SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Program Overview

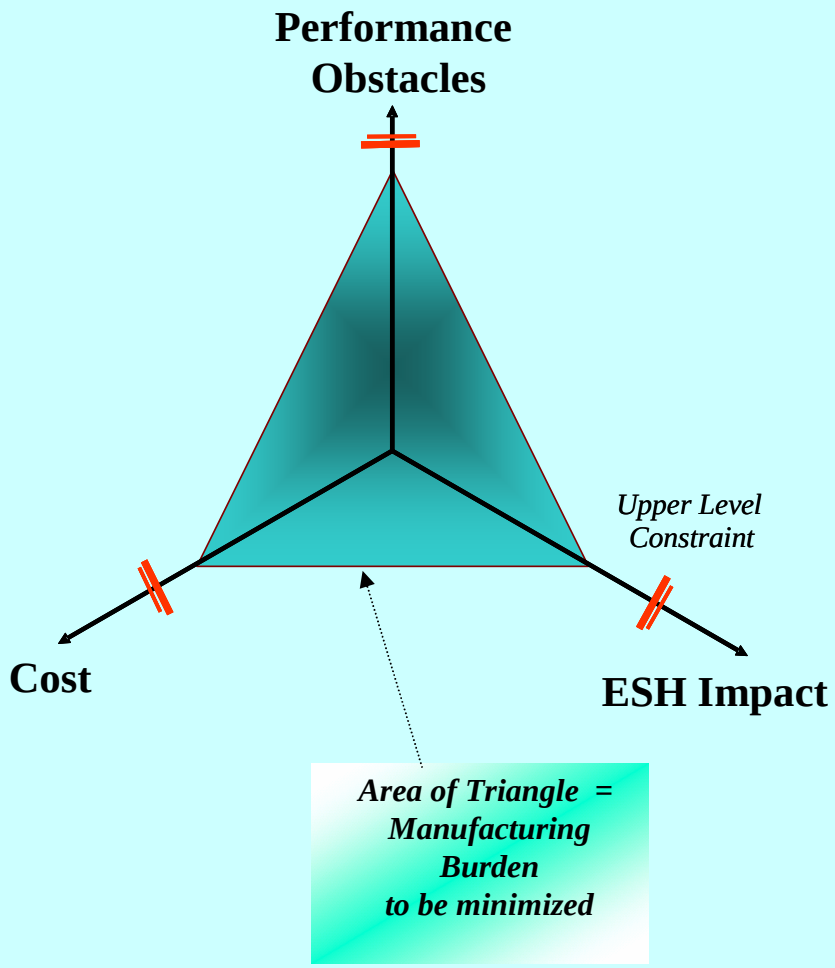
Annual ERC Meeting
February 22-23, 2007

Outline of Presentation

- A short background and some statistics on the ERC
- Report on overall ERC activities and progress during the last year
- Future plan and proposed changes

ERC Mission and Objectives

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

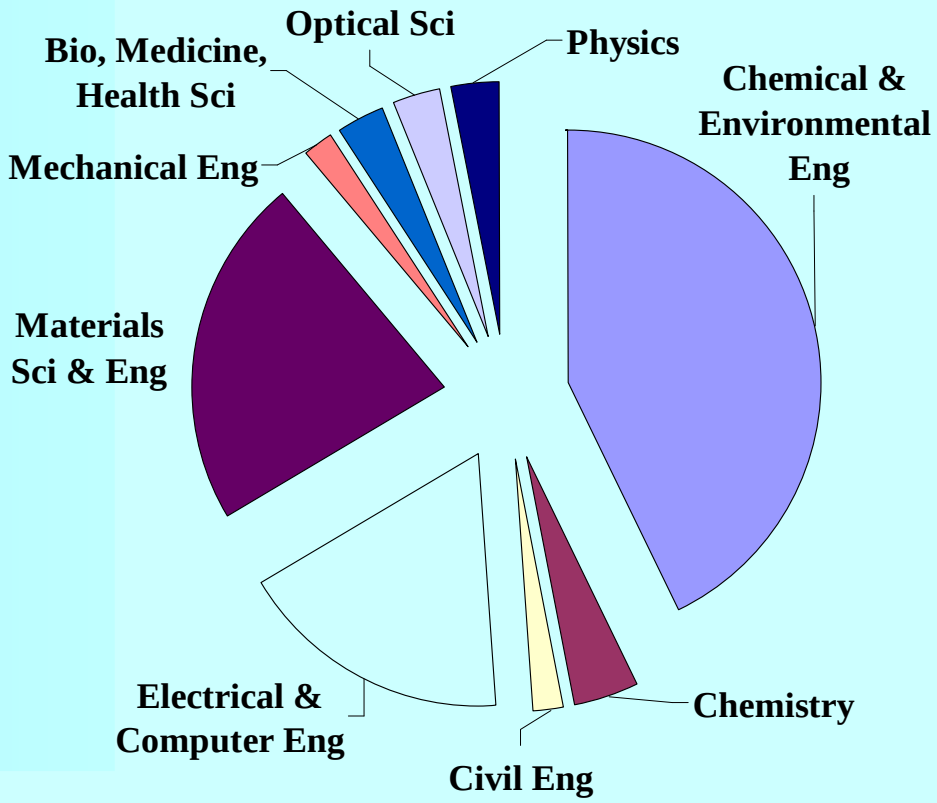


Emphasis on Interdisciplinary Approach

8 Universities
11 Academic disciplines
25 Faculty members

Students Cumulative:
235 PhD and MS
192 Undergraduates

Employment of graduates:
> 80% joining SC industry & suppliers; mostly by ERC members



ERC Member Institutions

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

} Founders 1996

- Cornell University (1998 -)
- Lincoln Laboratory (1998 -)
- Arizona State University (1998 - 2003)
- University of Maryland (1999-2003)
- Purdue University (2003 -)
- Tufts University (2005 -)
- Columbia University (April 2006 -)

Principal Investigators at the ERC

Year 1

1. Boning (MIT)
2. Chidsey (Stanford)
3. Gleason (MIT)
4. Graves (UCB)
5. Helms (Stanford)
6. Kimerling (MIT)
7. Kovacs (Stanford)
8. McVittie (Stanford)
9. O'Hanlon (UA)
10. Peterson (UA)
11. Peyghambarian (UA)
12. Raghavan (UA)
13. Reif (MIT)
14. Shadman (UA)
15. Sinclair (UA)

Years 4-6

1. *Baygents (UA)*
2. *Bent (Stanford)*
3. *Blowers (UA)*
4. Boning (MIT)
5. *Dornfeld (UCB)*
6. Gleason (MIT)
7. Graves (UCB)
8. *Kimerling (MIT)*
9. *Khuri-Yakub (Stanford)*
10. *McIntyre (Stanford)*
11. *McRae (MIT)*
12. *Muscat (UA)*
13. *Musgrave (Stanford)*
14. *Ober (Cornell)*
15. *Ogden (UA)*
16. O'Hanlon (UA)
17. Peterson (UA)
18. *Philipossian (UA)*
19. Raghavan (UA)
20. *Raupp (ASU)*
21. Reif (MIT)
22. *Rubloff (U Maryland)*
23. *Saraswat (Stanford)*
24. Shadman (UA)

Years 9-11

1. *Bahl (UA)*
2. *Baygents (UA)*
3. Beaudoin (Purdue)
4. Boning (MIT)
5. Farrell (UA)
6. Gleason (MIT)
7. Graves (UCB)
8. Jacobsen (UA)
9. Manno (Tufts)
10. Mathine (UA)
11. *McIntyre (Stanford)*
12. *Muscat (UA)*
13. Nishi (Stanford)
14. *Ober (Cornell)*
15. *Philipossian (UA)*
16. Raghavan (UA)
17. Rogers (Tufts)
18. Runyan (UA)
19. *Saraswat (Stanford)*
20. Shadman (UA)
21. Sierra (UA)
22. Vermeire (ASU)
23. Watkins (U Mass)
24. West (Columbia)
25. Wysocki (UA)

Elements of a New Strategic Plan

New Initiatives, Focus Areas, and Plans

Current ERC Research Projects

- **Two types of projects:**
  - **12 core projects (funded by the core SRC/Sematech contract)**
  - **12 (started) + 2 (new) customized projects (non-core funding)**
- **Core projects were selected through RFP, white papers, and full proposals; then reviewed by a committee appointed by SRC and Sematech**
- **Customized projects are added throughout the year. Review and selection procedures depend on sponsors.**

Current and Projected Sources of Funding

- **SRC and Sematech (core)**
- **Sematech (customized projects)**
- **Industrial members (membership)**
- **Industrial members (customized projects)**
- **Cost sharing by participating universities**
- **Grants from Federal and State agencies; examples:**
  - **Educational grants from NSF**
  - **Arizona TRIF Initiative**
  - **Science Foundation of Arizona (cost-sharing proposal is submitted on *low-energy, low-water nano-scale manufacturing*; *PI: A. Muscat*)**

Significant funding leverage for the benefit of S/C industry

Core Projects Selected for 2006-2007

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

Customized Projects in 2006-2007

- **Process Optimization and Modeling of Metal CMP** (D. Rosales-Yeomans, L. Borucki, W. Worth and A. Philipossian**);** *sponsor: Sematech*
- **Post-Planarization Waste Minimization** (T. Sun, L. Borucki, W. Worth and A. Philipossian); *sponsor: Sematech*
- **Mechanistic Study and Modeling of Orbital Polisher for Cu CMP** (H. Lee, L. Borucki, F. O'Moore, S. Joh and A. Philipossian); *co-sponsors: SRC and Novellus*
- **Screening Options for PFOS Removal from Litho-Track Wastewater** (V. Ochoa and R. Sierra); *sponsor: Sematech*
- **Impact of Fluoride and Copper in Wastewater on Publicly-Owned Treatment Works** (R. Sierra, G. Leon); *sponsor: Sematech*
- **Ultra Low-k Film Repair and Pore Sealing Using Supercritical Fluids** (L. Hatch and A. Muscat); *sponsor: Sematech*

Customized Projects in 2006-2007

- **Evaluation of Radical- and Ion-Induced Damage on Low-*k* Films** (D. Graves); *sponsor: Sematech*
- **Lowering Purge-Gas Consumption During Dry-down of Gas Distribution Systems** (J. Yao, H. Juneja, A. Iqbal, F. Shadman, and C. Geisert); *seed project sponsor: Intel*
- **Biomimetic Manufacturing of Nanoscale Devices** (A. Muscat, M. McEvoy, M. Mansuripur); *seed funding by Arizona TRIF Initiative*
- **Low-Energy-Hybrid (LEH) Technology for Water Purification and Recycling** (K. Chen, M. Schmotzer, F. Shadman); *co-sponsors: ERC and Arizona TRIF Initiative*
- **A Survey of Water Use, Reuse, and Policies Affecting Semiconductor Industry in Southwest US** (S. Megdal UA-WRRC); *sponsor: Arizona TRIF initiative*
- **Electro-Coagulation Applied to Water Conservation & Wastewater Treatment** *(*J. Baygents, J. Farrell, A. Boyce, A. Fuerst, Z. Georgousis), *co-sponsors: WSP and Intel*

Program Organization Under NSF/SRC

Thrust A
BEOL Processes
- PFC Alternatives
- Solventless Low-k Dielectric
- Novel Barrier Film Deposition Methods
- CMP Waste Minimization
- Environmentally Benign Planarization

Thrust B
FEOL Processes
- Novel Surface Cleaning and Passivation
- Selective Deposition for Gate Stack Manufacturing
- Etching of New High-k and Electrode Materials

Thrust C
Factory Integration
- Low-Energy Water Purification and Wastewater Treatment
- Efficient Wafer Rinsing and Cleaning
- Water Recycle and Reuse
- Integrated ESH Impact Assessment

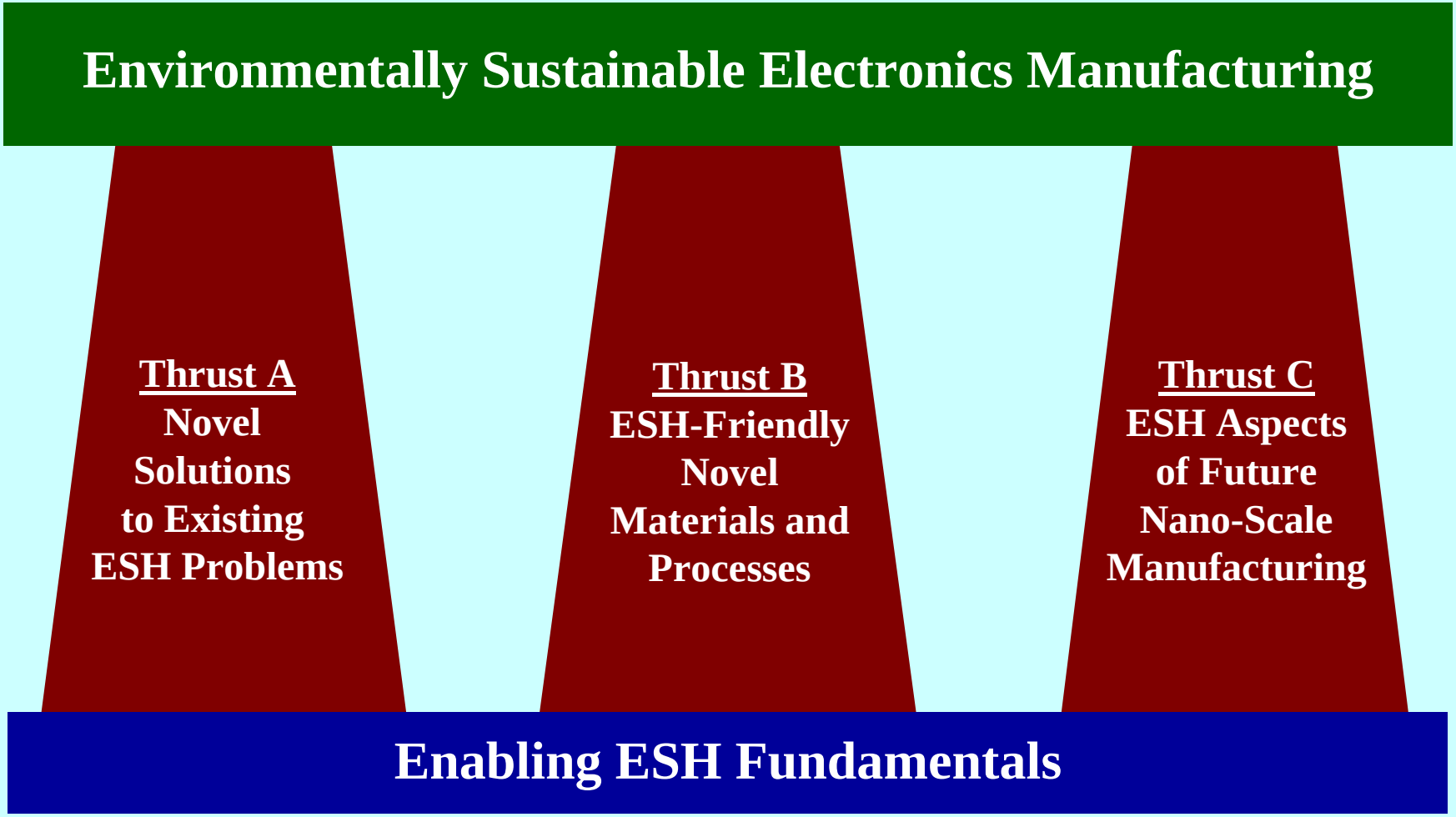
Thrust D
Patterning
- Solventless Lithography
- Additive Processing

Education
- ESH concepts in Science/Engineering Curricula
- Continuing Education and Short Courses
- Outreach

Justification for Re-defining the Thrust Areas

- **Focus on future technology areas that need ESH consideration.**
- **Better balance of size and focus among ERC thrust areas.**
- **Better representation, grouping, and linkage of projects and initiatives.**
- **Better alignment of thrust areas with the needs and plans of ERC sponsors.**

Proposed New Focus and Thrust Areas



Proposed New Focus and Thrust Areas

- **Thrust A: Novel Solutions to Existing ESH Problems**

  Examples:
  - **Organics (e.g. PFOS) and ionic (F^- and Cu^{++}) removal from wastewater**
  - **CMP slurry use reduction**
  - **Water recycling**

- **Thrust B: ESH-Friendly Novel Materials and Processes**

  Examples:
  - **Novel PAG materials to replace PFOS**
  - **Low-energy and low-chemical deposition and pattering methods**
  - **Low-waste planarization beyond CMP**

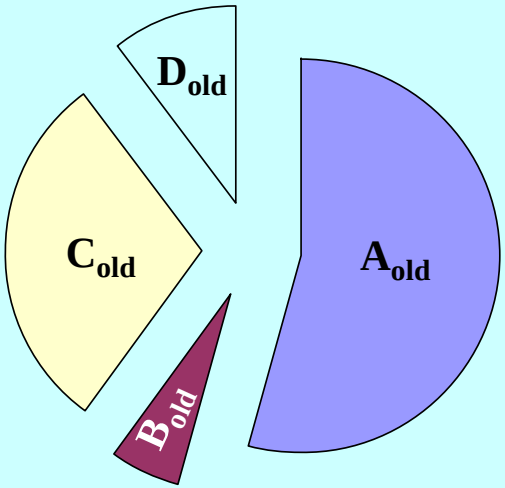
- **Thrust C: ESH Aspects of Future Nano-Scale Manufacturing**

  Examples:
  - **New low-energy and low-chemical processes specific to nano-scale fabrication (e.g. mimicking bio systems for patterning and selective deposition)**
  - **ESH aspects of nano-particles and other nano-structures**
  - **Environmentally sustainable processes for cleaning nano-structures**

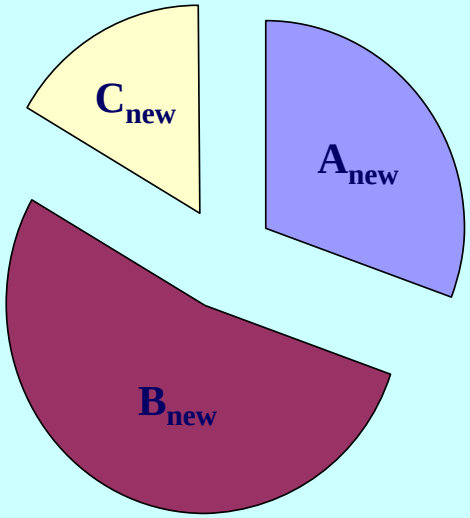
New Thrust Designation of Core Projects

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

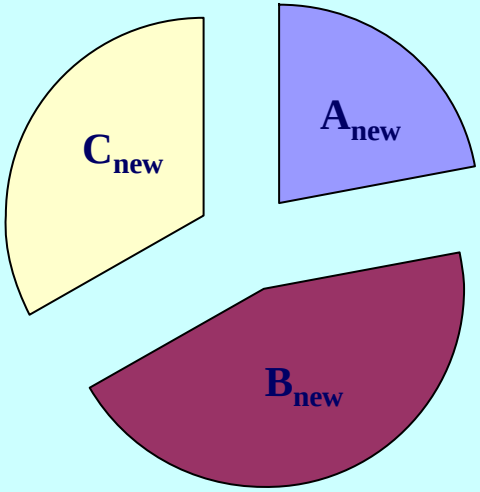
Resource (Funding) Distribution



Current Funding in Current Thrust Areas



Current Funding in Proposed Thrust Areas



Goal in Funding Distribution

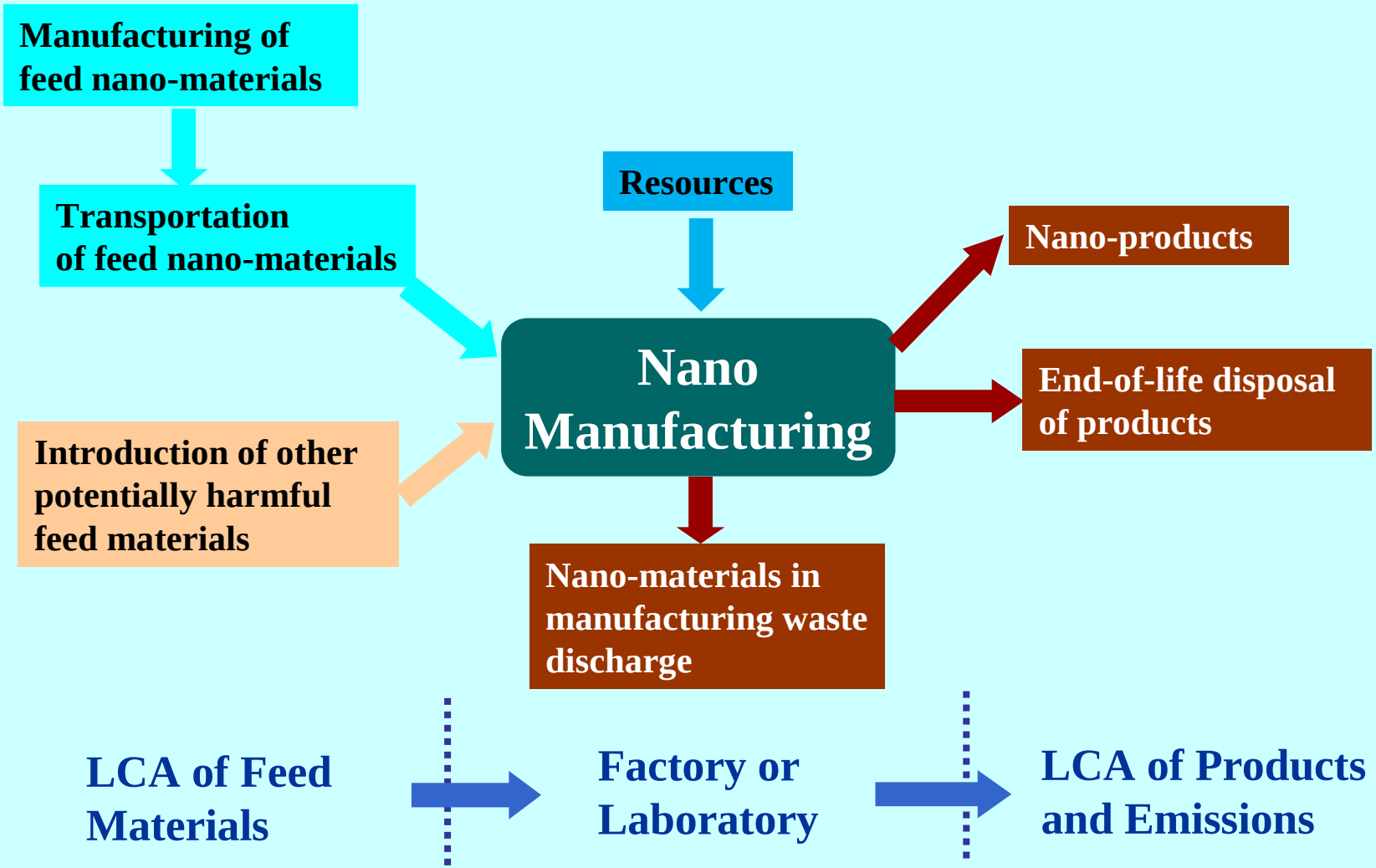
Strategic Plan

New Focus Area

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

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Broad Scope of ESH in Nano-Manufacturing



ESH Aspects of Nano-Manufacturing

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

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

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

4. Positive Environmental Impact
   - Opportunities for major ESH gain

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Facts and Fictions about Nano-Particles

- **Our environment is full of nano-particles. Examples are wide variety of man-made carbon nano-particles, various macromolecules, and atmospheric aerosols.**
- **Research on nano-particles is needed, but has attracted disproportionate consideration compared to other more critical sustainability issues of nano-manufacturing that are based on science and not fear.**

Functionalized Fabricated Nano-Particles

New name for some old materials

Aerosil = fumed SiO_2

Particle size:

4-20 *milli-micron* (nanometers)

New additive for coating industry

Colorants & Coatings

(Farbe & Lack Journal; April 1949)

Facts and Fictions about Nano-Particles

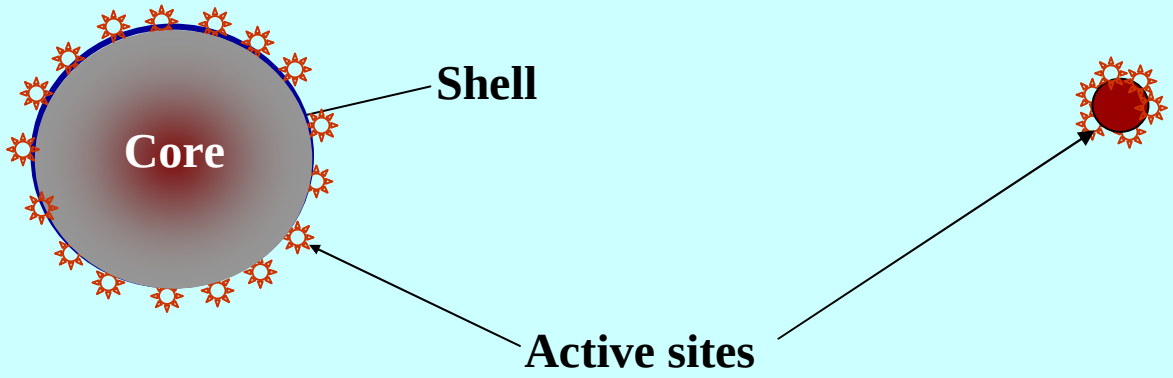
- **Effect of nano-particles and macro-molecules on biological systems has been the subject of years of extensive research.**
- **Primary effect is due to interactions of particle surface with other contaminants. Therefore, study of nano-particles without knowing and simulating the process environment around them is irrelevant and waste of research resources.**

Nano-Particles in CMP Process

Two types of CMP nano-particles:

Primary Nano-Particles
(engineered particles; 5-90nm)

Secondary Nano-Particles
(very active surface; <10nm)



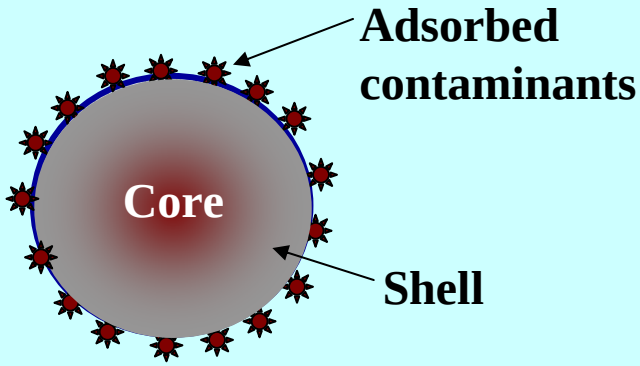
What is Unique About Nano-Particles?

Treatment problem:

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

Synergistic ESH impact of nano-particles:

- ***Active surface***
- ***Selective adsorption***
- ***Pore condensation*** ***(Kelvin Effect)***
- ***Concentration***
- ***Facilitated transport***
- ***Enhanced life-time***



Other Applications and Sources of Nano-Particles

- Nano-particles of porogens used in deposition of porous low-k films (a current ERC project)
- Nano-droplets in sprays
- Aerosols formed in vents and in cooling towers due to chemical reactions in vapor phase (a graduated ERC project)
- Nano-tubes and nano-wires; potential release and handling issues if fabricated ex-situ.

ESH Aspects of Nano-Manufacturing

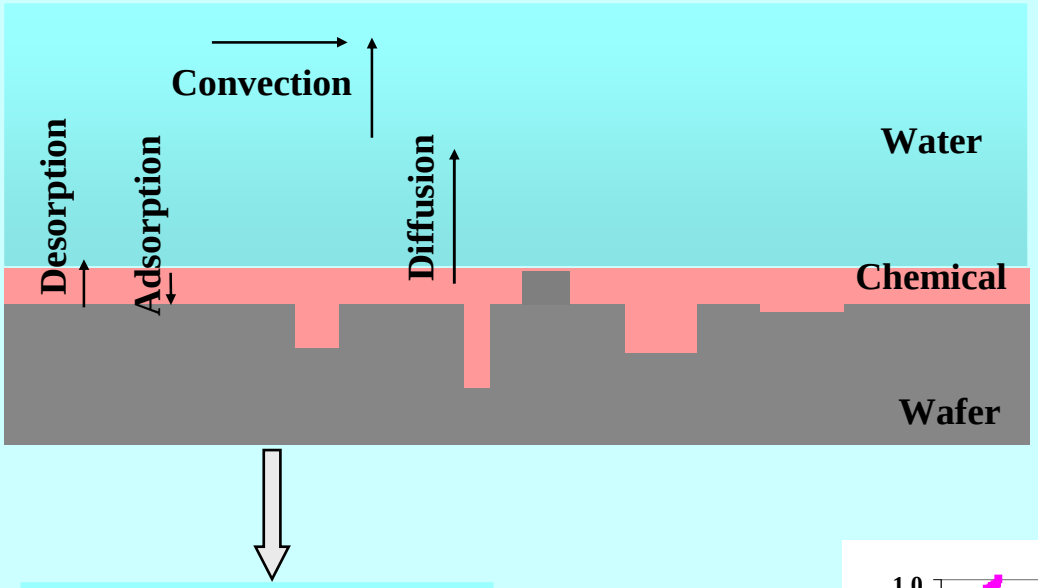
1. Nano-Particles in Manufacturing
   - Workers exposure to nano-particles in the fabs
   - Emission of nano-particles through fab waste streams

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

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

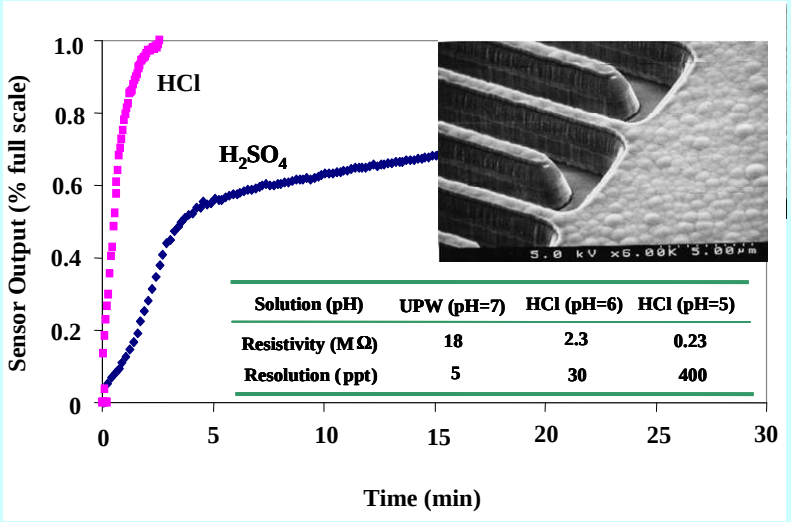
4. Positive Environmental Impact
   - Opportunities for major ESH gain

Cleaning Challenges in Nano-Manufacturing

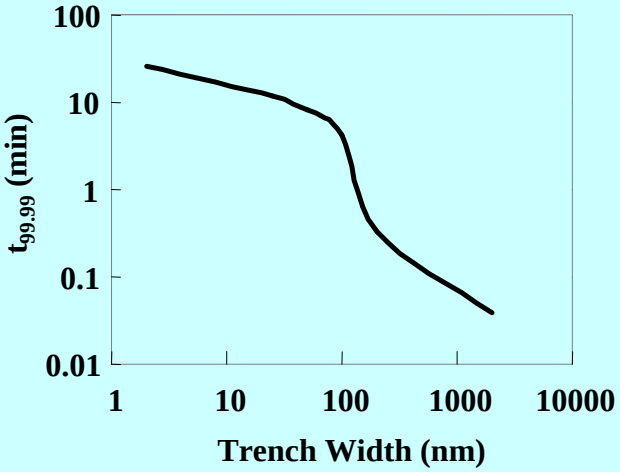


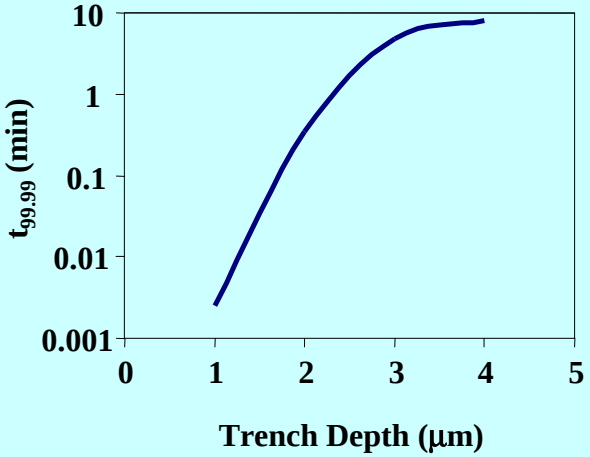
Transport in Nano-Features:

- Charge-influenced diffusion
- Wall interactions
- Re-adsorption
- Activated desorption



Cleaning Challenges in Nano-Manufacturing





- Change in transport mechanisms for cleaning liquid and by-products
- More activated processes due to strong surface interactions
- Surface charge effects
- More issues with interfacial contamination (high surface to volume)
- More processing steps
- More issues with drying and surface conditioning

ESH Aspects of Nano-Manufacturing

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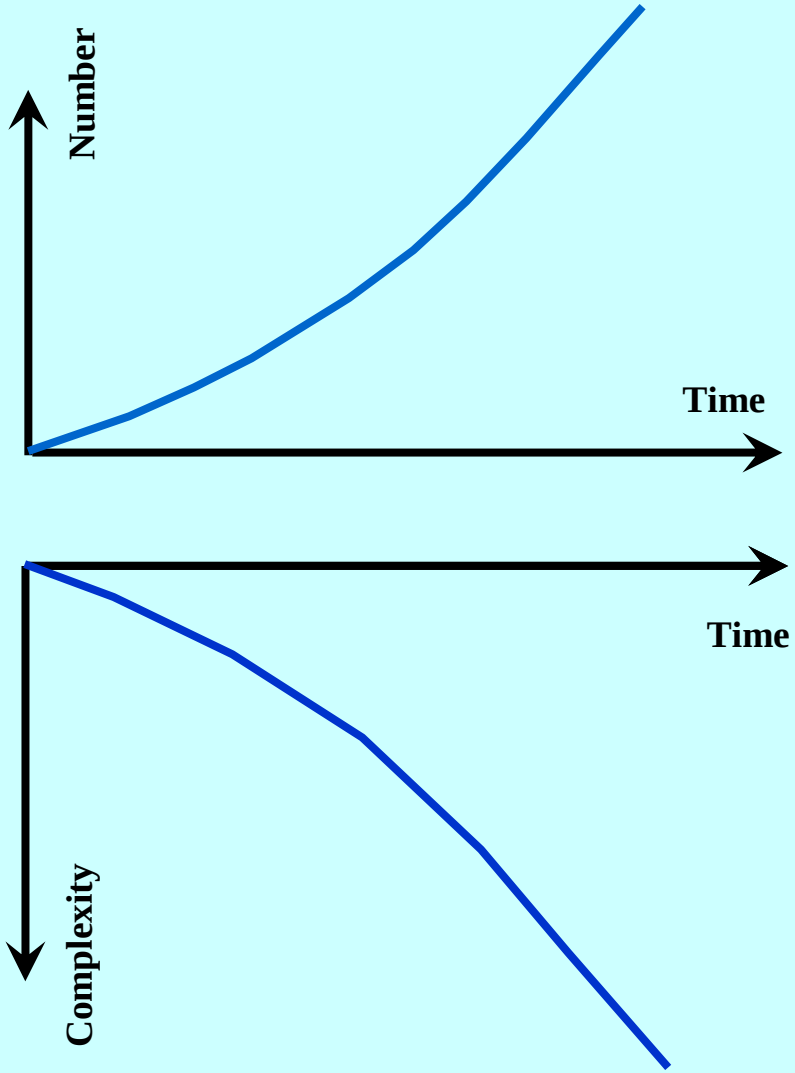
Introduction of New Materials



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   - **Opportunities for major ESH gain**

Positive Environmental Impact

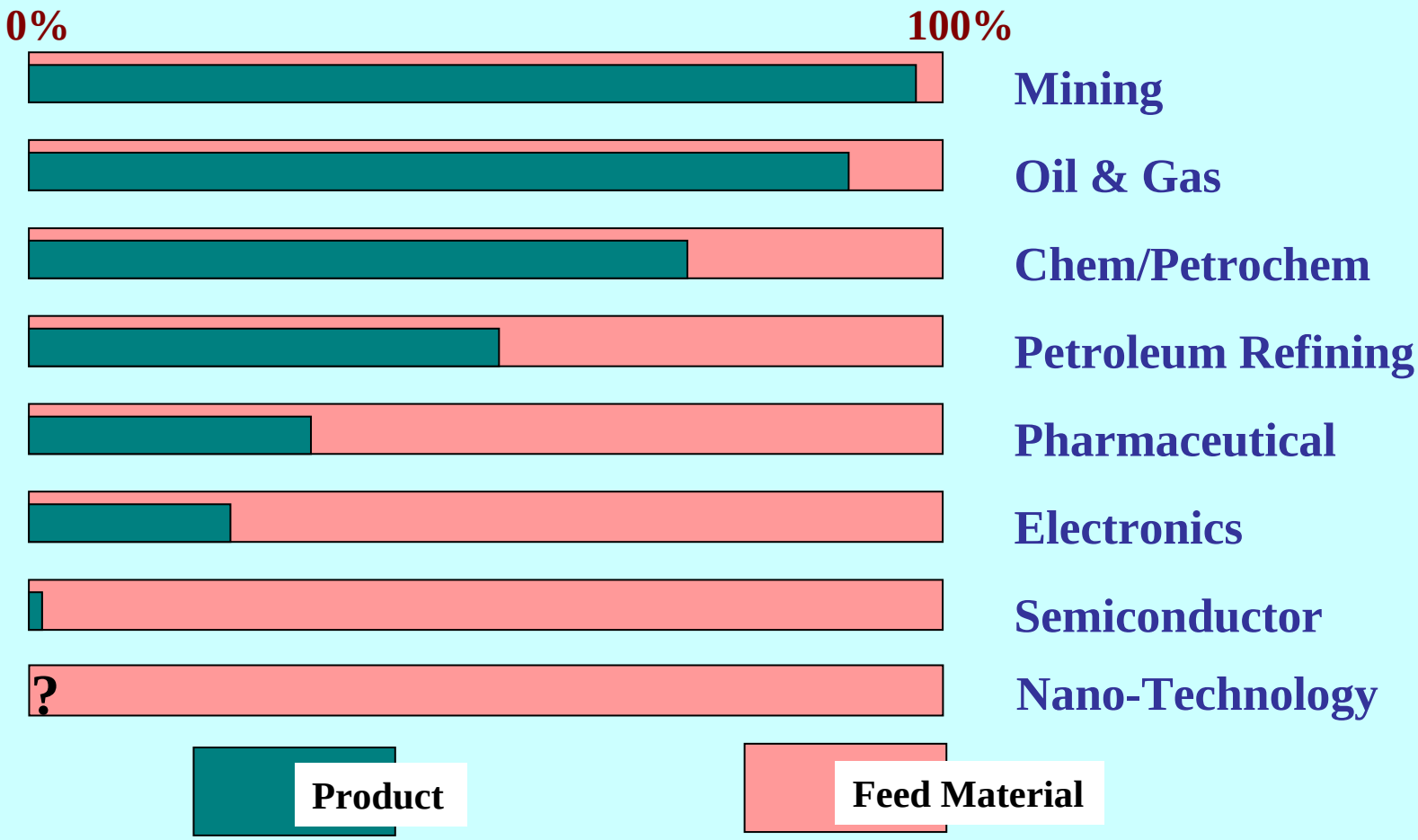
Evolutionary

- **Opportunity to phase out problematic materials which are deeply rooted in present manufacturing (e.g. PFCs, PFOS)**

Revolutionary

- **Opportunity to phase out problematic process paradigms and replace them with more friendly processes (e.g. move from *subtractive* to *additive* processing):**

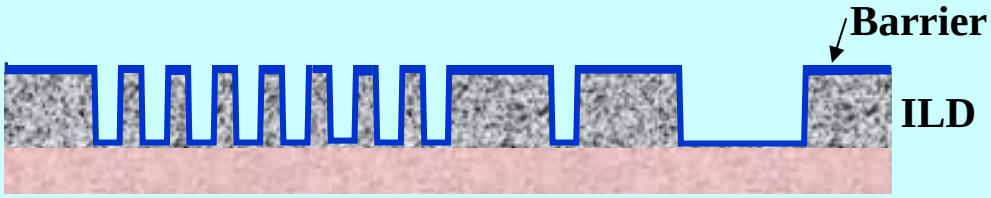
Material Usage Index in Various Industries



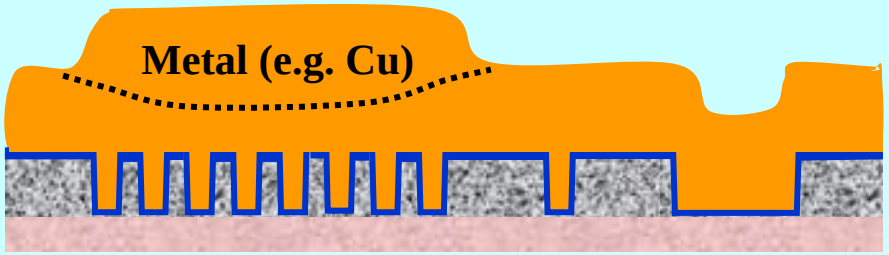
Conventional CMP of Interconnect Copper

Duane Boning (MIT)

Dielectric patterning
Barrier deposition



Copper deposition
(seed, fill)



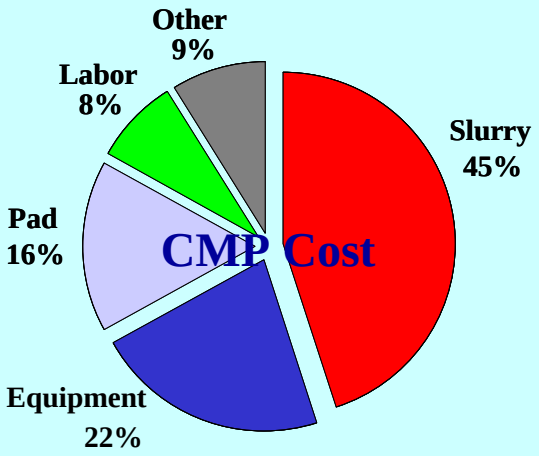
CMP

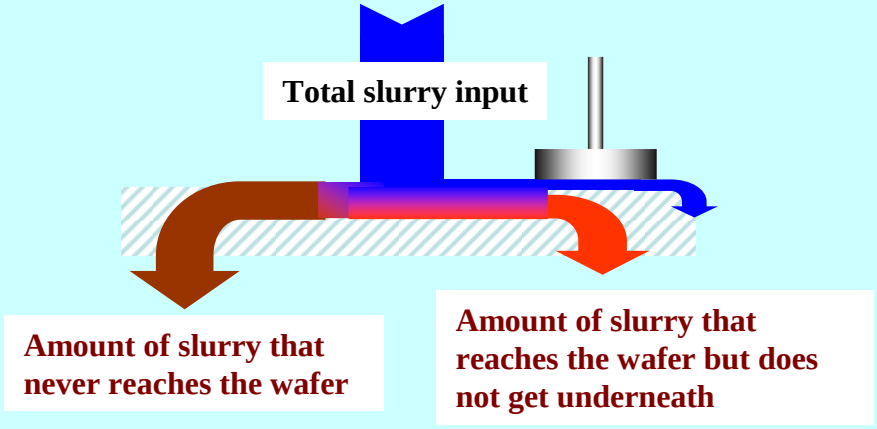
Top barrier removal

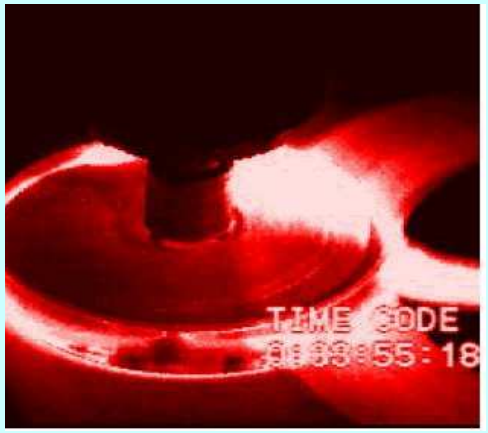
Chemical Mechanical Planarization (CMP)

Ara Philipossian (UA)

- One of the fast growing processing segments
- Major source of nano particle emission in S/C fabs
- Costly and wasteful operation: For a typical 200-mm factory:
  - 6,000,000 liters of slurry ($20M) per year
  - 300 metric tons of solid waste per year



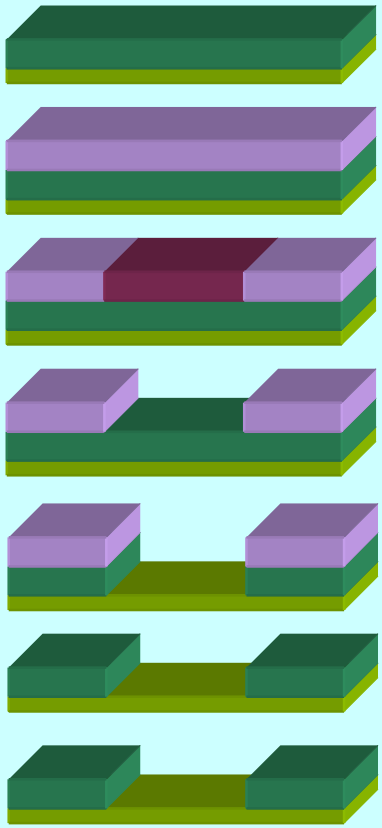




Amount of slurry that does the actual polishing is often less than 10%

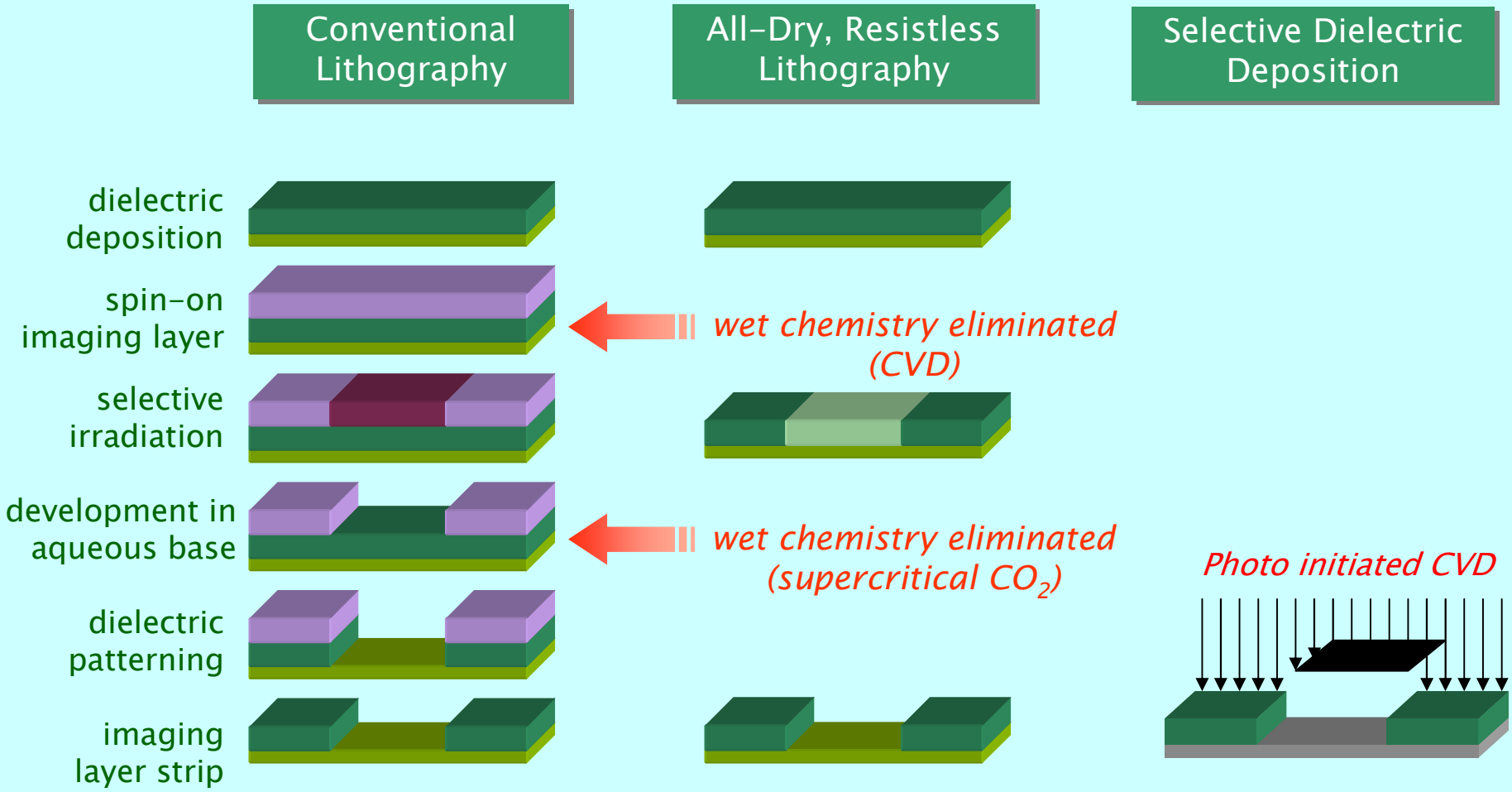
Deposition and Patterning of Dielectrics

Karen Gleason (MIT), Chris Ober (Cornell)

Conventional Lithography		ESH Issues
dielectric deposition		Precursors, HAPs, wastes
spin-on imaging layer		VOCs, waste
selective irradiation		VOCs, radiation
development in aqueous base		VOCs, HAPs
dielectric patterning		HAPs, PFCs
resist strip		A/B chemicals, solvents
imaging layer strip		A/B chemicals, UPW

Deposition and Patterning of Dielectrics

Karen Gleason (MIT), Chris Ober (Cornell)



SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Best Examples of Additive Processing

Dan Herr and Victor Zhirnov (SRC)

	EUV Lithographic Subtractive Patterning 32 nm	Growth of a Baby [Bio-Assisted Self-Assembly]	Bio Advantage
Bits patterned per second	8.59E+09 bits/s/masking layer	7.53E+17 amino acid equivalents/s	8.77E+07
Energy required per bit	1.46E-12 J/bit/masking layer	1.29E-20 J/amino acid equivalent	1.13E+8

Evolution = Environmentally Friendly

Novel Manufacturing Concept for ESH Gain

- **Exploring *biological* systems/methods to develop *environmentally efficient and benign* processes for manufacturing nano-electronics**
- **ERC was awarded funding by Arizona TRIF Initiative to start a joint project in this area with two other large centers at UA (BIO5 and Optics)**
- **Three ERC seed projects for 2007 ($300k; overhead free) related to *resource utilization and sustainability of micro- and nano-electronics manufacturing***

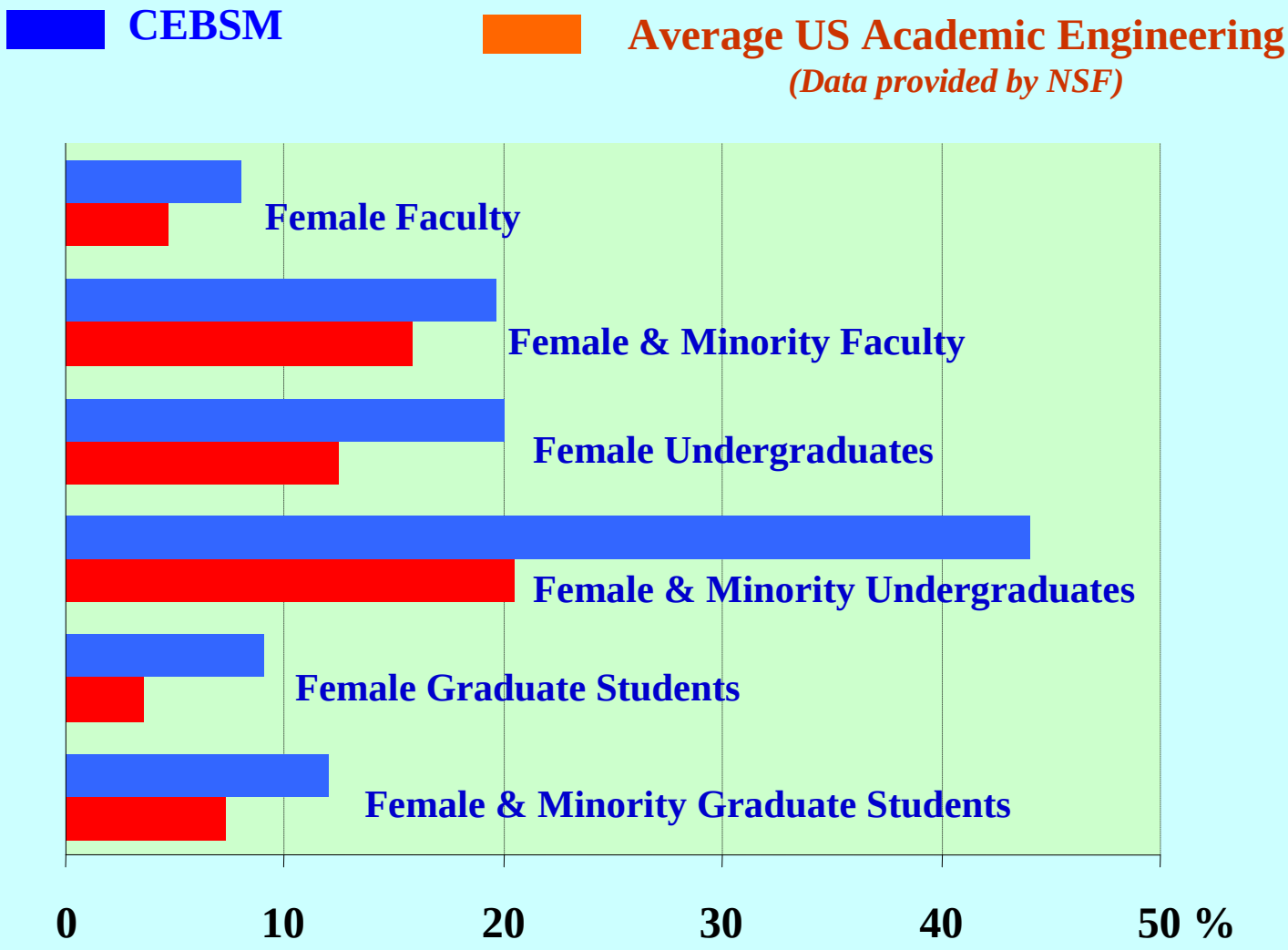
Selected Accomplishments

- **Research: 67 research projects; 224 peer-reviewed publications**
- **Technology Development: 16 patents**
- **21 national/international awards for faculty**
- **51 students national/international awards and fellow positions; many institutional fellowships and scholarships**
- **Simon Karecki Fellowship and Award**
- **22 technology transfer projects directly with member companies**
- **$1 M Fujimi Endowment and Professorship in Planarization**
- **Five new spin-off companies**

Selected Accomplishments

- **Pre-University Outreach**
  - **Wide range of activities (example: *Teachers Institute* for science teachers; 25 schools have participated and graduated)**
- **University Education:**
  - **Industry internship for students**
  - **REU Program for undergraduates (60% are women and minorities)**
  - **New courses in *benign manufacturing***
- **Post-University Education:**
  - **Short courses and workshops for practicing scientists and engineers; bi-weekly tele-seminars; distance learning courses; internships for industry residents at universities; faculty sabbaticals sponsored by industry**

Gender, Racial, and Ethnic Diversity



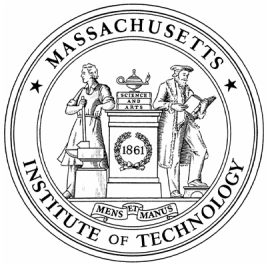
Partial List of Student Awards in 2006

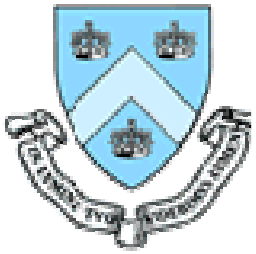
- **Yasa Adi Sampurno, Best Student Poster, International Planarization Technology Conference, Foster City, CA 2006.**
- **Rachel Morrish, AWIS (association for women in science) Award.**
- **Daniel Rosales-Yeomans, Best Student Paper, Techcon, Portland, OR 2006.**
- **Ashok Muthukumaran, "Sandia Mountain Scholarship Award" from NACE foundation.**
- **Hyosang Lee, Best Student Poster, International Planarization Technology Conference, Foster City, CA 2006.**
- **Iqbal, A., Juneja, H., Yao, J., Shadman, F., Best Paper Award, SRC Student Symposium, October, 2006, Raleigh, North Carolina.**

Important Dates and Program Schedule

- **Annual report to SRC, Sematech, and other members companies (February 1, 2007)**
- **Annual Review Meeting (February 22-23, 2007)**
- **Review feedback and recommendations (by March 1, 2007)**
- **Project-level decisions and adjustments based on the review (by April 1, 2007**
- **Decision on funds available for new projects (in consultation with SRC, Sematech, and EAC; finalized by April 1, 2007)**
- **Review of the new core proposals (March and April; selection by April 15, 2007).**
- **Plan on adding new projects (both core and customized) this year.**

Planarization Long Range Plan





SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Team

- **PIs:**
  - Ara Philipossian (UA)
  - Duane Boning (MIT)
  - Srini Raghavan (UA)
  - Vincent Manno (Tufts)
  - Chris Rogers (Tufts)
  - Robert White (Tufts)
  - Stephen Beaudoin (Purdue)
  - Alan West (Columbia)
- **Other Researchers:**
  - Ed Paul (MIT)
  - Len Borucki (Araca)
  - Yun Zhuang (UA)
  - Fransisca Sudargho (UA)
  - Yoshi Nishimura (Inoac)
- **Advisory Committee**
  - Paul Fischer (Intel)
  - Laertis Economikos (IBM)
  - Cliff Spiro (Cabot)
  - Chris Borst (University at Albany)

Team

- **Graduate (PhD) Students:**
  - Ashok Muthukumaran (UA)
  - Yasa Sampurno (UA)
  - Ting Sun (UA)
  - Daniel Rosales-Yeomans (UA)
  - Hyosang Lee (UA)
  - Xiaomin Wei (UA)
  - Rumin Zhuang (UA)
  - Nicole Braun (Tufts)
  - Caprice Gray (Tufts)
  - Andrew Mueller (Tufts)
  - James Vlahakis (Tufts)
  - Hong Cai (MIT)
- **Graduate (PhD) Students (continued):**
  - Daniel Truque (MIT)
  - Xiaolin Xie (MIT)
  - Kristin Shattuck (Columbia)
  - Bum Soo Kim (Purdue)
  - Caitlin Kilroy (Purdue)
  - Gautam Kumar (Purdue)
- **Undergraduate Students:**
  - Anita Lee (UA)
  - Geoff Steward (UA)
  - Jessica Torres (Purdue)

Next Five Years

- **Landscape:**
  - **Research, fundamental in nature yet industrially relevant, addressing the technological, economic and environmental challenges of planarizing:**
    - **Copper**
    - **Tantalum and Ruthenium**
    - **Dielectrics (STI, and ILD as it relates to barrier polish)**
    - **New materials (as they relate to new memory devices)**
- **Gaps to be Filled:**
  - **Processes & consumables for:**
    - **Advanced processes and consumables for planarization**
    - **Electrochemically assisted planarization**
    - **Post-planarization cleaning and surface preparation**

Advanced Processes & Consumables for Planarization

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

Advanced Processes & Consumables for Planarization

- **Objectives**
  - **Real-time detection and modeling of pattern evolution**
    - **Develop novel force-spectra endpoint detection methods by determining how various wafer and pad surface states during polish affect the frictional energy in particular frequency bands**
    - **Relate these signals to details of the wafer topography evolution by integrating pattern evolution models with the above endpoint or diagnostic signal analysis**
  - **Effect of pad grooving on process performance**
    - **Empirical and numerical investigation of the effect of various pad designs (materials, groove shapes and dimensions) as well as different types of slurries on RR, COF and pad temperature for copper and tantalum CMP**
    - **Identification and verification of optimal pad designs for technology transfer to 300-mm platforms**

Advanced Processes & Consumables for Planarization

- **Objectives (continued)**
  - **Wear phenomena and their effect on process performance**
    - **Isolate, quantify and model the hydrodynamic, van der Waals, hydrophobic and electrostatic processes that determine how nanoparticles (both silica and ceria), pads, diamonds and wafers interact with one another in representative systems and how these interactions evolve with extended use.**
    - **Develop methods to visualize and measure local wafer-pad mechanical interactions using laser-induced fluorescence and micro-machined shear stress sensors**

Once fundamentals of pad asperity evolution & the effect of the multitude of contacting bodies on pad asperities are understood, their impact on planarization capability can be modeled.

This will lead to the design of new polishing protocols & consumables that will deliver superior performance with reduced environmental consequences.

Advanced Processes & Consumables for Electrochemically Assisted Planarization

- **Focus and Objectives:**

  - Development and implementation of a 'full' process that includes clearing of copper AND planarization of the barrier (i.e. tantalum) layer

  - **Novel chemistries** to enhance and control electrochemical removal and passivation of copper, tantalum and ruthenium
  - **Novel pads** to ensure electrical contact with isolated copper islands during clearing (requires development of conducting pad technology, with appropriate mechanical, electrochemical & environmental properties)
  - **Modeling and characterization** of tool, pad and wafer interactions for design and control (particularly endpoint detection) are needed to minimize process cost and environmental impact

Advanced Post-Planarization Cleaning Processes & Consumables

- **Focus and Objectives:**
  - Fundamental study of the effects of brush (new and used) material and design on shear force, creep, rebound and cleaning efficiency of insulator and metal films

  - **Novel surface mechanical testing methodologies** to perform cyclic and incremental brush deformation measurements before and after extended wear to understand failure mechanisms
  - **Design and use of novel tribometers** to study the frictional forces in post-planarization scrubbing
  - **Modeling and characterization** of brush, cleaning fluid and wafer interactions within the realm of nano-lubrication theories

Philipossian Selected Projects Update

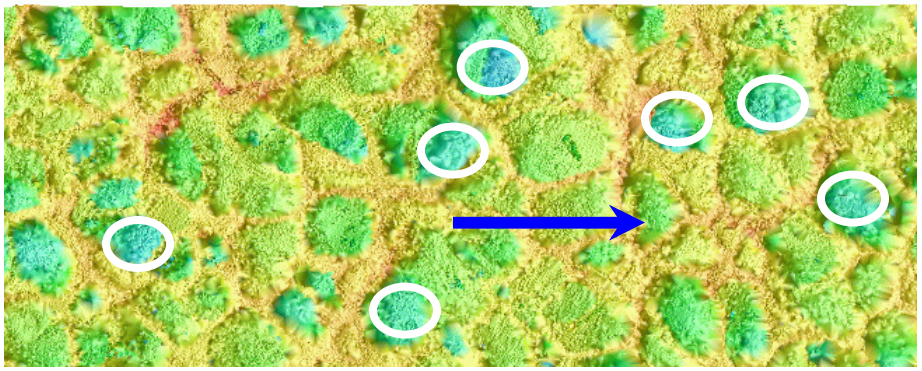
Advanced Processes & Consumables for Planarization

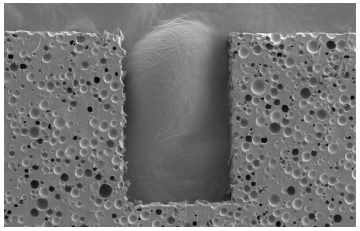
- **Wear Phenomena … Interactions among slurry, pad, wafer and diamonds**

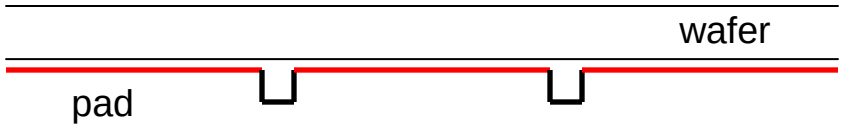
- **Real-Time Detection of Pattern Evolution … STI polish with cerium oxide abrasives**

Wear Phenomena

Slurry Transport by Land Areas due to Topography







Valleys in the land areas of pad surface topography carry fluid directly

The effect of valleys on fluid transport can be quantified from interferometry with a shear flow factor (0 for a smooth surface and > 0 as valleys become deeper)

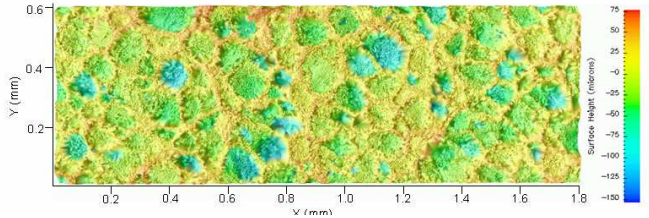
Total fluid flux is proportional to the product of the shear flow factor and the surface height standard deviation

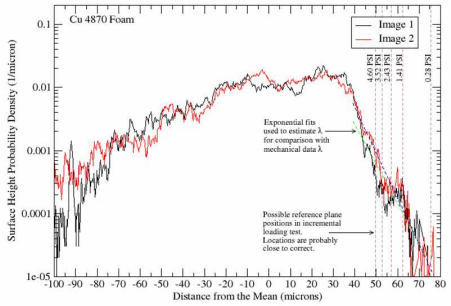
Shear flow factor is relevant for evaluating transport by the land areas of grooved pads

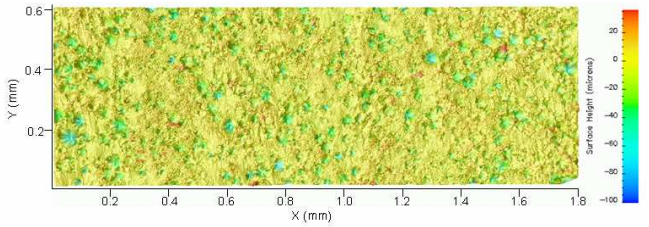
Wear Phenomena

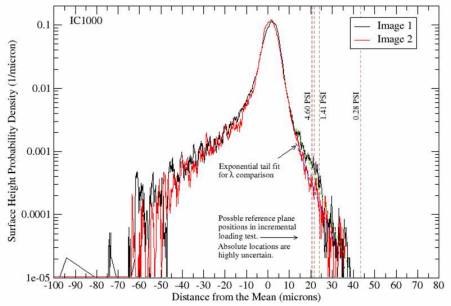
Slurry Transport by Land Areas due to Topography

- **Team:**
  - T. Sun, Y. Zhuang, L. Borucki and A. Philipossian
- **EHS Impact:**
  - Slurry consumption reduction
- **Key Results:**
  - Developed and qualified contact method to analyze mechanical pad surface properties (i.e. top 50 – 100 microns) in dry conditions
  - 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.
  - The psiloQuest Cu 4870 (top) shows 5X the fluid carrying capacity compared to the Rohm and Haas IC1000 (bottom)
- **Plans:**
  - Extend contact method to analyze moist pads at different temperatures
  - Demonstrate, through polishing tests, that higher fluid carrying capacity translates to less slurry use
  - Extend the study to other pads and conditioning methods





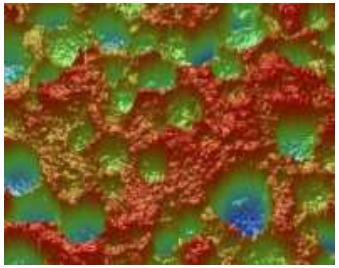


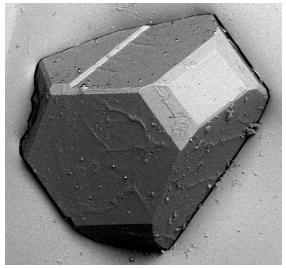


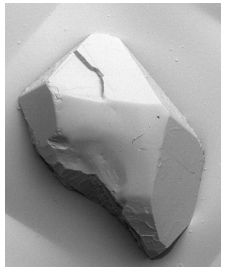
Wear Phenomena

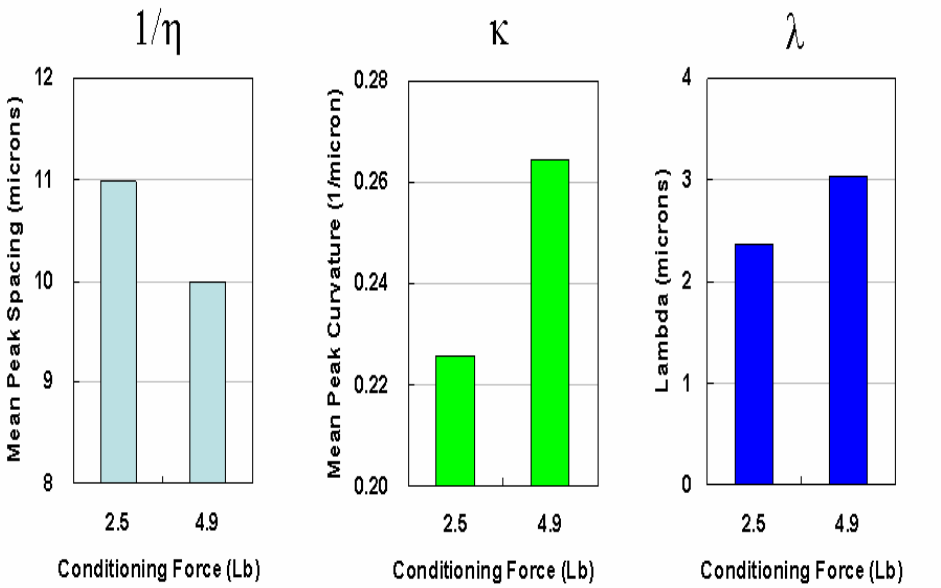
Conditioner Pressure Effect on RR and Pad Surface Properties

Higher diamond conditioner pressure means faster pad & diamond wear









- **Team:**
  - R. Zhuang, Y. Zhuang, L. Borucki and A. Philipossian
- **EHS Impact:**
  - Pad and diamond wear reduction
- **Key Results:**
  - Copper RR is higher at lower conditioner pressures
  - RR simulations indicate that lower conditioner pressure cause removal to be more 'mechanically limited'
  - Higher conditioning pressure cause lower peak spacing, higher peak curvature and rougher surface
  - Parameters independently calculated from pad surface data are consistent with extracted values from the L – H model
  - FIRST experimental & theoretical evidence that a strong correlation exists between pad surface profile and kinetic rate constants
- **Plans:**
  - Explore whether these trends hold for other pads, diamonds, slurries and CMP applications

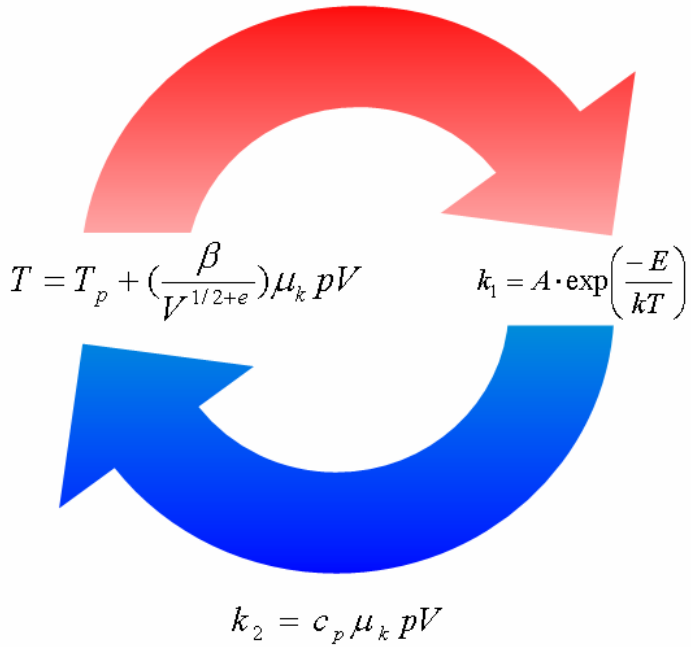
Wear Phenomena

Conditioner Pressure Effect on RR and Pad Surface Properties

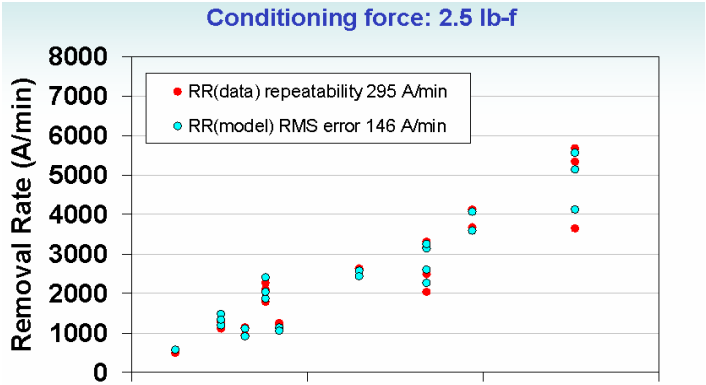
$$\underline{Cu} + nR \xrightarrow{k_1} \underline{L}$$

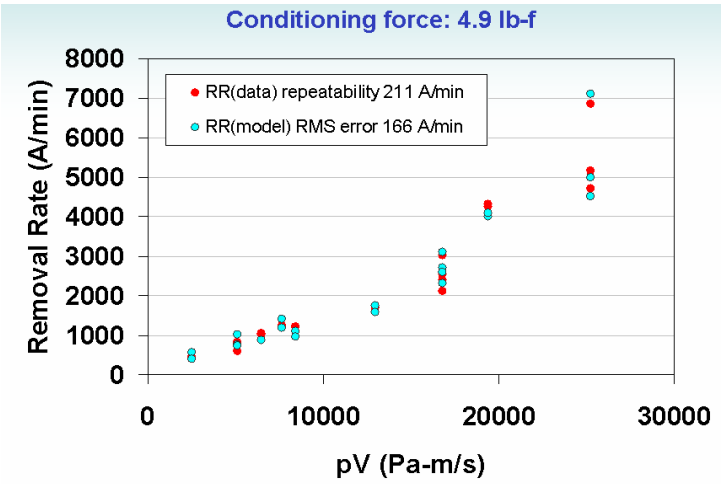
$$\underline{L} \xrightarrow{k_2} L$$

$$RR = \frac{M_w}{\rho} \frac{k_1 C}{1 + \frac{k_1 C}{k_2}}$$



***C_p* and *ß* are fitting parameters that depend on pad thermal and mechanical properties and also on conditioning**





$$C_p \propto \frac{1}{\lambda^{0.5} \kappa^{0.5}} \quad \text{and} \quad \beta \propto \frac{\kappa^{0.75}}{\lambda^{0.25} \eta}$$

Wear Phenomena

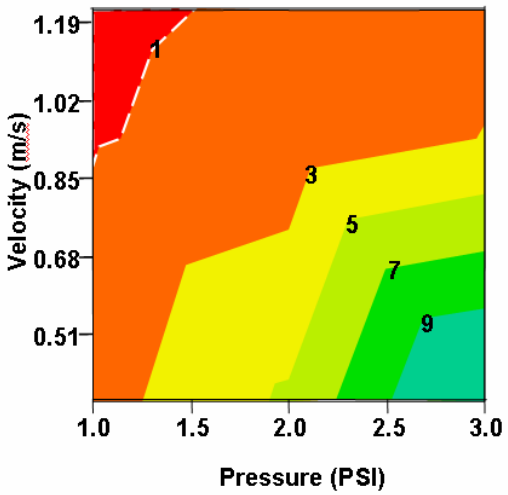
Conditioner Pressure Effect on RR and Pad Surface Properties

		2.5 lb-f	4.9 lb-f
c_p	Pad surface analysis and conditioning theory	1.60E-07	1.24E-07
	Langmuir-Hinshelwood model	1.50E-07	1.31E-07
β	Pad surface analysis and conditioning theory	5.84E-03	5.46E-03
	Langmuir-Hinshelwood model	5.95E-03	5.36E-03

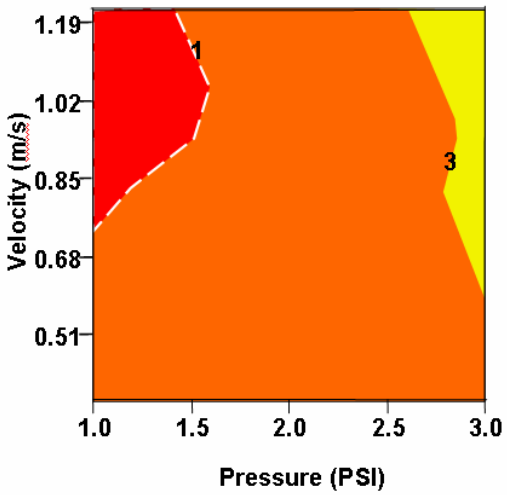
The differences between the two methods are 2 – 7 percent

k_1/k_2 Simulation Comparison

2.5 lb-f



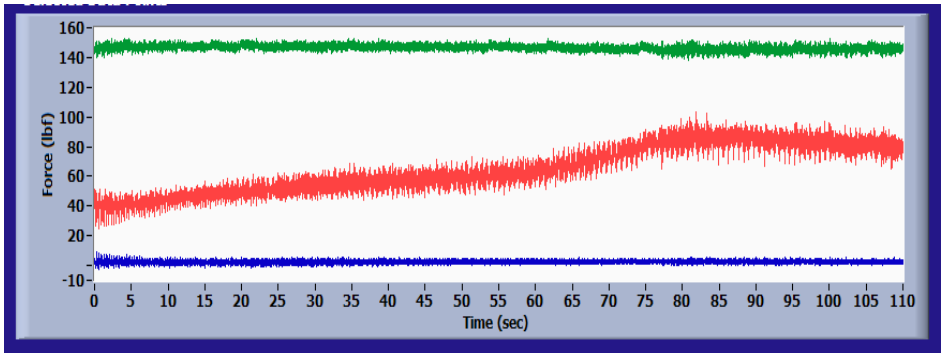
4.9 lb-f



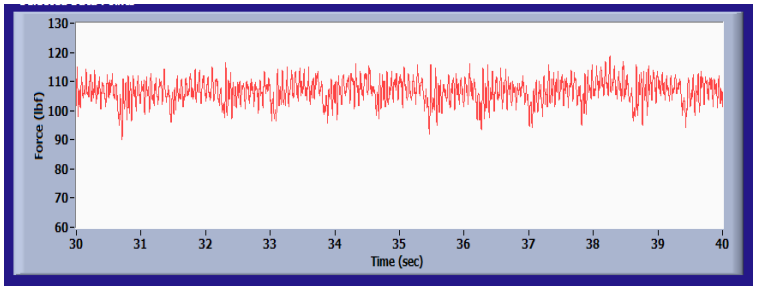
Detection and Modeling of Pattern Evolution

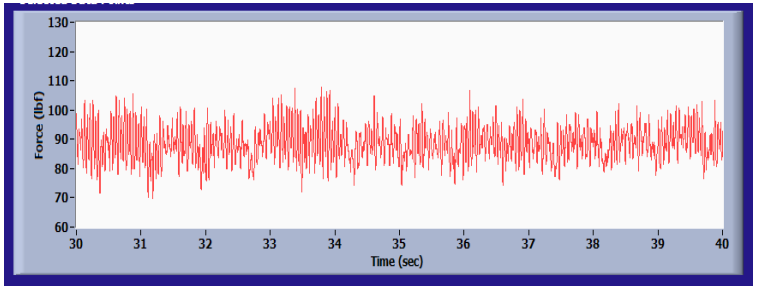
Real-Time 'Force Spectroscopy'

Shear force and down force during a 2 – minute polish of a 200 – mm STI patterned wafer with cerium oxide slurry



Shear force during blanket Copper (top) and blanket Tantalum (bottom) CMP with colloidal silica slurry

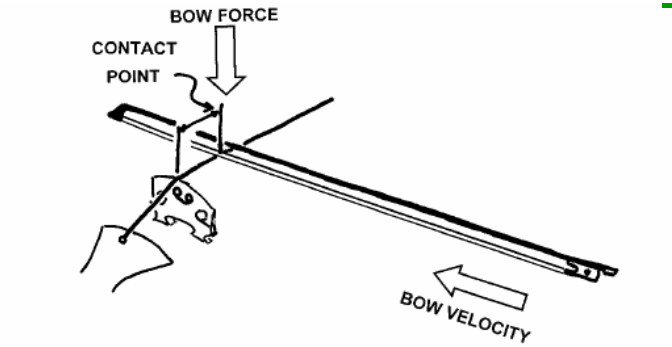




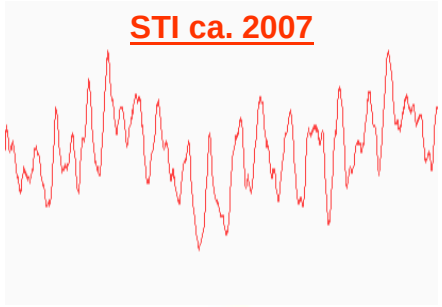
Detection and Modeling of Pattern Evolution

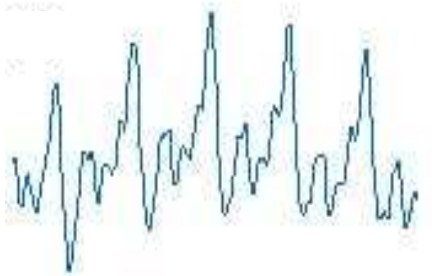
Real-Time 'Force Spectroscopy'

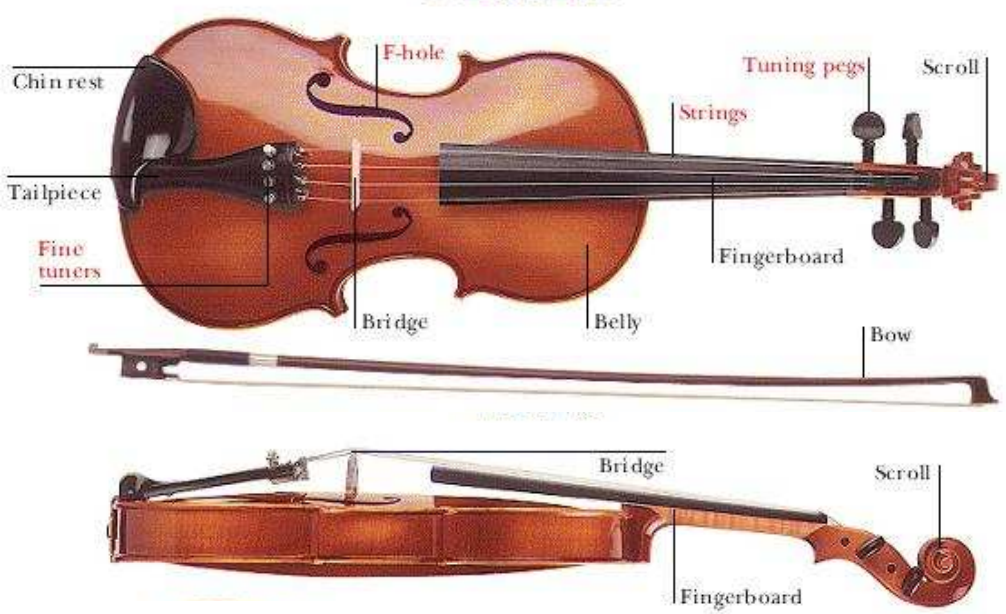
CMP and the Violin



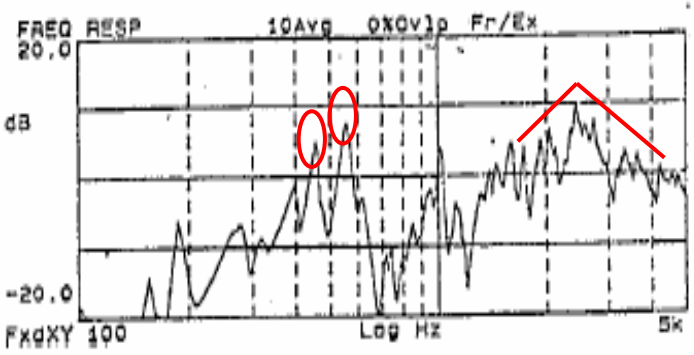
STI ca. 2007





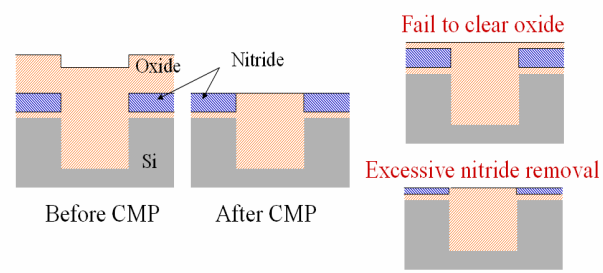


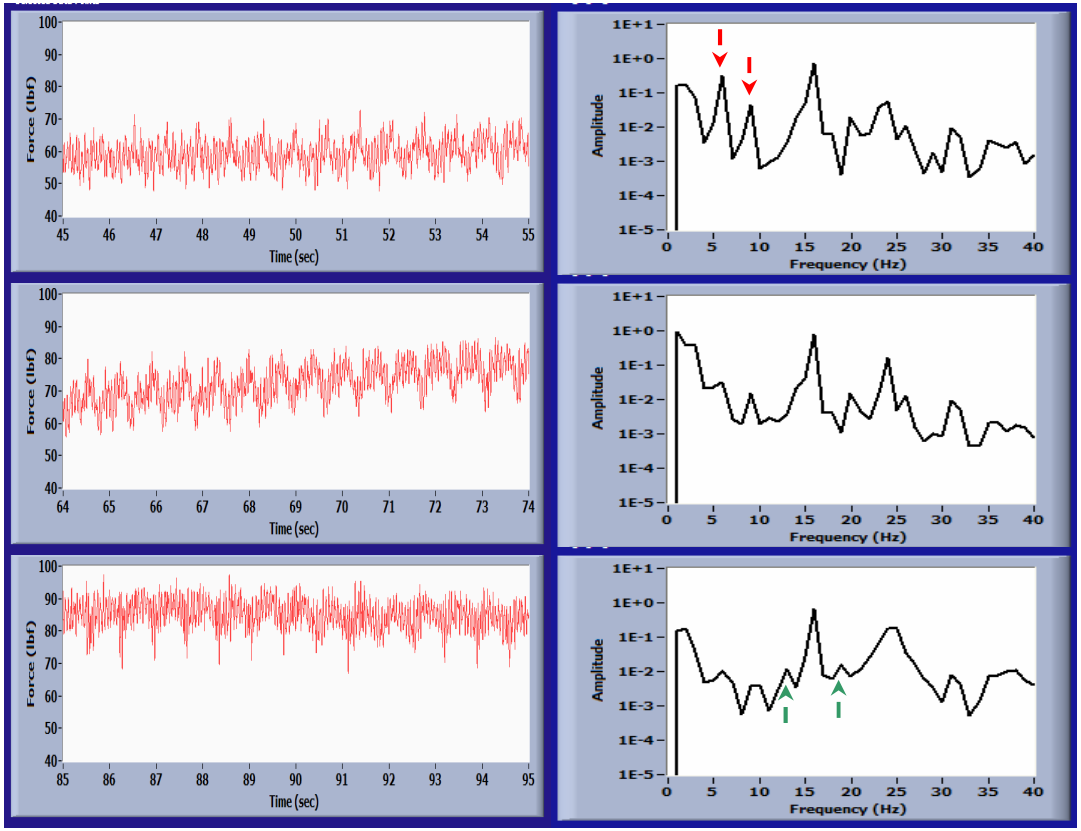
Stradivarius ca. 1715



Detection and Modeling of Pattern Evolution

Real-Time 'Force Spectroscopy'



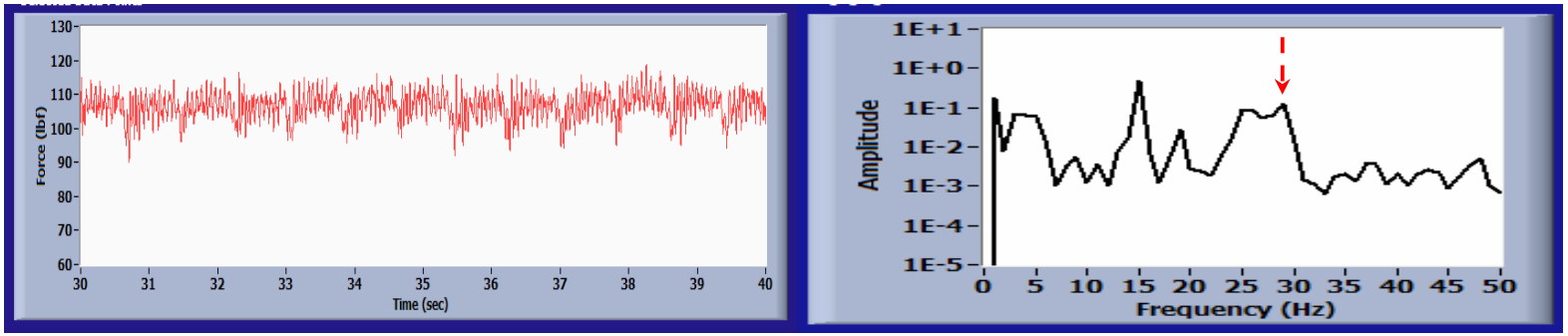


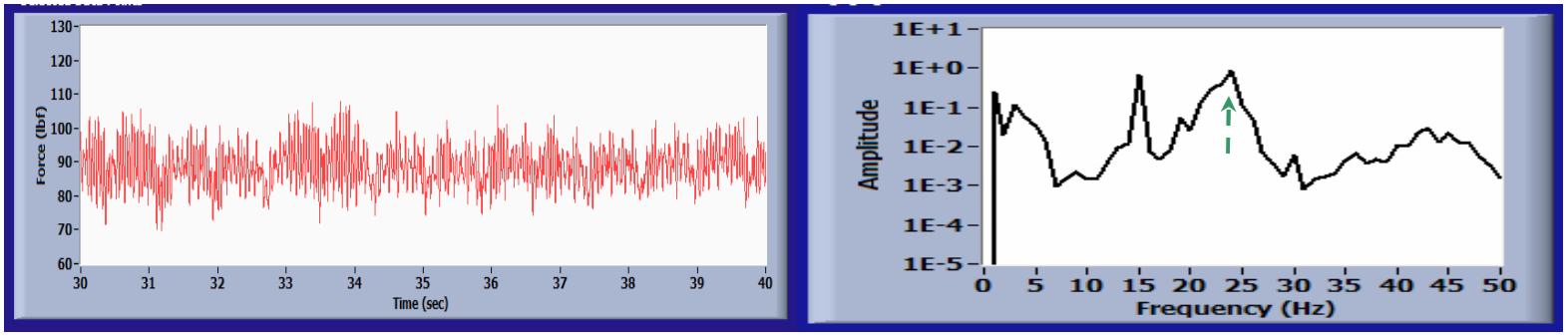
- **Team:**
  - **Y. Sampurno, F. Sudargho, Y. Zhuang and A. Philipossian**
- **EHS Impact:**
  - **Slurry and other consumables reduction (shorter over-polish & use of ceria slurries)**
- **Key Results:**
  - **Developed and qualified 200 – mm polisher for real-time XYZ force analysis**
  - **Demonstrated feasibility of 'force spectroscopy' for the detection of:**
    - **STI pattern evolution**
    - **Silica and ceria-based ILD & STI slurry abnormalities**
    - **Pad and diamond EOL (copper CMP)**
    - **Insufficient diamond conditioning (STI)**
    - **Blanket copper and tantalum wafers**
- **Plans:**
  - **Demonstrate feasibility of 'force spectroscopy' for Step – 2 and Step – 3 copper & barrier polish**
  - **Integrate and validate results with MIT's pattern evolution and nano-topography models**

Detection and Modeling of Pattern Evolution

Real-Time 'Force Spectroscopy'

Blanket Copper Wafer





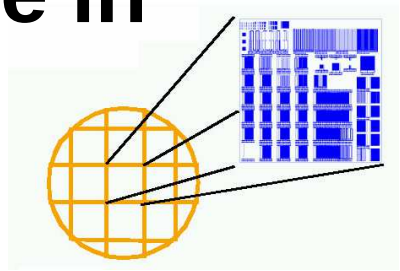
Blanket Tantalum Wafer

Relating Pad Properties to Feature/Chip-Scale Topography Evolution

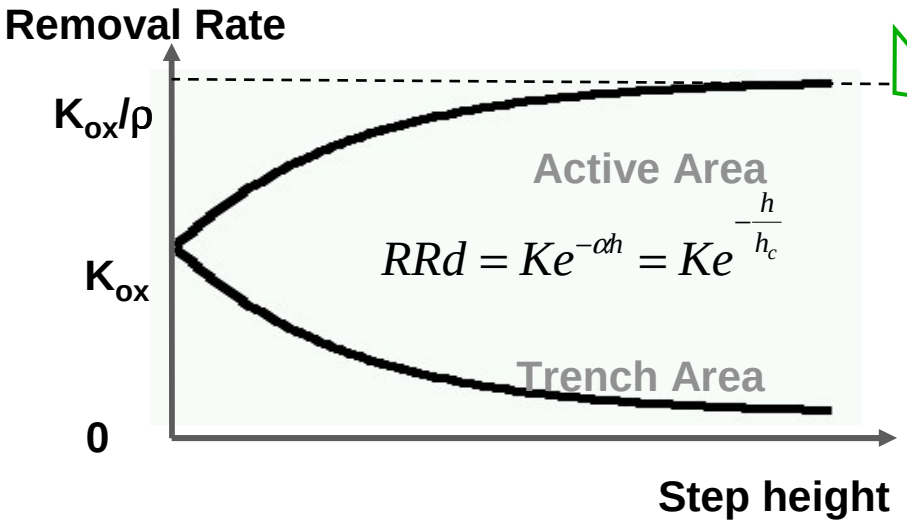
Subtask 1: Wear phenomena and their effect on process performance

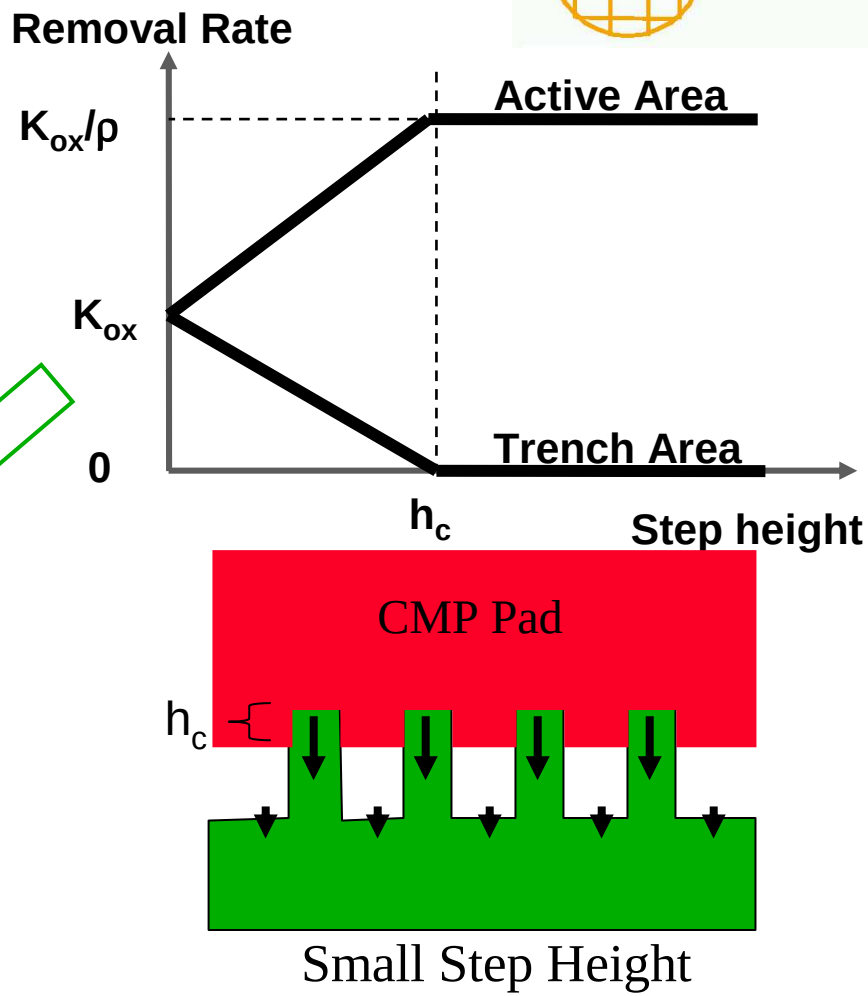
- Key issue: how can we relate pad structure and parameters to the efficiency of planarization?
- Approach:
  - Extend previous *empirical* CMP model, specifically to…
  - Address the role of surface asperities in planarization, dishing, and erosion
  - Enable integration with detailed experiments and models of larger ERC team (UA, Tufts, Purdue) in pad/slurry effects
- Results:
  - Model extensions which improve physical basic for chip-scale CMP model, and explicitly account for pad surface properties

Review: Step Height Dependence in Chip-Scale CMP Model



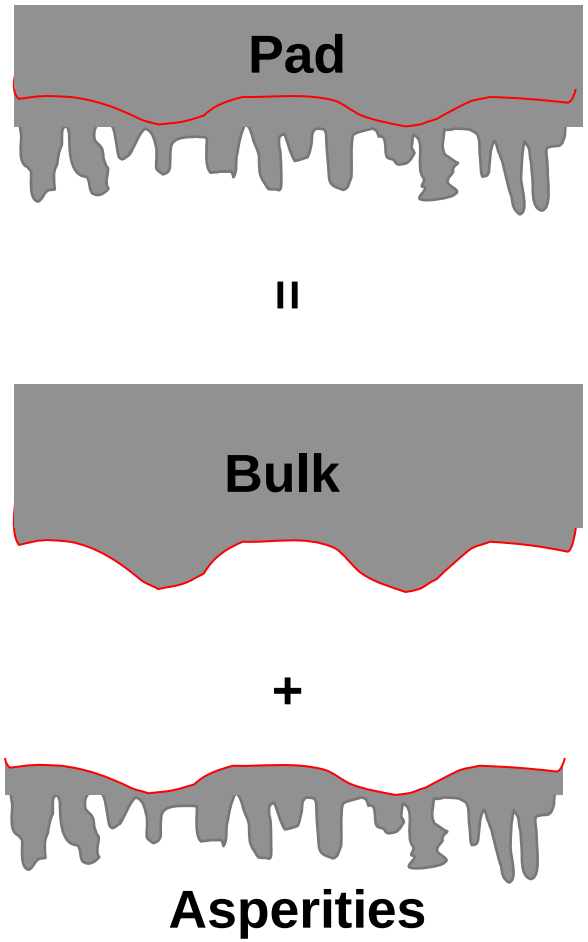
- Step-Height Model
  - Removal rate depends on the step height
  - Exponential model assumes a continuous transition between the two phases





Basis for Extended Model

- Pad is assumed to consist of a “bulk” material with surface asperities
- Bulk material obeys
  - contact wear model
- Asperities are assumed to
  - have negligible width
  - observe Hook’s law, i.e. the force it exerts is proportional to its compression



Combine Bulk and Asperities

- Bulk surface displacement *w* and pressure *P*

$$w_0 - w = F¢\ (P - P_0)$$

- Asperities compression requires

$$P = \rho\, k\, \Psi(w) + (1-\rho)\, k\, \Psi(w+h)$$

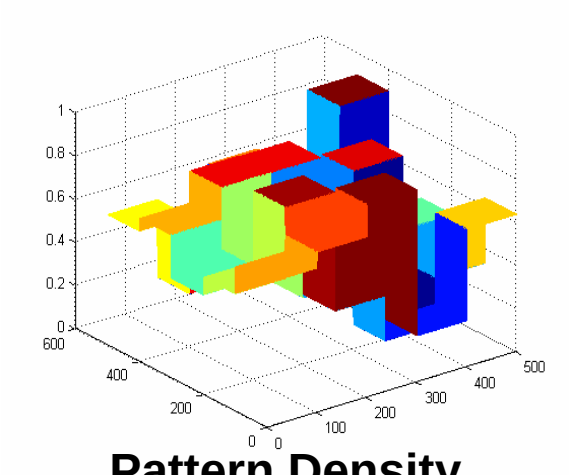
  - ρ is local pattern density
  - k is Hook's coefficient
  - h is local step height
  - Define asperities height distribution: p(ξ)

$$\Psi(w) = s_w^{1} d\eta\, s_\eta^{1} d\xi\ p(\xi)$$

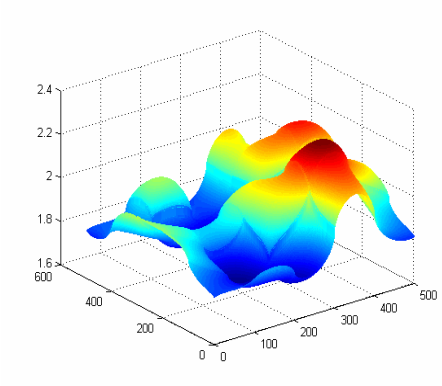
- From two eqns, *w* and *P* can be solved
  - Removal rate is proportional to *P*

Verify Pattern-Density/Step-Height (PDSH) Model, case 1

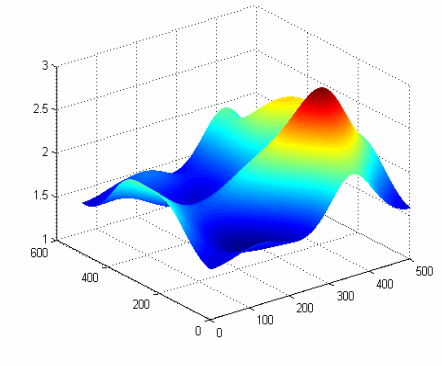
- Assumptions
  - Uniform asperities height
  - i.e. $p(\xi) = \delta(\xi_c - \xi)$
- Physical model predicts similar removal rate as our older pattern density model



Pattern Density



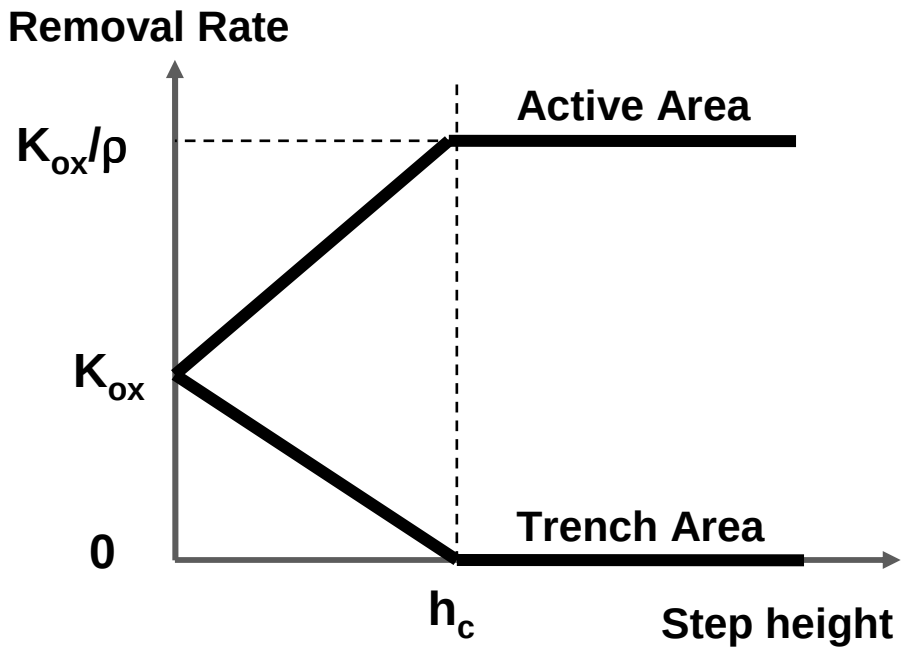
P_{raised} Map



Pattern Density Model

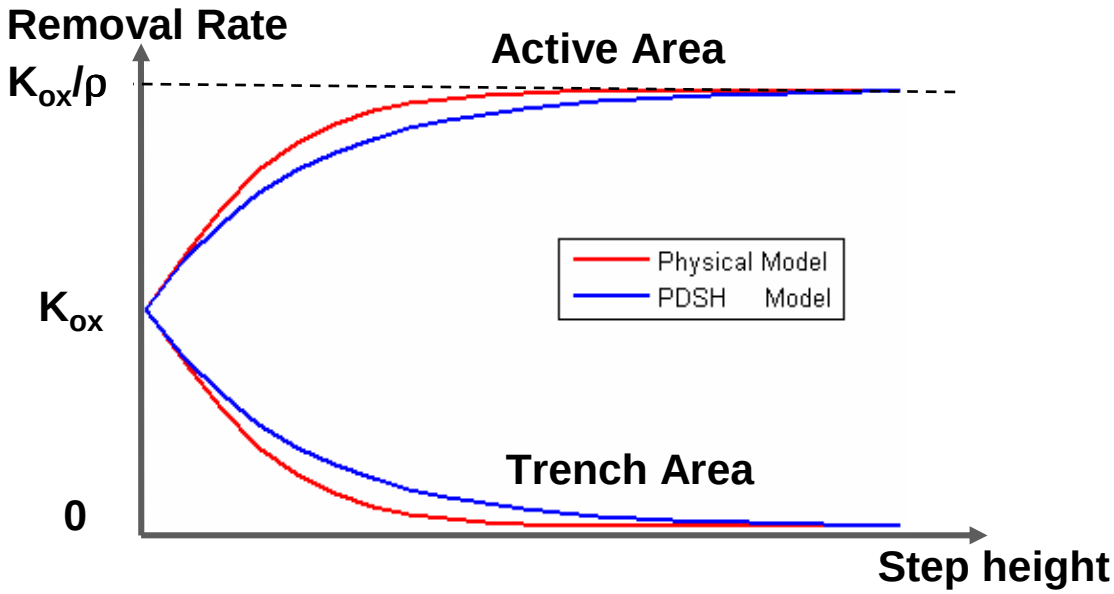
Verify PDSH Model, case 1

- When $h<\xi_c-w$
  - $P_{raised}=P_0+(1-\rho)kh$
  - $P_{trench}=P_0-\rho\ kh$
- When $h_{,}\ \xi_c-w$
  - $P_{raised} = P_0/\rho$
  - $P_{trench}=0$
- Transition height
  - $h_c = P_0/k/\rho$
- That is the assumption in PDSH model



Verify PDSH Model, case 2

- Assumptions
  - Exponential distribution of asperity heights: $p(\xi) = e^{-\xi/\lambda} / \lambda$
- Step height dependence
  - $P_{raised} = P_0 / (\rho + (1-\rho)e^{-h/\lambda})$
  - $P_{trench} = P_0 \, ¢ \, e^{-h/\lambda} / (\rho+(1-\rho) e^{-h/\lambda}))$



Opportunities: Pad Properties Integrated with Chip-Scale Model

- Physical-based model
  - Uses reasonable assumptions
  - Computationally feasible
  - Verifies and extends previous CMP models
  - Link empirical model parameters with physical pad property parameters (bulk modulus; pad surface asperity height distributions)
- Next steps
  - Implement time-step CMP model
  - Verify with experimental data
    - Empirical pad asperity height info (UA, Tufts interaction)

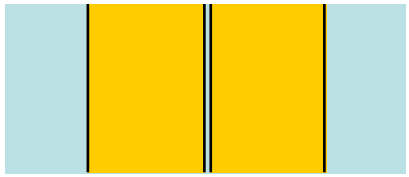
Control of Dishing/Erosion in Copper Interconnect

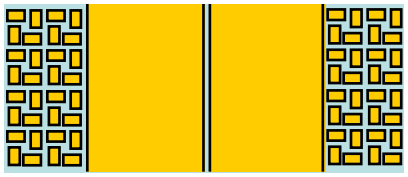
Subtask 2: Real-time detection and modeling of pattern evolution

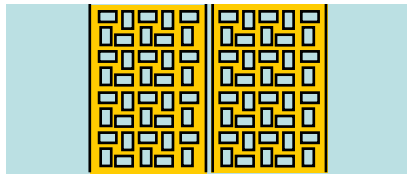
- Key issue: how do we reduce and *control* pattern dependent variations in copper plating/CMP?
- Approach:
  - Design “in-pattern” dummy fill structures
  - Use new integrated ECD/CMP chip-scale model to jointly optimize process and dummy fill design
- Results:
  - In-pattern dummy fill can dramatically reduce dishing *and* required fill thicknesses in future CMP
- Future:
  - Relate real-time signals (UA) to pattern evolution on the chip, to improve process endpoint and control

Alternative Dummy Fill Strategies

Top view







Side view

(a) Without dummy fills

(b) With between-pattern dummy fills

(c) With in-pattern dummy fills

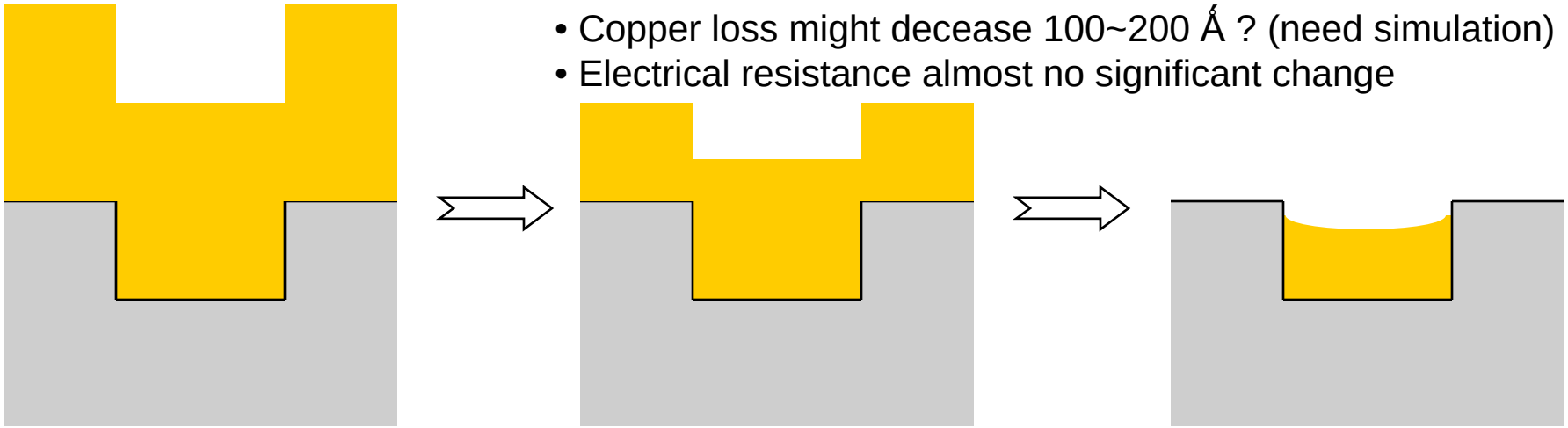
Conventional Approach

Alternative Approach

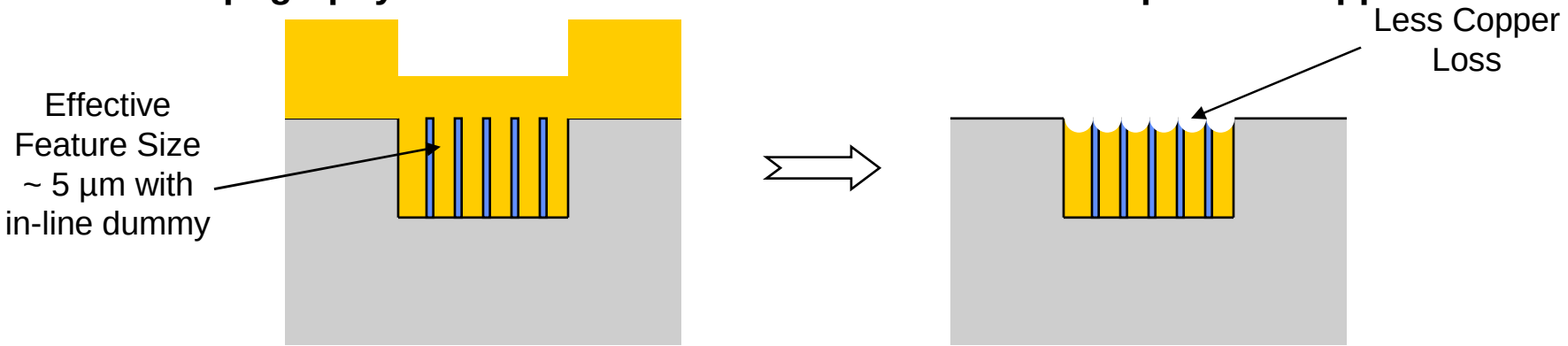
In-Pattern Dummy Fill

In-Line Dummy

- Total effective line width decreases 5 ~10%
- Copper loss might decease 100~200 Å ? (need simulation)
- Electrical resistance almost no significant change

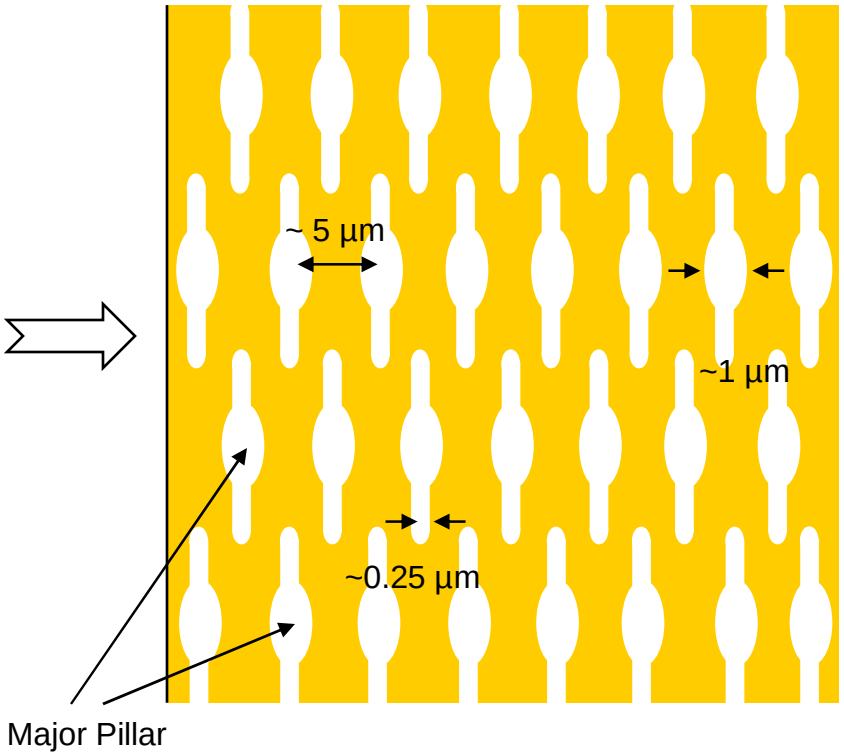


CMP Topography Evolution for Wide Feature with Thick Deposited Copper Film



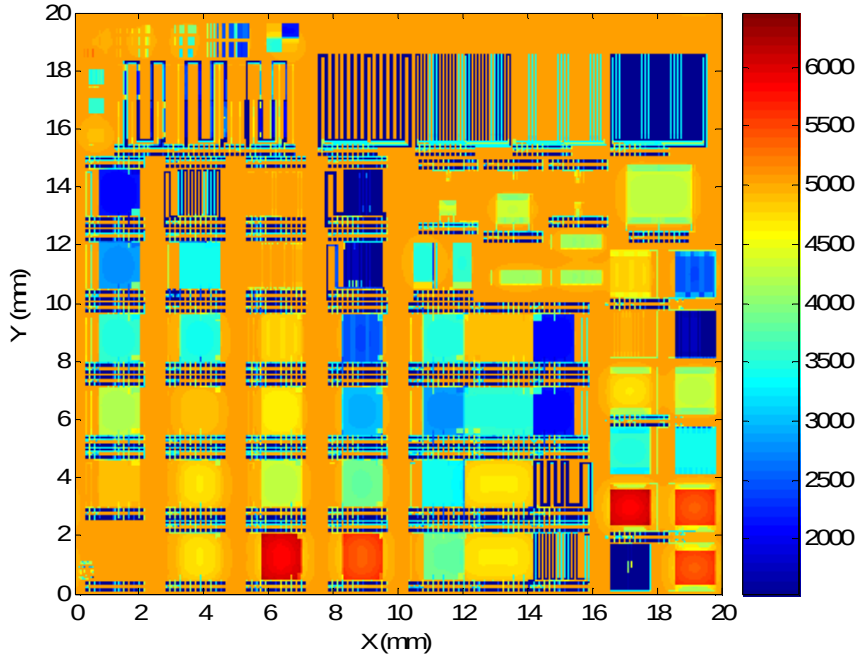
CMP Topography Evolution for Wide Feature with Thin Deposited Copper Film and In-Line Dummy

In-Pattern Dummy Design



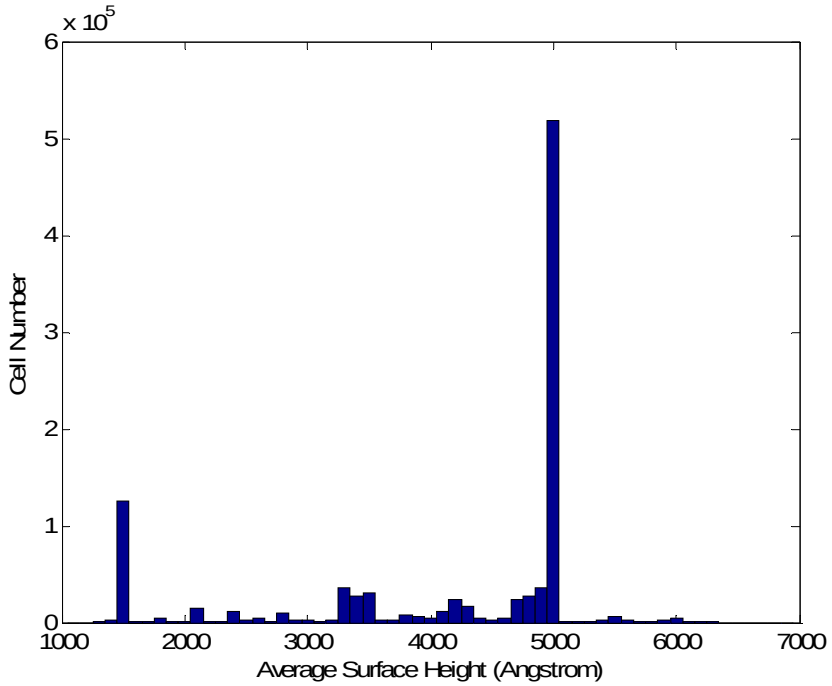
- Goals:
  - Optimize dummy design to improve *both* plating and post-CMP topography
- Approach:
  - Add “slot” to increase trench wall surface areas, thus increasing plated copper thicknesses
  - Add “pillar” oxide structures to support the pressure of the pad, and restrict ability of asperities to reach copper between fill structures

ECD Simulation w/o Dummy Fills



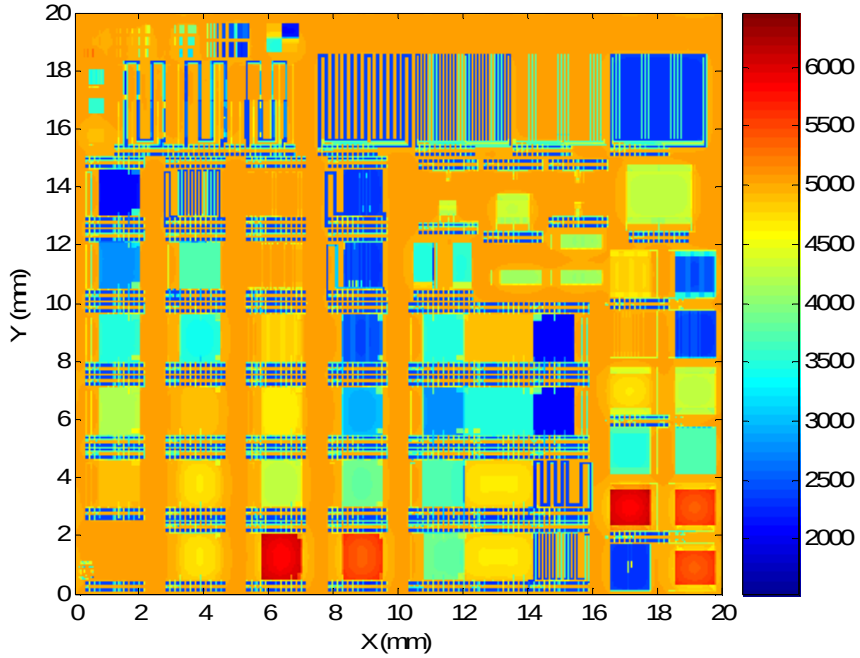
Average surface height map (Å)

Histogram of average surface height



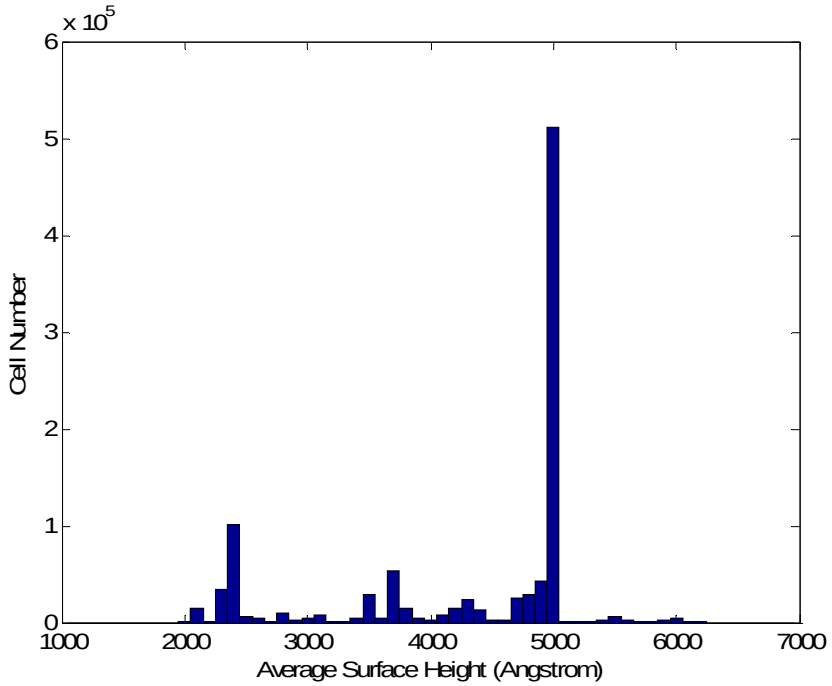
Chip-Scale ECD Modeling at t=100 sec

ECD Simulation w/ Dummy Fills



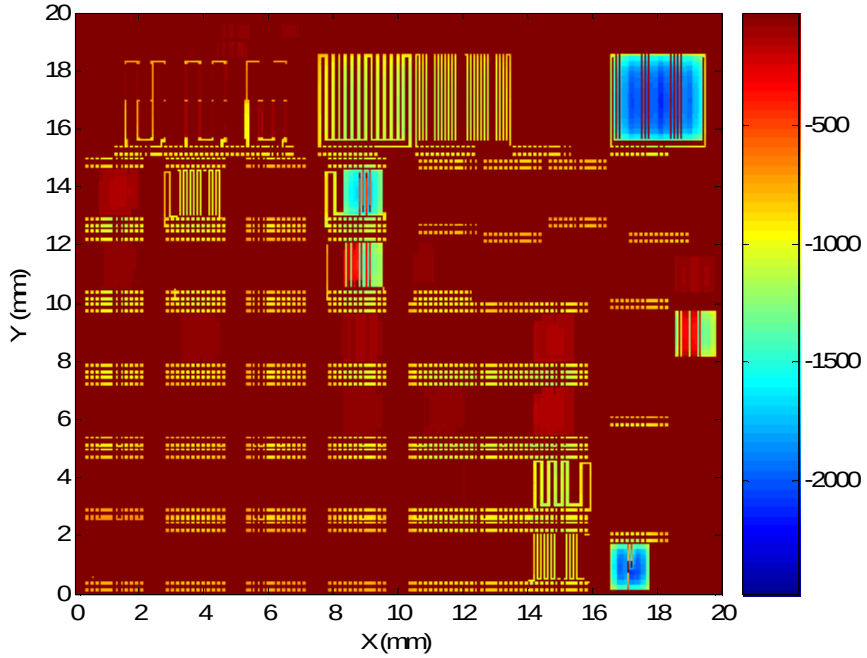
Average surface height map (Å)

Histogram of average surface height



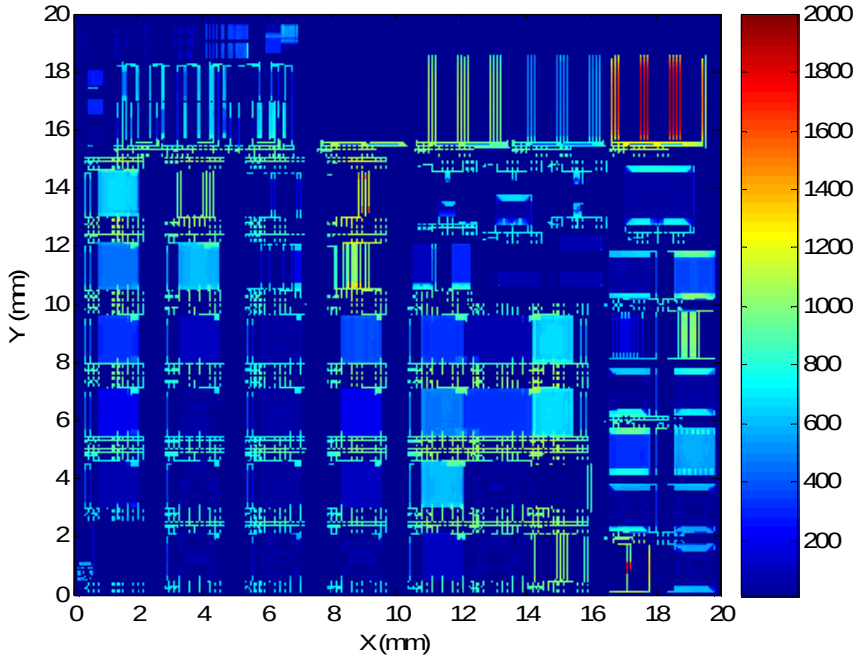
Chip-Scale ECD Modeling at t=100 sec

CMP Simulation w/o Dummy Fills



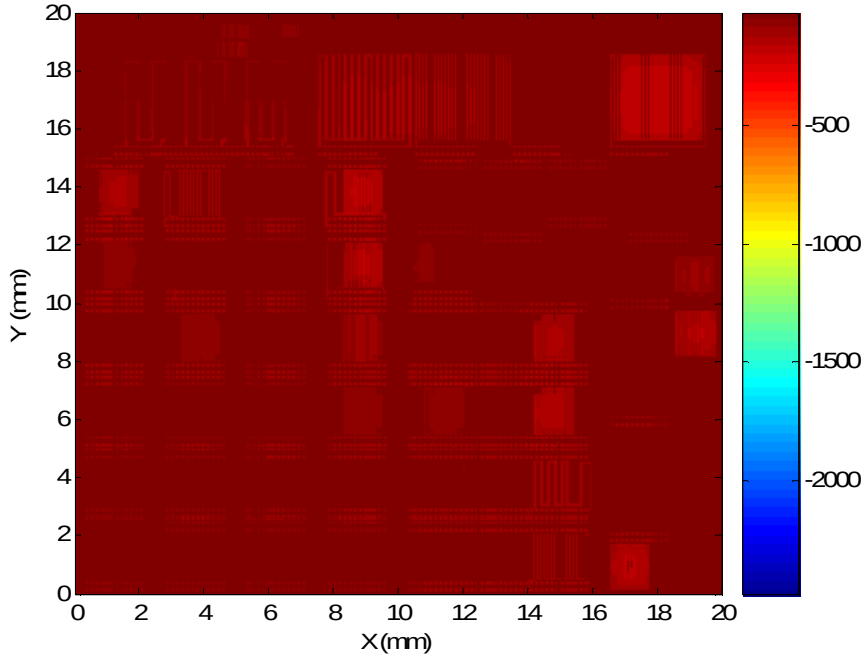
Envelope map (Å)

Step height map (Å)



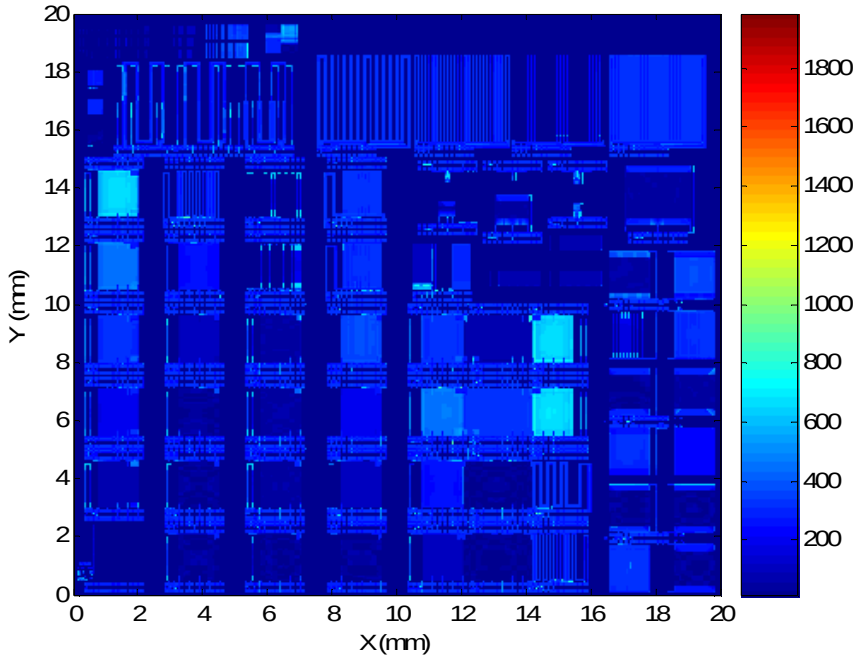
Chip-Scale CMP Modeling at t=120 sec

CMP Simulation w/ Dummy Fills



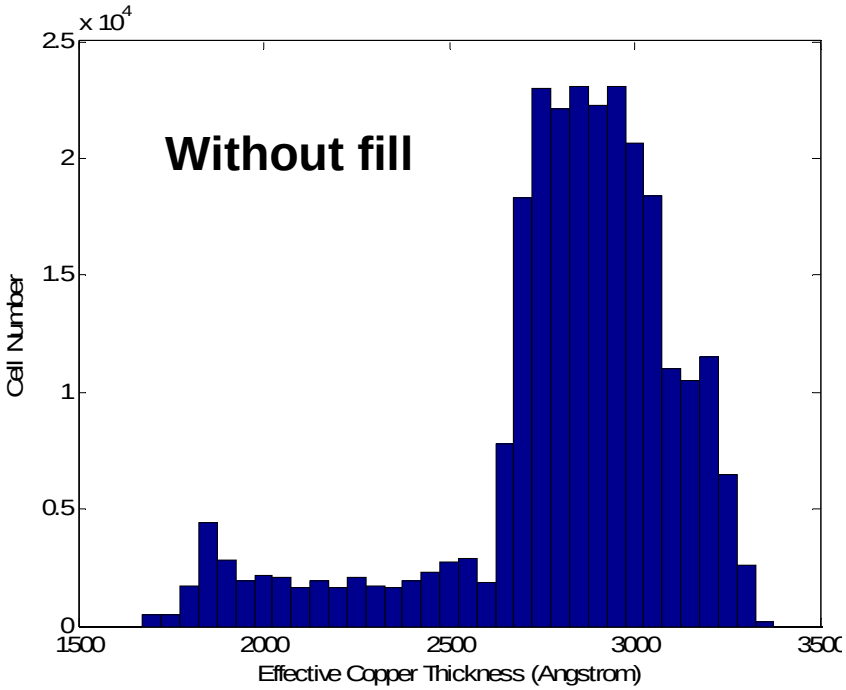
Envelope map (Å)

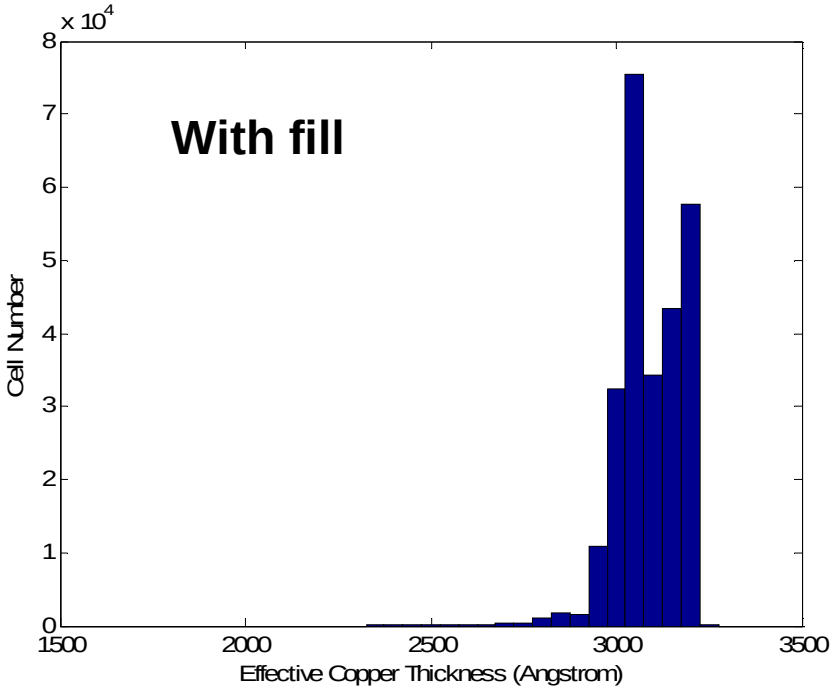
Step height map (Å)



Chip-Scale CMP Modeling at t=120 sec

Comparison: Effective Copper Thickness w/o and w/ In-Pattern Dummy Fills





- Key results
  - Dramatically improved topography based on fills designed with *both* ECD and CMP in mind
  - Reduction of copper thickness required, from 8500 Å to 5000 Å, results in >40% reduction in plating and polishing

Summary and Next Steps

- Team
  - Xiaolin Xie (Ph.D. candidate, Physics, finishing this spring)
  - Hong Cai (Ph.D. candidate, Materials Science, finishing this spring)
  - Daniel Truque (S.M. student, EECS, finishing this spring)
  - Visiting Professor: Dr. Ed Paul (2006-2007 academic year)
- Results
  - Extended our previous *empirical* chip-scale CMP model to include pad surface asperity effects and statistics
  - Completed an integrated ECD/CMP chip-scale model
  - Developed an “in-pattern” dummy fill strategy to control and reduce dishing/erosion loss
- Next Steps
  - Relate additional pad/slurry properties to planarization performance
  - Explore real-time endpoint signal relationships with pattern evolution model

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

SRC ID #425.020 / ERC Thrust A / Subtask 1.2

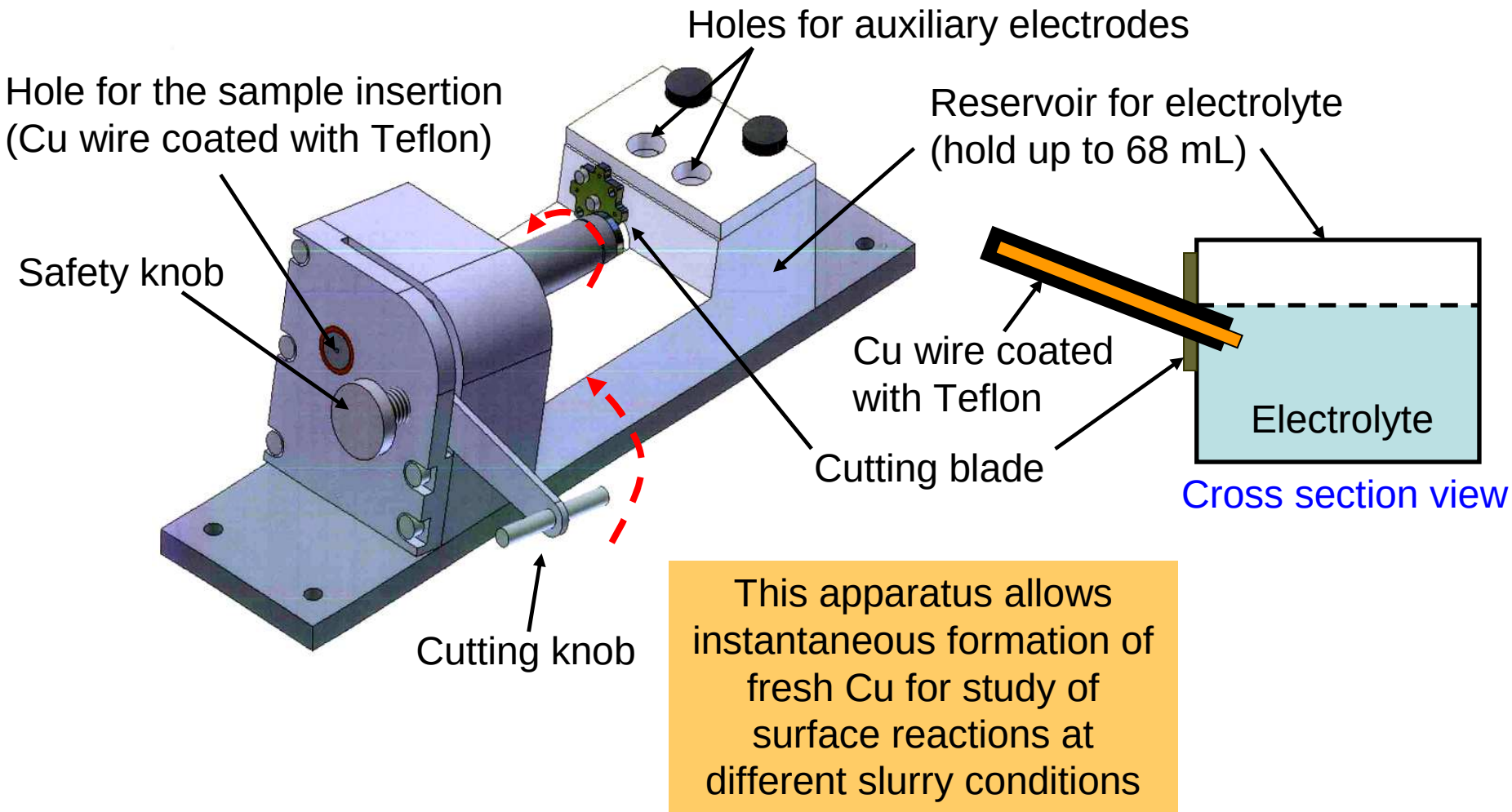
Bum Soo Kim
Caiti Kilroy
Steve Beaudoin
School of Chemical Engineering
Purdue University

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Project Objective

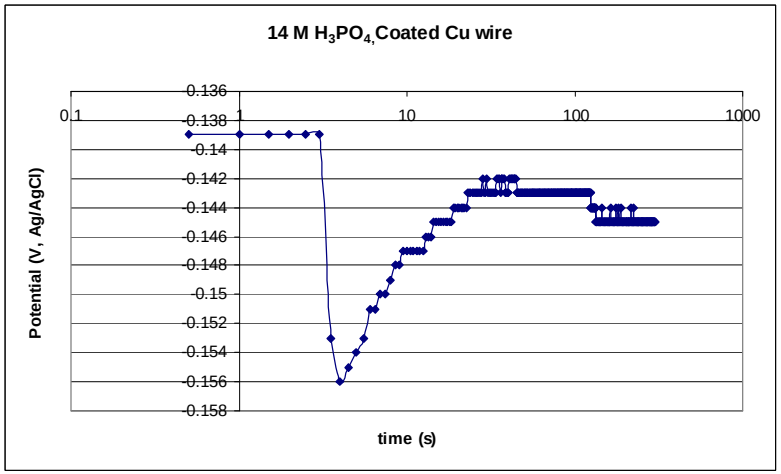
- Evaluate electrochemical processes occurring on Cu surfaces in slurry
  - CMP-relevant timeframes
  - Provides information on chemical state, mechanical properties of Cu surface
- Develop, validate models for Cu removal based on dissolution, abrasion
  - Including submodels for particle interactions with Cu surface

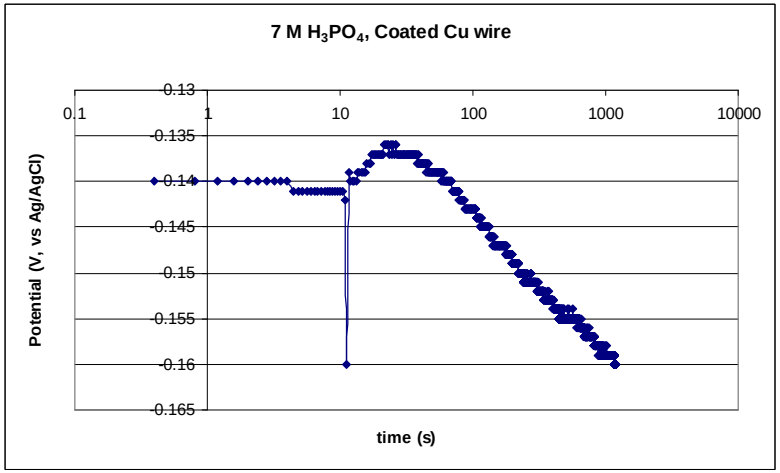
Guillotine Electrode: Reactions on CMP Timeframes

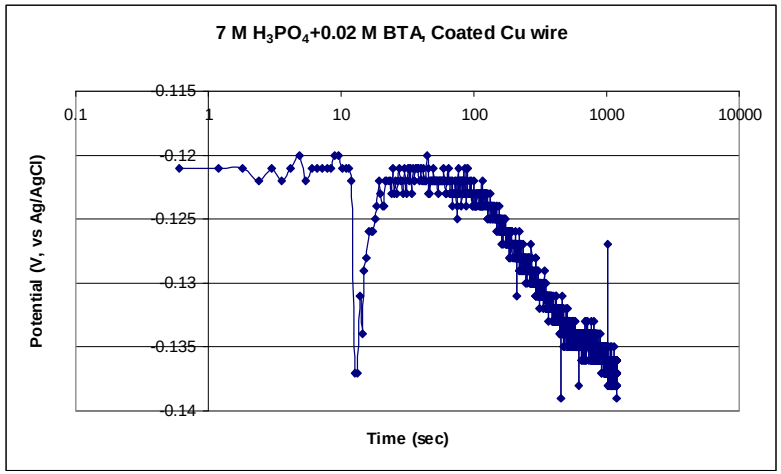


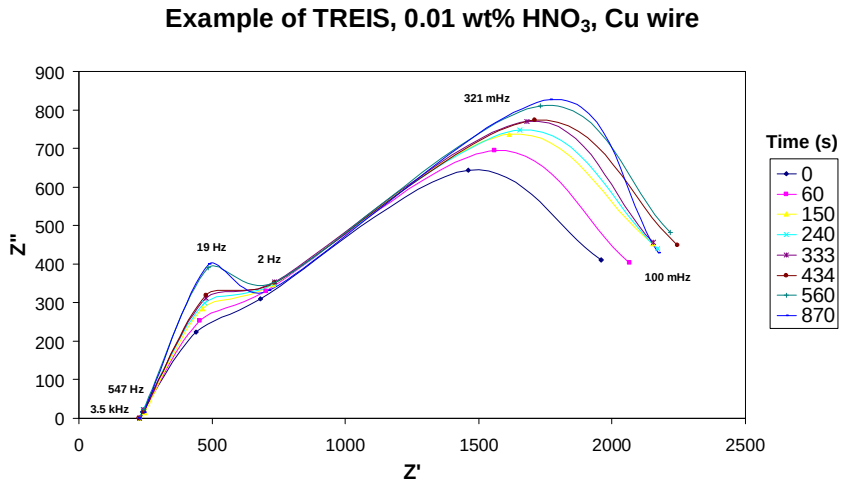
This apparatus allows instantaneous formation of fresh Cu for study of surface reactions at different slurry conditions

Preliminary Results









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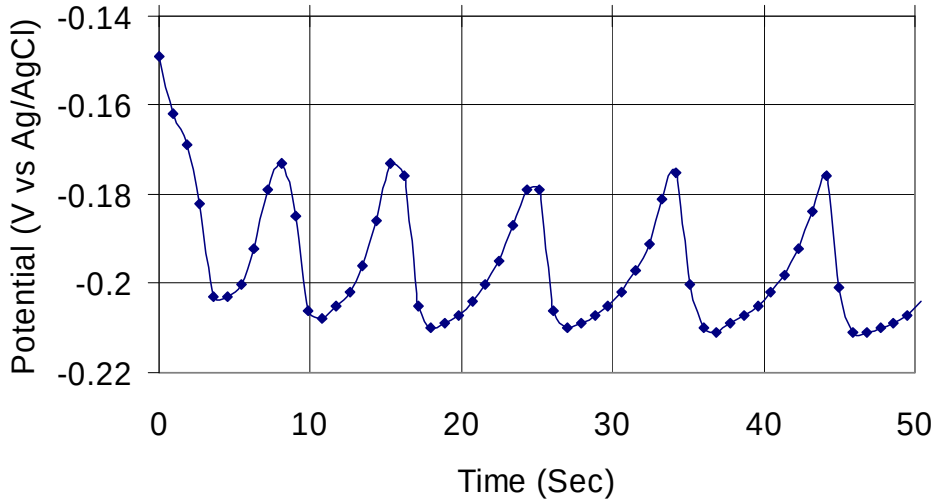
Reactions on Copper: E-Chem Oscillation



Copper disk at 0 rpm
- Electrolyte
  - 2.25 M HCl
  - 0.43 M H_2O_2
- OCP (Open Circuit Potential)

❖ Rising potential
  ▶ Net passivation

❖ Decreasing potential
  ▶ Net dissolution

❖ OCP (Open Circuit Potential) oscillation due to
  ▶ Balance of mass transfer to electrode surface, surface reaction
  ▶ Local pH fluctuation due to surface reaction
  ▶ Instability of the surface film

❖ Repetitive passivation and dissolution of Cu surface while the surface itself is being smoothed → possible ***ECMP*** application

Modeling E-Chem Oscillation

$$\frac{de}{dt} = \frac{v-e}{r} - m_1 k_1 u_1 - m_2 k_2 u_2$$

$$\frac{du_1}{dt} = -1.25 d^{1/2} k_1 u_1 + 2d(w_1 - u_1)$$

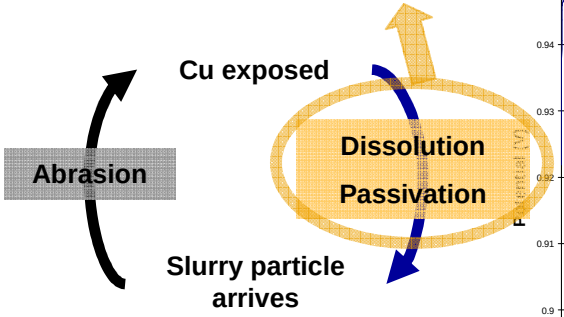
$$\frac{du_2}{dt} = 1.24 d^{1/2} k_2 u_2 - 1.54 d(w_2 - u_2)$$

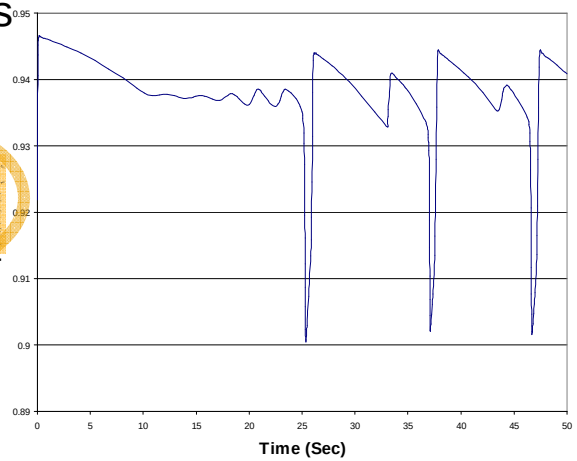
$$\frac{dw_1}{dt} = 1.6 d(2 - 3w_1 + u_1)$$

$$\frac{dw_2}{dt} = 0.386 d(1 - 2w_2 + u_2)$$

e: dimensionless electrode potential
v: dimensionless applied potential
u_i: dimensionless concentration in boundary layer 1 which contacts the electrode surface (H^+(i=1), Cu^{2+} (i=2))
w_i: dimensionless concentration in layer 2 (H^+(i=1), Cu^{2+} (i=2))
k_i: dimensionless surface reaction constant (H^+(i=1), Cu^{2+} (i=2))
r: dimensionless solution resistance
d: dimensionless rotational speed
m_1 and m_2: dimensionless numbers containing electrode surface area, Faraday number, capacitance, solution concentration, temperature

Potential oscillations

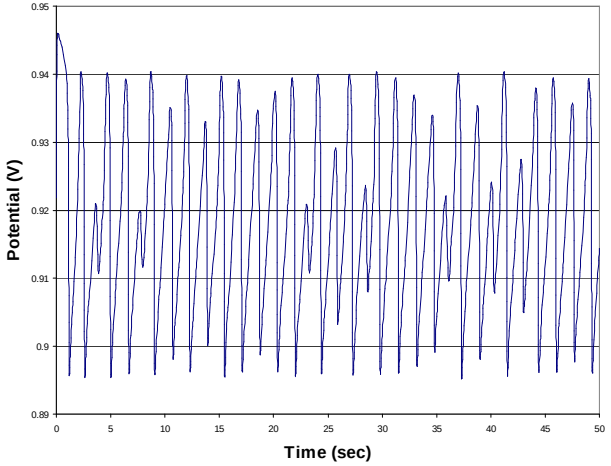




- Allows description of mass transfer and surface reaction effects in Cu CMP
- Following generalization and validation, may allow prediction of Cu reaction, dissolution, and passivation rates

Modified model proposed: Koper *et al.*, *J. Chem. Phys*. **96(10)**, (1992)

Large (above) and small (below) diffusion coefficient



Conclusion

- Corrosion reaction on Cu surface
  - Corrosion rate dynamics obtained in presence of BTA
- Guillotine electrode: reaction on ‘fresh’ metal surface
  - Surface repassivation and dissolution can be monitored
    - Independent of any prior oxide film
  - TREIS can be achieved
- Electrochemical oscillation
  - Continuous passivation and dissolution under various solution compositions observed
  - Can predict mass transfer and surface reaction effects in Cu CMP
  - Coupled with electrochemical polishing, has potential to be utilized in ECMP

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

Task ID : 425.014

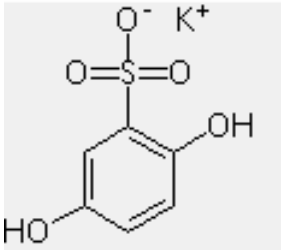
Srini Raghavan (PI)

Ashok Muthukumaran (Graduate student)

Department of Materials Science and Engineering
The University of Arizona

Ta CMP

- Conventional Ta CMP
  - Silica particles in slurry ~ 5-10 weight %
  - Alkaline pH ; H_2O_2 as oxidant
  - Mostly *mechanical* in nature
- Literature information
  - Benzene sulfonic acid
    - Recent patent applications mention derivatives of benzene sulfonic acid as oxidant under acidic condition
      - United States Patent Application 20060030158, Cabot Microelectronics (2006)
      - United States Patent Application 2005090109, EKC Technology (2005)
    - Etching and polishing of Ta
    - pKa of dihydroxy benzene sulfonic acid ~12.2



Potassium salt of dihydroxy benzene sulfonic acid

  - Aryl disulfonic acid (e.g: dihydroxy benzene disulfonic acid or Tiron)
    - Complexes with refractory metals

Objective

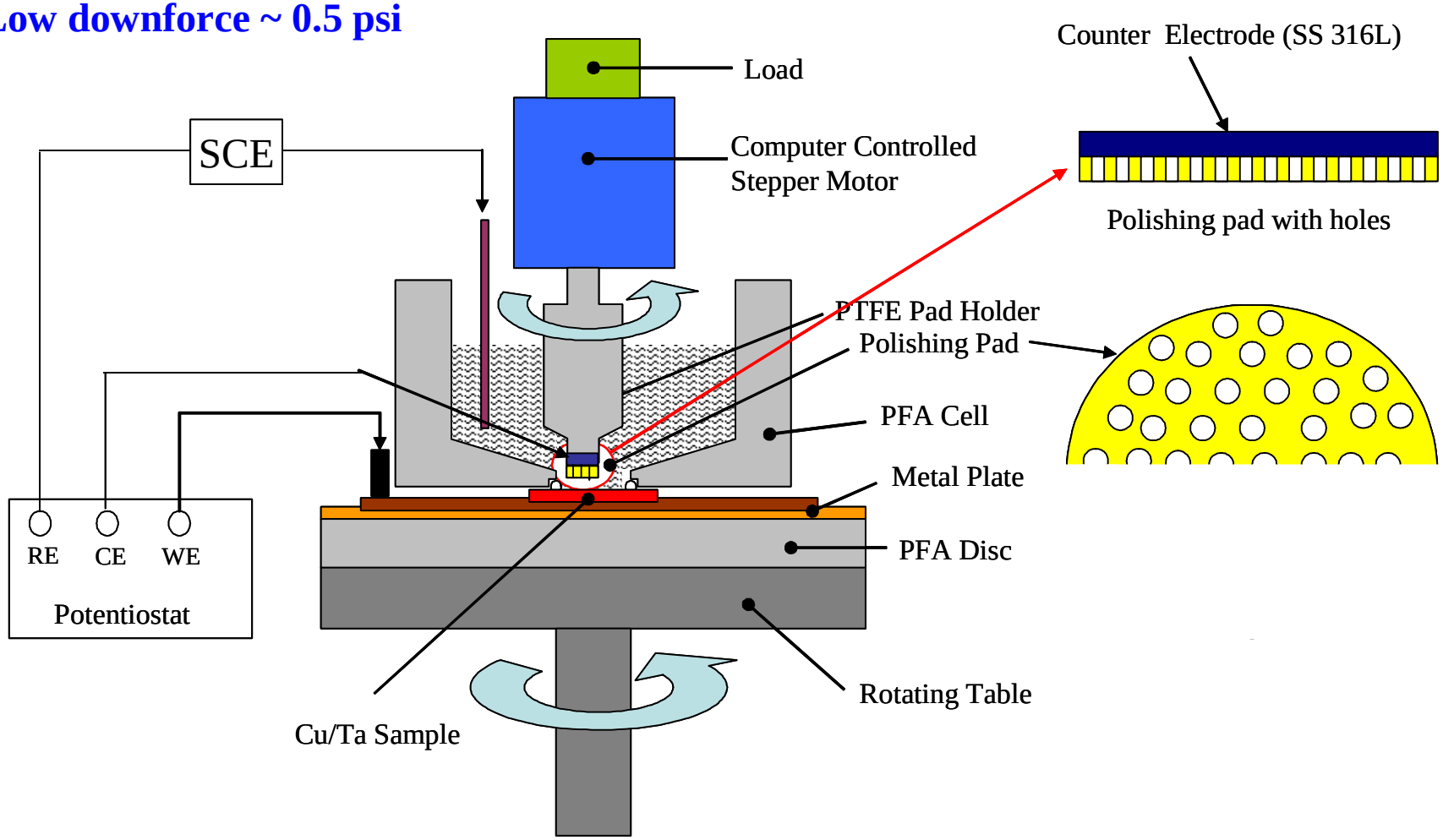
- To develop chemical system suitable for electrochemical mechanical removal of tantalum films with a 1:1 selectivity with respect to copper under ECMP conditions.

Accomplishments During the Current Contract Year

- Developed sulfonic acid based chemical system suitable for electrochemical mechanical removal of tantalum films.

Modified ECMP Tool

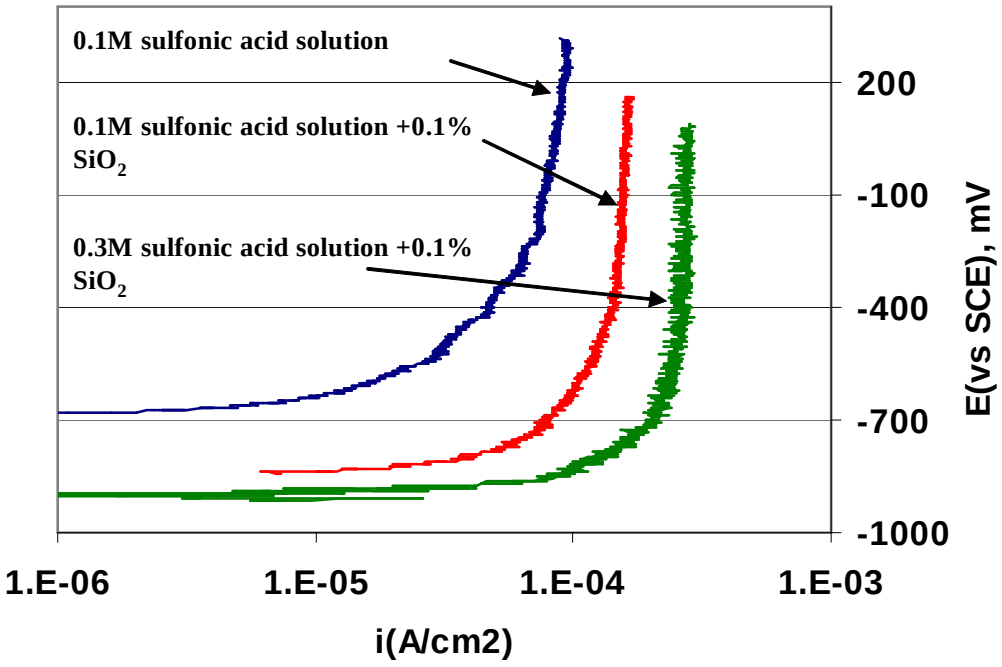
Polishing area = 22 cm^2
Low downforce ~ 0.5 psi



Note: Picture drawn not to scale

Anodic Polarization of Tantalum (under abrasion)

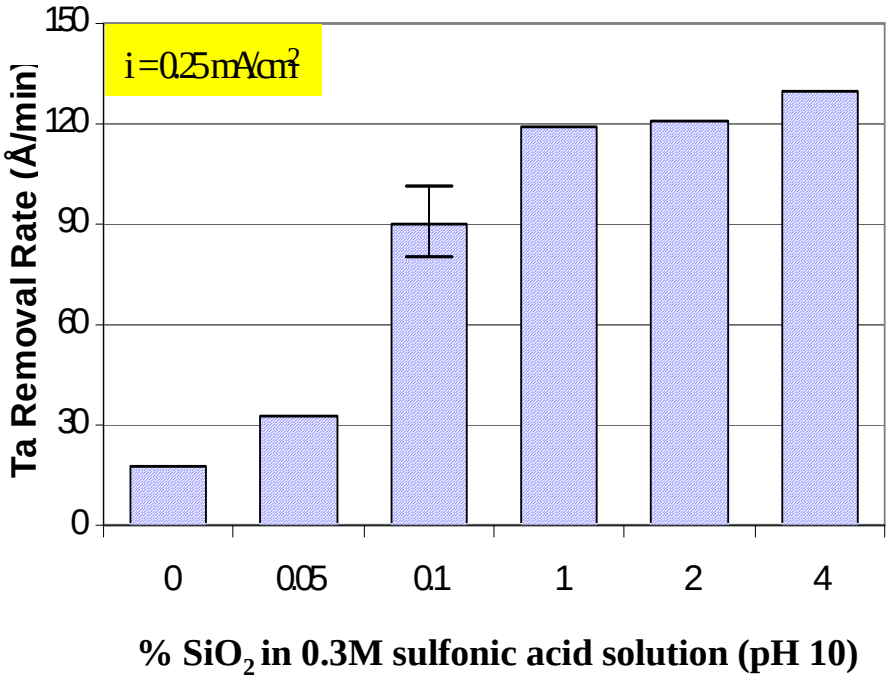
Load ~ 0.5 psi



Note: Maximum solubility of 2, 5 dihydroxybenzene sulfonic acid ~ 0.3M

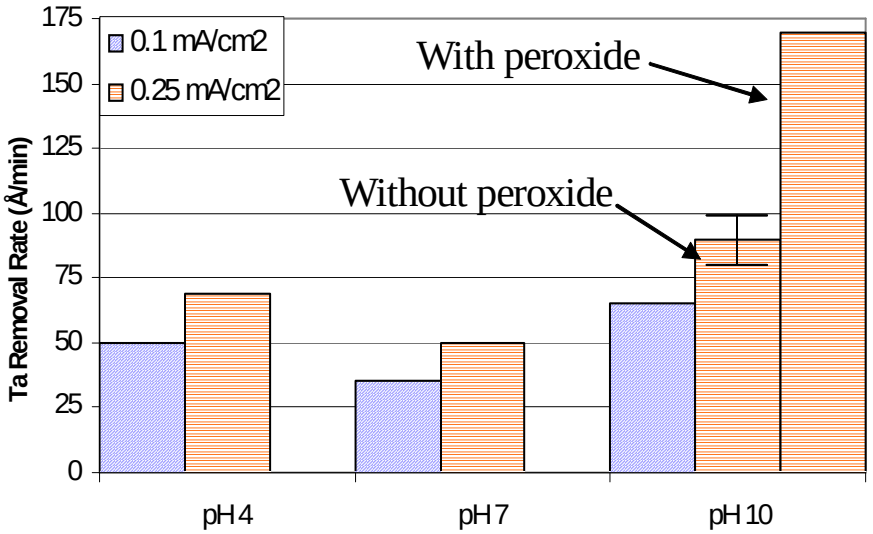
- 2,5 Dihydroxybenzene sulfonic acid solutions, in the presence and absence of silica at pH 10
- Potential sweep = OCP to 1V vs. OCP ; Scan rate = 5 mV/s
- Low current density in 0.1M sulfonic acid solution in the absence of silica particles
- Addition of silica (0.1%) to 0.1M sulfonic acid solution slightly increases the current density
- Higher current density of 0.3 mA/cm^2 was observed in solution containing 0.3 M sulfonic acid and 0.1% SiO_2

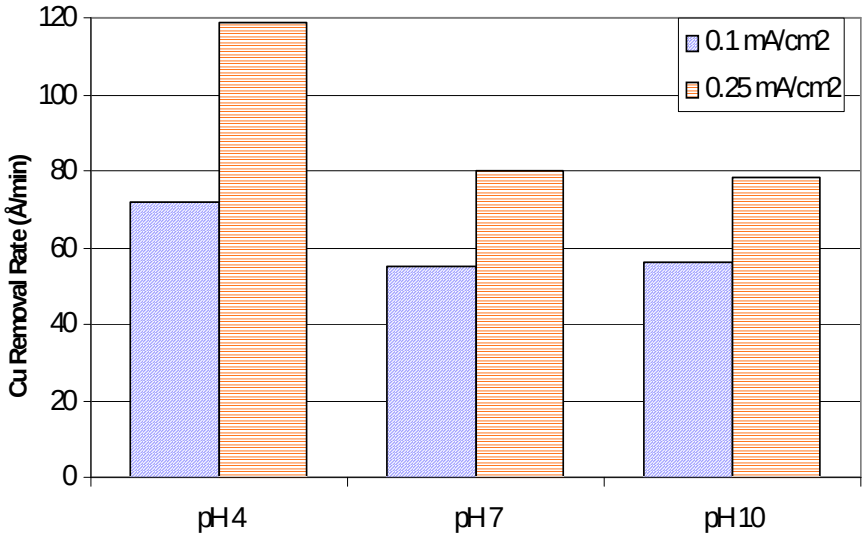
Effect of Silica Concentration



- 0.3 M sulfonic acid solution (pH 10), at a current density of 0.25 mA/cm^2
- Very low Ta removal rate in the absence of SiO_2 ~ 20 Å/min
- Addition of 0.05% SiO_2 slightly increases the removal rate to 35 Å/min
- At 0.1% SiO_2 removal rate nearly doubles ~ 90 ± 10 Å/min
- Above 0.1% SiO_2 removal rate does not significantly increase

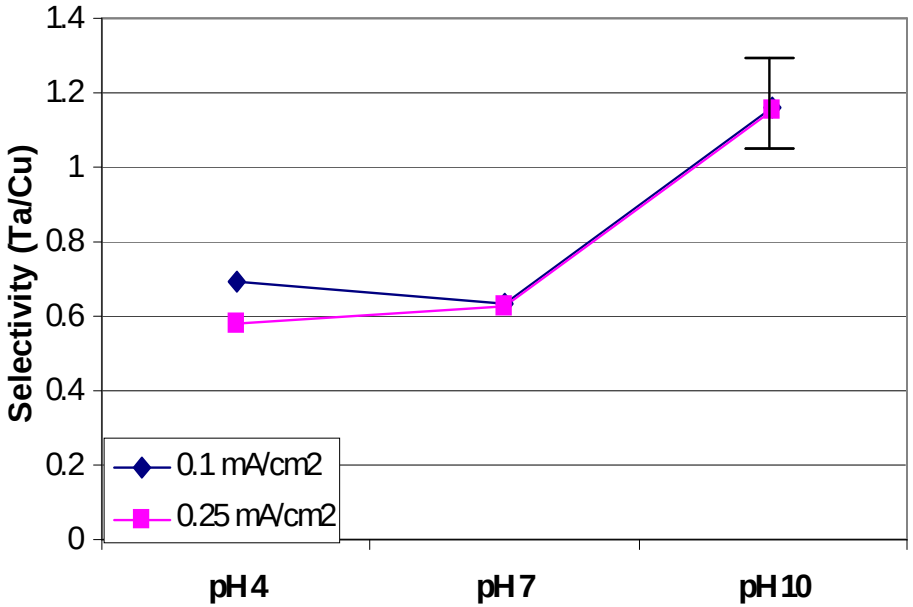
Electrochemical Mechanical Removal of Tantalum and Copper





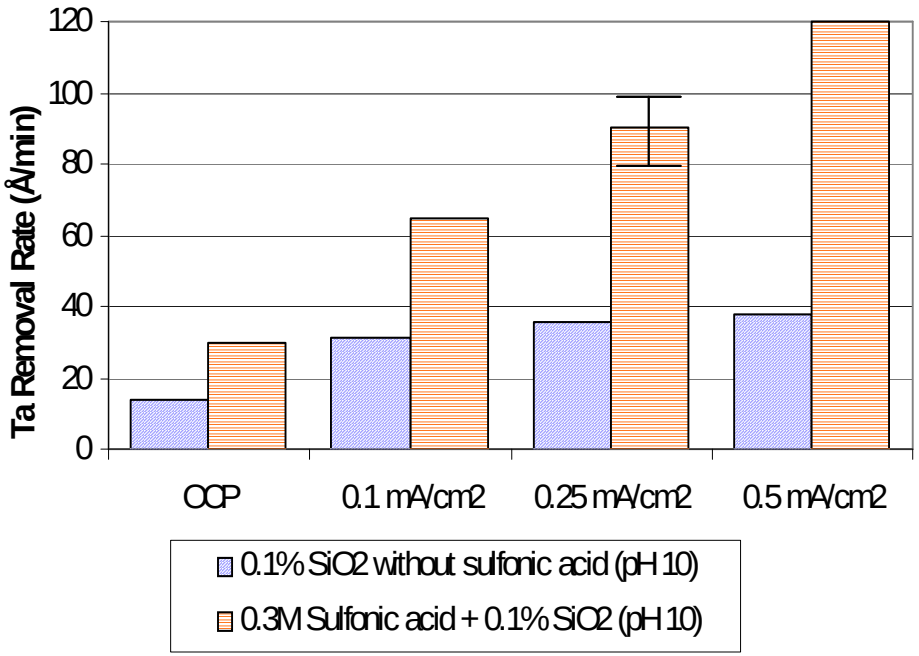
- 0.3 M Sulfonic acid solution + 0.1% SiO_2
- At pH 10, removal rate of Ta is higher ~ 90 ± 10 Å/min for i = 0.25 mA/cm^2
- Addition of 1.2M H_2O_2, removal rate of Ta increases to ~ 170 Å/min for the same current density
- At pH 10, Cu removal rate is 80 Å/min for a current density of 0.25 mA/cm^2

Selectivity



- 0.3 M sulfonic acid solution + 0.1 % SiO_2 at pH 10
- At pH 4 and 7, selectivity is ~ 0.6
- At pH 10, ideal selectivity of 1.1 ± 0.1 was obtained

Effect of Applied Current Density on Tantalum Removal



- Absence of sulfonic acid solution
  - Removal rate of Ta *plateaus* above 0.25mA/cm^2
  - Higher removal rate of Ta ~ 36 Å/min
- Presence of sulfonic acid solution
  - Removal rate of Ta increases *linearly* with increasing applied current densities
  - Highest removal rate ~ 120 Å/min, observed in 0.3 M Sulfonic acid + 0.1% SiO_2 (pH 10) at current density of 0.5 mA/cm^2

Current Efficiency

Applied current density (mA/cm^2)	Estimated Removal Rate of Ta (Å/min)	Actual Removal Rate of Ta (Å/min)			Current efficiency (%) after correcting for OCP removal rate		
		pH4	pH7	pH10	pH4	pH7	pH10
OCP	-	23	12	30	-	-	-
0.1	23	52	35	65	120*	102*	142*
0.25	56	71	52	100	84	69	119*
0.5	112	-	-	119	-	-	77

* Current efficiency greater than 100% indicates some *mechanical removal of metallic Ta*

➢Current efficiency calculated after correcting for OCP removal rate and based on *three electron transfer*

Future Directions

- Possibility of increasing removal rate by peroxide addition
- Develop chemical systems for the removal of other barrier layers (TaN, Ru)
- Electrochemical endpoint detection

Industrial Interactions and Technology Transfer

- Had many telephone discussions with Dr. Renhe Jia of Applied Materials on tantalum removal under ECMP conditions

Summary

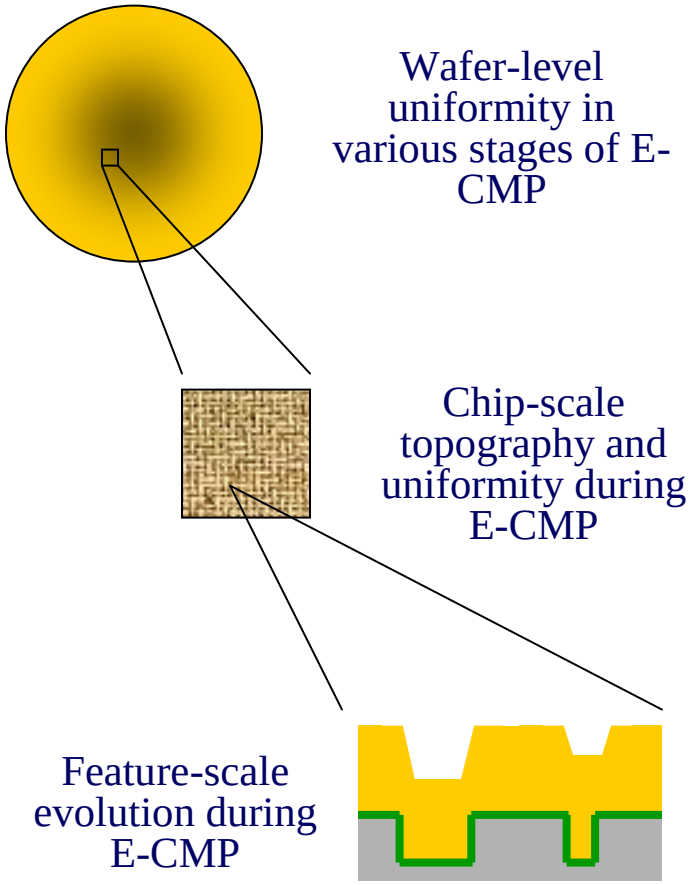
- Ta removal rate of ~ 100Å/min obtained in 0.3 M Sulfonic acid solution containing 0.1% SiO_2 (pH 10) at a current density of 0.25 mA/cm^2
- Ta/Cu selectivity of ~ 1:1 observed at pH 10
- Small amount (~ 0.1%) of silica is required for good removal rates of Ta
- 2,5 dihydroxy benzene sulfonic acid is a promising chemical for electrochemical mechanical removal of Ta barrier layer under ECMP conditions

Subtask 3: Modeling, Optimization and Control

- **PI:**
  - Prof. Duane Boning, EECS, MIT
- **Research Personnel:**
  - Daniel Truque (S.M. student, EECS, finishing this spring)
  - Visiting Scientist: Prof. Ed Paul (2006-2007 academic year)
- **Results**
  - Preliminary wafer scale E-CMP removal rate model (D. Truque)
  - Explored a model for surface film formation and removal dynamics in E-CMP, appropriate for use in feature-scale evolution modeling (E. Paul)
- **Publications**
  - D. Truque, X. Xie, and D. Boning, "Wafer Level Modeling of Electrochemical-Mechanical Polishing (ECMP)," to be presented, CMP Symposium, MRS Spring Meeting, April 2007.

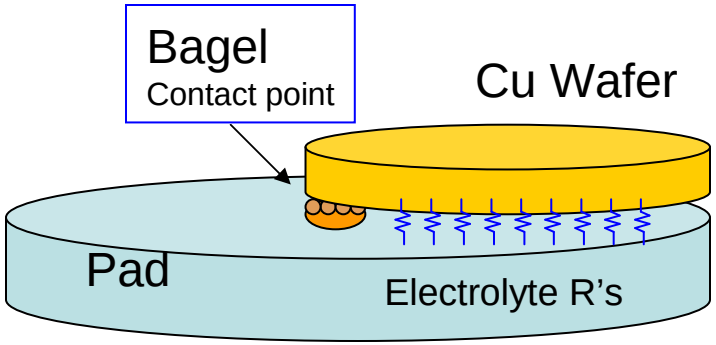
E-CMP Modeling and Control

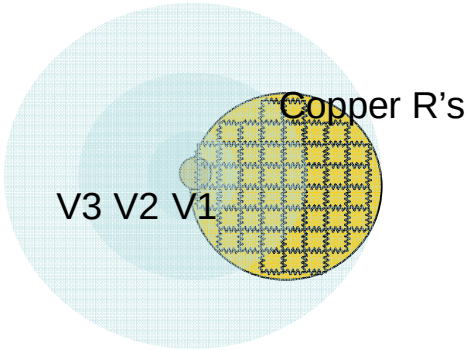
- **Novel methods and approaches for modeling and control of patterned wafer performance:**
- **Tool, pad and wafer interactions**
  - For tool design and control (particularly endpoint detection)
  - Minimize process cost & environmental impact
- **Patterned features (at completion of ECMP/CMP)**
  - Develop feature-scale, chip-scale, and wafer-scale models of process
  - Integrate/couple with plating and CMP models for chip-scale interconnect structure/geometry prediction



E-CMP Modeling and Control Highlights

- **Wafer scale uniformity is a key concern:**
  - Motivates existing tool design: current zones to achieve uniformity
  - Future: alternative tool/pad designs to improve uniformity





- **Preliminary wafer-scale modeling:**
  - Consider distributed current paths and voltage drops from contact points to wafer surface
  - Future: interactions with chip & feature-scale topography evolution

- **E-CMP tool and process learning**
  - Collaboration with IBM/Albany Nanotech (L. Economikos)
  - Assist in installation of new Applied Materials ECMP at Albany (summer 2006 – D. Truque internship at Albany/IBM)
  - Initial characterization fabrication runs

Environmental Health and Safety (EHS) Impact of Electrochemical Planarization Technologies

Kristin G. Shattuck

February 22, 2007

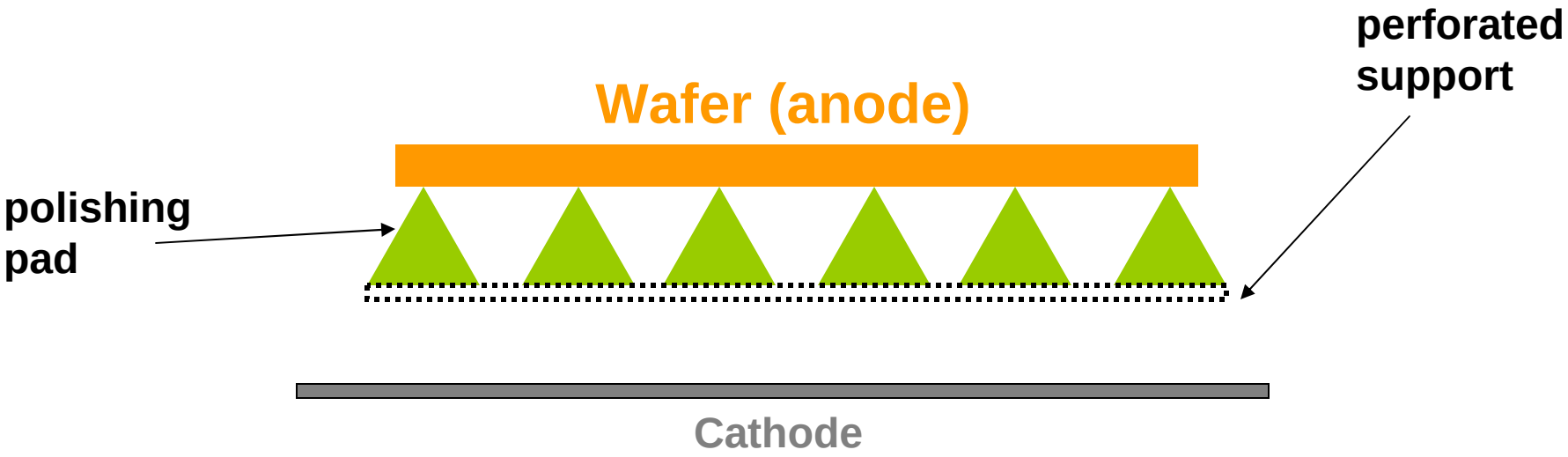
Task Number
425.016

Faculty Research Advisor
Alan West

Project Commenced
May 2006

Affiliation
Columbia University

What is eCMP?



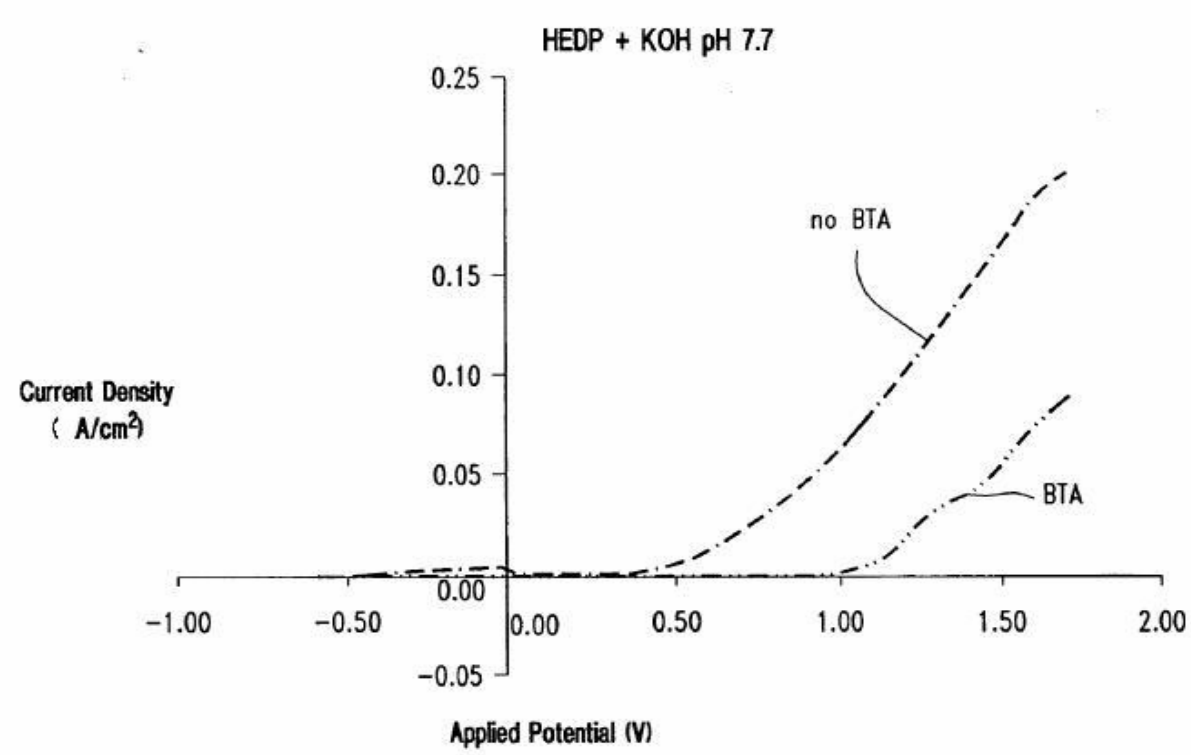
- **Potentially eliminates need for particles in slurry**
- **Reduce/eliminate use of strong oxidizers**
  - **electrons supplied by external circuit oxidize Cu**

Project Objectives

- **Develop and characterize novel chemistries to control Cu/barrier selectivity**
  - **Ru and Ta-based liners**
- **Determination of planarization mechanisms for Cu e-CMP**
  - **Role of inhibitors**
    - **BTA (Benzotriazole), PTA (Phenyl-1H-Tetrazole)**
    - **Pad/Additive Interactions**
- **Current Focus**
  - **Effect of BTA concentration & pH in phosphate-based electrolyte**
  - **e-CMP Tool**
    - **Design Completed**
    - **Preliminary Polishing results**

BACKGROUND: Previous Results

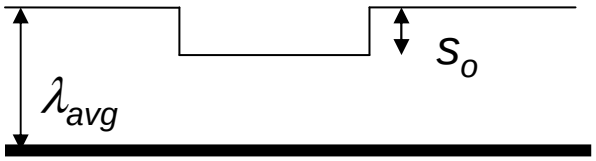
- **Ratio of currents seen with and without BTA indicate planarization capabilities**



*US Patent Application 20060163083A1 – Andricacos et al., IBM Yorktown. July 27, 2006

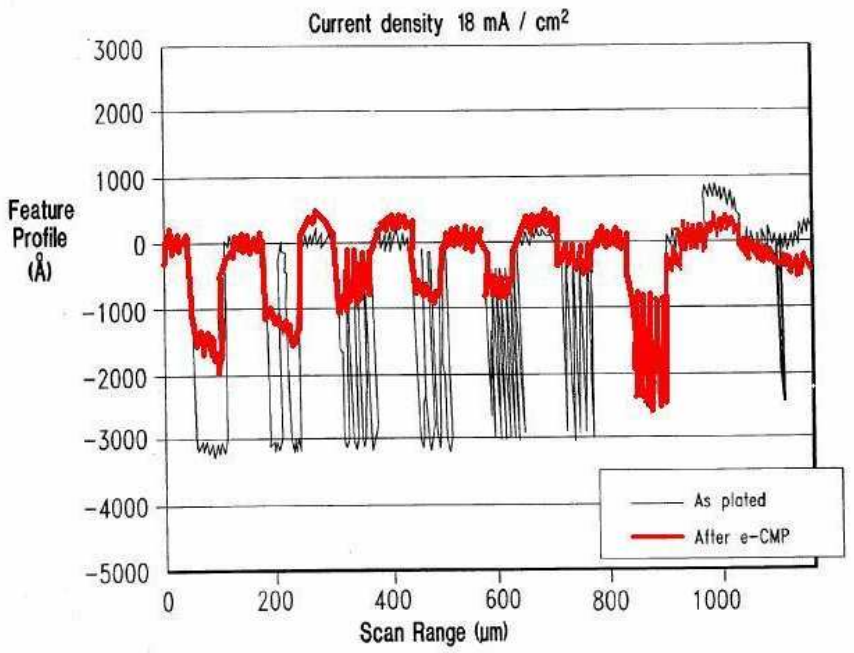
PF of BTA/HEDP System

- **Define Planarization Factor: PF**
  - **PF = s / λ**
    - **S = decrease in average step height**
    - **λ = the decrease in the average metal layer thickness**



- **Planarization results using eCMP test structure**
  - **Utilizing electrolyte with pH = 7.7**
    - **Figure 2 - PF ~ 0.65**
      - **18 mA/cm^2**

Profilometry data Before and After eCMP



*US Patent 20060163083A1 – Andricacos et al., IBM Yorktown. July 27, 2006

Electrolyte Characterization

- **Phosphoric acid based systems similar to HEDP**

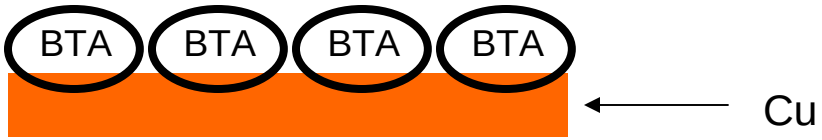
- **Current Studies Focus on:**
  - **KPO_3 – H_3PO_4 / BTA**
  - **H_3PO_4 /PTA**

- **Experimental Parameters**
  - **pH**
    - **Range 0 – 10.3**
  - **BTA Concentration**
    - **Range 0- 0.01 M**
  - **Mass Transfer**

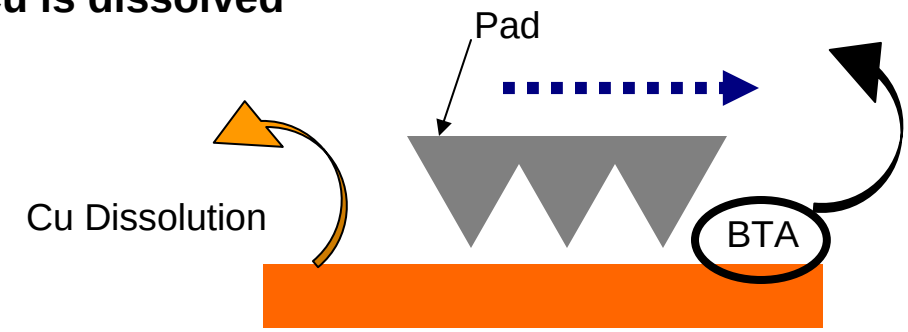
- **Characterization**
  - **Electrochemical Impedance Spectroscopy (EIS)**
  - **Linear Sweep Voltametry (LSV)**
  - **Cyclic Voltametry (CV)**

Proposed eCMP Mechanism Utilizing BTA

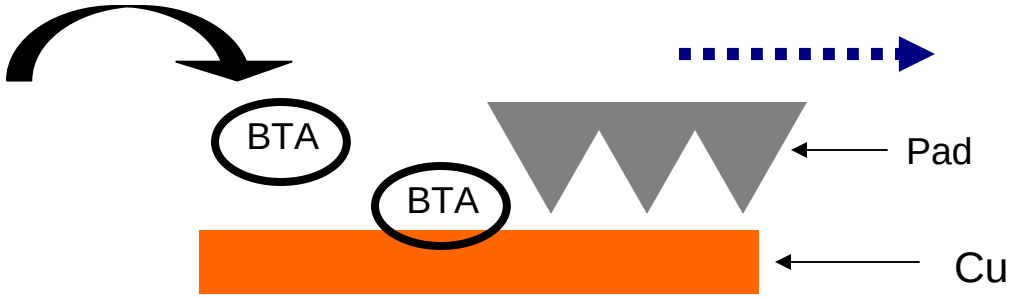
1. **BTA adheres to surface**
   - **Forms BTA-Cu complex**



2. **Pad mechanically removes Protective BTA layer**
   - **Exposed Cu is dissolved**

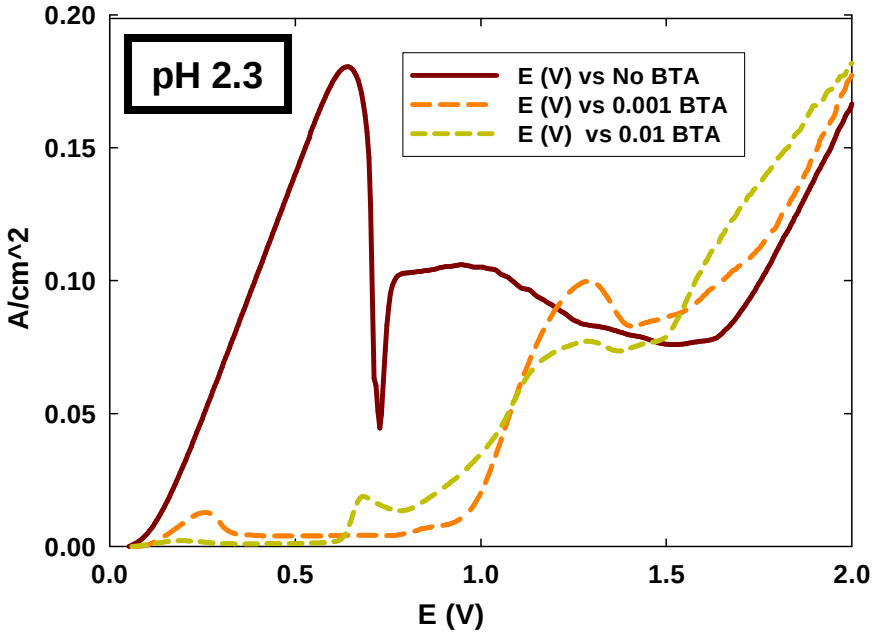


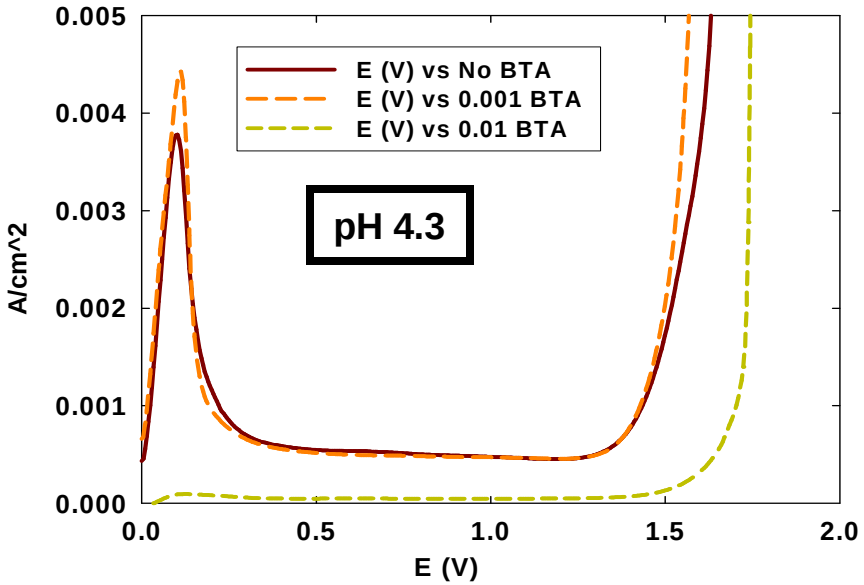
3. **BTA re-attaches to protect new CU surface**

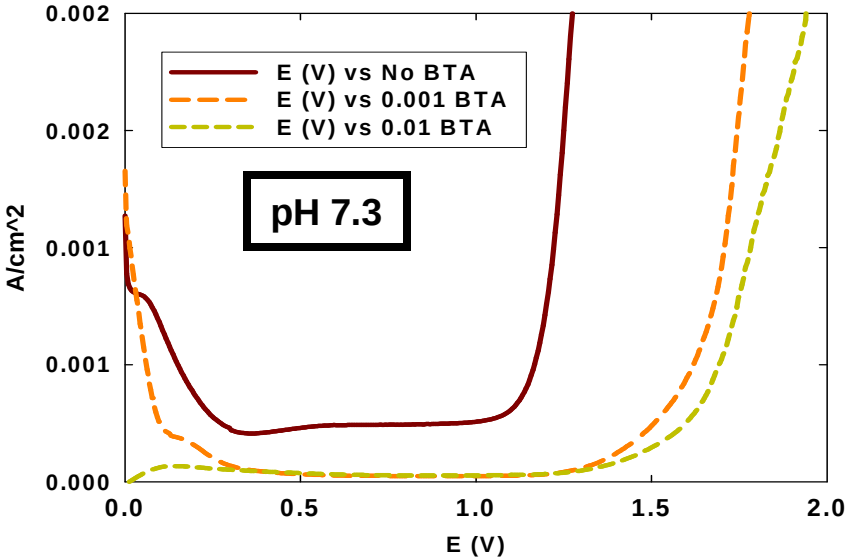


Results of BTA Inhibitor Study

- **Effect of pH and Concentration**
  - **Scan rate 5 mV/s – RT – 100 RPM**
- **BTA effect changes with pH**



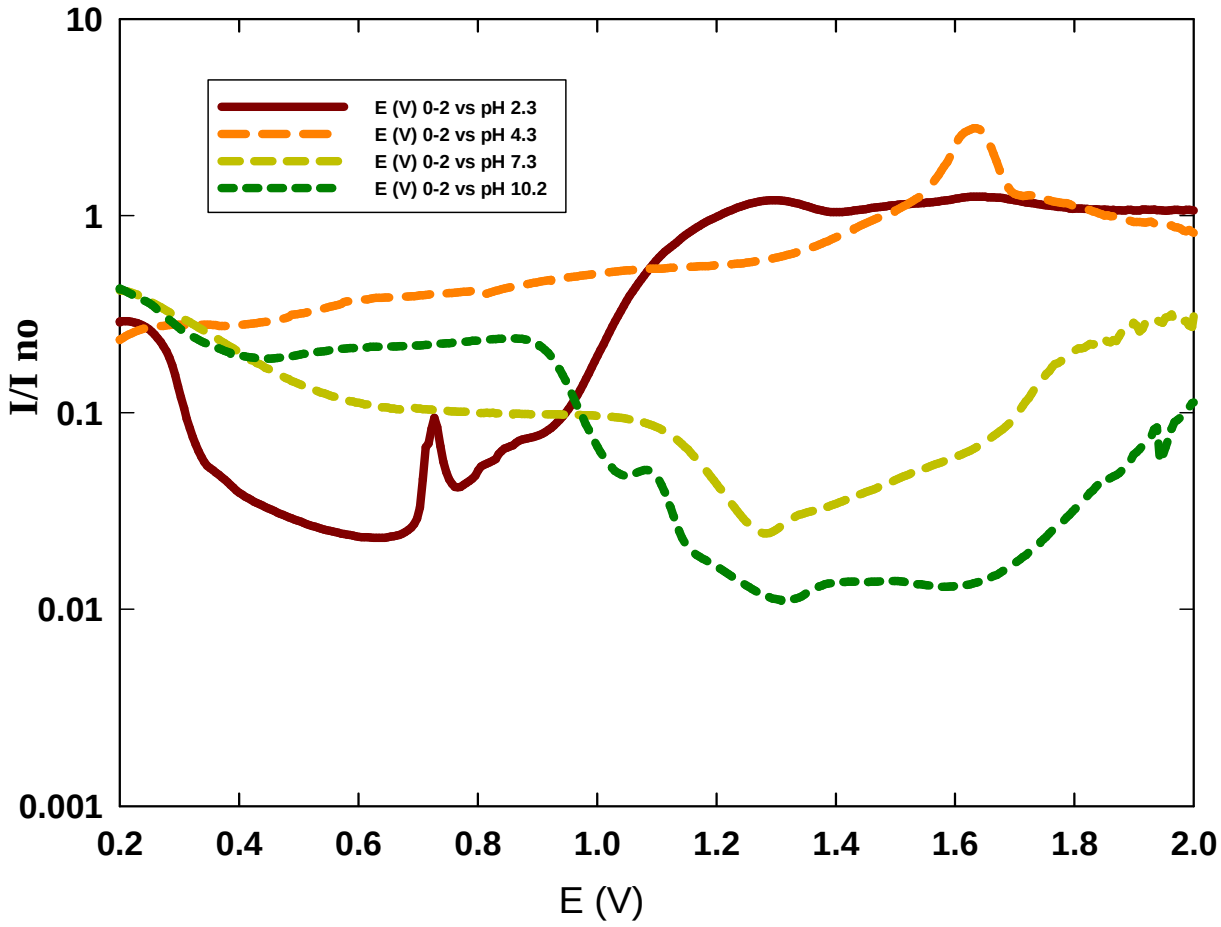




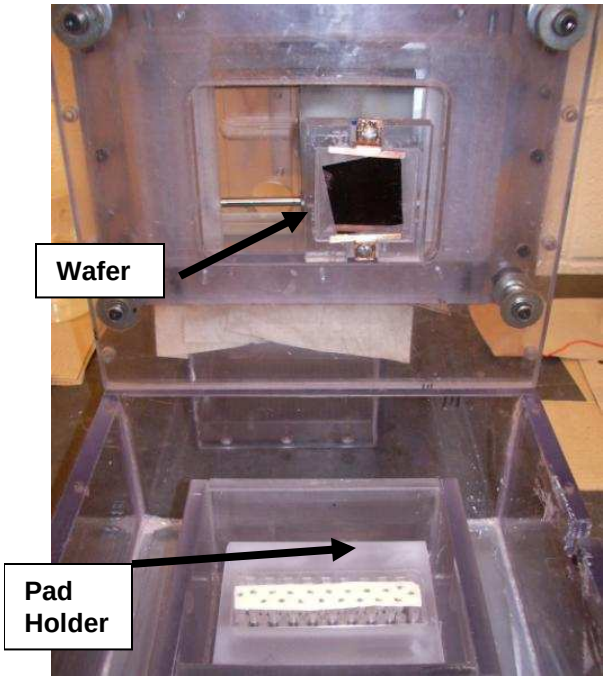
Planarization Capability

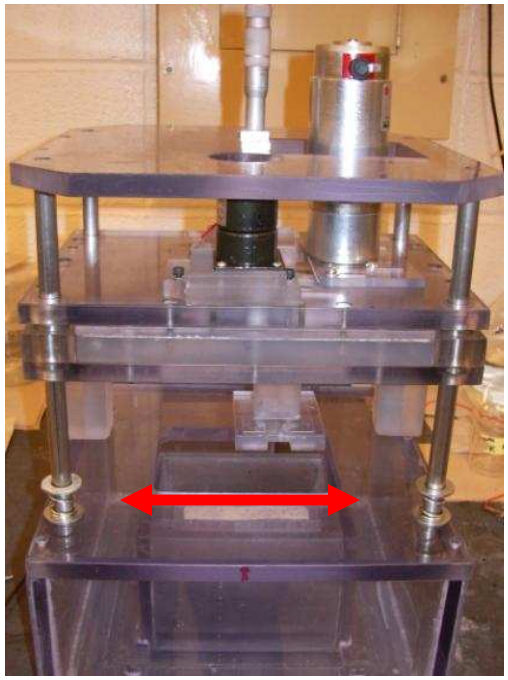
- **Where:**
  - **I = current with 0.001 M BTA**
  - **I_{No} = current with No BTA**

- **Related to dissolution rate with and without a polishing pad**

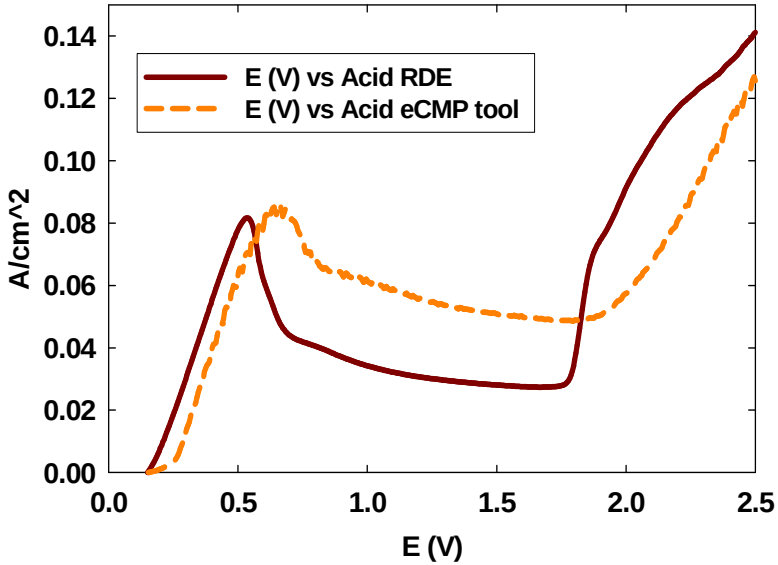


eCMP Tool





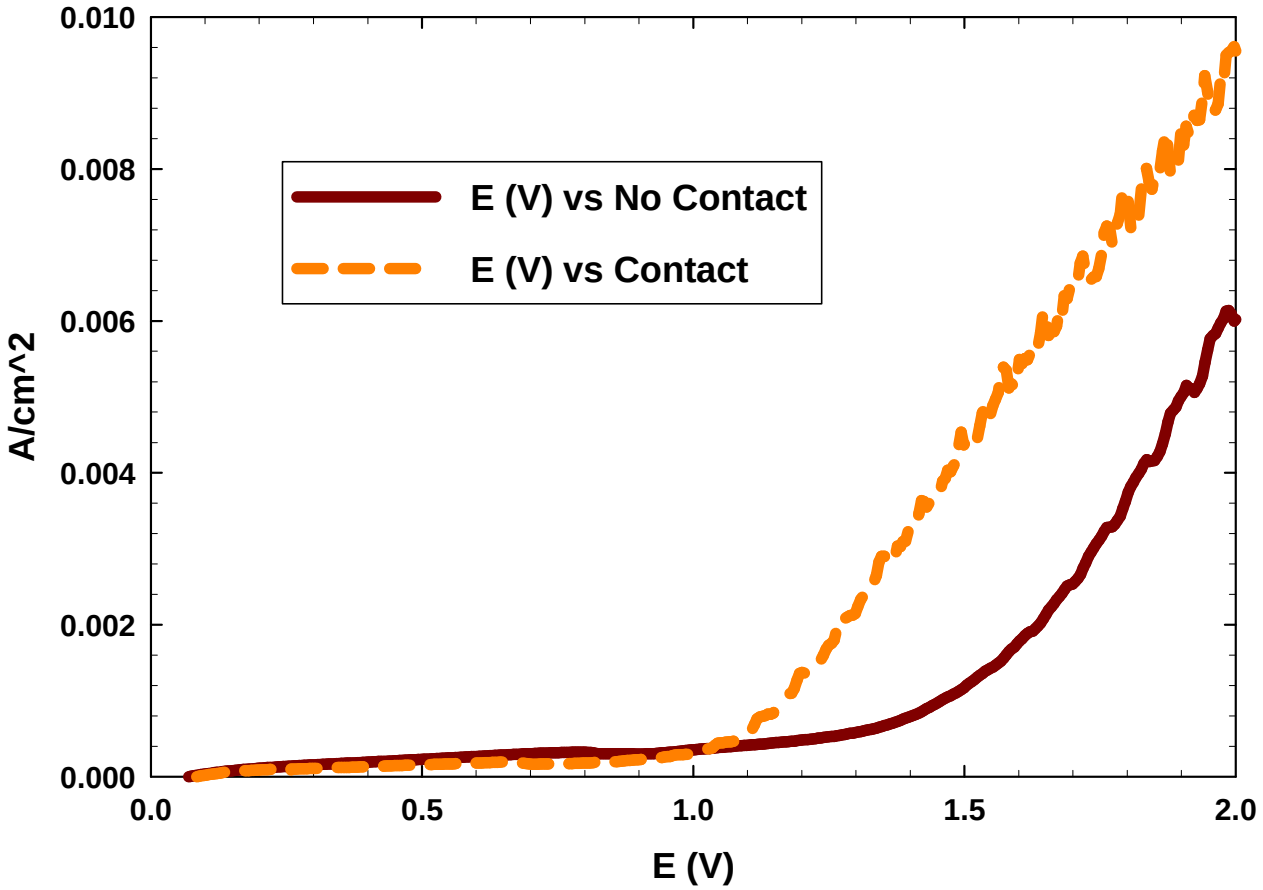
- **Ablility to compare results obtained with RDE to eCMP tool**



- **Design features:**
  - Apply and control low downforces (<0.3 PSI)
  - Operate in contact and non-contact modes
- **Major Characterization**
  - Metal-removal rates
  - Selectivity
  - Planarization efficiency

Preliminary Polishing Results

- **pH 2.3 - Pad Contact vs. No Pad Contact**
  - **Rohm & Haas: Suba™ 500 Pad**



Summary

- **H_3PO_4/BTA Electrolytes**
  - **pH lower than 4**
    - **BTA had little passivation effect**
    - **PTA had slight passivation effect at pH 0**
  - **pH above 4**
    - **Inhibition of Cu dissolution increased with both 0.001 and 0.01 M BTA concentrations**
    - **Change in RPM did not effect current density**
- **eCMP Tool successfully completed**
  - **Device accuracy confirmed with RDE experiments**
  - **Initial wafer testing has begin**
- **Future Work**
  - **Perform eCMP experiments on wafers to determine optimal electrolyte composition**
  - **Closely monitor effect of pad type on planarization**
  - **Begin investigation on polishing liner materials**

Acknowledgements

- **Columbia University**
  - **Dr. Alan West**
  - **Paula Cojocaru – visiting scholar**
- **Industry mentors/contacts**
  - **Intel**
  - **Novellus**
  - **Texas Instruments**
- **CMP Pads**
  - **Cabot**
  - **Rohm & Haas**
- **SRC/ Sematech**

Cabot Microelectronics

R & D Directions for Chemical Mechanical Planarization Solutions

Jim Dirksen

Director of Enabling Technology
Research and Development

2/22/2007

Outline

- Industry Technology Trends.
- Planarization Technology Trends.
- Environmental Considerations.
- Conclusions.

Cabot Microelectronics

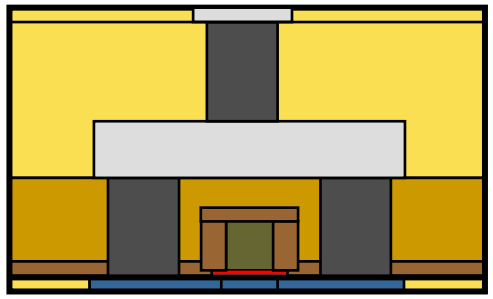
Industry Technology Trends

- Moore's law continues.
- Increasing integration complexity.
  - New uses of known materials
  - Introduction of new materials.
  - Minimization of overburden.
  - More CMP passes.
- Continued cost pressure.
- Nano-scale effects.
  - Critical stress deviations from bulk effects.
  - Size-dependent resistivity factors into materials choice.

Cabot Microelectronics

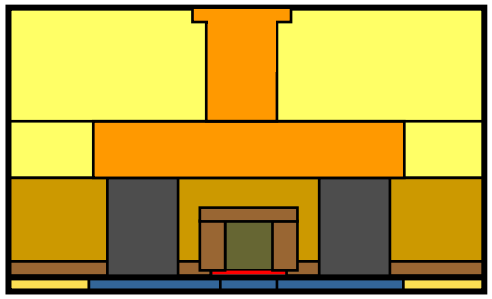
Moore's Law Requires

New Materials/Structures



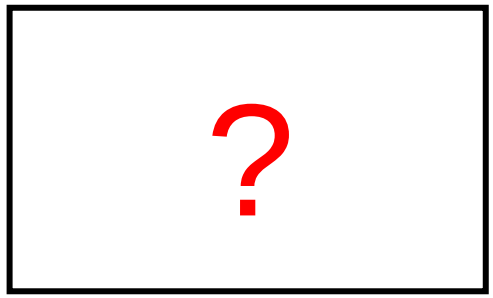
Al wire & W Via in Oxide

Mature Logic, Current DRAM



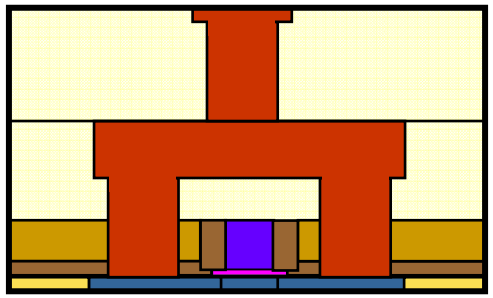
Cu wire in LowK dielectric

Advanced Logic, DRAM 65nm



?

Future Interconnects



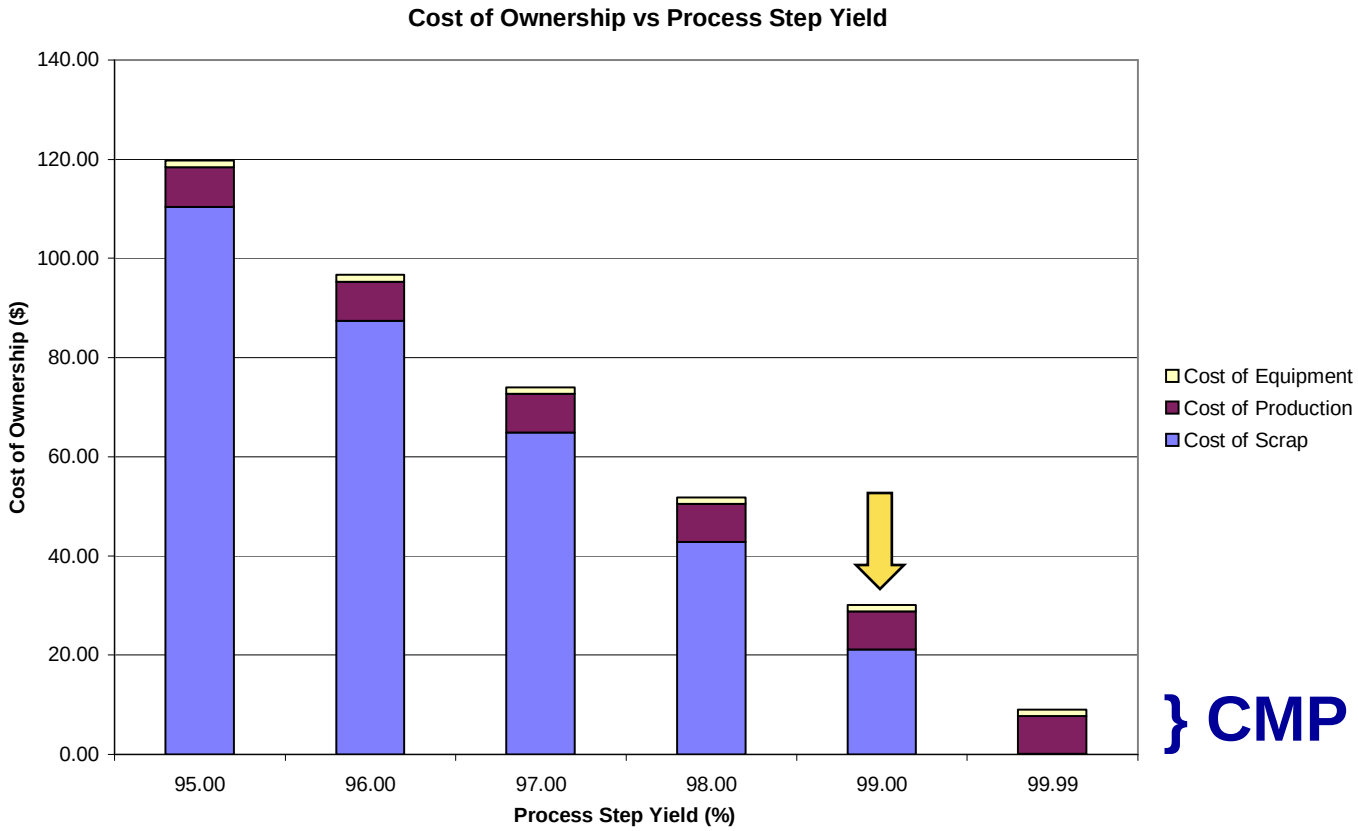
Cu wire in UltraLowK

45/32nm Logic

- Doped Si
- Oxide
- SiON
- Poly
- Nitride
- Doped Ox
- Doped Si
- Ti(N)+W
- Ti+Al(Cu)
- Ta(N)+Cu
- Low K
- High K
- Metal
- RuTa+Cu
- ULK

Cabot Microelectronics

Total Cost = CMP CoO + Yield Loss



} CMP CoO

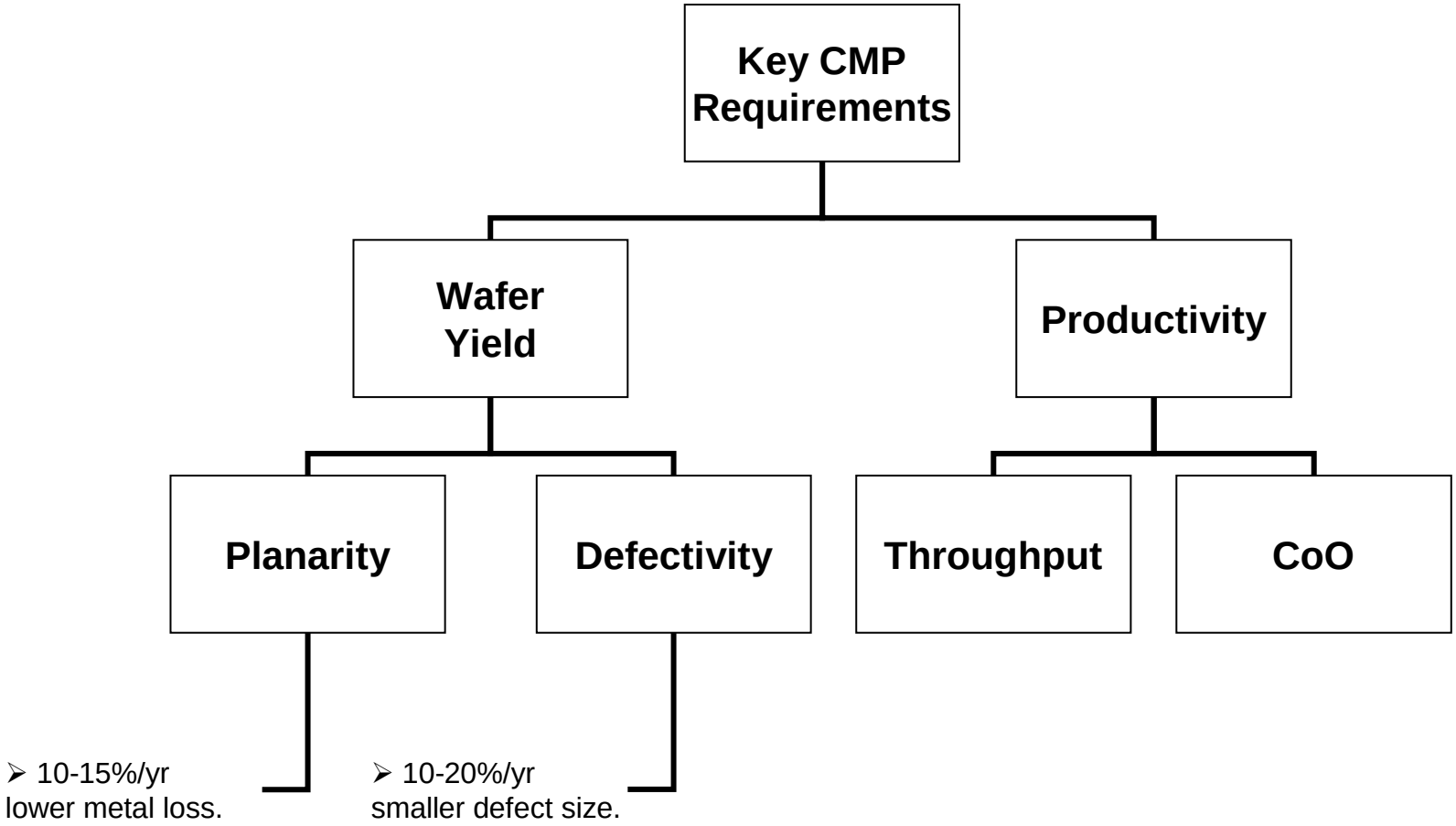
Re-Qual Interval = 875 wafers, Final Value of Wafer =$2100
Line Loading = 100%, Slurry Price = $30/gal, Usage = 500 ml/wafer

Source: Lucia Markert CoO

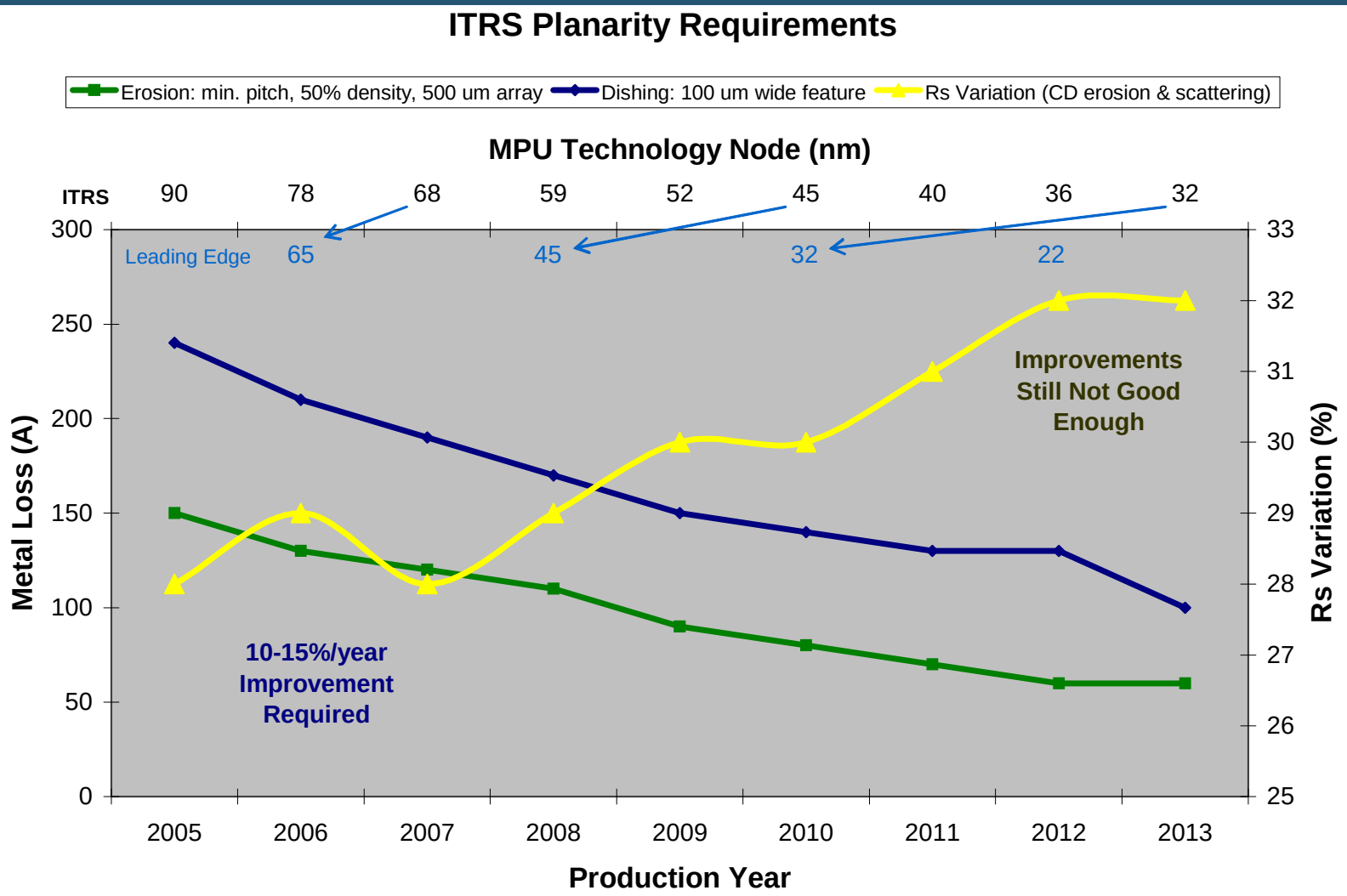
- **1 Bad Chip in 100 Caused by CMP = 2X the Total Cost of CMP.**
- **The Cost of Slurry and Pads is only 1 part of the Total Cost of CMP.**

Critical Customer Metrics

Early Demands—Yield Focused

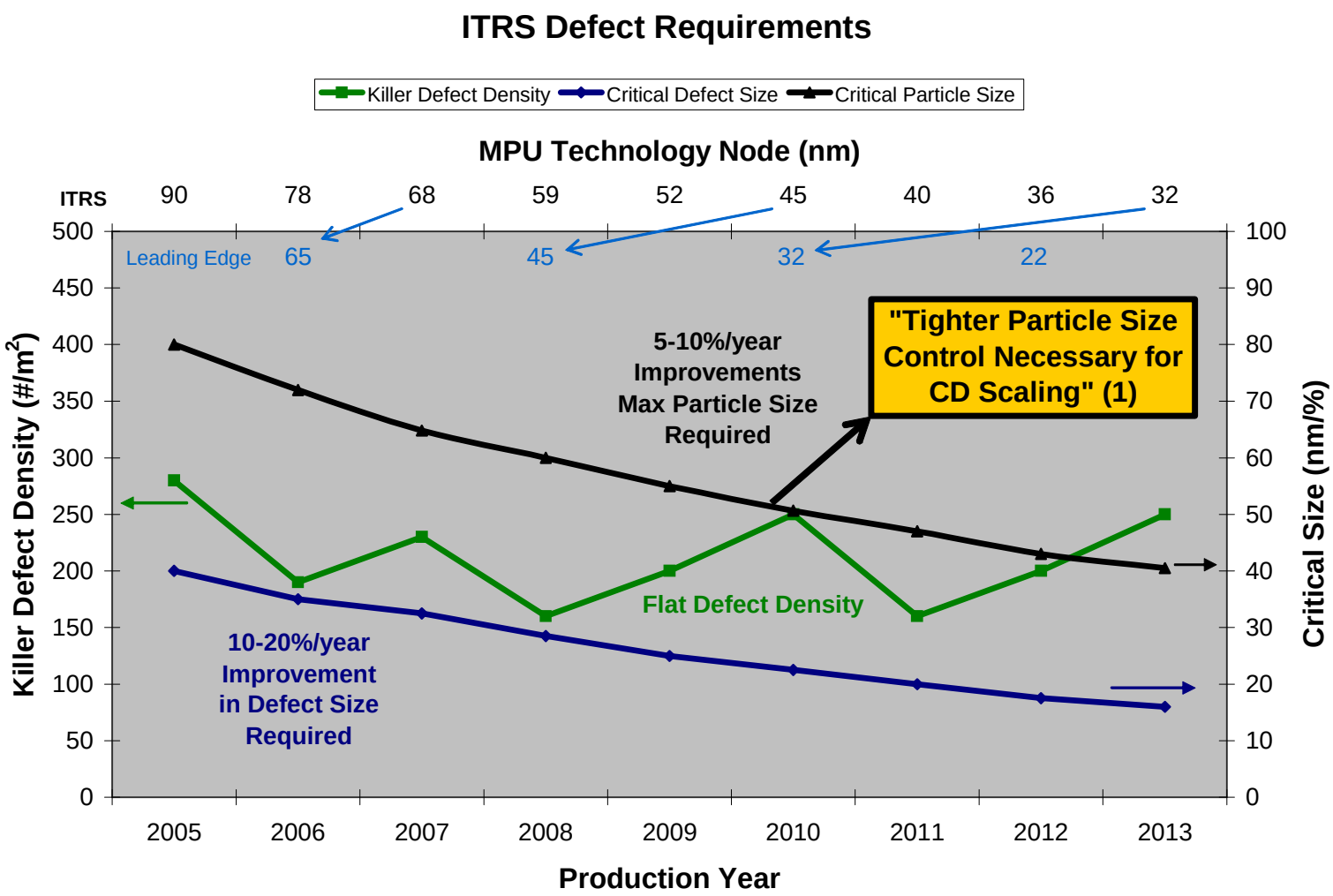


International Technology Roadmap for Semiconductors *(ITRS): Planarity Requirements*



Cabot Microelectronics

International Technology Roadmap for Semiconductors *(ITRS): Defectivity Requirements*

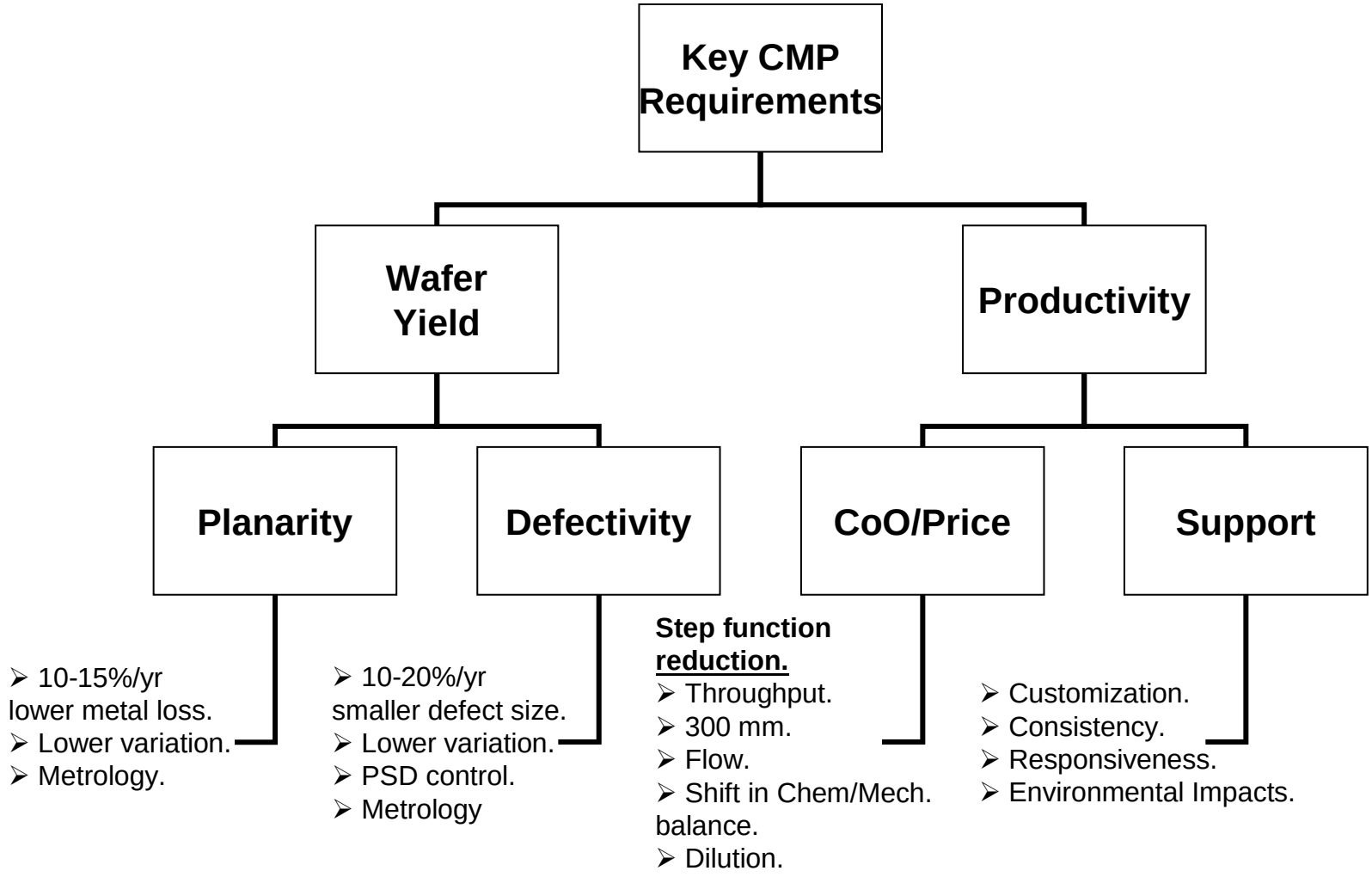


(1) C. Barns, L. Jiang, T. Younkin & **P. Fischer** (2006), *CAMP's Eleventh International Symposium on Chemical-Mechanical Planarization (CMP),* Lake Placid, NY, Aug. 13-16, 2006.

Cabot Microelectronics

Critical Customer Metrics

World of Additional Constraints



Planarization Technology Trends

- Reduction in:
  - Mechanical stress.
    - Solids content.
    - Downforce.
  - Costs.
- Increase in:
  - New materials to planarize.
  - Chemical activity.
  - Planarization efficiency.
  - Customization.
  - Technical support.

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Environmental Considerations

- Wastewater treatment.
  - Heavy metals.
    - Customers sensitive to Cu, innovate on Al.
  - Total oxygen demand (TOD).
    - Customer sensitive to TOD, requires novel oxidizers.
  - Complexing agents.
    - More sensitivity towards complexation efficiency.
- Toxicity.
  - Introduction of Ru as an alternative barrier material.

- Total Solutions are Essential.
  - Yield drives success.
    - One misstep erases all the benefits of previous steps.
  - Solutions must be cost effective.

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Summary

- More demanding integration schemes.
- Challenging planarization and defectivity requirements stay on 2 year cycles.
- Advanced nodes require lower mechanical stress.
- Total number of CMP passes increasing.
- Focus on lower cost of ownership for consumables.
- Additional pressure on wastewater treatment.
  - Slurry complexity increasing to achieve performance.

Cabot Microelectronics

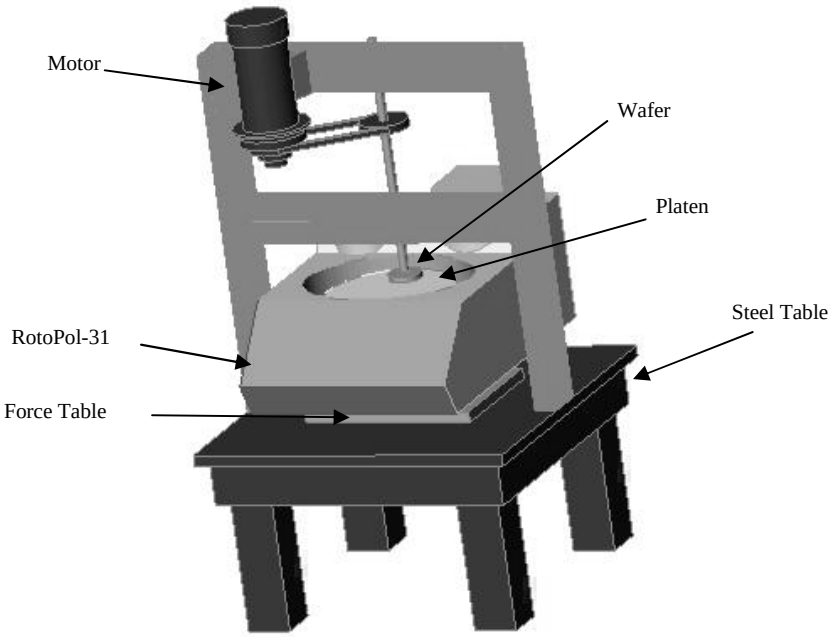
In-Situ Thickness and Friction Measurements during CMP

ERC Task # 425.020

PIs: C. B. Rogers, V. P. Manno, and R. D. White

RAs: N. Braun (MS), C. Gray (PhD), A. Mueller (MS), J. Vlahakis (PhD)

Tufts University
Department of Mechanical Engineering
Medford, MA



Objectives

Coordinated Projects Focused on Advanced Planarization Characterization – Benchtop

- **Use Dual Emission Laser Induced Fluorescence (DELIF) to obtain in-situ images of the slurry layer during CMP and quantify wafer-pad contact during polishing – Caprice Gray**
- **Develop a model of Oxide CMP MRR through a corresponding series of macroscale friction and wafer position experiments – James Vlahakis**
- **Design and fabricate micromachined shear stress sensors to measure local, real-time shear stress at the pad-wafer interface during CMP due to slurry and asperity interactions – Andrew Mueller**
- **Investigate the feasibility of using PIV to track slurry particle-slurry flow at the asperity level in-situ (collateral study) – Nicole Braun**

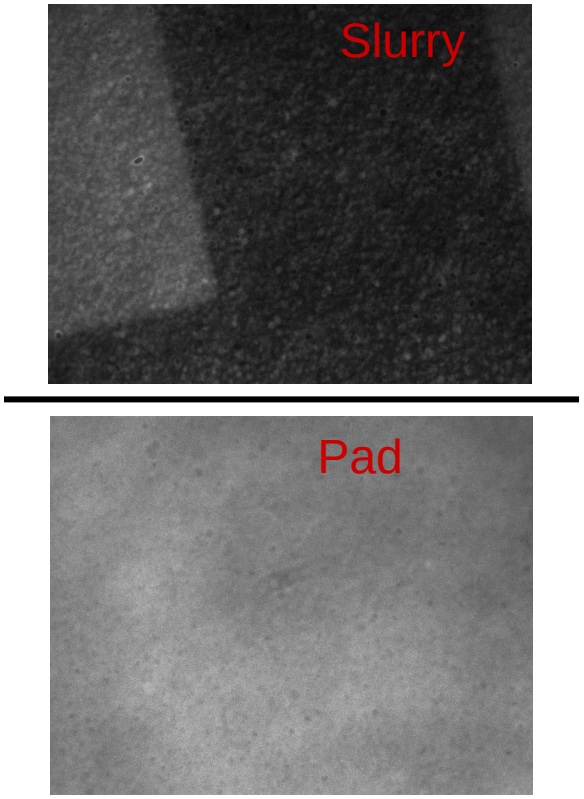
Environmental Safety and Health (ESH) Metrics and Impacts

METRIC	IMPACT
Energy Consumption During Process	Understanding wafer-pad interactions during polish leads to reduced time to polish and tool energy consumption
DI Water Consumption During Process	Optimized process parameters based on in-situ characterization of contact, and forces leads to reduced time to polish and slurry consumption optimization
Process Chemical Consumption (Slurry Chemicals)	

Project 1 - DELIF Studies

- Use Dual Emission Laser Induced Fluorescence (DELIF) to attain in-situ images of the slurry layer during CMP
  - Images are instantaneous (6 ns time integration), taken at a rate of 2 images/sec
  - High spatial resolution (>3 mm/pixel) to resolve micron sized features
- Detect in-situ pad-wafer contact
  - Pads (all polyurethane based): CMC D100, CMC D200, Fruedenburg FX9, IC1000
  - Process variables: applied wafer down force, pad-wafer relative velocity, slurry particle concentration, pad conditioning

DELIF Theory



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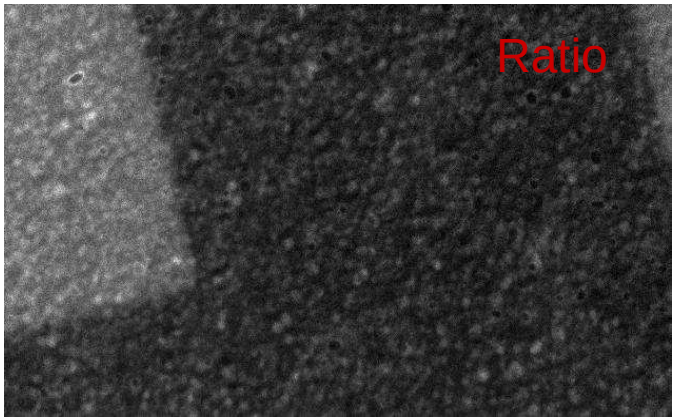
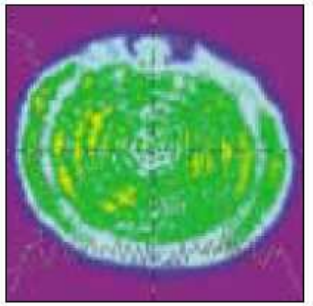
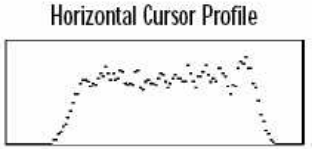
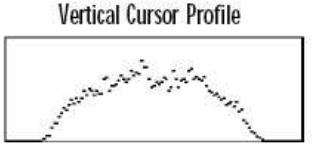


Division of 2 images cancels variations in image source intensity

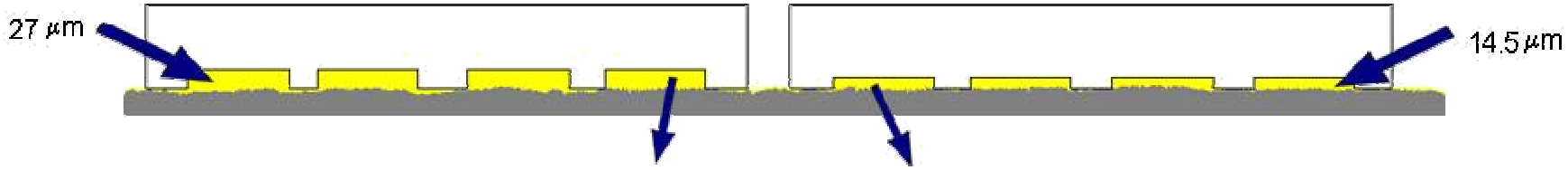
Laser Profile







Linear calibration technique to correlate image intensity to fluid layer thickness



Intensity (27) - Intensity (14.5) = Intensity (12.5)

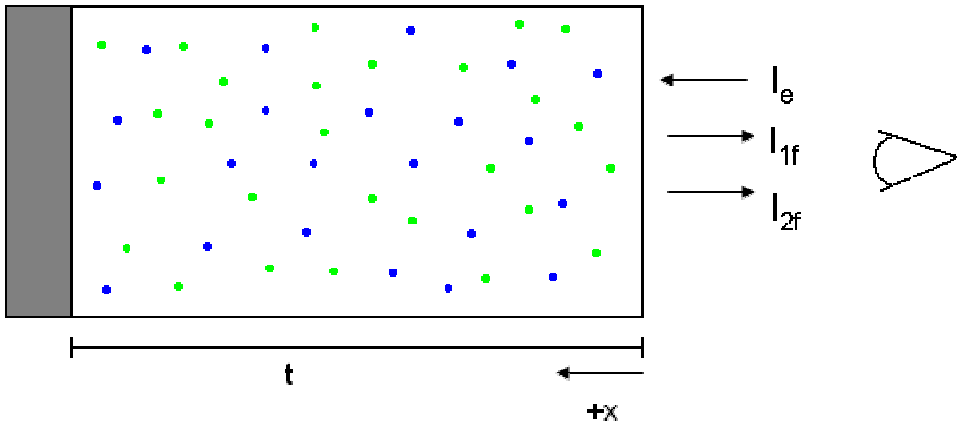
$$X = \frac{27 - 14.5}{I_{27} - I_{14.5}}$$

X = Calibration factor (μm/intensity-unit)

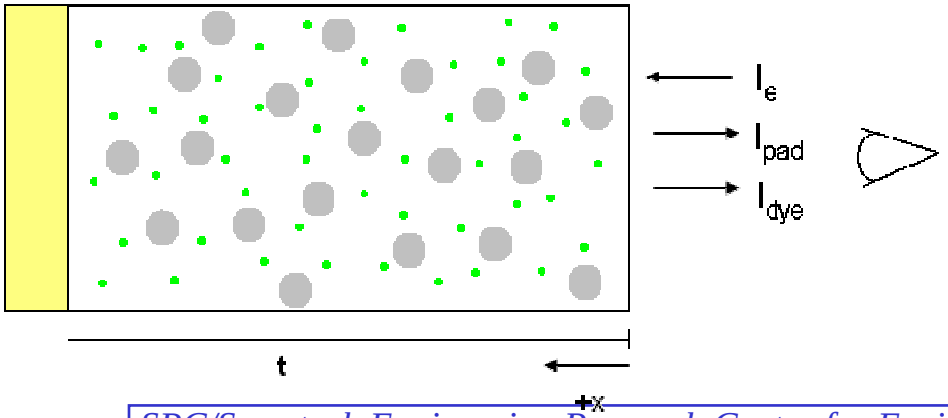
DELIF Modeling

- **Goals:**
  - Examine how comparable our actual system is to existing DELIF models
  - Develop rigorous theory
  - Use theory to test if ratio intensity calibration is linear or quadratic (Ratio Intensity → Fluid layer thickness)

Existing Model Geometry



CMP Model Geometry



Existing Model Solution $\frac{I_{2f}}{I_{1f}} = At + B$

Reduced Model Results

$$\begin{bmatrix} \dot{I}_e^+ \\ \dot{I}_p^- \\ \dot{I}_d^+ \\ \dot{I}_d^- \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ 0 & k_2 & 0 & 0 \\ k_4(\lambda_l) & k_4(\lambda_p) & 0 & 0 \\ -k_4(\lambda_l) & -k_4(\lambda_p) & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} I_e^+ \\ I_p^- \\ I_d^+ \\ I_d^- \end{bmatrix}$$

$$k_1 = \varepsilon_d(\lambda_l) C_d$$
$$k_2 = \varepsilon_d(\lambda_p C_d)$$
$$k_4(\lambda) = \tfrac{\phi_d}{2} \eta_d(\lambda) C_d \varepsilon_d(\lambda)$$

Simplification Assumptions:
1. No scattering particles
2. All excitation light is absorbed and no excitation light is reflected

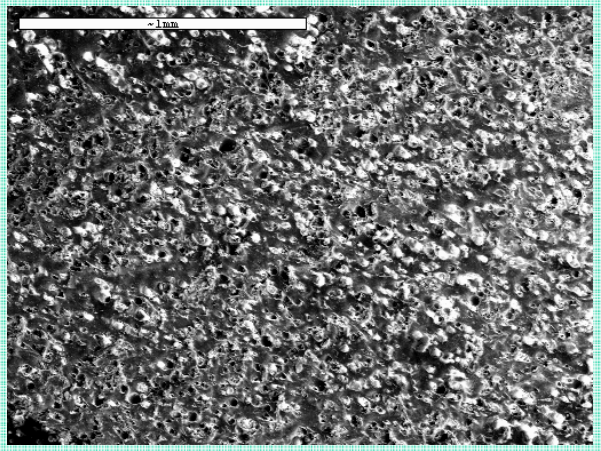
Boundary Conditions

1. $\mathrm{I}_e^+(0) = \mathrm{I}_0$
2. $\mathrm{I}_p^-(\mathrm{L}) = \mathrm{I}_e^+(\mathrm{L}) \alpha(\lambda_l) \phi_p \eta_p(\lambda_p)$
3. $\mathrm{I}_d^+(0) = 0$
4. $\mathrm{I}_d^-(\mathrm{L}) = \mathrm{I}_d^+(\mathrm{L})$ for 100% reflection of $\mathrm{I}_d^+(\mathrm{x})$

Solution:

$$R_{pad} = \frac{I_d^{-,pad}}{I_p^-} = \left(1 + \frac{1}{\alpha(\lambda_l)\phi_p\eta_p(\lambda_p)}\right) 2k_4 L \longrightarrow$$ LINEAR Calibration

Image Quality Benchmarking

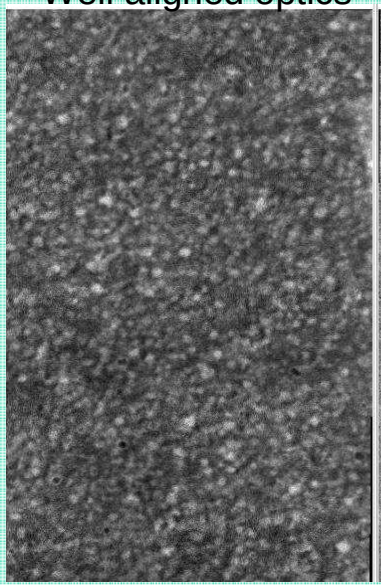


SEM

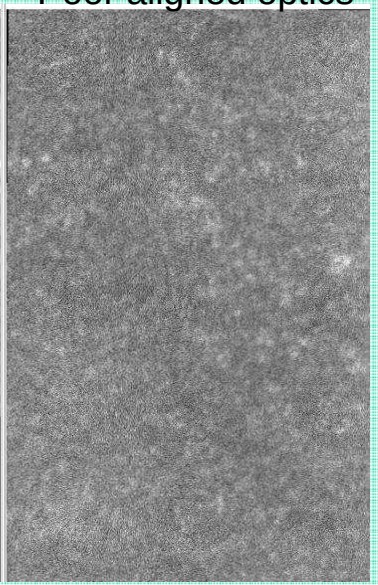
NO Z RESOLUTION

Optical Microscope

Well aligned optics



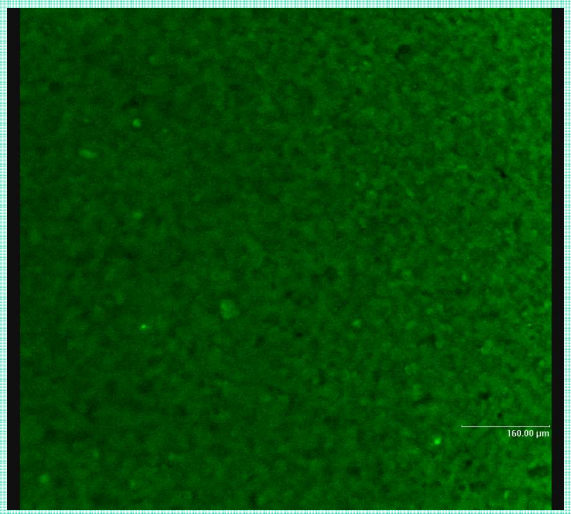
Poor aligned optics



DELIF

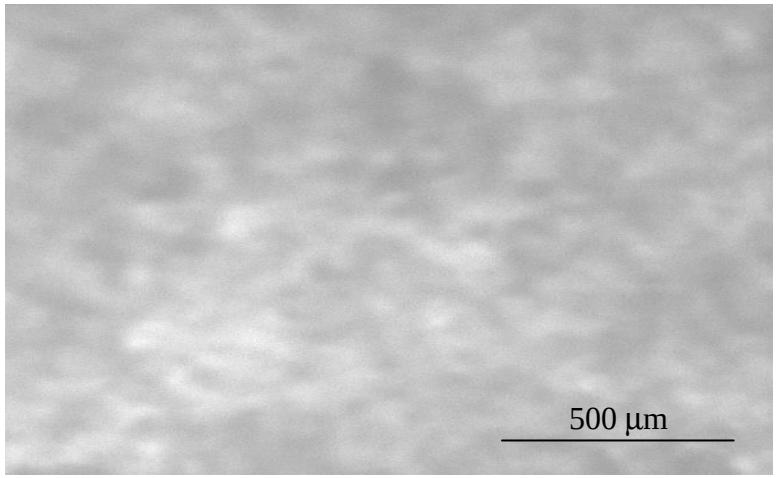
GOOD Z RESOLUTION

Confocal Microscope

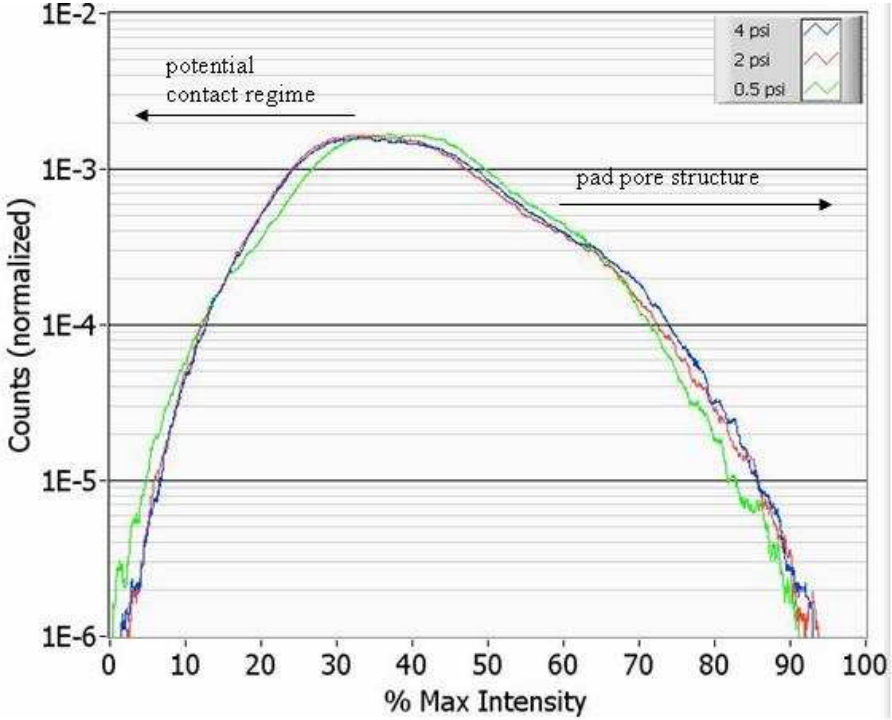


DELIF for Contact

- 360,000+ pixels → 2% ~ 7200 pixels
- 50 μm² ~ 7-8 pixels (6.7 μm²/pixel)
  - Focus must be really good
  - We are at the resolution limit for our system
- At this resolution, we are seeing contact region intensity smoothing



Data for static DELIF on CMC D100



DELIF – Status and Next Steps

Status:

- **We had developed an optical model that helps us understand calibration of image intensity to fluid layer thickness.**
- **We have made optical system improvements to optimize detection of pad-wafer contact.**
- **We have begun to benchmark DELIF method by making pad surface measurements using other techniques**
- **We have established a data processing method for detecting pad-wafer contact.**

Future Work:

- **Calculate results of full CMP DELIF model including slurry particle scattering effects**
- **Determine pad to pad DELIF variations**
- **Choose a slurry for optimal DELIF and polishing**
- **Observe pad-wafer contact on various polishing pads and differing CMP run parameters (down-force, pad-wafer speed, etc.)**

Project 2 - CMP Friction Studies – Modeling

Goal – To develop a predictive, microscale model of CMP and a corresponding series of macroscale experiments that serve to both inform and develop our model

Chemical forces associated with actual material removal

- **F_p = force due to wafer-pad interaction**
- **F_a = force due to wafer-abrasive interaction**
- **We can write**

$$\mu = \frac{F_p + F_a}{(pressure \times area_{wafer})}$$

- **We can separate the terms so that**

$$F_p = \mu_p (press \times area_{pad})$$

$$F_a = \mu_a (press \times area_{abrasive})$$

- **The area fraction has been shown to be**

$$\frac{A_{abrasive}}{A_{pad}} = \frac{[A]}{K_{pad} + [A]}$$

- **Ultimately, this simple, preliminary analysis arrives at**

$$F_{drag} = \left(\frac{\mu_p K_{pad} + \mu_a [A]}{K_{pad} + [A]}\right) F_z$$

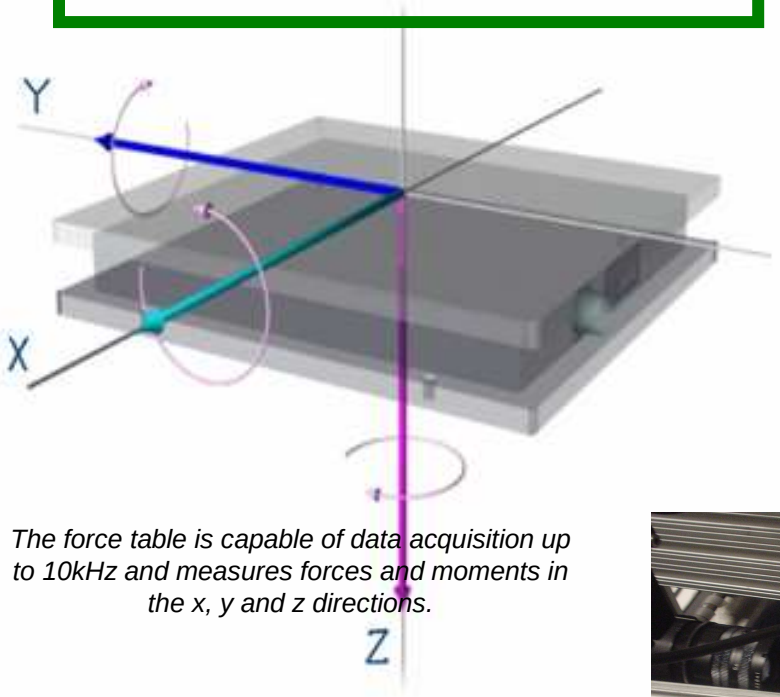
[A] – abrasive concentration

K_{pad} – fitting parameter dependent on pad properties

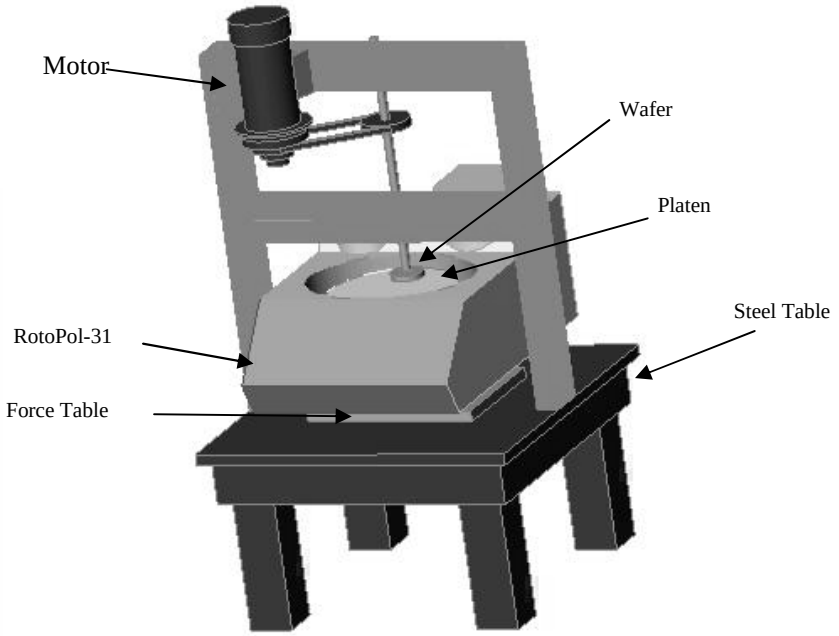
- **Develop experiments that test modeling**

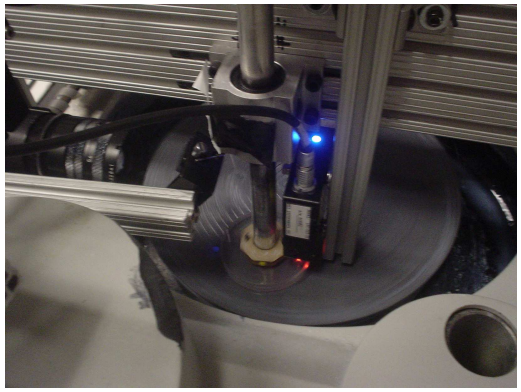
Friction and MRR Studies

- Measure friction – force table
- Position – laser sensors
- MRR – patterned wafer



The force table is capable of data acquisition up to 10kHz and measures forces and moments in the x, y and z directions.



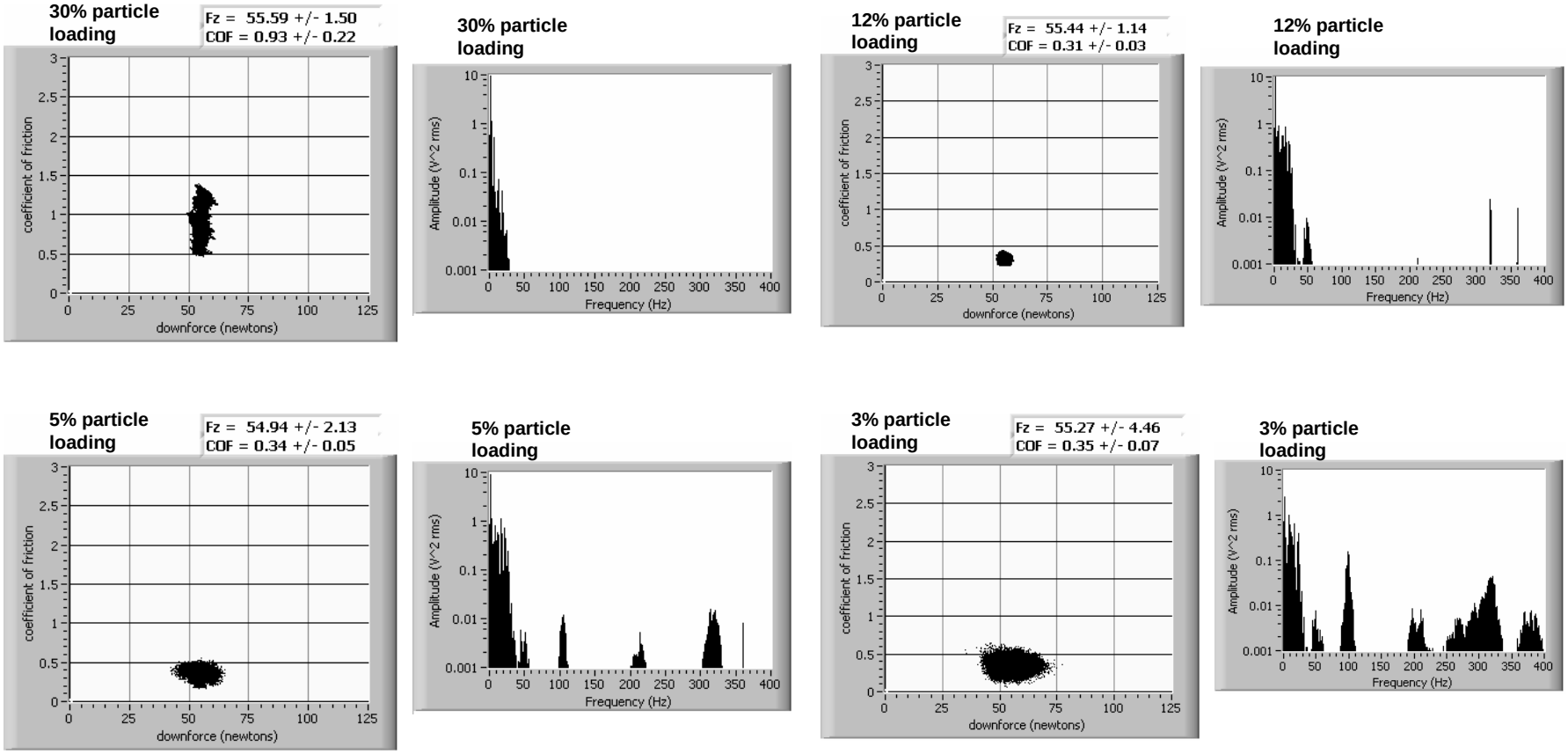


CMP Friction Studies – Typical Data

CoF vs. slurry dilution,

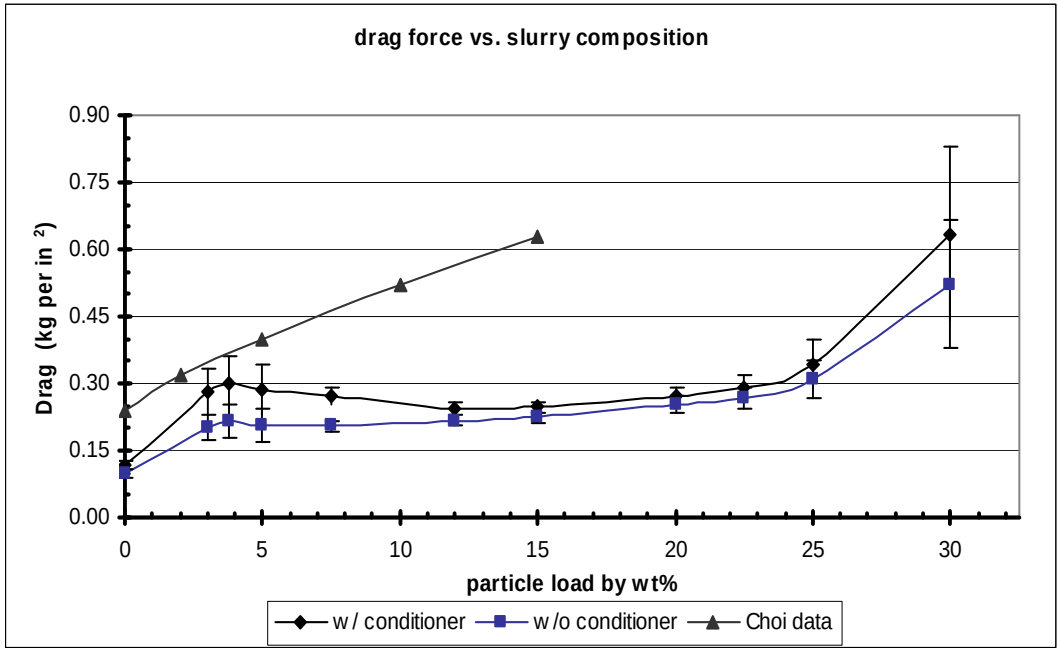
- **stick-slip response grows as we dilute the slurry**
- **note how CoF plots and spectra develop as stick-slip grows**

CoF vs. Downforce | **Fx Spectra** | **CoF vs. Downforce** | **Fx Spectra**



CMP Friction Studies – Latest Data

- **Drag Force vs. slurry dilution**
  - **60rpm (~.5m/s) & 1.7psi**
  - **Note large CoF (and large σ) for pure slurry. A result of shear thickening?**
  - **CoF remains fairly constant over a wide range of slurry dilutions**
  - **Our experiments indicate that for pure H_2O, pH plays a role in determining CoF**
  - **Next steps**
    - **Explore particle loadings in the 0 - 5% range. Specifically, where does the "up and over" nature of the curve begin to manifest?**
    - **Investigate pH dependence for H_2O**
    - **Perform experiment "backwards" – if we begin with pure slurry and work towards pure H_2O, would we see different results than if we started with pure H_2O and worked towards pure slurry? If so, what does this tell us about slurry/pad interactions?**



Choi data – Choi, Lee and Singh, "Effects of Particle Concentration in CMP," Mat. Res. Soc. Symp. Proc. Vol. 671, 2001

Choi's parameters	Our parameters
2psi	1.7psi
Particle size ~0.2μm	Particle size ~.09μm
$V_{relative}$ = 2.2 m/s	$V_{relative}$ = .5 m/s
.64in^2 sapphire	7in^2 BK7 glass

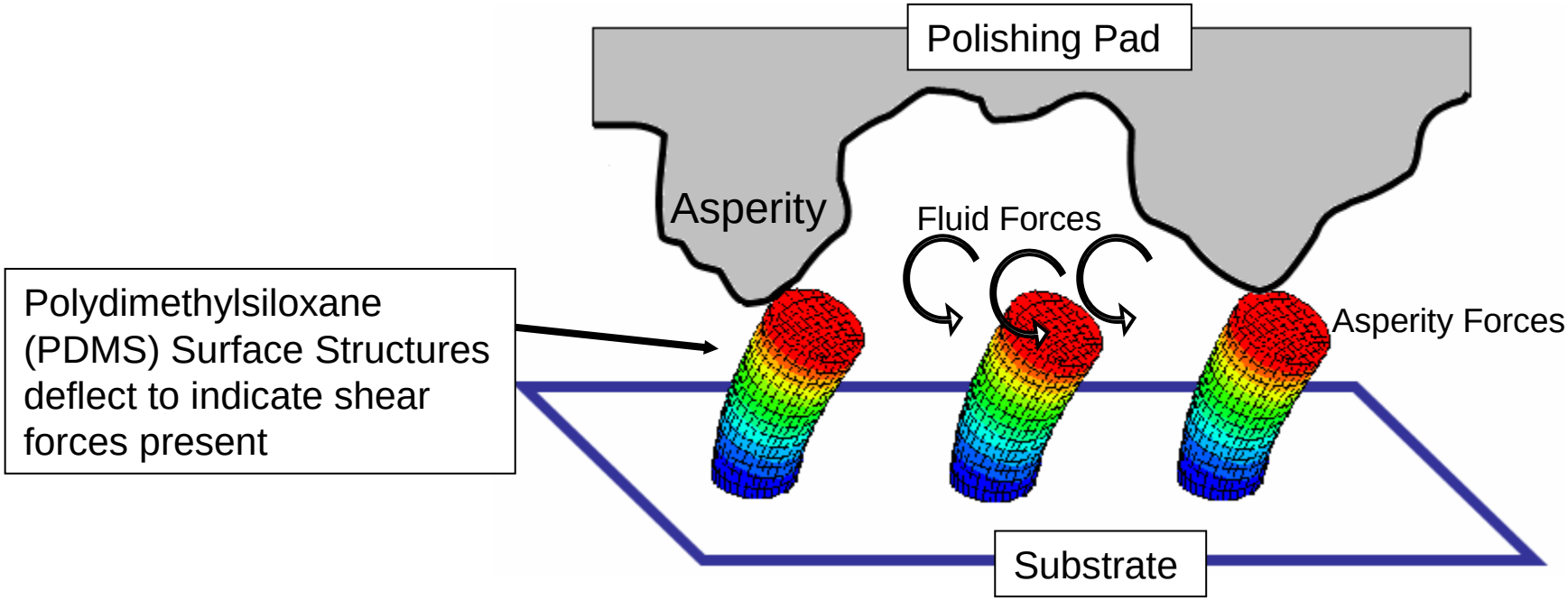
CMP Friction Studies – Status and Future Work

- **Install position sensors and calibrate patterned wafer**
- **Continue model development leveraging knowledge base that exists among this and other SRC groups**
- **Identify experiments that test model veracity and coordinate data acquisition with contact and shear force measurements**
- **Perform the experiments and iterate until our model and data are compatible**

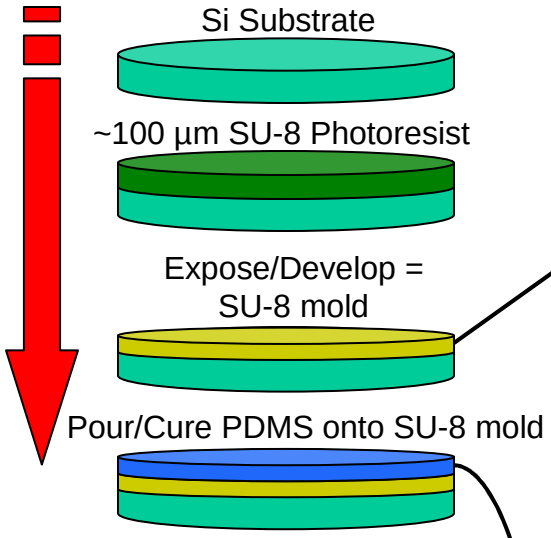
Thanks to both the SRC/Sematech ERC and our industrial partners, Cabot Microelectronics and Intel, and partner researchers at U of A and MIT

Project 3 - Micromachined Shear Sensors

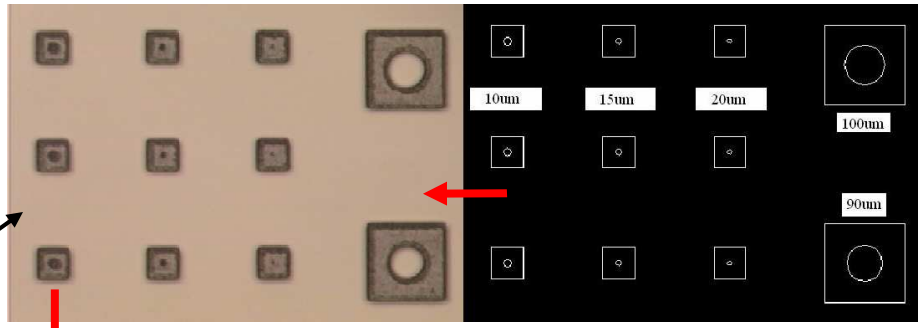
- Fabricate and implement micromachined shear stress sensors for characterization of surface forces during chemical-mechanical polishing (CMP).
- Measure local, real-time shear stress at the pad-wafer interface during CMP due to slurry and asperity interactions with the wafer.



Sensor Process & Design Overview

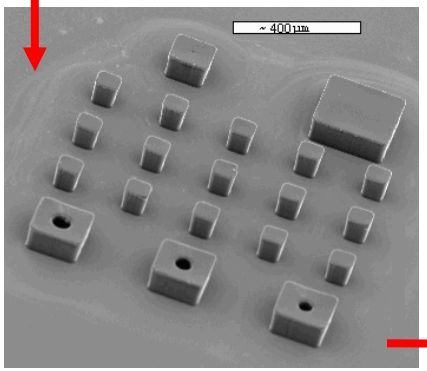


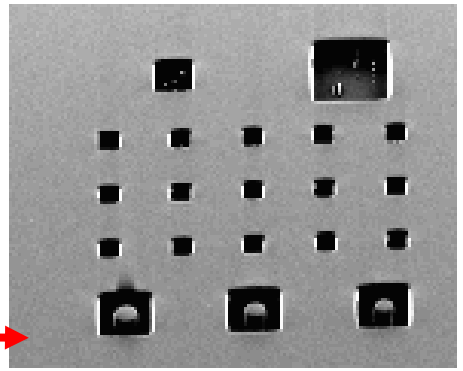
Light microscope image of SU-8 mold from design 1



Design 1 CAD Layout

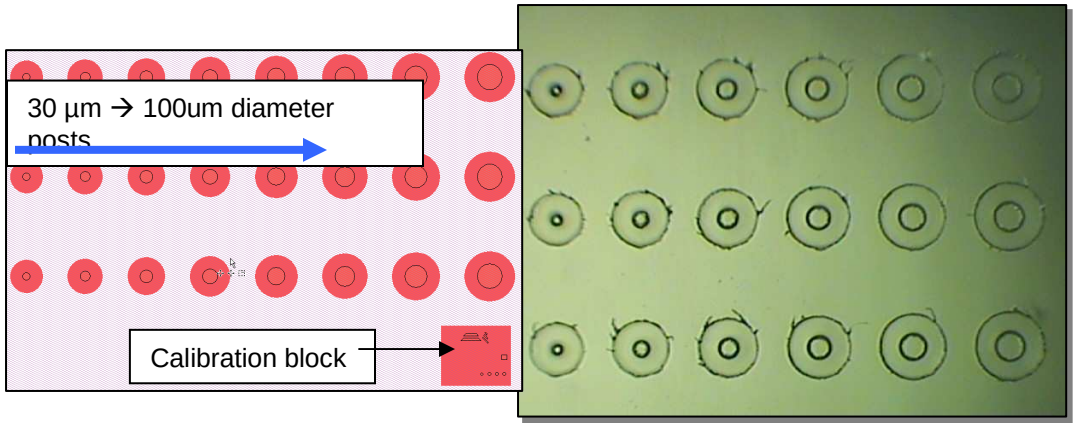
SEM image of SU-8 mold from design 1





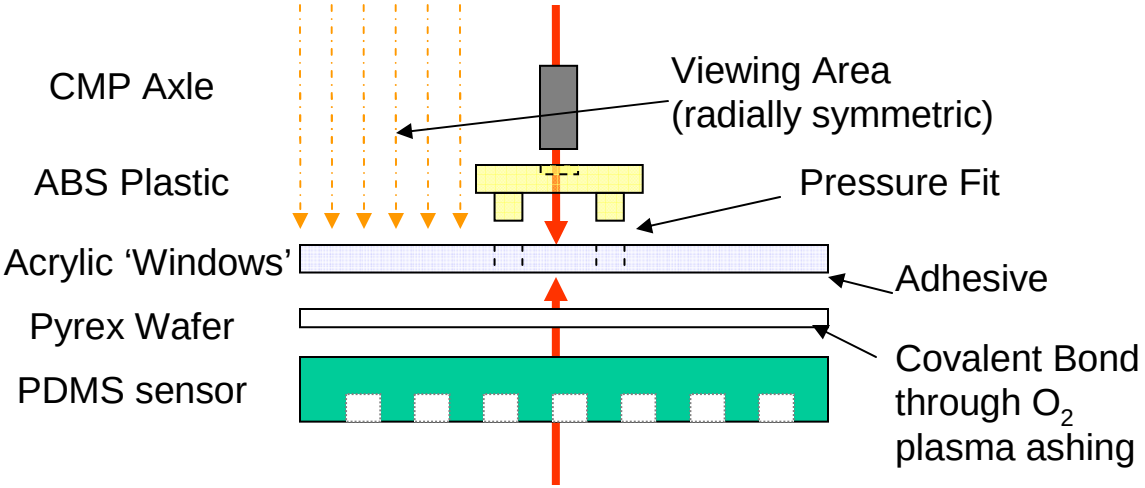
SEM image of PDMS structure from design 1

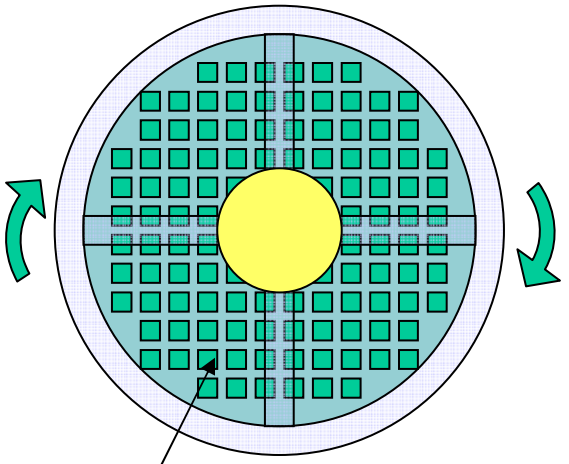
Final Design



- Initial Design
  - 85 µm high posts: successful
  - 80, 90, 100 µm diameter: successful
  - 10, 15, 20 µm : not fully formed; incomplete formation of mold
- Final Design
  - Fabrication limits for final design: 30-40 µm minimum diameter at 85-100 µm high.
  - Camera resolution: 5-10 µm deflection
  - Dyeing may improve resolution

Mounting





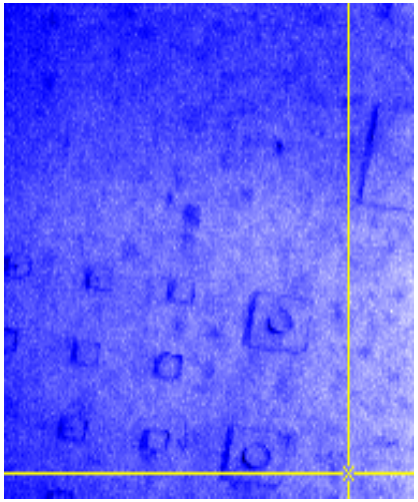
Sensors seen through acrylic viewing window, Pyrex, and the back of the PDMS wafer

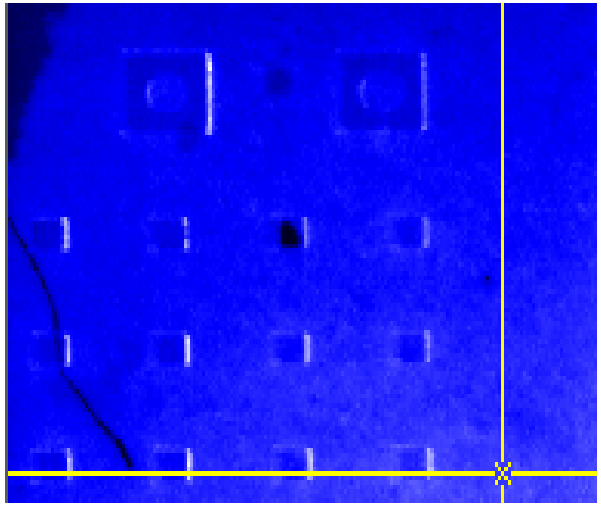
Imaging

Current Optics

Without dye: 80-100 µm structures visible.

Expect to be able to resolve ~5-10 µm displacement with existing optics.





Rhodamine B

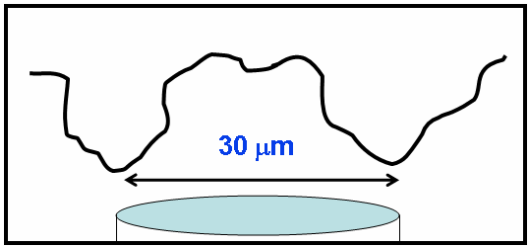
With dye: some edges are very bright.

Additional experiments are planned to attempt to achieve uniform edge dyeing.

Asperity Force Estimations

Total shear force load is COF·Downforce·Wafer Area (for 4" wafer) ≈ 0.5 (1.8 psi) (π (50 mm)^2) ≈ 50 N

Option #1 : Assume 30 µm center to center spacing on asperity tips with a square grid.



Number of Asperities in Contact: Wafer Area/Asperity Neighborhood Area (for 4" wafer)

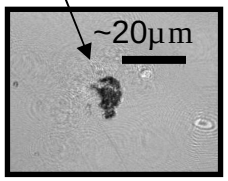
≈ (π (50 mm)^2)/ ((30 µm)^2)

≈ 8.7 · 10^6 asperity contacts/wafer

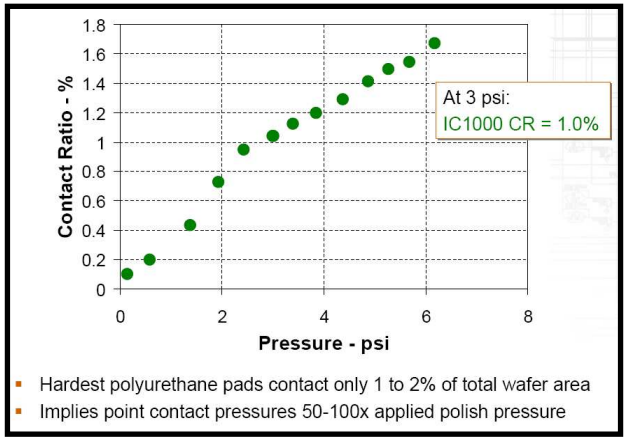
Force per asperity is total force over number of asperities ≈ 50 N/(8.7·10^6 asperities) ≈ 6 µN

Option #2 : Determine number of contacts based on ratio of total contact area to individual asperity contact area.

≈ π(5 µm)2 ≈ 80 µm^2



Carolina L. Elmufdi and Gregory P. Muldowney, "The Impact of Pad Microtexture The Impact of Pad Microtexture and Material Properties and Material Properties on Surface Contact and Defectivity in CMP on Surface Contact and Defectivity in CMP"



Estimate of static wafer contact % area for IC1000 pad at 1.8 psi downforce is **0.7%.**

Number of Asperities in Contact:

≈ (0.007·π (50 mm)^2)/ 80 µm ^{2}

≈ 6.9 · 10^5 asperity contacts/wafer

Force per asperity is total force over number of asperities ≈ 50 N/(6.9·10^5 asperities) ≈ 70 µN

Micromachined Sensors – Status and Next Steps

Status:

- **The sensors developed will allow measurement of shear forces during CMP at an estimated force resolution of 1-100 µN and spatial resolution of 300 µm.**
- **Sensor fabrication feasibility has been proven and diameter limitations have been established at 30 µm.**
- **Calibration and implementation of the shear sensors are ongoing.**

Next Steps:

- **Develop experimental apparatus for calibrating post deflection under known:**
  - **Fluid flow loads**
  - **Mechanical loads**
- **Improve dyeing ability to improve optical post resolution.**
- **Integrate with CMP rig for *in situ* surface force measurements.**

Industrial Collaboration/Technology Transfer

- Close collaboration with industry partners – Cabot Microelectronics and Intel
  - Monthly telecons – secure website for information exchange
  - Semi-annual face-to-face meetings
  - Thesis committees and joint publication authorship
  - Metrology and analysis methodology technology transfer
  - In-kind support – specialized supplies and equipment
  - Student internships (e.g. C. Gray at Intel during Summer 2005)
  - Close coordination with A. Philipossian research group at U of Arizona
- Information and results exchange with MIT (D. Boning) ERC project
  - Monthly joint meetings of PIs and research students
  - Discussion of findings with other colleagues (e.g. E. Paul – Stockton College on leave at MIT)

In-Situ Thickness and Friction Measurements during CMP – Global Last Year Goals

- **Demonstrate reliable in-situ contact measurement**
- **Determine if pad optical properties can be used as practical performance measures**
- **Correlate contact-macroscale friction-MRR-MEMS sensor data**
- **Develop oxide CMP MRR model that maps small scale phenomena and large scale, integrated data acquisition**

Thanks to SRC/Sematech ERC, our industrial sponsors, Cabot Microelectronics and Intel, and partner researchers at University of Arizona and MIT and OUR STUDENTS!

QUESTIONS?

Low Environmental Impact Processing of Sub-50 nm Interconnect Structures

Chia-Hua Lee and Karen Gleason

Department of Chemical Engineering

Department of Materials Science and Engineering

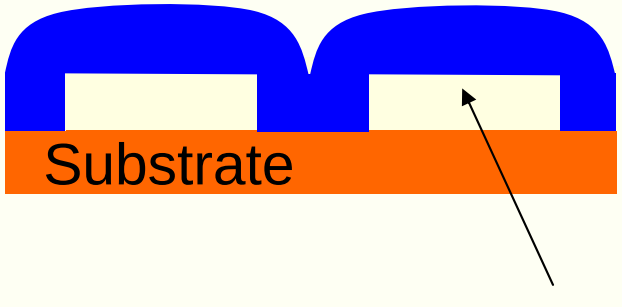
Massachusetts Institute of Technology

Approach

- Direct deposition patterned sacrificial layers rather than blanket
- Use of Dip-Pen Nanolithography (DPN) to create surface patterns (expected resolution sub 50nm) (collaboration with Prof. Angela Belcher's (MIT) group)
- Use supercritical CO_2 to remove sacrificial materials (collaboration with Prof. Muscat (UA) group)

Sacrificial Materials for Air Gap

- Use of Sacrificial Materials (or Porogens) for Low-Dielectric-Constant Integration
  - Air has the lowest k of 1.0 (reduce RC delay, power, noise)



Direct Patterning Deposition

↓

Deposition of bridge layer

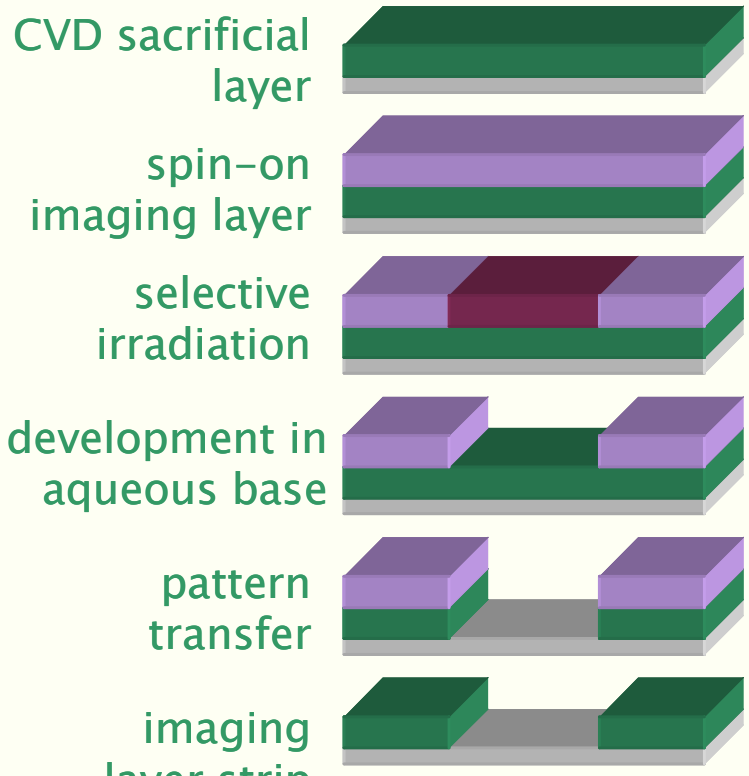
↓

Decomposition

Patterning Approaches

Subtractive Processing

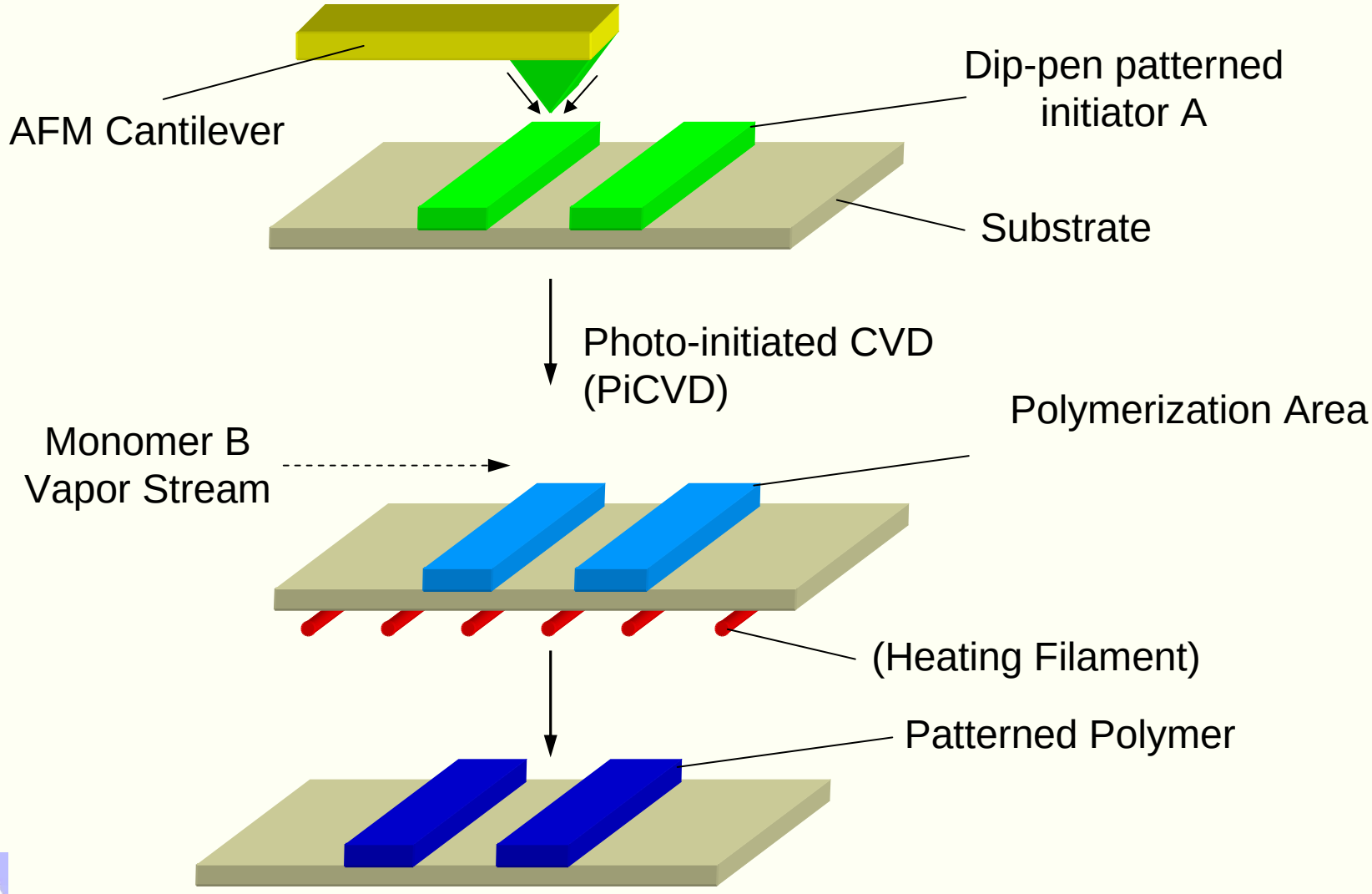
Additive Processing



Selective CVD of sacrificial layer

- Photolithography;
- Microcontact Printing ;
- Dip-pen Nanolithography

Pattern Fabrication



Patterned Sacrificial Polymers

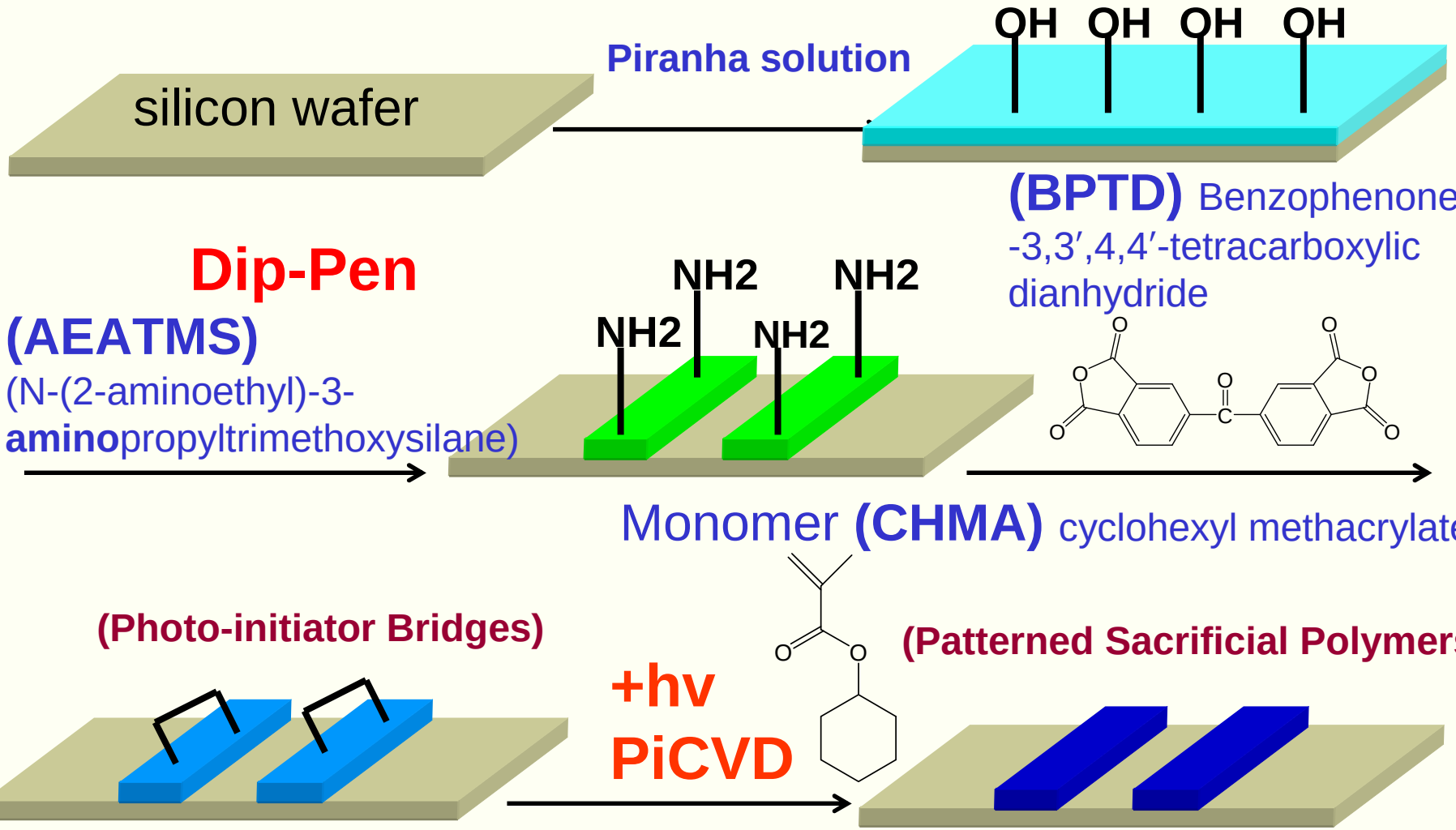
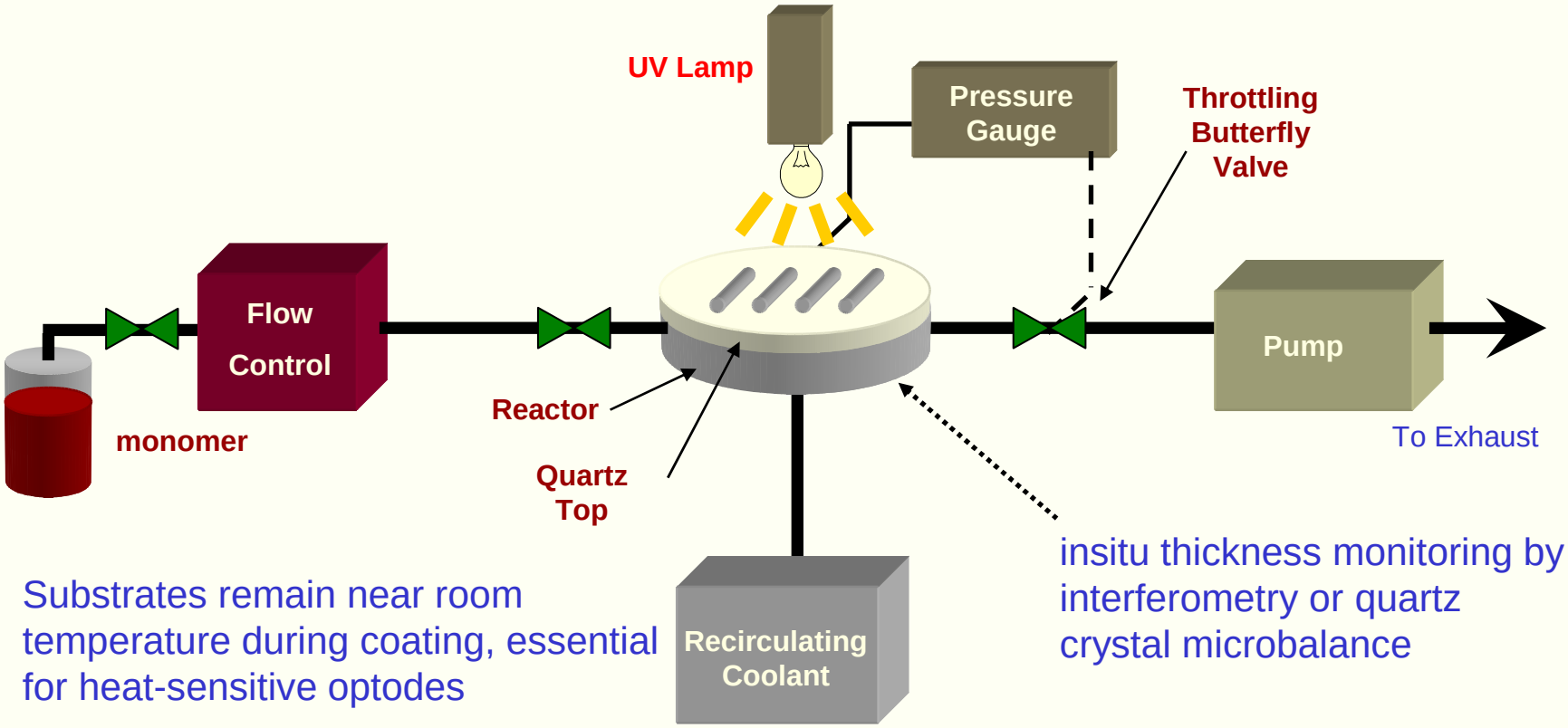


Photo-initiated CVD for sacrificial Polymers

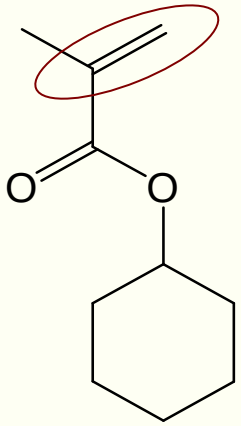


PiCVD process characteristics:

- All-dry process, no worker exposure to solvents
- low-temperature process
  (substrate at ~ room temperature; no high-temperature filament)

PiCVD Sacrificial Layer Chemistry

Monomer Cyclohexyl Methacrylate (CHMA)

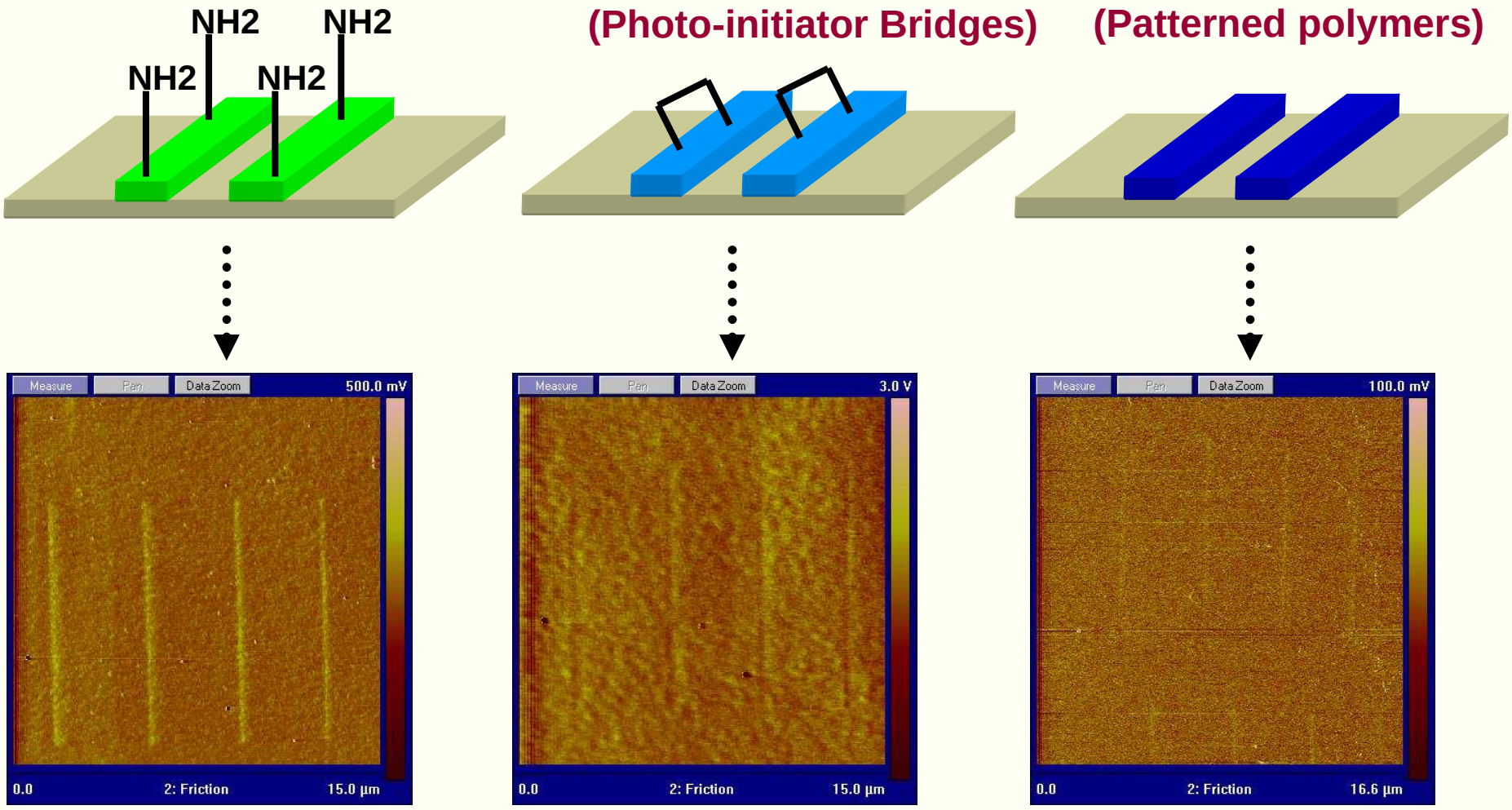


- •selective bond scission
- •systematic compositional variation using feed gas

- CHMA is not a photosensitive monomer
- Decomposition > 99.7% by thickness
- Onset temperature of decomp ~ 270 °C
- A environmental improvement over previously-reported spin-on sacrificial materials

Reference: K. Chan and K. K. Gleason, J. Electrochem. Soc., 153, 4, C223-C228 (2006)

Lateral Force Microscope (LFM) Friction Images



Acknowledgement: Chung-Yi Chiang and Prof. Angela Belcher

Conclusion and Future Work

- The direct pattering of sacrificial polymer has been demonstrated prepared by the combination of DPN and PiCVD technology. (collaboration with Belcher group)
- PiCVD processes for additive processing will be optimized for growth rate, uniformity, absence of surface defects, chemical structure, minimization of EHS impact, and compatibility with dry polymeric removal.
- Air gap structures will be tested for removal of the sacrificial layer. (collaboration with Muscat group)

Low Environmental Impact Processing of Sub-50 nm Interconnect Structures

Air gap fabrication through sacrificial polymer removal in supercritical CO_2

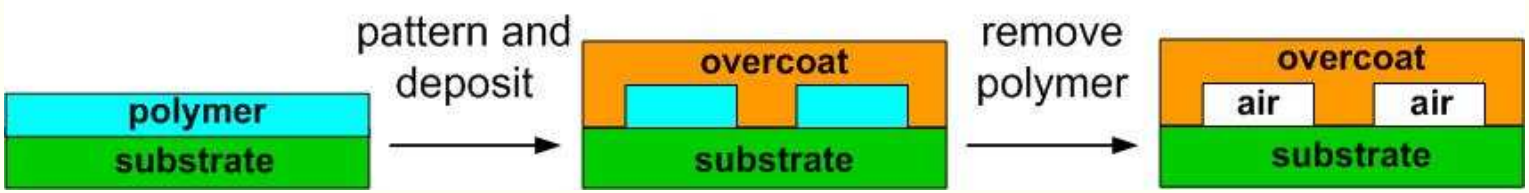
Rachel Morrish and Anthony Muscat

Department of Chemical and Environmental Engineering

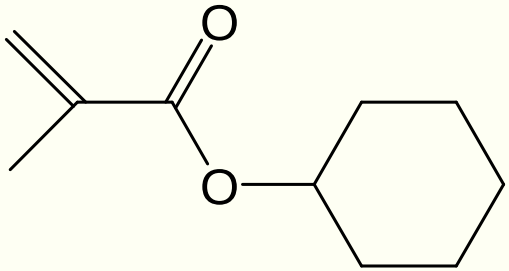
University of Arizona

Sacrificial Polymer Removal

- Air gap structure fabrication by etching sacrificial polymer

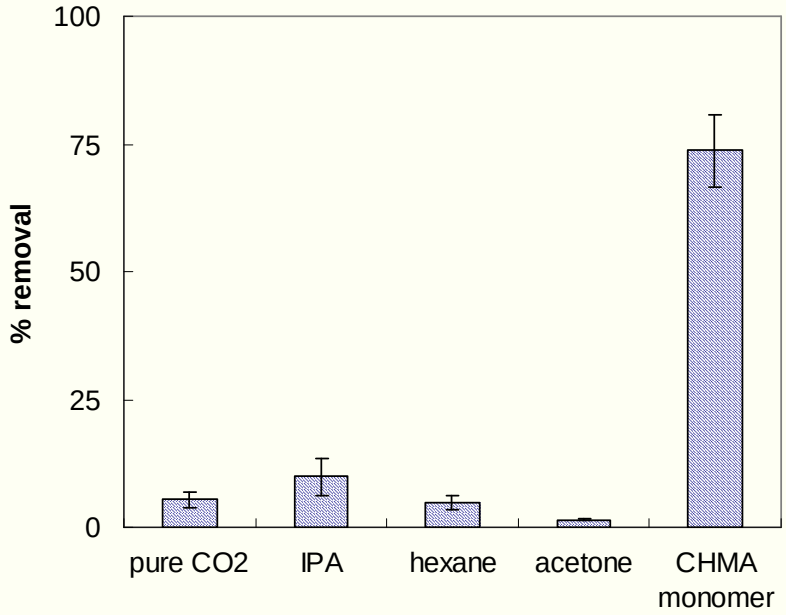


- Removing sacrificial polymer in supercritical CO_2 ($scCO_2$)
  - high density, low surface tension, low temperature
  - EHS benefits
- Polymer solubility in $scCO_2$
  - polycyclohexyl methacrylate (CHMA)
  - polymerized methacrylates > 2000 bar



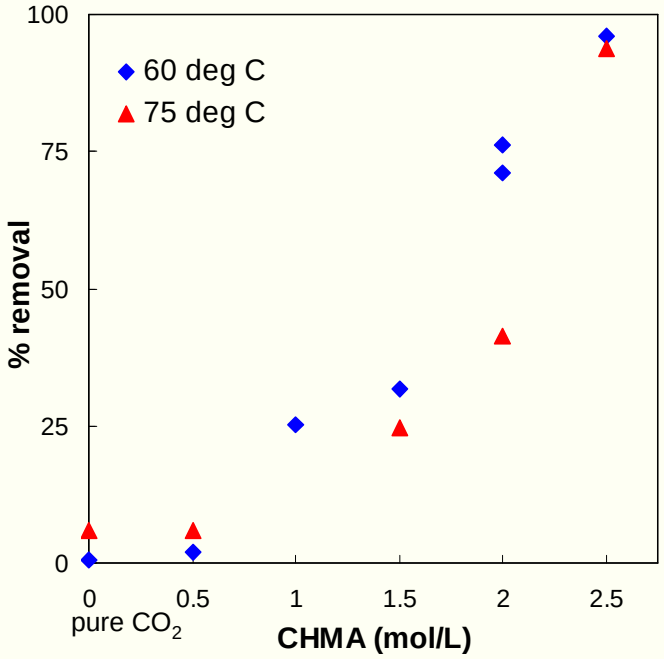
Sacrificial Polymer Removal

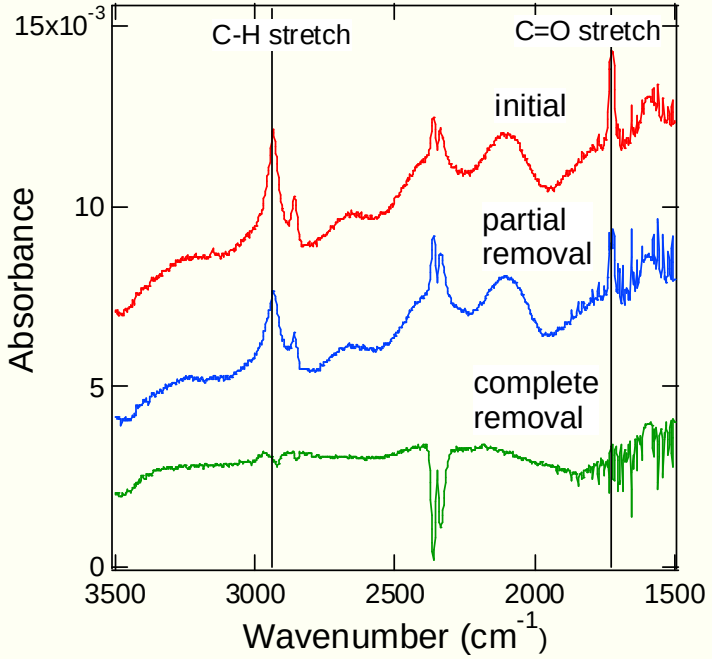
- Polymerized CHMA thin film in cosolvent/CO_2 mixture
  - compared IPA, hexane, acetone, CHMA monomer cosolvents
  - film thickness measured by ellipsometry, initial 100 – 250 nm
  - 1 – 2.5 M cosolvent mixed in CO_2
  - T = 60 ± 3°C, P = 170 ± 15 bar
  - reaction time = 30 minutes
- CHMA monomer exhibited highest removal
  - increases solution density
  - favorable intermolecular interactions for dissolution



Sacrificial Polymer Removal

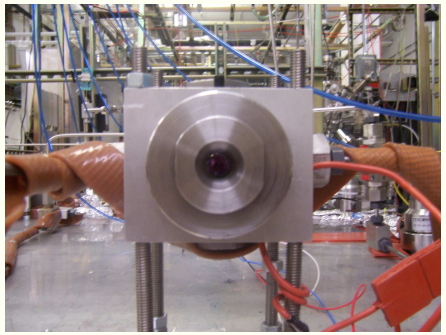
- Removed sacrificial polymer with CHMA monomer in $scCO_2$ at 170 bar
  - solubility increased with increasing CHMA concentration
  - verified removal using FTIR





Conclusion and Future Work

- Conclusion
  - Demonstrated removal of sacrificial polymer using CHMA monomer in $scCO_2$ solution
- Future Work
  - Determine optimum processing conditions for etching
  - Investigate dissolution kinetics using *in-situ* FTIR reactor
  - Test sacrificial polymer removal on patterned substrates
  - Explore viability of recycling CO_2 and monomer cosolvent
- Acknowledgments
  - Gleason group
  - SRC/Sematech Engineering Research Center



Cornell University

MIT

ERC/SRC Task ID #425.017

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

W. Shannan O'Shaughnessy[1], Sal Baxamusa[1], Sivakumar Nagarajan[2], Nelson Felix[3], Jin Kyun Lee[3], Prof. Karen K. Gleason[1], Prof. James J. Watkins[2] and Prof. Christopher K. Ober[3]

[1]Chemical Engineering, Massachusetts Institute of Technology

[2]Polymer Science & Engineering, UMass Amherst

[3]Materials Science & Engineering, Cornell University

Approaches

- Molecular glass precursors and porogens
  - Vapor phase
  - Supercritical CO_2
- Photoinitiated (pi)CVD patterned growth of dielectrics
- Supercritical (sc)CO_2 processing of low-k dielectric films

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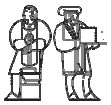
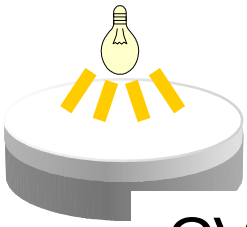
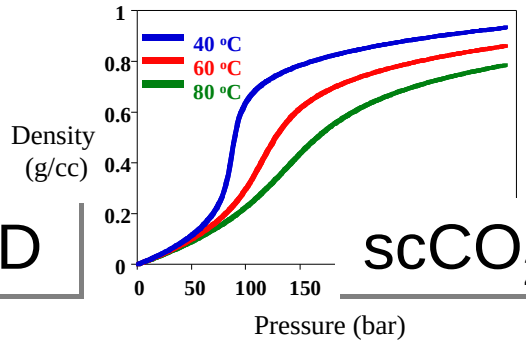


MIT

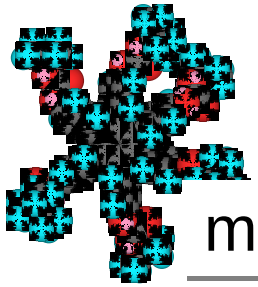
Rationale and ESH Benefits



CVD



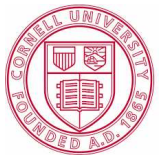
$scCO_2$



materials

all dry semiconductor processing

- Low k materials require fundamental understanding and novel approaches to dielectric deposition, patterning, processing and repair
- Complementary research program combines innovative deposition and processing of low k materials to meet ITRS roadmap goal of dielectric constants lower than 2.0
- Program designed to test new concepts in ESH friendly semiconductor production based on dry deposition and supercritical CO_2 processing
- Team provides access to unique tools (CVD deposition tools [MIT], $scCO_2$ processing equipment and nanoimprint lithography [UMASS], nanofabrication facility [Cornell CNF]).



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Photoinitiated CVD

- Photoinitiated CVD invented by **Gleason** is evolutionary from plasma enhanced CVD (PECVD) of low k Si:O:C:H films.
- Photoinitiated patterning of growth sites drives the assembly and free radical gas phase low k precursors and porogens (designed by **Ober**).
- High resolution initiator deposition carried out by **Ober** (Cornell) and **Watkins** (UMASS)

plasma-enhanced CVD
(electric field, blanket films for subtractive processing)

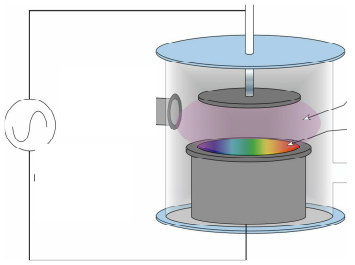
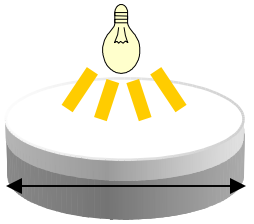


photo-initiated CVD
(UV photons, patterned films for additive processing)



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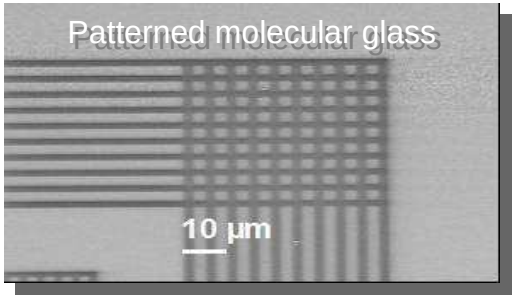
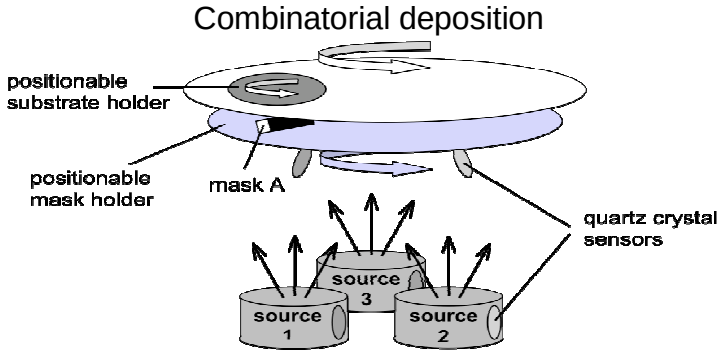
Low k Molecular Glasses

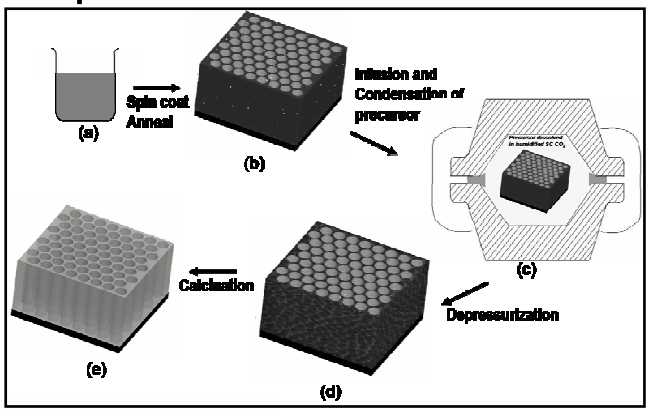
- Investigate molecular glasses for patterning and as low k precursors
- Molecular glass precursors will be prepared by **Ober** using synthetic schemes developed expressly for these studies.
- Low k films deposited from glass and porogen precursors in collaboration with **Gleason** and **Schmidt** (Bayreuth).
- Porogen and film processing using $scCO_2$ by **Ober** and **Watkins**.

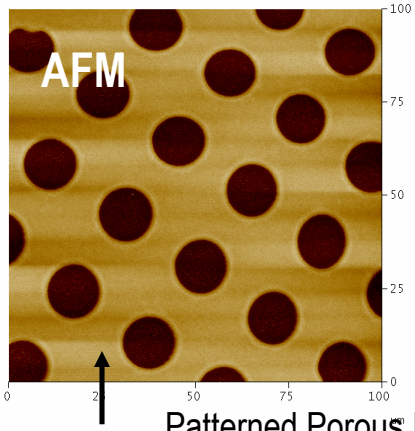


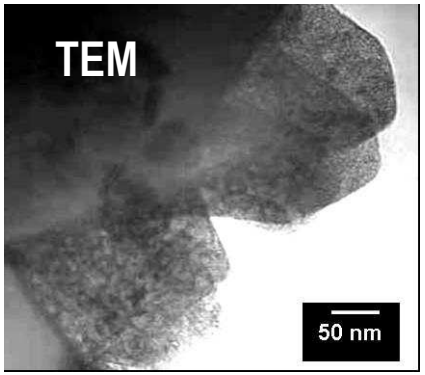


$scCO_2$ Processing of Low k Materials from Self-assembled Templates

- Develop new approach to mesoporous ultralow k (ULK) silicate films involving 3-D replication of self-assembled block copolymer templates in $scCO_2$ (**Watkins**)
- With **Ober**, synthesized new block copolymers capable of template formation and direct lithographic processing.
- Advantage of this approach is the separation of photopatternable template preparation (via spin coating and self-assembly) and silicate network formation into discrete steps.







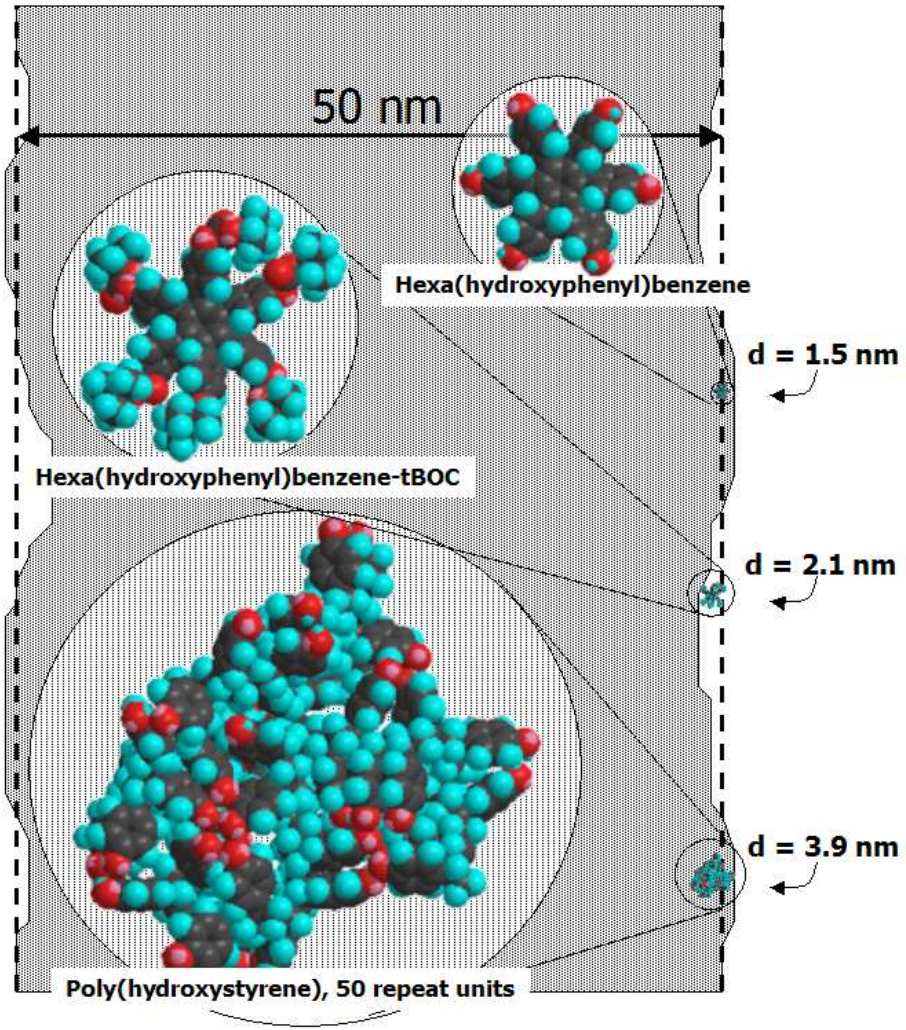
Patterned Porous Inorganic Network

Presentations

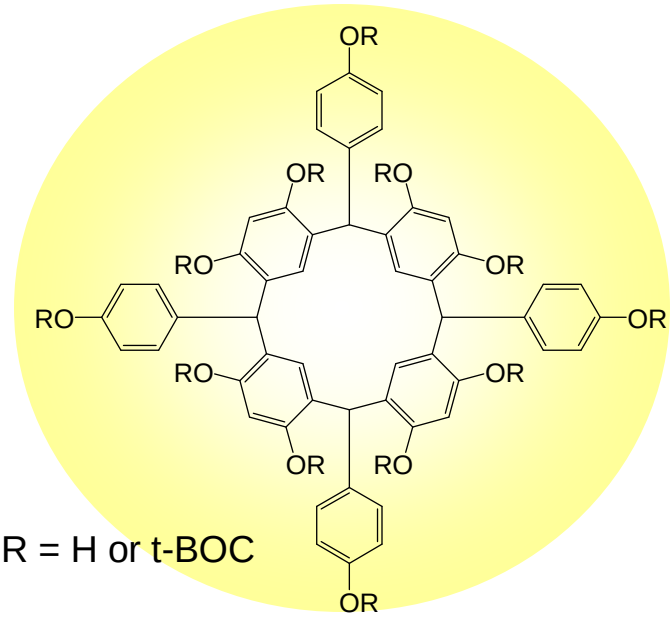
- Molecular glasses: lithographic processing and porogen precursors
  - Nelson Felix (Cornell)
- piCVD patterning of low K films
  - Shannan O'Shaughnessy (MIT)
- Well-Ordered ULK Films via SCF Processing
  - Sivakumar Nagarajan(UMASS)

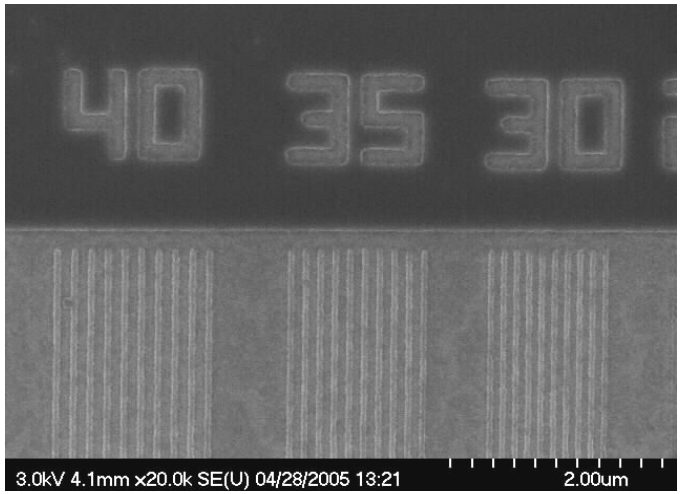
Molecular Glasses

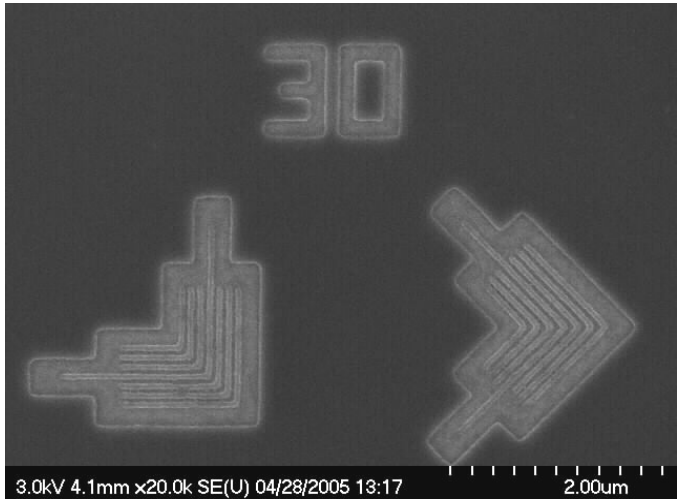
- Small molecule size ~1-2nm
  - Potential for lower Line-Edge Roughness (LER)
- Well defined molecular structures
  - No distribution of mass
- Low tendency towards crystallization
  - bulky irregular shape or different conformation states
- Strong intermolecular attractive forces for high Tg
  - Specific interactions such as H-bonding
- Better miscibility with other small components



Performance as Resists





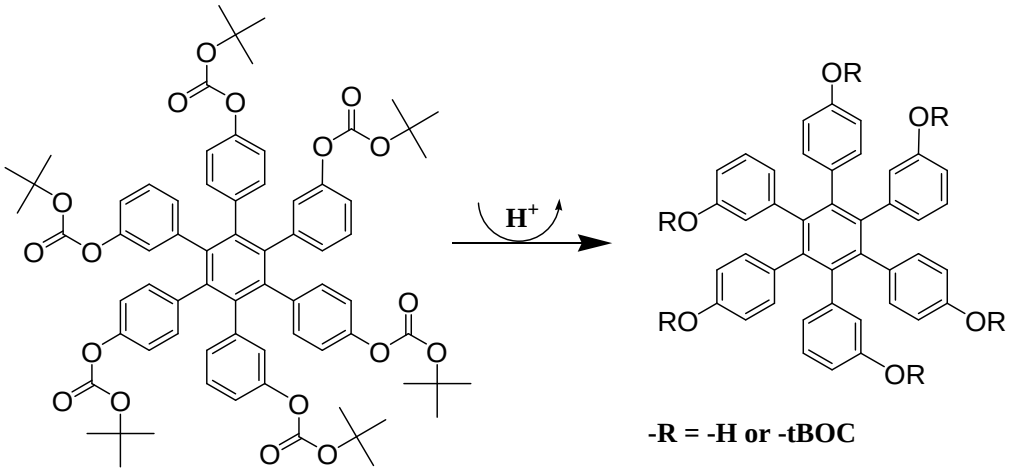


- 30 nm L/S, LER ~ 5 nm
- Best EUV exposure results with molecular glasses

S. W. Chang, R. Ayothi, D. Bratton, D. Yang, N. Felix, H. B. Cao, H. Deng and C. K. Ober, *J. Mater. Chem.*, **16** (2006), 1470-74.

Images obtained at Lawrence Berkeley National Laboratories by EUV microexposure tool

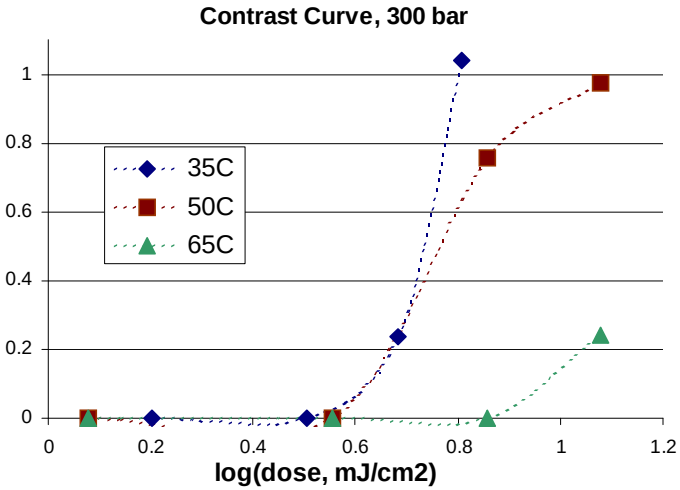
Supercritical CO_2 Solubility

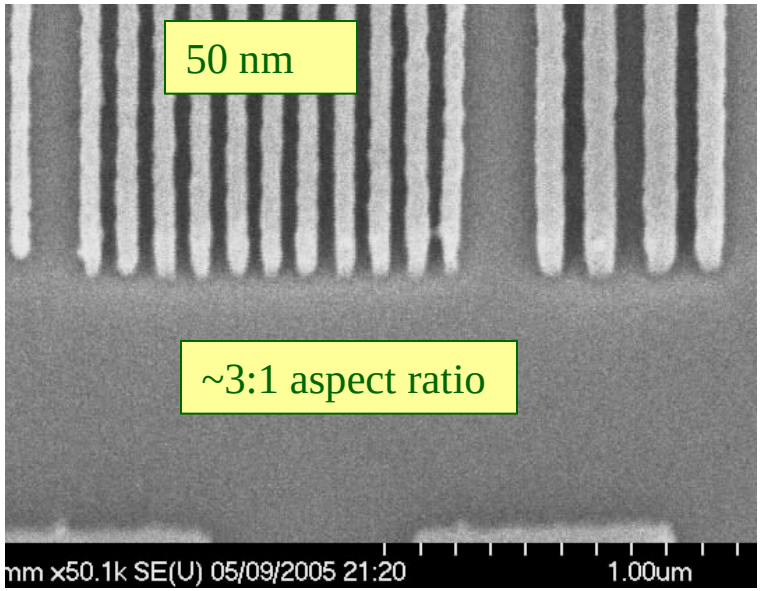


-R = -H or -tBOC

Developed in scCO2

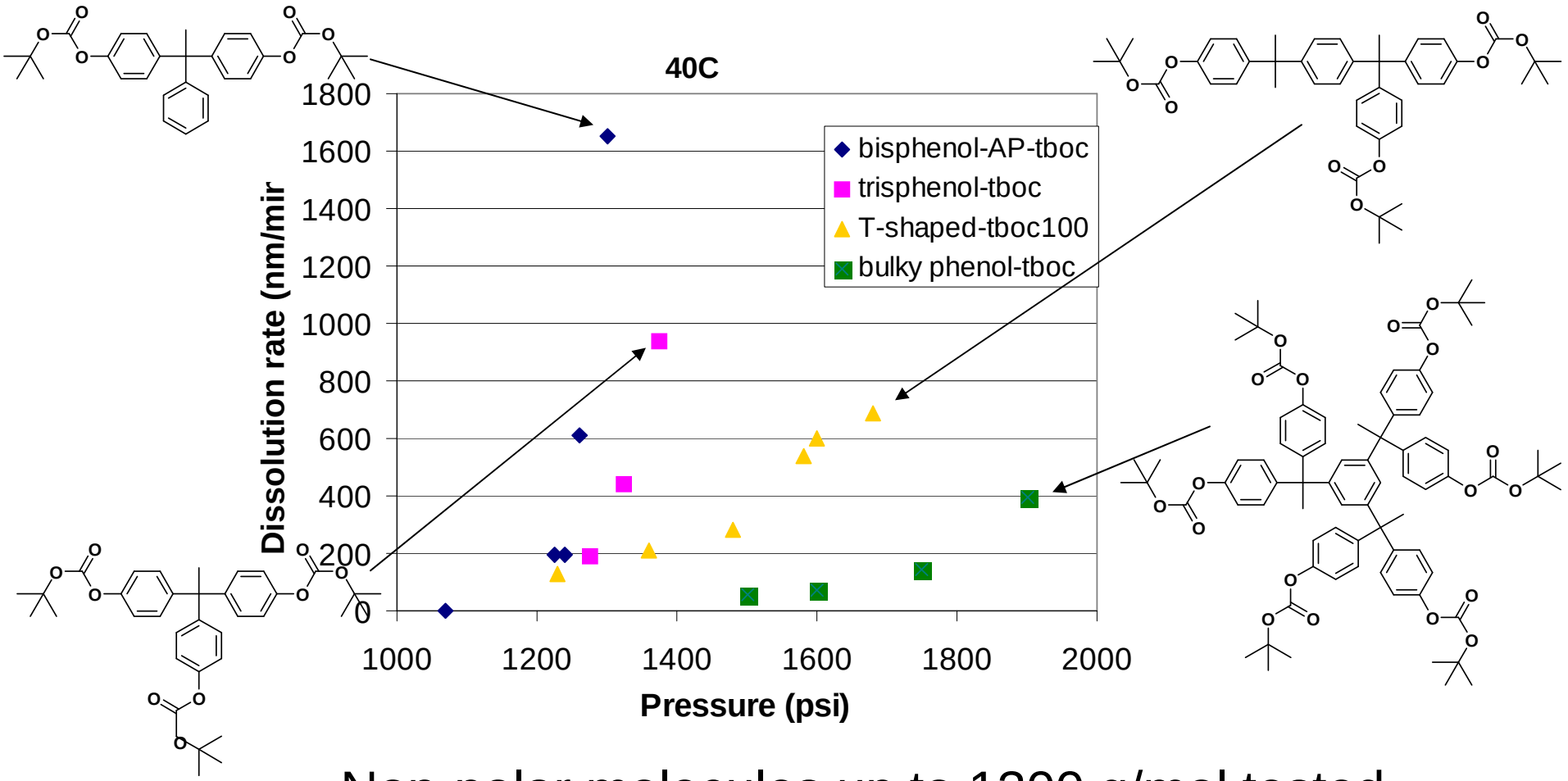
LER ~ 7nm





Felix, N. M, Tsuchiya, K., and C. K. Ober, *Adv. Mater.*, 18(4), 2006, p 442-446.

CO_2 Dissolution Rates of Small Molecule Films



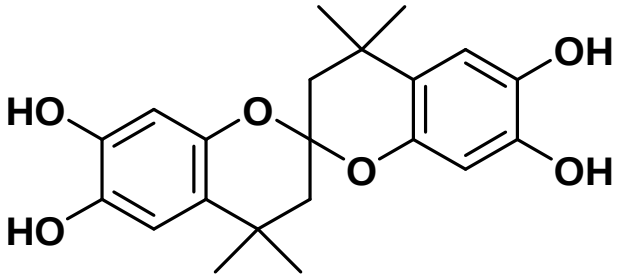
- Non-polar molecules up to 1300 g/mol tested
- Solubility varies predictably with molecular wt.

Vapor Deposition of Molecular Glasses

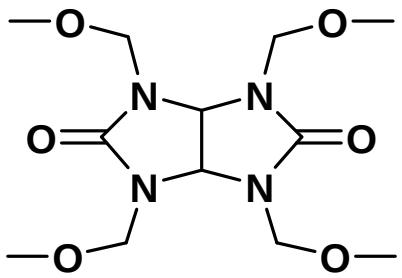
ERC/SRC Task ID #425.017

- Small molecules sufficiently volatile and stable to deposit by dry deposition technique without degradation
- Allows for precise control of resist components - deposition on curved surfaces

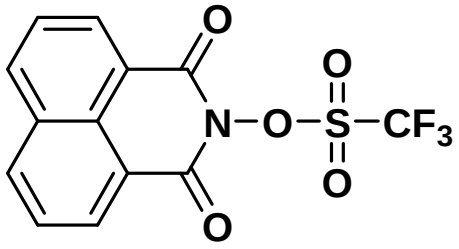
Sample System Used



Glass-former



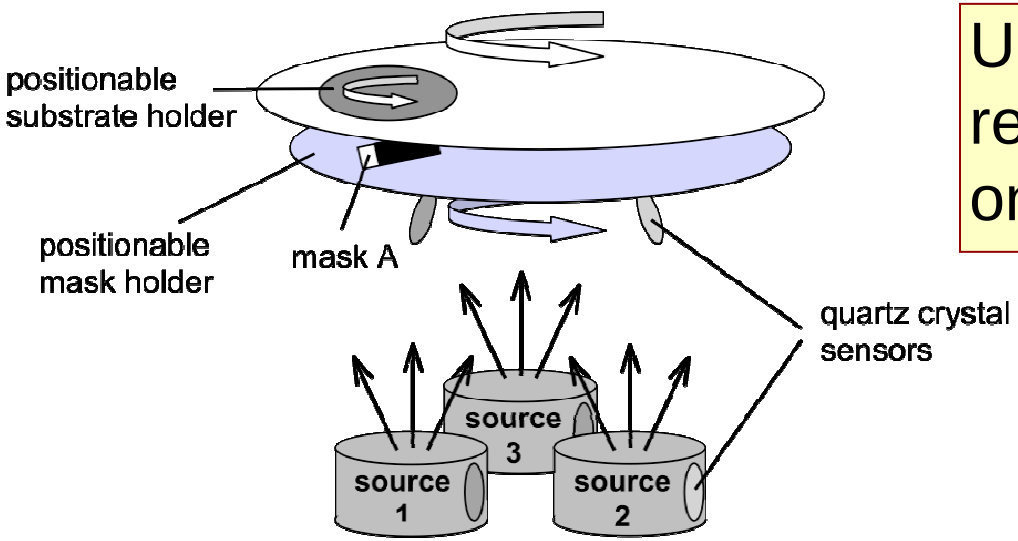
Crosslinker



Photoacid Generator

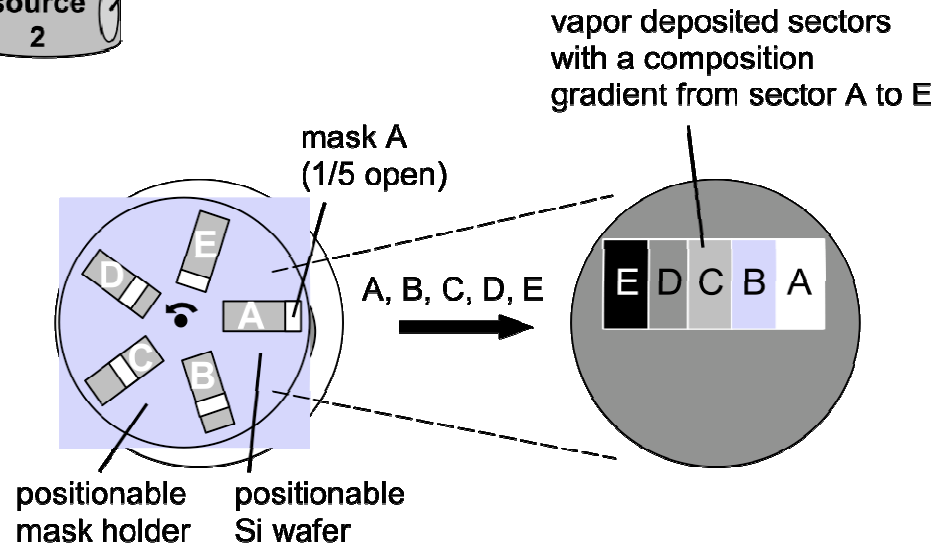
Deposition and Screening

ERC/SRC Task ID #425.017



Up to 10 different resist compositions on one wafer

Gradients, controlled mixtures, and rapid screening

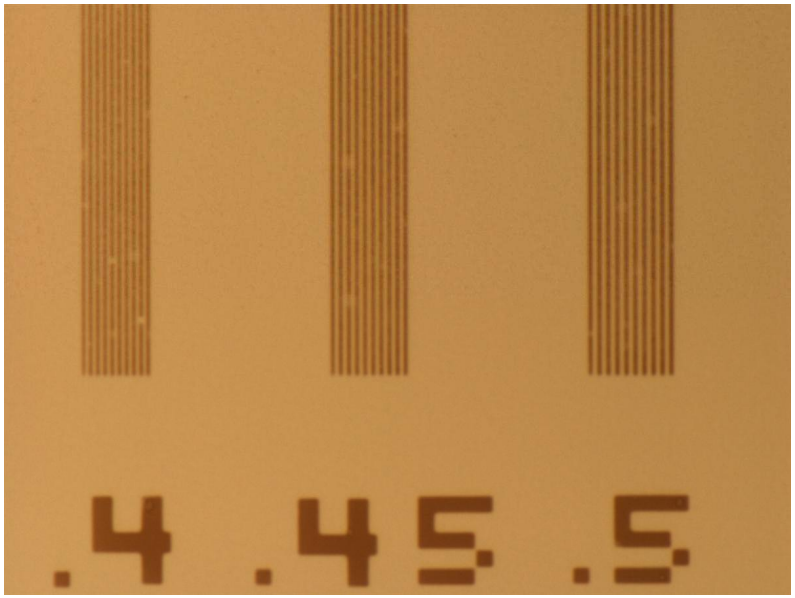


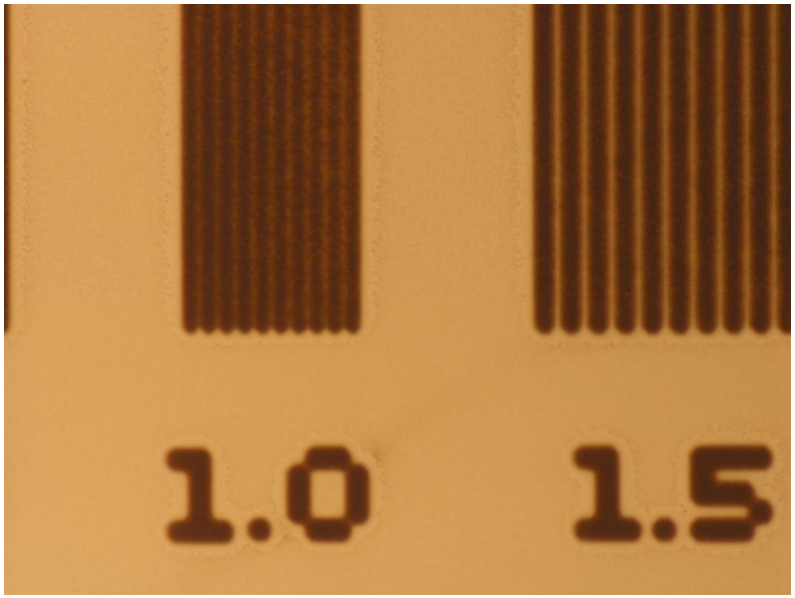
Cornell University

UNIVERSITÄT BAYREUTH

Results

- Test exposure using 365 nm Stepper
- Developable in water



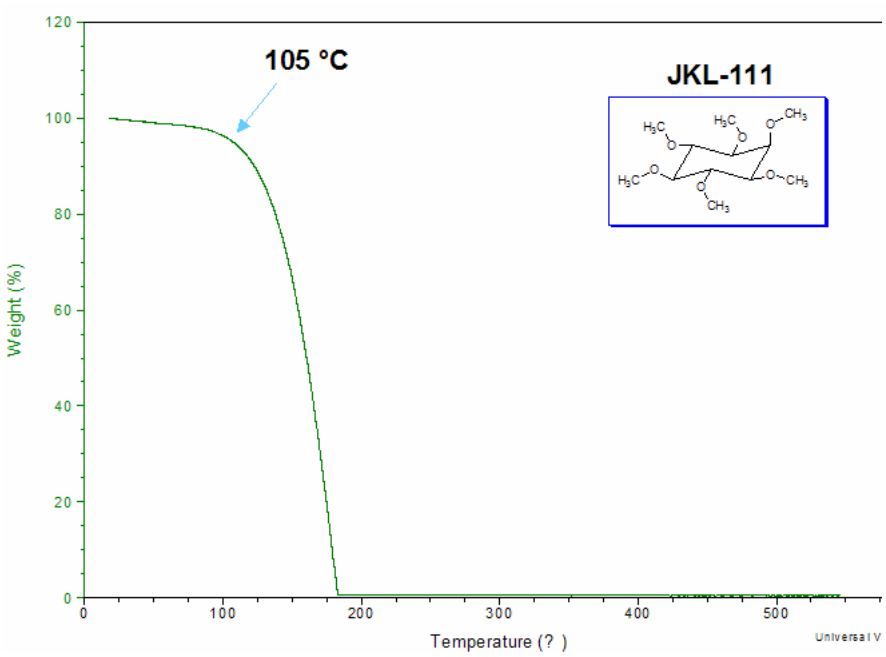


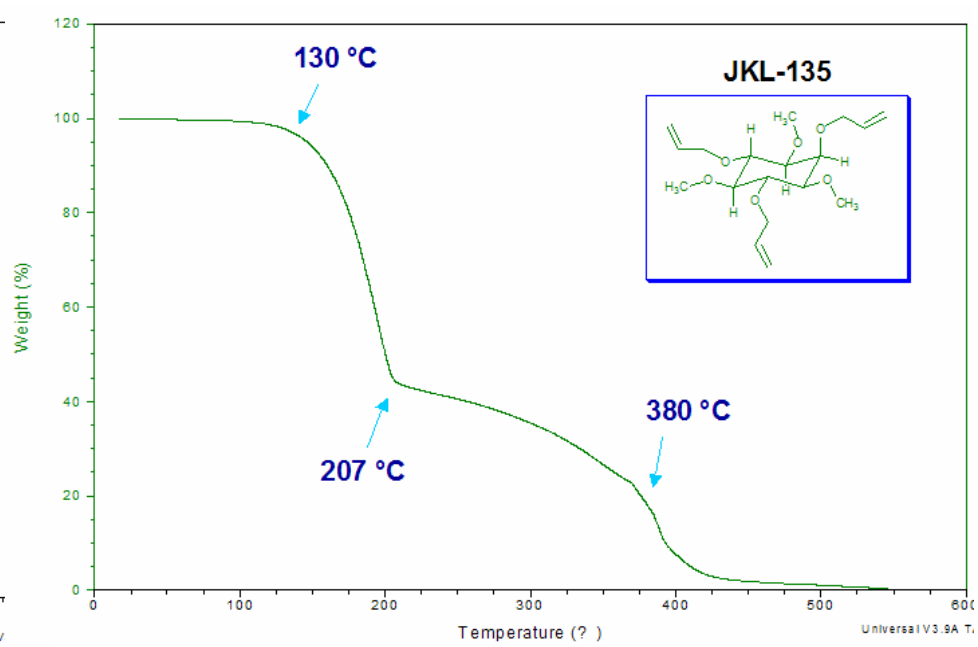
Cornell University

UNIVERSITÄT BAYREUTH

Inspiration: MG-type Porogens

- Small molecule porogens with low decomposition temperatures
- Simple, easily-synthesized structures
- Potential for lower annealing temperature, time.





Summary

ERC/SRC Task ID #425.017

- Molecular glass components have shown great synergy with environmentally-friendly processing
  - Demonstrated ability to process a variety of small molecules with $scCO_2$
  - Vapor Deposition possible
    - Deposition of blanket films of resist components
    - Compatibility with vapor-based low-k dielectric processes

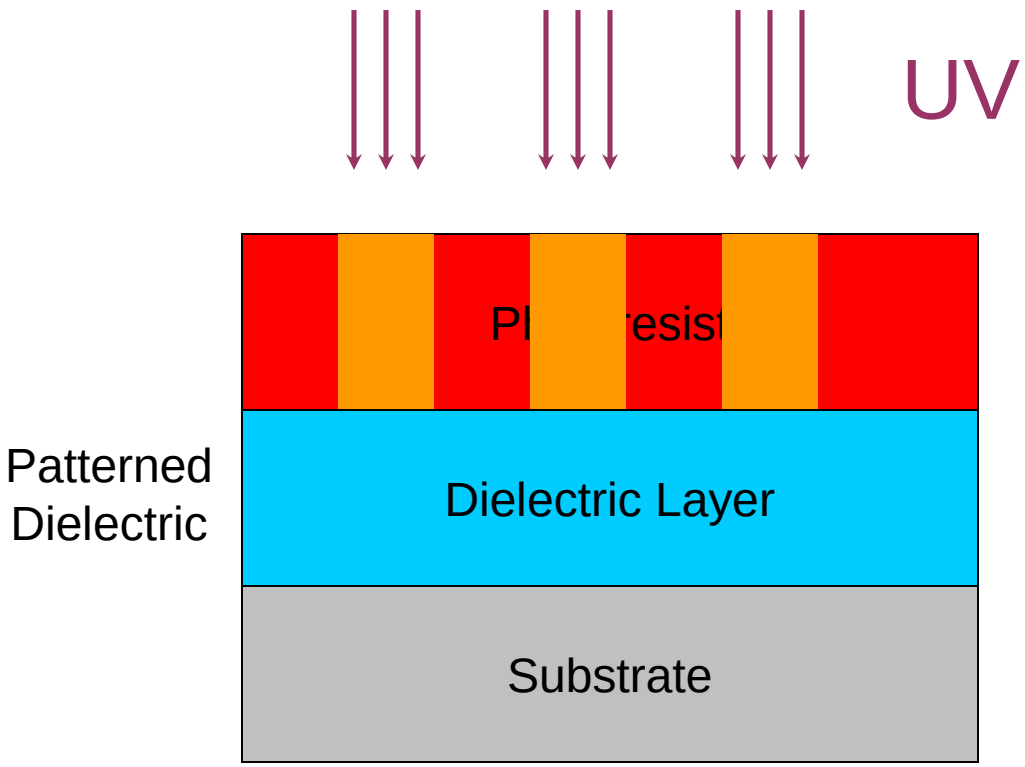
Presentations

- Molecular glasses: lithographic processing and porogen precursors
  - Nelson Felix (Cornell)
- piCVD patterning of low K films
  - Shannan O'Shaughnessy (MIT)
- Well-Ordered ULK Films via SCF Processing
  - Sivakumar Nagarajan(UMASS)

piCVD - Project Goals

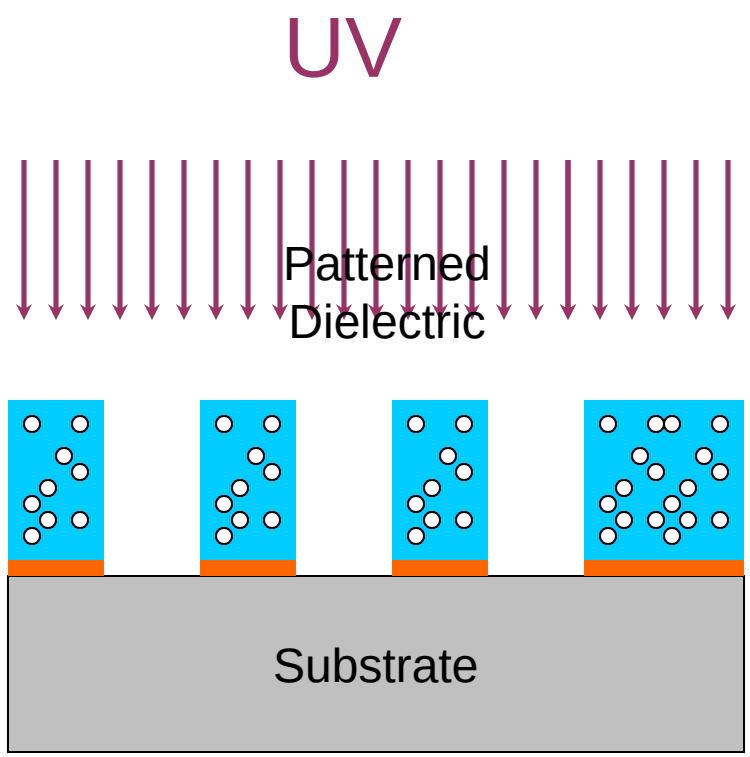
ERC/SRC Task ID #425.017

- Patterned Dielectric Growth
- Current Technology
  - Resist based lithography of blanket dielectric layer
- Reduce time & ESH impact



New Approach

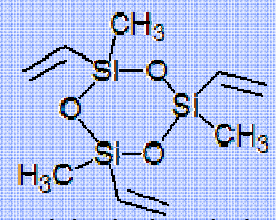
- In situ Patterned Growth
  - Apply Initiator
  - Lithographic Patterning
    - Microcontact Printing
    - E-beam lithography
    - Dip pen lithography
    - Photobleaching
  - Grow piCVD material
    - Gas phase monomer & porogen
  - Remove porogen
- Improves cost and ESH
  - Fewer steps
  - Less solvent
- Complementary to sacrificial materials patterning



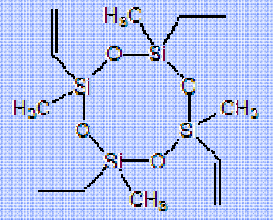
Chemistry

ERC/SRC Task ID #425.017

piCVD Monomers



Trivinyl-trimethyl-cyclotrisiloxane (V_3D_3)

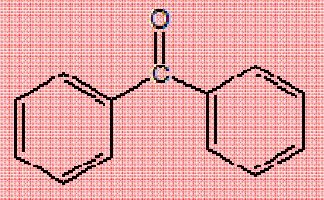


Tetravinyl-Tetramethyl-cyclotrisiloxane (V_4D_4)

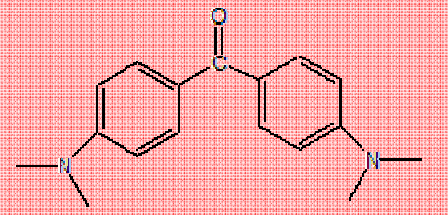
Dielectric Constant ≈ 2.5

Model Systems:
Cyclohexyl Methacrylate
Hydroxyethyl Methacrylate
Plasma Organosilicate Glass

piCVD Initiators



Benzophenone

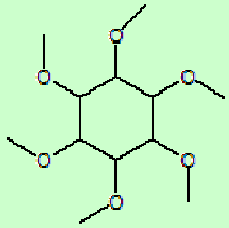


Michler's Ketone

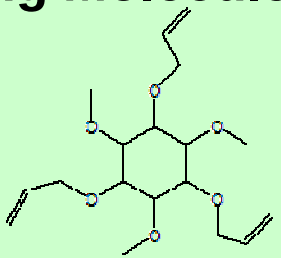
Surface tethered Benzophenone derivatives (Cornell)

Active @ 254nm & 365nm

Novel Pore Generating Molecules



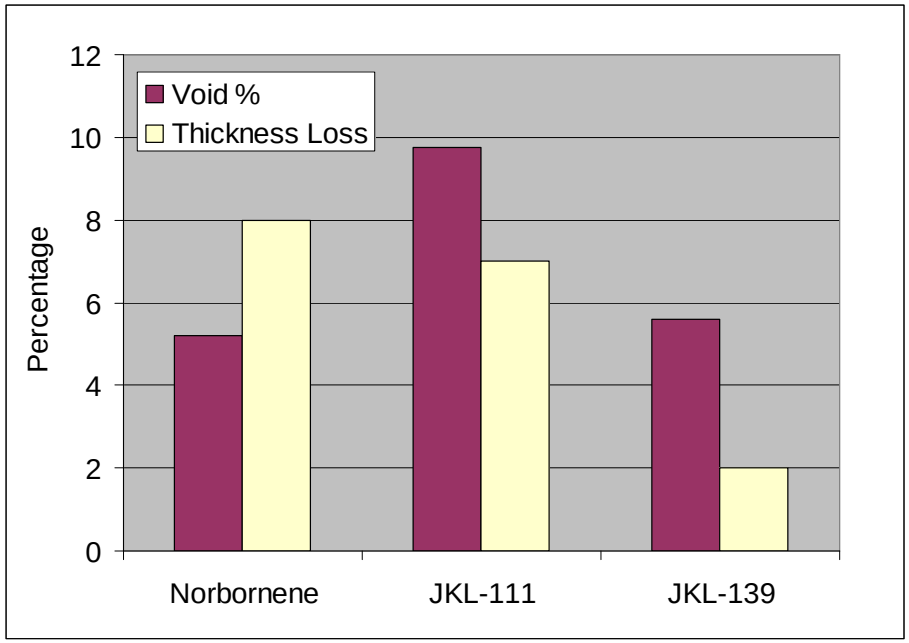
Hexamethyl ether of *myo*-inositol
JKL-111

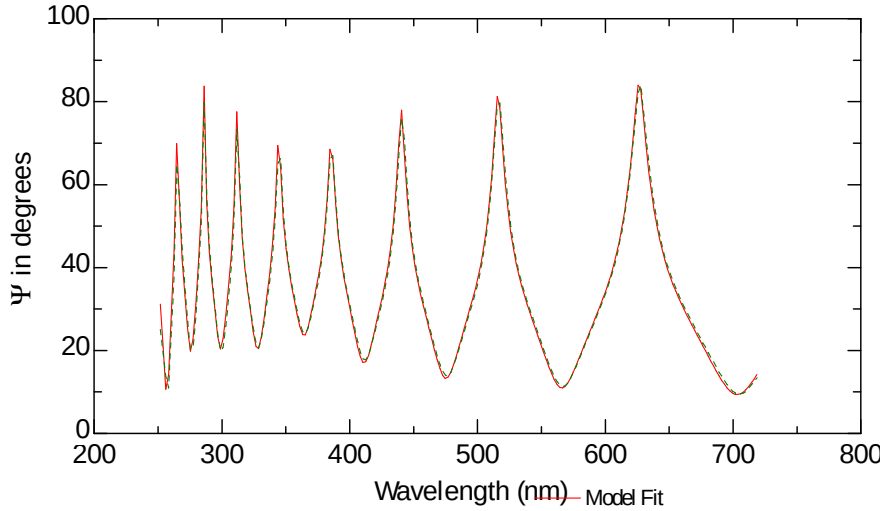


JKL-139

Results – Novel Porogens

ERC/SRC Task ID #425.017

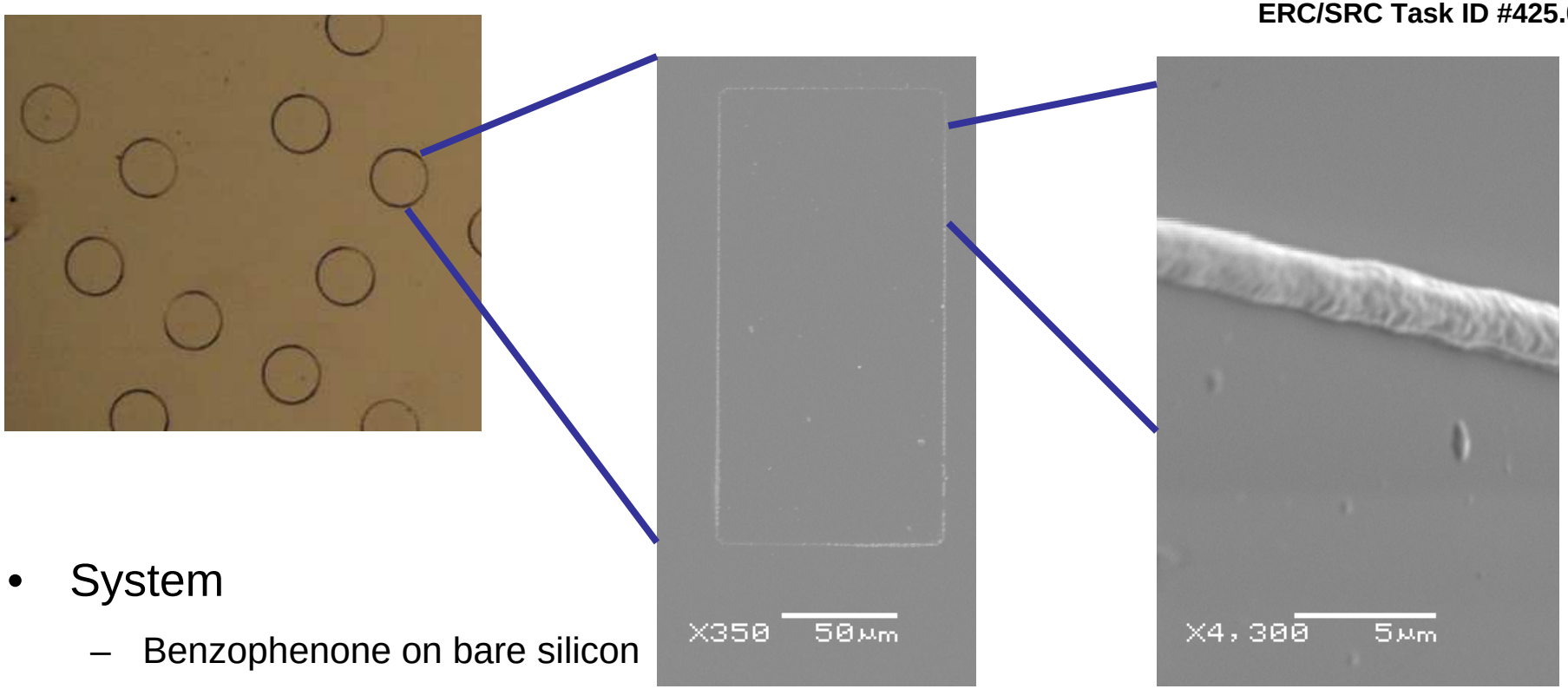




Ellipsometry data plus model fit for porous film

- Test properties of novel molecules as porogens
  - Ensure incorporation and thermal removal
  - Compare to Norbornene
    - Commercially available porogen
  - Void percentage modeled using spectroscopic ellipsometry
    - Effective medium approximation

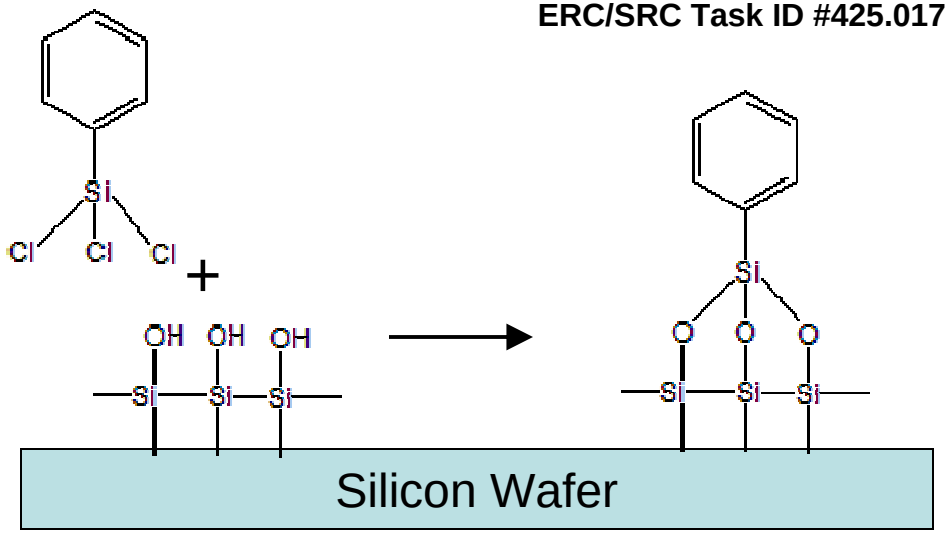
Initial Patterning Results

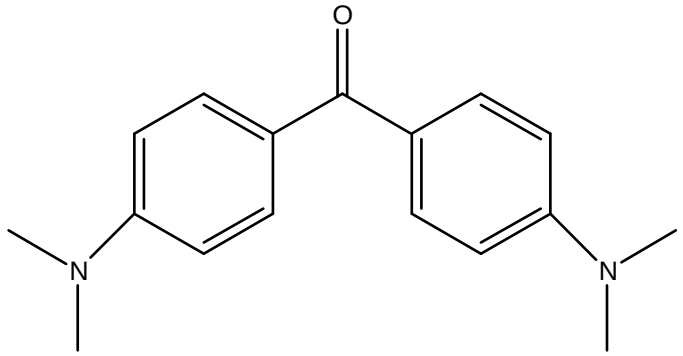


- System
  - Benzophenone on bare silicon
  - 100µm circles and rectangles
- See patterned growth but no fill in

Patterning- Issues & Solutions

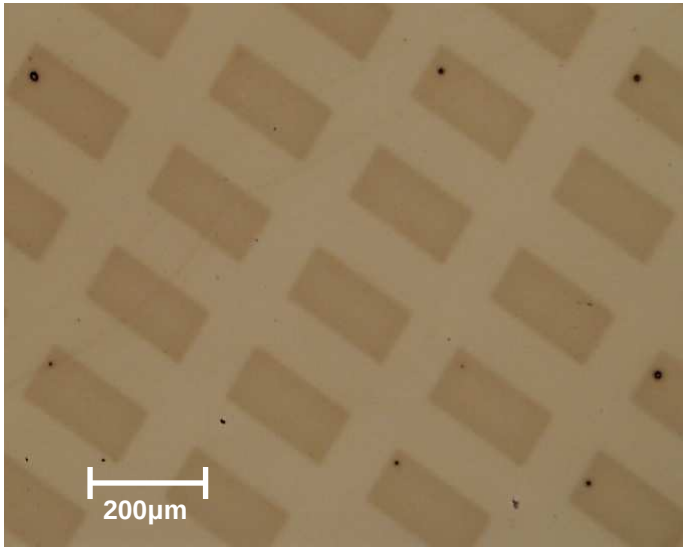
- Issues
  - Limited initiator surface affinity
    - Poor coverage
  - Max initiator concentration limited by onset of crystalization
    - Results in thin structures
- Solutions
  - Modify substrate surface
    - Create more favorable interactions
  - Switch Initiators
    - Same mode of action
    - Less solvent affinity & crystallization



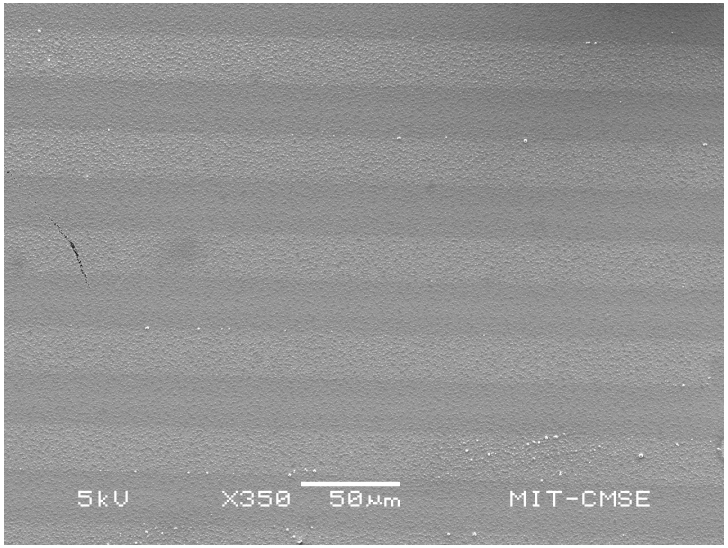


Michler's Ketone

Results – Patterned Films



Optical micrograph of 100µm X 200µm rectangles created through piCVD on pre-patterned initiator



SEM image of 25µm lines created through piCVD on pre-patterned initiator

- Full coverage of patterned area achieved
- Feature thickness increased
  - 25µm features at >200nm thickness

Milestones and Future Work

ERC/SRC Task ID #425.017

- Milestones
  - Patterned dielectric growth
    - Proof of concept achieved
    - 25μm features with >200nm thickness
  - Novel Porogen materials validated
    - 9.7% porosity achieved with novel porogen JKL-111
    - >93% thickness retention
- Future Work
  - Optimize initiator lithography
    - Smaller Features
    - Tethered initiators
  - Optimize porogen incorporation and chemistry
  - Integrate pattern film growth with porogen addition

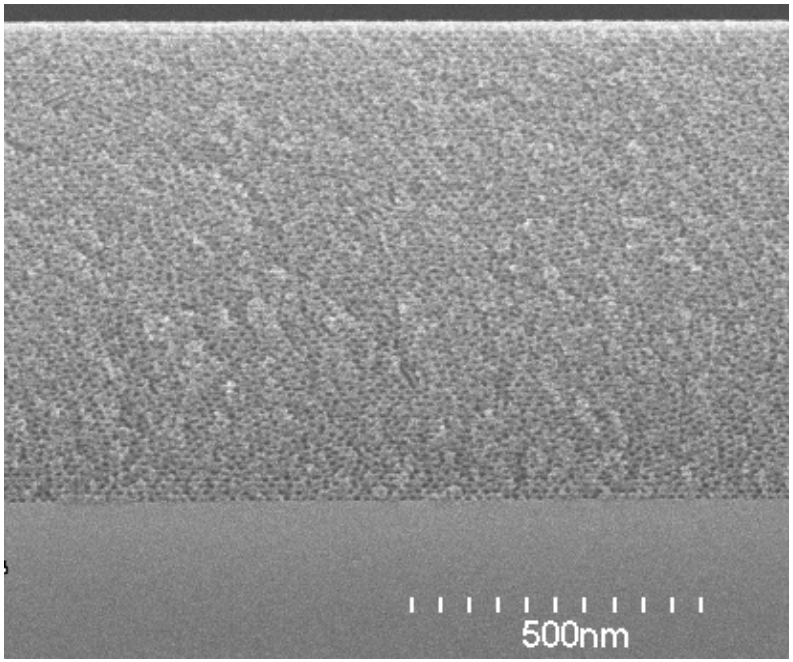
Milestones and Future Work

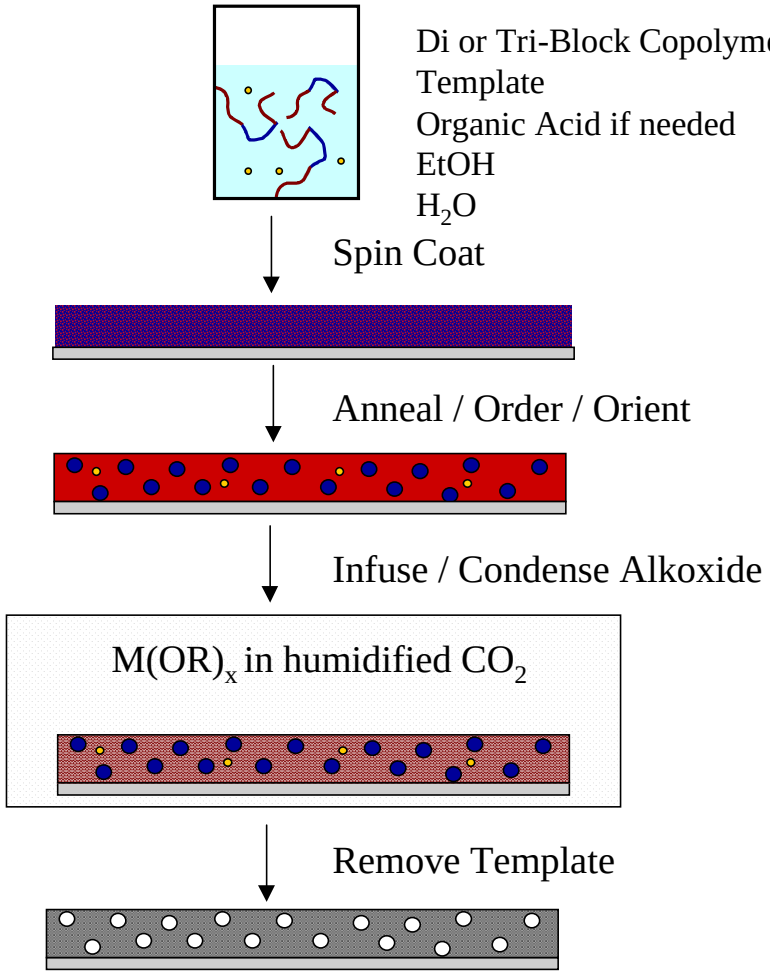
- Milestones
  - scCO2 processing of small molecules
    - Patterning and development
  - Vapor deposition of molecular glasses
    - Deposition of blanket films of resist components
    - Compatibility with vapor-based low-k dielectric processes
  - Novel porogen materials synthesized
    - Clean decomposition at relatively low temperatures
- Future work
  - Optimize porogen chemistry
  - Continue exploration of vapor-depositable and scCO2-soluble molecular glass systems

Presentations

- Molecular glasses: lithographic processing and porogen precursors
  - Nelson Felix (Cornell)
- piCVD patterning of low K films
  - Shannan O'Shaughnessy (MIT)
- Well-Ordered ULK Films via SCF Processing
  - Sivakumar Nagarajan(UMASS)

Well-Ordered ULK Films via SCF Processing





- mutual solubility of template and precursor is not required
- extraction of ROH from incipient film drives condensation
- alkoxide condensation is decoupled from template assembly
- rapid process cycle
- **heterogeneous approach preserves structural details of pre-formed BCP template**

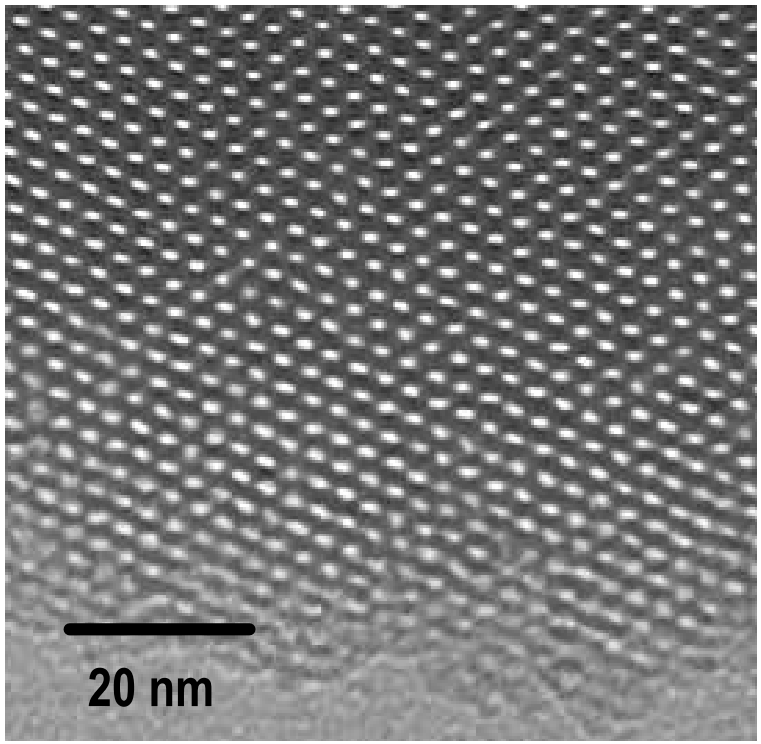
Supercritical fluids provide a unique, environmentally friendly, reaction environment that is ideally suited for materials chemistry for semiconductor and nanostructured devices

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

ULK Mesoporous Films Prepared in CO_2

First Generation Films Exhibit Excellent Performance

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



Can we do better?

Yes, Through Engineered ULKs

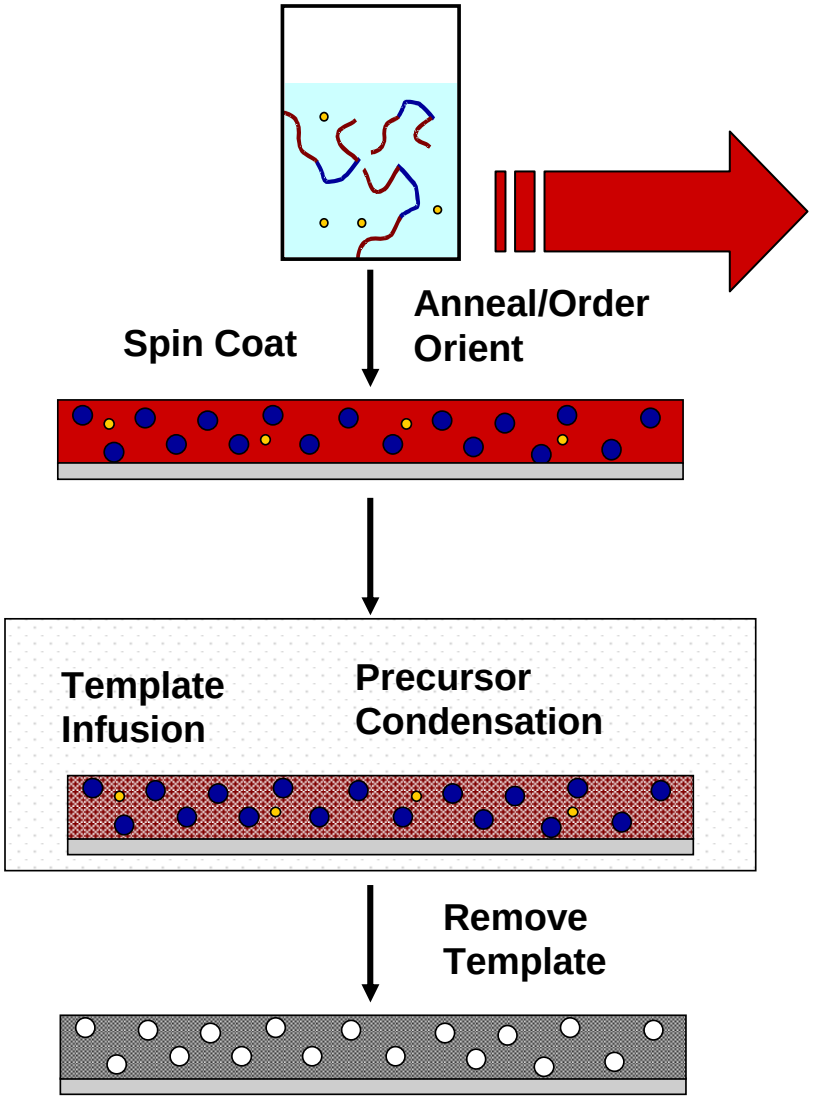
Mechanical properties can be optimized

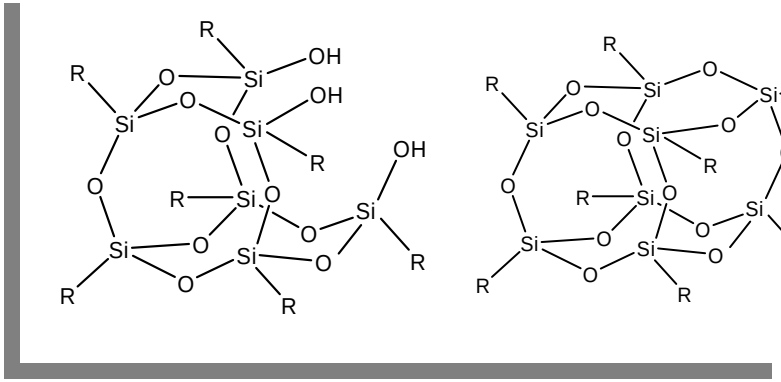
Inclusion of POSS (see A. Romang poster)
Use of bridged silsesquioxanes
Fully condensed networks via new catalysts

Direct patterning provides process differentiation

Directly patterned fat lines for BEOL process compression (cost savings + resource reduction).
Subsequent entry point for ULK < 2.2

Doping Templates with "Nanoparticle" Fillers to Improve Mechanical Properties





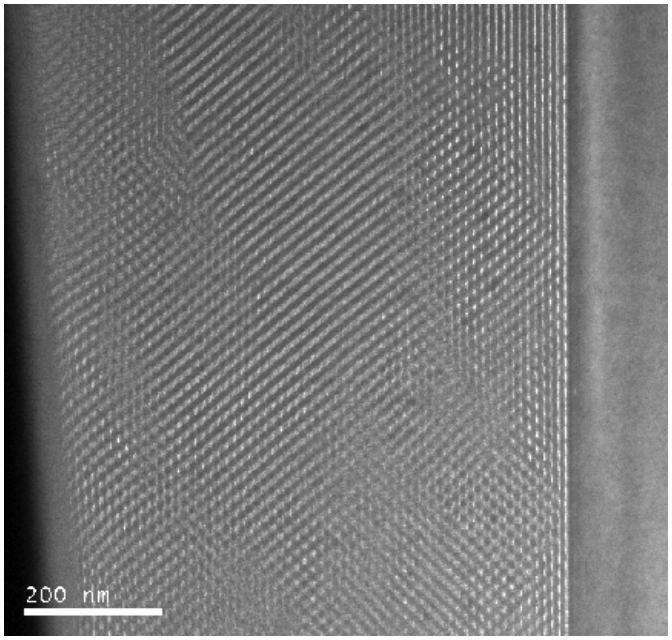
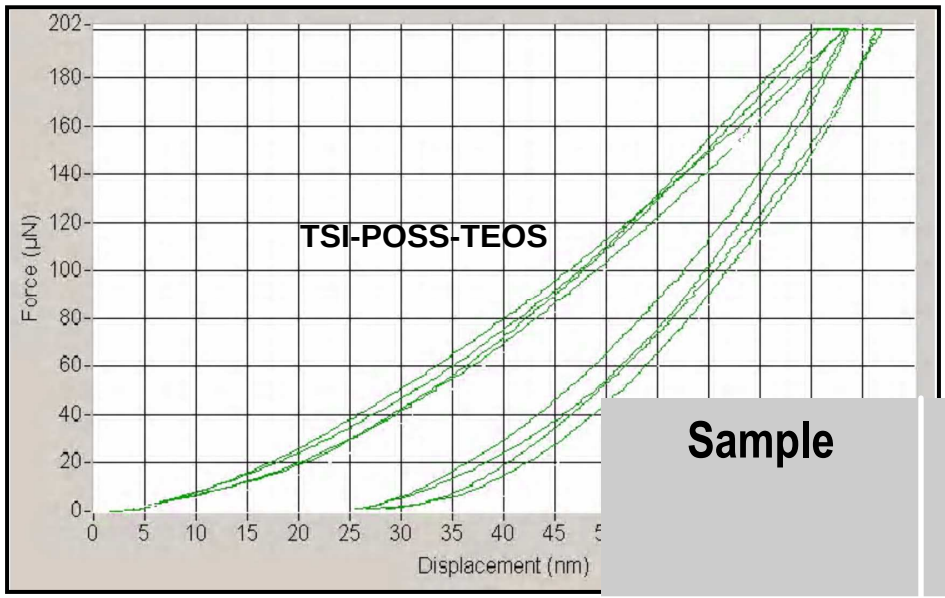


Image: Prof. Brian Gorman, UNT

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Nanoindentation of Mesoporous Silica Thin films

- A standard Berkovich probe (3 sided pyramidal shape) was used to perform load-controlled indents using Hysitron Nanoindenter.
- In load-control mode, the instrument applies a normal force to the indenter tip while continually measuring tip displacement into the sample.

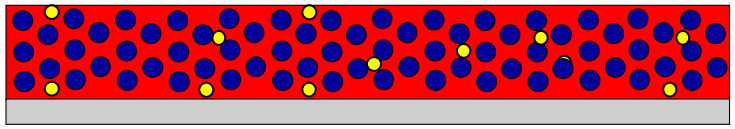


Sample	Reduced Modulus (GPa)	Hardness (GPa)	Hardness Normalized to TEOS
1. TEOS	4.19 ± 0.11	0.18 ± 0.004	1.0
2. BTESM	4.69 ± 0.19	0.47 ± 0.03	2.6
3. TSI-POSS/TEOS	21.45 ± 2.06	1.92 ± 0.12	10.7

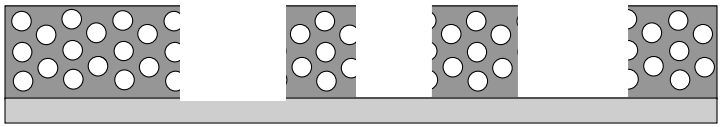
Fabrication of Micro-patterned Mesoporous Silica Films

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

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



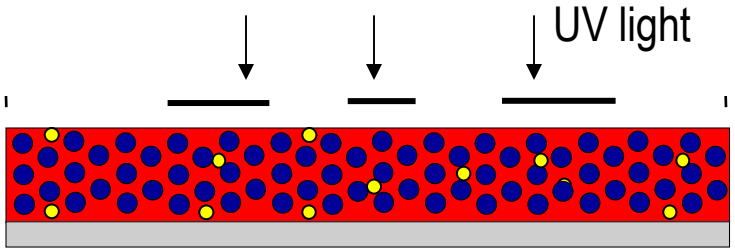
Block copolymer template with
Photo acid generator (PAG)



Patterned Inorganic network

Patterning

Calcination



Phase selective Deposition

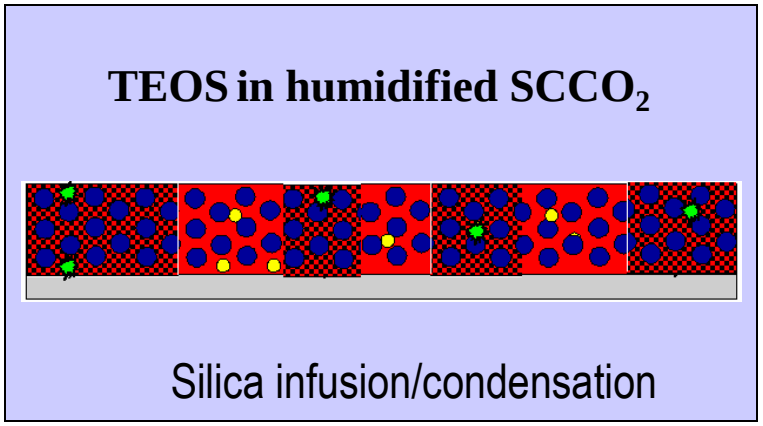


Photo acid generator
Generated Acid

Patterned Mesoporous Silica Films from Pluronics(F108)

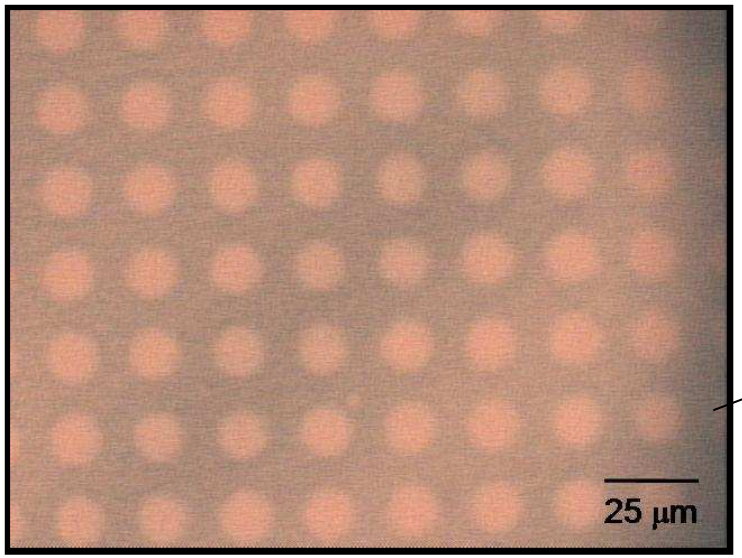
Photo acid generator: Tri phenyl sulfonium triflate – generates Triflic acid.

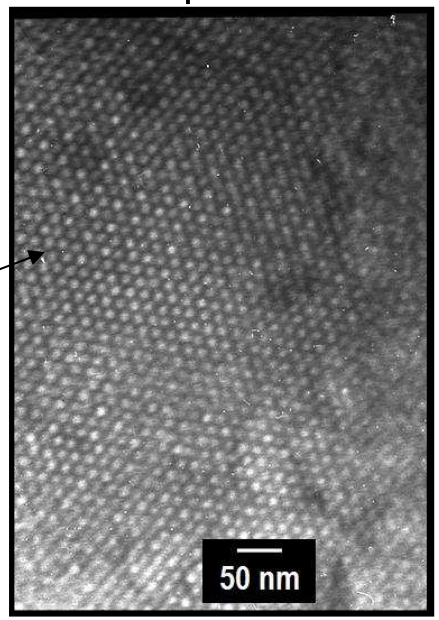
$$(C_6H_5)_3S^+CF_3SO_3^- \xrightarrow[254\ nm]{UV} CF_3SO_3H + \text{Various decomposition products}$$

Device Level Replication:
Microscopic structures.

Mesoporous silica film

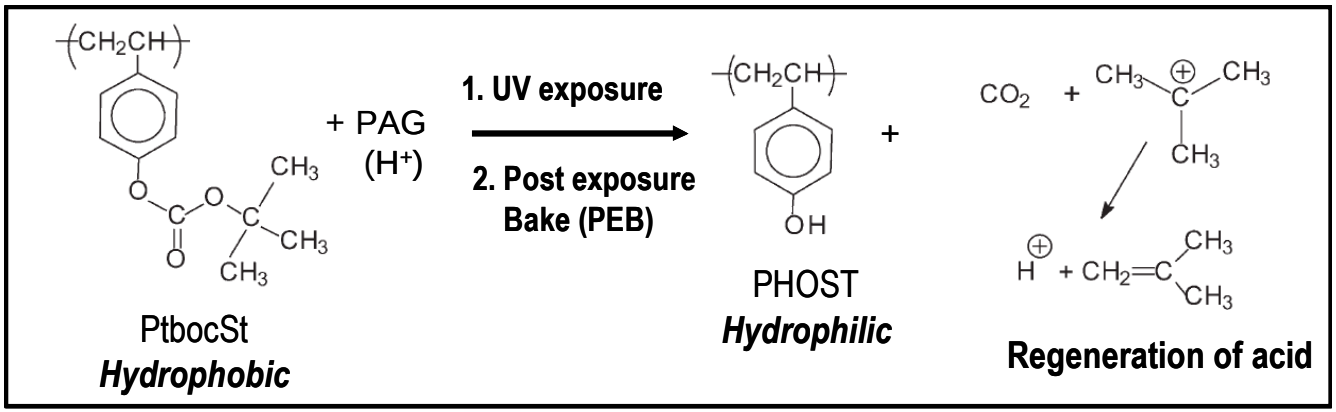
Domain level Replication:
Nanoscopic structures

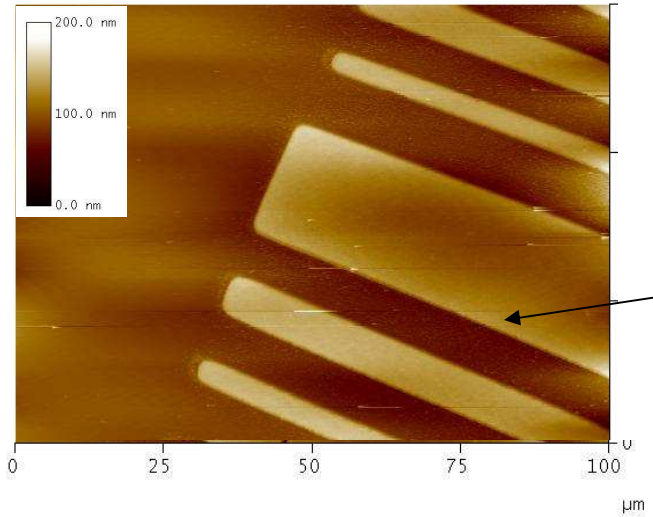




- OM Images lack sharp boundaries – Possibility of PAG diffusion to unexposed area.

Patterned Mesoporous Silica Films from PtbocStyrene Films: Crude Contact Mask



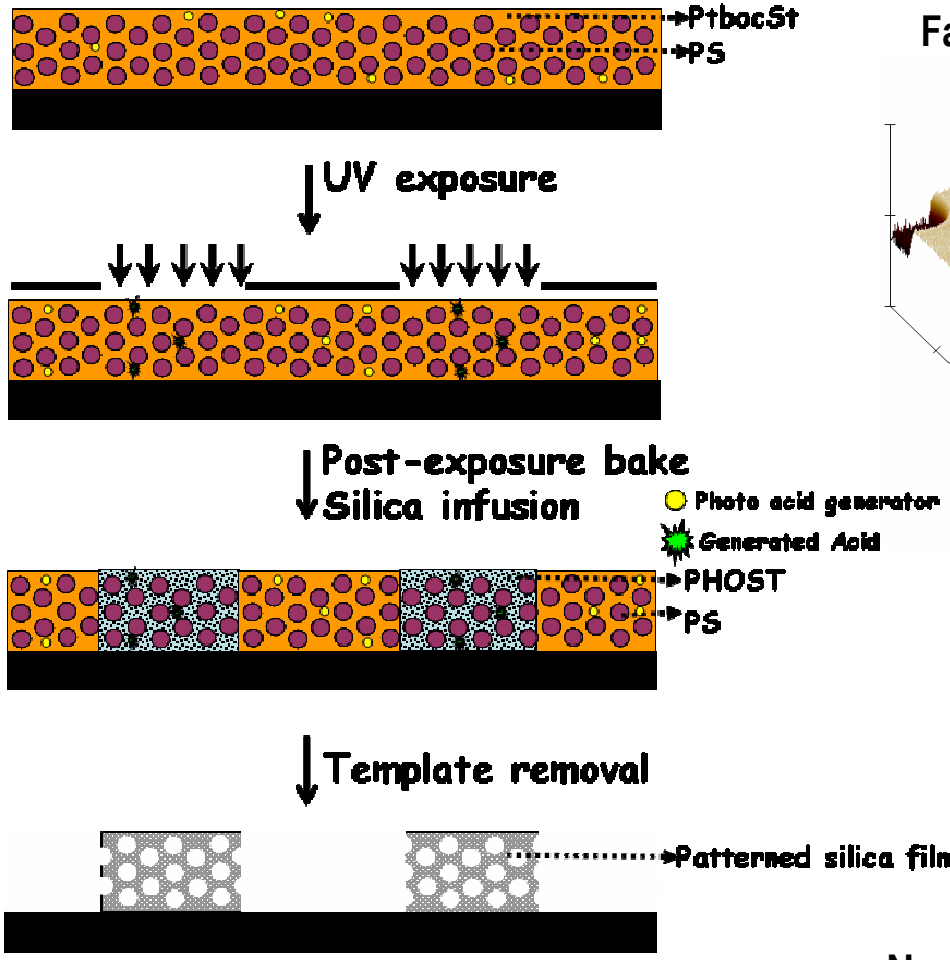


directly patterned silica film

- Good pattern replication with sharp boundaries.
- Device level features down to few microns in size
- Resolution determined by lithography, not materials

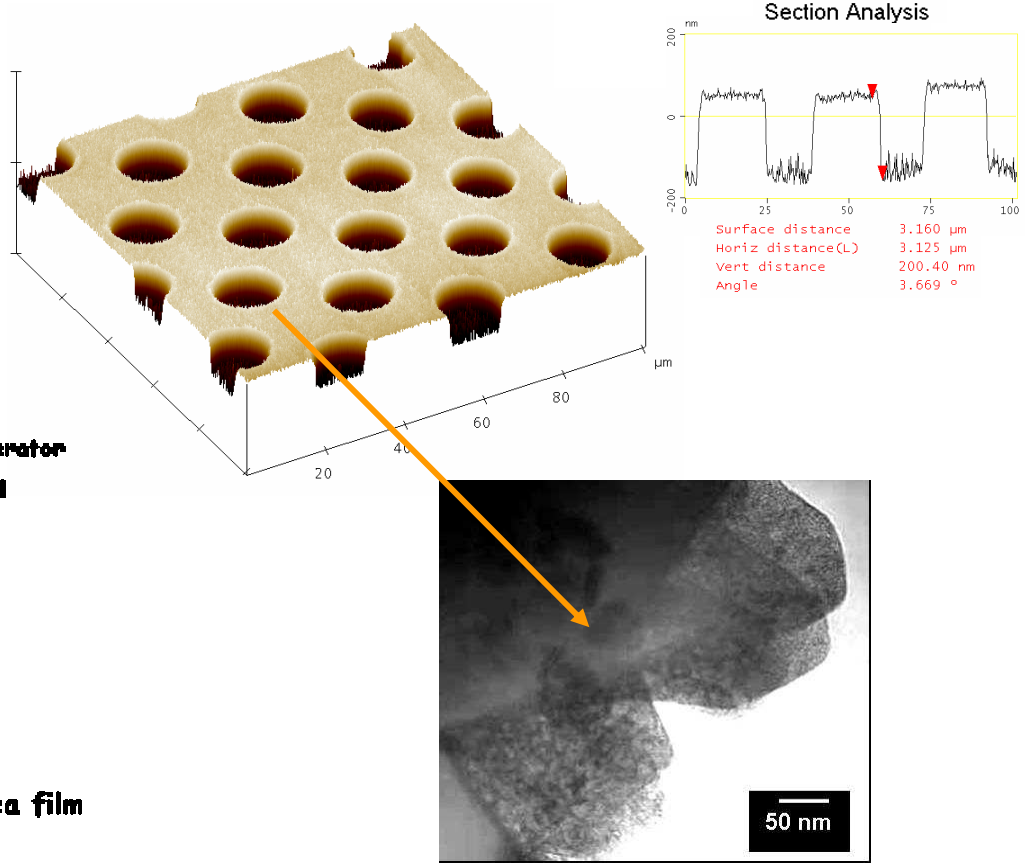
Micro-patterned Mesoporous silica films from PS-b-PtbocSt films

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



Feasibility Test – Crude Contact Mask

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



Next: Litho by 248 stepper at partner company

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Well-Ordered ULK Films via SCF Processing: Conclusions

Use of POSS additives substantially improves mechanicals

-Same approach is applicable to zeolites

Direct Patterning Shows Promise

feasibility using contacts masks demonstrated

first target: fat lines

process compression offers cost and ESH benefits

Recent acquisition of 200 mm tool will permit scale-up

Acknowledgments

Additional funding: UMass Center for Hierarchical Manufacturing and NSF NIRT

BOC Edwards 200 mm Tool Donation

ESH Metrics

- Comparison to
  - Current subtractive processing with resist application, development, and pattern transfer
  - Spin-on photoresist for lithography

Goals/ Possibilities	Usage Reduction			Emission Reduction			
	Energy	Water	Chemicals	PFCx	VOCs	HAPs	Other Hazardous Wastes
Selective deposition of dielectric layers by photoinitiated Chemical Vapor Deposition	>90% reduction	NA	> 90% reduction	Potentially higher emissions for CVD due to chamber cleans	>90% reduction	NA	Spin-on resists requires solids waste disposal

Thrust D-425.013

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

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

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

Project Background & Objectives

- This project aims to develop novel PFOS-free PAGs that meet the stringent performance demands required by semiconductor manufacturing and do not pose a risk to public health or the environment.
- Work on the development of the novel non-PFOS/non-PFAS PAGS is conducted at Cornell University (Ober group).
- Environmental studies of these new materials in progress at the University of Arizona (Sierra group).
- Studies of new PAGs and research to evaluate the inhibitory potential of the new chemistries are presented here.

ESH Benefits

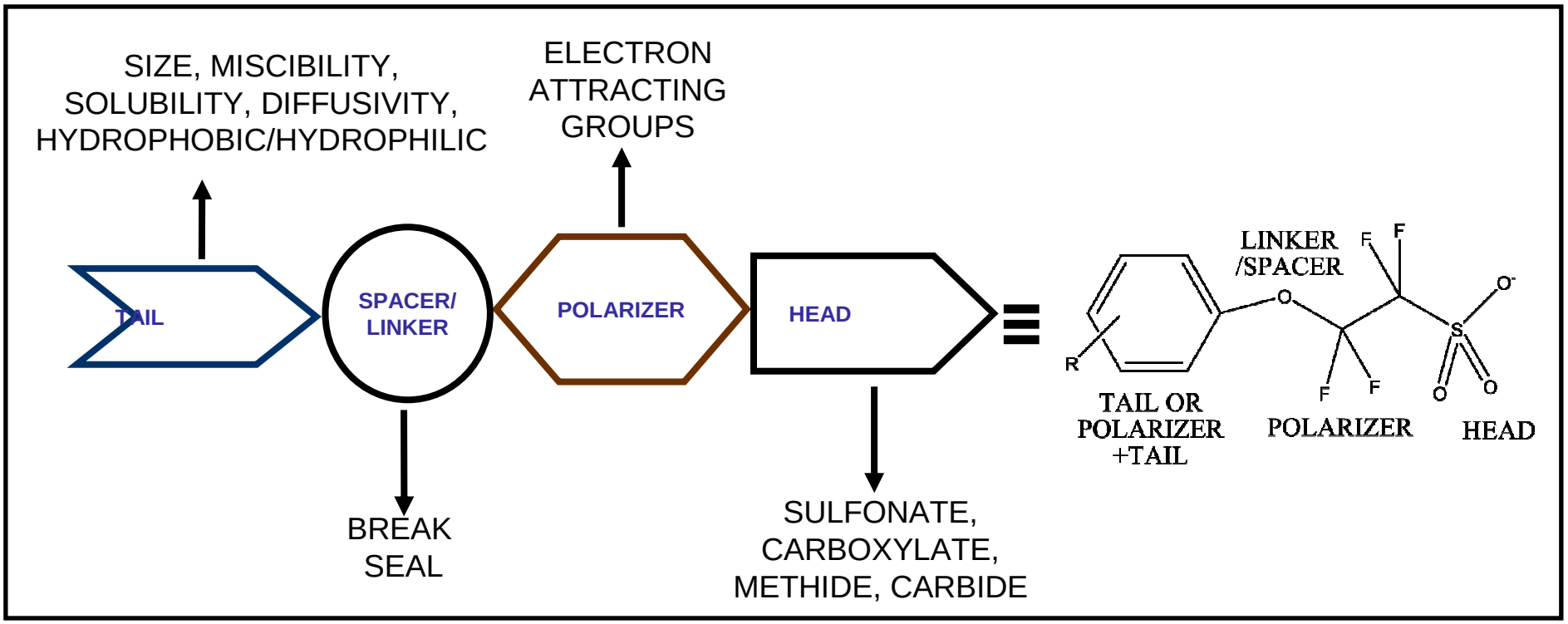
- These studies will be of critical importance in assessing synthetic strategies for environmental acceptability and will be used to guide the design of new PFOS-free photoacid generators.

Requirements for EUV Resists

- **Resolution : 32 nm node and beyond**
- **DOF: ≥ 0.2um**
- **Line Width Roughness (LWR) (3σ) : < 1.5 nm**
- **Sensitivity: 2- 5 mJ/cm^2**
- **Absorption (μm^{-1}) : Low**
- **Outgassing: < 10^{11} molecules/cm^2 at E_{size}**

Cao, Heidi, et al., Proceeding SPIE 2003, 5039, 484

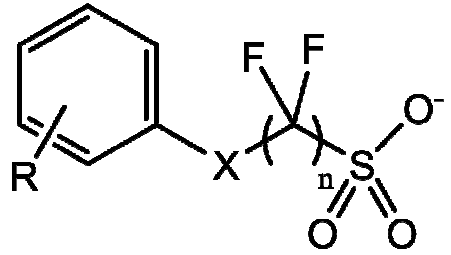
Non-PFOS PAG Anion Design Strategy



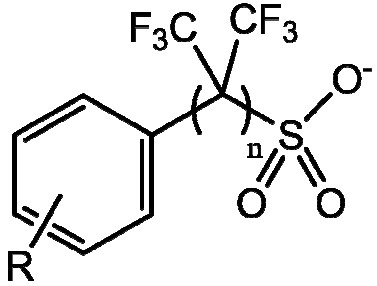
- **Non-PFOS PAG anion features**
  - **Lithography : pKa, size, functional group, element composition**
  - **ESH : ≤ CF_2, log $P_{oil/water}$, Bioconcentration Factor (BCF)**

Non-PFOS PAG Anions For EUV

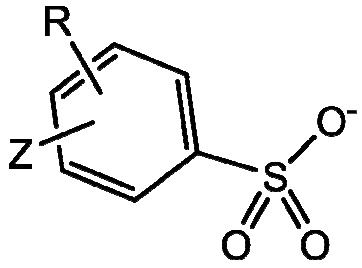
- **Acid strength**
  - **Few fluorine atoms**
  - **Non-fluorinated electron attracting group**



- **Transparency/radiation effect**
  - **Phenyl group/Reduced fluorine**

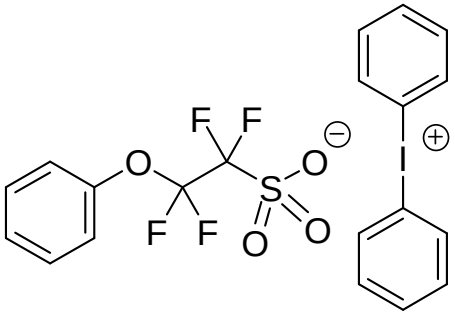


- **PAG or Photoacid miscibility**
  - **Phenyl group/Functional group**

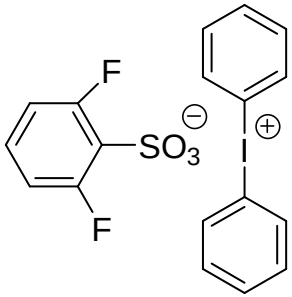


- **Size/volatility/solubility**
  - **Variation of R group**

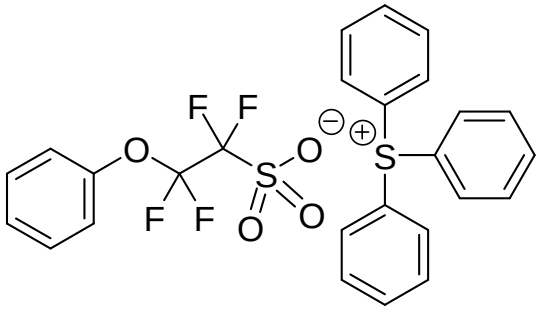
Non-PFOS PAGs



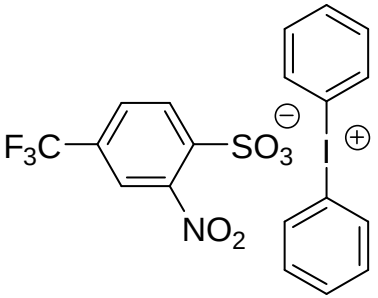
PF1



SF1

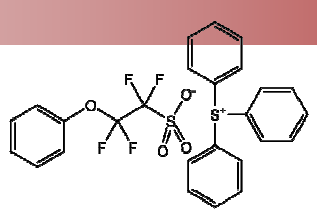


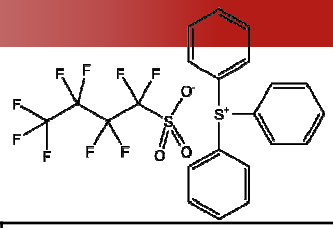
PF2



SF2

Comparison of Properties of Non-PFOS PAGs vs PFBS PAG

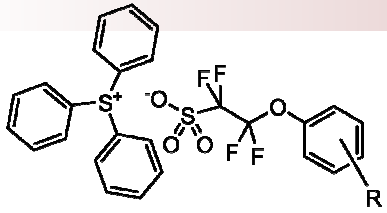




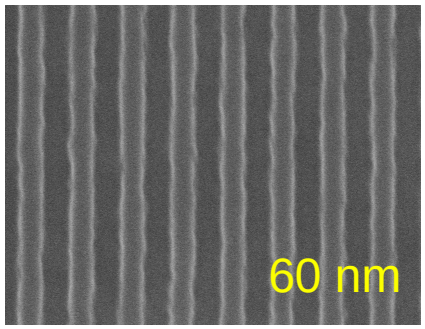
PAG Structure	$C_6H_5OCF_2CF_2\text{-}SO_3^-\ ^+S(C_6H_5)_3$	$CF_3\text{-}CF_2\text{-}CF_2CF_2\text{-}SO_3^-\ ^+S(C_6H_5)_3$
Molecular Weight	537	562
Purity	NMR, DSC, Elemental analysis	99 %
Decomposition [Td] (°C), DSC	305	398
Melting Point [Tm] (°C), DSC	93 , White solid	84 - 88, White solid
Solubility	GBL, PGME, EL, DPM, PGMEA	GBL, PGME, EL, DPM, PGMEA
Solubility in Poly(4-hydroxy styrene), ESCAP, Methacrylate/PGMEA	10 wt %	10 wt %
*Molar volume of photoacid (± 3 cm^3)	170	162
*Acid Strength pKa (Taft)	-4.86	-4.99
*Partition coefficient ($P_{oil/water}$)	2.3298	2.4113
*Bioconcentration Factor (BCF)	3.162	3.162

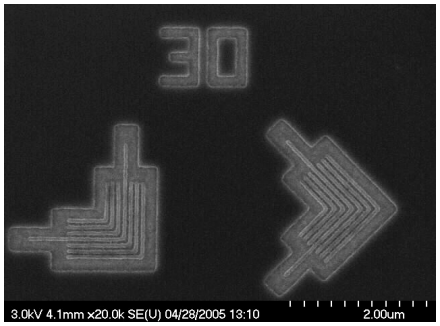
*Estimated Properties

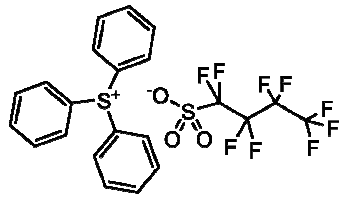
Molecular Glass Resist: Comparison of Non-PFOS PAG Performance with PFBS PAG at EUV



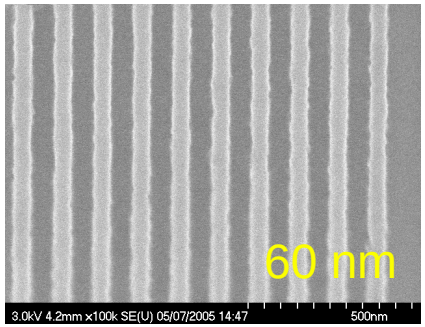
E_s = 21.0 mJ/cm^2
R = 25 - 30 nm
LER (60 nm) = 5.0 nm

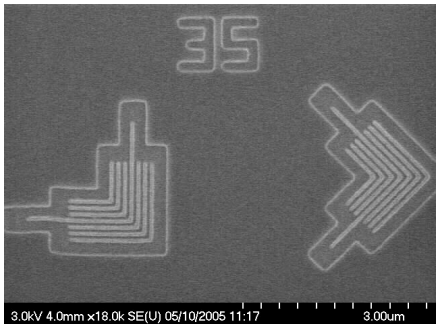


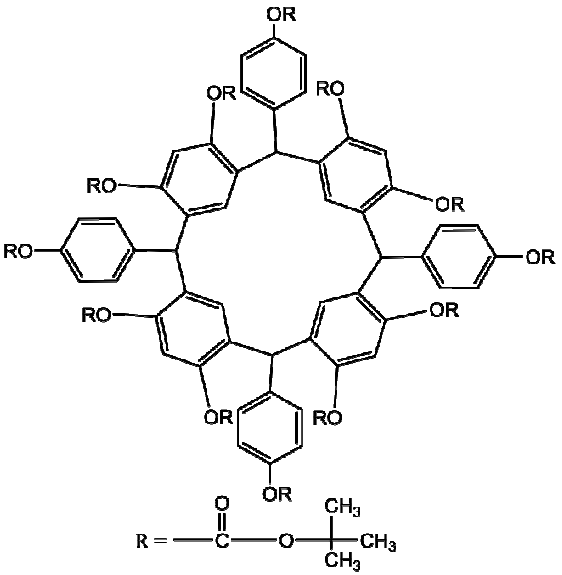




E_s = 39.0 mJ/cm^2
R = 30 - 35 nm
LER (60 nm) = 4.3 nm





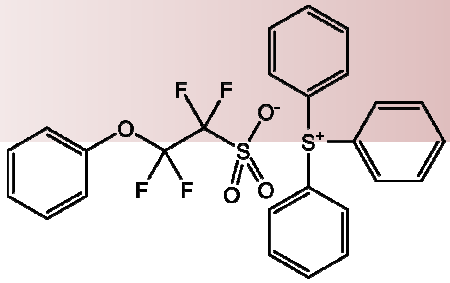


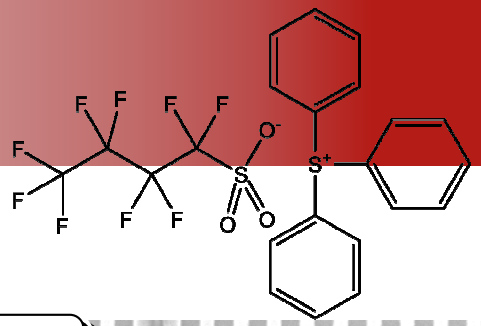
Molecular Glass Resist

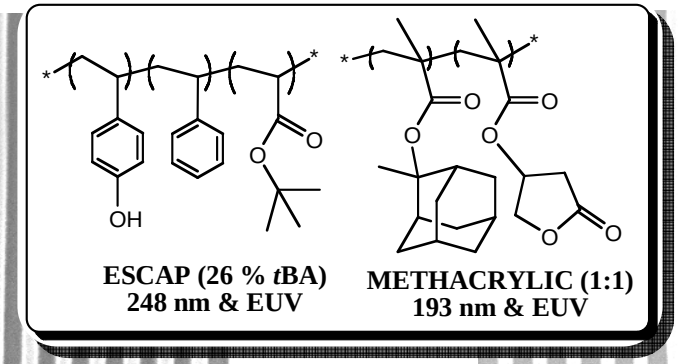
"Better sensitivity, resolution and acceptable LER for PFBS free resist"

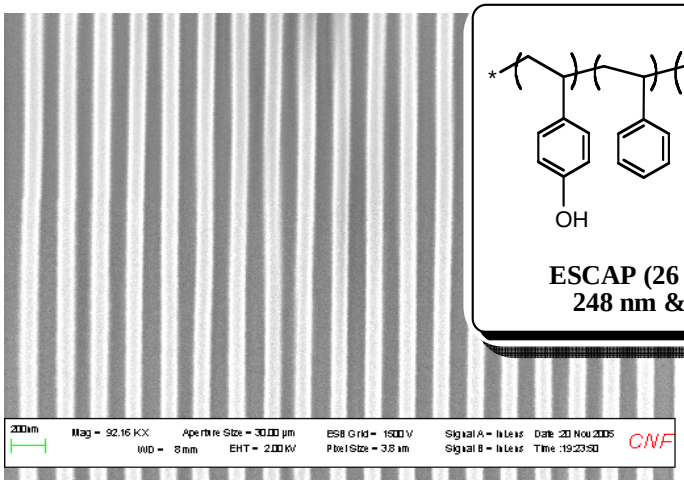
Formulation: MG = 5 wt %; PAG = mole % (5 wt % wrt polymer); Thickness = 90 nm; TOA = 0.12 %; PAB = 100 °C/120 s; PEB = 80 °C/30 s; 0.026M TMAH/ 10 s. HMDS substrate for Non-PFOS PAG and BARC for PFBS PAG

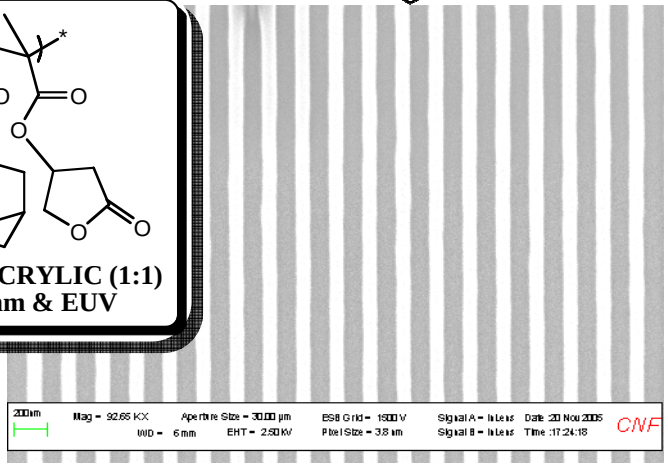
E-beam Lithography: Non-PFOS PAG vs. PFBS PAG









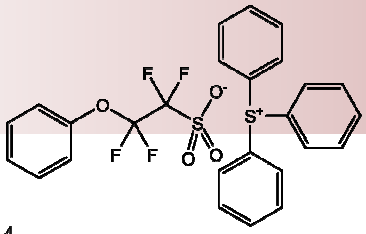


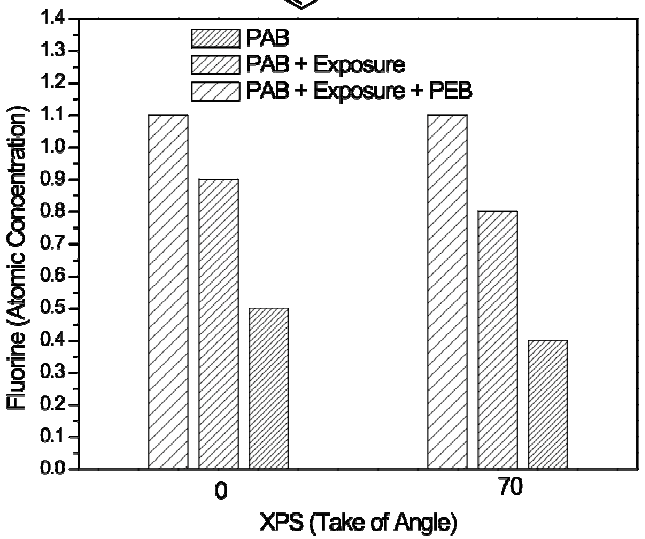
E_s = 28 µC/cm²
LER = 5.3 ± 0.6
R = 70 nm (2:1,1:1,1:2 lines)

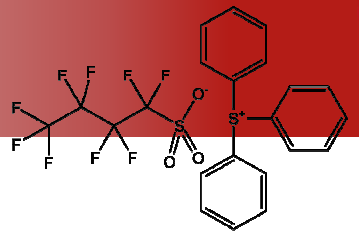
E_s = 24 µC/cm²
LER = 4.9 ± 1.1
R = 60 nm (2:1,1:1,1:2 lines)

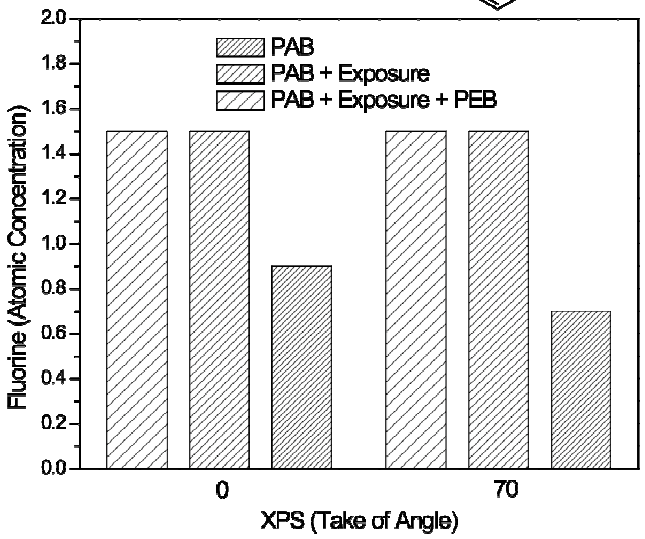
Formulation: Poly (GBL-*co*-MAdMA) = 6 %; PAG = 1.633 * 10^{-5} mole (~ 5 wrt to polymer); Solvent = PGMEA/2-butanone; TOA – 0.06 %; Film = 3000 rpm ; PAB = 115 °C/60 s; Dose = 12 µC/cm² to 40 µC/cm² (Step Size 4 µC/cm²); PEB = 120 °C/60 s; Development = 0.26 N TMAH

PAG Miscibility in Methacrylate Resist by XPS





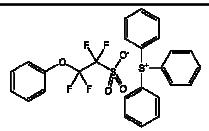
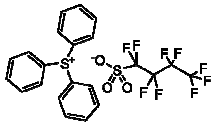




- **XPS TOA 70°(surface ~ 1- 3 nm) and 0°(~ 3- 7 nm)**
- **Depth dependent variation in fluorine concentration is negligible**
- **Concentration of PAG used in XPS studies are higher**
- **Comparable lithographic performance at EUV and e-beam /PAG miscibility**

Poly (GBL-*co*-MAdMA) = 6 wt %; PAG = same molar concentration **(~ 10 wt % wrt to polymer**); Solvent = PGMEA; Film Thickness = 150 ± 10 nm; PAB = 115 °C/60 s; Exposure = 90 mJ/cm^2; PEB = 115 °C/60 s

Comparison of Non-PFOS Vs PFBS PAGs Performance at EUV and E-beam

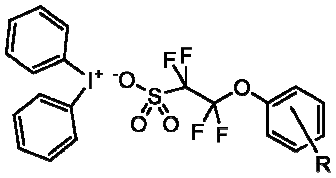
PAG Structure	EUV @ ALS MET				E-Beam (100 kV) @ CNF			
	E_0 for 100 nm lines (mJ/cm^2)	E_s for 40nm lines (mJ/cm^2)	LER for 100 nm lines	R (nm) (1:1 elbow)	E_0 for 500 nm lines ($\mu C/cm^2$)	E_s for 100 nm lines and below ($\mu C/cm^2$)	LER for 100 nm lines	R (nm) (1:2, 1:1, 2:1)
	<4.9	7.5	7.7 ± 0.8	30	16	28	5.3 ± 0.6	70
	<6	8.6	8.0 ± 0.6	30	16	24	4.9 ± 1.1	60

Sensitivity, resolution and LER are comparable at e-beam and EUV

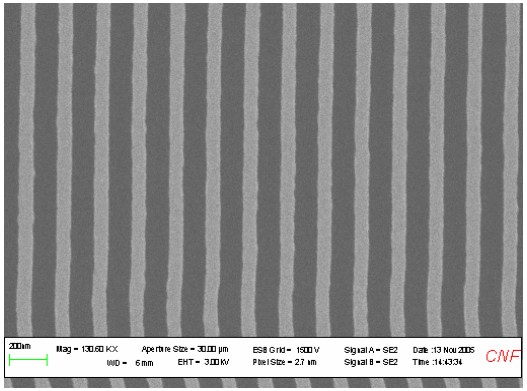
Formulation: Poly (GBL-*co*-MAdMA) = 6 %; PAG = 1.633 * 10^{-5} mol % (~ 5 wrt to polymer); Solvent = PGMEA/2-butanone; TOA – 0.06 %; Film = 3000 rpm ; PAB = 115 °C/60 s; PEB = 120 °C/60 s; Development = 0.26 N TMAH

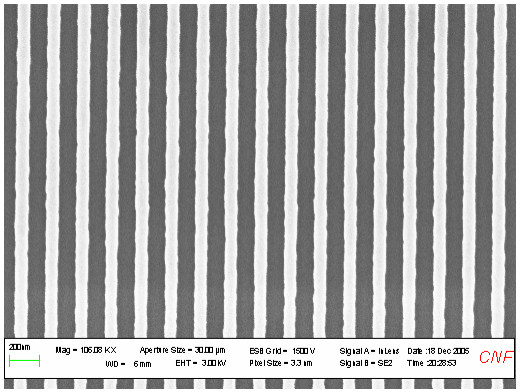
E-beam Lithography: Effect of Photoresist Matrix

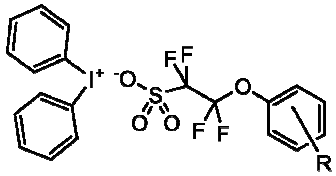
Poly (GBL-*co*-MAdMA) | **ESCAP**



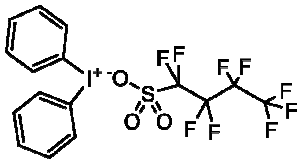
E_s = 24 μC/cm²
LER = 8.5 ±1.0
R = 60 nm (2:1,1:1,1:2)



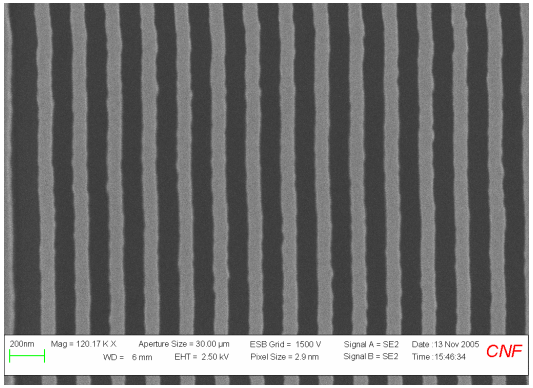


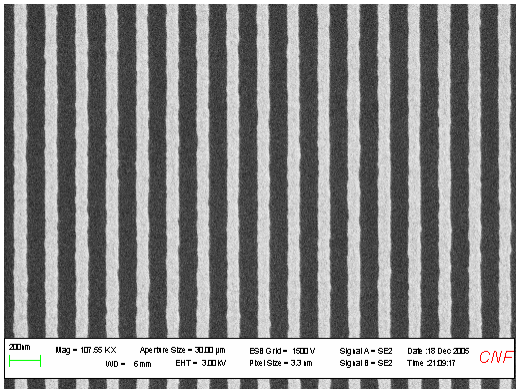


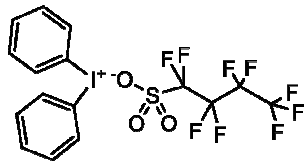
E_s = 12 μC/cm²
LER = 6.3 ± 0.7 nm
R = 80 nm (2:1,1:1,1:2)



E_s = 16 μC/cm²
LER = 9.3 ± 1.1
R = 70 nm (2:1,1:1,1:2)







E_s = 18 μC/cm²
LER = 7.1 ± 0.7 nm
R = 100 nm (2:1,1:1,1:2)

- **Sensitivity and LER improvement for non-PFOS PAG in ESCAP resist – PAG miscibility**
- **Non-PFOS PAG and PFBS PAG performance are comparable in different resist**

Material and Methods

- The inhibitory potential of three non-PFOS PAGs (SF1, SF2 and PF1) and their counter ions, **diphenyl iodonium (DPI)** and **triphenyl sulfonium (TPS**), was evaluated using three different bioassays:
  - Mitochondrial Toxicity Test (MTT);
  - Microtox® (a widely-used, commercial assay utilizing a marine bacterium that emits fluorescence), and
  - Methanogenic inhibition test.

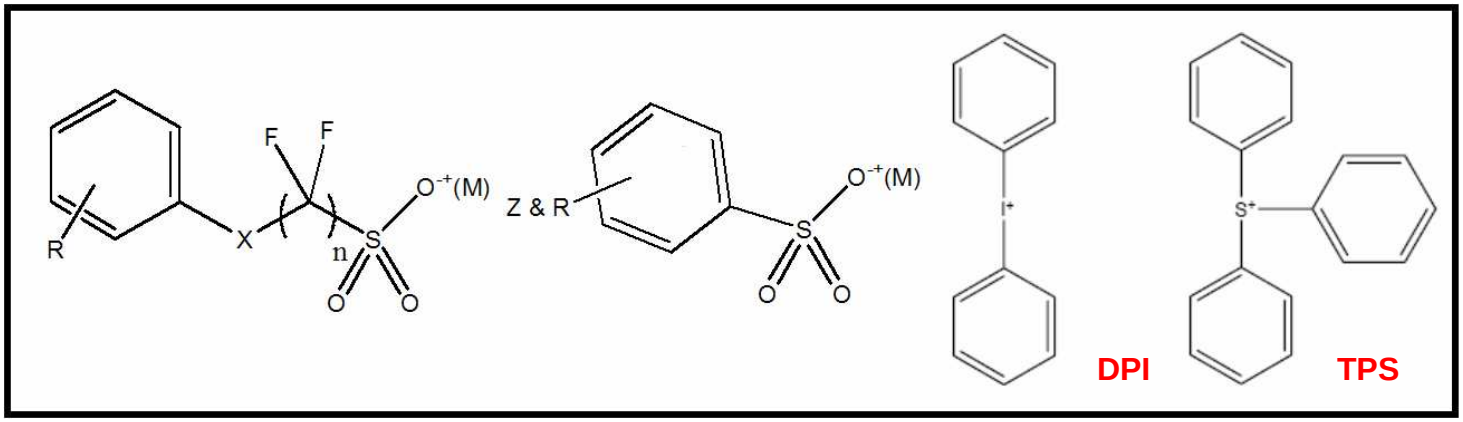


Fig. 1- Non-PFOS PAGs that will be synthesized and studied. Counter ions studied.

Results: MTT Assay

- The PAG counter ions, DPI and TPS, showed the highest toxic effects in the MTT assay (Fig. 2). PF1 was the only PAG displaying toxicity in this bioassay.

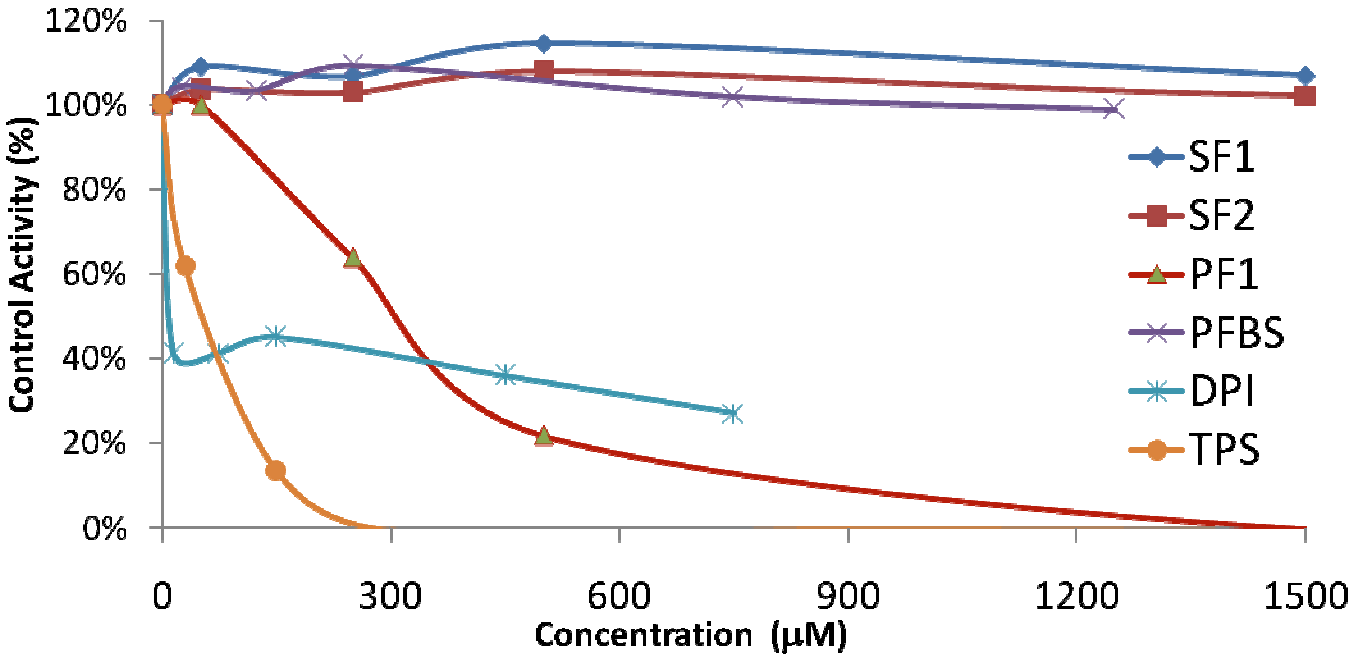


Fig. 2- Inhibitory effect of the new non-PFOS PAGs and the PAG counter ions in the MTT bioassay.

Results: Microtox Assay

- In agreement with the findings of the MTT assay, the PAG counter ions were also the most inhibitory compounds in the Microtox assay. PF1 also displayed microbial inhibition, albeit at relatively high concentrations (50% inhibitory concn. (IC_{50})= 1.6-2.2 mM).

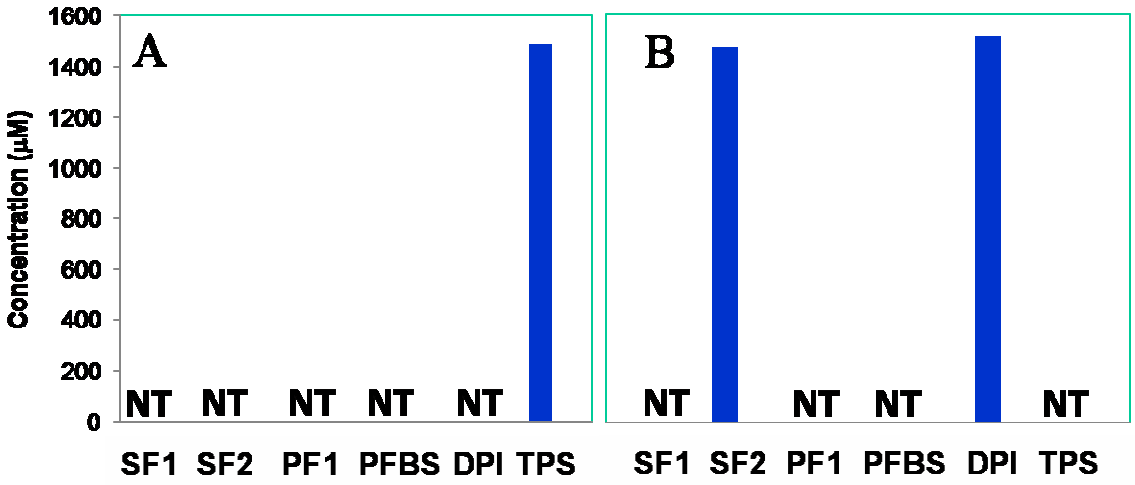
Inhibitory effect of the new PAGs and their counter ions in the Microtox bioassay. IC50 and IC80 are the concentrations of the compounds causing 50 and 80% inhibition in the assay.

	IC50 (µM)			IC80 (µM)		
Compound	**5 min**	**15 min**	**30 min**	**5 min**	**15 min**	**30 min**
SF1	NT*	NT	NT	NT	NT	NT
SF2	NT	NT	NT	NT	NT	NT
PF1	2,195	1,705	1,614	9,698	5,467	4,371
PFBS	NT	NT	NT	NT	NT	NT
DPI	40	10	5	179	48	22
TPS	40	29	38	145	78	76

*NT= Not toxic at the highest concn. tested for SF1, SF2 and PFBS (11,250 µM).

Results: Methanogenic Inhibition

- The counter ions displayed inhibition towards H_2 and acetate-utilizing methanogens. In contrast, the PAGs were generally not toxic. SF2 was an exception, with an IC50 value of 1,470 µM. Methanogens constitute an important microbial population in anaerobic sludge digestors. Severe methanogenic inhibition can result in process failure.



Inhibitory effect (IC50) of the new PAGs and counter ions in (**A**) autotrophic methanogens and (**B**) acetoclastic methanogens in anaerobic sludge. *NT= Not toxic at the highest concn. tested (in µM): SF1 (2,560); SF2 (1,850), PF1 (1,830), PFBS (1,670).

Conclusions

- The counter ions, diphenyl iodonium (DPI) and triphenyl sulfonium (TPS), showed the highest toxic effects in all three tests.
- The new PAGs, SF1 and SF2, were not inhibitory or only at very high concentrations.
- PF1 displayed inhibition in the MTT and Microtox assays but the IC50 levels were 1-2 orders of magnitude higher compared to those determined for the counter ions.

Future Work

- Complete ongoing studies of the toxicity of PAGs and counter ions under aerobic and nitrifying conditions.
- Investigate the susceptibility of the novel PAGs to biodegradation by microorganisms commonly found in wastewater treatment systems.
- Investigate the treatability of the most promising PAG(s) by conventional biological and/pr physio-chemical methods.

Industrial Collaboration / Technology Transfer

Industrial Collaboration:

Jim Jewett, Intel Corporation

Ralph Dammel, AZ-Microelectronic Materials, Inc.

George Barclay, Rohm and Haas Microelectronics

Disclosures and Patents:

A patent application has been filed on ionic non-PFOS/non-PFAS PAGs following the general design strategy described in the proposal.

Biochips and Micro-Arrays for Rapid Assessment of Chemical Toxicity

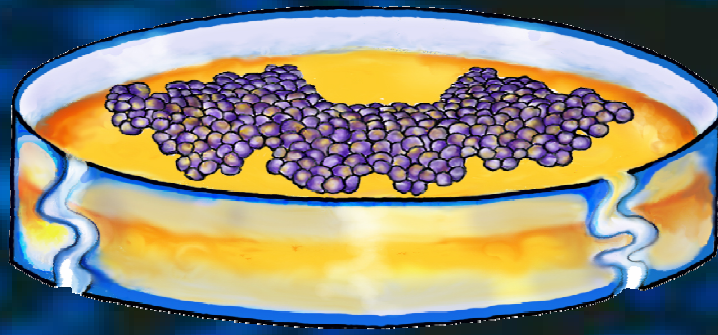
Sub Task C-4; SRC 425.012

by

David L. Mathine[1], Joseph J. Bahl[2], and Raymond B. Runyan[3]

[1]Optical Sciences, University of Arizona, Tuscon, AZ
[2]Sarver Heart Center, University of Arizona, Tucson, AZ
[3]Department of Anatomy and Cell Biology, University of Arizona, Tucson, AZ

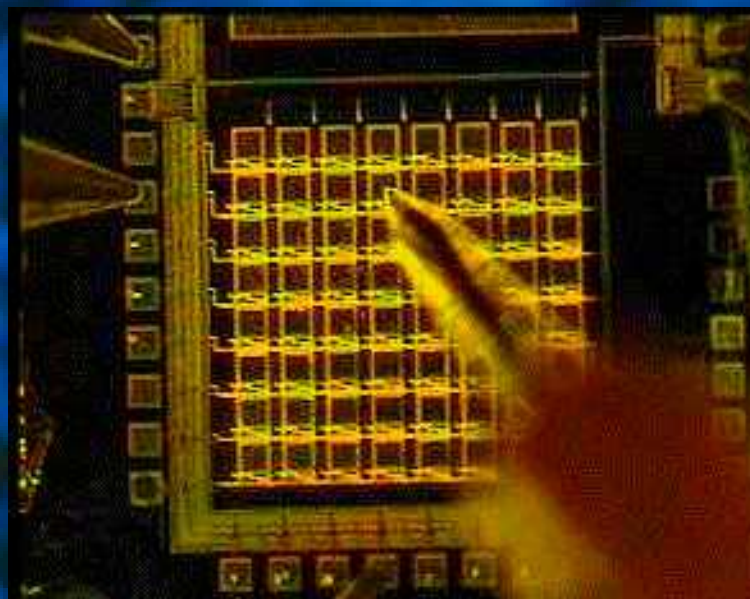
Rapid Assessment of Chemicals and Process Chemistries



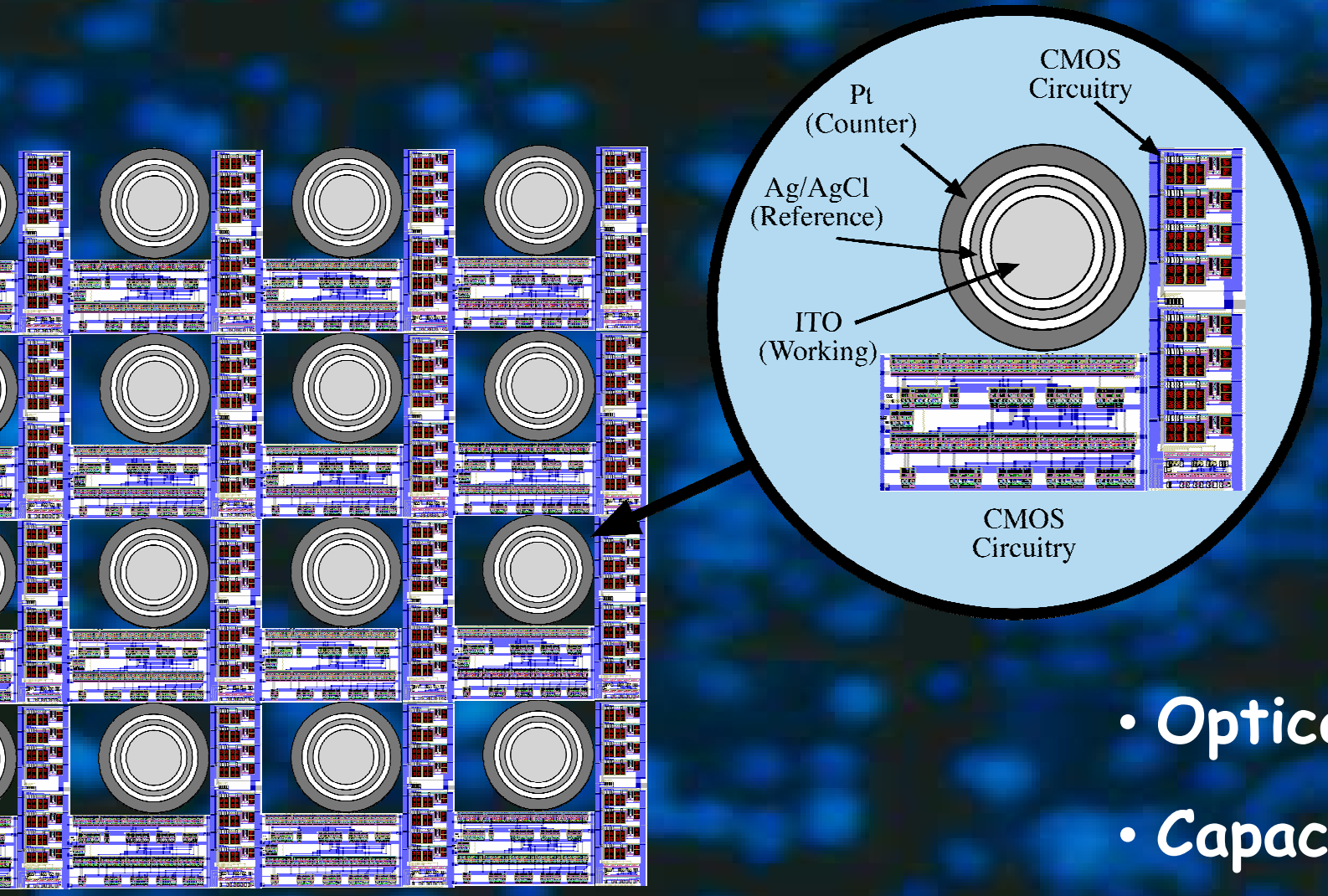
Rapid assessment of chemicals and process chemistries

Important for both chemical suppliers (starting materials) and equipment suppliers/end users (for process-generated by-products, interactions of multiple chemicals, proprietary chemistries in R/D stage, etc.)

A first step towards an on-line ESH monitor.



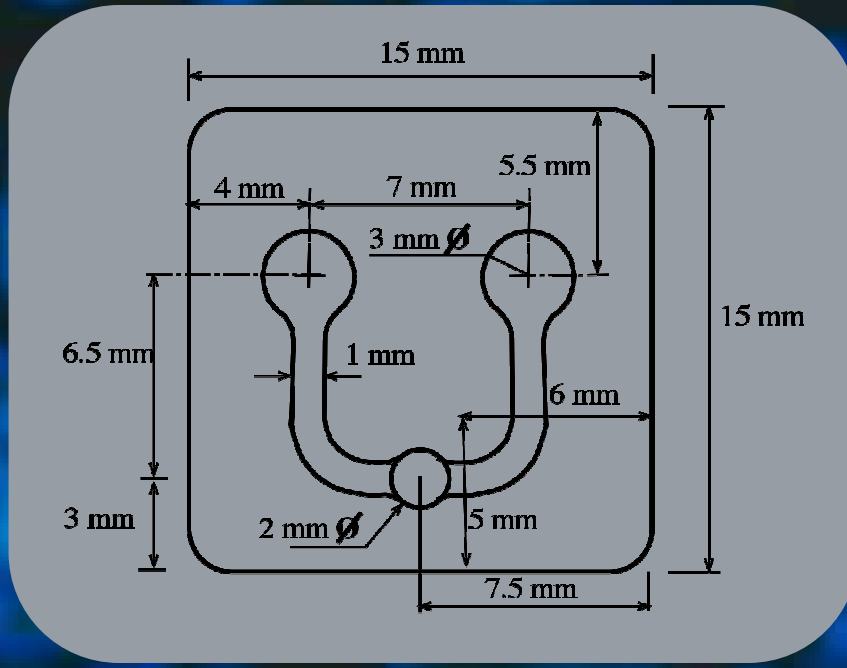
Biosensor Fusion



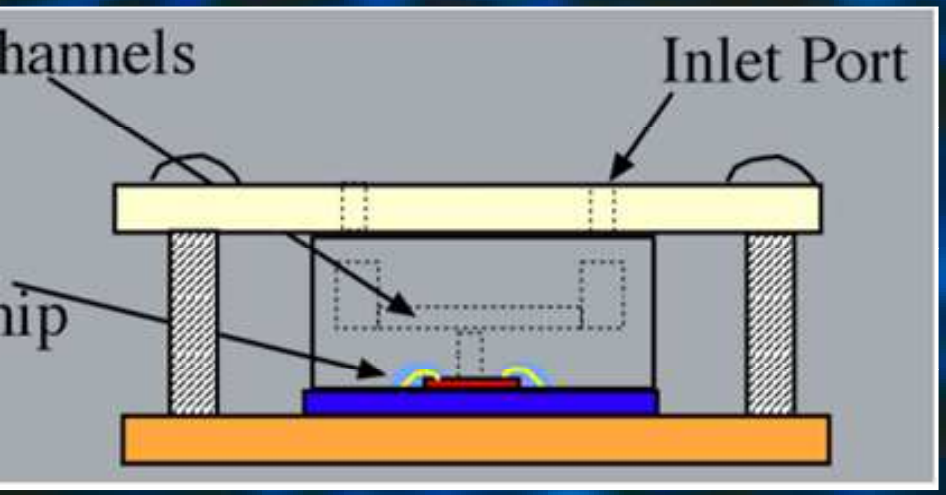
- Optical Sensors
- Capacitance Sensors
- Electrochemical Sensors
- Electrical Sensors

Biochamber Design

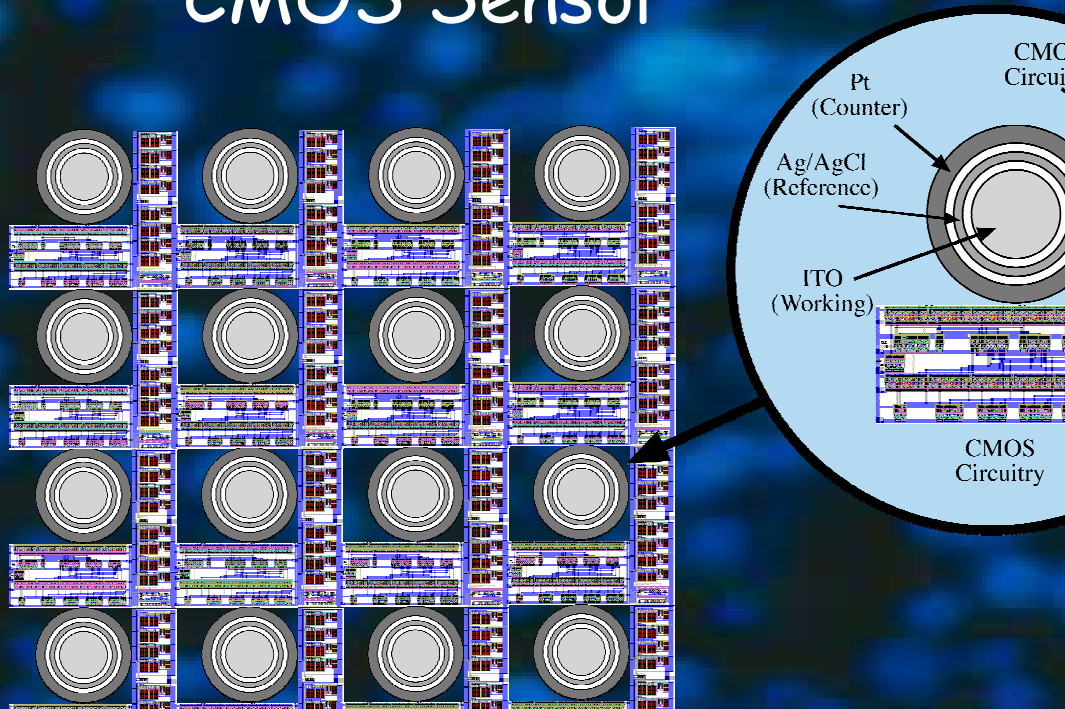
Biofluidics



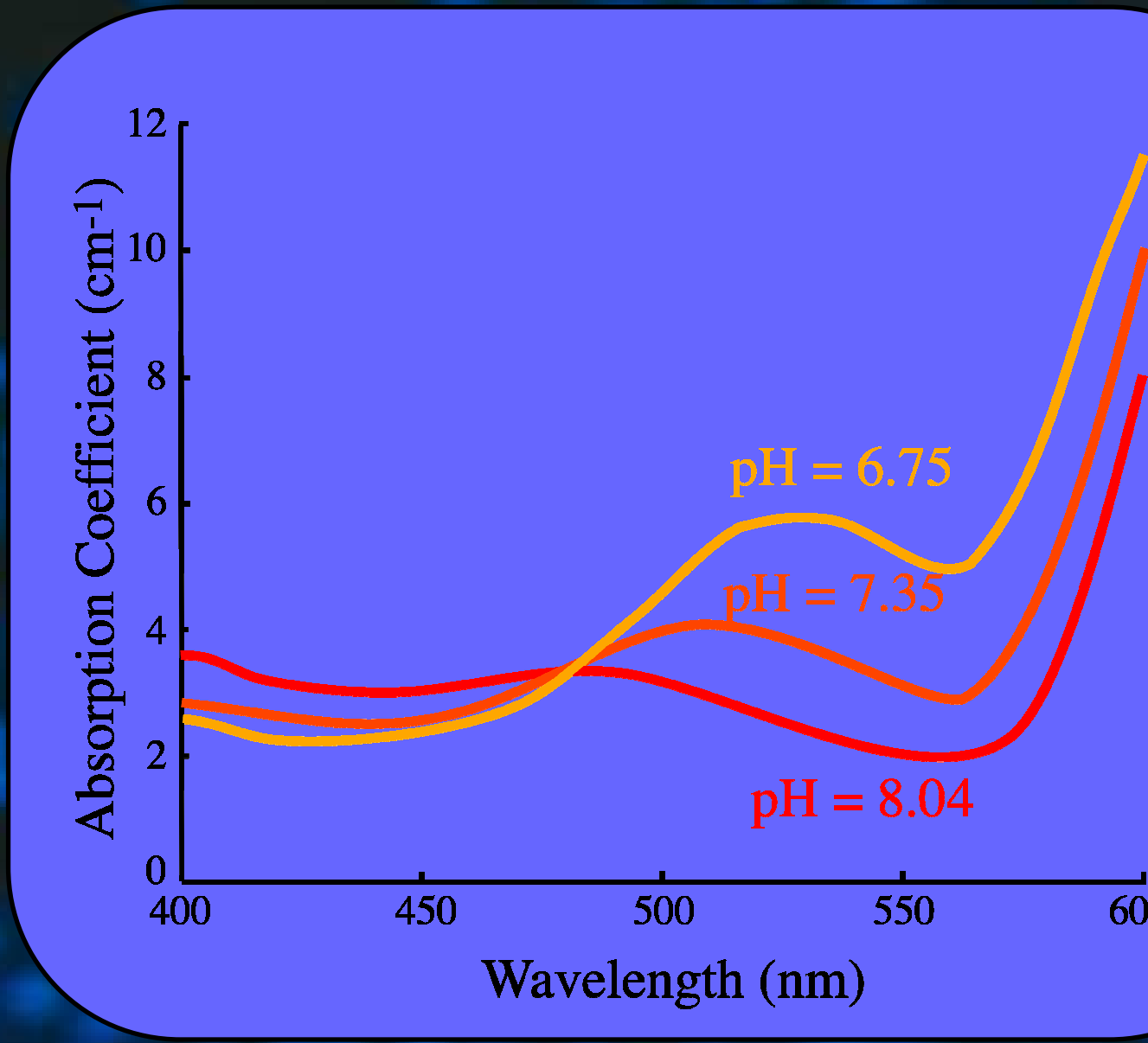
ironmental Chamber



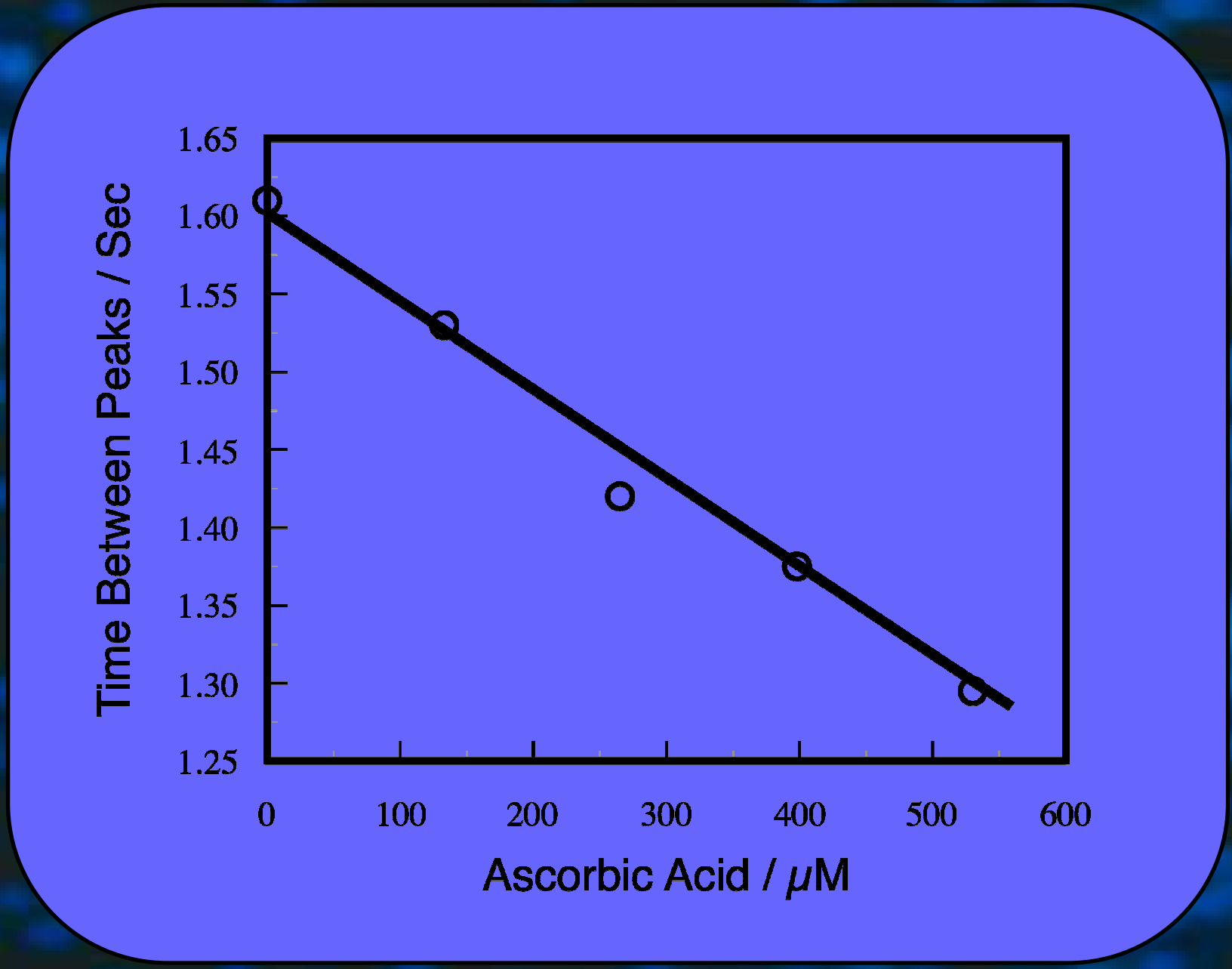
CMOS Sensor



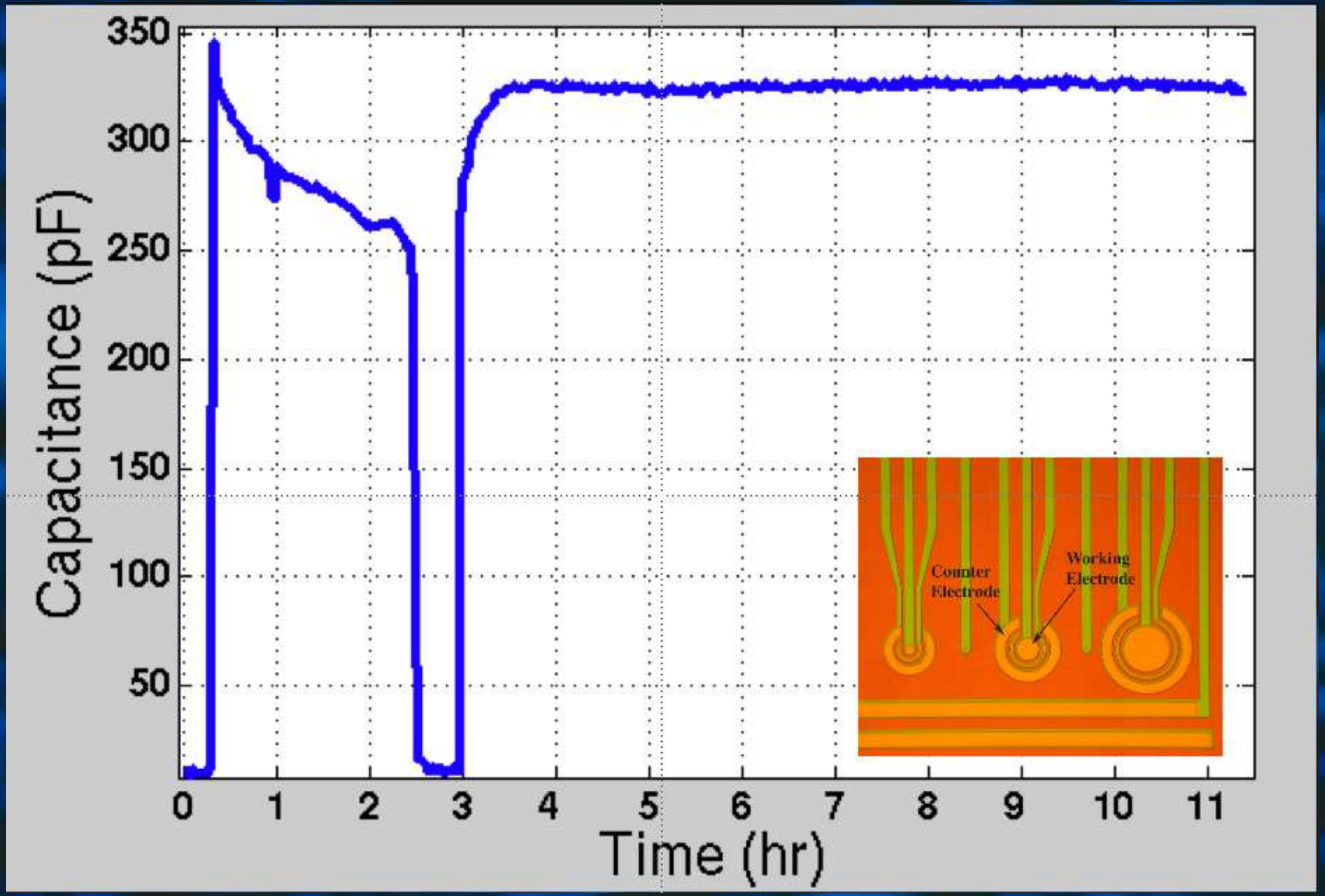
Optical Measurements



Chemical Measurements

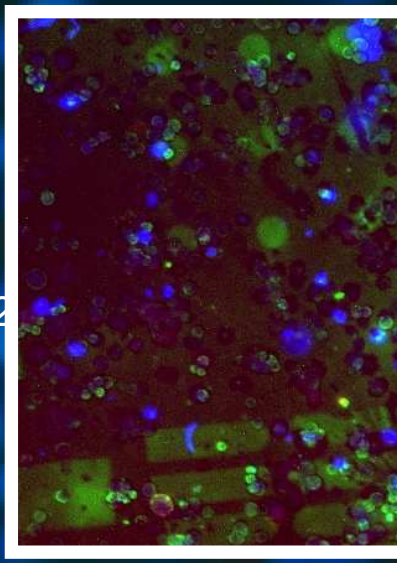


Electrical Measurements

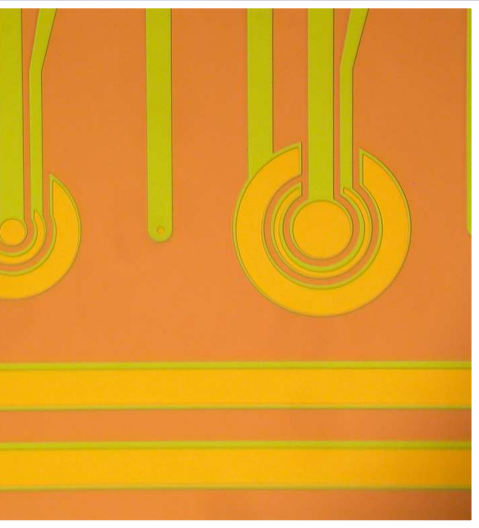


Cell Attachment

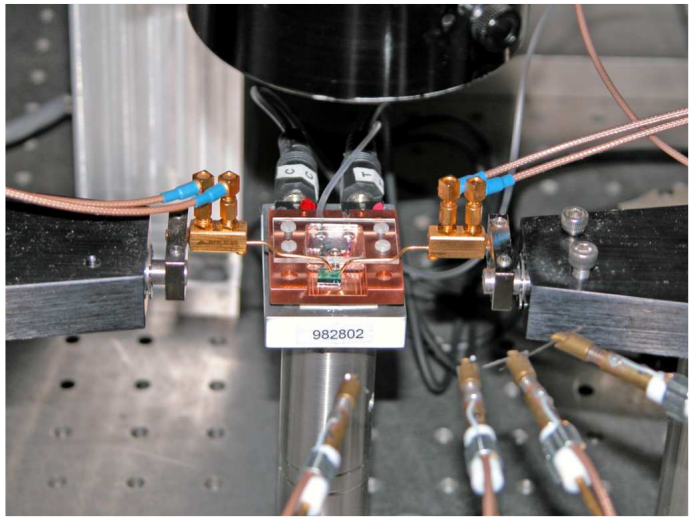
DU145 on
Poly-L-lysine
Patterned SiO_2



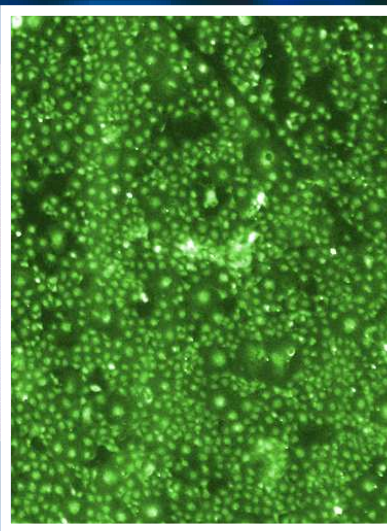
Electrodes



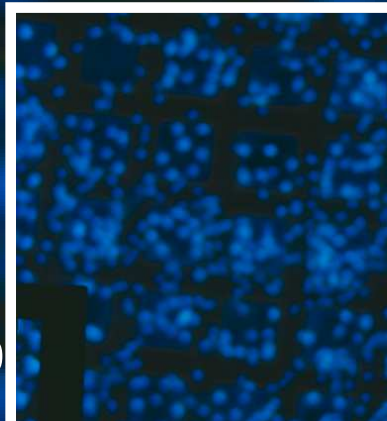
Biochamber



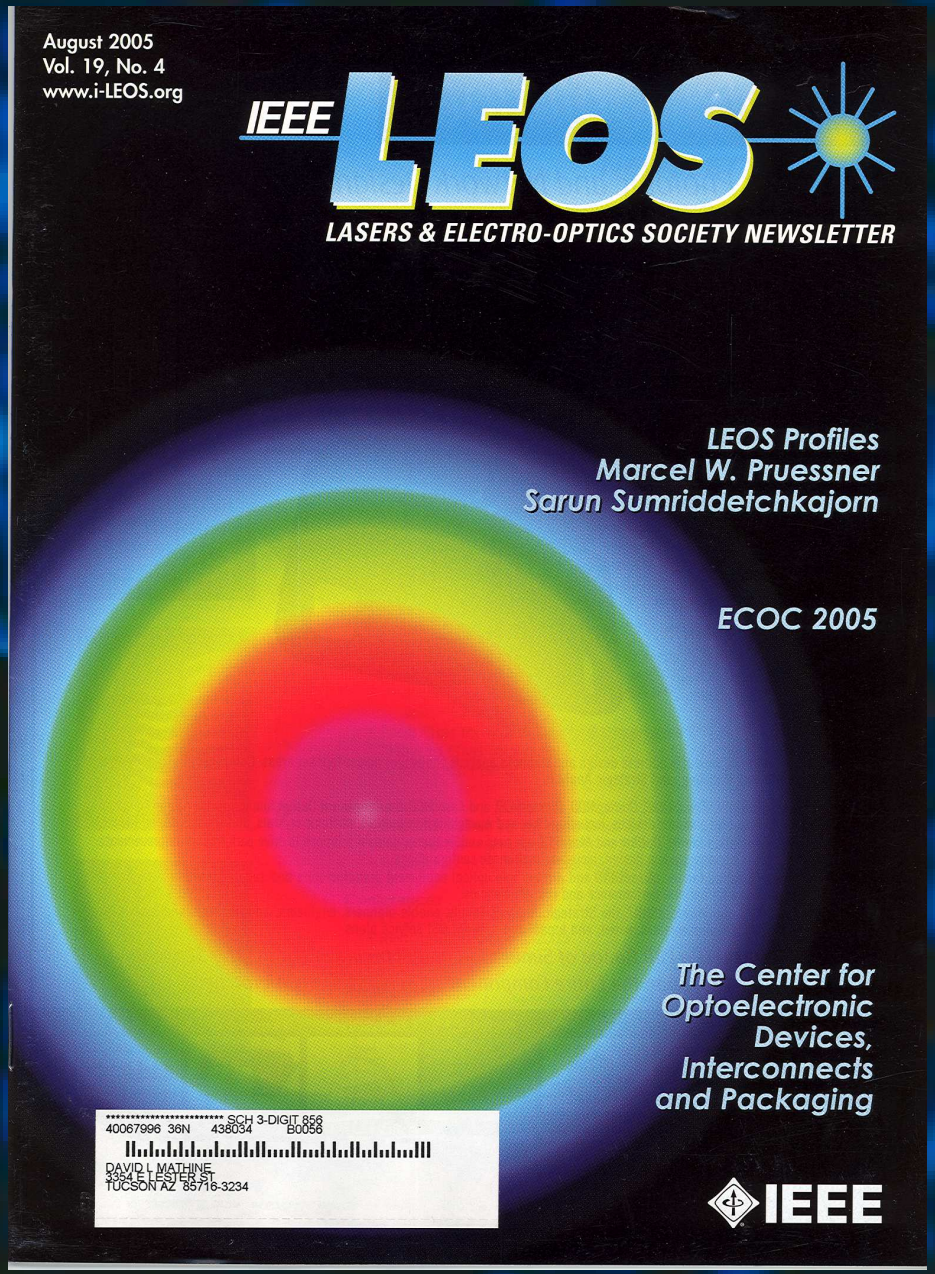
COS-7
on ITO Coated
Silicon

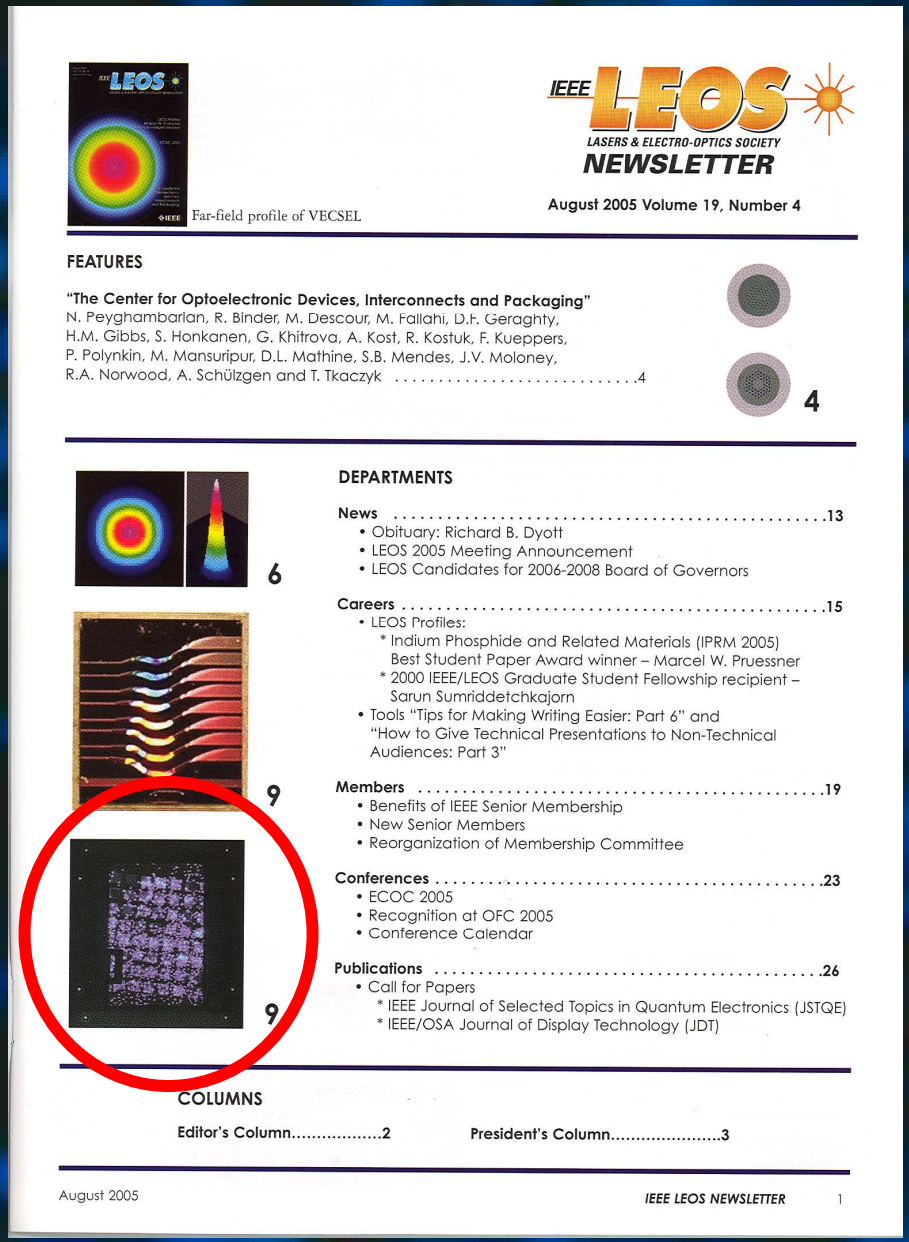


COS-7
on CMOS Chip



LEOS Newsletter





Far-field profile of VECSEL

IEEE LEOS
LASERS & ELECTRO-OPTICS SOCIETY
NEWSLETTER

August 2005 Volume 19, Number 4

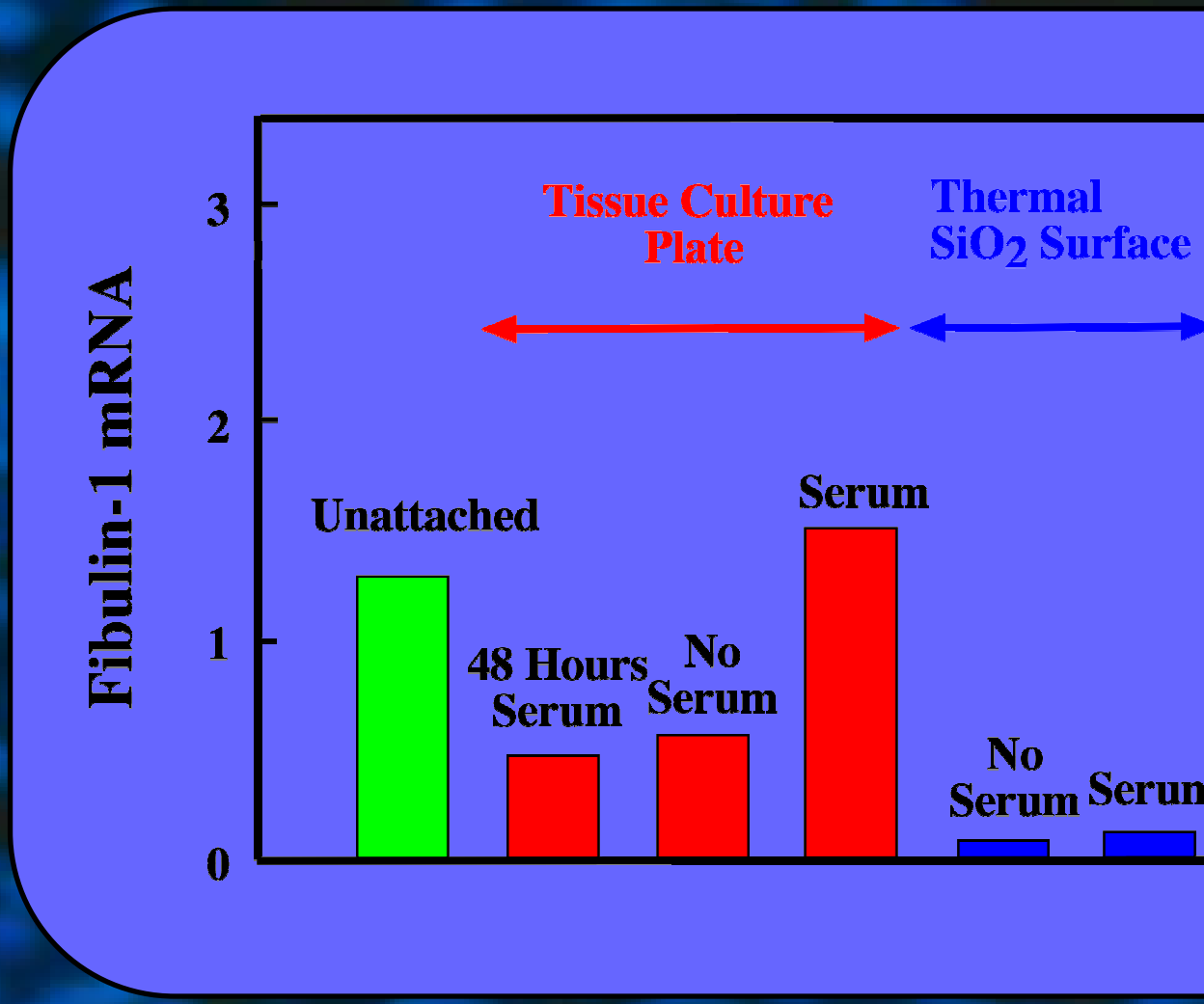
FEATURES

Fibulin-1 Expression

ibulin-1 is an
xtracellular matrix
roduced by COS-7 cells.

rovides a measure of
ne cellular response to
ne substrate.

iO_2 provides a smaller
timulus than tissue
ulture plate!

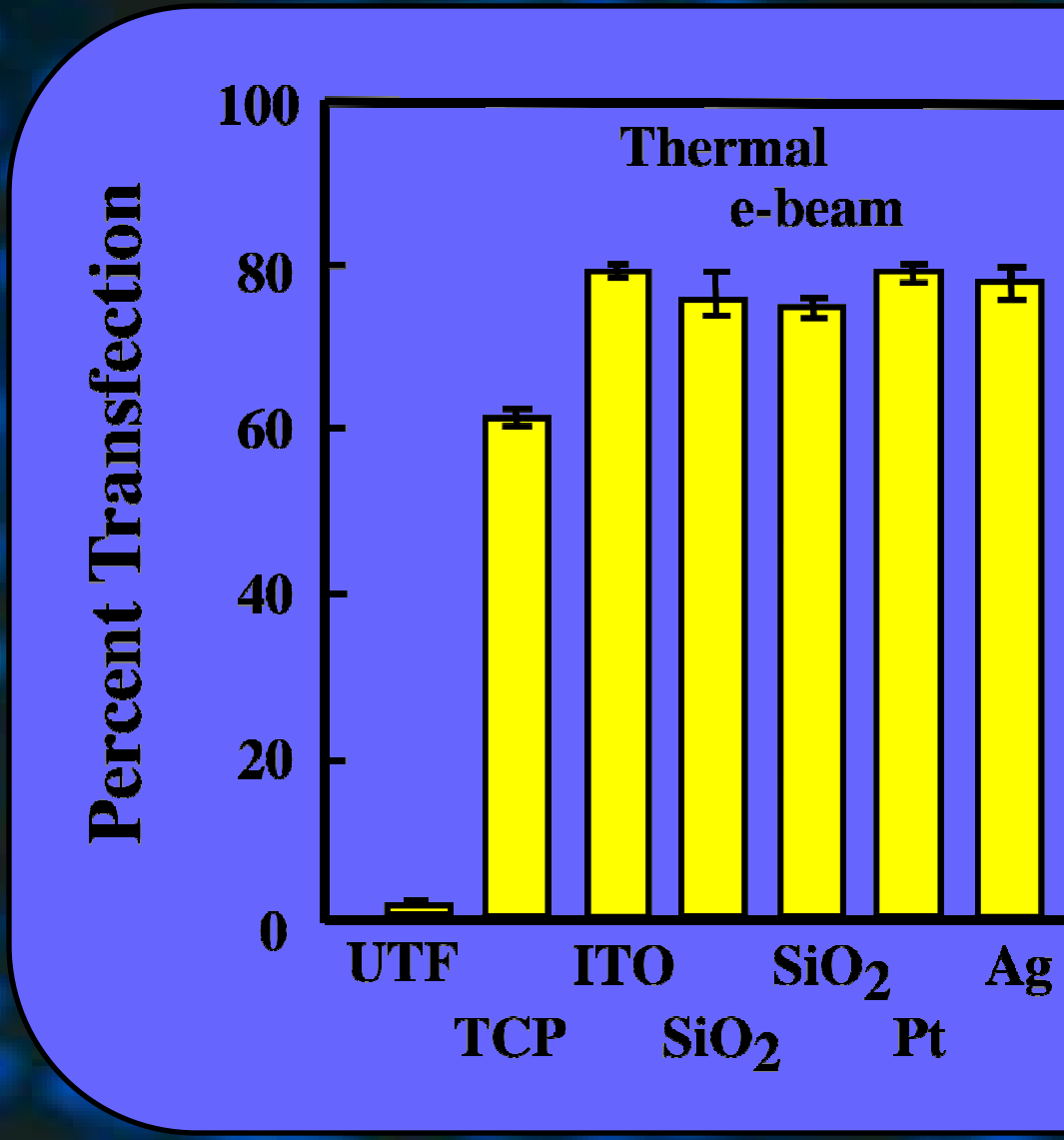


Percent Transfection

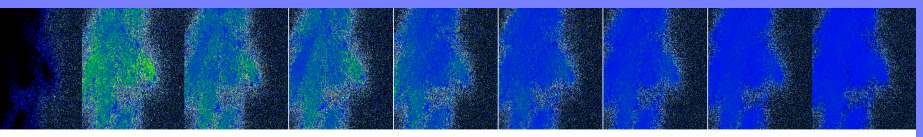
ransfection is the
ntroduction of DNA into
nimal cells.

hanges in gene
xpression can be readily
valuated.

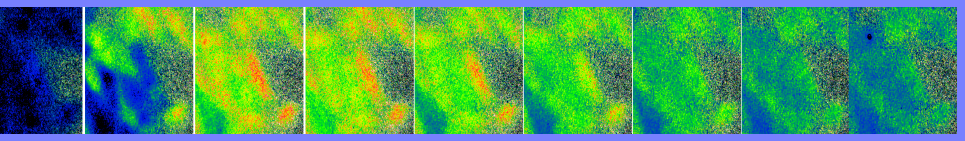
esigned for real time
onitoring with the
iochip.



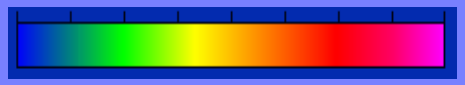
Chemical Toxicity Measurement



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



Treated: 10ppb TCE cells @ 10nM VP



Low Calcium flow High Calcium flow

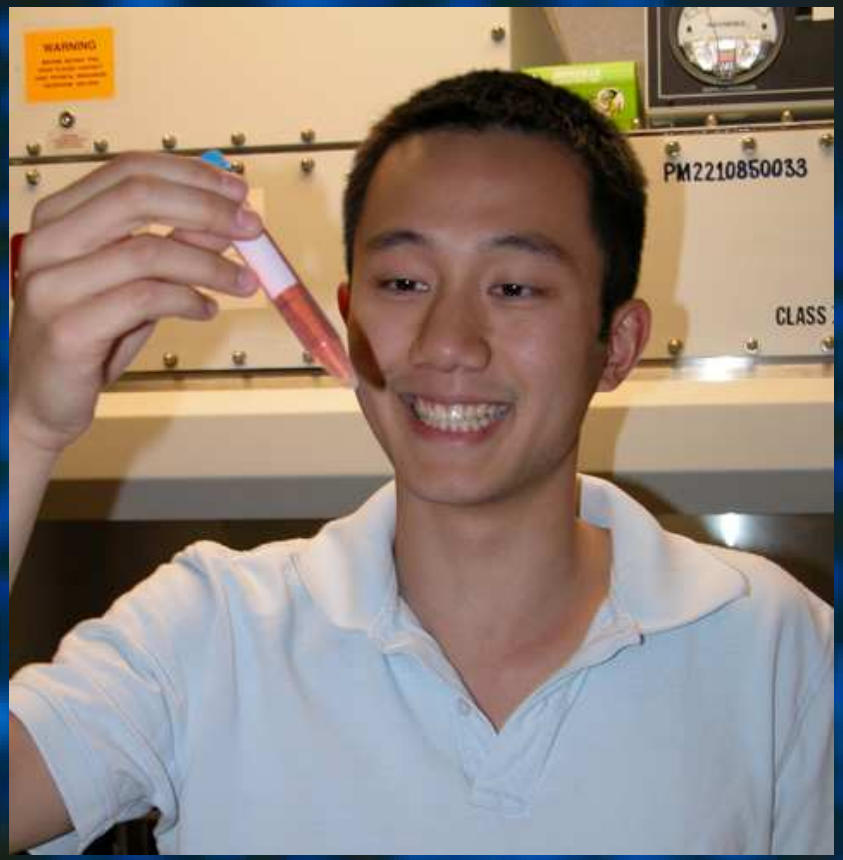
- Developed novel technique based on calcium handling cells.
- P19 cells were exposed to levels of TCE for 24 hour then treated with vassopression to measure intracellular flux of calciu
- Measured calcium flux by changes in fluorescence.

Summary

Developed techniques for cell attachment to semiconductor and insulator surfaces

Demonstrated calcium measurement for toxicity.

Next step is to evaluate new chemicals



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

(SRC 425.022)

Part 1: Ge Surface Clean and Passivation
Jungyup Kim and Yoshio Nishi
Speaker: Jungyup Kim

Part 2: BEOL cleaning of Copper Structures
Nandini Venkataraman and Srini Raghavan
Speaker: Srini Raghavan

Part 3: Drying of Thin Porous Low-k Films
Asad Iqbal, Junpin Yao, Harpreet Juneja, Farhang Shadman
Speaker: Asad Iqbal

Ge Surface Clean and Passivation

J. Kim, J. McVittie, K. Saraswat and Y. Nishi

Stanford University

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

1. Introduction
2. Etch Rate Aspects/Surface Roughness
3. Native Oxide Removal and Passivation
4. Metal Removal
5. Environmental Considerations
6. Conclusions

1. Introduction
2. Etch Rate Aspects/Surface Roughness
3. Native Oxide Removal and Passivation
4. Metal Removal
5. Environmental Considerations
6. Conclusions

Why Germanium ?

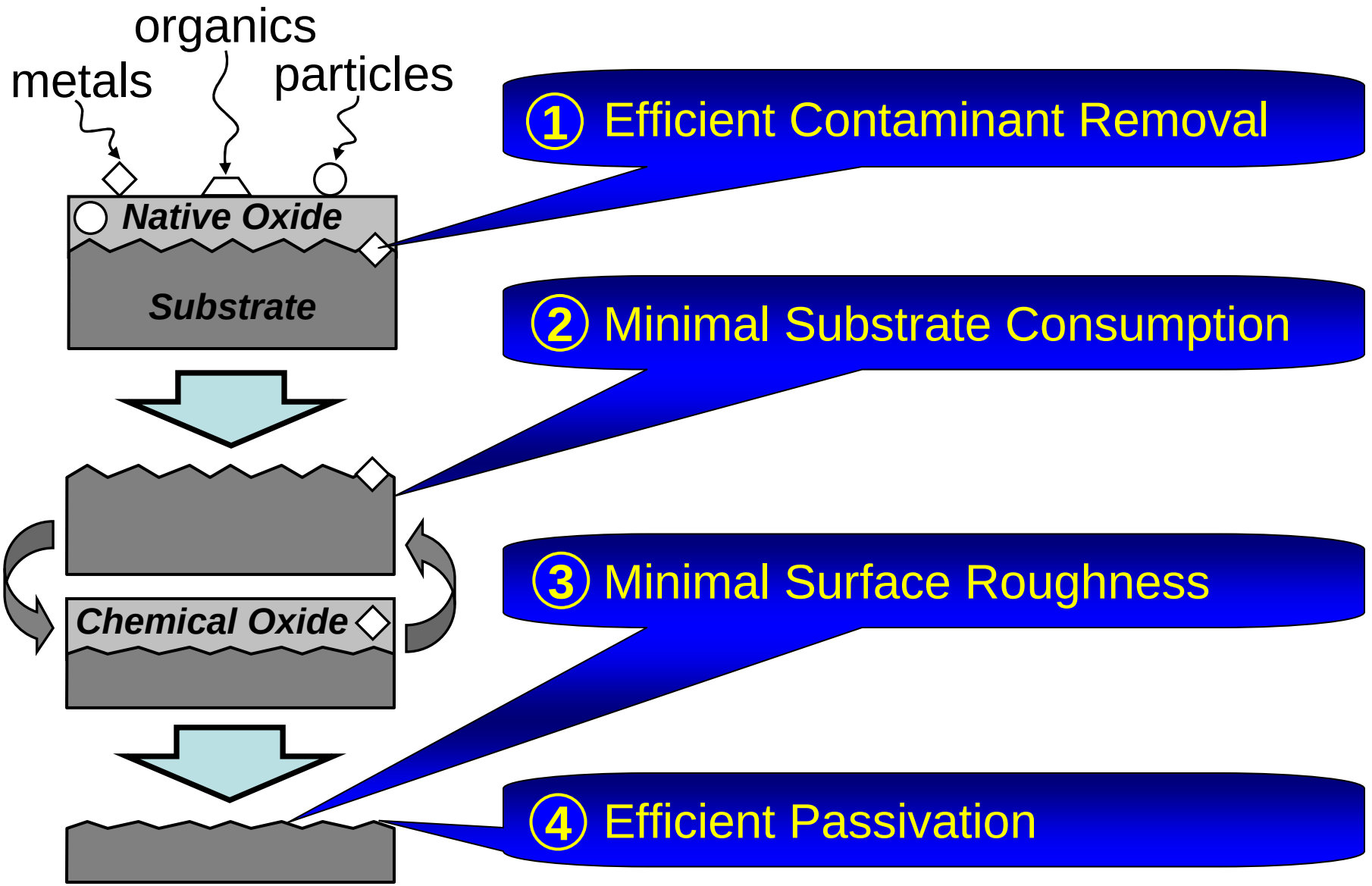
- Ge is gaining interest as a substrate for high mobility applications because of higher carrier mobility.
(2X electron & 4X hole mobility of Si)

($cm^2V^{-1}s^{-1}$)	Si	Ge
Electron	1450	3900
Hole	505	1800

Schäffler et al, *Semiconductor Sci. Tech.* (1997)

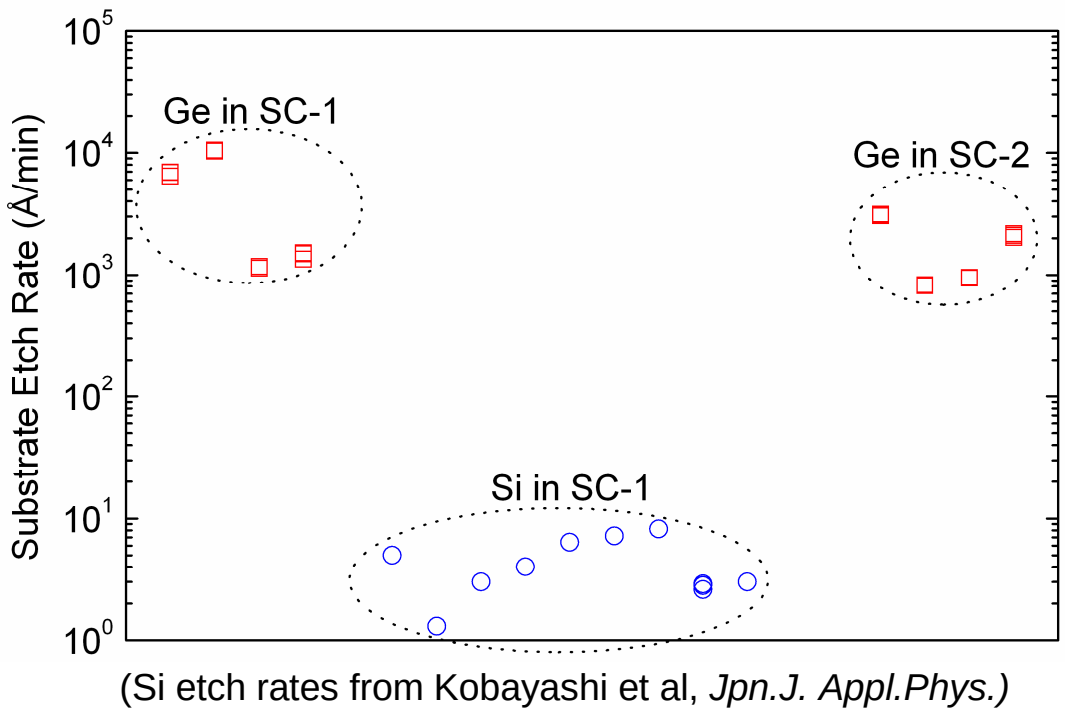
- Effective surface preparation is required to fully utilize the high mobility properties of Ge in process integration.

Wet Cleaning of Germanium Surface

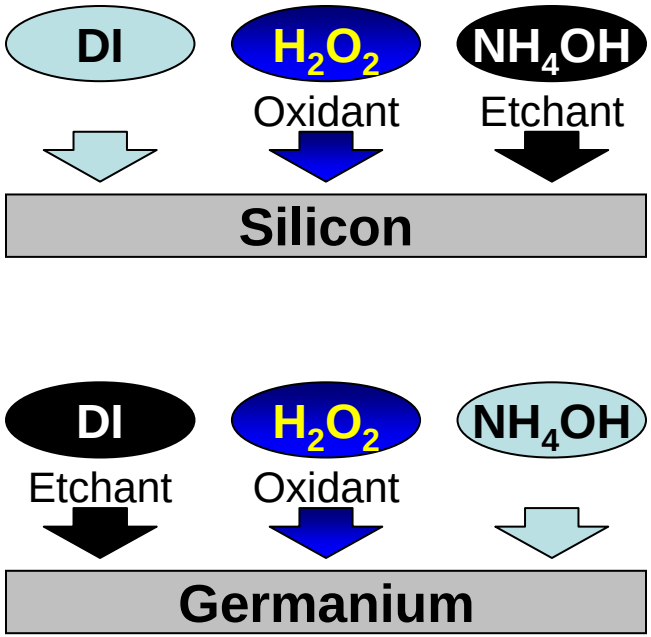


1. Introduction
2. Etch Rate Aspects/Surface Roughness
3. Native Oxide Removal and Passivation
4. Metal Removal
5. Environmental Considerations
6. Conclusions

Etch Rate in Standard Clean Solutions

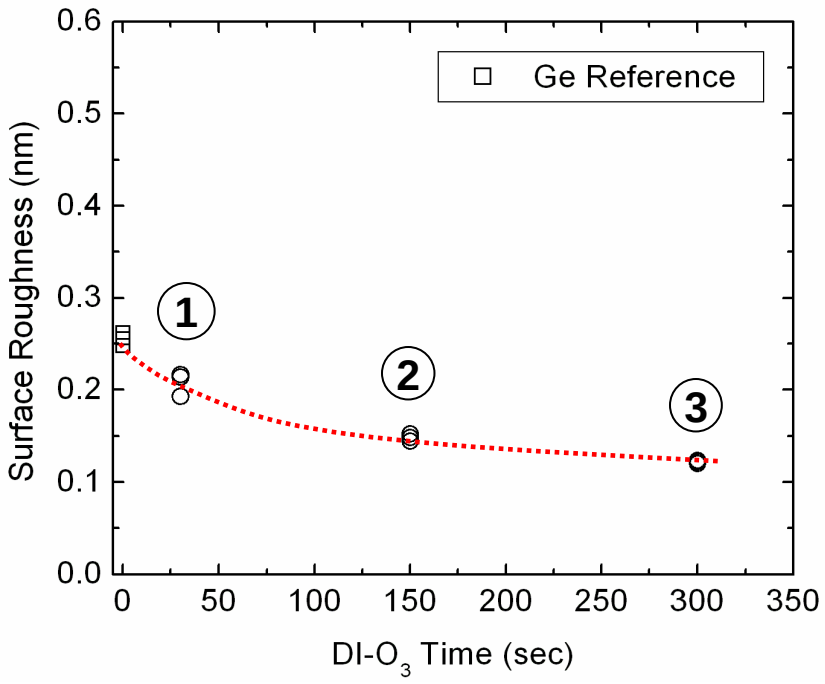


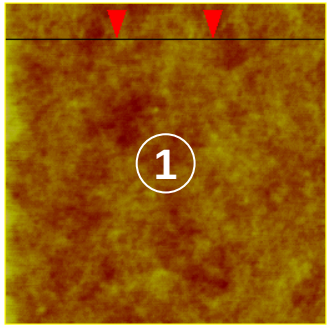
(Si etch rates from Kobayashi et al, *Jpn.J. Appl.Phys.)*

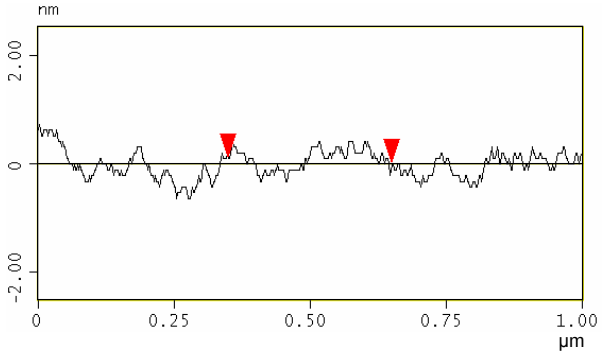


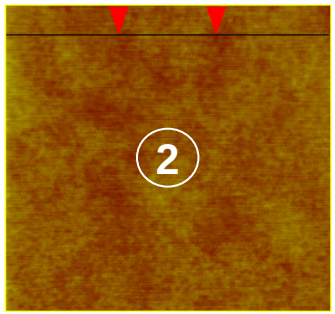
- Water solubility of GeO_2 (2 µm/min) results in high Ge etch rates for room temp SC-1 & SC-2. (Si etch rates <10 Å/min)
- Need alternative **minimal-etching** clean solution for Ge.

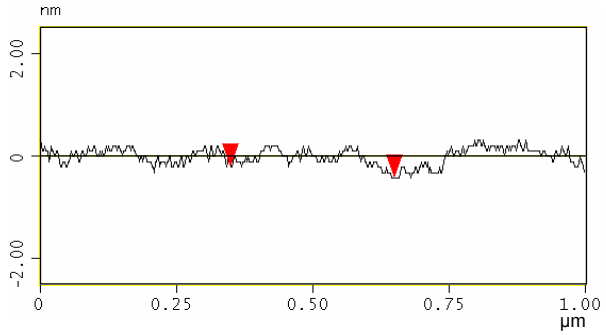
Roughness Improvement with DI-O_3

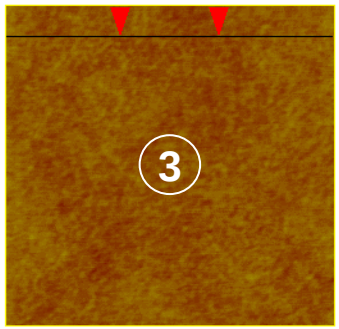


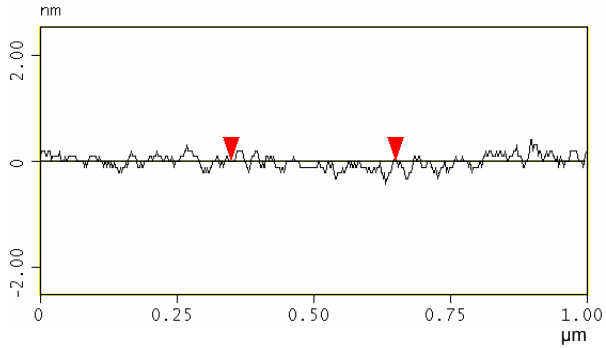












- Ozonated DI water (DI-O_3) smoothensGe surface while etching.

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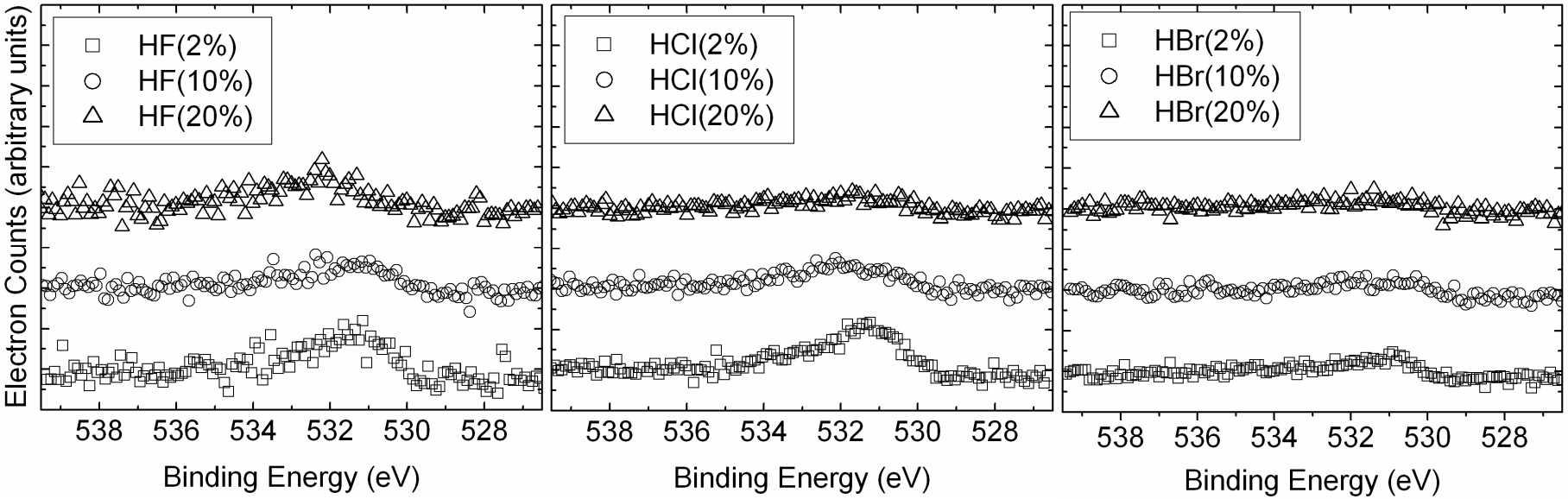
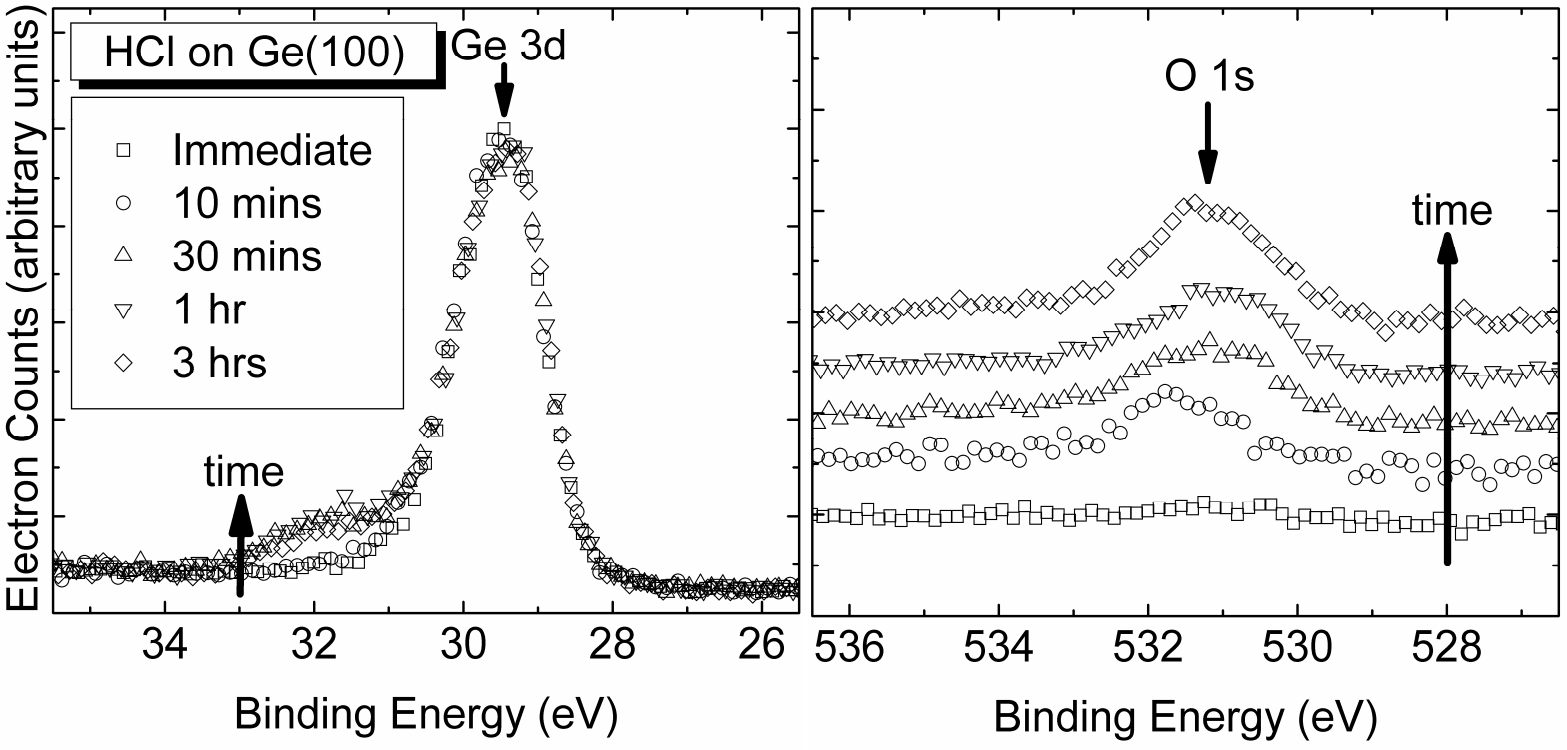
Native Oxide Removal

High Resolution Scans of Oxygen (1s) on Ge



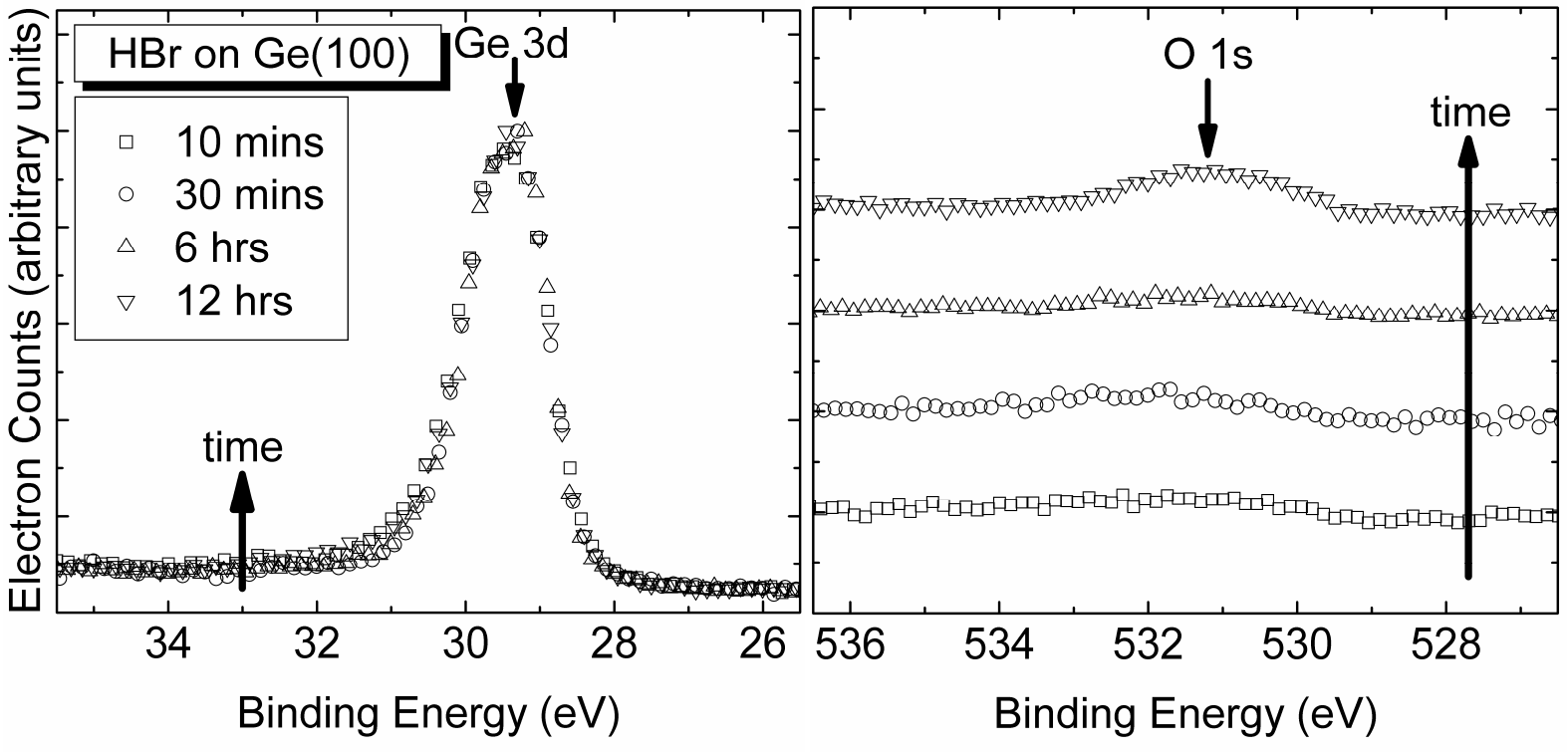
- Relative O(1s) signal represent remaining oxide.
- HF (all concentration @2mins) does not remove oxide layer.
- Concentrated HCl and HBr gives complete removal of the contaminant containing native oxide.

Passivation of HCl Treated Ge Surface



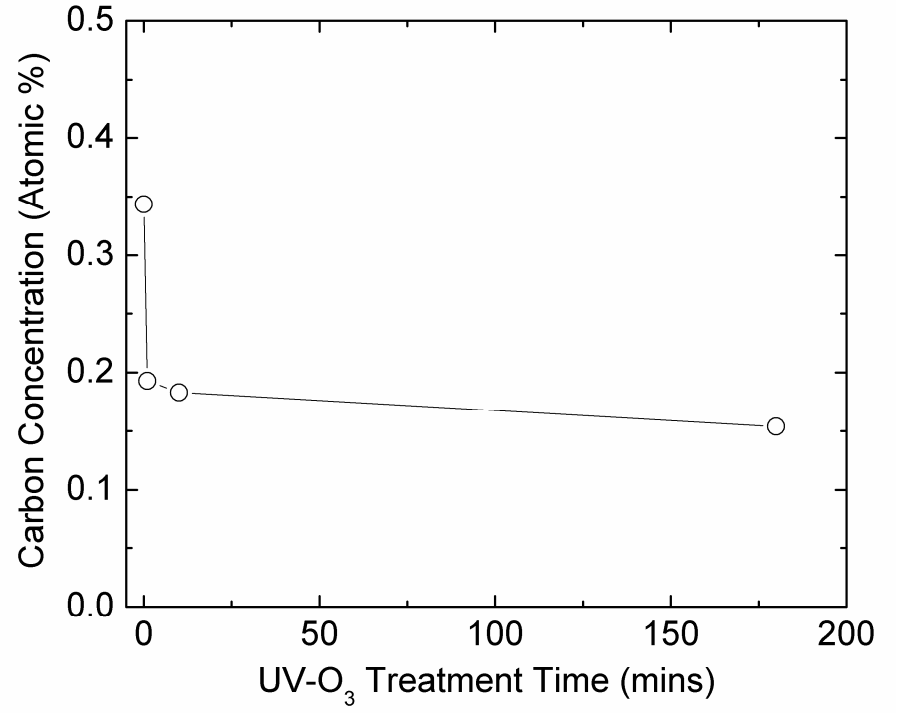
- Complete removal of oxide achieved.
- Oxide re-growth in 10mins.

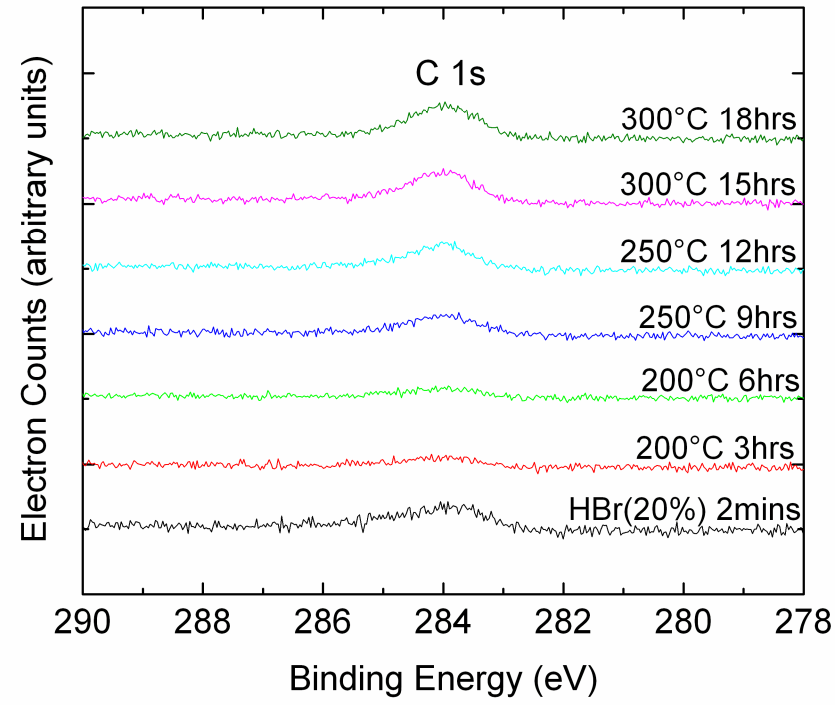
Passivation of HBr Treated Ge Surface



- Complete removal of oxide achieved.
- Passivation effective for 6 hours

Organic Removal





- UV-O3 decrease the carbon contamination level
- Thermal treatment decreases the carbon level but prolonged treatment at high temperatures redeposit carbon.

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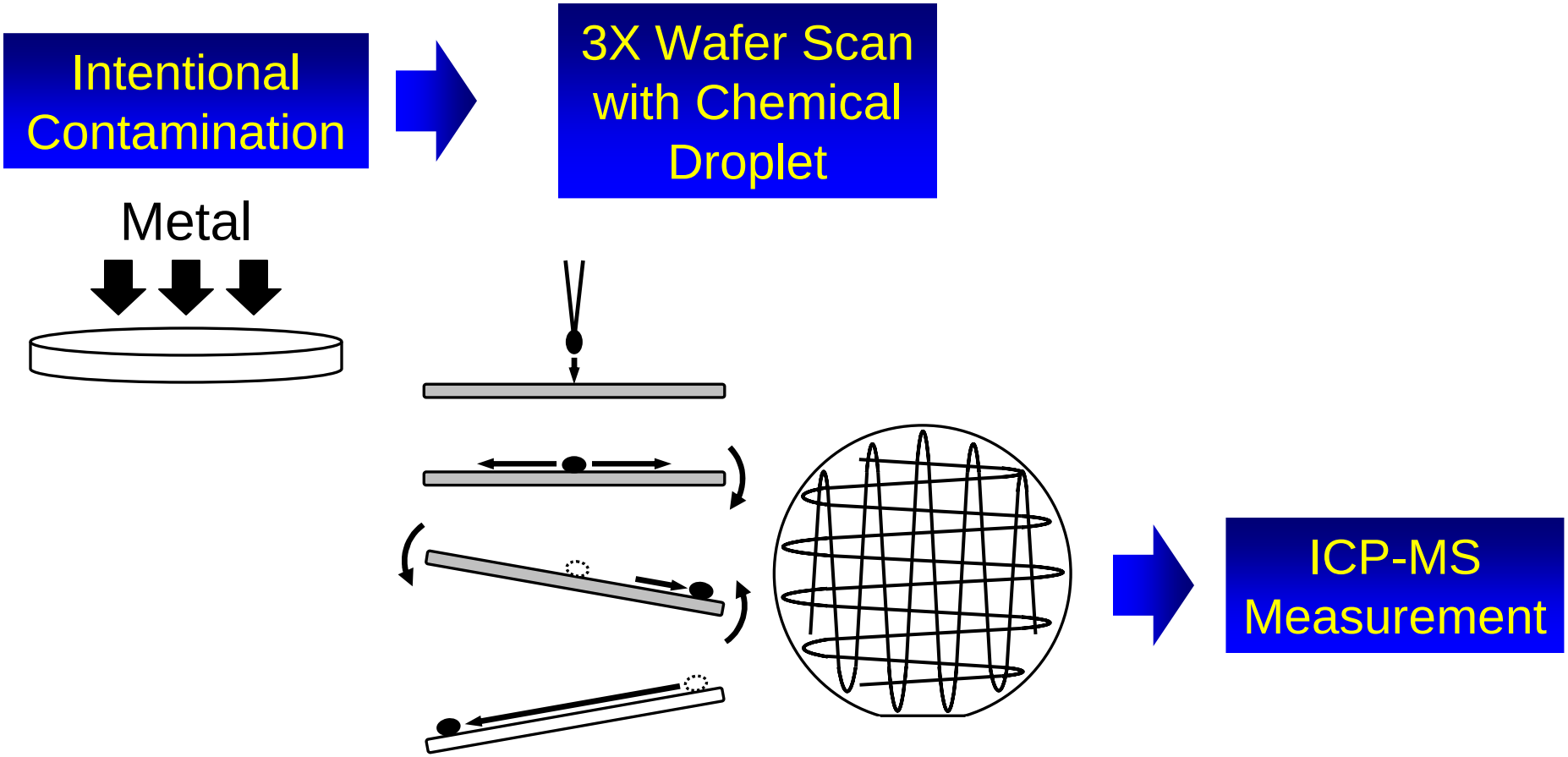
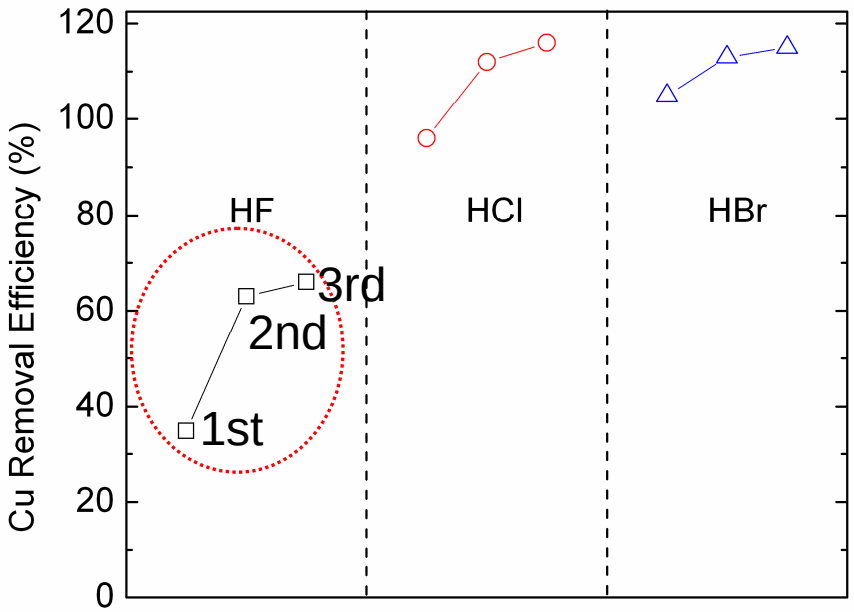
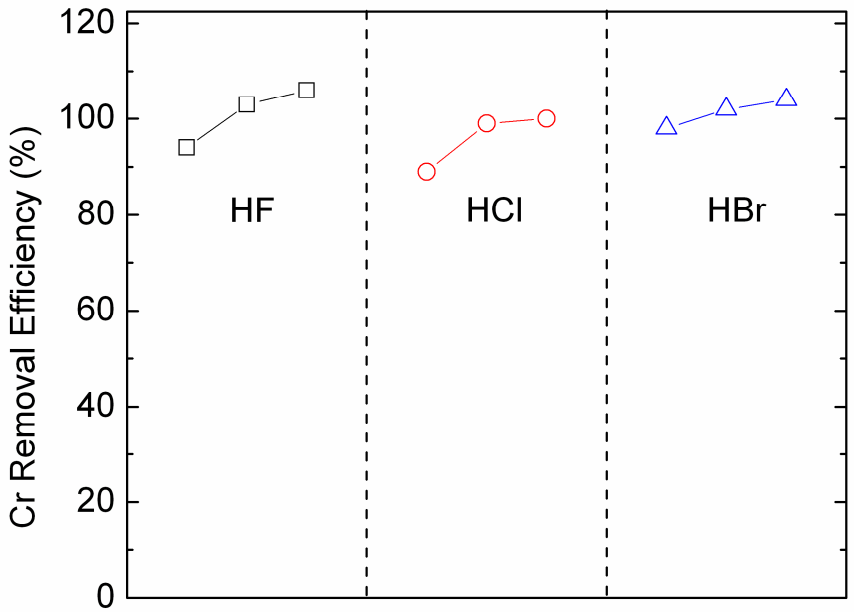
Wafer Surface Analysis (WSA) Method



- ICP-MS : Inductively Coupled Plasma Mass Spectroscopy

Metal Removal Efficiency (MRE)

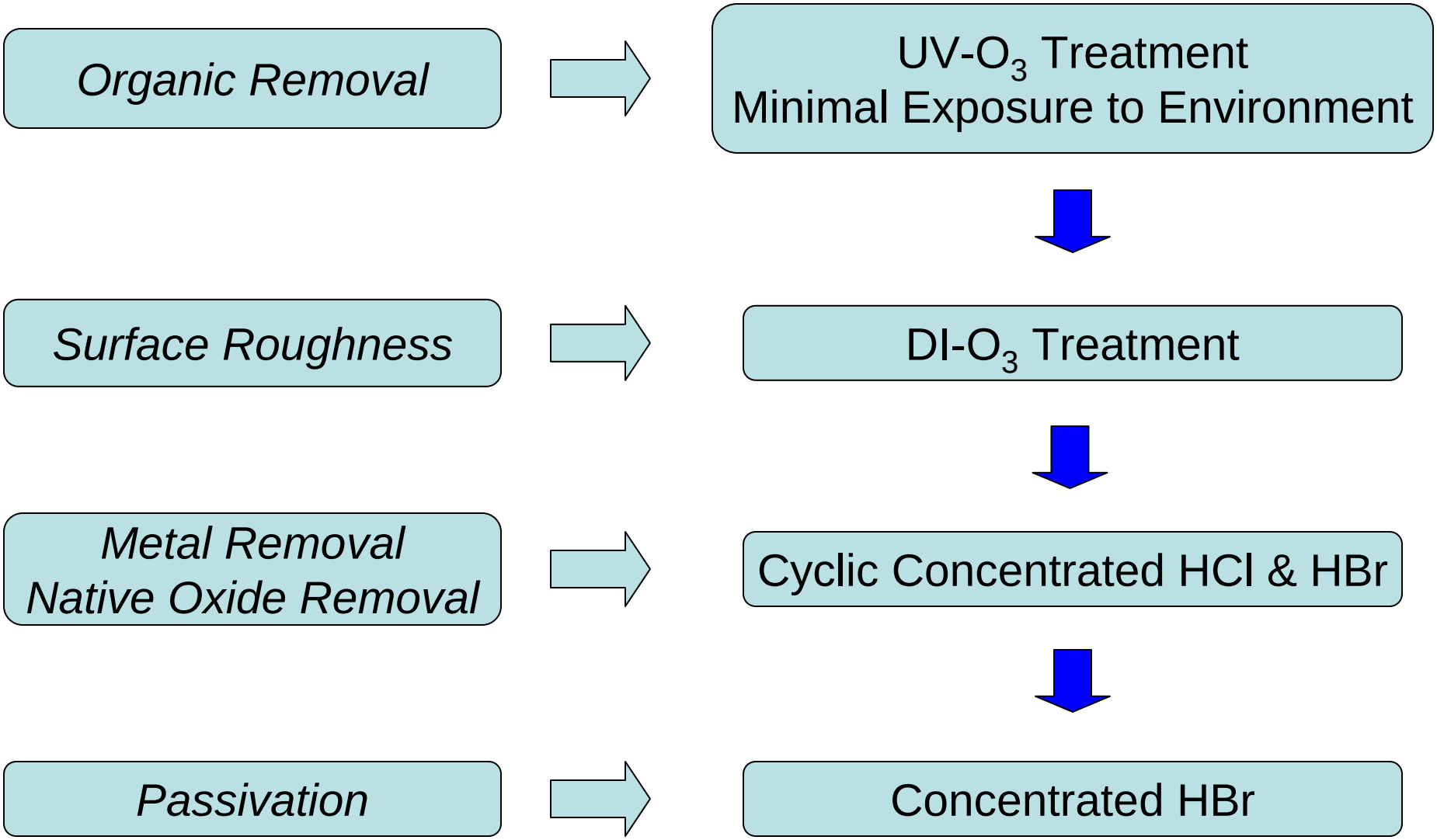




$$\text{Metal Removal Efficiency} = \frac{\text{Metal Recovered by WSA Method}}{\text{Initial Contamination on Wafer}} \text{ X } 100$$

- MRE → “Effectiveness of Clean”
- Fe, Al, Ni, Ti, Co, Cr, Cu show >80% MRE for HF,HCl and HBr except Cu with HF solution.

Proposed Ge Cleaning Solution



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ESH Benefits of Ge Cleaning Solution

Process	Advantages
• UV-O_3 (Organics) • DI-O_3 (Surface Roughness)	O_3 breaks down naturally to O_2. (non-toxic by-product)
• Cyclic HCl (Metal)	Room temp process: does not require heat as in SC-2 (65~85°C) for Si. (energy conservation)

▸ Water-soluble GeO_2 allows the use of DI water instead of HF as oxide etchant. HF usage can be eliminated.

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Conclusions

1. Ge has abnormally high etch rates in room temp. SC-1 & SC-2.
2. Surface roughness is improved with DI-O_3.
3. Native oxide is efficiently removed with conc. HCl & HBr.
4. Ge is passivated efficiently by HBr.
5. Metals are removed efficiently by HCl & HBr.
6. Proposed Ge clean process uses O_3 chemistry and room temp processes.

Future Work

- Further work with DI-O_3 and DI-O_3/Acid mixtures on contamination removal of Ge surfaces.
- Establish correlation of contaminants on electrical properties of Ge surfaces.
- *ab-initio* modeling of oxidation of halide-passivated surface.

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

Task ID : 425.022

Srini Raghavan (PI)

Graduate Student

Nandini Venkataraman

Department of Materials Science & Engineering,

The University of Arizona

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

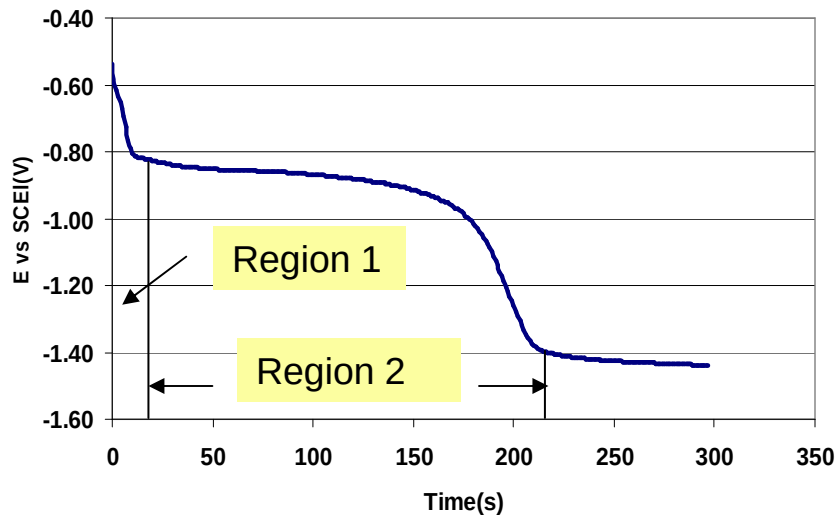
Project Objectives

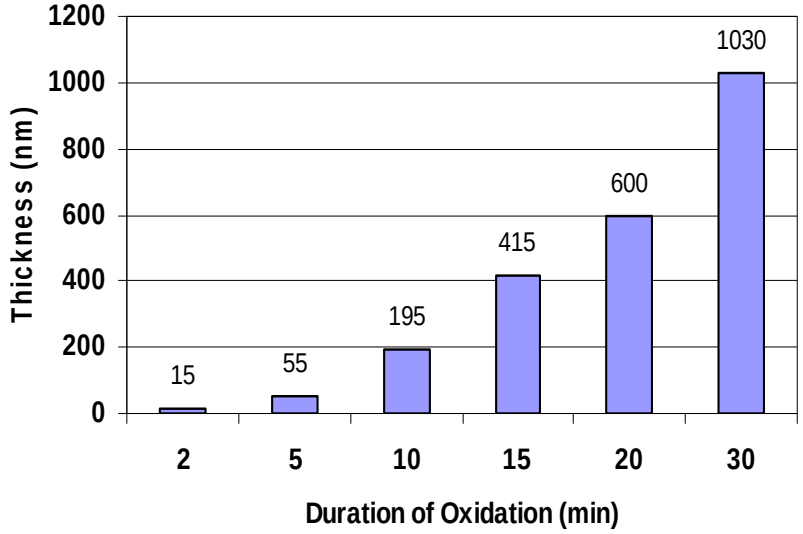
- Identify and evaluate novel chemistries suitable for BEOL cleaning that selectively remove copper oxide residues without corroding copper
- Examine the feasibility of using Electrochemical Impedance Spectroscopy (EIS) as a technique to determine the end point of copper oxide removal and detect the transition from copper oxide to copper

BEOL cleaning of Cu/low k structures

- Involves removal of post etch residues including copper oxide residues from the sidewalls and bottom of the copper lines
- Formulations required to exhibit high selectivity between copper oxide and underlying copper lines and should not alter the low k dielectric material
- Semi-aqueous fluoride (SAF) and some all-aqueous chemical systems (based on ammonium phosphate and organic acids) have been reported in literature
- Mechanism of action largely unknown due to proprietary nature of formulations

Preparation of Samples by Controlled oxidation of copper



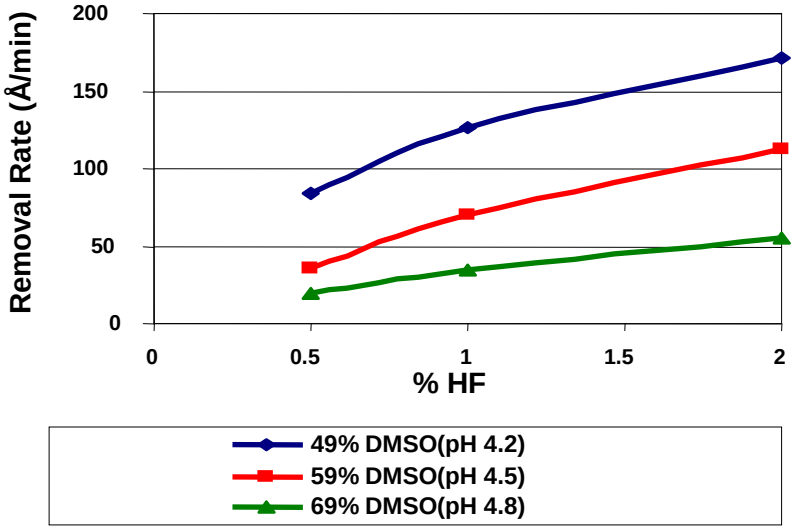


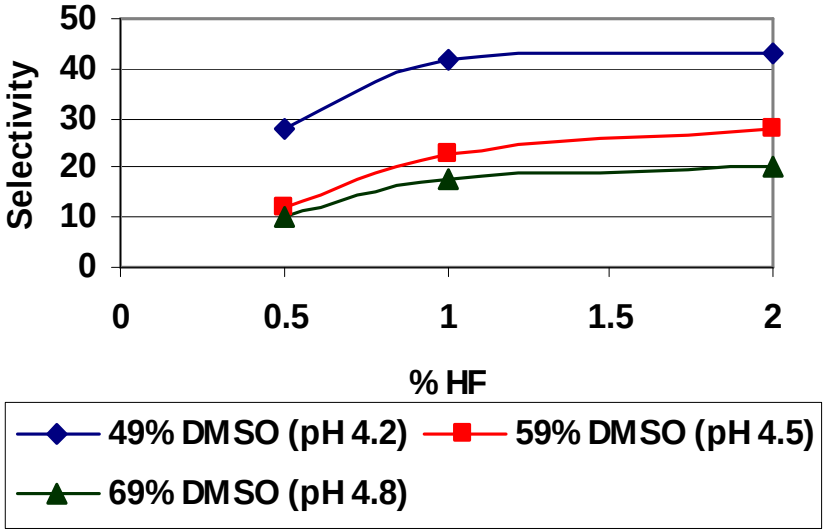
- Electroplated copper (~ 0.65 µm) oxidized at 300°C in high purity air ambient
- Thickness of copper oxide estimated using electrochemical reduction technique and calculated using Faraday's law
- Three electrode setup with SCE as reference electrode and Pt counter electrode

Applied current density: 0.75 mA/cm^2
Electrolyte: 0.1 M $NaHCO_3$

- Copper oxide reduces at two potentials
  - -0.6 V vs SCE corresponding to reduction of copper (II) oxide (CuO)
  - -0.8 V vs SCE corresponding to reduction of copper (I) oxide (Cu_2O)
- 55 nm copper oxide (mostly Cu_2O) formed by oxidation for 5 minutes used for all further experiments.

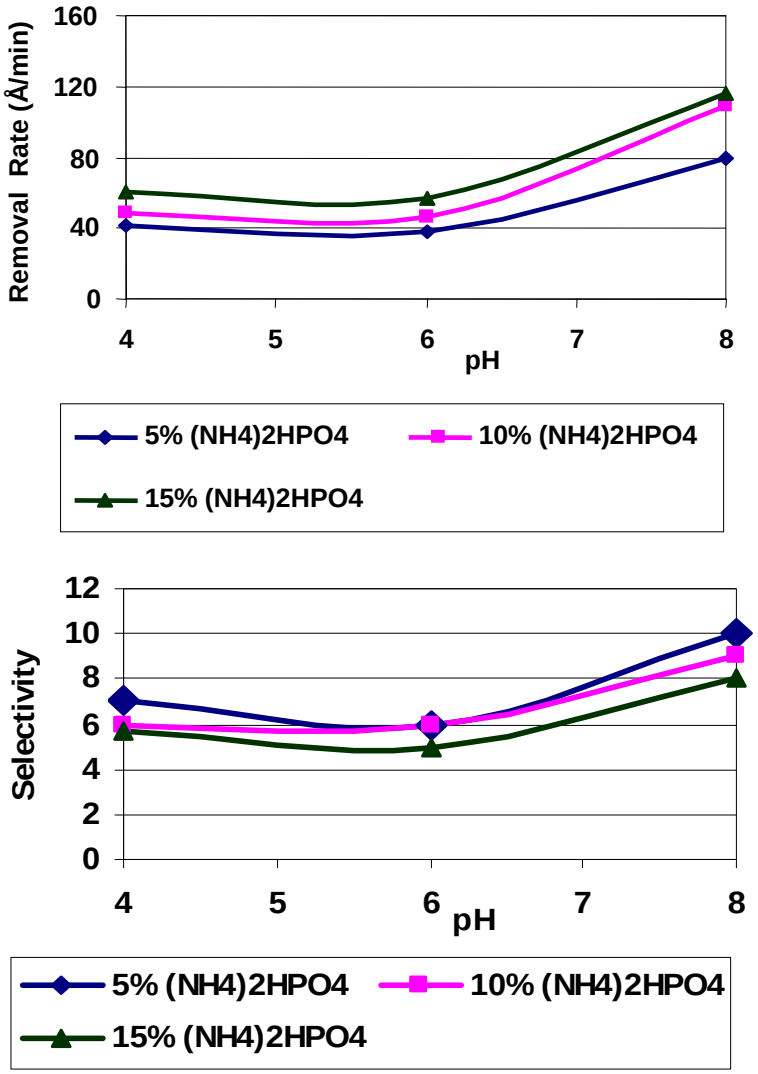
Investigation of SAF formulations





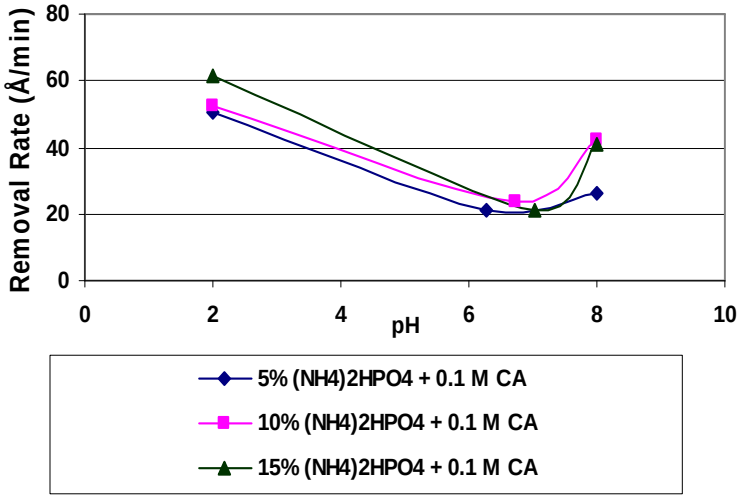
- Immersion tests in formulations containing Dimethyl Sulfoxide (DMSO), HF and H_2O
- Immersed area: 4 cm^2
- Duration of Immersion : 3 minutes
- Solution analyzed for copper by Atomic Absorption Spectroscopy and removal rate calculated
- Selectivity = $\frac{\text{Removal rate of copper oxide}}{\text{Etch rate of copper}}$
- Removal rate of copper oxide and selectivity increase when
  - % HF increases
  - % DMSO decreases
- 49% DMSO, 2% HF, 49% H_2O (pH 4.2) shows
  - Highest Cleaning Rate ~ 170 Å/min
  - Highest Selectivity ~ 42:1

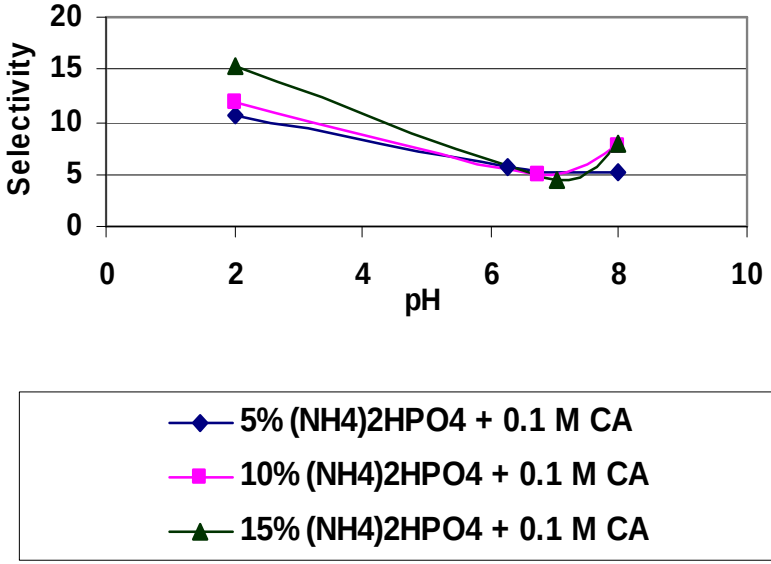
All aqueous $(NH_4)_2HPO_4$ formulations



- Removal rate of copper oxide and selectivity increases when
  - $(NH_4)_2HPO_4$ concentration is increased
  - pH is alkaline (pH 8)
- Highest removal rate ~ 115 Å/min in formulation containing 15% $(NH_4)_2HPO_4$ at pH 8, (with selectivity of 8:1)
- Highest selectivity ~ 10:1 obtained in formulation containing 5% $(NH_4)_2HPO_4$ at pH 8, (with removal rate of 80 Å/min)

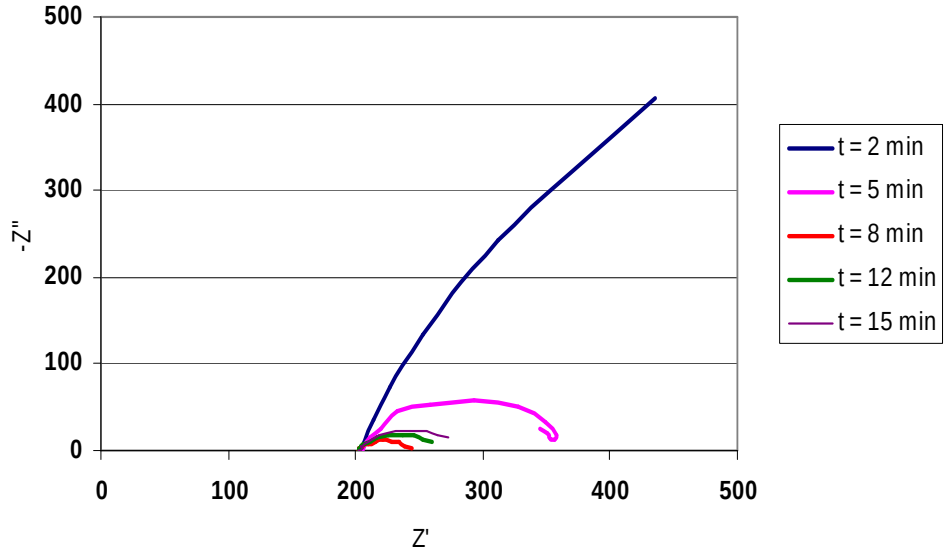
Combination of $(NH_4)_2HPO_4$ and Citric Acid

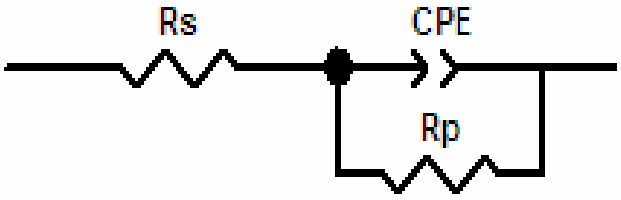




- Increasing $(NH_4)_2HPO_4$ concentration increases removal rate of copper oxide and selectivity
- Higher removal rates at acidic pH (pH 2)
- Formulation containing 15% $(NH_4)_2HPO_4$ and 0.1 M Citric Acid (pH 2)
  - Highest removal rate ~ 60 Å/min
  - Highest selectivity ~15:1

Electrochemical Impedance Spectroscopy Investigations



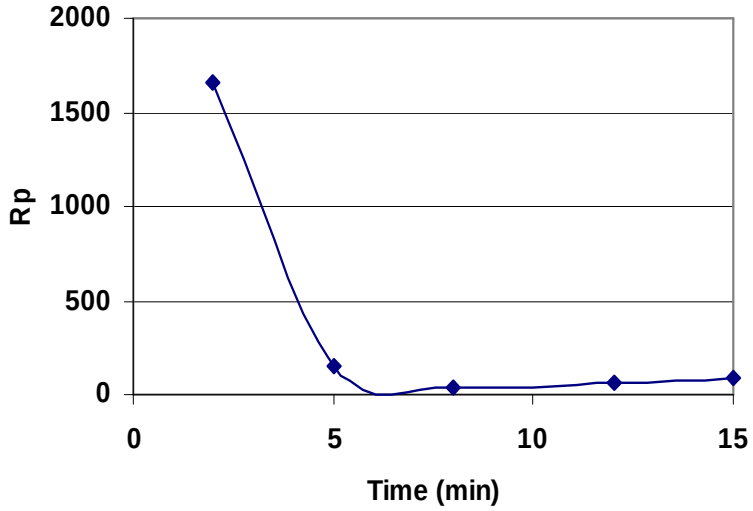


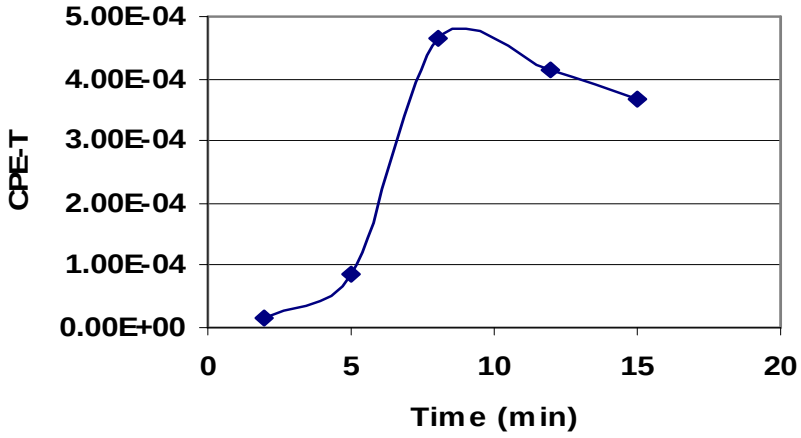
$$Z_{CPE} = \frac{1}{[T^*(i\omega)^P]} \qquad 0 \le P \le 1$$

When P = 1, $Z_{CPE} = Z_C$

- **Sample : 55 nm copper oxide with 2 cm^2 area**
- **Three electrode setup : Pt wire reference electrode, Pt counter electrode**
- **Electrolyte : 49% DMSO, 1% HF, 50% H_2O (pH 4.2)**
- **Amplitude of AC signal : 5 mV**
- **Frequency range used : 10^5 Hz to 0.1 Hz**
- **Impedance spectra measured as a function of time**
- **Simple equivalent circuit consists of solution resistance (Rs), in series with a parallel combination of interfacial resistance (Rp) and a Constant Phase Element (CPE)**

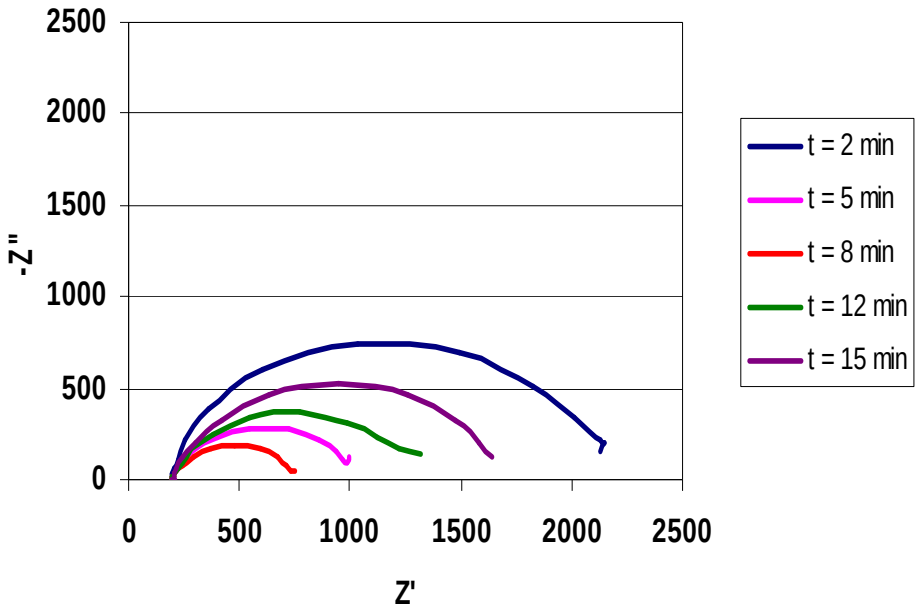
Time evolution of equivalent circuit parameters





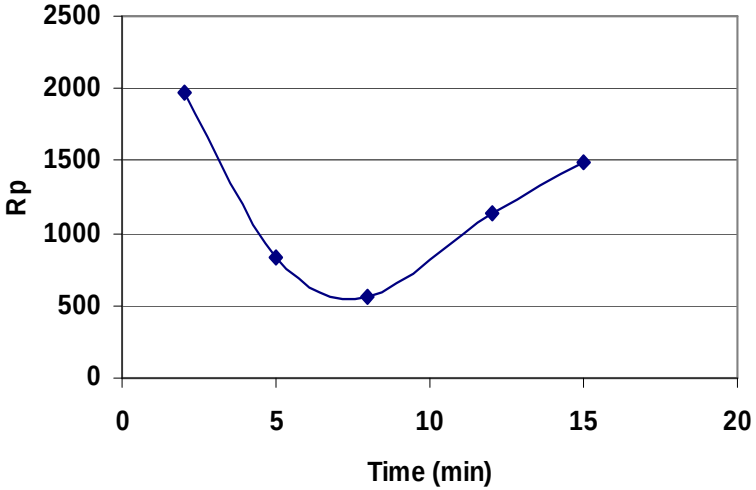
- Component R_p
  - decrease with time corresponds to reduction in copper oxide thickness
  - minimum corresponds to complete dissolution of copper oxide
  - slight increase corresponds to corrosion of copper.
- Component CPE-T
  - Analogous to capacitance, inversely proportional to thickness
  - increases with time – decrease in copper oxide thickness
  - reaches maximum, corresponds to complete removal of copper oxide

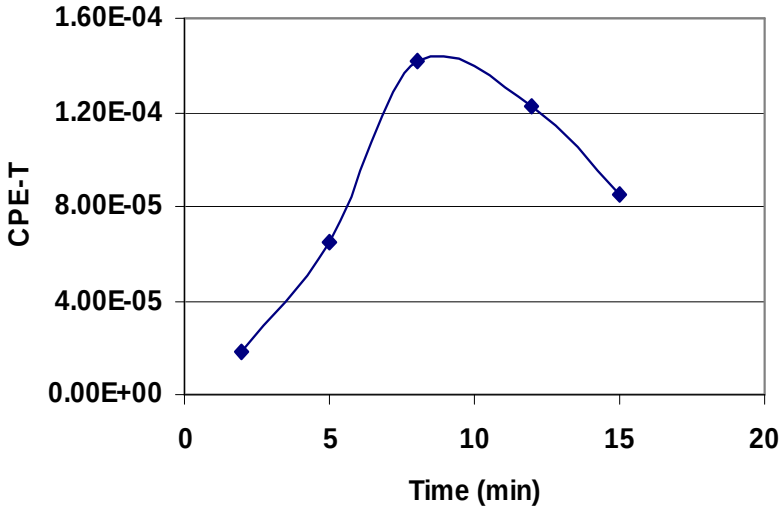
Effect of BTA on evolution of EIS spectra



- **Sample : 55 nm copper oxide with 2 cm^2 area**
- **Electrolyte : 49% DMSO, 1% HF, 50% H_2O + 0.001 M BTA (pH 4.2)**
- **Amplitude of AC signal : 5 mV**
- **Frequency range used : 10^5 Hz to 0.1 Hz**
- **Impedance spectra measured as a function of time and the data fit to the proposed equivalent circuit**

Effect of BTA on equivalent circuit parameters





- Component R_p
  - Addition of BTA results in overall increase in magnitude of R_p
  - Indicates greater resistance to charge transfer at the interface due to adsorption of BTA on the surface
- Component CPE-T
  - Decrease in magnitude of CPE-T upon addition of BTA
  - CPE-T analogous to capacitance. Adsorption of BTA increases the capacitance component.

Conclusions

- DMSO based semi aqueous fluoride chemistry (SAF) and all-aqueous chemistries based on ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and citric acid have been investigated for cleaning copper oxide residues.
- Electrochemical Impedance Spectroscopy has been demonstrated as a technique to determine the end point of removal of copper oxide and detect the transition from copper oxide to copper on the surface.

Future Directions

- Determine the applicability of the EIS technique to evaluate cleaning performance of these formulations in patterned test structures with high aspect ratio features
- Work with Prof. Shadman's group in using the technique to follow rinsing of structures after cleaning

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

Drying of Thin Porous Low-*k* Films

SRC 425.022

Asad Iqbal, Junpin Yao, Harpreet Juneja, Farhang Shadman

Chemical and Environmental Engineering

University of Arizona

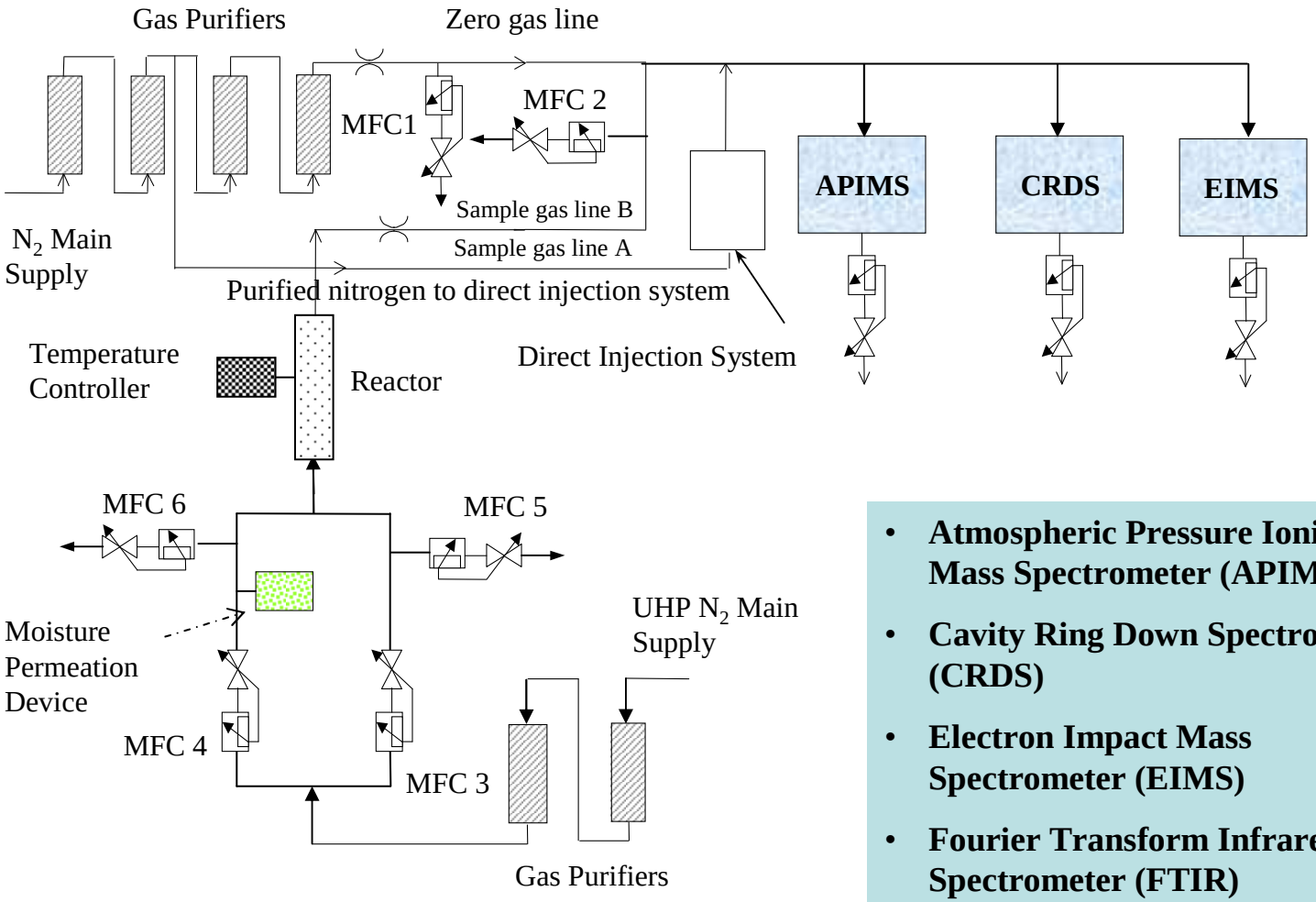
Background

- **Moisture can deteriorate the *k* value, create adhesion problems, and cause reliability issues.**

Objectives

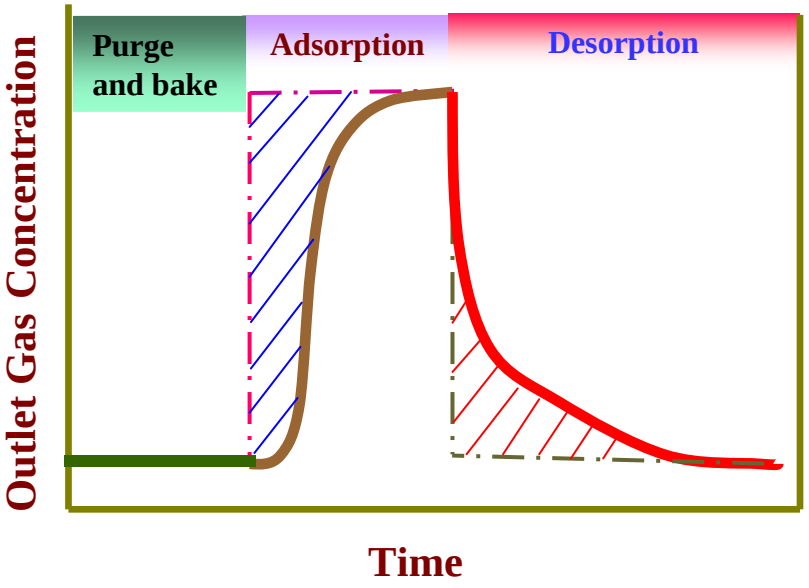
- **Determine the fundamentals of moisture interactions and outgassing in both uniform and non-uniform porous low-*k* films:**
  - **loading**
  - **molecular transport**
  - **chemical interactions**
  - **removal**
- **Develop experimental and process modeling techniques for minimizing the chemical and energy usage during cleaning and purging of low-*k* films.**

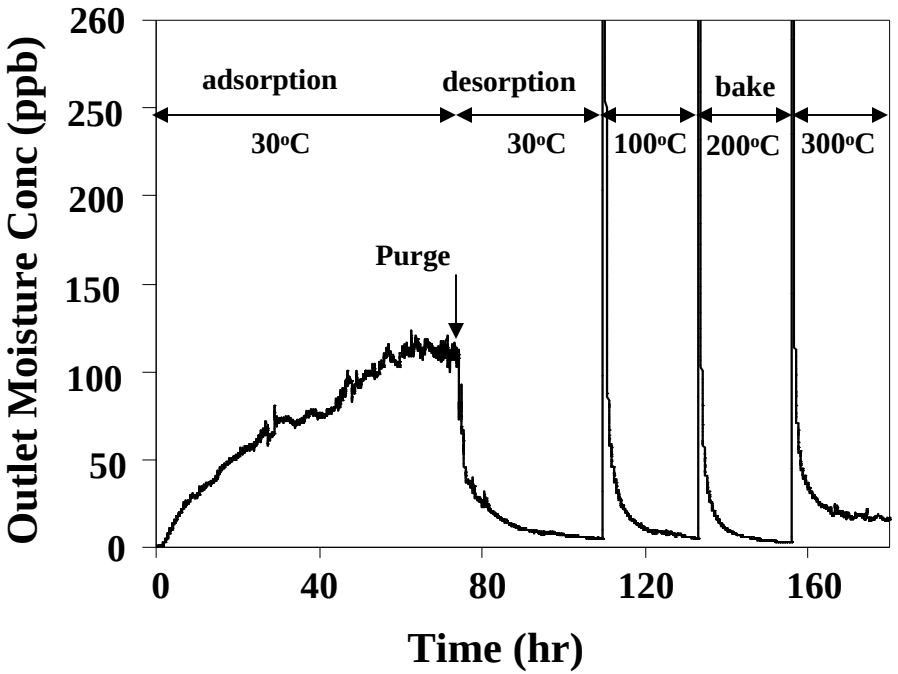
Experimental Setup



- **Atmospheric Pressure Ionization Mass Spectrometer (APIMS)**
- **Cavity Ring Down Spectroscope (CRDS)**
- **Electron Impact Mass Spectrometer (EIMS)**
- **Fourier Transform Infrared Spectrometer (FTIR)**

Experimental Procedure





Experimental procedure

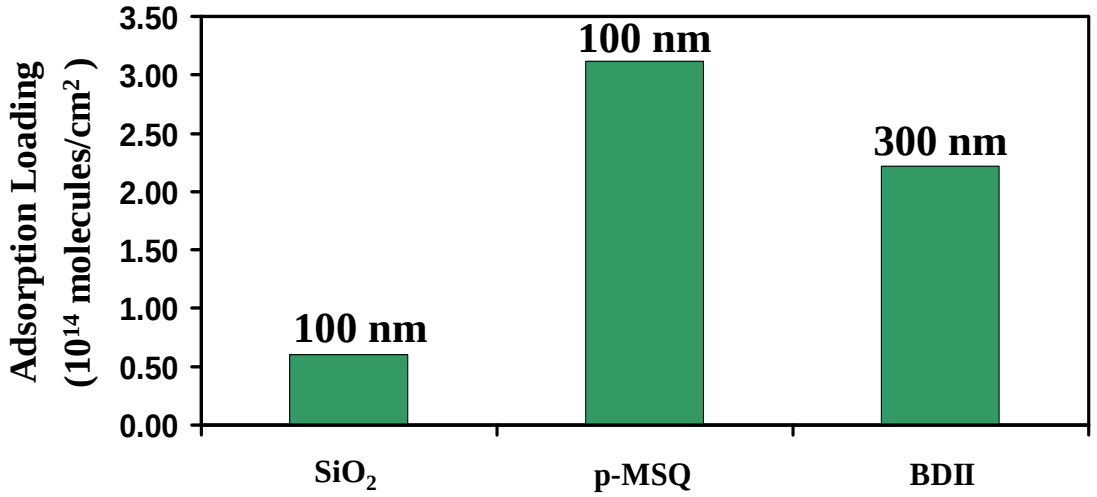
Adsorption at 30°C; then desorption at 30°C; followed by bake-out at 100, 200 & 300°C

Temporal profile

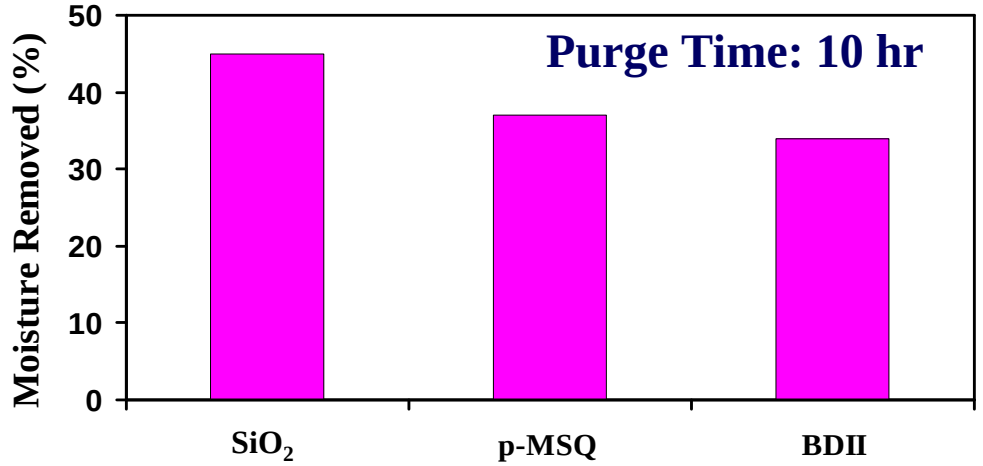
Exposure to 110 ppb moisture; followed by temperature-programmed desorption

Moisture Loading and Retention Comparison

Challenge Concentration: 56 ppb

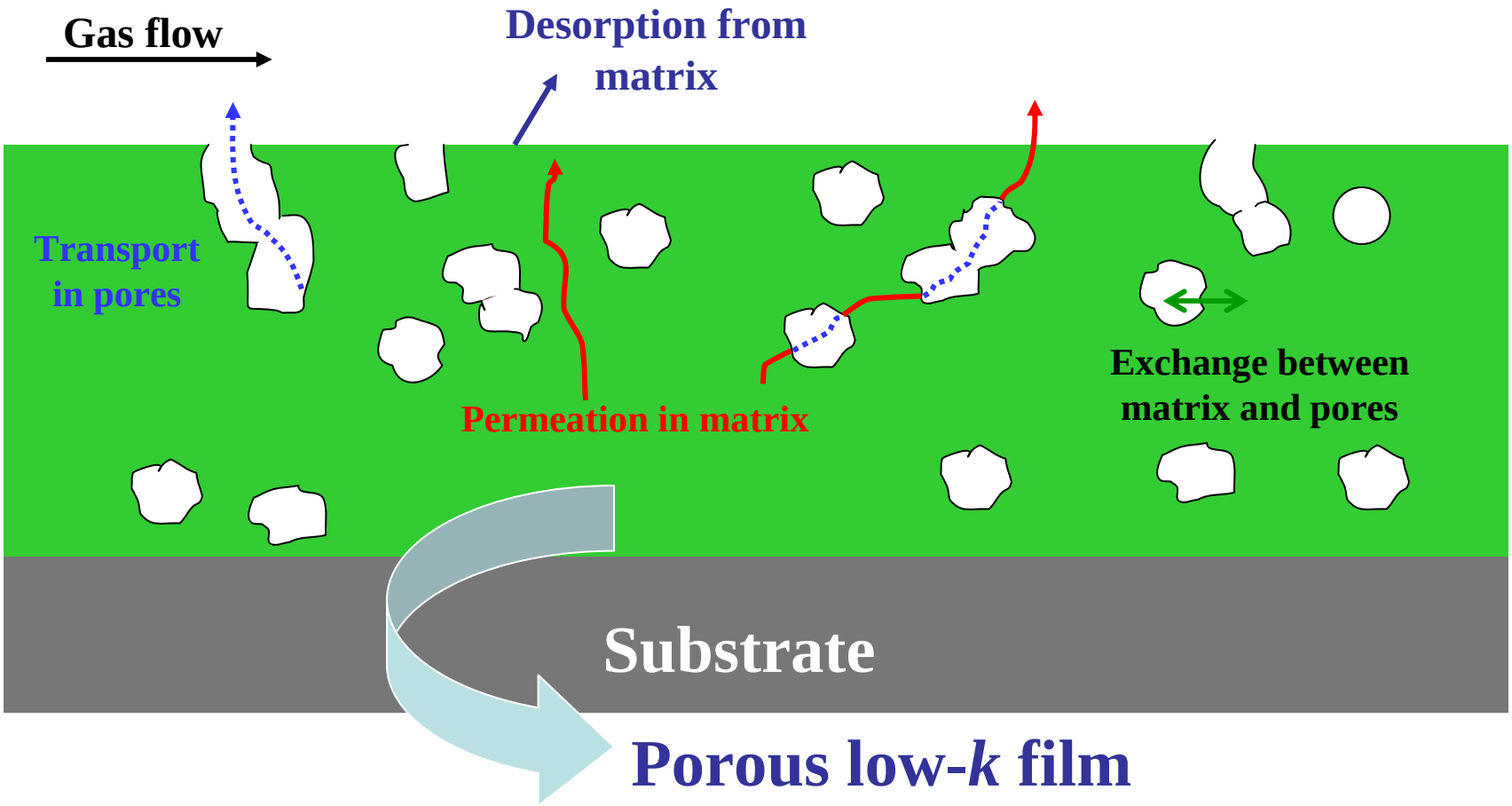


Porous low-*k* films have much higher sorption loading than SiO_2



Moisture removal is a very slow process

Moisture Transport Pathways in Porous Low-*k* Film



Process Model for Non-Uniform Films

Transport of moisture in matrix:

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

Transport of moisture in pore:

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

C_S / C_g: Moisture concentration in matrix / pore;

D_S / D_g: Moisture diffusivity in matrix / pore;

ε: Film porosity;

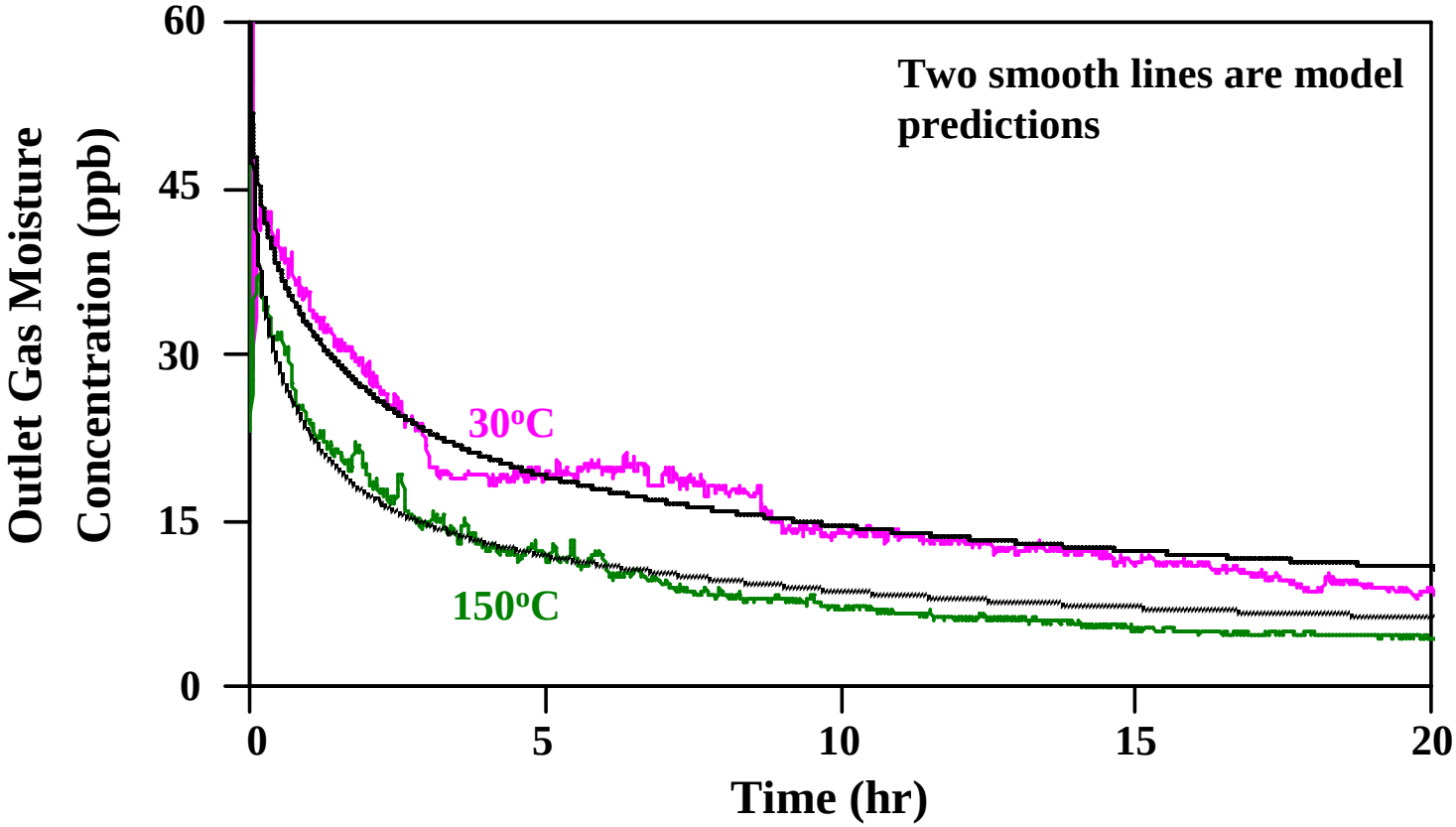
S_p: Specific surface area;

S: Moisture solubility in matrix;

k_m: Interphase transport coefficient between pore and matrix;

Validation of Model

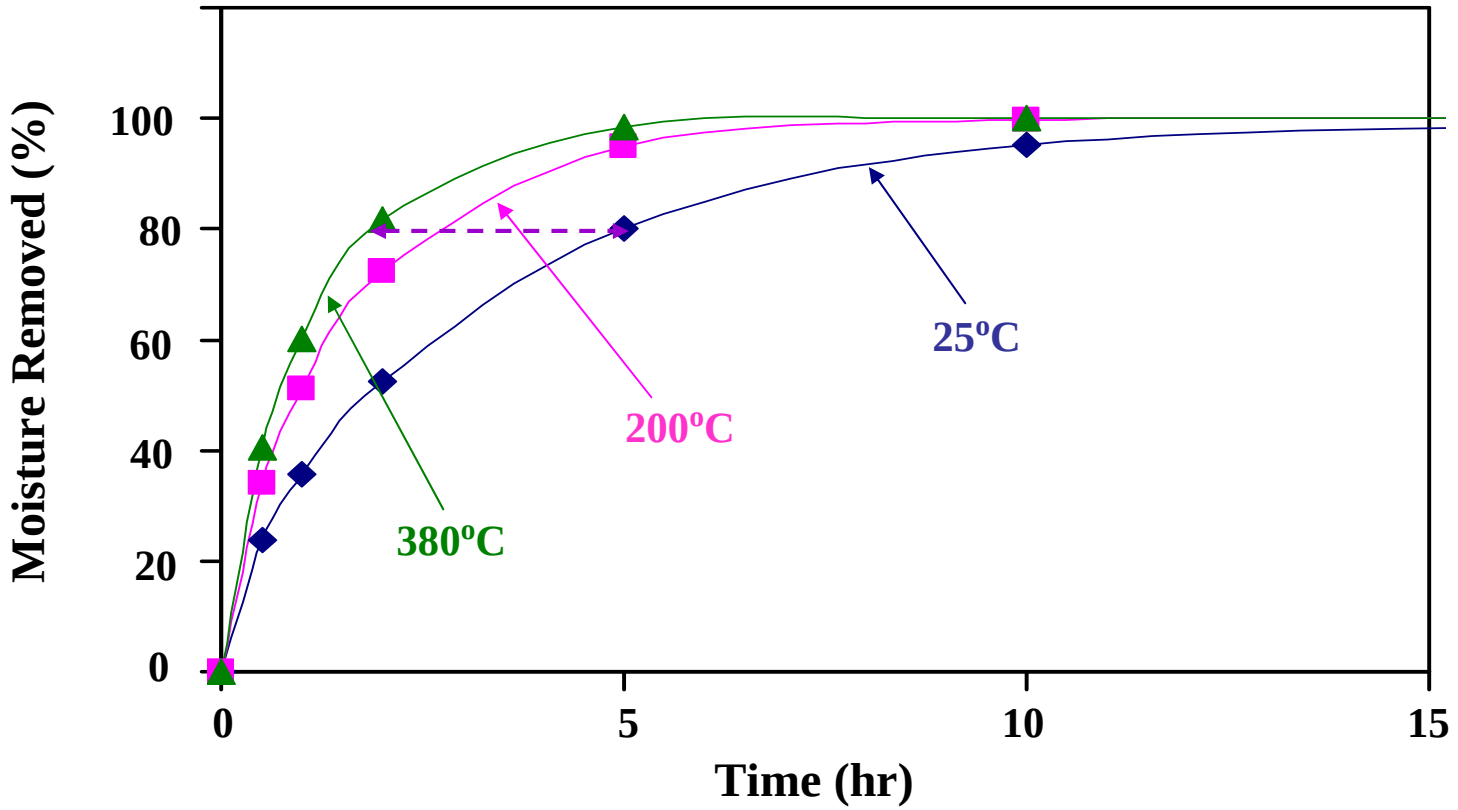
p-MSQ (JSR LKD 5109); Challenge Concentration: 56 ppb;
Purge Gas Purity: 1 ppb; Purge Gas Flow Rate: 318 sccm;
Film Thickness: 4000 Å



Good agreement between the model and the experimental data

Effect of Temperature on Moisture Removal

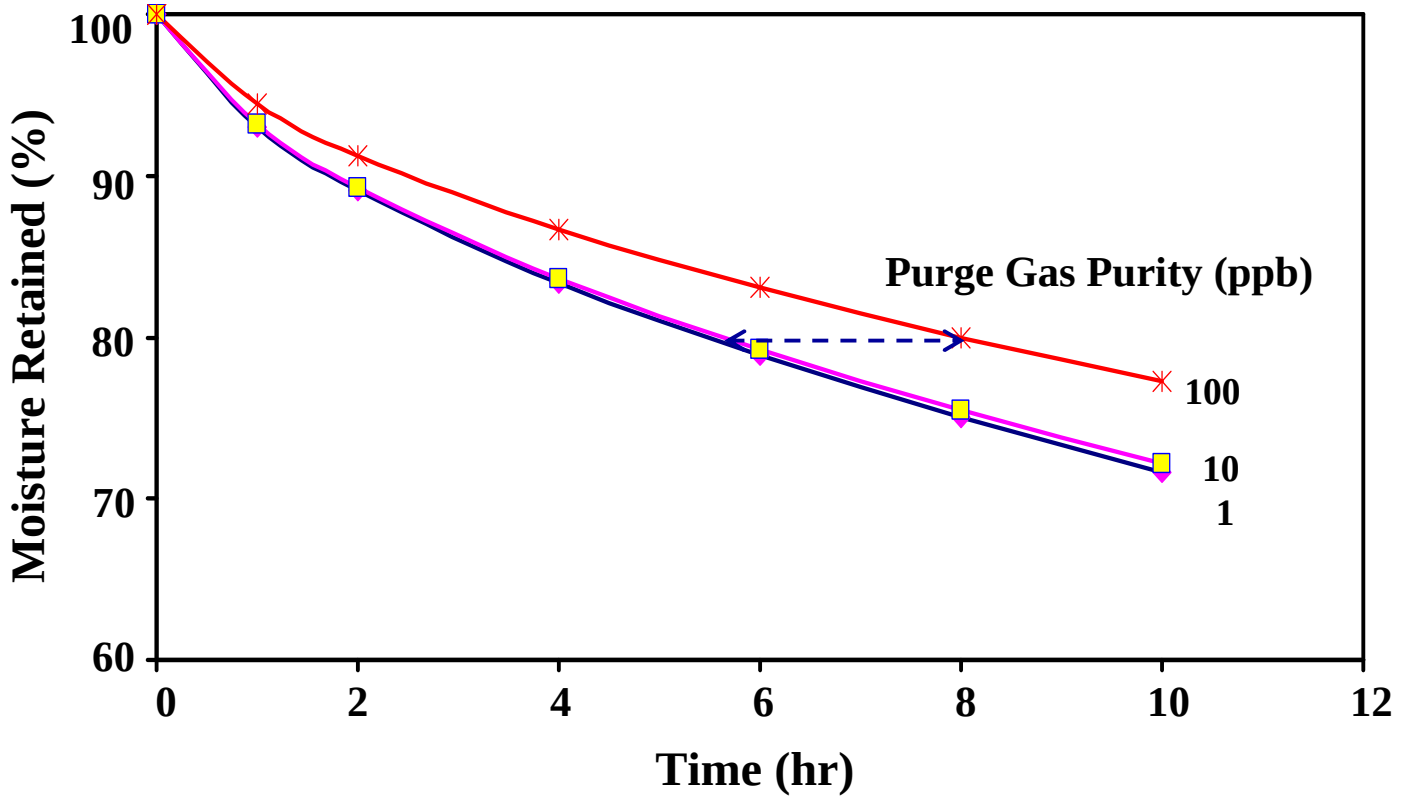
p-MSQ (partial etch, N_2H_2 ash); Challenge Concentration: 1500 ppm;
Film Thickness: 1000 Å; Purge Gas Flow Rate: 350 sccm;
Purge Gas Purity: 1 ppb



There is an optimum extent of heating for enhancing the desorption

Dependence of Moisture Removal on Purge Purity

p-MSQ (LKD 5109); Challenge Concentration: 500 ppb; Temperature: 250°C; Film Thickness: 4000 Å; Purge Gas Flow Rate: 600 sccm

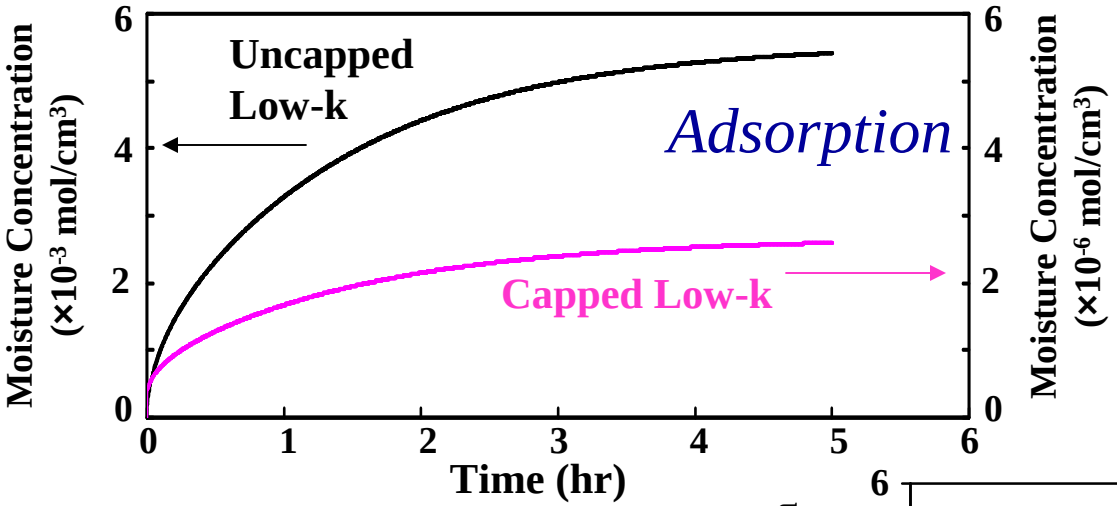


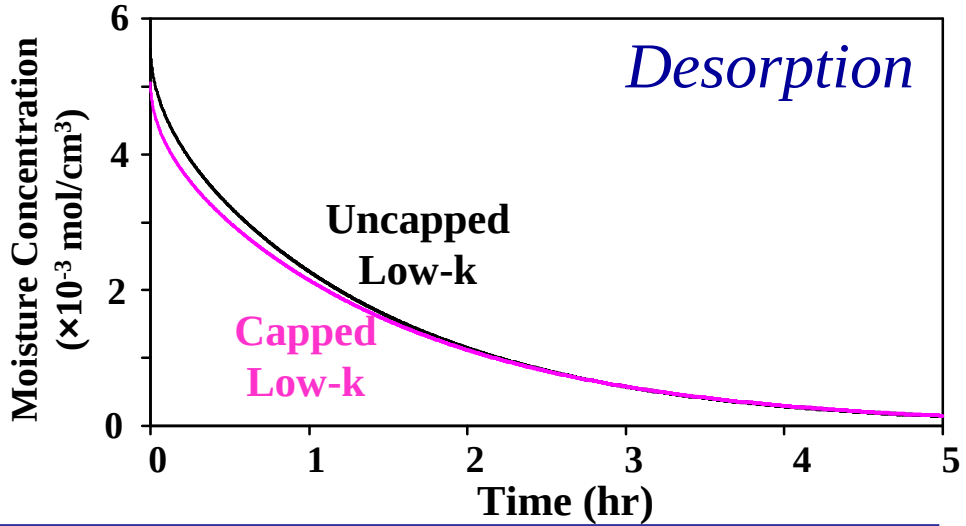
Purge purity enhances drying primarily at the late stages of desorption

Effect of Capping on Moisture Uptake/Removal

Temperature: 25°C; Challenge Concentration: 1500 ppm; Low-*k* Film Thickness: 100 nm; Cap Layer Thickness: 10 nm;

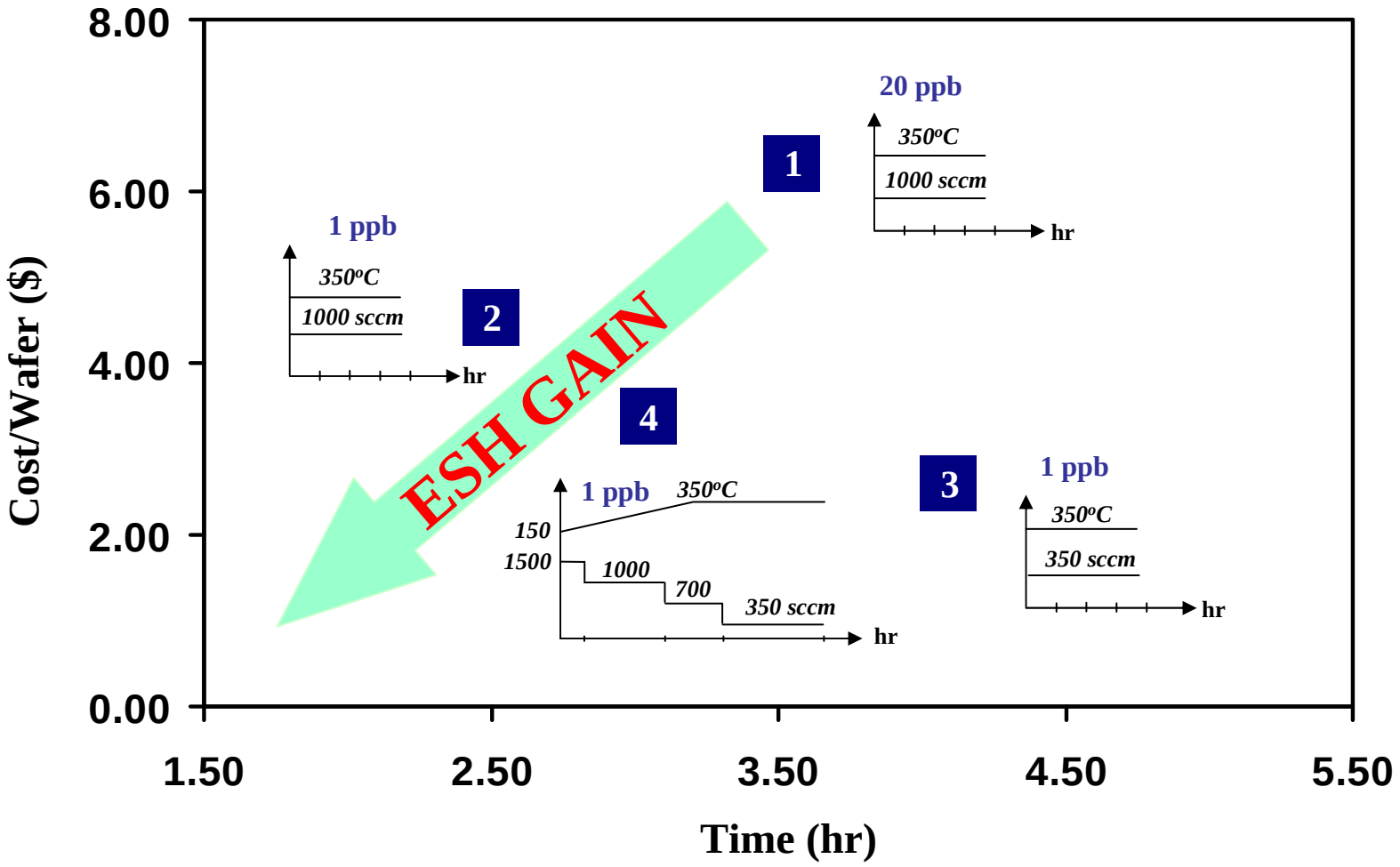
Ds (low-*k*)=Ds (cap)=7e-13 cm^2/s; Solubility (low-*k*) = 350,000; Solubility (cap) = 60 cm^3(gas)/ cm^3(solid);





ESH Gain in Optimizing the Purge Process

Challenge Conditions: 500 ppb moisture at 30°C for 1 hr. Purge for 80% moisture removal



Conclusions

- **Moisture removal is a slow and highly activated process.**
- **Porous low-*k* films has a higher uptake capacity as compared to SiO_2.**
- **There is an optimum extent of heating for enhancing the desorption.**
- **Purge gas purity primarily help the late stages of outgassing.**
- **Cap layer with low moisture solubility prevents moisture intrusion, but does not affect moisture removal.**
- **A process model is developed for data analysis and purge optimization. This model can be used to minimize the chemical and energy consumption, reduce the purge time, and increase the throughput.**

Acknowledgement

University of Arizona	
Dr. Farhang Shadman	**Advisor, Regents Professor in Chemical Engineering and Optical Sciences Department, U of A**
Dr. Roger Sperline	**Professor in Chemistry Department, U of A for helping with FTIR Analysis**
Dr. Ting Tsui	**Texas Instruments, Austin, Texas**
Sematech (Interconnect Group) and Texas Instruments (SiTD)	**For partial support of this research and providing samples**
SRC/Sematech	**Engineering Research Center for Environmentally Benign Semiconductor Manufacturing**

Low-Water and Low-Energy Rinsing and Drying of Patterned Wafers and Nanostructures

SRC: 425.021

Jun Yan, Kedar Dhane, Farhang Shadman
University of Arizona

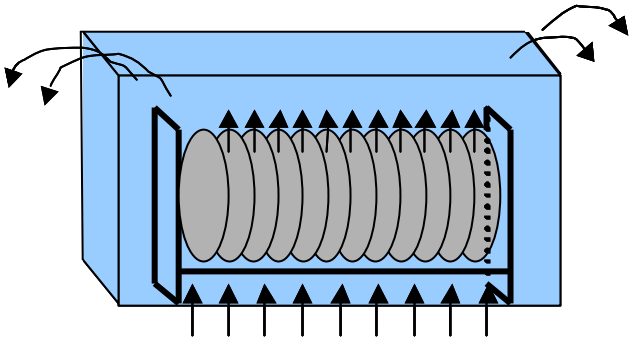
Bert Vermeire
Arizona State University

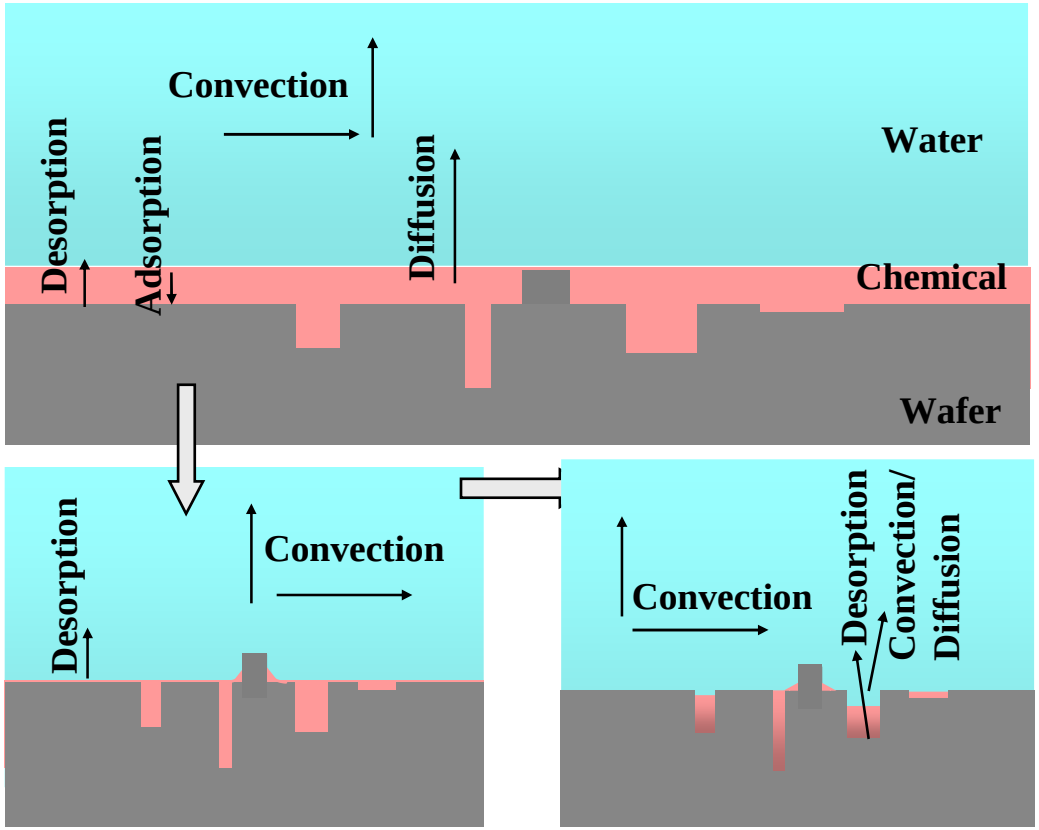
Joint work with Freescale:
Hsi-An Kwong, Tom Roche, Jack Shively

Industrial Liaisons: Marie Burnham (Freescale) and Douglas Goodman (Environmental Metrology Corp.)

Rinsing of Patterned Wafers

Over-Flow Rinse Process





- **Fundamentals of rinsing patterned wafers are poorly understood**
- **Key to low-water rinse is on-line metrology; technology not available presently**

Objective and Method of Approach

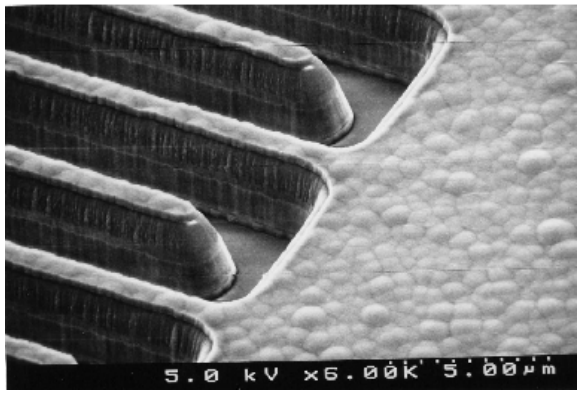
Objective:

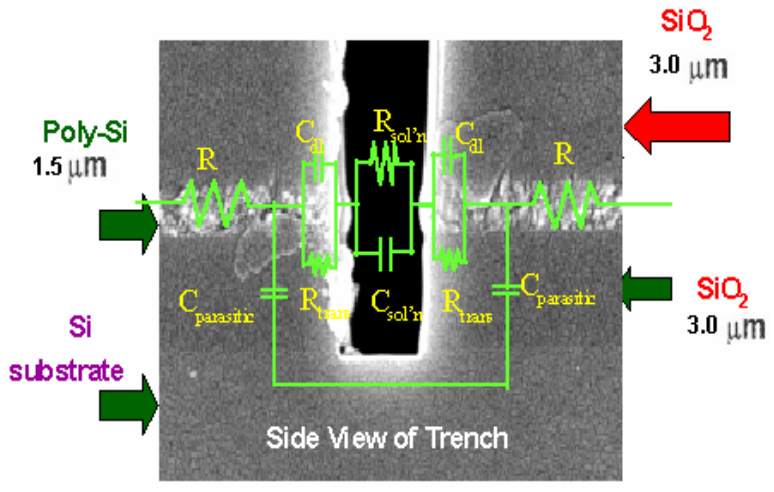
- Develop technology for reducing water, energy, and chemicals used during cleaning of patterned wafers, without sacrificing the cleaning performance

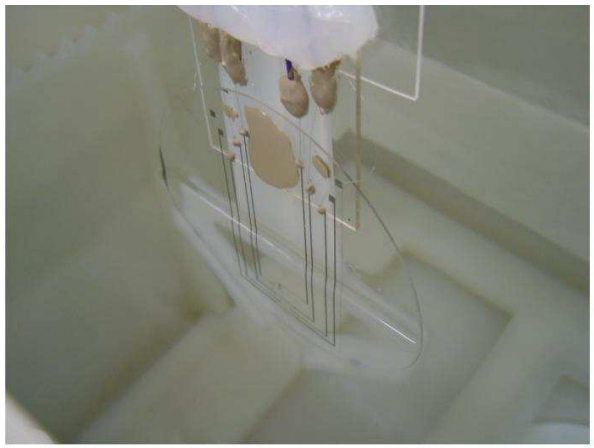
Method of Approach:

- Develop a novel sensor for in-situ and real-time measurement of residual contamination in microstructures during wafer cleaning, rinsing, and drying
- Develop new cleaning methods, using sensor measurements and process modeling

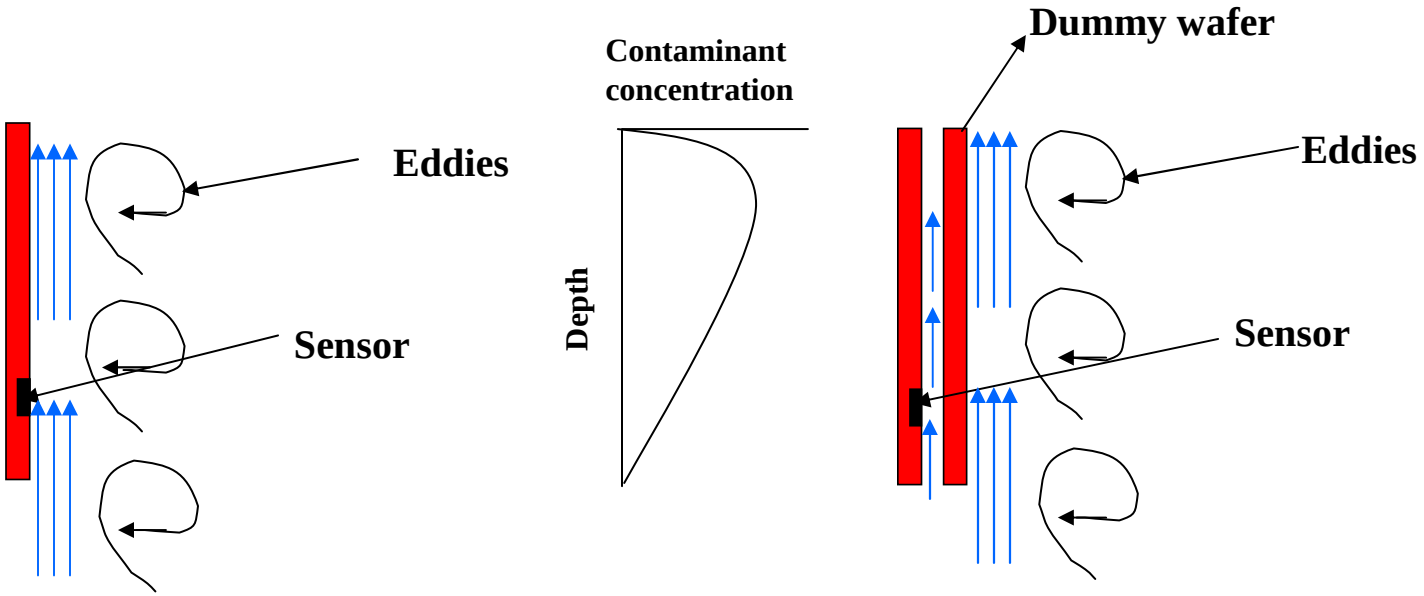
Novel Electro-Chemical Residue Sensor (ECRS)







Experimental Configurations

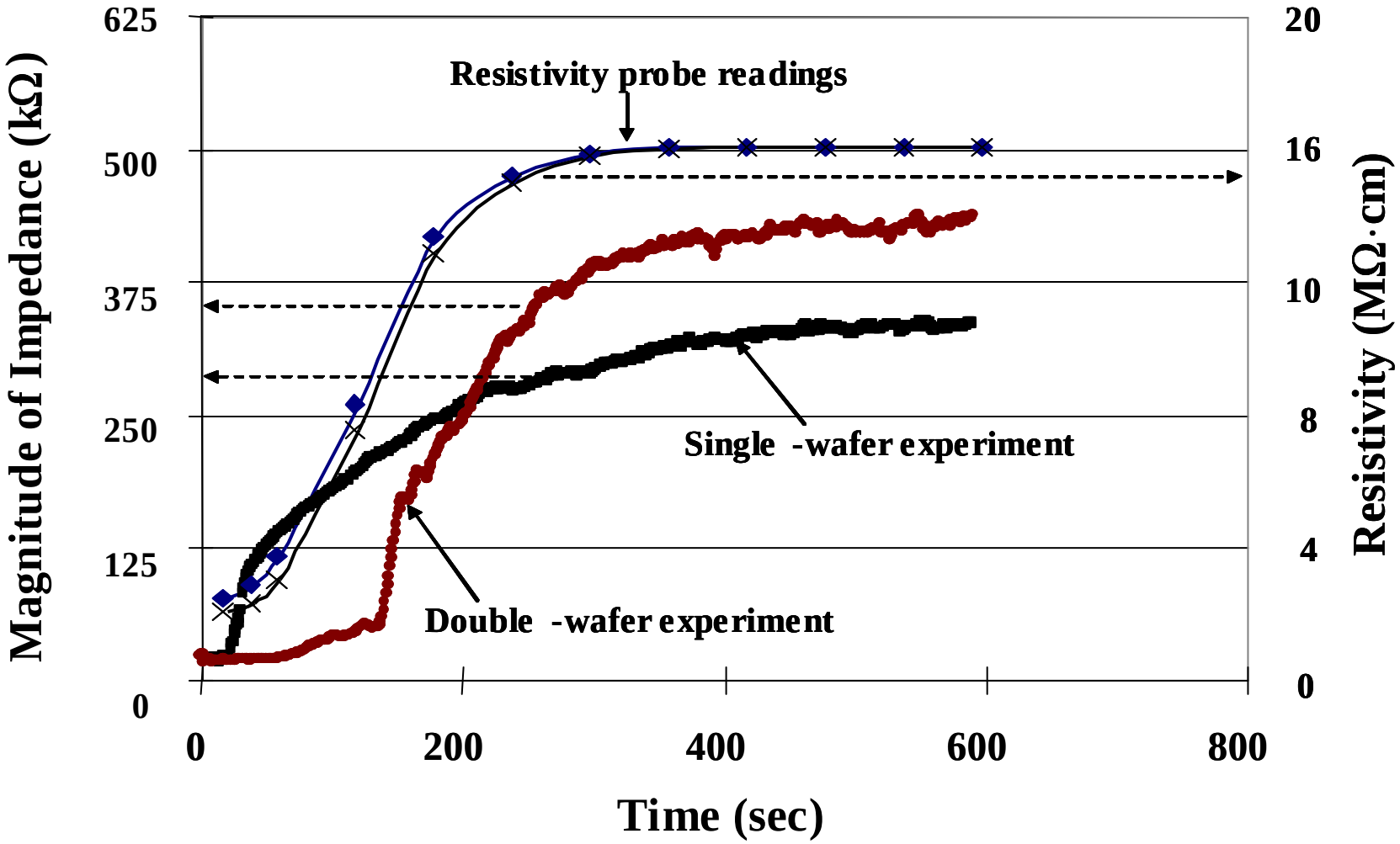


- Single-wafer configuration
- High convective and turbulent flow
- Good mixing

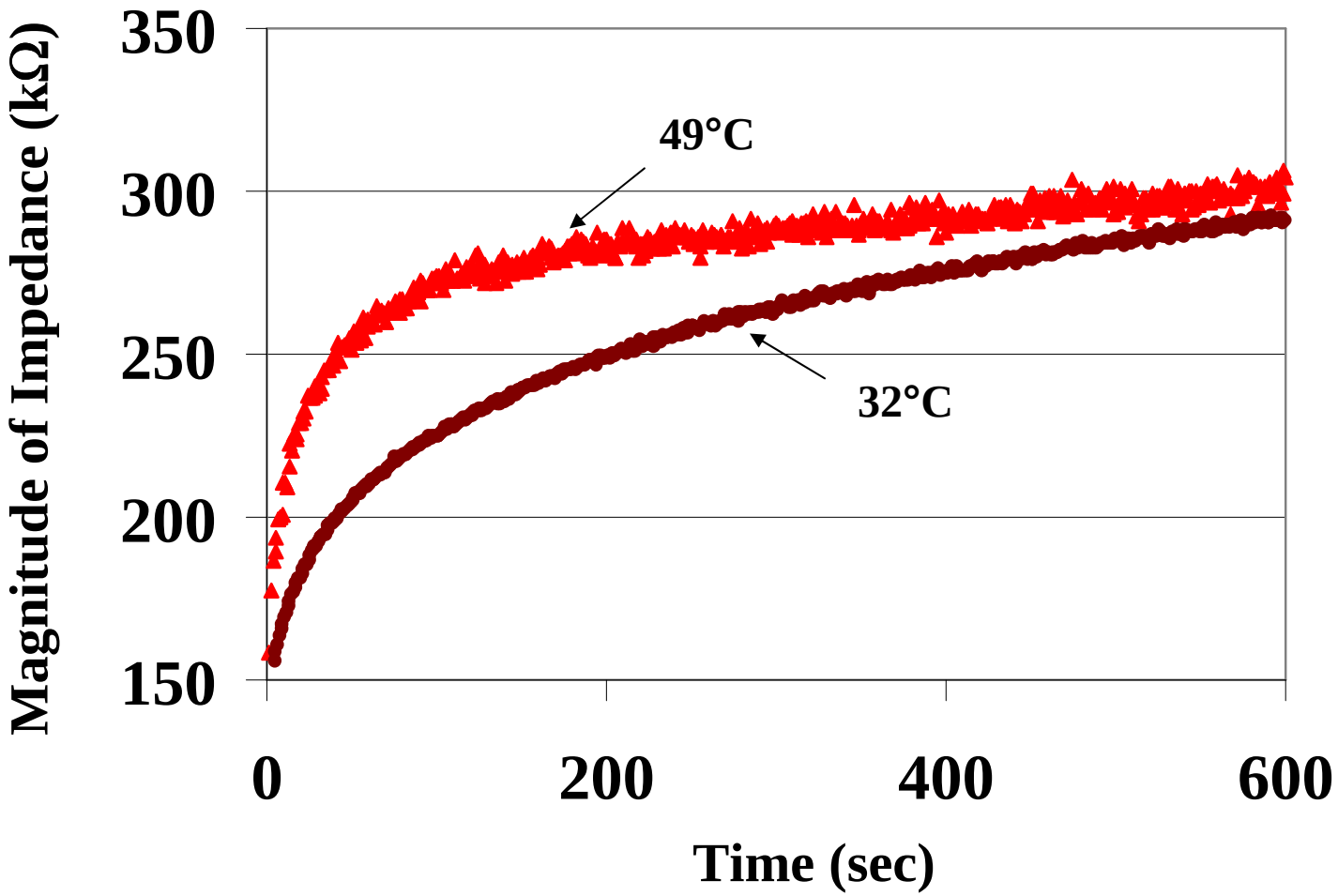
- Multi-wafer configuration
- Slow laminar flow between wafers
- Poor mixing

Sensor Performance and Capabilities

H_2SO_4 Rinsing



Effect of Temperature



Comprehensive Simulation of Rinse Process

Transport equation for H^+, OH^-, NH_4^+ and SO_4^{-2} :

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

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:

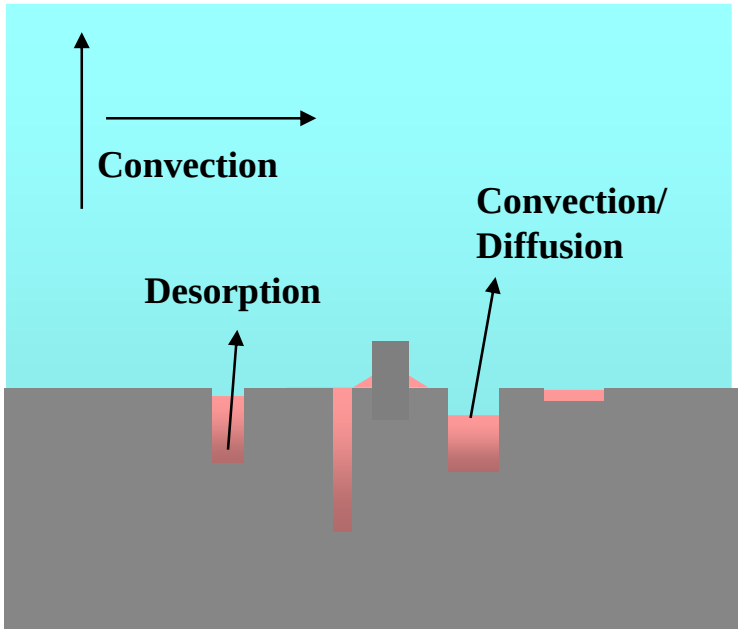
$$\rho = F \sum_i z_i C_i$$

Ohm's law:

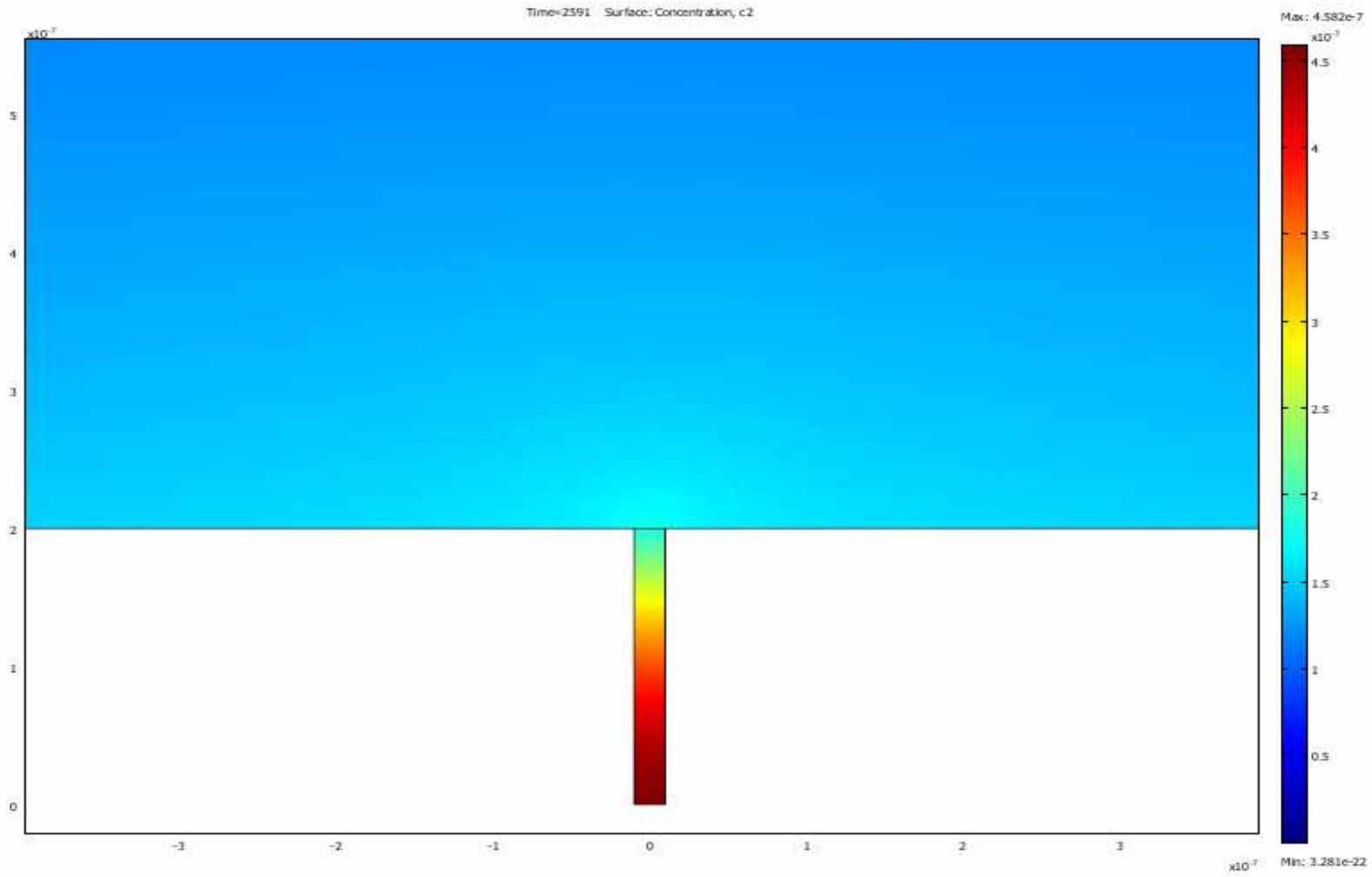
$$J = \sigma E \qquad \nabla E = 0$$

where electrical conductivity:

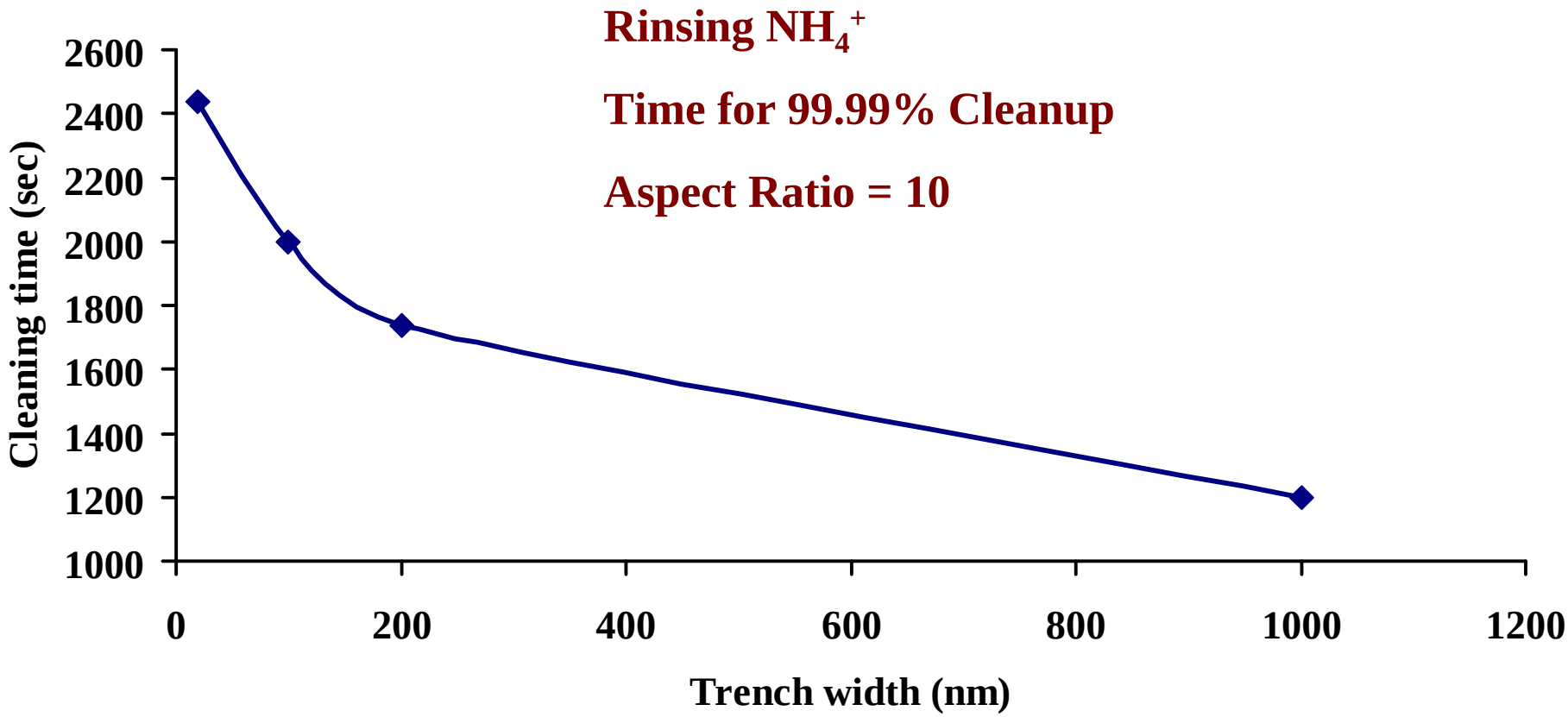
$$\sigma = \sum_i \lambda_i C_i$$



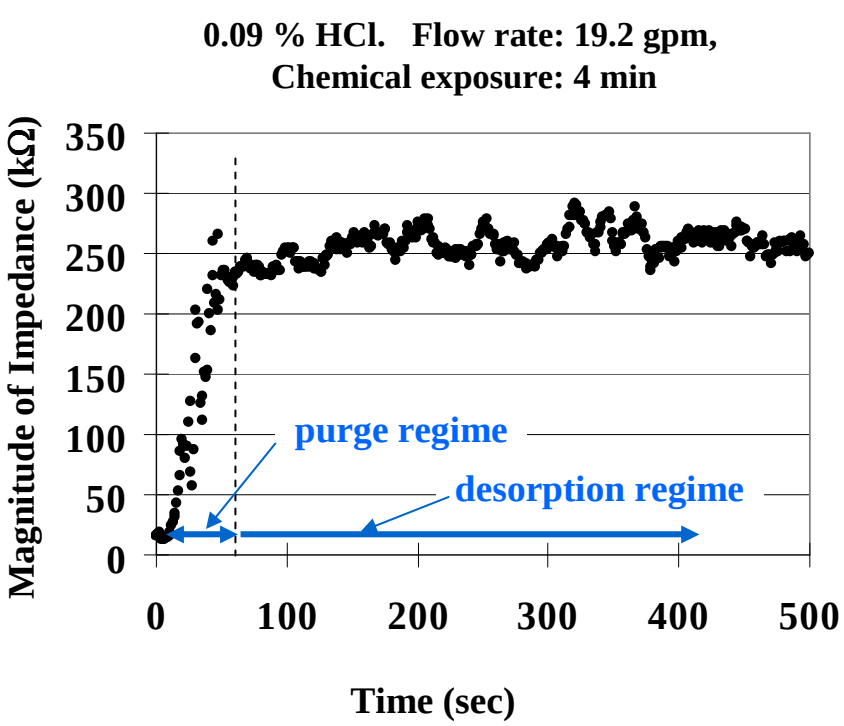
NH_4^+ Rinse out of 20nm Trench

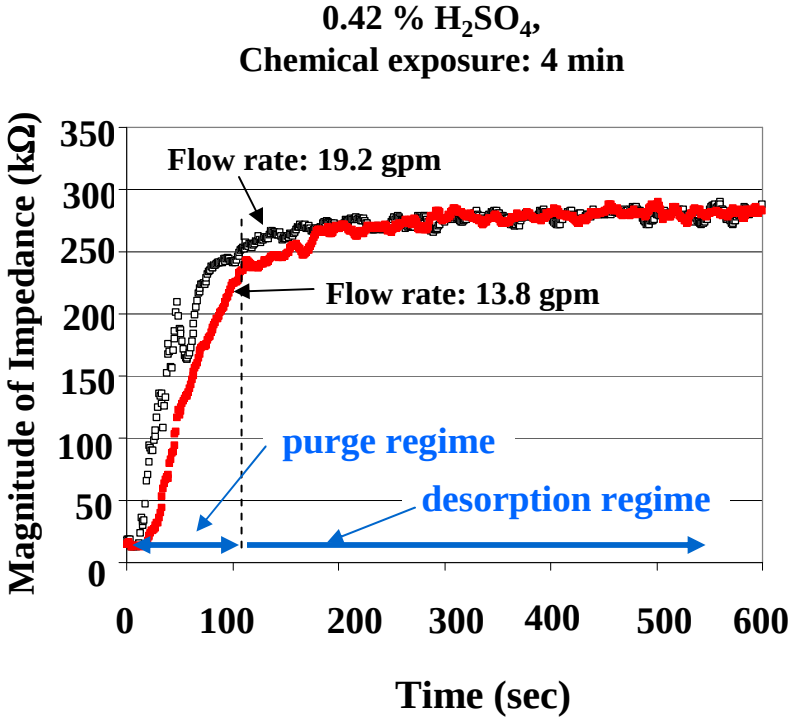


Effect of Feature Size on Cleaning



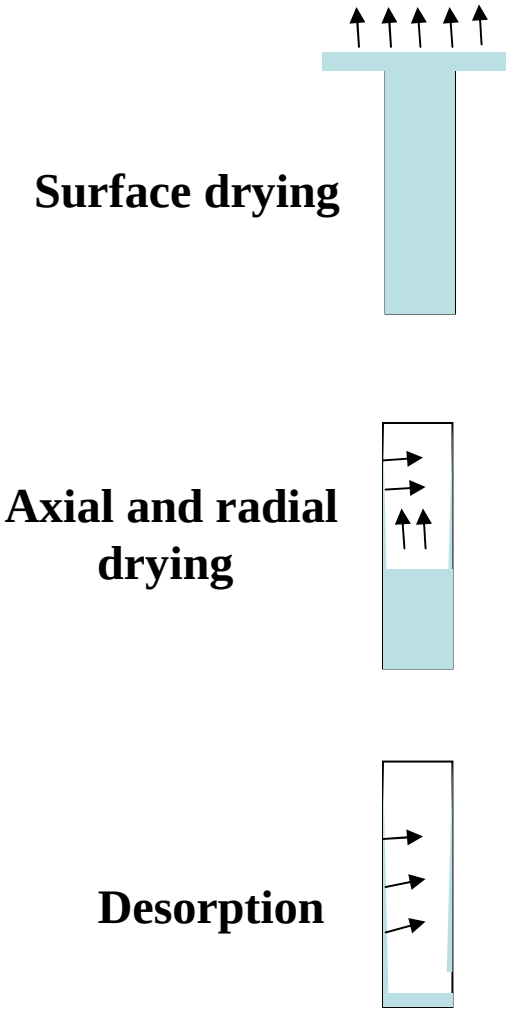
Rinse Optimization Using ECRS

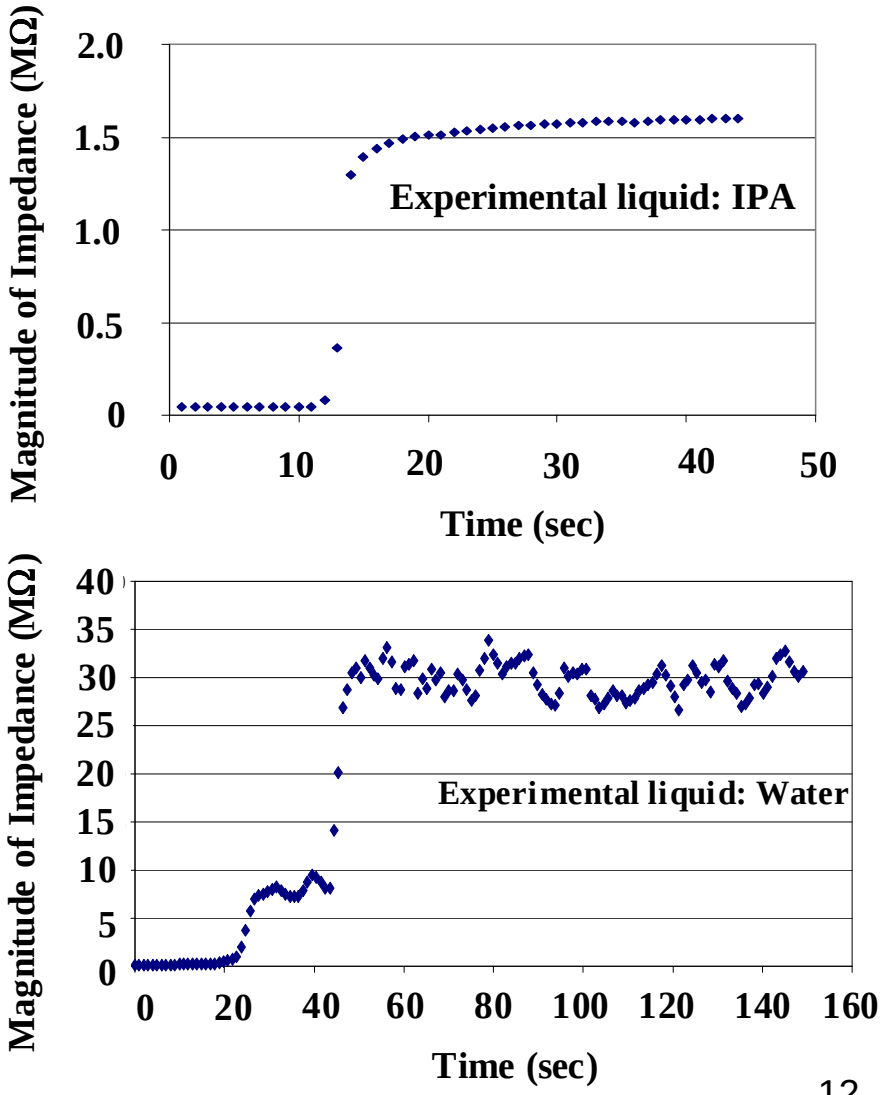




- **Transitions from *purge regime* to *desorption regime***
- **Strategy: Optimum change in flow rate and temperature, based on the transition, detected by ECRS**

Material/Energy Use Reduction during Drying





Summary and Conclusions

- Improved the ECSR design for better S/N and direct tool integration
- Developed and verified a comprehensive process model; the model is applicable to rinsing and cleaning of fine structures on patterned wafers.
- Used ECRS measurements and process modeling to develop rinse processes that require significantly less water and energy.
- Have been working with Freescale team towards developing a new rinse recipe based on staged flow rate.
- Based on preliminary tests, concluded that water use reduction of 40% (cold rinse) and 50% (hot rinse) is achievable.

Future Plans and Technology Transfer

- **Investigate the application of ECRS technology for other applications (drying and post-etch cleaning of sidewalls)**
- **Continue joint work with Sematech and the Freescale task force to validate and implement the project results.**
- **Commercialize the ECRS through joint work with Environmental Metrology Corp.**
- **Continue collaboration and technology transfer that has been initiated with other members (e.g. Samsung)**

Acknowledgement

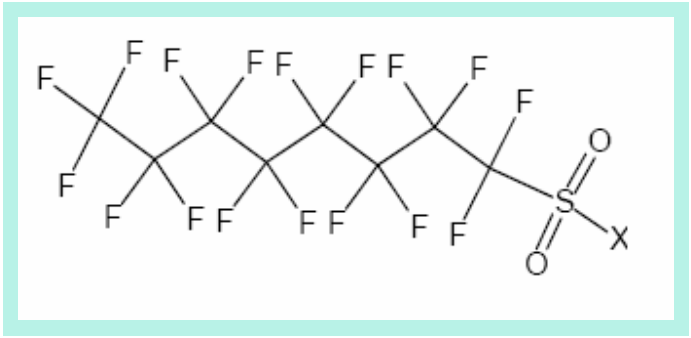
- **Primary Funding by SRC/Sematech ERC**

- **Partial Funding by Environmental Metrology Corp**

- **Technology Transfer and Industrial Liaisons:**
  - **Marie Burnham (Freescale Semiconductor, Inc.)**
  - **Douglas Goodman (Environmental Metrology Corp.)**

- **Fabrication Assistance:**
  - **MFC (University of Arizona)**
  - **CSSER (Arizona State University)**
  - **SNF (Stanford University)**

Thrust C- 425.015 - Reductive Dehalogenation of Perfluoroalkyl Surfactants in Semiconductor Effluents



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

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

PFOS - Difficult for Treatment

Aerobic biotreatment: **Ineffective**

Sinclair & Kannan, EST, in press

Advanced oxidation treatment: **Ineffective**

O_3,O_3/UV,O_3/H_2O_2, H_2O_2/Fe^{2+} (Fenton's reagent)

Schroeder & Meester, J. Chromatog.A, 2005, 1082:110

Activated carbon: **Moderate effectiveness**

(Sierra et al. unpublished report, 2006)

Membrane processes: **Effective, but expensive**

Tang et al. EST, 2006, 40:7343

Disposal of concentrate!!

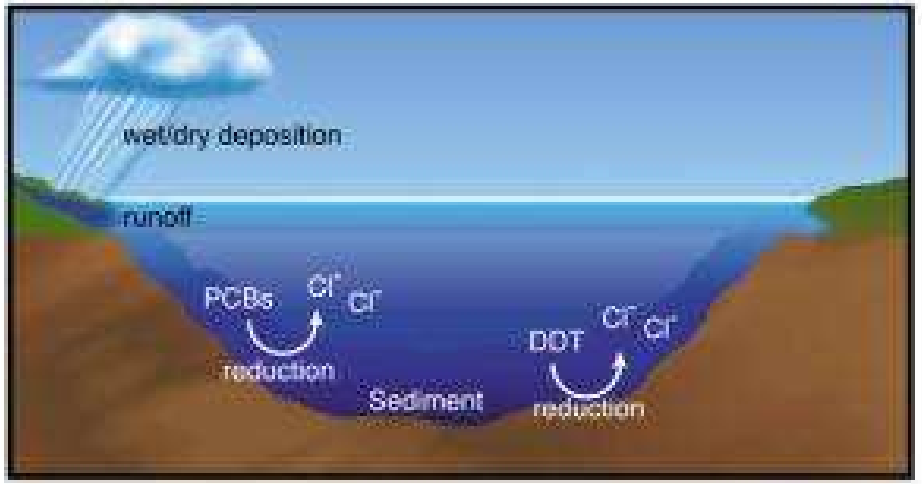
Objectives

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

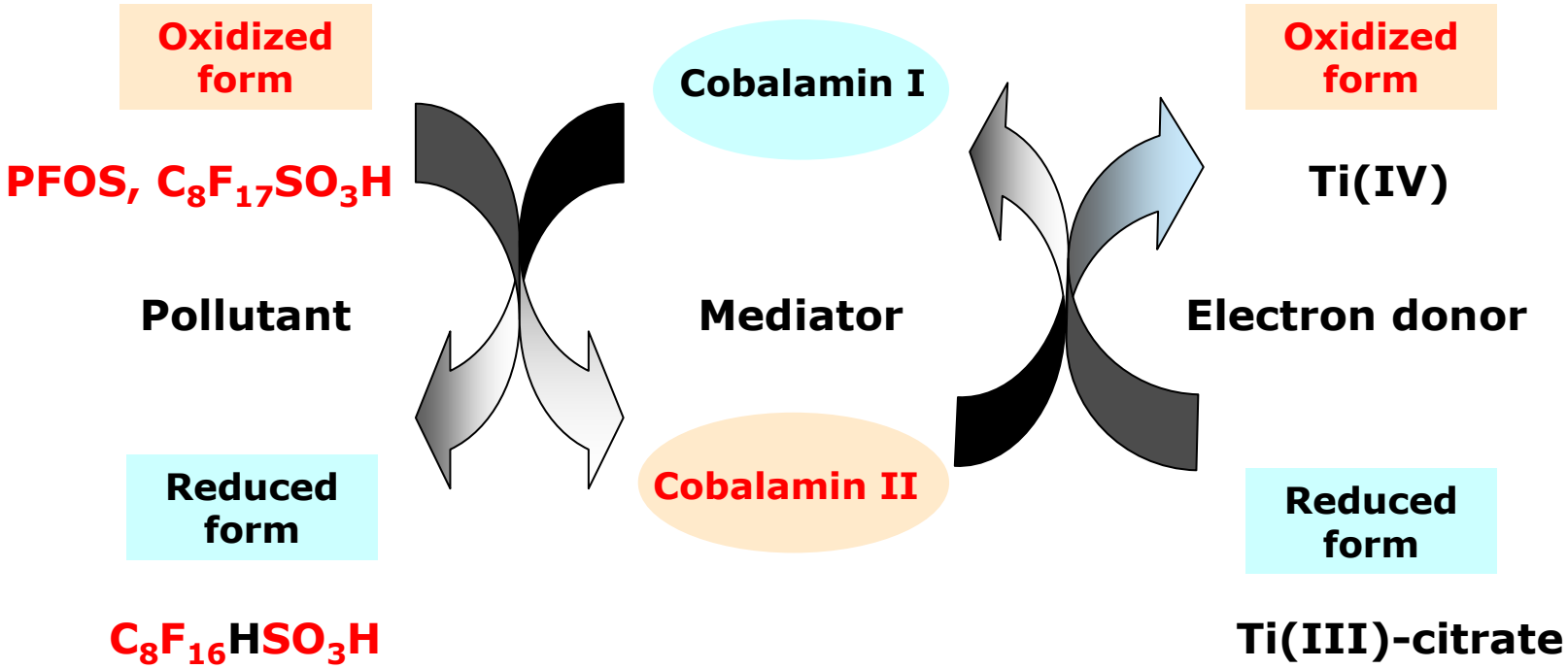
Reductive Dehalogenation

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

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



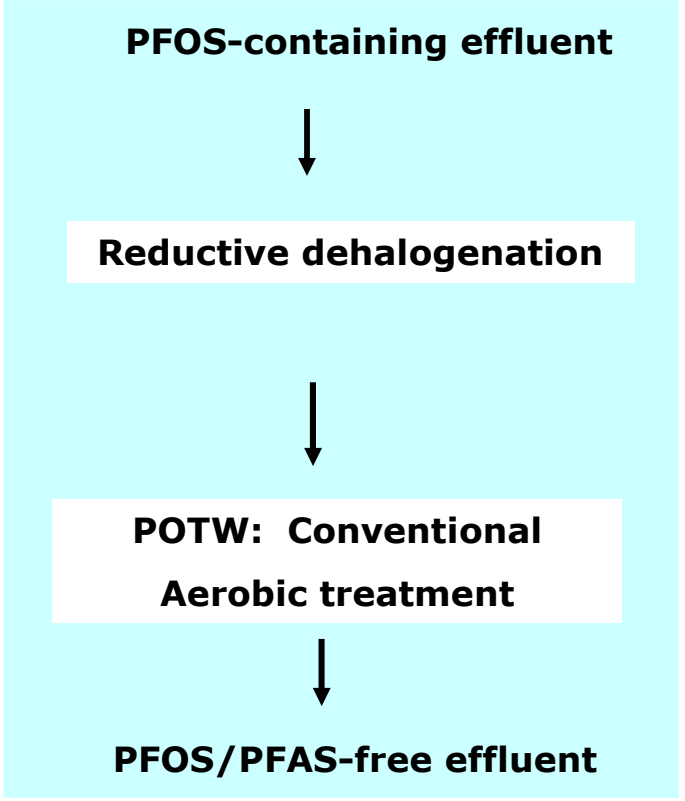
Mechanism of Reductive Dehalogenation



EHS Benefits

- Reductive dehalogenation of perfluorinated compounds is expected to lead to products amenable to biodegradation, which can be removed effectively in existing biological treatment infrastructure (eg. municipal wastewater treatment plants).

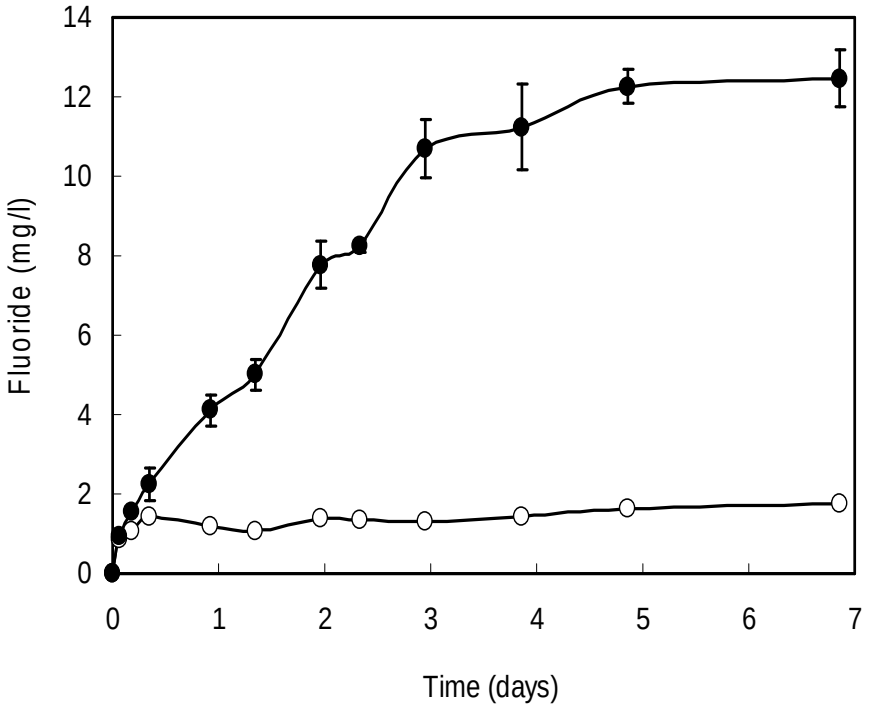
- Compound mineralization is advantageous over alternative techniques (e.g. adsorption, membrane processes, ion exchange) which generate residuals and brines.



Reductive Dehalogenation of PFOS by Vitamin B_{12} and Ti(III)-citrate

Time course of fluoride release in control samples (○) and treatment samples (●).

Biomimetic reductive dehalogenation of PFOS isomes with vitamin B12 (260 µM) and Ti(III) citrate (36 mM) in control samples (PFOS + Ti(III) citrate) and treatment samples (PFOS + Ti(III) citrate + Vitamin B_{12}). Samples were incubated at 70ºC and pH 9.0.

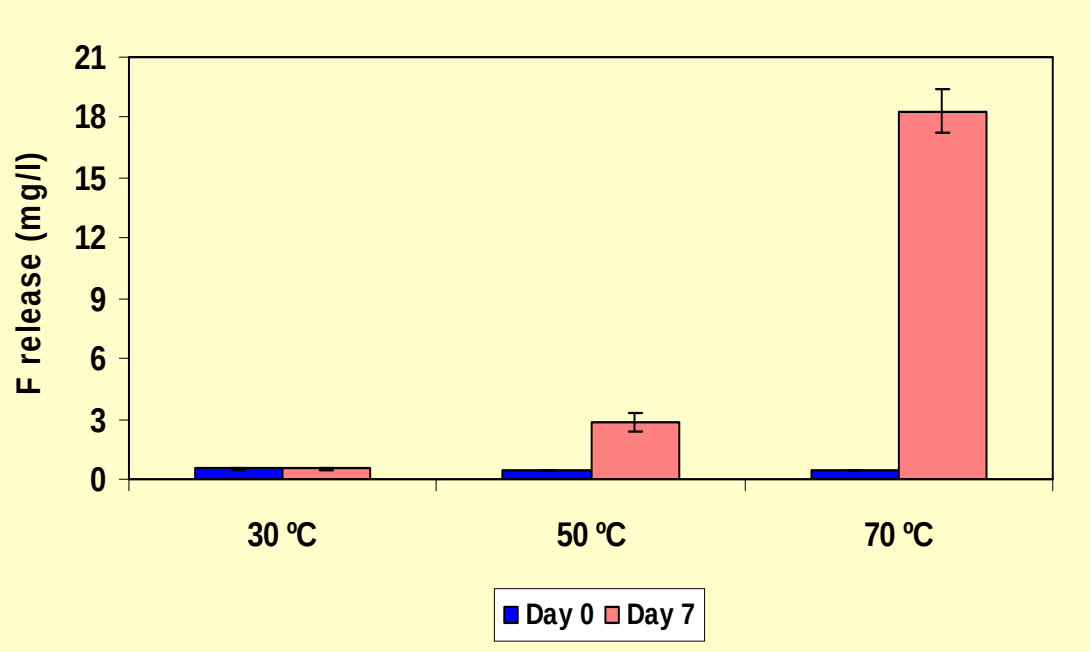


Reductive Dehalogenation of PFOS by Vitamin B_{12} and Ti(III)-citrate

- Reductive dehalogenation of PFOS did not occur in assays with cobalt(II) in lieu of vitamin B_{12}.
- Rate of PFOS degradation increased considerable with increasing temperature.
- Increase of the reaction pH from 7.5 to 9.0 also had a positive impact on the rate of PFOS defluorination, although less marked compared to the results obtained at high temperature.
- Vitamin B_{12} concentration affects rates.

Reductive Dehalogenation of PFOS

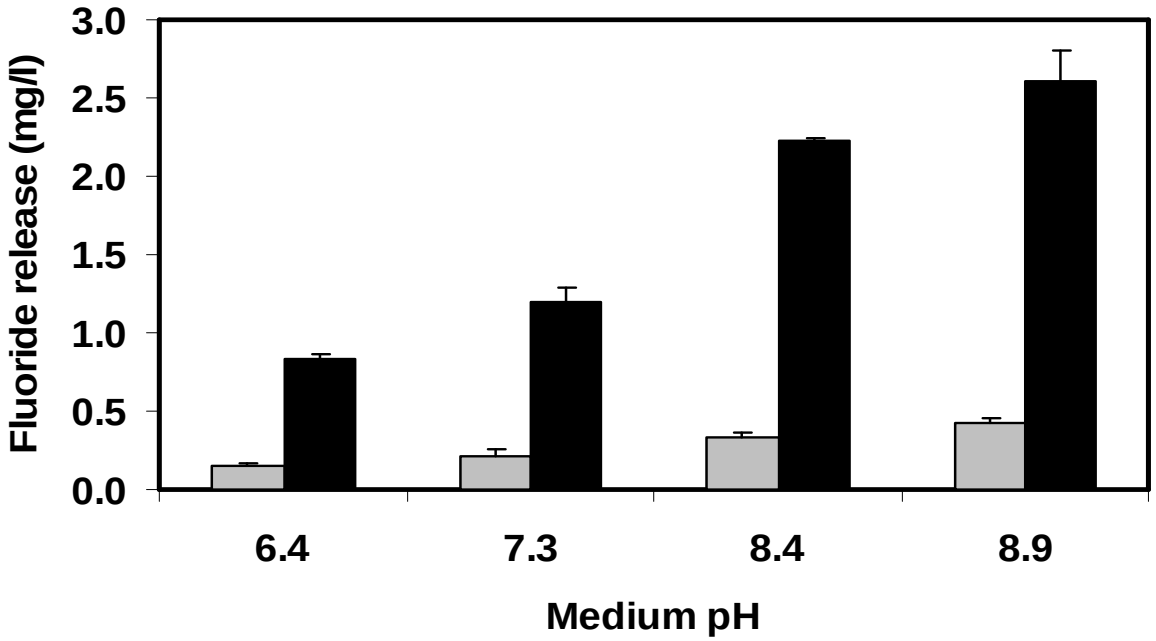
Effect of Temperature



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

Reductive Dehalogenation of PFOS

Effect of pH

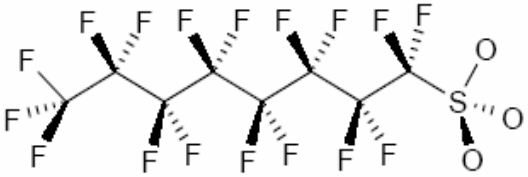


Gray bars = Controls with PFOS + Ti(III);
Black bars = Complete treatments with PFOS + Ti(III) + vitamin B12.

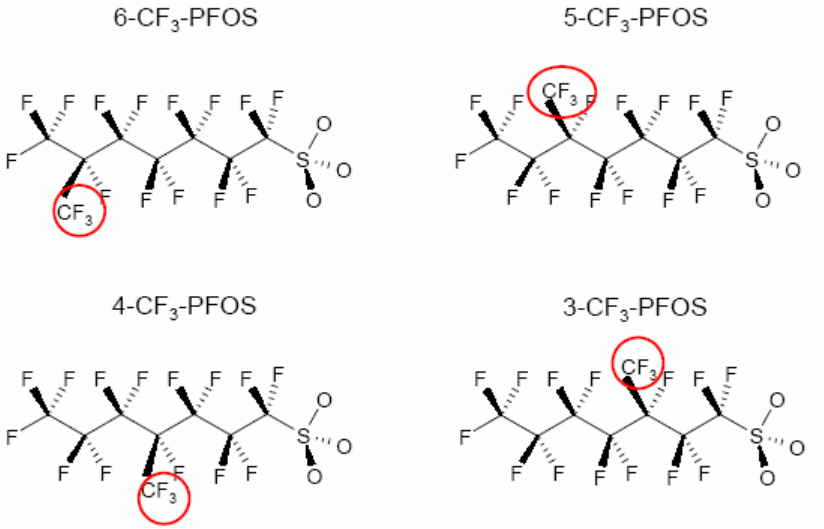
PFOS Isomers:

Linear *vs.* Branched PFOS

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

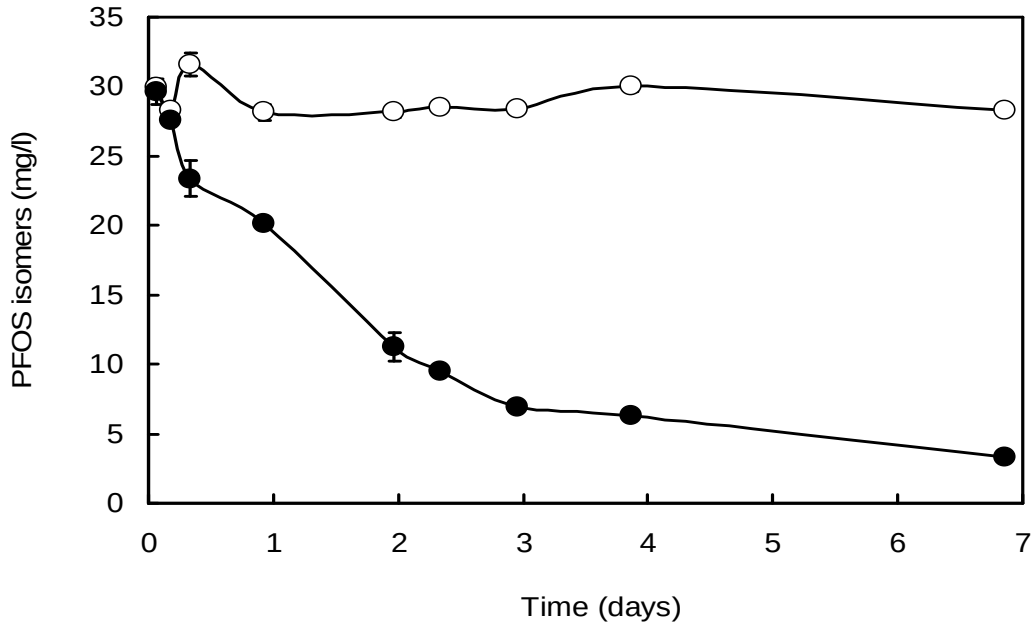


Linear isomer



Branched isomers

Biomimetic Reductive Dehalogenation of Branched PFOS Isomers



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

(o) **Control** (PFOS + Ti(III)-citrate)

Samples were incubated at 70ºC and pH 9.0

Conclusions

- PFOS is susceptible to biomimetic reductive dehalogenation by Ti(III) citrate/vitamin B_{12}.
- Important implications: partially defluorinated PFOS derivatives, comparable to the products expected from reductive defluorination, are susceptible to biodegradation by aerobic bacteria.
- These findings suggest that microbial reductive defluorination of PFOS might be possible.
- The observation that branched PFOS isomers are more susceptible to attack than linear PFOS provide clues for the design of perfluorinated chemicals more prone to degradation in the environment.

Industrial Collaboration/ Technology Transfer

Industrial Liaisons:

Walter Worth - Sematech

Tim Yeakley – TI

Disclosures:

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

Future Plans

- Obtain sediments from PFOS-impacted sediments for testing reductive defluorination by microorganisms
- Characterization of organic intermediates from biomimetic dehalogenation of PFOS.
- Study the mechanisms of biomimetic dehalogenation.
- Investigate the microbial degradation of partially defluorinated organics.

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

Task # 425.018 / Thrust C

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

Research Objectives

- Determine the feasibility of electrochemical destruction of PFAS in dilute aqueous waste streams.
- Determine the degree of electrolysis required to generate products that are readily biodegraded in municipal wastewater treatment plants.
- Develop an adsorptive method using hydrophobic zeolites or anion exchange resins for concentrating PFAS compounds from dilute aqueous solutions.

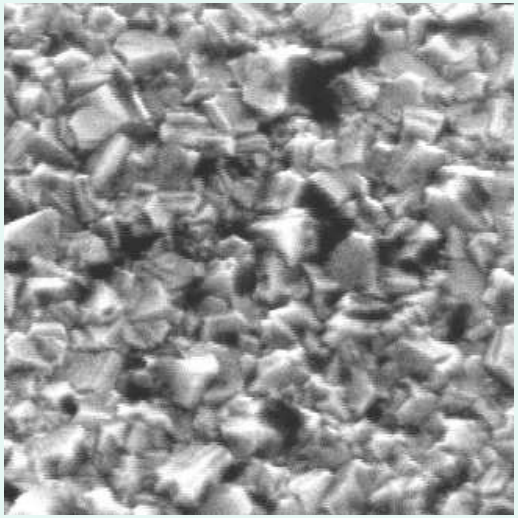
ESH Impact / ESH Metrics

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

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

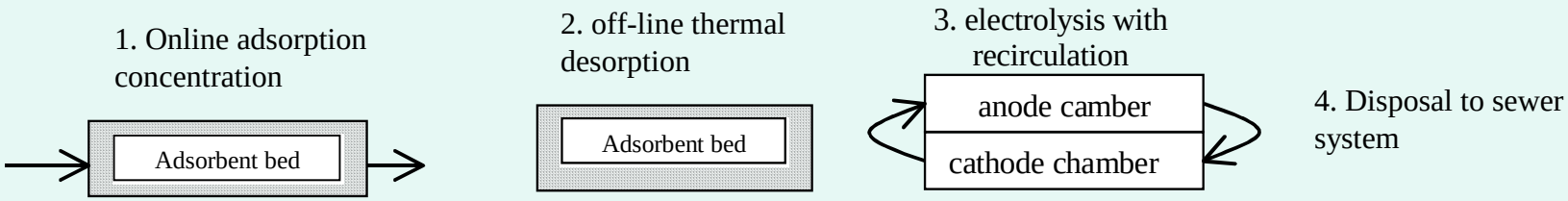
Boron-Doped Diamond Film (BDD) Electrodes

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



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

Proposed Treatment Scheme



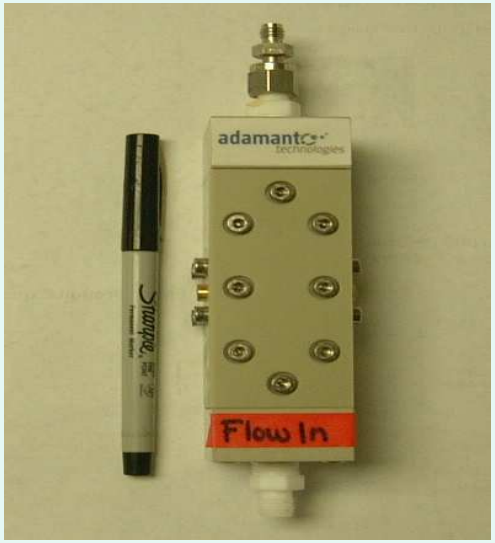
Multi-step treatment scheme:

1. Concentrate PFAS from dilute aqueous solutions on an adsorbent.
2. Thermally 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) in batch reactor.

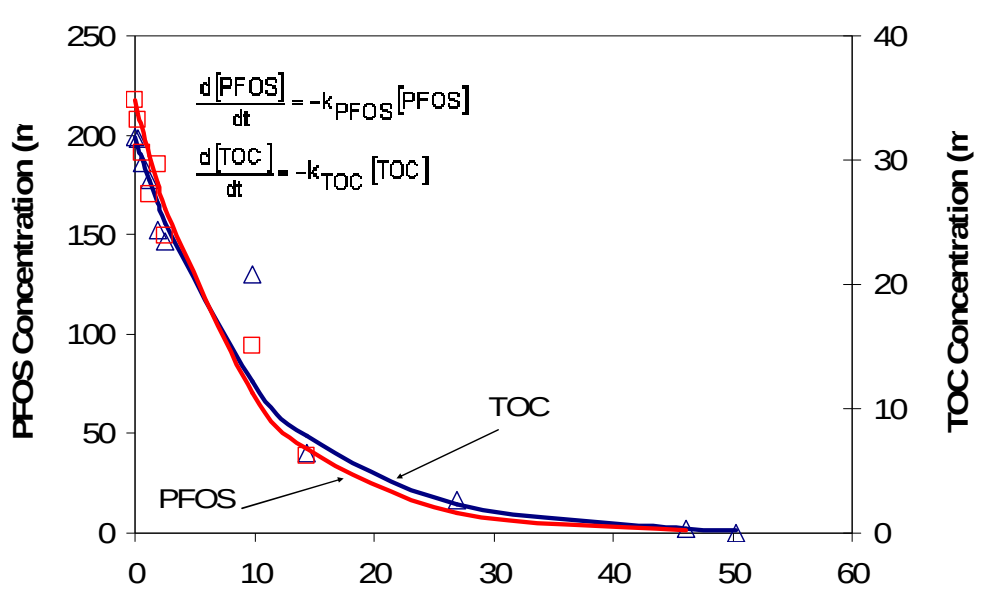
- no mass transfer limitations
- electrode surface area = 1 cm^2
- solution volume = 350 mL
- a_s = 0.00286 cm^2/mL



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

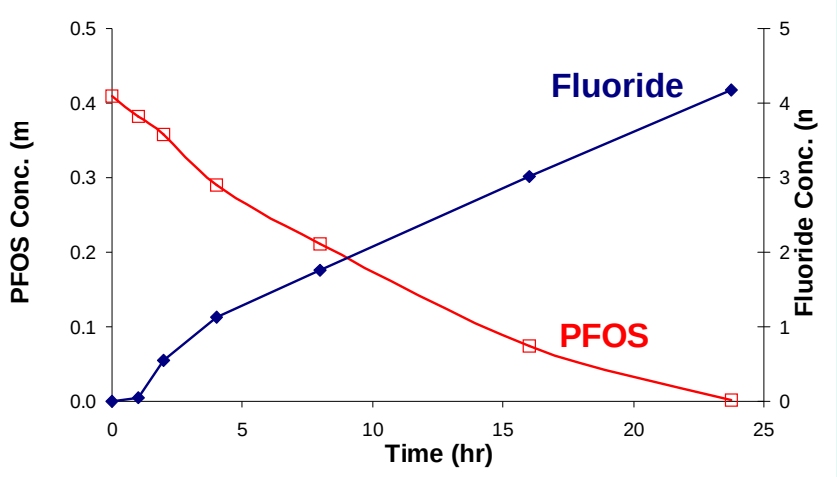
Experimental Results

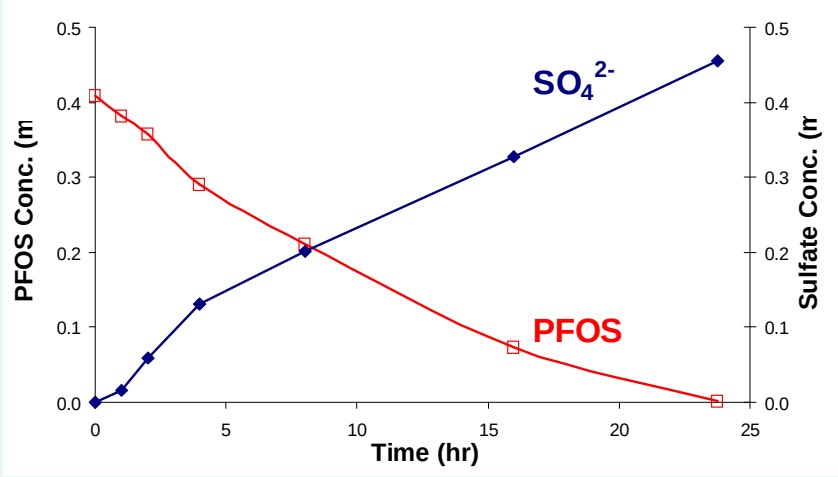


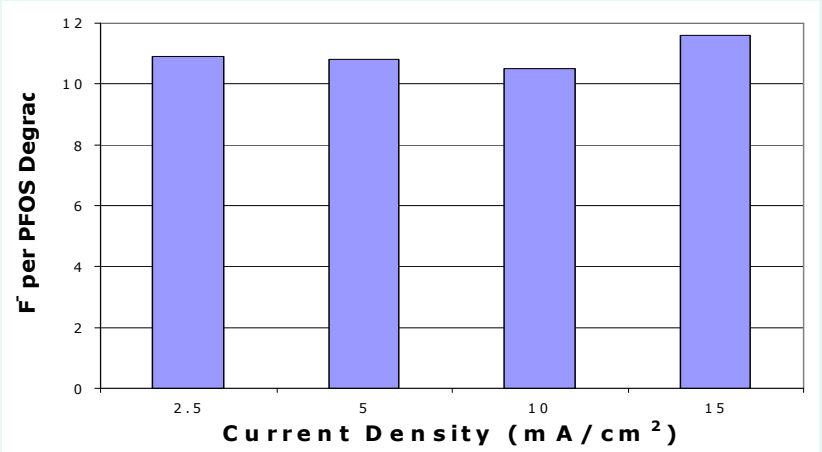
PFOS and total organic carbon concentration (TOC) in flow-cell operated at a current density of 15 mA/cm^2.

- PFOS can be rapidly removed from water
- Reaction rates are first order in concentration
- Treatment half-life of less than 10 minutes
- No build-up of reaction products

Reaction Products







Only trace quantities of:

1. Perfluorooctanoic acid
2. Perfluoroheptanoic acid
3. Perfluorohexanoic acid

Proposed Reaction Sequence

PFOS PFOA

$$C_8F_{17}SO_3H + 3H_20 \rightarrow C_7F_{15}CO_2H + SO_4^{2-} + 4H^+ + 2F^- + 2H_2$$

$$C_7F_{15}CO_2H + 2\ H_2O \rightarrow C_6F_{13}CO_2H + CO_2 + 2H^+ + 2F^- + H_2$$

$C_5F_{11}CO_2H$

$C_4F_9CO_2H$

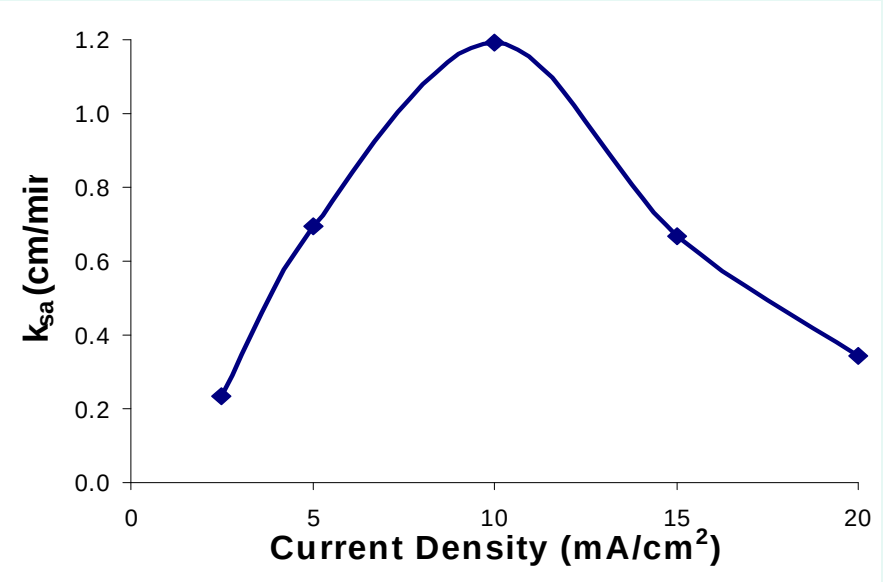
$C_3F_7CO_2H$

Pentafluoropropionic acid $C_2F_5CO_2H$ Volatile species

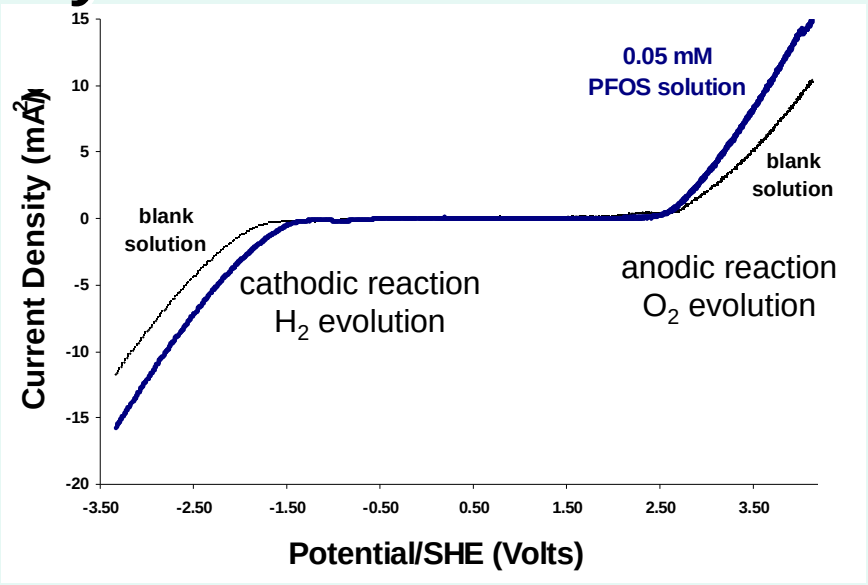
Trifluoroacetic acid CF_3CO_2H Volatile species

- Fluoride mass balance of 11 F^- released per PFOS degraded suggests that volatile species are lost from solution.
- No observation of intermediate products suggests near complete degradation in a single interaction with the electrode surface.

Effect of Current Density on Reaction Rates



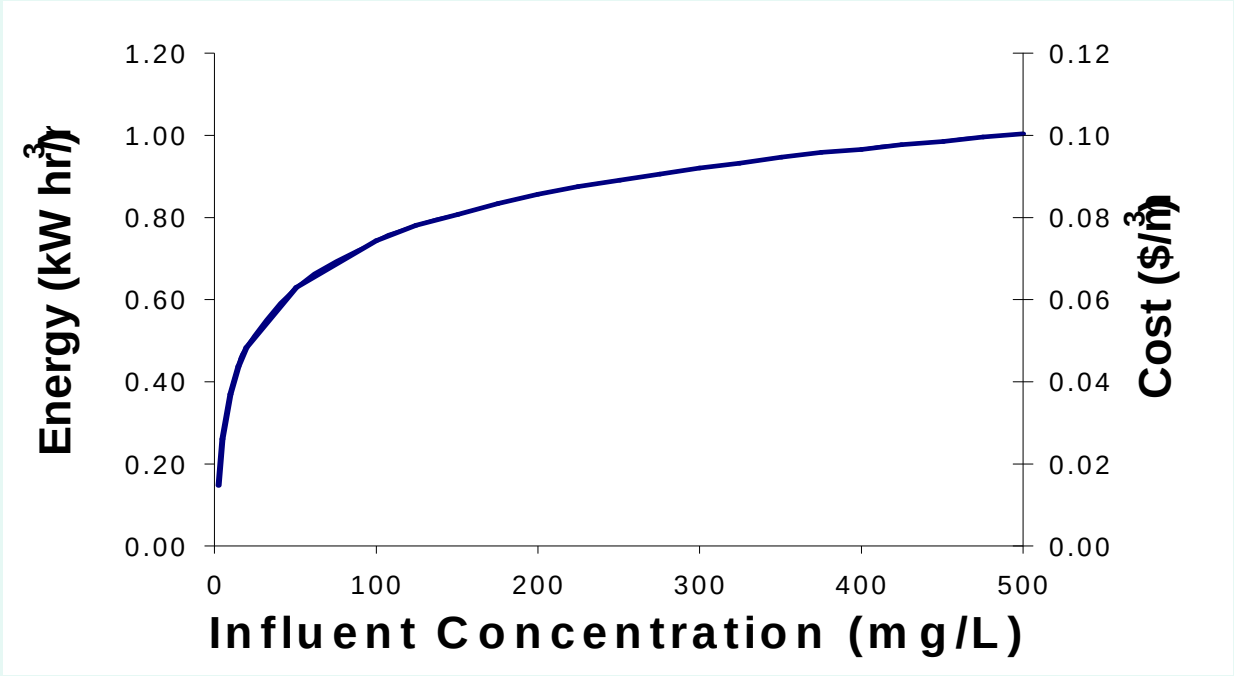
The effect of current density on the RDE surface area normalized rate constants (k_{sa}) for PFOS oxidation.



Linear sweep voltammograms from RDE in blank electrolyte and PFOS solutions.

- Oxygen gas bubbles at high current densities reduce the wetted surface area of the electrode and interfere with PFOS oxidation.
- Maximum practical reaction rates are limited by the competing reaction of oxygen evolution.

Treatment Costs



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 concentration. Costs based on flow-cell operated at a current density of 20 mA/cm^2.

- Electrical power costs are small compared to other treatment methods.
- Capital costs for a 10 liter per minute flow-cell are ~$5000.

Conclusions

1. **Developed analytical methods for measuring PFAS compounds.**

2. **Demonstrated that PFOS can be rapidly oxidized at BDD electrodes.**

3. **Determined the products of PFOS oxidation.**

Future Plans

1. **Determine the optimal operating conditions for oxidation of other PFAS compounds.**

2. **Determine the most effective adsorbents for PFAS concentration.**

3. **Determine the biodegradability of PFAS oxidation products**

4 **Pilot test treatment scheme on real process wastewaters.**

Acknowledgements

- Lily Liao and Arpad Somogyi
- NSF/SRC ERC 2001MC425
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- Petroleum Research Fund 43535-AC5

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Thomas P. Diamond	IBM
Jim Jewett	Intel
Laura Mendicino	Freescale Semiconductor

Novel Materials and Device Structures for High Mobility MOSFETs and Interconnects

Krishna Saraswat

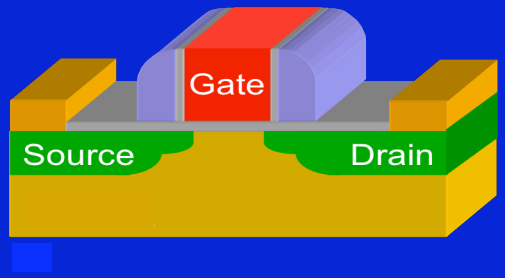
Department of Electrical Engineering
Stanford University, CA, USA

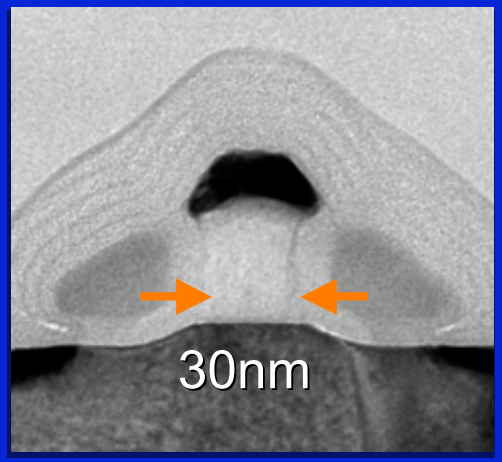
Outline

- Need for high mobility channel
- Ge PMOS
- Is high mobility the only criterion for high performance?
- NMOS Ge or III-V ?
- Future interconnect technologies
- Summary

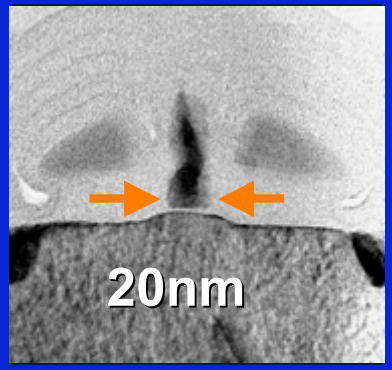
Scaling of Si Bulk MOSFET

***Source*: Intel**

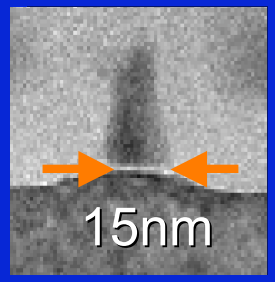




65nm process
2005 production

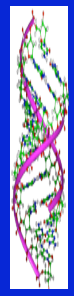


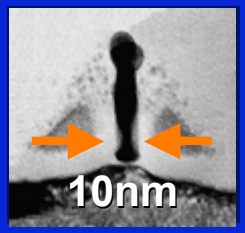
45nm process
2007 production



32nm process
2009 production

DNA is 15 nm wide



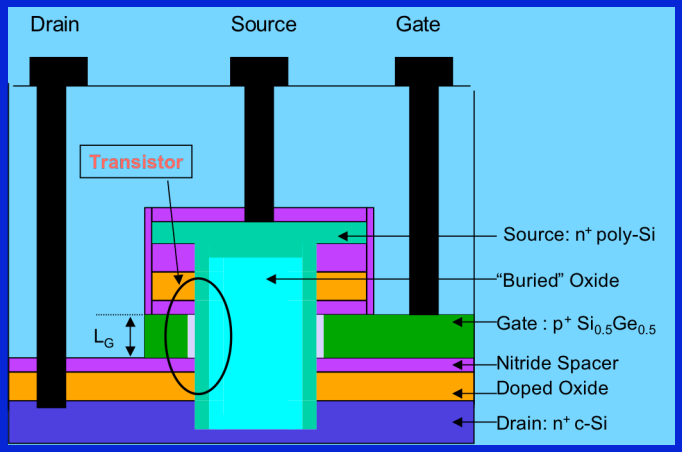


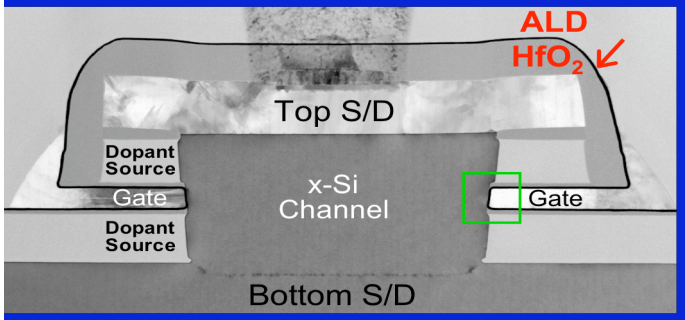
22nm process
2011 production

- Although devices can be scaled but performance is not improved
- Leakage keeps increasing
- Need new device structures for better electrostatic control

Non Planar MOSFETs

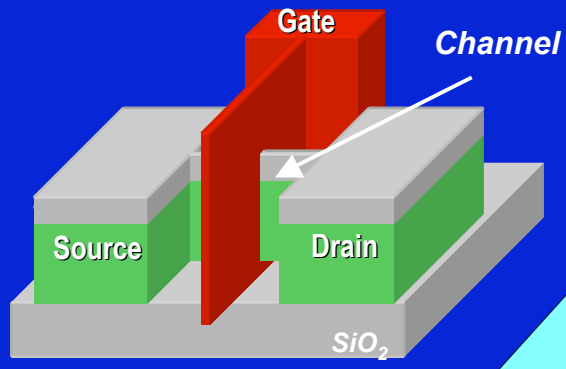
Vertical FET

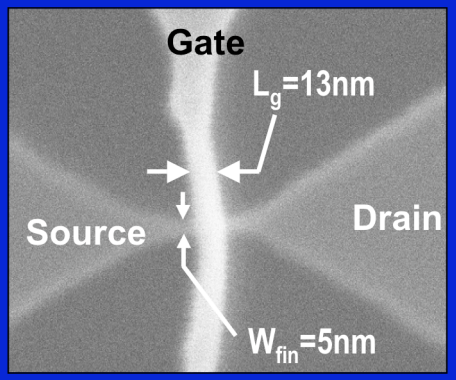




Stanford

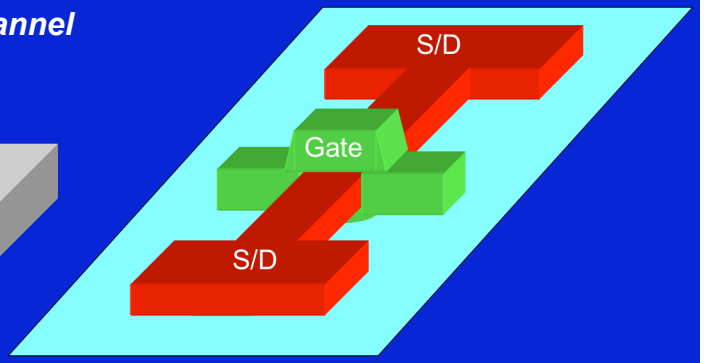
Double Gate FinFET

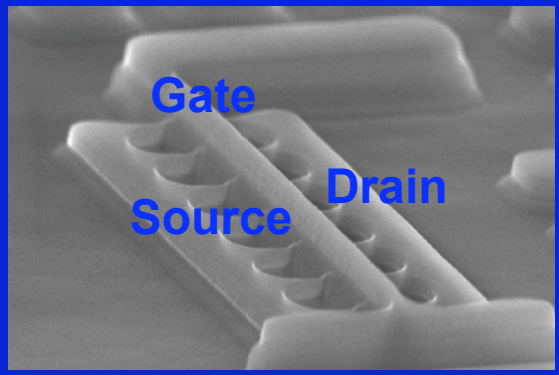




UC Berkeley

Tri Gate FET

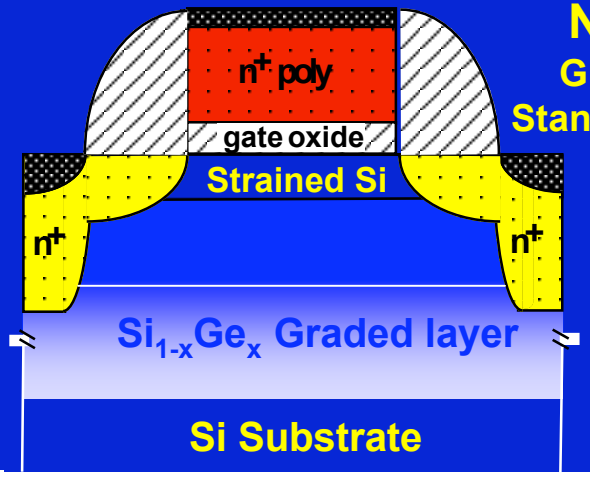




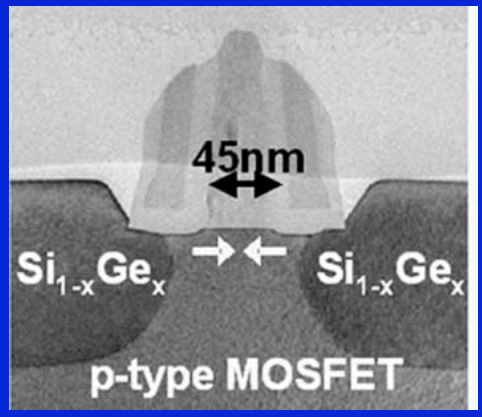
Intel

- New device structures for better electrostatic control ➔ low leakage
- On current still a problem

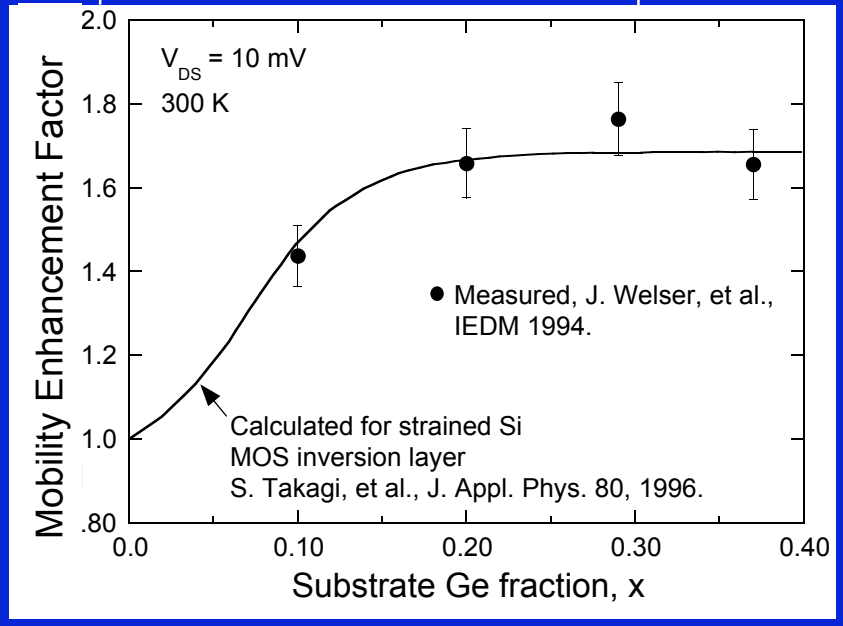
Mobility Enhancements in Strained-Si MOSFETs

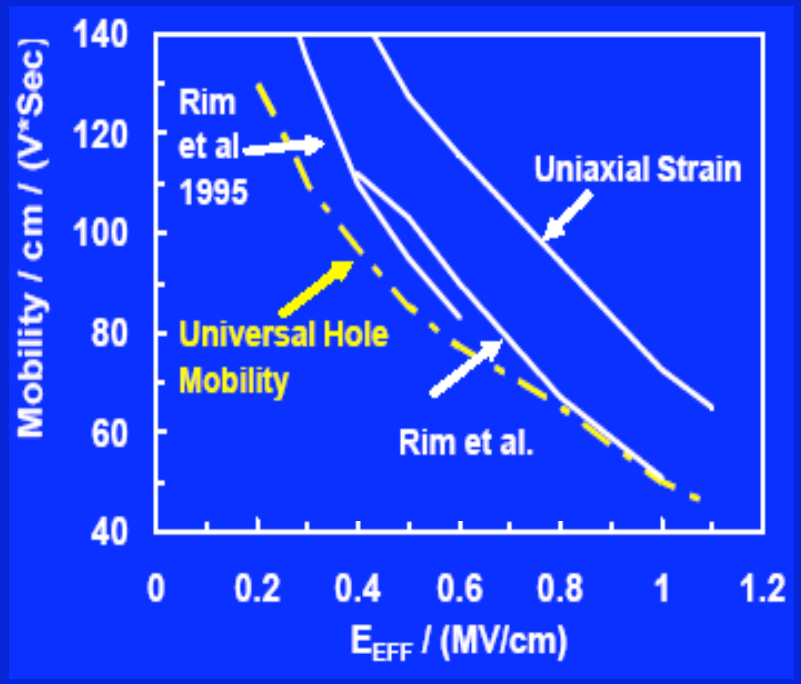


NMOS
Gibbons, Stanford, 1994



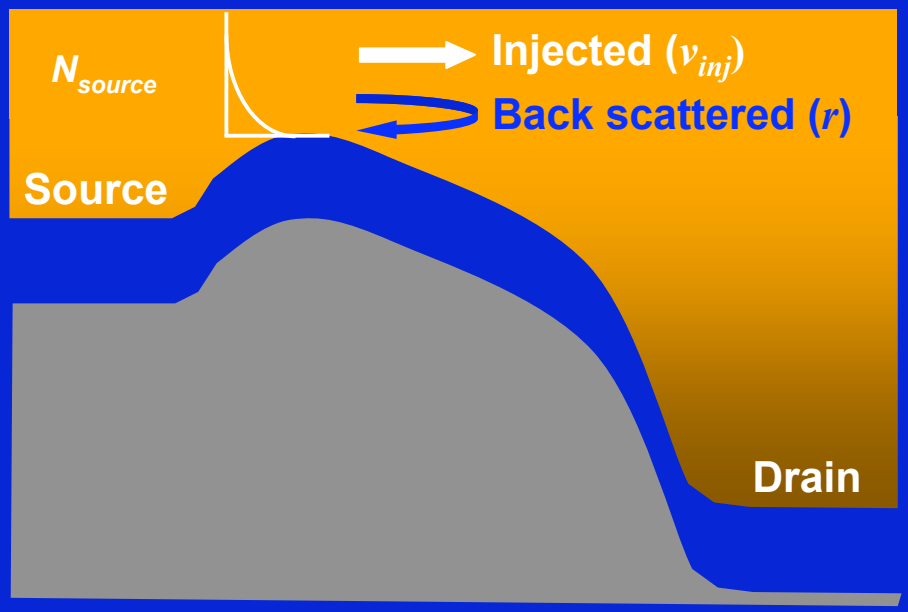
PMOS
Intel 2003





Mobility enhancement good for just 1 or 2 generations

High Mobility Channel Impact On Device Performance



After Natori, Lundstrom

$$I_{sat} = qN_{Source}v_{inj} \times \left(\frac{1-r}{1+r}\right)$$

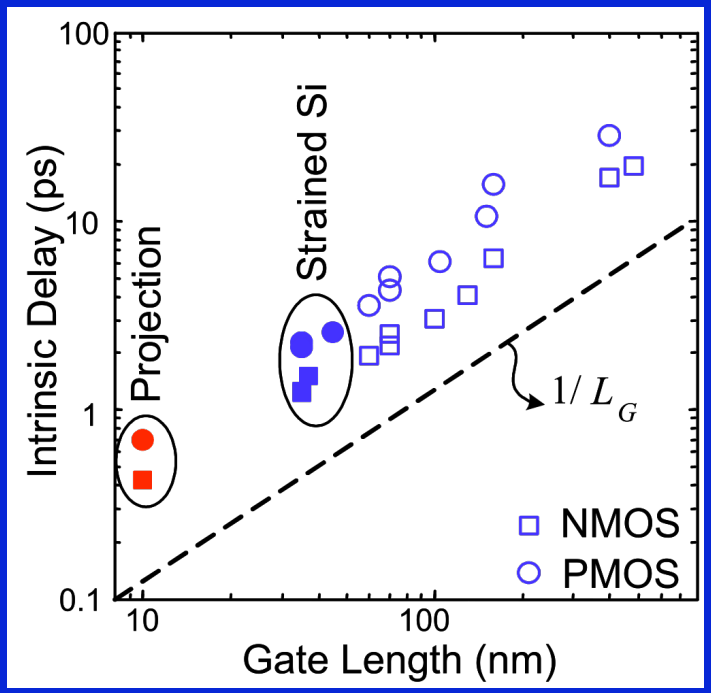
Low $m^*_{transport}$ → High v_{inj}
→ Low r

v_{inj} α low field mobility

Increasing μ brings us closer to the ballistic limit

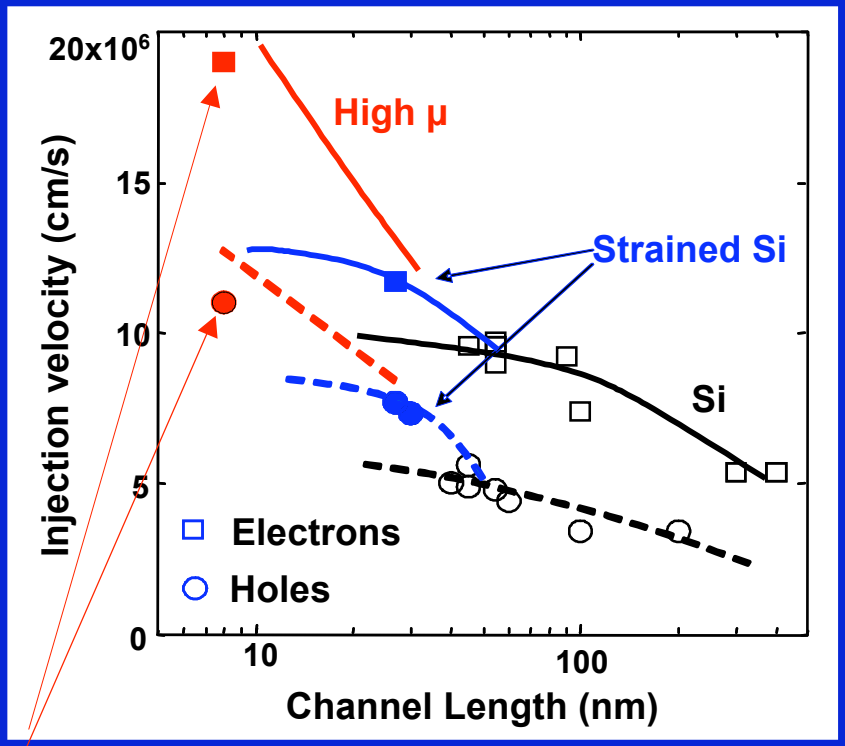
Motivating Focus for High-μ Channel

Historical CMOS Performance vs. Scaling: The 1/L_G "law"



Courtesy: D. Antoniadis (MIT)

Carrier velocity increase is paramount for performance scaling



- **But, carrier velocity increase has saturated with scaling…**
- **MOSFET delay has continued to decrease by use of Si strain to boost velocity…**
- **and, velocity boosting will also saturate with strain-based Si band engineering…**

High-μ channel: Getting there (L_G~10nm) and proceeding beyond

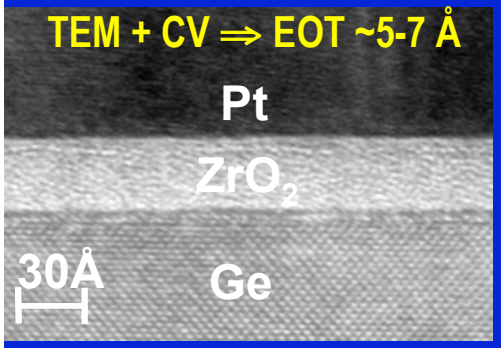
Picking the Right High-μ Material

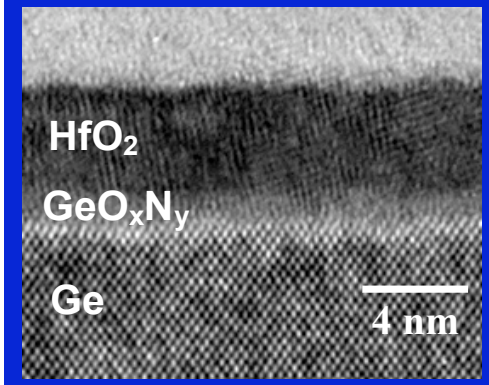
Material ⇒ Property ⇓	Si	Ge	GaAs	InAs	InSb
Electron mobility	1600	3900	9200	40000	77000
Hole mobility	430	1900	400	500	850
Bandgap (eV)	1.12	0.66	1.424	0.36	0.17
Dielectric constant	11.8	16	12.4	14.8	17.7

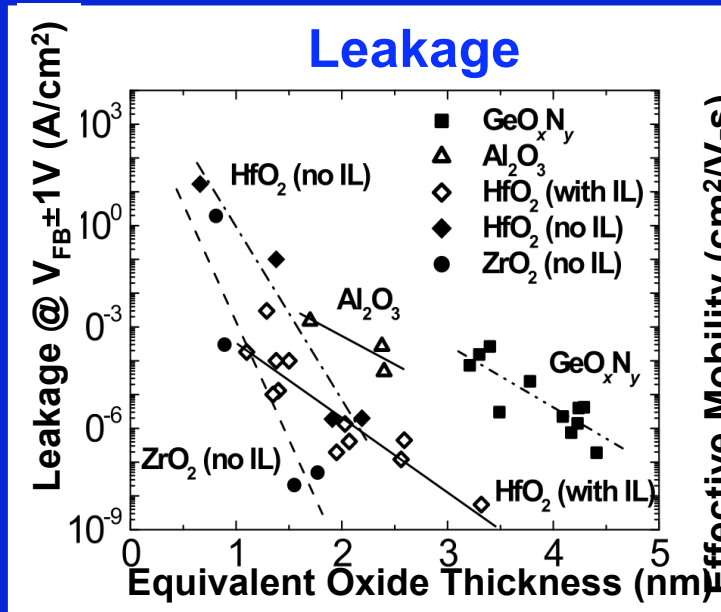
Questions we must answer

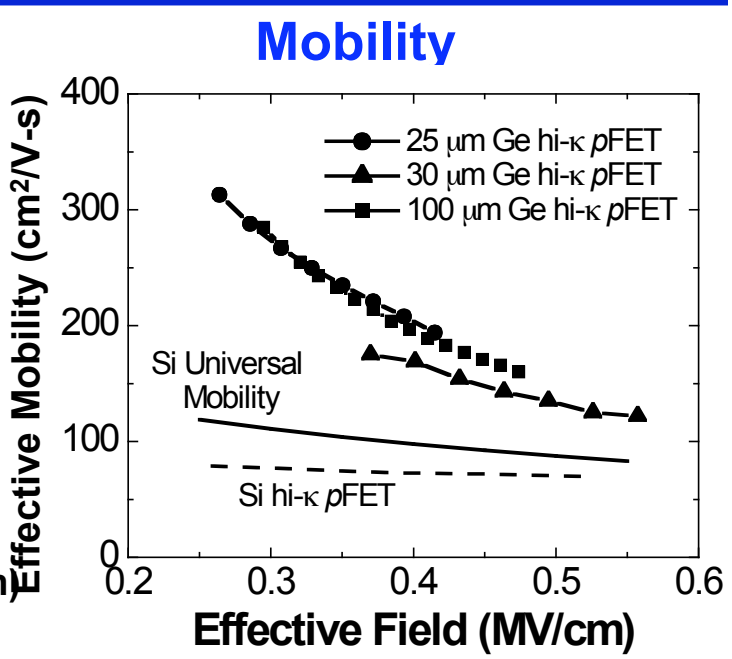
- Does the high μ translate into a high I_{ON} and high switching frequency?
- What is the minimum obtainable I_{OFF}?
- What are the parasitic R and C of transistor with high μ materials?
- Is the transistor with high μ scalable to nanoscale?

High Mobility PMOSFETs with High-k Gate Dielectric on Bulk Ge







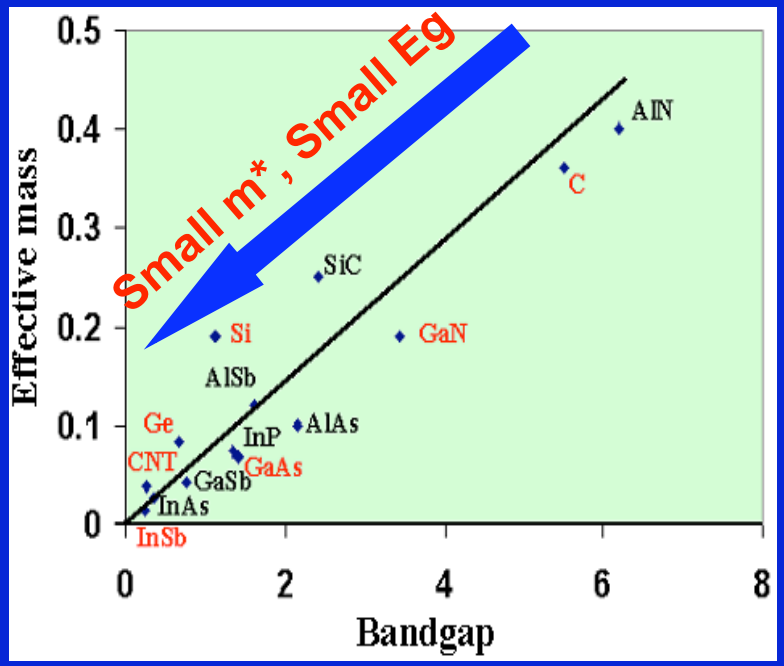


- Passivation of Ge with GeO_xN_y, ZrO_2 and HfO_2
- High-κ dielectrics reduce leakage by several orders of magnitude
- Field isolation by GeO_xN_y + CVD SiO_2
- 1st demo of Ge MOSFETs with metal gate and hi-κ

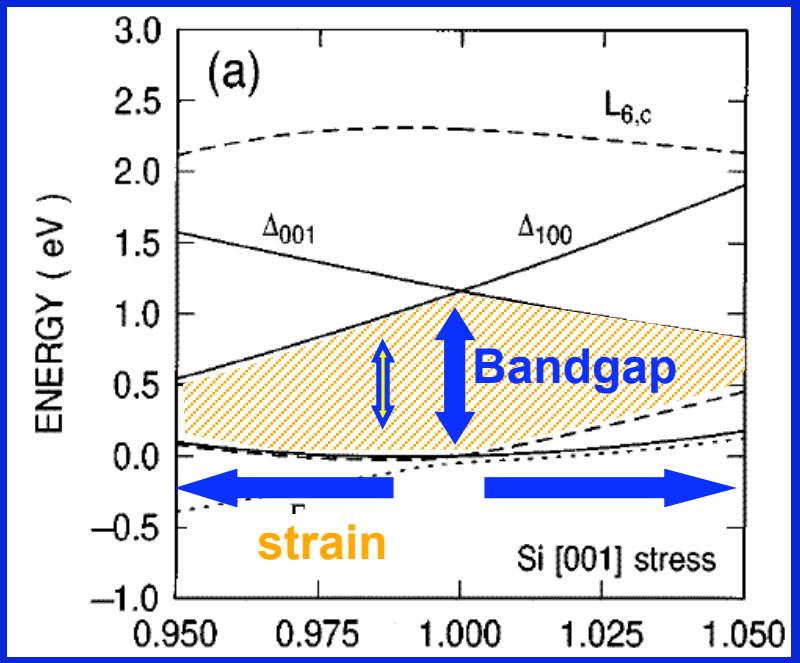
Chui, Saraswat, et al., IEDM 02 & IEEE TED, July, 2006.

High Mobility Materials

Effective mass vs. Bandgap



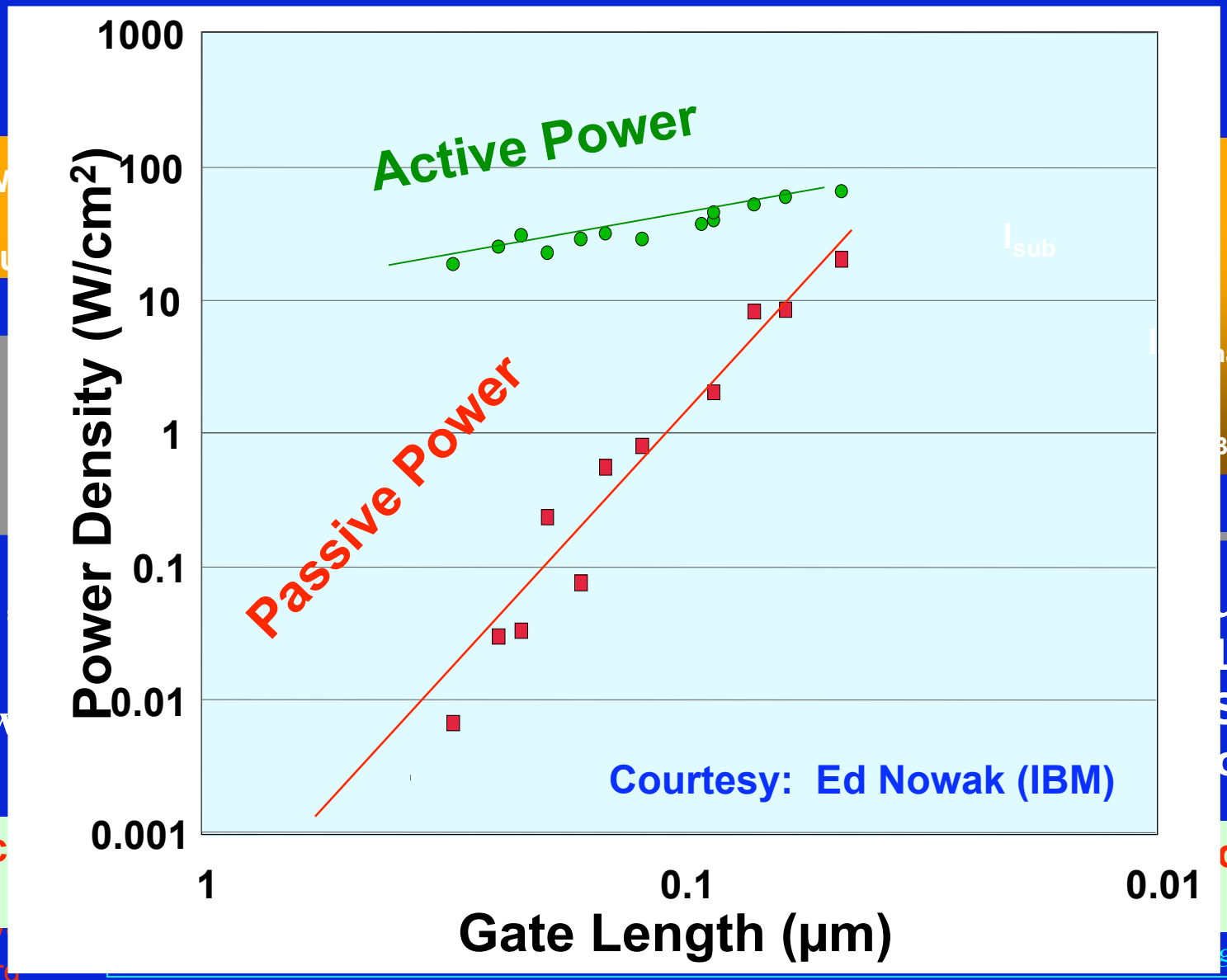
Strain vs. Bandgap



(Fischetti et al, JAP 1996)

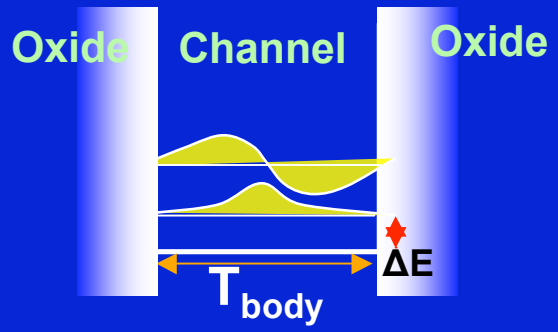
Smaller Effective Mass and Smaller Bandgap
→ Larger BTBT and Larger Off State Current.

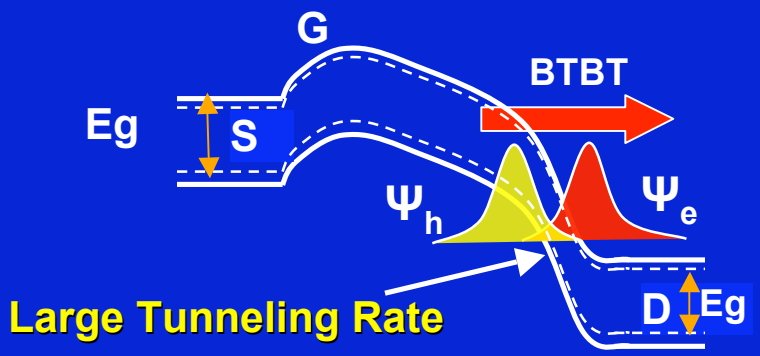
High Mobility Channel Impact On Device Performance



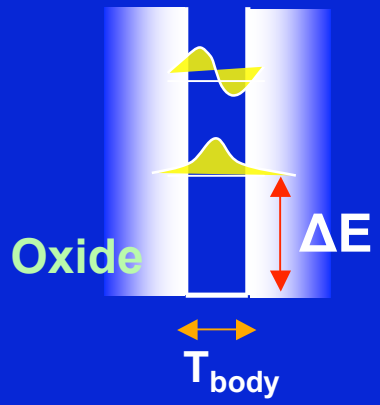
Quantization Effects at the Nanoscale

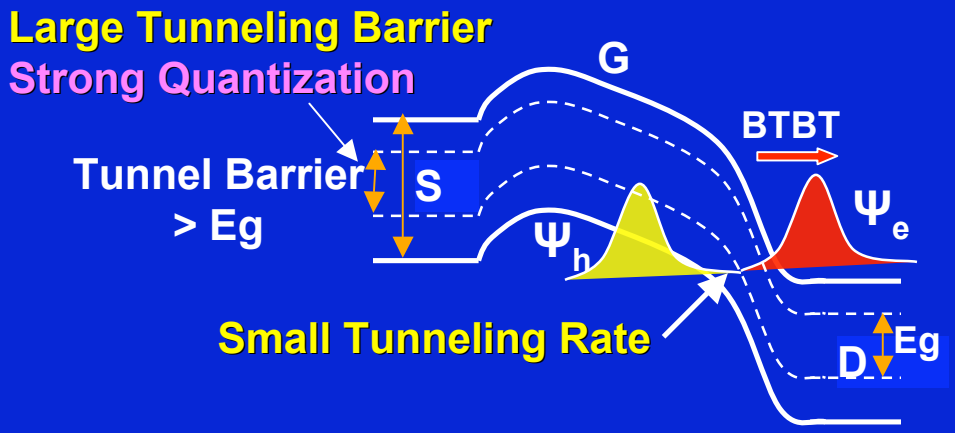
Thick Body DGFET





Thin Body DGFET

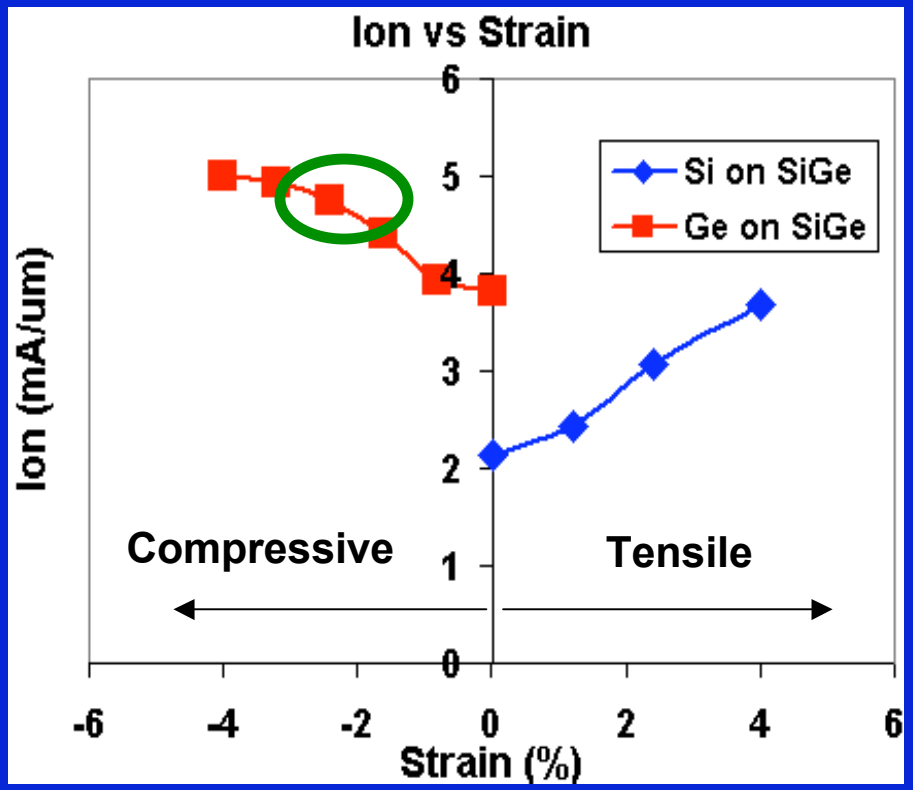




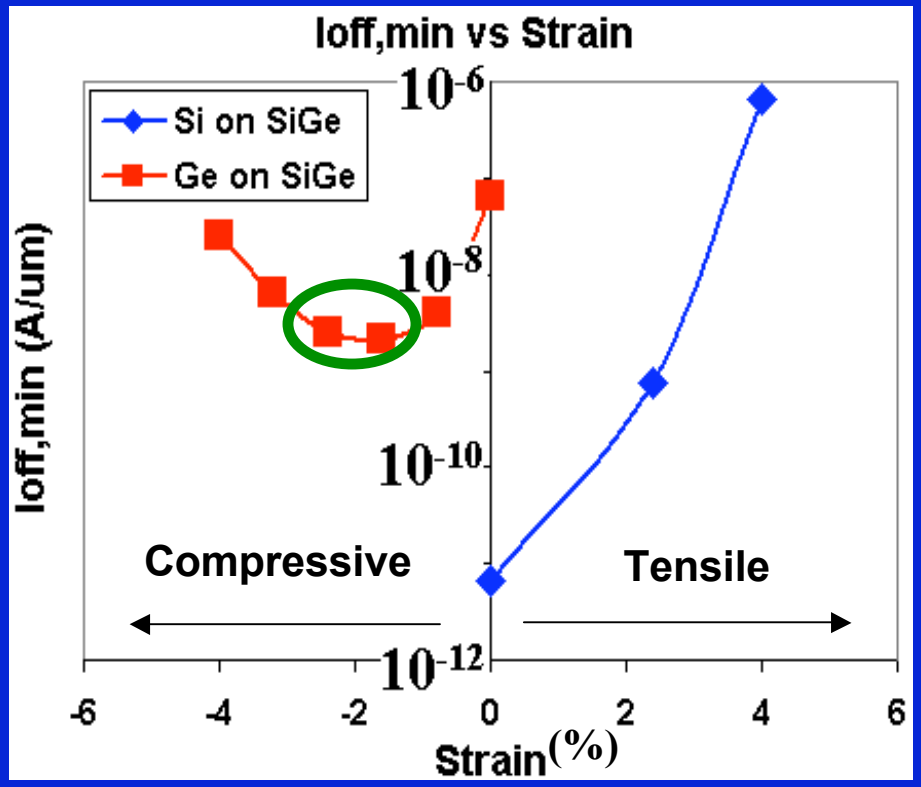
- Thin Body Increases Tunneling Barrier Height ⇒ Lower BTBT

Performance – Biaxial Strain

I_{ON}



I_{OFF}



L_G=16nm, T_{body} = 5nm, T_{ox} = 0.9nm, V_{dd}=0.7V

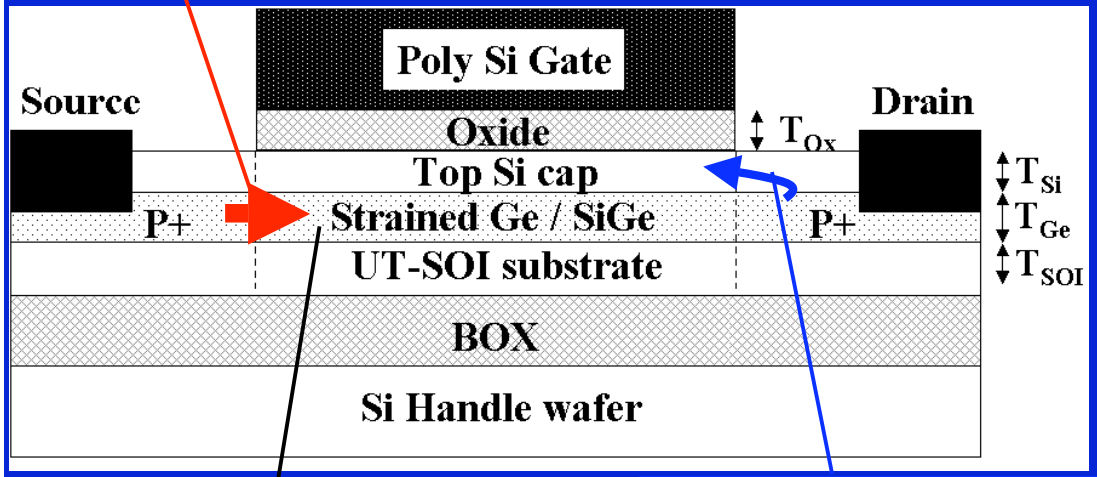
Optimal Performance Tradeoff:

- Biaxial Compressively Strained (2-3%) Germanium

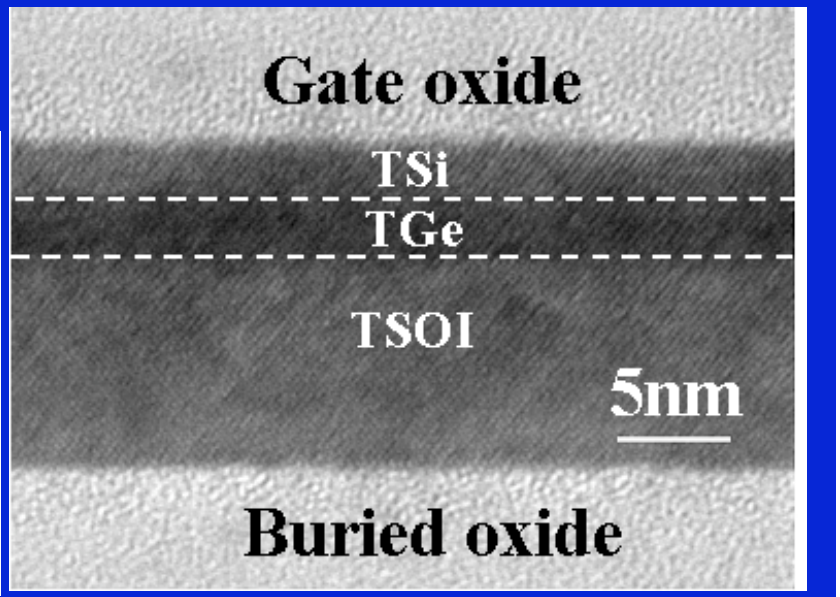
Krishnamohan et al.IEEE IEDM 06

Strained-Ge Heterostructure SOI PMOS

Transport in high μ Ge
➢ High I_{on}



TEM

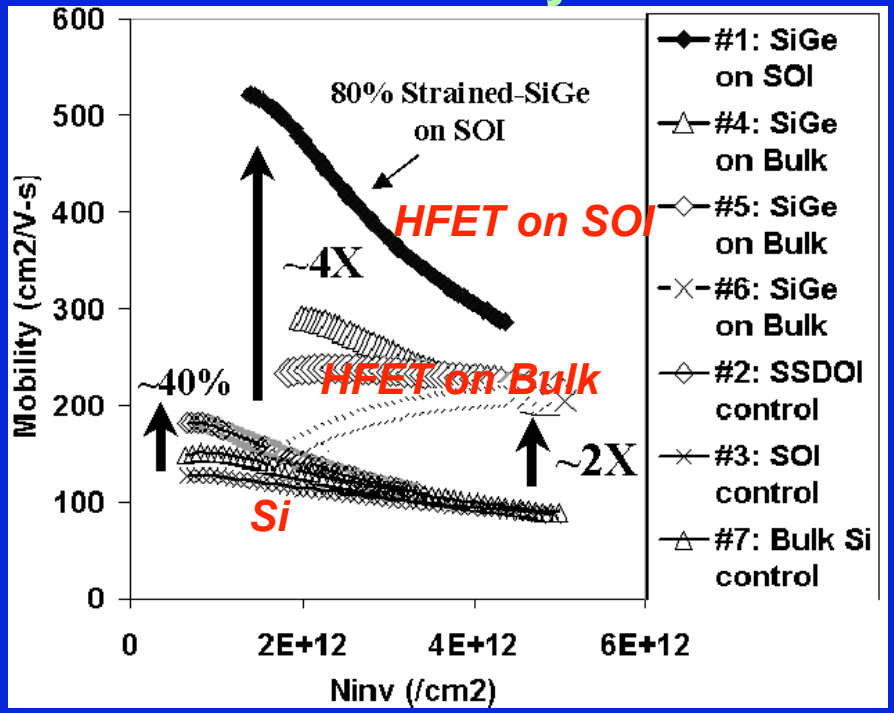


High E-field in wide bandgap Si
Low E-field in Ge
➢ Low leakage

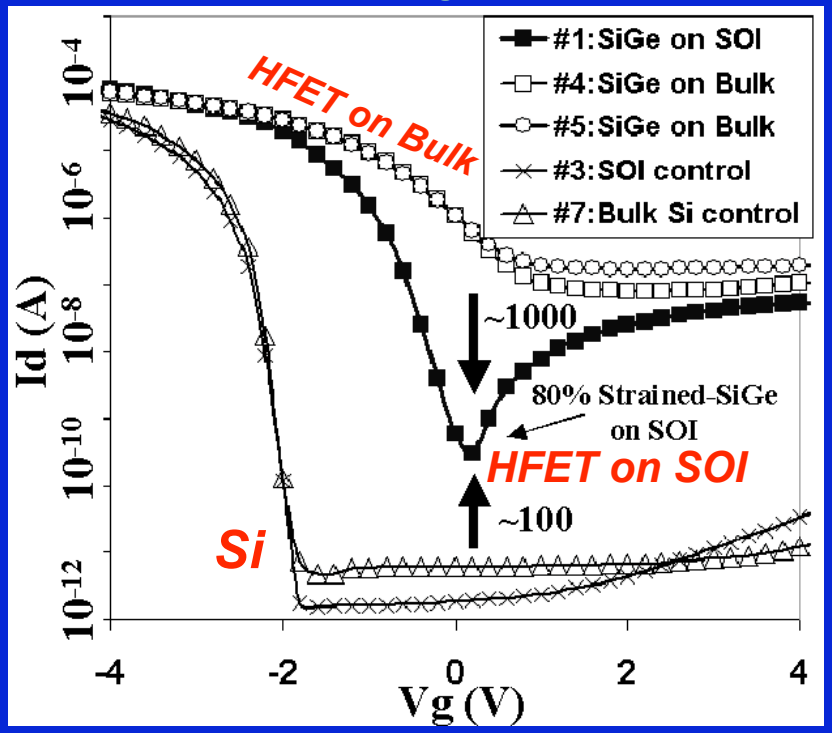
Eg ⇑ due to quantization in Ge thin film
➢ Low leakage

Strained-Ge Heterostructure SOI PMOS

Mobility



I_d-V_g



4X improvement over Si due to:

- ✓ Strain in Ge
- ✓ Reduced scattering due to
  - – Reduced E-field in Ge
  - – Channel away from the interface

Low BTBT leakage:

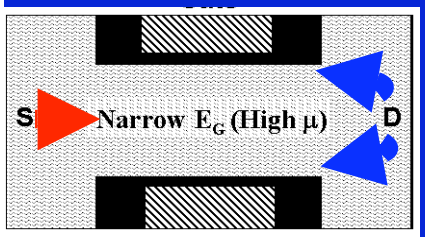
- ✓ Eg ⇑ due to quantization in Ge thin film
- ✓ Reduced E-field in Ge

Krishnamohan, Krivokapic, Uchida, Nish and Saraswat, IEEE TED, May 2006,

Ge/Si PMOS Ultimate Performance Comparison

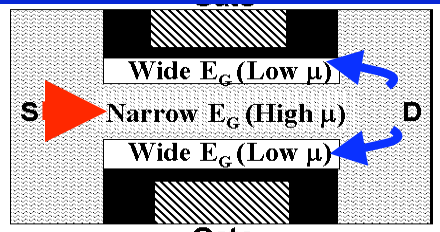
Structures

Monomaterial



High mobility DG MOSFET
(Surface Channel)

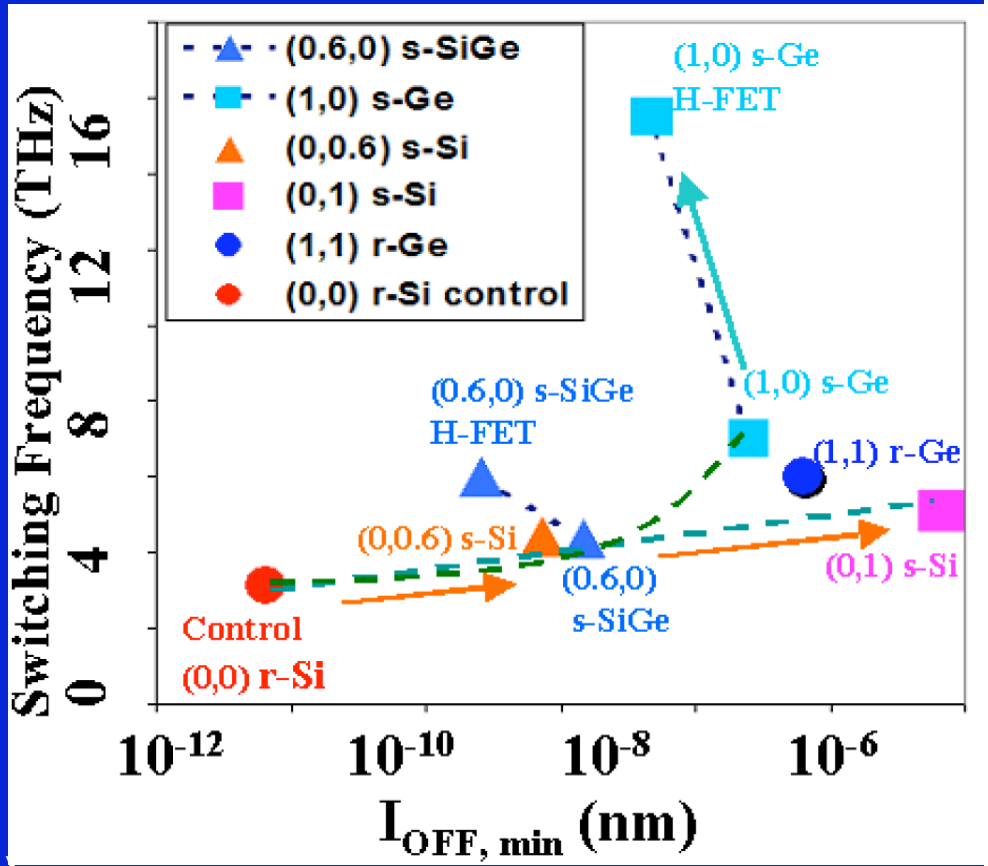
Heterostructure-FET



Heterostructure DG MOSFET
(Center Channel)

Power-Performance

L_G=16nm, T_S = 5nm, V_{dd}=0.7V



Materials:

Relexed Si (r-Si), Strained Si (s-Si), Relaxed-Ge (r-Ge), Strained-Ge (s-Ge), Strained-SiGe (s-SiGe)

Terminology (x,y) for channel material

x = Ge content in the channel material and

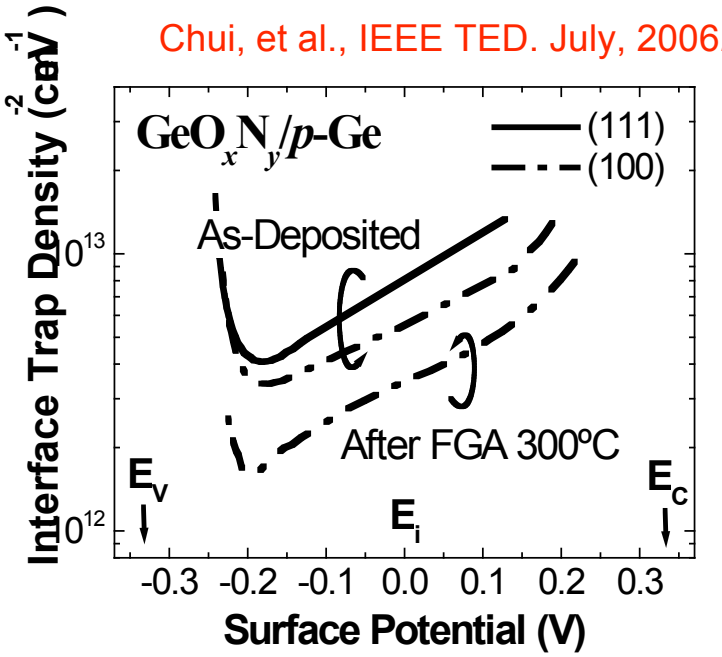
y = Ge content in an imaginary relaxed (r) substrate to which the channel is strained (s)

Saraswat, et al. IEEE IEDM, Dec. 2006,

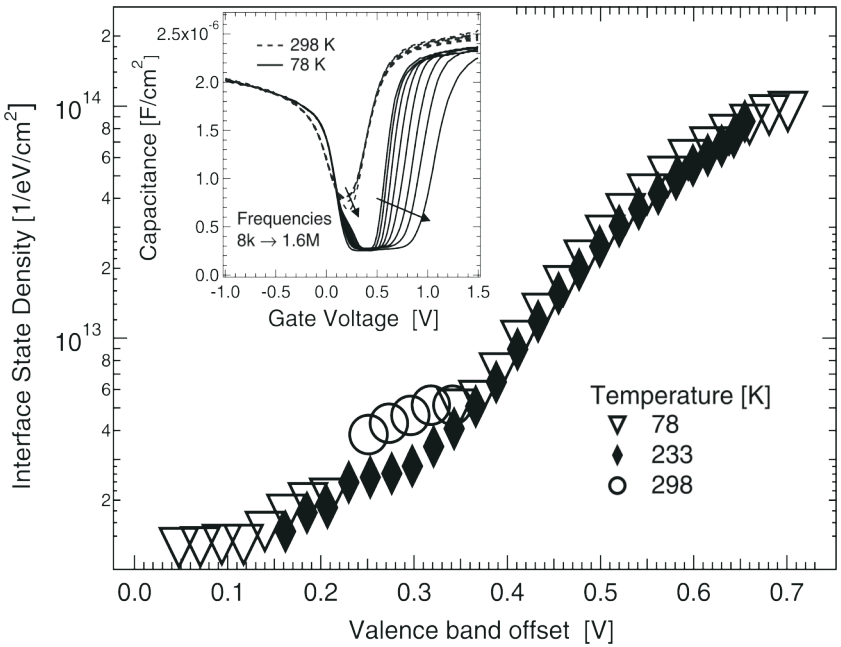
Ge NMOS Performance

- Low Ge *n*-MOS electron mobility
  - ☹ Best μ_n ~ 370
- I_{ON} limited by high D_{it}
  - ☹ Asymmetric interface state density distribution

Chui, et al., IEEE TED. July, 2006.

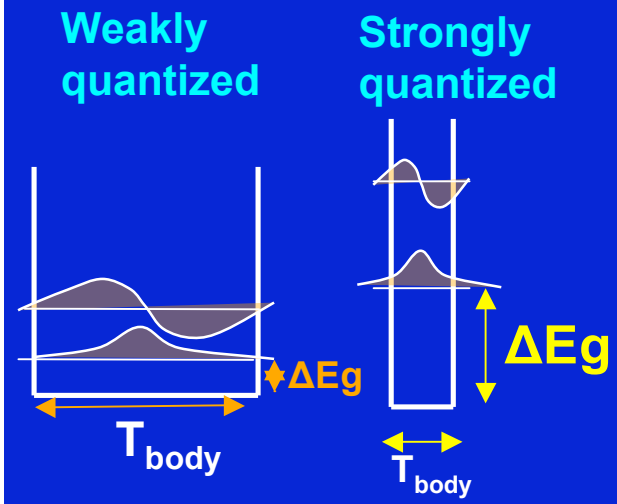


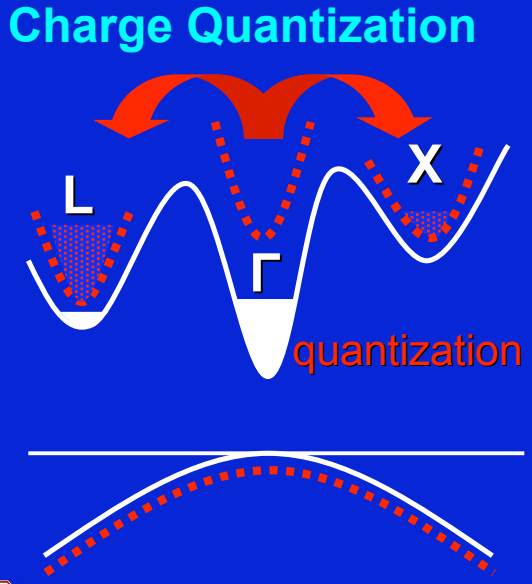
(Martens *et al.*, to be published)



- Need improved dielectric stack achieve high mobilities
- Need atomic level modeling to understand interface states on Ge and III-V

High Mobility III-V Channel NMOS?





Main question

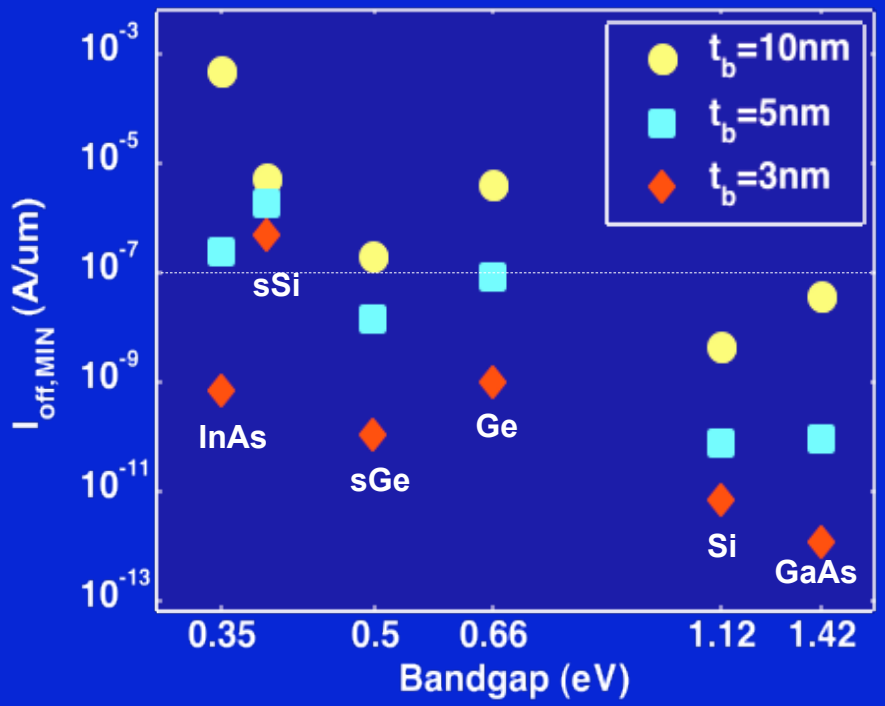
- Will high mobility provide high performance?

Problems

- low density of states in the Γ-valley → reduced $Q_{inversion}$ and hence I_{ON}
- Quantization in thin films and high surface E-field → Charge occupies high DOS L and X valleys with heavy mass
- Materials like InAs and InSb, have a much smaller band gap → high leakage
- High dielectric constant and hence inferior short-channel effects

Off Current: Band Engineering

T_{body} Dependence (V_{DD}=0.9V)



Thin body :

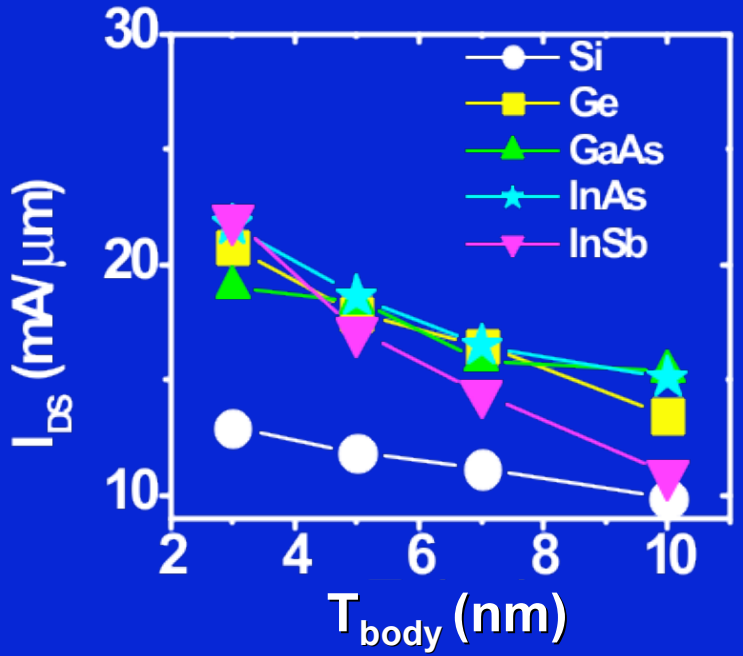
- **Small bandgap materials → large BTBT**
- **Quantization → E_G ⇑ → small BTBT**

It is possible to engineer a material with low I_{OFF}, but……

Saraswat, et al. IEEE IEDM, Dec. 2006,

NMOS Drive Currents (Ballistic)

Body Thickness Effect (V_{DD}=0.9V)

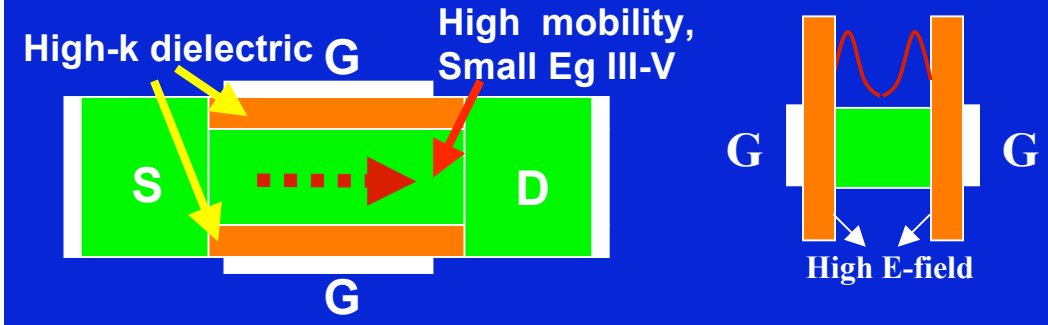


T_{OX} = 1nm,
L_G = 15nm,
I_{OFF} = 0.1μA/μm

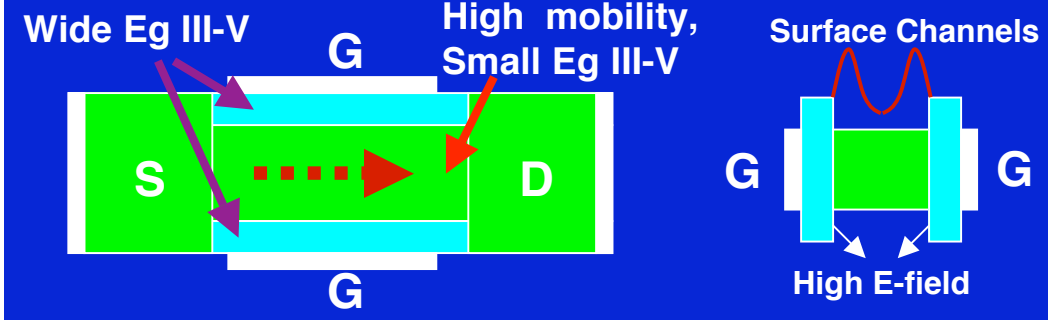
- I_{ON} for III-V materials is similar to Ge at higher V_{dd}
- For low T_{body} charge spills into L and X → low I_{ON}
- Innovative device structures needed to improve I_{ON}

Saraswat, et al. IEEE IEDM, Dec. 2006,

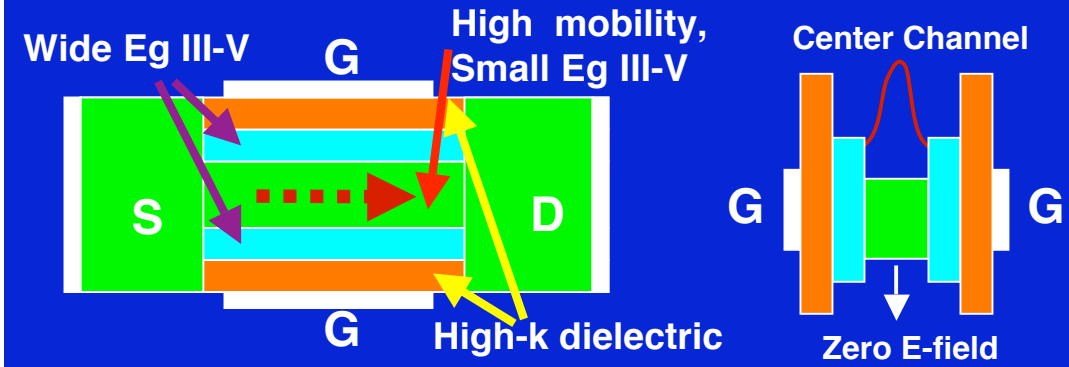
"MOSFET"-like structures using III-V



Structure 1:
High-k dielectric as Insulator for a Surface Channel MOSFET



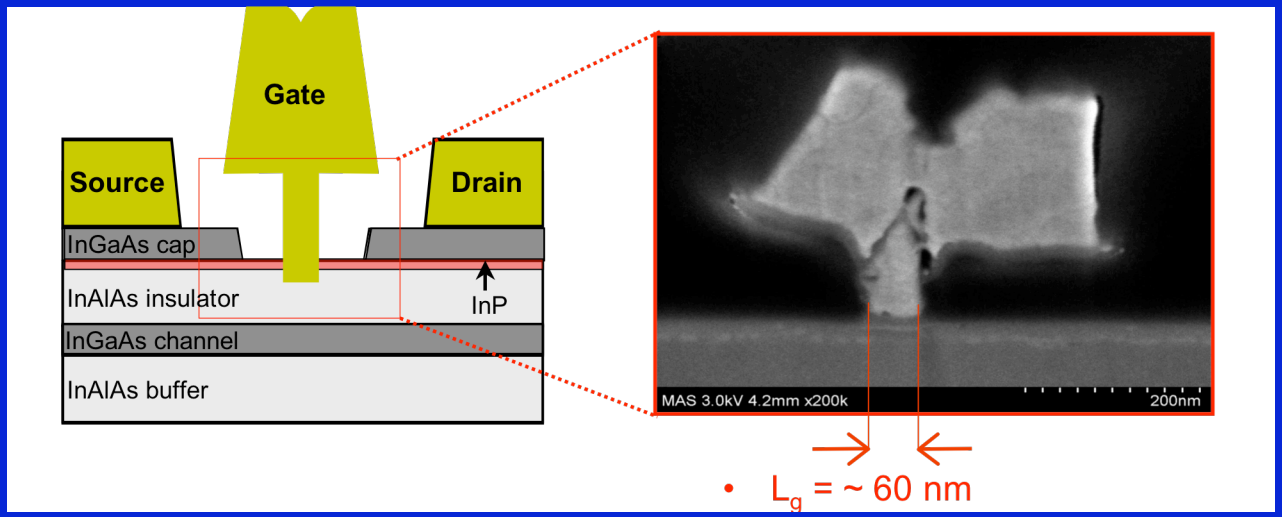
Structure 2:
Wide bandgap III-V as Insulator for a Surface Channel MOSFET

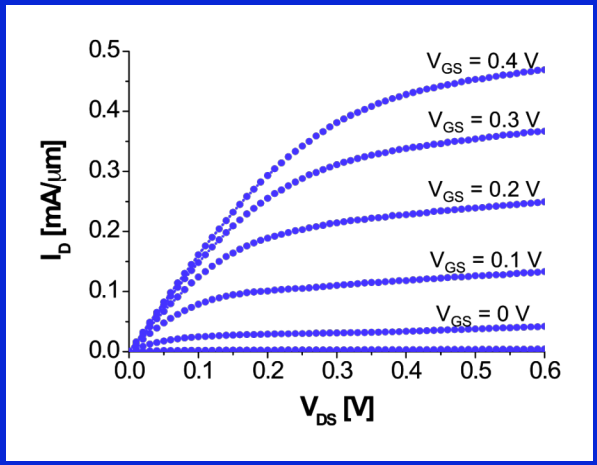


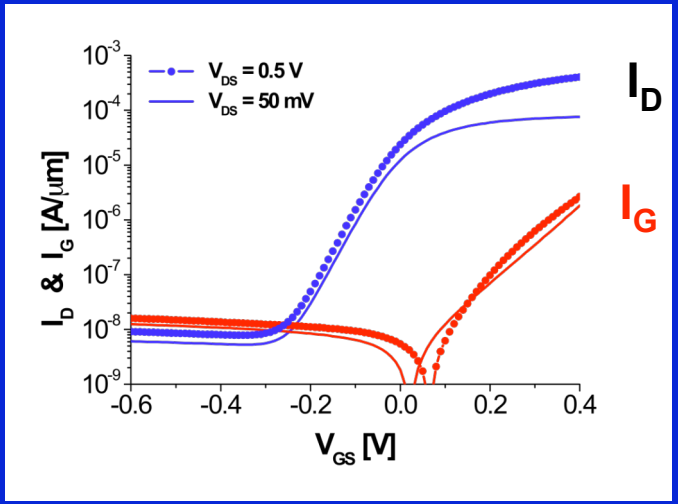
Structure 3:
High-k dielectric as Insulator for a Center Channel MOSFET

Picking the right structure?

60 nm $In_{0.7}Ga_{0.3}As$ HEMTs







J. A. del Alamo, MIT

araswat
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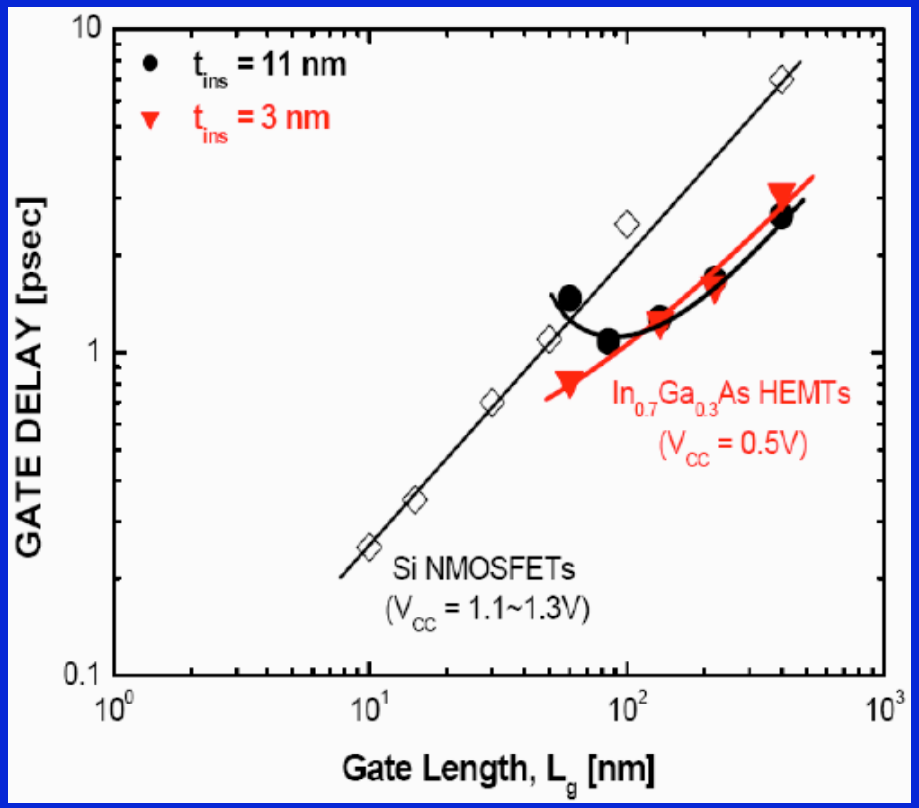
SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Performance of InGaAs HEMT

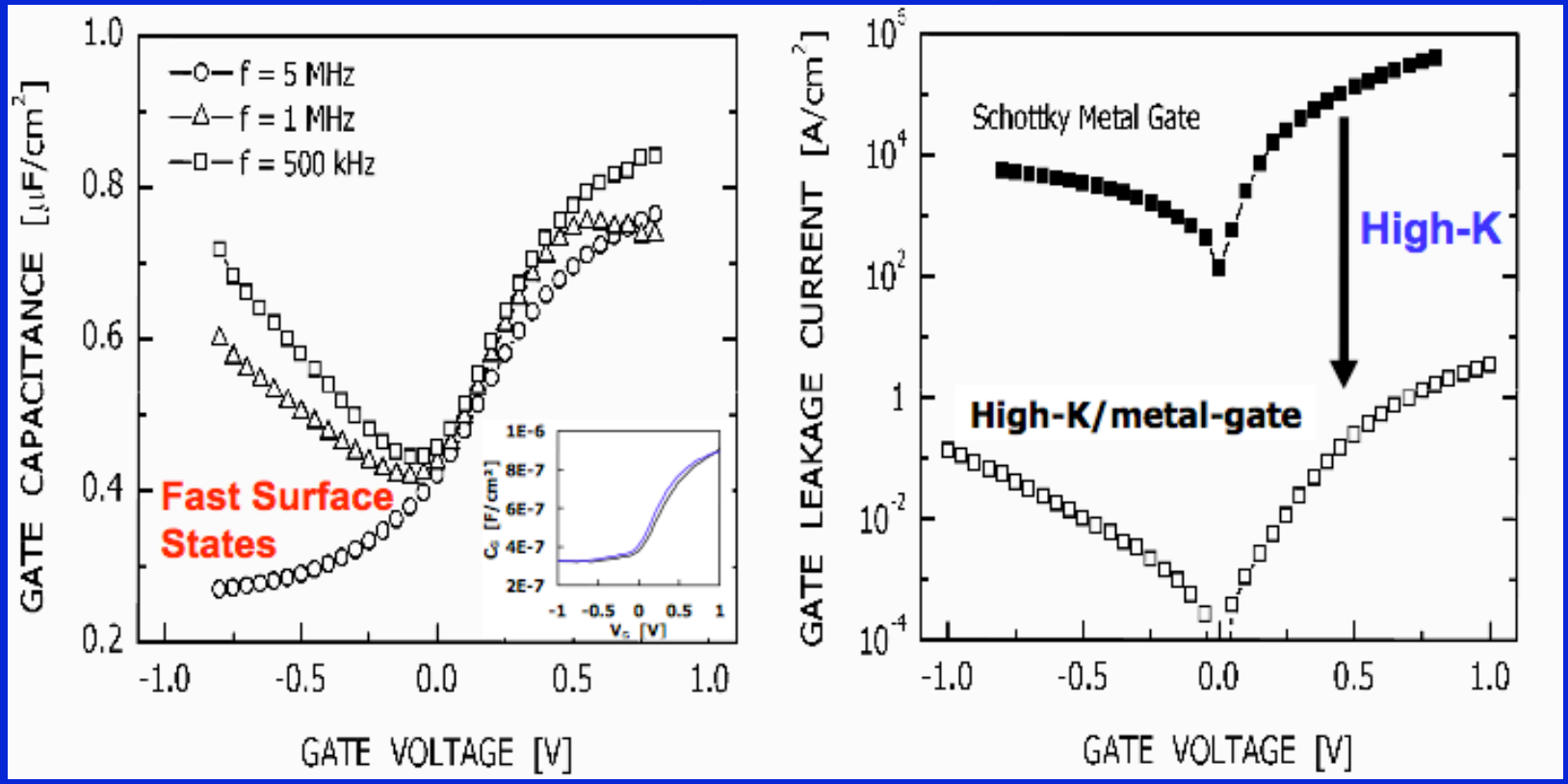


- III-V QW devices show very high performance at low V_{cc} (0.5V).
- Compare favorably with 65 nm Si CMOS Logic Suitability
- Low S/D leakage but Schottky gate leakage high

D. Kim, J. Alamo et al. (MIT), IEDM 2006

Grand Challenge in III-V MOSFETs: Compatibility of III-V and High-K/Metal-gate Stack

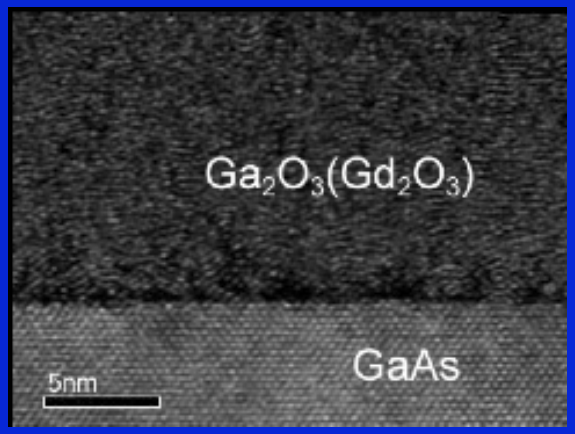
AlInSb / High-K / metal-gate



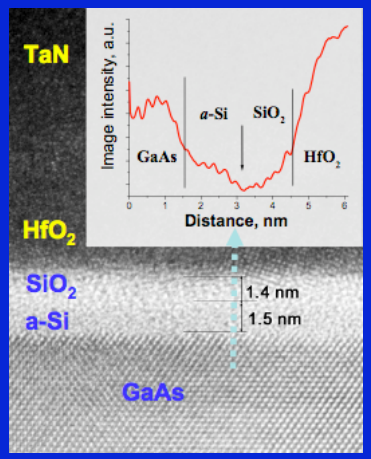
R. Chau , INFOS, Leuven 6/05

High-K / metal-gate technology needed for III-V MOSFET

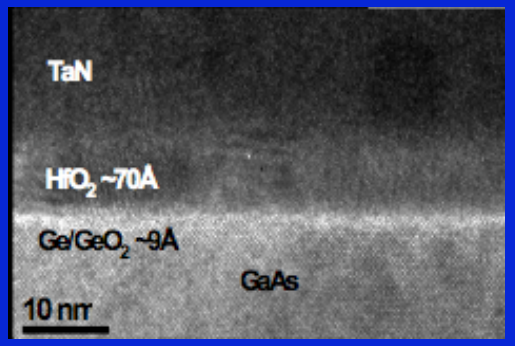
Examples of Efforts to Passivate III-V



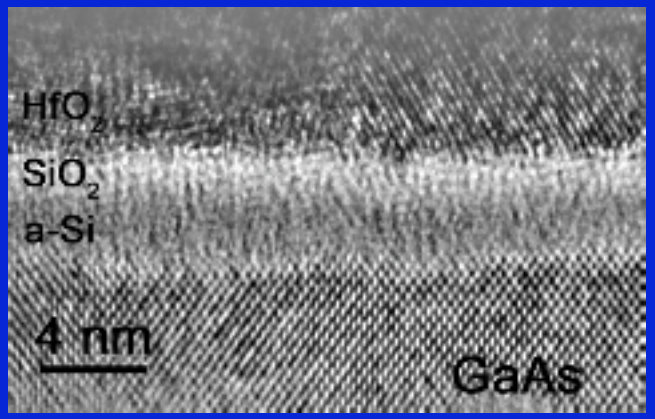
M. Hong (Tsinghua)



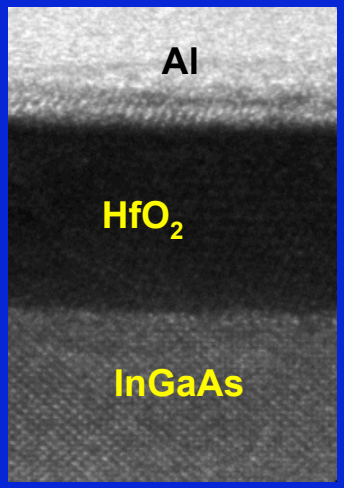
Oktyabrsky (Albany)



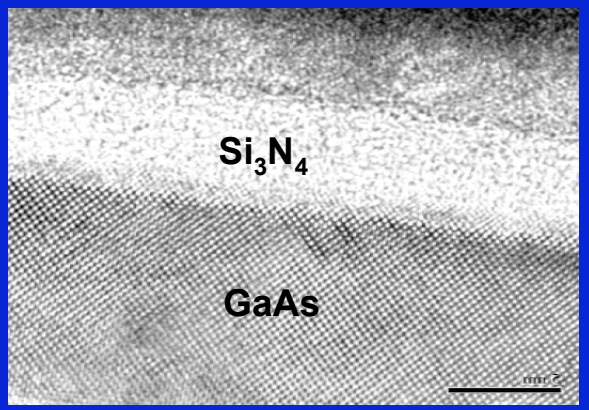
J. Lee (UT Austin)



Kummel (UCSD)



McIntyre (Stanford)
N. Goel (Intel)

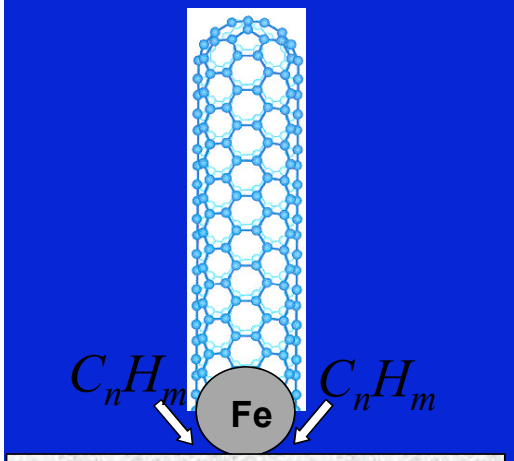


T. P. Ma -Yale

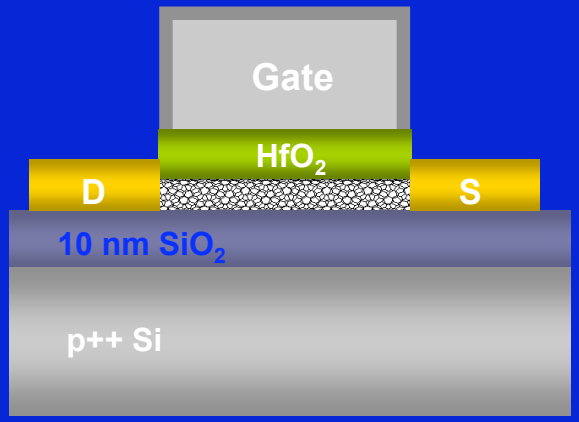
araswat
tanford

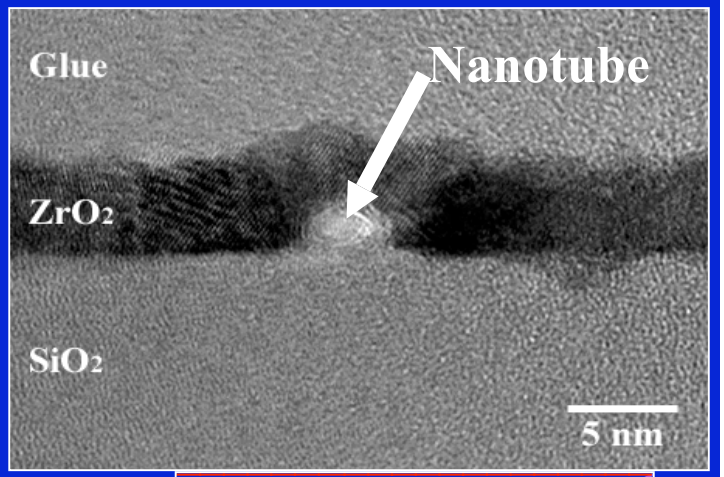
Ballistic Nanotube Transistors

Growth

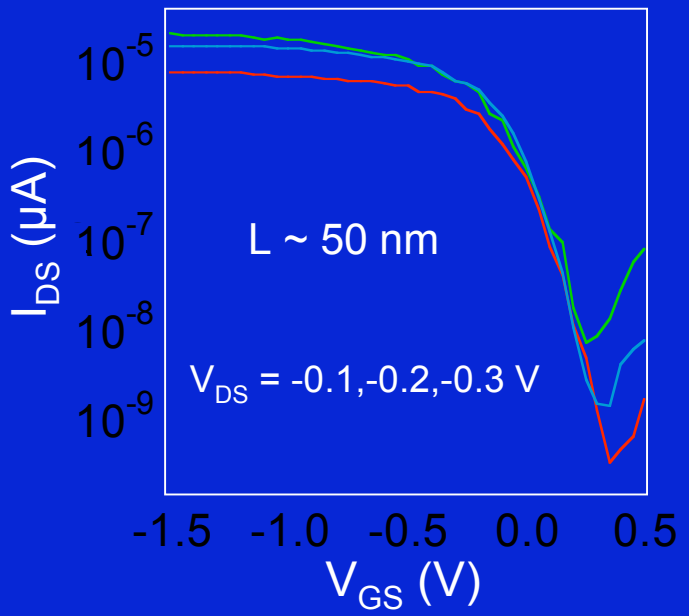


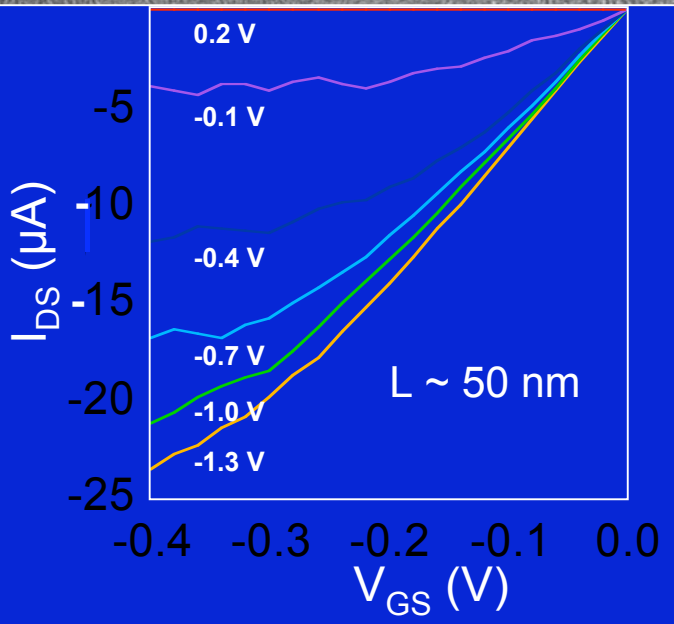
MOS Transistor





Dai (Stanford)
McIntyre (Stanford)
Gordon (Harvard)
Lundstrom (Purdue)





Key Challenge: Low thermal budget controlled growth

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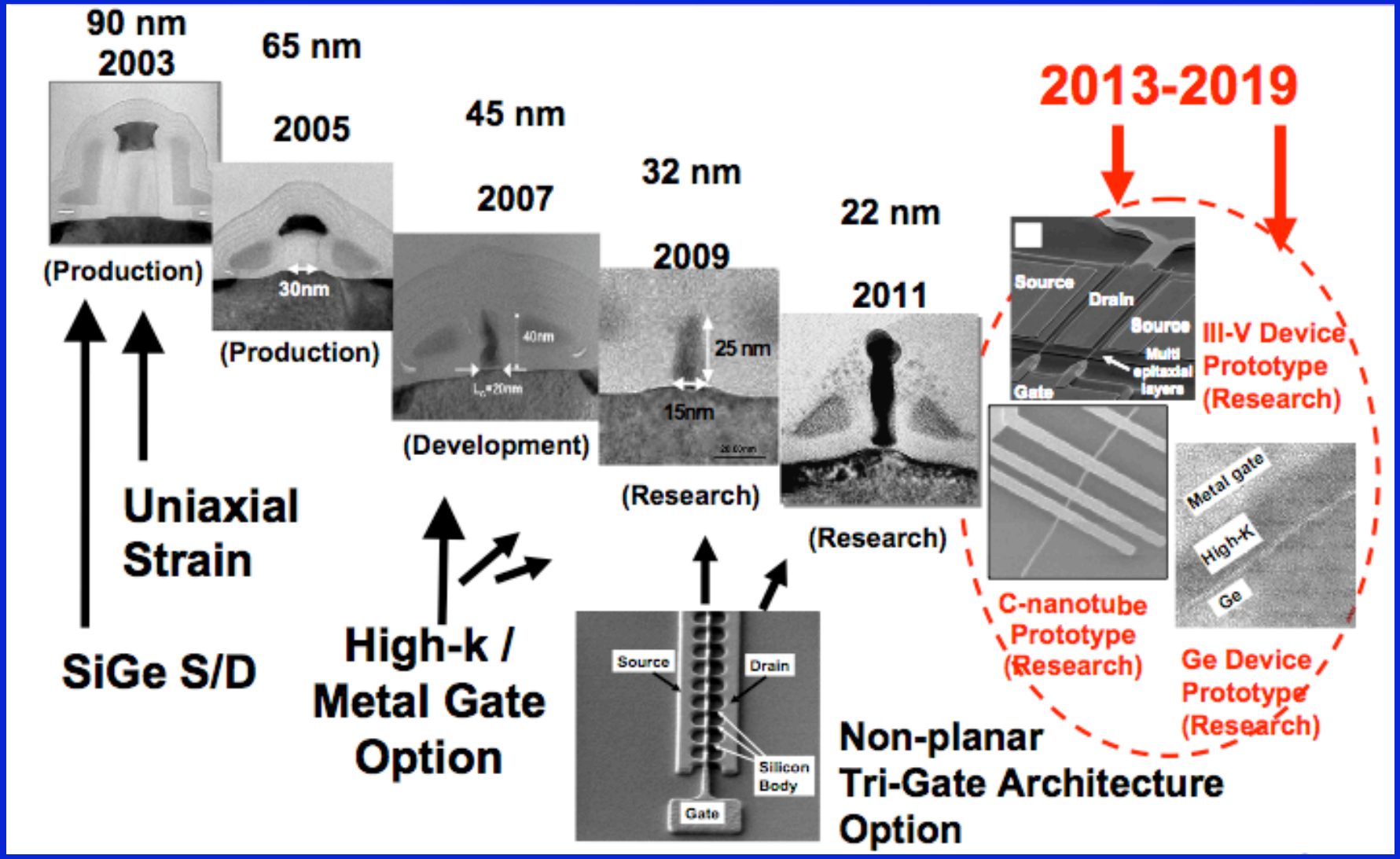
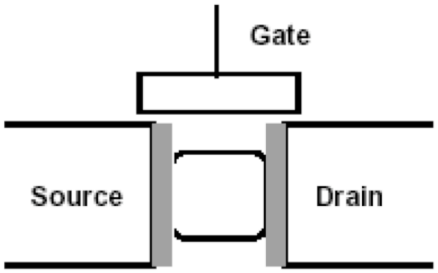
Transistor Scaling: Future Options



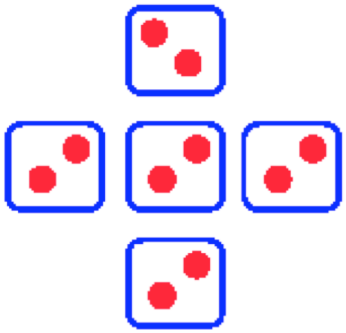
Source: W. Tsai (Intel)

Seemingly Useful Devices



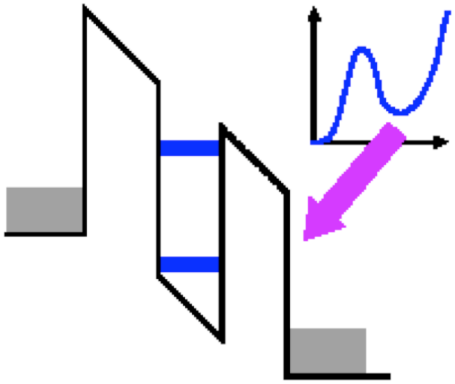
Single Electron Transistors (SET)

Limited Current Drive
Cryogenic operation



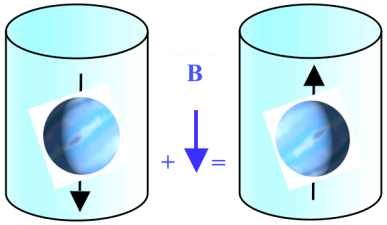
Quantum Dot

Limited Fan-Out
Critical dimension control



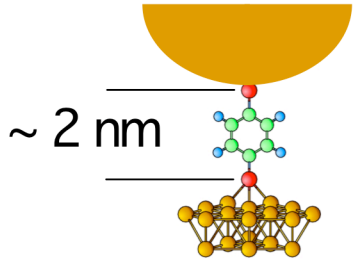
Resonant Tunneling Diode

Challenging fabrication and process integration



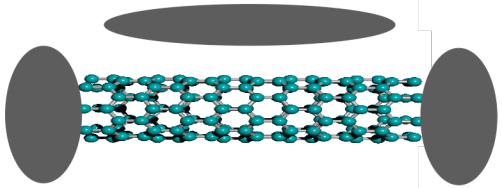
Spintronics

Need high spin injection and long spin coherence time



Molecular Device

Limited thermal stability
New architectures needed



Carbon Nanotubes

Controlled growth

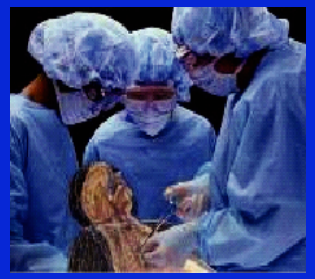
Future Terascale Integration

Entertainment

Ref: J. Bautista (Intel)

Learning & Travel

Personal Media Creation and Management



Health

Performance

TIPS

GIPS

MIPS

KIPS

RMS

3D & Video

Mult-Media

Text

Tera-scale

Multi-core

Single-core

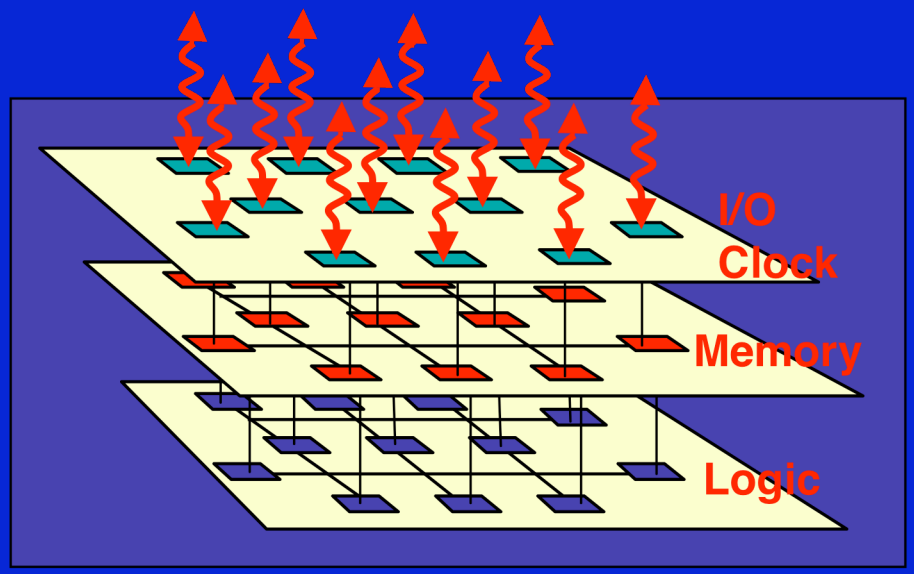
Kilobytes Megabytes Gigabytes Terabytes

Dataset Size

*Tera-scale Applications:
Visual Media Indexing

Interconnects will have not only latency but also enormous bandwidth requirement

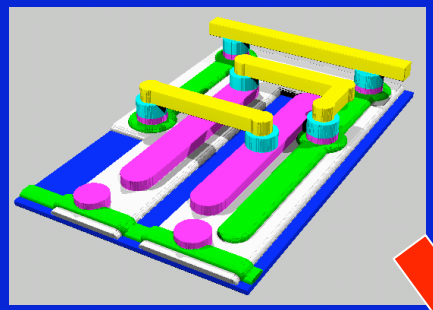
Future Processor Requirements



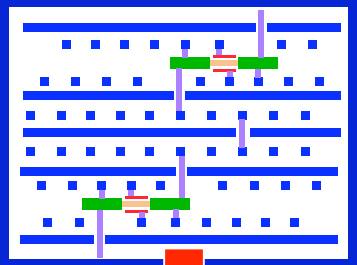
- **High-BW, low-power on-chip wires**
  > 100 Tb/s
- **Clocking and Synchronization**
  < 5ps jitter and skew
- **High-BW, off-chip links**
  > 40 Tb/s, 80 Gb/s/link
- **Heat Removal**
  Manage average > 200W, 64W/cm^2, local 'hot-spots' 250 - 400 W/cm^2
- **Power Distribution**
  Manage ~ 300A current at 0.7V V_{dd}
- **Optical/Electrical Packaging**
- **3D heterogeneous integration of novel devices and materials**

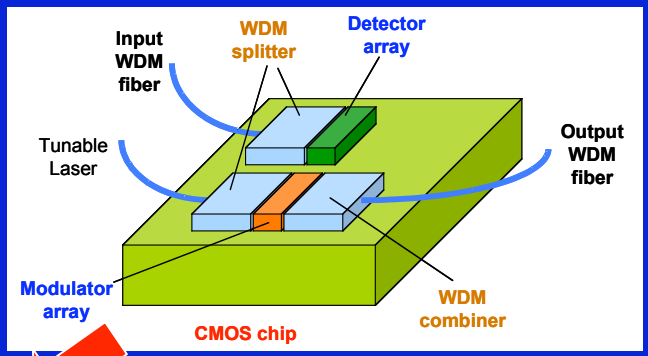
Interconnect Technologies for Future

Metal nanowires

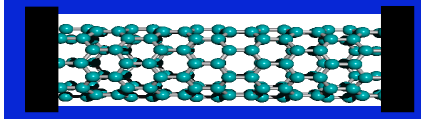


3D

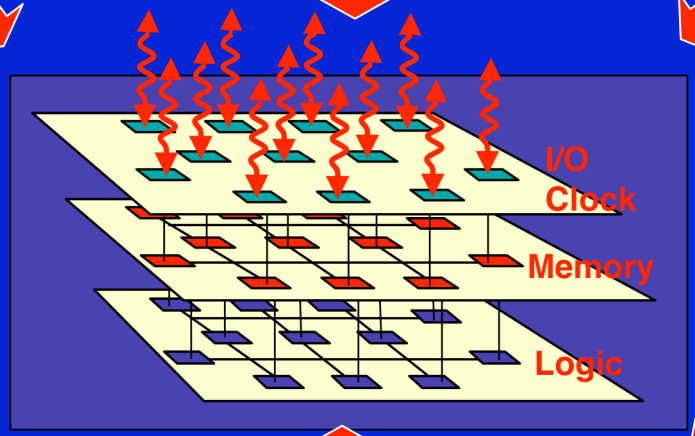


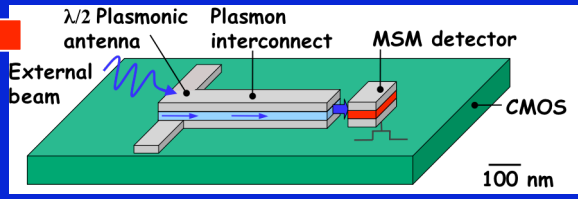


Optical interconnect
Lasers,modulators,detectors, WDM components

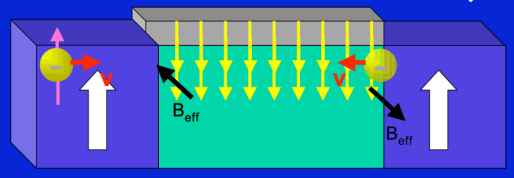


Nanotube interconnect

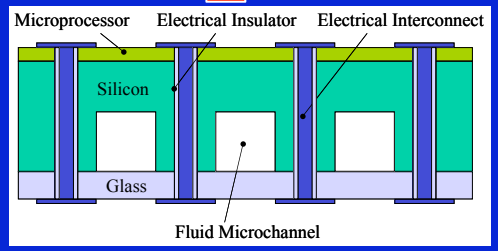




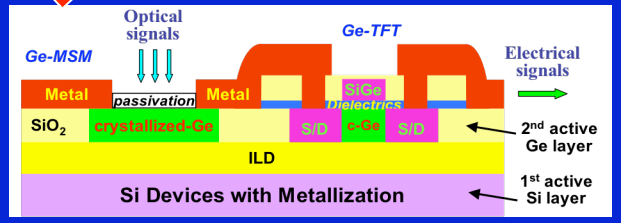
Nanoscale photonics and plasmonics



Spintronic interconnect



Heat Transfer



Si compatible photonics

araswat
tanford

Summary

- Moore's Law increasingly relies on material innovations
- There is an implosion of new materials
- We need to worry about the EHS issues at the time of technology development

Materials, Structures and Processes for Nanoscale MOSFETs with High-Mobility Channels: ESH Assessments

Thrust B

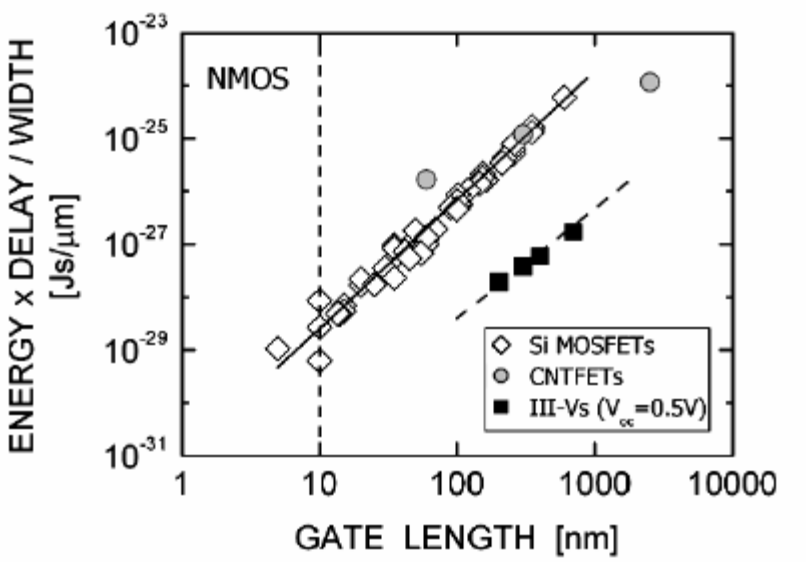
Eunji Kim[1], K.C. Saraswat[1,2] and P.C. McIntyre[1]

[1] Department of Materials Science & Engineering, Stanford University
[2] Department of Electrical Engineering, Stanford University

Acknowledgements:
Collaborators - Joseph Chen and Prof. Yoshio Nishi
Leveraged Support – Intel unrestricted gift funds

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Background



III-V channel devices

- Higher effective carrier mobilities
- Lower power dissipation (operating voltage)

R.Chau et. al, IEEE Trans. Nanotechnology. 4, 153 (2005)

✓ A high quality interface between gate dielectrics and III-V semiconductors is essential to integrate a nanoscale III-V-based MOS device.

✓ However, a large density of defect states exists at the interface between the native oxide and GaAs, InGaS, InP, etc.

✓ III-V materials are new to MOS device fabrication and present special ESH problems

Objective

• Conventional methods to remove native oxides of III-V semiconductors do not produce a stable oxide-free surface, but generate potentially toxic effluents from III-V compounds.

Alternatively, many passivation methods followed by wet cleaning have been reported.

• S-passivation using S-containing aqueous solution ($(NH_4)_2S$, Cl_2S_2, etc.)

• Deposition of a capping/passivation layer (Si, As, Sb, Bi, etc.) : Additional energy cost, complexity of decapping/surface oxidation

✓ Find an effective way to remove the native oxide of III-V compounds.

✓ Passivate the oxide-free surface with low thermal budget ***so that multiple surface cleans are not needed*** prior to gate dielectric growth

✓ Demonstrate effects on MOS capacitor and transistor properties

Cleaning Procedure (Si vs GaAs)

H_2SO_4/H_2O_2 : 120~150°C 10min
Strips organics

H_2O/HF : Room T 1min
Strips chemical oxide

DI H_2O Rinse : Room T

$NH_4OH:H_2O_2/H_2O$ SC-1 : 80~90°C 10min
Strips organics, metals, particles

DI H_2O Rinse : Room T

$HCl/H_2O_2/H_2O$ SC-2 : 80~90°C 10min
Strips alkali ions, metals

DI H_2O Rinse : Room T

Acetone : Sonication, Room T 5min
Strips organics

Dilute (HF or HCl or NH_4OH)
removes native oxide

DI H_2O Rinse : Room T

Passivation

DI H_2O Rinse : Room T

✓Low thermal budget passivation method to minimize the number of wet cleaning steps?

Standard RCA cleaning procedure for Si wafer

Potential ESH Impact

Native oxide removal process

HCl-etching

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

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

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

Toxic or harmful effluents :

$AsCl_3$, $AsCl_5$, $GaCl_3$

HF-etching

$As_2O_3 + 6HF \rightarrow 2AsF_3 + 3H_2O$

$As_2O_5 + 10HF \rightarrow 2AsF_5 + 5H_2O$

$Ga_2O_3 + 6HF \rightarrow 2GaF_3 + 3H_2O$

Toxic or harmful effluents :

AsF_3, $AsCl_5$, GaF_3

Special care must be taken for disposal of HF

S-passivation

$(NH_4)_2S$ solution

Hardly produce any As-containing effluents

Disposal as hazardous waste

HfO_2 deposition

Atomic Layer Deposition

150°C : low thermal budget

relatively lower vacuum : lower energy cost compared to MBE

Sample Fabrication

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

Surface treatment

- **Sonication in acetone for 5min**
- **Short DI water dip**
- **18% HCl etching for 3min (2% HF etching for 3min)**
- **Short DI water dip**
- **5% $(NH_4)_2S$ for 15min**
- **Short DI water dip**

Gate dielectric deposition

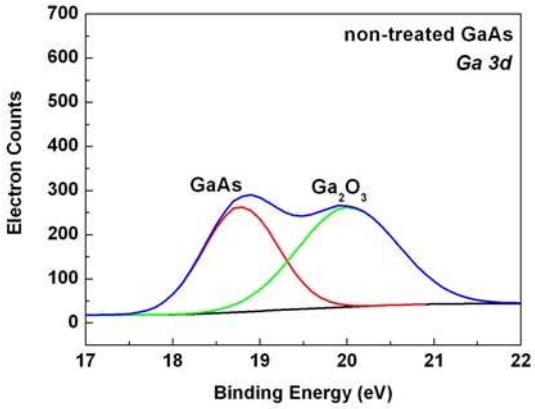
- **Atomic Layer Deposition of HfO_2**
- **TDEAH, water, 150°C, 250cy**

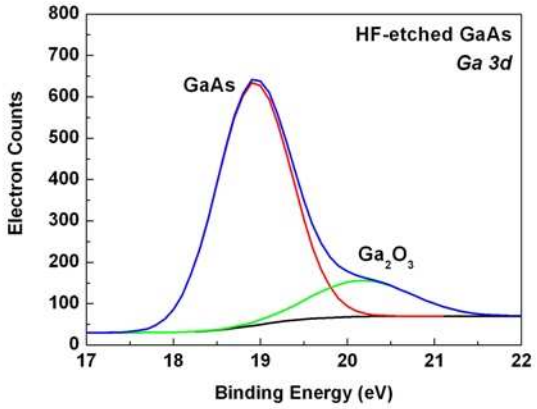
Metal gate deposition

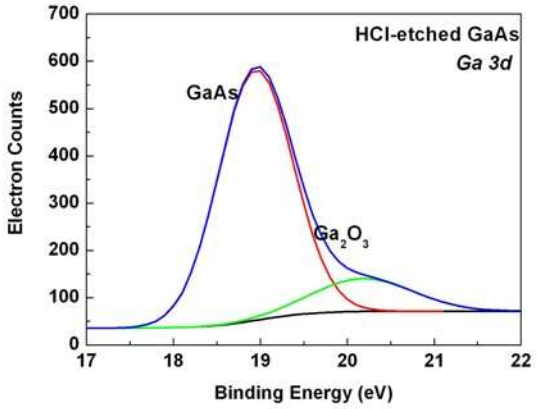
- **50nm W for front contact,**
- **Ti(50nm)/Au(150nm) for back contact by e-beam evaporation**

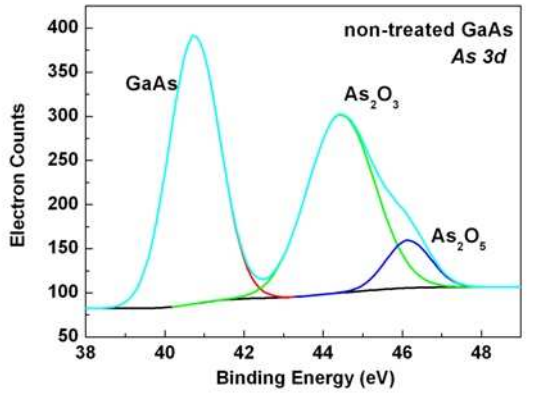
Surface Treatments

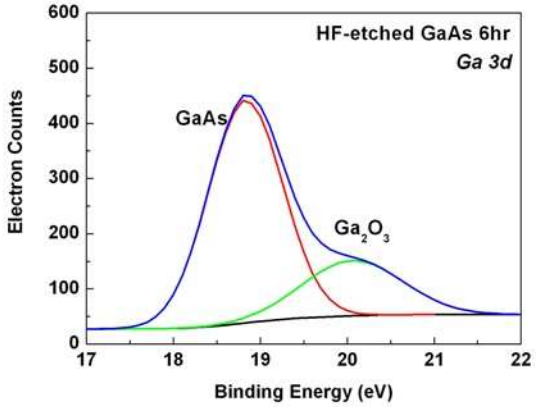
Non-treated GaAs | HF-etched GaAs | HCl-etched GaAs

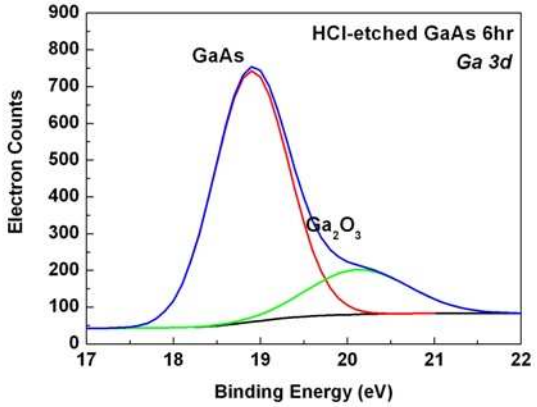












Ga_2O_3, As_2O_3, As_2O_5

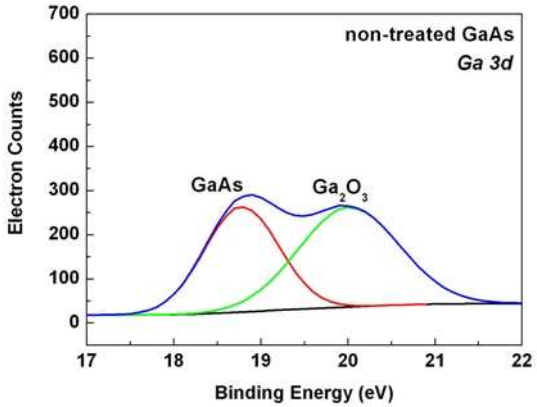
Reduced Ga_2O_3

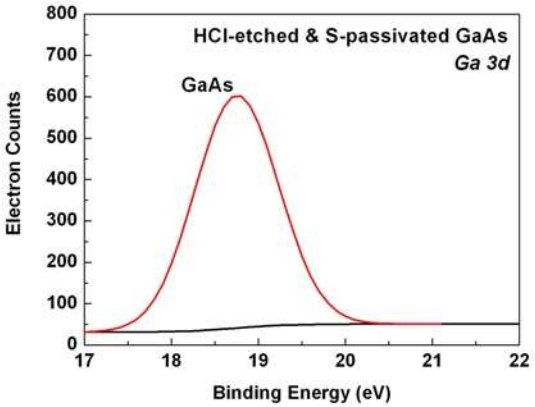
Reduced Ga_2O_3

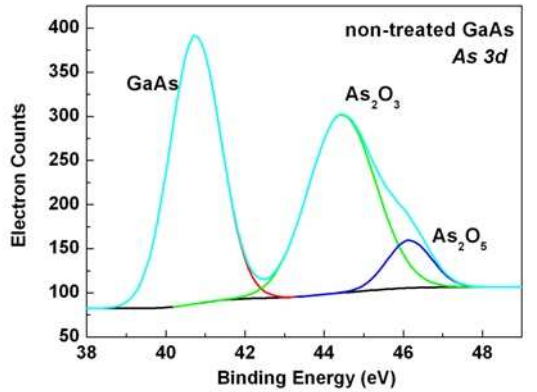
Surface Treatments

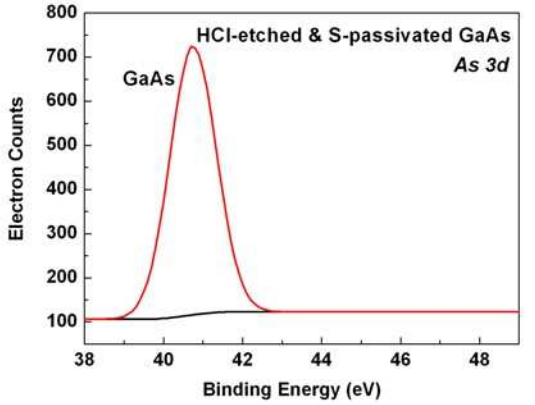
Before S-passivatoin

After S-passivation









Ga_2O_3, As_2O_3, As_2O_5

Oxide-free surface

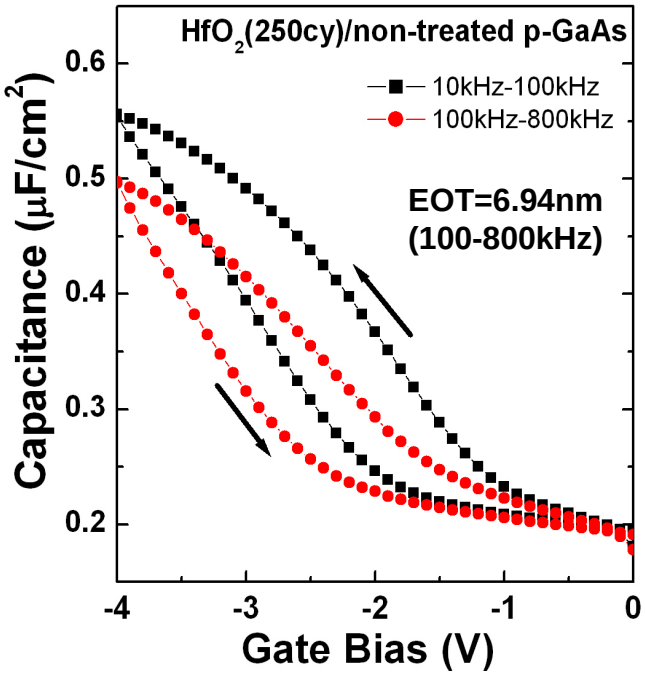
Surface Treatment Summary

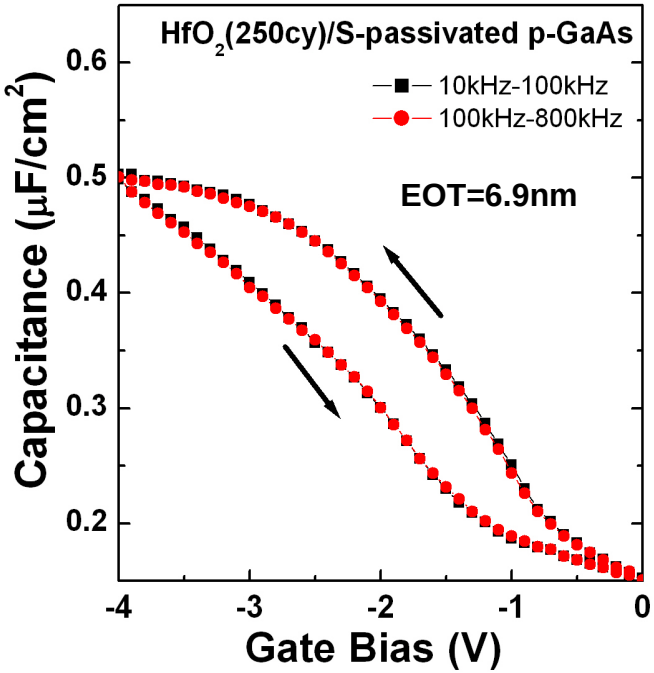
	Non-treated GaAs	HF-etched GaAs	HCl-etched GaAs	HF-etched & S-passivated GaAS	HCl-etched & S-passivated GaAs
Ga_2O_3/total Ga After surface treatment	**56%** (reference, no surface treatment)	**17%**	**14%**	**11%**	**~0%**
Ga_2O_3/total Ga After 6 hour exposure to lab atmosphere	**56%** (reference, no surface treatment)	**25%**	**19%**	**13%**	**11%**

- **HCl-etching exhibits better performance in removing native oxides of GaAs than HF-etching**
- **Native oxide removal followed by S-passivation using dilute aqueous $(NH_4)_2S$ produces a more stable oxide-free surface**

✓ **S-passivation has ESH benefits by potentially reducing the number of wet cleaning steps used prior to gate dielectric deposition**

C-V Charcteristics





✓ **S-passivated (HCl-etched) sample shows improved CV characteristics**

- **complete elimination of frequency dispersion**
- **recovery of a near-ideal flat band voltage**
- **modest decrease in CV hysteresis**

Summary

- We have performed an assessment of ESH impact of chemistries used in this research
- We have shown that HCl-etching is more efficient in terms of removing the native oxide of GaAs than HF-etching.
- We have studied the surface stability of various surface treatments and confirmed that S-passivation using $(NH_4)_2S$ solution followed by HCl-etching produces a more stable oxide-free surface
  - Important to minimize the number of wet cleaning steps (effluent generation) prior to gate dielectric deposition
- We have demonstrated improved electrical properties of W/ALD-HfO_2/p-GaAs such as complete elimination of frequency dispersion, a decrease in CV hysteresis, and recovery of flat band voltage shift by S-passivation.

Future Plan

- Improve properties of HfO_2/GaAs (& InGaAs) by post-deposition anneals under various conditions.
- Study *in-situ* hydrogen thermal anneals and hydrogen plasma anneals to remove the S-layer adsorbed on GaAs surface prior to HfO_2 deposition (S may dope the surface of such crystals, which may have negative consequences in terms of electrical control of MOS devices. By removing S-layer prior to gate dielectric deposition, we will be also able to minimize potential S contamination in the subsequent device fabrication process.)
- Perform a systematic assessment of ESH benefits from a stable chemical passivation of III-V surfaces in a realistic device fabrication flow (jointly with the Nishi and Shadman groups)
- Investigate possible issues associated with removal of residual passivating agent (e.g. S) either before or after gate dielectric deposition (jointly with the Nishi and Shadman groups)

* This research involves active collaboration with researchers at Intel Corporation: Dr. Niti Goel, and Dr. Wilman Tsai

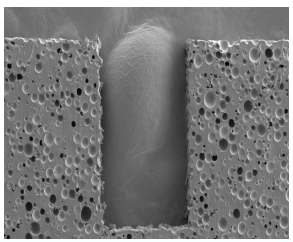
Sematech Project Update

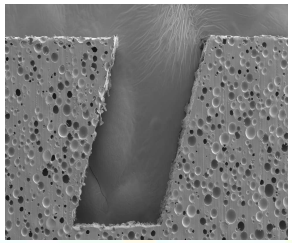
Process Optimization and Modeling of Metal CMP

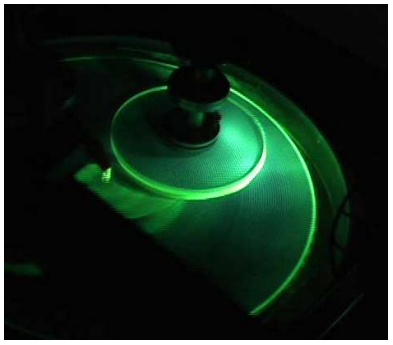
- **Team:**
  - D. Rosales-Yeomans, L. Borucki, W. Worth and A. Philipossian
- **Goal: (EHS Impact … Slurry and Pad Consumption Reduction)**
  - Analyze effect of novel grooves on kinetic, thermal and tribological attributes of metal CMP
- **Key Results:**
  - Design & manufacture of pads with novel grooves
  - Application of new 3-step Cu removal model to explain data in terms of chemical, mechanical & dissolution rate constants
  - Significant increase in pad life due to nearly 50 percent reduction in required wafer pressure with certain grooves
  - Significant reduction in slurry consumption associated with certain grooves
- **Plans:**
  - Refine 3-step model by incorporating the role of process parameters on passivation film growth
  - Prove mechanism of slurry transport by flow visualization using DEUVEF

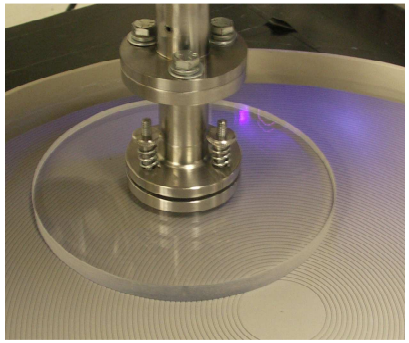
Sematech Project Update

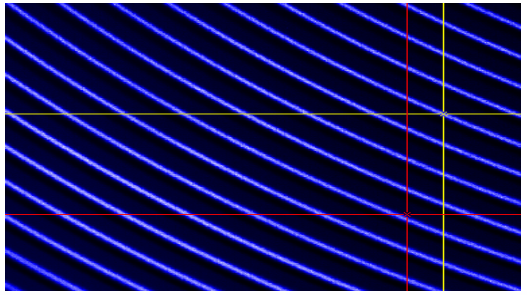
Process Optimization and Modeling of Metal CMP

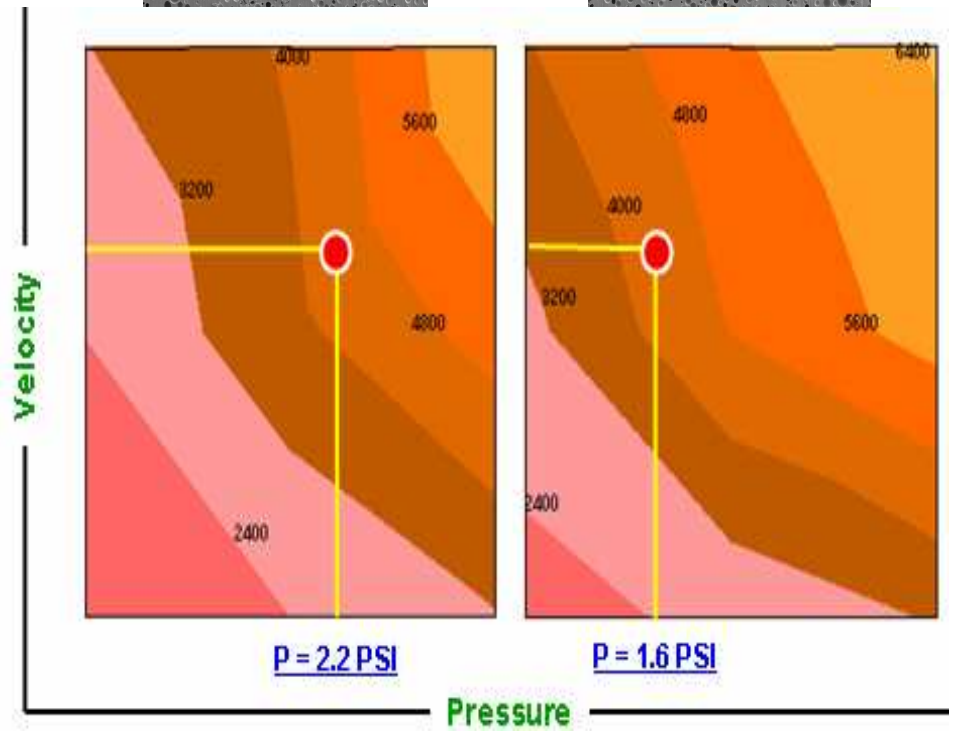


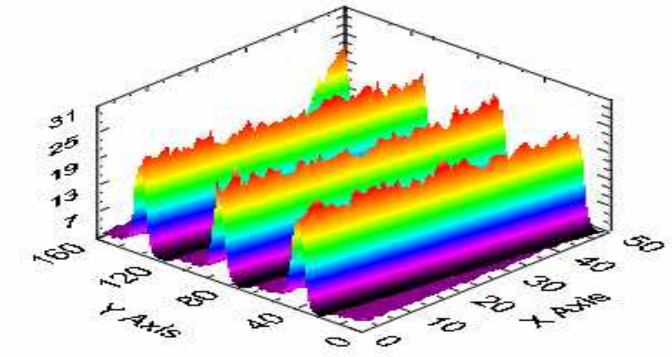












SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

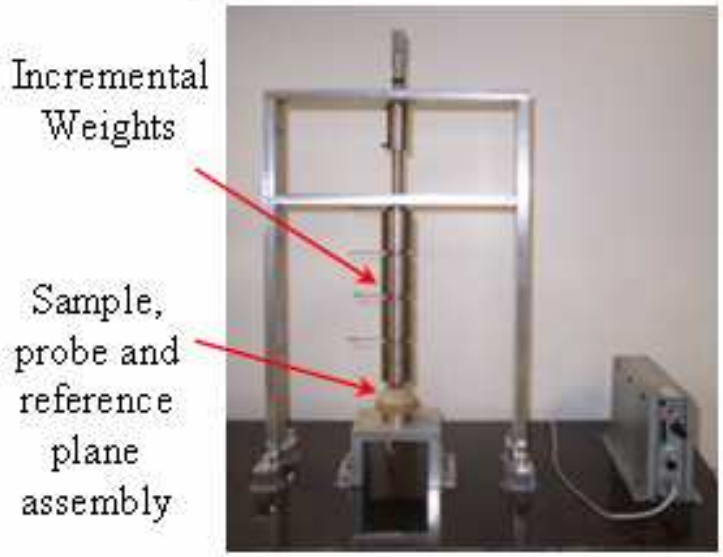
Sematech Project Update

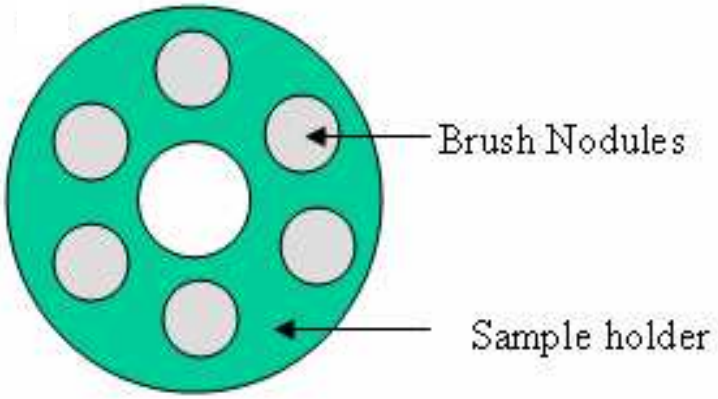
Post-Planarization Waste Minimization

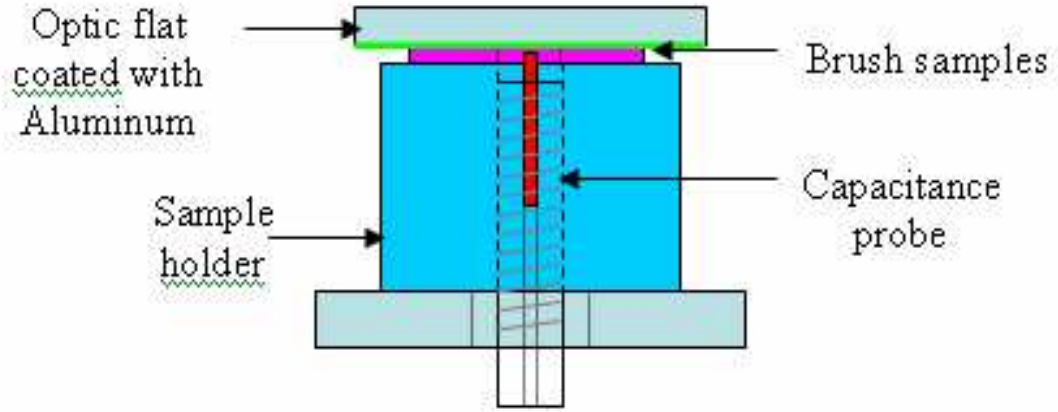
- **Team:**
  - T. Sun, L. Borucki, W. Worth and A. Philipossian
- **Goal: (EHS Impact … Pad Consumption Reduction)**
  - Investigate effect of brush physical properties on tribological behavior during post-CMP cleaning
  - Investigate brush asperity deformation as a function of applied load and extended use
- **Key Results:**
  - Harder brushes were less stable than softer brushes in terms of COF and they also exhibited a greater degree of hydrodynamic chattering
  - COF showed a power law dependence with sliding velocity
- **Plans:**
  - Theoretically explain the power law dependence of COF on sliding velocity using modified nano-lubrication models
  - Qualify and adopt incremental and cyclic loading methods to perform brush deformation measurements before and after extended wear to understand failure mechanisms of PVA brushes during post-CMP scrubbing

Sematech Project Update

Post-Planarization Waste Minimization







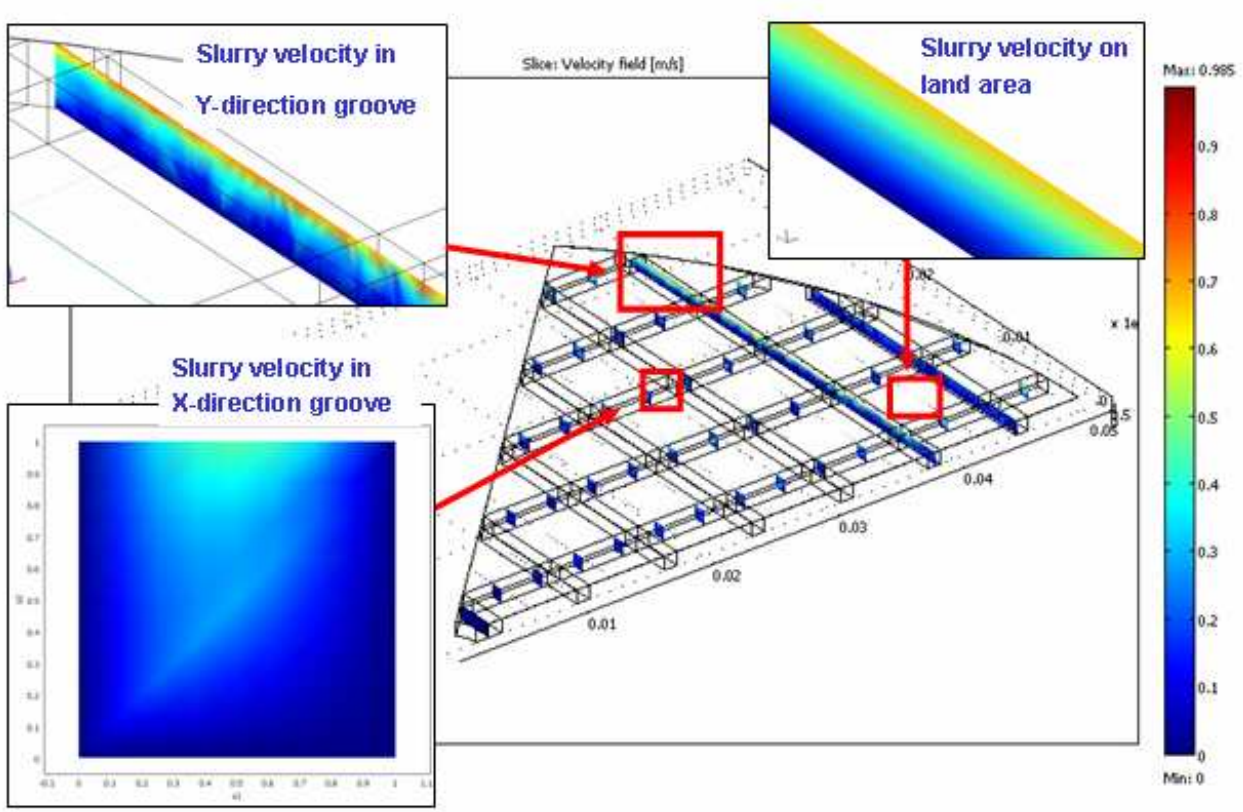
Novellus-SRC Customized Project

Mechanistic Study and Modeling of Orbital Polisher for Cu CMP

- **Team:**
  - **H. Lee, L. Borucki, F. O'Moore, S. Joh and A. Philipossian**
- **Goal: (EHS Impact … Slurry and Pad Consumption Reduction)**
  - **Characterize by-product build up on pad surface and investigate how process parameters affect by-product build up & polish performance**
  - **Develop a 3D fluid transport model for fluid flow and couple it with a model for transport and consumption of reactant and for production and deposition of by-products to predict pad staining and compare with experimental results**
- **Key Results:**
  - **Staining due to mechanical action during polishing which was then advected downstream by slurry flow**
  - **Staining increased with polishing pressure, wafer rotation rate, slurry flow rate and polish time**
  - **Simulated slurry velocity increased gradually on the wafer surface in the radial direction due to wafer rotation. This affected velocity in the grooves. Simulation results showed shear flow on land areas and wafer-driven circulation in the grooves**

Novellus-SRC Customized Project

Mechanistic Study and Modeling of Orbital Polisher for Cu CMP



- **Plans (already completed in February 2007):**
  - **With simulated slurry velocity and temperature profiles, by-product generation, transport, and deposition on pad will be simulated to illustrate the mechanism of stain formation**

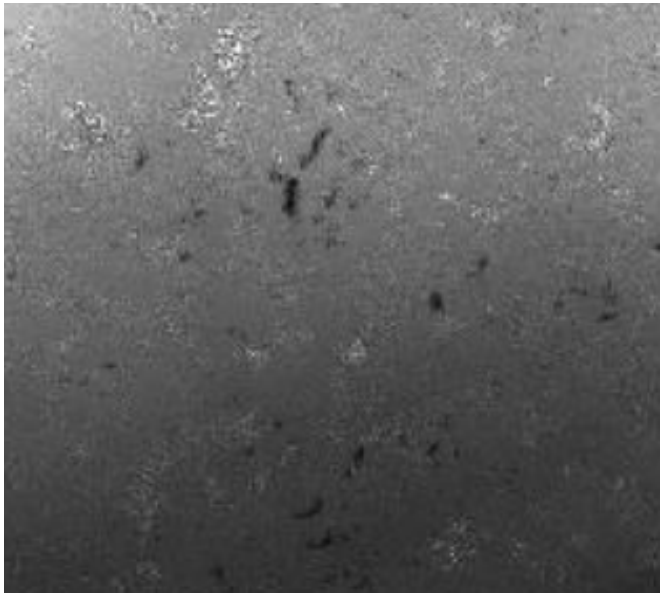
Proposed New Seed Project

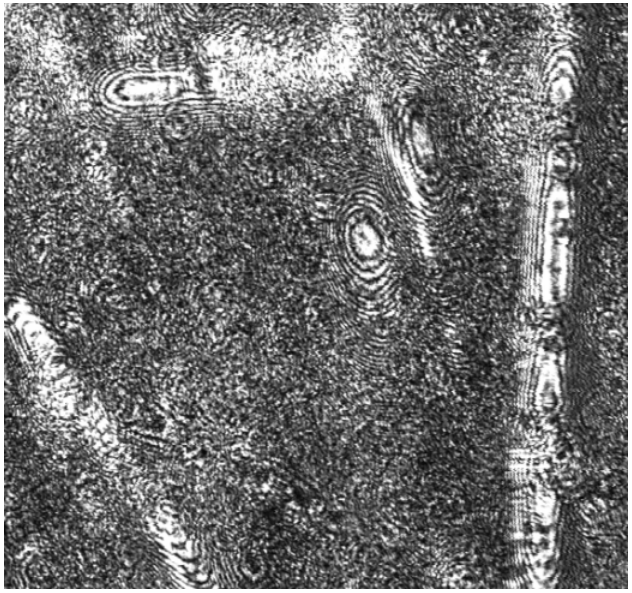
Quantifying Pad-Wafer Contact Area using Confocal Microscopy

- **Team:**
  - X. Wei, L. Borucki and A. Philipossian
- **Background:**
  - Several new types of pads with vastly different bulk and surface mechanical properties are being introduced in the planarization space
    - Porous open or closed cell
    - Non-porous with water-soluble particles or fibers
    - Conductive closed cell for E-CMP
    - Micro-replicated asperity
  - Actual contact area (caused by surface topography, mechanical properties and process conditions) affects surface abrasion as well as defectivity
- **Goal: (EHS Impact … Pad Consumption Reduction)**
  - Use confocal microscopy to get high-resolution images from a single focal plane of samples under typical pressures used in planarization
  - Develop reflectance-interference contrast methods for improved imaging
  - Recommend general pad structures and micro-textures that provide high contact area, better contact uniformity and less contact pressure for improved planarity, less defects and longer pad life

Proposed New Seed Project

Quantifying Pad-Wafer Contact Area using Confocal Microscopy





Subtask C-1-5 : *Screening of four options for PFOS removal from litho-track wastewater*

- 1 year Sematech seed project –

(Completed)

Reyes Sierra and Valeria Ochoa

Chemical and Environmental Engineering
University of Arizona

OBJECTIVES

The aim of this seed project was to evaluate the effectiveness of four different approaches for the removal of PFOS, *i.e.*,

1) Biomimetic dehalogenation (vitamin B_{12}-Ti(III)-citrate).
2) Anaerobic reductive dehalogenation.
3) Activated carbon adsorption.
4) Biosorption by wastewater treatment sludge.

CONCLUSIONS

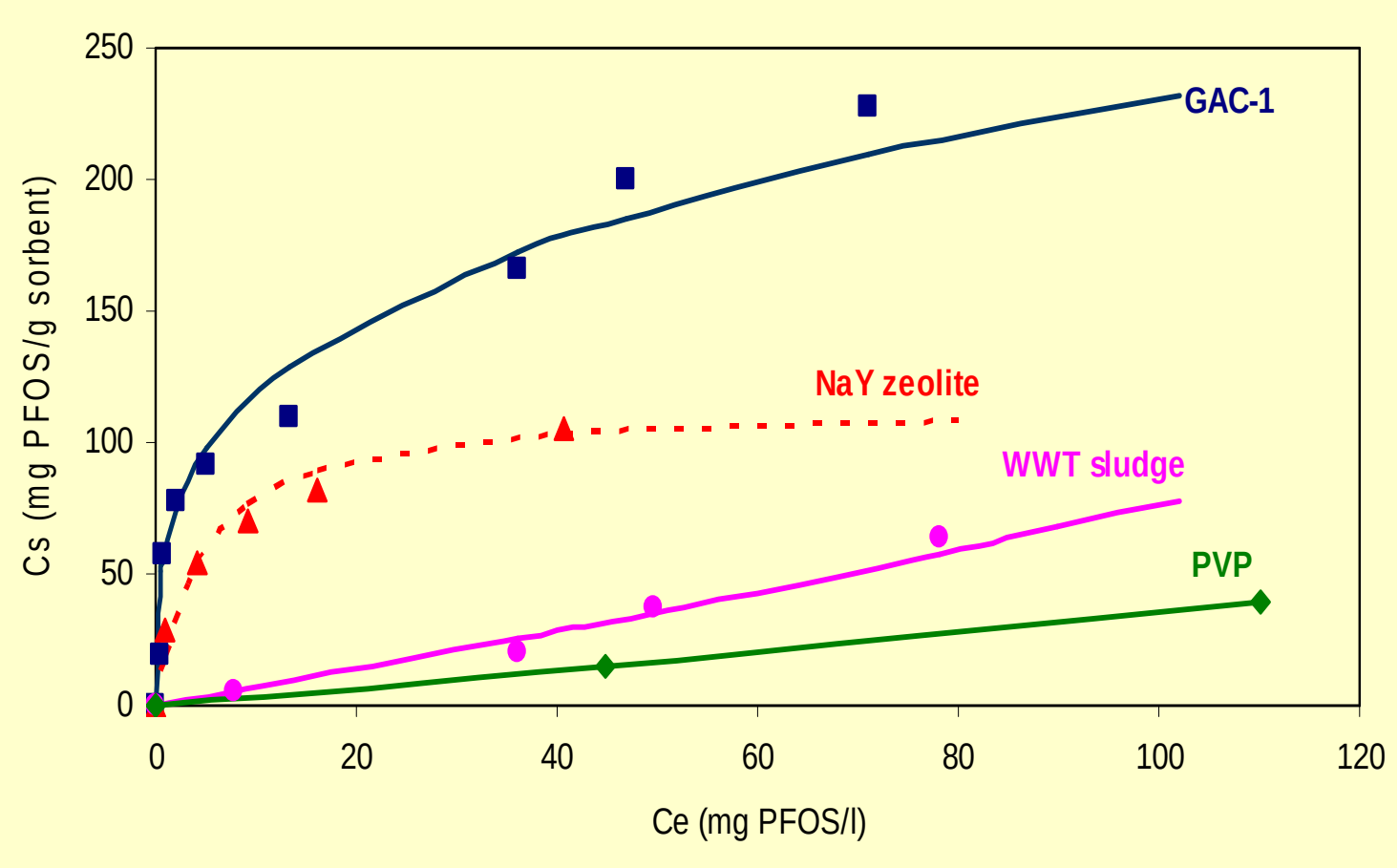
1) PFOS is susceptible to biomimetic dehalogenation with vitamin B_{12}-Ti(III)-citrate -> 3 moles Fluoride released/mol PFOS.

2) Biodegradation of PFOS and PFBS was not observed after 6 months of incubation under anaerobic conditions.

3) Adsorption onto granular activated carbon (GAC) is a promising method for the removal of PFOS from dilute aqueous streams. Affinity of GAC for PFOS > PFOA ≈ PFBS.

4) Partial removal of PFOS should be expected during wastewater treatment due to biosorption.

Adsorption of PFOS on Different Media



Impact of Fluoride and Copper in Wastewater on Publicly-Owned Treatment Works (POTWs)

- New Sematech Project -

Reyes Sierra and Glendy Leon

Dept Chemical and Environmental Engineering
The University of Arizona
PO Box 210011, Tucson, AZ 85721

Fluoride and Copper in Semiconductor Manufacturing Effluents

Fluoride (F^-) and **copper** (Cu^{2+}) often present in combined semiconductor manufacturing effluents.

F^- - Max. conc. (mg/L): 4.7 - 72.0 mg/L; Avg Conc. (mg/L): 4.3 - 26.8 mg/L

Cu^{2+} - Max. conc. (mg/L): 0.03 - 4.0 mg/L; Avg Conc. (mg/L): 0.01 – 0.9 mg/L

There is a lack of information regarding the toxicity of F^- to microorganisms in POTWs and higher aquatic organisms.

The inhibitory potential of Cu is well established. However, no evidence is available to judge the hypothesis that F^- has a synergistic effect on Cu toxicity.

Project Objectives

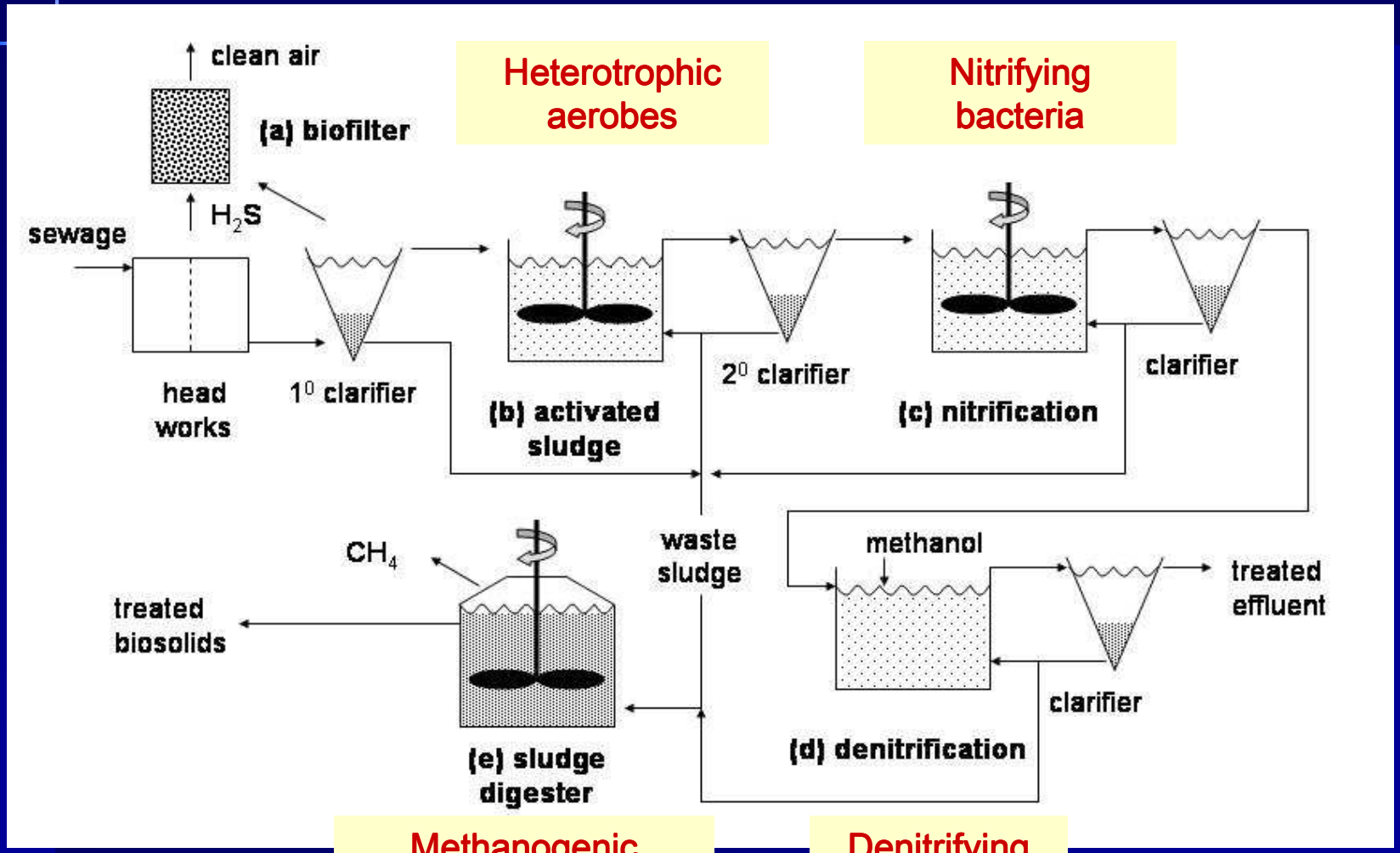
Literature review - Impact of F^- and Cu^{2+} on:

- Biological wastewater treatment
- Species used in effluent ecotoxicology monitoring

Determine the inhibitory effect of F^- and Cu^{2+} to:

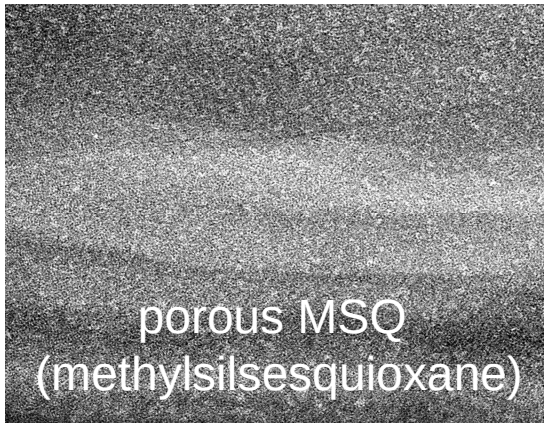
- Main microbial populations in POTWs
- Common effluent monitoring species

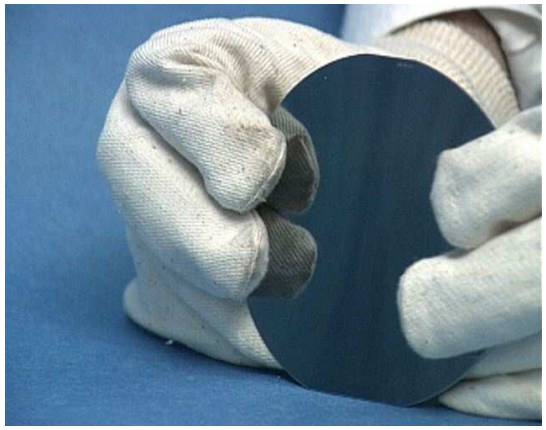
Unit processes and key microbial populations in a typical municipal wastewater treatment plant

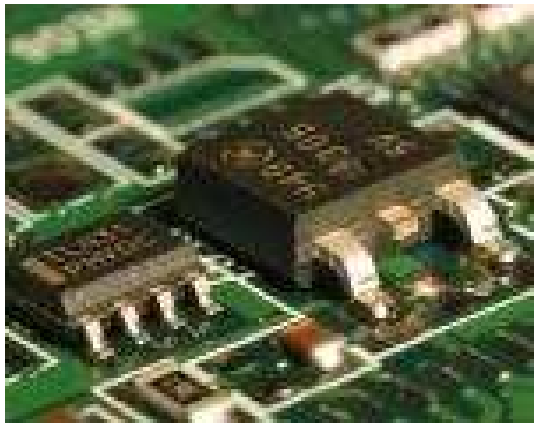


Ultra Low-*k* Film Repair and Pore Sealing Using Supercritical Fluids

Sematech Final Project Report
SRC/TI Customization







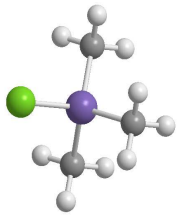
Lieschen Hatch and Anthony Muscat
Department of Chemical & Environmental Engineering
University of Arizona, Tucson, AZ 85721

Acknowledgements: Sematech, SRC, and Texas Instruments

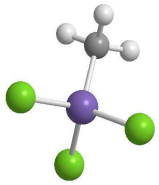
Chemistry of Chlorosilanes and p-MSQ

Repair chemistries

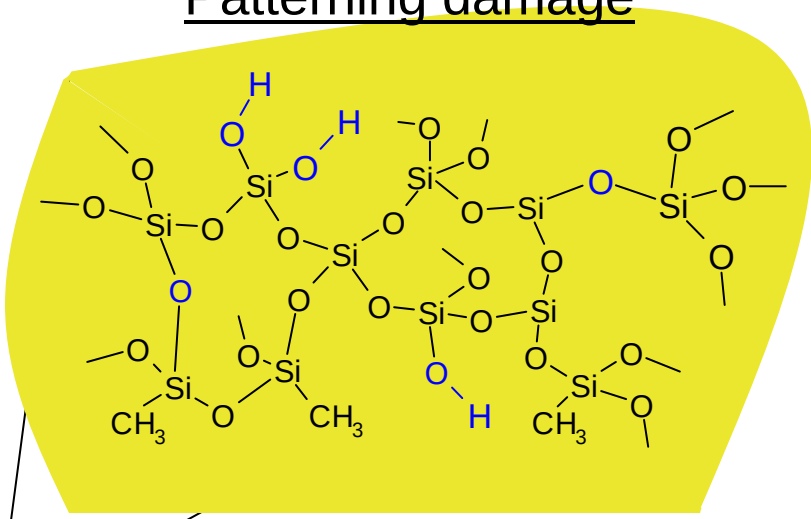
Trimethylchlorosilane
(TMCS, 0.44 nm)

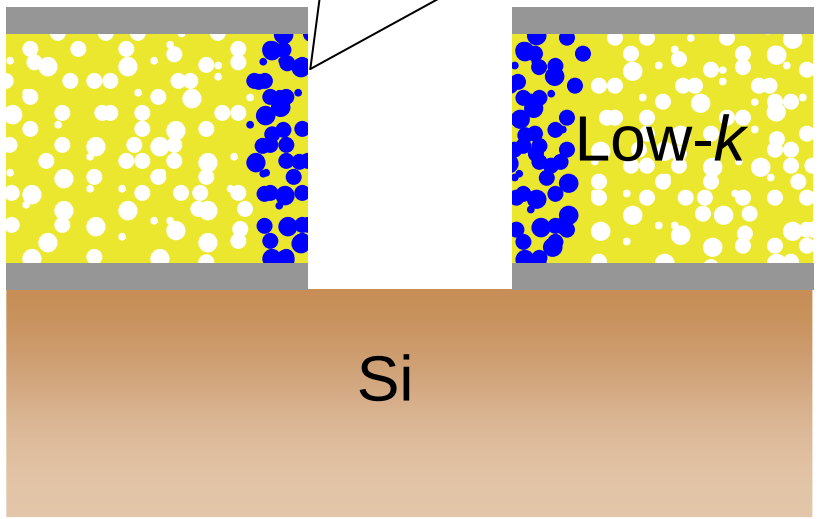


Methyltrichlorosilane
(MTCS, 0.43 nm)



Patterning damage

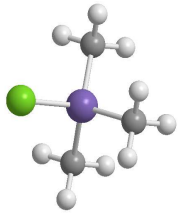




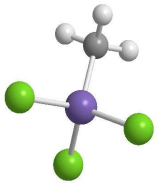
40% porosity p-MSQ
3.4 nm avg pore D

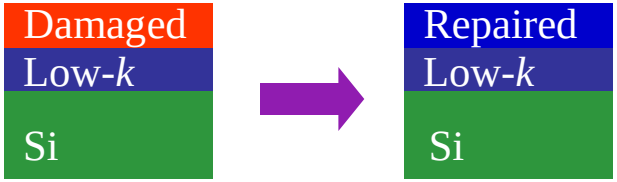
Chlorosilane Repair and Sealing of p-MSQ

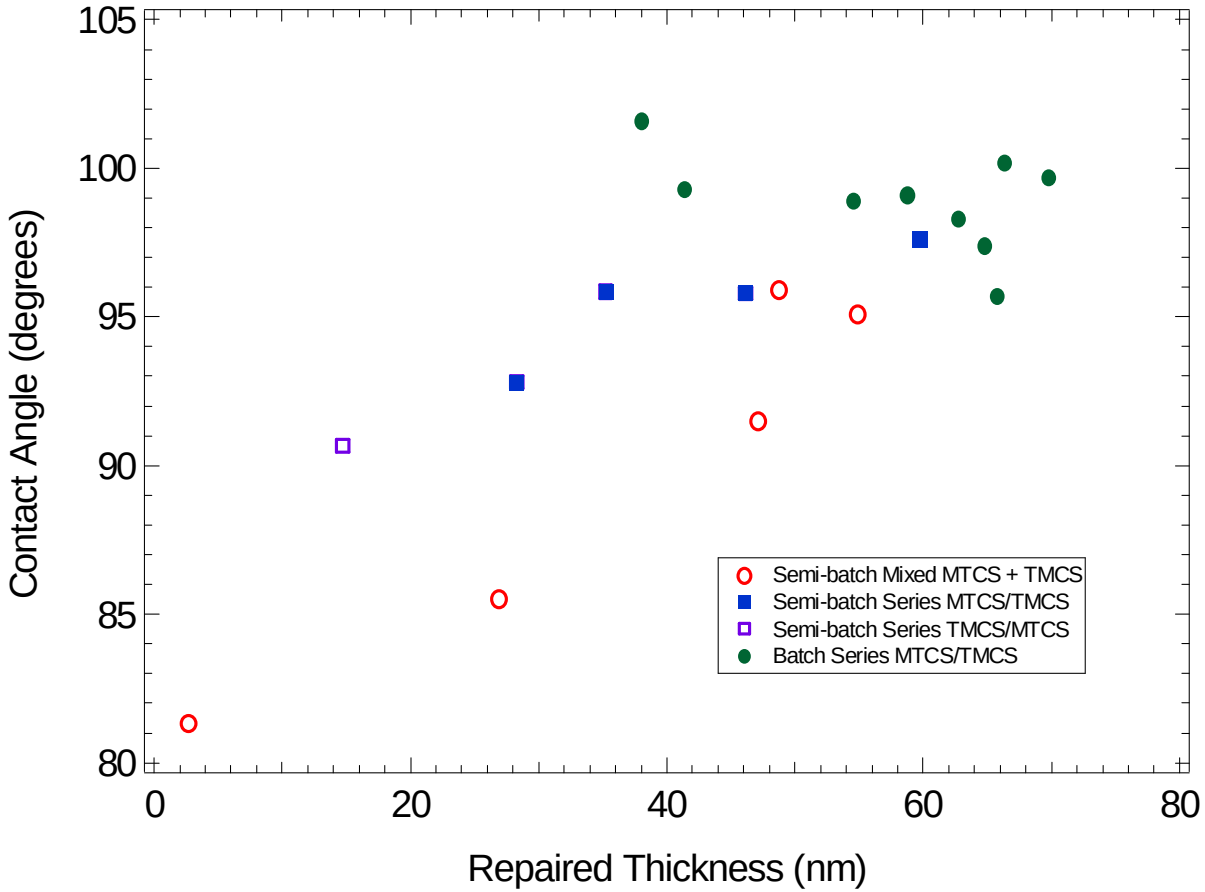
Trimethylchlorosilane
(TMCS)



Methyltrichlorosilane
(MTCS)

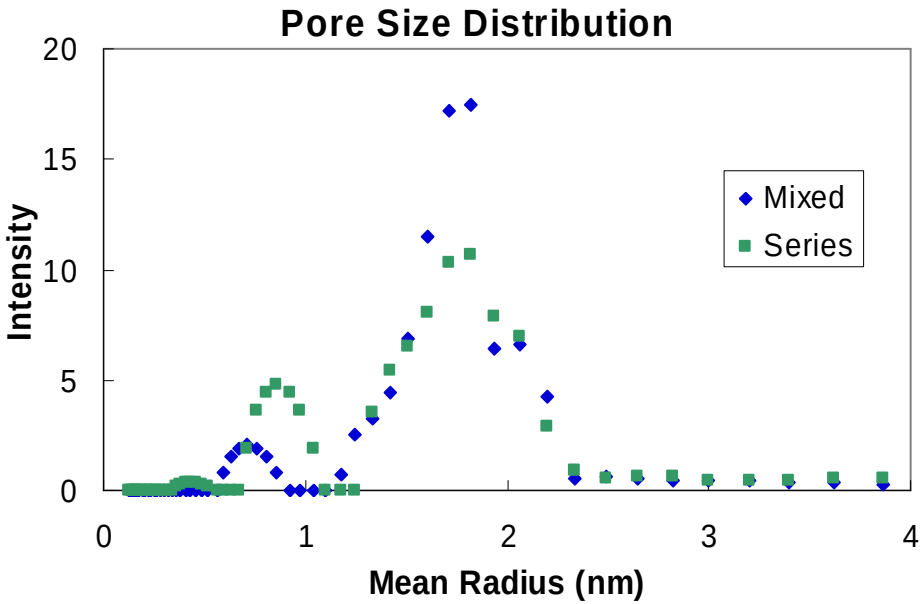


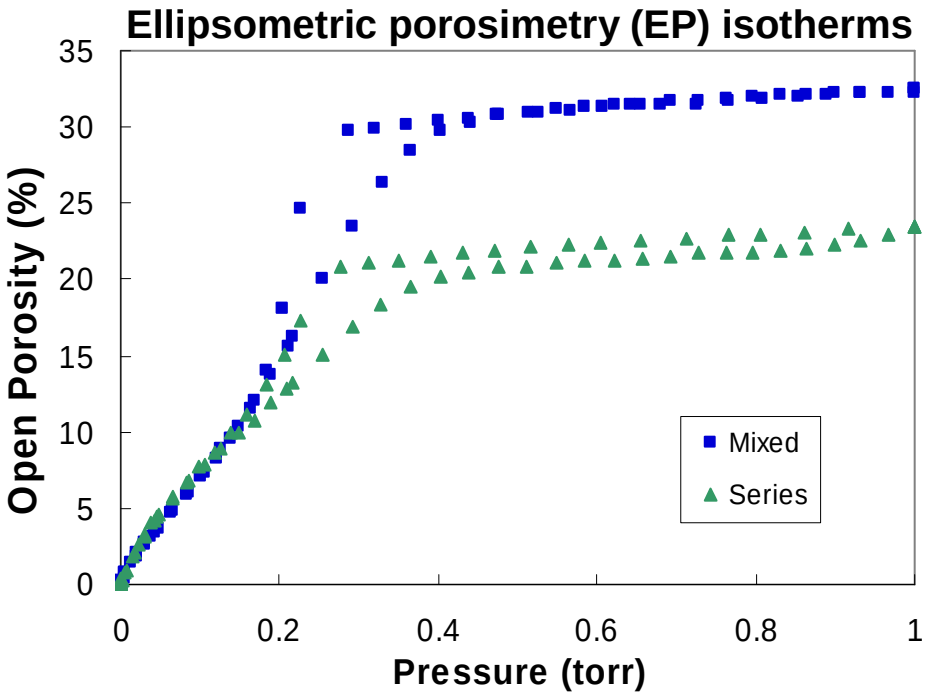




- Goal: MTCS/TMCS to decouple contact angle and thickness
- Series MTCS/TMCS higher contact angles with thinner film

Pore Size Distribution and EP

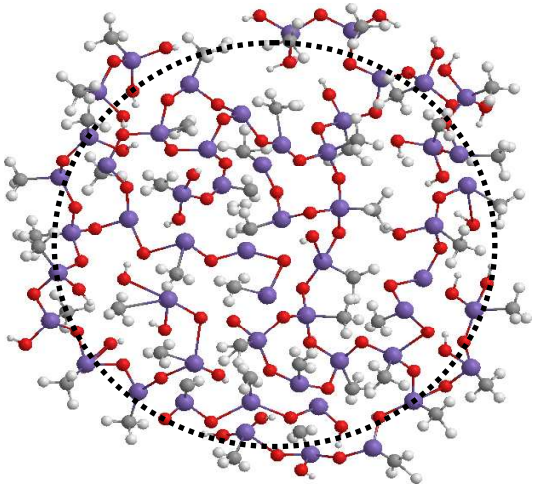




- Series MTCS/TMCS decrease porosity by 50 %
- Series MTCS/TMCS better at capping pores than Mixed MTCS + TMCS

Conclusions

- Repaired p-MSQ (mesoporous) with chlorosilanes dissolved in $scCO_2$ (*k=3.4* damaged film $\rightarrow$ *2.4*)
  - Hydrophobic surface
  - Removed/reacted OH groups
  - Repaired films stable in air for 30 days



- Demonstrated sequential MTCS/TMCS process sealed pores of plasma-treated p-MSQ
  - Polymerization reactions in fluid and on surface

- Controlled sealing layer thickness
  - Chorosilane concentration
  - Moisture
  - Process T and p

Accomplishments

- Students:
  - Dr. Bo Xie (Applied Materials)
  - Eduardo Vyhmeister (Ph.D. candidate, UPRM)

- Publications:

B. Xie, A. J. Muscat, E. Busch, T. Rhoad. Advanced Metallization Conference Proceedings, 2004.
B. Xie, A. J. Muscat. Proceedings – Electrochemical Society, 2004.
B. Xie, A. J. Muscat. Microelectronic Engineering, 2004
B. Xie, A. J. Muscat. Materials Research Society Symposium Proceedings, 2004.
B. Xie, A. J. Muscat. Solid State Phenomena, 2005.
B. Xie, A. J. Muscat. Microelectronic Engineering, 2005.
B. Xie, G. Montano-Miranda, C. C. Finstad, A. J. Muscat. Materials in Semiconductor Proc., 2005.
B. Xie, C. C. Finstad, A. J. Muscat. Chemistry of Materials, 2005.
B. Xie, L. Choate, A. J. Muscat. Microelectronic Engineering, 2005.

Biomimetic Manufacturing of Nanoscale Devices

Anthony Muscat[1], Megan McEvoy[2], Masud Mansuripur[3]

[1]Department of Chemical and Environmental Engineering

[2]Department of Biochemistry and Molecular Biophysics

[3]College of Optical Sciences

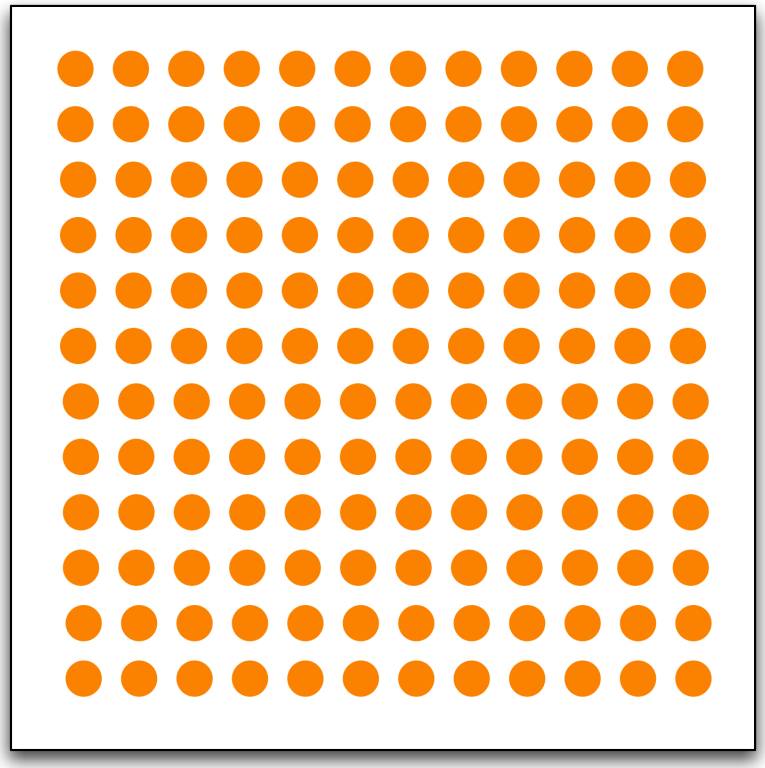
University of Arizona, Tucson, AZ 85721

Initial phase, seed project, funded by Arizona TRIF, January 2007

Proposal submitted to NSF NIRT program

Objective

- Harness biomolecules isolated from bacteria to rapidly and selectively deposit materials on semiconductor substrates to create uniform arrays of dots and grow nanowires in 3D



Rationale

- Minimize costs of materials, energy, and water to fabricate nanoscale devices using bio-based strategy
- Exploit homogeneity, mild reaction conditions, and specificity of of biological molecules
  - Other biomolecule work grows wires based on passive electrostatic adsorption on viruses, DNA, etc.
- Grow 3D structures to achieve scalable architecture
  - Address current show stopper to grow oriented arrangement of nanowires
- Employ additive, bottom up patterning methods

Lowering Purge-Gas Consumption during Dry-down of Gas Distribution Systems

A Joint ERC-Intel Seed Project

Junpin Yao*, Harpreet Juneja*, Asad Iqbal*, Farhang Shadman*, and Carl Geisert#

Department of Chemical and Environmental Engineering
University of Arizona

#Intel Corporation, Chandler, Arizona

February 2007

Outline

- **Experimental procedure and model development**
- **Experimental results and model validation**
- **Parametric study and model application**
- **Summary and Conclusion**

Summary and Conclusions

- **Moisture removal from stainless steel surfaces is a slow and activated process.**

- **A technique, that combines measurement and process modeling, is developed to study the dynamics of moisture absorption and desorption, moisture loading, and moisture profile in a gas distribution network.**

- **The technique can be used to optimize the dry-down time and lower the purge-gas consumption during system start-up or recovery.**

Etching of Metals and Polysilicon During Megasonic Cleaning

Srini Raghavan

Pierre Deymier

Department of Materials Science and Engineering

University of Arizona

Project Justification

- Megasonic cleaning after CMP exposes metal and polysilicon features
- Corrosion (pitting and intergranular) and feature damage is known to be a problem during cleaning but the interaction between sound field and chemistry in causing the damage has not been established
- Literature reports on systematic investigations of etching of metals in megasonic field are virtually nil

Proposed Work

- Investigate the etching of W, Cu and polysilicon films in solutions of interest to post-CMP cleaning in megasonic field using an electrochemical quartz crystal microbalance (ECQCM)
- Characterize the cavitation characteristics (intensity and bubble size) in different cleaning solutions using a cavitation probe and hydrophone and relate them to etching
- Identify megasonic conditions (power, frequency, angle of impingement) that could reduce the extent of etching and feature damage
- Experiments will be correlated to modeling and simulation results

- Experience of the PI, Infrastructure and Industrial Collaborations

  - PIs have an immersion megasonic system, cavitation probe, hydrophone and a ECQCM to carry out experiments

  - Professor Deymier has been active in developing MD (Molecular Dynamics) simulations on cavity formation in liquids and on substrates immersed in liquids as well as capabilities for modeling linear and non-linear acoustic wave propagation in inhomogeneous fluid/solid media.

  - PIs have a working collaboration with Prosys Megasonics, a leading megasonic tool manufacturer

- ESH Impacts

  - Proposed work can help in the development of cleaning systems that can provide effective cleaning in dilute chemical systems at reduced megasonic power

Quantitative Structure-Biodegradability Relationships for Organofluorine Compounds

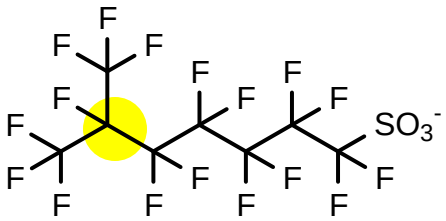
Dr. Jim Field, Dr. Reyes Sierra	UA ChEE	Biodegradation
Dr. Paul Blowers	UA ChEE	Computational Chemistry
Dr. Chris Ober	Cornell	PAG Chemistry

Background PFOS and new PAG substitutes contain fluorine groups

Small changes in PAG chemistries have large impacts on biotransformation

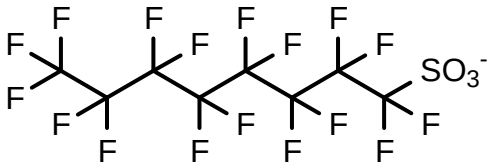
Reductive Dehalogenation (Vit B12): Linear *versus* Branched

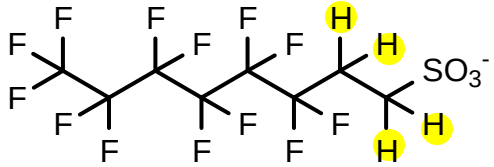
Cooxidation (monooxygenase): F groups versus H groups



Vit B12

Sierra *et. al.* 2007





monooxygenase

Key *et. al.* 1998

Objective

Identify key structural characteristics of organofluorine compounds promoting environmental biodegradability without compromising PAG quality

Methods

- **Test Series of Structurally Related PFOS and New PAGs for Biodegradability**

  (variations on F, H, branching, O-groups, NO2-groups *etc*)

  Reductive dehalogenation: biomimic Vit B12; anaerobic sludge

  Cooxidation: methane monooxygenase

  Aerobic Growth: activated sludge

- **Computational Chemistry**

  Correlations: HOMO energies, total atomic charges, ring angles, solvation energies, and dipole moments

  Calculations: B3LYP/6-31g* for molecular geometry predictions

- **PAG Chemistry**

  Organic Synthesis: structural series

  PAG: performance in photolithography