium*, May-2009- accepted for oral presentation.

Technical & Environmental Challenges in Nano Scale Semiconductor Manufacturing

Ann Kelleher
Intel Fab 12 Plant Manager

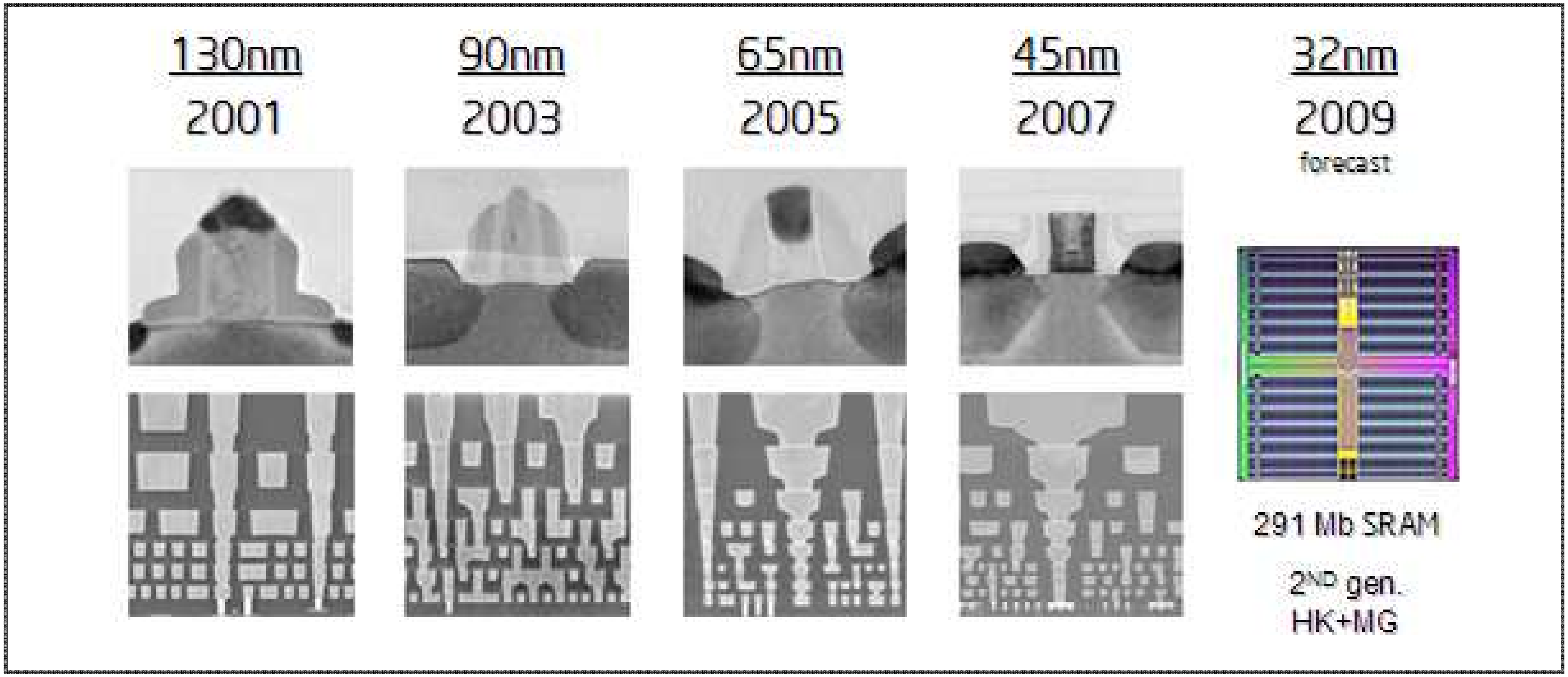
Agenda

- Intel HVM Overview
- Technical Challenges
- Environmental Challenges
- Summary

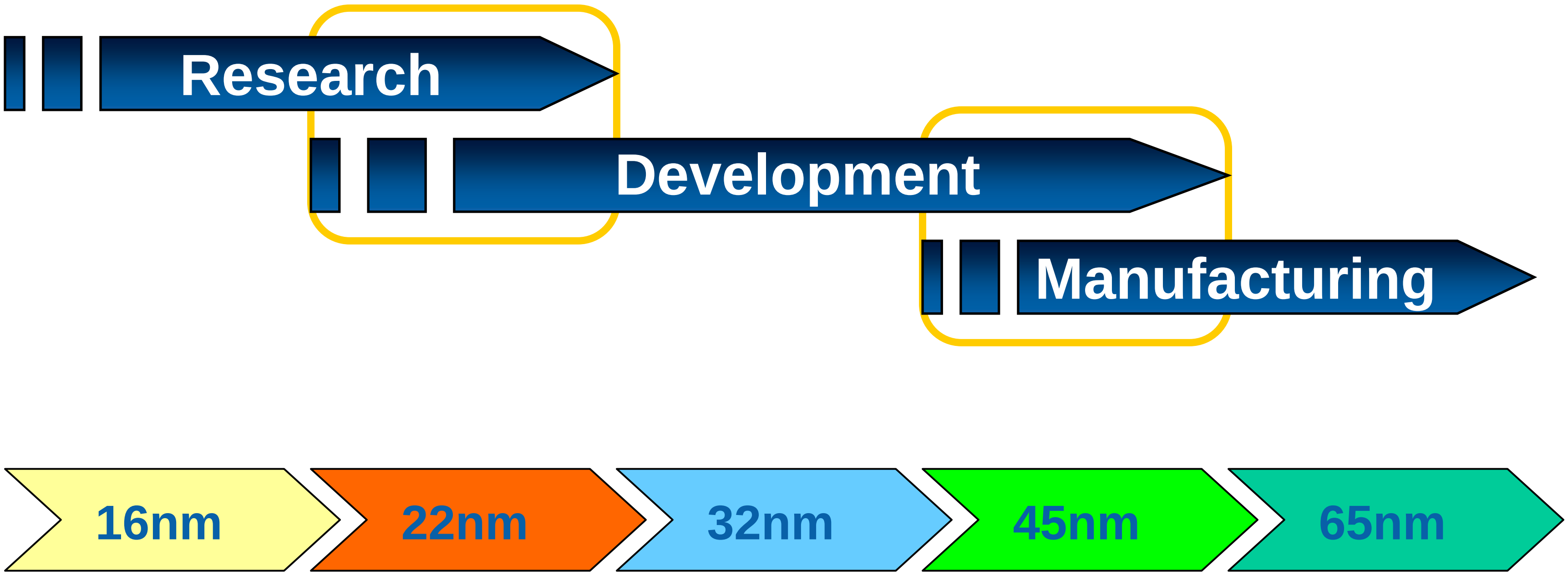
Wafer Fab and Assembly/Test Sites

Technical Challenges

- Development Cycle
  - 2 year new technology cadence
  - Development & HVM overlap



Intel's Silicon R-D-M Pipeline

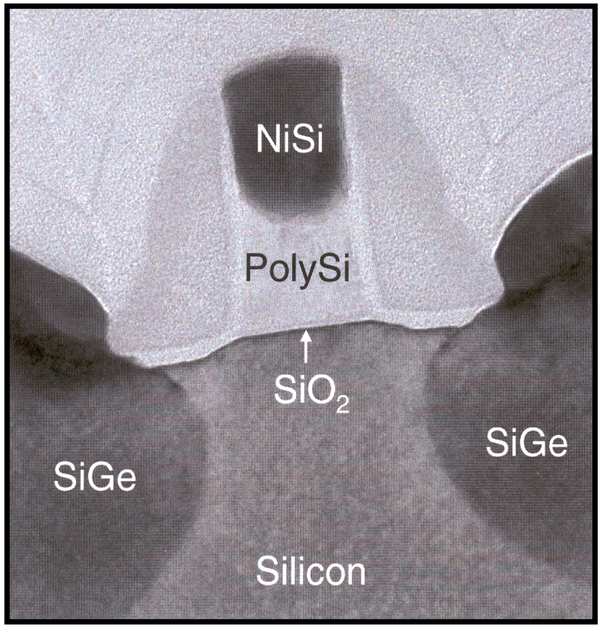


Continuous stream of new technologies in pipeline

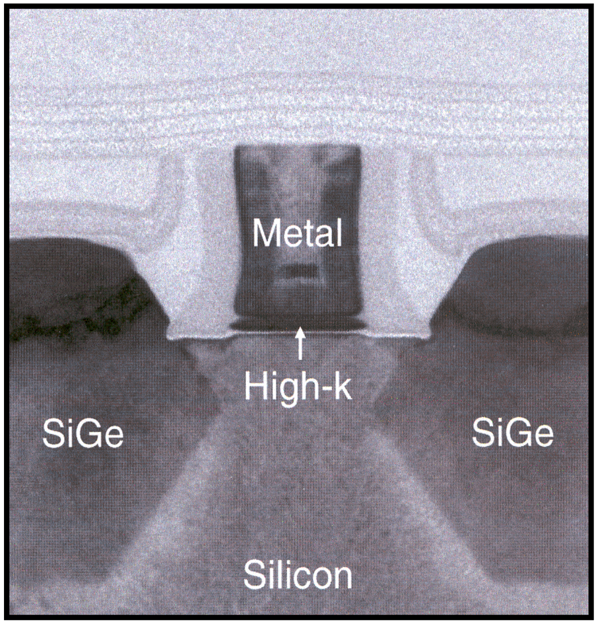
Technical Challenges

- Process Technology
  - Shrinking geometry sensitivity, new materials, new layers
  - Pattern, etch & clean geometries < lithography wavelength

65 nm Transistor



45 nm HK + MG



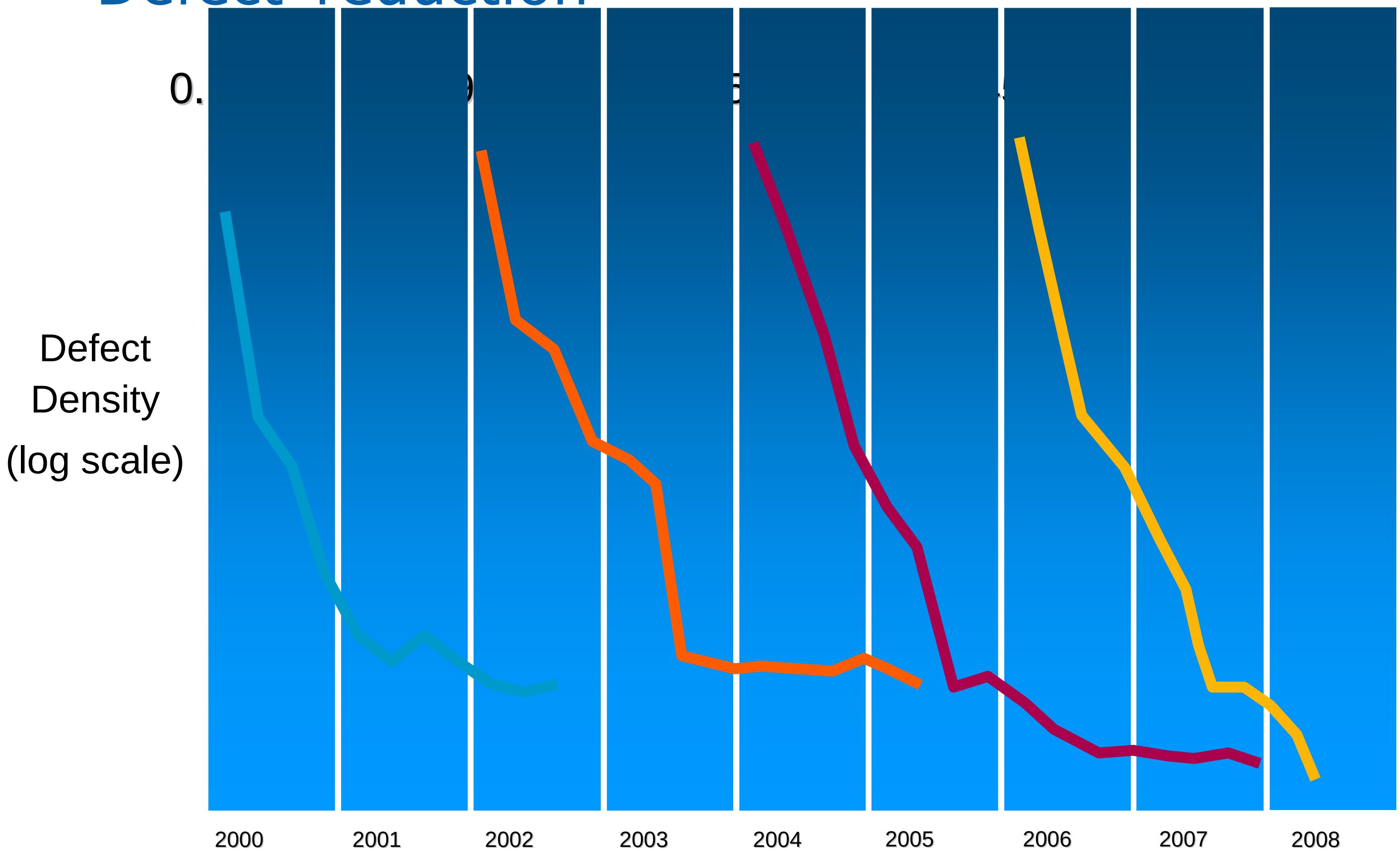
Hafnium-based high-k + metal gate transistors are the biggest advancement in transistor technology since the late 1960s

Technical Challenges

- Cost & Cycle Time Improvements
  - Alternative supplier qualification, in house development
    - Trace contaminant comparisons
    - Analytical equipment differences, lower detection limits
  - Cycle time reduction
    - Manufacturing waste elimination
    - Legacy monitors, que times
    - Risk of going too far, loosing signal visibility
  - Defect reduction learning rate reset with new technology

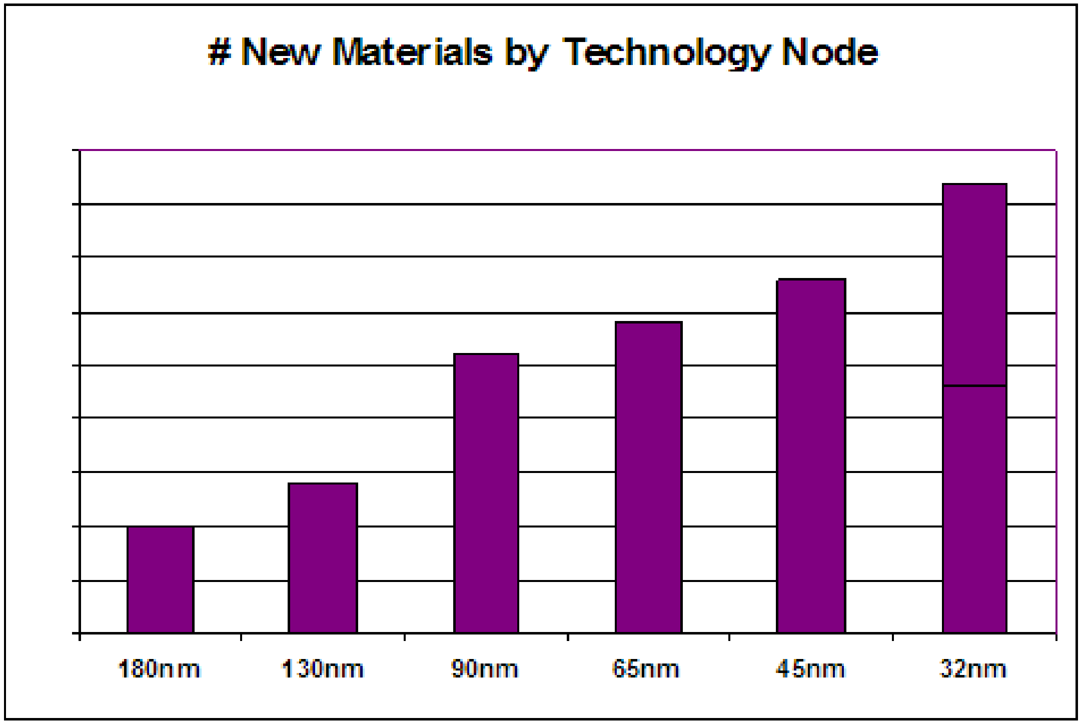
Technical Challenges

- Defect reduction



Technical Challenges

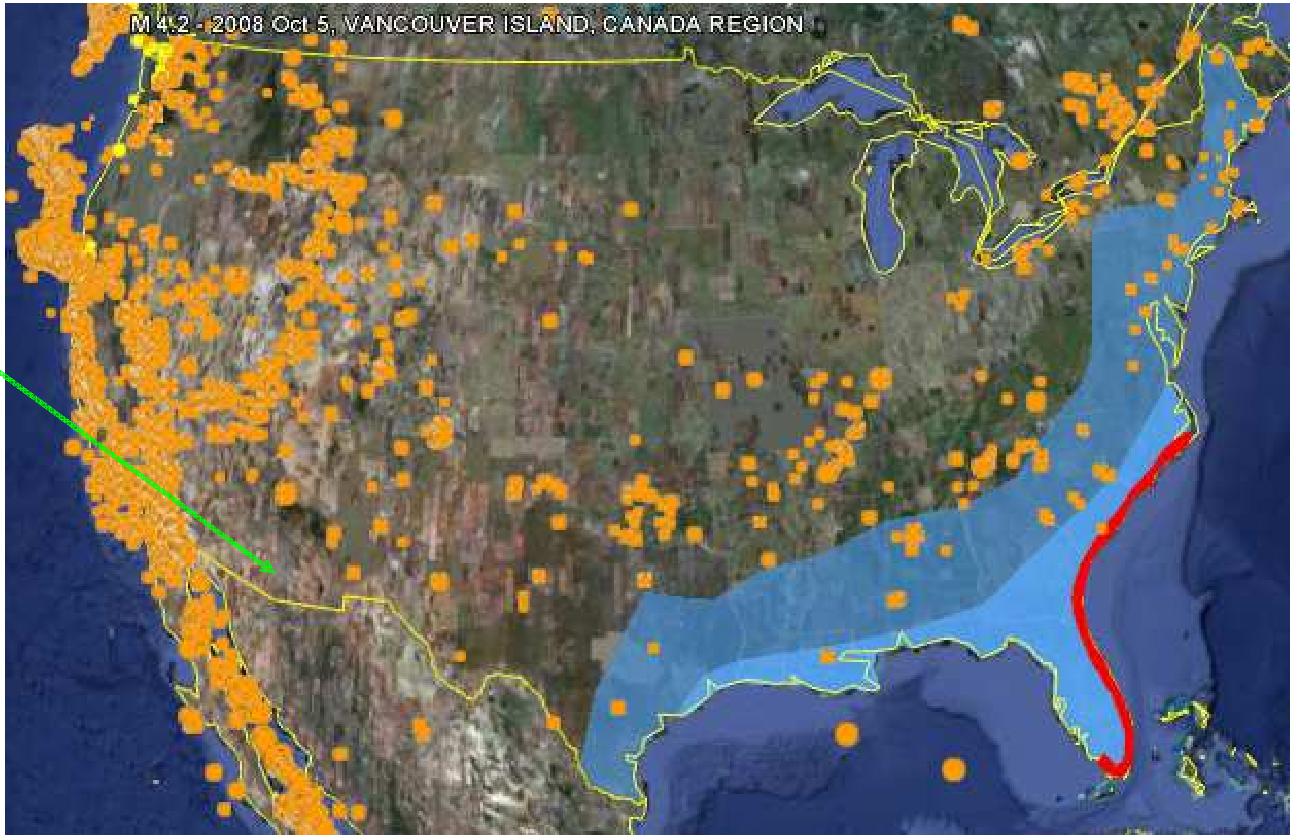
- Materials Supply Chain Challenges
  - New chemistries, suppliers with each technology
  - Quality requirement learning & gaps ("cherry picking")
  - Supplier health financially, environmentally



Technical Challenges

- Supplier disruption due to financial, environmental risks

(You're Safe)



4+ Mag Earthquakes 2005-2008

Hurricane History
- 20-40 every 100 yrs
- 40-60
- 60+

Environmental Challenges

- Increasing Water, Chemical & Gas Usage
  - Shrinking dimensions & defect reduction driving industry from batch etching/cleaning to single wafer processing
  - Single wafer chemical & water usage can increase 2-10X
  - Water recycling opportunities reduced (chemical concentration)
  - Increased waste water treatment, dealing with by products
  - Backend metal layer #s increases/becomes more complex, more PFC's are used for etch and CVD cleaning steps, additional abatement

Opportunities

  - Improved efficiency of chemical / water cleans, water recycle
  - Green alternatives for the cleaning chemicals & PFC's
  - More efficient, cost effective abatement technology

Environmental Challenges

- Energy Consumption
  - Lithography heading towards EUV per ITRS, higher energy use
  - Reduce overall utility demands for manufacturing tools
- Governmental & Customer Expectations
  - Green being used as marketing tool, differentiator, customer requests & demands to suppliers increasing
  - Government increasing action to make products “safer”
  - Nanomaterials – we all need to understand if there are any issues related to EHS and detection/metrology (in both the air & water)

Summary

- Challenges
  - Technology introduction cadence
  - Defect reduction
  - Chemical & Gas usage, cost, recycling & abatement
  - Analytical capabilities
  - Supply chain health, risks
  - Green expectations

There have been a few surprises, let’s work together to be better prepared for future challenges

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

(*Task Number: 425.022*)

PIs:

- **Yoshio Nishi, Electrical Engineering, Stanford University**
- **Srini Raghavan, Materials Science and Engineering, UA**

Part 1. Ge Surface Clean and Passivation

PIs:

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

Graduate Students:

- **Masaharu Kobayashi: PhD candidate, Electrical 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, high-k Ge gate stack**
- **Establish novel oxidation technique to grow high quality GeO_2 interfacial dielectric layer at low temperature**
- **Achieve clean interface between gate dielectric insulator and Ge substrate with low interface state density (D_{it})**

ESH Metrics and Impact

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:

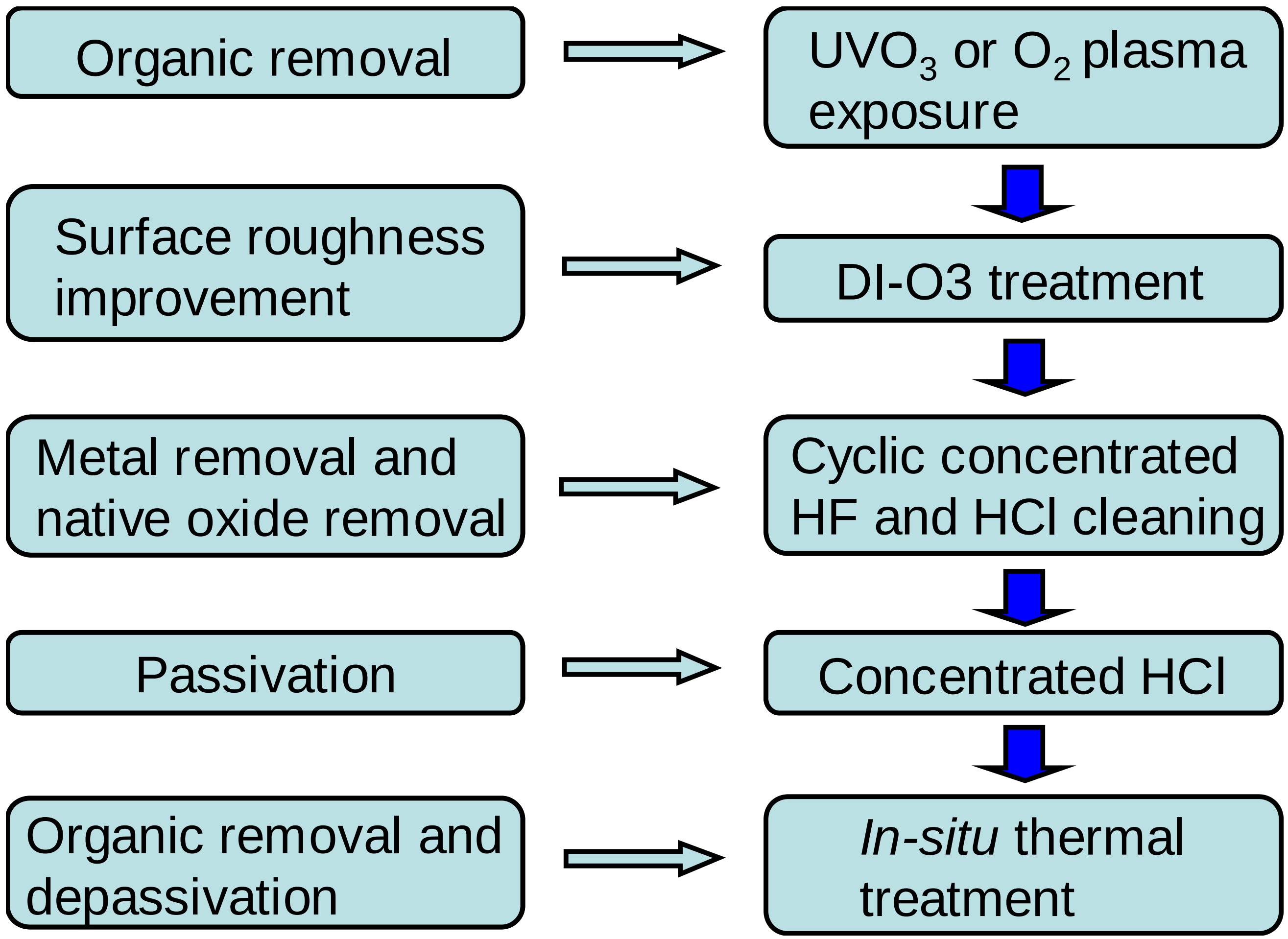
1. **Oxidation of Ge only costs oxygen. Compared to other novel surface passivation such as Si and P passivation by SiH_4 and PH_3 in CVD respectively, the poisonous gasses are not necessary to introduce.**
2. **Power reduction due to lower operating voltage which will reduce consumption of natural resources in energy generation.**

Importance of Ge surface clean/passivation

- Appropriate Ge surface clean is essential for reliable and high yield process.
  - Carbon contamination removal
  - Metal contamination removal
  - Native oxide removal
- Ge surface is more reactive to oxygen so that defective Ge native oxide is easily grown.
- Proper oxide removal and surface passivation are necessary to obtain sharp interface for high performance/low power Ge device fabrication.

Proposed Ge surface cleaning/passivation

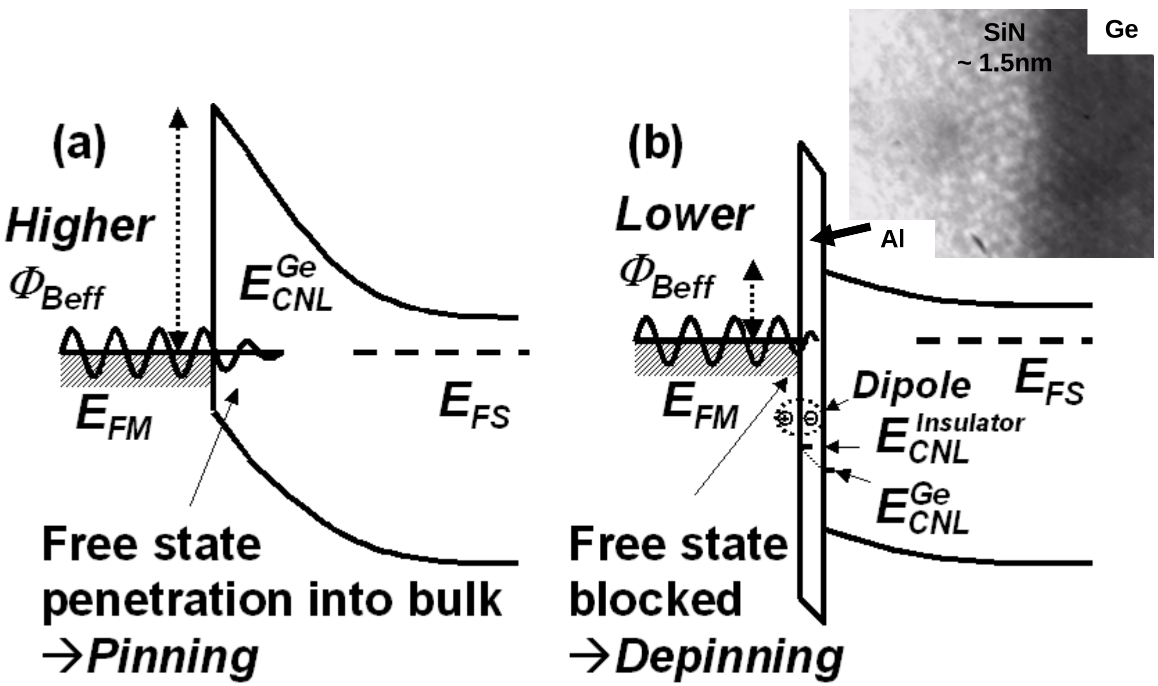
(2007- 2008 review)

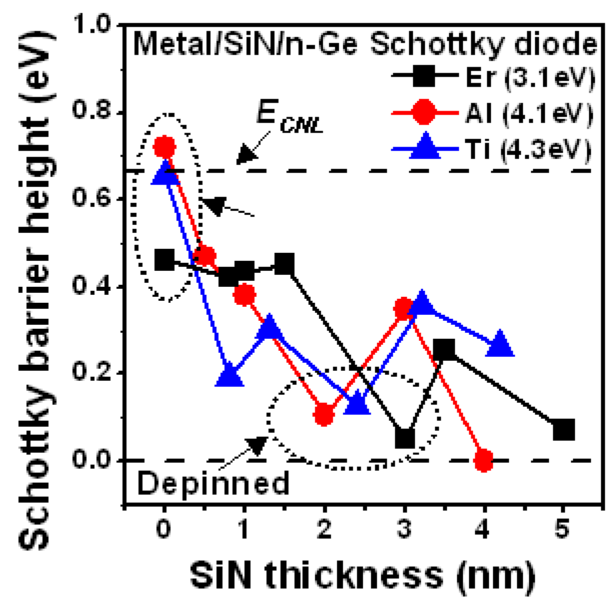


Problem/solution in metal/Ge contact

(2007- 2008 review)

- Fermi-level is strongly pinned at charge neutrality level (E_{CNL}) close to Ge valence band* based on MIGS theory
  - Very high Schottky barrier height for electron conduction
- Appropriate passivation layer can block wavefunction pentration and release Fermi-level pinning
  - Leads to low contact resistance in n-type metal/Ge Schottky jucntion



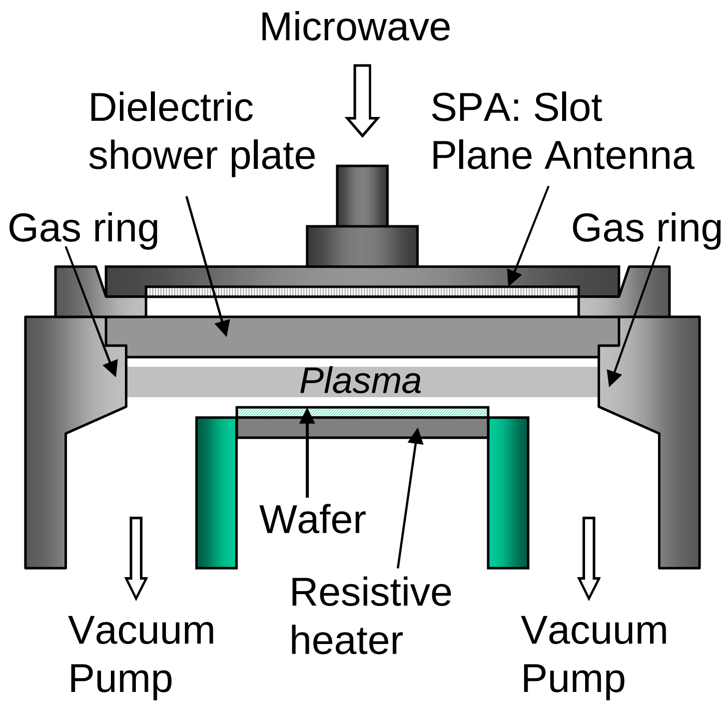


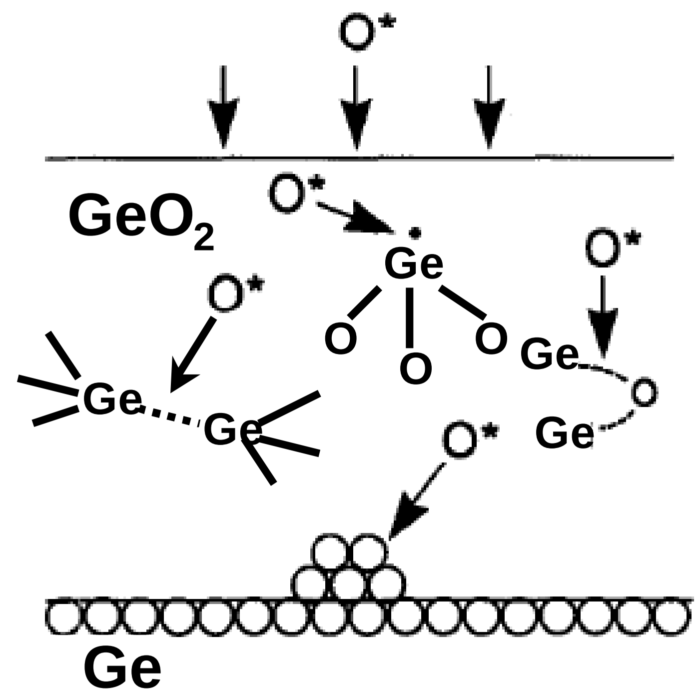
Slot-Plane-Antenna (SPA) radical oxidation

- Advantages of radical oxidation*
  - Smaller and reactive atomic oxygen radicals repair oxide defects and densify the oxide layer
  - Surface orientation independent growth
  - Lower temperature dependence

T. Ohmi et al., Proc. of IEEE, 89 394 2001

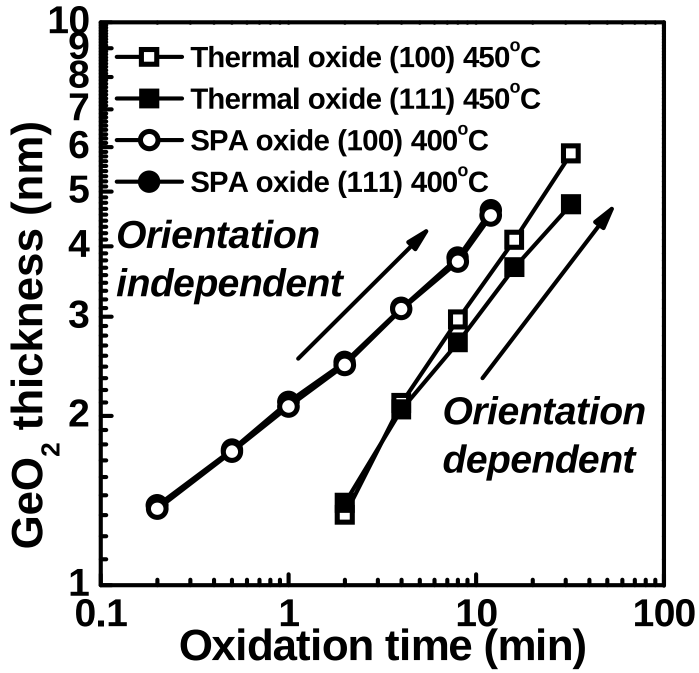
M. Nagamine et al., IEDM 1998 p. 593

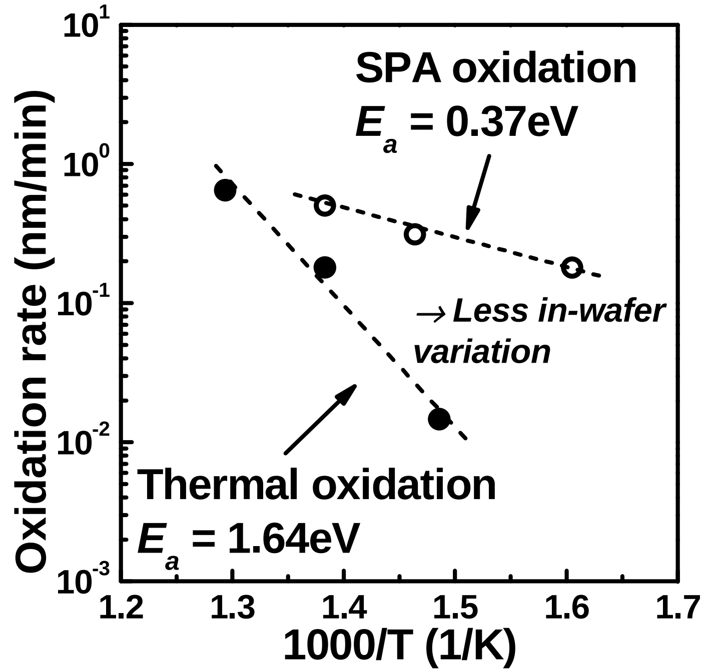




Oxidation rate

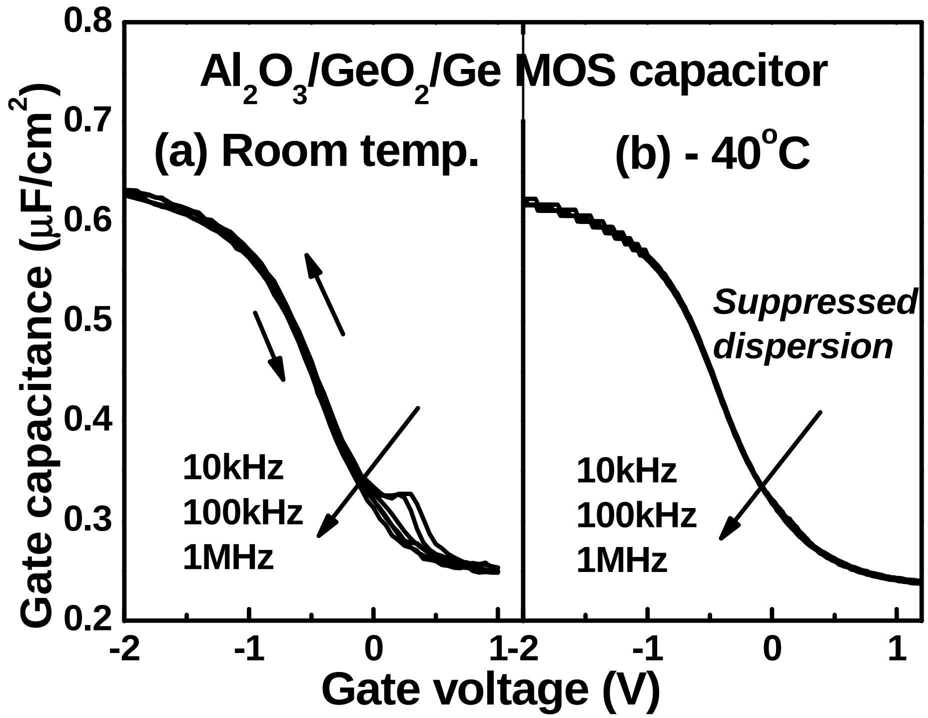
- Orientation independent growth
  - Suitable for uniform oxide growth on multi-gate FET
- Lower temperature dependent growth
  - Less in-wafer thickness variation





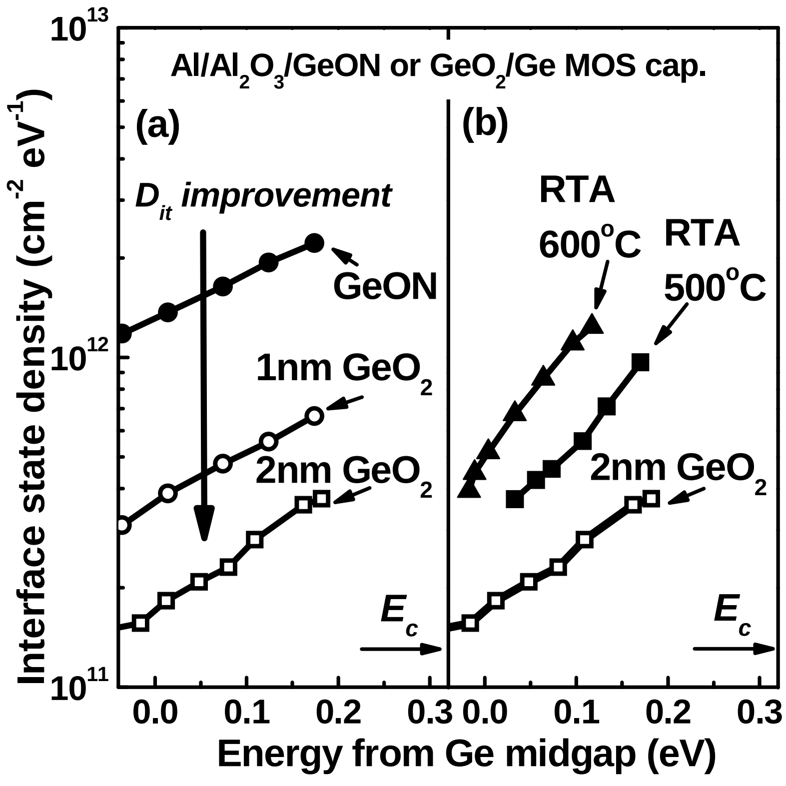
C-V characteristics

- $Al_2O_3/GeO_2/Ge$ MOS capacitor
  - Very small hysteresis and frequency dispersion
  - Fast minority carrier response is suppressed and no frequency dispersion at low temperature
    - → enable precise D_{it} measurement by conductance method



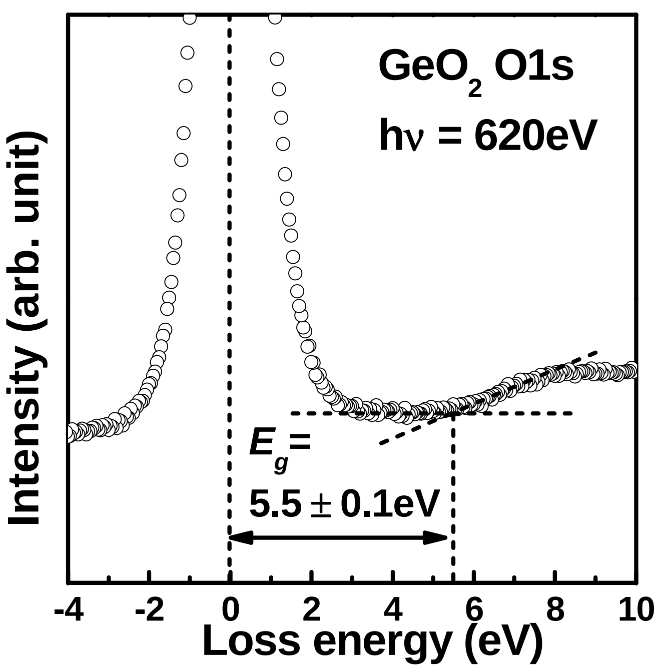
Interface state density (D_{it})

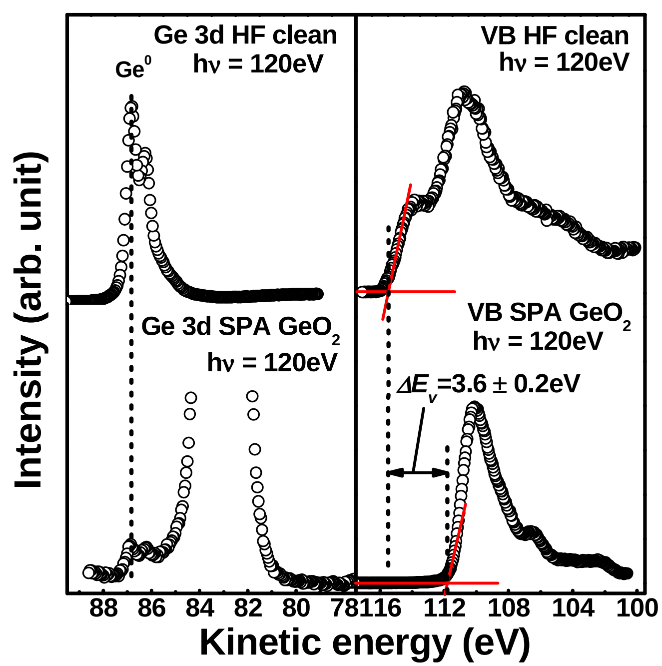
- GeO_2 significantly improved D_{it} compared to GeON
- D_{it} degradation after RTA was kept small on the order to $10^{11} cm^{-2}/eV$

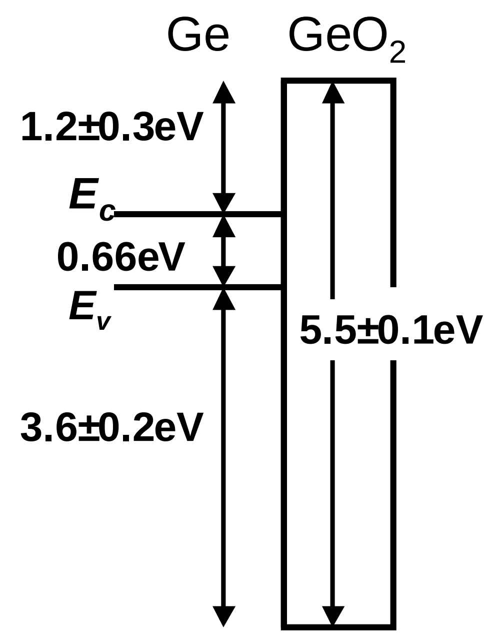


Band gap (E_g) and band offsets (ΔE_c, ΔE_v)

- E_g and $\Delta E_c / \Delta E_v$ were measured by SRPES
  - E_g = 5.5eV, ΔE_c = 1.2eV, ΔE_v = 3.6eV
  - Wide enough E_g and moderately high ΔE_c
    - → Feasible to Ge CMOS integration



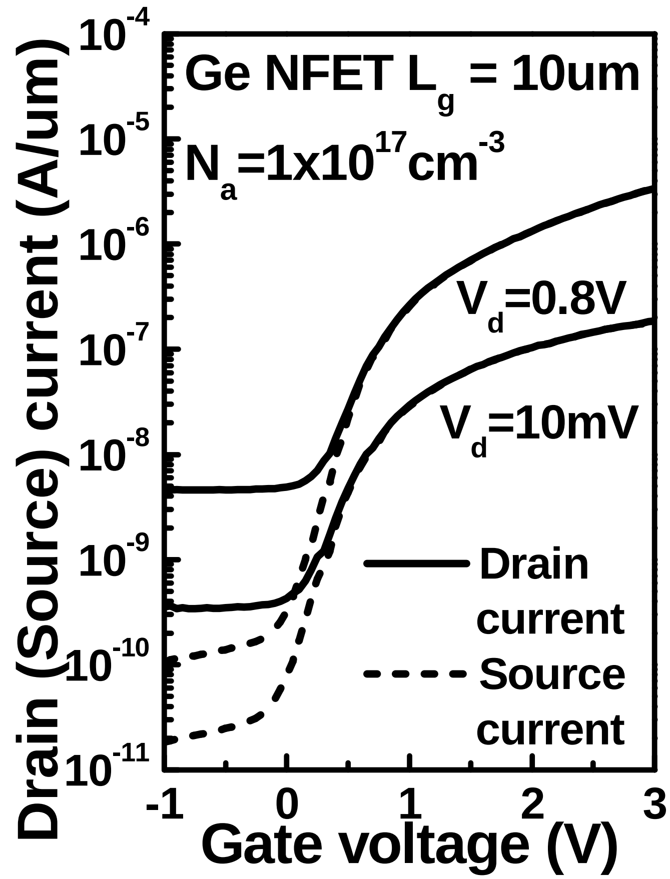




Demonstration on Ge NMOSFET

- Demonstration of Ge NMOSFET
  - Moderately low leakage current and reasonable subthreshold slope

- 2μm Ge epitaxial growth on Si
  - MHA and *in-situ* channel doping
- Field isolation
- Si capping layer growth
  - *In-situ* H_2 bake + 500°C SiH_4
- SPA radical oxidation at 400°C
  - SiO_2/GeO_2 dielectric formation
- Metal gate definition
- P^+ S/D implantation
- Passivation LTO deposition
- Dopant activation at 400°C
- Contact formation
- Al/Ti metallization



Summary

- Established novel oxidation process
  - Orientation independent/low temperature dependent oxidation
- Demonstrated high quality GeO_2/Ge interface
  - Excellent electrical characteristics with low interface state density
  - Low leakage/good subthreshold slope in Ge NFET

Industrial Interactions and Technology Transfer

This research has collaborative interactions with Initiative for Nanoscale Materials and Processes, INMP, at Stanford which is supported by 8 semiconductor and semiconductor equipment manufacturing companies*.

*** AMAT, AMD, IBM, Intel, NEC, TEL, Toshiba, TSMC**

Future Plans

Next Year Plans

- **Characterize effective mobility of Ge MOSFET with this novel oxidation process and investigate transport property of Ge MOSFET**
- **Integration of gate stack formation by radical oxidation and metal source/drain technique proposed in the last review.**

Long-Term Plans

- **Fabrication of multi-gate Ge FET by utilizing radical oxidation**
- **Development of process for high performance/low power Ge CMOS integration**

Publications and Presentations

1. *M. Kobayashi, A. Kinoshita, K. Saraswat, H. –S. P. Wong and Y. Nishi, "Fermi-Level Depinning in Metal/Ge Schottky Junction and Its Application to Metal Source/Drain Ge NMOSFET", VLSI technology symposium 2009, p. 54*
2. *M. Kobayashi, A. Kinoshita, K. Saraswat, H. –S. P. Wong and Y. Nishi, "Fermi Level Depinning in Metal/Ge Schottky junction for Metal Source/Drain Ge Metal-Oxide-Semiconductor Field-Effect Transistor Application", Journal of Applied Physics, accepted*

Part 2. Post Etch Residue Removal in Copper Damascene Structures

PI:

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

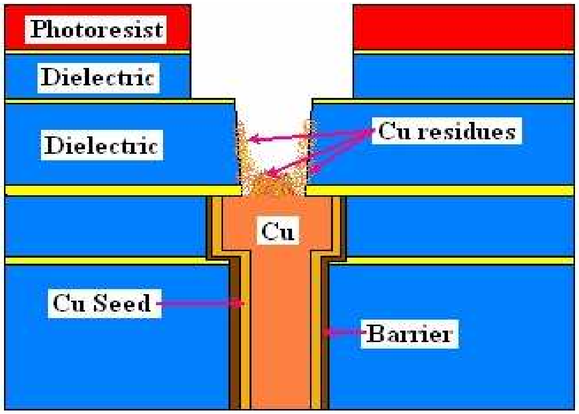
Graduate Students:

- **Dinesh P R Thanu, PhD candidate, Materials Science and Engineering, University of Arizona**

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

Objectives

- Eliminate solvent from fluoride based strippers used for BEOL cleaning of copper based structures. In this context, evaluate an *all-aqueous* dilute HF based chemical system for the selective removal of copper oxide films (CuO_X) from copper and dielectric surfaces
- Identify conditions under which copper can be passivated in this chemical system and study the effect of dissolved oxygen and HF concentration



ESH Metrics and Impact

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

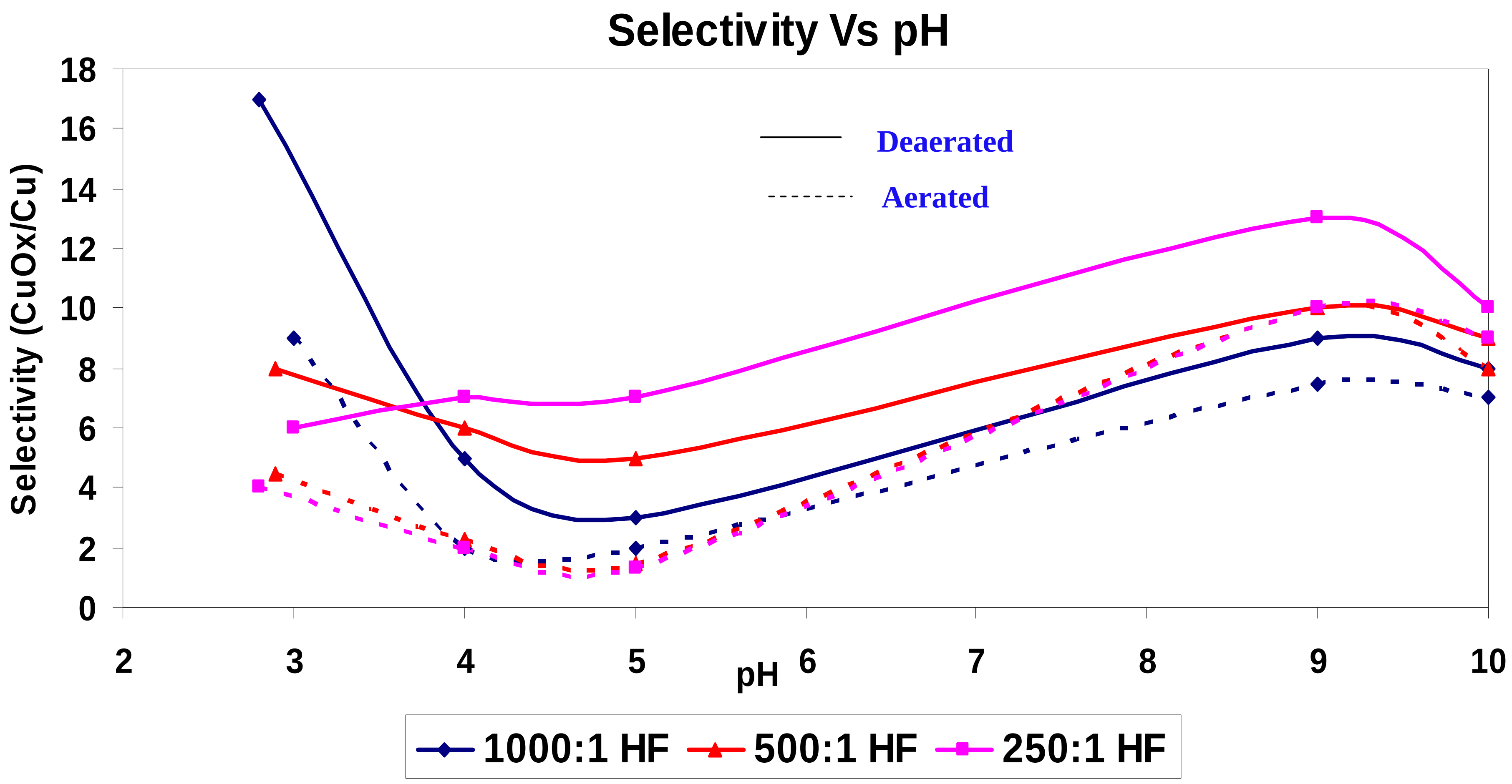
Solution components	**Weight % in typical formulations**	**Weight % in best formulation in this study**	**% Reduction**
Solvent	> 60%	0%	100%
Water	< 40%	99.9%	Increase of ~ 150%
Fluoride	~ 1-2%	0.05%	>95%

Solution	**LD_{50} (Oral Rat) mg/kg**
Hydrofluoric acid	**1276**

Solvent	**Vapor Pressure (@20^0C) mm Hg**
Hydrofluoric acid (1wt%)	**<0.1 mm**
DMSO	**0.417**

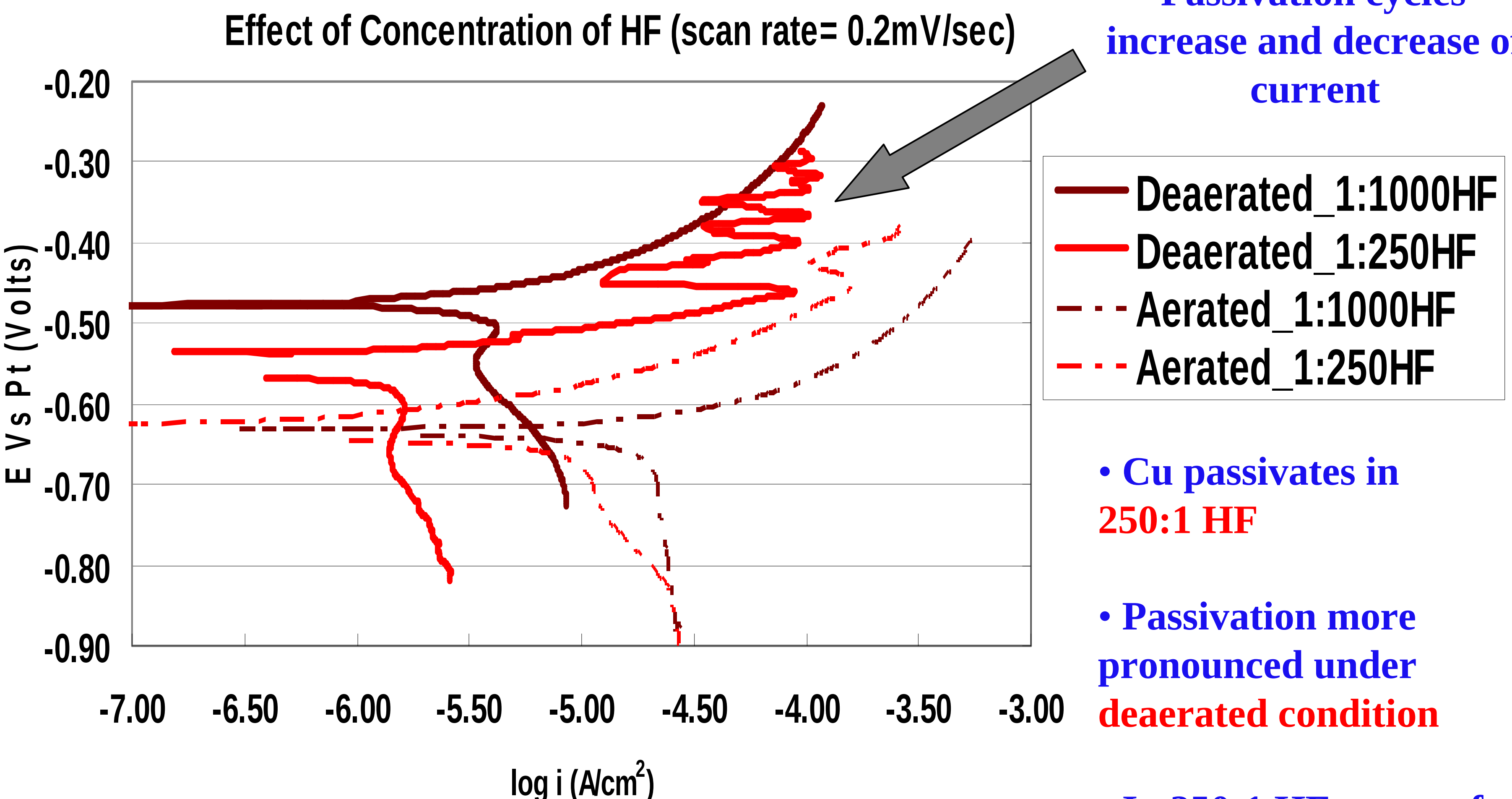
2008 – 2009 Contract Year Research Highlights

Etch Selectivity of CuO_X over Cu



- ***1000:1 dilute HF (pH 3 – Deaerated condition)***
  - ***CuO_X removal rate ~ 30 Å/min; CuO_X/Cu selectivity ~ 20:1***
- ***Aeration reduces selectivity***

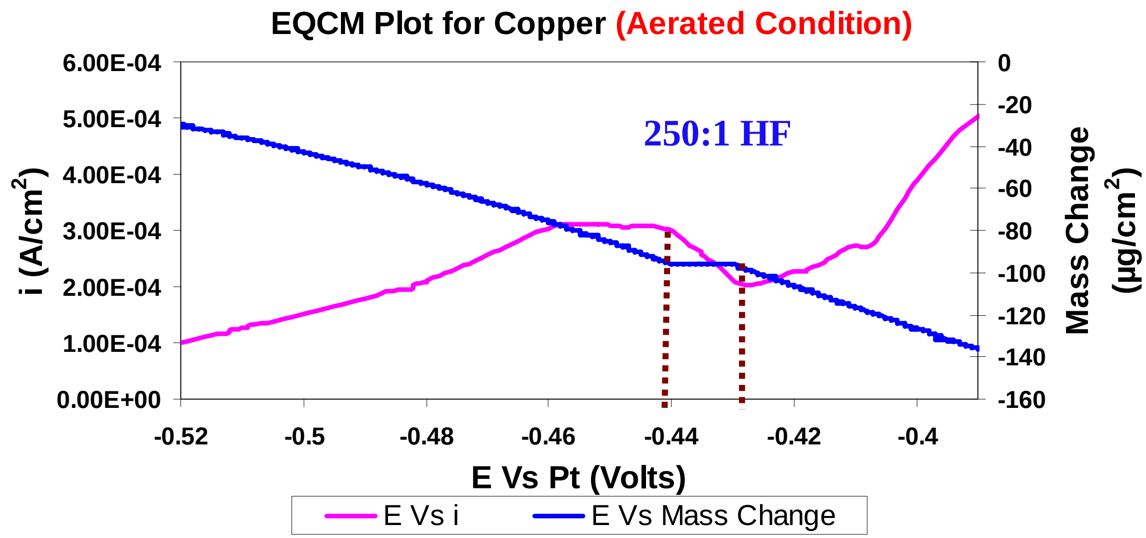
Why does deaeration provide better selectivity? Electrochemical Study

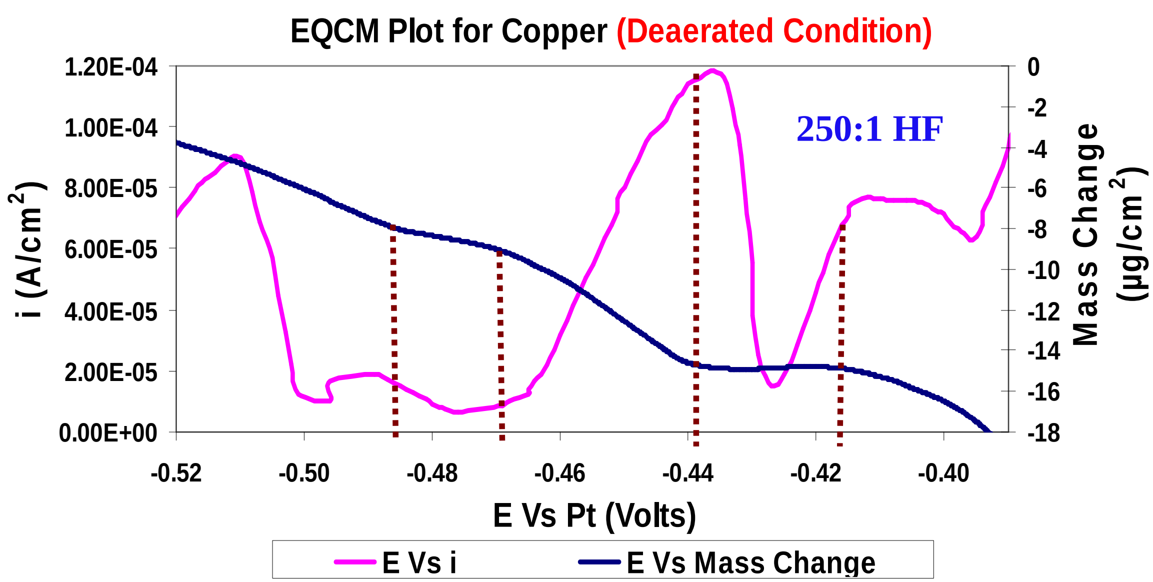


Passivation cycles- increase and decrease of current

- Cu passivates in 250:1 HF
- Passivation more pronounced under deaerated condition
- In 250:1 HF, onset of passivation is at -0.45V

Monitoring of Dissolution/Passivation of Copper by Electrochemical Quartz Crystal Microbalance (EQCM)





- Copper (820 nm) plated onto gold electrode of quartz crystal and anodically polarized at 0.2 mV/sec
- Mass change plateaus can be seen in potential regions where there is passivation
- Improved copper passivation would improve selectivity
- Copper passivation seen at SPECIFIC ANODIC POTENTIALS

Conclusions

- *Dilute HF* (~250:1) can be used to remove CuO_x
- Deaeration improves CuOx/Cu selectivity through *decreased copper etching*

Highlights of Work Done During the 3-Year Contract Period

• Systematically investigated and optimized a semi-aqueous fluoride (SAF) based formulation for the selective removal of copper oxides over copper and TEOS – identified optimal solvent and active fluoride species concentration as well as pH

• Developed an electrochemical impedance based methodology to detect CuO_X to Cu transition during etching

• Investigated the use of dilute HF (no solvent) based formulation for the selective removal of CuO_x over Cu and dielectrics and identified the conditions where copper can be passivated

Role of Semiconductor Industry in Development of Future Solar Energy Technology

February 19, 2009

Tadahiro Ohmi
Masaki Hirayama
Koji Tanaka

New Industry Creation Hatchery Center,
Tohoku University

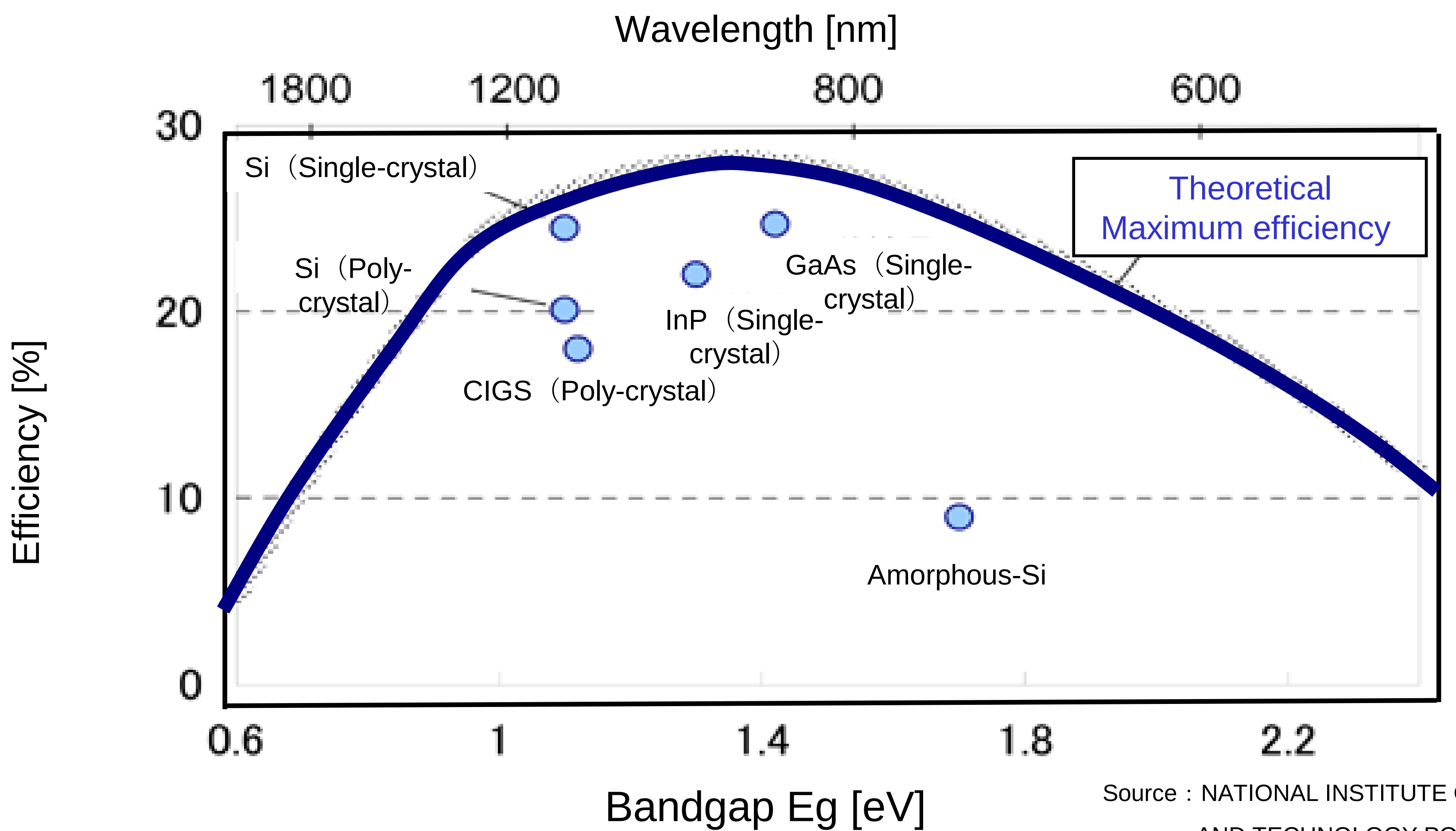
Introduction

☆ Global Heating Issues will be overcome by developing New Solar Cells where the total generation energy of the Solar Cell must be completely larger than the entire energy required to produce the solar cells !!

☆ Current manufacturing technologies are completely far from this requirement.

☆ Different thin film continues deposition in the same process chamber only by changing process gases, and different thin film continuous etching in the same process chamber only by changing process gases must be established to achieve this requirement.

theoretical efficiency vs bandgap



Source：NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY POLICY

Only amorphous-Silicon much different from the theoretical efficiency.
Current CVD plasma made a lot of defects and damages into amorphous silicon.

Bandgap vs Voc

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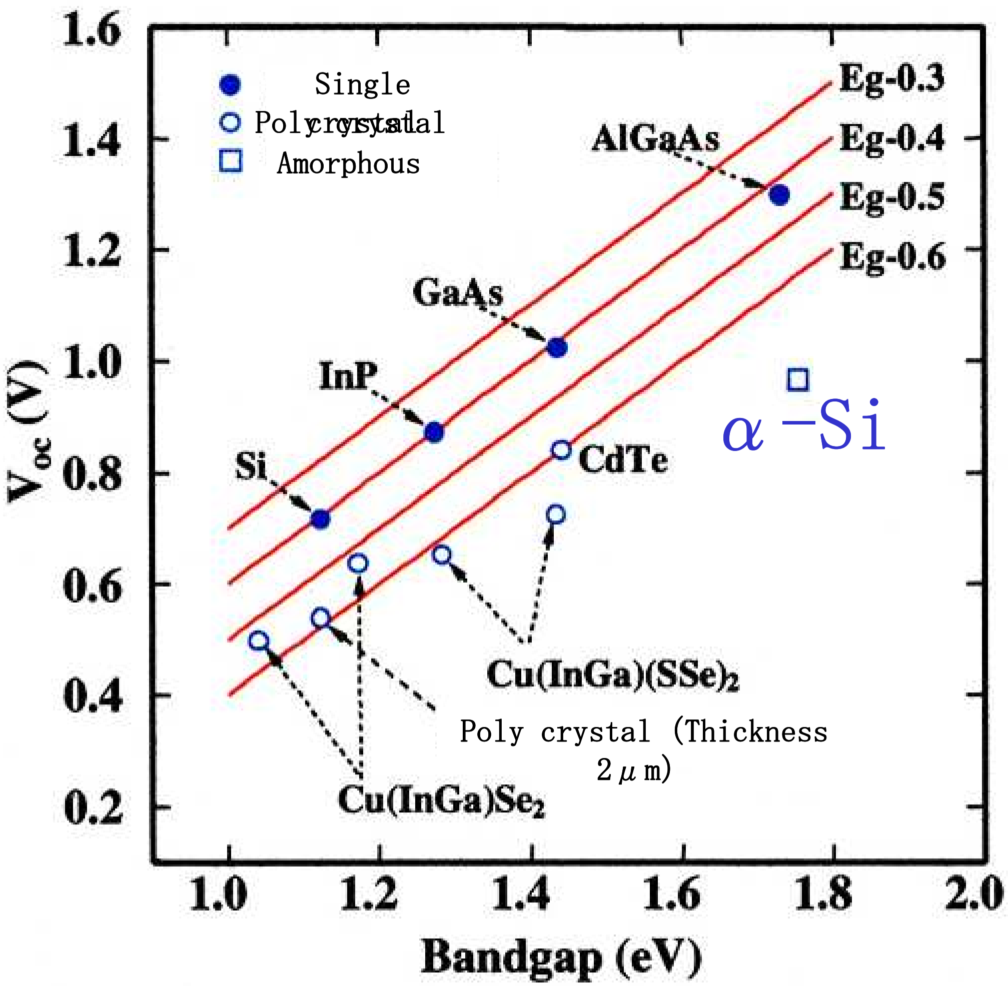

High film quality

Voc = Eg − 0.4

Plasma of conventional equipment make a large amount of damage and contamination in amorphous Si.

Voc = Eg(18)− 0.9

＊「5th New generation solar cell system」 M.Konagai (Tokyo Institute of Technology) 2008.

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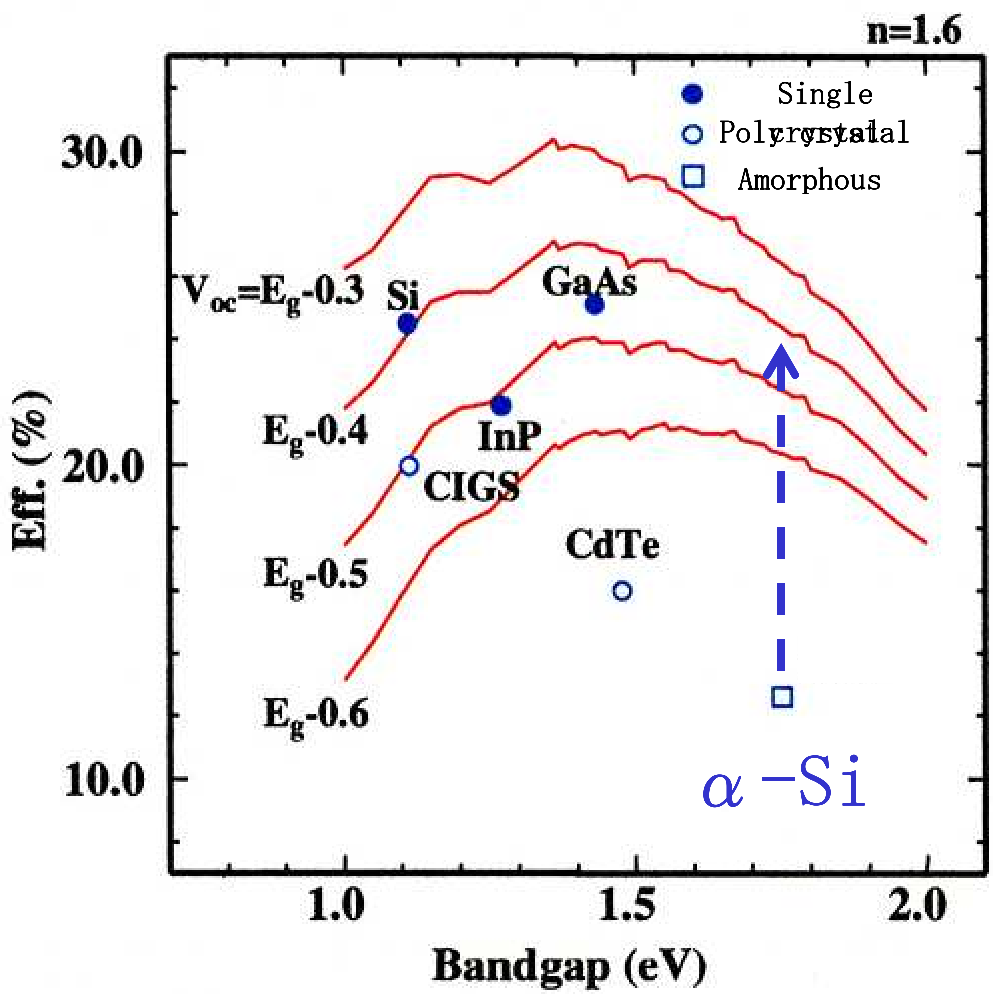
Efficiency of solar cell



New plasma source MSEP makes high quality amorphous Si with no damage and no contamination.

Efficiency becomes 20% or more

＊「 5th New generation solar cell system 」 M.Konagai (Tokyo Institute of Technology) 2008.

Efficiency of single crystal solar cell

☆ Solar Cells of Single Crystal Si, Single Crystal GaAs and Single Crystal InP have been confirmed to exhibit high conversion efficiency very near to the theoretically speculated efficiency.

⇒ These single crystal solar cells are fabricated by using high temperature processing without using plasma processing, resulting in no damages and no defects in fabricated solar cells, so that electrons and holes excited by sunlight completely contribute to power generation. i.e. ,higher conversion efficiency.

Efficiency of amorphous silicon solar cell

☆ Conversion efficiency of amorphous Si solar cells is very low far from the theoretically speculated conversion efficiency. Why?

⇒ Terminated hydrogen of amorphous silicon dangling bonds are going to eliminate if the temperature becomes higher than 300℃, so that the amorphous Si solar cells must be essentially fabricated by using plasma process equipment at the temperature around 200℃.

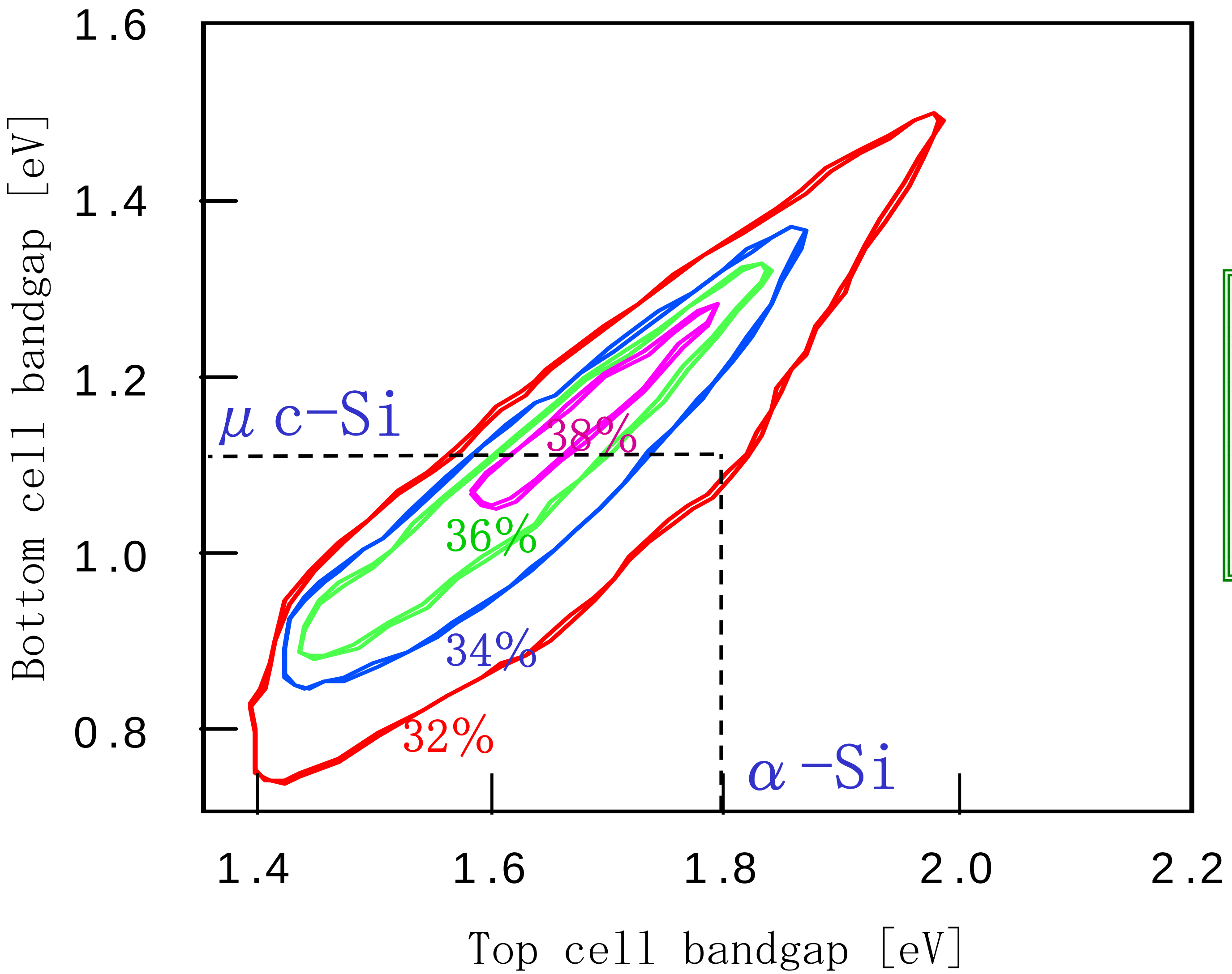
⇒ Current plasma processing equipment is very well known to accompany very severe damages such as charge-up damages and ion bombardment induced damages, so that they are used only in interconnect fabrications but not used for transistor fabrications in LSI manufacturing.

Amorphous Si Solar Cells

⇒ There inevitably remain huge amount of damages and defect in current amorphous Si solar cells, so that most of electrons and holes excited by sunlight do not contribute to the power generation, resulting in very low convention efficiency solar cells!!

☆ Our target is very clear to establish amorphous Si solar cells having very high convention efficiency greater than 20% by developing very high quality plasma process equipment completely free from damages having very new functions, i.e., different thing film continuous depositions and continuous etching in the same process chamber only by changing process gases.

Efficiency of 2 junctions solar cell



＊Yamaguchi (Toyota Technological Institute)

When solar cell has 2 junctions（α -Si/ μ c-Si）, Efficiency becomes **30%** or more.

Social Impact of solar cell by realizing very high conversion efficiency

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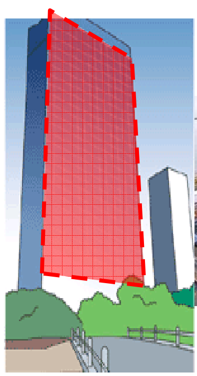
Solar Energy
(1kW/m^2、1million kW/km^2)

⮤ Data of Japan

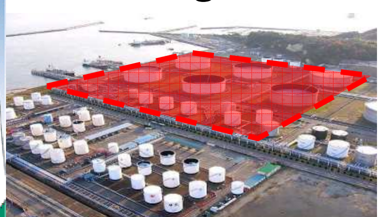
Ex.) Total Electrical Power in the world 25 trillion kWh/year (2020)

Efficiency	20 %	30%
Area	300km × 400km = 120,000km^2 (1/3 of area of Japan)	200km × 400km = 80,000km^2 (1/4.5 of area of Japan)
Output	22.8 billion kW	22.8 billion kW
Output in 1 year	22.8 billion kW × 3hour/day × 365day/year ≒ 26 trillion kWh	22.8 billion kW × 3hour/day × 365day/year ≒ 26 trillion kWh

Data of Japan



Building

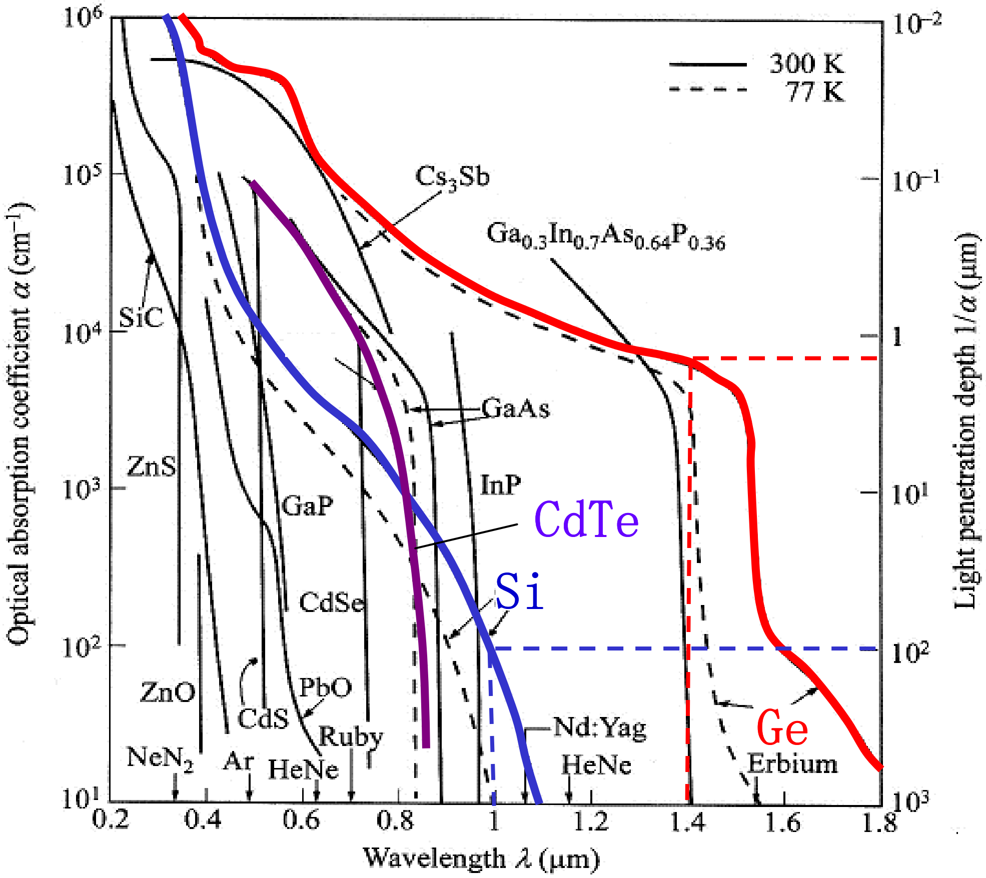


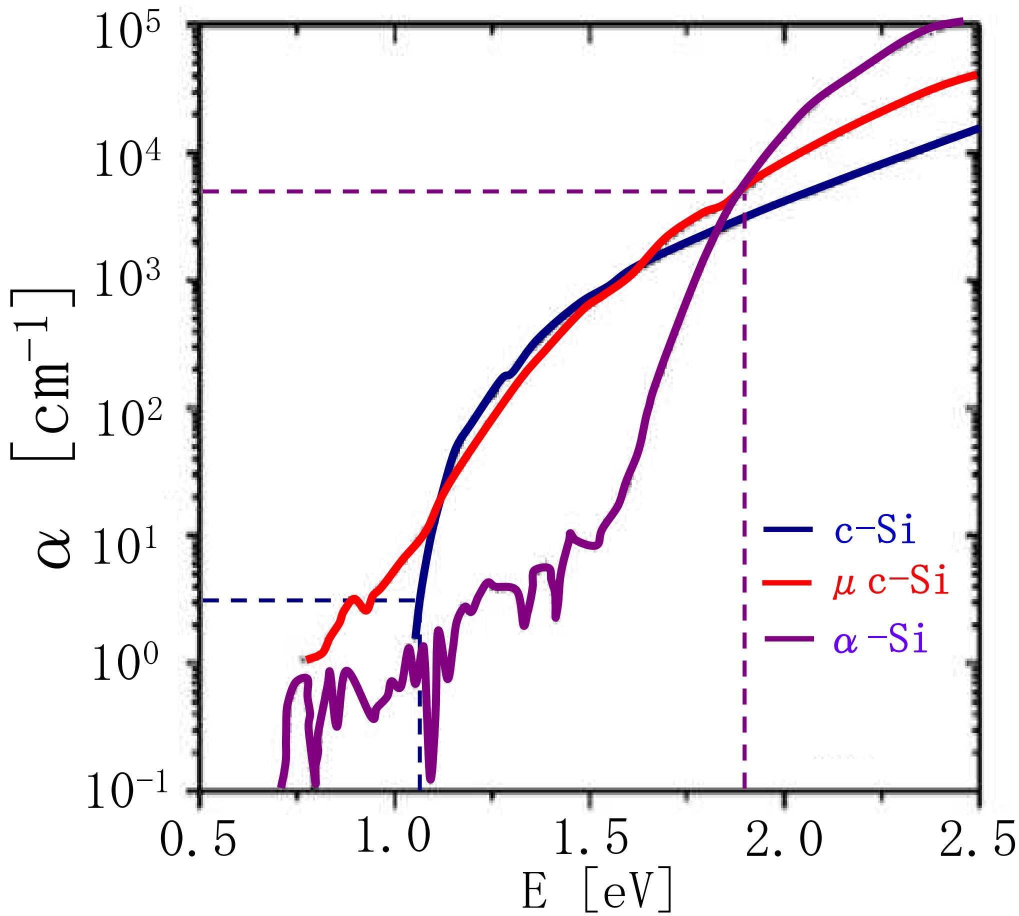
Complex

All the electrical power for the entire world can be generated by developed solar cell!!

DO NOT DUPLICATE

Optical absorption coefficient





＊H. Melchior,” Demodulation and Photodetection Techniques,”
in F. T. Arecchi and E. O. Schulz-Dubois, Eds.,
Laser Handbook, vol. 1, North-Holland, Amsterdam, 1972, pp. 725-835

α -Si	0.5 μ m
μ c-Si	2 μ m
c-Si	100 μ m

Requested resource

Si

	α-Si	**α-Si／μc-Si**	c-Si
Thickness	0.5μm	**0.5／2μm**	100μm
Efficiency	20%	**30%**	30%
Area	120,000km^2	**80,000km^2**	80,000km^2
Number of modules	$6.1x10^{10}$	**$4.1x10^{10}$**	$4.1x10^{10}$
Consumption	140,000ton	**466,000ton**	18,640,000ton

＊Module size ： 1.20m x 1.64m

＊Silicon crystal production volume 40,000～50,000 ton/year

Others

	Ge	Cd	Te
Thickness	**0.5μm**	5μm	5μm
Efficiency	**40%**	30%	30%
Area	**60,000km^2**	80,000km^2	80,000km^2
Consumption	**160,000ton**	3,460,000ton	2,500,000ton

Recoverable reserves

	Recoverable reserves [ton]	Requirement [ton]	Cost [$/ton]
Si	Enough	140,000～17,732,000	2,000
Ge	500	160,000	130,000
Cd	600,000	3,460,000	2,000
Te	21,000	2,500,000	100,000
In	2,800		1,000,000
Zn	220,000		2,000
Se	82,000	5,748	30,000

＊Se thickness ： 10nm

1$=100yen

Si is unique material to solve the energy issue of the entire world !!

Proposal of New Solar Cell Structure

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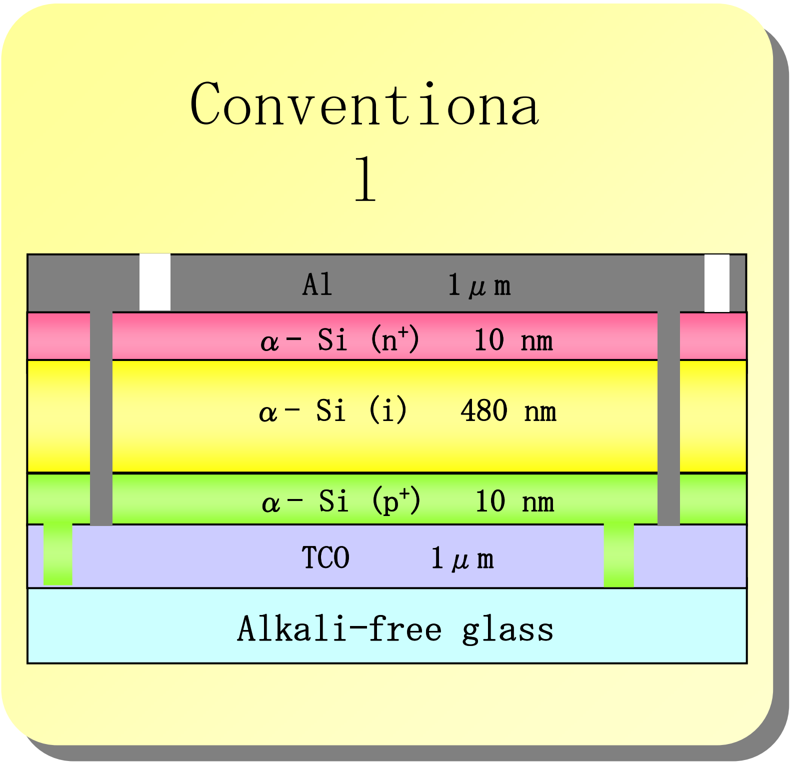

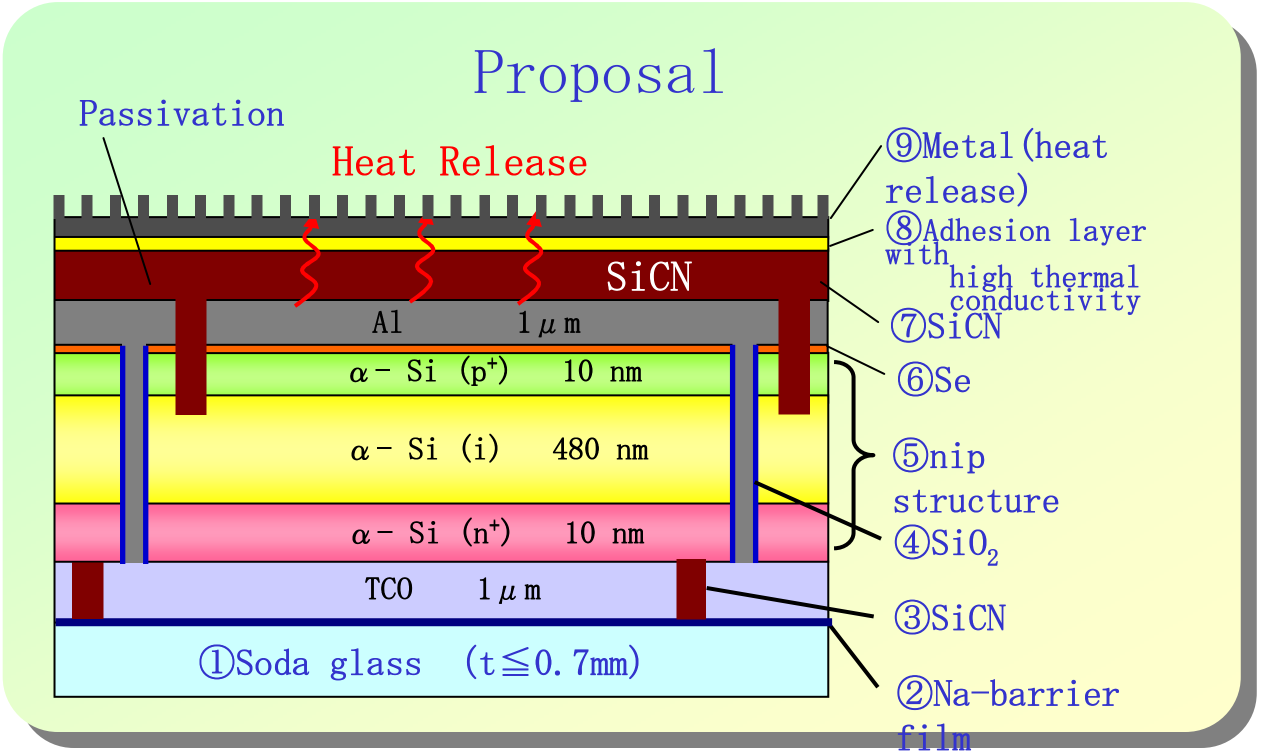

New Structure1 (①②) Low-cost **Sodium Glass** is used (Na barrier is indispensable)

New Structure2 (③④⑦) Device Isolation and Passivation for **SiCN・SiO_2**

New Structure3 (⑤) **nip** structure

New Structure4 (⑥) Decrease of Contact Resistance (**Se**)

New Structure5 (⑧⑨) Low Temperature Operation of the module (**Heat Release**)

New Structure6 Patterning by **Etching**

DO NOT DUPLICATE

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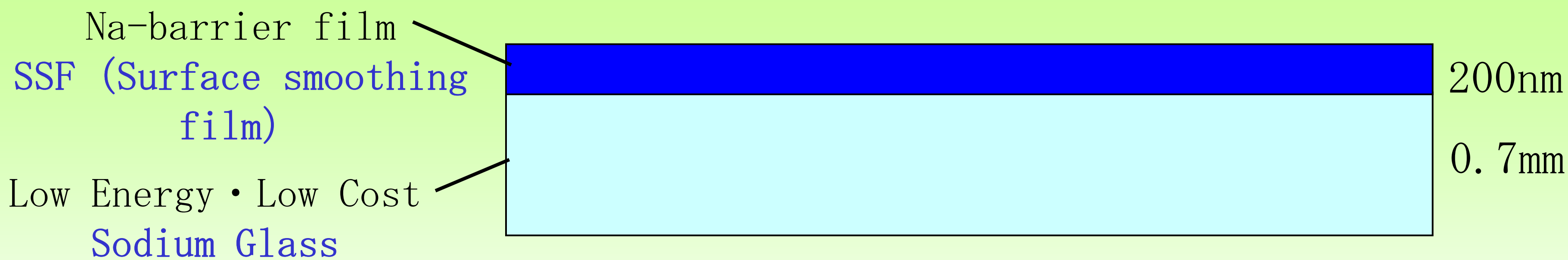
Alkali Free Glass to Soda Glass

Current：Alkali Free Glass
Melting Point 1800℃
Cost 5,000yen/m^2

Low Energy
Low Cost

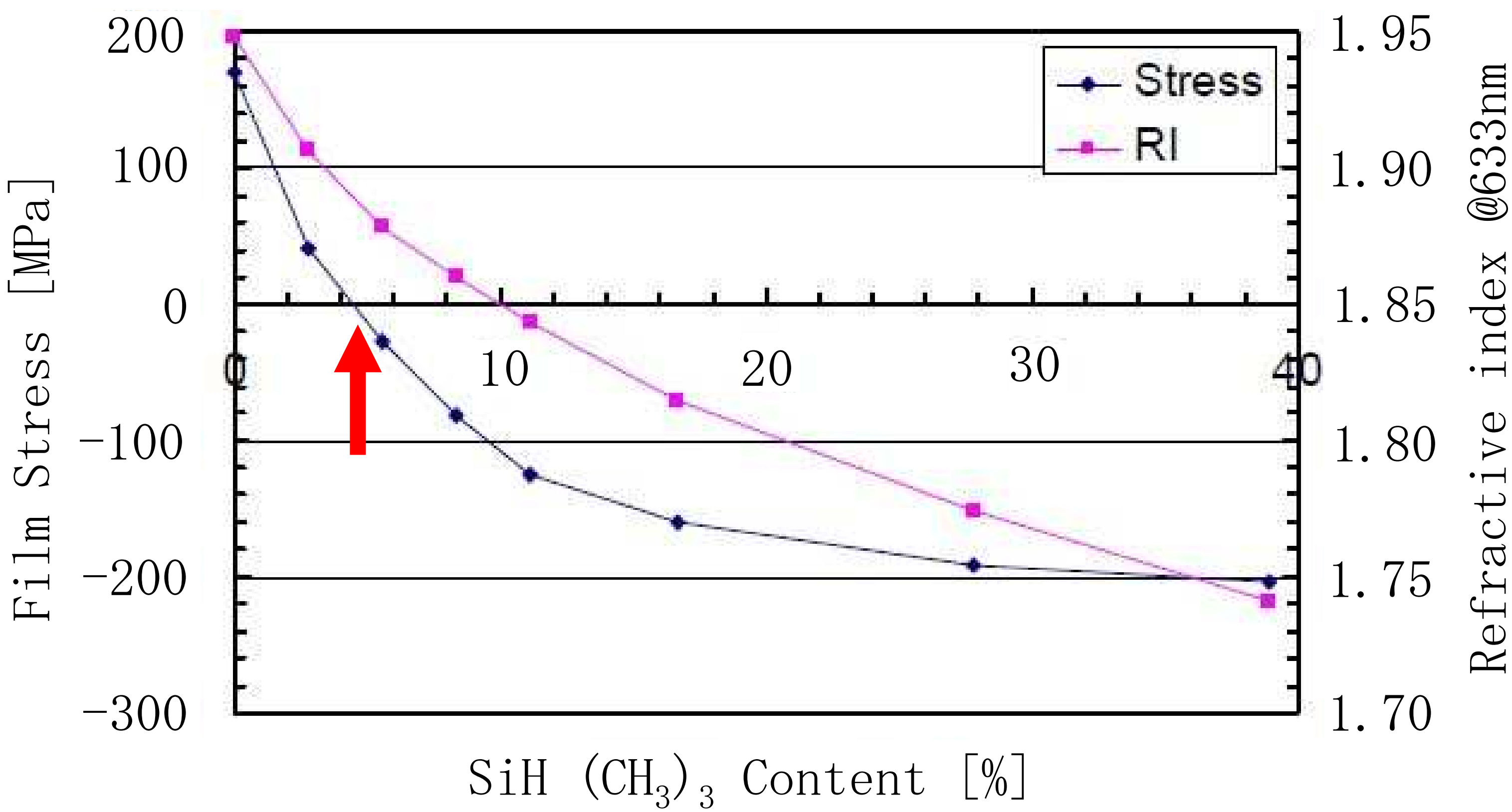
New：Sodium （Na） Glas
Melting Point 1300℃
Cost 500yen/

Difficulty ： Sodium is diffused into deposited films.



Solution ： SSF is introduced by slit coating
To avoid diffusion of Sodium

Optimization of CVD process conditions



MW：2.5kW, Press.: 26.6Pa, Gap： 110mm, Stage Temp: 70℃, Time: 300sec

Gas: (Upper) Ar/NH_3=1150/113sccm

Stress free SiCN film deposition will become available !!

Solar Cell Structure Ⅰ and process step①

①Na-barrier Film Slit Coating (0.2μm)
②Low pressure Drying (400℃,5Torr,N_2)

③Deposition of n+ ZnO(Ga) (1.0μm) **[MSEP 1]**

<u>Kr / O_2 , Ar / $Zn(CH_3)_2$ + $Ga(CH_3)_3$</u>

④Photoresist Coating (Slit coating) :
Photolithography

⑤Pattern Etching of n+ ZnO(Ga) **[MSEP 2]**

<u>Ar , Ar / Cl_2 / HBr</u>

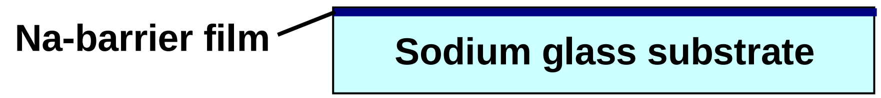
⑥Photoresist Removing by Kr/O_2 plasma **[MSEP 3]**

Photoresist + O* = nCO_2 + mH_2O
ZnO + O* = ZnO
SiOC + O* = SiOC

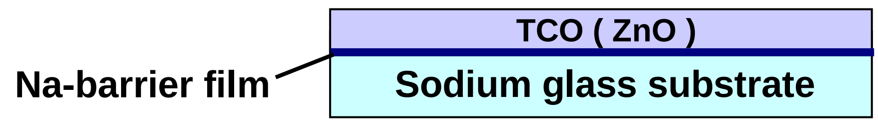
Surface and Side Wall of ZnO are improved thier performance by the reaction with O*.

Na Barrier Film surface is improved by the reaction with O*.

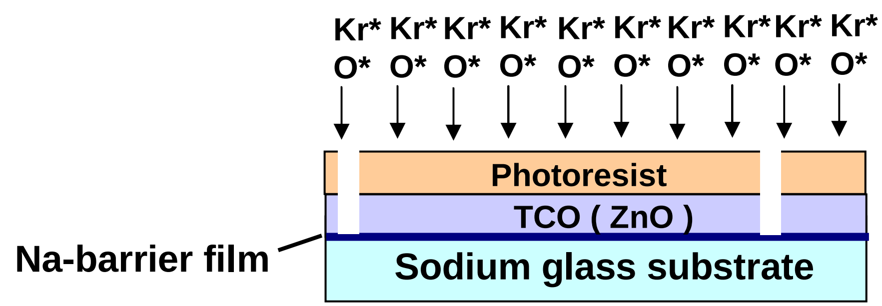
①Na-barrier Film Coating
②Low pressure Drying



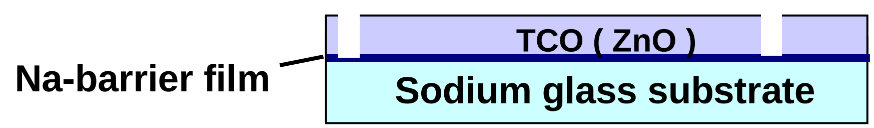
③Deposition of TCO



④Photoresist Coating
⑤Pattern Etching



⑥Photoresist Removing



Solar Cell Structure Ⅰ and process step②

⑦

(1)Deposition of SiCN
Xe / NH_3 , SiH_4 + $SiH(CH_3)_3$ [MSEP 4]

(2)Etching of SiCN
Ar , CF_4 [MSEP 4]

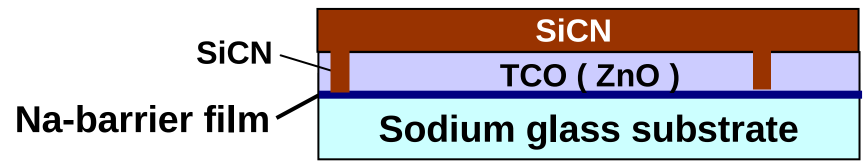
(3)Deposition of n+ α-Si (10nm)
Ar / H_2 , SiH_4 + pH_3 [MSEP 4]

(4)Deposition of i α-Si (480nm)
Ar / H_2 , SiH_4 [MSEP 4]

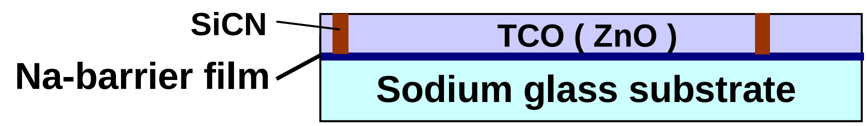
(5)Deposition of p+ α-Si (10nm)
Ar / H_2 , SiH_4 + B_2H_6 [MSEP 4]

(6)Deposition of Se
Ar / H_2 , H_2Se [MSEP 4]

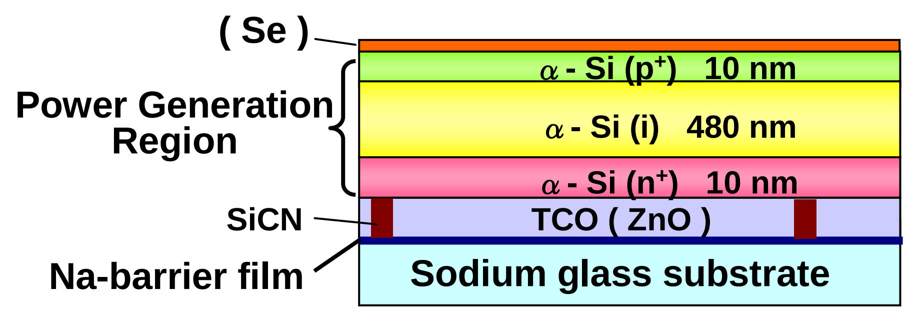
⑦(1) Deposition of SiCN



⑦(2)Etching of SiCN



⑦(3)~(6) 4 layers continuous deposition



Deposition. Etching. 4 layers continuous deposition in the same process chamber only by changing process gas.

Solar Cell Structure Ⅰ and process step③

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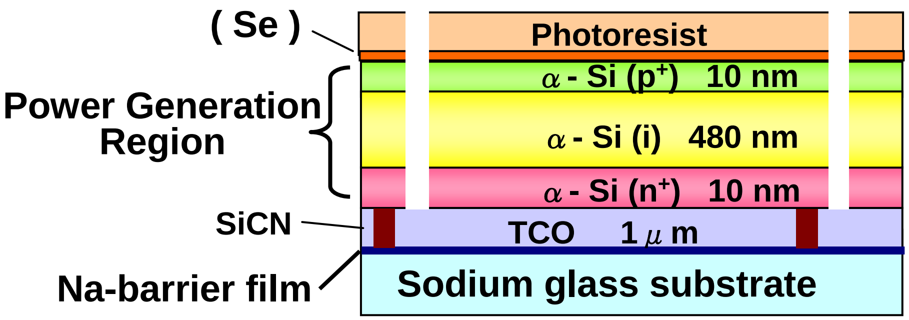
⑧Photoresist Coating (Slit coating) :
Photolithography

⑨
- (1)Etching of Se — Ar / H_2 , CH_4 [MSEP 5]
- (2)Etching of p⁺a-Si — Ar , HBr [MSEP 5]
- (2)Etching of ia-Si — Ar , HBr [MSEP 5]
- (2) Etching of n⁺a-Si — Ar , HBr [MSEP 5]

⑧Photoresist Coating
⑨4 layers continuous etching

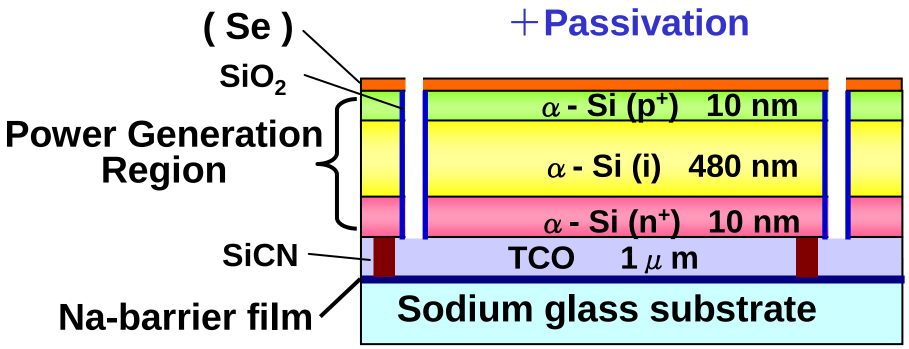


4 layers continuous etching in the same process chamber.

⑩Photoresist removing by Kr/O_2 plasma [MSEP 3]

$$\text{Photoresist} + O^* = nCO_2 + mH_2O$$

⑩Photoresist removing
＋Passivation



Inner Surface of amorphous-Sillicon etched holes
are covered by SiO2 by amorphos-silicon surface oxidation by O*.

DO NOT DUPLICATE

Solar Cell Structure Ⅰ and process step④

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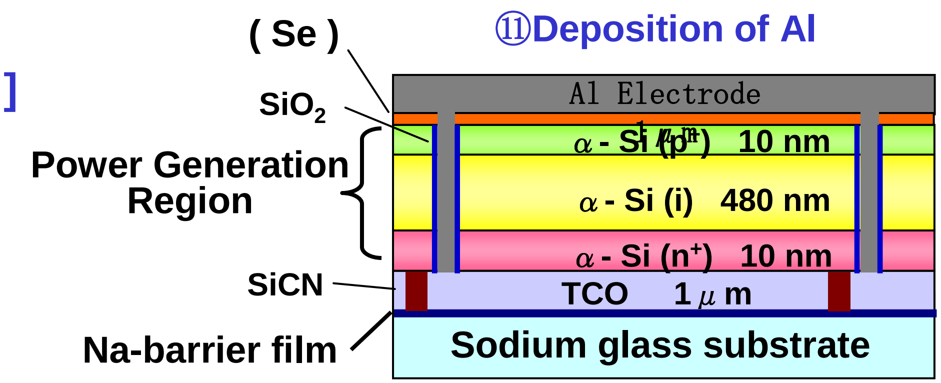
⑪Deposition of Al (1 μm) [MSEP 6]

⑫Photoresist Coating (Slit coating) :
Photolithography

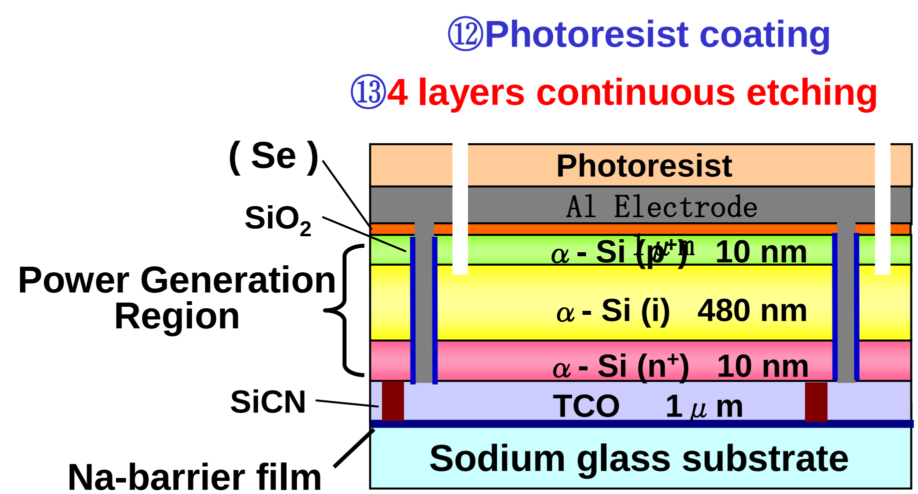


⑬
(1)Etching of Al [MSEP 7]
Ar , Cl_2

(2)Etching of Se [MSEP 7]
Ar / H_2 , CH_4

(3)Etching of p^+a-Si [MSEP 7]
Ar , HBr

(3)Etching of ia-Si [MSEP 7]
Ar , HBr



4 layers continuous etching in the same process chamber.

Solar Cell Structure Ⅰ and process step⑤

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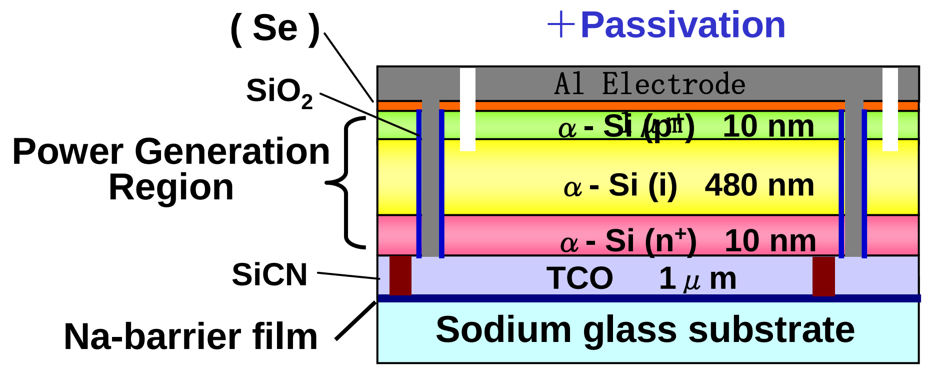
⑭Photoresist removing by Kr/O2 plasma [MSEP 3]

Photoresist + O* = nCO_2 + mH_2O

Amorphos silicon surface is converted to SiO2 through the reaction with O*.

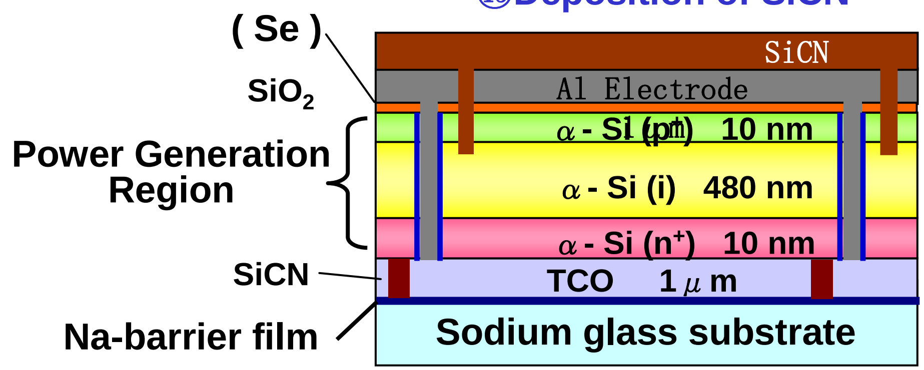
⑭Photoresist removing
＋Passivation



⑮Deposition of SiCN [MSEP 8]

Xe / NH_3 , SiH_4 + $SiH(CH_3)_3$

⑮Deposition of SiCN



Current technology : 16 plasma chambers are required.
New technology : only 8 plasma chambers are required⇒Drastic energy saving in manufacturing !!

Module cost

2020 : 25 trillion kWh/year

10yen/kWh (0.1dollar/kWh) → 250 trillion yen/year (2.5 trillion dollar/year)

Based on sunshine condition in Japan.

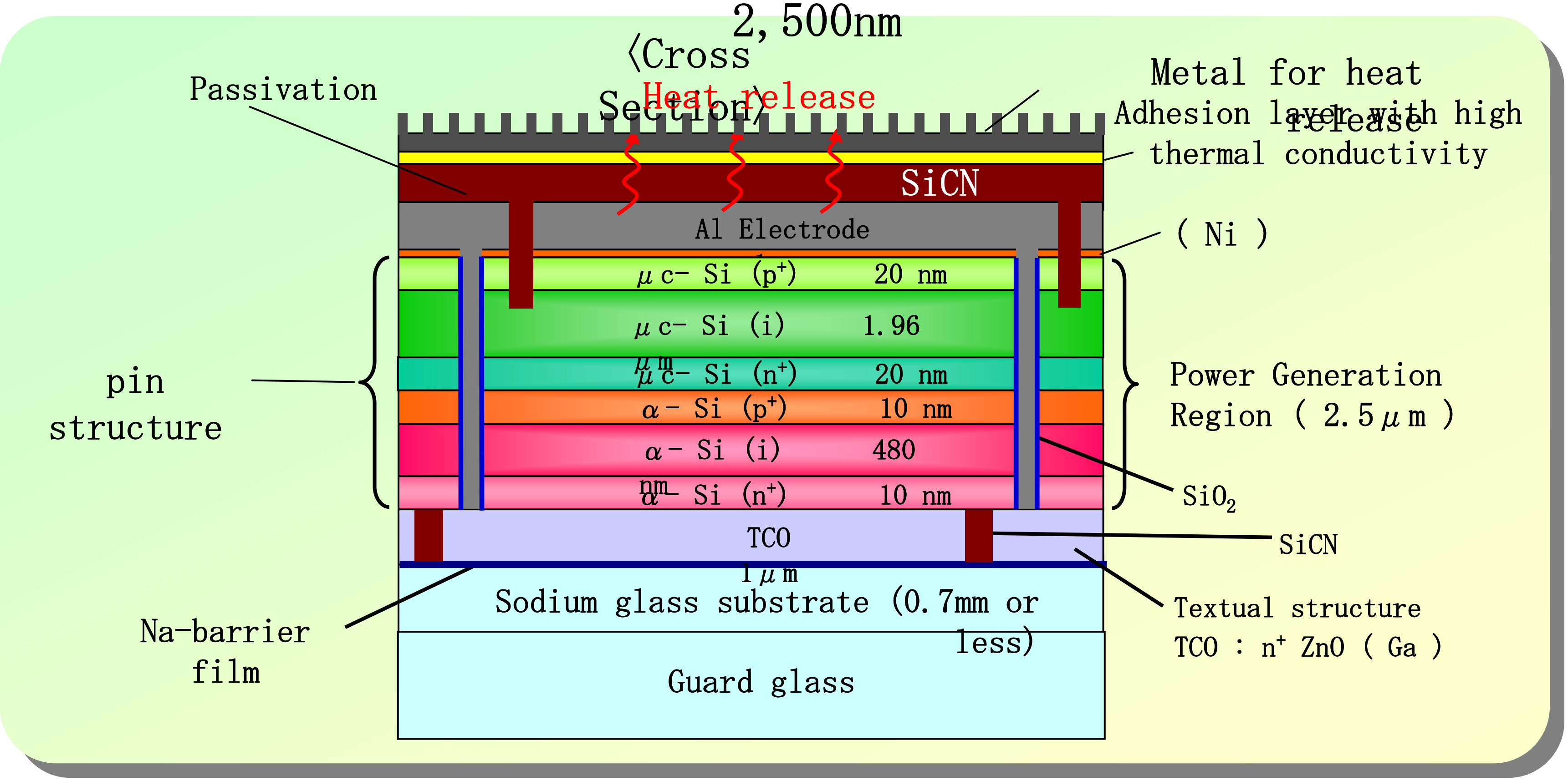
(1kW/m^2, 3hours/day)

Conversion efficiency	Solar cell area
20%	120,000km^2
30%	80,000km^2

	Amorphous-Si p^+in^+	α-Si p^+in^+/μc-Si p^+in^+
Thickness	0.5 μm	2.5 μm
Conversion efficiency	**20%**	**30%**
Solar cell area	120,000km^2	80,000km^2
Requested Si volume	140,000ton	466,000ton
Price of Si	**280 million dollar**	**932 million dollar**
Price of sodium glass	**600 billion dollar**	**400 billion dollar**

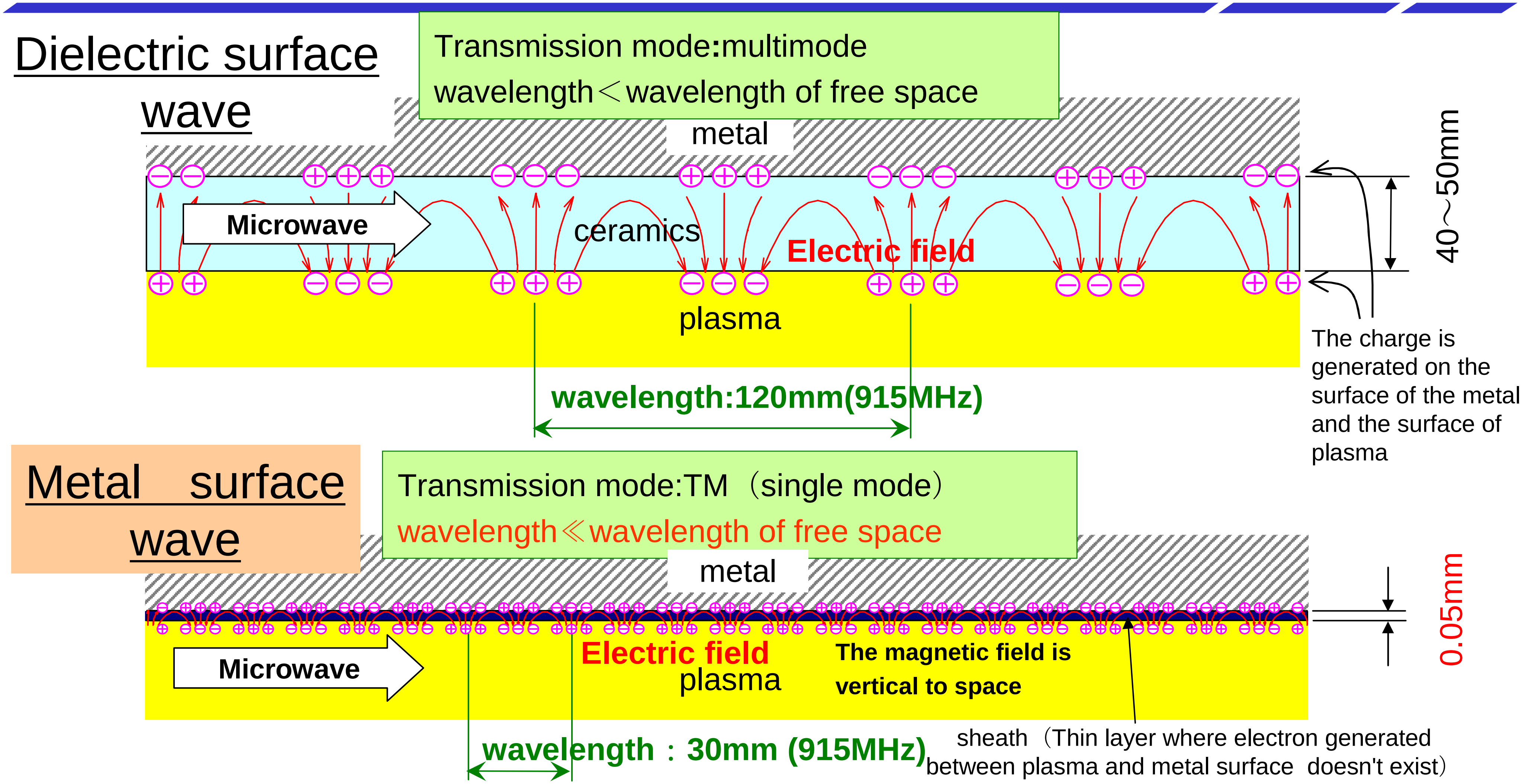
Solar Cell Structure Ⅱ

6 stacked layer (α-Si／μc-Si pin diodes) Total thickness of 2,500nm



【Simulation value】 Output : 555W (282V, 1.97A)
Cell conv. Efficiency 30.0% Module Conv. Efficiency : 28.2%
Glass size 1.20m×1.64m

propagation modes of microwave



In other propagation forms, the size in the section on the propagation road is about fractions of wavelength（several 10 mm or more）.On the other hand, the metal surface wave propagates along with an extremely thin layer compared with wavelength. (about 0.05mm) Therefore, no one was noticed for a long time!!!

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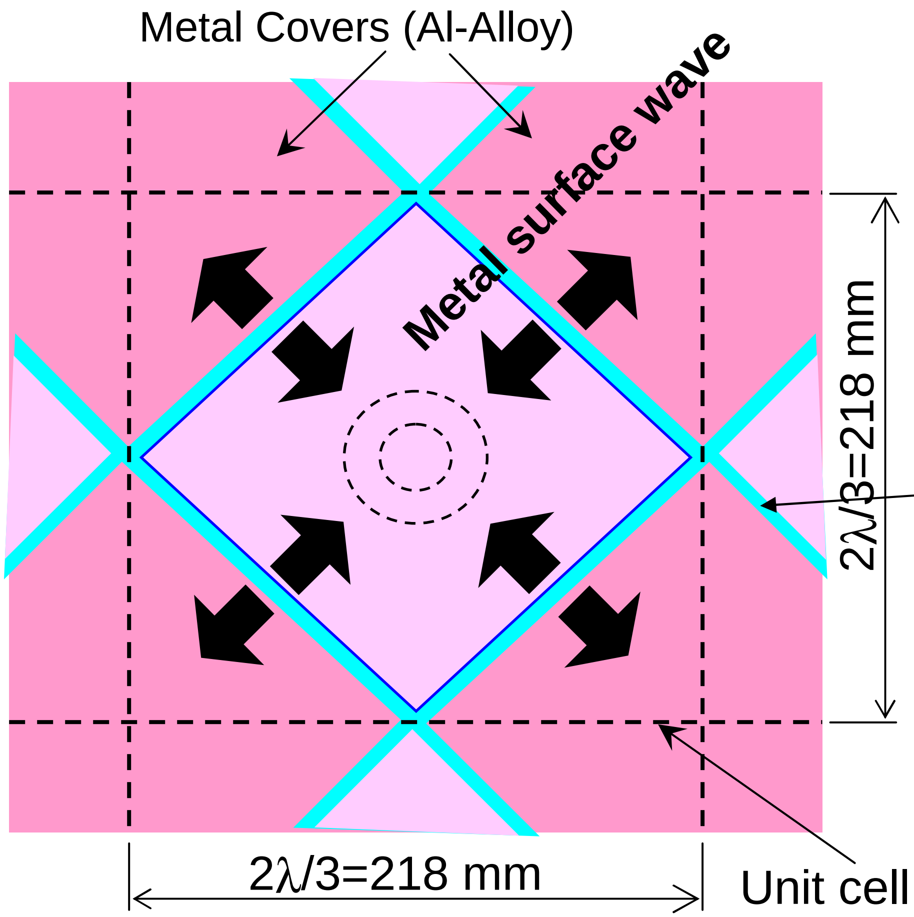
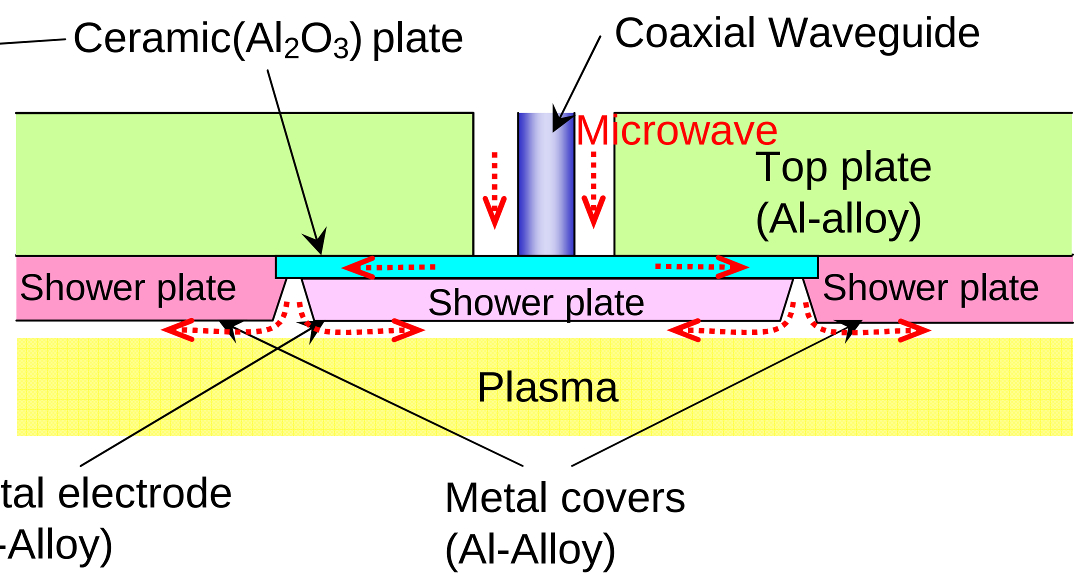
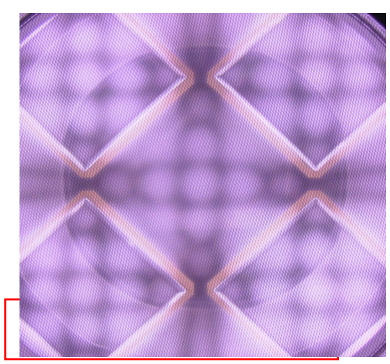
Structure of MSEP cell



- Shape of the metal electrode is same as the metal cover.
- Minimum unit area is halved.
- Required propagation distance is minimized.

➡ Uniform plasma is excited at arbitrary conditions.





←Photograph of actual plasma

Two dimensional standing wave patterns the same in a metal electrode and a metal cover.

All the surface of the Al-alloy is covered with the 0.3 μ m～0.5 μ m thick Al_2O_3 passivation film having perfect anti-corrosion capability.

Summary

☆ We must overcome global warming issues by developing Si thin film solar cells on the sodium glass covered with sodium diffusion barrier film having very high conversion efficiency higher than 20% and 30% by establishing very high quality plasma process equipment completely free from damages having very new functions such as different thin film continuous depositions and continuous etchings in the same process chamber only by changing process gases succeedingly. i.e., 915MHz Metal Surfacewave Excitation Plasma（MSEP）.

☆ Total generation energy of new solar cells during around 5 years must be completely larger than the entire energy required to produce these solar cells!!

Reductive Dehalogenation of Perfluoroalkyl Surfactants in Semiconductor Effluents

(*Task #: 425.015)*

PIs:

- **Reyes Sierra, Chemical and Environmental Engineering, UA**
- **Neil Jacobsen, Chemistry Department, UA**
- **Vicki Wysocki, Chemistry Department, UA**

Graduate Students:

- **Valeria Ochoa, PhD candidate, Chemical and Environmental Engineering, UA**

Undergraduate Students:

- **Chandra Khatri, Chemical and Environmental Engineering, UA**

Other Researchers:

- **Antonia Luna, Postdoc, Chemical and Environmental Engineering, UA**
- **Javier Torres, Research Assoc., Chemical and Environmental Engineering, UA**
- **Jim A Field, Professor, Chemical and Environmental Engineering, UA**

Cost Share (other than core ERC funding):

UA/NASA grant (to C. Khatri)

NWIR grant $12K

Objectives

- **Investigate the feasibility of reductive dehalogenation of PFOS and related perfluorinated compounds using two different approaches:**
  - Chemical biomimetic treatment by vitamin B_{12} and Ti(III) citrate.
  - Anaerobic microbial degradation.
- **Optimize the kinetics of reductive dehalogenation.**
- **Characterize the mechanisms and products of reductive dehalogenation.**
- **Investigate the degradation of partially dehalogenated PFOS compounds in assays simulating municipal wastewater treatment.**

ESH Metrics and Impact

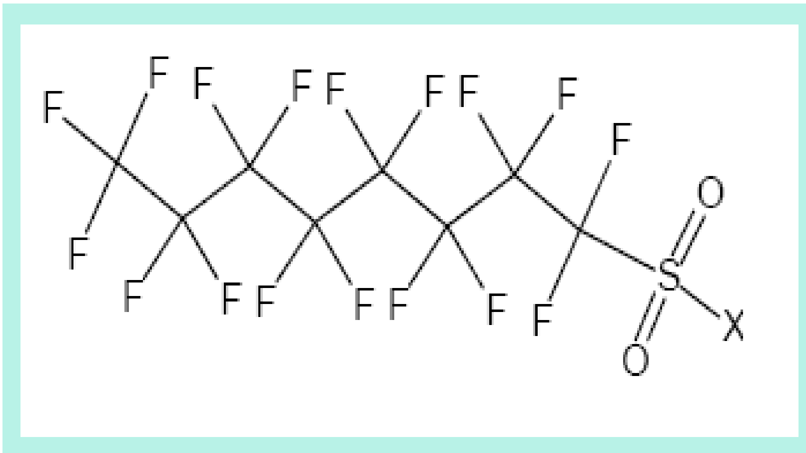
1. *Reduction in the use or replacement of ESH-problematic materials*
   New strategies to design biodegradable PFAS.

2. *Reduction in emission of ESH-problematic material to environment*
   ≈ 100% removal of PFOS from aqueous waste streams.

3. *Reduction in the use of natural resources (water and energy)*
   Considerable reduction in energy consumption compared to alternative treatment methods such as reverse osmosis, ultrasonic treatment, etc.

4. *Reduction in the use of chemicals: ----*

PFOS in Semiconductor Manufacturing



Perfluorooctane sulfonate (PFOS)

- **PFOS/PFAS are critical constituents of leading edge photoresists for use as photoacid generators (PAGs) and surfactants in anti-reflective coatings (ARCs).**

Treatment Methods for Removing PFOS Needed

- **Increasing evidence of the significance of PFOS/PFAS as persistent - bioaccumulative – toxic (PBT) contaminants.**

- **Significant new use rule (SNUR, 2002) restricting the use of PFOS with exemptions for semiconductor industry.**

PFOS in the Serum of Adult American Blood Donors

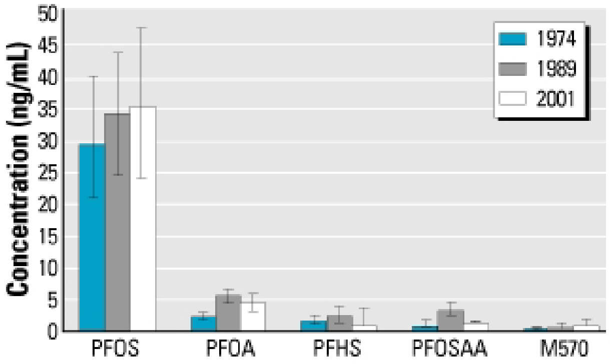


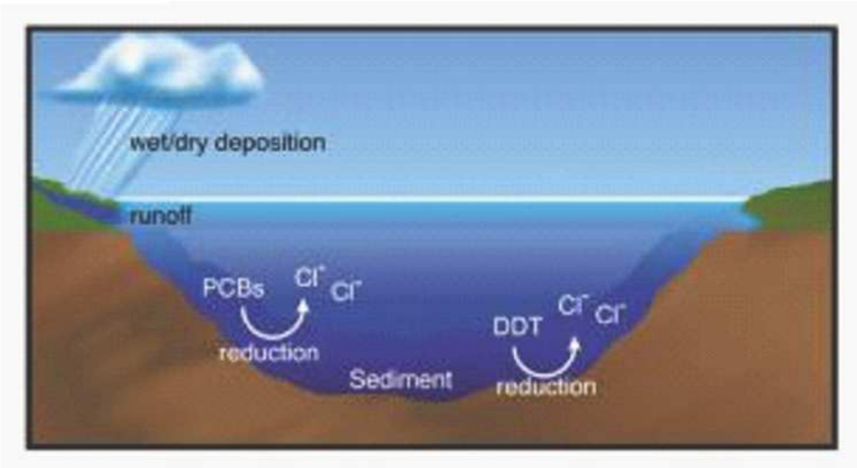
Figure 1. Median fluorochemical concentrations and IQRs for blood samples collected in Washington County, Maryland, from adults living in proximity in 1974 (*n* = 178 serum samples) and 1989 (*n* = 178 plasma samples) and in the county in 2001 (*n* = 108 serum samples; Olsen et al. 2003c).

Olsen et al. 2005. Environ. Health Perspect.

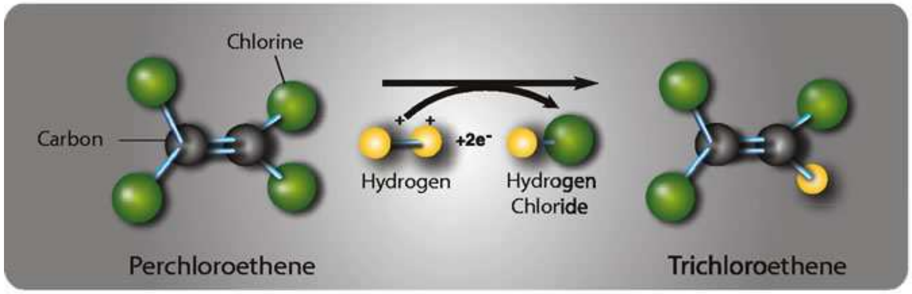
- **Effective methods to minimize environmental emissions of PFOS and maintain existing regulatory exemptions are needed.**

Reductive Dehalogenation

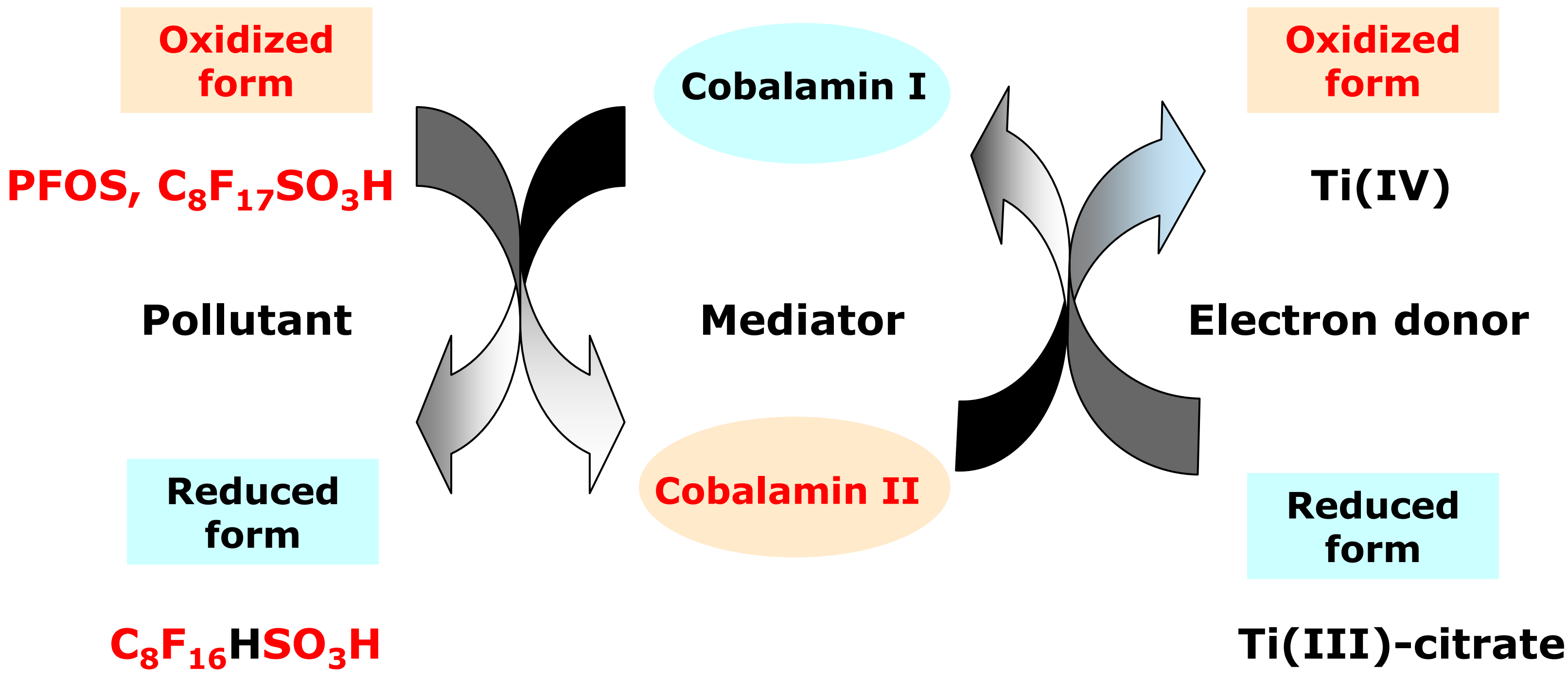
Microbial reductive dehalogenation is the main means of degradation of highly halogenated organics. Eg. PCE, PCBs, PBDEs.



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



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



Method of Approach

- ***Development of analytical techniques***

  Analysis of PFOS and PFOS degradation products by HPLC, LC-MS-MS, GC-MS and F-NMR. Concentration/clean-up by SPE.

- ***Microbial reductive dehalogenation:***

  Shaken batch bioassays supplemented with H_2/vitamin B_{12} and different inocula, including sludges/sediments exposed to fluoroorganics.

- ***Biomimetic reductive dehalogenation***

  Batch bioassays with vitamin B_{12} as catalyst and Ti(III) citrate as reducing agent.

- ***Monitoring of PFOS and PFOS degradation products***

  Fluoride release, Analysis of PFOS and PFOS degradation products by HPLC, LC-MS-MS, and F-NMR

Method of Approach

- ***Optimization of chemical reductive dehalogenation:***

  Technical PFOS with vitamin B_{12}/ Ti(III)

  Temperature, pH, [vitamin B_{12}] and [Ti (III) citrate]

- ***Mechanisms of reductive dehalogenation***

  Role of vitamin B_{12} on chemical reductive dehalogenation

  Electron Paramagnetic Resonance (EPR) – radical mechanism

- ***Enhanced Vitamin B_{12} catalysis via reactive surfaces***

  Solid supports (e.g., Zeolites and activated carbon).

- ***Biodegradation by microorganisms in municipal wastewater treatment systems***

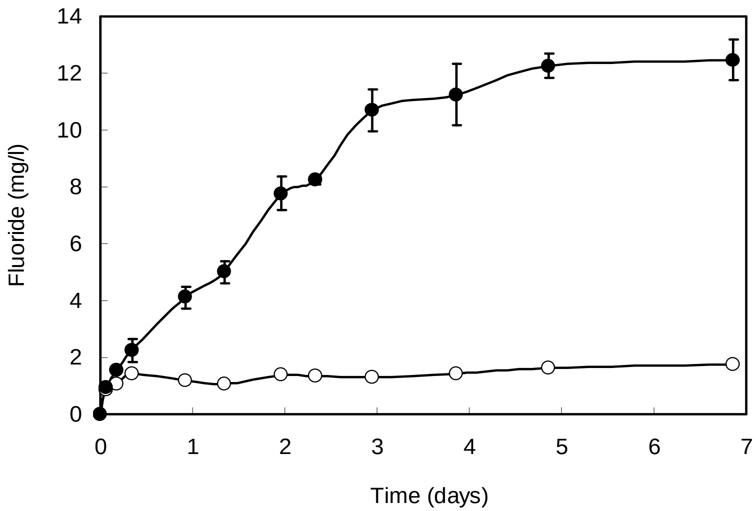
  Biodegradation and toxicity bioassays under different redox conditions

Results

Chemical *vs.* Microbial Reductive Dehalogenation

- PFOS is reductively dehalogenated by vitamin B_{12}/Ti(III) citrate.

A



Technical PFOS:
18% defluorination (3 atoms F^-/mol PFOS)

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.

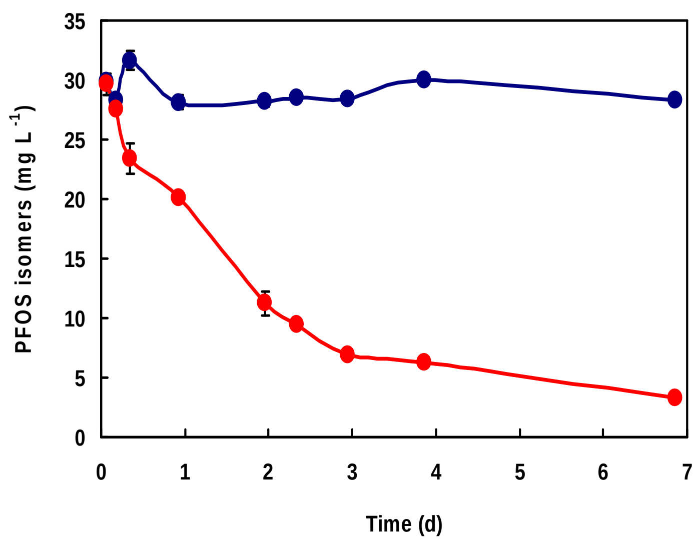
- PFOS is highly resistant to microbial reductive degradation by natural mixed inocula after long periods of incubation (> 2 years)

Results

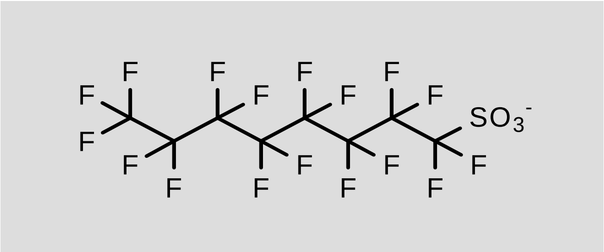
Chemical Reductive Dehalogenation

- ❖ Technical PFOS contains 20-30% branched isomers.
- ❖ Branched PFOS isomers more susceptible to reductive dehalogenation compared to the linear PFOS isomer.

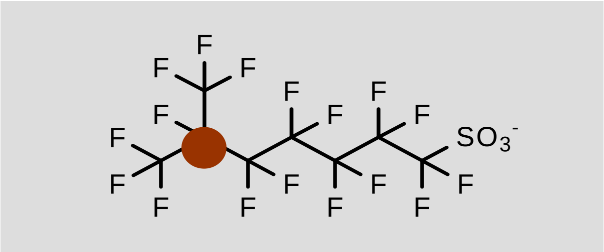
Branched PFOS: 71% defluorination



Time course of disappearance of branched PFOS isomers with vitamin B12 and Ti(III) citrate (36 mM) by HPLC-IC



Linear isomer

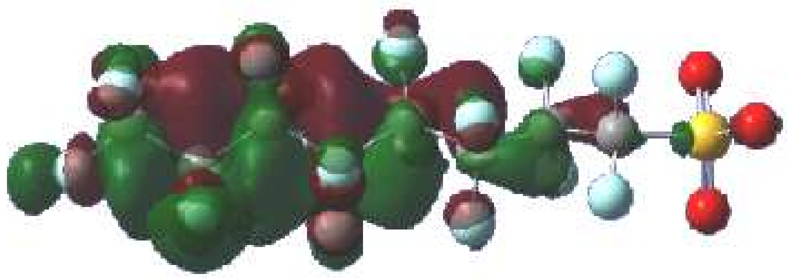


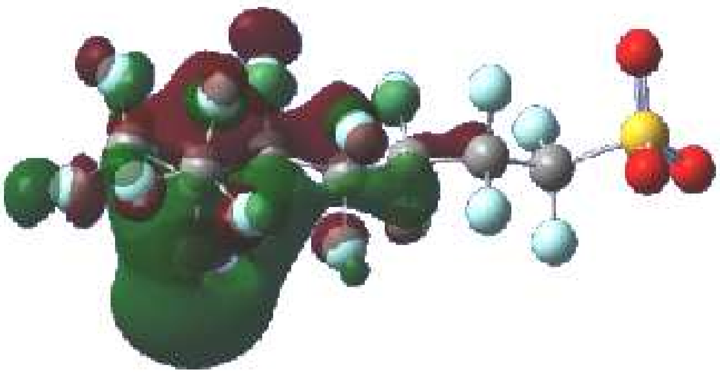
Branched isomer

† Ochoa-Herrera et. al. *Environ. Sci. Tech*, 2008,**42**:3260-3264

Results:

Ab-initio Calculations for Linear and Branched isomers





LUMO molecular orbitals of linear PFOS *(a)* and branched isomer, 6-CF3-PFOS *(b)* anions. Isosurface plots of the MOs were generated with an isodensity value of 0.02 a.u.

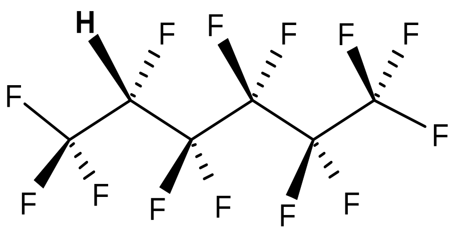
- **Branched PFOS isomers (*e.g.* 6-CF3-PFOS) expected to be more reactive with free radicals than linear PFOS isomer, their LUMO orbital is more accessible.**

Results:

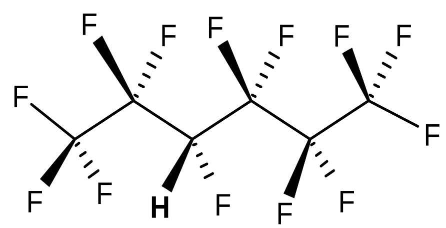
Identification of Degradation Products

- LC-MS/MS, solid and liquid F-NMR and GC/MS studies were conducted to identify the products of the PFOS dehalogenation.

- Release of carbon dioxide (CO_2) from PFOS (≈15%) and traces of volatile fluorinated compounds detected in the gas phase.



2H-Perfluorohexane



3H-Perfluorohexane

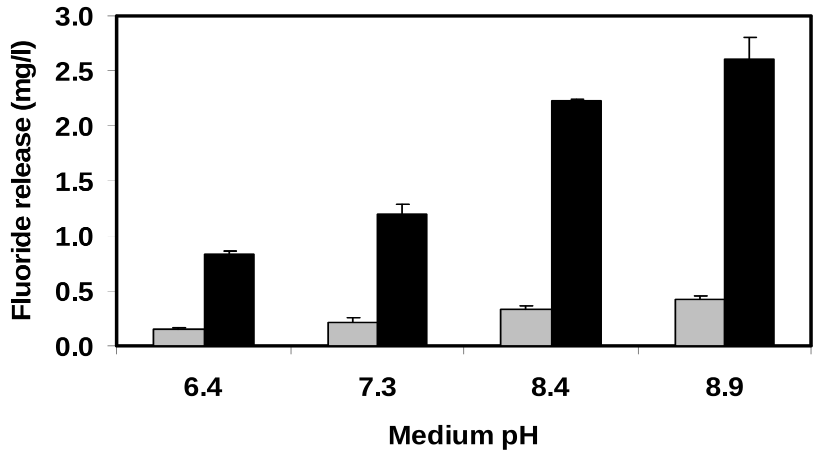
- No PFOS degradation products were detected in the reaction solution or in the insoluble/colloidal fraction.

Results

Optimization of Chemical Reductive Dehalogenation

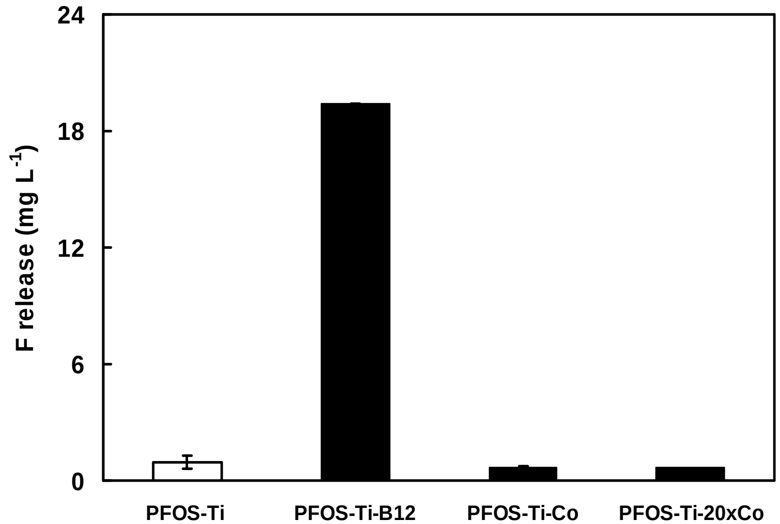
- Kinetics of chemical reductive dehalogenation of PFOS with vitamin B_{12}/ Ti(III) citrate: pseudo-first order reaction (K = 0.0204 h^{-1}).

- The optimal conditions for reductive dehalogenation were: 260 μM vitamin B_{12}, 36 mM Ti(III) citrate, temperature of 70°C and pH 9.0.



Gray bars = Controls with PFOS + Ti(III);
Black bars = Complete treatments with PFOS + Ti(III) + vitamin B12.

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 B_{12}.
- Electron paramagnetic resonance (EPR) results confirmed the involvement of a radical-mediated mechanism.

Conclusions

- **PFOS is susceptible to chemical reductive dehalogenation by vitamin B_{12}/Ti(III).**

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

  Branched PFOS better ESH characteristics (more prone to biodegradation)

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

- **Optimized temperature and pH greatly enhances PFOS reductive dehalogenation kinetics**. T = 70ºC ; pH = 9

- **Catalysis of vitamin B_{12} not enhanced by reactive surfaces.**

  Activated carbon and zeolites did not increase defluorination rates

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

  No F^- release in 2 years from technical PFOS

Industrial Interactions and Technology Transfer

- **Sematech/ISMI (Walter Worth, Steve Trammell)**
- **TI (Tim Yeakley – TI)**

Future Plans

Next Year Plans

- **Summarize previous studies and submit several manuscripts for transfer of know-how to technical community.**

Publications, Presentations, and Recognitions/Awards

- **Publications**

Ochoa-Herrera V, Sierra-Alvarez R, Somogyi A, Jacobsen NE, Wysocki VH, Field JA. 2008. Reductive defluorination of perfluorooctanesulfonate (PFOS). *Environ. Sci. Technol.* 42(9):3260-3264.

Torres, F.J., Ochoa-Herrera, V., Blowers, P; Sierra-Alvarez, R. 2009. *Ab initio* study of the structural, electronic, vibrational, and thermodynamic properties of linear perfluorooctane sulfonate (PFOS) and its branched isomers. *Chemosphere (Submitted)*.

Ochoa-Herrera. 2008. Removal of perfluorooctane sulfonate (PFOS) and related compounds from industrial effluents. PhD dissertation, University of Arizona, December 2008.

- **Awards**

Ochoa-Herrera, V. Outstanding teaching assistant of the Dept. Chemical and Environmental Engineering, academic year 2006/2007.

Deliverables

Report on the susceptibility of PFOS and related perfluoroalkyl surfactants to chemical biomimetic degradation (June 2007 and 2008)
- *Completed*

Report on the susceptibility of PFOS and related perfluoroalkyl surfactants to microbial reductive dehalogenation (June 2007 and 2008)
- *Completed*

Report on the removal of dehalogenated products from PFOS and related perfluorinated compounds under conditions relevant to municipal wastewater treatment plants (Dec 2008).
- *Completed*

Pilot testing and design of a pretreatment method based on reductive dehalogenation to enhance the removal of perfluoroalkyl surfactants during conventional biological wastewater treatment (March 2009)
- *Chemical reductive dehalogenation only effective to remove branched isomers*

Destruction of Perfluoroalkyl Surfactants using Boron Doped Diamond Film Electrodes (*Task Number: 425.018)*

PI:

- **James Farrell, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Kimberly C. Carter, PhD candidate, Chemical and Environmental Engineering, UA**

Undergraduate Students:

- **none**

Other Researchers:

- **Zhahui Liao, Postdoctoral Fellow, Chemical and Environmental Engineering, UA**

Cost Share (other than core ERC funding):

- **$100 k from National Science Foundation, Small Grants for Exploratory Research**

Destruction of Perfluoroalkyl Surfactants in Semiconductor Process Waters Using Boron Doped Diamond Film Electrodes

(Task Number: 425.018)

Subtask Subtitles:

 # Susceptibility of PFAS oxidation and reduction products to biodegradation under conditions relevant to municipal wastewater treatment plants.

 # Development of an adsorptive method using hydrophobic zeolites and/or anion exchange resins for concentrating PFAS compounds from dilute aqueous solutions.

PI:

- **Reyes Sierra, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Valeria Ochoa, PhD candidate, Chemical and Environmental Engineering, UA**

Undergraduate Students:

- **Chandra Kathri, Chemical and Environmental Engineering, UA**

Other researchers

- **Sandra Hernandez, PhD candidate, University Autonomous of Coahuila, Mexico**

Cost Share (other than core ERC funding):

UA/NASA grant (to C. Kathri) / CONACyT grant (to S. Hernandez)

Objectives

- Determine the feasibility of electrochemical destruction of perfluoroalkyl surfactants (PFAS) in aqueous waste streams.
- Determine the susceptibility of PFAS compounds and their oxidation products to microbial degradation.
- Determine the degree of electrolysis required to generate products that are readily biodegraded in municipal wastewater treatment plants.
- Develop an adsorptive method for concentrating PFAS compounds from dilute aqueous solutions.
- Test the proposed multistep treatment scheme on real semiconductor wastewaters containing PFAS compounds.

ESH Metrics and Impact

1. Reduction in emission of ESH-problematic material to environment.

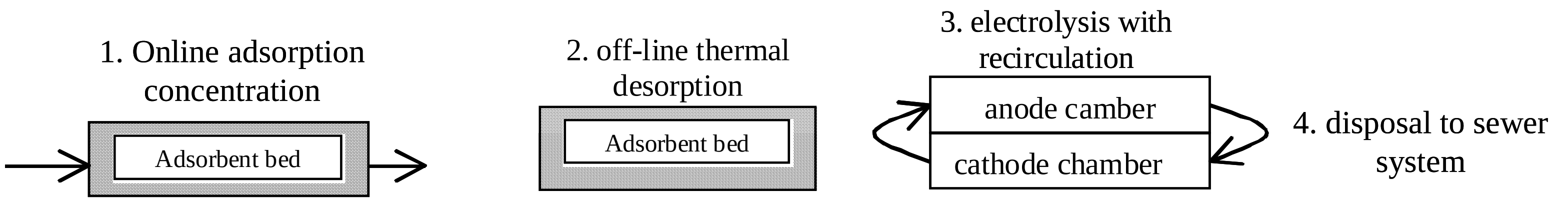
- 100% destruction of perfluoroalkyl surfactants in wastewaters
- technology can also be used for destruction of other ESH-problematic organic compounds

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

- energy savings by avoiding costly reverse osmosis (RO) separation
- water savings by recovering all the treated wastewater (no RO retentate disposal)
- energy savings by avoiding combustion of PFAS compounds in RO retentate

3. Securing the critical use exemption status for PFAS and related compounds in the semiconductor industry.

Proposed Treatment Scheme



Multi-step treatment scheme:

1. **Concentrate PFAS from dilute aqueous solutions on an adsorbent or ion exchange resin.**

2. **Desorb PFAS into a concentrated solution.**

3. **Recirculate concentrated PFAS solution through a BDD electrode reactor for electrolytic destruction.**

4. **Dispose of biodegradable electrolysis products to the sanitary sewer system.**

Experimental Systems

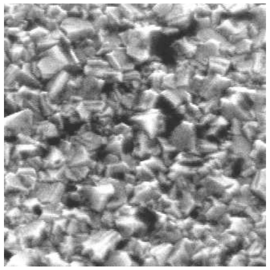
Rotating Disk Electrode (RDE) Reactor

- **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**

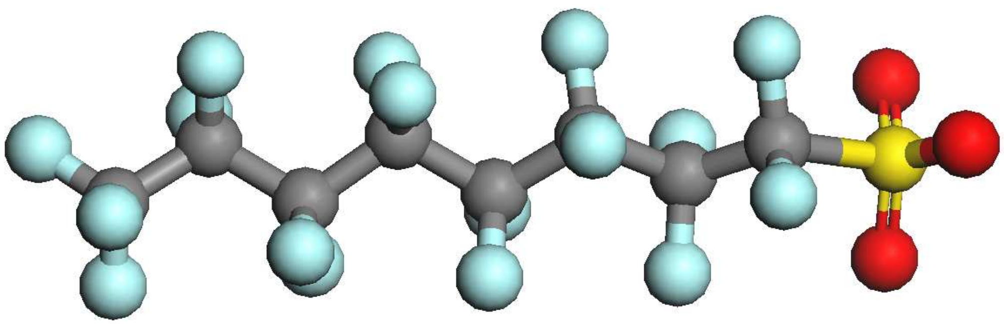
Boron Doped Diamond Film Electrodes



- **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**

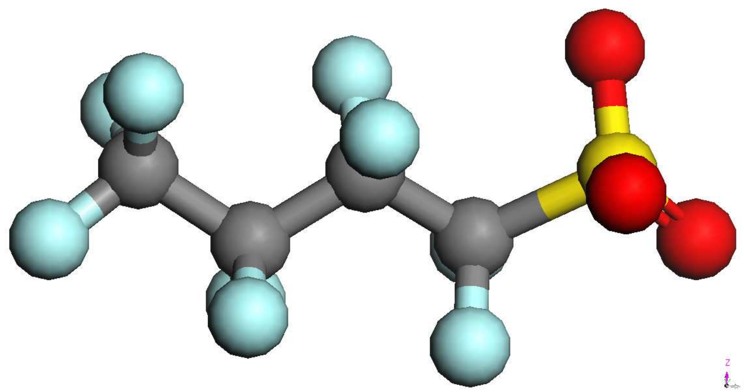
Target Compounds:

perfluorooctyl sulfonate (PFOS)



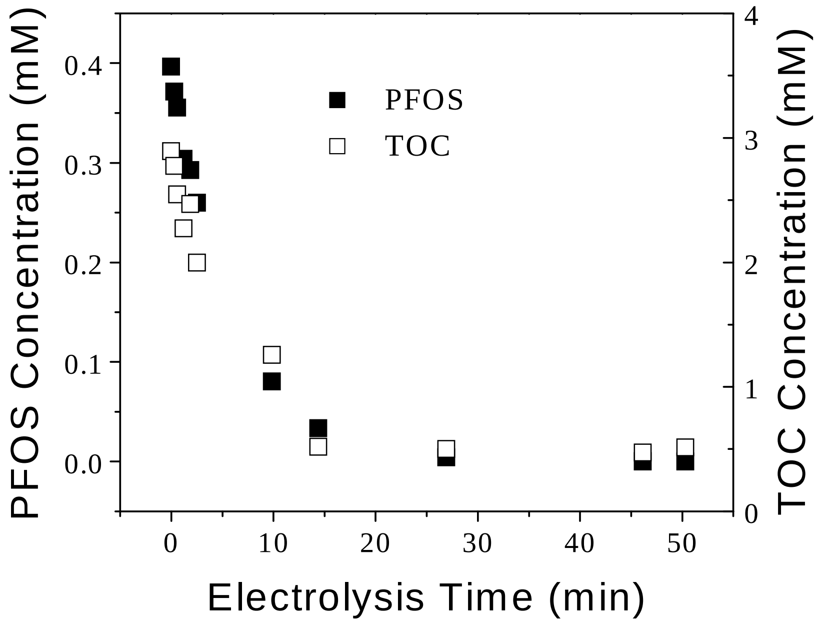
Most widely used PFAS.

perfluorobutyl sulfonate (PFBS)



Potential replacement for PFOS.

Experimental Results:
Flow Through Reactor



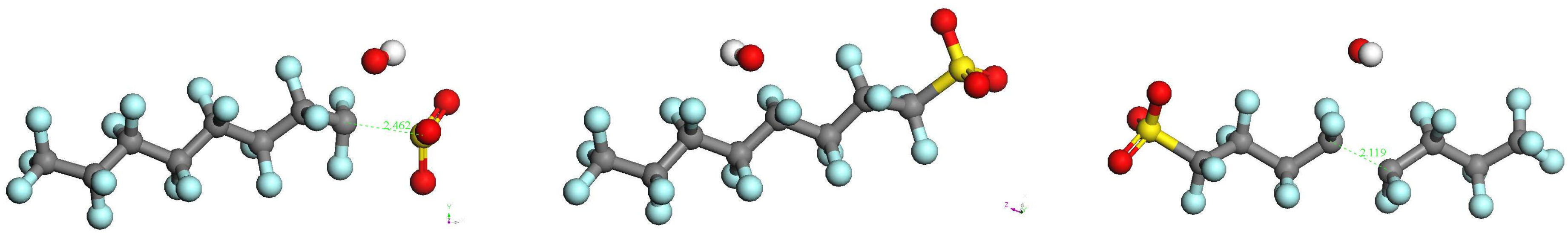
PFOS & total organic carbon (TOC) concentrations as a function of electrolysis time for the flow-cell operated at a current density of 20 mA/cm^2.

- 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.
- Measured activation energy for PFOS oxidation is 4.2 kJ/mol.

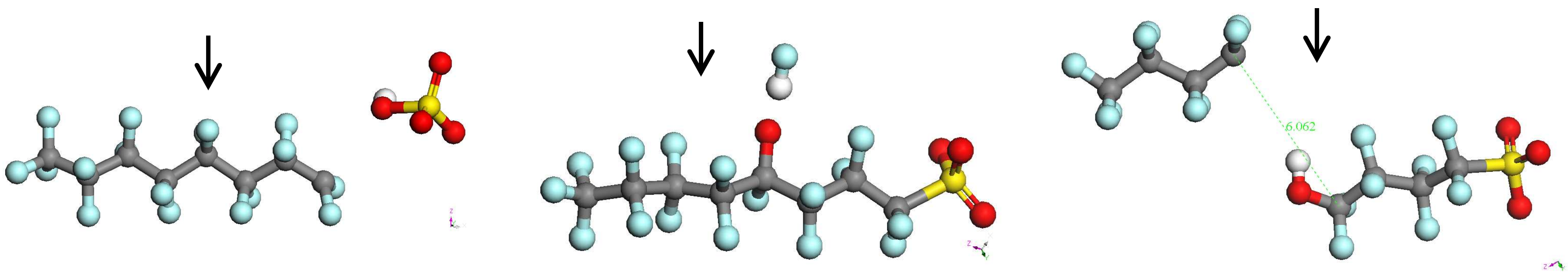
Quantum Chemistry Modeling: Activation Energies for HO• Attack

Transition State Structures

E_a= 123 kJ/mol E_a= 241 kJ/mol E_a= 169 kJ/mol



Final Products



- **Activation energies are much higher than those observed for compounds that readily react at room temperature.**

Reaction Mechanisms

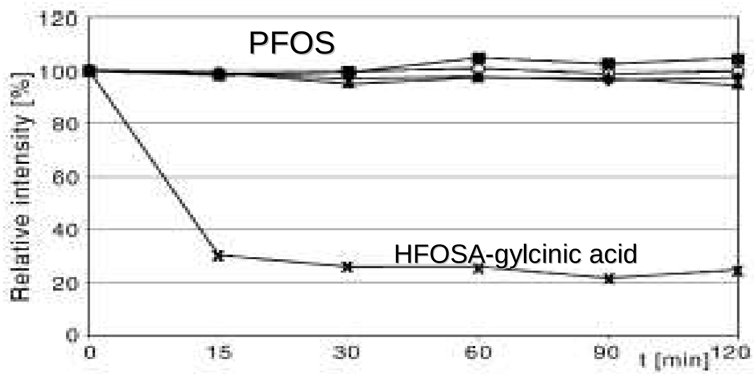


Fig. 1. Graphs of elimination for PFOS and HFOSA-glycinic acid under AOP treatment over a period of 120 min applying different AOP reagents (PFOS treated with: O_3 ▲; O_3/UV ■; O_3/H_2O_2 ♦; Fenton ○; HFOSA-glycinic acid treated with: O_3/UV ×).

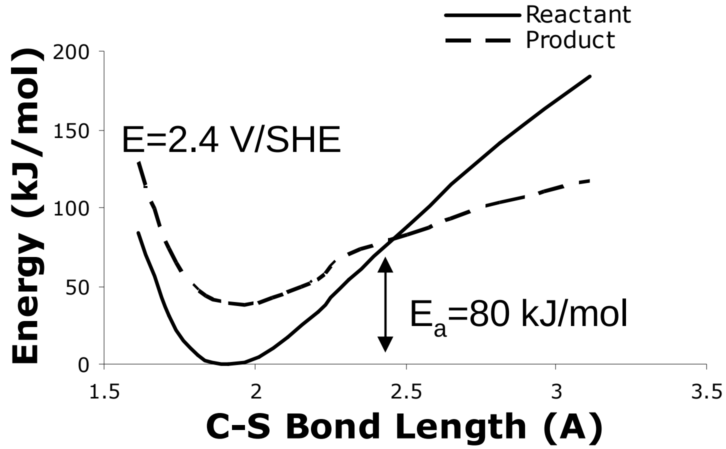
Schroder and Meesters, *J. Chromatog. A*., 2005.

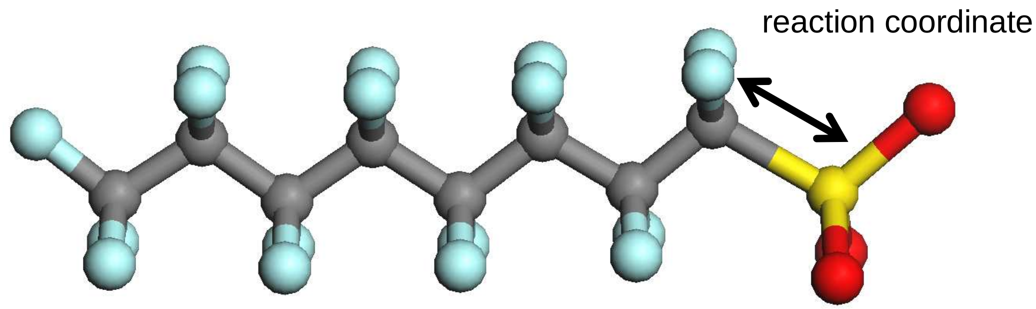
PFOS unreactive with:

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 oxidation methods.
- **Oxidation by BDD electrodes is much more powerful than peroxide based oxidation methods.**

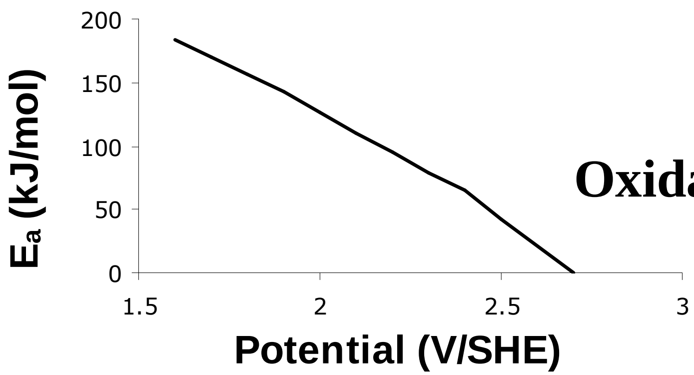
Quantum Chemistry Modeling: E_a for Direct Electron Transfer





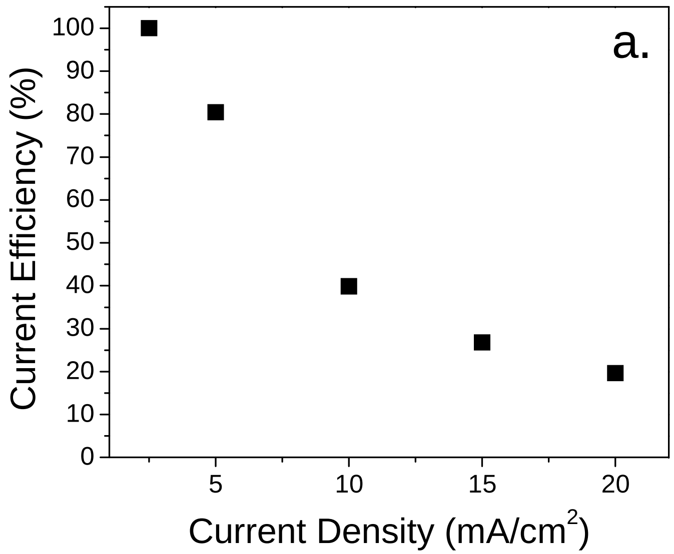
$$C_8F_{17}SO_3^- \rightarrow C_8F_{17}\text{-}SO_3^{\bullet} + e^-$$

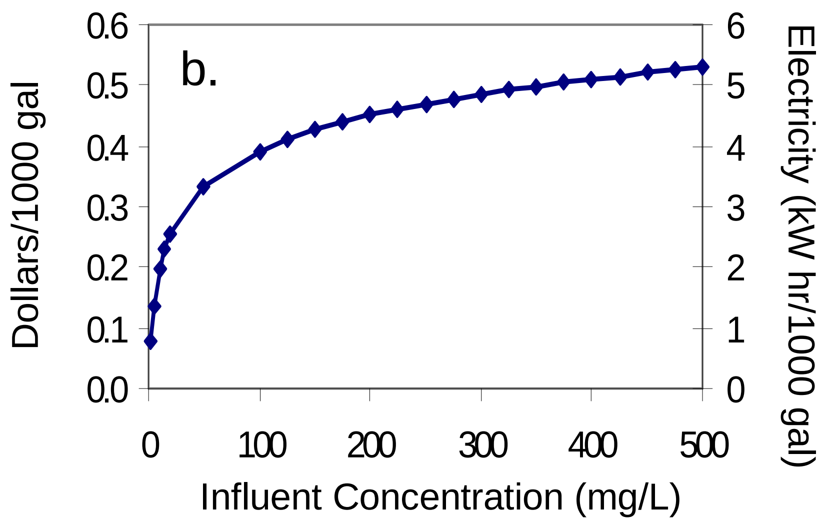
reactant $\rightarrow$ products



Oxidation becomes activationless at E>2.7 V/SHE.

Current Efficiencies and Treatment Costs





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

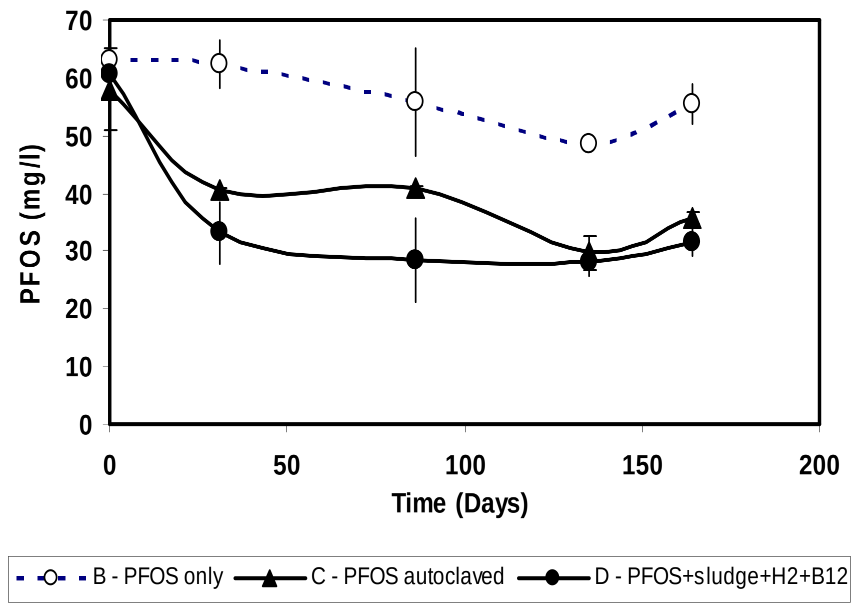
b) Electrical power requirements and costs required to reach a final PFOS concentration of 1 mg/L (2.5 µM) as a function of the influent PFOS concentration. Costs based on flow-cell operated at a current density of 20 mA/cm^2 and an energy cost of $0.10/kWhr.

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

Results:

Microbial Degradation of PFOS and PFBS Electrolysis Products

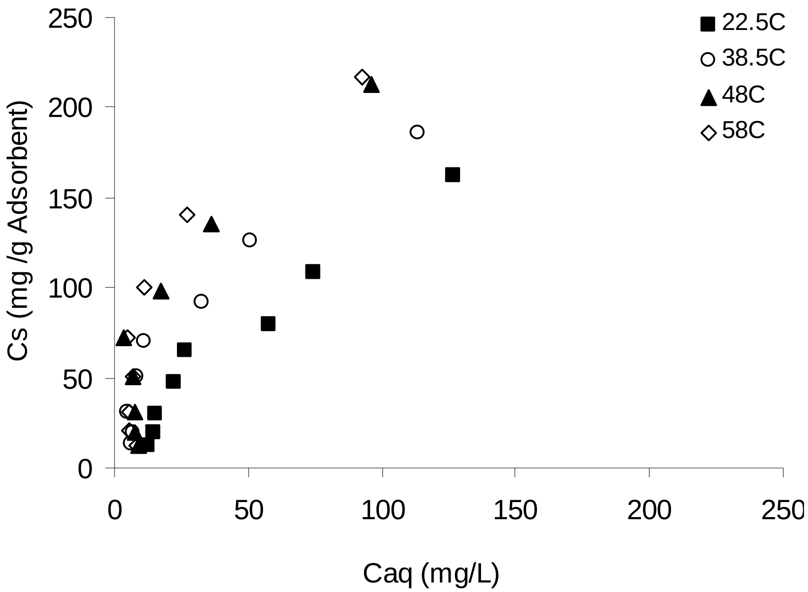
Time course of the anaerobic degradation of PFOS electrolyzed for 24 h. Abiotic control(■), killed sludge control (▲) and full treatment (●).

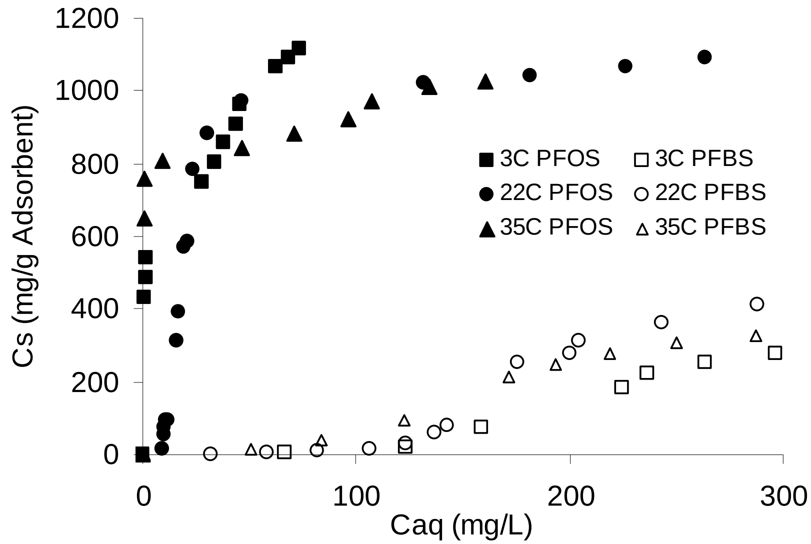


Products of PFOS and PFBS electrolysis are very persistent.

- Electrochemical treatment of FPOS and PFBS for up to 24 and 96 h, resp., did not enhance the compound's anaerobic biodegradation even after extended incubation (> 1.1 years).
- PFOS partly adsorbed by microbial sludge.

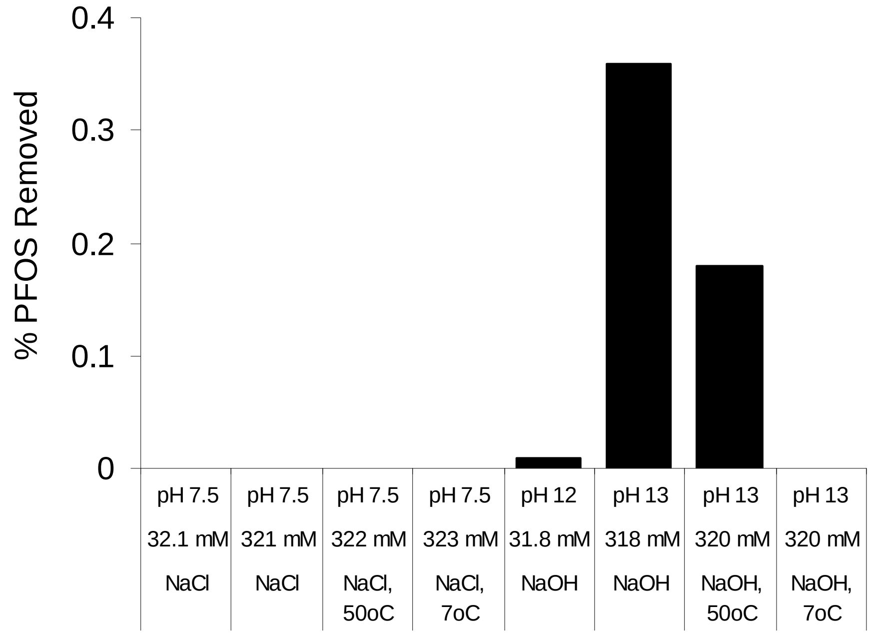
Adsorbent Testing





- Measured adsorption isotherms on GAC, ion exchange resins and zeolites
- Greater adsorption at higher temperatures (endothermic)
- Thermal desorption of not possible

Adsorbent Regeneration Testing



- PFOS is irreversibly adsorbed to ion exchange resin.
- Reverse osmosis (RO) is only viable concentration method.

Conclusions

- PFOS and PFBS are rapidly mineralized to CO_2 and F^- at BDD electrodes without detectable intermediate products.

- No evidence for the microbial degradation of PFOS and PFBS was observed after extended incubation (> 1.0 y).

  - PFOS and PFBS are adsorbed by hydrophobic zeolites, activated carbon, and ion exchange resins.

  - Adsorption to ion exchange resins is irreversible.

Industrial Interactions and Technology Transfer

- **Walter Worth, Sematech, Walter.Worth@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**

Future Plans

Next Year Plans

- **Finish adsorbent regeneration tests by April 1, 2009.**

Long-Term Plans

- **Identify partners for pilot testing on RO concentrates containing organic compounds.**

Publications, Presentations, and Recognitions/Awards

- **K. E. Carter and J. Farrell, "Oxidative Destruction of Perfluorooctane Sulfonate using Boron Doped Diamond Film Electrodes," *Environ. Sci. Technol.* 2008, 42, 6111.**
- **Z. Liao and J. Farrell, "Electrochemical Oxidation of Perfluorobutane Sulfonate using Boron Doped Diamond Film Electrodes," *J. Applied Electrochem.*, in review.**
- **J. Farrell, "Electrochemical Water Purification using Boron Doped Diamond Film Electrodes" presented at the University of California at Los Angeles, 10/30/07.**
- **J. Farrell, "Electrochemical Water Treatment using Diamond Film Electrodes," presented at the University of Illinois at Urbana-Champaign, 11/7/08.**
- **James Baygents and James Farrell. "Electrochemical Methods for Water Reclaim in Semiconductor Manufacturing," presented at the International Conference on Microelectronics Pure Water, November 11-12, 2008, Mesa, AZ.**

Non-PFOS Photoacid Generators: Environmentally Friendly Candidates 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:

- **Jing Sha: PhD candidate, Materials Science and Engineering, Cornell University**
- **Victor Gamez, PhD candidate, Chemical & Environmental Engineering, UA**

Undergraduate Students:

- **Matthew West, , Chemical & Environmental Engineering, UA**

Other Researchers:

- **Woo Jin Bae, Postdoctoral Fellow, Materials Science and Engineering, Cornell Univ.**
- **Yi Yi, Postdoctoral Fellow, Materials Science and Engineering, Cornell University**

Cost Share (other than core ERC funding):

- **Rohm & Haas Support ($20K) Yi Yi**

Objectives

- **Develop PFOS free and environmentally friendly photoacid generators (PAGs) with easily degradable, biomolecular structures for chemically amplified resist application**

- **Develop PAGs with superior imaging performance**

- **Evaluate lithographic performance in selected model 193 nm and EUV resists**

- **Evaluate the environmental aspects of new environmentally friendly PAGs**

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)*

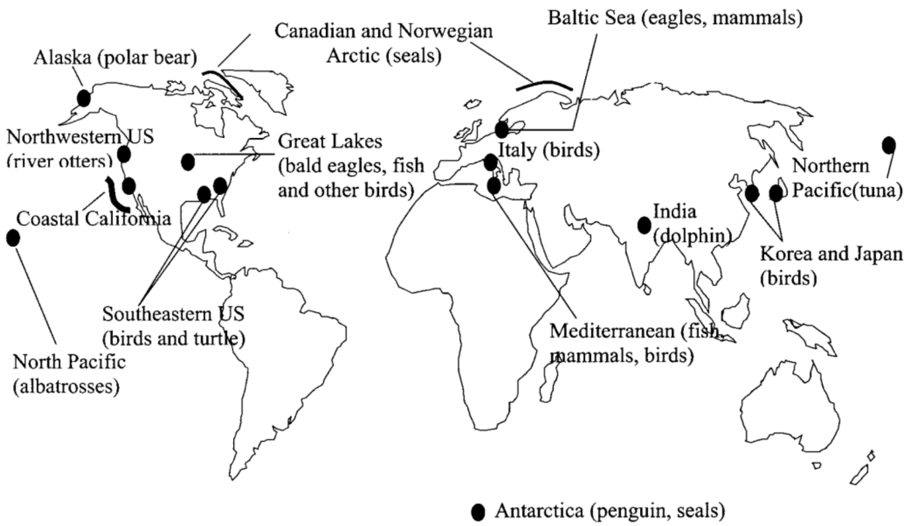
   Prepare new PAGs using simple, energy reduced chemistry in high yields and purity to reduce water use and the use of organic solvents.

4. *Reduction in the use of chemicals*

   By preparing new PAGs using simple chemistry in high yields and purity, we reduce the use of fluorinated chemicals.

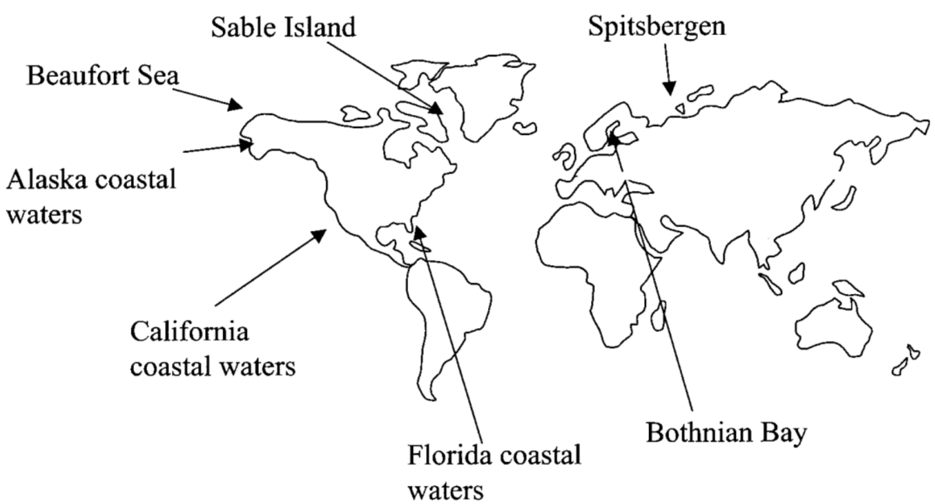
Bioaccumulation of PFOS

Global Distribution of PFOS in Wildlife



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

Accumulation of PFOS in Marine Mammals



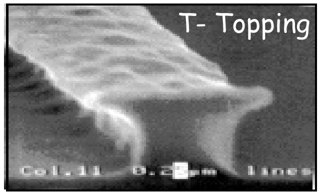
Environ. Sci. Technol. **2001, *35*, 1593.**

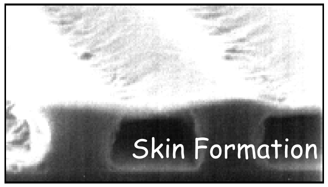
The EPA proposed a significant new use rule (SNUR) for PFOS in 2000.

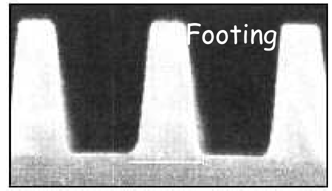
Next Generation PAGs – environmentally friendly, no bioaccumulation

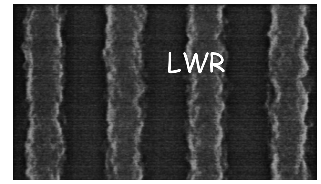
PFOS PAG Performance Issues

"Segregation or non-uniform distribution of PAG"



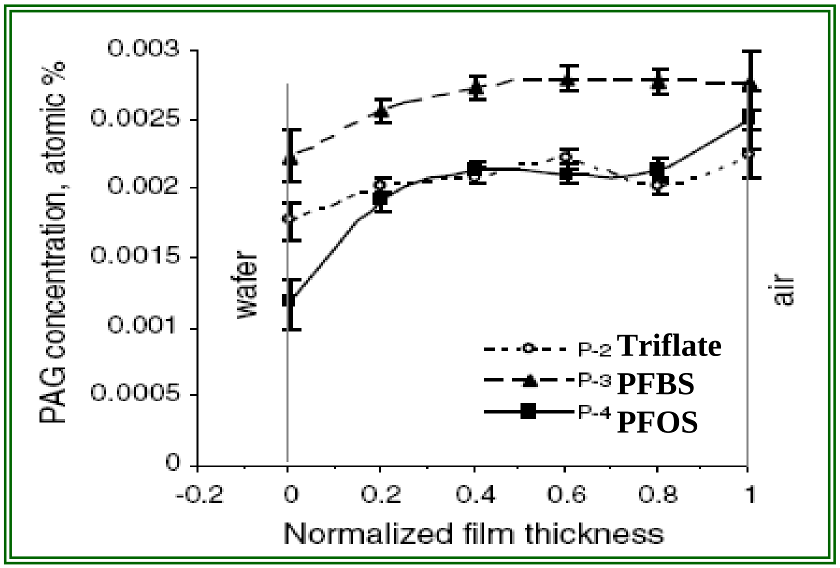




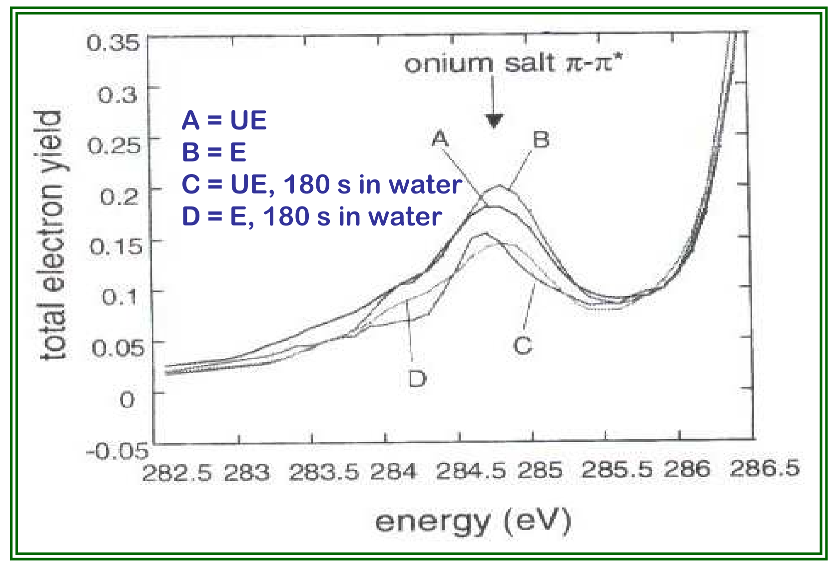


"Surface segregation increases with increase in fluorine content"

"PAG leaching Surface Phenomena"



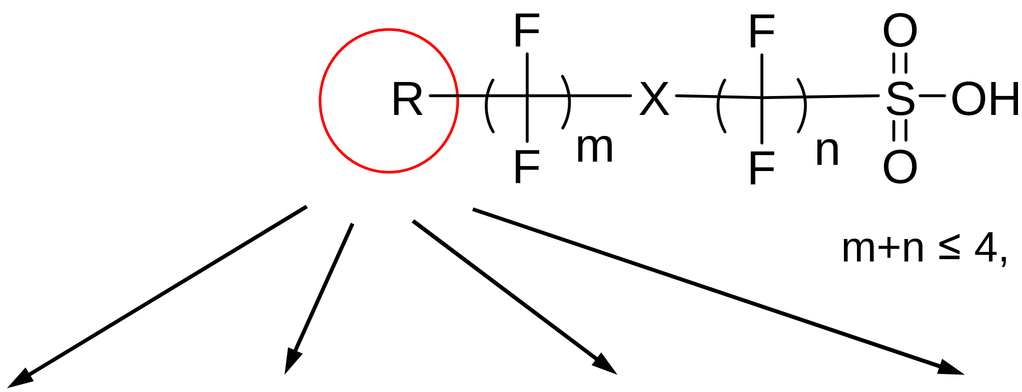
RBS Depth Profile of polar PAGs in a IBMA-MMA-MAA-t-BMA matrix



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



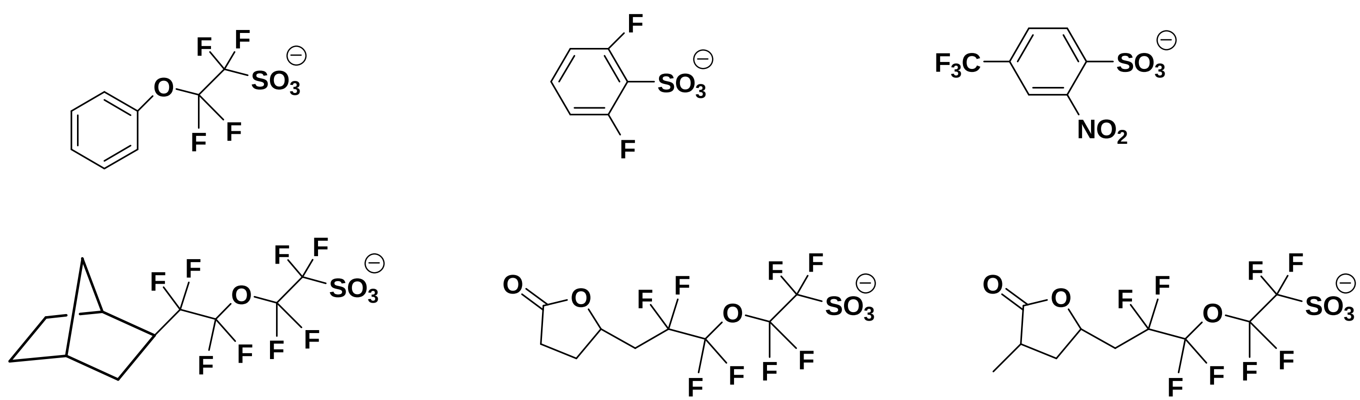
polar	**hydrophilic**	**aromatic**	**linear**
			branch
nonpolar	**hydrophobic**	**aliphatic**	**ring**

Practical synthetic chemistry considerations:

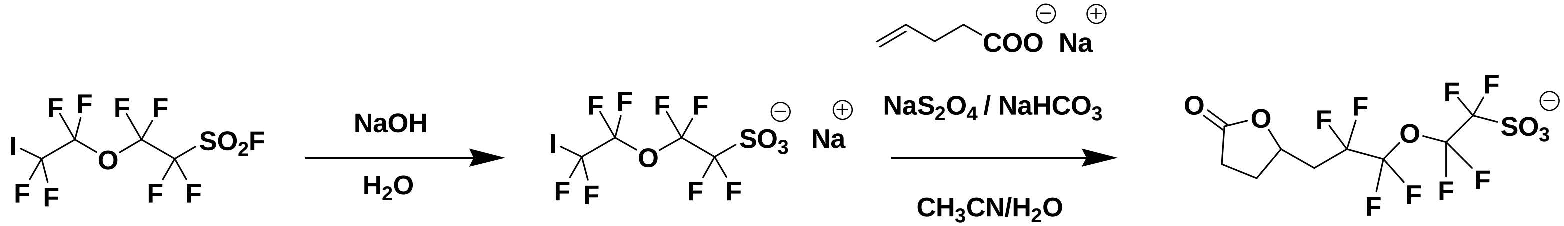
- **Simple chemistry — low cost & less time**
- **Efficient reactions — high yield & high purity**

New non-PFOS PAG Anions

Selected examples:

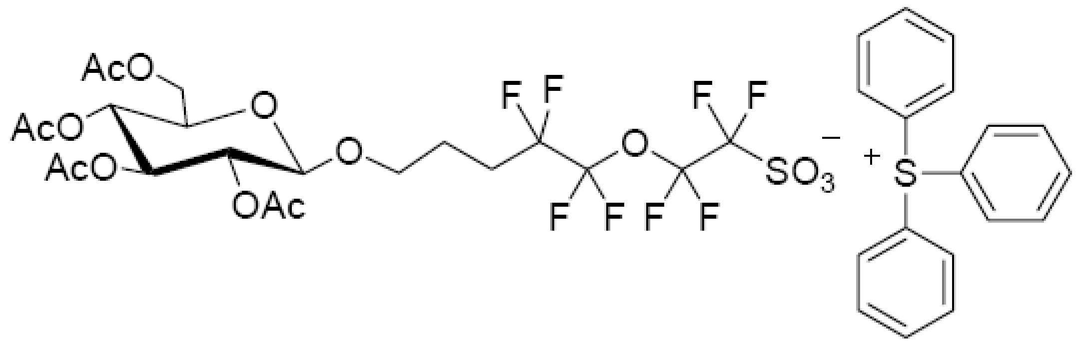


Synthetic scheme of a PAG anion:

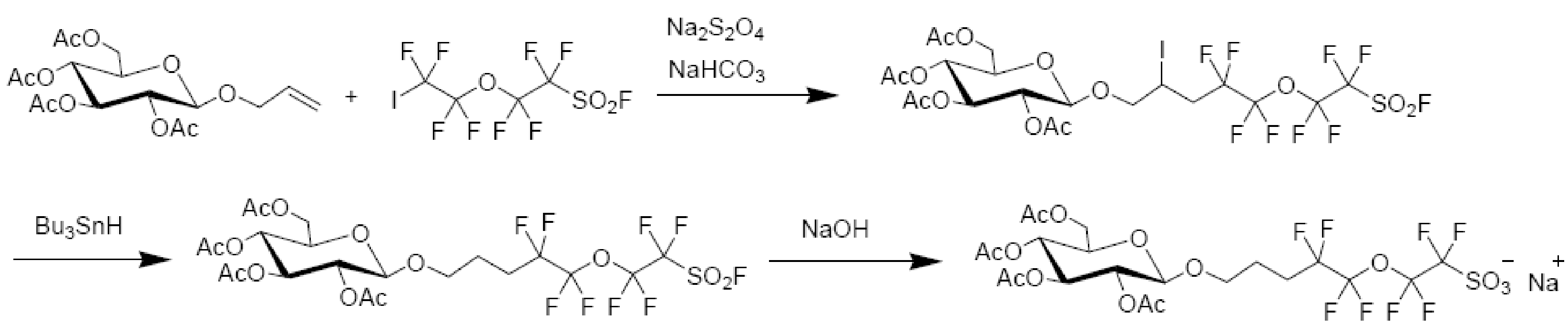


Synthesis of “Sweet” PAG

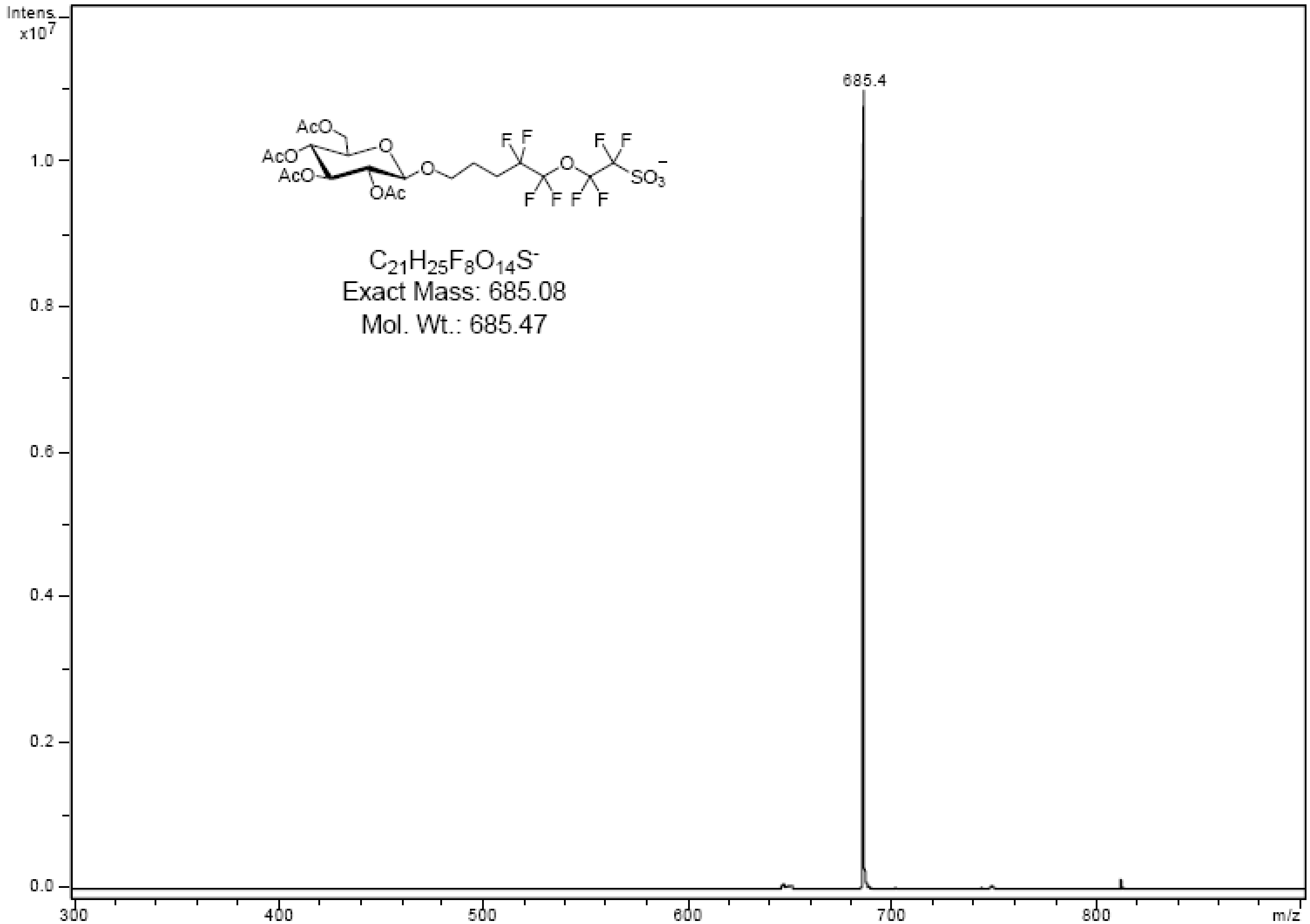
Final structure:



Synthetic Scheme:

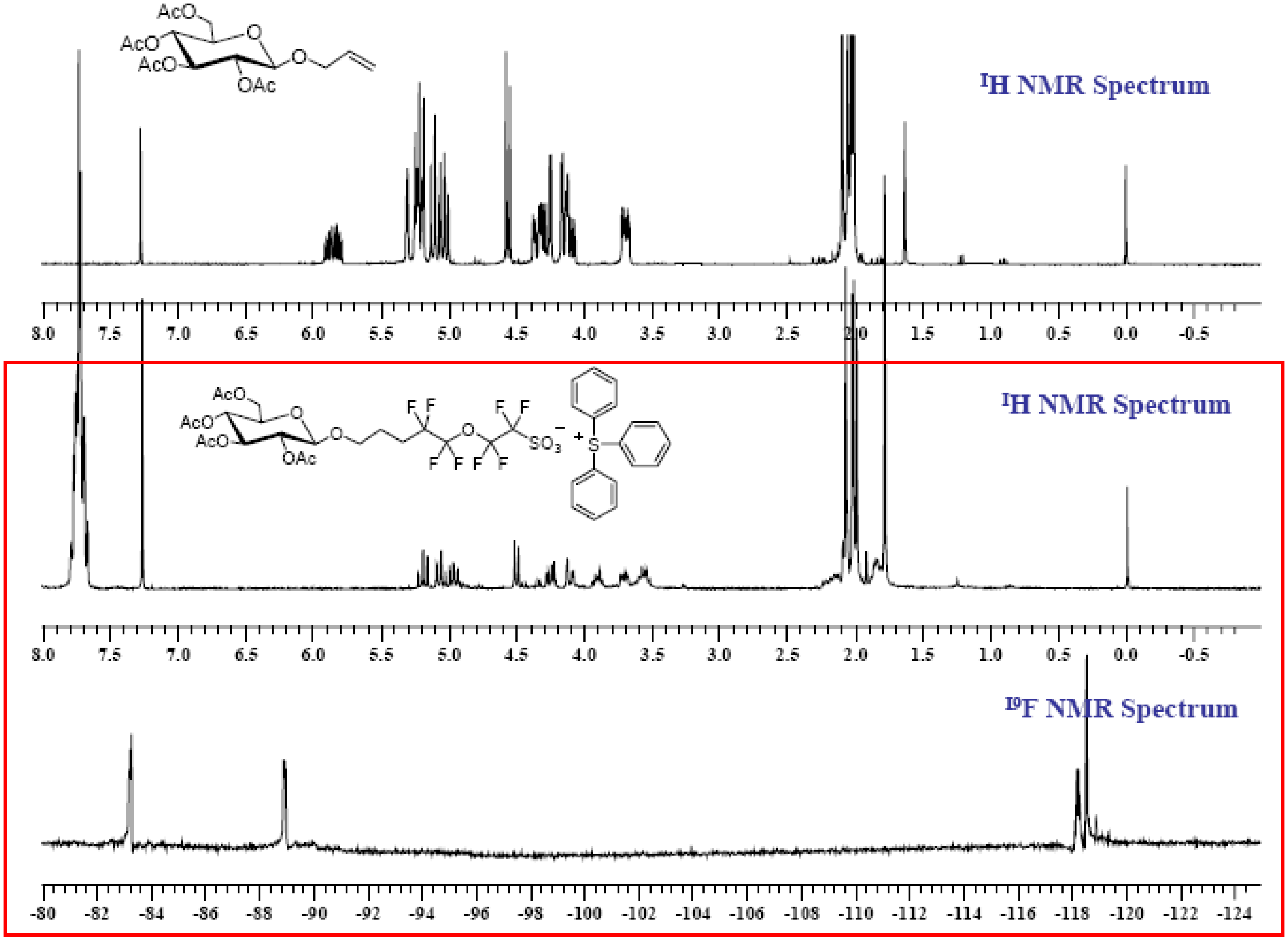


High Purity Sweet PAG (via MS)

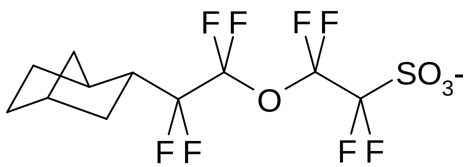


SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

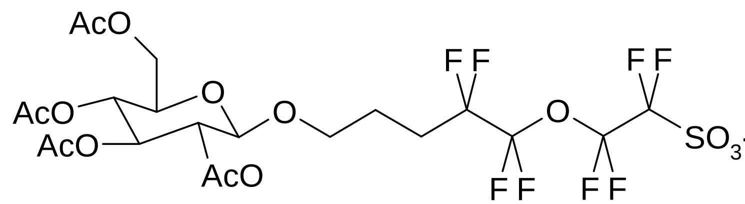
Characterization of Sweet PAG



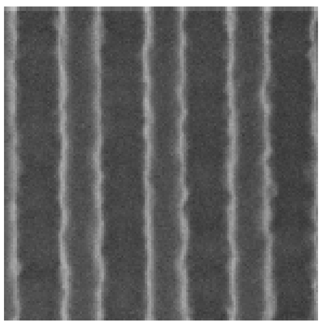
Evaluation of Lithographic Performance



NBPFEES (NB)



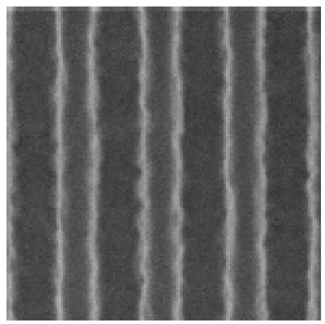
Sweet PAG (Sweet)



TPS-NB

90.8nm @ 23.8mJ/cm²

LER: 5.8±0.4



TPS-Sweet

92.2nm @ 27.3mJ/cm²

LER: 6.5±0.4

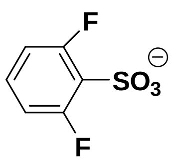
PAG	Esize@Target	MEF	EL by +/- 10% of target CD
TPS-NB	25.48	3.18	12.94
Sweet PAG	49.78	3.20	12.90

MEF (Mask Error Factor. The lower, the better)
EL (Exposure latitude. The higher, the better)

Collaboration with Rohm & Haas

Environmental Compatibility of New Non-PFOS PAG Anions

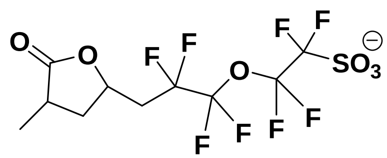
Selected examples:



PAG-1

1st generation PAG

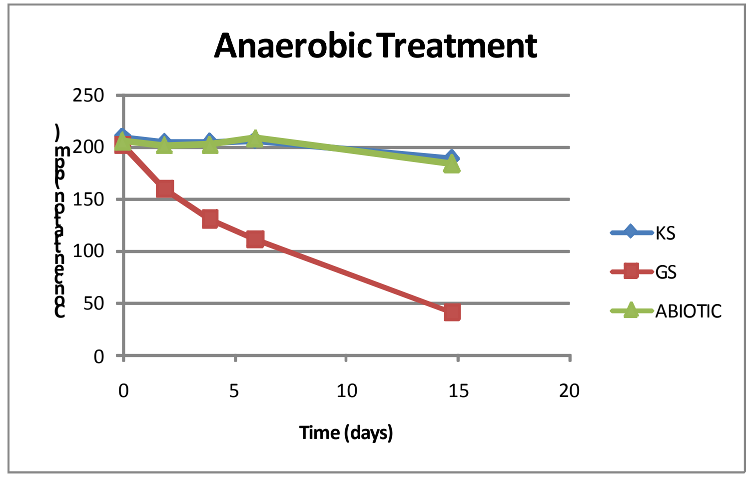
(Aromatic structure)



PAG-2

2nd generation PAG

(Aliphatic structure)



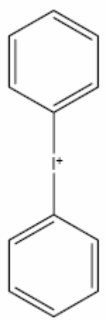
Degradation for PAG-2 in anaerobic batch bioassays. (KS) Abiotic sterilized control; (GS) complete treatment with active sludge; (ABIOTIC) sterile, non-inoculated control.

- **1st Generation Non-PFOS PAGs: Low toxicity and low bioaccumulation potential, but relatively persistent to microbial degradation.**

- **2nd Generation Non-PFOS PAGs: Preliminary results show that replacing the phenyl group with a UV-transparent alicyclic moiety increases the susceptibility of the PAG compound to biodegradation.**

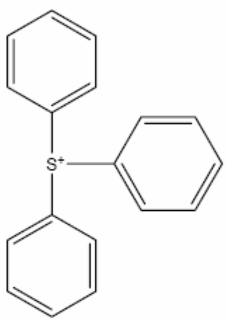
Environmental Compatibility of PAG Counterions

Selected examples of common PAG counterions:



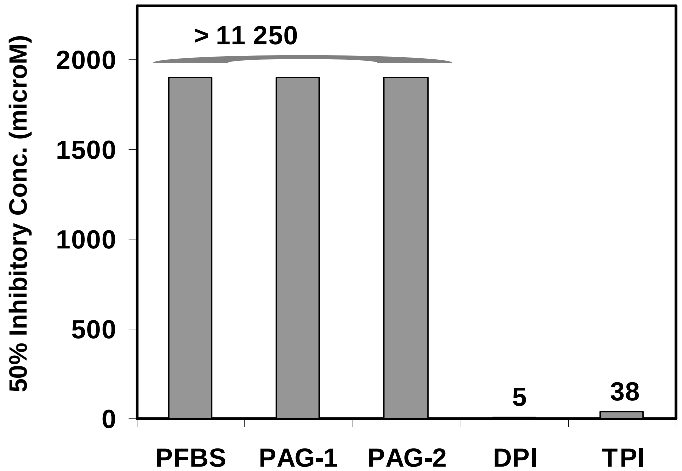
Diphenyliodonium

(DPI)



Triphenylsulfonium

(TPI)



Toxic response of the new PAG anions and selected PAG counterions in the Microtox assay. The most toxic compounds are those with the lowest inhibitory concentrations.

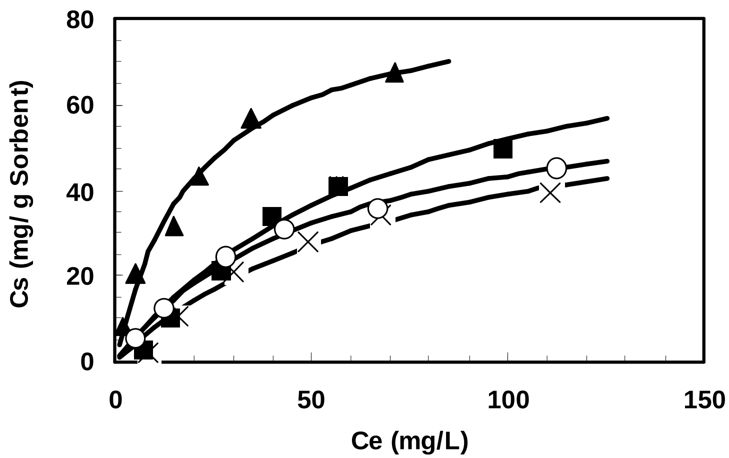
- **DPI and TPI should be replaced by more benign alternatives. Both counterions were highly toxic in assays with microbial and human cells.**

- **The EPA environmental compatibility software, PBT *Profiler,* estimated that triphenylsulfonium may be a PBT (persistent-bioaccumulative-toxic) pollutant.**

Treatability of New Non-PFOS PAG Anions (1st generation compounds)

The new non-PFOS PAG anions (1st generation) are amenable to removal by several physico-chemical treatment methods

- **Activated carbon adsorption**: PAGs can be removed with activated carbon. Adsorption increased with increasing side chain length.
- **Advanced chemical oxidation** (Fenton's reagent): Very efficient in the removal of new PAGs. PFOS and PFBS are recalcitrant to oxidative attack.
- **Chemical reduction with zero-valent iron:** Low or no removal of new PAGs, PFOS and PFBS.



Comparison of non-PFOS PAG adsorption on activated carbon. (X) PAG-1; (□) PAG-2; other first-generation non-PFOS PAGs: (▲) SF2; (■) PF1; Continuous lines show the fitting of the isotherm data to the Langmuir model.

Industrial Interactions and Technology Transfer

- **Samples provided to Rohm & Haas Electronic Materials**
- **Collaboration with Rohm & Haas Electronic Materials for photolithography tests of Sweet PAG**
- **Samples provided to TOK**
- **Samples provided to AZ Microelectronics**
- **Performance at 193 nm and EUV evaluated with the assistance of International Sematech and Albany Nanotech**
- **Interactions with Intel on LER issues**

Task Deliverables

- **Report on the completion of testing of new PFOS-free photoacid generators for 193 nm and EUV performance (Dec 06)**
  - ***completed***
- **Report on the assessment of the environmental compatibility of new PFOS-free photoacid generators. (Dec 07)**
  - ***completed***
- **Report on the completion of testing to determine the removal of PFOS-free photoacid generators by biological and physico-chemical treatment methods. (May 08)**
  - ***completed***
- **Report on new PFOS-free PAGs with improved performance and improved environmental impact. (Mar 09)**
  - ***On schedule***

Future Plans

Next Year's Plans

- Prepare next generation sugar-based Sweet PAG
- Reduce synthetic steps and use more environmentally friendly chemicals
- Environmental evaluation of the new Sweet PAGs
- Summarize previous studies and submit manuscripts for transfer of know-how to technical community

- More details during discussion of new projects

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.

•Yi, Yi; Ayothi, Ramakrishnan; Ober, Christopher K.; Yueh, Wang; Cao, Heidi. Ionic photoacid generators containing functionalized semifluorinated sulfonates for high-resolution lithography. Proceedings of SPIE (2008), 6923 69231B-69231B-8.

•Yi Yi, Ramakrishnan Ayothi, Yueh Wang, Mingqi Li, George Barclay, Heidi Cao and Christopher K. Ober, "Ionic Photoacid Generators for 193 nm & EUV Lithography", *J. Mater. Chem*., in preparation.

Presentations

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

•SPIE Conference, San Jose, CA, Feb. 26, 2008. "New Architectures for High Resolution Patterning"

•Sematech Workshop on Approaching the Optical Limit, Sagamore Hotel, Bolton Landing, NY, May 15, 2008. "LCAR 193nm Resists", invited talk with Bruce Smith (RIT)

•Rochester Institute of Technology, Rochester, NY, Oct. 22, 2008. "New Approaches to Sub-50 nm Lithography: Molecular Glasses and Block Copolymers", invited talk.

•CNMS Discovery Lecture Series, Oak Ridge National Laboratory and University of Tennessee, Knoxville, TN, Dec. 5, 2008. "Rethinking Photoresists: New Approaches to Making Very Small Structures", invited talk.

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
  - Victor Gamez, March 2009
- Internships (Task and related students)
  - Katy Bosworth, IBM
  - Evan Schwartz, Intel
  - Anuja de Silva, IBM

Toxicity Evaluation of HfO_2 Nanoparticles

(Sematech Customized Project)

Principle Investigators:

- **Jim A Field**, Chemical and Environmental Engineering, UA
- **Scott Boitano**, Physiology and Arizona Respiratory Center, UA
- **Buddy Ratner**, University of Washington Engineered Biomaterials Center, UWEB
- **Reyes Sierra**, Chemical and Environmental Engineering, UA
- **Farhang Shadman**, Chemical and Environmental Engineering, UA

Graduate Students:

- **Cara L Sherwood**: PhD candidate, Cell Biology and Anatomy, UA
- **Jeff Rottman**: PhD candidate, Chemical and Environmental Engineering, UA
- **Chris Barnes**: PhD candidate, Chemical Engineering, UW

Undergraduate Students:

- **Ivann Hsu**, Chemical and Environmental Engineering, UA

Other Researchers:

- **Antonia Luna**, Postdoctoral Fellow, Chemical and Environmental Engineering, UA

Cost Share (other than core ERC funding):

- **$80k from UA Water Sustainability Program**

Objectives

- **Develop useful toxicity assays for hafnium oxide (HfO_2) nanoparticles (NP)**
- **Develop characterization techniques to determine contaminants on NPs**

ESH Metrics and Impact

- **Identification of ESH-problematic materials (if any) during NP production**

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

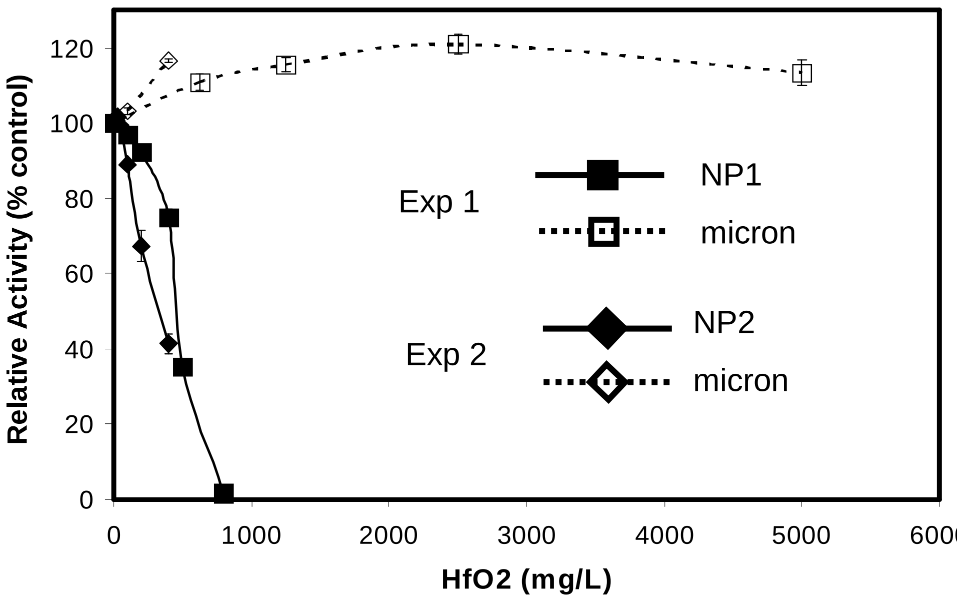
Samples Obtained/Particles Tested

- **Batch 1 nano-sized HfO_2 particles: "<u>NP1</u>"**
  (Average particle size: approx. 20 nm)
- **Batch 2 nano-sized HfO_2 particles: "<u>NP2</u>"**
  (Average particle size: approx. 1-2 nm; *HfO_2 with acetic acid)
- **Reference: Micron-sized HfO_2 particles**
  (Particle Size Distribution: 0.2 to 30 microns)

Toxicity Evaluations

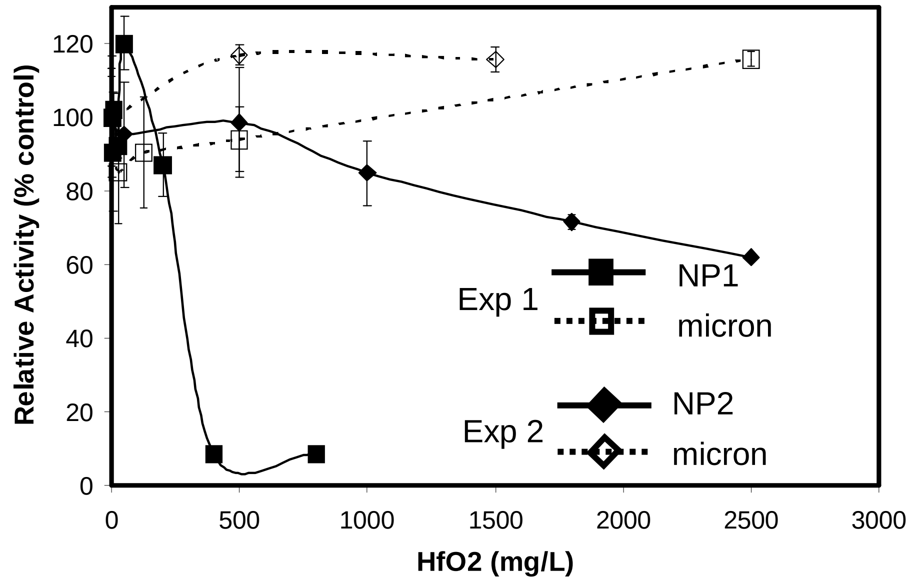
- **Microtox** (bacterium, *Vibrio fischeri*)
- **Mitochondrion Toxicity Test** (mammalian ureter epithelium cells)
- **Methanogenic Toxicity** (anaerobic microbial consortium)
- **Live-Dead Assay (**human skin cells (Ha-Cat)**)**

Microtox Assay



- **NP1 (20 nm) HfO_2 nanoparticles have moderate toxicity**
- **NP2 (1-2 nm) HfO_2 nanoparticles have moderate toxicity**
- **Reference, micron-sized HfO_2 particles non-toxic**

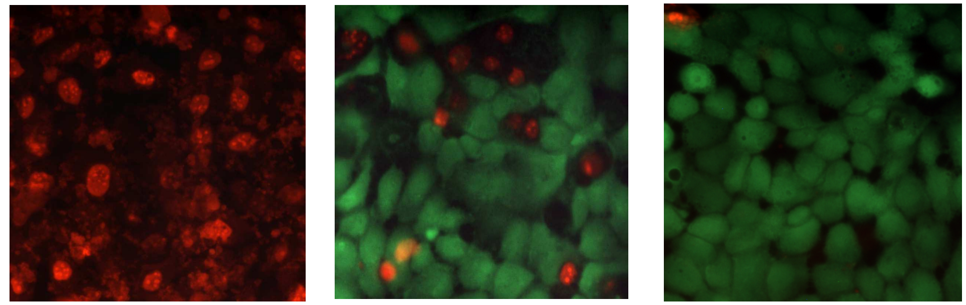
MTT Assay



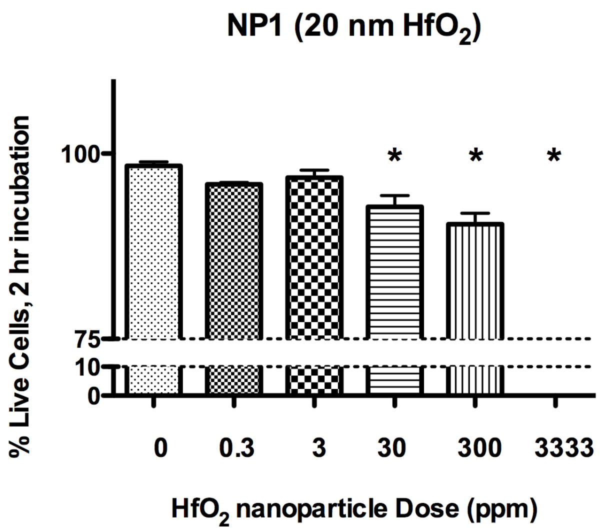
- **NP1 (20 nm) HfO_2 nanoparticles have moderate toxicity**
- **NP2 (1-2 nm) HfO_2 nanoparticles have low toxicity**
- **Reference, micron-sized HfO_2 particles non-toxic**

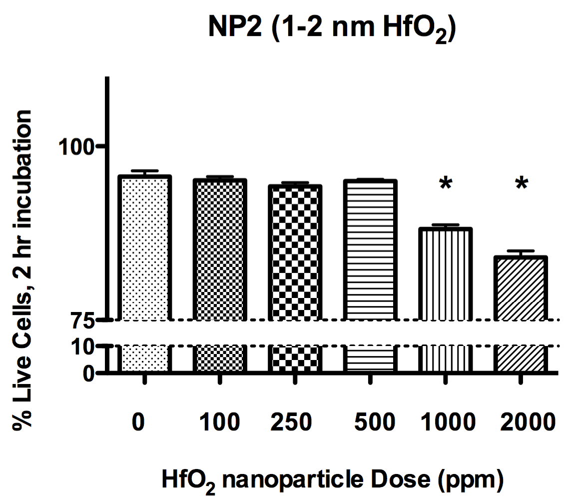
Live-Dead Assays (Ha-Cat)

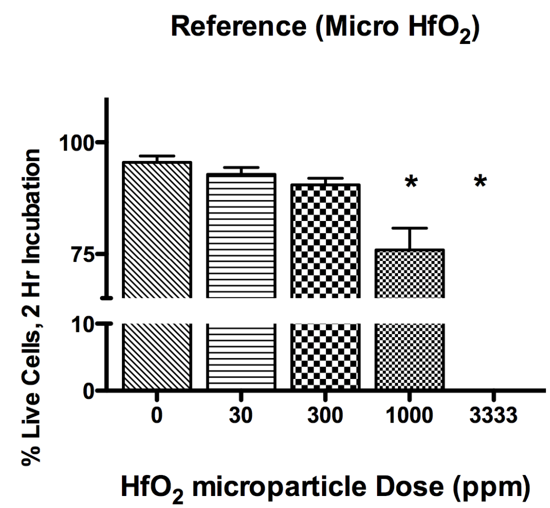
- Dual color fluorescent assay
- Dead cells stain Red; Live cells stain Green
- Example with NP1-HfO_2 (20 nm size)



3000 ppm   300 ppm   3 ppm







- NP1 HfO_2 nanoparticles (20 nm) have moderate toxicity
- NP2 HfO_2 nanoparticles (1-2 nm) and micron-sized HfO_2 particles have low toxicity

Toxicity Summary

	NP1 (20 nm)	NP2 (1-2 nm)	Ref-Micron (200-3000 nm)
	50% Effective concentration (mg/L)		
Microtox	<u>463</u>[+]	<u>300</u>	>5000
MTT	294	>2500	>2500
Live/Dead	<u>1700</u>*	<u>>2000</u>	<u>1800</u>*
Methanogenic	>2500	>2500	>5000

[+] underlined numbers indicate that inhibition observed, in some cases at levels less than 50%

* preliminary data for estimate purposes only

Preliminary Conclusions

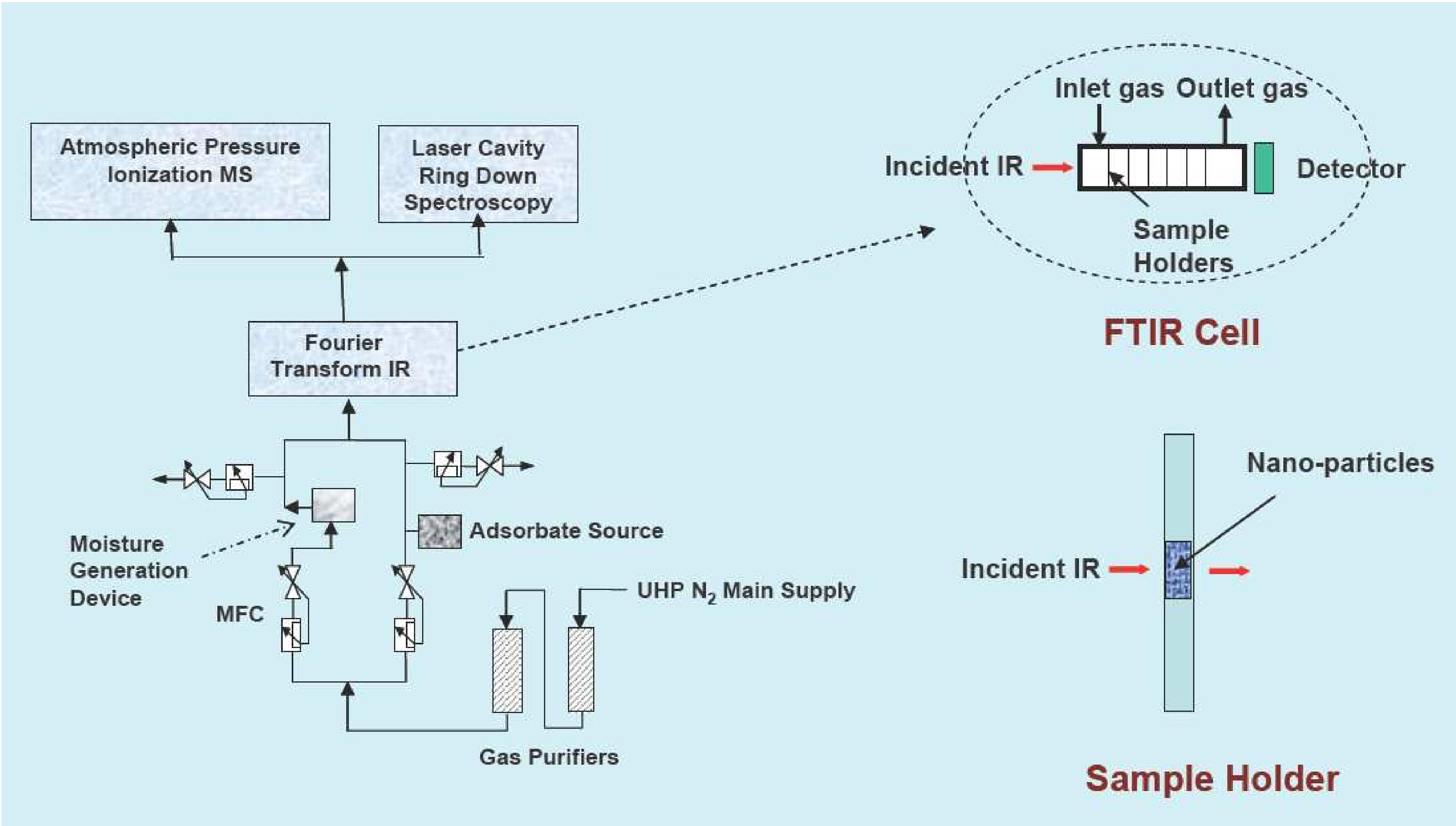
- **Reference micron-sized HfO_2 were <u>not toxic</u> in various assays with microbial and mammalian cells**
- **HfO_2 nanoparticles were <u>moderately toxic</u> in most bioassays, but their toxicity did not correlate with particle size alone**
- **Lack of O_2 in methanogenic assay corresponded with lack of toxicity**

Surface Physical Characterization

- **Particle size distribution (dynamic light scattering)**
- **Specific area (area/volume or area/mass of NP)**
- **Active site density; Site energetics**
- **Physical adsorption vs chemical adsorption**
- **Ability of the surface to concentrate bulk contaminants (selective adsorption)**
- **Retention of contaminants**

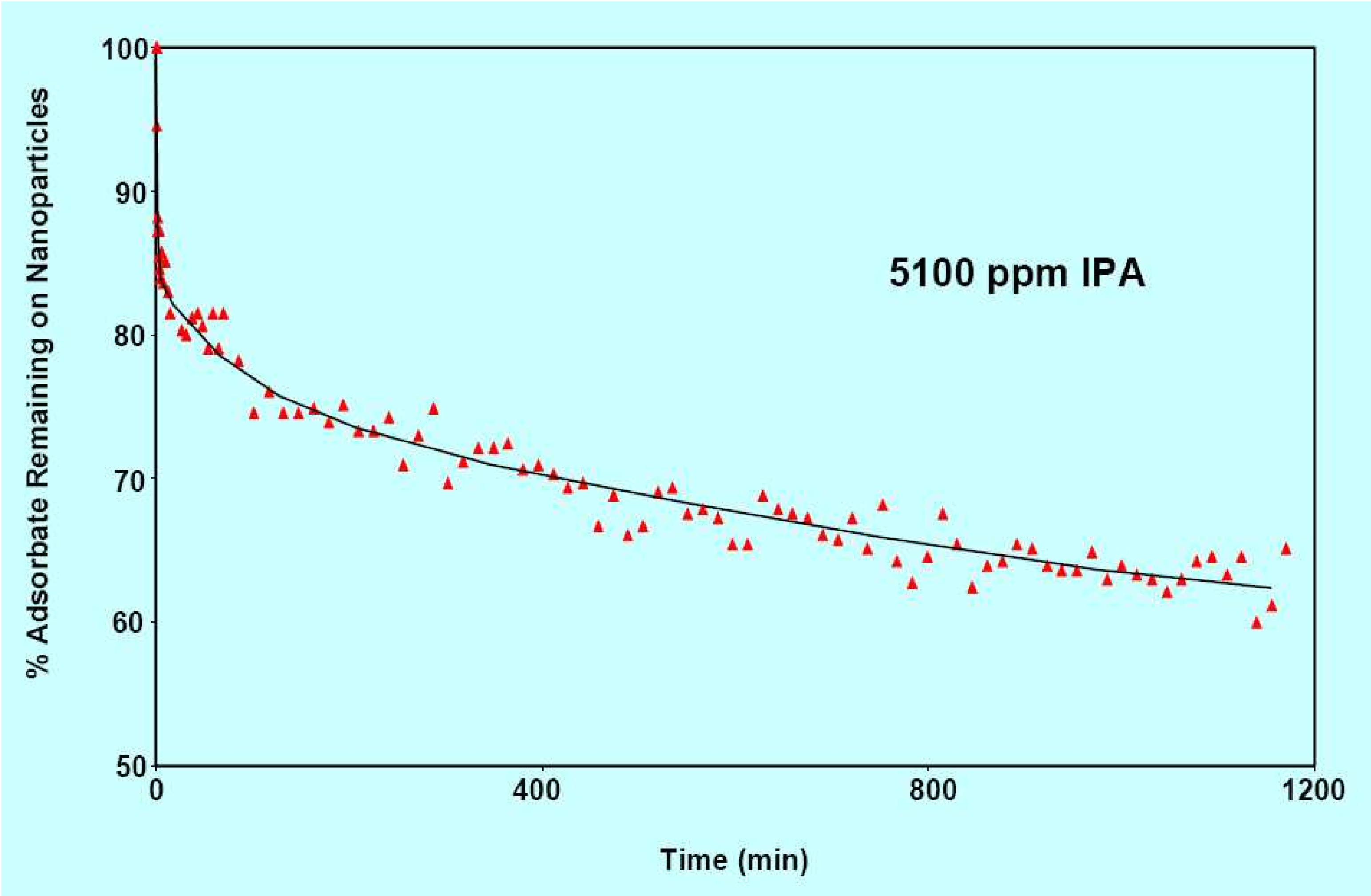
Adsorption Desorption

Experimental Set Up



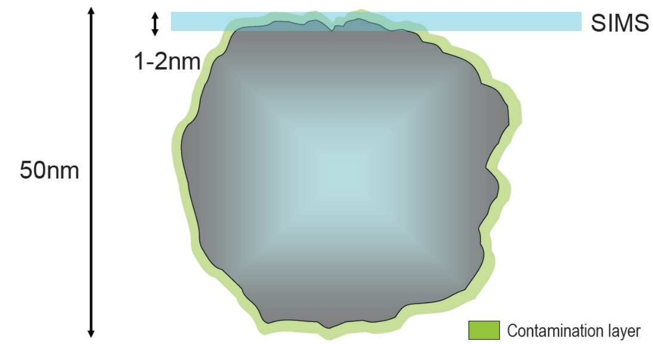
Adsorption Desorption

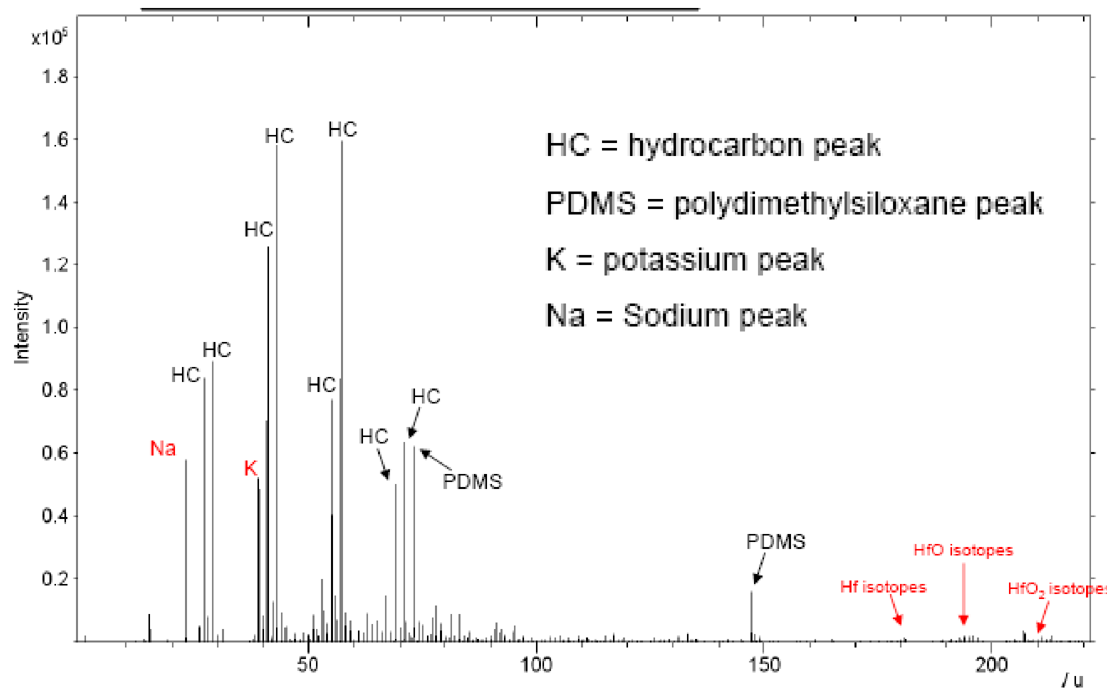
Example Results Desorption Experiment



Secondary Ion Mass Spectrometry (SIMS) Time-of-flight (ToF) SIMS; Static SIMS

- Probably the most information-rich of the modern surface analysis methods
- Various organic/inorganic contaminants detected on the surface of HfO_2 NPs





- Positive and negative spectra can be used to identify impurities including metals from fabrication or organics from unidentified sources

Nanoparticle Impurities

Negative Spectra Impurities

mass	ID	Ref Micron	NP1 20 nm	NP2 1-2 nm
13	CH			X
16	O	X	X	X
17	OH	X	X	X
24	C_2			X
25	C_2H			X
35	Cl	X		
37	C_3H	X		
63	COCl		X	
79	^{79}Br		X	
81	^{81}Br		X	
221	AuS		X	

- **"X" represents presence of molecule**
- **Molecules representative of influential loadings using PCA for negative spectra vs. tape**

Positive Spectra Impurities

mass	ID	Ref Micron	NP1 20 nm	NP2 1-2 nm
27	C_2H_3	X	X	X
29	C_2H_5	X	X	X
39	C_3H_3	X	X	X
41	C_3H_5	X	X	X
43	C_2H_3O	X	X	X
45	C_2H_5O	X		X
55	C_4H_7	X	X	X
57	C_4H_9	X	X	X
77	C_2H_9OSi (?)	X		X
91	C_7H_7			X
115	C_9H_7			X
118	$C_5H_{12}NO_2$			X
135	$C_7H_9N_3$			X
161	$C_{11}H_{13}O$			X

Surface Characterization Summary/Preliminary Conclusions

SIMS Analysis

Impurity	Ref Micro	NP1 20 nm	NP2 1-2 nm
Light Organics (<100 MW)	+	+	+
Heavy Organics (>100 MW)			+
Silicon	+		+
Chlorine	+	+	
Bromine		+	
Rare Earth Metals	+	+	+

- **The nature of the impurities varied depending on the source of the NPs**
- **Nano-sized HfO_2 particles adsorbed organic contaminants more energetically than micron-sized particles *<u>(higher activation energy)</u>***

Adsorption/Desorption Analysis

	NP1 (20 nm)	Ref Micro
Time to remove 90% of organics at 25^{o}C	Long time; very little change	25 hrs
Time to remove 90% of organics at 50^{o}C	> 25 hrs	16 hrs
Time to remove 90% of organics at 100^{o}C	1.2 hrs	55 min
Capacity (adsorbed IPA molecule per unit area; 55 ppb exposure)	9.1×10^{15}	8.6×10^{15}

- **Nano-sized particles have slightly higher *<u>capacity</u>* for adsorption and retention of secondary contaminants**

Industrial Interactions and Technology Transfer

- **ISMI-Sematech (Steve Trammell, Laurie Beu)**
- **AMD (Reed Content)**
- **IBM (Arthur T. Fong)**
- **Intel (Steve W. Brown, Paul Zimmerman, Mansour Moinpour)**

Future Plans

Immediate Plans

- Test the hypothesis that reactive oxygen species (ROS) are responsible for nanoparticle toxicity.

- Investigate the impact of surface contaminants and particle size on the toxicity displayed by HfO_2 nanoparticles.

Other Plans

- Characterize the potential toxicity of current and future NPs and NP-byproducts of SC manufacturing.

- Develop new methodologies for assessing and predicting toxicity.

Biologically Inspired Nano-Manufacturing (BIN-M)

Science Foundation Arizona Customized Project

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
- Rahul Jain, PhD candidate, Chemical and Environmental Engineering, UA

Other Researchers:

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

Cost Share (other than core ERC funding):

- Science Foundation Arizona, ASM, SEZ-LAM

Objectives

- Minimize cost 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

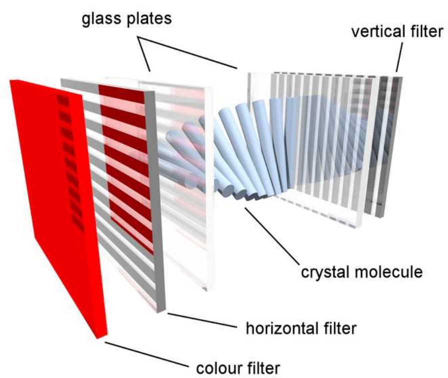
ESH Metrics and Impact

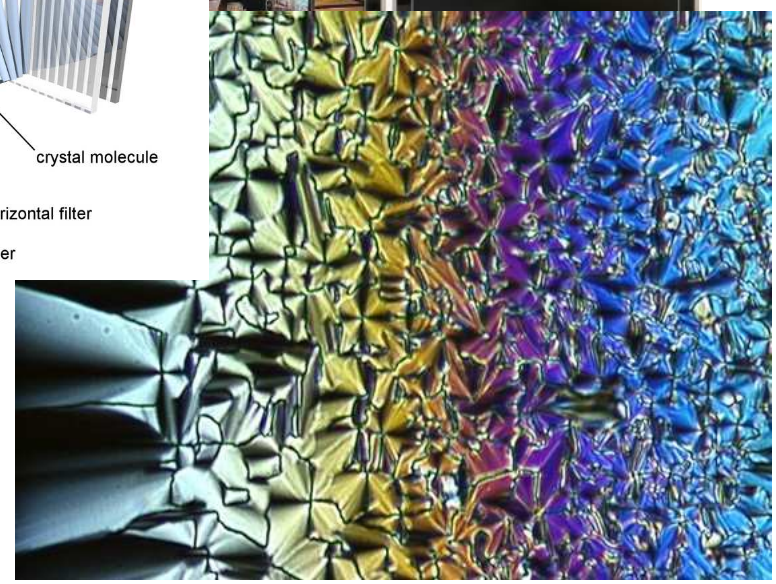
Sustainability metrics			
Process	Water l/bit/masking layer	Energy J/bit/masking layer	Materials g/bit/masking layer
Subtractive 32 nm*	$3.3x10^{-10}$	$1.5x10^{-12}$ EUV	$2.9x10^{-16}$
Additive	$3.6x10^{-13}$	$9.2x10^{-17}$	$1.8x10^{-19}$

*****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.

Self Assembled Structures

DNA



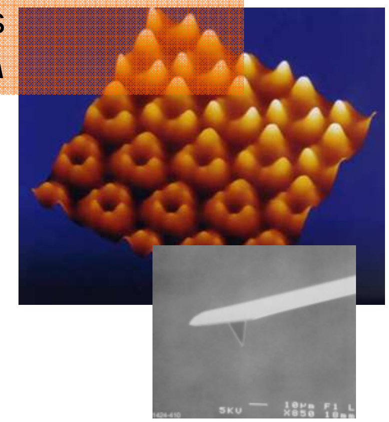


Liquid crystal display

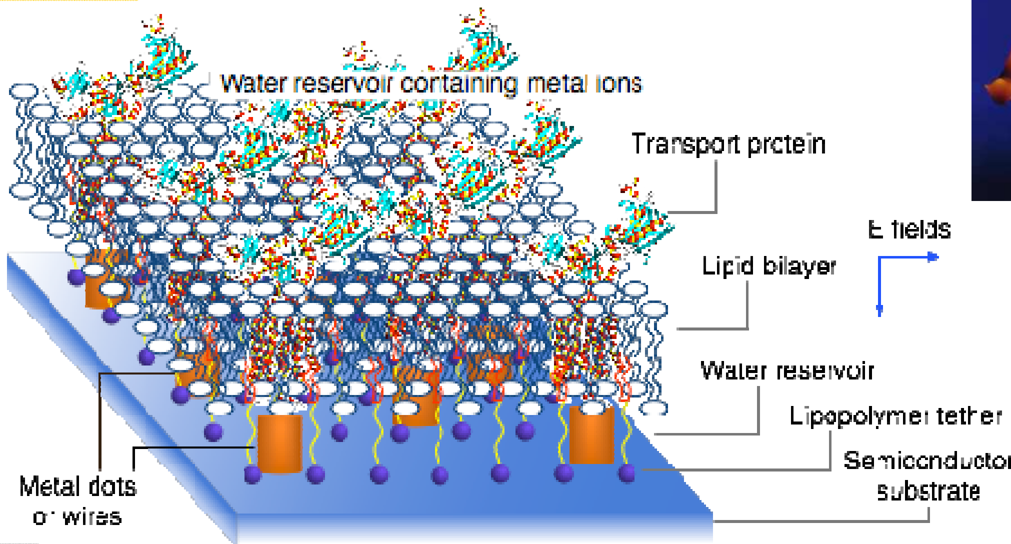
Process Goal: Deposit Array of Metal Dots

Biochemistry of metal transport proteins
Megan McEvoy/UA

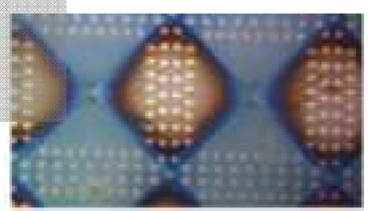
Characterize bio & inorganic structures using scanning probe and optical techniques
Masud Mansuripur/UA



Selective deposition
Glen Wilk, Eric Shero, Christophe Pomarede Steve Marcus/ASM



Pattern surfaces and build structures
Anthony Muscat/UA

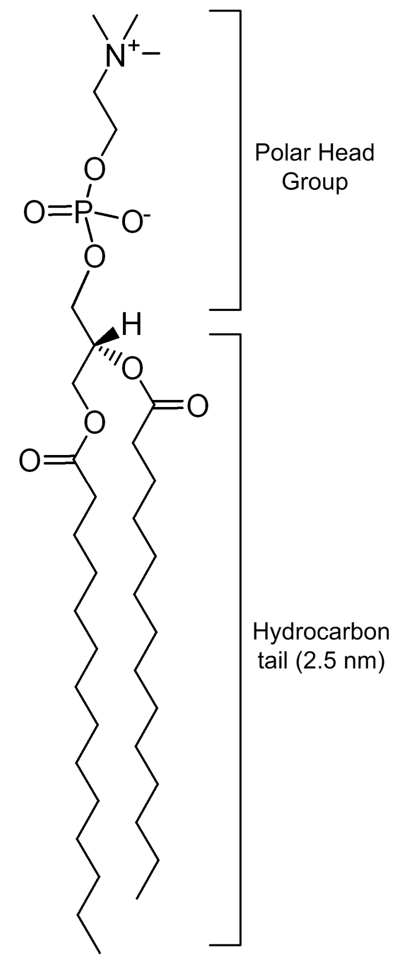


Semiconductor surface preparation
Harald Okorn-Schmidt, Zach Hatcher, Leo Archer/SEZ-LAM

Lipid Bilayer Formation

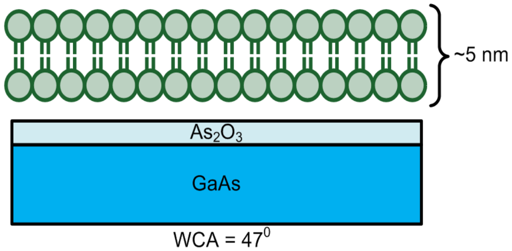
(Mask in Traditional Subtractive Process)

- Lipid bilayer deposited on substrate by vesicle fusion method
- Non polar hydrocarbon tail of DMPC is estimated to be 2.5 nm long
- Vesicle fusion
  - Droplet of vesicle placed on a substrate, where it adsorbs, breaks up and spreads, forming a bilayer
- AFM is an ideal tool to study the characteristics of these membranes since it can generate high resolution images

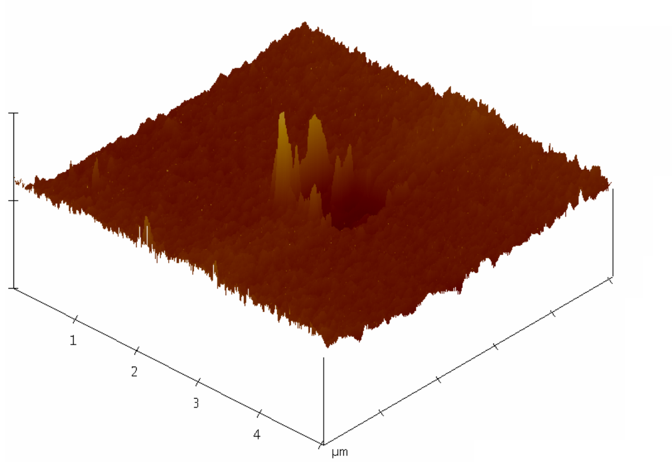


1,2-Dimyristoyl-*sn*-Glycero-3-Phosphocholine (DMPC)

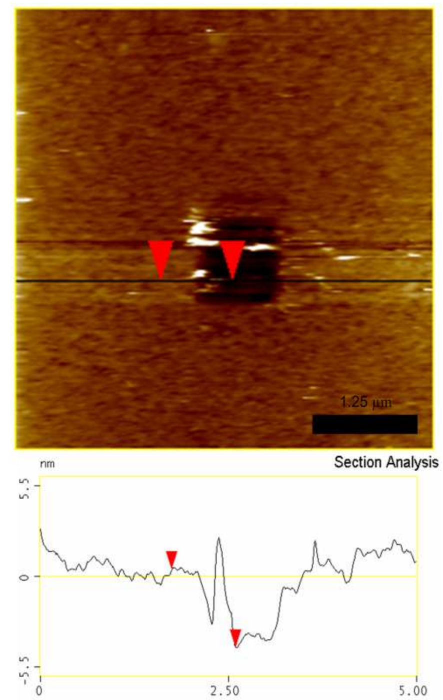
Lipid Bilayer formed on GaAs



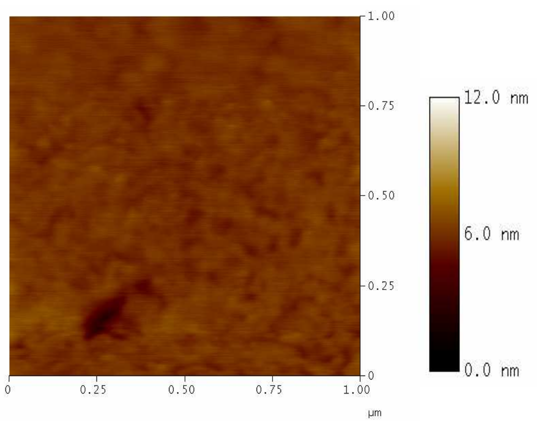
Schematic of lipid bilayer on As_2O_3 terminated GaAs



3D view of the tip induced rupture.



AFM image showing 1 x 1 µm^2 of tip induced rupture of bilayer.



AFM image of lipid bilayer on As_2O_3 terminated GaAs surface.

- Bare GaAs surface:
  - RMS roughness <0.4 nm over 1x1 µm^2 region.
- Bilayer on As_2O_3 terminated GaAs
  - AFM confirmed the formation of lipid bilayer.
  - RMS roughness <0.2 nm over 1x1 µm^2 region.
  - AFM height image and corresponding cross section analysis of the tip induced rupture process. The height difference indicated by markers is ~5nm.

Preparation of CopB

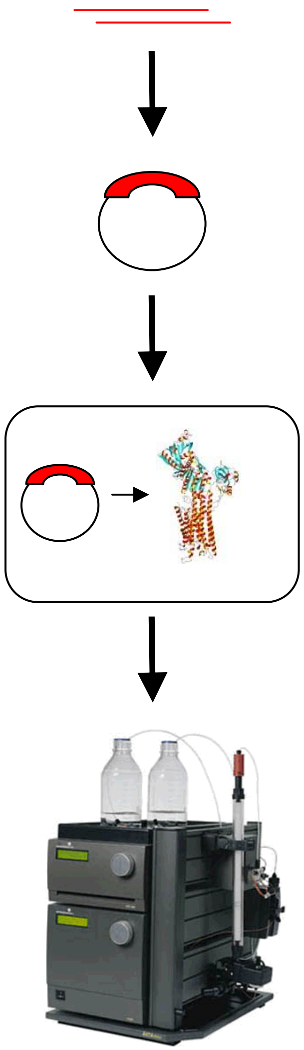
- The *copB* gene from *Archaeoglobus fulgidus* has been isolated using the polymerase chain reaction (PCR)
- The *copB* gene has been inserted into a plasmid for expression in *E. coli*
- CopB will be expressed in *E. coli* and purified using an affinity tag
- CopB containing vesicles will be fused with lipid bilayers

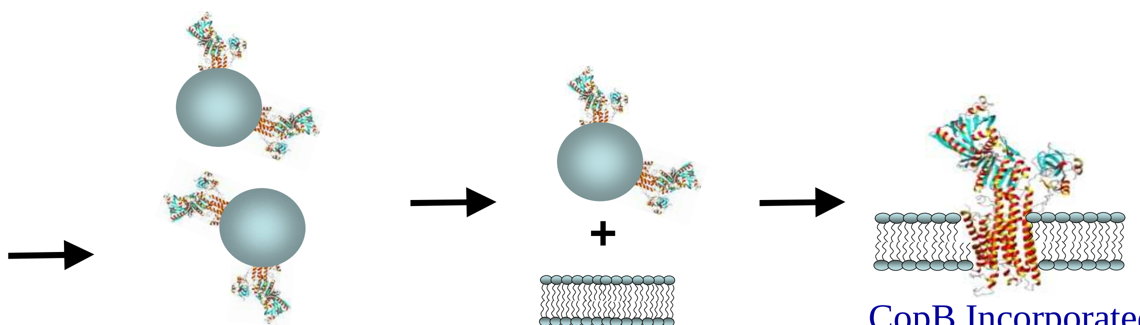
copB gene

E. coli expression plasmid

CopB protein expression in *E. coli*

Affinity chromatography to isolate CopB protein



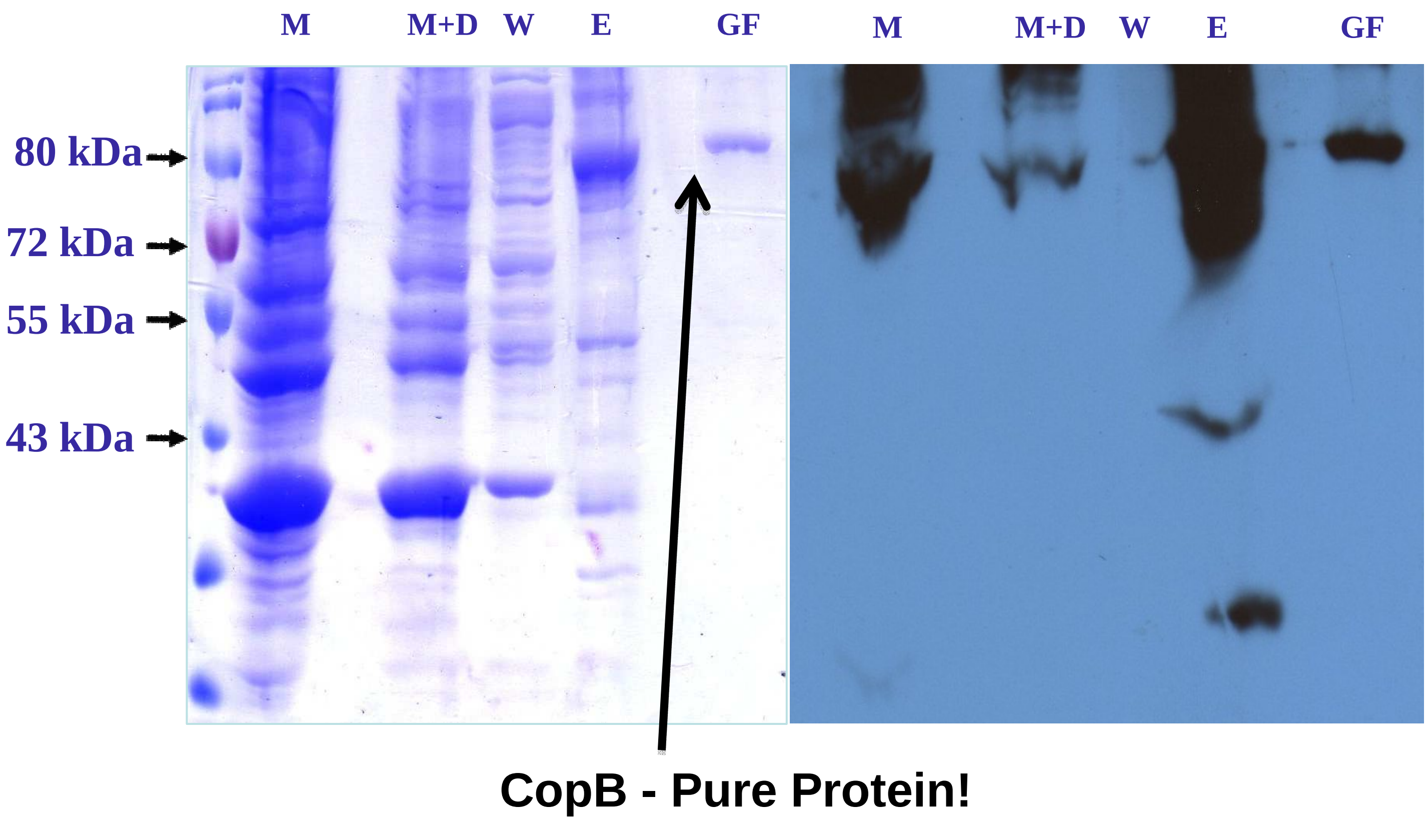


Purified CopB in vesicles

Fusion of vesicles and lipid bilayer

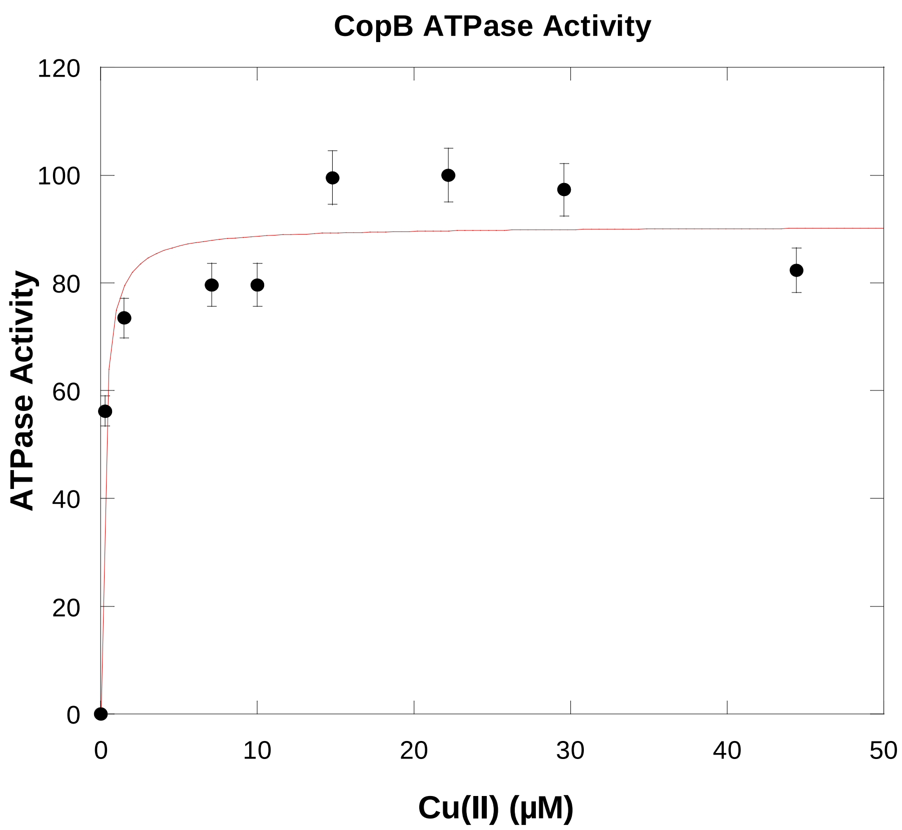
CopB Incorporated in lipid bilayer for selective deposition

Transport Protein Synthesized and Purified



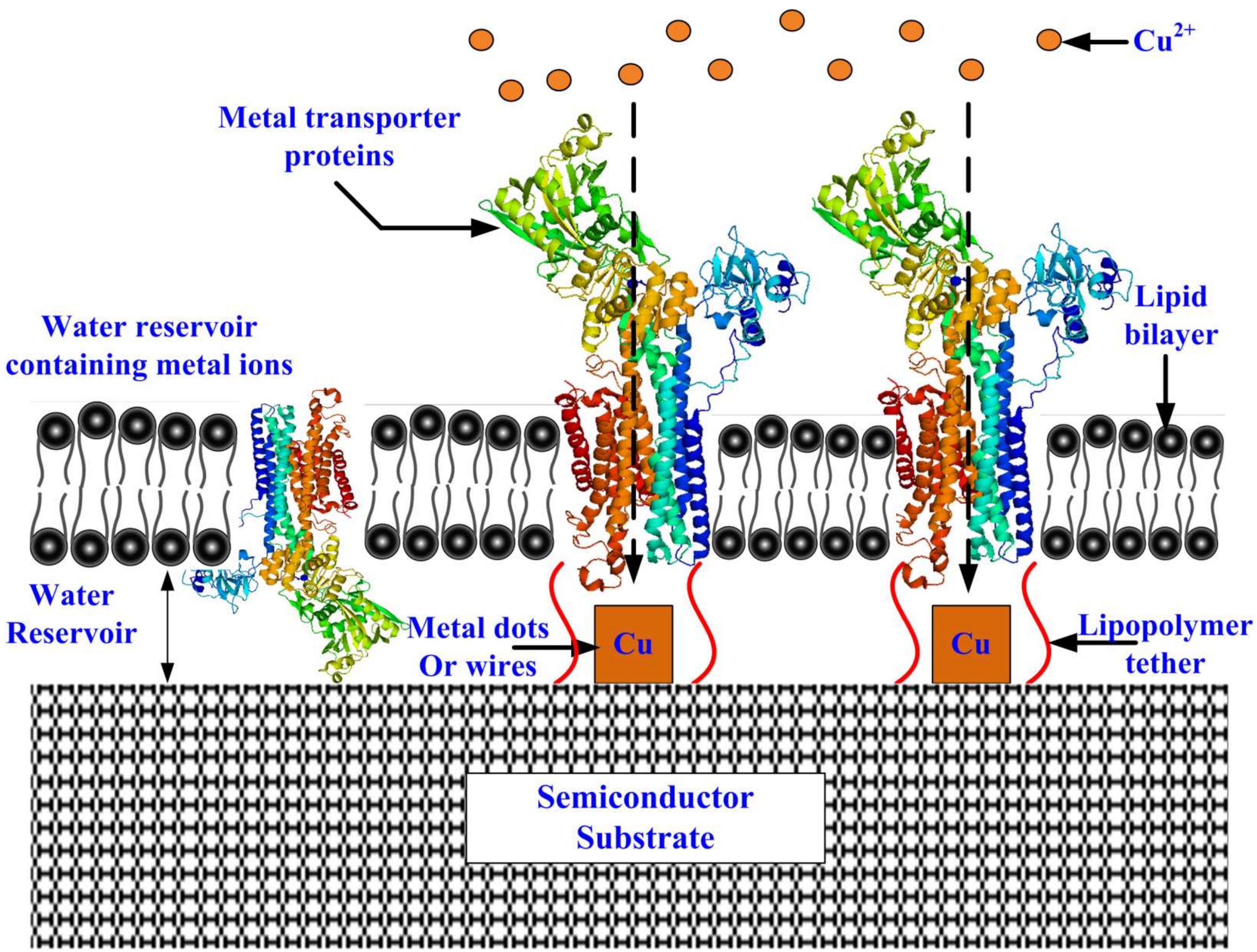
SDS-PAGE gel of a Histidine tagged protein prep performed on a Ni(II) affinity column (Left), western blot of the same gel (Right). Lanes: M – total membrane protein, M+D – detergent solubilized protein, W – wash with 30 mM imidazole, E – Elution with 400 mM imidazole, GF – sample purified through gel filtration (Sephacryl S-300).

<u>Activity & Copper transport by *A.fulgidus* CopB</u>

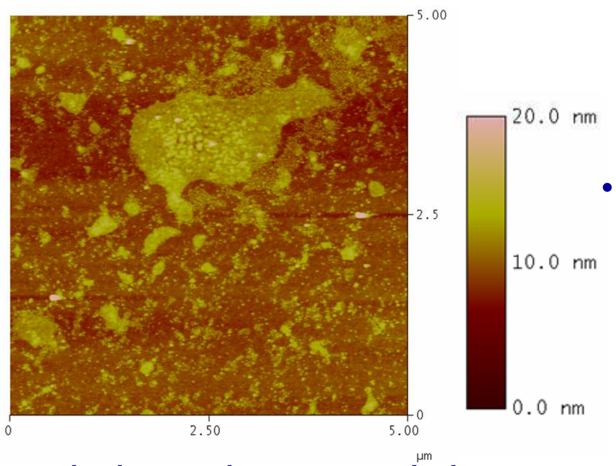


- Enzyme activity as determined by plotting the rate of release of inorganic phosphate as a function of copper concentration.
- The data was fit to the Michaelis-Menton kinetics to measure the maximum velocity at which the enzyme hydrolyses ATP.
- The Michaelis constant was determined to be K_m=0.20 ± 0.08 μM.
- The enzyme was found to have a maximum velocity of V_{max}= 90.48 ± 3.6, where 100%= 6.22 nmol/mg. of Enz/h.

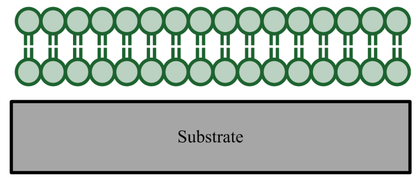
Integration



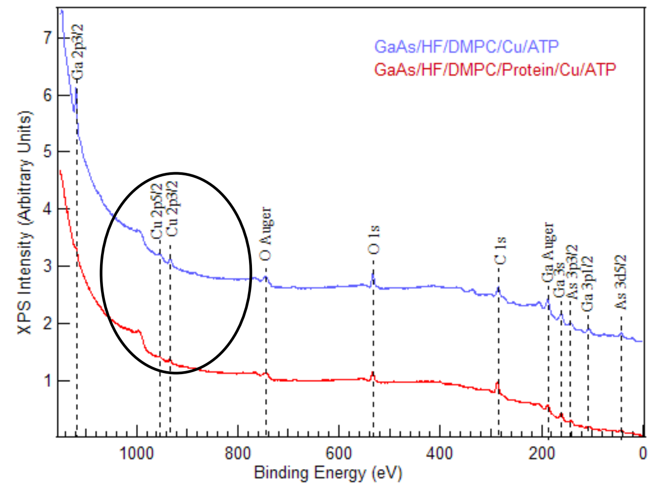
Copper Transport through *A. fulgidus* CopB

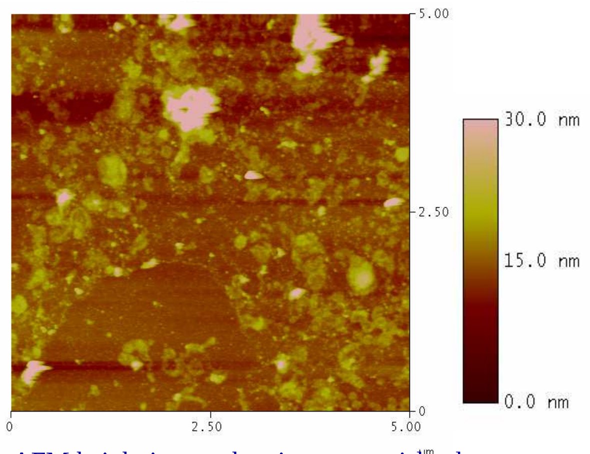


AFM height image showing copper islands on HF etched GaAs surface 5-15 nm high without the use of protein

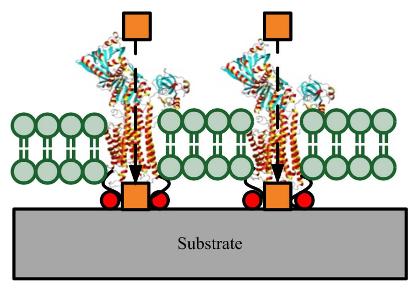


- HF treated GaAs surface:
  - Addition of ATP to the already formed lipid bilayer
  - Addition of Cu^{2+} for verification of deposition of Cu without the proteins
  - Cu deposited on the substrate due to a non continuous bilayer or contamination while washing the bilayer

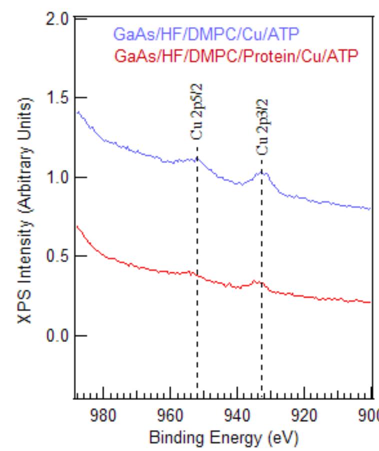




AFM height image showing copper islands on HF etched GaAs surface 20-50 nm high using protein



- HF treated GaAs surface:
  - Incorporation of protein in the lipid bilayer followed by ATP addition
  - Addition of Cu^{2+} to deposit as Cu^0 on the substrate through transporter proteins
  - Cu deposited on the substrate



XPS data showing copper deposition on HF etched GaAs surface with and without protein

Industrial Interactions & Technology Transfer

- Presentation on liquid and gas phase cleaning of high mobility substrates to SEZ
- Jeremy Klitzke from SEZ visiting scientist at UA
- Surface modification development with ASM and LAM/SEZ projects

Future Plans

Next Year Plans

- Liquid and gas phase cleaning of high mobility substrates
- ALD film nucleation on high mobility substrates
- Find conditions for maximum activity – and thereby enhance Cu(II) transport
- Study stability and activity of *A. fulgidus* CopB in different lipid compositions
- Solve the crystal structure of the transporter using X-ray crystallography
- Demonstrate chemically patterned surface
- Incorporate proteins into the lipid bilayer
- Check compatibility of proteins in different lipid molecules
- Characterize proteins and structures using q-dots

Long-Term Plans

- Develop characterization techniques for nanostructures
- Demonstrate patterned nanostructures over cm length scale

Publications, Presentations, and Recognitions/Awards

- "Biologically Inspired Nano-Manufacturing Using a Cu(II) ATPase" - Poster presented at The 22nd Protein Society Symposium, July 18th, 2008, San Diego, CA. Presented by Sam Jayakanthan.

- "Structural and Functional Characterization of the Copper Transporting P1B-ATPase CopB from *Archaeoglobus fulgidus"* – Seminar presented at the Biological Chemistry Program Journal Club Feb 5th 2009. Presented by Sam Jayakanthan

ERC – Intel
Customized Joint Pilot Program

Expected Outcome: New Technologies on Environmentally–Friendly High-Volume Nano-Manufacturing

Gopal Rao, Intel

Intel/ERC Steering Committee: Gopal Rao (Co-Chair), Prof Farhang Shadman (Co-Chair), Prof Ara Philipossian, Avi Fuerst, Jim Jewett, Mansour Moinpour, Don Hooper, Carl Geisert, Dan Hodges, John Harland, David Harman

Acknowledgements

Executive Initiative:

Dr. Robert Shelton (President of UA)

Josh Walden (VP/GM of FSM)

Gabe Quenneville (Plant Manager, FSM)

Intel FSM Research Management Review Committee

PIs Team:

Intel : Avi Fuerst, Don Hooper, Mansour Moinpour, Carl Geisert, Dan Hodges

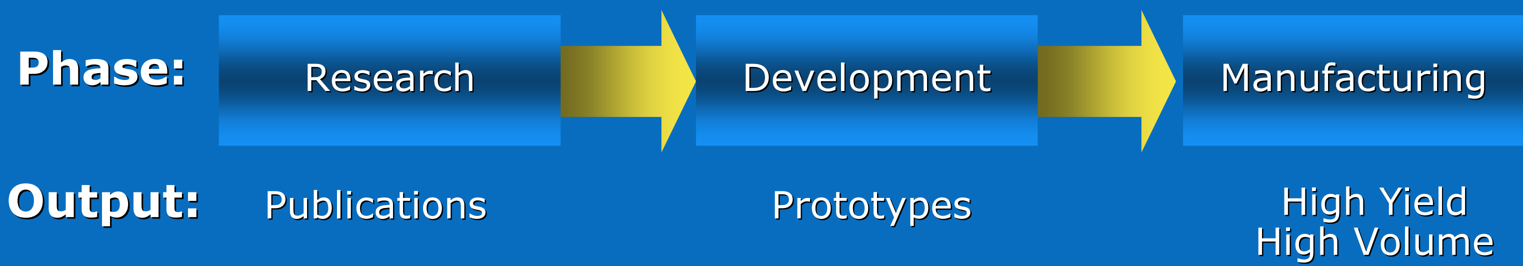
UA: Farhang Shadman, Ara Philipossian, Srini Raghavan, Jim Baygents, Jim Farrell

Current Intel/ERC Customized Research Projects

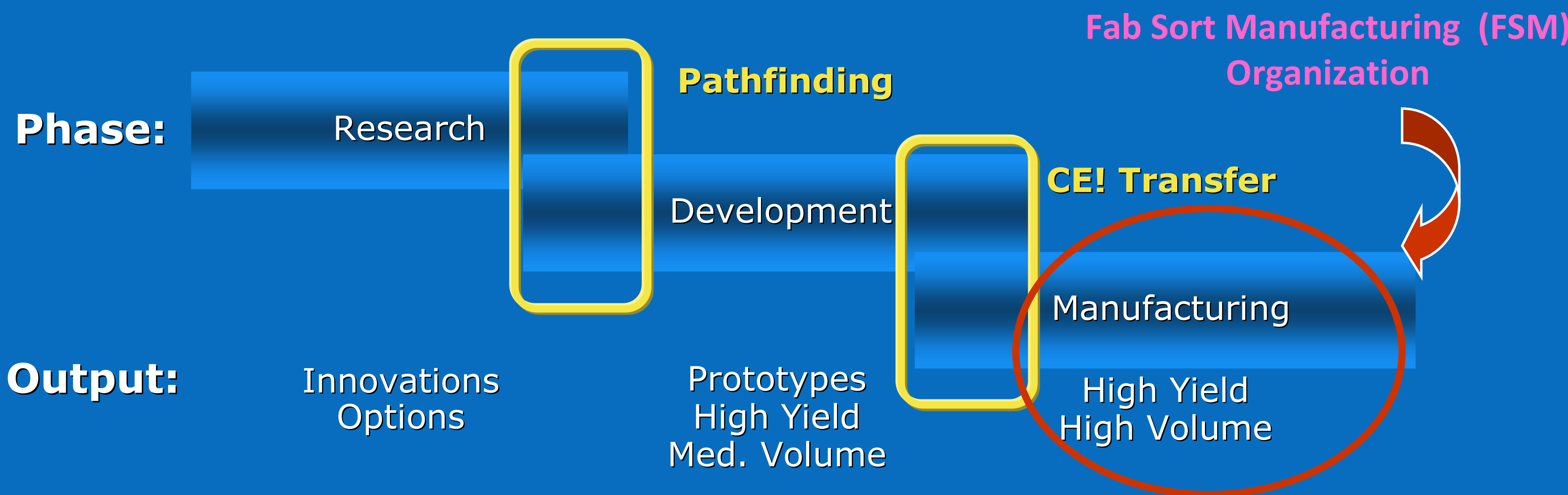
No	Project	Lead ERC PI	Lead Intel PI	Research Duration
1.	Investigation of the Relationship between Planarization & Pad Surface Micro-Topography	Ara Philipossian	Mansour Moinpour	3 yrs
2.	Retaining Ring and Conditioner Interactions	Ara Philipossian	Don Hooper	2 yrs
3.	Contamination Control in Gas Distribution Systems of Semiconductor Fabs	Farhang Shadman	Carl Geisert	1.5 yrs
4.	Develop an AFM based methodology to determine the optimal APM composition to remove particles from surfaces	Srini Raghavan	Avi Fuerst	2 yrs
5.	Integrated Electrochemical Treatment of CMP waste streams for water reclaim and conservation	James Baygents James Farrell	Don Hooper	2 yrs

Intel's Process Technology R-D-M Flow

Traditional R-D-M Method:



Intel's R-D-M Method:

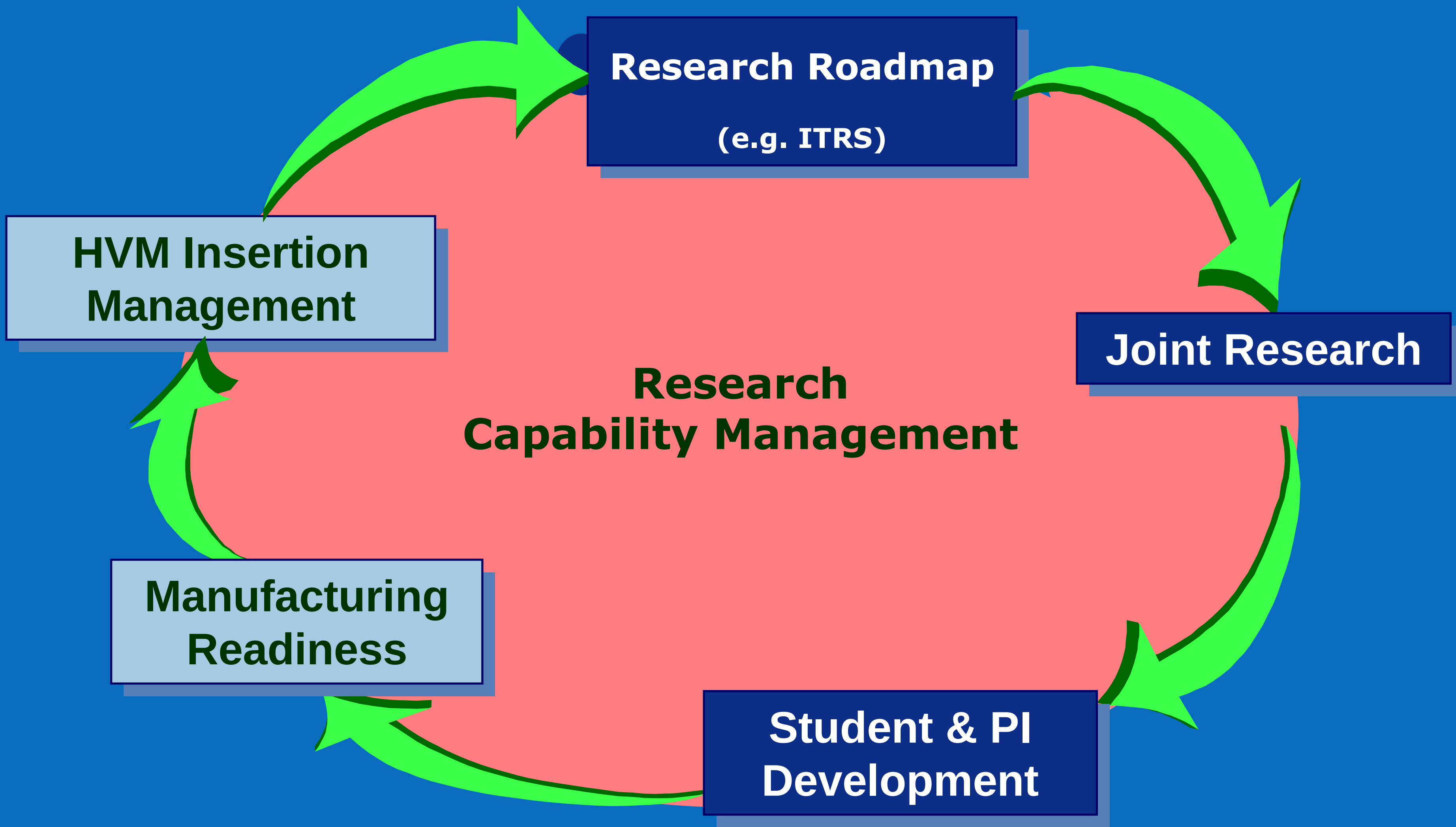


Justification for Research in Manufacturing

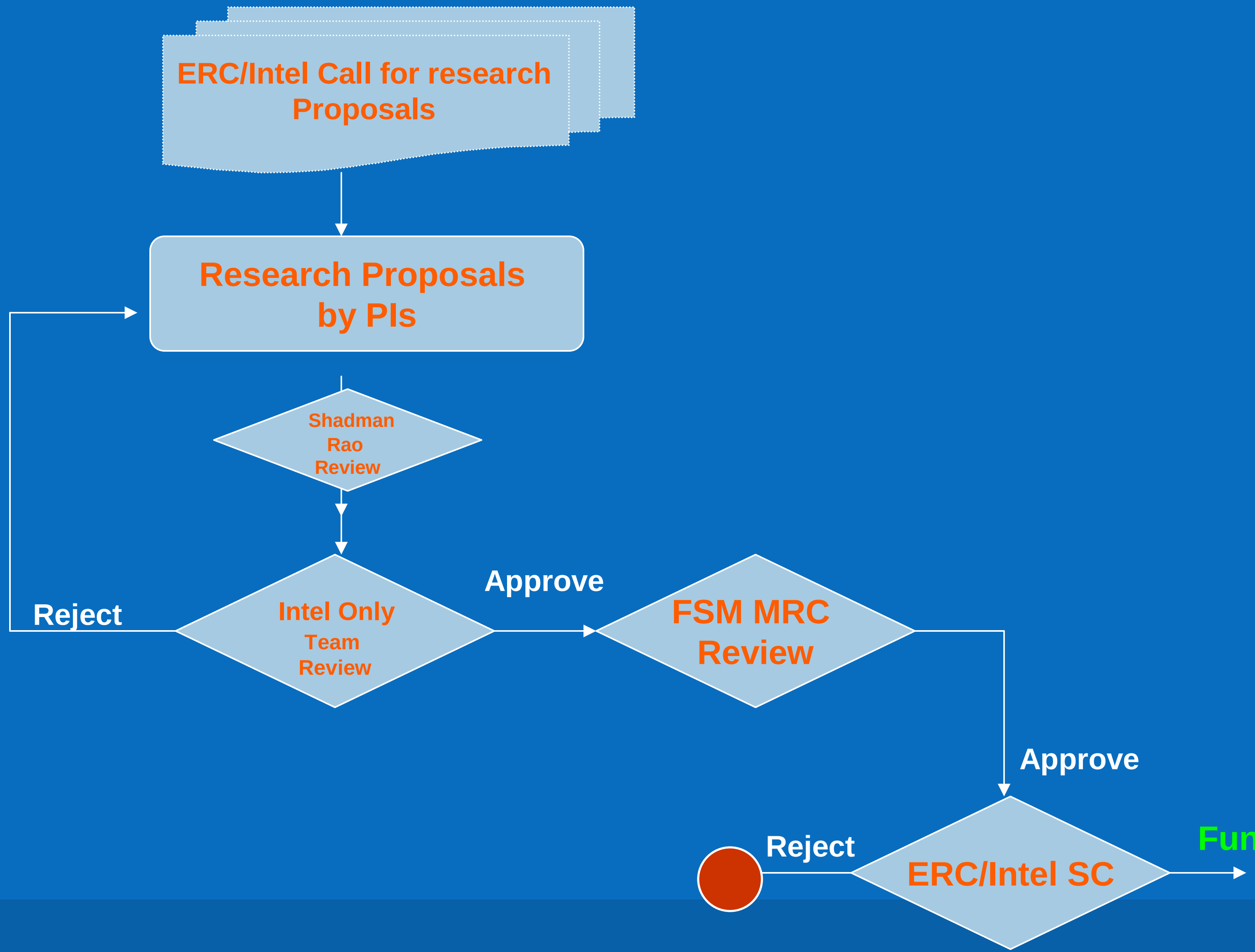
- Moore's Law enabling significant technology development
- Manufacturing methods, techniques and innovation must keep pace with our technology roadmap
- Leveraging universities for manufacturing research is a good option to explore fundamental and innovative concepts and theories
- FSM resources optimized for performing research in manufacturing

FSM Research Themes

Intel/ERC Initiative Scope

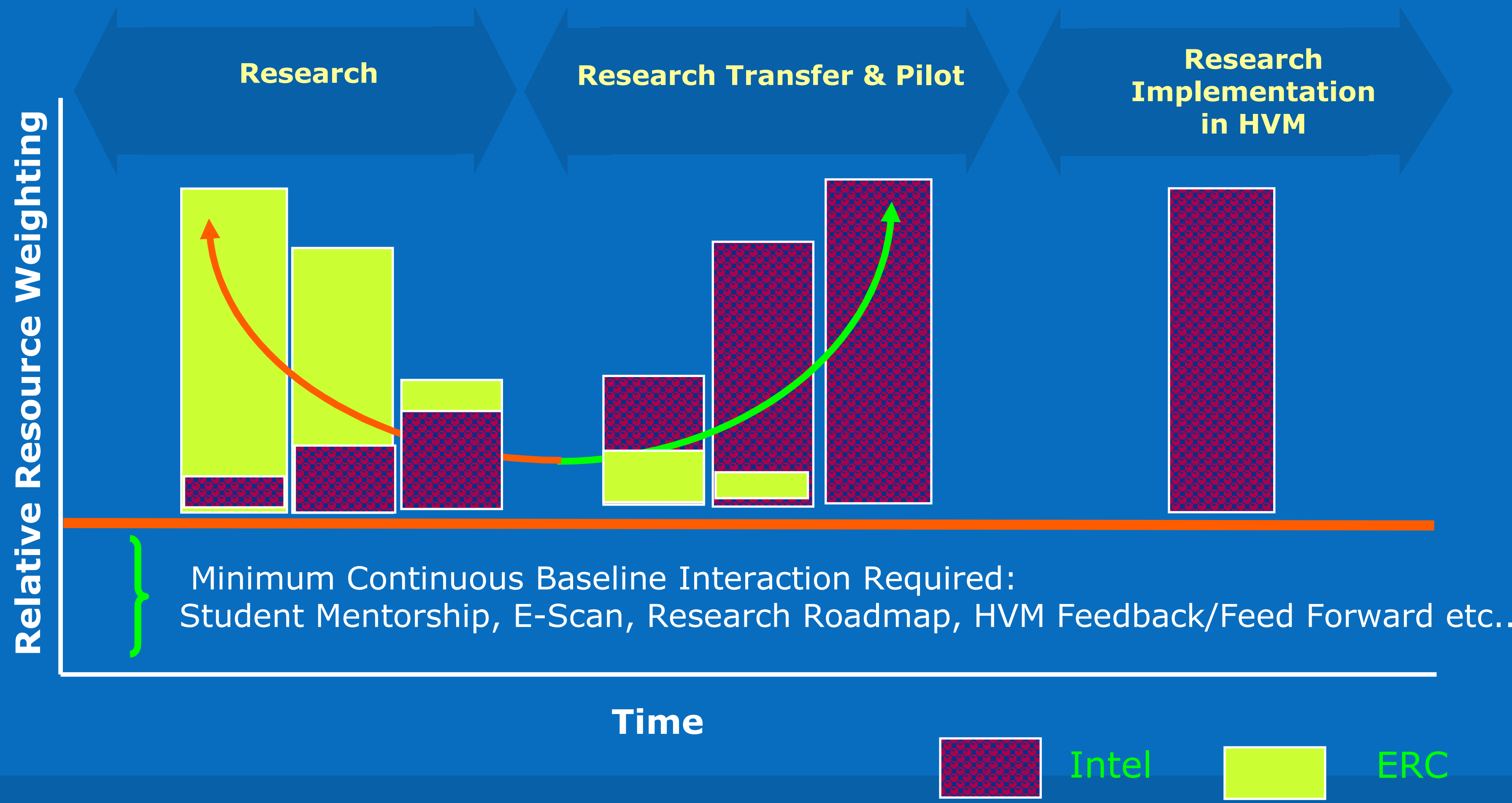


Research Proposal Ratification Process



Joint Intel/ERC Collaborative Research Model Resource Weighting

"Focusing on Research With HVM Implementation is Critical to Effectively Managing the Research/Student Supply Chain"



Conclusions

- Total Value of Intel/ERC Customized Research: ~$1.3M
- Good collaboration between Intel and ERC PIs
- Research Program managed well by Intel/ERC Steering Committee
- Research Projects on track
- ‘For FSM’, ‘By FSM’, ‘In FSM’ Concept applied to harvesting research gaining traction

Thank You!

Retaining Ring Induced Frictional Pad Heating and its Effect on Pad Wear

PI:

- Ara Philipossian, ChEE, UA

Graduate Student:

- Zhenxing Han, PhD candidate, ChEE, UA

Other Researchers:

- Jiang Cheng, Visiting Scholar, ChEE, UA
- Yasa Sampurno, Research Associate, ChEE, UA
- Yun Zhuang, Research Associate, ChEE, UA
- Siannie Theng, Research Technician, ChEE, UA
- Len Borucki, Araca Incorporated

Cost Share (other than core ERC funding):

- In-kind donation (retaining rings) from Entegris
- In-kind donation (slurry) from Fujimi
- In-kind donation (conditioner disc) from Shinhan
- In-kind donation (conditioner disc) from 3M
- In-kind donation (polishing pad) from Rohm and Haas
- In-kind donation (polishing pad) from CMC
- In-kind donation (wafer) from Intel

Objectives, ESH Metrics and Impact

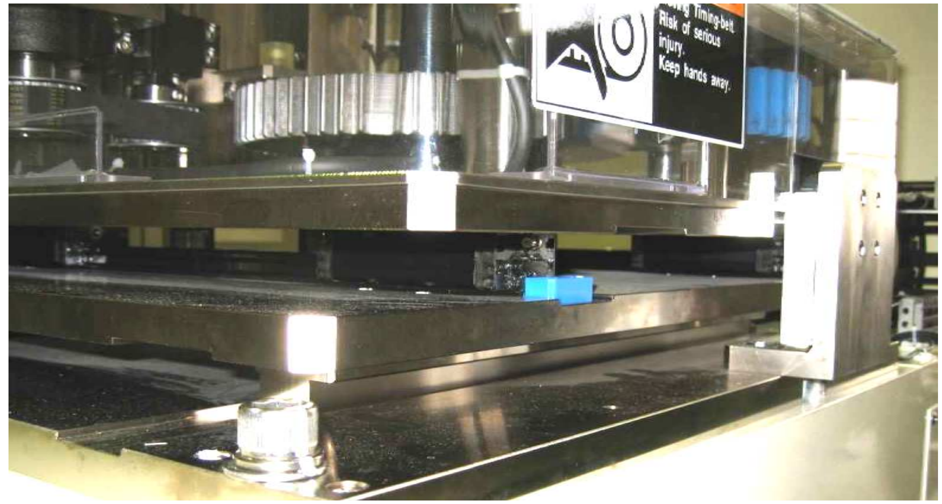
Objectives

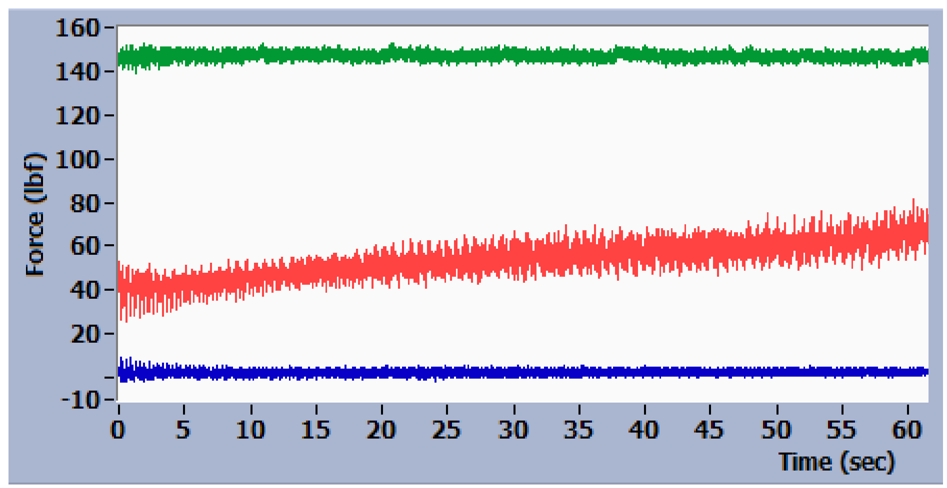
- **Quantify the effect retaining ring materials, diamond disc conditioners, polishing pads and process conditions (i.e. pad temperature and polishing time) on pad cut rate and pad wear profile**
- **Determine whether or not temperature and/or time effects are the full explanation for pad wear profile differences in different processes**

ESH Metrics and Impact

- **Reduce CMP slurry consumption by 10 – 20 %**
- **Reduce energy consumption by 10 – 20 %**
- **Increase pad life by 20 – 30 %**

APD – 800 Polisher and Tribometer

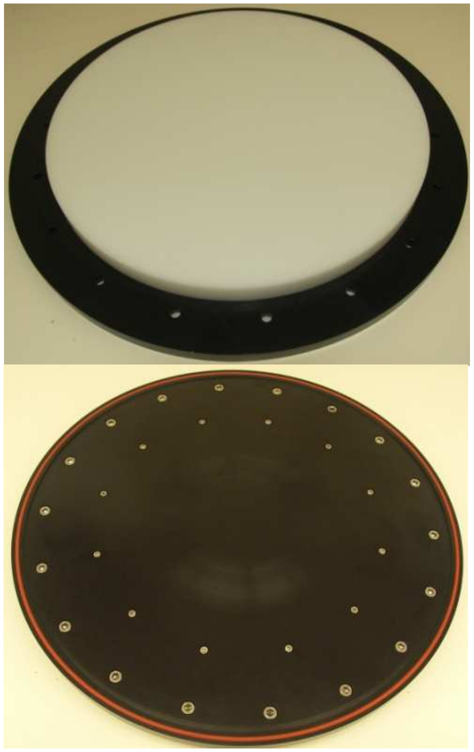




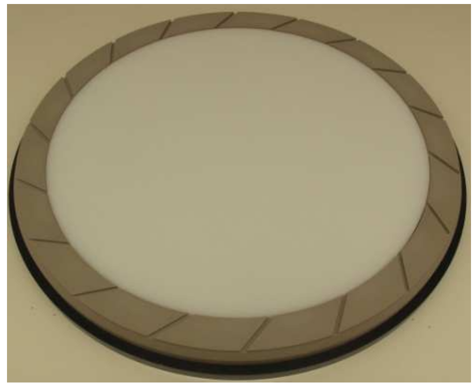
Experimental Conditions

- Pad
  - IC1000 K-Groove Pad with Suba IV Sub-pad
- Slurry
  - 2 volume parts of Fujimi PL- 4217 slurry with 3 volume parts of UPW
  - Flow rate: 250 ml/min
- Retaining Ring
  - PEEK – 1
  - PEEK – 2
  - PPS – 1
  - PPS – 2
- Pad Conditioning
  - 4-inch 3M diamond disc rotating at 95 RPM and sweeping at 10 times per min
  - In-situ conditioning in 5.8 lbf
- Retaining Ring Polishing
  - Polishing pressure: 6 PSI
  - Sliding velocity: 1 m/s

Retaining Ring Adaptor



Adaptor



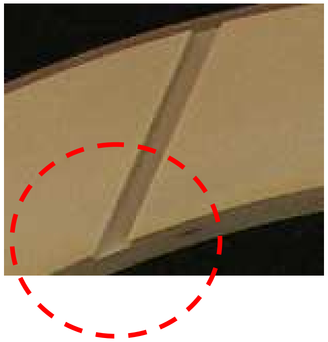
Adaptor with the retaining ring installed

Overall setup on the APD – 800 carrier head

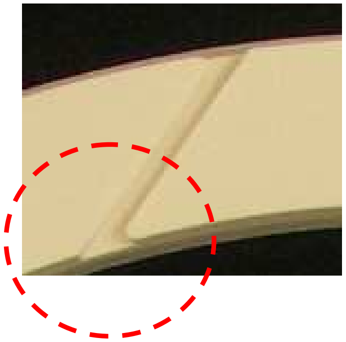
Retaining ring adaptor has been successfully developed and implemented. The adaptor enables the use of 300-mm industry standard retaining rings (i.e. for the AMAT Reflexion polisher) on UA's APD – 800 300-mm polisher and tribometer

Retaining Ring Materials and Slot Designs

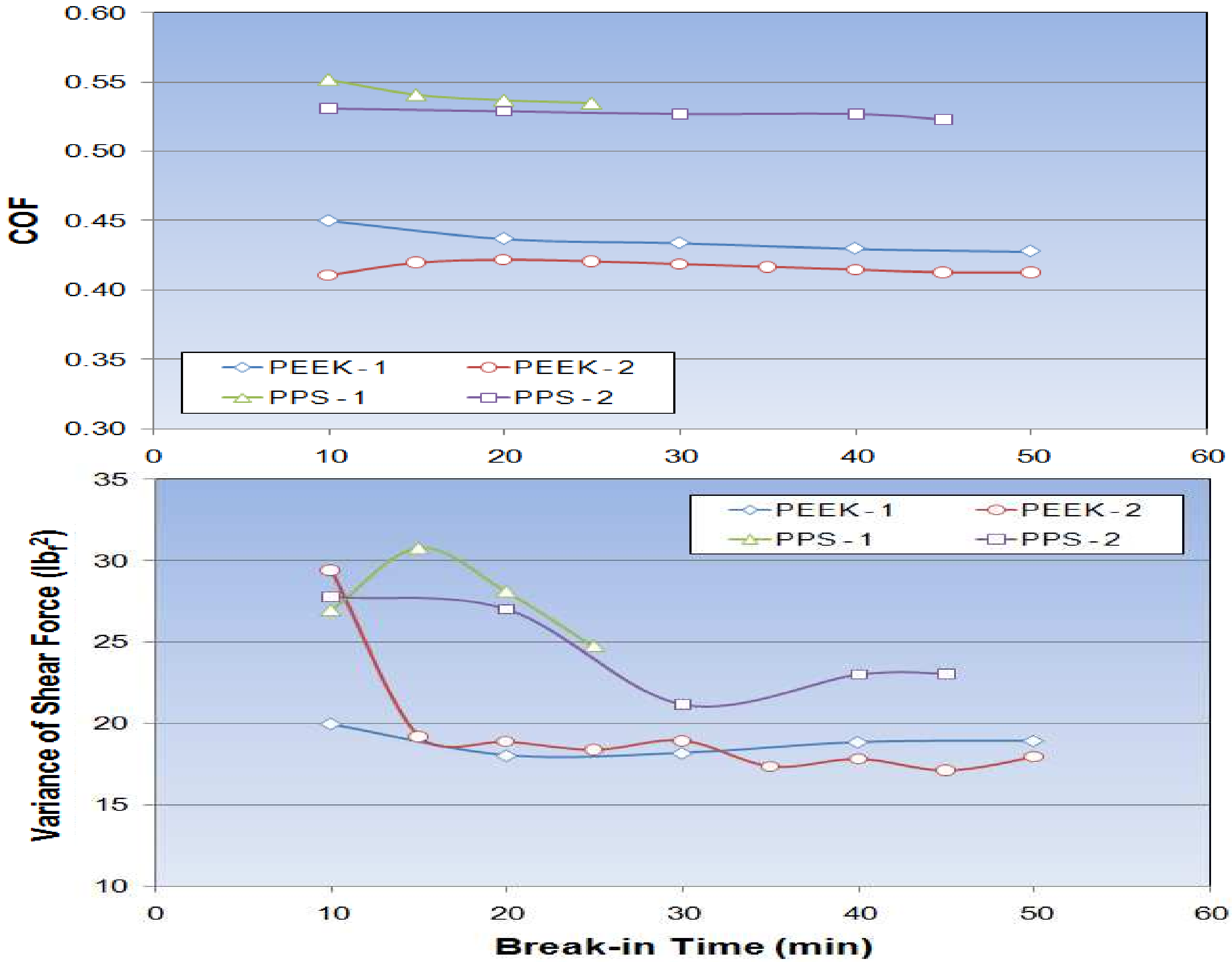
PEEK with Slot Design 1



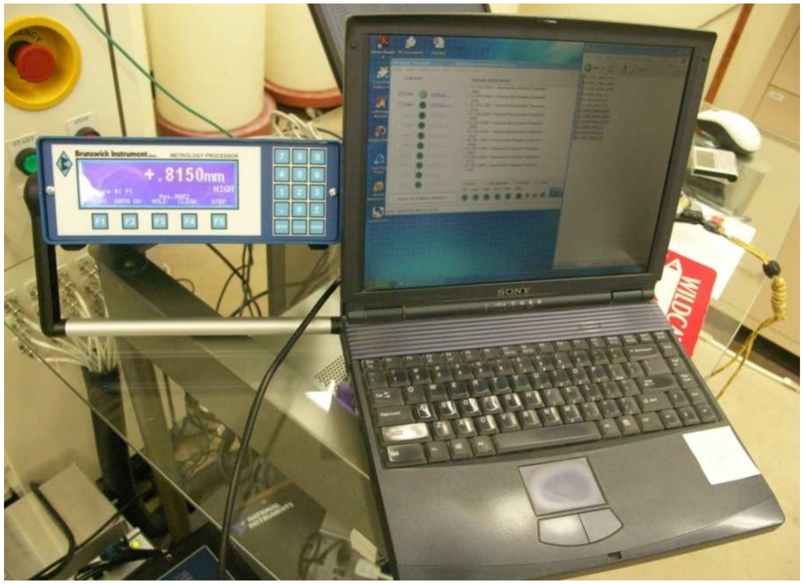
PPS with Slot Design 2



Coefficient of Friction and Force Variance

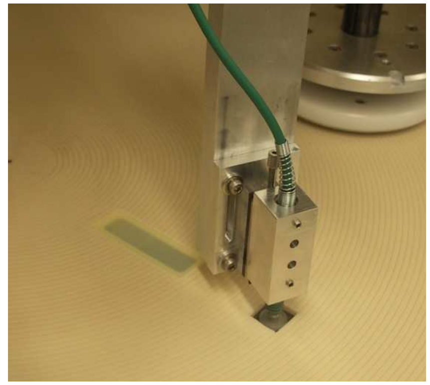


Pad Cut Rate Measurement Device & Data

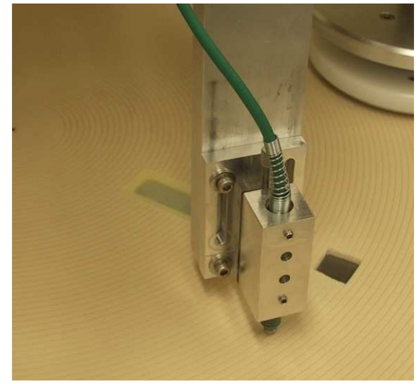


Computer and signal processing system associated with the pad cut rate measurement device

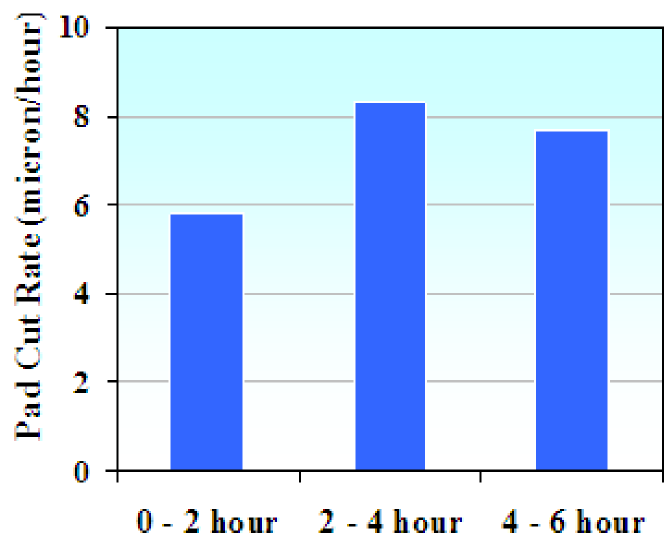
- Accuracy is appx. 0.2 micron
- Measurement is in contact mode



Probe on reference surface



Probe on pad surface



Summary

- **Retaining ring adaptor and pat cut rate measurement device are successfully implemented in this project**
- **PPS retaining rings with Slot Design – 2 have higher COF and variance of shear force than PEEK retaining rings with Slot Design – 1**
- **COF and variance of shear force decreases with polish time**
- **Pad cut rate is relatively stable over three segmented polishing time**

Industrial Interactions and Future Plans

Industrial mentors and contacts:

- **Don Hooper (Intel)**
- **Chris Wargo (Entegris)**
- **Ralph Stankowski (Entegris)**
- **Leonard Borucki (Araca)**

Next Year Plans:

- **Investigate the effect of polishing pad materials, retaining rings materials, conditioner disc and pad temperature on pad cut rate and pad wear profile**

Long-Term Plan:

- **Complete theoretical analysis and refine previously developed pad cut rate models to comprehend the effect of process temperature**

Investigation of the Relationship between Planarization and Pad Surface Micro-Topography

PI:

- **Ara Philipossian, ChEE, UA**

Graduate Student:

- **Yubo Jiao, PhD candidate, ChEE, UA**

Other Researchers:

- **Jiang Cheng, Visiting Scholar, ChEE, UA**
- **Yasa Sampurno, Research Associate, ChEE, UA**
- **Yun Zhuang, Research Associate, ChEE, UA**
- **Siannie Theng, Research Technician, ChEE, UA**
- **Len Borucki, Araca Incorporated**

Cost Share (other than core ERC funding):

- **In-kind donation (conditioner disc) from Shinhan**
- **In-kind donation (conditioner disc) from 3M**
- **In-kind donation (polishing pad) from Rohm and Haas**
- **In-kind donation (polishing pad and slurry) from CMC**
- **In-kind donation (wafer) from Intel**

Objectives, ESH Metrics and Impact

Objectives

- Gain a deeper understanding and control of factors related to pad topography that affect planarization.
- Once we prove that contact area is a sharp predictor of planarization behavior, this work will result in a dramatic reduction in the number of patterned test wafers needed to develop, tune or diagnose a process.
- The work will also result in lower slurry and pad consumption (along with associated waste treatment) and improved productivity.

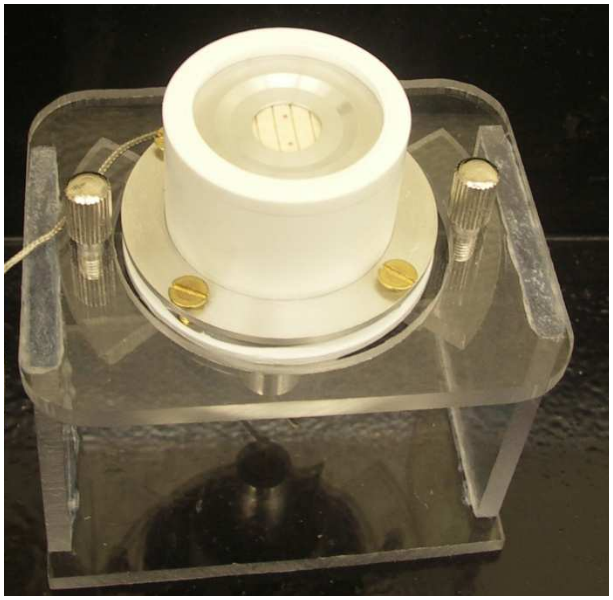
ESH Metrics and Impact

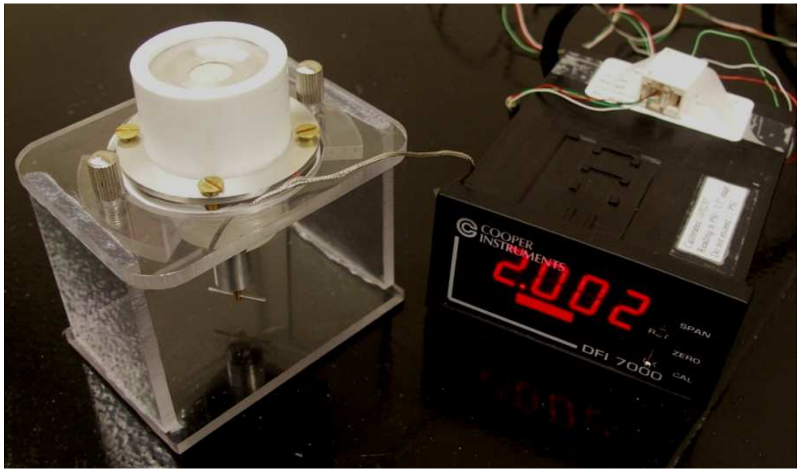
- Reduce CMP slurry consumption by 10 – 20 %
- Reduce energy consumption by 10 – 20 %
- Increase pad life by 20 – 30 %

Approach

- **Polish 300-mm wafers using a variety of conditions and consumables (i.e. pads with different hardness and porosity and diamonds with different levels of aggressiveness) known or expected to improve or degrade planarization efficiency**
- **Examine pad samples under static loading (at CMP-relevant pressures) using flat and possibly patterned sapphire windows. Patterned windows would replicate the contact conditions on patterned wafers and would make it feasible to actually see which pad features affect planarization**
- **Correlate planarization behavior with contact area characterizations**
- **Tie observational data together with rough surface contact and removal rate models**

Pad Sample Holder for Confocal Microscopy



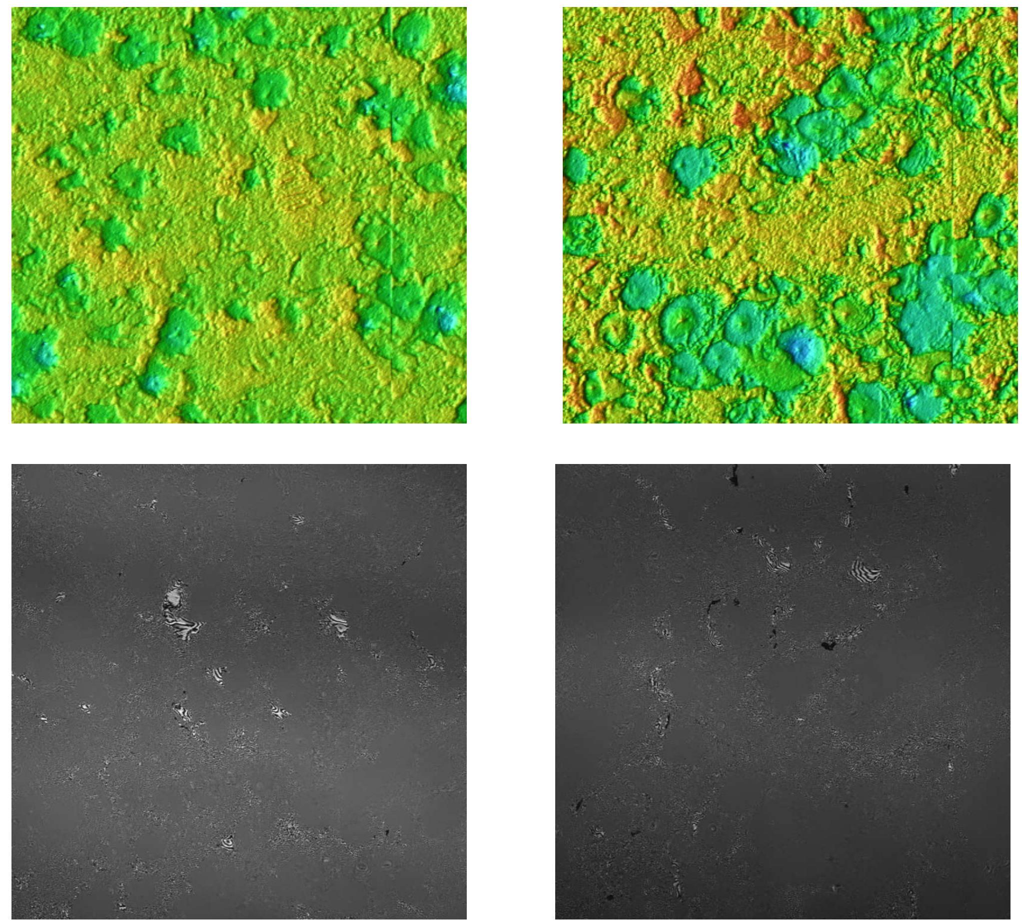


2nd generation pad sample holder for confocal microscopy has been qualified. Compared to the 1st generation, the 2nd generation system has an enhanced down force control on the pad sample.

Data Extraction and Analysis

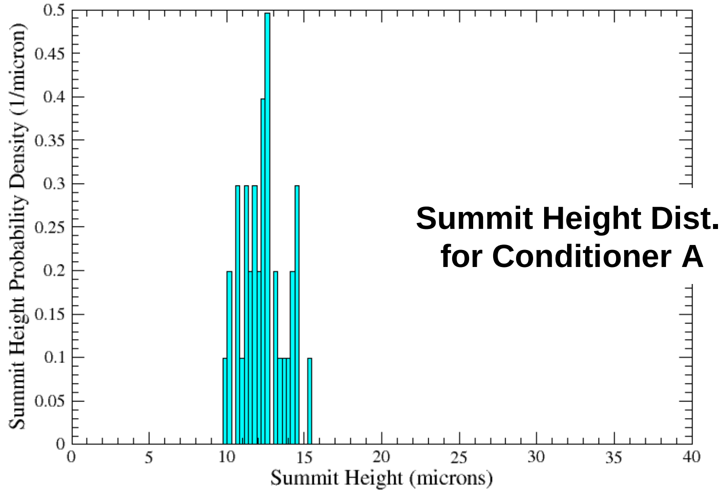
Algorithms and numerical methods for determination of the following have been refined:

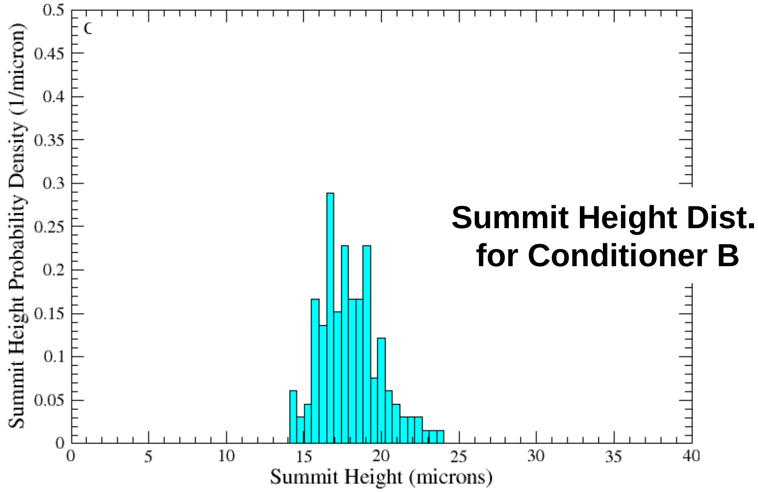
- **Contact area fraction**
- **Asperity height distribution**
- **Asperity density**
- **Asperity curvature**

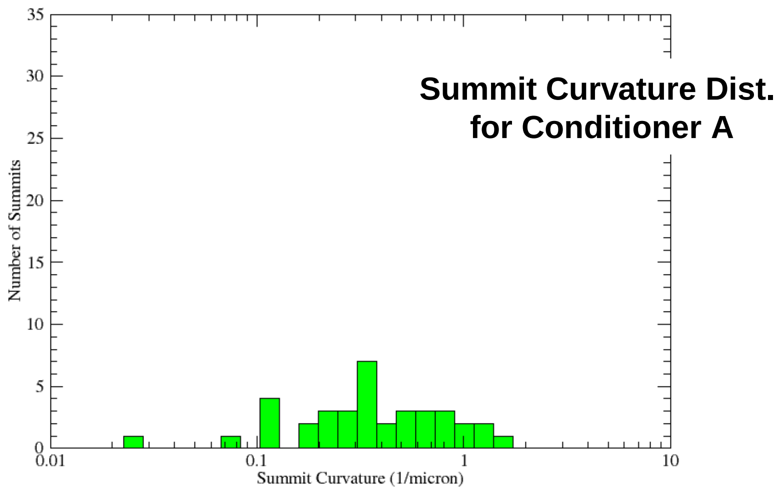


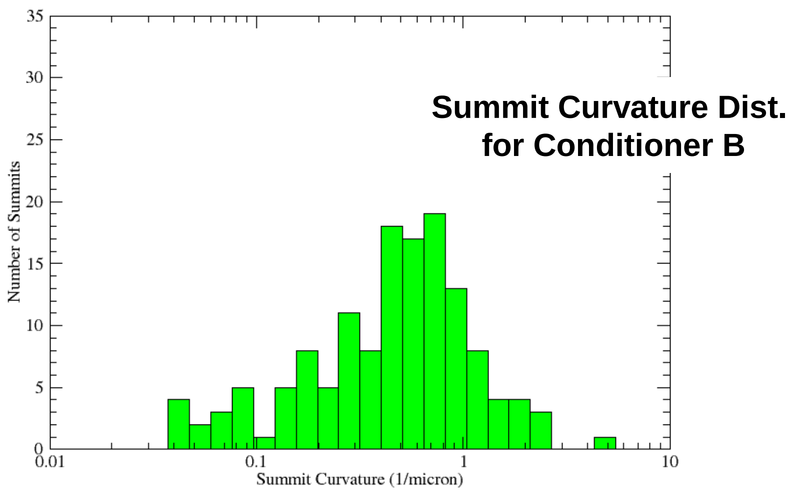
Conditioner A   Conditioner B

Data Extraction and Analysis









Industrial Interactions and Future Plans

Industrial mentors and contacts:

- **Don Hooper (Intel)**
- **Mansour Moinpour (Intel)**
- **Cliff Spiro (CMC)**

Next Year Plans:

- **Investigate effect of polishing pad material, conditioner disc and process parameters**
- **Correlate observed polishing results with observed confocal microscopy data**

Long-Term Plan:

- **Propose methodology for using confocal microscopy as part of a screening process or diagnostic technique for new consumables and processes and demonstrate the effectiveness of the methodology**

Lowering Material and Energy Usage During Purging of Gas Distribution Systems

High-Volume Nano-Manufacturing Customized Project

PI:

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

Co-PI:

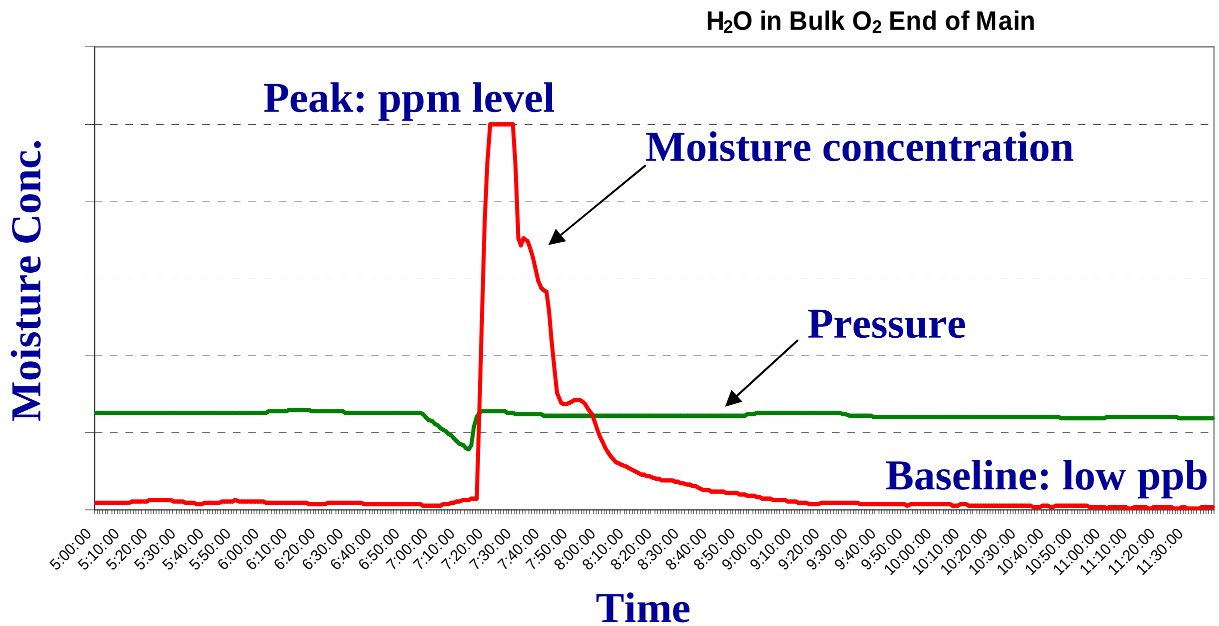
- **Carl Geisert, Sr. Principal Engineer, Intel**

Graduate Students:

- **Junpin Yao, Postdoctoral, Chemical and Environmental Engineering, UA**
- **Hao Wang: Ph.D. candidate, Chemical and Environmental Engineering, UA**

Background

1. **Surface adsorption/desorption, system pressure fluctuation, back diffusion from dead legs, and stagnant sections can cause significant contamination in ultra-pure gas distribution systems.**

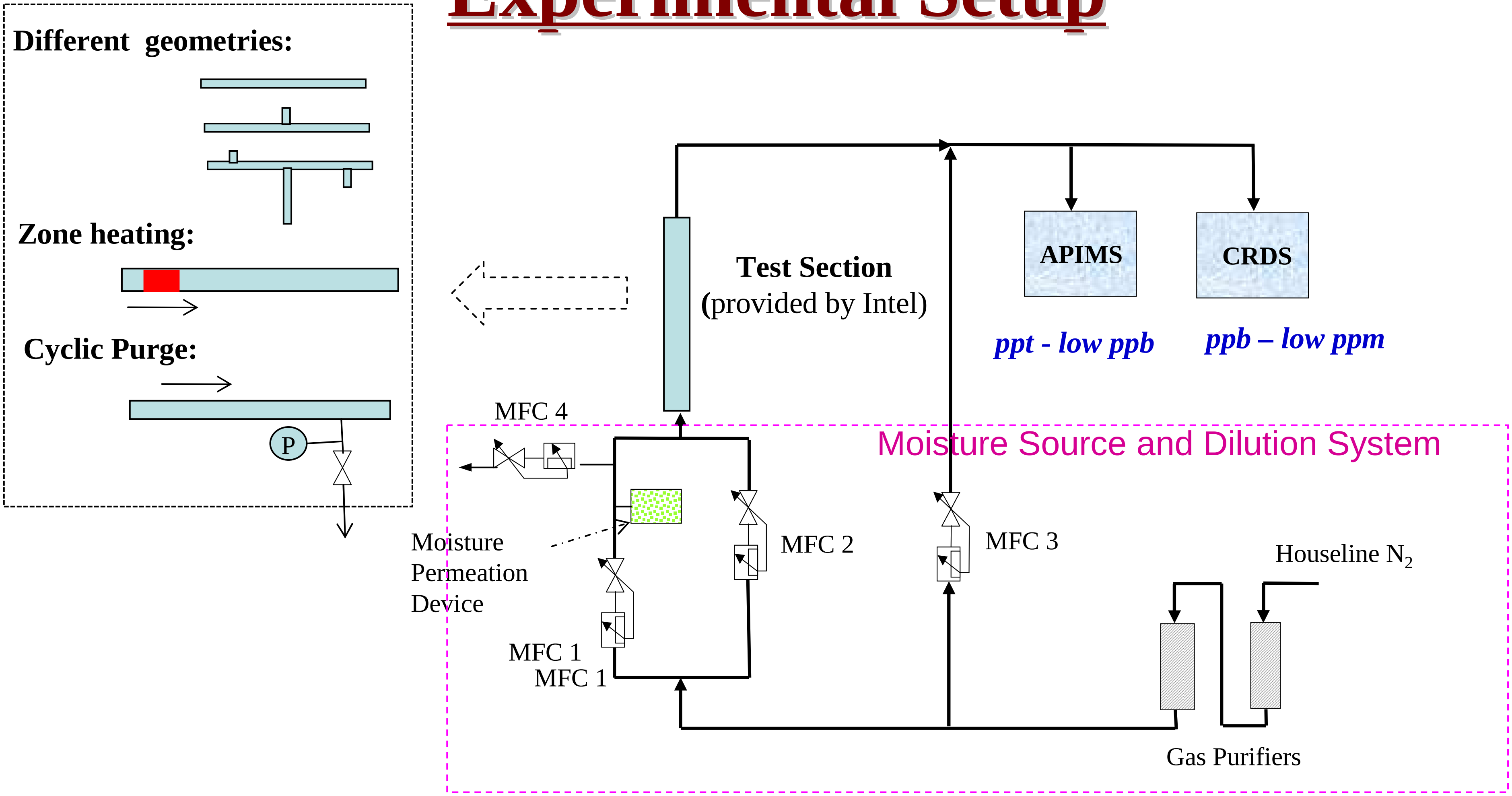


2. **Significant reduction in purge time and gas usage can be accomplished by applying programmed purge and cleaning processes that are based on process simulation combined with direct monitoring at key points.**

Objectives and ESH Impact

1. Determine the effects of purge gas temperature/zone heating, flow rate, purity, and cyclic purge on moisture removal during purging of gas distribution lines;
2. Determine the impacts of dead legs and trickle purge at laterals on dry down of gas distribution systems;
3. Develop and verify a gas distribution simulator for field application; develop a user-friendly tool that can be utilized to minimize gas usage during purging and cleaning processes at the system start up, during system recovery or during the operation of gas distribution systems.

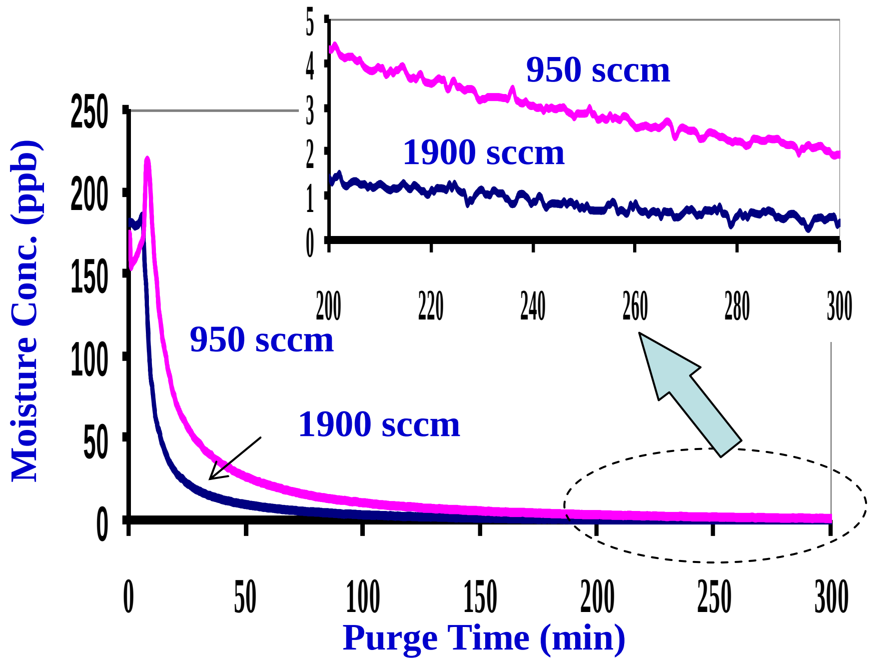
Experimental Setup

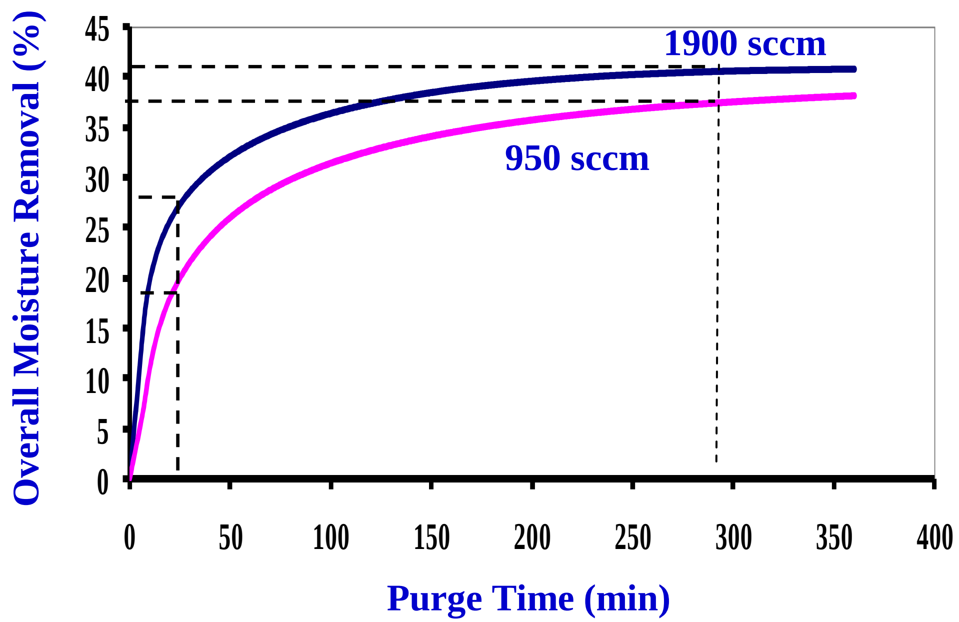


- **Atmospheric Pressure Ionization Mass Spectrometer (APIMS): fast response, low detection limit**
- **Cavity Ring Down Spectroscope (CRDS): robust, no vacuum, easy to maintain and operate, direct ppb reading**

Effect of Purge Flow Rate

EP SS pipe with 1.5 in. OD and 70 in. length. Initially the whole system was equilibrated with 180 ppb of moisture at 25 ^{0}C. Purge with 0.01 ppb purge gas at room temperature at 1900 and 950 sccm.

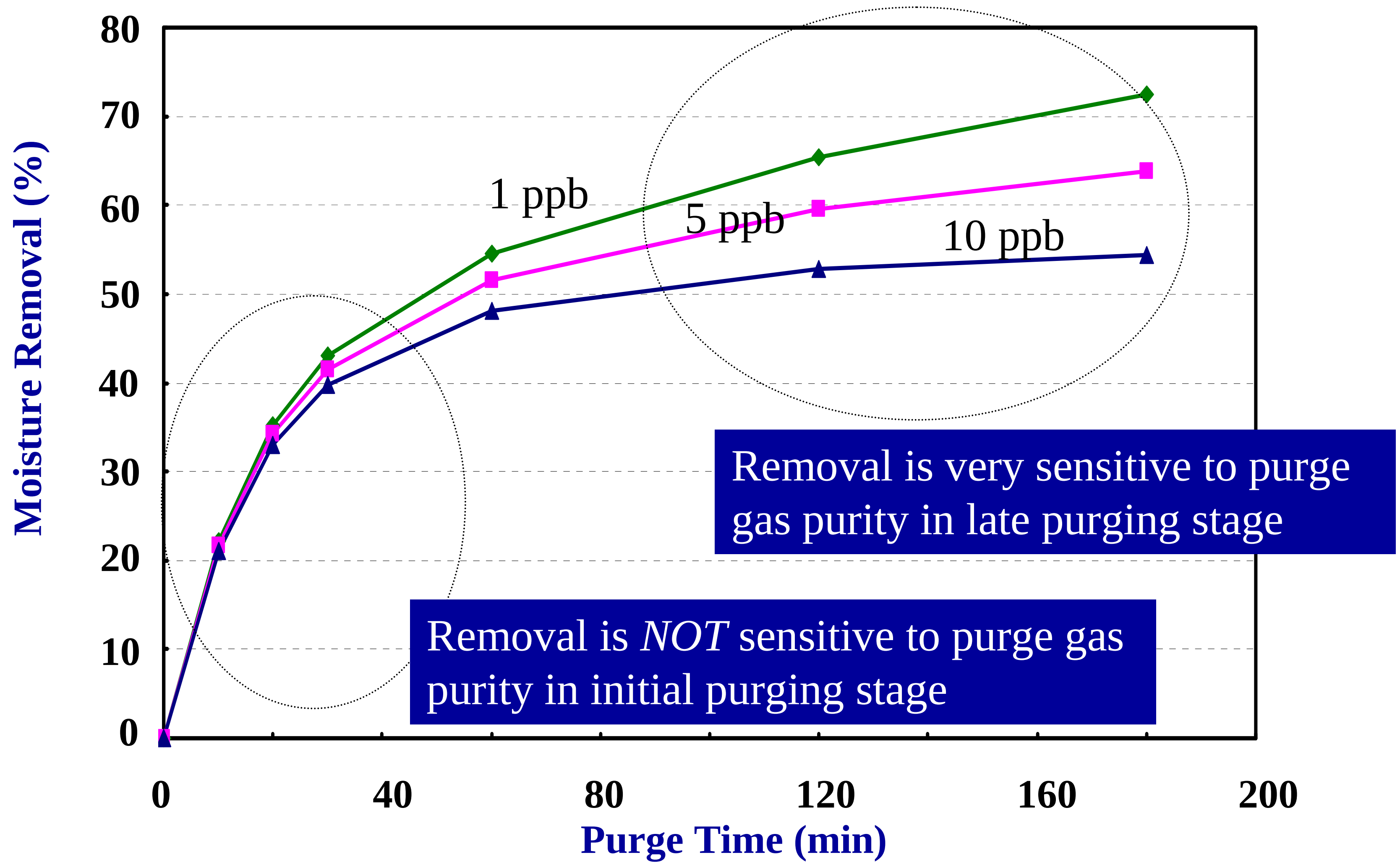




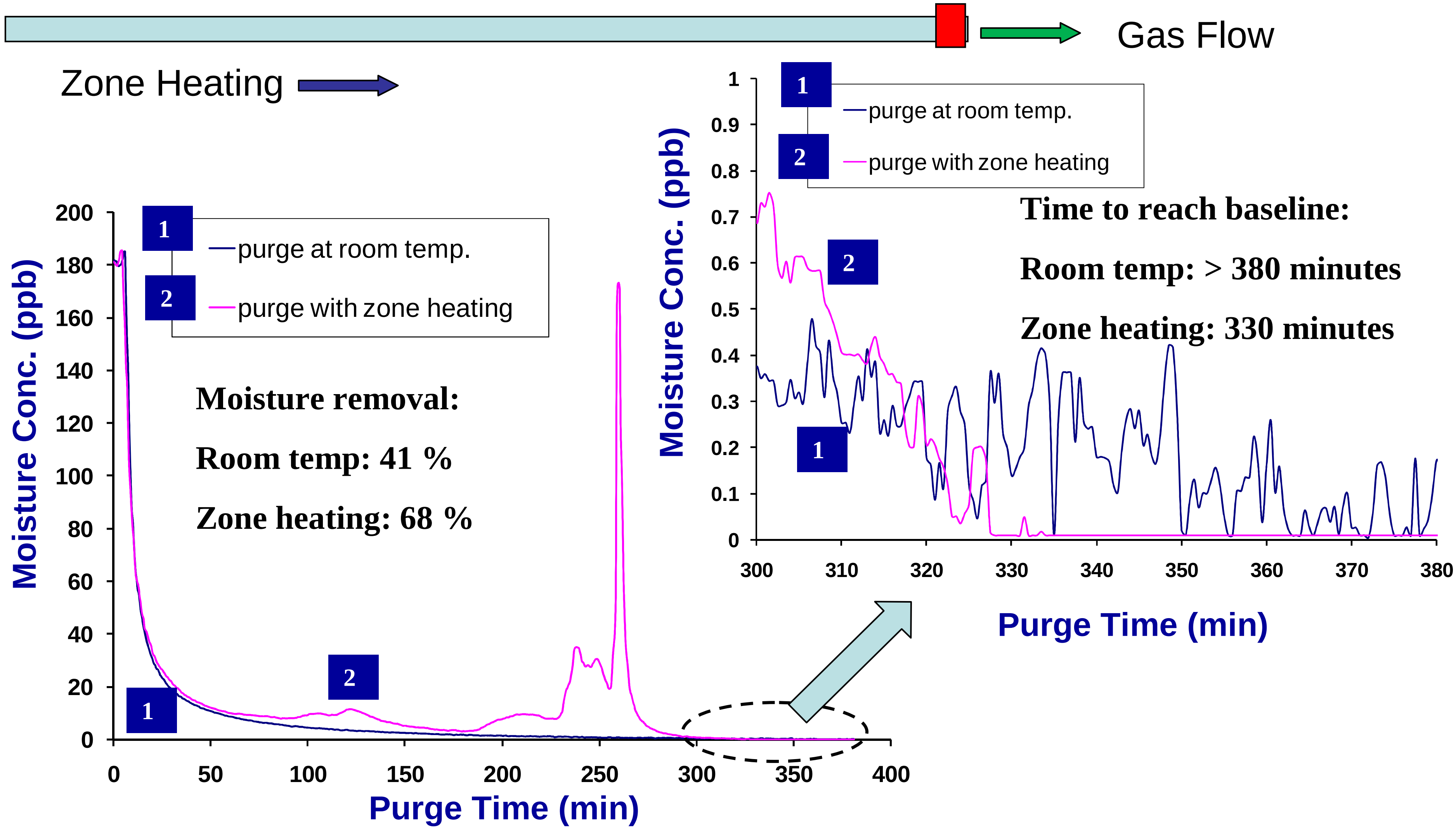
During initial purge stage, moisture removal is very sensitive to purge gas flow rate.

Effect of Purge Gas Purity

EP SS pipe with 1.5 inch OD and 36 inch length. Initially the whole system was equilibrated with 180 ppb of moisture at 25 ^{0}C. Isothermal purge with 350 sccm and 0.01 ppb purge gas.



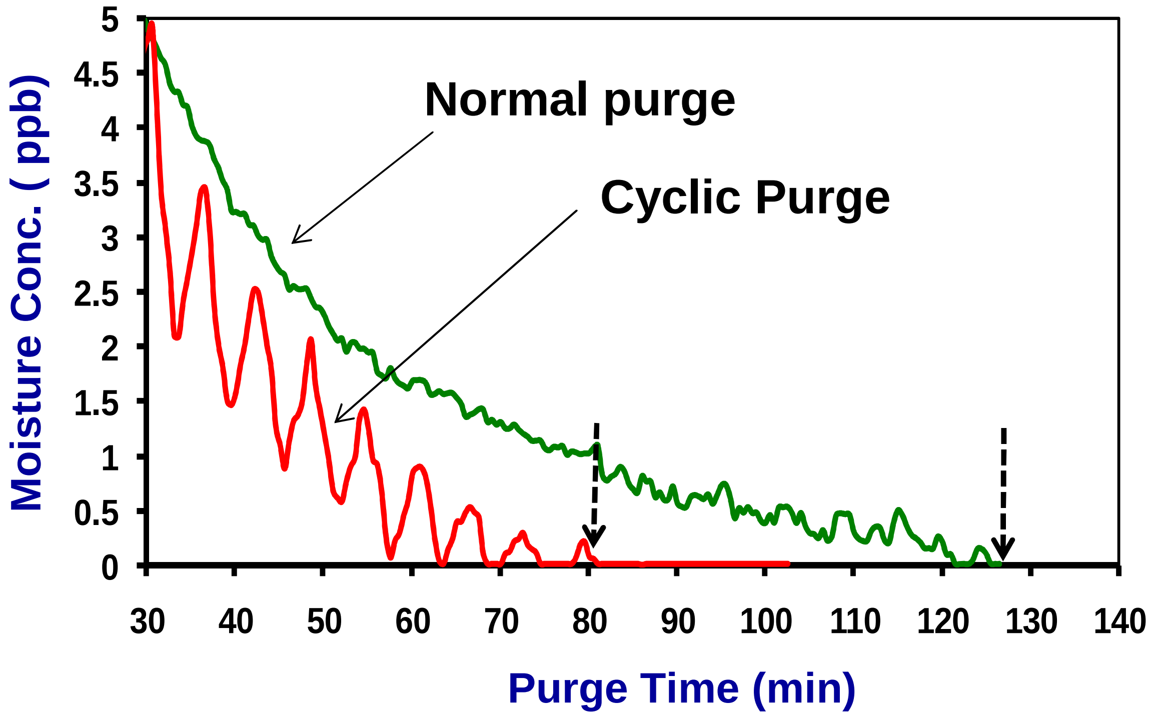
Application of Zone Heating



Zone heating enhances moisture removal: higher overall removal and less time to reach baseline

Application of Cyclic Purge

EP SS pipe with 1.5 inch OD and 70 inch length. Challenge conc. 90 ppb; Isothermal purge with 1900 sccm and 0.01 ppb purge gas.



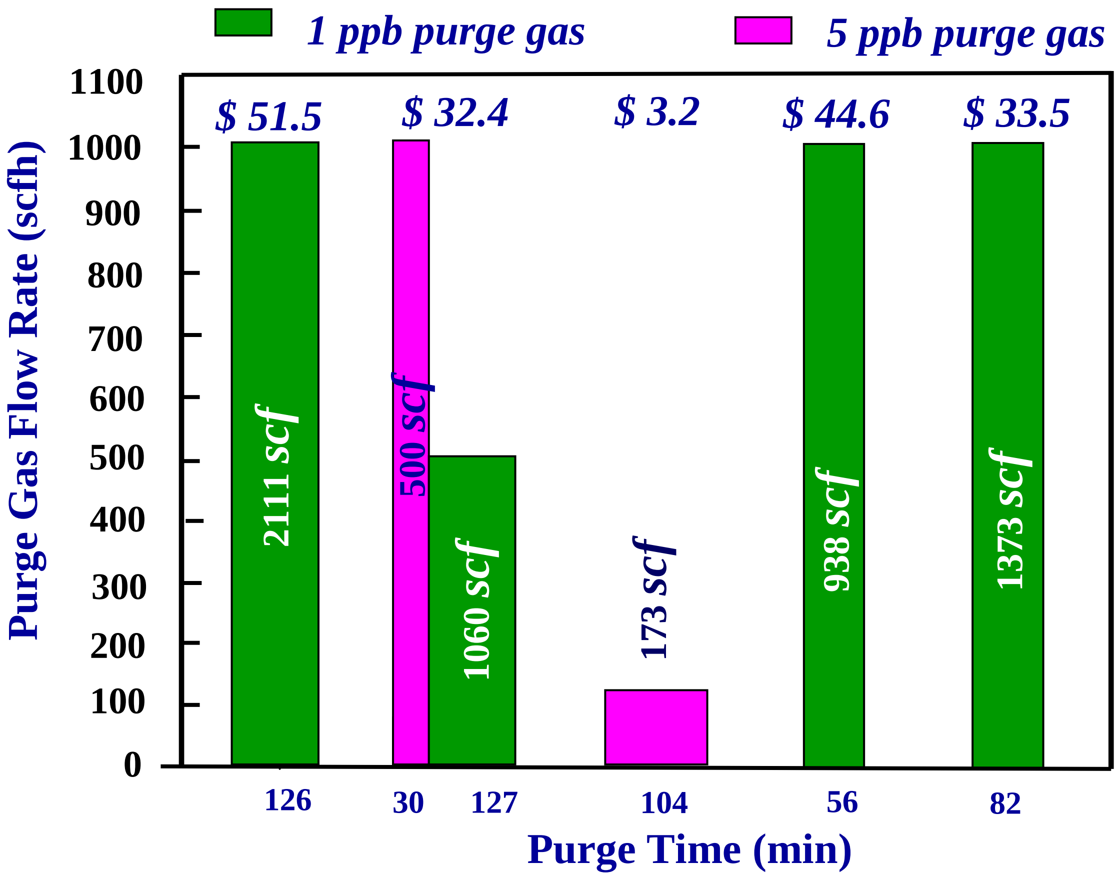
Time to reach baseline:

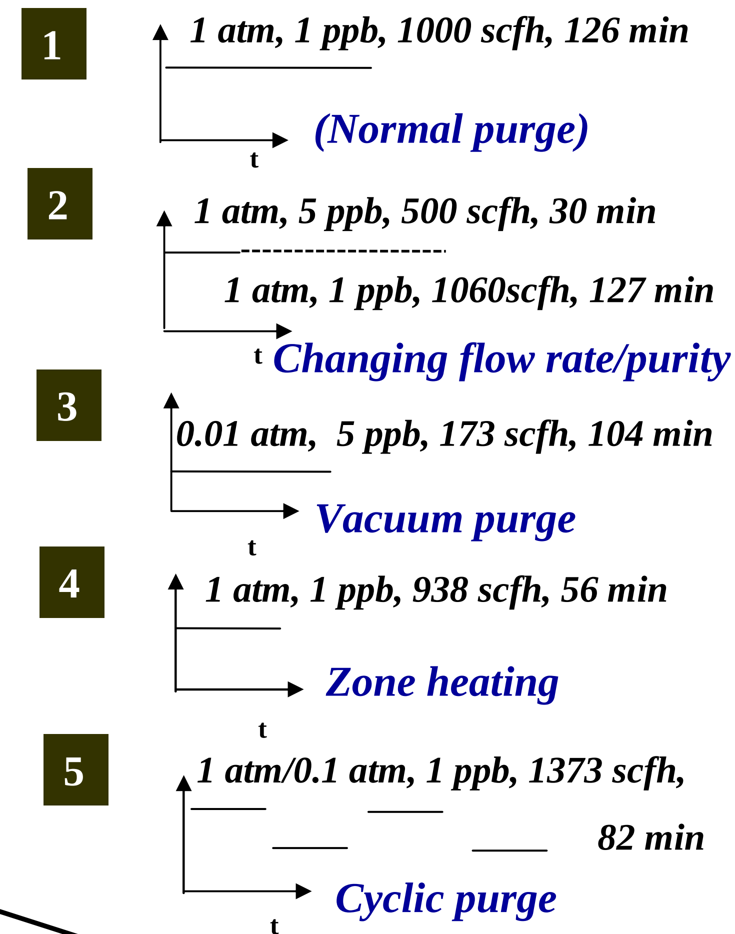
Cyclic purge: 82 minutes; Normal purge: 126 minutes

Cyclic purge enhances moisture removal: less time to reach baseline

Low-ESH Impact Purge Strategies

Sample: 10 meter, 1.5 inch OD; Initially was equilibrated with 200 ppb of moisture; 90% moisture removal. All operations are performed at room temp. except zone heating at 100 °C.





Options: 1 2 3 4 5

- 3 → **Minimum cost**
- 4 → **Minimum purge time**
- 5 → **Medium purge time and cost**

Highlights

- Moisture removal can be enhanced significantly by heating the pipe: zone heating achieves higher overall moisture removal and less time to reach baseline as compared to normal purge at room temperature.
- During initial purge stage, high purge flow rate and low purge gas purity are recommended, while during late purge stage, low purge flow rate and high purge gas purity are recommended.
- Cyclic purge enhances moisture removal.
- The process model developed in this research can help us to optimize purging processes with minimized time, gas usage and total cost.

Interactions and Future Plans

- Continue working with Intel; initiate similar applications and studies for other members
- More study on zone heating and cyclic purge
- Prepare a software package for use in industry

Acknowledgements

- Lisa Bergson, CEO, Tiger Optics LLC
- Val Strazds, Sr. Engineer, Intel
- Asad Iqbal, Ph.D., Process Engineer (graduated in 2007), Intel
- Harpreet Juneja, Ph.D., Application Engineer (graduated in 2008), Applied Materials

Integrated Electrochemical Treatment of CMP Waste Streams for Water Reclaim and Conservation (Customized Project)

PIs:

- **James Farrell, Chemical and Environmental Engineering, UA**
- **James C. Baygents, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Francis Dakubo: PhD candidate, Chemical and Environmental Engineering, UA**
- **Mark Brown, MS candidate, Chemical and Environmental Engineering, UA**

Undergraduate Students:

- **Jake Davis, Chemical Engineering, UA**
- **Ritika Mohan, Chemical Engineering, UA**
- **Kyle Kryger, Chemical Engineering, UA**
- **Ehab Tamimi, Chemical Engineeering, UA**

Cost Share (other than core ERC funding):

- **NASA Space Grant Fellowship (K. Kryger)**
- **Water Sustainability Program Fellowship (R. Mohan)**

Objectives

- **Develop an electrochemical method for removing Cu^{2+}, H_2O_2, colloidal abrasives, chelating agents and corrosion inhibitors from wastewater generated during CMP.**
- **Compare contaminant removal with industry benchmarks for use of reclaimed water.**
- **Build a prototype reactor and pilot test on real CMP wastewater.**
- **Compare economic value of reclaimed water versus freshwater.**

ESH Metrics and Impact

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

- Eliminate the disposal problems associated with membrane concentrates.
- Eliminate the disposal of Cu-laden nanoparticles into hazardous waste landfills.

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

- Reclaim CMP wastewater for use in mechanical systems.
- CMP wastewater accounts for up to 30% of fab water use.

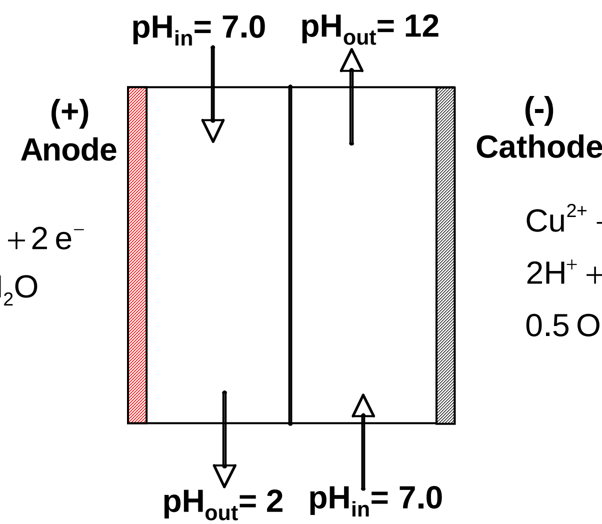
3. Reduction in the use of chemicals

- Eliminate the need for pH adjusting chemicals and reducing agents that add to TDS load.
- Eliminate the need for activated carbon regeneration.

Electrochemical Treatment

$H_2O \rightarrow 0.5\,O_2 + 2H^+ + 2\,e^-$

$\text{organics} \rightarrow CO_2 + H_2O$



$Cu^{2+} + 2e^- \rightarrow Cu^0$

$2H^+ + 2\,e^- \rightarrow H_2$

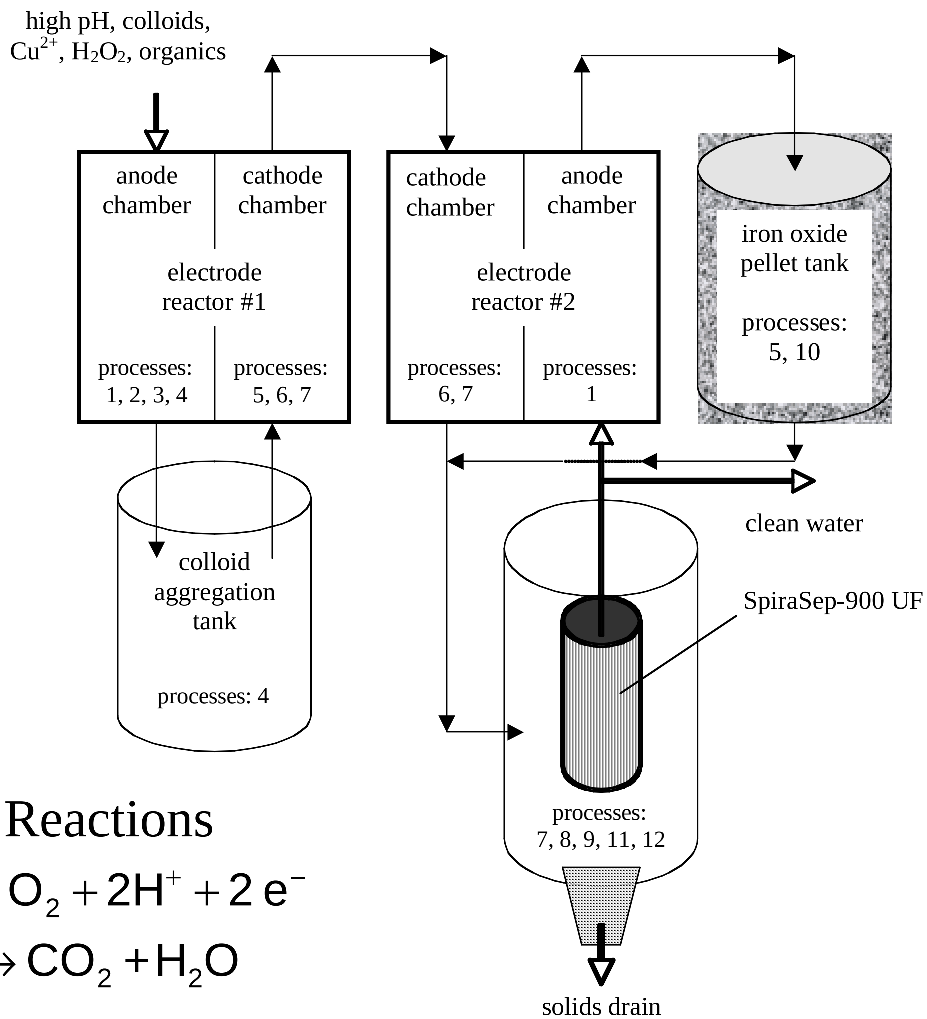
$0.5\,O_2 + 2H^+ + 2\,e^- \rightarrow H_2O$

Advantages of electrochemical reactors over other methods of water treatment include:

1. Elimination of chemical additives (*e.g.*, pH adjusting chemicals)
2. Elimination of secondary waste stream production requiring further treatment or disposal (*e.g.*, RO reject, ion exchange brines)
3. Low capital and operating costs

Example of Proposed Application:

Treatment of Cu-CMP wastewater



Process Key:

1. solution acidification
2. colloid charge neutralization
3. organic compound oxidation
4. colloid aggregation
5. solution pH neutralization
6. copper electrowinning
7. H_2O_2 reduction
8. colloid flocculation
9. organic compound adsorption
10. ferric ion addition
11. particle filtration
12. solids sedimentation

Cathode Reactions

$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

$$2H^+ + 2\,e^- \rightarrow H_2$$

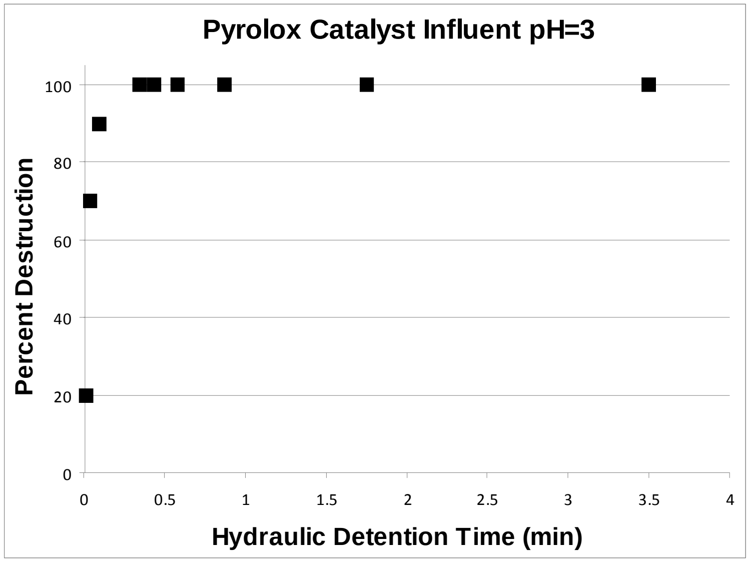
$$0.5\,O_2 + 2H^+ + 2\,e^- \rightarrow H_2O$$

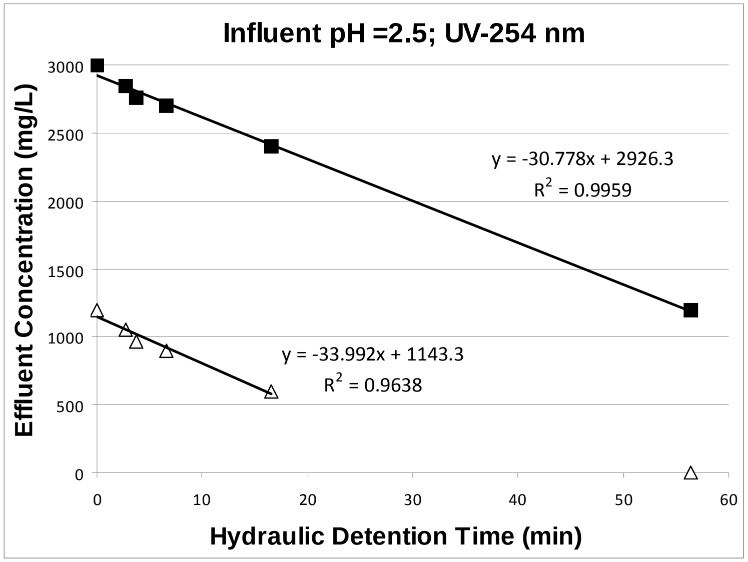
Anode Reactions

$$H_2O \rightarrow 0.5\,O_2 + 2H^+ + 2\,e^-$$

$$\text{organics} \rightarrow CO_2 + H_2O$$

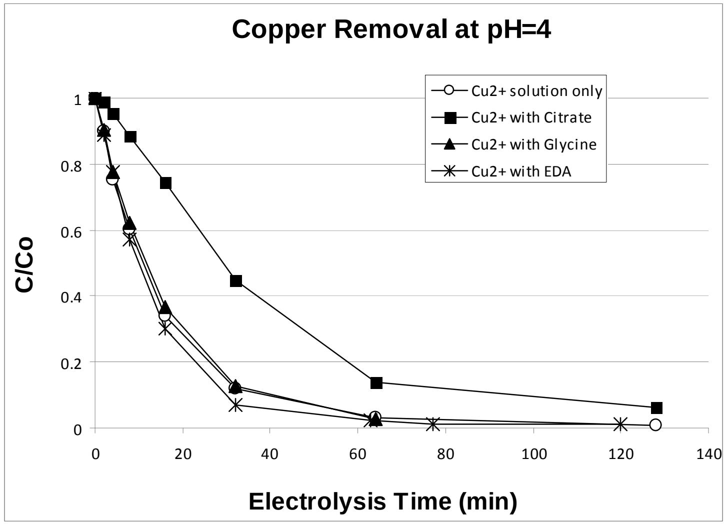
Peroxide Destruction

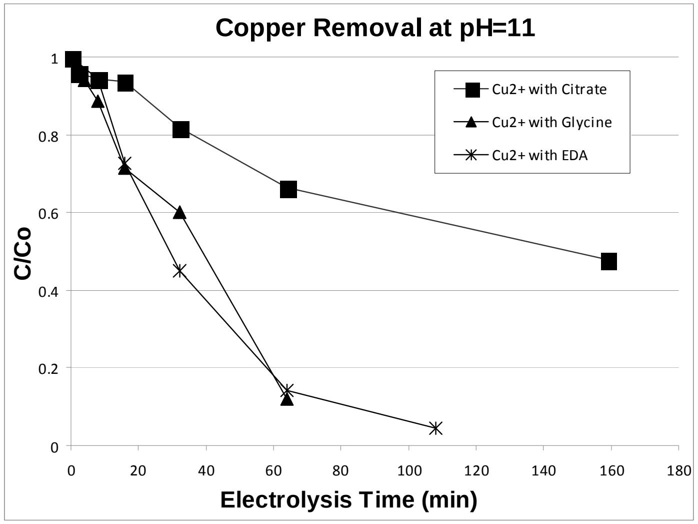




- **Conducted tests on six possible peroxide destruction catalysts.**
- **Conducted tests on ultrasonic and UV-light peroxide destruction.**
- **Pyrolox® (pyrolusite-MnO_2) catalyst determined to be the most effective.**
- **H_2O_2 destruction rates with both 185 and 354 nm UV light were too slow for practical implementations.**

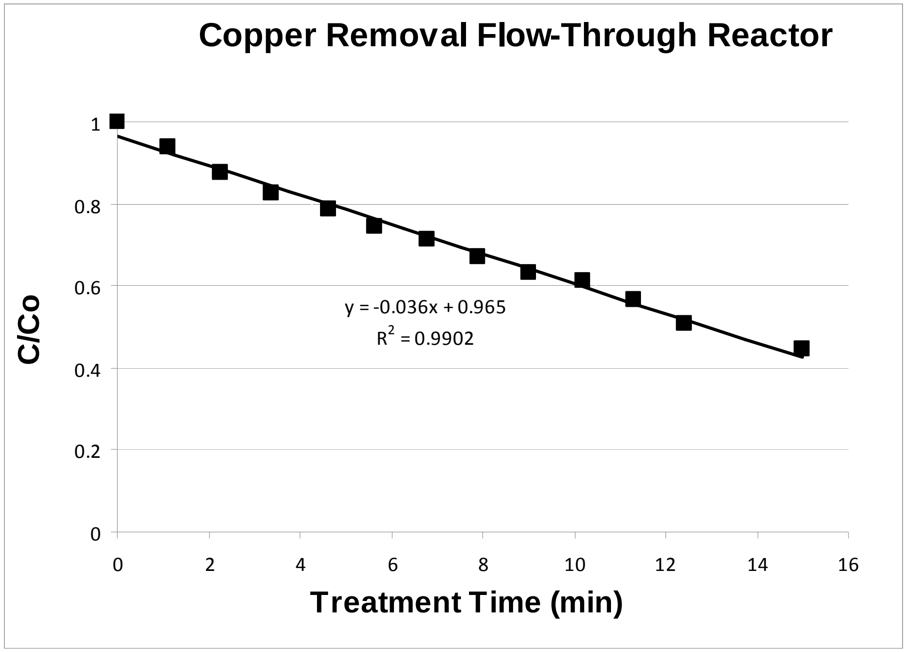
Electrodeposition of Cu on Carbon Cloth Cathode





- **Investigated the effect of chelating agents on electrodeposition of Cu in batch reactors in solutions with low and high pH values.**
- **Ethylenediamine (EDA) and glycine do not affect Cu deposition rates.**
- **Cu deposition occurs at both low and high solution pH values.**

Electrodeposition of Cu^{2+} in Flow-through Reactor



- **Cu deposition occurs rapidly in flow-through reactor.**

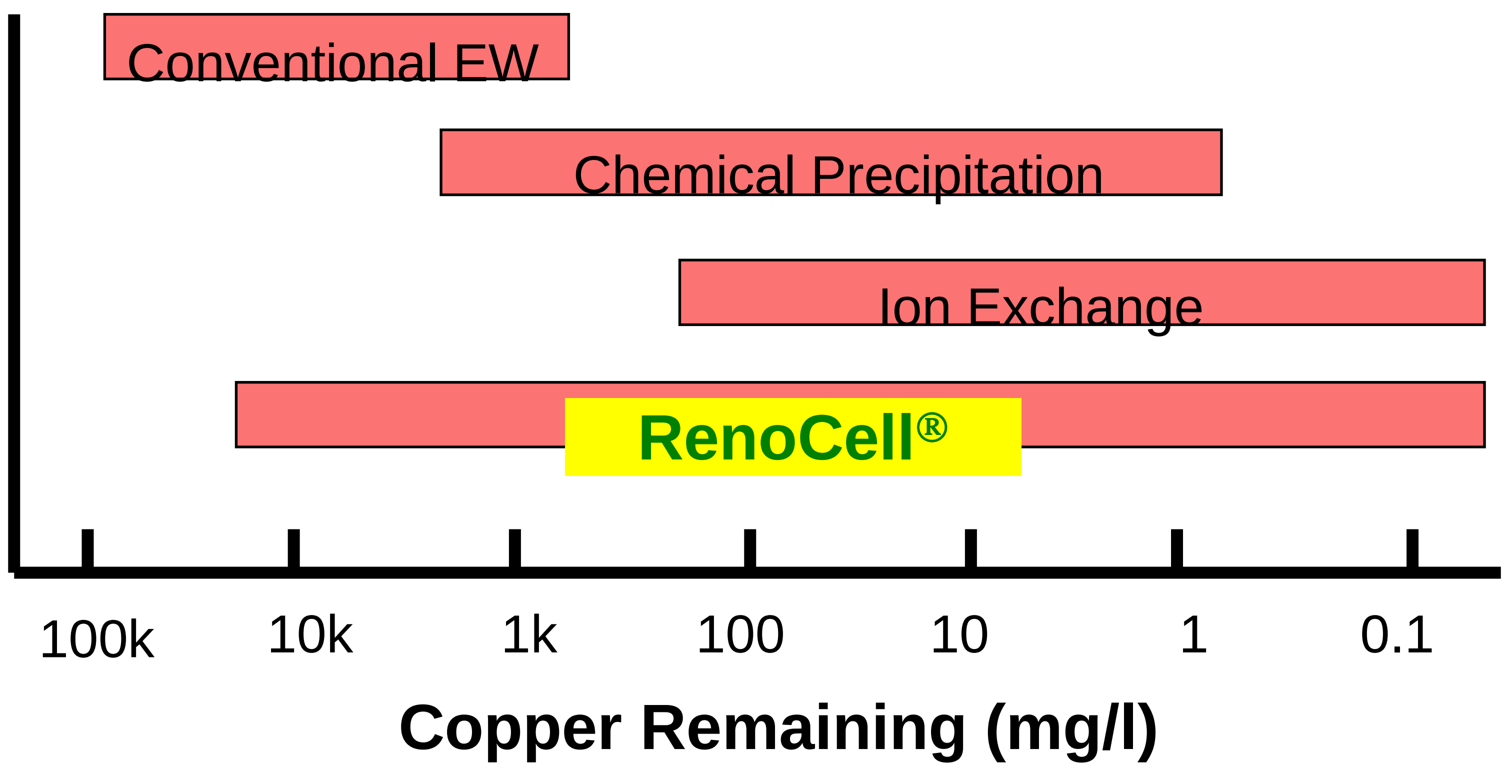
Commercial Scale Reactors

POROUS CARBON CATHODE

Before Test

After Metal Deposit

EFFECTIVE OPERATING RANGES FOR METAL REMOVAL TECHNOLOGIES



Industrial Interactions and Technology Transfer

- **Don Hooper, Intel Corporation**
- **Dan Hodges, Intel Corporation**
- **Allen Boyce, Intel Corporation**
- **Avi Fuerst, Intel Corporation**

Future Plans

Next Year Plans

- **Bench test RenoCell® electrochemical reactor for Cu^{2+} removal and colloid destabilization**
- **Pilot test peroxide destruction catalyst with Allen Boyce**
- **Bench test SpiraSep-900® ultrafilter for colloid filtration**

Long-Term Plans

- **Apply electrochemical treatment methods to other wastewater streams**

Publications, Presentations, and Recognitions/Awards

- **James Farrell. "Electrochemical Water Treatment using Diamond Film Electrodes," presented at the University of Illinois at Urbana-Champaign, 11/7/08.**

- **James Baygents and James Farrell. "Electrochemical Methods for Water Reclaim in Semiconductor Manufacturing," presented at the International Conference on Microelectronics Pure Water, November 11-12, 2008, Mesa, AZ.**

OPTIMIZATION OF DILUTE AMMONIA-PEROXIDE-MIXTURE (APM) FOR HIGH VOLUME MANUFACTURING THROUGH SURFACE CHEMICAL INVESTIGATIONS

Shariq Siddiqui[1], Jinhong Zhang[2] and Srini Raghavan[1]

[1]Material Science and Engineering Department

[2]Department of Mining and Geological Engineering

University of Arizona, Tucson, AZ 85721

Objectives

1. Develop atomic force microscope (AFM) based methodology for optimizing ammonia-peroxide mixture (APM) composition for particle removal

2. Investigate the stability of dilute ammonia-peroxide solutions using Horiba SC-1 monitor and develop a model

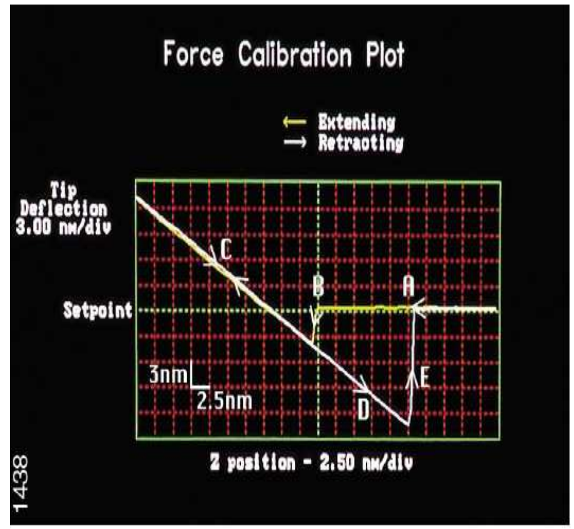
3. Introduce cost effective processes into high volume manufacturing (HVM) based on models developed through surface chemical investigations

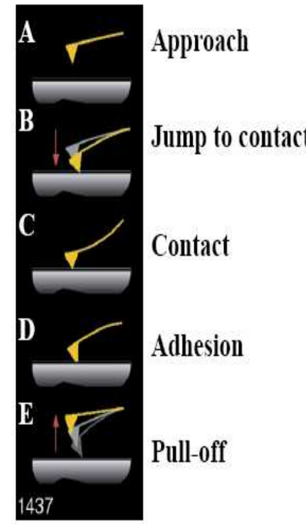
Methods and Approach

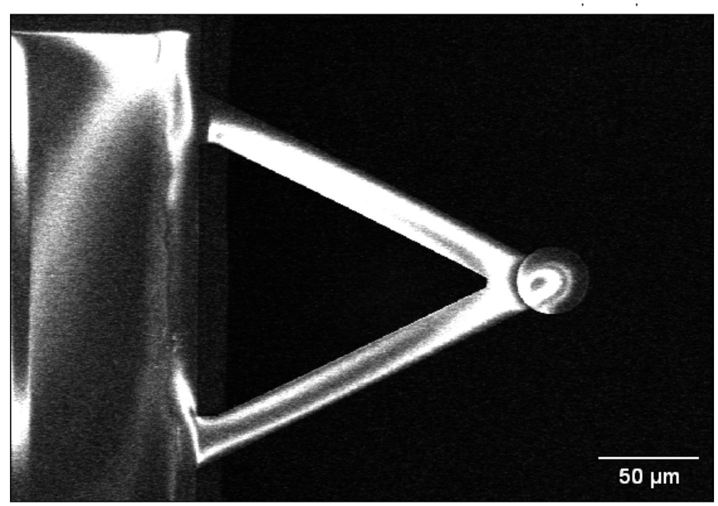
1. Measure attractive or repulsive forces between a particle and a surface using the colloidal probe technique.

2. Measure interaction forces between a *hydrophilic* surface and a *hydrophilic* particle in de-ionized water and electrolyte solutions.

3. Measure interaction forces between a *hydrophobic* surface and a *hydrophobic* particle in de-ionized water, ammonium hydroxide solutions and in dilute APM solutions.







Experimental Procedures

Hydrophilic surface – hydrophilic particle interactions

- Thermal oxide (1000 Å) surface cleaning
  - Acetone and methanol sonication for 5 min
  - N_2 blow dry
  - H_2SO_4:H_2O_2 (4:1) for 10 min
  - DI-H_2O rinse
  - N_2 blow dry
- Si_3N_4 AFM Tip cleaning
  - Soaked in ethanol overnight
  - UV (254 nm) irradiated for 1 hour to remove carbon contamination before attaching a particle.
- Silica particle size ≈ 5 µm

Hydrophobic surface – hydrophobic particle interactions

- Si (100) p-type surface cleaning
  - Acetone and methanol sonication for 5 min
  - N_2 blow dry
  - Dilute HF (1:100) for 10 min
  - DI-H_2O rinse
  - N_2 blow dry
- Octadecyltrichlorosilane (OTS), $CH_3(CH_2)_{17}SiCl_3$,coated glass particle size ≈ 10 µm
- Ammonium hydroxide solutions ranging from 1:6 to 1:50.
- Surface treated with a dilute APM (1:1:100) solution for 10 min and rinsed with DI water before force-distance measurement.

RESULTS I

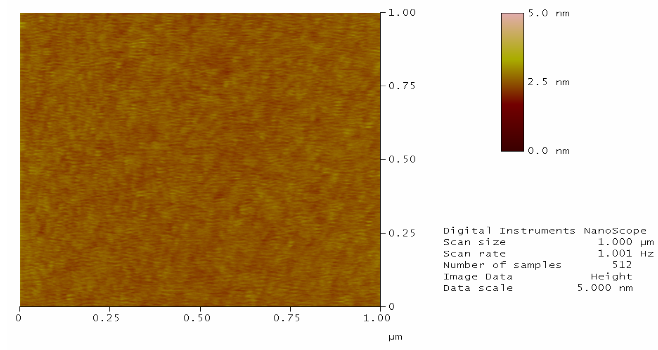
The interaction force between *hydrophilic* silica surface and *a hydrophilic* silica particle in de-ionized water and in electrolyte solutions.

Silica surface-Silica particle in DI water

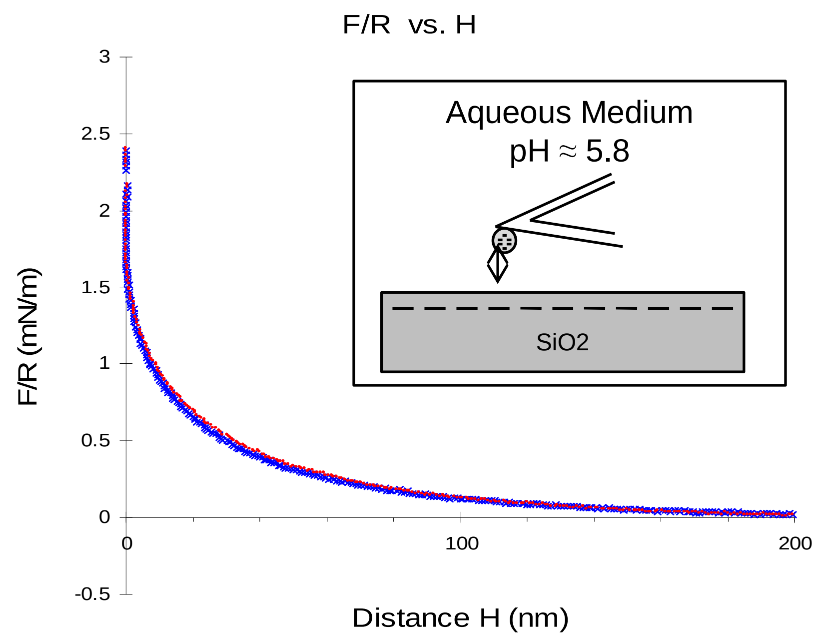
- The surface imaging of silica substrate in contact mode showed a smooth surface with a RMS roughness of 0.1 nm.

- Contact angle of water on silica surface was measured to be <10º indicating that the surface was hydrophilic.

- The interaction force between silica surface and a silica particle in DI water was found to be repulsive due to similar (negative) charge on both surfaces at pH of 5.8.

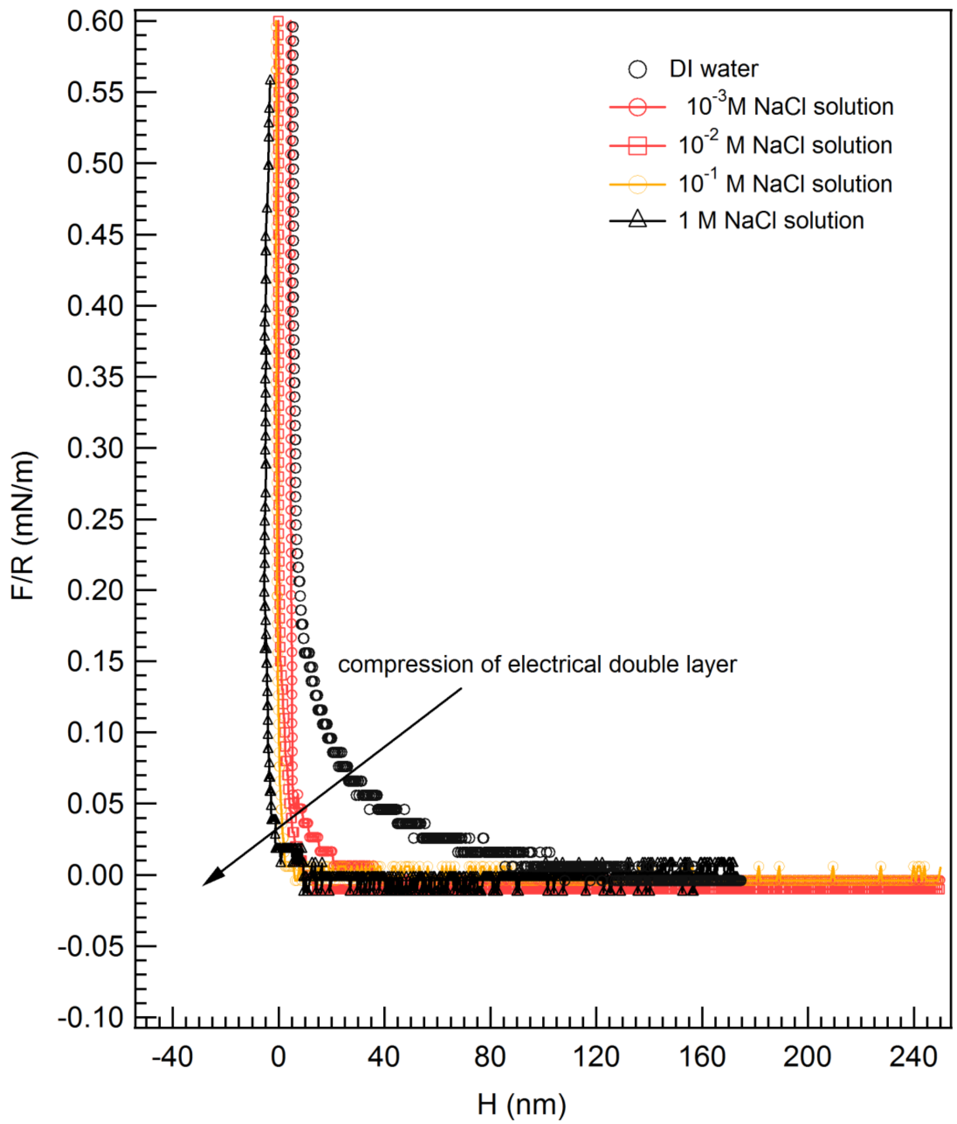


RMS: 0.1 nm



Silica surface-Silica particle in NaCl solutions

- In electrolyte solutions, the force-distance curve exhibits a much steeper profile than in DI water due to the compression of the electrical-double layer.



RESULTS II

The interaction force between *hydrophobic* silicon surface and a *hydrophobic* octadecyltrichlorosilane (OTS) coated glass particle in DI water, ammonium hydroxide solutions and in a dilute APM solution.

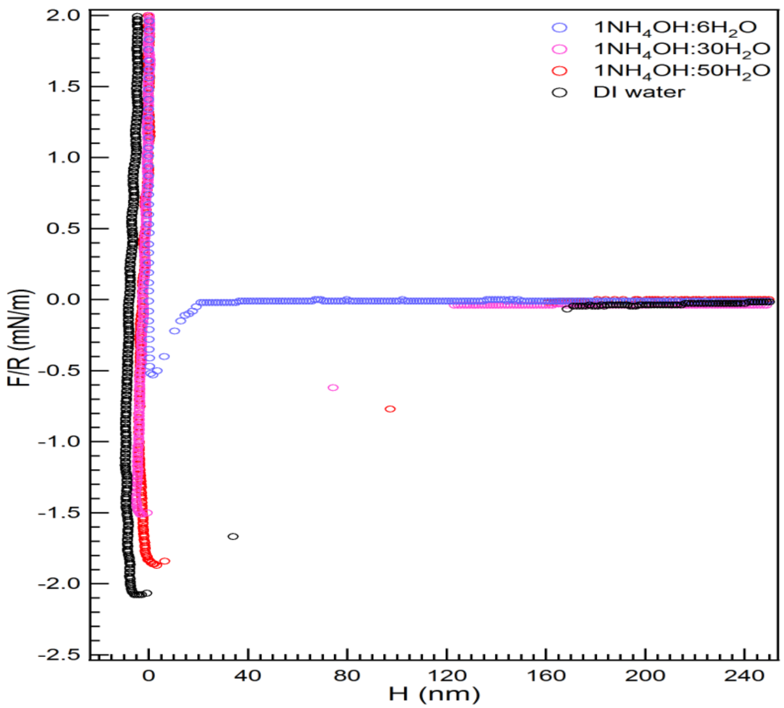
Si surface-OTS coated glass particle in DI water & $NH_4OH:H_2O$ solutions

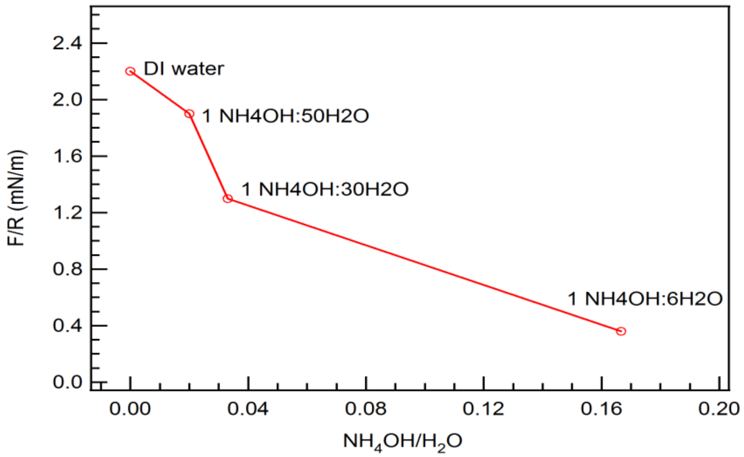
o HF treated silicon substrate results in H-terminated surface, which is hydrophobic and prone to attract particles, particularly hydrophobic particles.

o A strong adhesion force (negative value) of 2.2 mN/m ± 0.3 mN/m was measured between hydrophobic silicon surface and a hydrophobic OTS coated glass particle in de-ionized water.

o The adhesion force in $NH_4OH:H_2O$ (1:50) solution was similar to that measured in de-ionized water indicating that more dilute ammonium hydroxide solutions may not be very effective in removing particles.

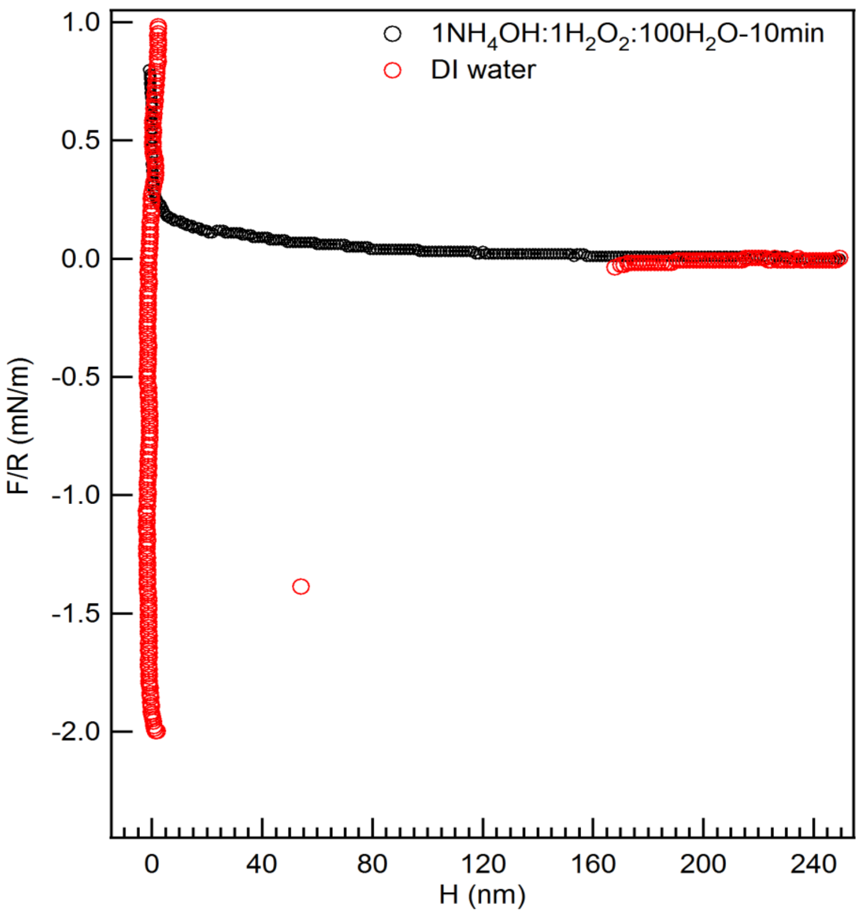
o The adhesion force was observed to decrease with increasing ammonium hydroxide concentrations.





Si surface-OTS coated glass particle in a dilute APM (1:1:100) solution

o A dilute ammonium-peroxide mixture resulted in a net repulsive interaction due to the oxidation of the silicon surface and the removal of OTS coating from the glass particle.



Summary

- Colloidal probe technique has been successfully used to measure the interaction force between: (1) hydrophilic silicon dioxide surface and hydrophilic glass particle and (2) hydrogen terminated silicon surface and hydrophobic glass particle
- The force of interaction between silicon dioxide surface and silicon dioxide particle is repulsive in DI water and its magnitude decreases in electrolyte solutions
- A strong *adhesion force* was measured between hydrogen terminated silicon surface and a glass particle made hydrophobic through an alkyl silane in DI water. This adhesion force was observed to decrease with increasing ammonium hydroxide concentration in solution.
- No adhesion force was observed between a hydrogen terminated silicon surface and hydrophobic glass particle in dilute APM (1:1:100) solution.

FUTURE EXPERIMENTS

- To measure the effect of contaminant particle size on interaction force ; initial plan is to use a *hydrophobic* Si AFM probe (nominal radius ~ 10 nm) to simulate a particle

- Use a particle such as aluminum oxide, which would exhibit strong electrostatic attraction to the silica surface and measure the effect of APM ratio on adhesion force

- Collect stability data on dilute APM solutions using Horiba SC-1 composition monitor.

Industrial Interactions and Technology Transfer

- Barry Brooks, Intel Corporation
- Avi Fuerst, Intel Corporation

SRC® Semiconductor Research Corporation

PIONEERS IN COLLABORATIVE RESEARCH®

Cooperative SRC-IMEC-CEBSM R&D Initiative

imec

Green manufacturing for semiconductor industry

- Semiconductor Research Corporation (SRC) and IMEC intend to set up an international collaboration aimed at creation of novel processes and materials for advanced semiconductor manufacturing.
- The memorandum of understanding (MOU) calls for the consortia to apply their more than 50 years of combined expertise to finding *more environmentally friendly ways to make chips* for use by the worldwide electronics industry.
- The research will be conducted among IMEC and the joint SRC/SEMATECH Center for Environmentally Benign Semiconductor Manufacturing (CEBSM).
- The cooperative work will aim at two objectives:
  - Creation of leading-edge technologies that protect the environment
  - More effective processes for lowering the costs of chip manufacturing.

Focus topics in first phase of the joint initiative

- Sustainable cleaning and surface preparation of new materials and nano-structures.
  - Processes for the introduction of new channel and gate materials, such as Germanium and III/V compounds; precursors for deposition, etch chemicals and cleaning agents.
  - Establish options for minimizing emissions and decreasing the usage of chemicals, water and energy during processing.
  - Explore novel in-line and real-time approaches for monitoring the efficacy of nano-structure cleaning processes.
- Sustainable high-performance material planarization processes.
  - Advance the design and feasibility of process options that eliminate the release and discharge of nanoparticles in the manufacturing waste streams.

New materials and nano-structures

- ***Project 1: Cleaning and introduction of new materials and new nano-structures***
  - For the integration of high mobility channel materials in future device technologies several key challenges must be addressed.
    - Cleaning, dry and wet etching of III/V materials and treatment of waste from these etch processes.
    - Environmentally benign substitutes for solvents for cleaning and removal of photoresist and post-etch residues.
    - Environmentally benign and safe MOCVD precursors.
  - Goal of the project:
    - Finding high performance, environmentally benign solvents, methods, and metrology technology for cleaning of new materials (like Ge and III/V) and nano-structures, including high aspect ratio structures and post-etch residue cleaning.
    - Develop a fundamental understanding and proactive management of critical mass balance factors.

CMP of new materials

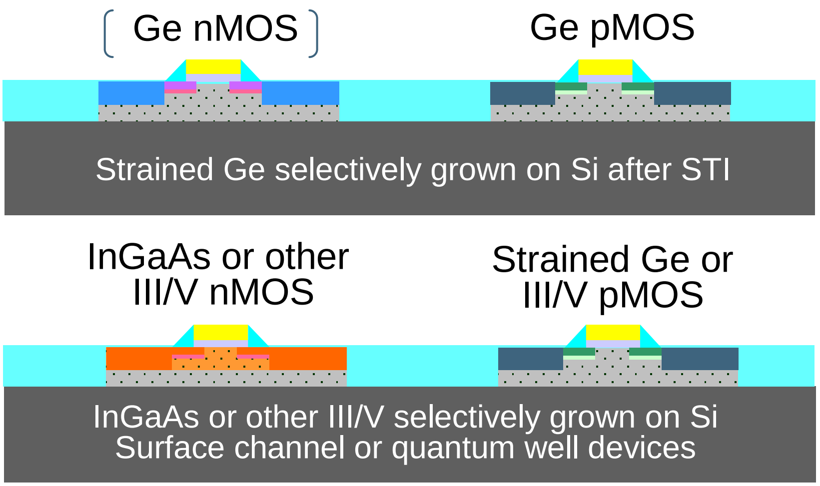
- ***Project 2: CMP issues involving new materials and CNT interconnect; i.e. effect of nanoparticles during CMP, Ge and III/V CMP***
  - CMP of CNT's in VIA's for advanced interconnects
    - Effect of CNT's in CMP slurry.
    - Avoid release of CNT's to the environment.
  - CMP of Ge and III/V materials
    - Optimize processes for CMP of Ge and III/V's
    - Treatment of CMP waste with III/V materials
  - Goal of the project:
    - Characterization of CMP issues in heterogeneous substrates /surfaces involving low k and CNT's, Ge, III/V's and other materials as warranted.
    - Characterization of CMP waste generated.
    - Study of treatability and ESH issues of this new CMP waste.

CMOS with high-mobility channel materials

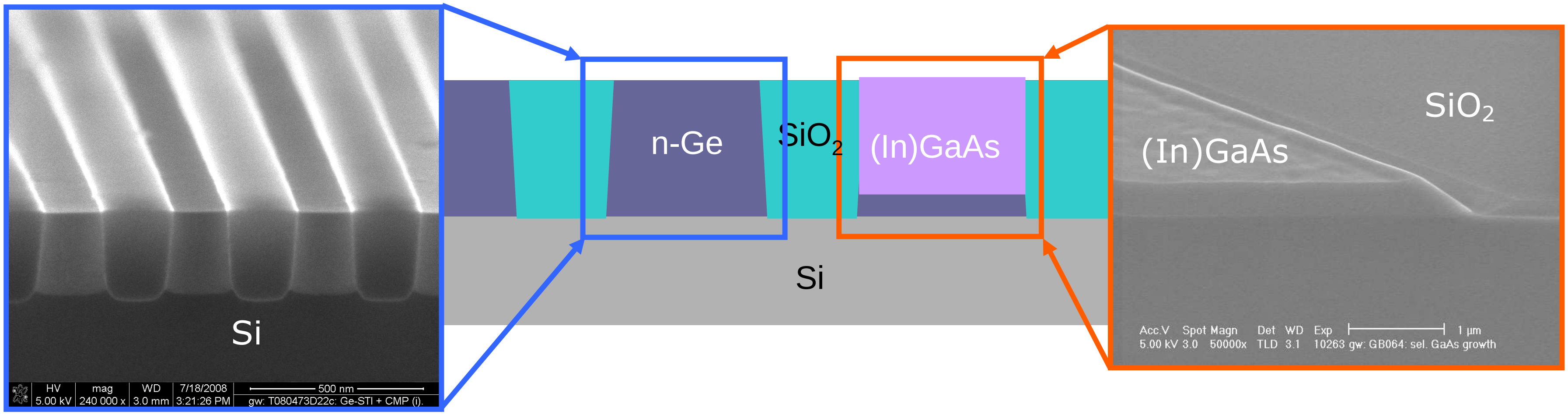
- ❑ CMOS performance can be enhanced by using high-mobility channel materials
  - Various studies suggest that higher mobility leads to improved transistor performance even for very short channel devices
- ❑ Most high-μ materials do no have a stable electrically passivating natural oxide
  - The use of deposited high-κ dielectrics potentially allows the use of high mobility channel materials that do not have a stable thermal oxide
  - Electrical passivation of the high-μ material / high-κ interface is a major challenge

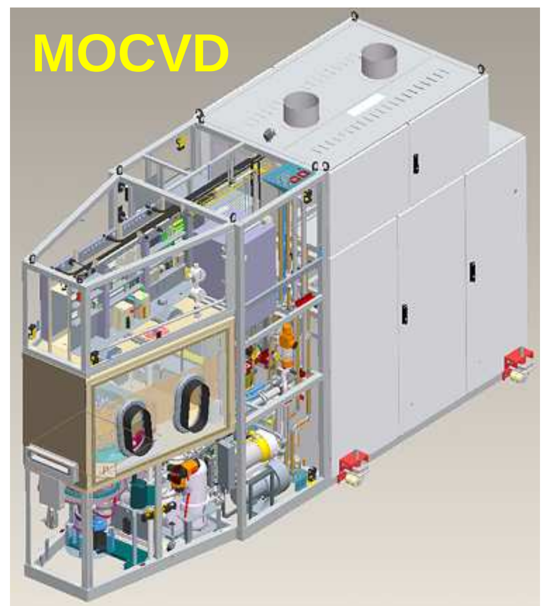
S. Takagi, The University of Tokyo, INC4 2008

	Si	Ge	GaAs	InP	InAs	InSb
electron mob. (cm^2/Vs)	1600	3900	9200	5400	40000	77000
electron effective mass ($/m_0$)	m_t: 0.19 m_l: 0. 916	m_t: 0.082 m_t: 1.467	0.067	0.082	0.023	0.014
hole mob. (cm^2/Vs)	430	1900	400	200	500	850
hole effective mass ($/m_0$)	m_{HH}: 0.49 m_{LH}: 0.16	m_{HH}: 0.28 m_{LH}: 0.044	m_{HH}: 0.45 m_{LH}: 0.082	m_{HH}: 0.45 m_{LH}: 0.12	m_{HH}: 0.57 m_{LH}: 0.35	m_{HH}: 0.44 m_{LH}: 0.016
band gap (eV)	1.12	0.66	1.42	1.34	0.36	0.17
permittivity	11.8	16	12	12.6	14.8	17



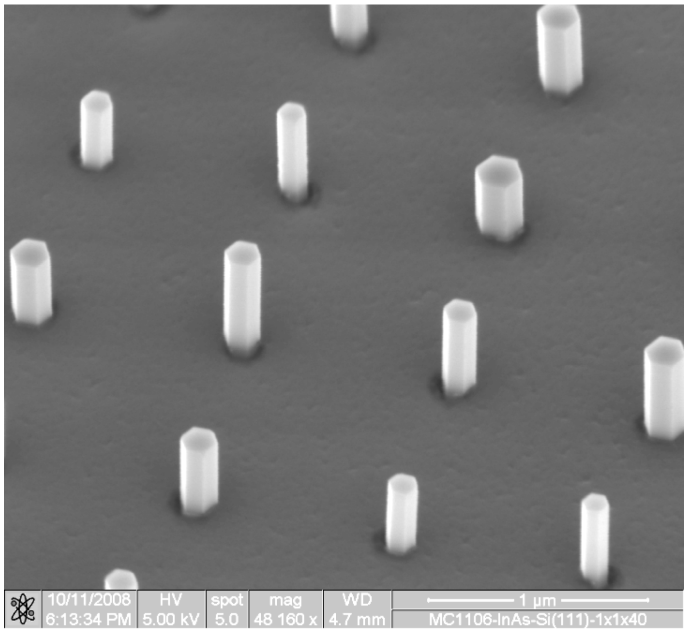
Selective growth of Ge and III/V on Si wafers

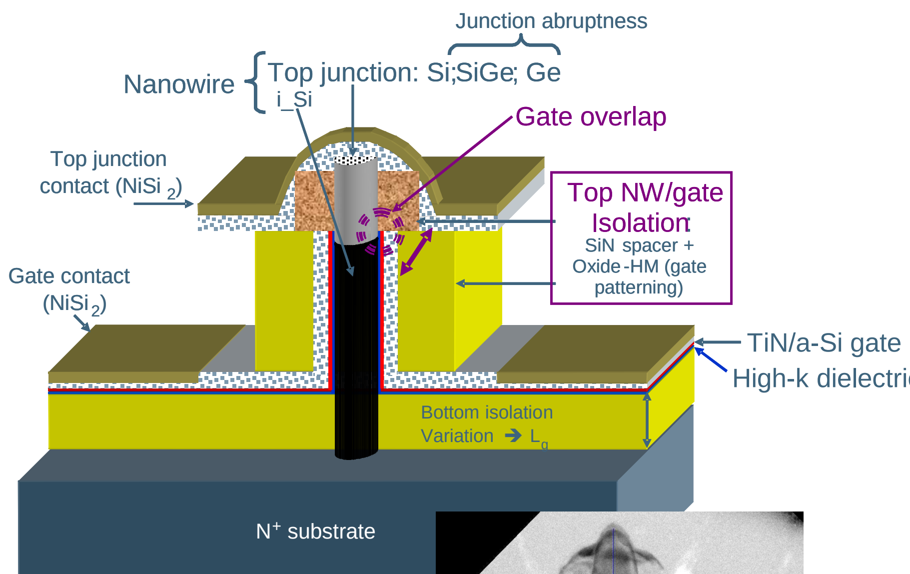




InAs NW growth on patterned Si(111)

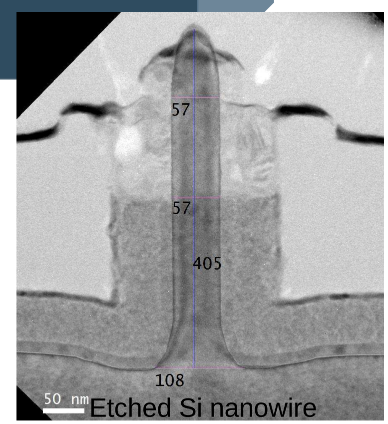
- ❑ InAs NW growth on patterned Si(111)
- ❑ Implementation of TFETs (shown with etched nanowires)





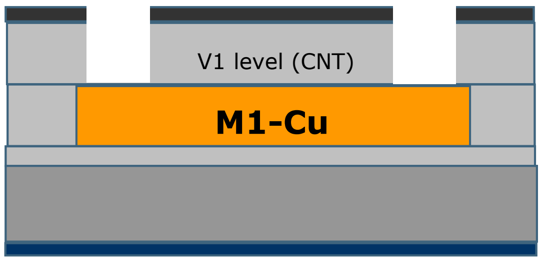
11.6% lattice mismatch between Si and InAs

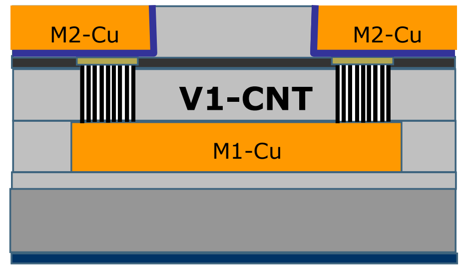
- (111) growth direction
- High growth selectivity
- ~0.5 nm/s growth rate



CNT interconnects

❑ CNT exhibit enhanced electrical and thermal properties over Cu

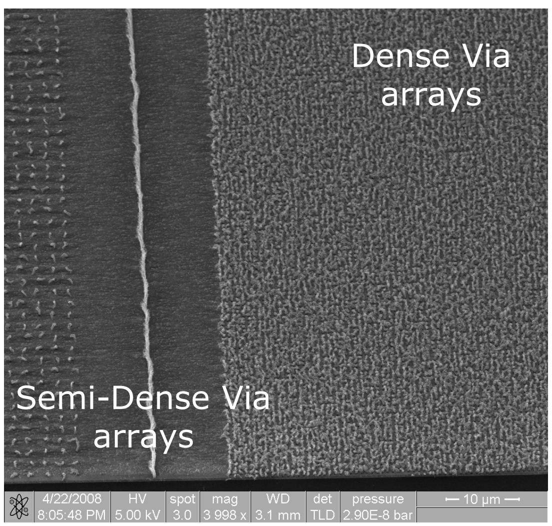




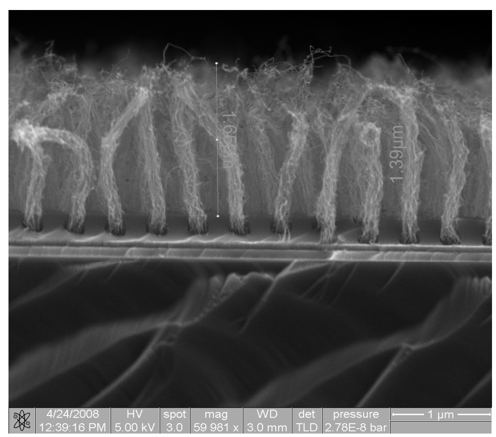
Current capacity:
- Cu ~ 10^6 A/cm^2
- CNTs ~ 10^9 A/cm^2

Thermal conductivity:
- Cu ~ 400 W/m·K
- CNTs ~ 5000 W/m·K

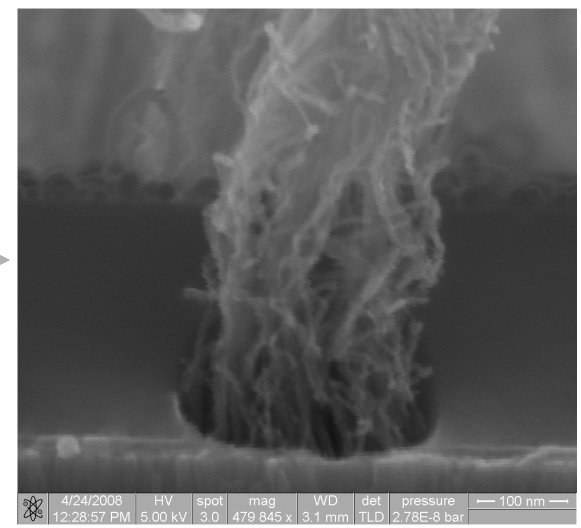
❑ High-density of MW CNT obtained with selective growth in Via structures



Selective CNT growth at via bottom



X-section: Vertically Aligned CNT via arrays



Individual 200nm Via
High % CNT filling
Density ~10^{11} cm^{-2}

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Development of Quantitative Structure-Activity Relationship for Prediction of Biological Effects of Nanoparticles Associated with Semiconductor Industries

Principle Investigators: Yongsheng Chen, Trevor Thornton, Jonathan Posner

Objectives

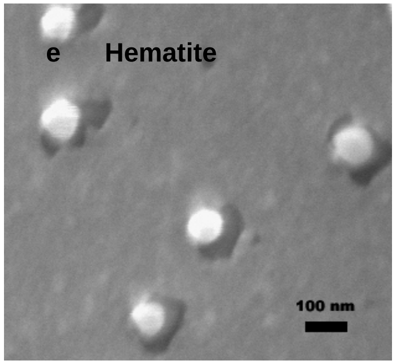
The value of the proposed approach is to predict the toxic effects and fate of both currently conceived (QD, CNT, Si nanowires) as well as future MNMs that will be used in the semiconductor industry.

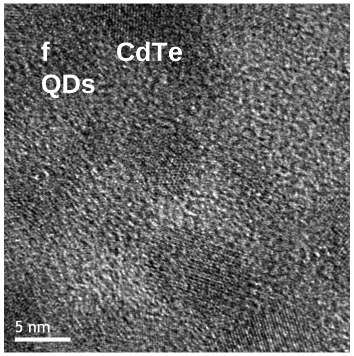
The long term goal is to better understand the potential adverse effects of MNMs to prior to their commercialization and to allow semiconductor industries to have better position in the potential commercial submissions of MNMs for Federal approval.

Approach

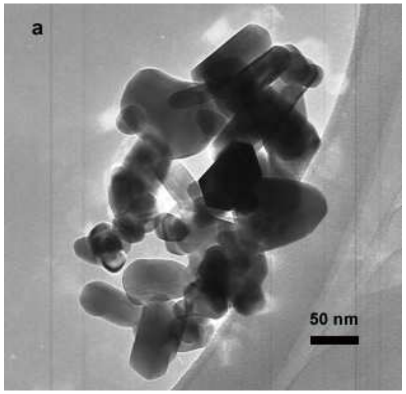
Physiochemical Property Characterization of NPs

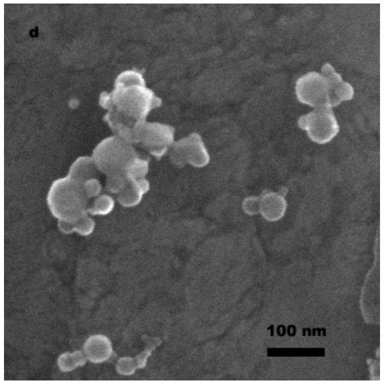
1. the shape, size distribution, particle number, surface charge,





2. surface reactivity, surface composition, and aggregation/disaggregation state of NPs



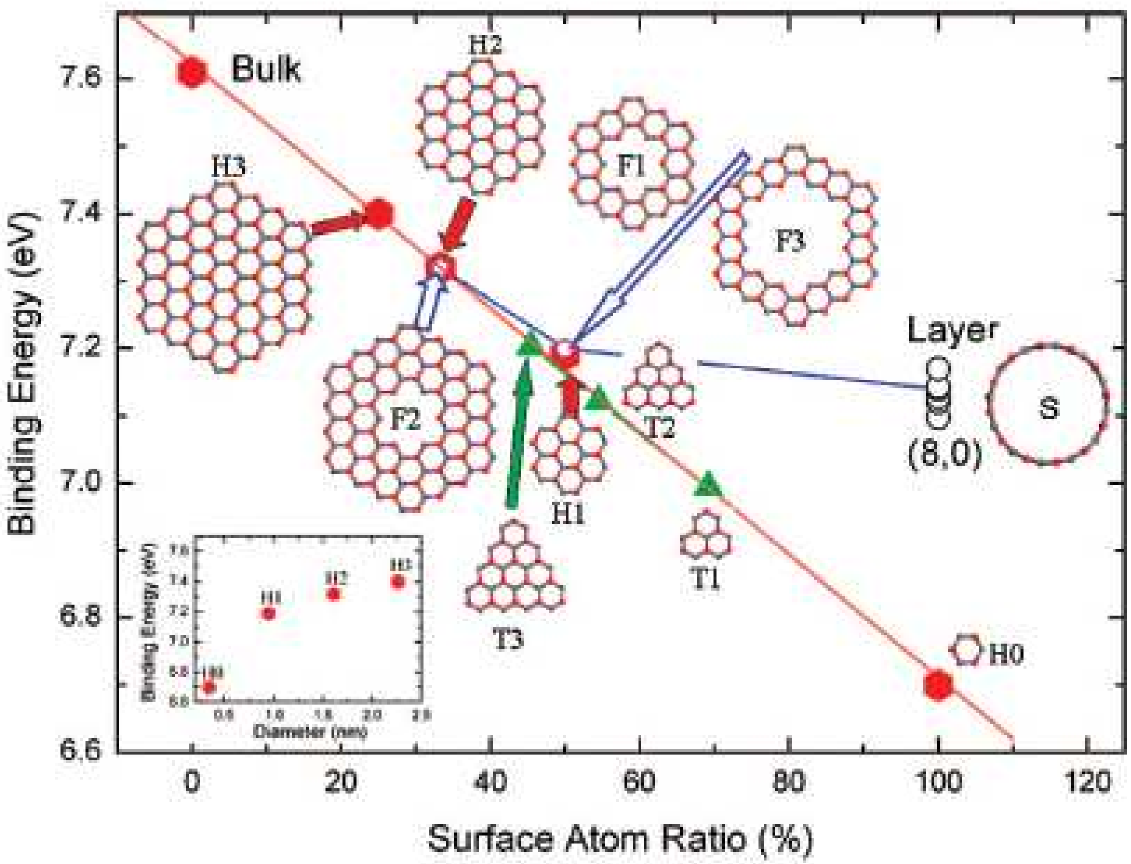


To Obtain Physicochemical Parameters by Theoretical Computations

Quantum chemistry. Both global descriptors (such as molecular weight, topological surface area, diameter, surface atom ratio, surface charge, dipole moment and polarizability, highest occupied molecular orbitals and lowest unoccupied molecular orbitals (HOMO-LUMO) gap energy)

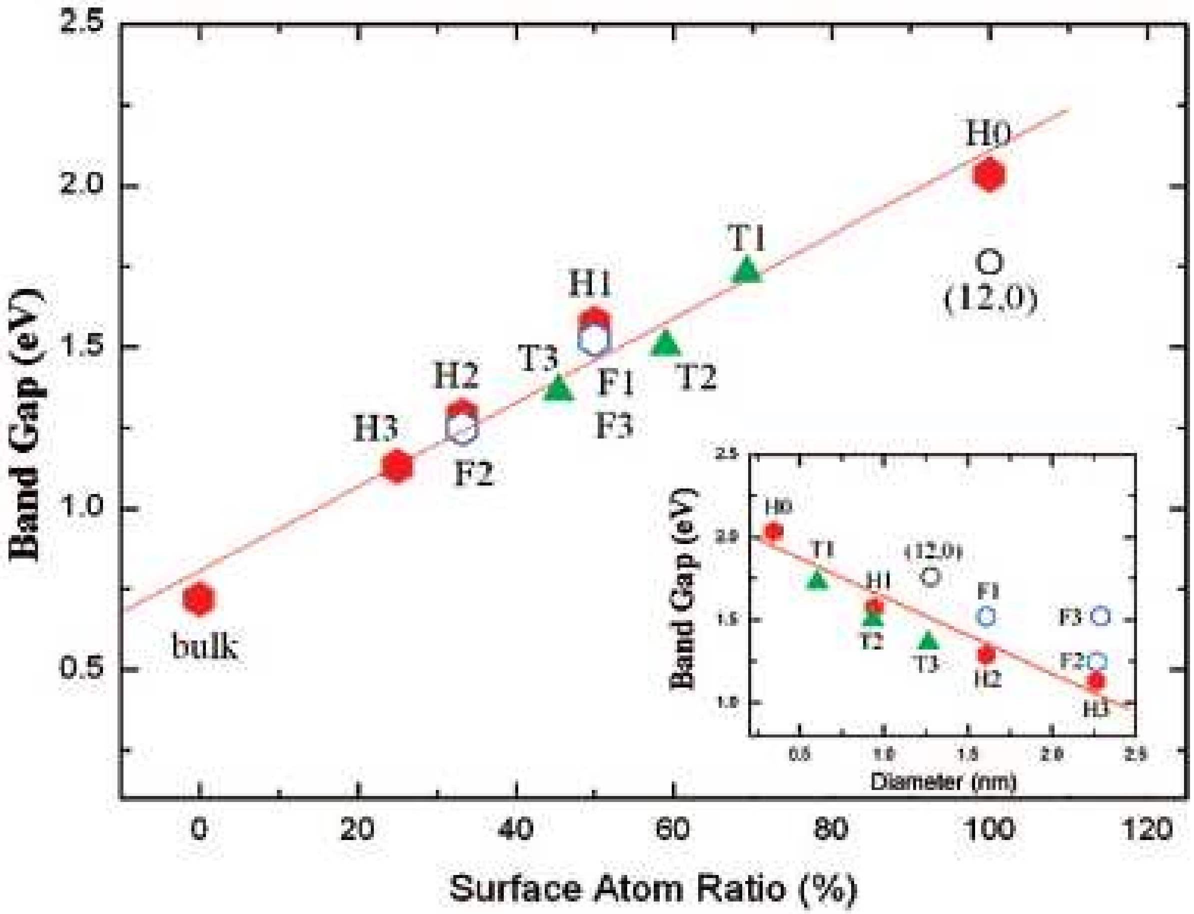
Density-Functional Theory. Local descriptors (such as local charge and the hydrogen bonding potential of the most extrusive sites) will be considered. These parameters will be computed at the density-functional theory (DFT) or density-functional based tight-binding (DFTB) theory level. Figure 1 shows an example of our calculated binding energies with atom ratios for various ZnO nanostructures.

Binding Energies of ZnO One Dimension Nanostructures



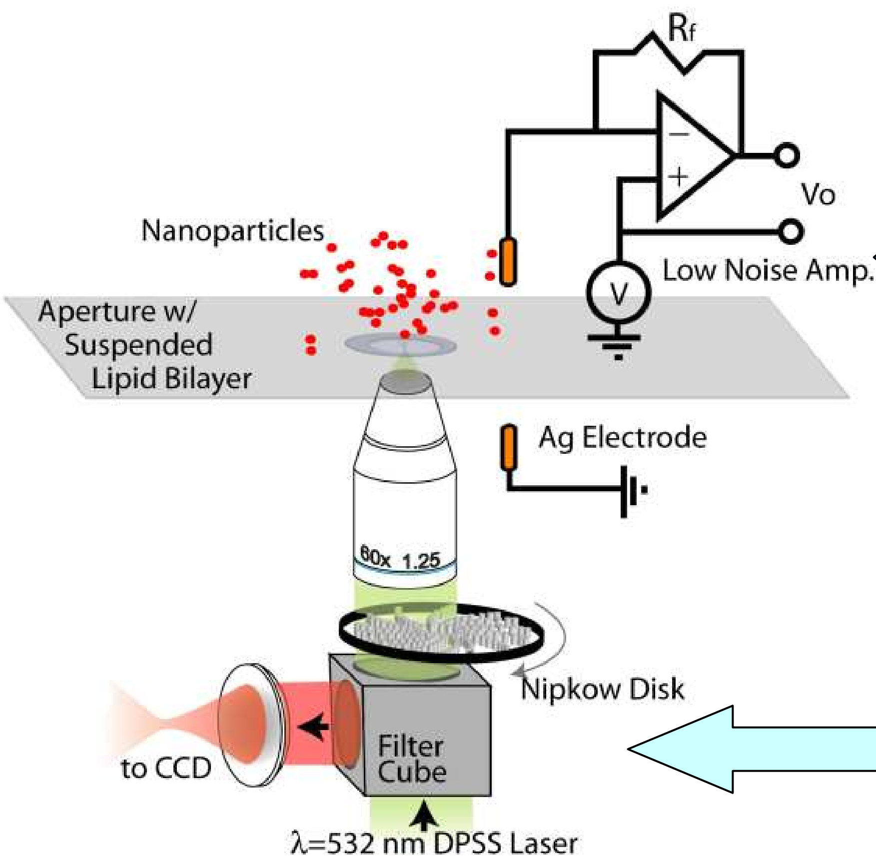
Variation of binding energies with surface atom ratios for various 1 D ZnO nanostructures. The inset shows binding energy as a function of diameter for the nanowires with hexagonal cross sections.

Band Gap of ZnO One Dimension Nanostructures



Variation of band gaps with surface atom ratios for various 1 D ZnO nanostructures. The inset shows band gap as a function of diameter for the 1 D nanostructures.

Quick Measurements of NPs Biological Effects/Toxicity

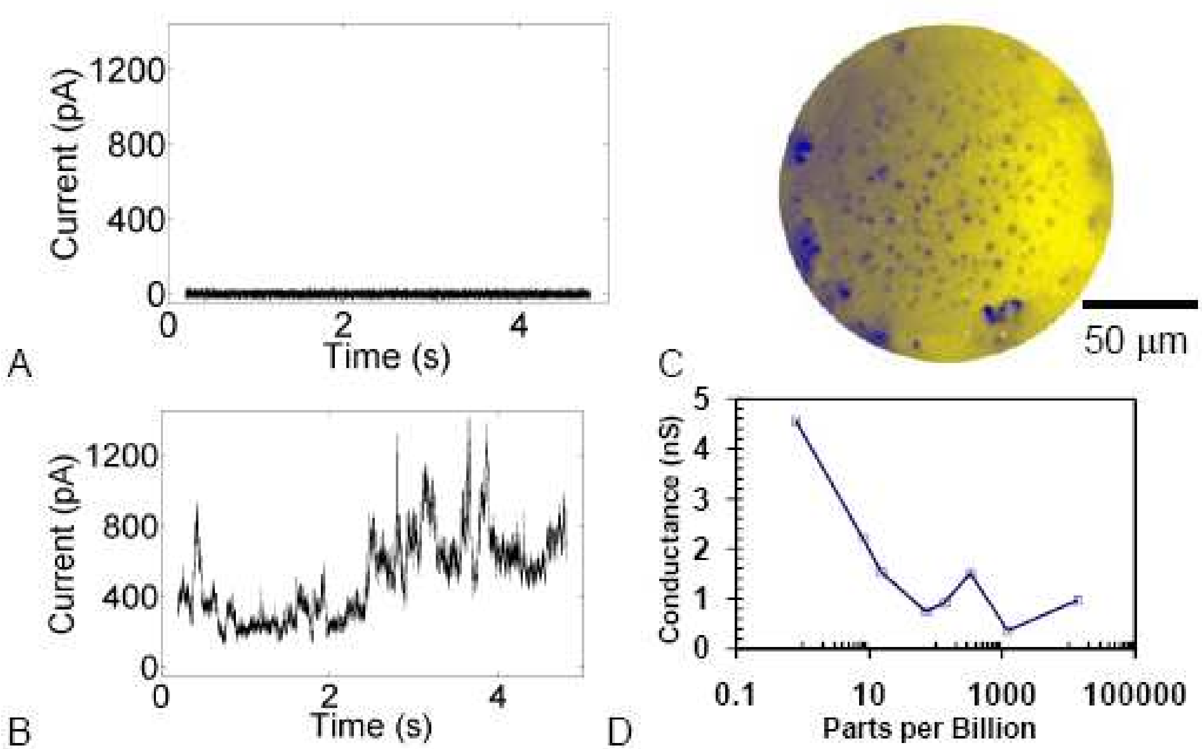


Platform for quick measurements of NP biological effects/toxicity

A low noise amplifier with Ag/AgCl electrodes is used to record the electrical currents through the aperture.

A standard epifluorescence microscope with cooled CCD camera is used to image the NPs aggregation and fluorescent dye transport.

Quick Measurements of NPs Biological Effects/Toxicity



Panel A. : high sealing and no leakage across membrane. Panel B: leakage current due to NM interactions. Panel C: A epifluorescence micrograph of suspended lipid bilayer in a circular 150 µm aperture showing aggregated QDs (dark spots) on the membrane surface. Panel D: leakage can be detected at 1 PPB (µg/L) of nanoparticles. The conductance may depend on the shape, size, charge, concentration, and morphology.

Parameters from Literatures: Toxicity to Daphnia magna

The 48 h EC_{50} and LC_{50} of water suspensions of the tested materials to Daphnia magna

Material suspensions	EC_{50} (mg/L)	95% CI	LC_{50} (mg/L)	95% CI
nAl_2O_3	114.357	111.232-191.100	162.392	124.325-214.803
Al_2O_3/Bulk	>500	n.d.	>500	n.d.
$nTiO_2$	35.306	25.627-48.928	143.387	106.466-202.818
TiO_2/Bulk	275.277	170.661-570.045	>500	n.d.
nZnO	0.622	0.411-0.805	1.511	1.120-2.108
ZnO/Bulk	0.481	0.301-0.667	1.250	0.985-1.848
SWCNTs	1.306	0.821-1.994	2.425	1.639-3.550
MWCNTs	8.723	6.284-12.128	22.751	15.678-34.388
C_{60}	9.344	7.757-11.262	10.515	8.658-12.757
Carbon black	37.563	33.076-41.968	61.547	54.546-68.232

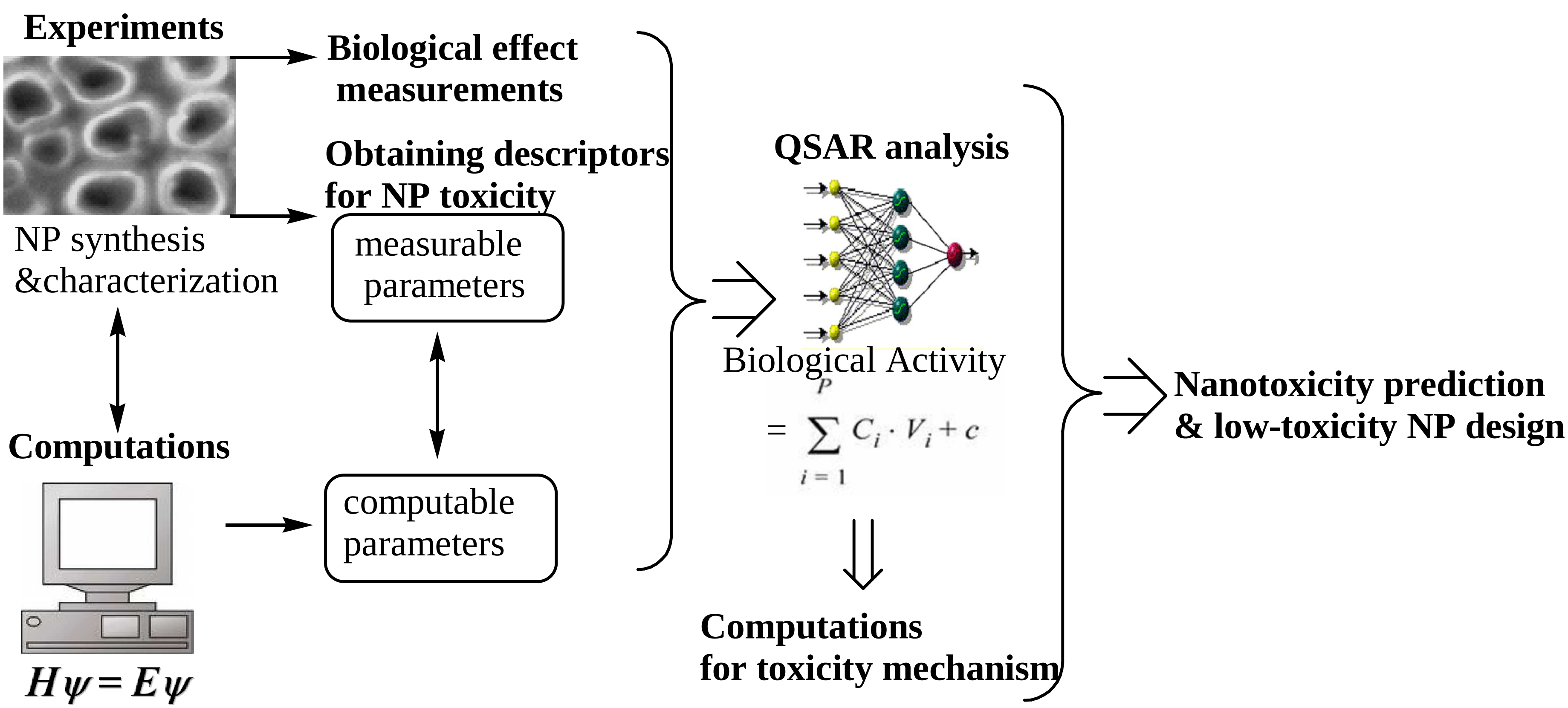
Note: n.d. = not determined

Parameters from Literatures: Toxicity to Fish– Carp Oxidative Stress and Growth Inhibition

Tissue	Biomarker	Exposure groups (mg/L)			
		control	0.04	0.20	1.0
Brain	SOD (U/mgprot)	49.4±5.28 (a)	46.8±6.69 (a)	58.7±10.4 (a)	49.8±14.7 (a)
	CAT (U/gprot)	4.25±1.10 (a)	4.24±0.54 (a)	6.47±1.54 (a)	4.78±1.57 (a)
	GSH (mg/gprot)	442.5±15.1 (a)	393.6±9.2 (b)	380.1±5.5 (b)	346.6±0.0 (c)
	LPO (nmoL/mgprot)	4.19±0.11 (a)	3.21±0.11 (b)	2.42±0.06 (c)	2.49±0.03 (c)
Liver	SOD (U/mgprot)	188.1±9.3 (a)	215.9±4.8 (b)	207.2±4.2 (b)	208.8±4.9 (b)
	CAT (U/gprot)	708.5±51.5 (a)	859.7±38.5 (b)	828.8±18.8 (bc)	755.9±35.1 (ac)
	GSH (mg/gprot)	213.4±5.8 (a)	223.6±5.3 (a)	186.0±1.8 (b)	192.8±2.0 (b)
	LPO (nmoL/mgprot)	3.54±0.02 (a)	2.88±0.02 (b)	2.83±0.07 (b)	3.81±0.03 (c)
Gill	SOD (U/mgprot)	17.0±4.9 (a)	22.6±1.2 (a)	13.7±3.7 (a)	16.9±4.8 (a)
	CAT (U/gprot)	4.75±0.86 (a)	6.86±0.39 (ab)	9.70±1.60 (c)	8.90±0.77 (bc)
	GSH (mg/gprot)	548.4±8.0 (a)	453.4±10.4 (b)	504.5±8.1 (c)	415.2±4.0 (d)
	LPO (nmoL/mgprot)	6.50±0.05 (a)	2.46±0.02 (b)	2.28±0.05 (c)	2.49±0.05 (b)

Note: Values for the control and C_{60} aggregates exposed groups are based on 32 d exposure and expressed as mean ± S.D. ($n = 3$). Different letters in the same row indicate significant differences between treatments within each tissue (ANOVA with Tukey's test, $p < 0.05$).

Environmental Implications –Predictive Model for Quick Evaluating Toxicity of Nanomaterials



Deliverables for Transfer to Industry

Year 1 12/2009: 1) **Report describing critical physicochemical parameters related to engineered nanomaterials toxicity; 2) This information largely is generated from extensive literature survey and provides industry with framework for properties governing toxicity**

Year 2 12/2010: 1) Catalogue of physicochemical measurements of semiconductor nanomaterials; 2) Data mining, theoretical computations, and original measurements; 3) Benchmark data describing relationship between physicochemical properties and bilayer assay

Year 3 12/2011: Operational QSAR modeling software tailored for semiconductor industry nanomaterials

Environmental Safety and Health (ESH) Impacts of Emerging Nanoparticles and Byproducts from Semiconductor Manufacturing

(Semiconductor Research Corporation Grant, P10367)

PIs:

- **Jim A Field, Dept. Chemical and Environmental Engineering, UA**
- **Scott Boitano, Dept. of Physiology & Arizona Respiratory Center, UA**
- **Buddy Ratner, University of Washington Engineered Biomaterials Center, UWEB**
- **Reyes Sierra, Dept. Chemical and Environmental Engineering, UA**
- **Farhang Shadman, Dept. Chemical and Environmental Engineering, UA**

Graduate Students:

- **Cara L Sherwood: PhD candidate, Cell Biology and Anatomy, UA**
- **Jeff Rottman: PhD candidate, Chemical and Environmental Engineering, UA**
- **Isa Barbero: PhD candidate, Chemical and Environmental Engineering, UA**
- **Rosa Daneshvar: PhD candidate, Chemical Engineering, UW**
- **Christopher Barnes: PhD candidate, Chemical Engineering, UW**

Other Researchers:

- **Antonia Luna, Postdoctoral Fellow, Chemical and Environmental Engineering, UA**

Cost Share (other than core ERC funding):

- **$80k from UA Water Sustainability Program**

Objectives

Overall: characterize toxicity of current and emerging nanoparticles (NP) & NP byproducts & develop new rapid methodologies for assessing and predicting toxicity

- Establish role for reactive oxygen species (ROS) and oxidative stress as a potential marker for NP toxicity assessment
- Develop predictable models of toxicity based on physico-chemical properties elucidated by advanced surface analysis techniques
- Validate toxicity assessments and predictions with organ skin cultures (and advanced lung cultures)

ESH Metrics and Impact

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

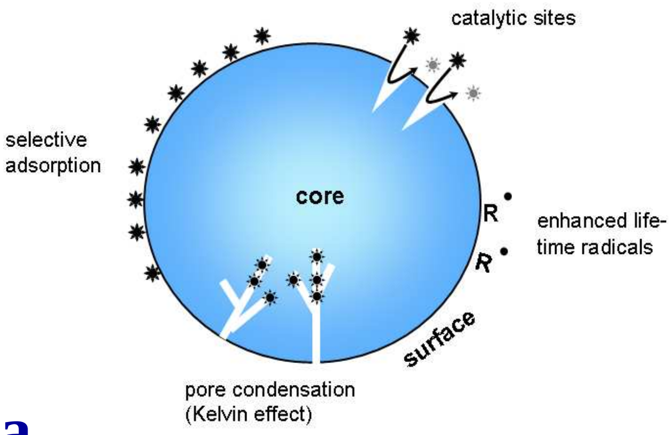
   This project will evaluate the toxicity of various types of nanoparticles utilized or considered for application in semiconductor manufacturing, and the impact of manufacturing steps on their toxicity. This information can assist in selecting materials which are candidates for replacement or use reduction.

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

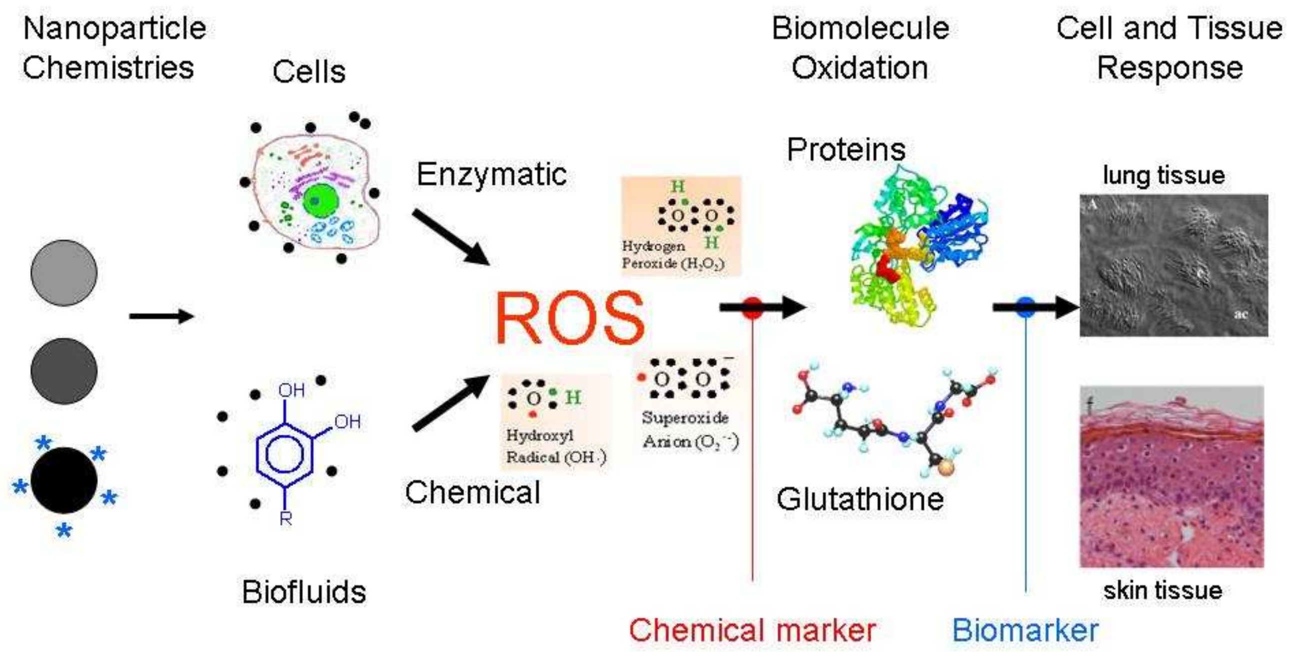
   The knowledge gained can be utilized to modify the manufacture of nanoparticles so that they have a lowered toxicity and thus a lowered environmental impact.

Hypotheses

- **Surface contamination plays an important role in NP toxicity**

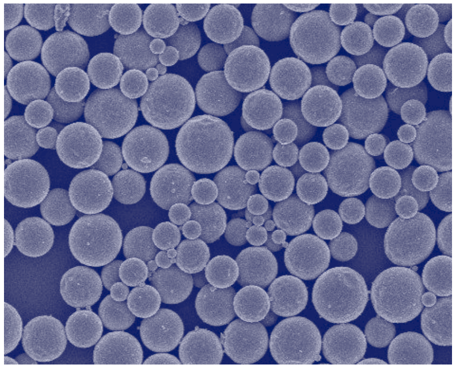


- **Oxidative stress provoked by ROS is a major contributing factor to NP toxicity**



Materials

- Nanoparticles



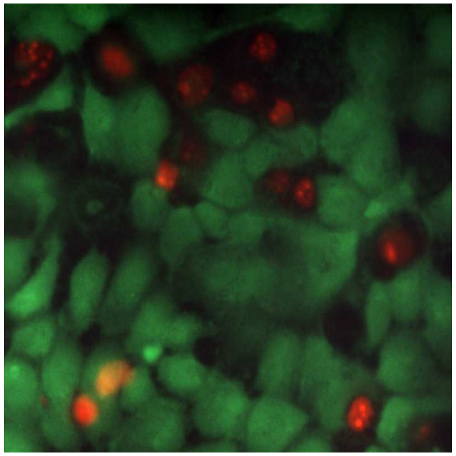
Hafnium Oxide (HfO_2), immersion lithography

Silica Oxide (SiO_2), CMP

Ceria Oxide (CeO_2), CMP

Others (Al_2O_3, carbon and germanium- nanotubes, quantum dots *etc*)

- Biological targets



Human skin cell line (HaCat)

Human lung epithelial cell line (16HBE14o-)

Human foreskin rafted organ culture (ROC)

Bacterium (*Vibrio fischeri*) Microtox test

Others (methanogens, microbial enrichment cultures, yeast *etc*)

Overview Tasks

- Task 1. Preparation and Characterization of NPS

  Subtask 1.1 Preparation of NPs

  Subtask 1.2 Physicochemical Characterization

  Subtask 1.3 Surface Analysis

- Task 2. Toxicity assessment and toxicity mechanisms

  Subtask 2.1 Screening NP Toxicity

  Subtask 2.2 Toxicity Mechanisms

  Subtask 2.3 Rapid Toxicity Assessment

  Subtask 2.4 Advanced Organ Cultures

  Subtask 2.5 Predictive Methods

Preparation and Characterization NP

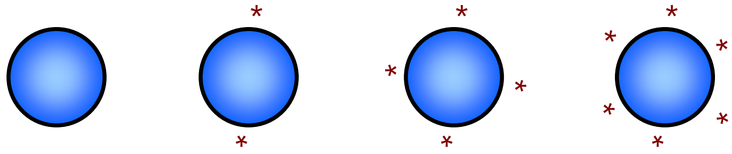
- Preparation

Gradients of surface contamination

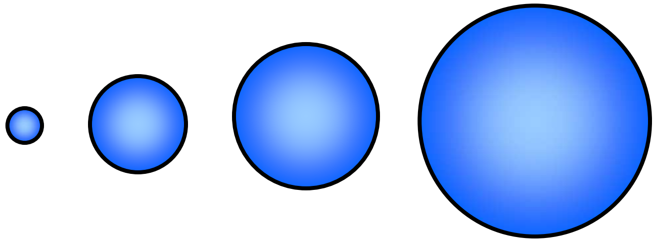
adsorption of defined contaminants

surface modification

removal of contaminants (chelators, solvents)



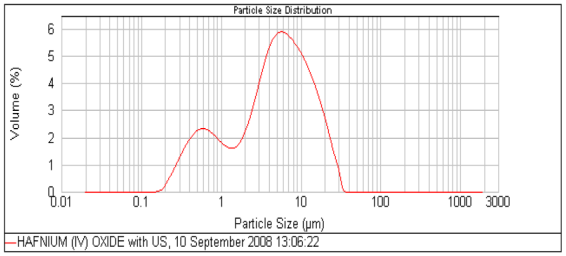
Gradients of particle size



- Characterizations

Particle size distribution, zeta-potentials

Adsorptive surfaces



- Surface Analysis (UW)

Electron spectroscopy for chemical analysis (ESCA or XPS)

depth 5 – 10 nm, elemental composition (1-10%), oxidation state

Static secondary ion mass spectrometry (sSIMS).

depth 1 – 2 nm, high mass resolution (precise identification)

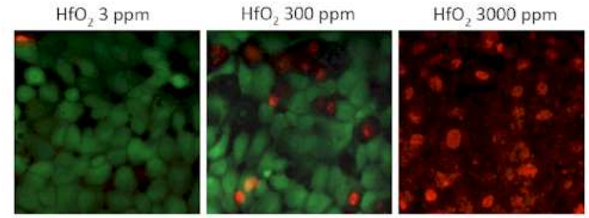
Toxicity of NP

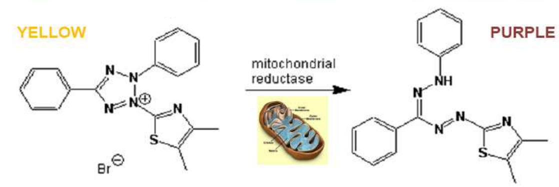
- Toxicity Screening

  Live/Dead

  Mitochondrial Toxicity Test (MTT)

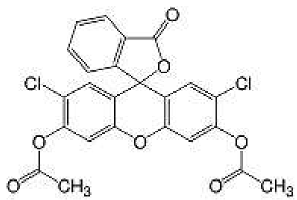
  Microtox



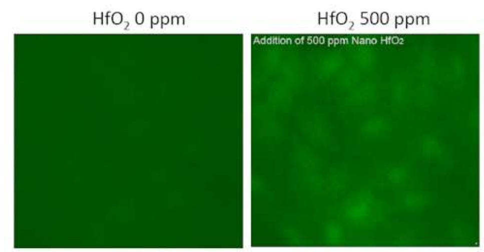


- Toxicity Mechanisms

  Reactive Oxygen Species



2',7'-dichlorofluorescin diacetate (DCF)



Oxidative Stress Markers

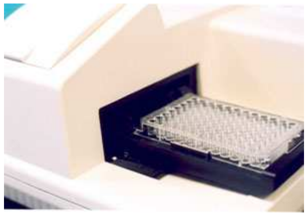
Damage to biomolecules	*e.g.* OxyBlot (Milipore): chemical-immunodetection assay for protein side chain carbonyl groups formed by oxidation
Proteomic	two dimensional differential gel electrophoresis (2D-DIGE) - nanoLC-MS/MS (modified for oxidized protein signatures)
Genomic	cDNA microarray technology (Affimetrix human oligo-nucleotide microarray of 19,200 genes) for gene expression

Toxicity of NP (continued)

- Rapid Toxicity Assessment

ROS production fluorescent dyes

ELISA Immunological assay: oxidized biomolecules

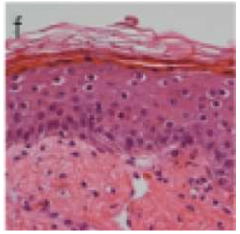


Fluorimeter - plate reader

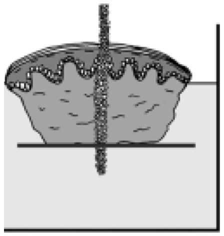
- Advanced Organ Cultures

Human Foreskin Rafted Organ Culture (UW)

Validate toxicity testing in cell lines with organ cultures



Fukano et al 2006



- Development Predictive Method(s) for Toxicity

Correlations and hypotheses

Multivariate Statistical Analysis.

e.g. principal component analysis SIMS data correlated with toxicity

Spectral Methods of Rapid Toxicity Predictions.

Advanced surface analysis to measure properties related to toxicity

Outcomes

- Experimental data on toxicity (or lack thereof) of emerging NPs and NP byproducts
- New rapid toxicity screening test for use in the industrial work place
- Predictive correlations between toxicity data and physicochemical parameters
- Rapid spectroscopic assessment method to predict NP toxicity (or lack thereof) for industrial use
- Clues on how to reduce and eliminate toxicity due to unavoidable surface contamination

Industrial Interactions and Technology Transfer

- •ISMI-Sematech (Steve Trammell, Laurie Beu)
- •AMD (Reed Content)
- •IBM (Arthur T. Fong)
- •Intel (Steve W. Brown, Paul Zimmerman, Mansour Moinpour)

Low ESH-impact Gate Stack Fabrication by Selective Surface Chemistry

New project P10370

Shawn Miller, Fee Li Lie, and Anthony Muscat
Department of Chemical and Environmental Engineering
University of Arizona, Tucson, AZ 85721

ERC Review Meeting
Feb 19-20, 2009
Tucson, AZ

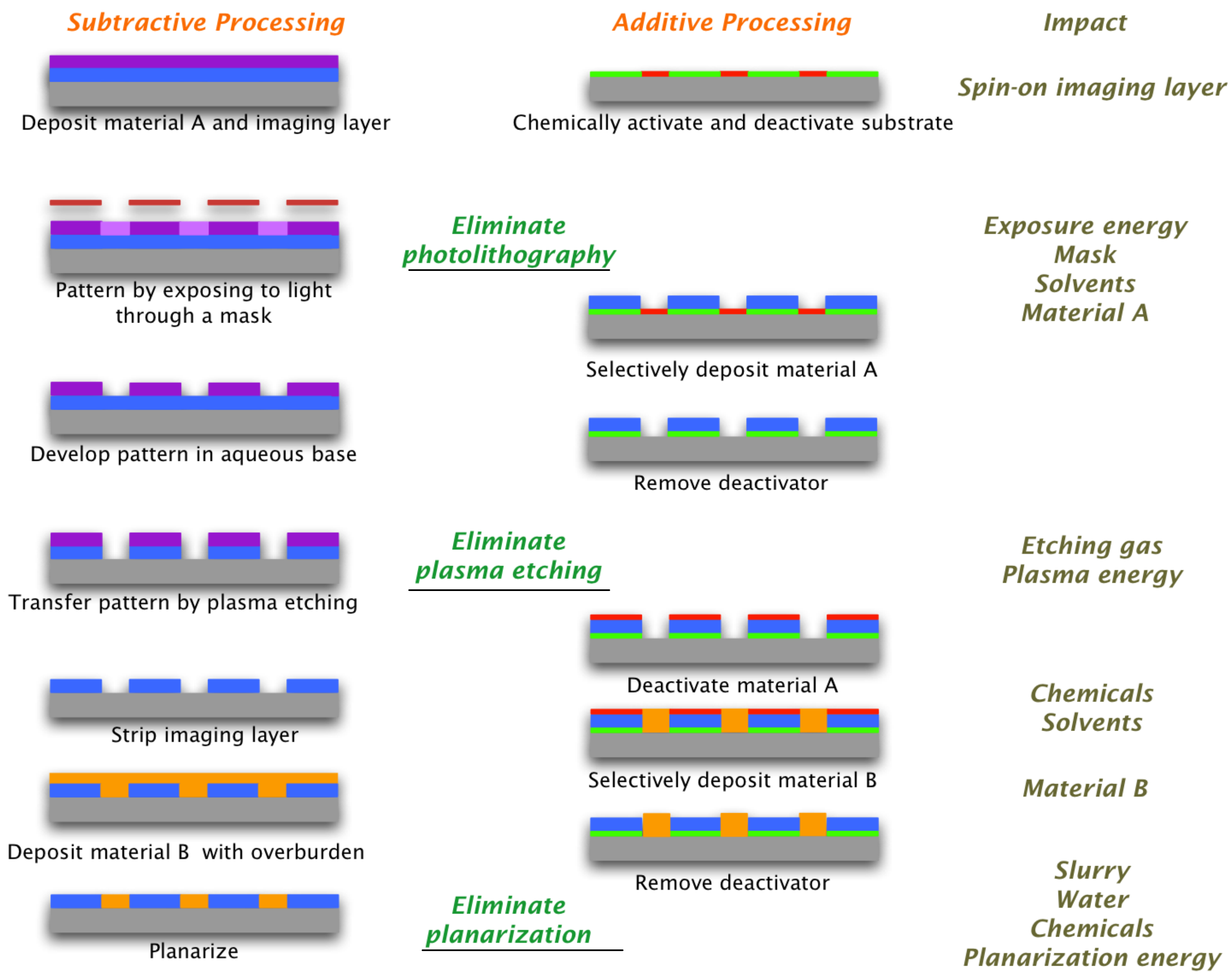
Industrial partners
Sematech
ASM, LAM/SEZ

Objectives

- **Simplify multistep subtractive processing used in microelectronic device manufacturing**
  - Develop new processes that can be integrated into current devices flows
  - Minimize water, energy, chemical, and materials consumption
  - Reduce costs

- **High-k gate stack is the testbed**
  - Fabricate low defect high-k/semiconductor interfaces

ESH Metrics and Impact: Additive Processing



ESH Metrics and Impact: Cost Reduction

- Integration of selective deposition processes into current front end process flow could reduce ~16% of the processing costs
  - Calculation based on Sematech cost model
  - Eliminate eight processing steps from the gate module
  - Tool depreciation, tool maintenance, direct personnel, indirect personnel, direct space, indirect space, direct material, and indirect material were included
  - Energy, waste disposal, and addition of two selective deposition steps were not included

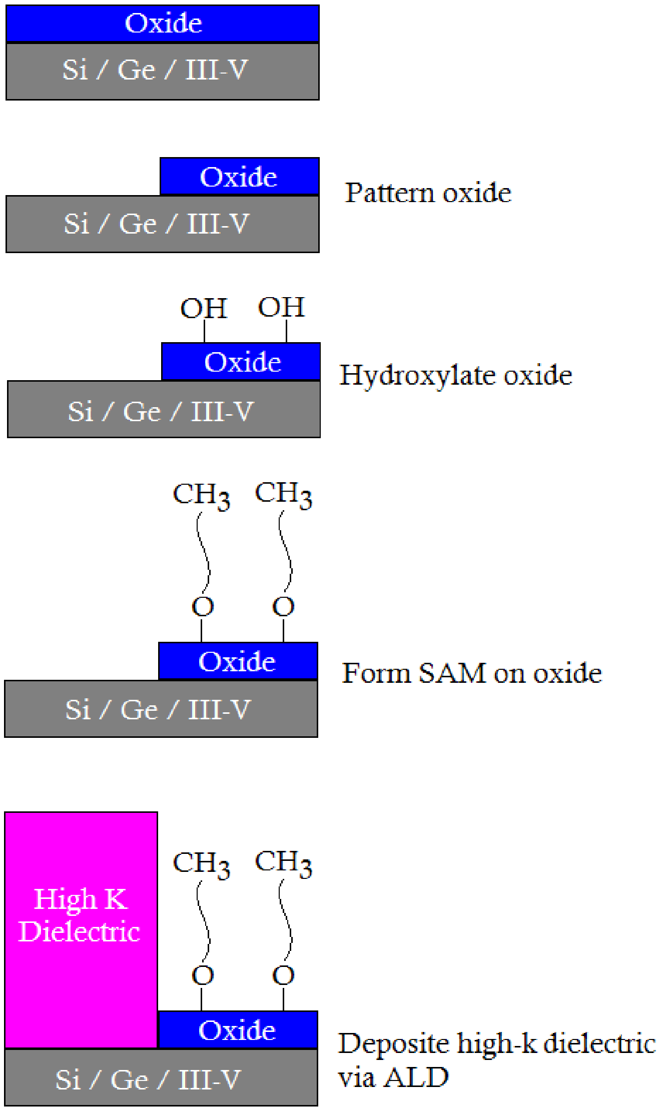
- There is potential for greater ESH benefit due to minimized cost of raw materials and waste generated

Novelty

- Develop industrially feasible processes to activate and deactivate surfaces
  - Significantly lower time scale
  - Extend to metal and semiconductor surfaces
- Integrate selective deposition steps at carefully chosen points in the CMOS process flow
  - Realize ESH and technical performance gains
- Quantify costs associated with selective deposition steps to refine industry models
  - Account for energy and waste disposal
  - More accurate prediction of the cost model

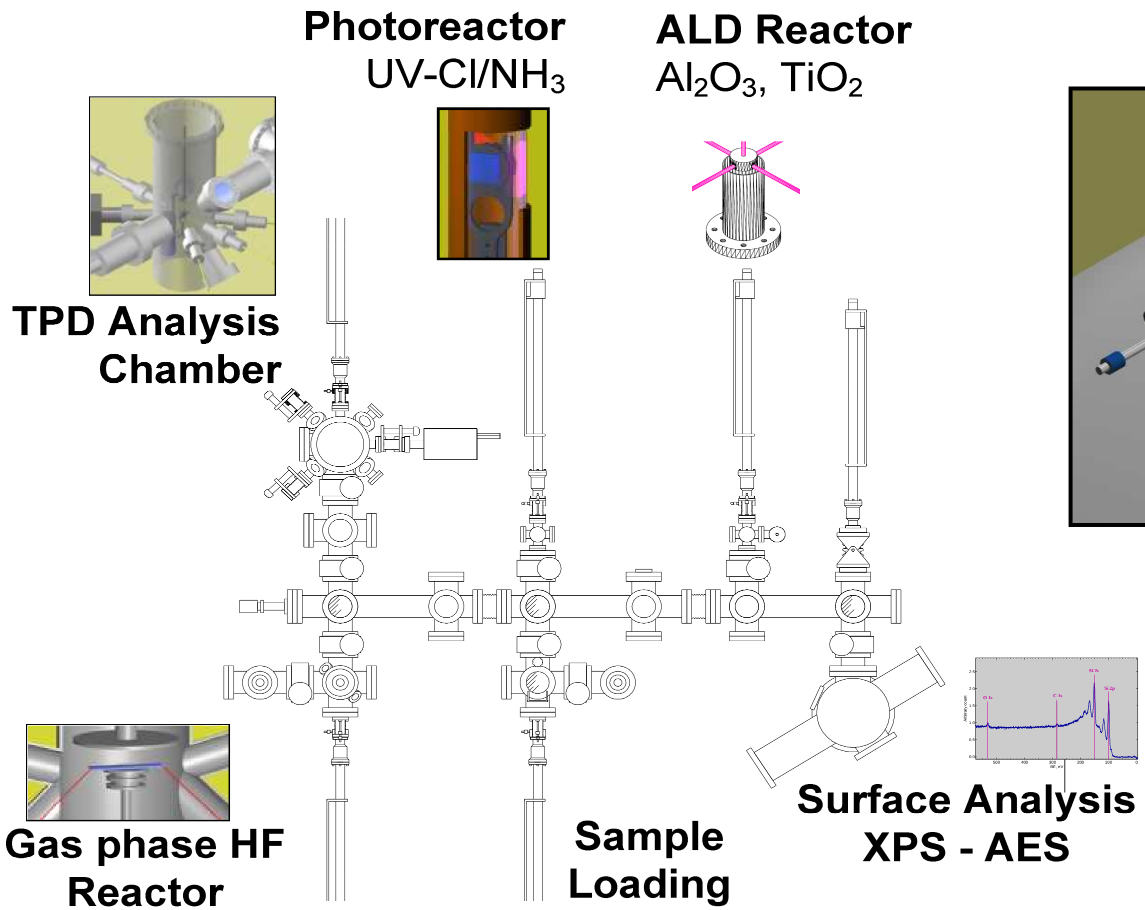
Methods and Approach

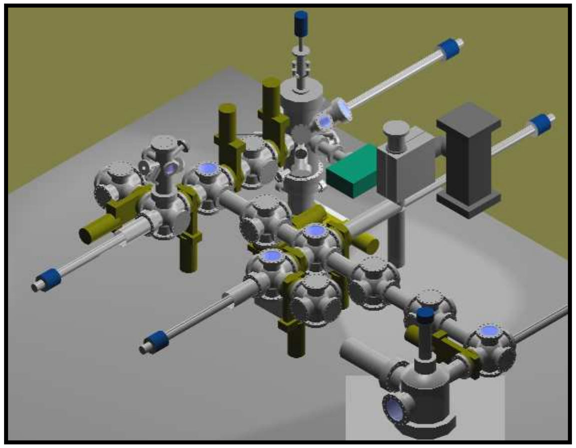
- Grow high-k films on semiconductors by activation and deactivation of surface sites
- Activation
  - Utilize surface chemistries to activate substrates for high-k film growth
  - Halogen, amine terminations
- Deactivation
  - Hydrophobic self assembled monolayer (SAM) prevents adsorption of H_2O
- Model systems
  - Si, Ge, and III-V substrates
  - High-k films
    - Al_2O_3
    - TiO_2
  - Atomic layer deposition (ALD)



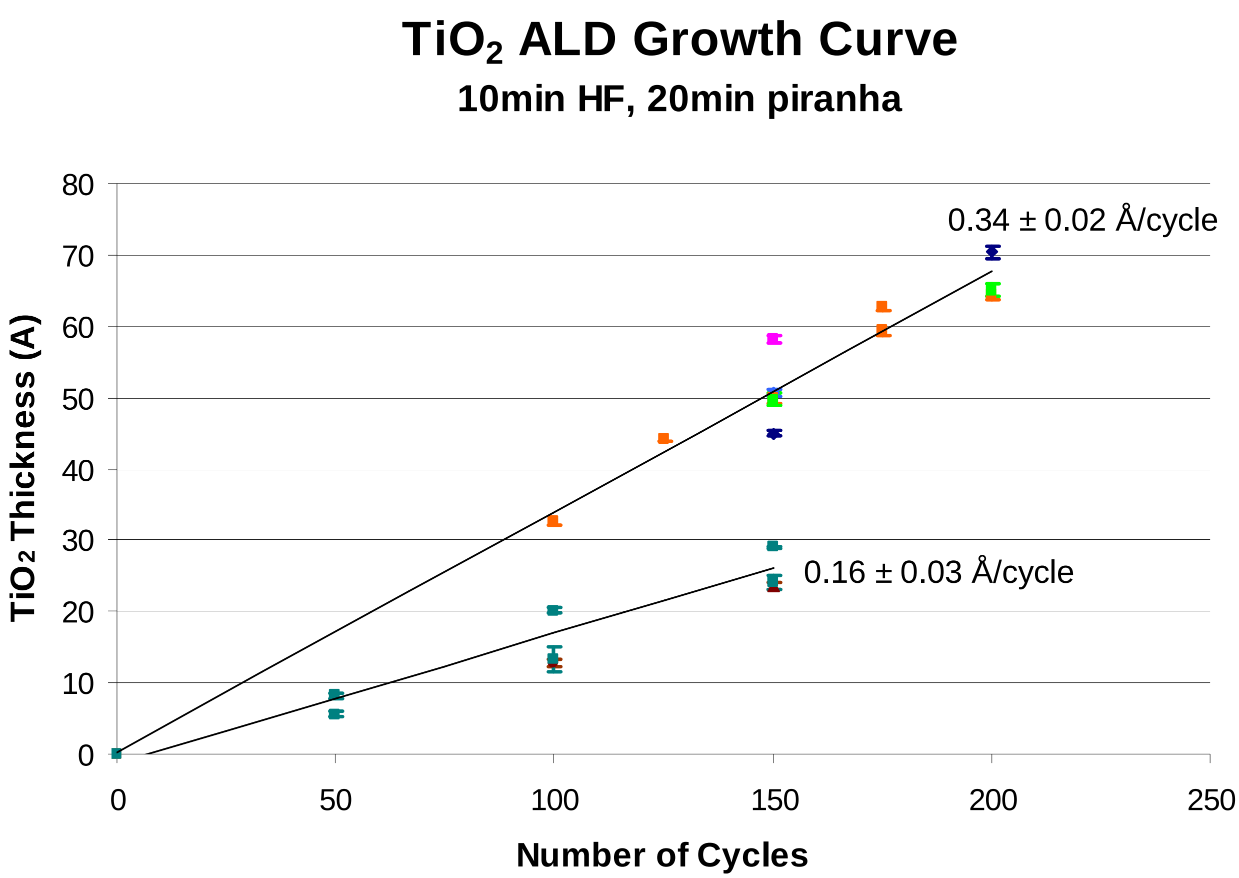
Clustered Research Apparatus

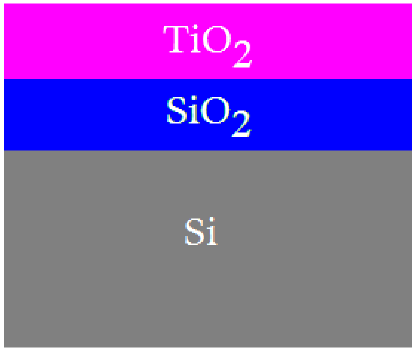
- In situ cleaning, high-k deposition, and surface analysis enables studies of surfaces without atmospheric contamination
  - Important for highly reactive substrate such as III-V materials





TiO_2 Growth Curve on Hydroxylated Si





- Deposition at 170℃

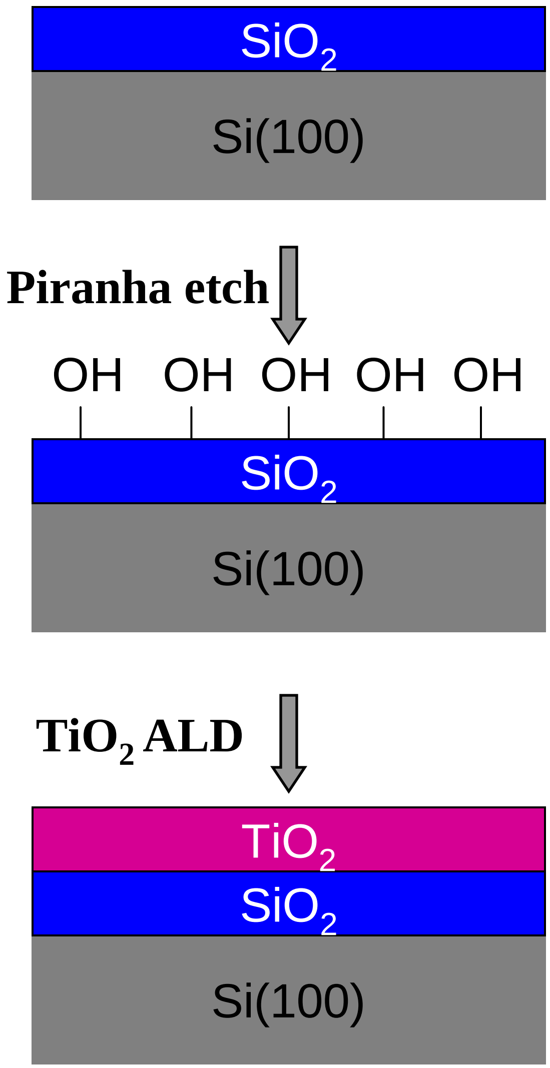
$TiCl_4$ / Purge / H_2O / Purge

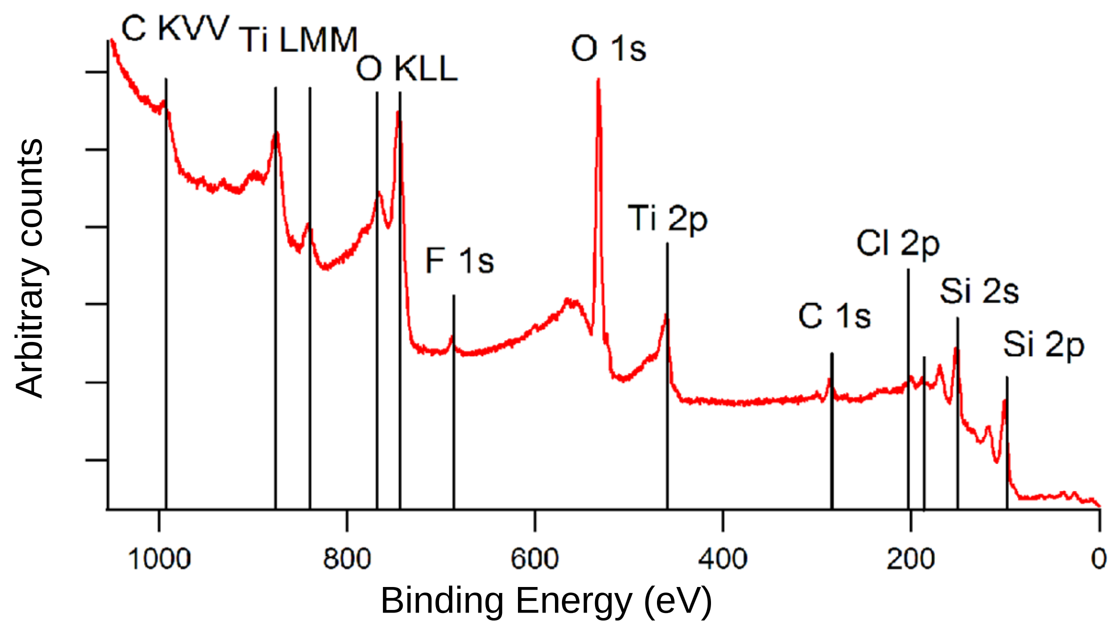
- 1s / 30s / 0.3s / 60s
- 1s / 30s / 0.3s / 30s
- 1s / 30s / 0.2s / 60s
- 1s / 30s / 0.2s / 30s
- 2s / 30s / 0.2s / 30s
- 2s / 30s / 0.1s / 30s
- 1s / 30s / 0.1s /30s

- Optimal deposition parameters:

  1s $TiCl_4$ pulse / 30s N_2 purge / 0.2s H_2O pulse / 30s N_2 purge

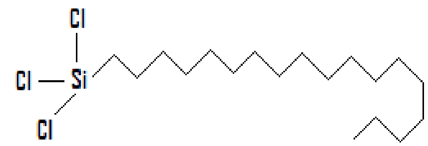
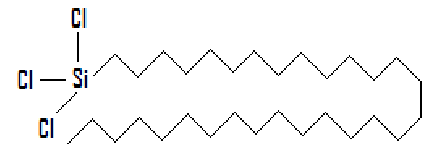
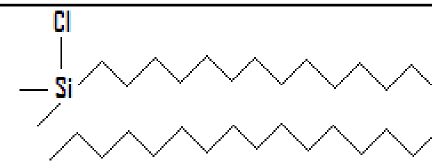
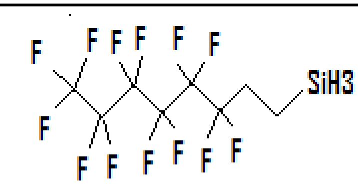
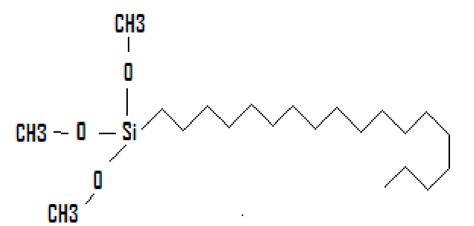
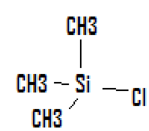
Si(100) high-k deposition: ALD of TiO_2





- Demonstrated TiO_2 deposition on hydroxylated Si(100)
  - Residual Cl present on surface
  - Si 2p peak still visible with ~9 Å thick TiO_2 layer

Deactivation using SAM Chemicals

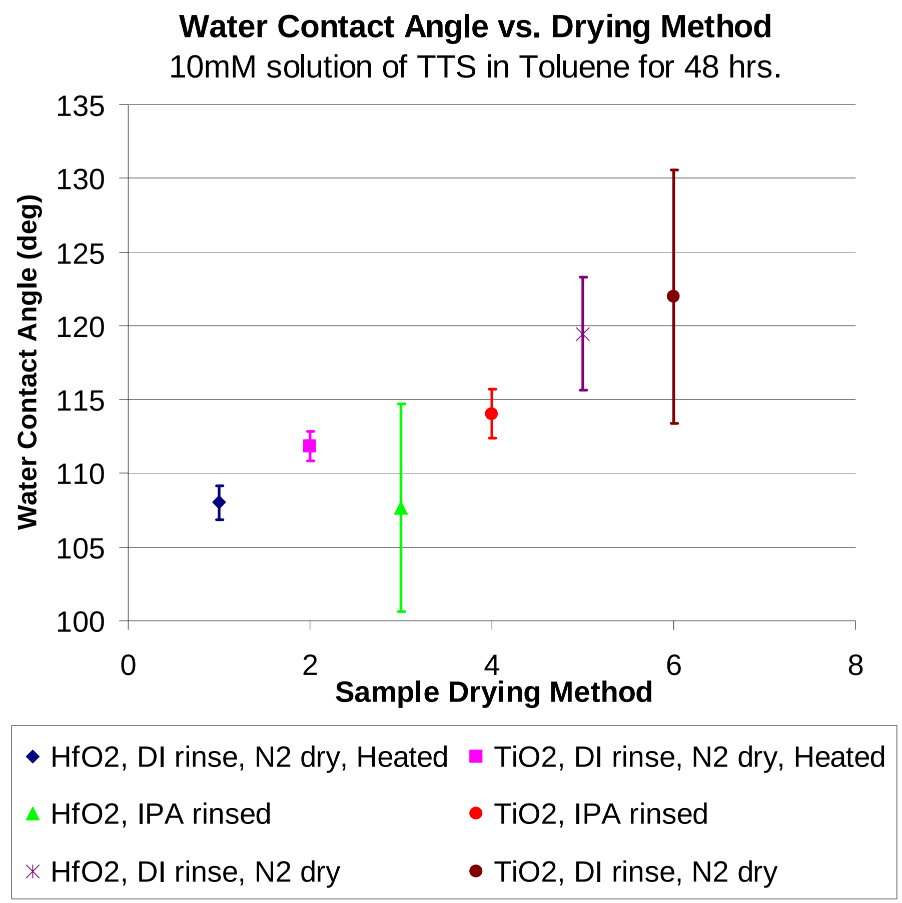
SAM molecules	Formula	Structure
Octadecyltrichlorosilane OTS	$C_{18}H_{37}Cl_3Si$	
Triacontyltrichlorosilane TTS	$C_{30}H_{61}Cl_3Si$	
Triacontyldimethylchlorosilane TDCS	$C_{32}H_{67}ClSi$	
Tridecafluoro-1,1,2,2-tetrahydrooctylsilane FOTS	$C_8H_7F_{13}Si$	
Octadecyldimethoxysilane ODS	$C_{21}H_{43}O_3Si$	
Trimethylchlorosilane TMCS	C_3H_9ClSi	

Surface Deactivation: SAM formation

Procedure

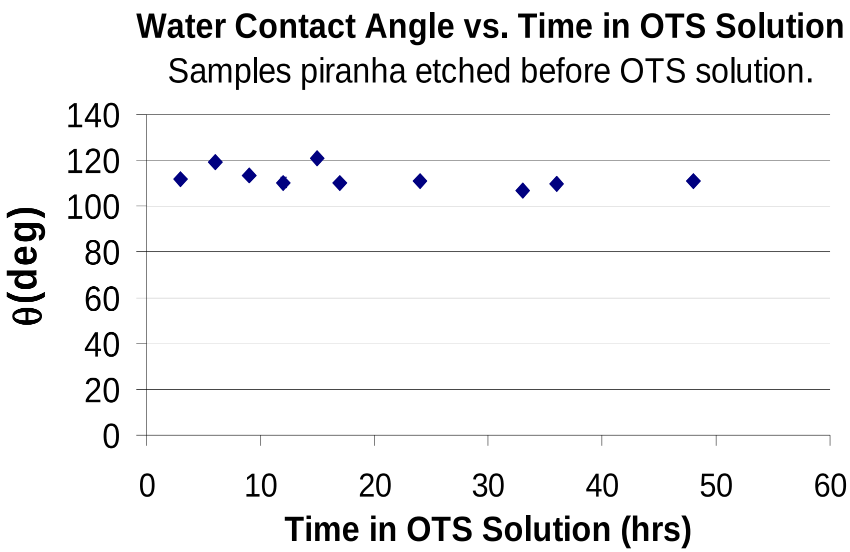
- 5 min sonication in acetone
- 5 min sonication in methanol
- 10 min etch in HF
  - 1 : 9 HF: H_2O
- 20 min etch in piranha
  - 110℃ ± 10℃
  - 4 : 1 $H_2SO_4 : H_2O_2$
- DI water rinsed, N_2 dried
- Remove adsorbed water
  - Heat samples at 200°C, 5 min
- SAM formation
  - 10mM solution of TTS in toluene for 48hrs
- Water contact angle measured

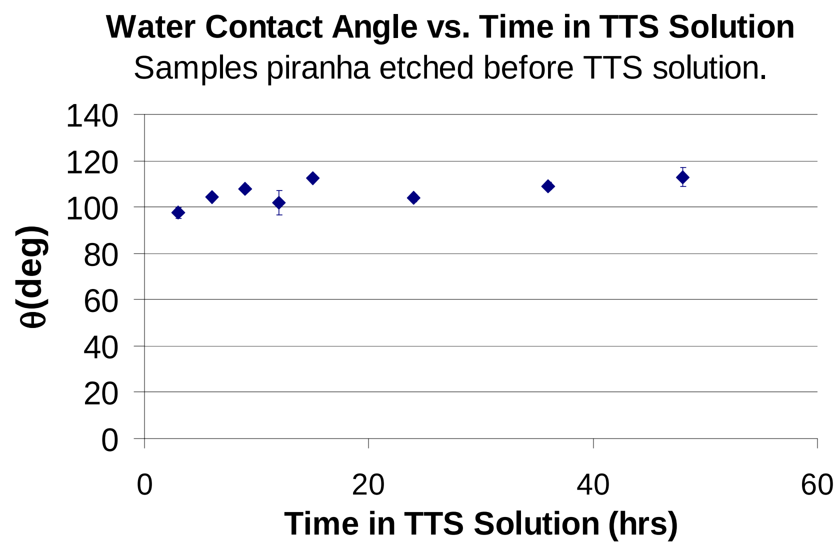
Adsorbed Water Removal



- Polymerization of the SAM molecule was observed due to reaction with adsorbed water producing large deviation in the water contact angle

Comparison of SAM Molecules: OTS and TTS

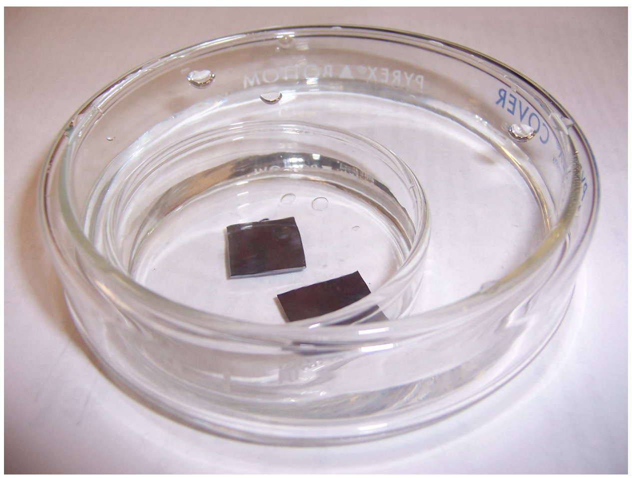


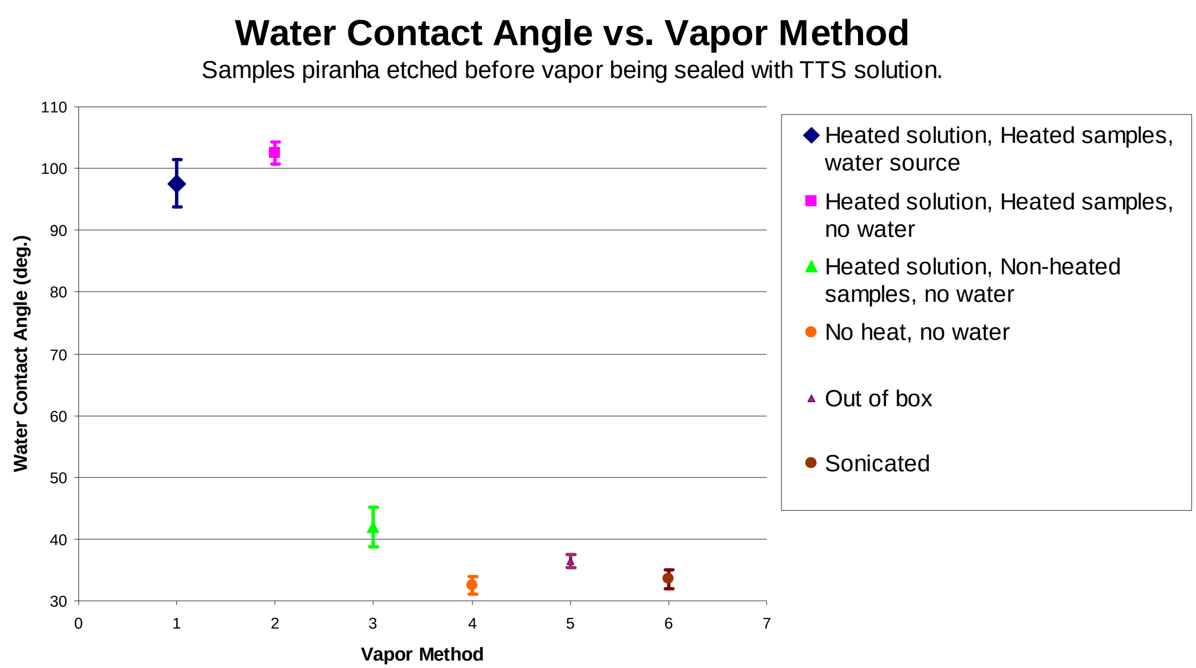


- Similar water contact angle obtained with OTS and TTS
- TTS potentially more effective deactivating agent
  - Higher steric hindrance due to longer carbon chain

Alternative SAM Delivery Method

- The long time scale for the formation of complete SAM in liquid phase is not feasible for industrial processes
- Vapor phase delivery of SAM potentially shortens time scale





- Demonstrate TTS SAM formation on piranha etched Si(100) by vapor exposure for 48 hours
- Temperature increase required for TTS deposition

Future Work

- Investigate vapor phase ozone and gas phase HF/vapor treatment to increase and control hydroxylation of oxide surfaces

- Characterize SAM layers
  - Thermal stability for deactivation
  - Durability for large numbers of ALD cycles
  - Chemical bonding between SAMs and surface
  - Degradation and repair of SAMs layers

- Extend deactivation study to Al_2O_3, TiO_2, HfO_2 surfaces

- Optimize vapor phase delivery of SAM molecules
  - Pulse and purge both water and SAM molecules as opposed to sealing vapor in a reactor for extended time

- Investigate optimized selective deposition method on III-V semiconductor surfaces

Predicting, Testing, and Neutralizing Nanoparticle Toxicity

The University of Texas at Dallas BioNanoSciences Group (EST. 2002)

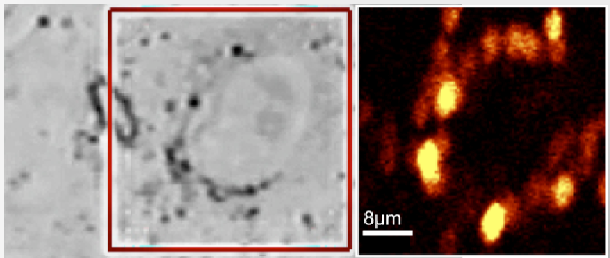
Paul Pantano – analytical chemist
Steve Nielsen – computational chemist
Gregg Dieckmann – synthetic chemist
Inga Musselman – surface scientist
Rocky Draper – cell biologist

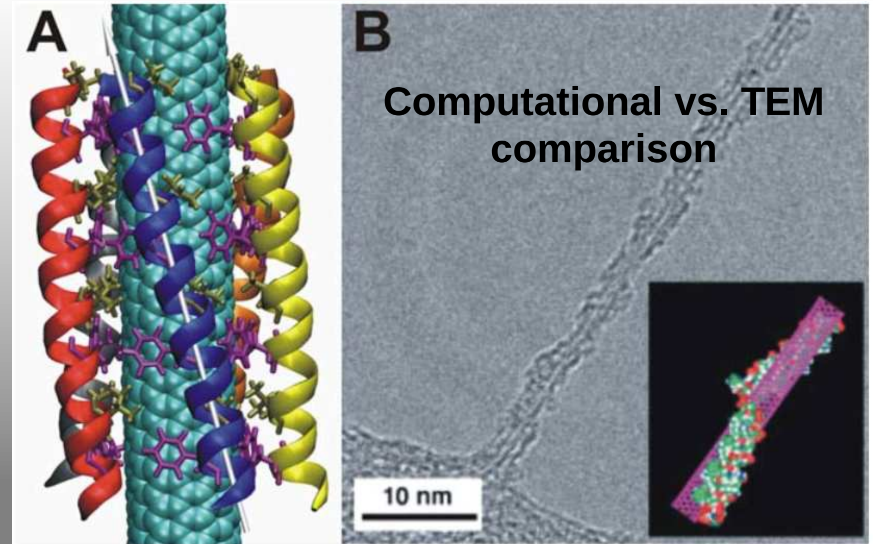
UTD Depts. of Biology, Chemistry, Engineering (Bob Helms)

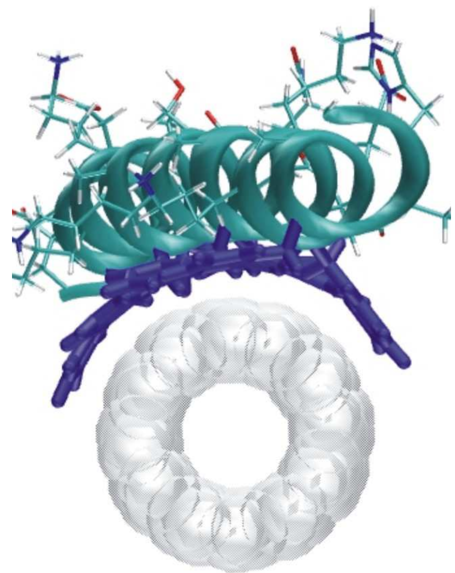
ARIZONA
co-PI: Ara Philipossian

Wide Range of Expertise at the *Nano-Bio* Interface

Live-cell imaging of CNTs using confocal Raman

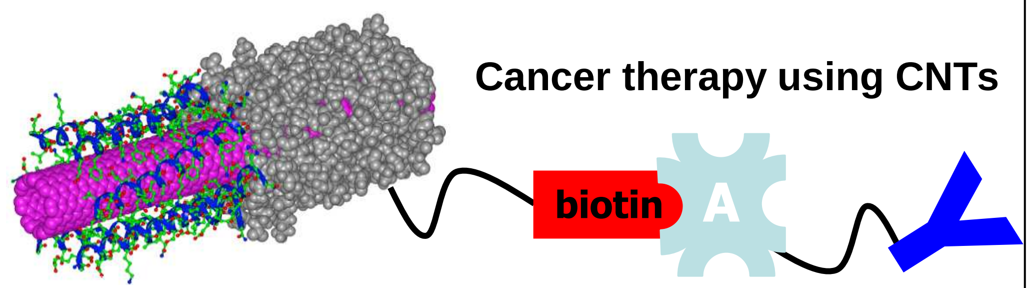






Molecular modeling of protein – CNT interactions

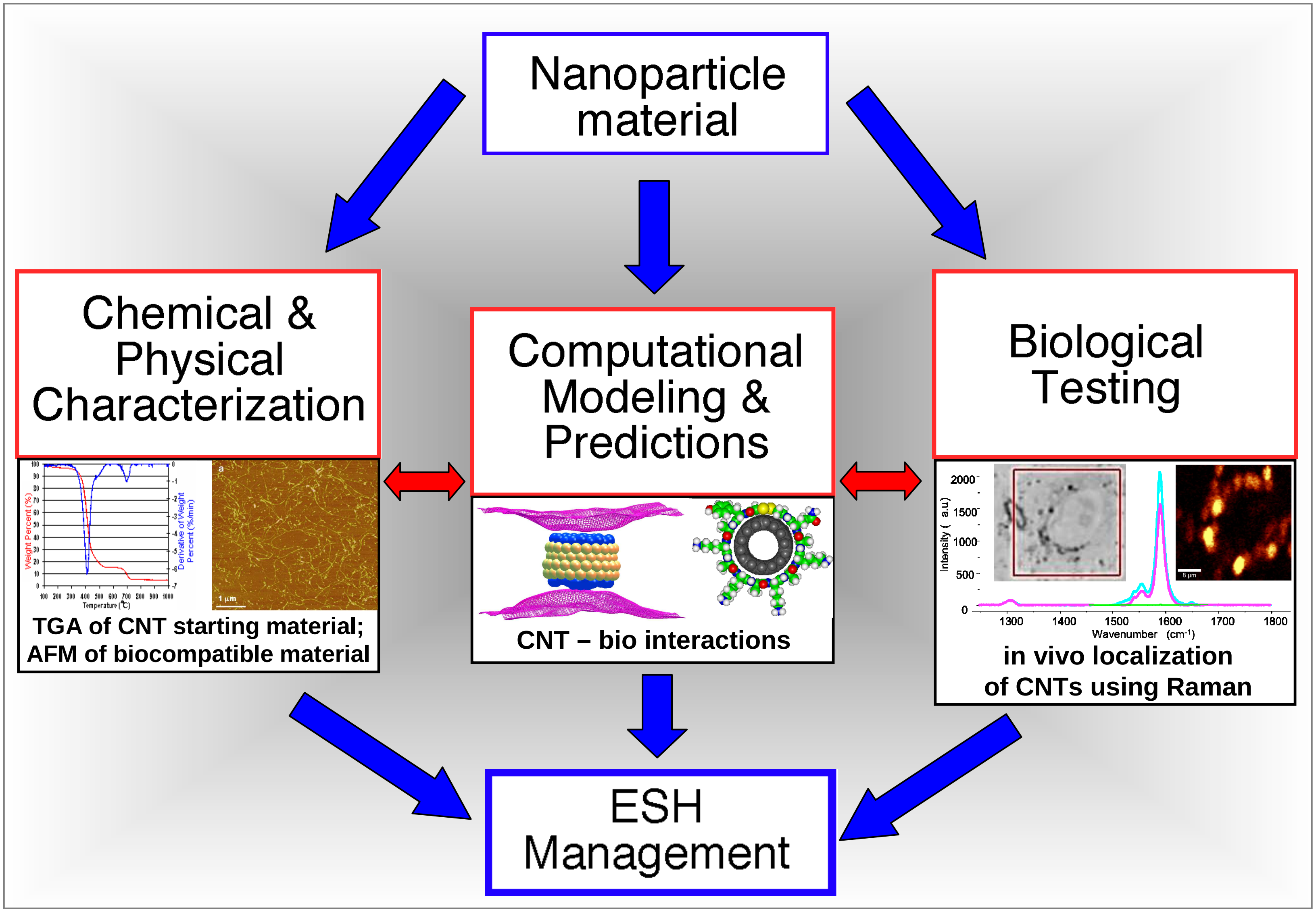
Cancer therapy using CNTs



Publication list available at poster

Current Goal: Focus our ESH expertise on needs of semiconductor industry

Predicting, Testing, and Neutralizing Nanoparticle Toxicity



SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Nanoparticle Material

Nano: does size matter?

Yes!
- -- electron confinement
- -- high surface area to volume ratio

→ **new and unanticipated reactivities**

Quality evaluations from an ESH impact perspective are needed to:
- support the semiconductor industry
- ensure public confidence in the use of nanotechnology

Handling CNT powder

Year 1 Focus: CARBON NANOTUBES (CNTs)
- unique properties have many potential applications in novel electronic devices
- only nanomaterial currently flagged by EPA under TSCA.

Future Focus: other nanoparticles of interest to semiconductor manufacturers
- e.g. CMPs supplied co-PI Ara Philipossian

We are very careful to first address batch-to-batch variation in nanomaterials before we assess biological activity.

Example: wt% of as-received CNT powders we have worked with

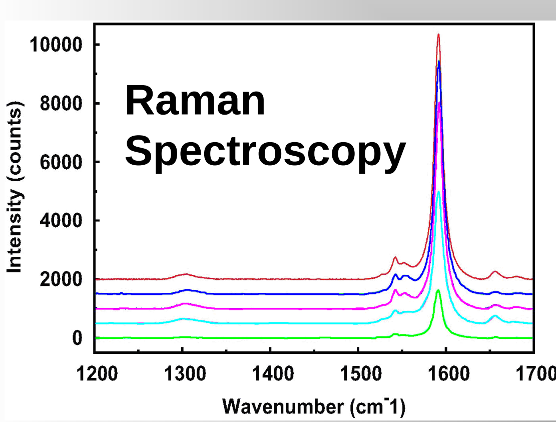
CNTs:	26 - 82%
Metals:	10 - 32%
Other:	5 - 44%

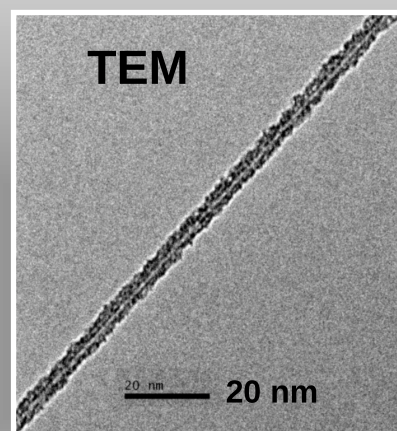
Chemical & Physical Characterization

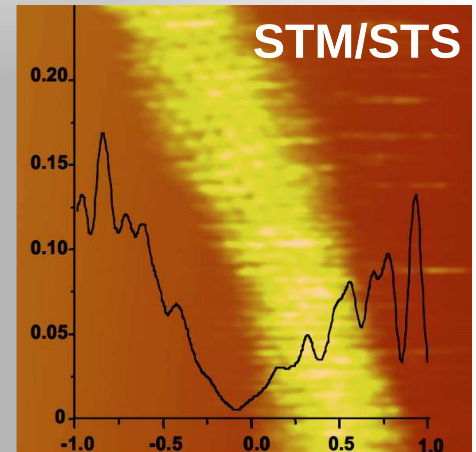
"We feel a sense of urgency that better characterization has to be done because we think there are numerous benefits of nanotechnology,"

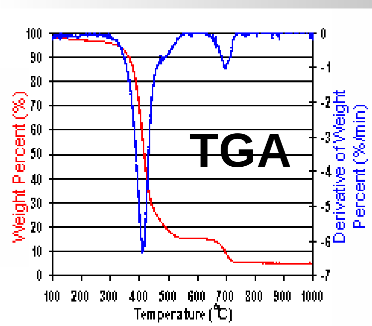
Mark D. Hoover, senior scientist at the National Institute for Occupational Safety & Health

Often the main driver of toxicity is not the nanomaterial itself but impurities like transition metals.



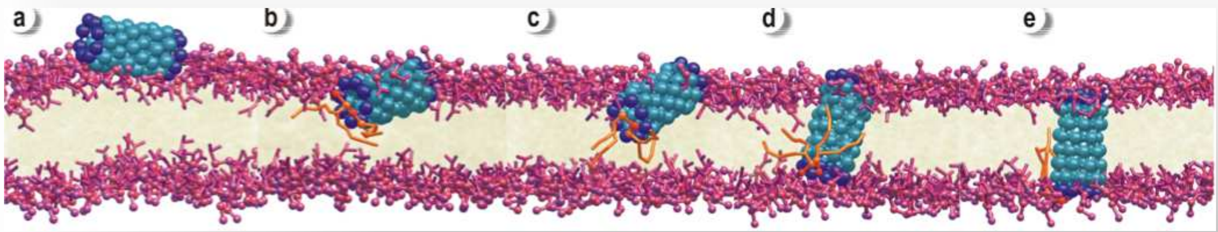


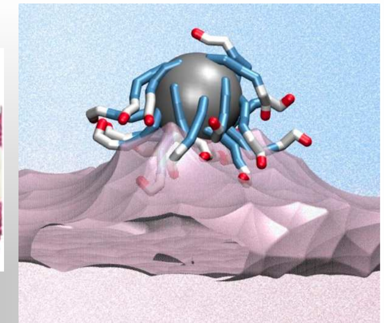




We have an extensive array of instrumentation and expertise that can be readily applied to any nanoparticle preparation:
-Bulk / solution / surface / single molecule measurements
-Elemental and functional group analysis
-Particle size and surface electronic properties
-Spectroscopy (UV-Vis-NIR, FTIR, Raman, ICP-mass spec., XPS)
-Microscopy (light, electron, and scanning probe)

Computational Modeling/Predictions

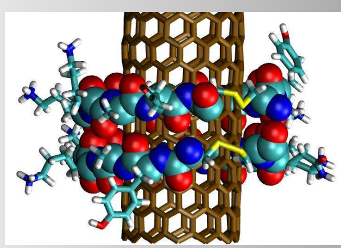




<u>Predictive power</u>: combine simulation, characterization and toxicity data to

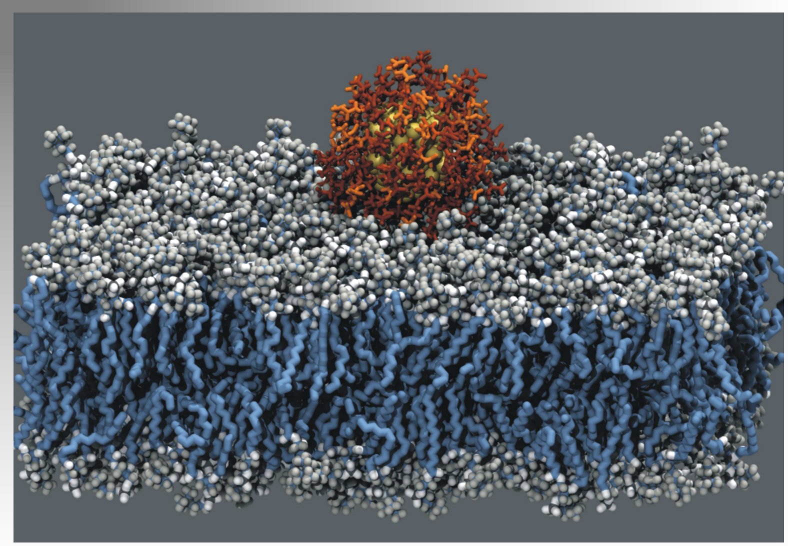
- predict trends
- deduce key indicators

→ linking nanoparticle properties to toxicity



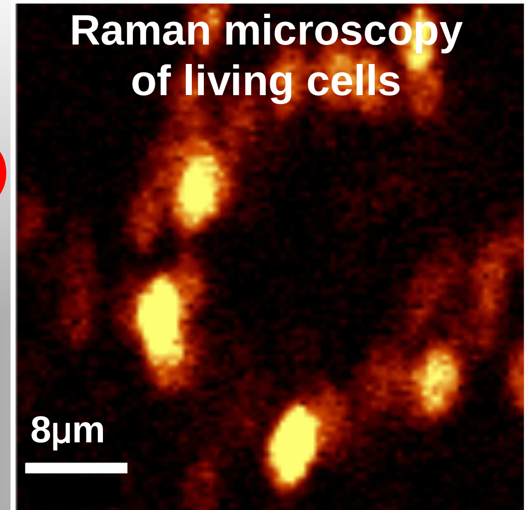
Molecular simulation captures unique properties of nanoparticles (NPs):

(1) NP – bio interactions
(2) NP reactivity
(3) NP surface properties
(4) NP aggregation states

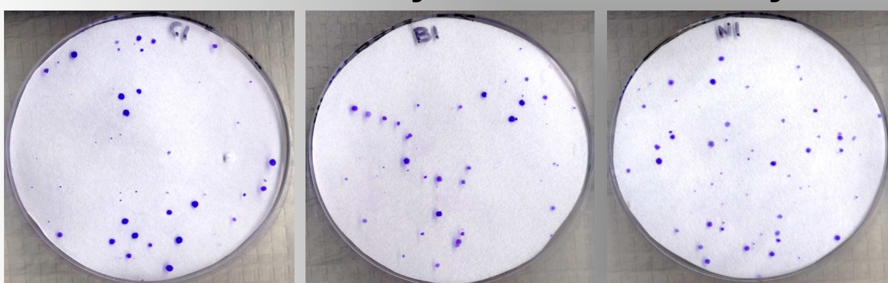


Biological Testing

Suite of protocols to assess
(1) material quantity (how much?)
(2) material fate (where is it?)
(3) biological activity (what does it do?)
(4) potential cytotoxicity (is it toxic?)



NRK Cell Colony Formation Assays



Control | BSA | BSA-SWNT

One of a variety of our methods to assess toxicity.

Our method (patent filed) to extract and measure CNTs from cells & tissues.

SWNT Bands

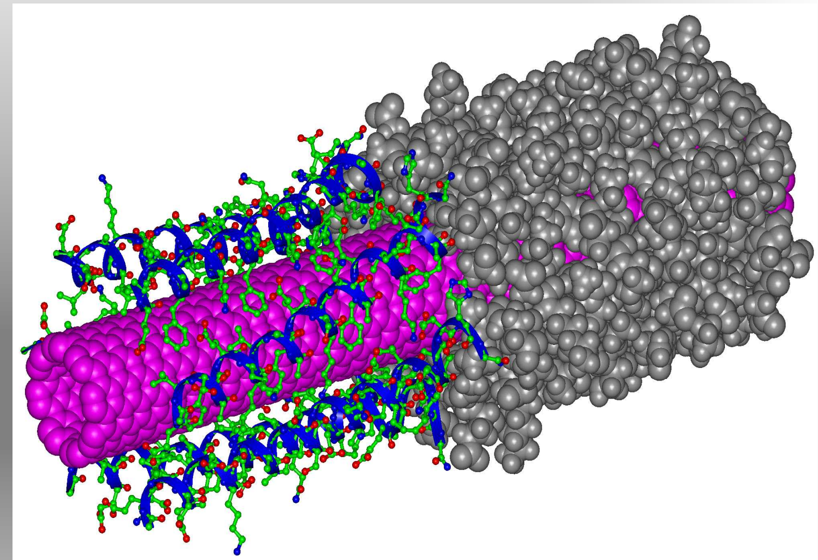
Currently being developed for semiconductor process analytical samples.

ESH Management

We plan to develop tools to enable near-concurrent screening of potential ESH impacts for novel nanomaterials in the R&D stage.

Our aims:

- **develop models for predicting toxicity**
- **determine how toxicity can be remediated**
  - **e.g. extract NPs from waste streams**
  - **e.g. modify NP surface with polymers to reduce toxicity**
- **work with companies to solve ESH management problems**



Possible coatings for remediation

UTD Bionanosciences Group committed to long-term vision of ESH research and management.

Predicting, Testing, and Neutralizing Nanoparticle Toxicity

Summary

We propose to characterize the properties of nanomaterials using analytical techniques, and correlate these properties through computer modeling with toxicity, mechanism & amount of uptake, and cellular fate.

TASK DELIVERABLES

Data on the characterization, fate, and toxicity (tested in model mammalian cells) of CNT nanoparticles.
(March 2010)

Data on physical and chemical characteristics of CNT and CMP nanoparticles with an initial attempt to correlate with structural modeling, interaction with model mammalian cells, toxicity, and bioactivity.
(March 2011)

Data on physical and chemical characteristics of CNT and CMP nanoparticles correlated with structural modeling, interaction with model mammalian cells, toxicity, and bioactivity.
(March 2012)

SRC

SEMATECH
Accelerating the next technology revolution.

Potential industrial partnerships
(ISMI, TI, Freescale, Intel, & others)

Wide Range of Expertise at the *Nano-Bio* Interface

SELECTED PUBLICATIONS RESULTING FROM ACTIVITIES OF THE UTD BIONANOSCIENCES GROUP

2003 Dieckmann, G. R.; Dalton, A. B.; Johnson, P. A.; Razal, J.; Chen, J.; Giordano, G. M.; Munoz, E.; Musselman, I. H.; Baughman, R. H.; Draper, R. K. Controlled assembly of carbon nanotubes by designed amphiphilic peptide helices, J. Am. Chem. Soc. 125: 1770-1777.

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Lowering the Environmental Impact of High-k and Metal Gate-Stack Surface Preparation Process

New Project P10375

PIs:

- **Yoshio Nishi, Electrical Engineering, Stanford**
- **Srini Raghavan, Materials Science and Engineering, UA**
- **Bert Vermeire, Electrical Engineering, ASU**
- **Farhang Shadman, Chemical Engineering, UA**

Project Subtasks

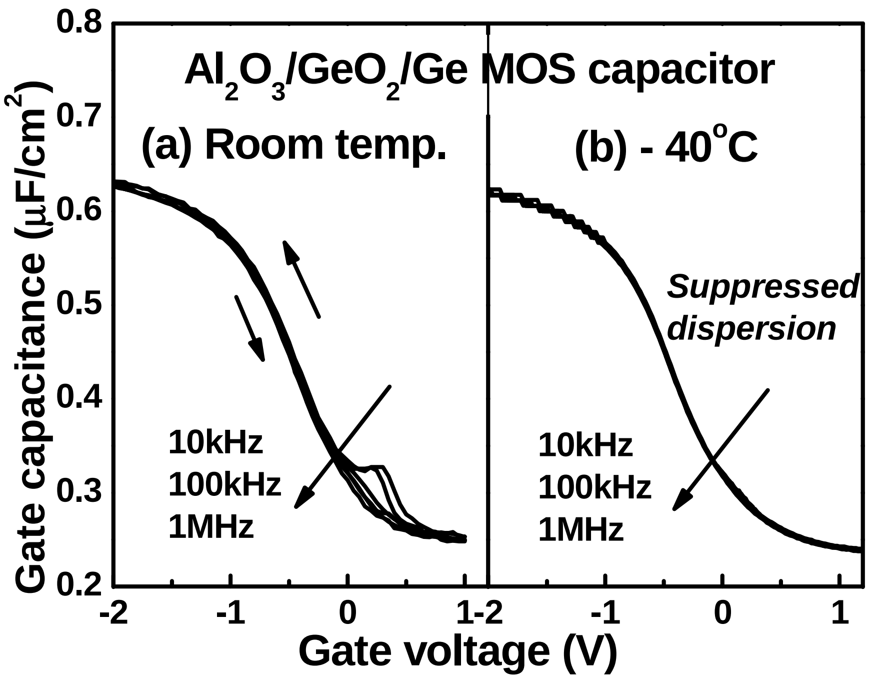
- **Subtask 1: Environmentally friendly chemical systems for patterning silicates and oxide of hafnium**
- **Subtask 2: Low-water and low-energy new rinse and drying recipes and methodologies**

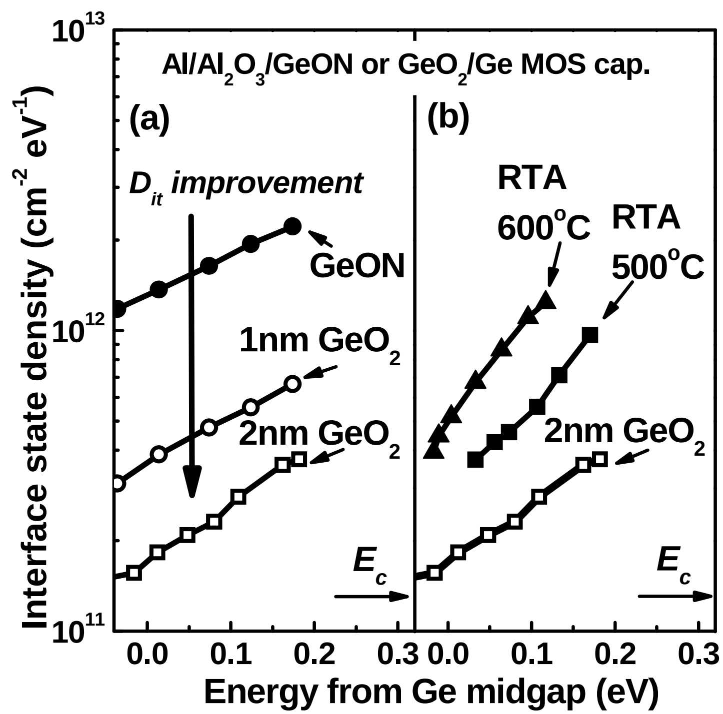
Objectives

Develop new chemistries, rinse methodologies, and reliable in-situ as well as post cleaning performance testing techniques that would lead to elimination and/or reduction in usage of hazardous cleaning chemicals, reduction in usage of water and energy, and gain in performance of high-k metal gate stacks.

High-k Metal Gate Stack Electrical Characterization

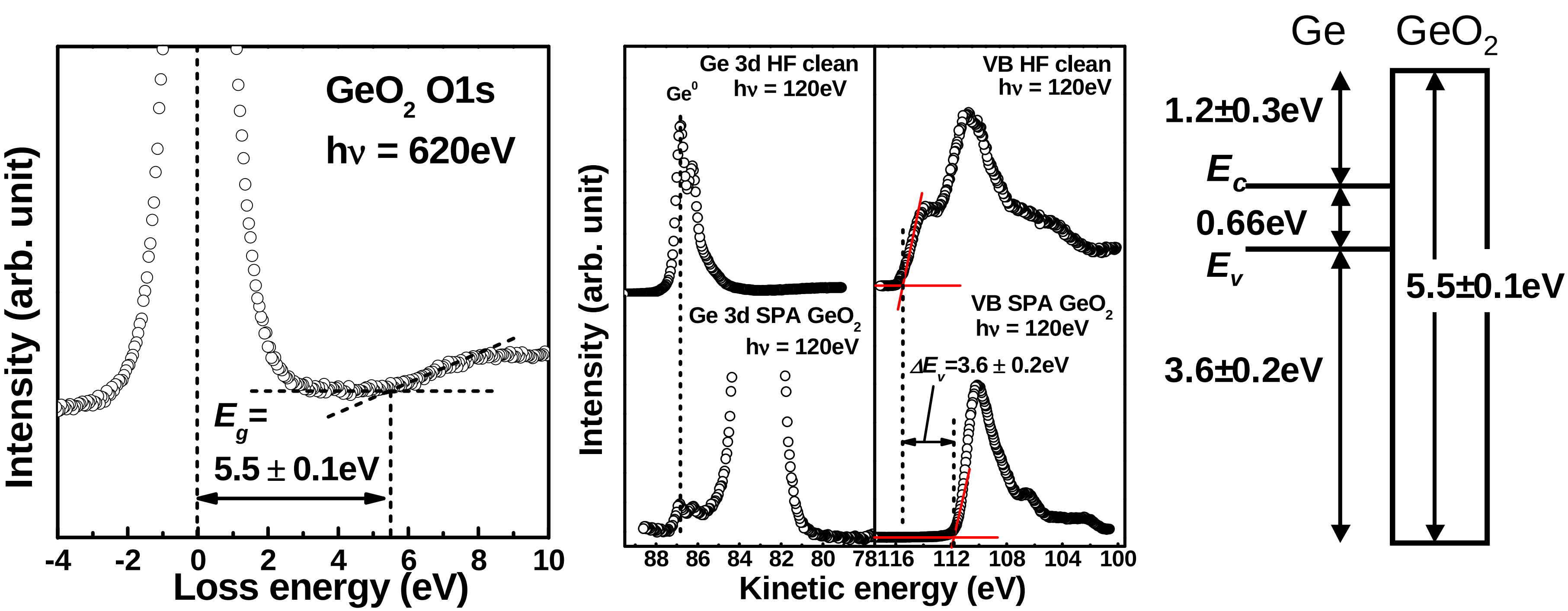
- Ex. C-V characteristics in MOS capacitor
  - Detect fixed charges, mobile ions and interface states (D_{it} can be precisely obtained by conductance method)
  - Reliability: PBTI, NBTI, TDDB etc.



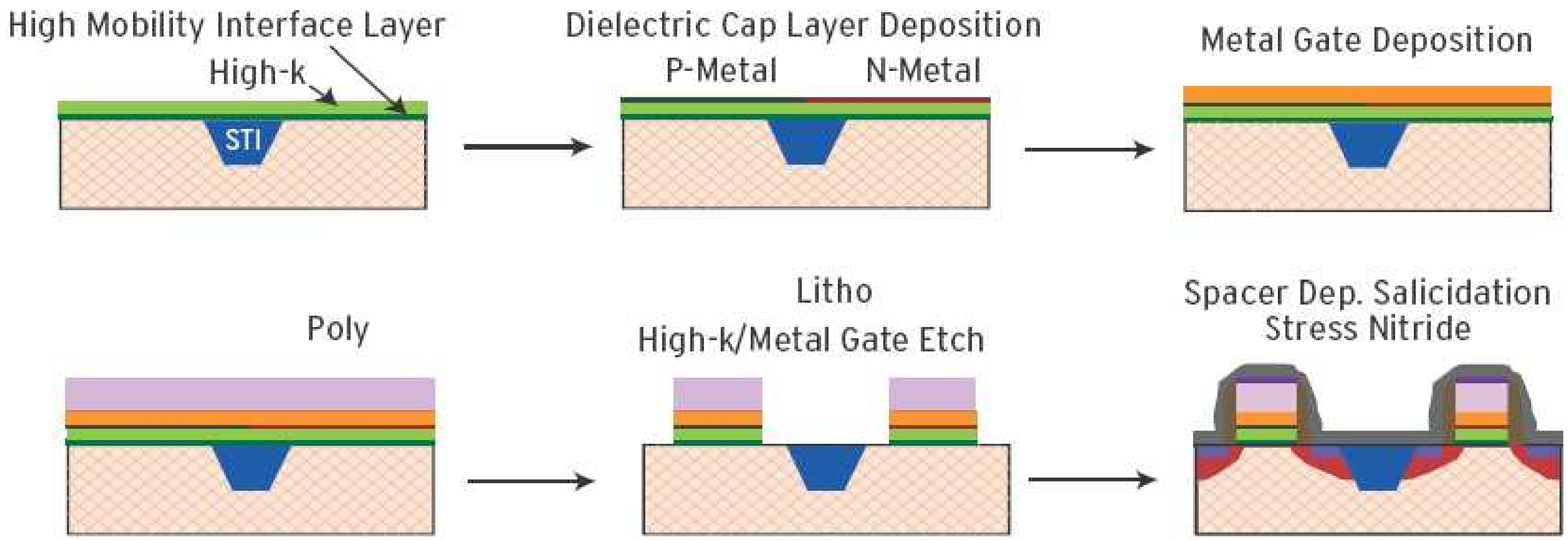


High-k Metal Gate Stack Physical Characterization

- Ex. XPS or SRPES analysis
  - Characterize chemical bonding on the surface and interface of High-k Metal gate stack
  - Construct band diagram correlating with electrical characterization

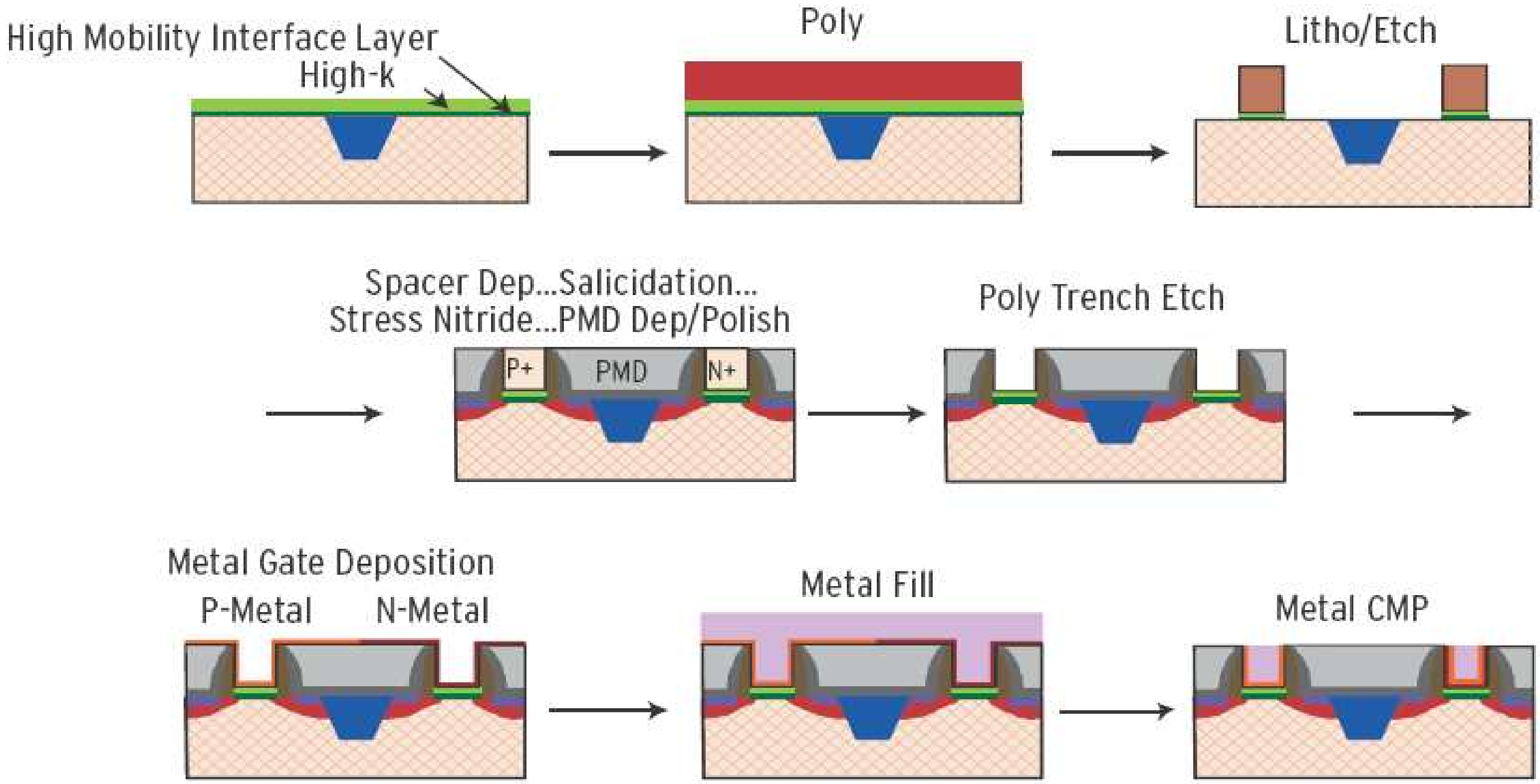


High k –Metal Gate Stack
Gate First Integration



Source: R. Arghavani, G. Miner, M. Agustin, "High-k/Metal gates for high-volume manufacturing", Nanochip Technology 5 (2), 2007.

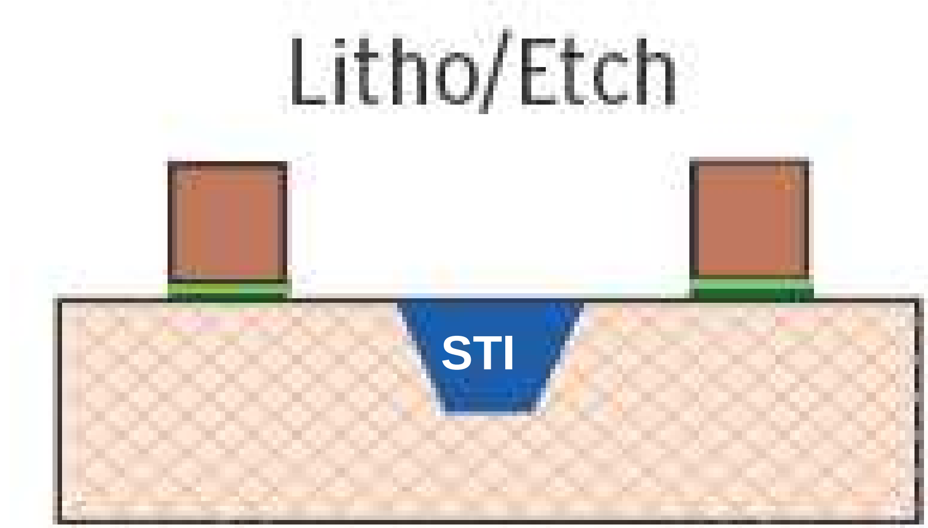
High k –Metal Gate Stack
Gate Last Integration



Source: R. Arghavani, G. Miner, M. Agustin, “High-k/Metal gates for high-volume manufacturing”, Nanochip Technology 5 (2), 2007.

Surface Preparation Challenges

- Both Gate First and Gate Last integration require removal of heat treated high-k dielectric
- Surface termination and chemistry loading impacts subsequent rinse and dry. The most severe rinse and dry problems originate on hydrophobic or mixed hydrophobic/hydrophilic surfaces
- Aspect ratios of features become more severe and new materials are introduced



Subtask 1: Environmentally Friendly Chemical Systems for Patterning Silicates and Hafnium Oxide

BACKGROUND

- **In the formation of high k- metal gate structures by the "gate first" process, etching of high k material after 'P-metal' removal to prepare the surface for 'N- metal' deposition is required. Additionally, selective etching of high k material with respect to SiO_2 is also needed**
- **Currently used chemical system for etching Hf based high-k materials is dilute HF containing HCl; however, these high k materials become very difficult to etch when subjected to a thermal treatment**
- **HF based systems appear to induce galvanic corrosion of polysilicon, which is in contact with metal gate materials; reducing the oxygen level of HF has been recommended to reduce corrosion**

Subtask 2: Low-Water and Low-Energy New Rinse and Drying Recipes and Methodologies

BACKGROUND

- **Formation of high-k metal gate structures requires cleaning of fine geometries containing materials not traditionally used by the semiconductor industry. Wet etching must be quenched at the appropriate time**
- **More single wafer tools are used for cleaning, rinsing and drying because of better yield. Optimization of cycle time is critical for throughput and reduced resource usage**
- **Elucidating rate-limiting mechanisms to make possible multi-stage, resource-efficient recipes requires in-situ and real-time measurements and accurate simulation capabilities**

Subtask 1 – Proposed Work

1. **Explore non-fluoride based chemical systems for etching heat treated hafnium silicates and oxide**
   - **Reductive thermal treatment followed by etching in ammoniacal solutions containing complexing agents**
2. **Investigate galvanic corrosion between representative gate metals (W, Mo, metal nitrides) and poly-silicon in developed formulations using patterned test structures**
   - **Key variable : polysilicon to metal area ratio**

Subtask 2 – Proposed Work

1. **Design test structures to measure the fundamental parameters that determine the dynamics of rinsing and drying of fine geometries containing these new materials.**
   - **Include surface loading, adsorption/desorption rate constants, electrostatic interactions, and surface tension**
2. **Develop simulation methods to investigate the contaminant profiles in the many possible gate stack configurations**
3. **Explore reduced resource usage and high throughput recipes for rinse and dry. Key parameters include:**
   - **Surface termination (from subtask 1), temperature, flow rates, and agitation**

Sugar-Based Photoacid Generators (“Sweet” PAGs): Environmentally Friendly Materials for Next Generation Photolithography

(Project Number: P10375)

PIs:

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

Graduate Students:

Undergraduate Students:

Other Researchers:

- **Wenjie Sun, Postdoctoral Fellow, Chemical and Environmental Engineering, UA**
- **Youngjin Cho, Postdoctoral Fellow, Materials Science and Engineering, CU**

Cost Share (other than core ERC funding)

Objectives

- **Develop PFOS free and environmentally friendly photoacid generators (PAGs) with superior imaging performance. The novel PAGs will be based on biological units such as sugars and cholic acids for chemically amplified resist application**

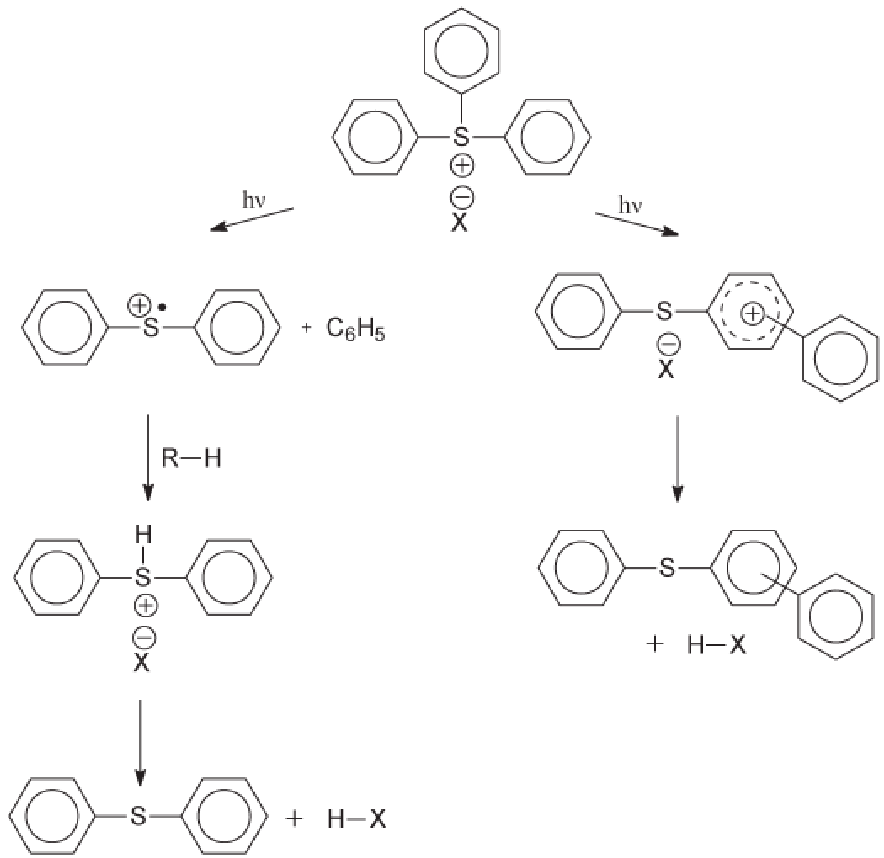
- **Identify modeling tools to predict the environmental fate of novel PAGs.**

Overview Tasks

- Develop and synthesize environmentally friendly PAGs based on biological units.
- Assess the lithographic performance of the novel "Sweet" PAGs at 193 nm wavelength (both under dry and immersion conditions).
- Evaluate key environmental properties of the novel PAGs
- Identify chemical functionalities contributing to increase the (bio)degradation potential of novel PAGs.
- Test the validity of selected computer models to predict the environmental fate of novel PAGs.

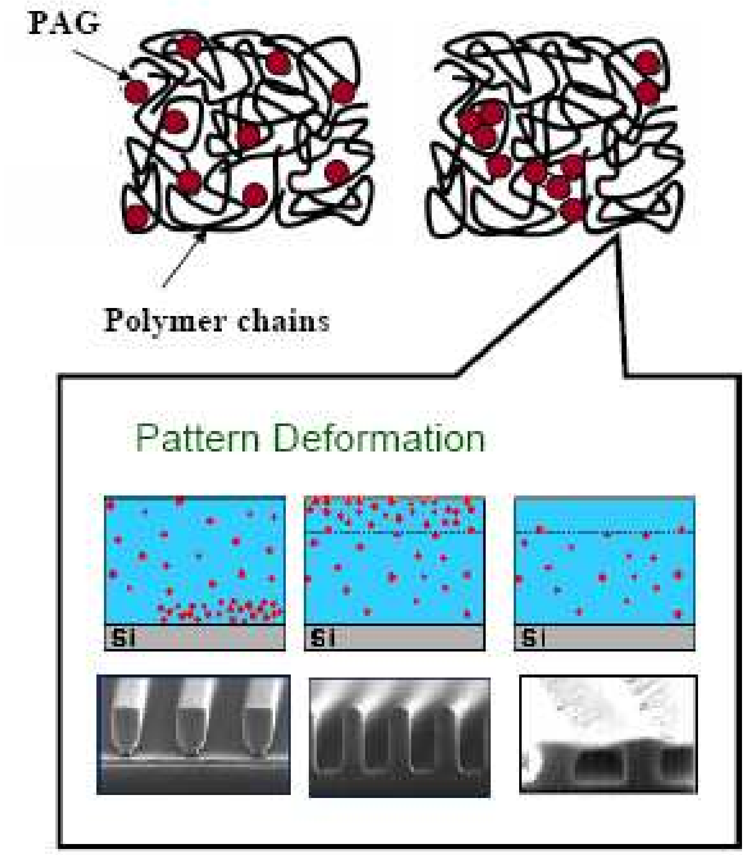
Photoacid Generator (PAG)

- PAG
  - ionic (onium salt)
    - metallic
    - sulfonate
    - sulfonylimide/sulfonylmethide
  - non-ionic
    - organohalide
    - sulfonate ester
      - 2-nitrobenzyl ester
      - aromatic sulfonate
      - oxime sulfonate
      - N-sulfonyloxyimide
      - sulfonyloxy ketone
      - DNQ 4-sulfonate
    - sulfone

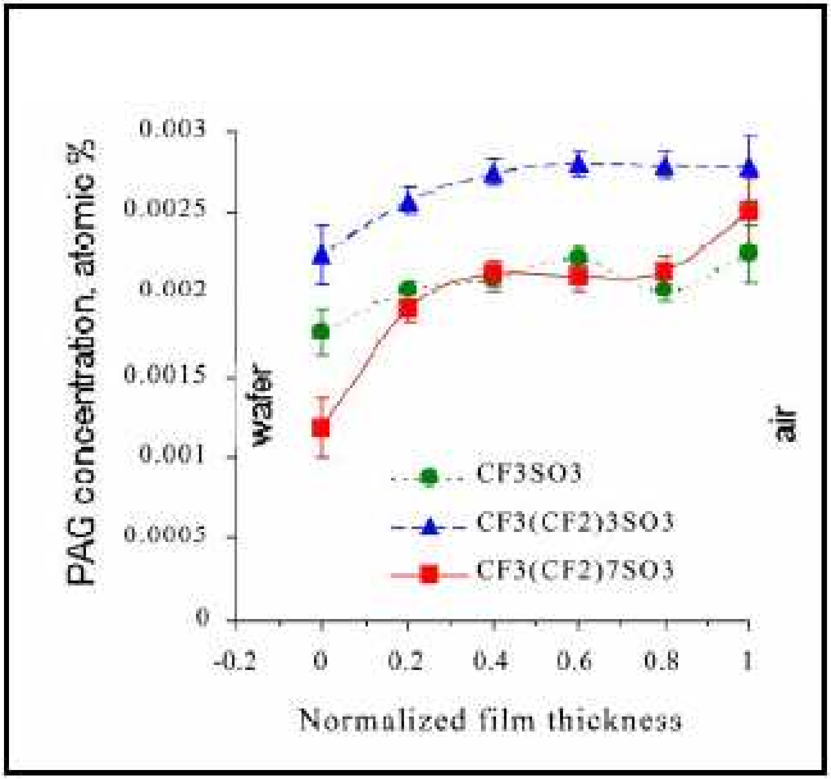


Photolysis mechanism of triphenylsulfonium salts

PAG Miscibility



Degree of segregation is dependent upon length of perfluorinated counter ion.



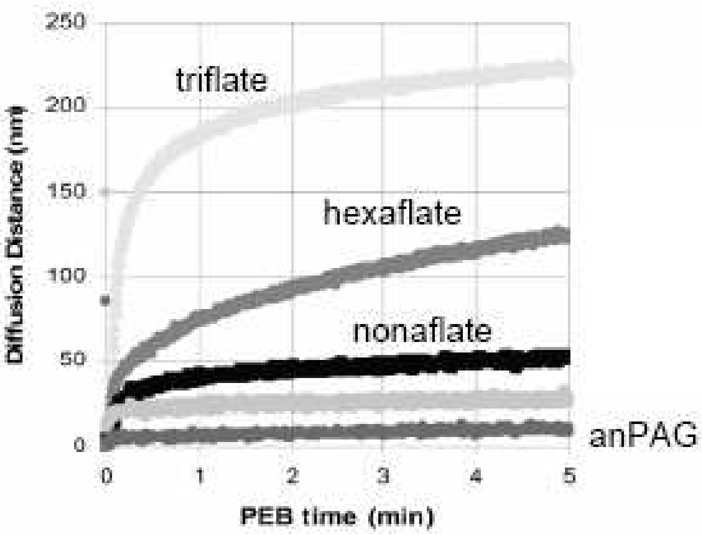
Ober C. K. et al., *J. Photopolym. Sci. Technol.* 1999, 3, 457.

Acid Diffusion Problem

> Excessive diffusion leads to **IMAGE BLUR** and **POOR RESOULUTION**.
> Effective acid diffusion is mainly determined by the counter anion due to Long range coulombic interactions. (Shi X. J. Vac. Aci. Technol. B 1999, 17, 350.)

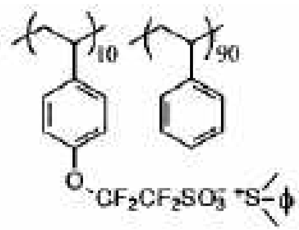
Diffusion distance:

triflate > hexaflate > nonaflate > anPAG

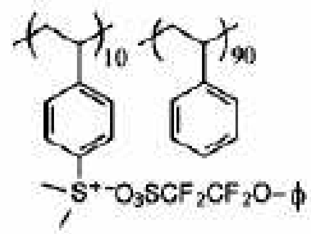


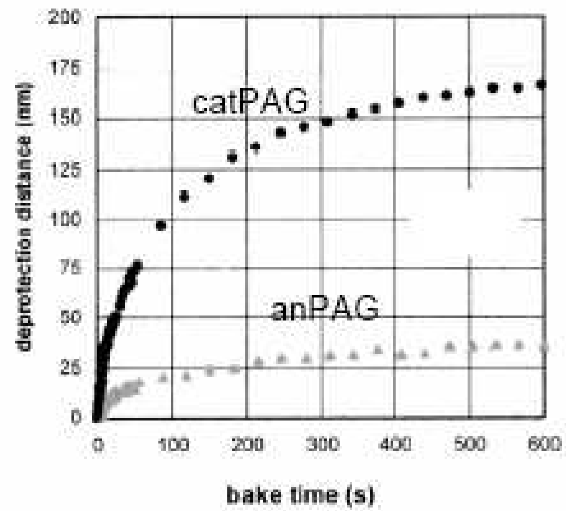
Stewart M. D. *Uinv. of Texas Dissertation 2003.*

anPAG



catPAG





"25 nm diffusion for PAG anion attached to polymer back bone"

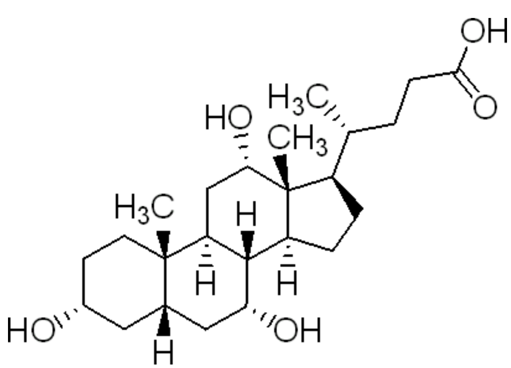
Stewart M. D. et al. *J. Vac. Sci. Technol. B* 2002, *20*, 2946.

Design of PAGs based on Steroids and their analogs

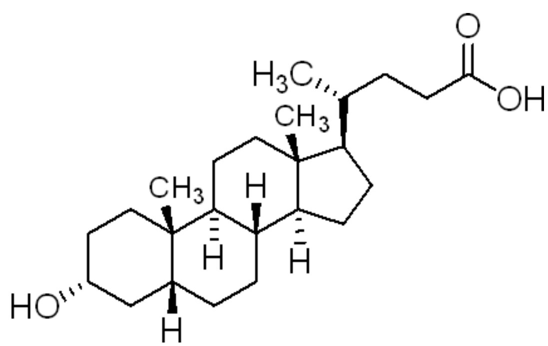
- Biodegradability and Biocompatibility

- Miscibility with 193 nm MG resists

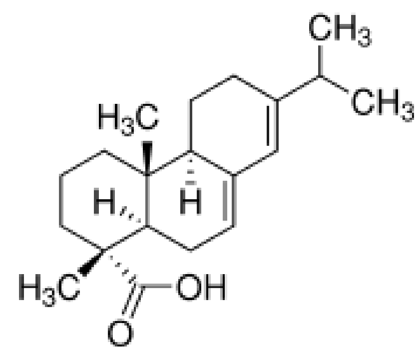
- Cholic acid, Lithocholic acid and Abietic acid (Pine resin acid)



Cholic acid

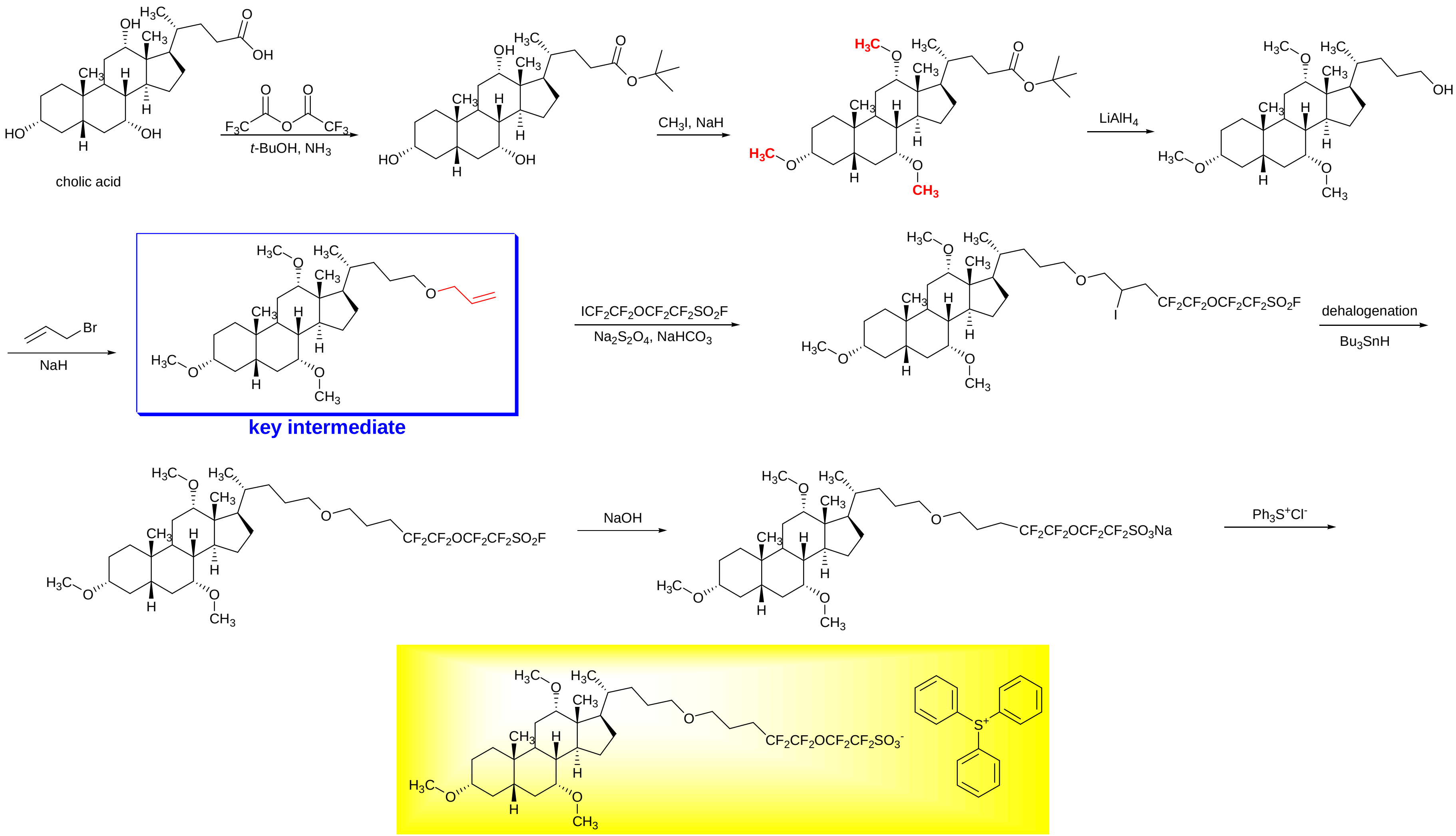


Lithocholic acid



Abietic acid

Synthetic Route for Biodegradable PAG



Environmental Compatibility

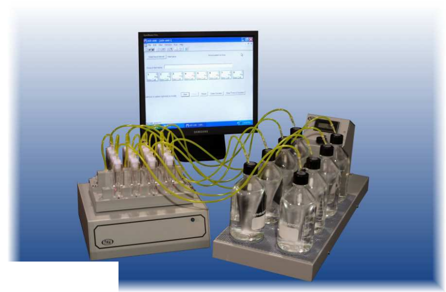
- **Biodegradation**
  - Batch bioassays: aerobic and anaerobic conditions
- **Toxicity**
  - Microbial inhibition (aerobic and anaerobic microorganisms)
  - Aquatic toxicity (Microtox^R w. bacterium, *Vibrio fischeri*)
  - MTT test (mitochondrion activity)
  - Live-Dead Assay

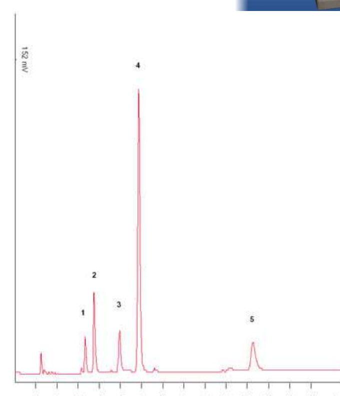
- **Bioaccumulation**
  - K_{ow}: water-octanol partition coefficient

Enhancing Degradation Potential

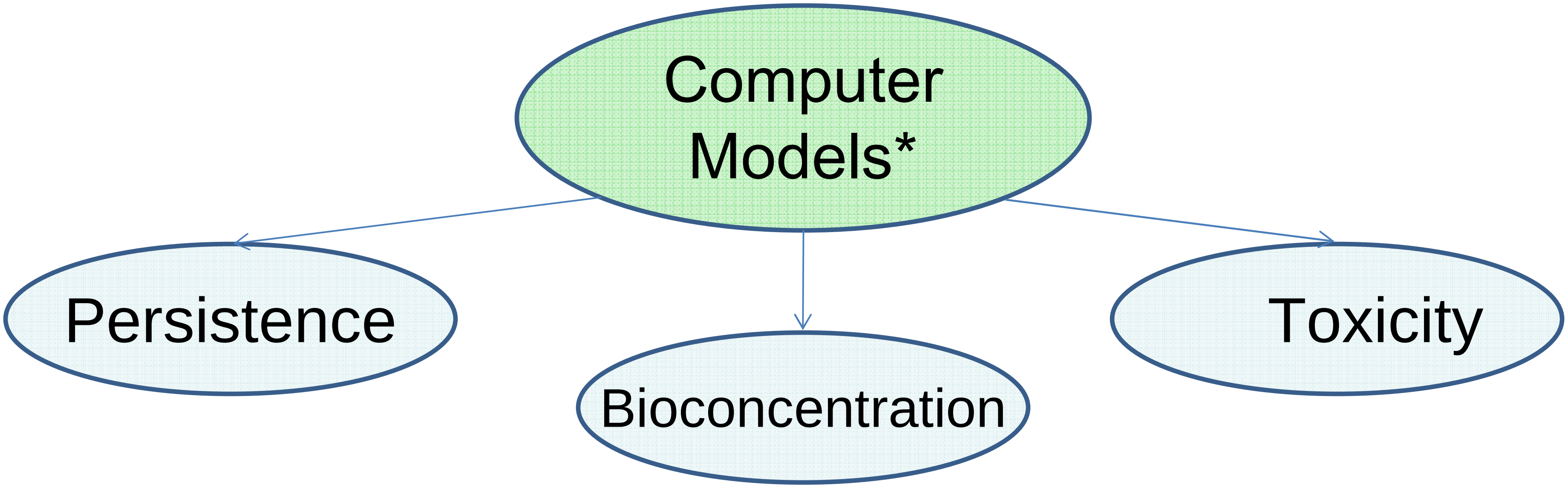
(Bio)degradability testing of structurally-related PAG compounds modified with selected functionalities.

- O_2 uptake (aerobic biodegradation)
- CH_4 production (anaerobic degradation)
- Parent compound removal
- Identification of intermediates
- Fluoride release





Predictive Tools for Environmental Fate Modeling



e.g. EPA PBT Profiler,
UM-BBD (University of Minnesota Biocatalysis/Biodegradation Database)
CATABOL

Outcomes

- Environmentally safe, high performance PAGs suitable for 193 nm lithography and other NGL wavelengths.
- Develop PAGs with superior imaging performance
- Identification of structural features to enhance PAG degradation under biotic and abiotic conditions.
- Selection of computer models to predict the environmental fate of PAGs.

Task Deliverables

- Report on the lithographic evaluation of new "Sweet" PAG Gen 2 materials (Cornell, June 2010)
- Report on the assessment of the environmental compatibility of 2nd generation "Sweet" photoacid generators (University of Arizona, Dec 2010)
- Report on the evaluation of selected computer models to predict PAG environmental fate (University of Arizona, Dec 2010).

Supercritical Carbon Dioxide Compatible Additives: Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography

PIs:

Christopher K. Ober, Materials Science and Engineering, Cornell

Juan de Pablo, Chemical Engineering, Wisconsin

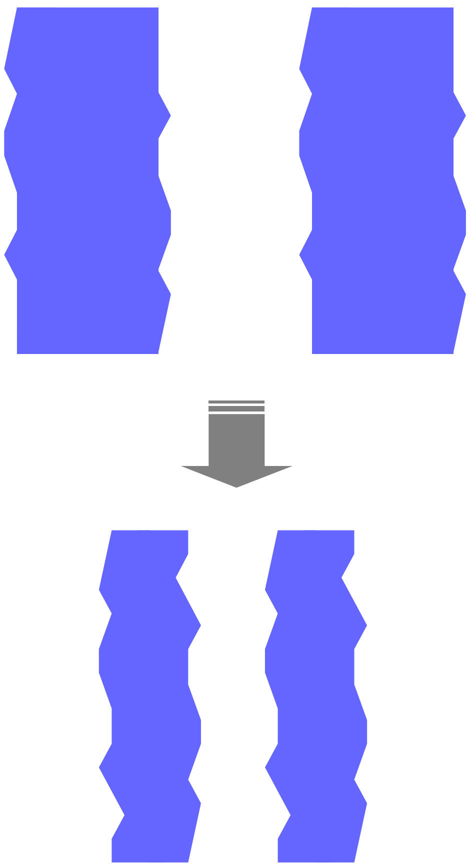
James Watkins, Polymer Science and Engineering, UMASS

Graduate Students:
To be determined.

Next Generation Lithography: Key Problems

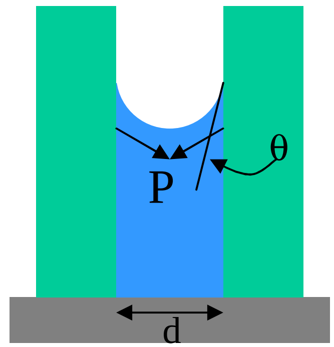
Pattern Variations

< 3nm for 32nm node



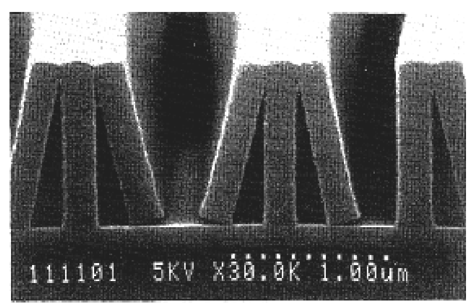
Pattern Collapse

Reduce surface tension



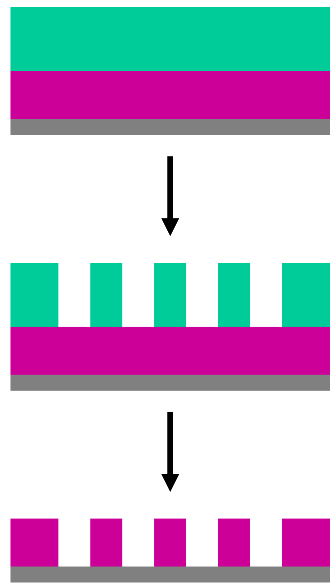
$$P = \frac{\sigma}{R} = \frac{2\sigma\cos\theta}{d}$$

@ 50nm L/S, aspect ratios >2:1 collapse w/water



Non-polar Materials

Low-k applications



Lack of appropriate non-polar developers → Must use mulitple subtractive steps

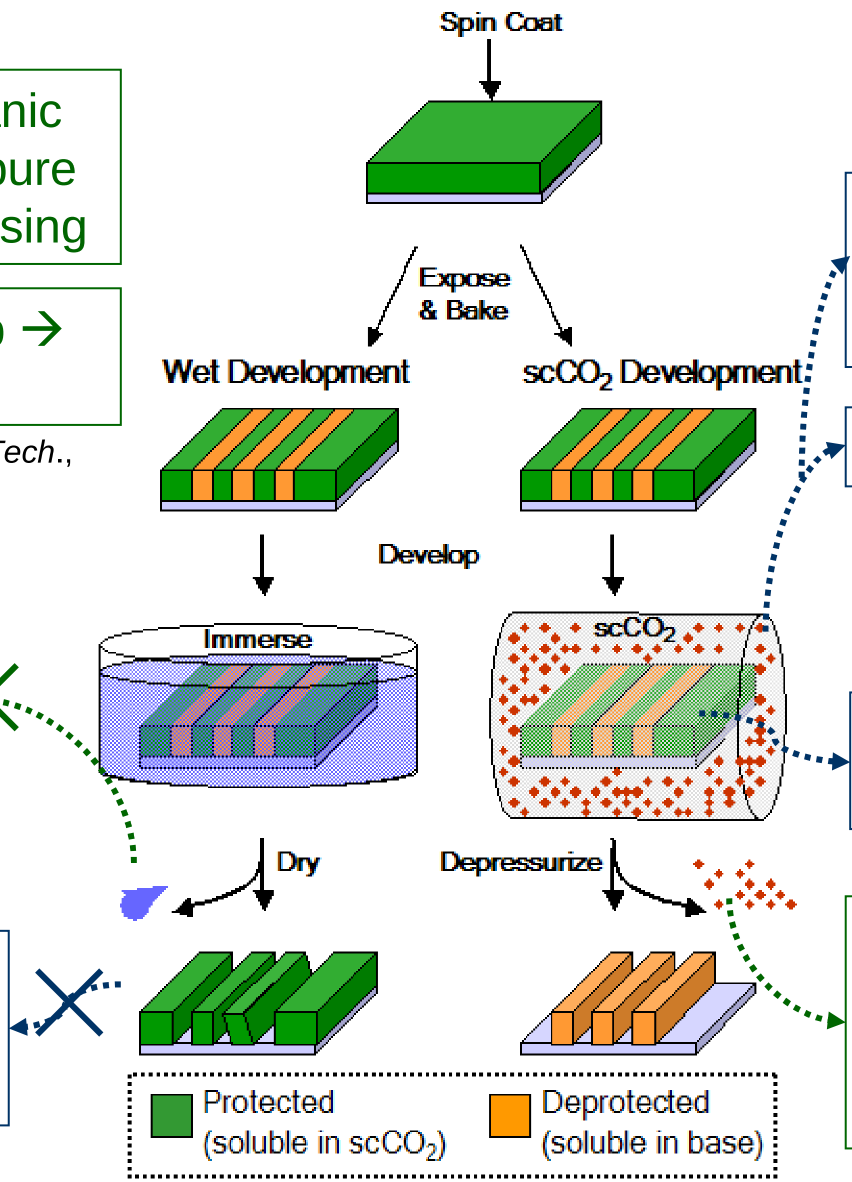
T. Tanaka et al., *JJAP* **1993**, 32, 6059.

Advantages of $scCO_2$ development

Elimination of organic solvents and ultra-pure water during processing

2 gram DRAM chip → 32 kg of water

Williams, et al., *Environ. Sci. Tech.*, **36**, 5504, (2002).



Liquid-like density, Tunable Solvating Power

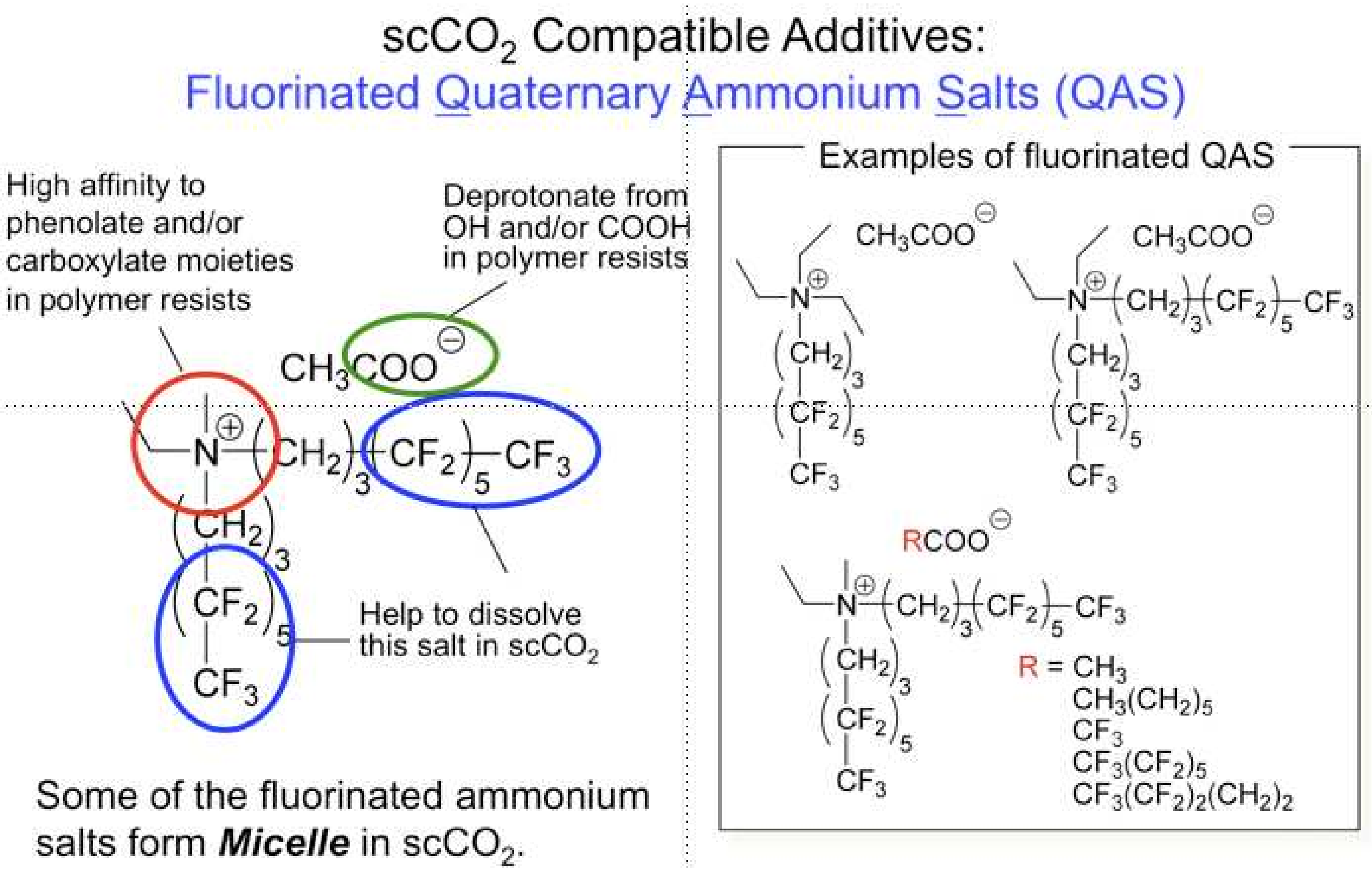
Gas-like transport

Penetrates crevices, no residue

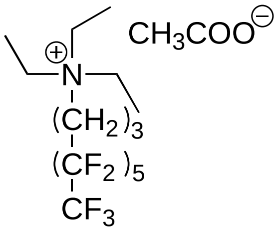
No surface tension, eliminates pattern collapse

Solvent is cleanly separated from resist residues via depressurization

Quaternary Ammonium Salts (QAS)

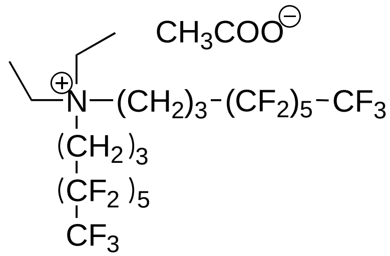


Series of QAS synthesized and tested as additives



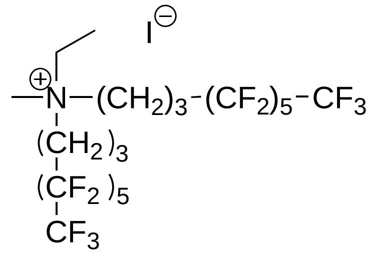
QAS-1

(Γ = -3.60)

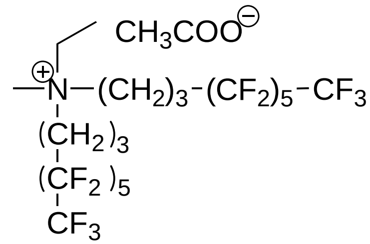


QAS-2

(Γ = -1.44)

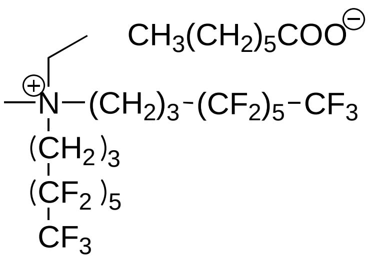


QAS-3

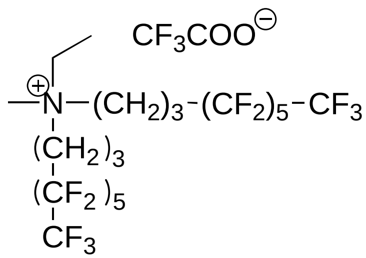


QAS-4

(Γ = +0.83)

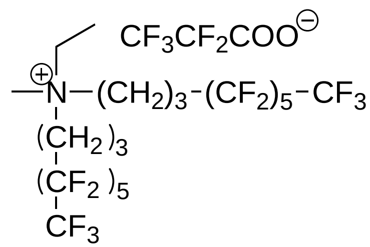


QAS-5



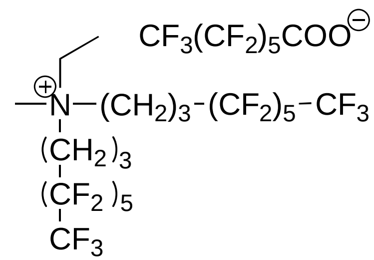
QAS-6

(Γ = +0.14)



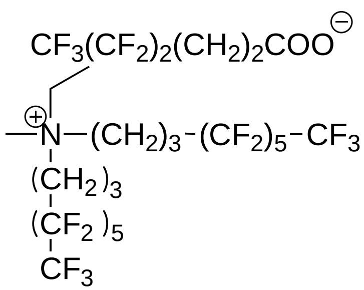
QAS-7

(Γ = +2.08)



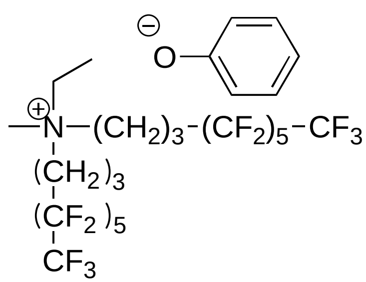
QAS-8

(Γ = +2.39)



QAS-9

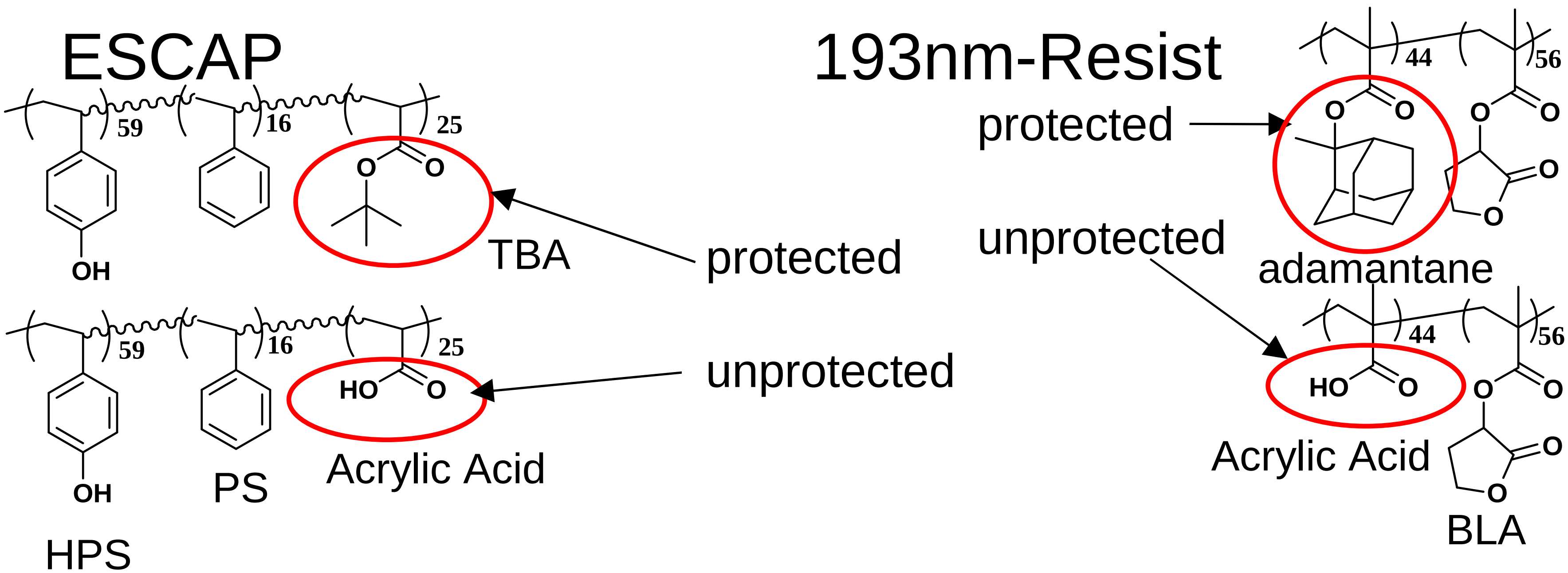
(G = +0.82)



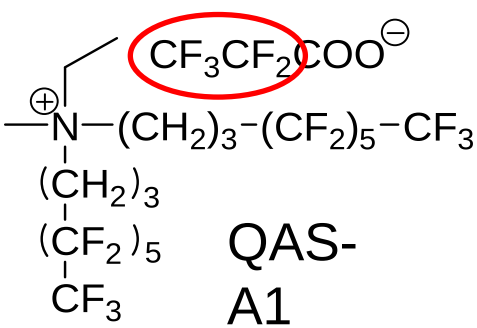
QAS-10

(Γ = +1.44)

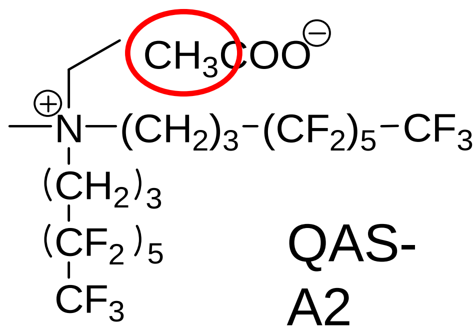
Future Work



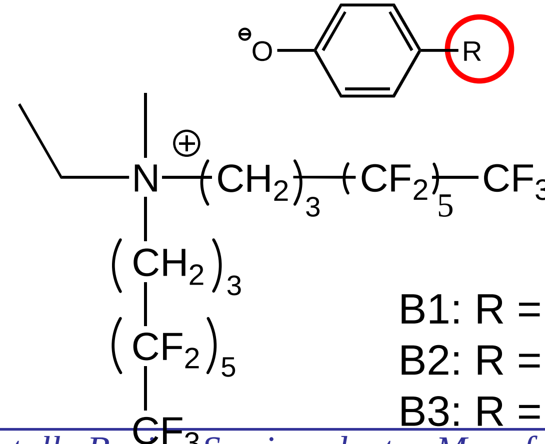
QAS-A: for ESCAP **QAS-B: for 193nm-resist**



QAS-A1



QAS-A2



B1: R = H
B2: R = CH_3
B3: R = CF_3
B4: R = NO_2

Example: Salt Solubility

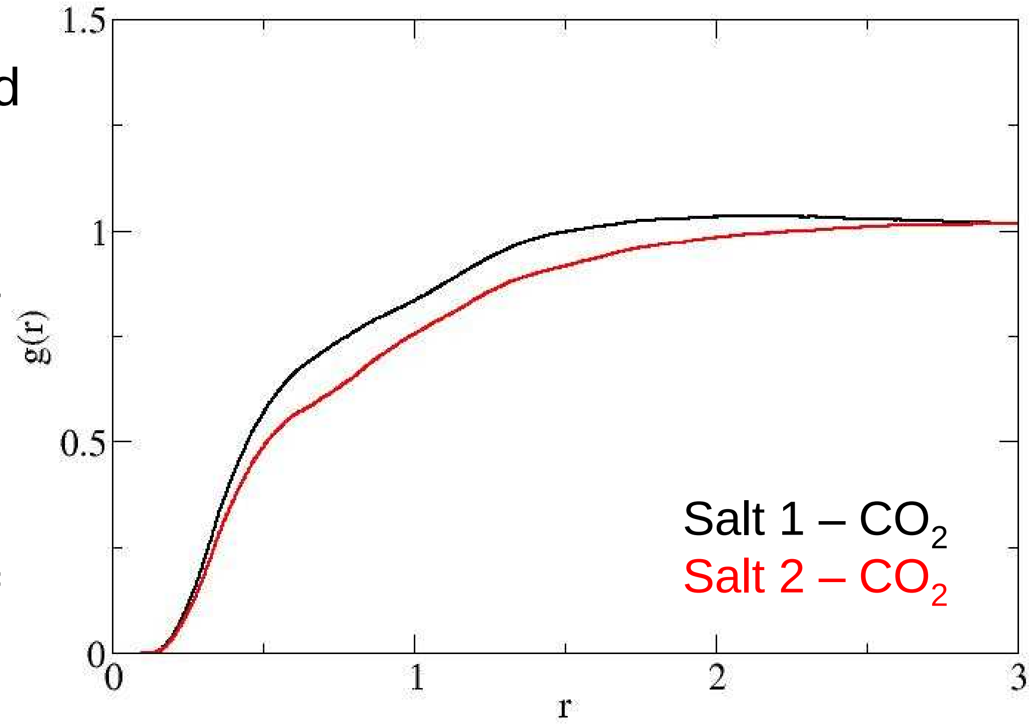
- g(r) is the local density as a function of distance from a fixed point

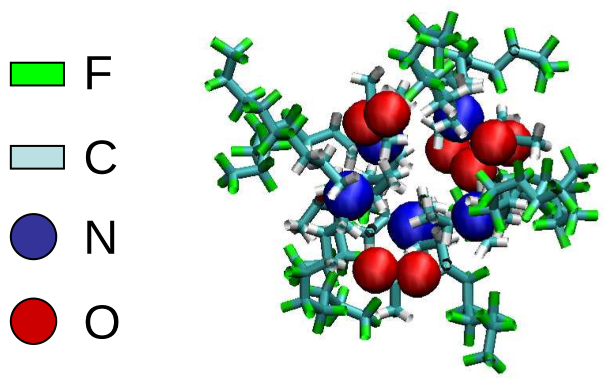
- Γ is the solubility enhancement factor

  Γ > 0 → miscible

  Γ < 0 → immiscible

- Screened solubility in $scCO_2$ of multiple candidates

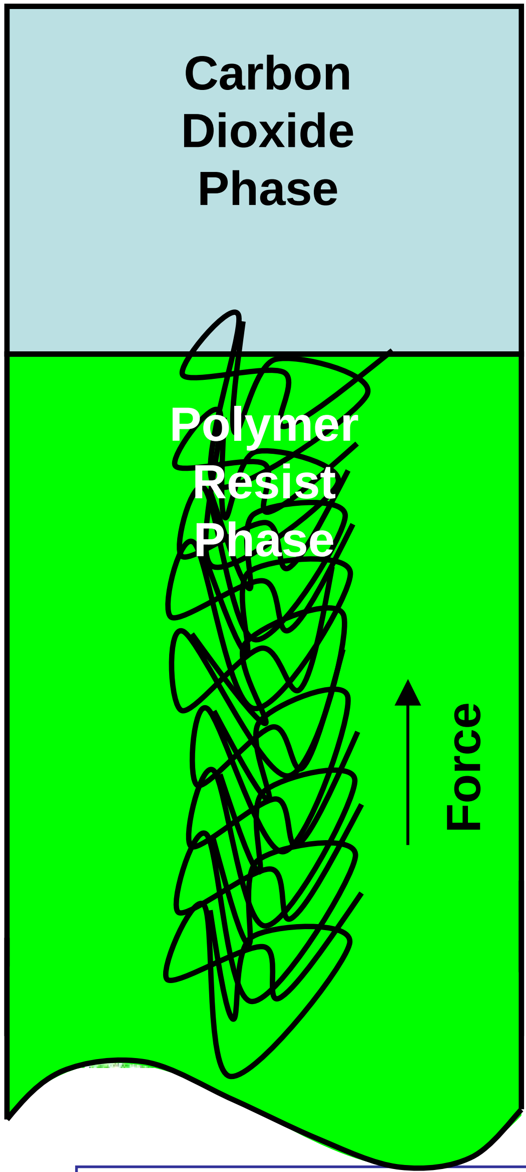




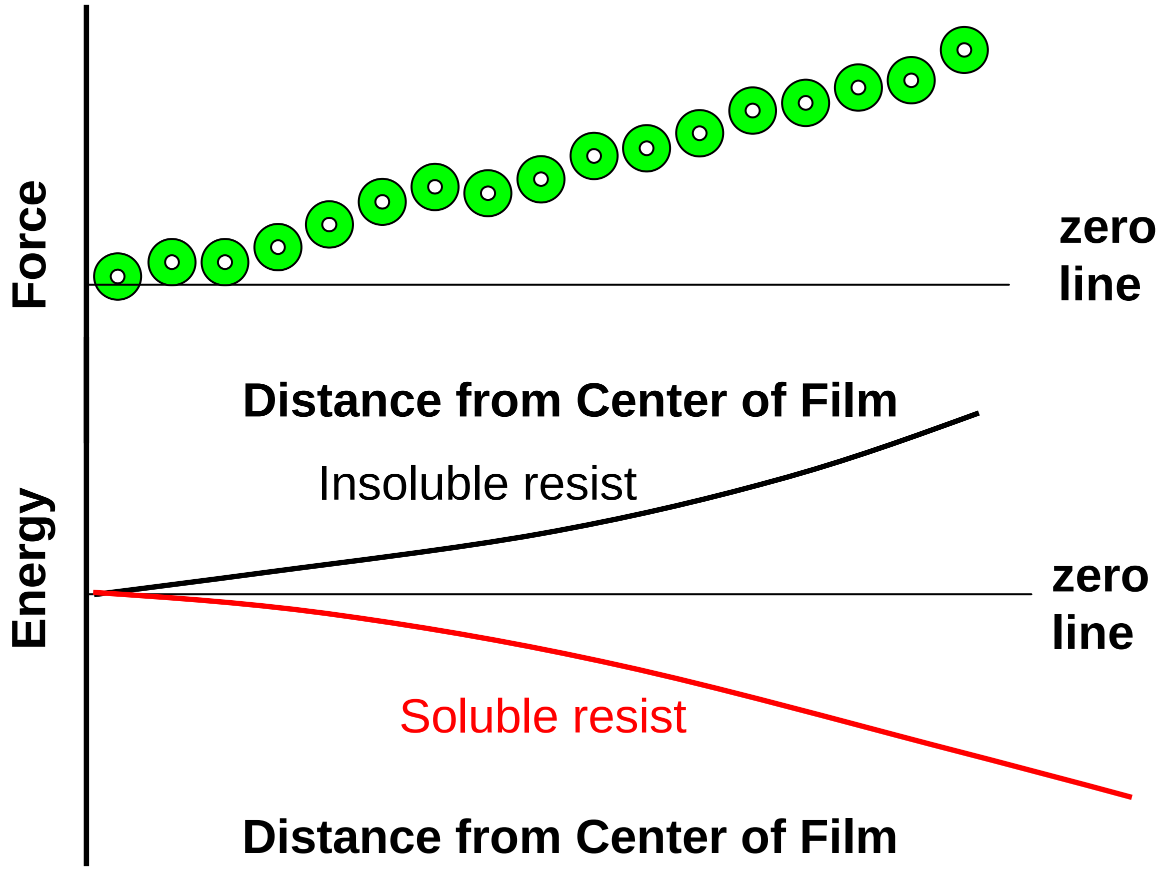
$$\Gamma_{i,j}(R) = \rho \int_0^R 4\pi r^2 \left(g(r)_{i,j} - 1\right) dr$$

$$\bar{v}_1^\infty = \frac{1}{\rho}\left[1 + x_2\left(\Gamma_{22}(\infty) - \Gamma_{12}(\infty)\right)\right]$$

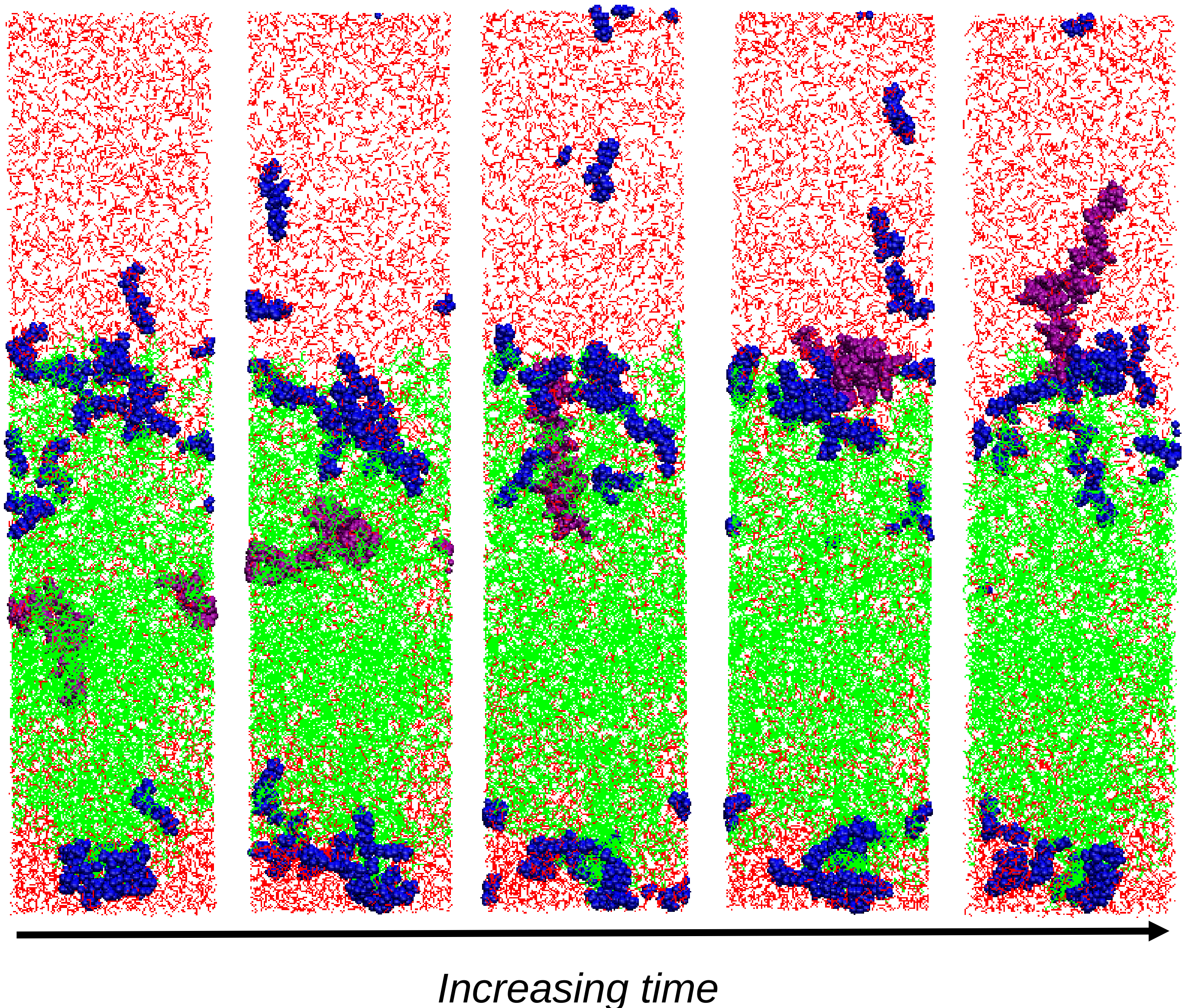
Thin Film Methods



$$F(z) = \int_{z}^{z_\infty} \langle f(z') \rangle \, dz' + F(z_o)$$

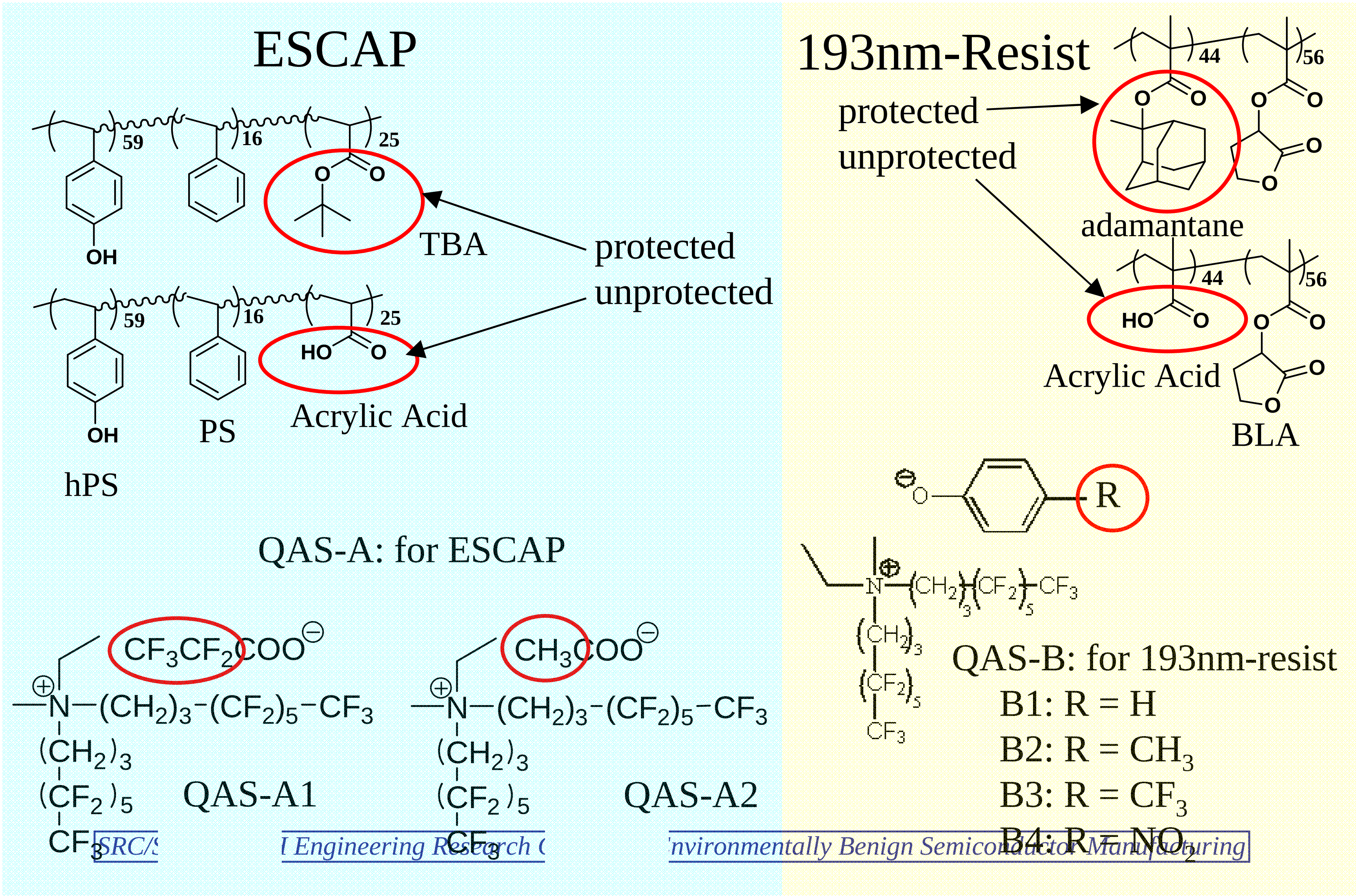


Chain Extraction: PHOST Configurations

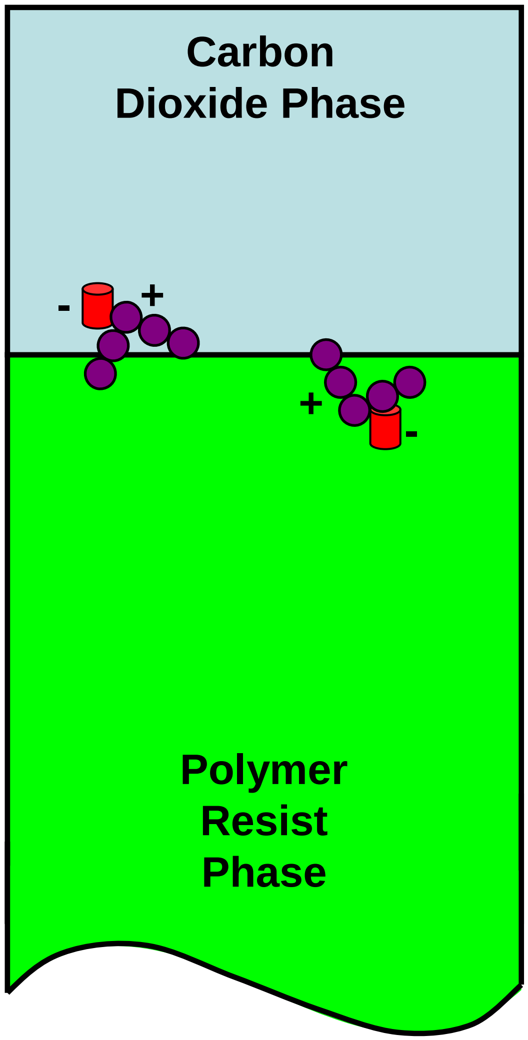


- **Purple** – pulled chain of PHOST
- **Red** – $scCO_2$
- **Green** – PHOST
- **Blue** – QAS-A2

Systems of Interest – Polymer Resists & Salts



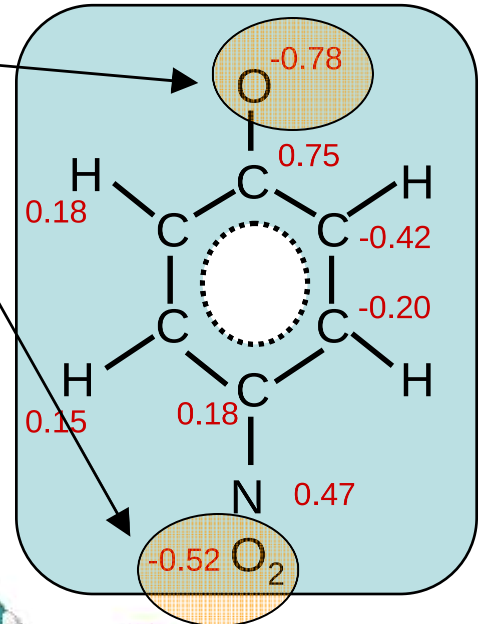
QAS-B4

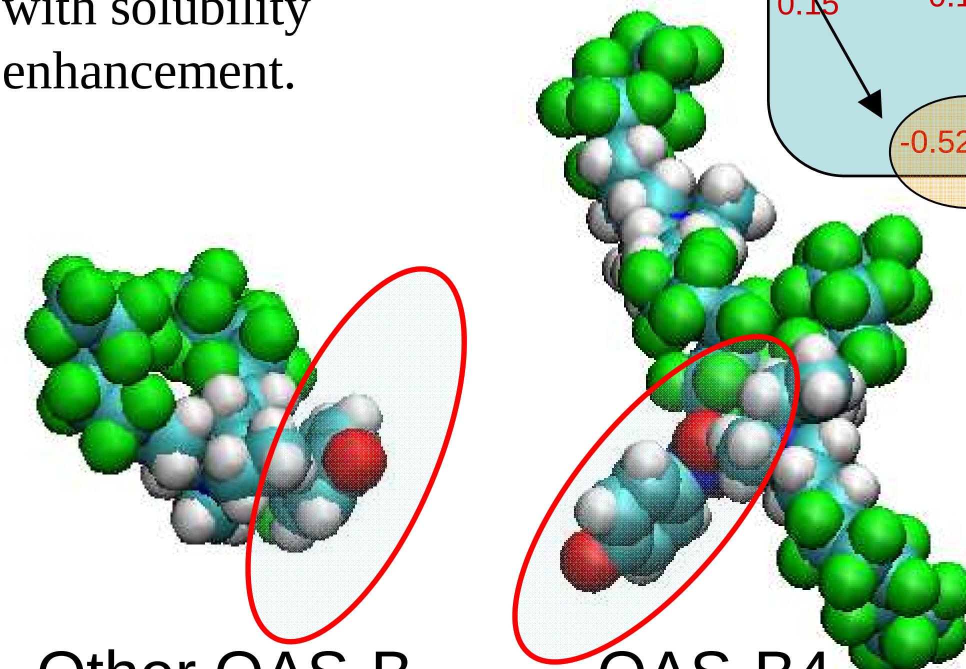


Surface Aggregation

- QAS-B4 charge delocalized
- QAS-B4 anion interacts with resist
- Surface aggregating salts with solubility enhancement.

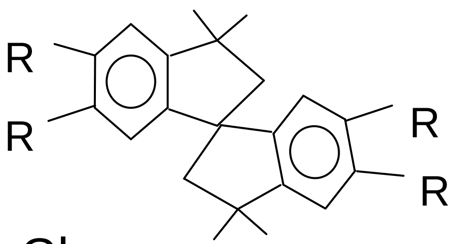
QAS-B4



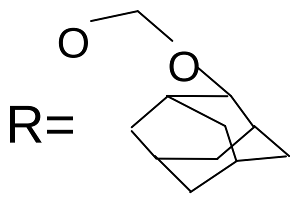


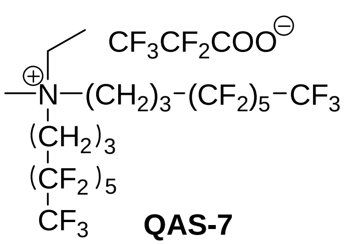
Other QAS-B QAS-B4

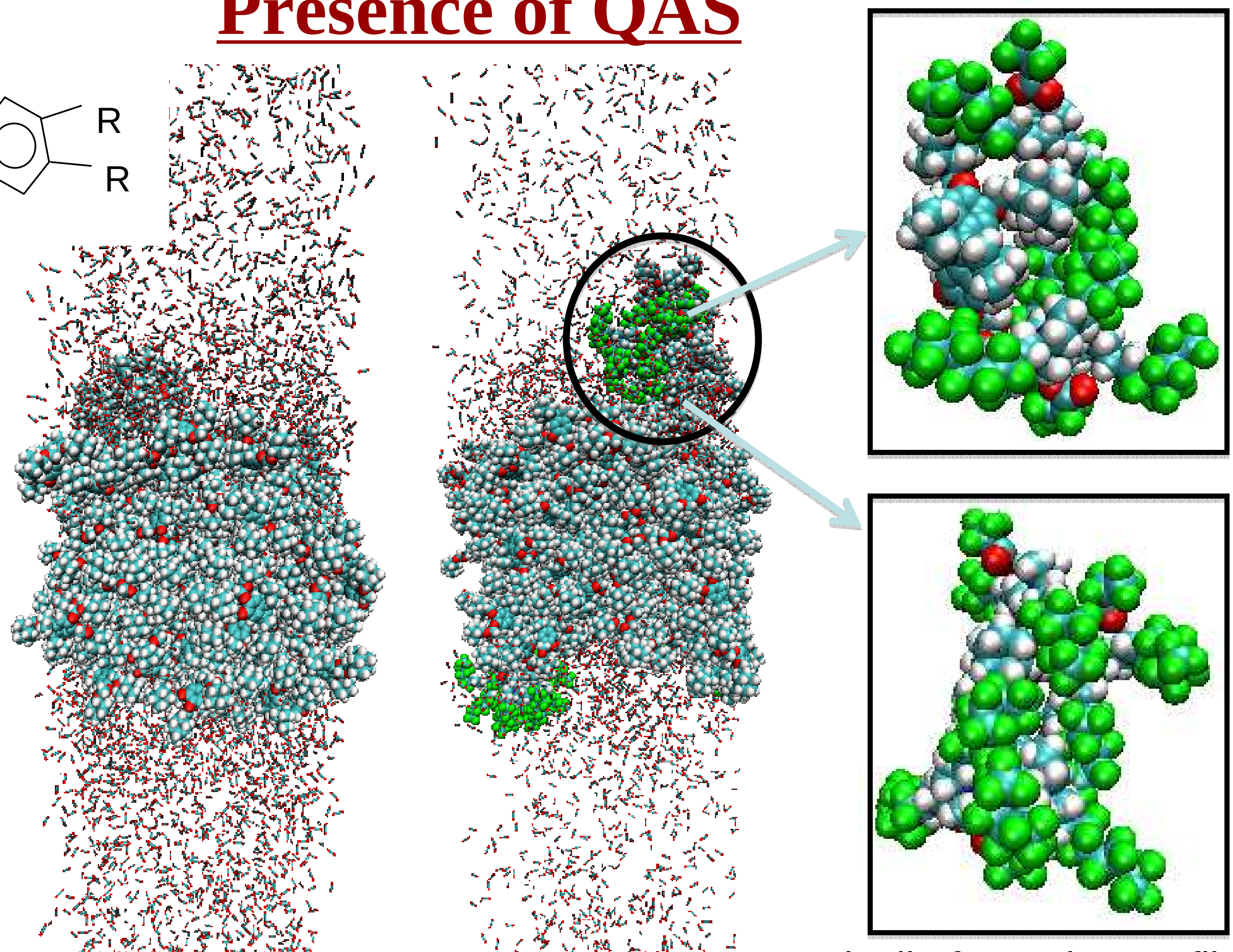
Ongoing Work: Molecular Glass in Presence of QAS



Glass







glass with no salt   glass with QAS7

Micelle formation on film surface

Delayed Activities (Watkins)

- Development of switchable additives to enhance solubility
- Release upon removal from CO_2 to enable recovery of the additive
- Use a cold-wall reactor to optimize performance, development conditions and reactor costs.
- Collaborative efforts with Ober (synthesis and processing) and (de Pablo) (computation) will help to better understand the relationships between additive structure and performance such that optimal materials can be designed.

A full-wafer high pressure CO_2 processing tool (DFP 200, BOC Edwards) located in the laboratories of Watkins at UMass.

Task Deliverables

- *Report on the simulation of a series of quaternary ammonium salts for resist development in $scCO_2$ and their mechanisms of dissolution (June 2009)*
- *Report on the preparation of a series of quaternary ammonium salts for resist development in $scCO_2$ (June 2009)*
- *Report on the use of a cold wall reactor for quaternary ammonium salts assisted resist development in $scCO_2$ (June 2009)*
- *Report on the simulation and molecular-level evaluation of new resist systems and processes for $scCO_2$ development (December 2009)*
- *Report on the preparation and lithographic evaluation of new QAS resist systems and processes for $scCO_2$ development (December 2009)*
- *Report on the interaction of base resist systems with supercritical CO_2 (December 2009)*

Fundamentals of Advanced Planarization: Pad Micro-Texture, Pad Conditioning, Slurry Flow and Retaining Ring Geometry

PI:

- **Ara Philipossian, ChEE, UA**
- **Duane Boning , EECS, MIT**

Graduate Students:

- **Yubo Jiao, ChEE, UA**
- **TBD, ChEE, UA**
- **Wei Fan, EECS, MIT**
- **Joy Johnson, EECS, MIT**

Other Researchers:

- **Yasa Sampurno, Research Associate, ChEE, UA**
- **Yun Zhuang, Research Associate, ChEE, UA**
- **Len Borucki, Araca**

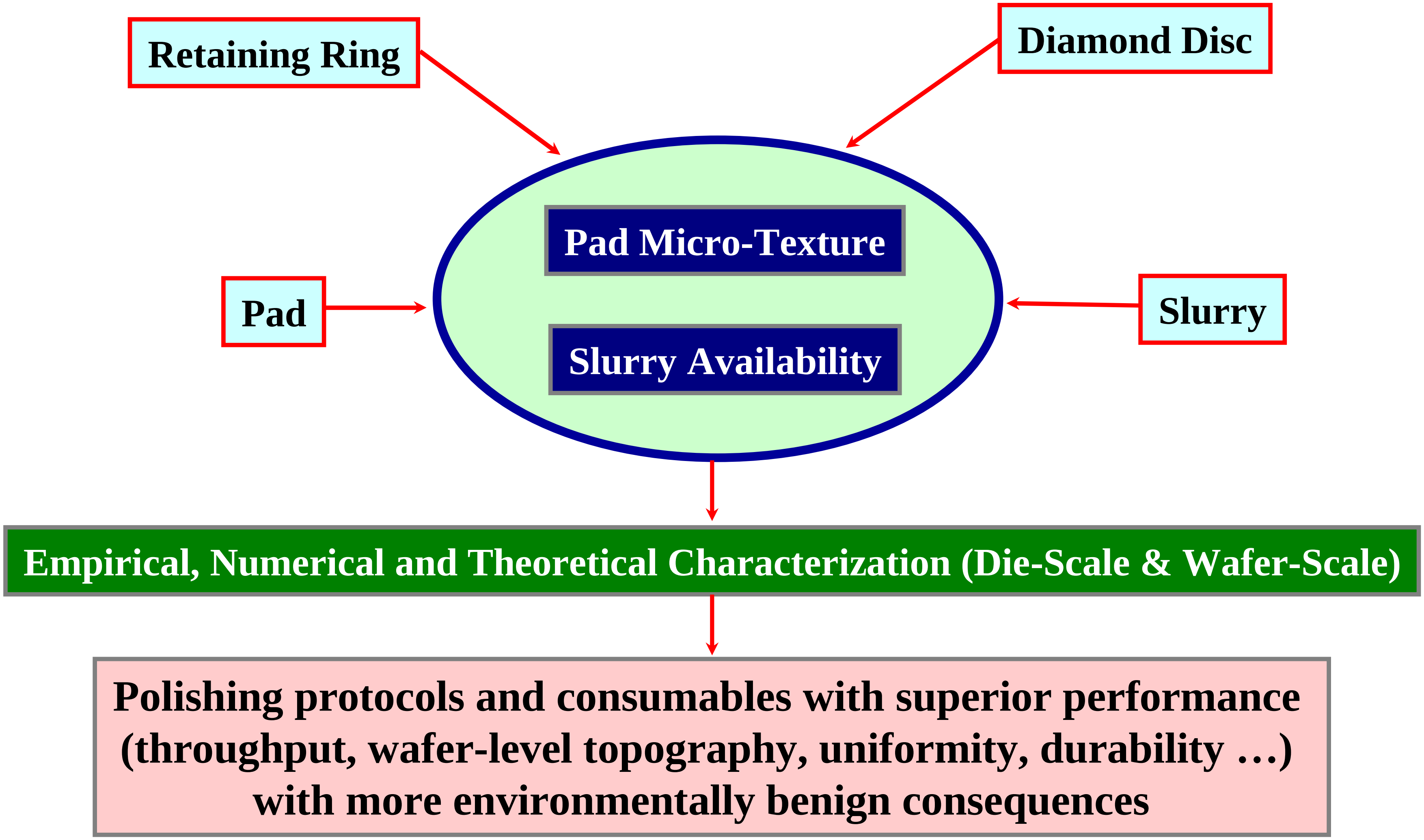
Primary Anticipated Result

- **Understand how pad micro-texture and slurry availability are fundamentally affected by:**
  - **Pad type (i.e. porous vs. non-porous, and various degrees of hardness)**
  - **Diamond disc type (i.e. grain size, and morphology)**
  - **Retaining ring type (i.e. PEEK vs. PPS, and various slot designs)**
  - **Slurry (i.e. flow rate and injection schemes)**

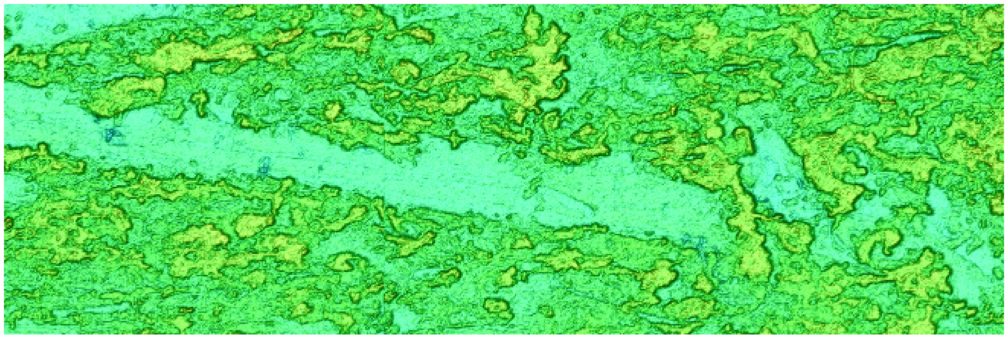
- **Via die-scale and wafer-scale empirical, theoretical and numerical methods, gain a deeper understanding of how the above:**
  - **Interact with one another**
  - **Affect polishing outcomes (on 200 and 300 mm rotary platforms)**
  - **Extendible to 450 mm rotary processes (theoretically)**

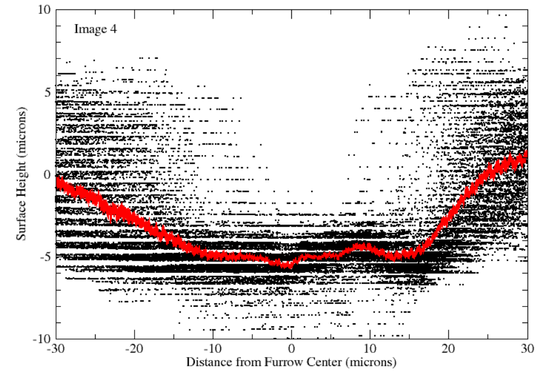
- **Ultimately, our goal is for this work to lead to new designs of polishing protocols and consumables with superior performance (i.e. wafer-level topography, uniformity, consumable durability, throughput …) and more environmentally benign consequences.**

Overall Scope

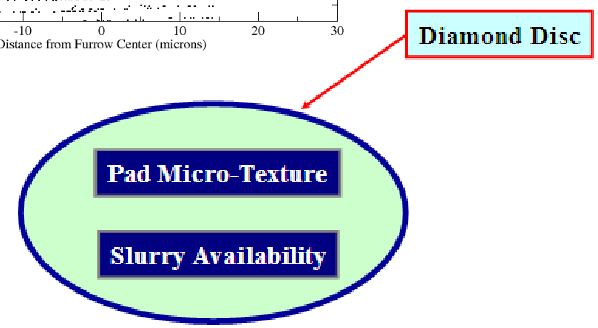


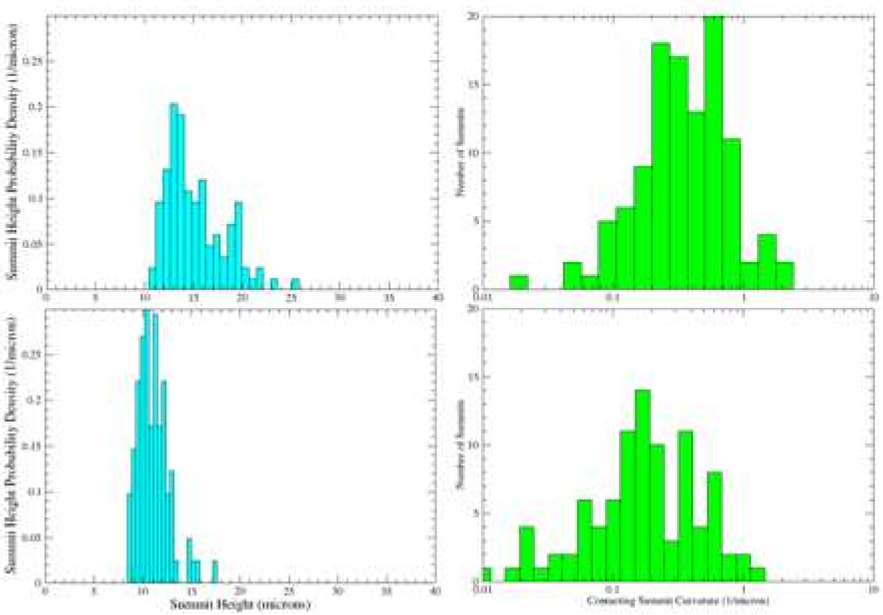
Diamond Morphology

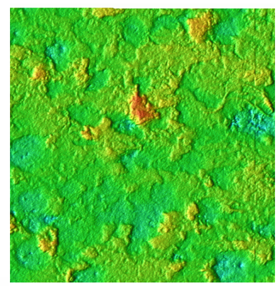




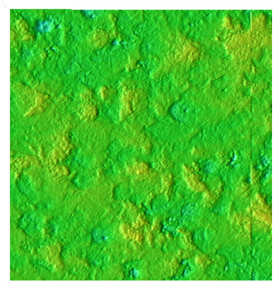
Source: Borucki (2008)





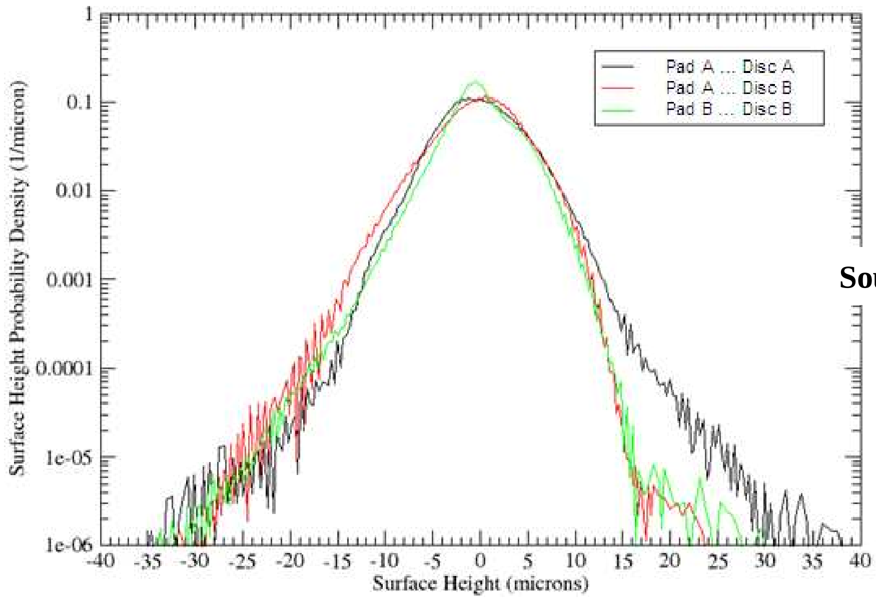


PCR = 44 micron per hr ; COF = 0.38 ;
Cu RR = 3,490 Angstrom per min

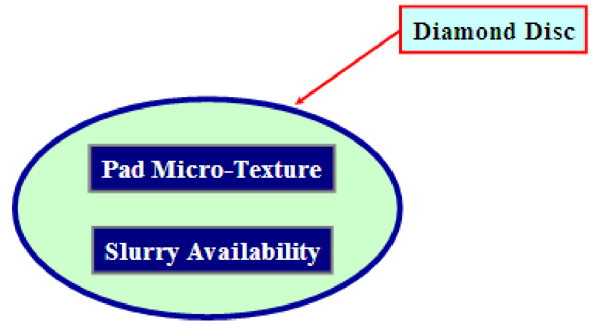


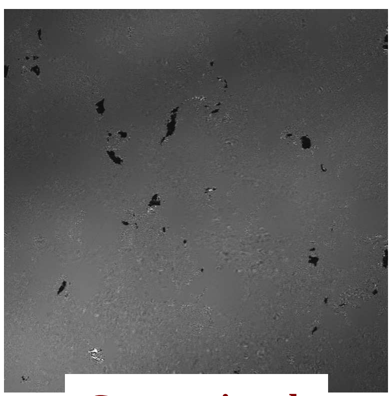
PCR = 19 micron per hr ; COF = 0.33 ;
Cu RR = 3,320 Angstrom per min

CVD vs. Conventional Diamonds

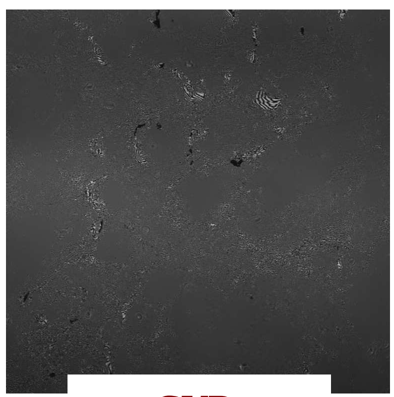


Source: Borucki (2008)

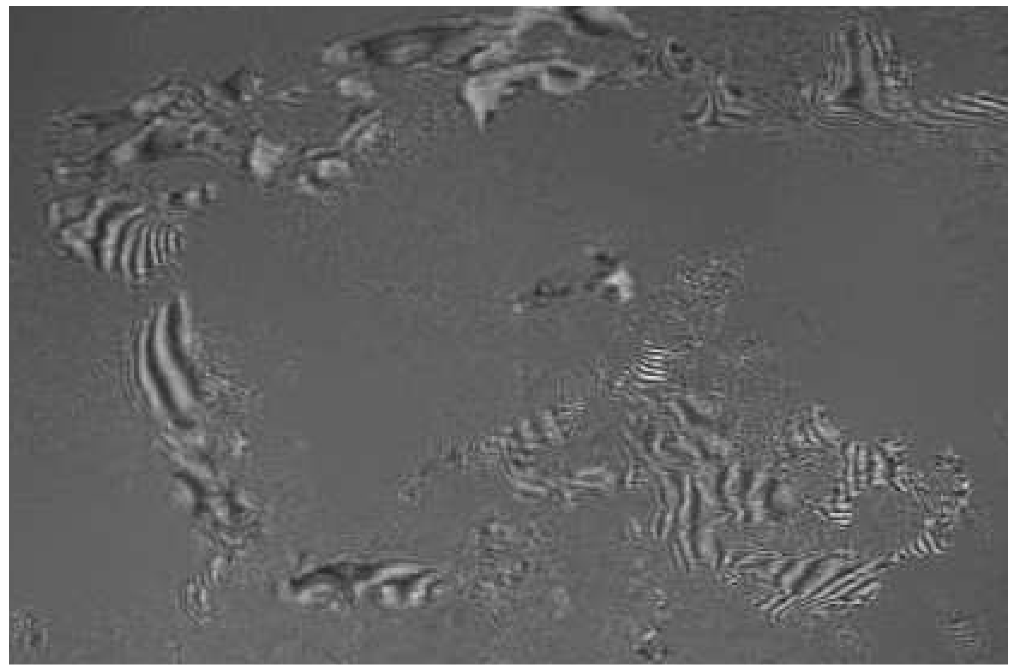




Conventional
Diamond Disc

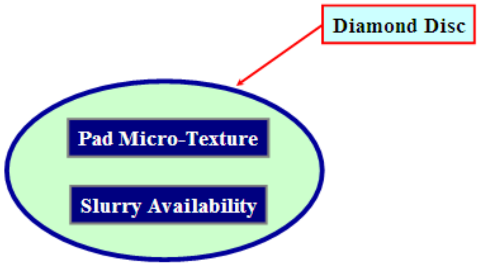


CVD
Diamond Disc

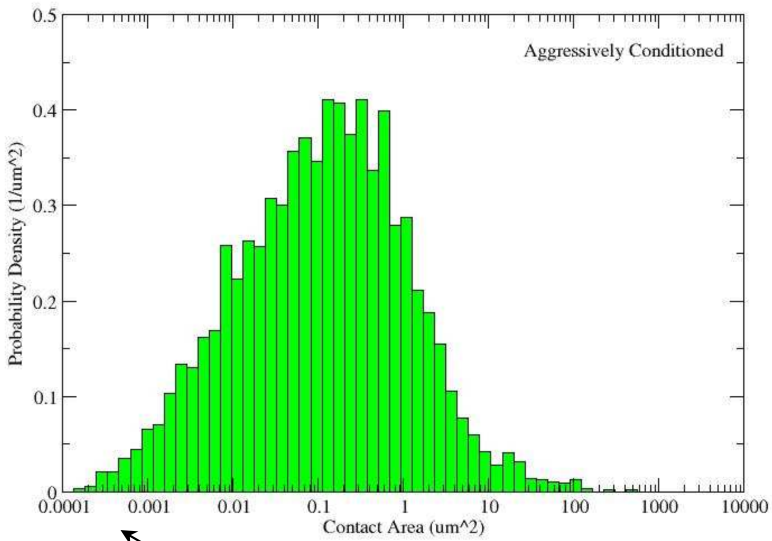


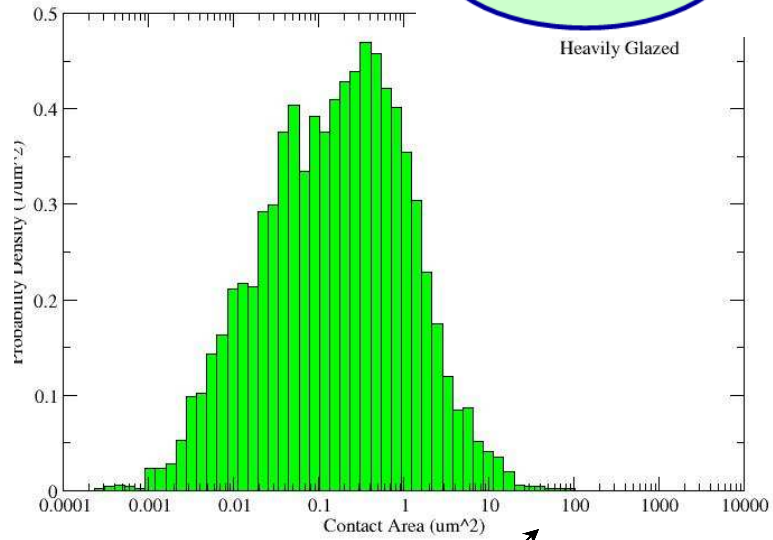
'Zebra Patterns' representing Near Contact Regions

Diamond Aggressiveness



Contact area histograms may be intimately related to polishing behavior



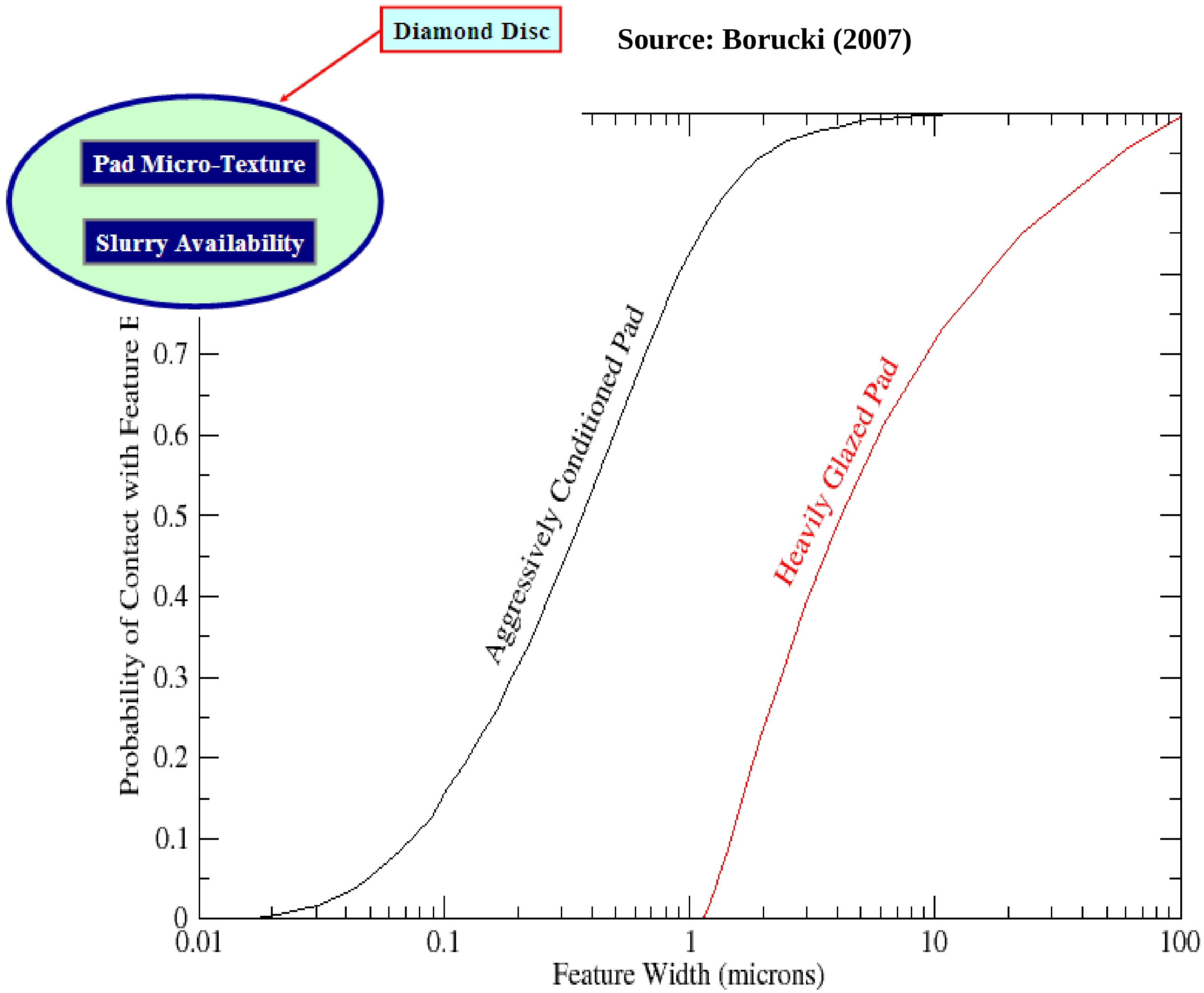


The aggressively conditioned pad has more contacts in the left-hand tail from tall "thin" asperities (i.e. 10 – 30 nm wide features). These presumably can reach into small features and reduce planarization efficiency. The heavily glazed pad by contrast has relatively few such contact areas.

The heavily glazed pad also has a deficit of large area contacts from tall "fat" asperities (i.e. 3 – 10 micron wide) relative to the aggressively conditioned pad. This may be responsible for a lower removal rate.

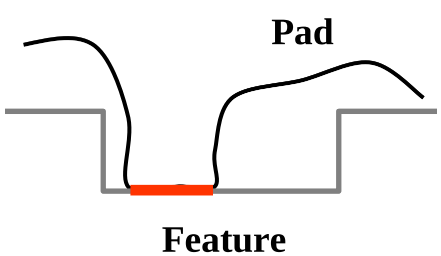
Diamond Aggressiveness

Source: Borucki (2007)



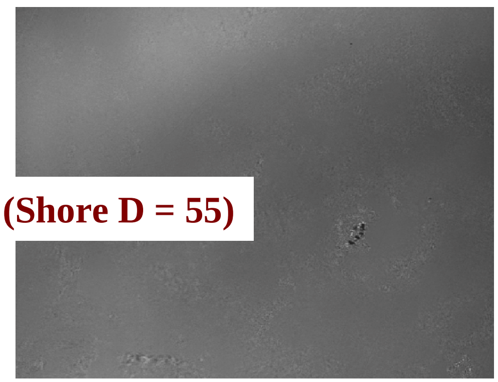
CONNECTION WITH PLANARIZATION

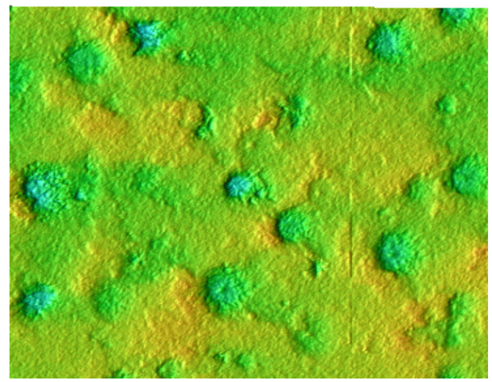
In this graph, the histograms from the previous slide have been processed to estimate the probability that a randomly chosen contacting asperity will be capable of contacting the bottom of a feature of a given width. While illustrated here for trenches, similar estimates can be made for other kinds of features.

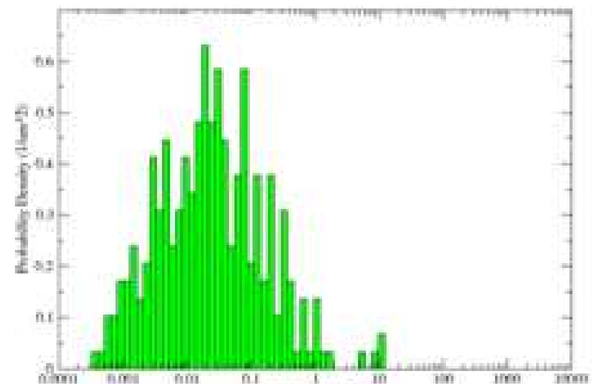


PU Pad Hardness

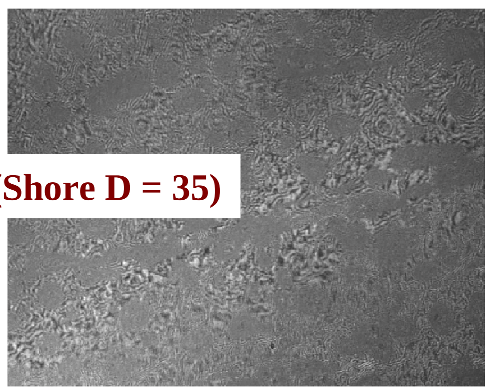
Hard Pad (Shore D = 55)

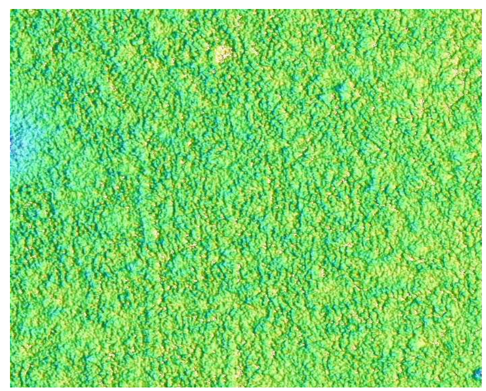


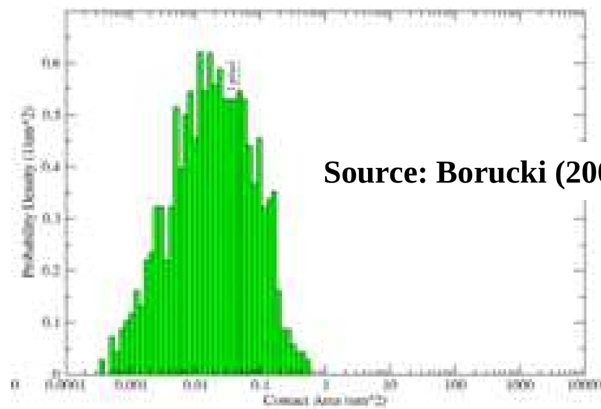




Soft Pad (Shore D = 35)

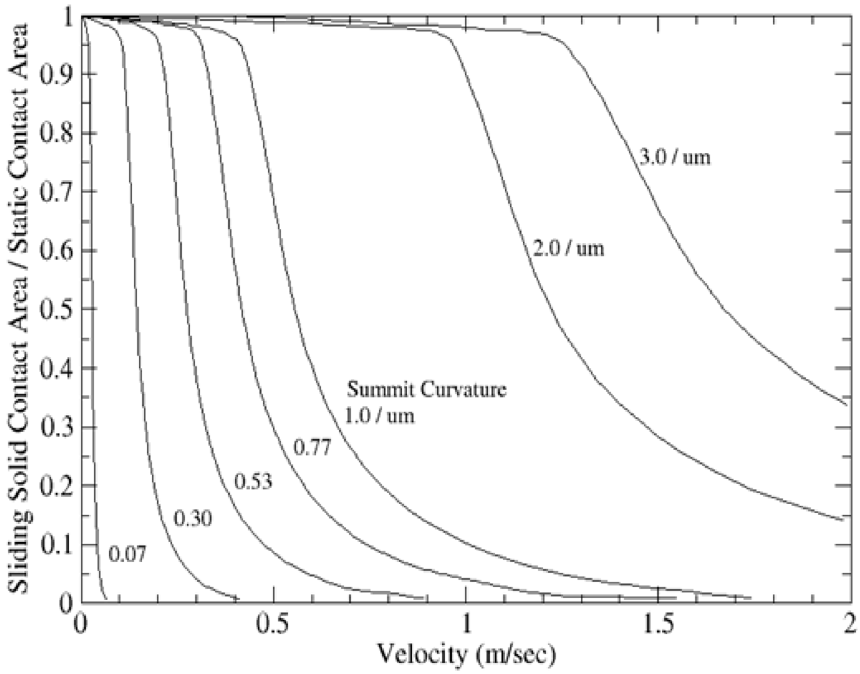




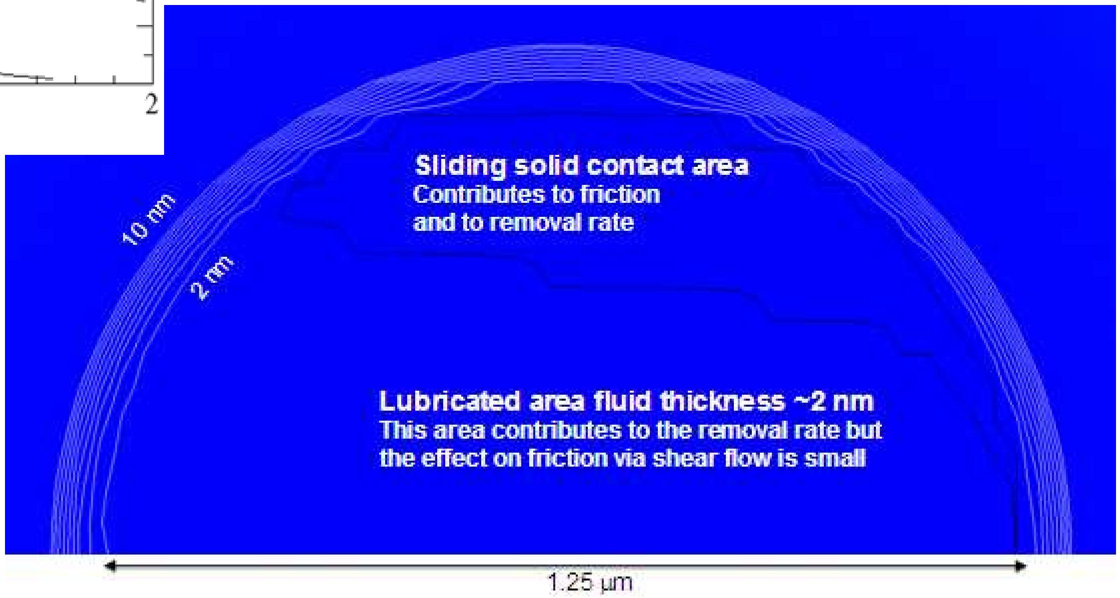


Source: Borucki (2009)

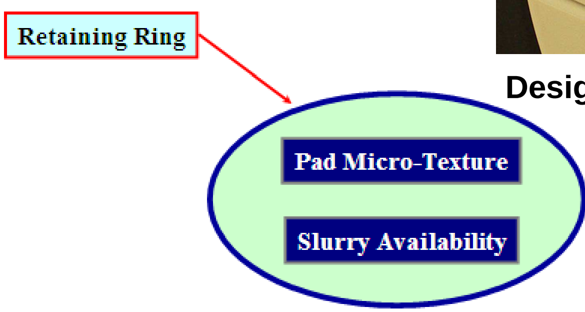
Modeling Contacting Solid Lubrication



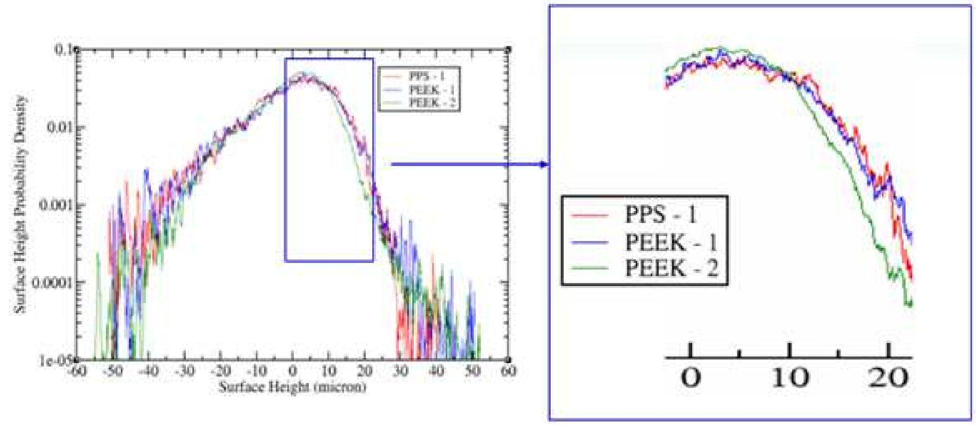
Source: L. Borucki (2009)



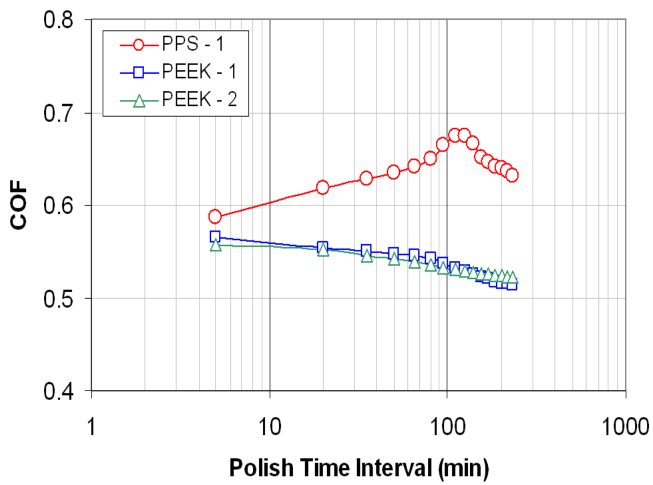
Retaining Ring Design

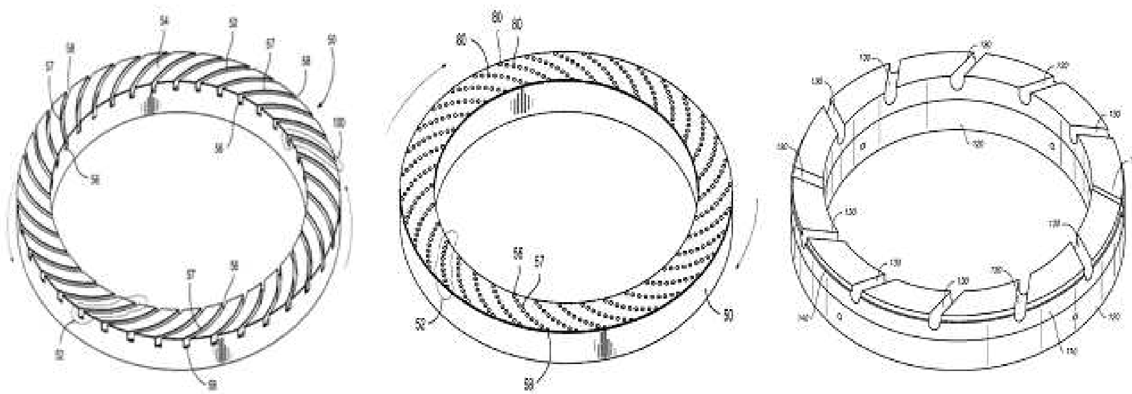


Design – 1   Design – 2



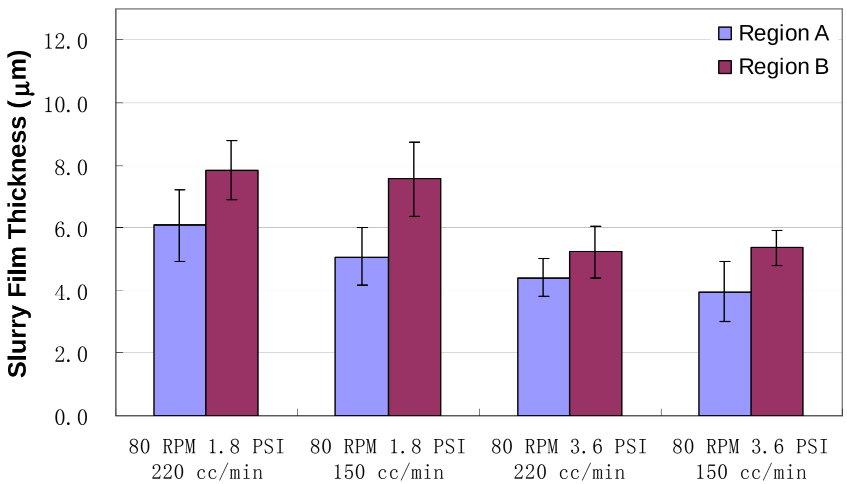
The PEEK – 2 ring achieves a narrower pad surface height distribution than the PPS – 1 and PEEK – 1 rings, suggesting that the slot design and the edge rounding plays significant roles in shaping the pad micro texture.

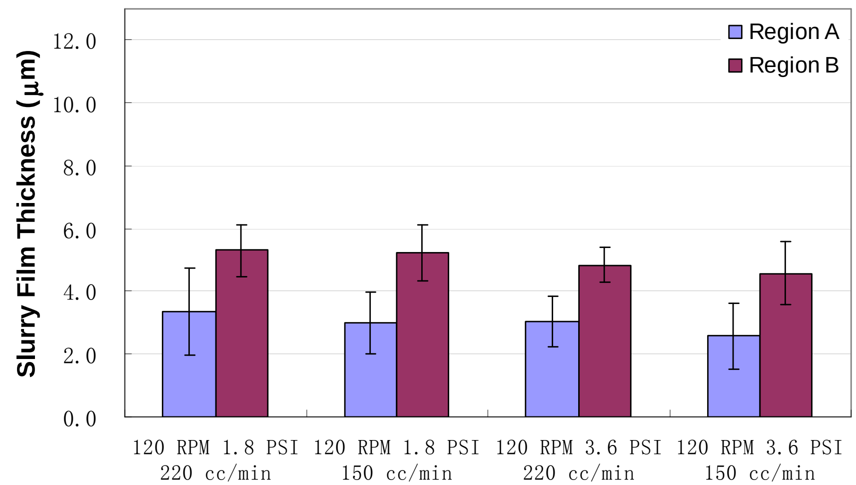


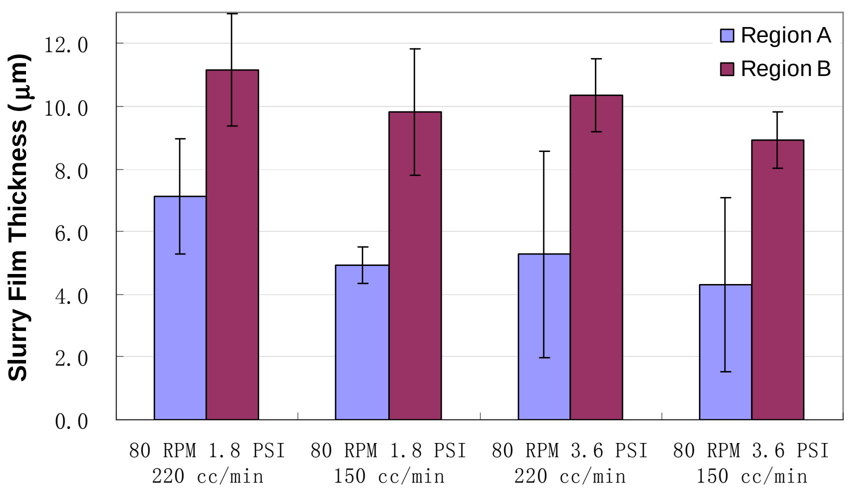


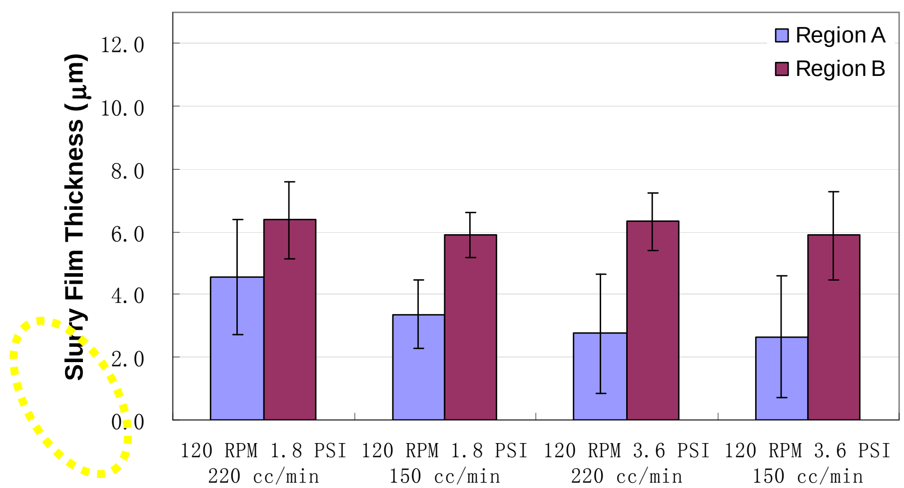
Slurry Film Thickness Measurement

STANDARD Ring (Top) and ALTERNATE Ring (Bottom)



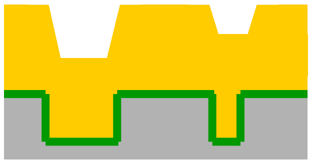




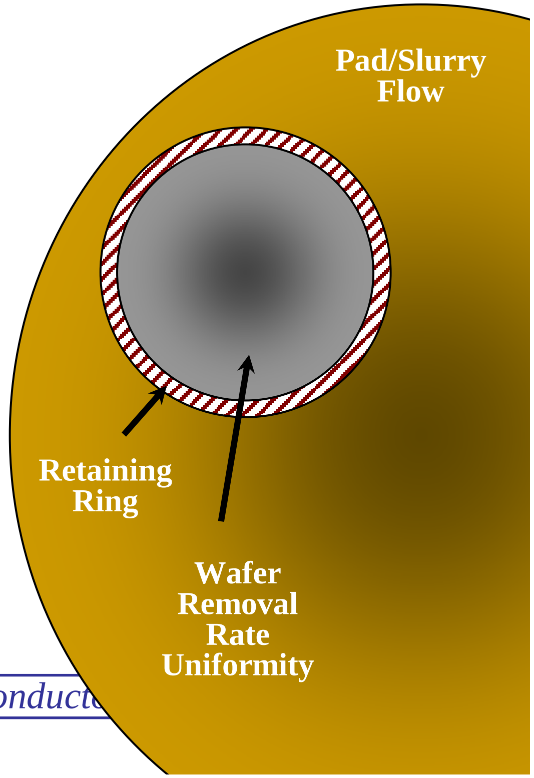


Wafer & Chip-Scale CMP Model: Retaining Ring Impact on Planarization

- **Previous work**
  - **Chip-scale and feature-scale layout pattern evolution**
  - **Pad modulus and pad asperity effects in a physically-based model**

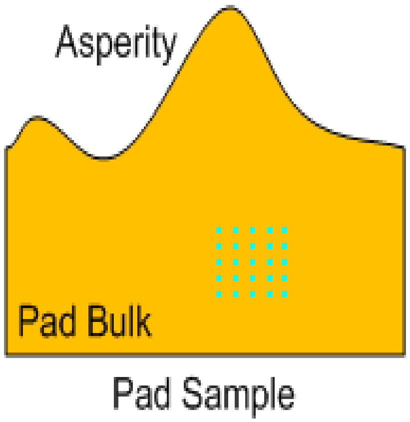


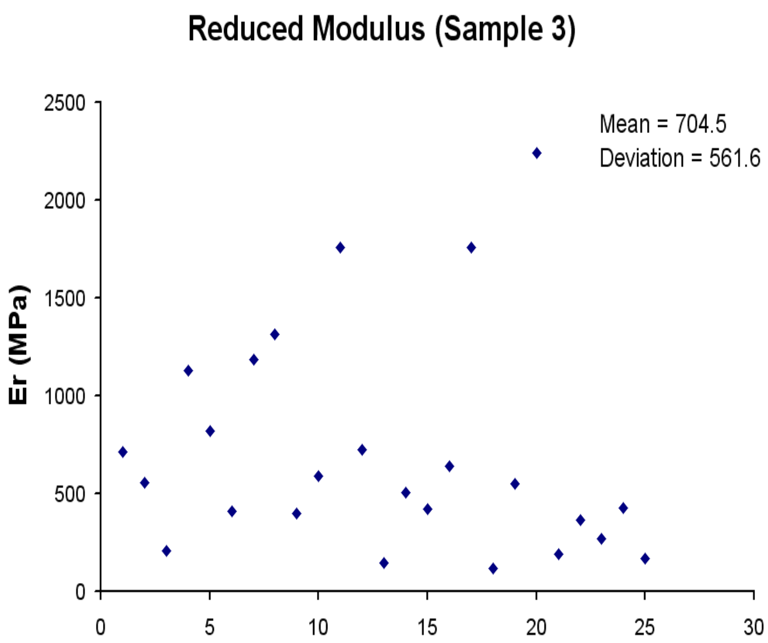
- **New work – CMP wafer scale model**
  - **Initial approach: empirical model relating retaining ring design options to wafer scale parameters:**
    - Pad microstructure (e.g. pad asperity distribution)
    - Other effects: slurry flow (affecting local removal rates)
- **New Work – Retaining ring/planarization model**
  - **Integrate wafer-level model with chip-scale and feature-scale model, to analyze impact on planarization**



Extended Die-Level CMP Model for Pad Microstructure Effects

- **Die-level models will be extended to incorporate key pad micro-structure dependencies to better predict dishing and erosion**
  - **Support pad-conditioning and retaining-ring studies**
- **Key effects:**
  - **Pad contact area**
  - **Asperity summit**
  - **Height distributions**
  - **Pad modulus *distributions***





Deliverables

- **Year – 1:**
  - **Build and qualify new portable dual emission UV-enhanced fluorescence (DEUVEF) system**
  - **Use DEUVEF technique to quantify slurry film thickness in pad-wafer interface, as well as bow wave effects, for various retaining rings**
  - **Complete initial wafer-level model relating pad-microstructure and slurry flow evolution to wafer-level planarity**
  - **Complete initial pad micro-texture analysis with laser confocal microscope for several industrially-relevant diamond discs**

- **Year – 2:**
  - **Quantify effect of retaining ring geometry design on slurry flow and pad micro-texture for several industrially-relevant pads (also with various groove designs)**
  - **Complete initial pad micro-texture analysis with laser confocal microscope for several industrially-relevant diamond discs**
  - **Complete extended die-level model incorporating pad-micro-structure and slurry dependencies in chip-scale prediction of dishing and erosion across each die**

Deliverables

- **Year – 3:**
  - **Relate pad micro-texture to shear forces during CMP**
  - **Complete integration of die-scale and wafer-scale models, relating uniformity of pad-microstructure and slurry flow characteristics across the wafer, to performance in multiple chips across the wafer**
  - **Harvest the predictability of the model to recommend new pad, diamond disc and retaining ring designs for improved polish performance and EHS metrics**
  - **Identify first-order scale up issue for 450 mm processes**

High-Dose Implant Resist Stripping (HDIS): Alternative to Ash/Strip Method

P10378

Srini Raghavan

Materials Science and Engineering
University of Arizona

High Dose, Low Energy Implants Used for

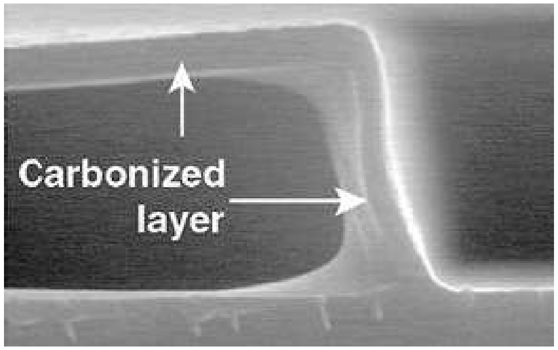
Formation of Shallow Junctions

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

PROPOSED WORK

***Overall Objective*:** **To find benign alternatives to super-hot SPM solutions currently being considered for *disrupting* carbonized crust on deep UV resist layers exposed to high dose (> 10^{15}/cm^2) arsenic ions**

Specific Tasks and Deliverables

- **Investigate suitable metal ion- hydrogen peroxide combinations (known as CHP) 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

. One doctoral student

- One undergraduate student

Improvement of ESH Impact of Back End of Line (BEOL) Cleaning Formulations Using Ionic Liquids to Replace Traditional Solvents
P10379

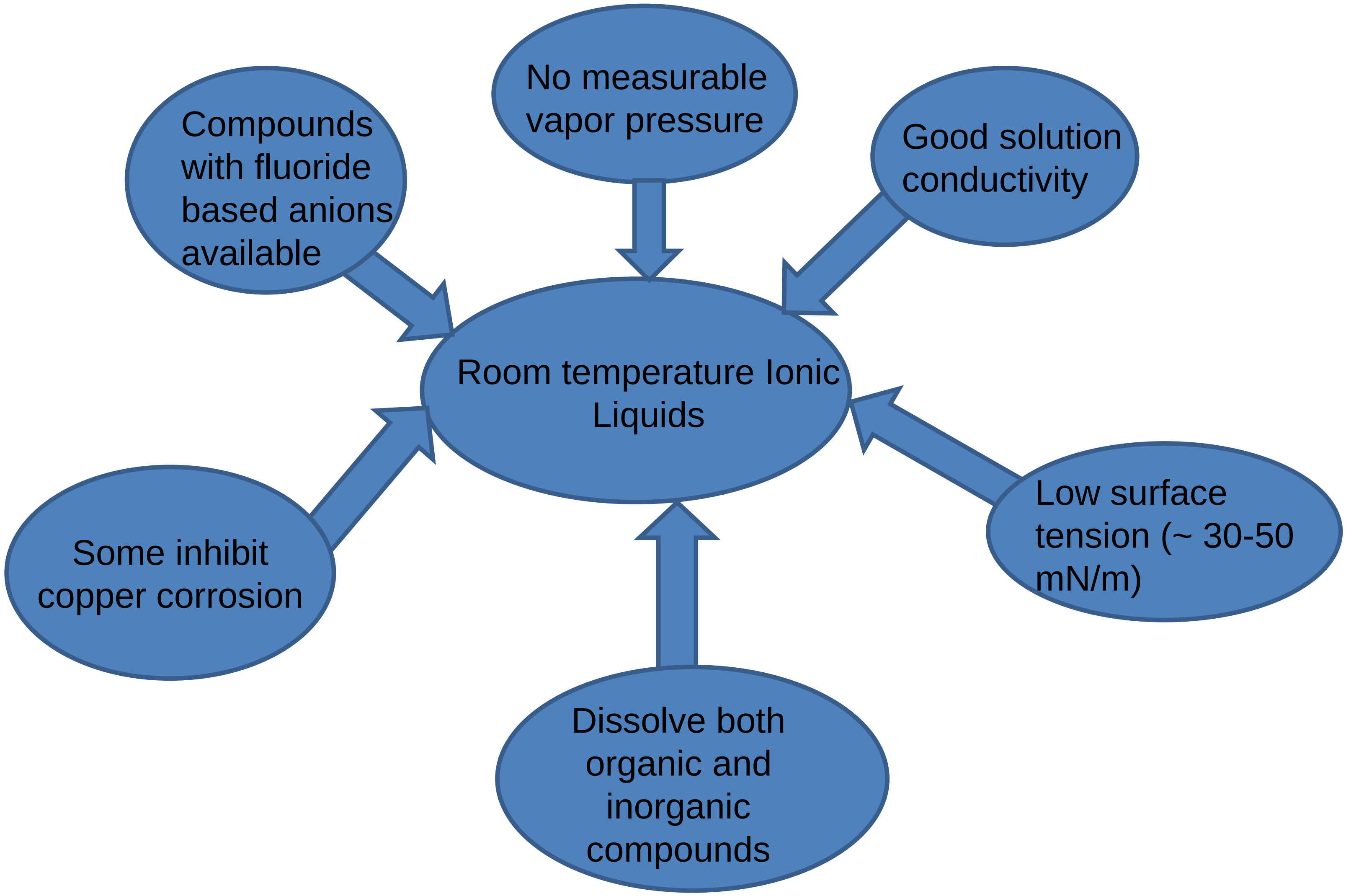
Srini Raghavan

Materials Science and Engineering
University of Arizona

OBJECTIVE

Explore Replacement of Traditional Solvents in BEOL Formulations with Room Temperature Ionic Liquids (RTIL)

- **IONIC LIQUIDS are ionic compounds that are liquid at room temperature**
- **Contain an organic cation and organic/inorganic anion**



Unique combination of properties makes ionic liquids an exciting choice for BEOL cleaning formulations

THREE SUBTASKS

Subtask 1:
Identify and Screen Suitable Ionic Liquids

Subtask 2:
Design cleaning formulations and evaluate them for Cu-low k cleaning

Subtask 3:
Determine Removal of Ionic Liquids by Rinsing

Industrial Mentors

- Dr. Robert Small , R. S Associates and formerly with Du Pont-EKC
- Dr. John Marsella , Air Products and Chemicals

PERSONNEL

- **One graduate student**
- **One undergraduate student**

Computational Models and High-Throughput Cellular-Based Toxicity Assays for Predictive Nanotoxicology

Task 1: High-Throughput Cellular-Based Toxicity Assays for Manufactured Nanoparticles

Task Leader: Dr. Russell J. Mumper, John A. McNeill Distinguished Professor;
Director, Center for Nanotechnology in Drug Delivery, School of Pharmacy, UNC-Chapel Hill

Task 2 : Develop Quantitative Nanostructure – Toxicity Relationships Models

Task Leader: Dr. Alexander Tropsha, K.H. Lee Distinguished Professor and Chair, Division of Medicinal Chemistry and Natural Products

Director, Carolina Exploratory Center for Cheminformatics Research, School of Pharmacy, UNC-Chapel Hill

Impact

ITRS Grand Challenge: 21. Chemical and Material Assessments (ESH)

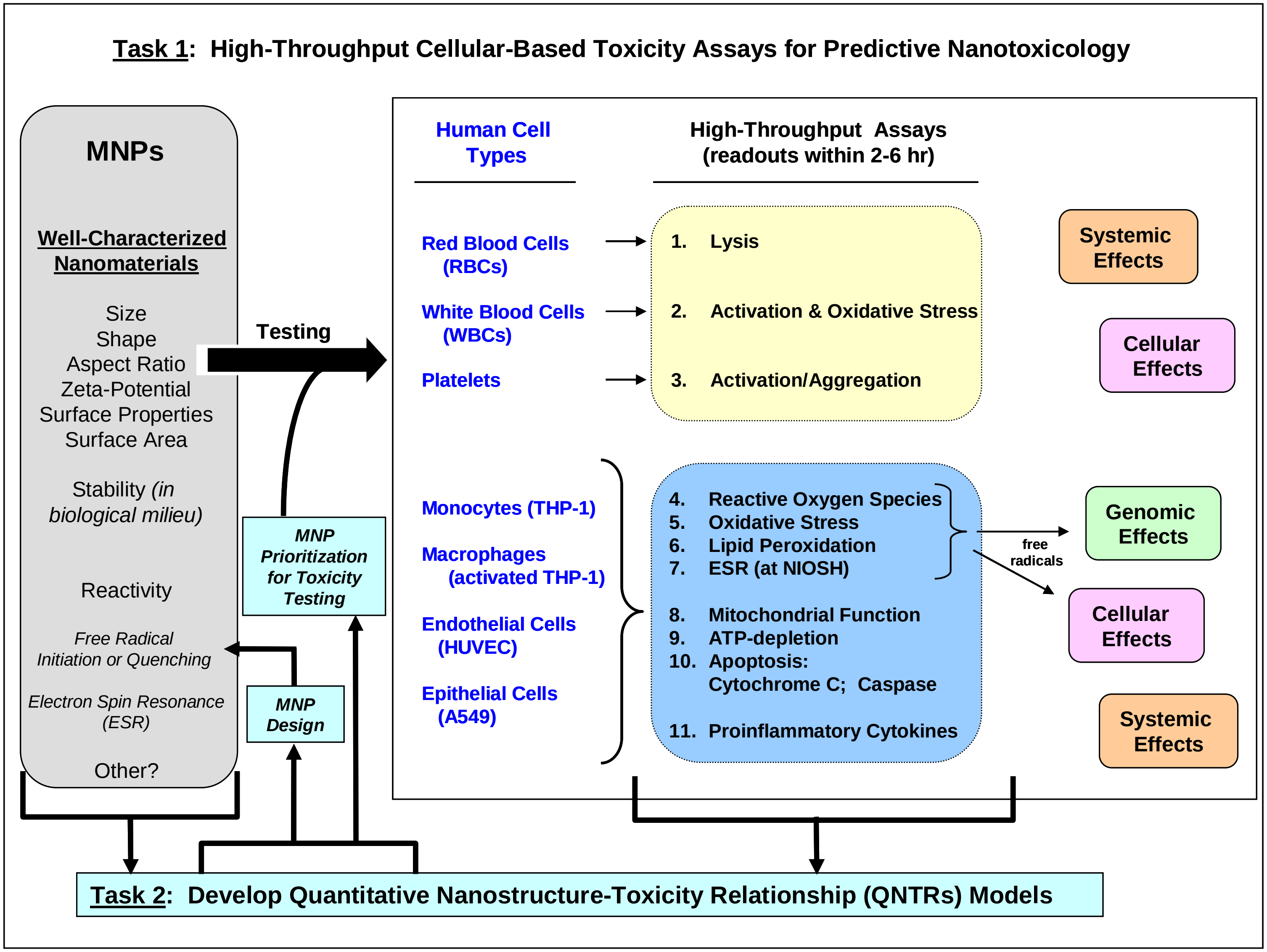
Anticipated Results

Obtain predictive knowledge of the physical/chemical properties of manufactured nanoparticles (MNP) that affect human cells and utilize this knowledge for improved MNP experimental design and prioritized toxicity testing.

Interaction with SRC/Partners

- ✓ **Potentially seamless interaction between the ESH Research Center and SRC member companies**
- ✓ **Send nanomaterials to UNC for characterization and analysis**
- ✓ **Analyze experimental data and build predictive QNTR models**
- ✓ **Prioritize MNP design and toxicity testing**
- ✓ **Provide continuous feedback of information for ESH and SRC member companies**

Approach



Task 1: High-Throughput Cellular-Based Toxicity Assays for Predictive Nanotoxicology
MNPs
Well-Characterized Nanomaterials
Size
Shape
Aspect Ratio
Zeta-Potential
Surface Properties
Surface Area
Stability (in biological milieu)
Reactivity
Free Radical Initiation or Quenching
Electron Spin Resonance (ESR)
Other?
Testing
MNP Prioritization for Toxicity Testing
MNP Design
Human Cell Types
High-Throughput Assays (readouts within 2-6 hr)
Red Blood Cells (RBCs)
White Blood Cells (WBCs)
Platelets
1. Lysis
2. Activation & Oxidative Stress
3. Activation/Aggregation
Systemic Effects
Cellular Effects
Monocytes (THP-1)
Macrophages (activated THP-1)
Endothelial Cells (HUVEC)
Epithelial Cells (A549)
4. Reactive Oxygen Species
5. Oxidative Stress
6. Lipid Peroxidation
7. ESR (at NIOSH)
8. Mitochondrial Function
9. ATP-depletion
10. Apoptosis: Cytochrome C; Caspase
11. Proinflammatory Cytokines
free radicals
Genomic Effects
Cellular Effects
Systemic Effects
Task 2: Develop Quantitative Nanostructure-Toxicity Relationship (QNTRs) Models

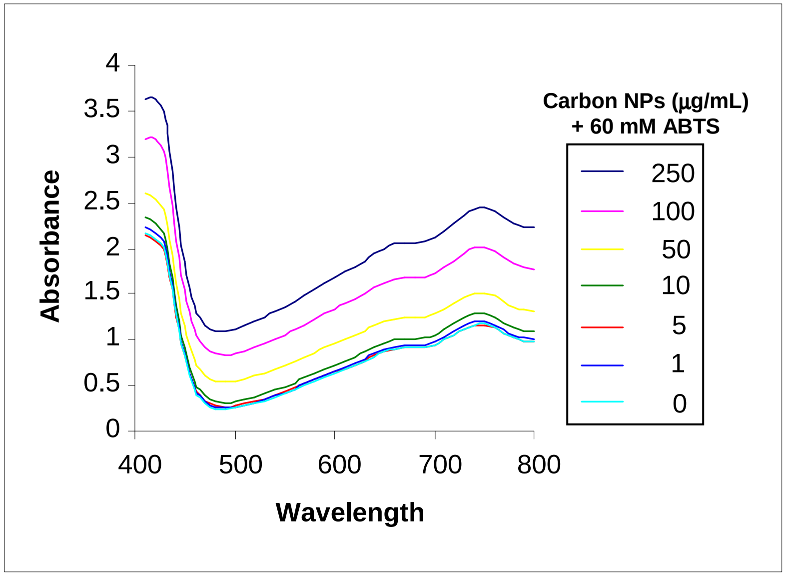
Current Cellular-based Assays

Human Cells	Assay	Description
Red Blood Cells (RBCs)	Lysis	Measure oxyhemoglobin at 540 nm
White Blood Cells (WBCs)	Activation	Measure reduction of ferricytochrome c caused by produced superoxide anions
	Oxidative Stress	Measure intracellular GSSG/GSH ratio; where GSSG is oxidized glutathione and GSH is reduced glutathione
Platelets	Activation	Flow cytometry to measure PAC-1-FITC binding to activated platelets
	Aggregation	Whole Blood Impedance Aggregometry

Human Cells	Assay	Description
Monocytes (THP-1) Macrophages (activated THP-1) Endothelial Cells (HUVEC) Epithelial Cells (A549)	Reactive Oxygen Species	1) Measure intracellular fluorescence produced with H_2DCFDA or carboxy-H_2DCFDA loaded cells; 2) Measure (a)cellular ESR
	Oxidative Stress	Measure intracellular GSSG/GSH ratio; where GSSG is oxidized glutathione and GSH is reduced glutathione
	Lipid Peroxidation	Lipid Hydroperoxide (LPO) Assay
	Mitochondrial Function	MTT assay & JC-1 assay
	ATP-depletion	ATPlite 1step® Assay Kit (PerkinElmer)
	Apoptosis:	
	Cytochrome C	Cytochrome C immunoassay
	Caspase-3	Caspase-3 Fluorometric Assay (R&D Systems); Quantify caspase-3 activation by cleavage of DEVD-AFC substrate
	Proinflammatory Cytokines	Cytokine assays by ELISA; NFKB, IL-1β, TNF-α, IFN-γ, IL-8

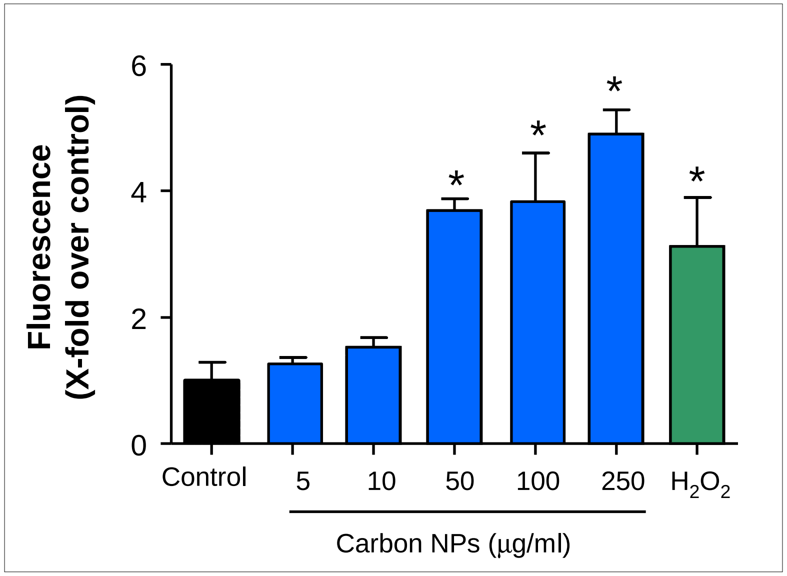
Example of (Bio)Reactivies of MNPs

Carbon NPs Initiate Free-Radical Reactions



Carbon NPs (n=3; at 0-250 µg/mL) in water were added to 60 mM ABTS at 25ºC for 24 hr and ABTS•+ was measured at 734 nm.

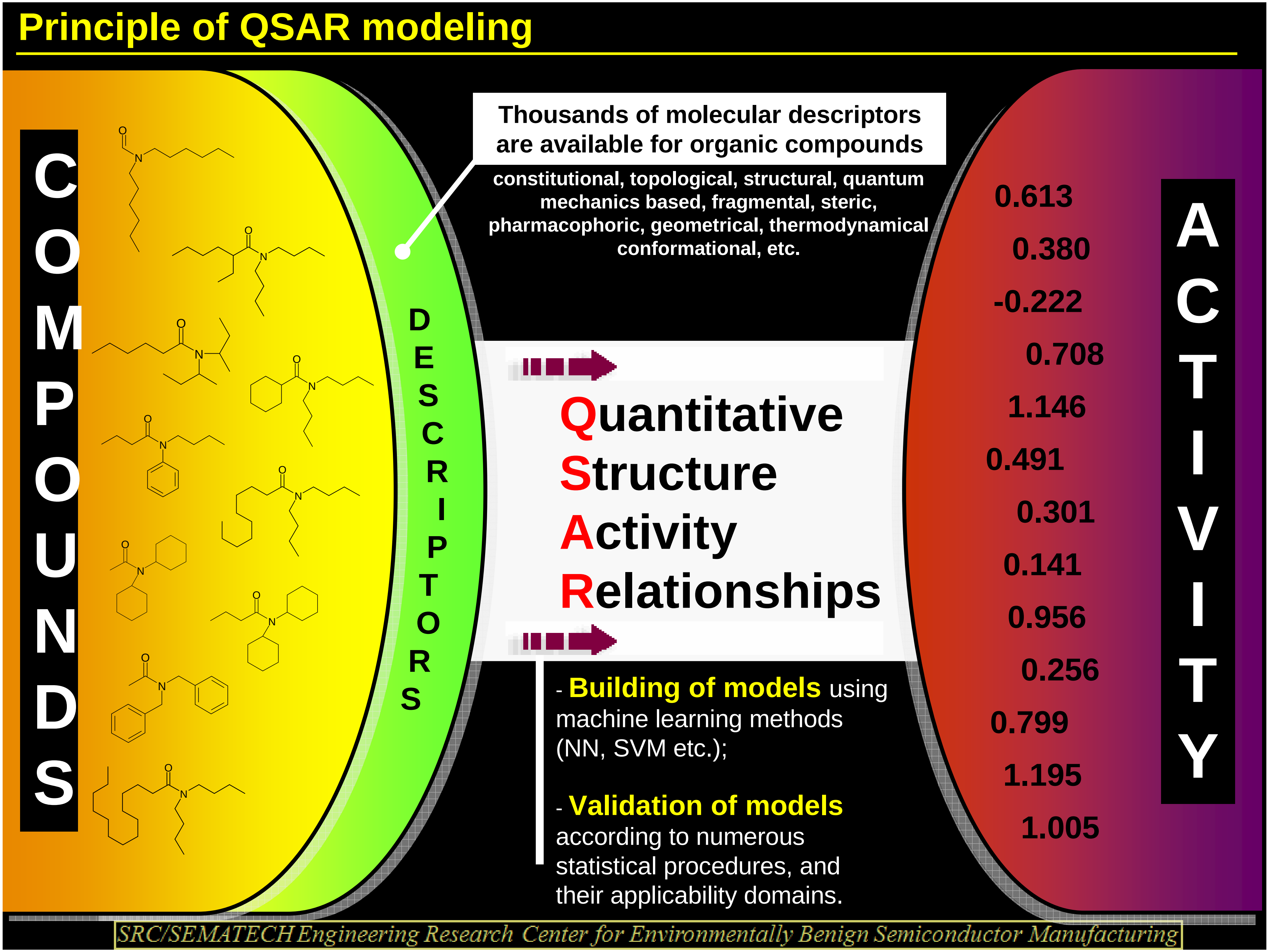
ROS Detection in A549 cells at 4 hr



25,000 cells; 25 µM carboxy H2DCFDA
100 mM H_2O_2 for 40 min was used as a positive control

Carbon NPs (55-100 nm)
American Elements
Cat. No. CM018 NP
Lot #: 117-139-217-9915

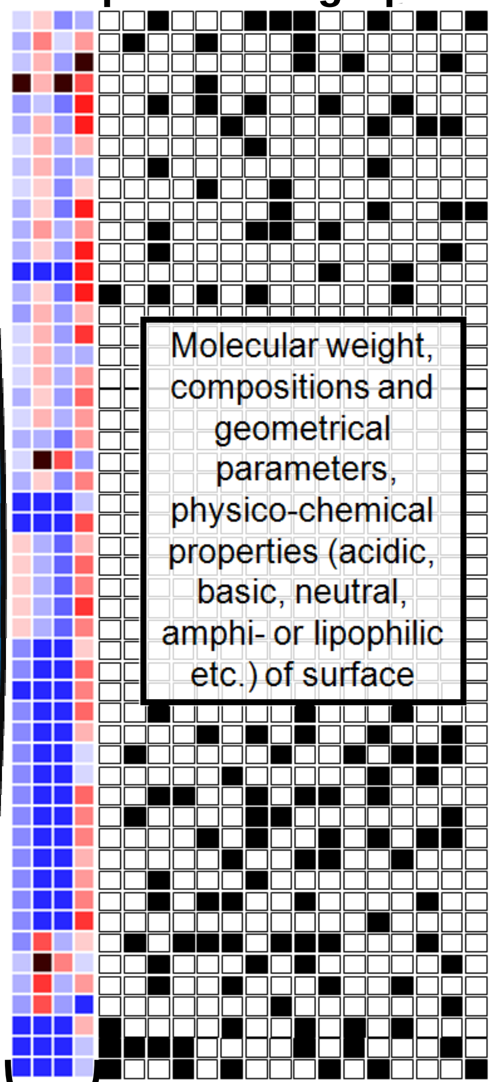
98% pure
Impurities include, among a few others:
Si (0.1%), Fe (0.08%), Cr (0.06%), Ni (0.05%)


Principle of QSAR modeling
COMPOUNDS
DESCRIPTORS
Thousands of molecular descriptors are available for organic compounds
constitutional, topological, structural, quantum mechanics based, fragmental, steric, pharmacophoric, geometrical, thermodynamical conformational, etc.
Quantitative
Structure
Activity
Relationships
- Building of models using machine learning methods (NN, SVM etc.);
- Validation of models according to numerous statistical procedures, and their applicability domains.
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
ACTIVITY
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Introducing the QNTR modeling

NANOMATERIALS

Nanoparticle fingerprints



DESCRIPTORS

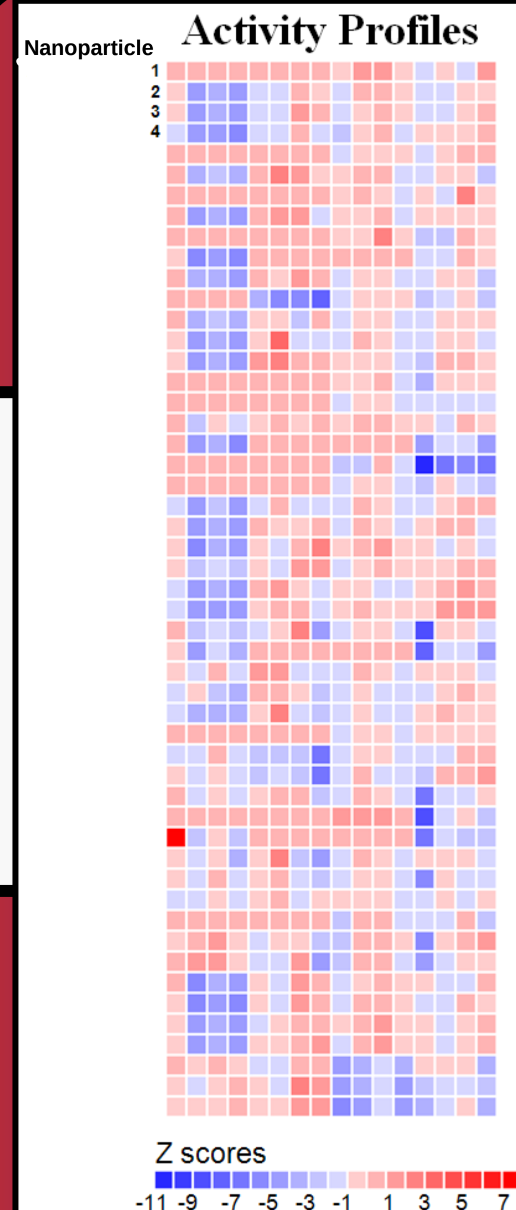
Experimental measurements
(size, relaxivities, zeta potential etc.)

Quantitative
Nanostructure
Toxicity
Relationships

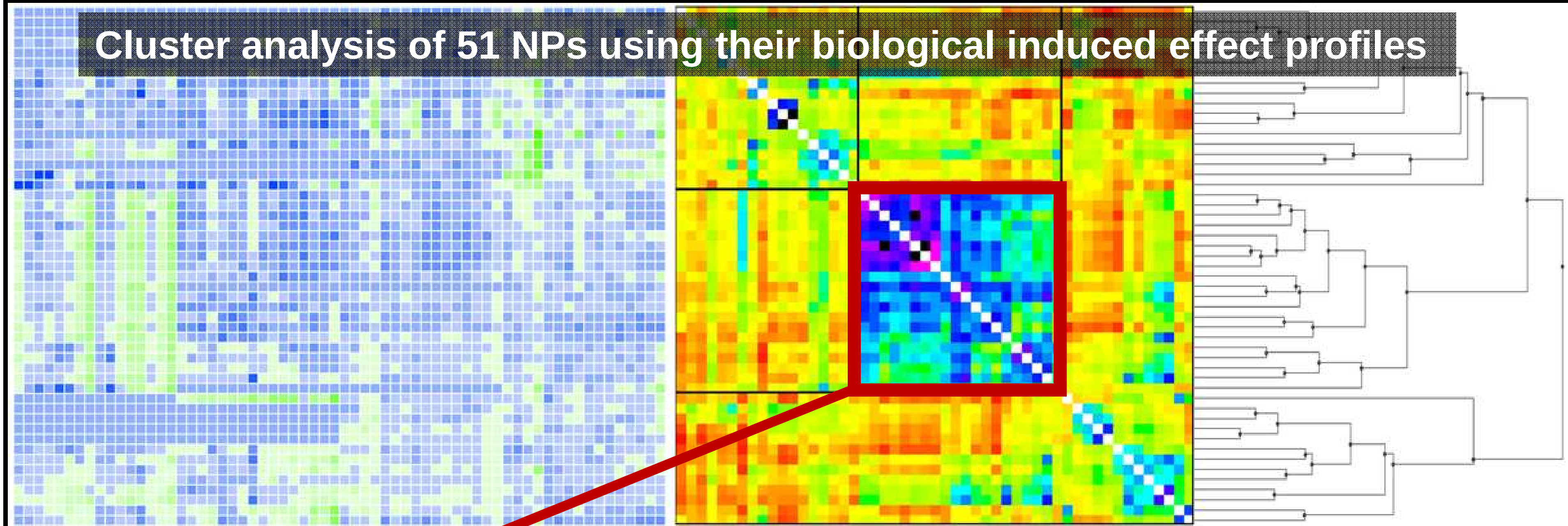
- **Building of models** using machine learning methods (NN, SVM etc.);

- **Validation of models** according to numerous statistical procedures, and their applicability domains.

Activity Profiles



Preliminary modeling results – case study 1



Recently[1], 51 NPs were tested in-vitro against 4 cell lines in 4 different assays at 4 different concentrations. We applied our QNTR approach to classify NPs according to their biological effects using 4 measured descriptors.

TYPE OF MNP	CLUSTER 1	CLUSTER 2	CLUSTER 3	Total
CLIO	7	13	3	23
PNP	7	2	10	19
MION	0	4	0	4
Qt-dot	3	0	0	3
Feridex	0	1	0	1
Ferrum Haussmann	1	0	0	1
Total	18	20	13	

MNP Core	CLUSTER 1	CLUSTER 2	CLUSTER 3	Total
Fe_2O_3	5	0	9	14
Fe_3O_4	9	20	4	33
Cd-Se	3	0	0	3
Fe(III)	1	0	0	1
Total	18	20	13	

QNTR modeling of the biological effects (Z score avg.) for 44 MNPs using MML-WinSVM program, 4 descriptors and a 5-fold cross validation procedure

Fold	MODELING SET				EXTERNAL SET				
	n	# models	% accuracy internal 5-fold CV	% accuracy	*n*	% accuracy	% CCR[a]	% Sensitivity	% Specificity
1	35	11	51.4 – 60.0	71.4 – 82.9	9	**78**	83	67	100
2	35	13	51.4 – 60.0	71.4 – 77.1	9	**78**	75	50	100
3	35	16	57.1 – 62.9	74.3 – 82.9	9	**78**	78	80	75
4	35	11	60.0 – 62.9	77.1 – 88.6	9	**56**	55	50	60
5	36	4	66.7	83.3 – 86.1	8	**75**	67	33	100
					44	**73**	**73**	**60**	**86**

[a]CCR – Correct Classification Rate.

PREDICTION ACCURACY

[1] Shaw et al. Perturbational profiling of nanomaterial biologic activity. PNAS, 2008, 105, 7387-7392

- Preliminary modeling results demonstrate that QNTR models can successfully predict the toxicological properties of existing NPs as well as their biological effects for certain cell lines.

- Novel cheminformatics QNTR approaches suggested in this study provide the ability to predict numerous biological effects induced by new or yet-to-discovered NPs.

- To increase the prediction performance, we need more experimental data to build our models. Therefore we are ready to collaborate with any SRC member. Our team will be able to analyze and build predictive QNTR models for experimental nanotoxicity data generated by EHS collaborators.

Deliverables

Task 1: High-Throughput Cellular-Based Toxicity Assays for Manufactured Nanoparticles

Year 1	Validation of high-throughput cellular-based toxicity assays for MNP assessment Completion of data package for initial set of MNPs Begin to test Maps from ESH and SRC member companies
Year 2	Test QNTR model using the predictive models developed in Task 2 Continue to test Maps from ESH and SRC member companies
Year 3	Complete data package for Maps from ESH and SRC member companies Complete final report with recommendations for future Cellular-Based Toxicity Assays for Maps

Task 2: Develop Quantitative Nanostructure – Toxicity Relationships Models

Year 1	Compile all available experimental data on MNPs; Develop QNTR models that correlate the compositional/physical/chemical/geometrical and biological descriptors of MNPs with known toxicological endpoints
Year 2	Improve the prediction performance of QNTR models with the availability of new experimental data from Task 1; Analyze the relationships between assays for experimental test prioritizations
Year 3	Create an integrated nanotoxicology web-portal to enable free access of the scientific community to data and models that are collected or generated in the course of this project