Environmentally Benign 3-D IC Technologies

Thrust A-1

Ajay Somani and Rafael Reif

Microsystems Technology Laboratories
M.I.T.

Objectives of project

- *Compare different 3-D process flows in terms of environmental issues (such as electricity, water usage, emissions, HAP's, VOC's…..) and performance.*
- *Identify non-environmentally benign processes.*
- *Develop alternative approaches / technologies that replaces non-environmentally benign processes without sacrificing performance.*

Evaluation Approach

- System Approach
  - Understand first order effects
  - Only fabrication processes are considered (i.e. no packaging).
- Compare different 3-D technologies
  - MIT,RPI and IBM.
- Focus on processes which are additional and/or different
- Use a standard/control circuit for comparison.
- Help from Industry/Sematech may be needed to quantify energy, water and emissions measurements associated with individual process steps.

First-Order Assumptions

- All 3-D processes have two wafers with devices.
- Cu is used as an interconnect metal layer.
- Surface preparation includes oxide CMP for global planarization and SC1 clean.
- All organic polymer deposition (e.g. BCB, dielectric glue and photoresist) require surface activation.
- Lift off is used to make Cu (metallic) pads.
- Processes are assumed to be linear in emissions, electricity and power usage.

Differences in 3-D processes

	MIT	RPI*[a]	IBM*[b]
1) Pre-Bonding treatment	Handle Si wafer attached by Cu-Cu bond a) CMP oxide on both wafers b) Deposit Al/Ta/Cu c) Bond	No Handle wafer	Handle glass wafer attached by glue bonding a) Surface preparation b) Spin coat organic glue c) Bond
2) Bonding	a) Etch 1 micron deep vias on thinned wafer b) Deposit Cu c) Lift off to form pads d) Bond it with second wafer	a) Surface preparation b) Spin coat BCB glue c) Bond	a) Deposit LPCVD oxide b) Surface preparation c) Bond
3) Post Bonding treatment	Release handle wafer	a) Etch 5 micron deep via for inter wafer interconnects b) Deposit Cu c) Lift off	a) Release handle wafer by laser ablation b) Etch 5 micron deep via for inter wafer interconnects c) Deposit Cu d) Lift off

* Process flows extracted from publications

[a] in *Advanced Metallization Conference 2000 (AMC 2000)*, v16, 515-521

[b] in IEDM, San Francisco, Dec.9-11 2002

Conclusion and Future Work

- 3 different 3-D wafer interconnect bonded approaches are being studied.
- Processes which are different have been identified and qualitatively categorized.
- We plan to quantify them on different factors such as emissions, electricity usage, HAPs, VOCs etc. (preliminary results in poster)
- Develop alternatives to non-environmentally benign processes without sacrificing 3-D performance.

TASK A2: Solventless Low-κ Dielectrics

Effect of Substrate Temperature on Plasma-Enhanced Chemical Vapor Deposition of Poly(methyl methacrylate) as a Sacrificial Material for Air Gap Fabrication

NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

Karen Gleason, Tom Casserly, SRC/Novellus Fellow

Department of Chemical Engineering, MIT

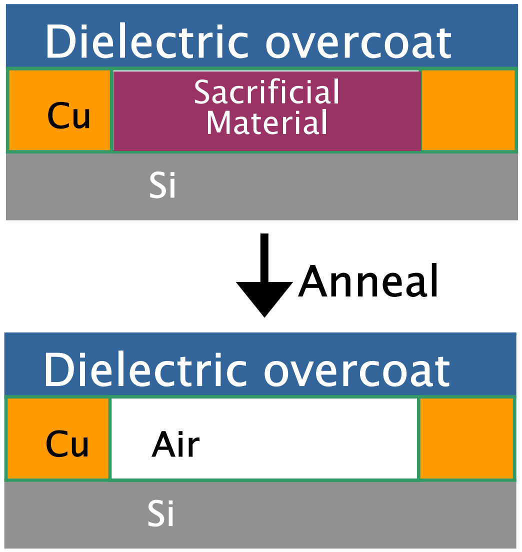
February 24, 2005

Thrust A2: Solventless Low-k Dielectrics

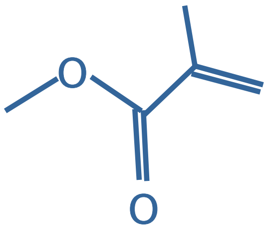
- **Why investigate air gaps?**
  - Dense solutions are approaching the limit for OSG materials
  - Integration of porous materials is an integration nightmare
  - Leap forward in performance increase as opposed to incremental improvements that face difficult challenges
- **Semiconductor International – January 1, 2005 Senior Editor, Laura Peters**
  - *Argues for air gaps as a low-k alternative needed at this time*
  - *"Porous dielectrics have too many problems — at least as many as their dense counterparts — and the overall benefit they deliver, represented as the effective k value, may be small given the integration, yield and reliability challenges they pose and the costs required to surmount them."*

Why Air Gaps: Low-κ Solution

- **Air has lowest dielectric constant**
  - Faster Integrated Circuits
  - Decrease power consumption
  - Reduce cross-talk
  - Leads to fewer levels of interconnect
- **Air has lowest refractive index**
  - Use in optical filters/reflectors/refractors
- **Closed cavity air gap**

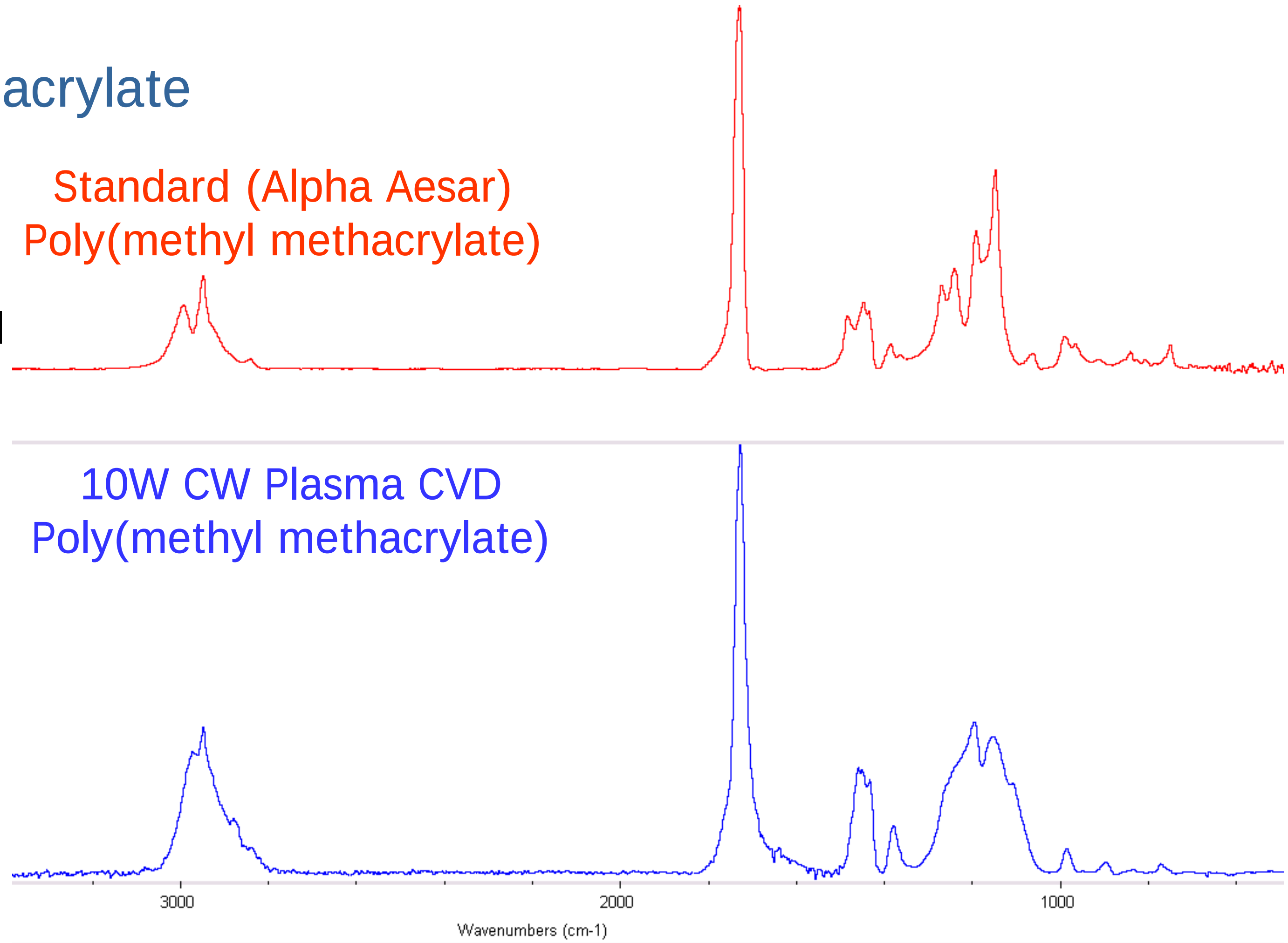


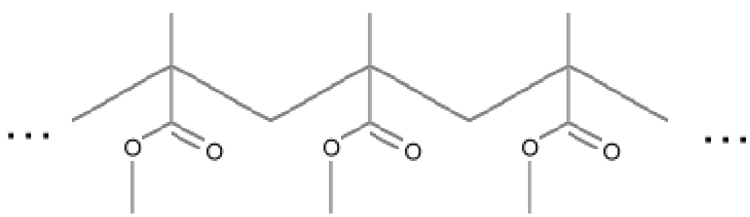
PMMA Deposition and Characterization



Methyl Methacrylate

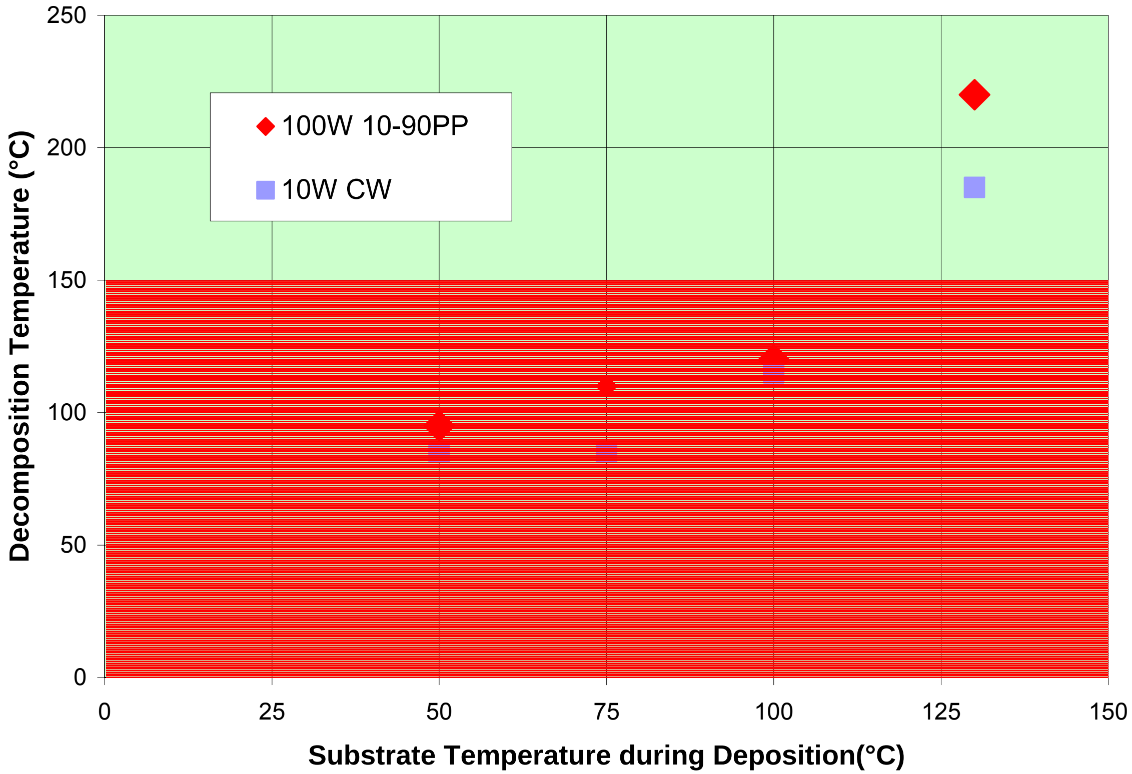
- **Free Radical Polymerization via vinyl bond to Poly(methyl methacrylate) (PMMA)**
- **Low power CW & Low duty cycle PPECVD retains much of PMMA functionality**
- **Thermally decomposes in the absence of oxygen to monomer form below 350°C**





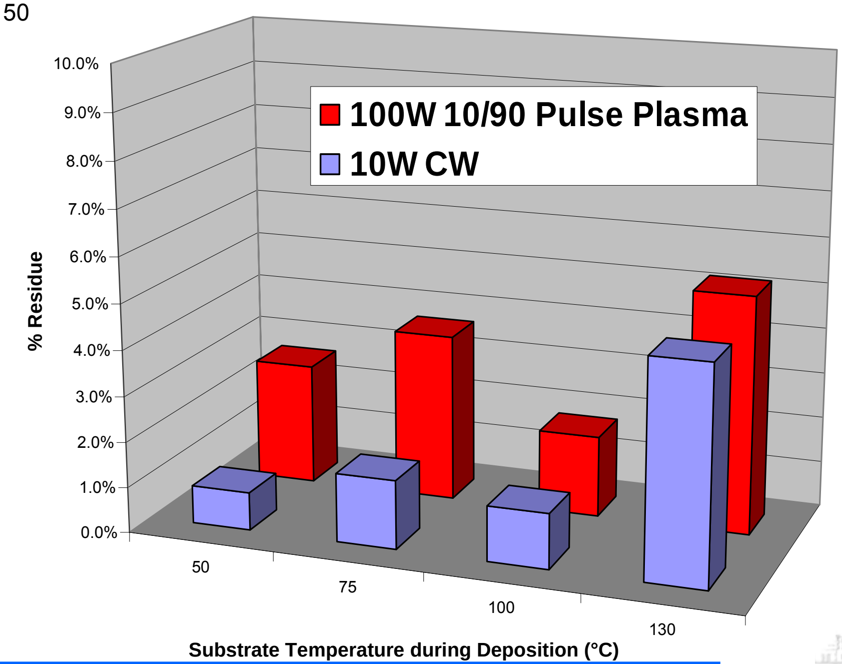
EAN decomposition →

Effect of Substrate Temperature on Thermal Properties



- Onset of Thermal Decomposition increases with increasing substrate temperature
  - Results from increased cross-linking and decreased presence of weak bonds in polymer backbone
  - Require thermal stability below 150°C for conventional hard bake of photoresist

- % Residue calculated by thickness increases with increasing substrate temperature and peak plasma power
  - Likely due to increased cross-linking at higher temperatures
  - Measured residue at low T, may be native thermal oxide – XPS is planned



Fabrication of Microscale Enclosed Void

Air-Gap Microchannels

No Hard Mask Required

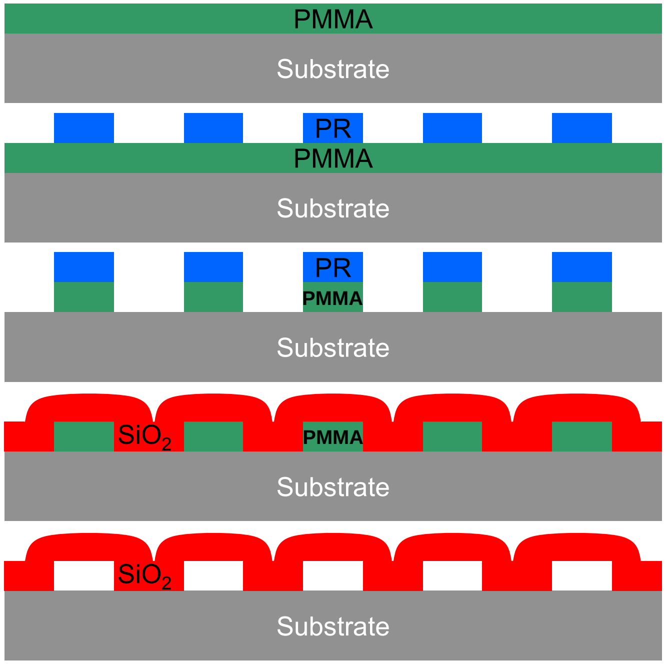
PMMA Deposition

Photolithography

O_2 Plasma Etching of PMMA

Photoresist Acetone Strip
SiO_2 Deposition

PMMA Decomposition

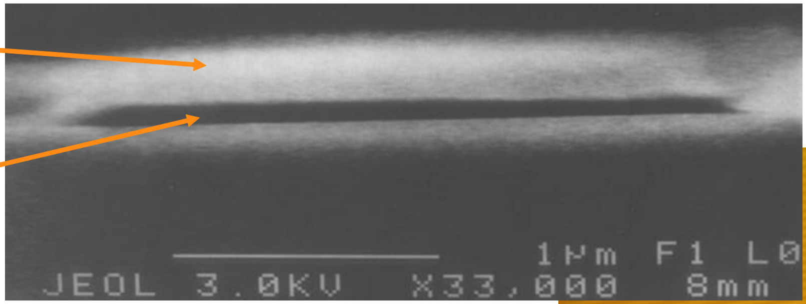


Width: 1 – 10 µm

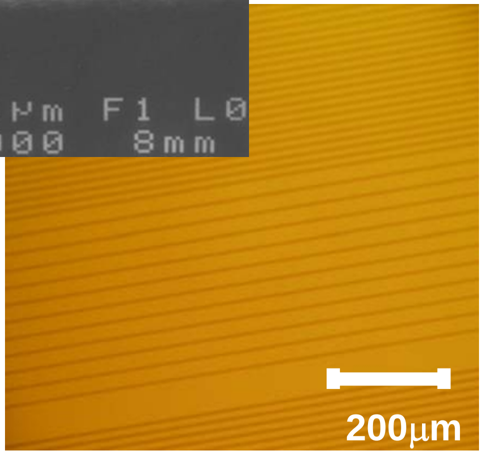
Etch Selectivity PMMA/PR ≥ 2

3000 Å SiO_2

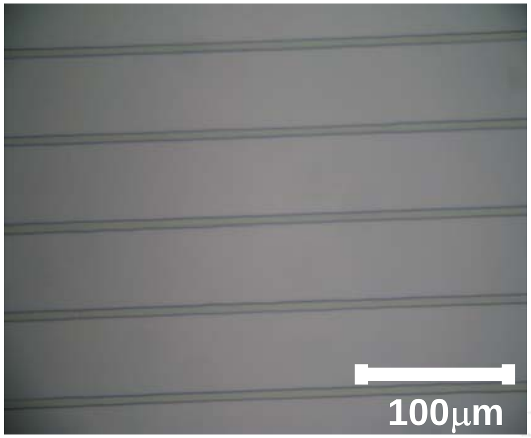
1000 Å Void



Cross sectional SEM
2µm x 100 nm Air Gap



200X – Spin Coated Resist over PMMA



500X – OSG over patterned PMMA

Resolution limited only by available lithography

Modeling of Pattern Dependency Effects in STI CMP

Xiaolin Xie – Ph.D. Candidate, Physics
Prof. Duane Boning, EECS

Microsystems Technology Laboratories
Massachusetts Institute of Technology

Thrust A: Back-End Processing
Subtasks A-4-1

ERC Annual Review, February 2005

Roadmap of the Research on STI CMP

- Recent Work
  - Simulation analysis of edge roll-off effect (this poster)
  - Verifying assumptions of step height pattern density model using 2D contact wear model (this poster)
  - Modeling and simulation of endpoint detection of STI CMP *(with Sandia, Rohm & Haas, IMEC)*
  - Design new STI CMP mask (at Retreat)
  - Improve existing step height pattern density model (at Retreat)
  - Development of die-level full contact wear model (at Retreat)

- In Progress
  - Characterization of new graded pad concepts (with Neopad)
  - Measurement on nanotopography effect on patterned wafer (*with Infineon, Siltronics)*
  - Modeling and simulation of endpoint detection of STI CMP with various slurries *(with Rohm & Haas, IMEC)*
  - Model improvement

Step-Height Pattern Density Model

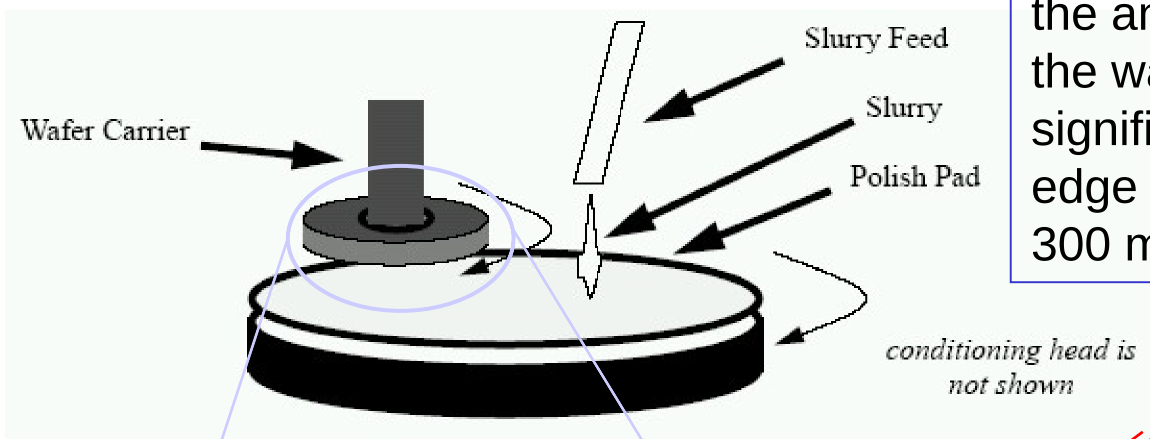
- Underlying assumptions
  - Pattern density is the dominant effect regardless of structure shapes
  - Stiffer pad has longer planarization length
  - Removal rate dependence on step height
  - Contact height decreases as Young's modulus increases

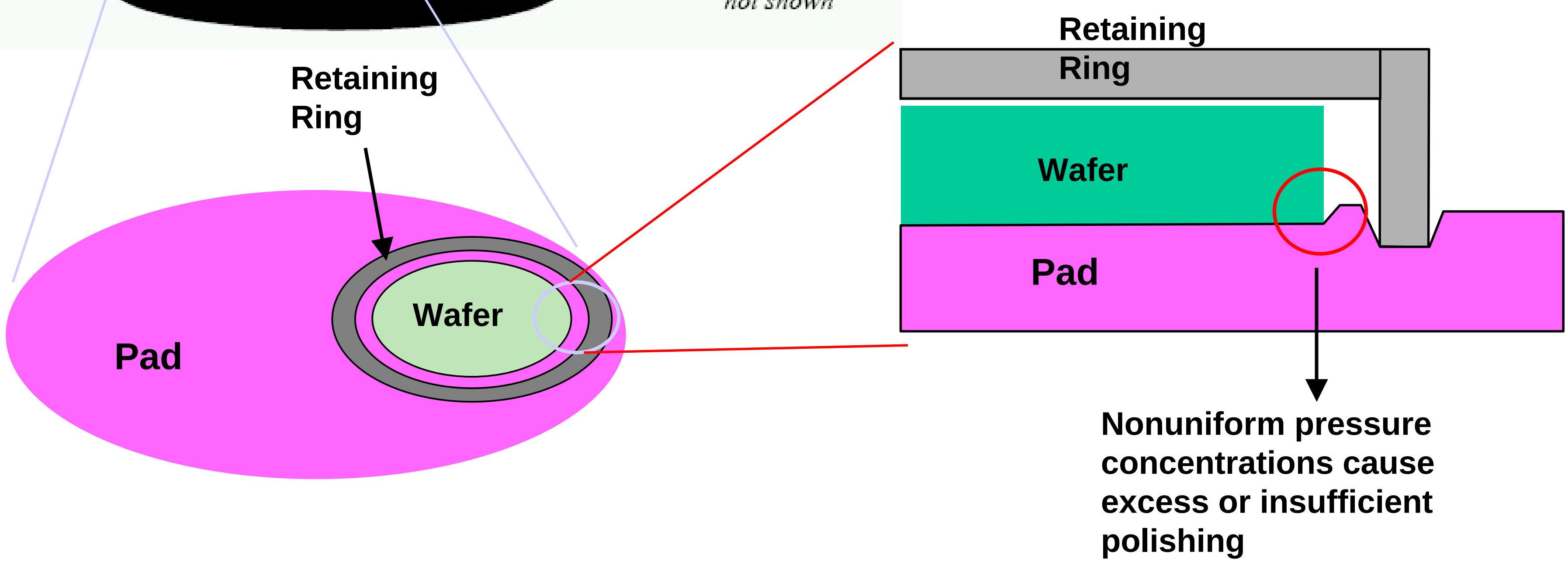
- Simulation by 2D die-level contact wear model is in agreement with the assumption above

Edge Roll-Off Effect

Problem: Edge roll-off effect refers to the anomaly polishing near the edge of the wafer caused by tool structure. It significantly reduces the yield near the edge of the wafer, especially for the 300 mm wafers.

CMP tool setup





Simulated with Contact Wear Model

- **Approach**
  - Contact wear model is used to simulate CMP near the edge of the wafer by considering the specific structure parameters and process conditions.
- Static dependence
  - Larger Young's modulus results in less deformation
  - Smaller gap results in less edge roll-off pressure
  - Smaller pressure results in less edge roll-off pressure
- Dynamic dependence
  - Large pressures and large gap lead to fast edge polishing
  - Good choice of pressures and gap lead to nearly uniform polishing
  - Small pressures and small gap lead to slow edge polishing

PMMA – Summary and Key Findings

- **Low power PECVD is a viable method for depositing PMMA**
  - **FT-IR confirms structural similarity to bulk PMMA**
- **PECVD PMMA has the desired properties**
  - **Decomposes at 230 to 350 °C**
  - **Negligible residue**
- **Closed-cavity air-gap microstructures successfully fabricated using conventional photolithographic and deposition tools**
- **Solubility of PMMA in acetone and isopropyl alcohol is inversely proportional to both the deposition power and substrate temperature**
- **Films deposited at lower temperatures contain CH_2-O-CH_2 linkages in the polymer backbone decreasing its thermal stability**
- **Onset of thermal decomposition increases with increased deposition temperature**

Conclusions

- The assumptions of step-height pattern density models are in agreement of 2D die-level contact wear model
- Edge roll-off effect is caused by tool structures near the edge of wafer
- Edge roll-off could be reduced with good combination of tool parameters

Future Plans

- Verify the Nanotopography simulation results with experiment data
- Improve CMP modeling with new STI CMP characterization mask
- Study the relationship between patterned wafer topography evolution and STI endpoint current signal with different slurries
- Characterization of new graded pad (Neopad)

Industrial Collaborations

- Rohm and Haas
- IMEC
- Neopad
- ADE Corp.
- Sandia National Laboratories
- NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

Effect of Slanted Groove on the Tribological and Removal Rate Characteristics of Copper CMP (Subtask A-5)

D. Rosales-Yeomans & A. Philipossian (University of Arizona, Tucson, AZ, USA)

T. Doi (Saitama University, Saitama, Japan)

L. Borucki (Intelligent Planar, Mesa, AZ, USA)

K. Ichikawa (Fujikoshi Machinery, Nagano Japan)

T. Suzuki (Toho Engineering Co., Yokkaichi, Japan)

SAITAMA UNIVERSITY

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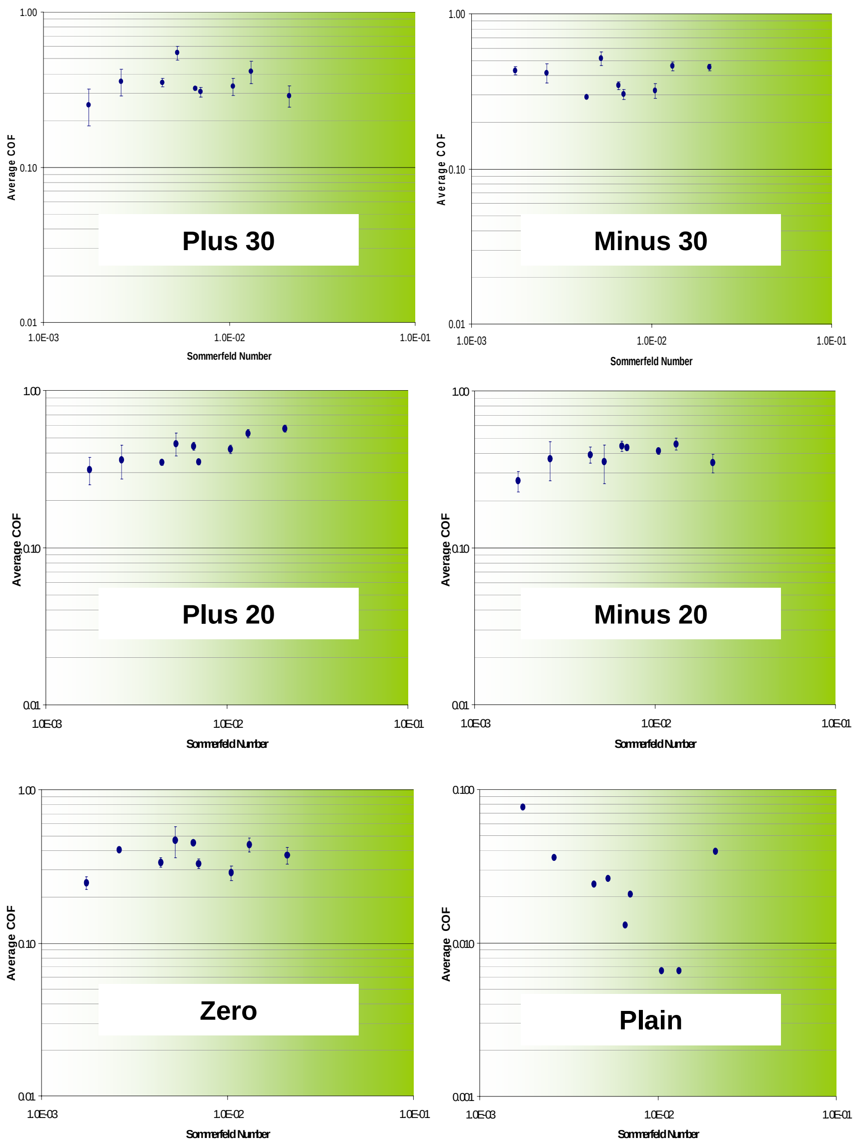
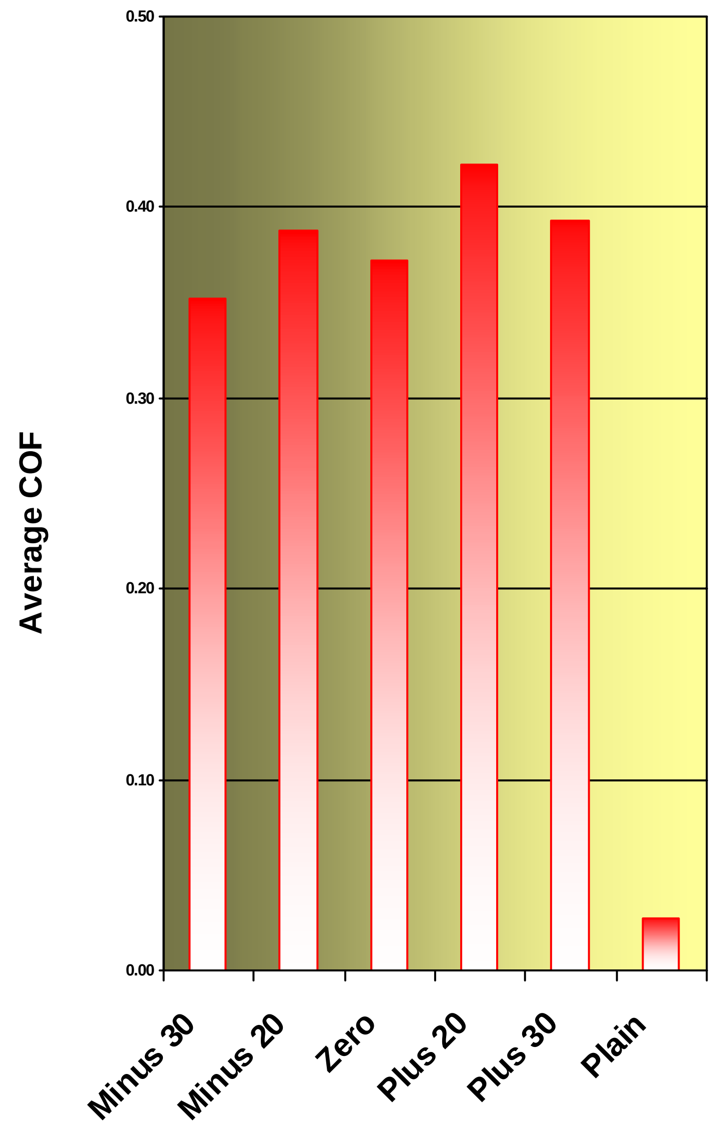
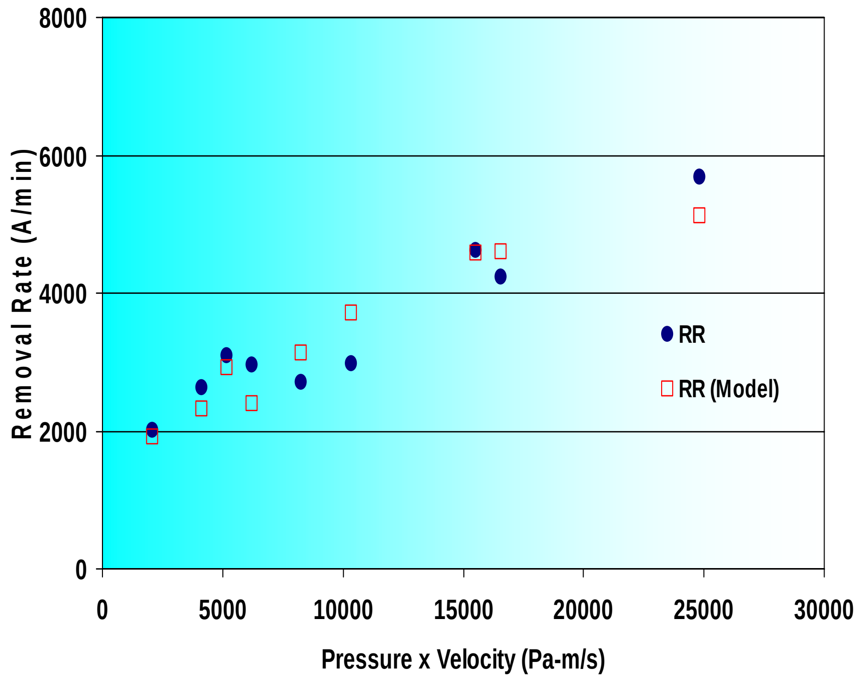
Stribeck Curves and Average COF Results

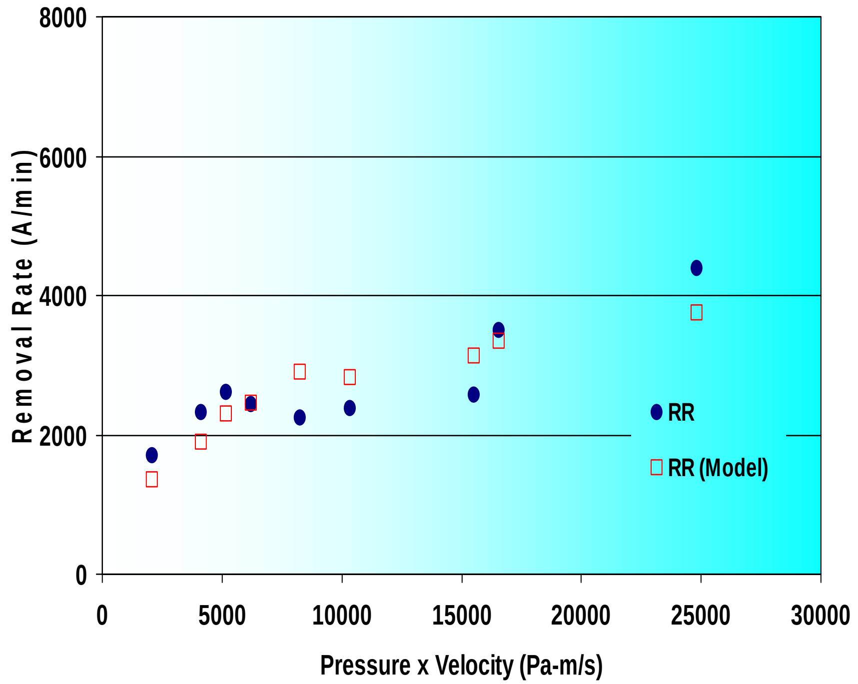




Removal Rate Data

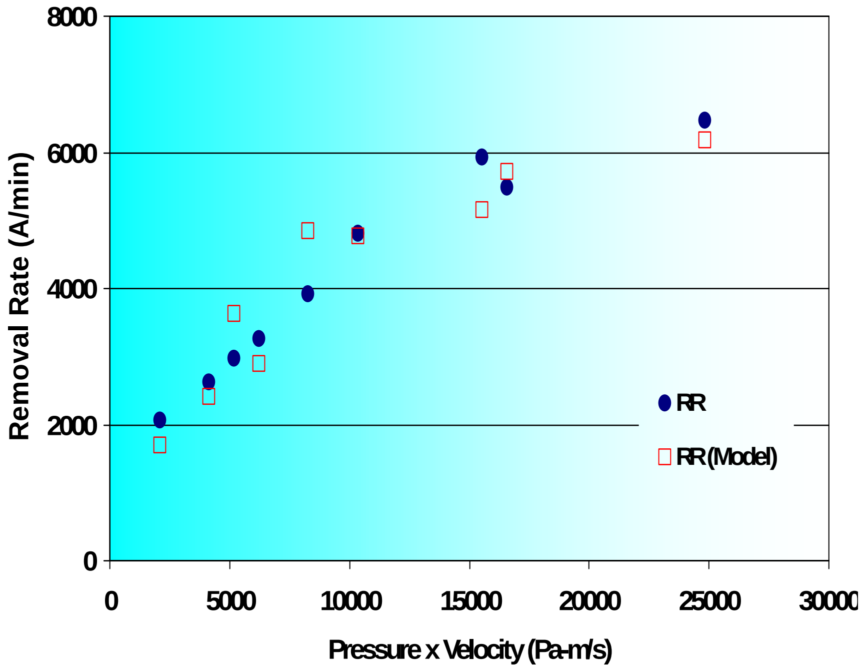
Plus 30 Degrees (left) and Minus 30 Degrees (right)

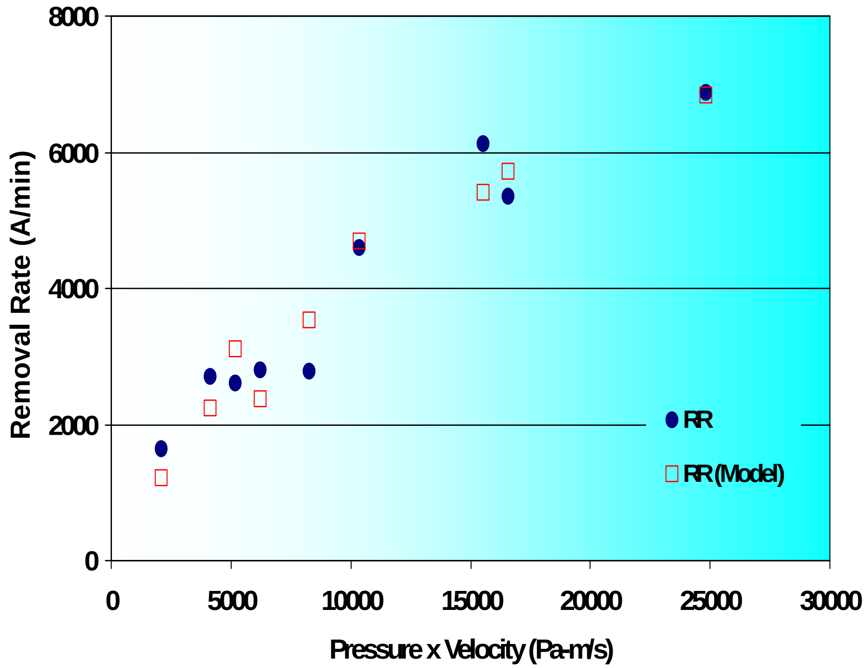




Removal Rate Data

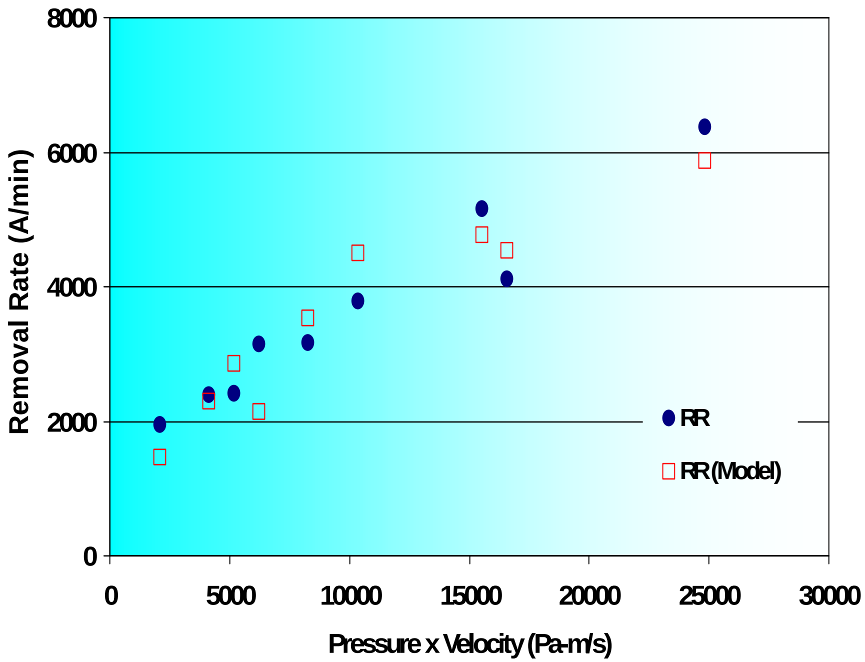
Plus 20 Degrees (left) and Minus 20 Degrees (right)

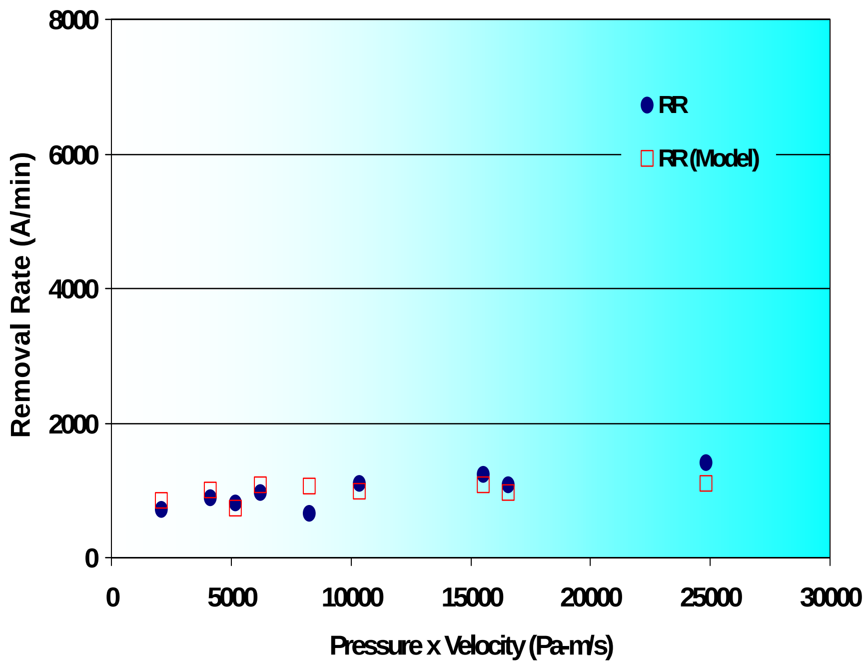




Removal Rate Data

Zero Degrees (left) and Plain (right)





Concluding Remarks

- Slanted grooves (positive and negative) can modify the RR behavior without significantly affecting COF

- Slanting the grooves in the positive direction results in higher RR

  - RR Plus 30 degrees > RR Minus 30 degrees
  - RR Plus 20 degrees > RR Minus 20 degrees
  - This is likely due to the fact that positive slanted grooves not only facilitate the discharge of used slurry and by-products but also ease the entrance of fresh slurry into the wafer pad interface
  - This will favor the copper complex formation, hence increasing RR.

- RR 20 degrees > RR zero degrees > RR 30 degrees

  - In the case of 30 degrees, groove pitch needs to be optimized to ensure acceptable mechanical strength

- Slanting of grooves:

  - Can be used to alter the balance between chemical and mechanical attributes of copper CMP
  - Does not affect the lubrication mechanism of the process

Alternative Planarization Technologies - Electrochemical Mechanical Planarization (ECMP) of Copper

Task ID : A-6-1

Srini Raghavan (PI)

Graduate students:
Subramanian Tamilmani
Viral Lowalekar

Materials Science and Engineering Department
University of Arizona

Objective

- To develop chemical systems suitable for ECMP of copper through electrochemical and surface chemical investigations

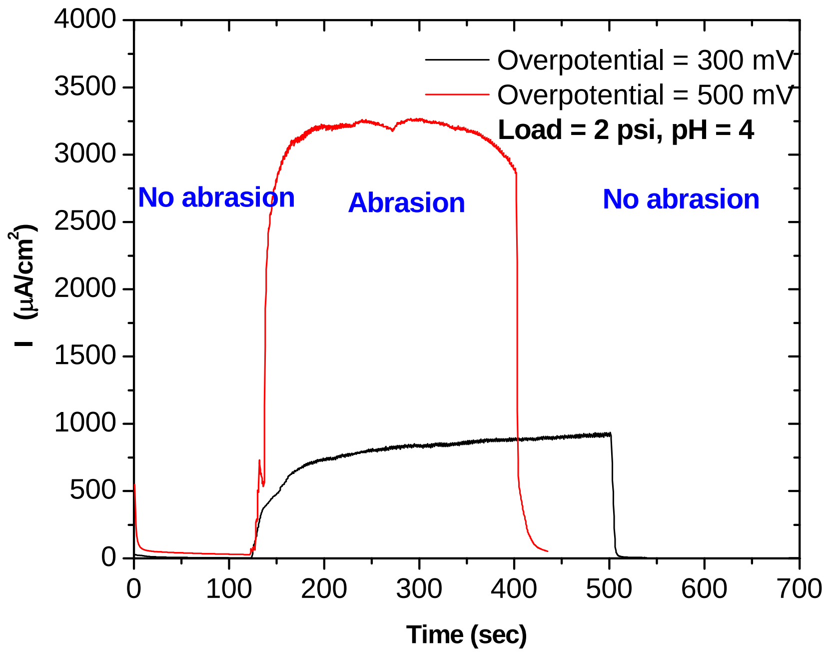
Accomplishments During the Current Contract Year

- Explored various chemical systems (organic acids, aqueous inorganic amine) that may be suitable for ECMP of copper

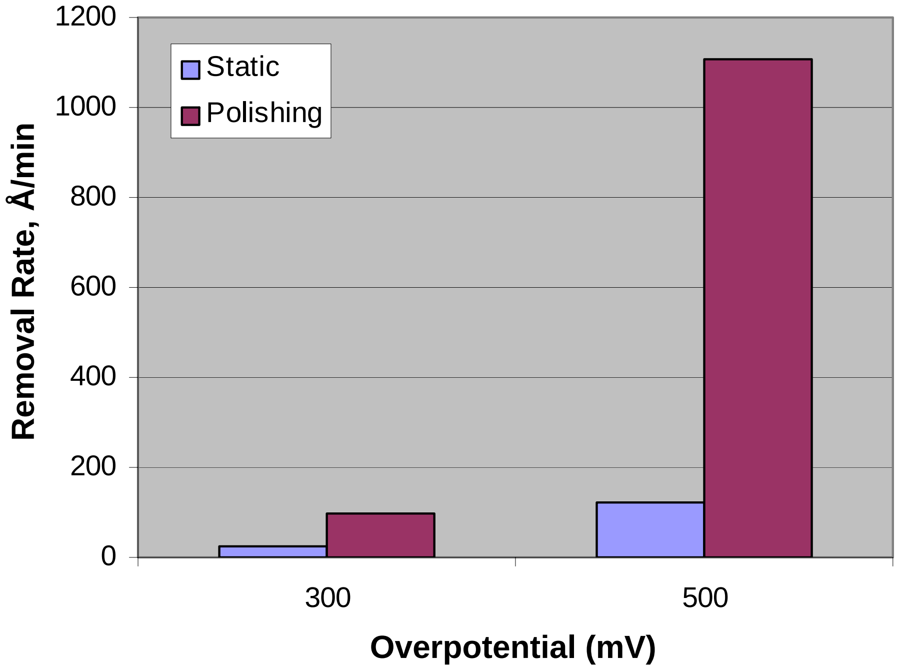
- Characterized the performance of additives (ex. corrosion inhibitors) that are critical to ECMP

ECMP of Copper in Oxalic Acid System

Current vs. Time Profile



Removal Rates

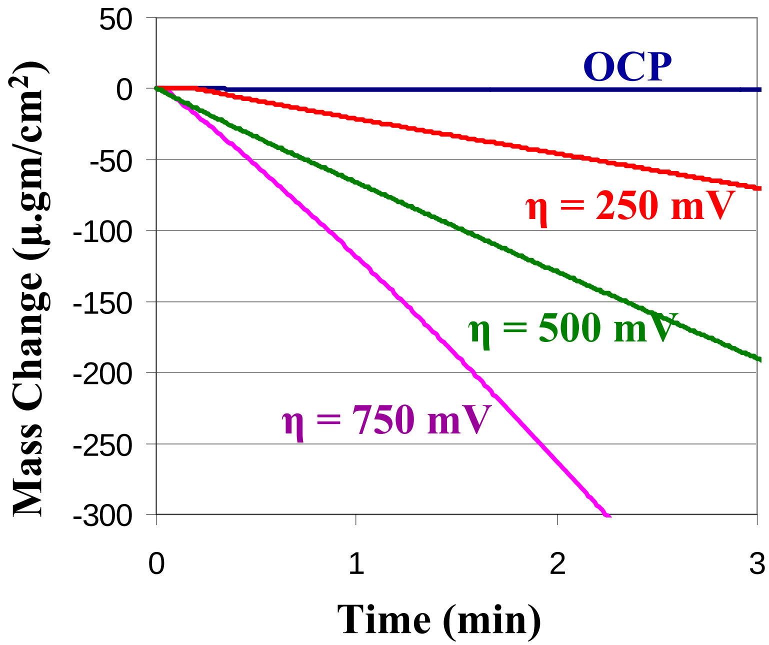


Removal rates determined by profilometry

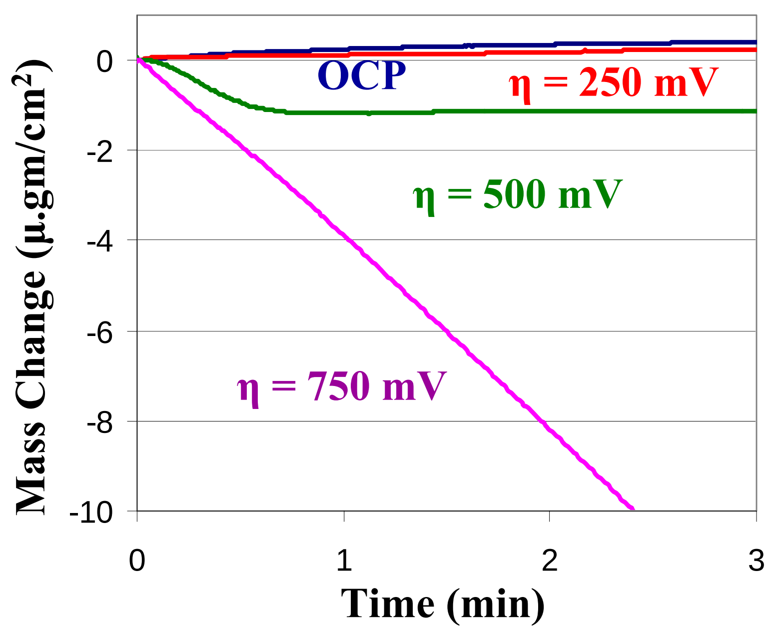
- 0.1M Oxalic Acid + 0.001M BTA + 1% SiO_2
- Higher removal rates with higher overpotential.

Effect of Potential on Copper dissolution – QCM studies

0.1M Citric acid (pH 4)



0.1M Citric acid + 0.01M BTA (pH 4)



- 1 µ.gm/cm^2 = 11 Å
- Dissolution rate increases with Overpotential (η)
- BTA offers complete protection up to η ~ 500 mV

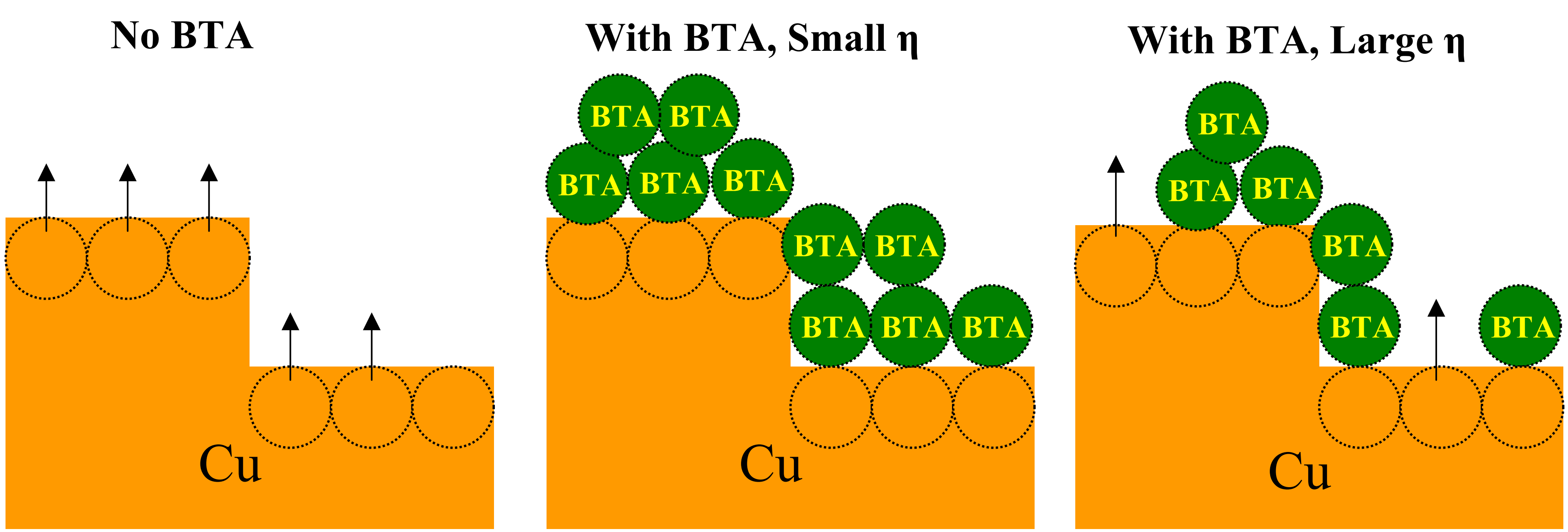
Adsorption model

At applied anodic overpotential "η",

$$i = i_o \exp(\beta F n\, \eta / RT) = i_o \exp(Const.\eta)$$

Copper dissolution rate,

$$-d(Cu)/dt = i/nF = -\,[k(\eta).\theta_{Cu}(\eta)]$$



Future Directions

- Investigate the feasibility of removal of barrier layers (Ta, TaN, W_xN_y) removal using ECMP technique.

Challenges:

  - "Inertness" of barrier layers
  - 1:1 selectivity between Cu and barrier layer

- Additives for improving surface finish.

Progress in Modeling and Optimization of Multilevel Copper Metallization

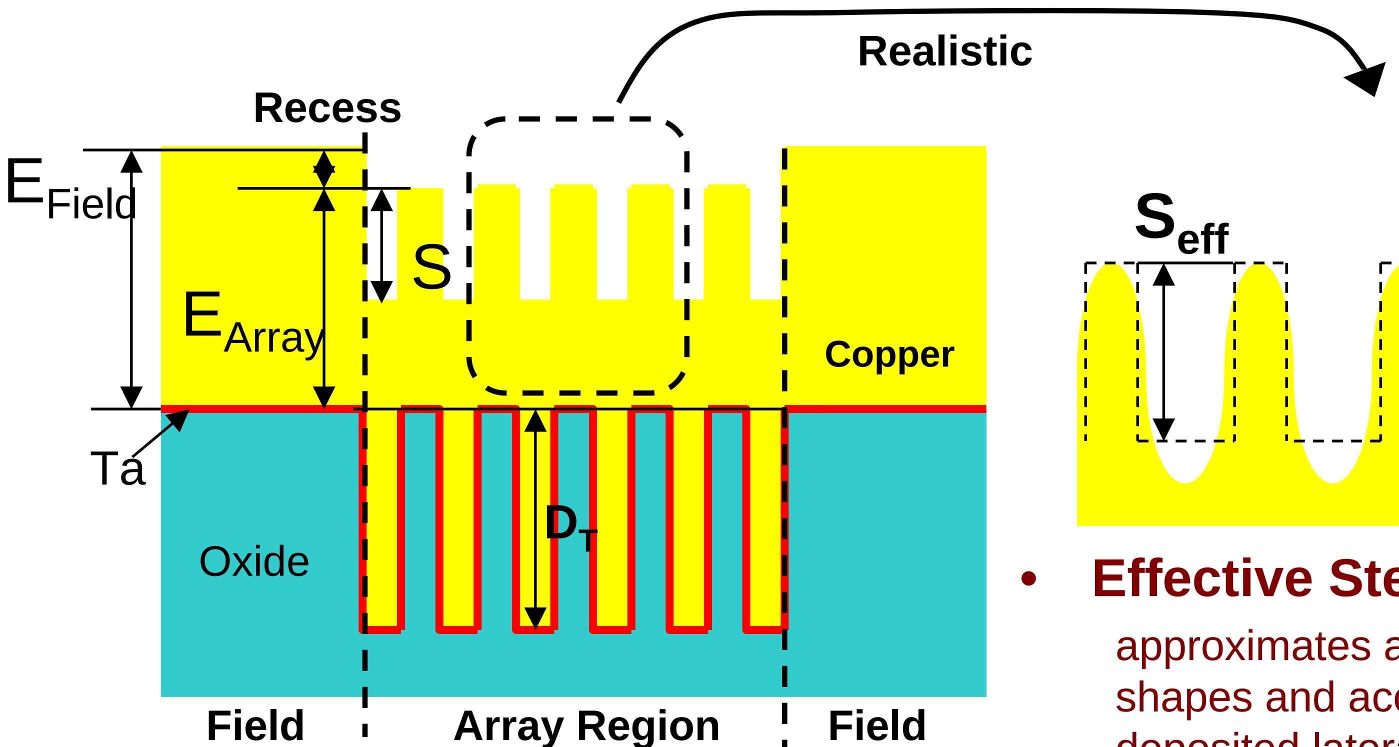
Hong Cai and Duane Boning
Microsystems Technology Laboratories, Massachusetts Institute of Technology

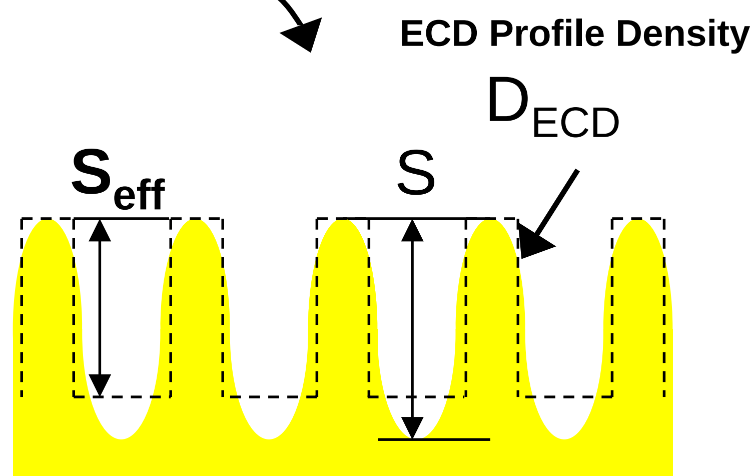
Highlights

- New electroplating model is developed with good accuracy, and can be extended into multi-level case. A more physics-based time-step version is under development.
- Newly-developed 3-step CMP model framework achieves good accuracy with reasonable computation load. The pad microstructure and the physical process in CMP will be considered in the next version.
- ECD and CMP model scripts are transferred for industrial application.
- Simulation results are incorporated in circuit variation analysis.

Variable Definition in ECD Model (1)

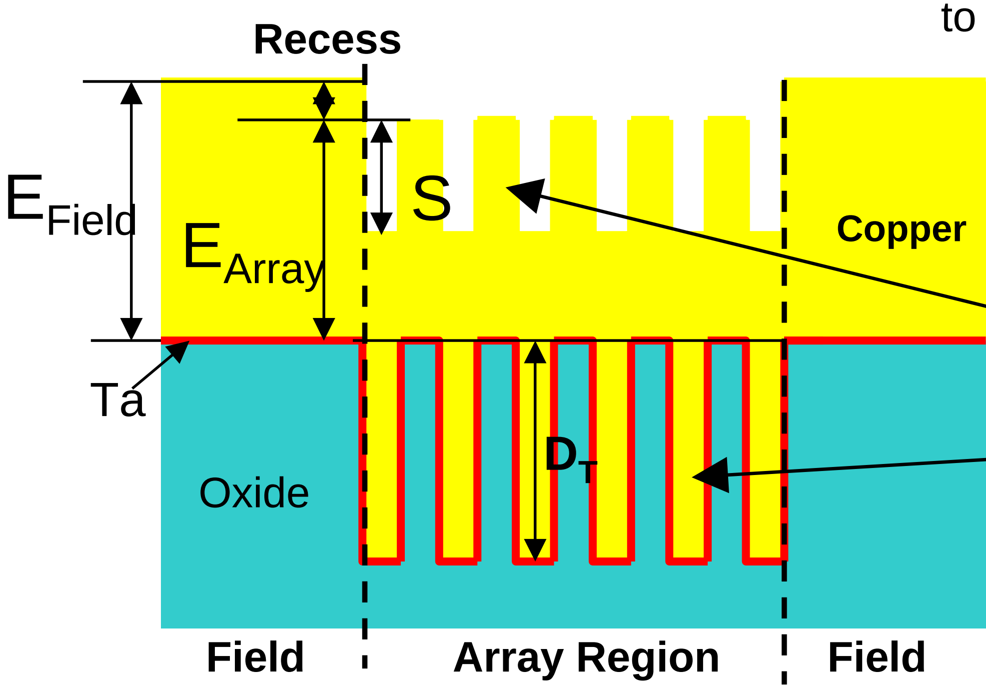
- Basic topography variables
  - Step Height (S): local step height
  - Envelope (E): Top surface of copper thicknesses referenced to barrier layer
  - Average Cu deposition thickness (T): total amount of copper deposited including the amount deposited in the trenches
    - ❖ Captures depletion effect in plating and its impact on plated profiles





- **Effective Step Height (S_{eff}):** approximates as rectangular shapes and accounts for as-deposited lateral bias

Variable Definition in ECD Model (2)



Simulated E is compared to measured E to obtain the optimal model parameters

$$T = E - S_{eff} * D_{ECD} + D_T \bullet D_{cell}$$

Amt. of Cu in step heights ($S_{eff} * D_{ECD}$)

Amt. of Cu in trenches ($D_T \bullet D_{cell}$)

$$D_{ECD} = \begin{cases} D_{cell} & (S_{eff} \geq 0) \\ 1 - D_{cell} & (S_{eff} < 0) \end{cases}$$

- Basic layout variables
  - Layout pattern density (D_{cell})
  - Effective line width (W_{eff})
    - All features in a cell are treated as rectangular objects with W_1 and W_2
    - captures 2D geometry information in each cell

$$\frac{1}{W_{eff}} = \frac{1}{W_{1avg}} + \frac{1}{W_{2avg}}$$

New Cu ECD Model

- Effective Step Height Surface Response Model

$$S_{eff} = Const_S + A_S \cdot \log W_{eff} + B_S \cdot D_{cell} \cdot \log W_{eff}$$

- *T* expressed in terms of the layout features

$$T = E - S_{eff} \cdot D_{ECD} + D_T \cdot D_{cell}$$

- *T* expressed in terms of the nominal *T* (without depletion effect) and Cu concentration factor F_{con} that describes the depletion effect

$$T = T_{nom} \cdot F_{con}$$

  - T_{nom} expressed by surface response model

$$T_{nom} = Const_T + A_T \cdot D_{cell} + B_T \cdot W_{eff}^{-1} + C_T \cdot D_{cell} \cdot \log W_{eff}$$

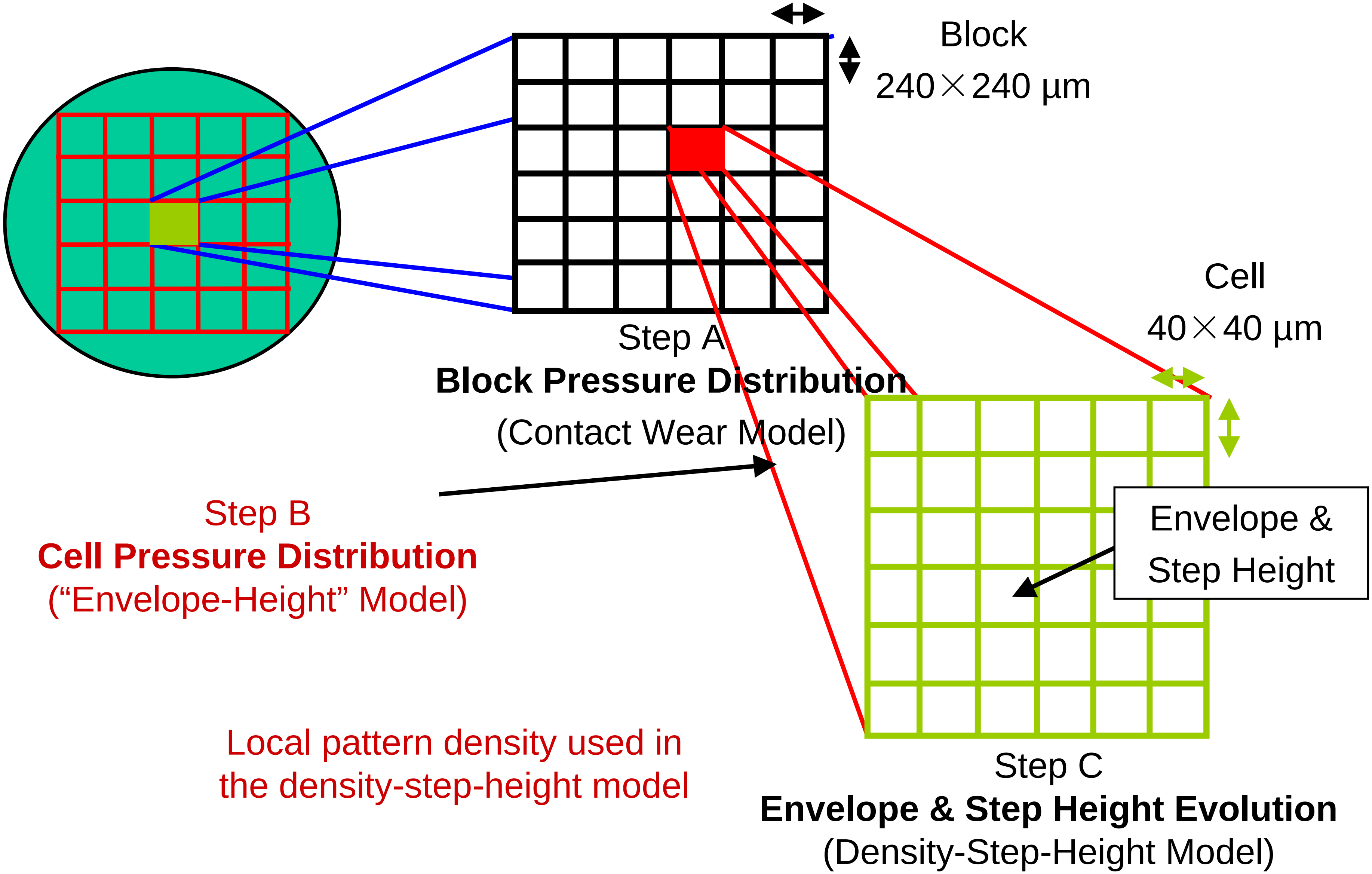
  - F_{con} *is* expressed by depletion factor F_{dep} that is a function of *T* and *ECD Depletion Length*

$$F_{con} = (F_{dep})^{-\alpha}$$

α is Cu ion transportation efficiency from 0 (no depletion) to 1

$$F_{dep} = f(T, ECD\, Depletion\, Length)$$

New Cu CMP Model Framework



Industrial Collaborations & Technology Transfer

- Praesagus, Inc. – layout interface data, oxide thickness, HRP and e-test
- Magna Chip, Inc. – experiments, measurement, financial support
- Neopad – CMP pad experiments
- Philips Analytical – copper thickness measurement

Future Plans

- Multi-level ECD and CMP modeling and simulation
- Time-step ECD & CMP physics-based chip-scale model improvement
- Co-optimize ECD and CMP processes with the modified time-step ECD and CMP models and assess improvements to process & environmental metrics
- Characterization and modeling of copper CMP for novel pads from Neopad
- Application of model to processes and layout optimization, smart dummy fill and abrasive-free polishing

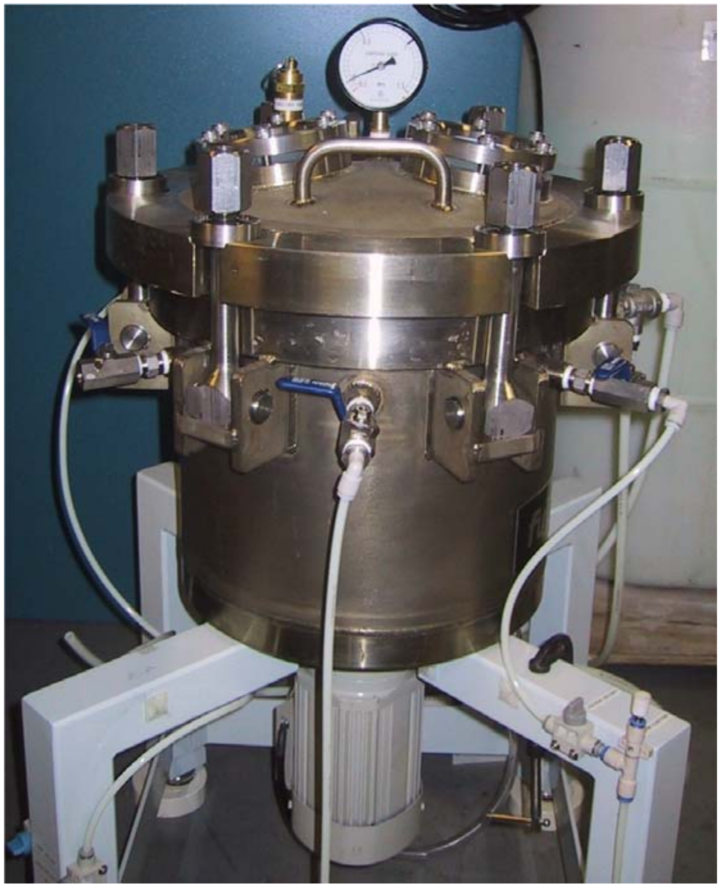
Subtask A-6-4: Impact of Aqueous and Gaseous Additives on Copper CMP Using a Controlled Atmosphere Polishing System

D. DeNardis, B. Hiskey, and A. Philipossian
(University of Arizona, Tucson, AZ, USA)

T. Doi
(Saitama University, Saitama, Japan)

K. Ichikawa and D. Ichikawa
(Fujikoshi Machinery Corporation, Nagano, Japan)

Objective and Driving Force



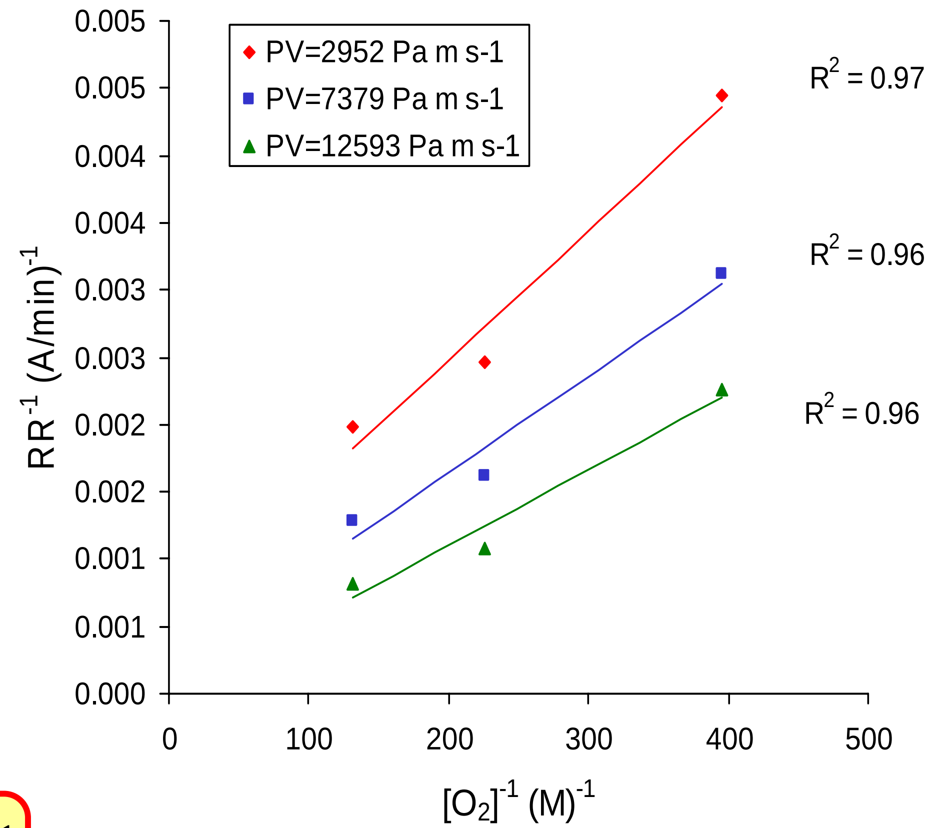
- To perform CMP under high pressure and vacuum (-1 ATM to 5 ATM) conditions with a variety of gases
- By controlling the chamber atmosphere, the species that are responsible for copper removal can be more accurately identified
- The possibility of decreasing non-uniformity by maintaining constant slurry composition
- Possibility of point-of-use chemical generation
- Ability to rapidly alter slurry chemistry during polishing allowing for converting multi-step polishes into a single step

Determining Rate Constants

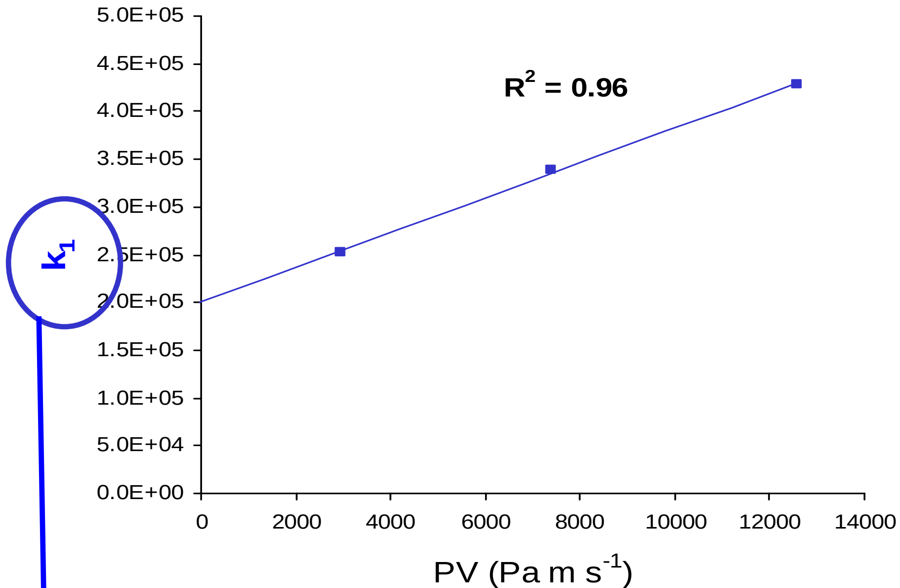
$$RR = \frac{k_2[R]}{\frac{k_2}{k_1} + [R]}$$

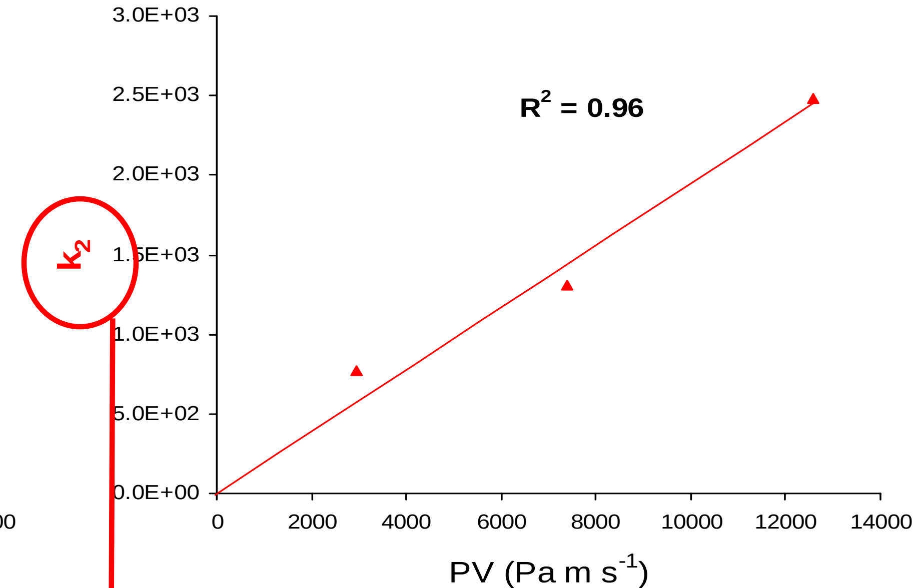
Inverting and replacing [R] with [O_2]

$$RR^{-1} = k_1^{-1} \cdot [O_2]^{-1} + k_2^{-1}$$



Mechanical Dependence





k_2 is the **rate constant of mechanical abrasion**

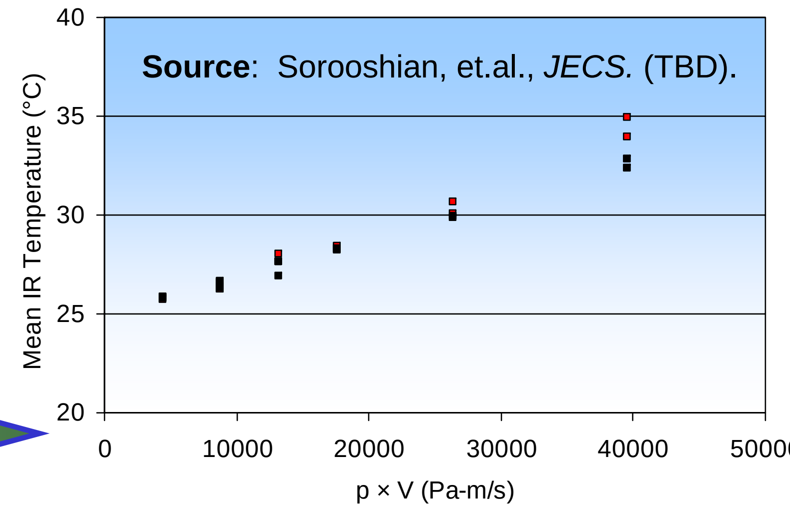
Should be f(PV)

k_2 should equal zero in the absence of mechanical action (PV = 0)!

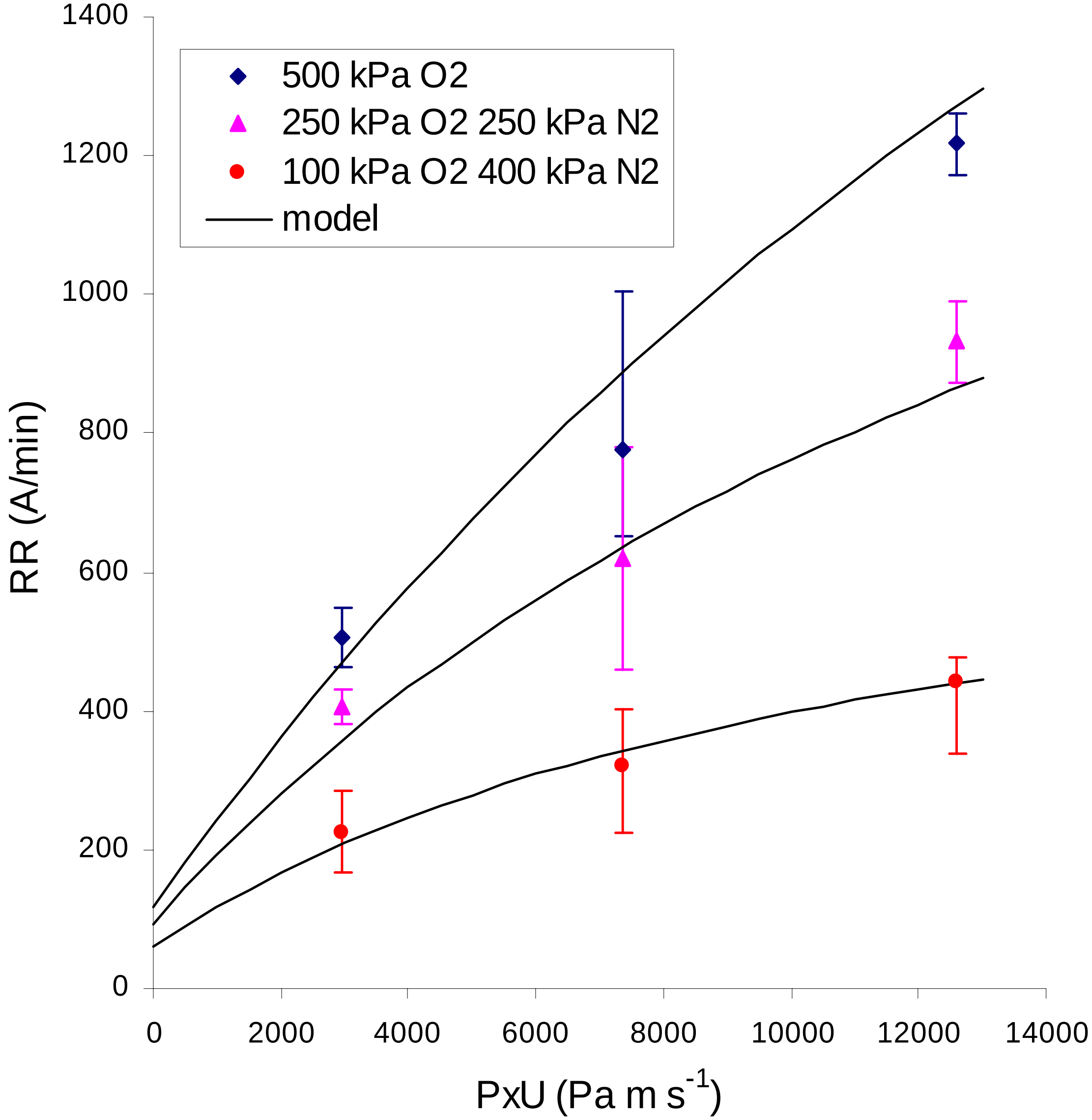
k_1 is the **chemical rate constant**

Should not be f(PV)

The increase in k_1 with PV may be due to **increases in temperature caused by friction**



Comparison of Model with Data



- **Robust model accounts for multiple pressures and velocities as well as different oxidant concentrations using 3 fitting parameters.**
- **If the PV dependence of k_1 could be accounted for by increases in temperature using and Arrhenius model, the number of fitting parameters could be reduced to two.**
- **Could this model adequately describe a system including additives other than oxidants?**

Conclusions & Future Work

- **A two-step removal mechanism is used to characterize copper CMP using dissolved oxygen**
  - **The fact that $k_2 = 0$ at $P \times V = 0$ coincides with model assumptions**
  - **Polishing experiments using different pads will assist in model validation: the chemical rate constant (k_1) should remain a f(T) only**
  - **Three empirical parameters are currently required to fully characterize the system for multiple pressures, velocities and oxidant concentrations**
  - **k_1 dependence on PV may be accounted for by temperature increases due to friction**
    - **If so, the number of parameters required will be reduced to two**
- **Addition of a complexing agent (NH_3) increases RR by 3X**
- **Oxidized copper species build-up, or re-deposit, on the wafer surface in the absence of complexants**
- **The system is not entirely controlled by oxidant or complexant concentration**
- **A three-step removal mechanism, including dissolution of abraded by-products, may prove useful to characterize systems including complexants**

Subtask A-6-4: Dual Emission UV-Enhanced Fluorescence (DEUVEF) Study of Slurry Residue in Pad Grooves

H. Lee, Z. Li, Y. Zhuang & A. Philipossian (University of Arizona)

Y. Seike, M. Takaoka & K. Miyachi (Asahi Sunac Corporation)

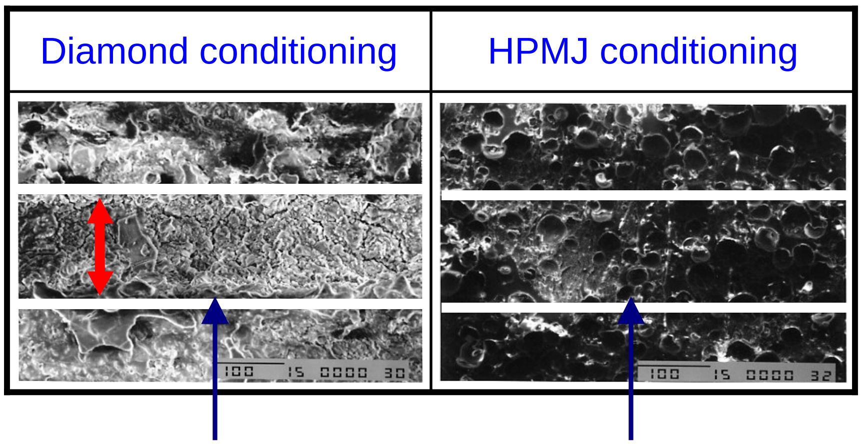
ASAHI SUNAC

U of ARIZONA . MIT . STANFORD . UC-BERKELEY

NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

Motivation

- **Previous results from ILD marathon runs show that**
  - **There is slurry residue in pad grooves with diamond disc conditioning**
  - **Residue-free groove is achieved by HPMJ pad conditioning**



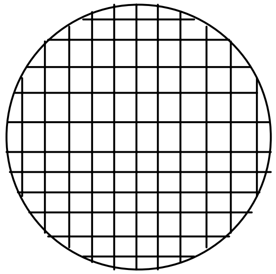
Slurry residue in the groove　　Residue-free groove

- **Dual Emission UV-Enhanced Fluorescence (DEUVEF) is used to quantify slurry residues in pad grooves for both diamond disc and HPMJ pad conditioning methods**

Procedure

- Constant
  - Polishing
    - Si wafer and Diamond disc conditioned at 30 RPM disk speed and 20 per min sweep frequency
    - 10 hrs with dyed slurry
    - Wafer pressure = 3PSI
    - Sliding velocity = 0.62 m/s
  - Dyed Slurry and flow rate
    - Fujimi PL-4217 (25% solids by weight) + 2 g/l Calcein
    - 80 cc/min
  - Drying of pad = 24 hrs (in dark)

- Variable
  - Pad type
    - FX-9 XY-Groove
    - FX-9 K-Groove
  - Pad Conditioning
    - Ex-situ Diamond disc conditioning
    - Ex-situ HPMJ conditioning



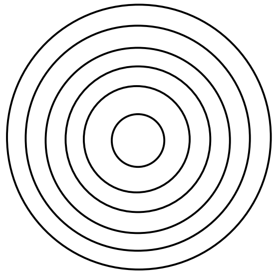
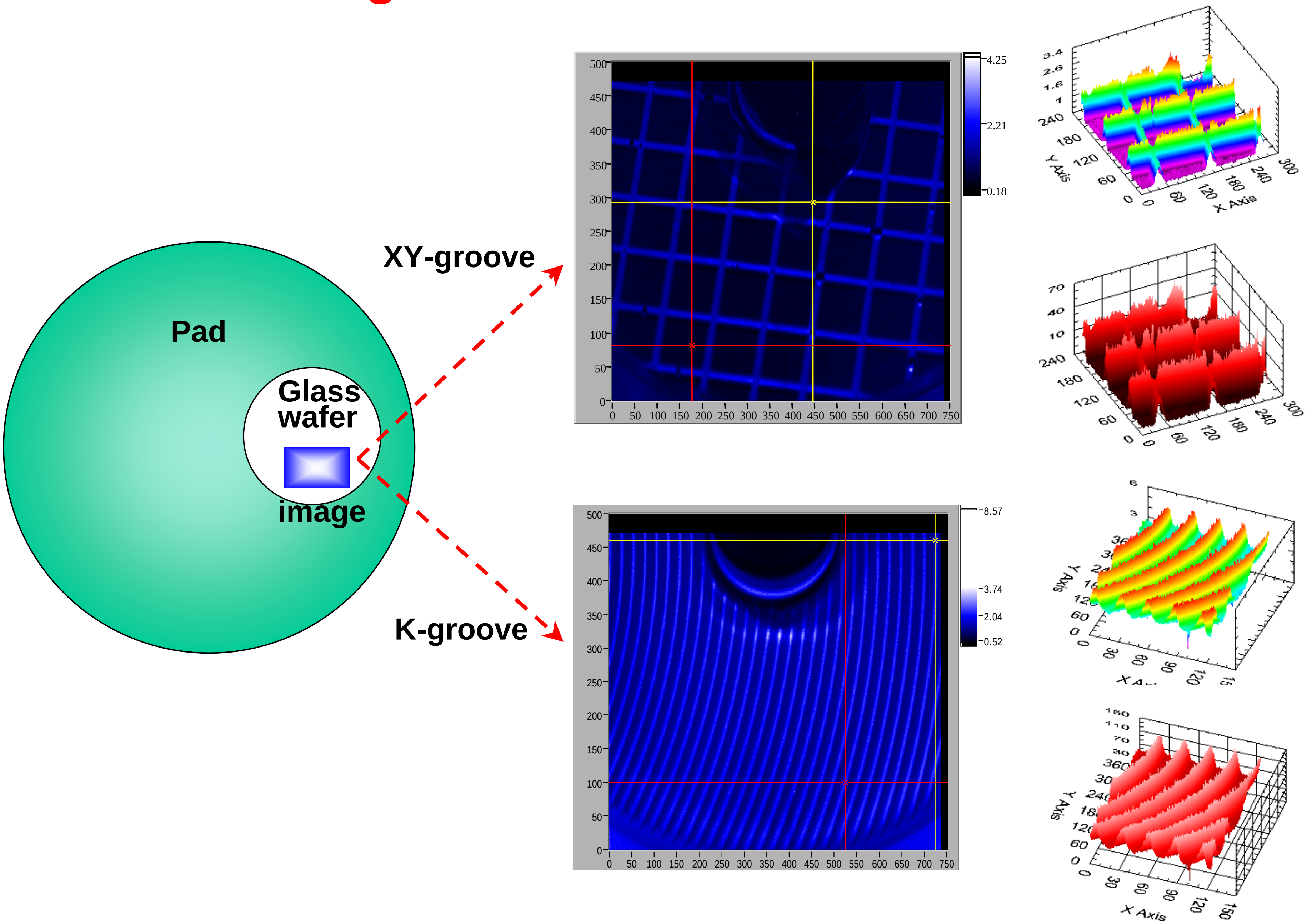
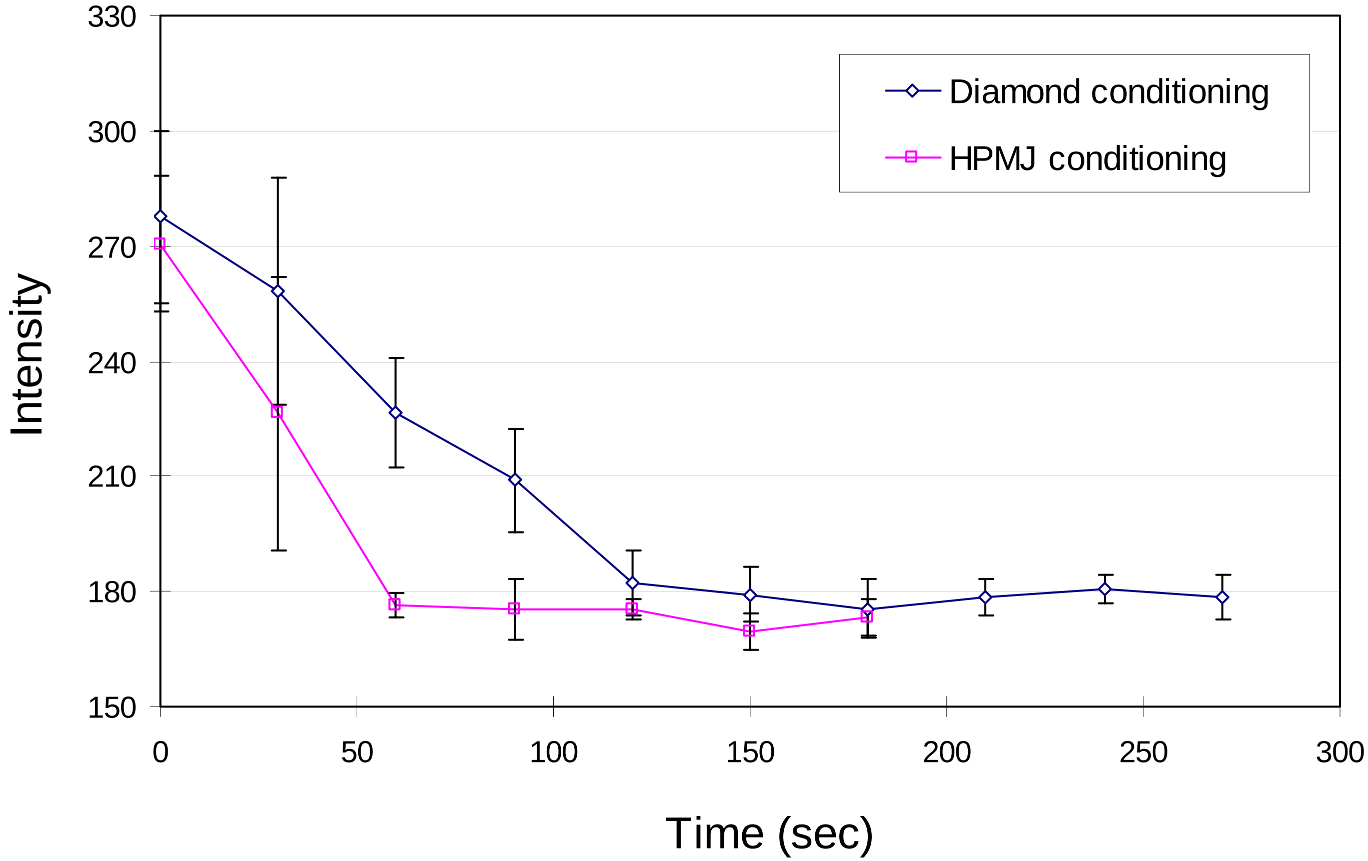


Image Under the Glass Wafer



Results … K-Groove



Summary

- Slurry residues in pad groove (X-Y Groove and K-Groove) were investigated by DE-UVEF technique with different pad conditioning methods – Diamond disc conditioning and HPMJ conditioning.

- For HPMJ conditioning, fluorescence intensity inside the groove is dramatically decreased with time for both XY-Groove and K-Groove pads.

- For Diamond disc conditioning, decrease in fluorescence intensity inside groove depends on pad type:
  - X-Y Groove : Inter-connection between groove
  - K-Groove : Concentric groove
  - The width of X-Y Groove is larger than the width of K-Groove

- HPMJ pad conditioning proved to be more efficient pad conditioning for removal of slurry residues from the groove.

Subtask A8

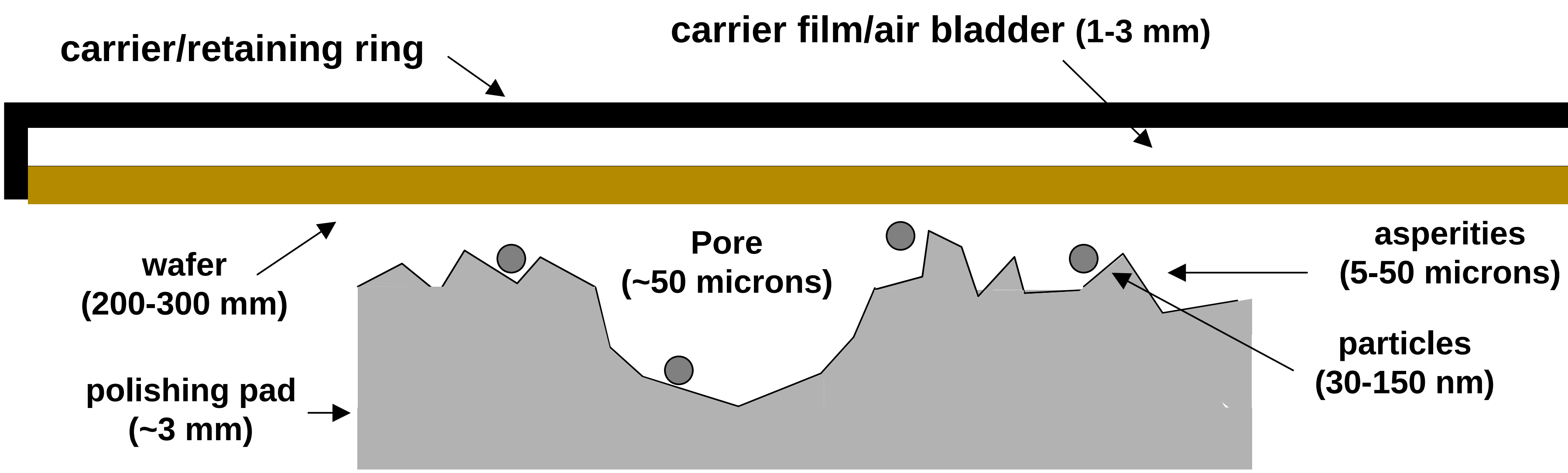
Copper Planarization for Integrated Circuit Manufacturing

Principal Investigator: Steve Beaudoin, Chemical Engineering, Purdue University

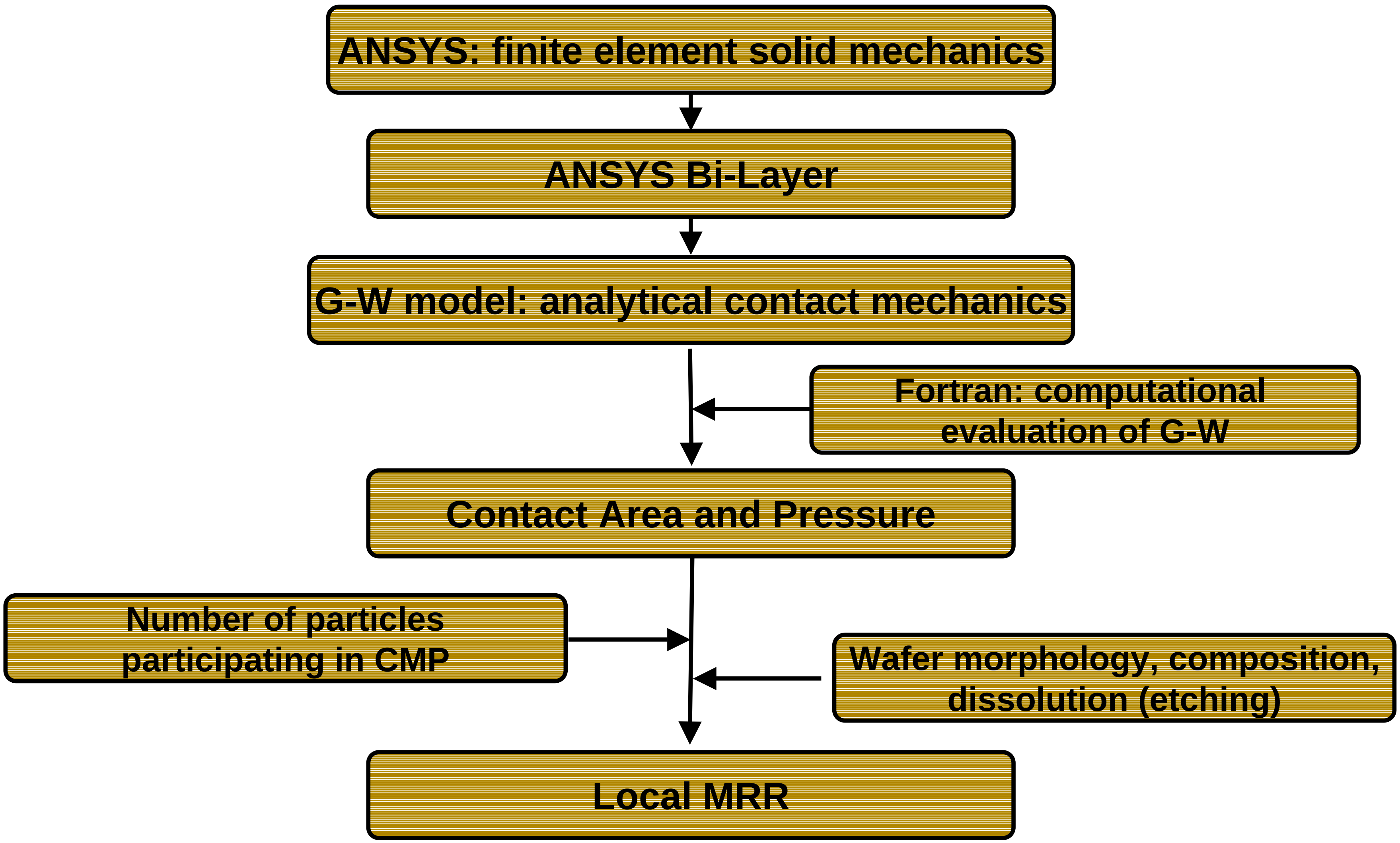
Graduate Students: Bum Soo Kim, Chemical Engineering, Purdue University
John Kelchner, Chemical Engineering, Purdue University

CMP Modeling Approach

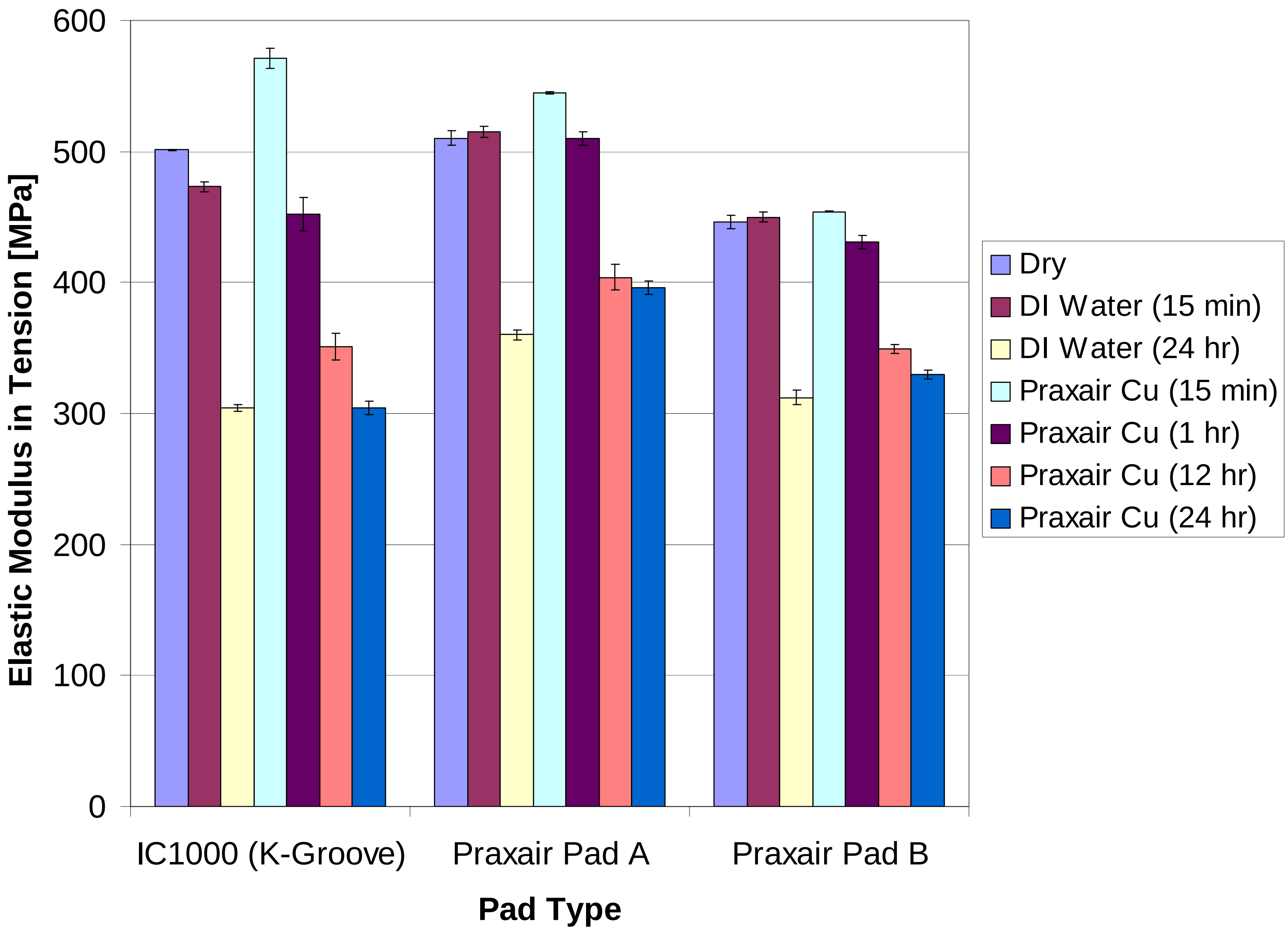
Behavior of bulk polishing pad and wafer	Behavior of asperities on pad and wafer	Pad-particle-wafer interactions	Polishing kinematics
Finite elements, solid mechanics	Bilayer model	Deformation, dissolution, indentation	Analytical vector operations
mm	microns	nanometers	mm



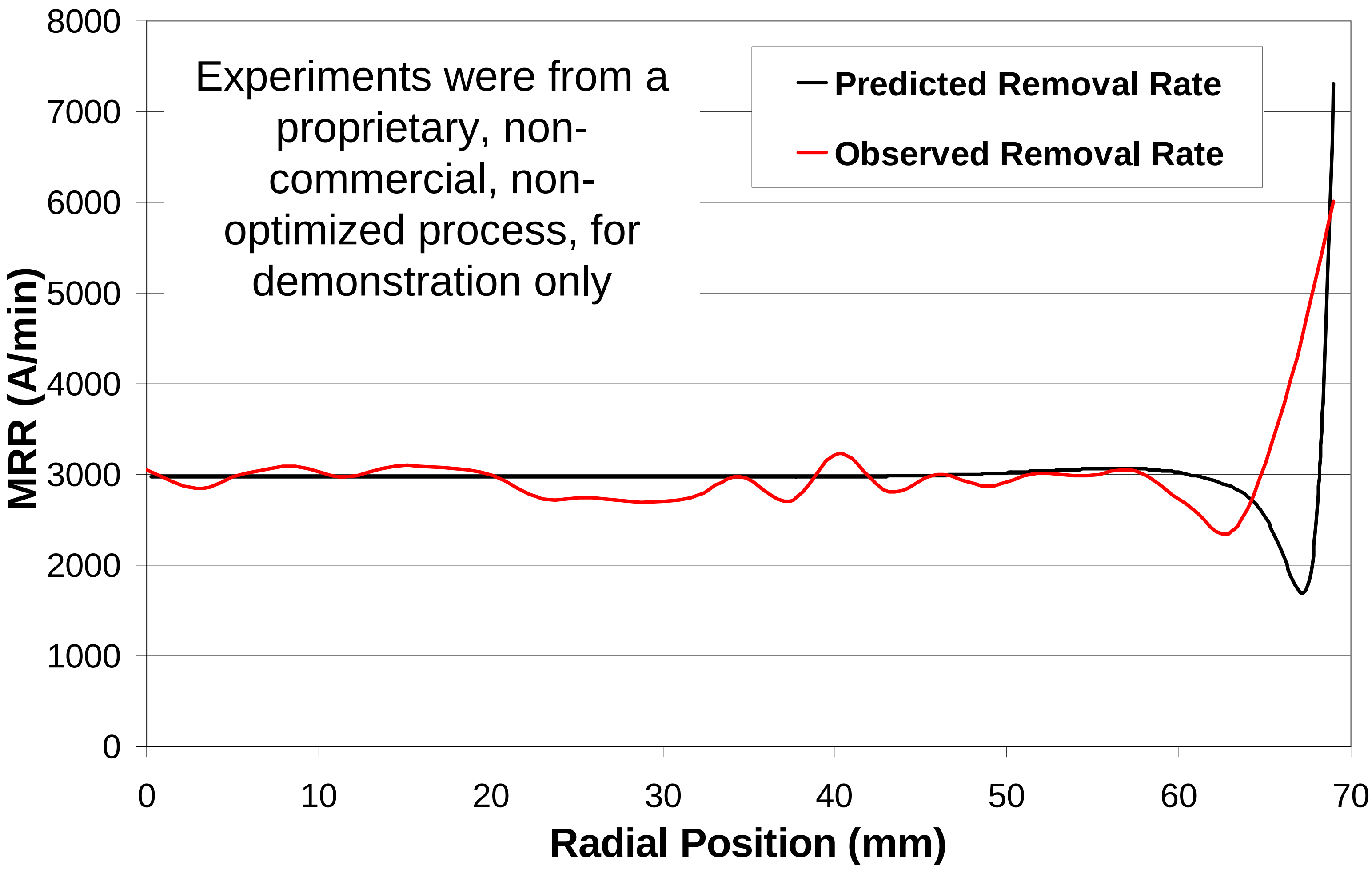
Pad-Wafer Interaction Studies



Measured Elastic Modulus in Tension



Local Predicted and Observed Material Removal Rate



Conclusions, Interactions and Acknowledgements

- Conclusions
  - CMP pad behavior studied in commercial slurries
  - Pad surface layer and bulk pad have different mechanical properties
  - Exposure to water or slurry affects properties of both regions of pad
- Future Work
  - Use validated approach in larger CMP model to predict polishing performance and identify low waste protocols
- Industrial Collaboration
  - Praxair Microelectronics, Rohm and Haas
- Acknowledgments
  - NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
  - State of Indiana 21st Century Fund
  - Praxair Electronics

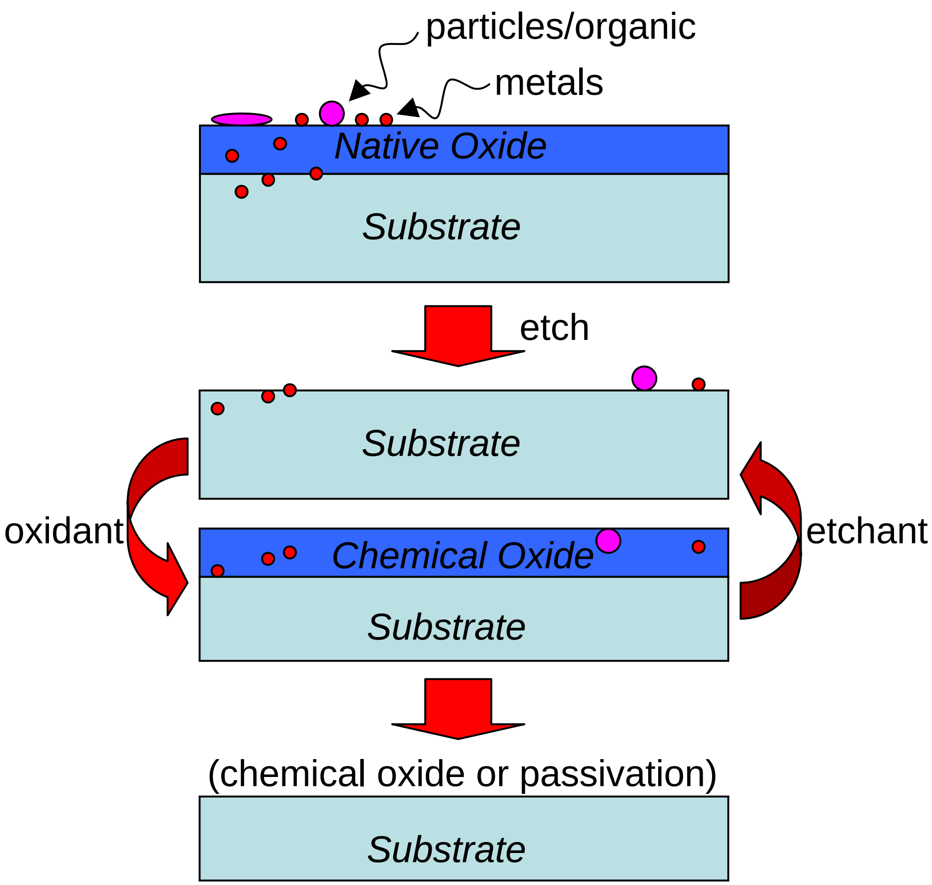
Subtask B-1-2

Nanoscopic Characterization of Ge Single Crystal Surfaces to Develop Environmentally Benign Chemical Treatment Processes for Manufacturing Ge-Based Devices

Jungyup Kim
Jim McVittie
Toshiyuki Homma
Krishna Saraswat
Yoshio Nishi

STANFORD UNIVERSITY

Germanium Cleaning : Background



Typical cleaning process flow

- Metal contaminants cause premature failure and electrical characteristic degradation in devices.
- Selection and process optimization of oxidant and etchant is important.
- Most of the cleaning process in IC manufacturing has been developed and optimized for silicon processes. No mature clean process is available for germanium.
- Cleaning development involves careful selection of the oxidant and etchant or a solution that would simultaneously do both oxidizing and etching.

Germanium Cleaning : Development Approach

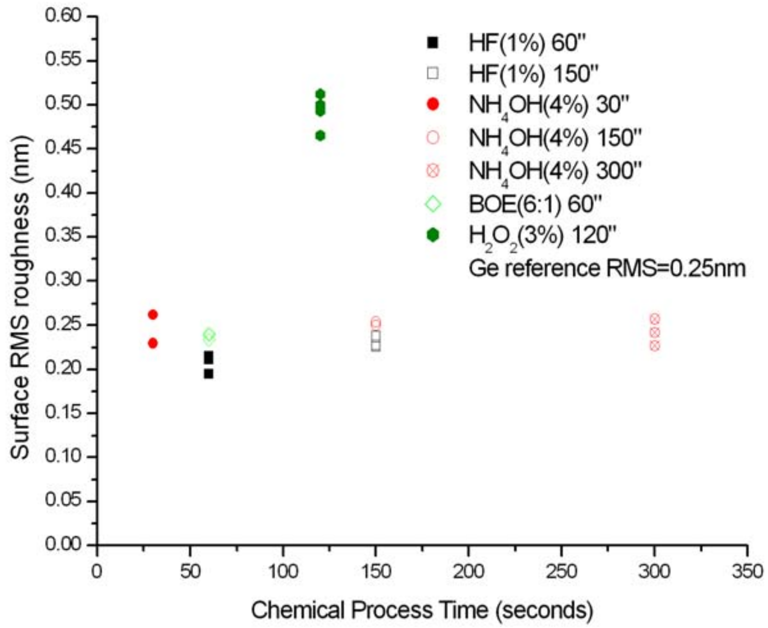
	Redox Reaction	Standard Oxidation Potential
K	$K = K^{+} + e^{-}$	2.931
Ca	$Ca = Ca^{2+} + 2e^{-}$	2.868
Na	$Na = Na^{+} + e^{-}$	2.710
Mg	$Mg = Mg^{2+} + 2e^{-}$	2.372
Al	$Al = Al^{3+} + 3e^{-}$	1.662
Au	$Au = Au^{3+} + 3e^{-}$	1.498
Si	$Si + 2H_2O = SiO_2 + 4H^{+} + 4e^{-}$	0.857
Zn	$Zn = Zn^{2+} + 2e^{-}$	0.762
Cr	$Cr = Cr^{3+} + 3e^{-}$	0.744
Cu	$Cu = Cu^{2+} + 2e^{-}$	0.342
Ni	$Ni = Ni^{2+} + 2e^{-}$	0.257
Fe	$Fe = Fe^{3+} + 3e^{-}$	0.037
Ge	$Ge + 2H_2O = GeO_2 + 4H^{+} + 4e^{-}$	0.019
H_2O_2	$2H_2O = H_2O_2 + 2H^{+} + 2e^{-}$	-1.776
O_3	$O_2 + 2H_2O = O_3 + 2H^{+} + 2e^{-}$	-2.076

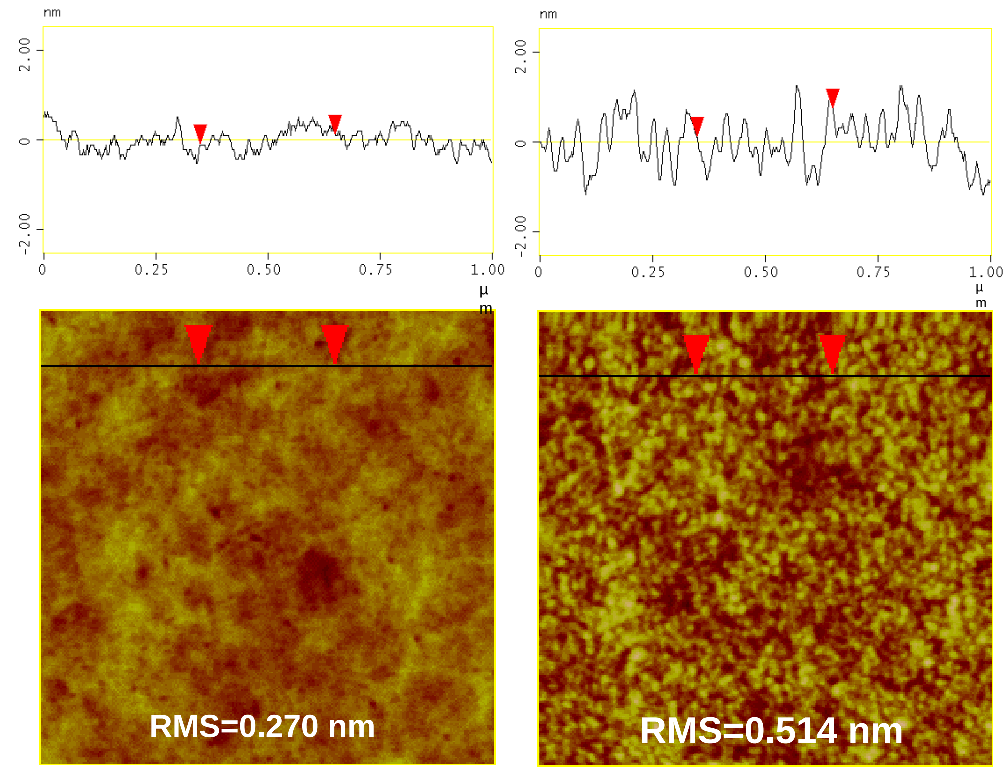
Reaction in the forward direction for metals indicates a thermodynamic driving force to lose an electron and go into the aqueous solution thus decontaminating the semiconductor surface.

This can be achieved by having a powerful oxidants such as hydrogen peroxide and ozone in the solution.

- Hydrogen peroxide and ozone has the highest oxidation potential for removal of the metals in solution and is being used in silicon cleans.

AFM study of chemically processed Ge surface



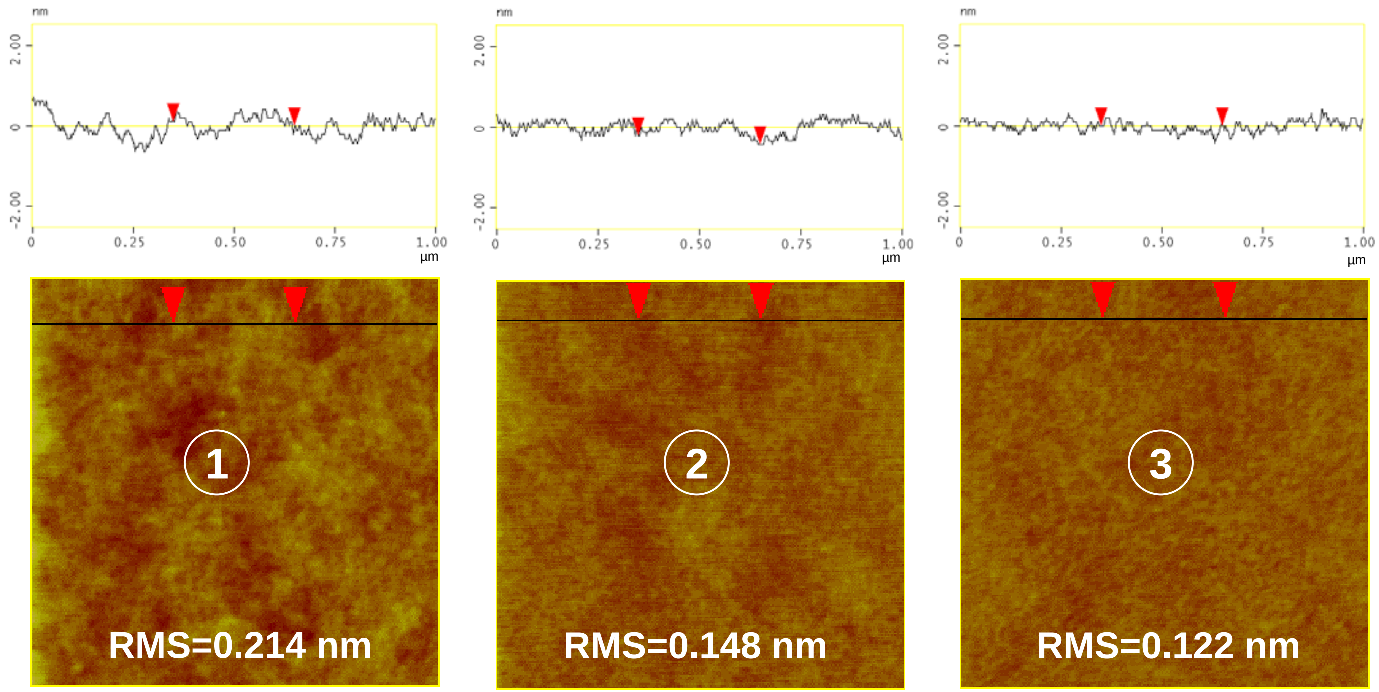


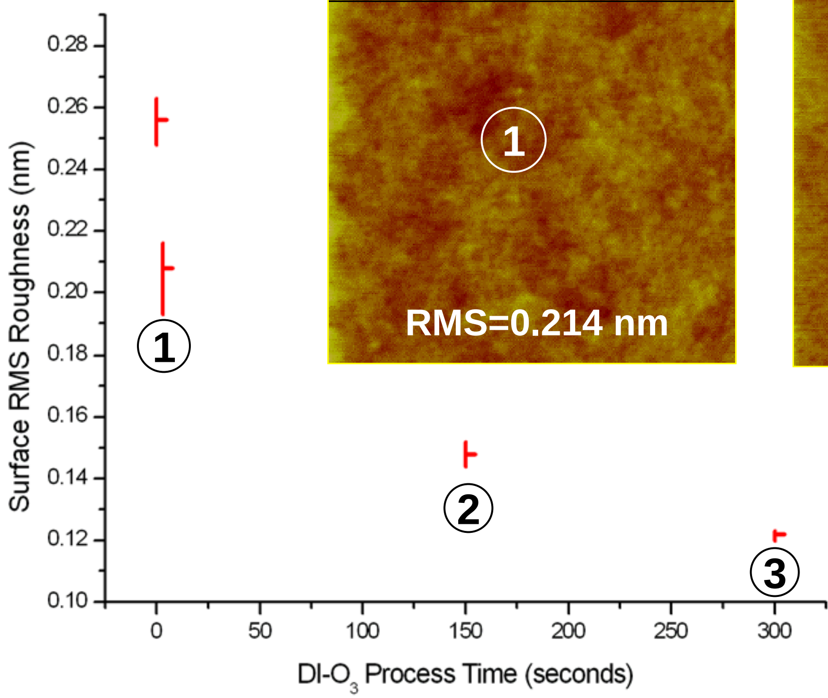
As received p-Ge

120 sec 30% H_2O_2

- Conventional cleaning chemicals (HF, BOE, NH_4OH) show no deterioration in surface roughness. Only H_2O_2 roughens the germanium surface. Surface RMS roughness increases from 0.270nm to 0.514nm. H_2O_2 is known to have an appreciable germanium etch rate.

AFM study of chemically processed Ge surface





DI-O_3 Process

1. DI-O_3 10”(organic removal)
2. DHF 60” (native oxide removal)
3. DI-O_3 Process (oxide re-growth)

- DI-O_3 decreases the surface roughness (AFM) of the germanium surface with increasing treatment time. DI-O_3 is a good candidate for germanium surface cleaning.

XPS Study of chemically processed Ge surface

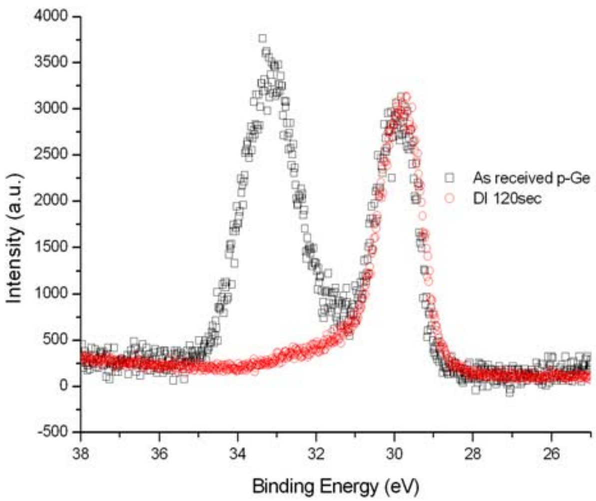


Figure 1

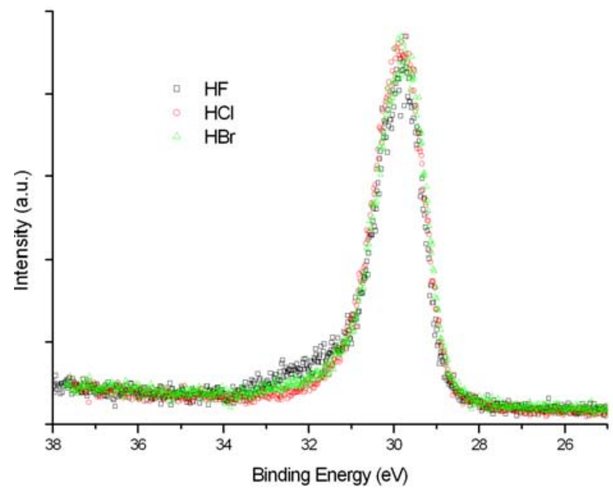


Figure 2

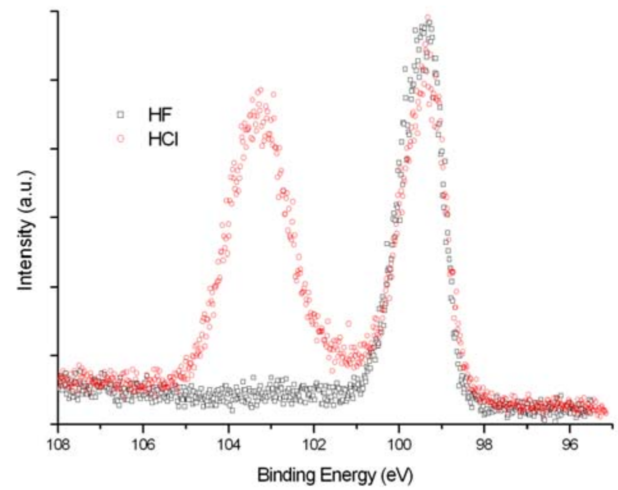


Figure 3

<u>Figure 1</u> → XPS of Ge-3d peak indicates that the germanium oxide layer has been dissolved after 120" of DI treatment. Indicates chemically prone oxide layer to conventional aqueous cleaning solutions.

<u>Figure 2,3</u> → XPS of Si-2p peak indicates that HF completely removes oxide and sub-oxide layer for silicon surface (Figure 3) but HX(X=F,Cl,Br) cannot completely remove oxide layers. Sub-oxide layers remain for all cases. HCl>HBr>HF in order of oxide removal efficiency.

Thrust B1: Surface Chemistry of High-k Barrier Layer Formation

Adam Thorsness, Shariq Siddiqui, Casey Finstad, and Anthony Muscat

Department of Chemical and Environmental Engineering

University of Arizona, Tucson, AZ 85721

agt@u.arizona.edu

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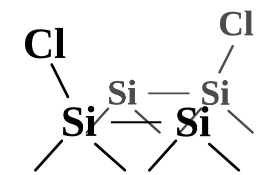
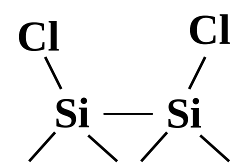
Feb. 2005

Summary/Conclusions

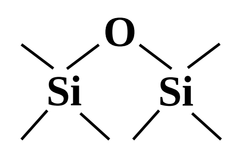
- Develop a starting surface for ALD of barrier layer (Si_xN_y tested) and/or metal oxide (TiO_2 tested)
  - First step - Investigated Cl adsorption
  - Second step – Reactivity of SiCl(a) with D_2O and NH_3
  - Third step – Form a nitride buffer layer and activate it with Cl
  - Forth step – Create a seed layer for high – *k* deposition

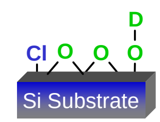


- Obtained Cl-terminated Si surface from a UV-Cl_2 process
  - Cl interacted with all Si-H and SiH_2 on the Si(100) surface
  - Only monochloride formed on the Si(100) surface during UV-Cl_2 process
  - No H remaining on surface



- Used D_2O to create a mostly very thin Si-O-Si surface

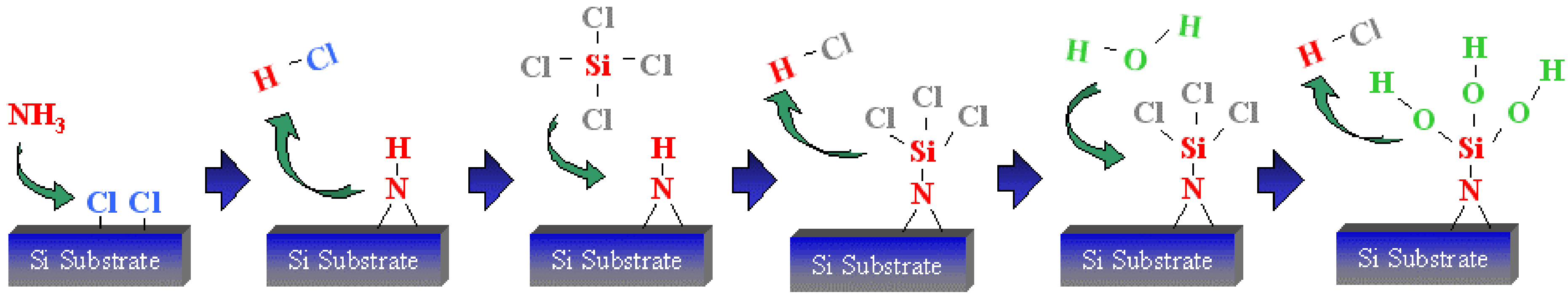




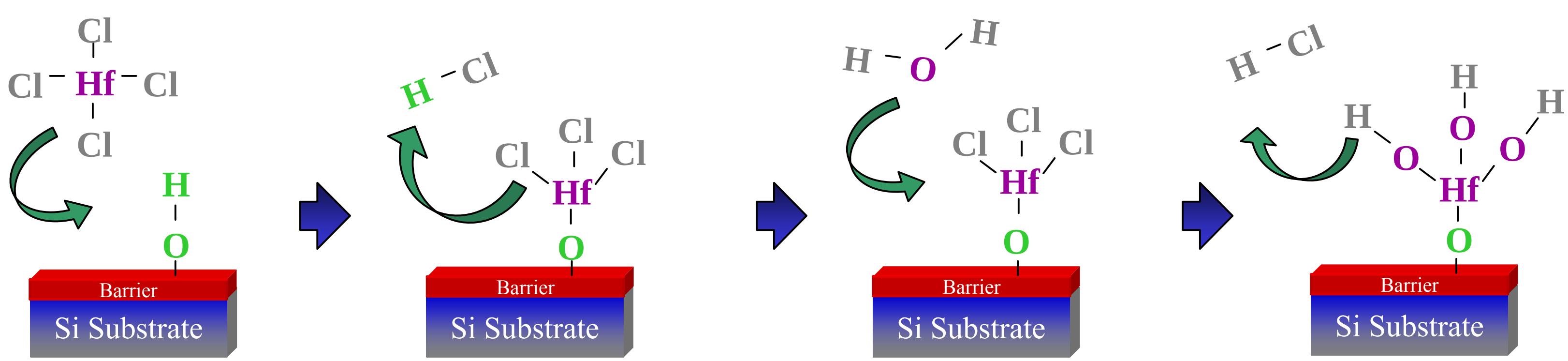
- Cl remaining on the Si surface after D_2O exposures produced both $SiCl_4$ and $SiCl_2$ TPD peaks at 580 K and 880 K, respectively

Barrier Layer and High-κ Formation

- A nitrogen-containing film, such as silicon nitride terminated with OH, has the potential of working as a barrier between the Si substrate and the gate dielectric.

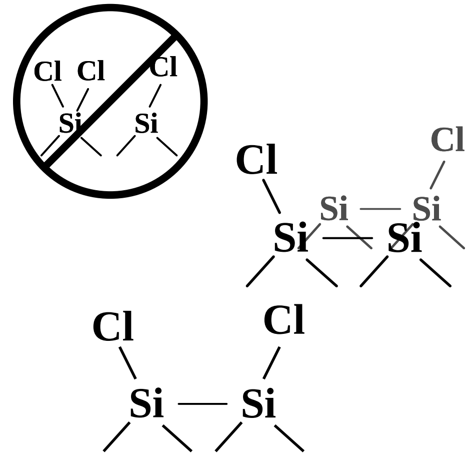


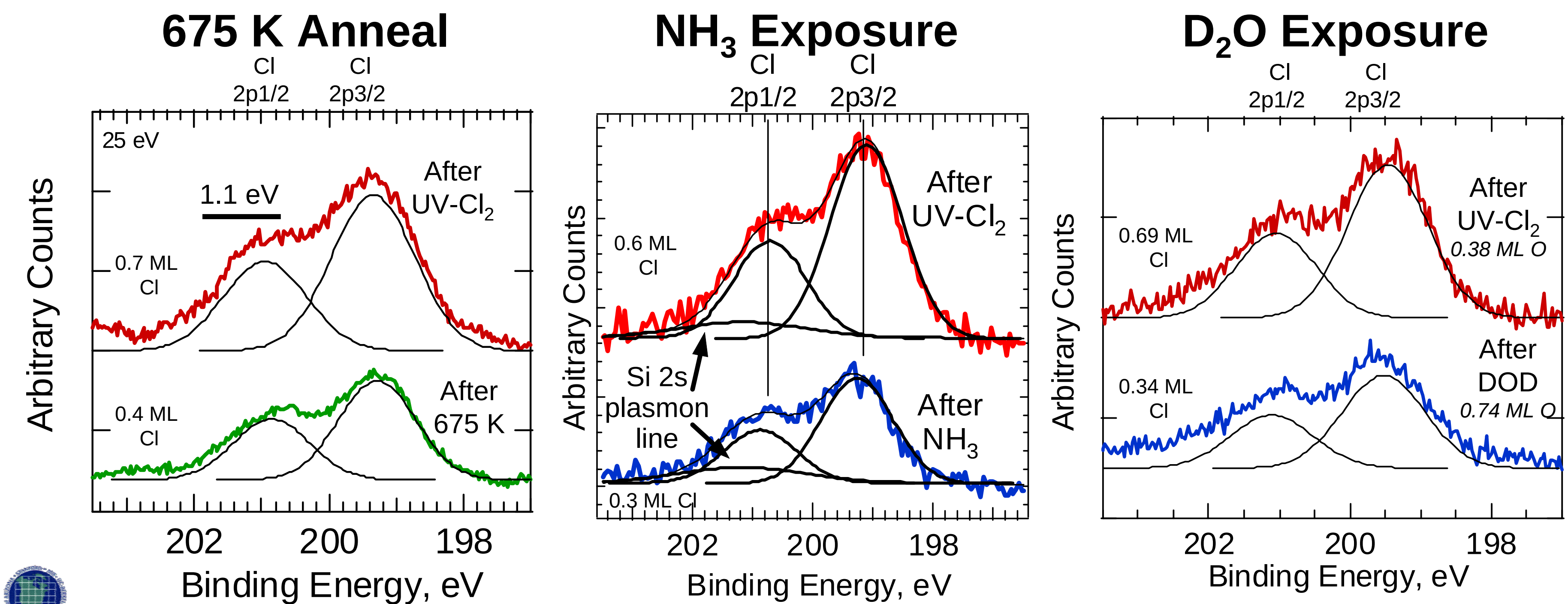
- For high-κ deposition using ALD a good surface would be terminated completely with –OH groups.



Only Monochloride (Symmetric Decrease in Cl 2p Peaks)

- Known chemical shift between monochloride and dichloride Si = 1.1 eV
- No obvious shift after the removal of what could be $SiCl_x$ after a 675 K anneal. (left plot)
  - TPD results show $SiCl_4$ desorbing during the 675 K anneal.
  - TPD results after the anneal show <u>only</u> $SiCl_2$ desorbing at TPD peak temperature of 880 K.
- Same symmetric decrease in the Cl signal after NH_3 and D_2O exposures. (middle and right plots)





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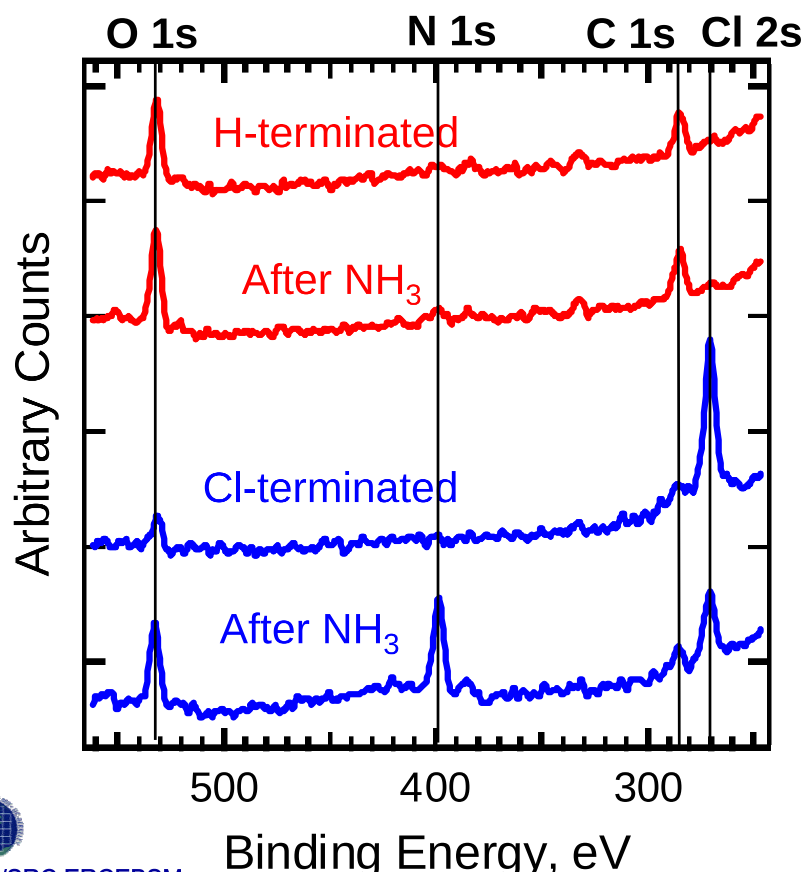
Creating a Thin Barrier Layer at Low Temperatures

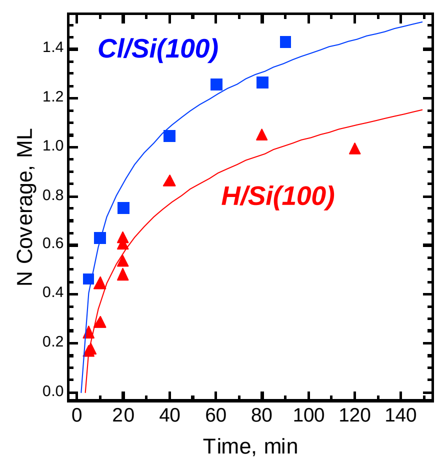
- NH_3 does not react with H-terminated Si(100) at 75°C
- NH_3 reacts with Cl-terminated Si(100) at 75°C (0.3 ML)

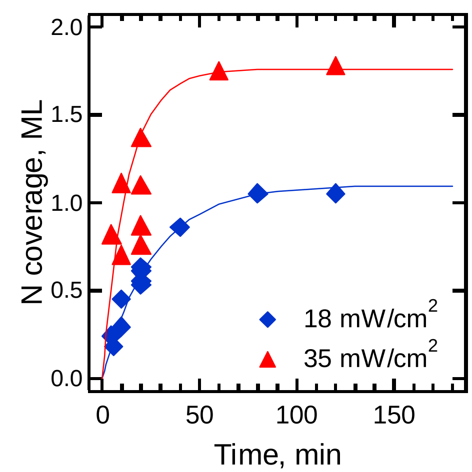
Halogen Termination To Activate Silicon Surface



- Higher coverage for pre-chlorinated surface
- 10 Torr NH_3, 75°C, 19 mW/cm² from 1000 W Xe arc lamp

- N coverage increases with time
- Higher saturation coverage with higher UV intensity
- Gas phase dissociation is photon limited ⇒ Control
- Surface structure
  - Subsurface diffusion?
  - N-H bond scission of surface amines?





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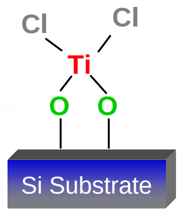
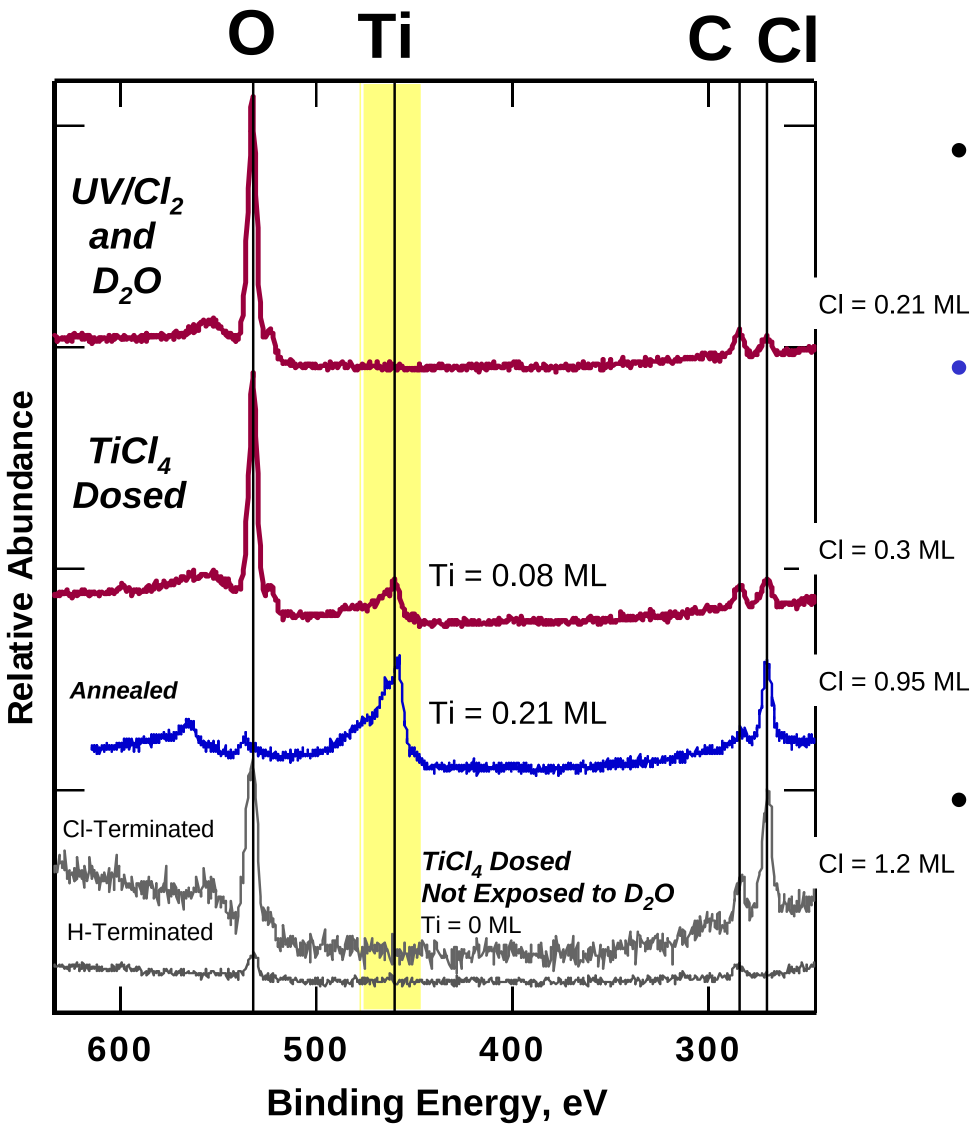
XPS of Exposures of D_2O to Different Si Surfaces





- Observed Ti adsorption onto UV/Cl_2 + D_2O exposed Si
- Ti-Si bonds on a Si surface with dangling bonds.
  - Cl adsorption
- No Ti adsorption
  - No Ti adsorption onto UV/Cl_2 exposed Si surface without D_2O treatment.
  - No Ti adsorption onto liquid cleaned surface. (H-terminated)

Thrust B: Front End Processing

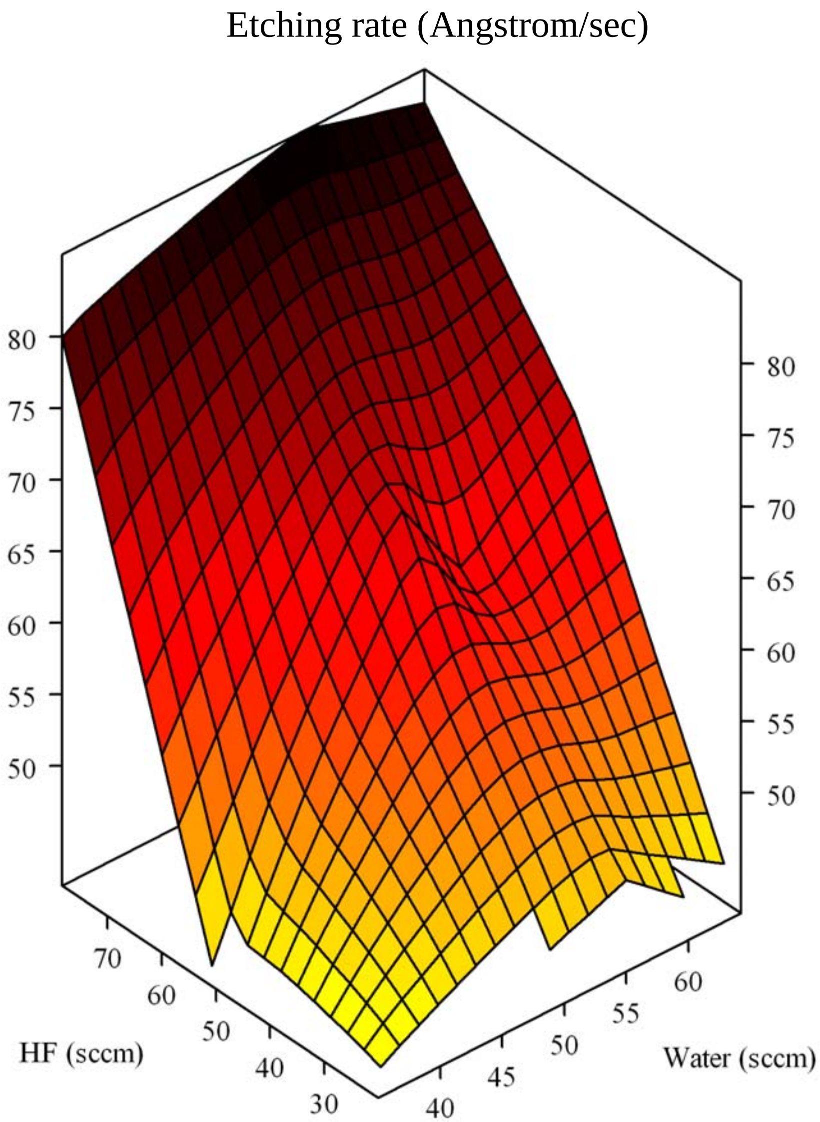
Task B-1: Wafer Surface Cleaning and Conditioning Processes that Minimize Resource Consumption:

Gas Phase Etching of Silicon Dioxide Films

Gerardo Montaño and Anthony Muscat
Department of Chemical and Environmental Engineering
University of Arizona
Tucson, AZ 85721

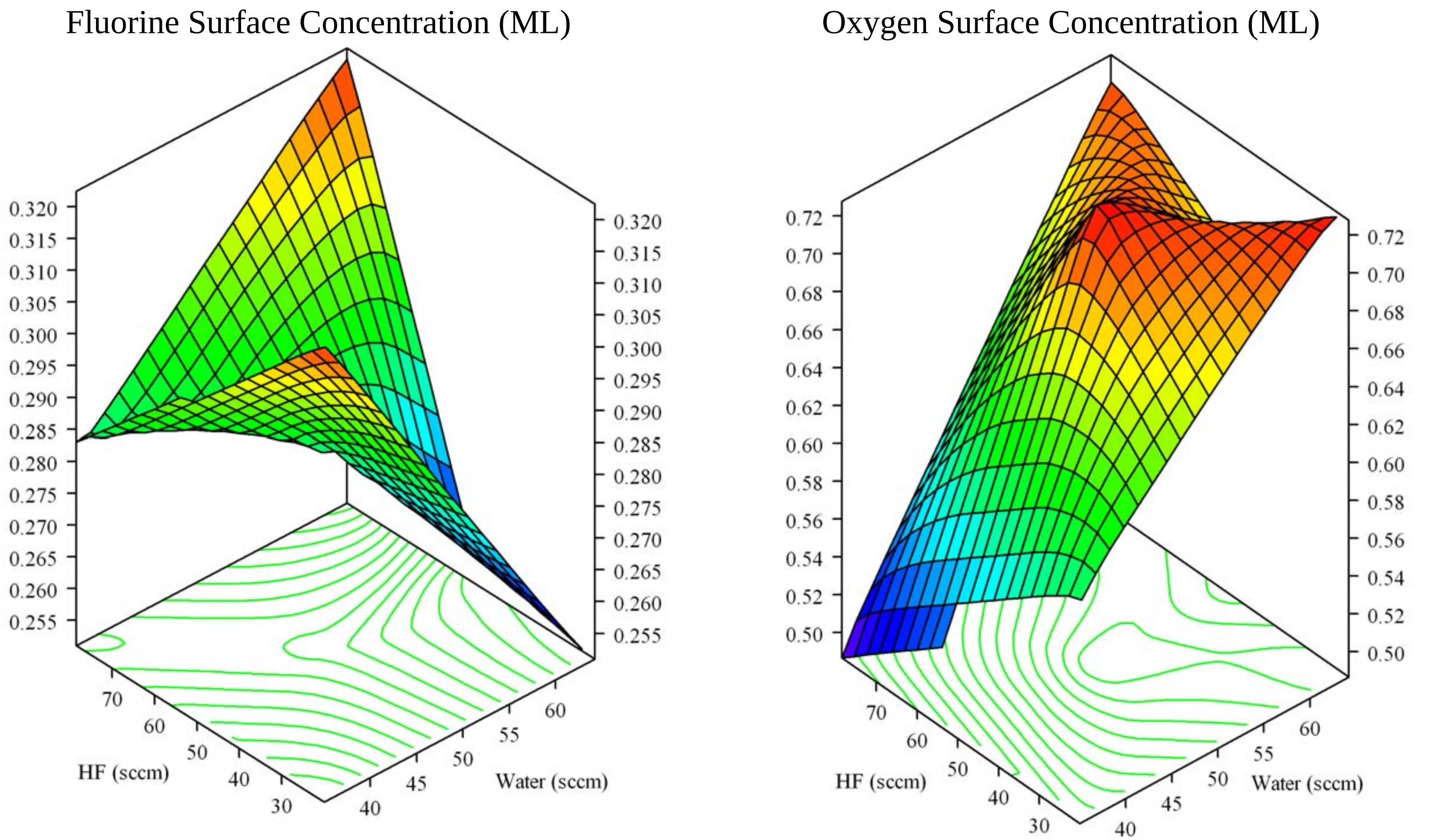
NSF/SRC EBSM ERC Annual Review
February 24-25, 2005

Etching Rate at 27ºC



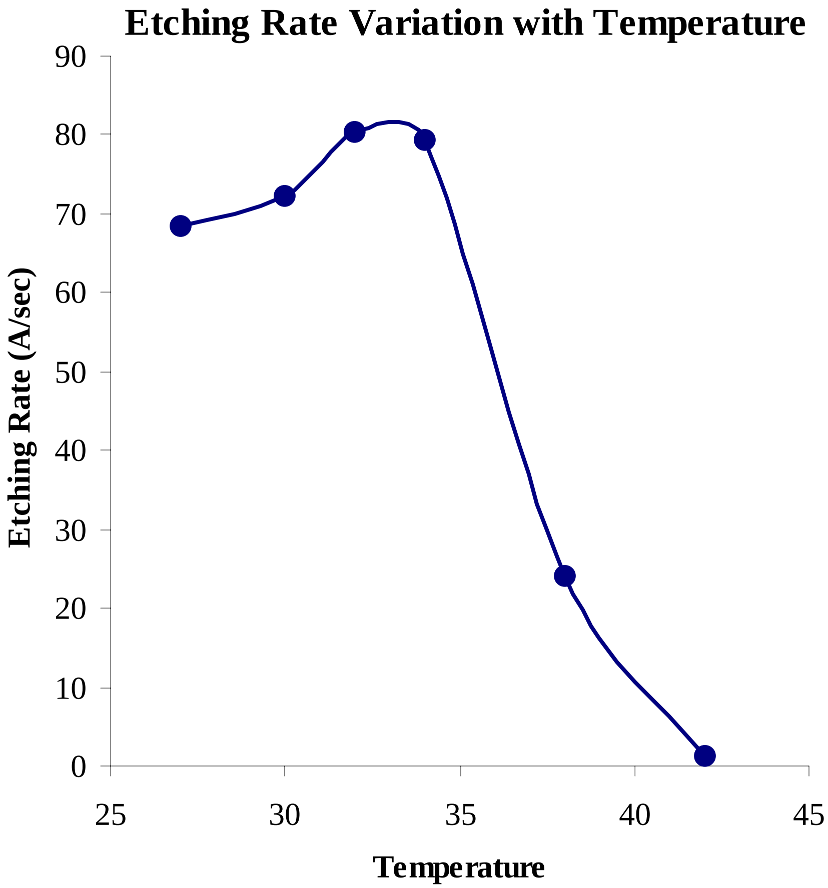
- Lowest rate (41 A/sec) is located at the lowest HF and H_2O flow rates.
- The highest reaction rate is not found at the highest reactant flow rates
- Water layer detected on surface of samples prior to HF dosing when water flow rates higher than 50 sccm. However, no noticeable change in etching rates is observed
- Etching rate increased linearly at high water flow rates
- Water impacts substantially the etching rate except at low HF flow rates. However, the effect decreases as the amount of water increases

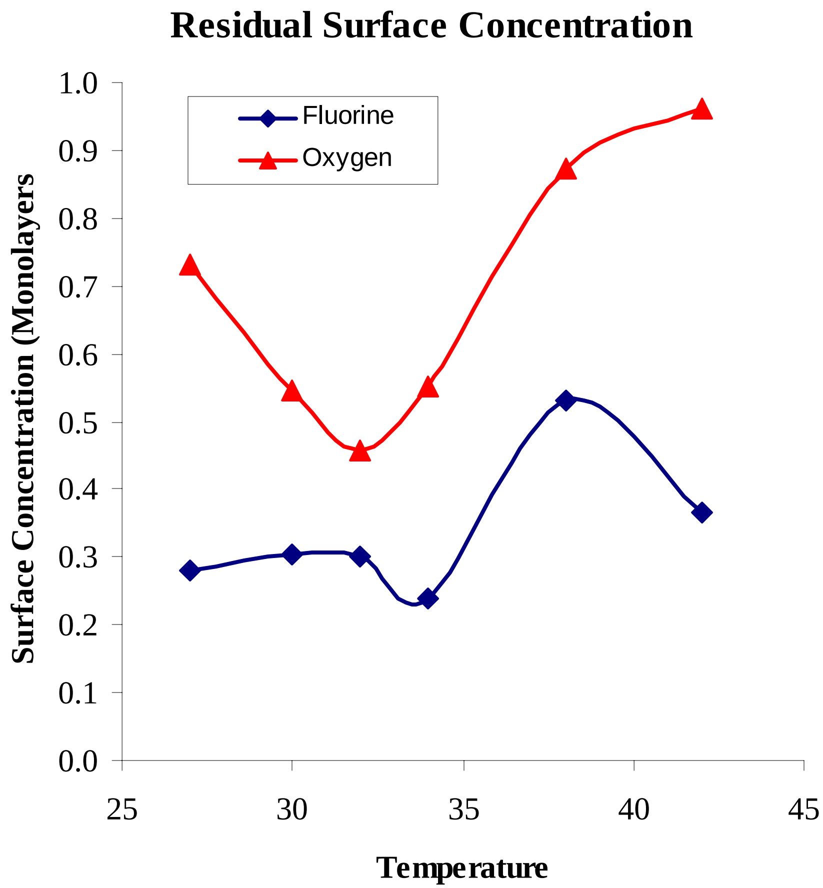
Residual Surface Composition at 27ºC



- Fluorine and Oxygen were calculated by using sensitivity factors and a calibration curve obtained with TXRF
- The smallest amount of residual F was obtained at low HF flow rates (below 50 sccm) and high water flow rates (above 50 sccm). This combination produced a high O surface concentration

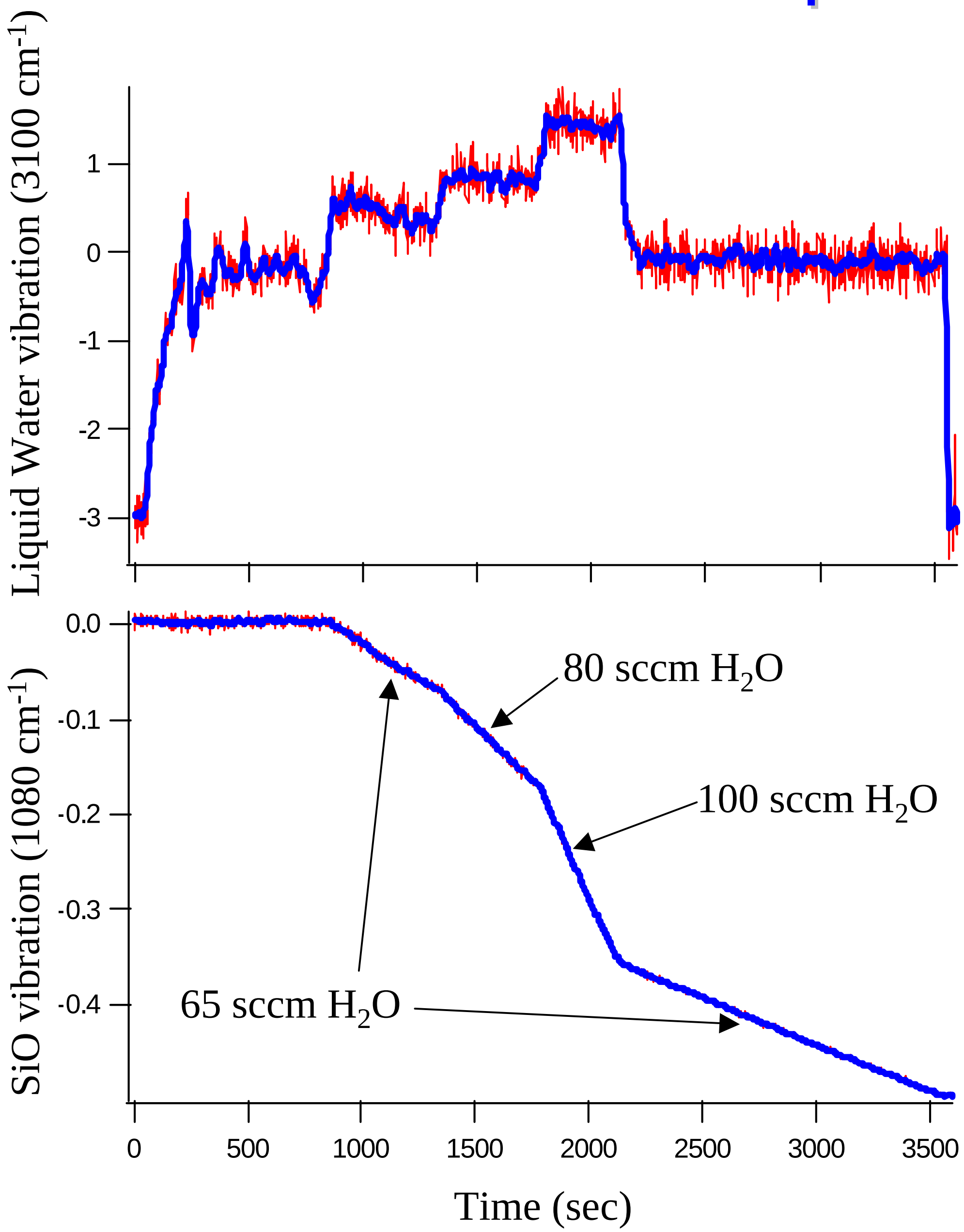
Behavior of Etching Rate with Temperature





- The plot shows the previously reported “volcano plot”, typical of gas phase etching of SiO_2
- Lowest F levels achieved when the produced water layer is the thickest during the reaction (more liquid like)

Influence of Gas Species in the Reaction



- When the etching process approximates the gas/solid regime, the water flow rate plays an increasing and important role in the reaction.
- During this experiment, the HF flow rate was kept constant and the water flow was changed from 65 sccm to 80, 100 sccm and back to 65 sccm
- The etching rate at the beginning was 0.41 A/sec, then it increased to 1.6 A/sec and then to 3.2 A/sec

Conclusions

- HF/Vapor Oxide Removal
  - A condensed layer prior to HF dosing was detected at low temperatures and high water flow rates. However, etching occurs regardless of the existence of a condensed layer. Moreover, it appears not to influence the overall etching rate trends.
  - Post process XPS analysis shows submonolayer coverages of F and O that are dependent on processing parameters. XPS also shows the inability to completely remove the oxide film layer
  - Surface is terminated by isolated silanols (FTIR)
  - Instantaneous availability of water (the amount of water available at any given time) appears to play a large role in etching rate
  - A wide range of etching rates can be obtained at any temperature. HF and H_2O flow rates have a more pronounced impact in etching rates

Gas Phase Methods for Alternative Passivation Layers on Monocrystalline Silicon

Task B-1: Wafer Surface Cleaning and Conditioning Processes that Minimize Resource Consumption

Sarah Perry and Anthony Muscat

Department of Chemical & Environmental Engineering

University of Arizona

Tucson, AZ 85721

NSF/SRC EBSM ERC Review

February 24-25, 2005

Motivation for Gas Phase Surface Passivation

Gas Phase Surface Passivation

Environmental Benefits

- Decreased water and solvent use
- Decreased energy use
- Decreased need for high cost cleanroom environments
- Safer working environment

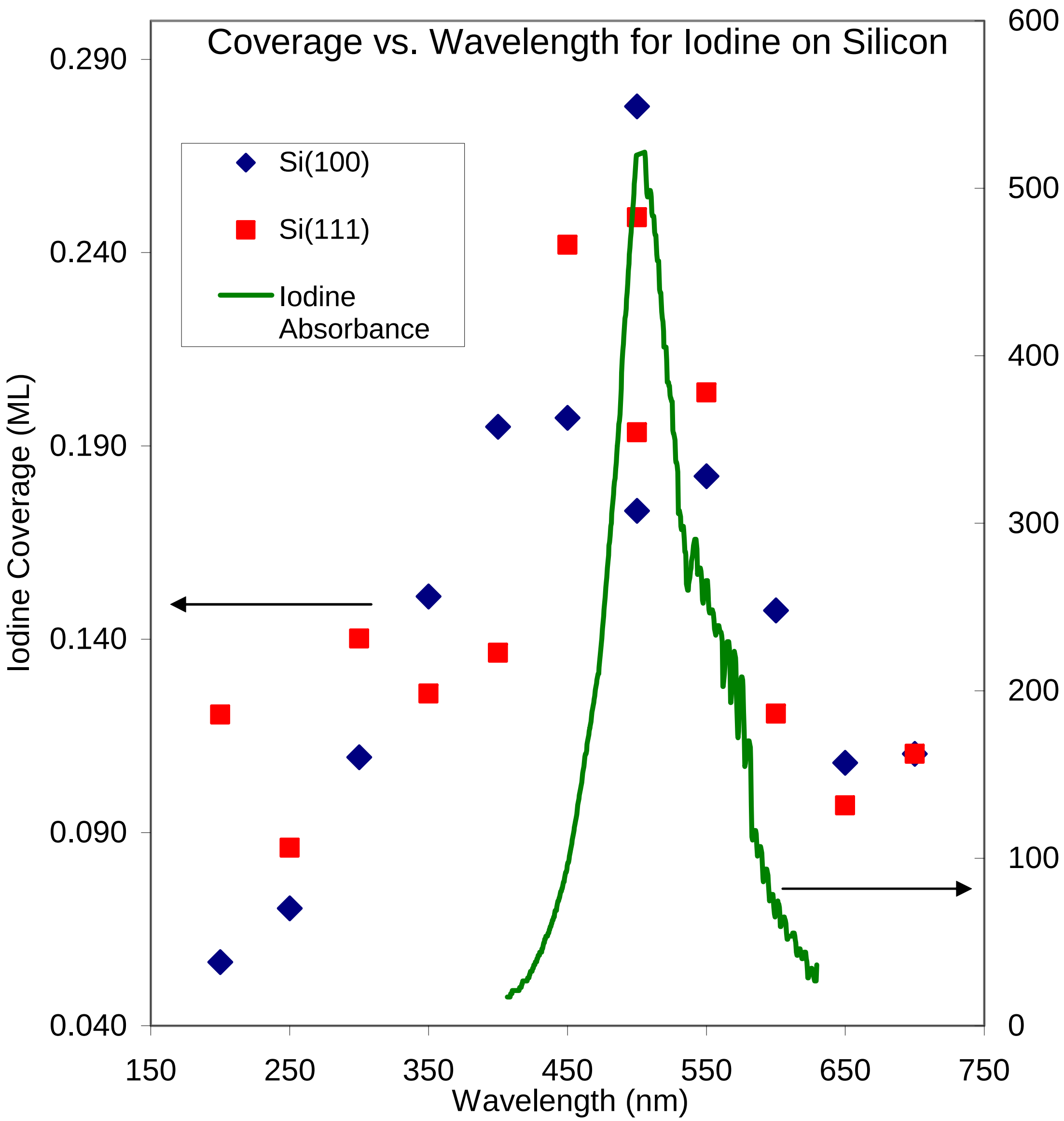
Better Surface Control

- Improved protection against oxidation and contamination
- Removal of duplicate cleaning steps
- Allows for even smaller features
- Higher device density
- Improved device yield
- Additive processing

Decreased Bottlenecking

- Increased factory-line efficiency
- Removal of duplicate cleaning steps
- Additive processing allows for fewer process steps

Iodine Termination – Photonic Activation



Spectrum from Okabe, Photochemistry of Small Molecules, (1978)

- Photonic enhancement corresponds to the UV-activation of the I-I bond at 500 nm
  - Similar coverage as compared to a full spectrum sample

I-I + hν → 2I·
2I · + Si-H → Si-I + HI

- No surface activation is observed
  - Si-H absorbs at 350 nm, no increase in adsorption seen
  - No difference between Si(100) and Si(111) crystal faces

Methoxy Termination

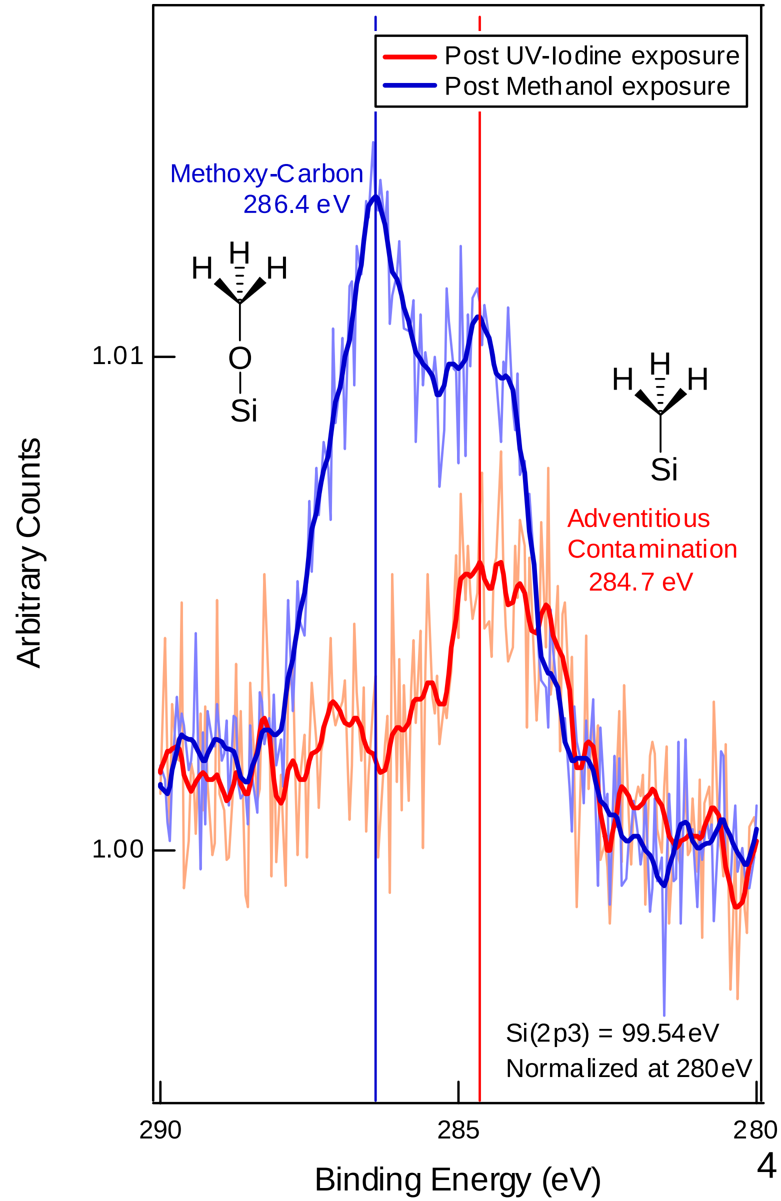
- Dissociative adsorption of methanol

$$CH_3OH + Si\text{-}H \rightarrow Si\text{-}OCH_3 + H_2$$

- Substitutive reaction of methanol on iodine terminated surface
  - Iodine provides a more reactive substrate
  - Iodine has the potential for selective adsorption for additive processing

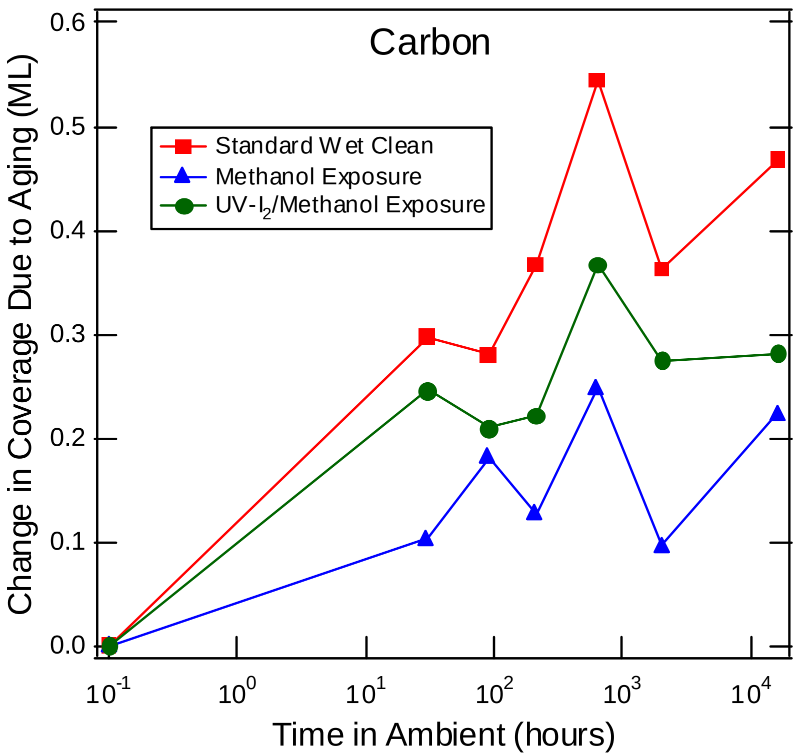
$$CH_3OH + Si\text{-}I \rightarrow Si\text{-}OCH_3 + HI$$

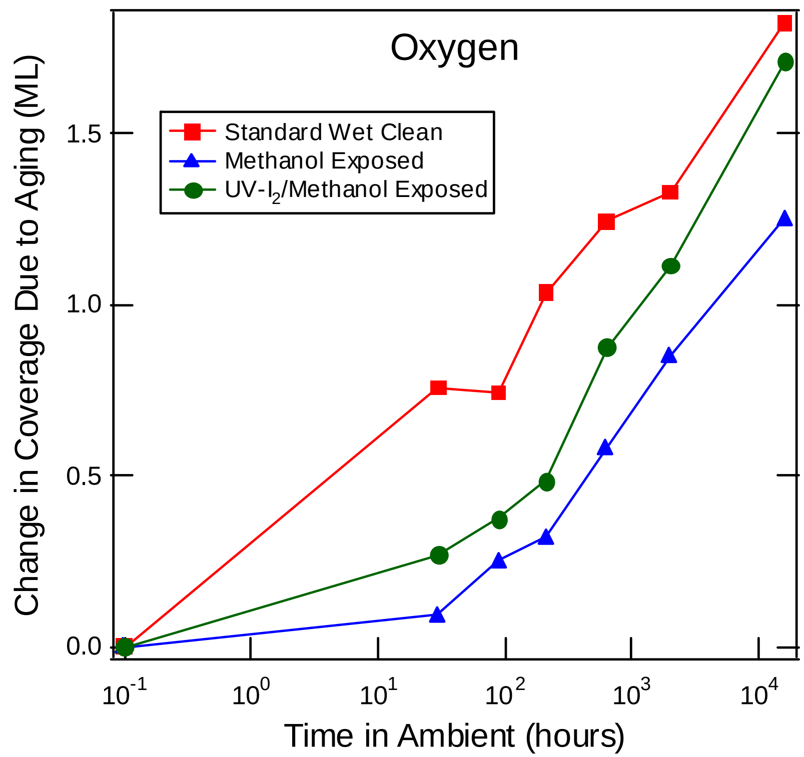
- Methoxy termination detected via a shift in the carbon (1s) peak of the XPS spectrum



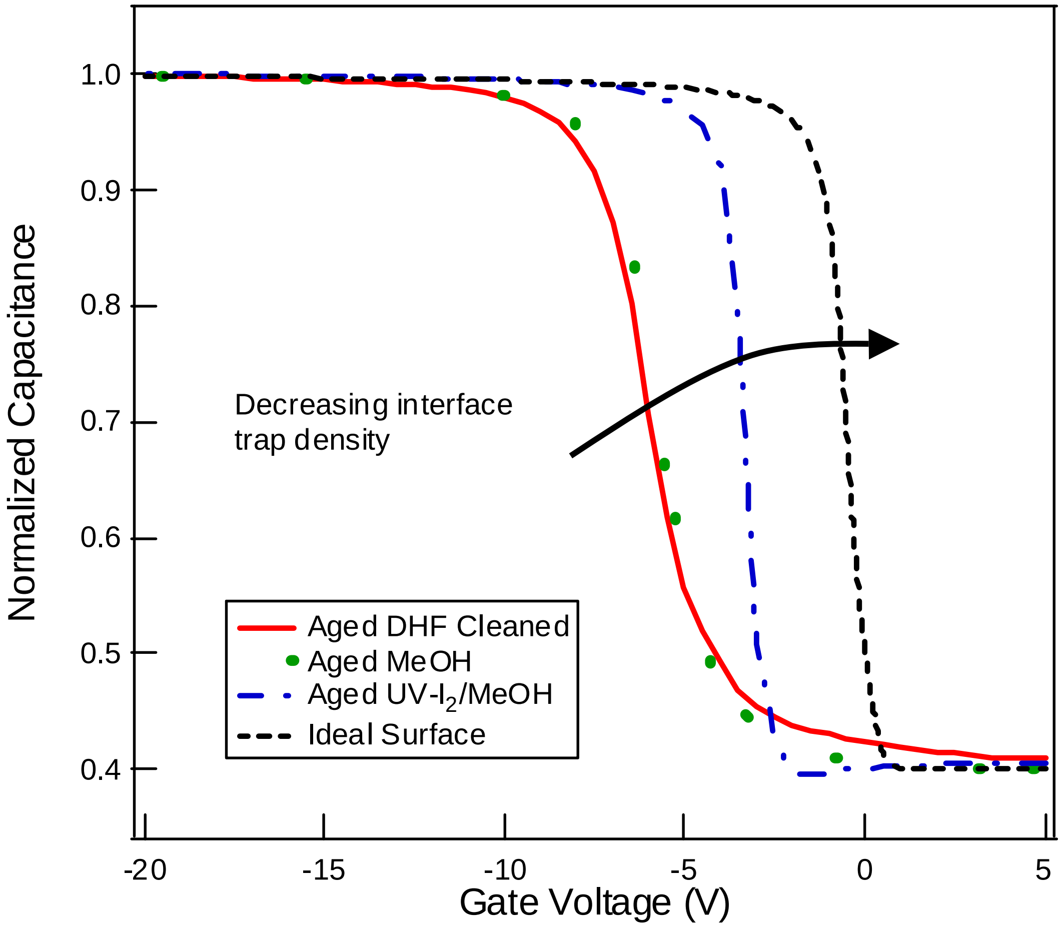
Aging Experiments

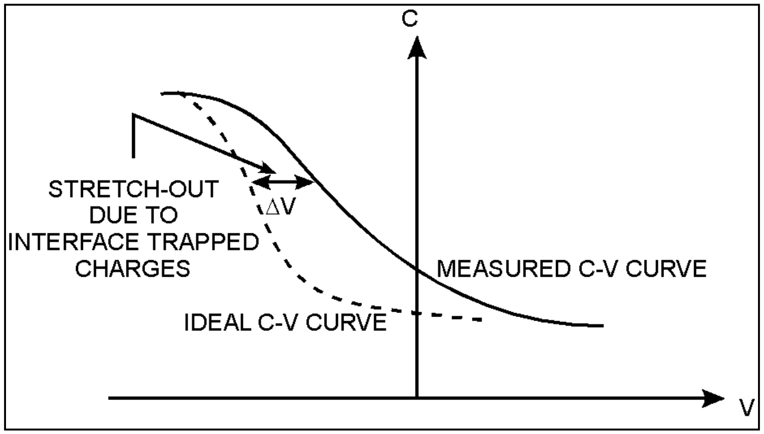
- Prepared samples were exposed to ambient conditions over time
- Methoxy passivation decreased carbon contamination and native oxidation as compared to a wet cleaned surface
  - 30-60% reduction in carbon contamination over time
  - 50-70% less oxidation within 10 hours
  - 10-35% less oxidation after 10 days





Capacitance-Voltage Measurements





Summary of Electrical Measurement Results				
	D_{it} ($cm^{-2}\,eV^{-1}$)	D_{it} % Change compared to I_2/MeOH	Q_{ox} (cm^{-2})	Q_{ox} % Change compared to I_2/MeOH
H terminated	1.9E+11	224%	3.1E+11	98%
MeOH-only	6.7E+10	16%	2.8E+11	79%
I_2/MeOH	5.8E+10	0%	1.6E+11	0%

- Interface traps result in a spreading of the depletion region in a *C-V* curve
- Methoxy-termination maintained a higher Si/SiO_2 interface quality, despite extended periods of exposure to ambient contamination
- In the range of industrial device defect densities (10^9 – 10^{11} cm^{-2})

Thrust B Task 2

Selective Surface Preparation and Templated Atomic Layer Deposition

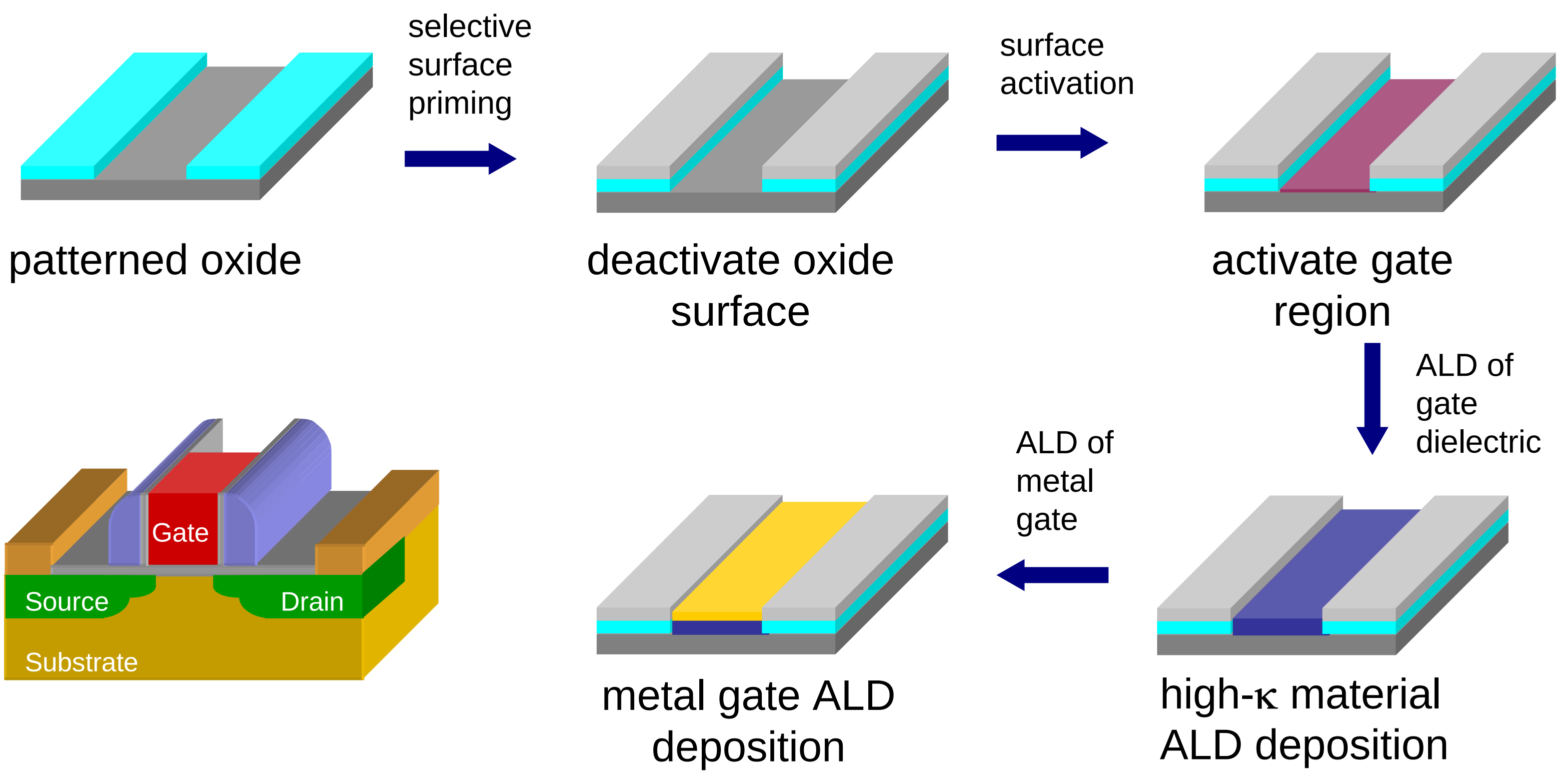
Junsic Hong, Rong Chen, David Porter, Stacey F. Bent

Stanford University

ERC Review Meeting, 24-Feb-2005

Process Flow for Area-Selective ALD for Gate Stack

- Goal: Self-aligned deposition process for gate dielectrics and gate metal

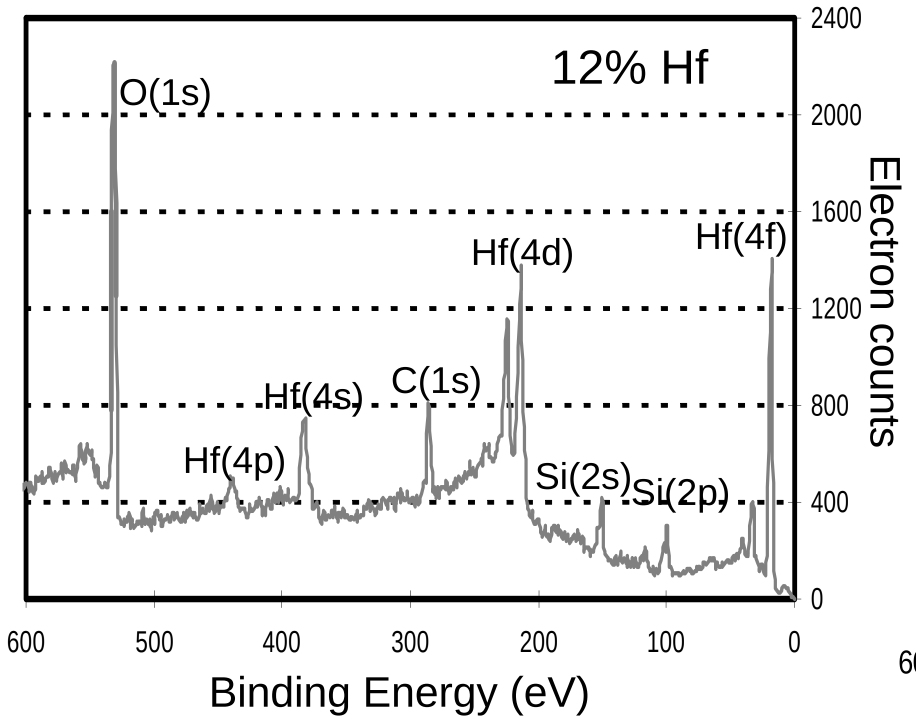


- Modifies process flow from a subtractive process (photolithography, etch) to an additive process (deposition).

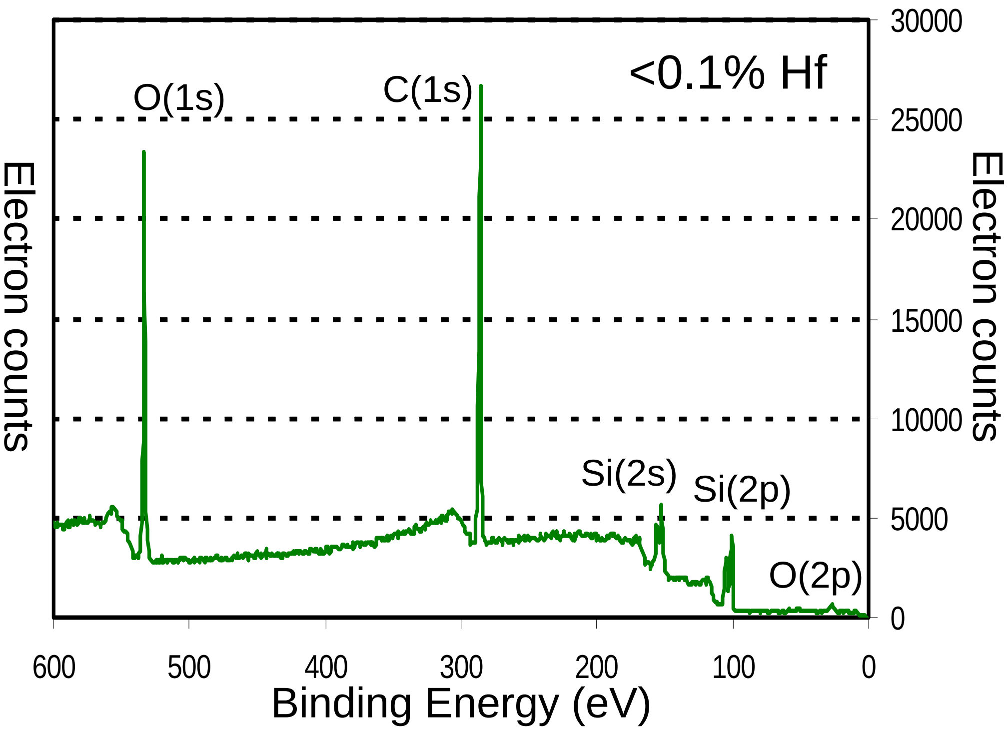
ALD Inhibition by Octadecyltrichlorosilane (ODTS) SAM

Vapor Phase Delivery

Bare Si(100) surface



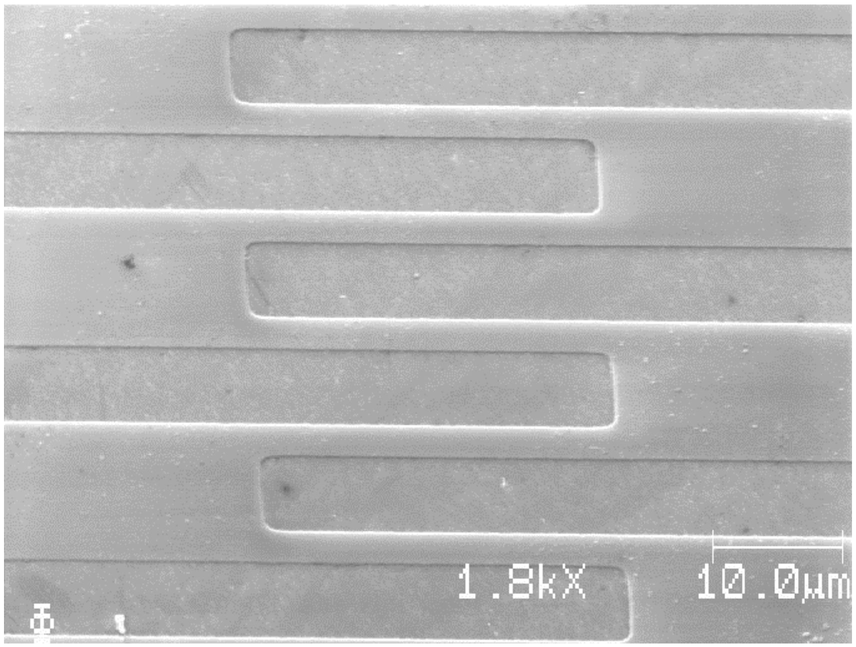
SAMs on Si(100) surface



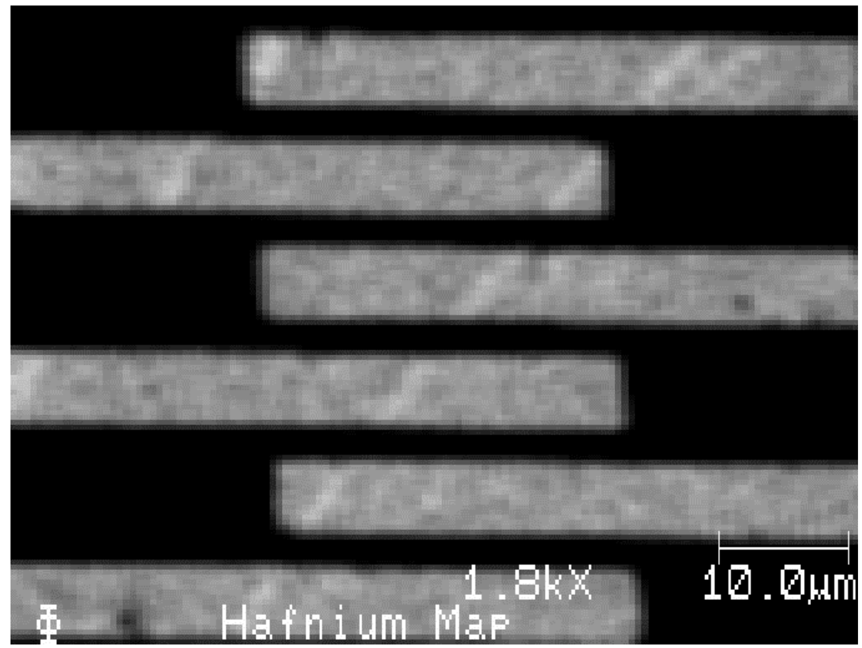
- Experimental Condition: SAM Precursors (Octadecyltrichlorosilane and water), Ts=170°C, t=2days

SEM Image vs. Hafnium Elemental Mapping

SEM image on patterned area

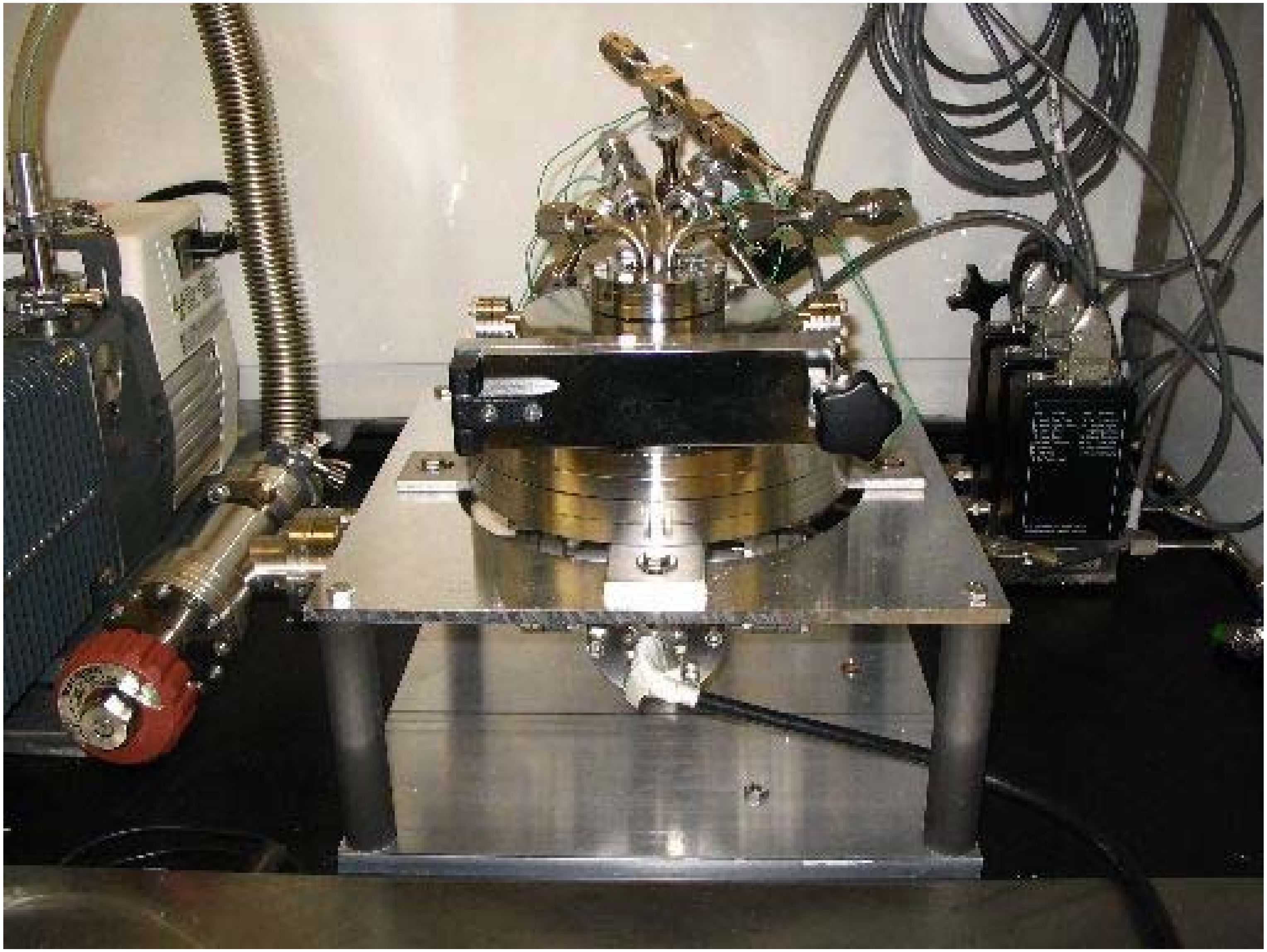


Hafnium elemental mapping on patterned area



Data: Charles Evans & Associates

Second Generation ALD Reactor



Conclusions

- Siloxane SAMs formed in vapor phase have been demonstrated as a monolayer resist for SiO2
- Properties of SAM required for successful deactivation have been delineated
- Area selective ALD on patterned oxide has been demonstrated
- 2nd generation ALD chamber is constructed and optimized for ALD run

Future Study

- Investigate SAMs formation with quartz crystal microbalance for mechanistic details
- Explore the way to form SAMs that can block ALD process at much shorter time
- Explore patterning and etching methods for deactivating agents

Chemical Structures and Band Alignment at HfO_2/Ge(001)

Kang-ill Seo and Paul. C. McIntyre
Department of Materials Sci. & Eng., Stanford Univ.

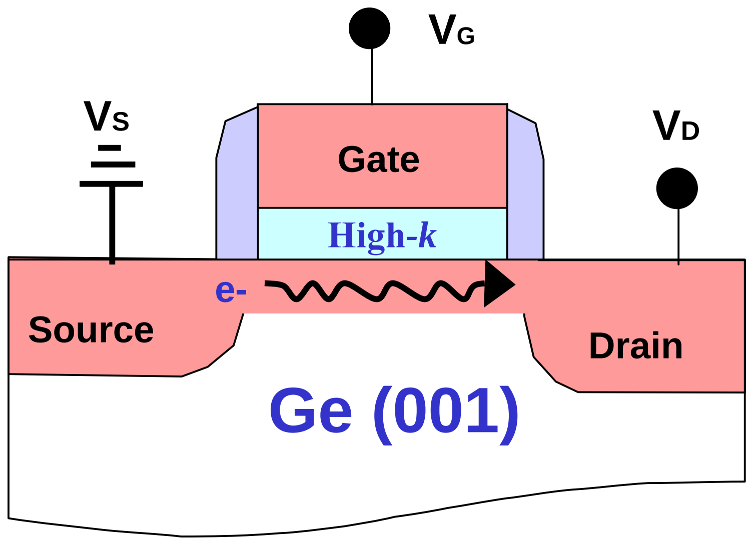
Krishna. C. Saraswat
Department of Electrical Eng., Stanford Univ.

Dong-Ick Lee, Shiyu Sun and Piero Pianetta
SSRL (Stanford Synchrotron Radiation Laboratory), Stanford Univ.

Task B-2

Selective Surface Preparation and Templated Atomic Layer Film Deposition: Novel Processes for Environmentally Benign Transistor Gate Stack Manufacturing

Benefit of High-*k* on Ge channel



- High-κ Gate Dielectrics → Avoid poor quality GeO_2 & Improve C_{ox}
- Ge channel → Intrinsic Mobility enhancement ; electron (2x) and hole (4x) compared to Si (001)

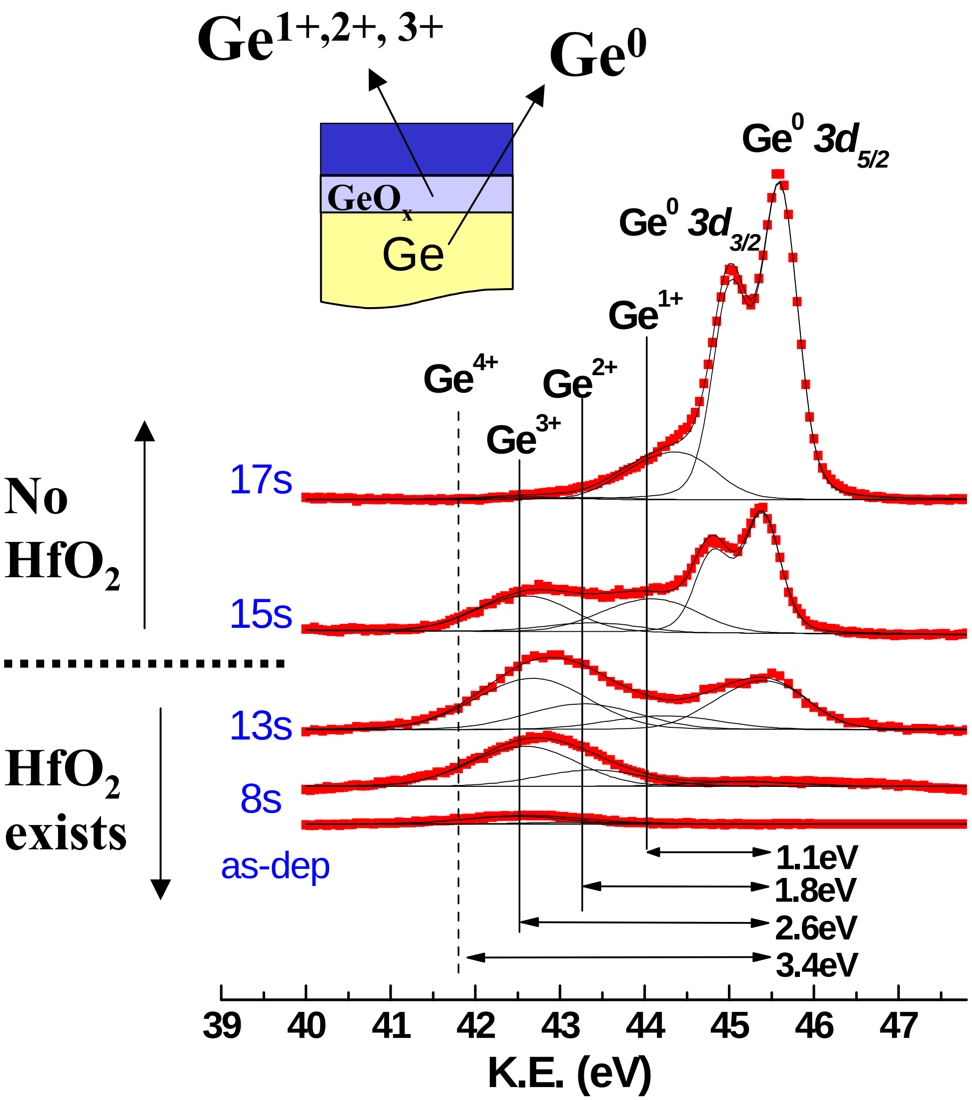
$I_{channel} \propto$ charge • source injection velocity

$$\propto (\varepsilon_r \varepsilon_o A / t_{ox}) \bullet (V_{GS} - V_{th}) \bullet (E_{source} \times \mu_{inj})$$

Better performance can be achieved by combining high-*k* gate dielectric and high mobility Ge channel

GeO_xN_y, Al_2O_3, ZrO_2, and HfO_2 have recently been studied as a high-*k* gate insulators on Ge,

Chemical Bonding of I.L. (Ge *3d* core level)

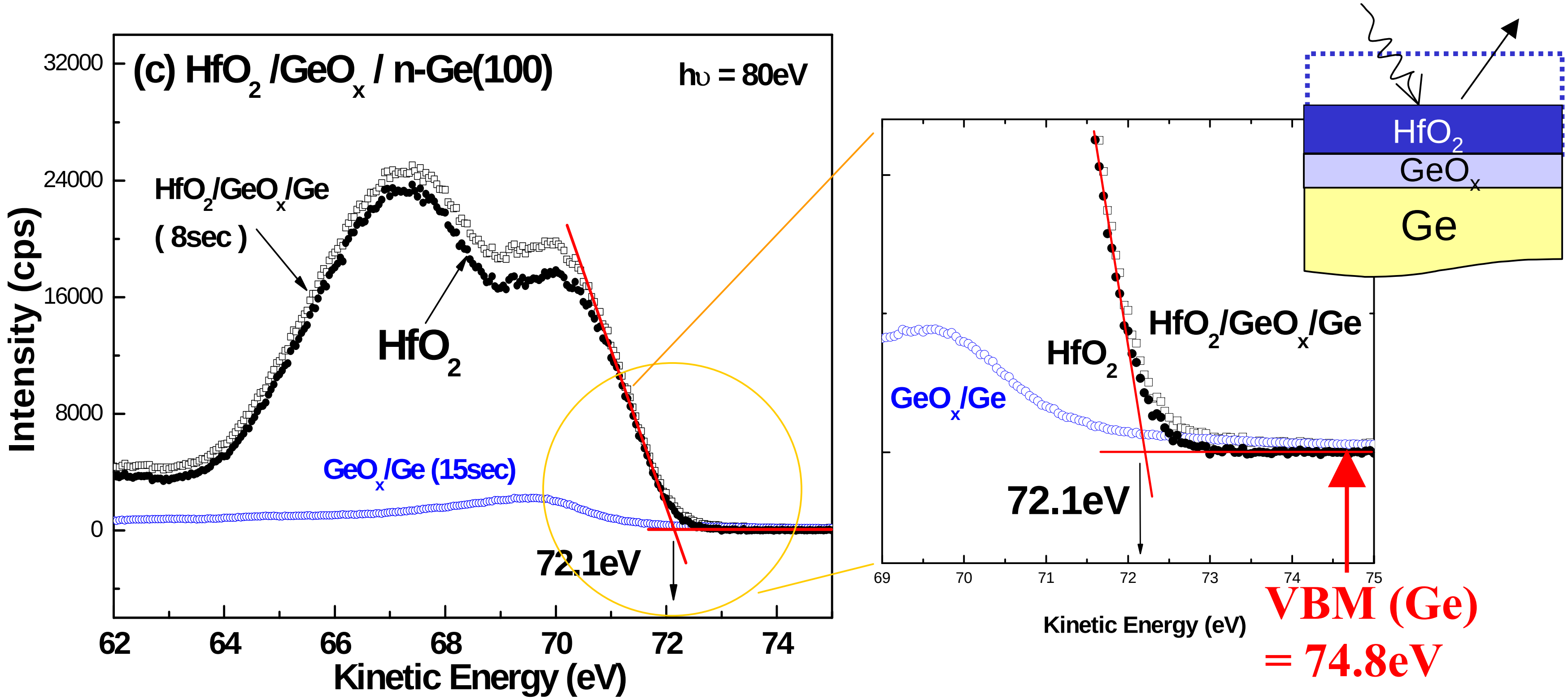


No Ge^{4+} feature associated with stoichiometric GeO_2.
→ Re-oxidation of Ge substrate following upper Hf metal oxidation leads to a very non-stoichiometric GeO_x layer at HfO_2/Ge interface

VB from HfO_2 / GeO_x / Ge (8sec HF-etching)

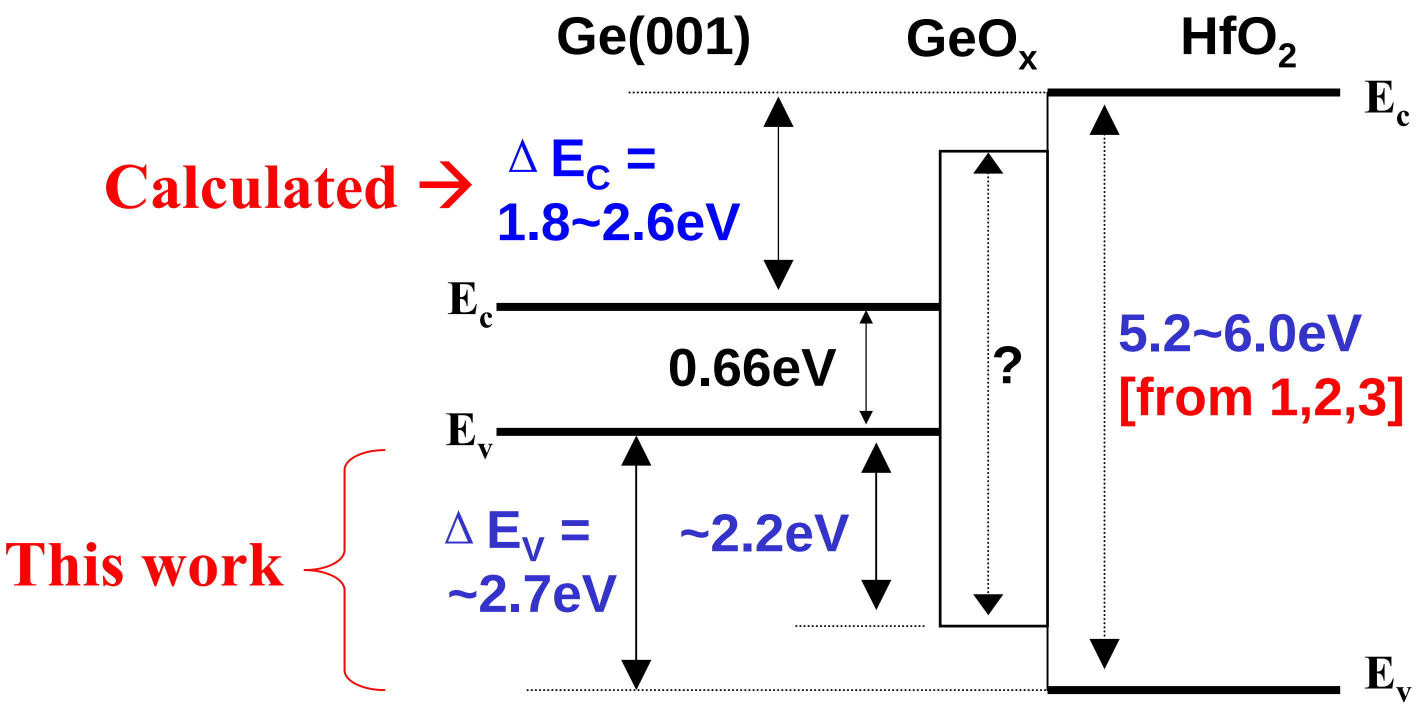
$$VB(HfO_2) = VB(HfO_2/GeO_x/Ge) - (\text{attenuation}) \bullet VB(GeO_x/Ge)$$

● □ ○



VBM (HfO_2) = 72.6eV → ΔE_v (Ge-HfO_2) = 2.7eV

Band Alignment of HfO_2/I.L.(GeO_x)/Ge(100) System



1 M. Oshima,et. al., Appl. Phys. Lett. **83**, 2172 (2003)
2 J. Robertson, J. Vac. Sci. Tech. B, **18**, 1785, (2000)
3 V. V. Afannas'ev, et. al., Appl. Phys. Lett. **81**, 1053 (2002)

Δ E_v and Δ E_c at HfO_2/Ge(001) are comparable to those of HfO_2/Si(001) → Promising in terms of leakage current

Conclusions

- **High-k (HfO_2) /I.L / Ge(001) ; By analyzing Ge *3d* core levels systematically, we found that a very thin non-stoichiometric chemical nature exists at the HfO_2/Ge interface.**
- **From the VB spectra, the VB offset between Ge(001) and HfO_2, ΔE_v (Ge-HfO_2) = ~2.7 eV and resulting CB offset, ΔE_c (Ge-HfO_2) = 1.8~2.6 eV. → Need better surface passivation layer, but promising in terms of gate leakage current**

Acknowledgement

- Special thanks to Prof. Yoshio Nishi and Prof. Baylor B. Triplett for helpful discussions, and Prof. Mike Kelly for analyzing XPS data.

- This work was supported in part by the NSF/SRC Center for Environmentally Benign Semiconductor Manufacturing and Initiative for Nanoscale Materials and Processes (INMP).

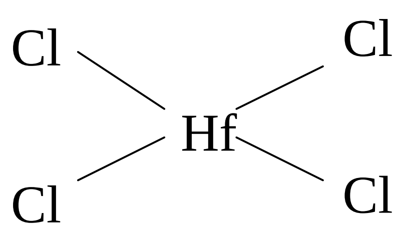
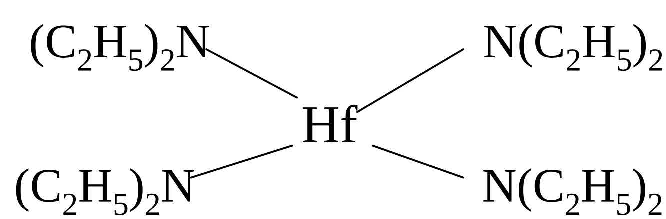
Effect of precursor on the characteristics of nanoscale ALD-HfO_2

R. Sreenivasan[1], P.C. McIntyre[1], K.C. Saraswat[2]

[1] Department of Materials Science Eng., Stanford University
[2] Department of Electrical Eng., Stanford University

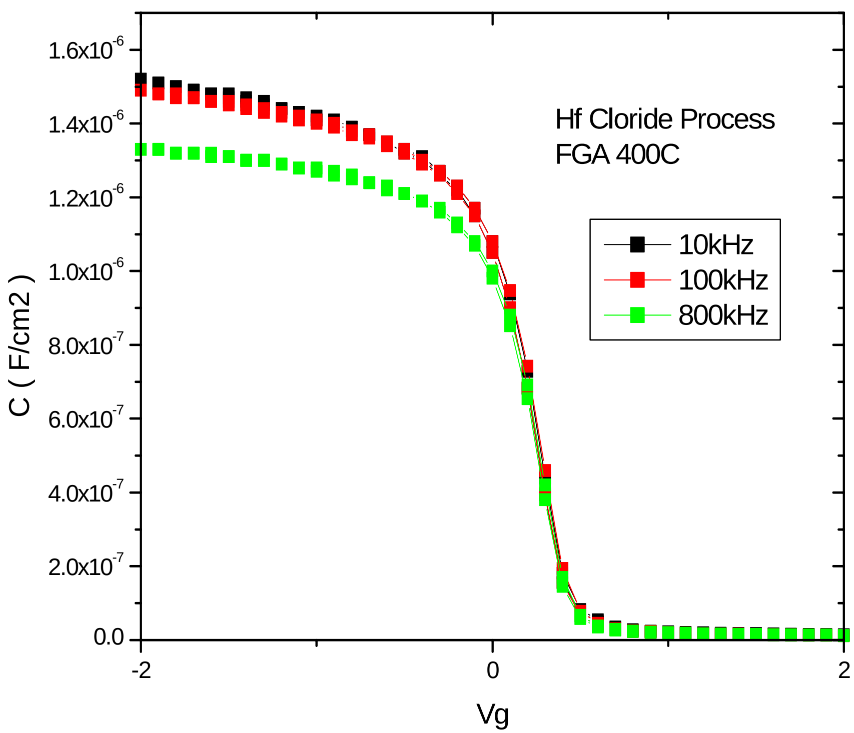
Thrust B, Project 2

ALD Process Parameters

	Chloride ($HfCl_4$)	Alkylamide (TDEAH)
Substrate temp	300 °C	150 °C
Bubbler temp	150 °C	65 °C
Pulsing	1-60-1-60	1-50-1-50
Dep rate	0.5Å/cycle	0.75Å/cycle
Chamber wall	R.T	75 °C
Oxidizer	H_2O	H_2O
N_2(carrier gas)	20 sccm	2.5 sccm
Process Pr	0.5 Torr	0.5 Torr
Chemical structure		

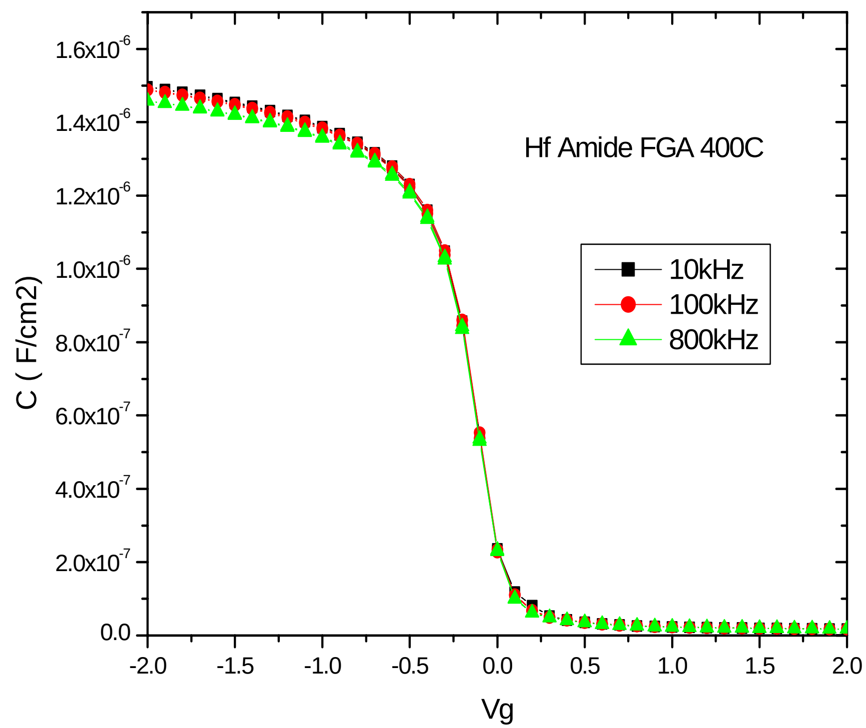
Choice of precursor

Chloride



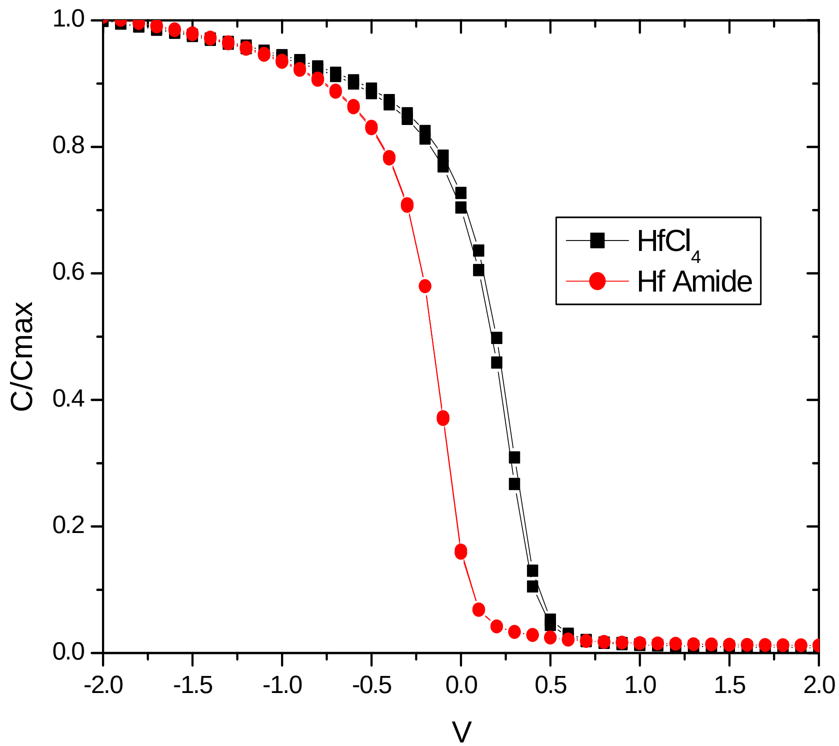
t_{HfO2} = 45Å, I.L = 15Å
Cap derived EOT = 23.1Å
Hysteresis ~ 20 mV

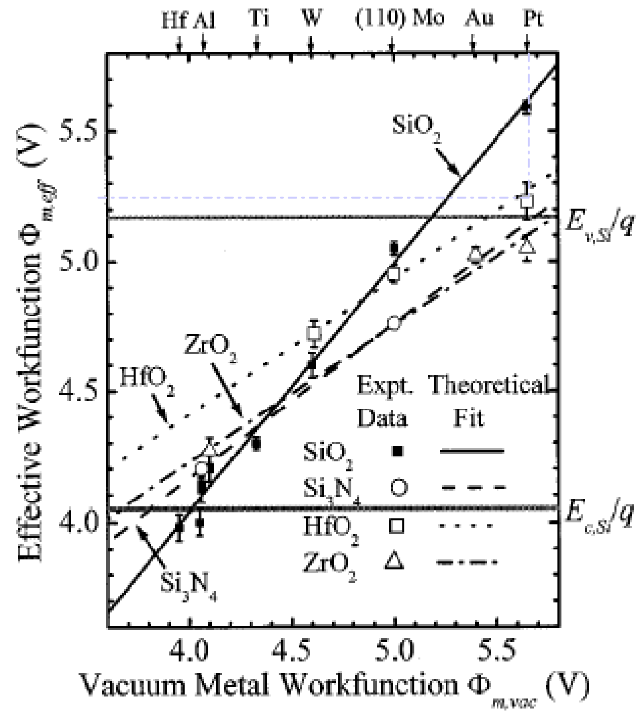
Alkylamide



t_{HfO2} = 50Å, I.L = 15Å
Cap derived EOT = 23.2Å
Hysteresis ~ 5 mV

Effect of Precursor on V_{FB}





V_{FB} (alkylamide) = 0.09V
V_{FB} (chloride) = 0.49V

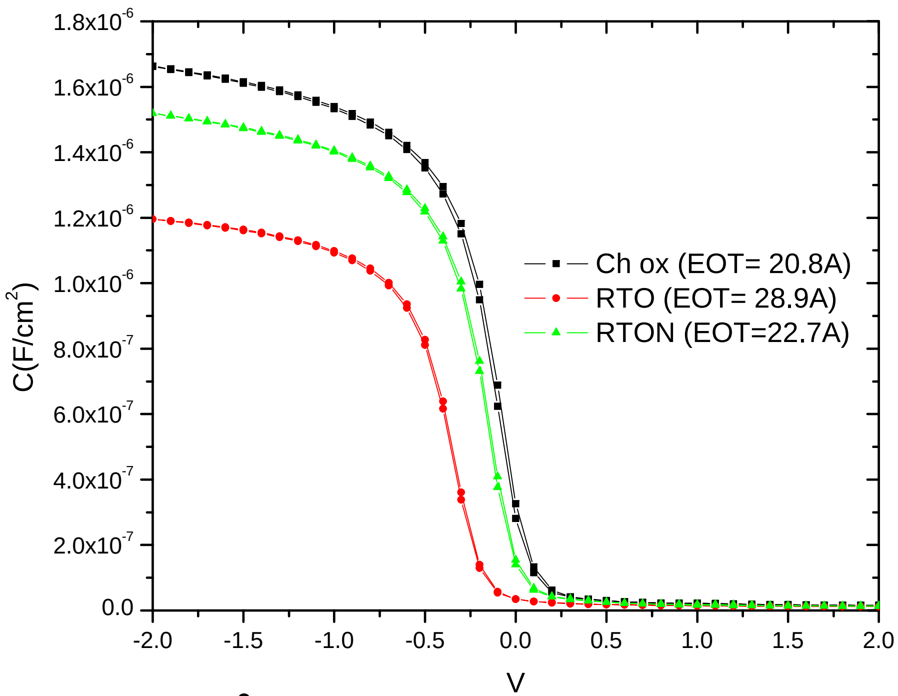
(Yee-Chia Yeo, *et. al. IEEE EDL, 2002*)

Q_F (alkylamide) = + 2.4E12
Q_F (chloride) = -1.29E12

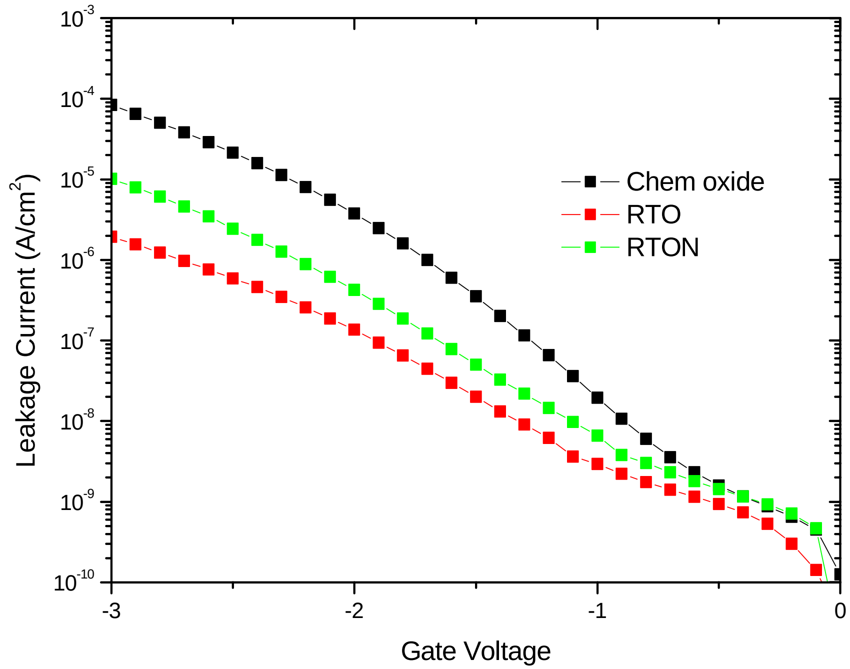
ϕ_{Pt} = 5.25 eV on HfO_2
"Ideal" V_{FB} = 0.35V

Electrical Characteristics

C-V Characteristics



Leakage Current



50Å HfO_2 was deposited on the Chem Ox, RTO and RTON samples

The electrical results indicate an excellent quality HfO_2 with very low leakage current.

Summary

- We have successfully grown high quality HfO_2 thin films on silicon substrates using the ALD process. The electrical characteristics of the HfO_2 films grown using TDEAH are far superior to those obtained using the chlorides.

- The carbon and nitrogen impurity levels in the films were below the detection limits of the XPS. A growth rate of 0.8Å/cycle was obtained.

- The low substrate temperature for the alkylamide process will facilitate area selective ALD on patterned substrates.

- The ESH implications of the different Hafnium precursors has been analyzed.

Thrust B: Front-End Processes

Task B-3: Evaluating EHS Impacts of New Dielectric and Conductor Materials Etch Processes

Cheng-Che Hsu, John Coburn, and David Graves

UC Berkeley

Victor Vartanian, Brian Goolsby, Peter Ventzek, Da Zhang, Shahid Rauf, and Laurie Beu

Motorola APRDL

Bing Ji

Air Products

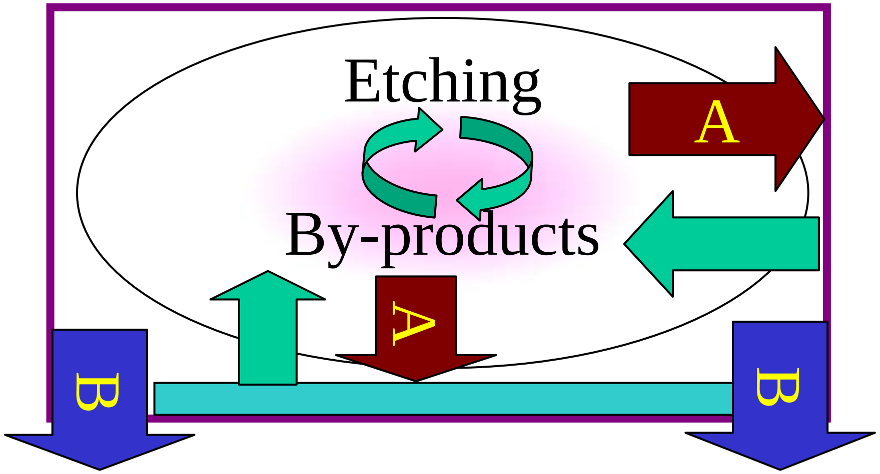
February 23-25, 2005

Project Objectives

By-products formation and transport have both processing and **ESH significance**.

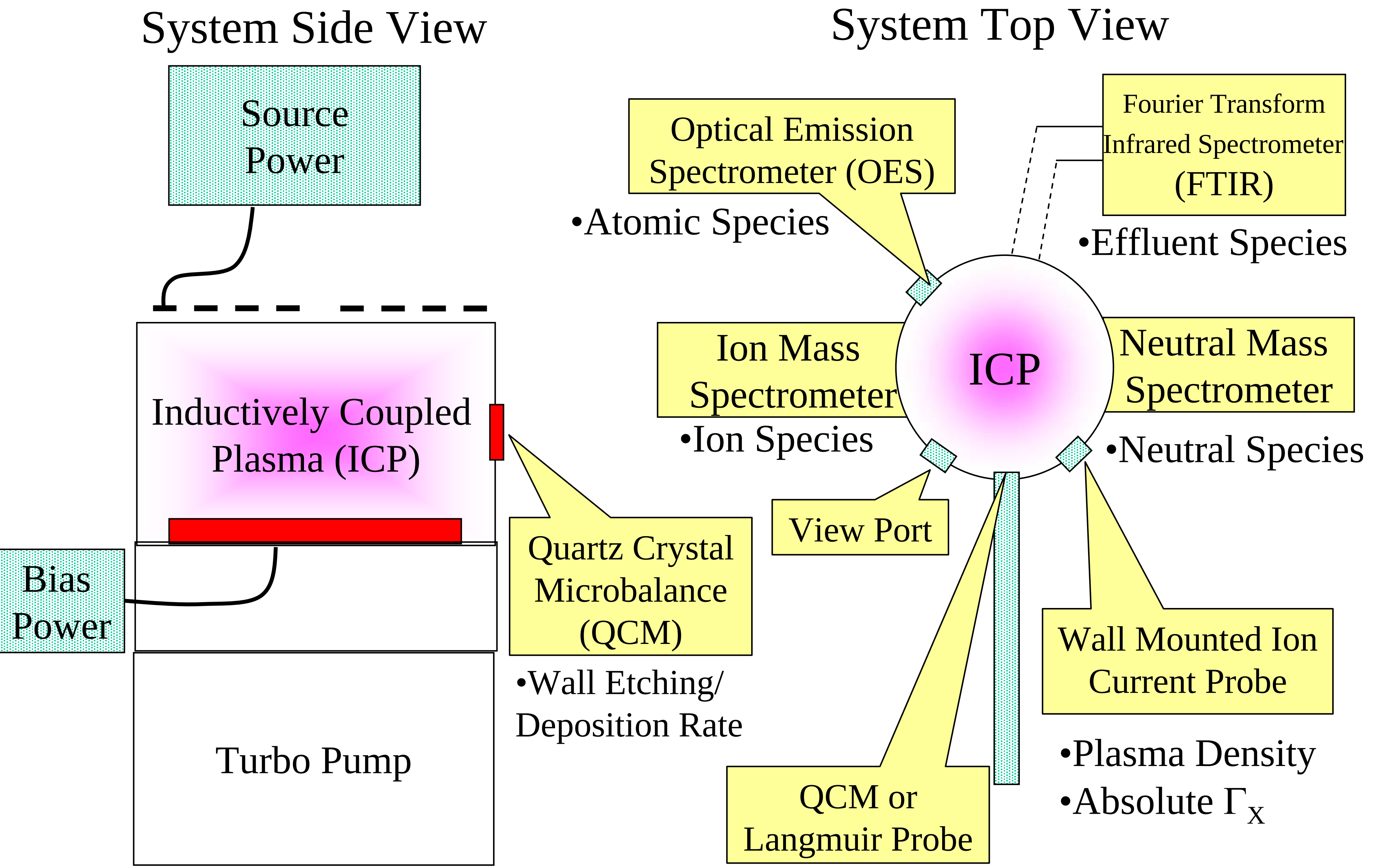
Goal: Identify the by-product, Investigate its formation mechanism and Identify the condition that minimizes the formation.

- **Novel materials etching**
  - **Large set of novel materials (metal gate, high k, 193nm PR)**
  - **Unknown and potential toxic etch by-products formed.**
  - **Process is complicated (through coupled gas phase or surface reactions): *very little is known*.**
- **By-products transport pathway:**
  - **A: Wall deposition: chamber clean safety?**
  - **B: Effluent: abatement possible?**



- **Testbed**: etch tool with multiple plasma diagnostics.
- **Model materials**
  - Ru: novel gate; potential toxic by-products: RuO_4
  - 193nm PR: novel PR; toxic by-products: chlorinated hydrocarbon with Cl_2-containing chemistries

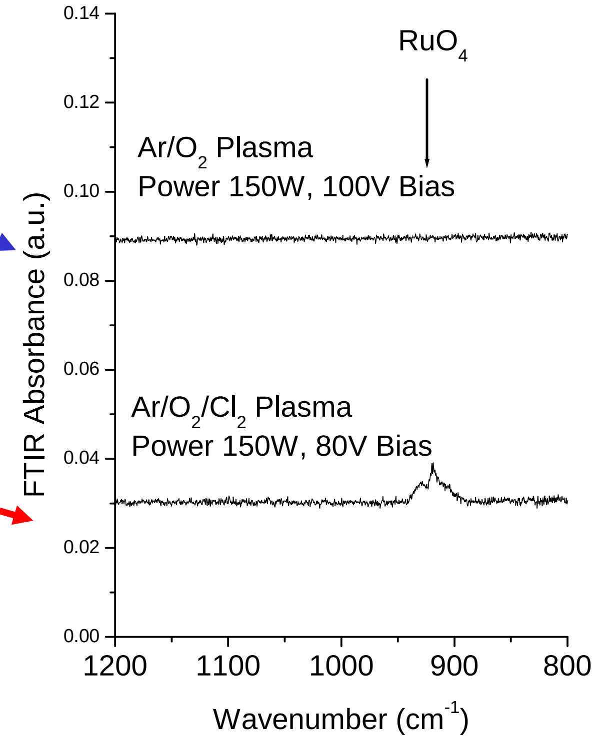
Experimental System: Diagnostic for ICP



Ru etching: by-product transport path

Effluent: downstream FTIR

- **Without Cl_2 addition (Ar/O_2 Plasma)**
  - Etching Rate ~ 60 A/min
  - Most etching by-product deposits on the wall.
  - No RuO_4 was found at the downstream FTIR
  - Neutral species dominate the wall deposition
- **With Cl_2 Addition ($Ar/O_2/Cl_2$ Plasma)**
  - Etching Rate ~ 300 A/min
  - Zero Wall Deposition Rate, i.e. all etching by-products leave the chamber.
  - RuO_4 was seen at the downstream FTIR



By Cl_2-addition, changing by-products transport pathway

- The effect can be explained by the formation of Ru-oxychloride.

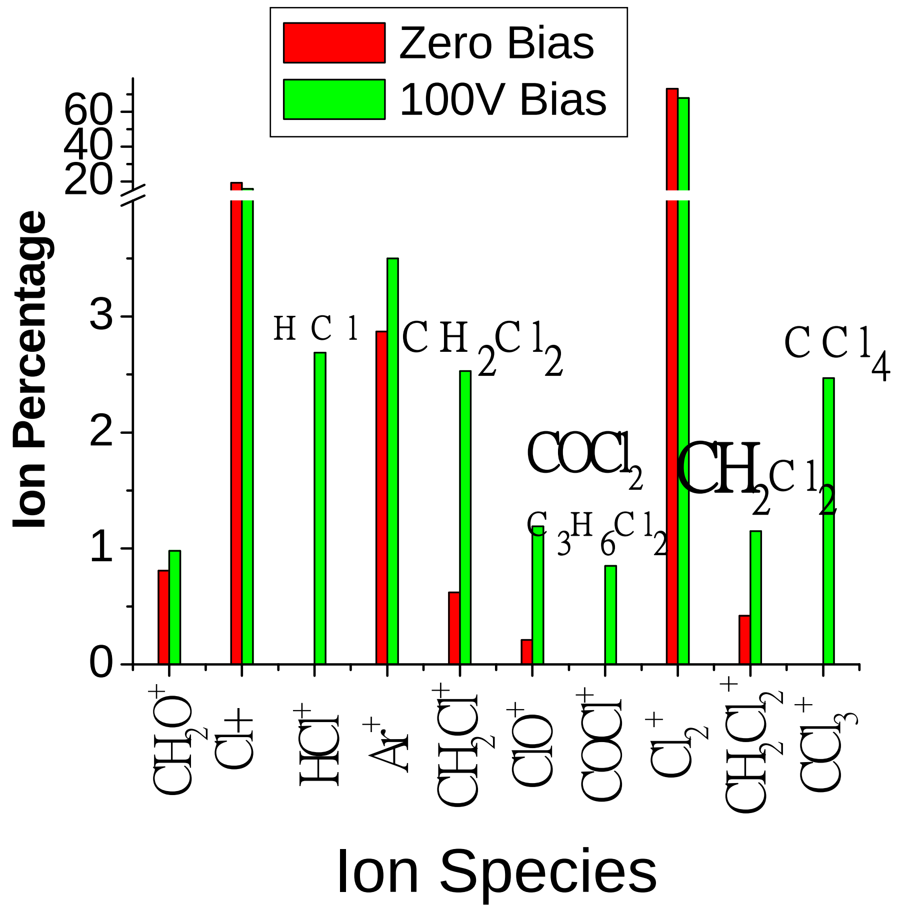
- In Cl_2-containing chemistries, the etching is dominated by both ions and neutrals.

193nm Photoresist Etching by-products

- Cl_2-containing photoresists etching/trimming processes: possible formation of carbon oxy-/hydro-chloride compounds, many of which are hazardous air pollutant (HAPs).

- Ion speciation implies the existence of HAPs:
  - HCl, CH_2Cl_2, CCl_4, $C_2H_4Cl_2$, $C_3H_6Cl_2$, and $COCl_2$
- Non-zero wall deposition rate suggests by-products deposition, represents a potential threat to workers during chamber wet clean.

Ar/Cl_2 Plasmas at 10mT



Conclusion and Accomplishments

- **Development of systematic analysis methodology**
- **Identification of potentially toxic by-products:**
  - RuO_4 in Ru etching w/ $Ar/O_2/Cl_2$.
  - Chlorinated hydrocarbons in 193nm PR etching w/ Cl_2-containing chemistry. Species: HCl, CH_2Cl_2, CCl_4, $C_2H_4Cl_2$, $C_3H_6Cl_2$, and $COCl_2$.
- **Mechanism study and manipulation of by-product transport:**
  - **By-products deposit on the wall: Ru etching by Ar/O_2 plasmas**
  - **By-products leave the system: Ru etching with Cl_2 addition ($Ar/O_2/Cl_2$).**
    - **Formation of Ru-oxychloride by the synergetic effect of ions and neutrals.**
- **Wall deposition precursor**
  - Dominated by neutrals in Ar/O_2 etching Ru.

Future Plans

- **Investigate wide range of material etch processes, e.g. Ru, RuO_2, HfO_2, W, MoN, Photoresist, high K materials etc.**
- **Identify conditions that minimize the toxic product emission.**

Low-Energy Hybrid Water Purification

A Novel Method for Removal of Recalcitrant Impurities

Subtask C-1-1

Mike Schmotzer, Elizabeth Castro, Farhang Shadman

Chemical and Environmental Engineering
University of Arizona

Objective:

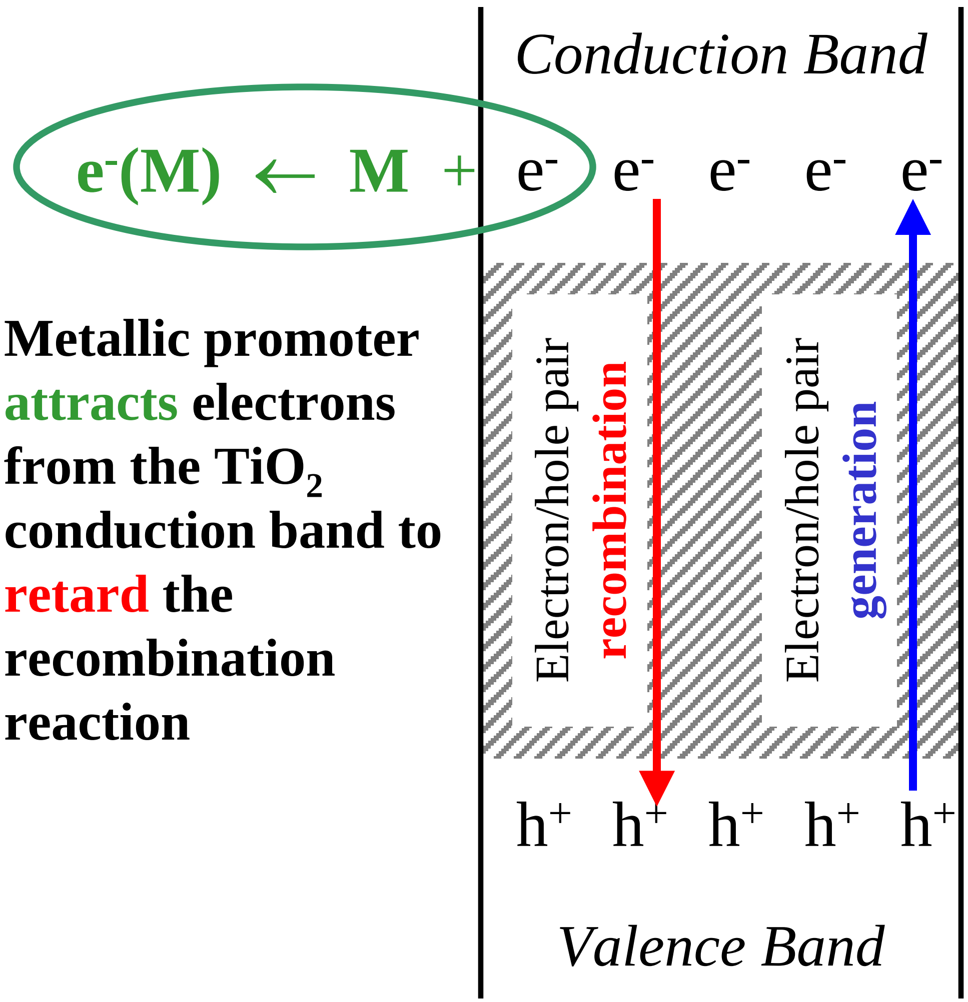
- **Develop a novel hybrid purification method for removal of recalcitrant organic impurities.**
- **Combine the following desirable advantages:**
  - **Lower energy use through enhanced catalytic oxidation**
  - **Low chemical use through extended ion-exchange life**
  - **Reduce waste through self-cleaning activated carbon**

Significance of Urea as a Challenge Impurity:

- **Urea contamination is a major concern for many UPW facilities due to seasonal run-off from agricultural fields.**
- **Current methods involve addition of other chemicals and high usage of energy.**
- **A technique that works for urea would definitely work for other impurities.**

Role of Promoters in TiO_2 Catalytic Oxidation

Metallic promoter attracts electrons from the TiO_2 conduction band to retard the recombination reaction



$TiO_2 + h\nu \rightarrow e^- + h^+$

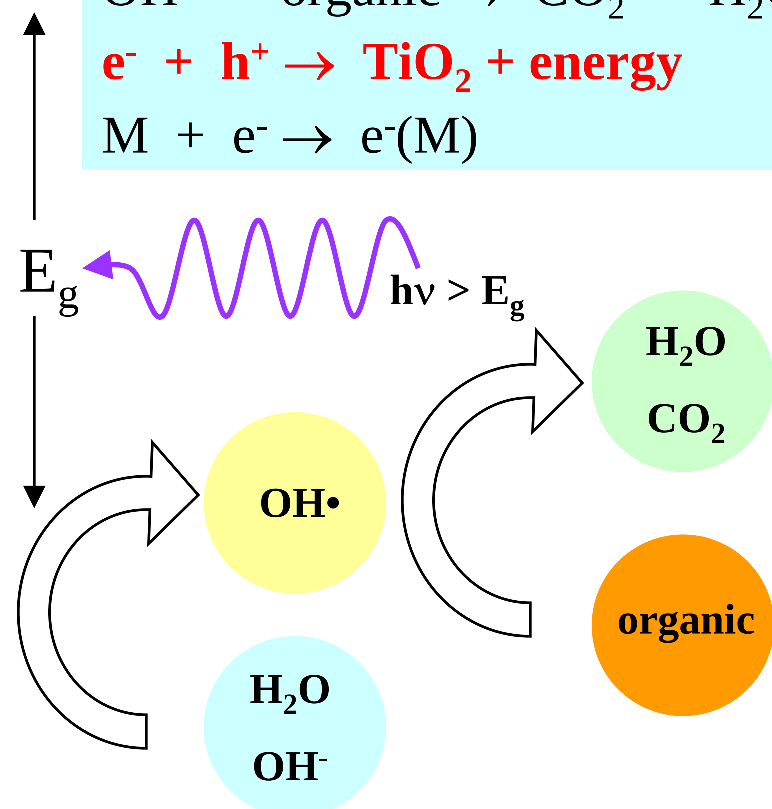
$h^+ + OH^- \rightarrow OH\bullet$

$h^+ + H_2O \rightarrow OH\bullet + H^+$

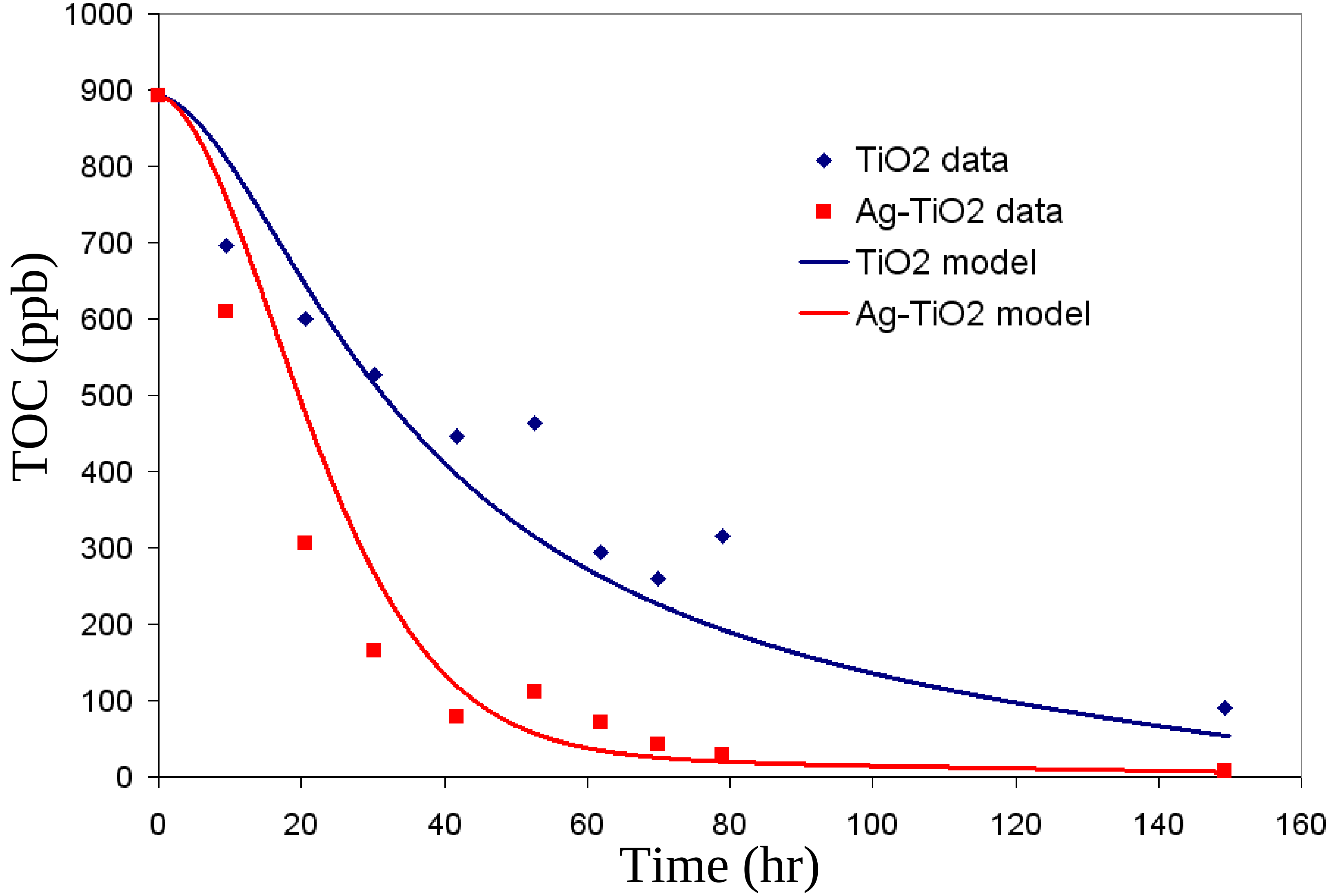
$OH\bullet + organic \rightarrow CO_2 + H_2O$

$e^- + h^+ \rightarrow TiO_2 + energy$

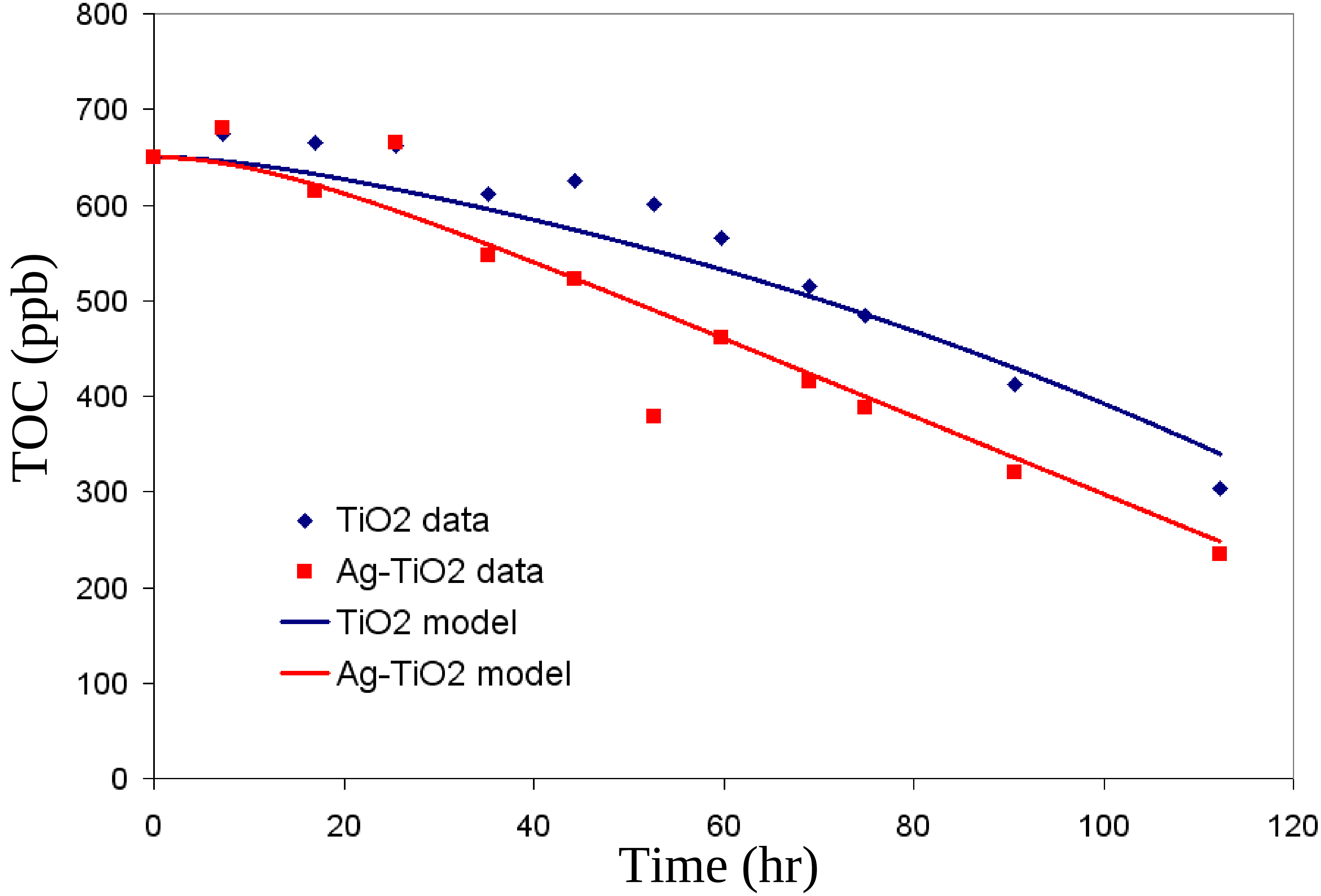
$M + e^- \rightarrow e^-(M)$



Photocatalytic Oxidation of Triton X-100
UV 254nm Illumination

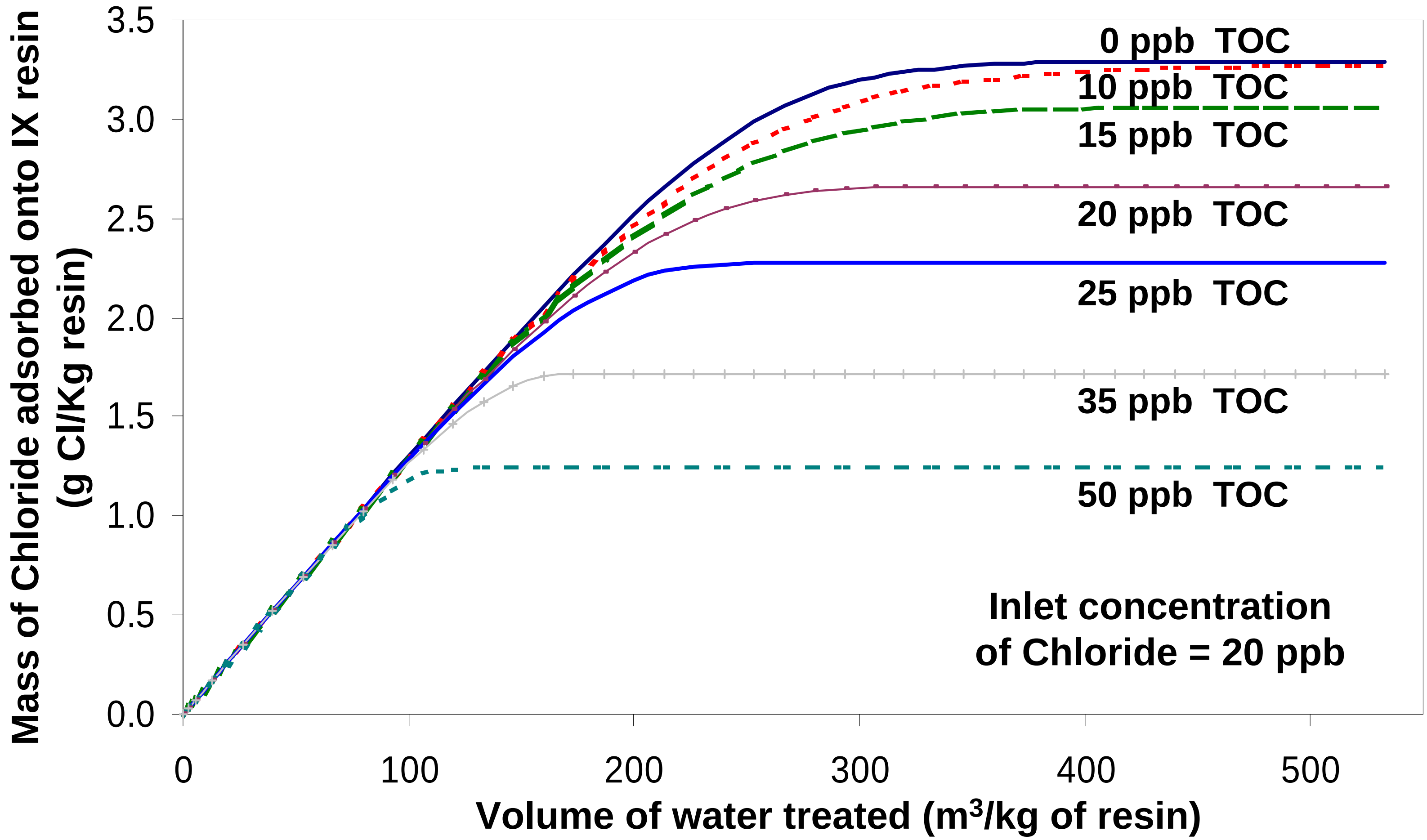


Photocatalytic Oxidation of Urea
UV 254nm Illumination



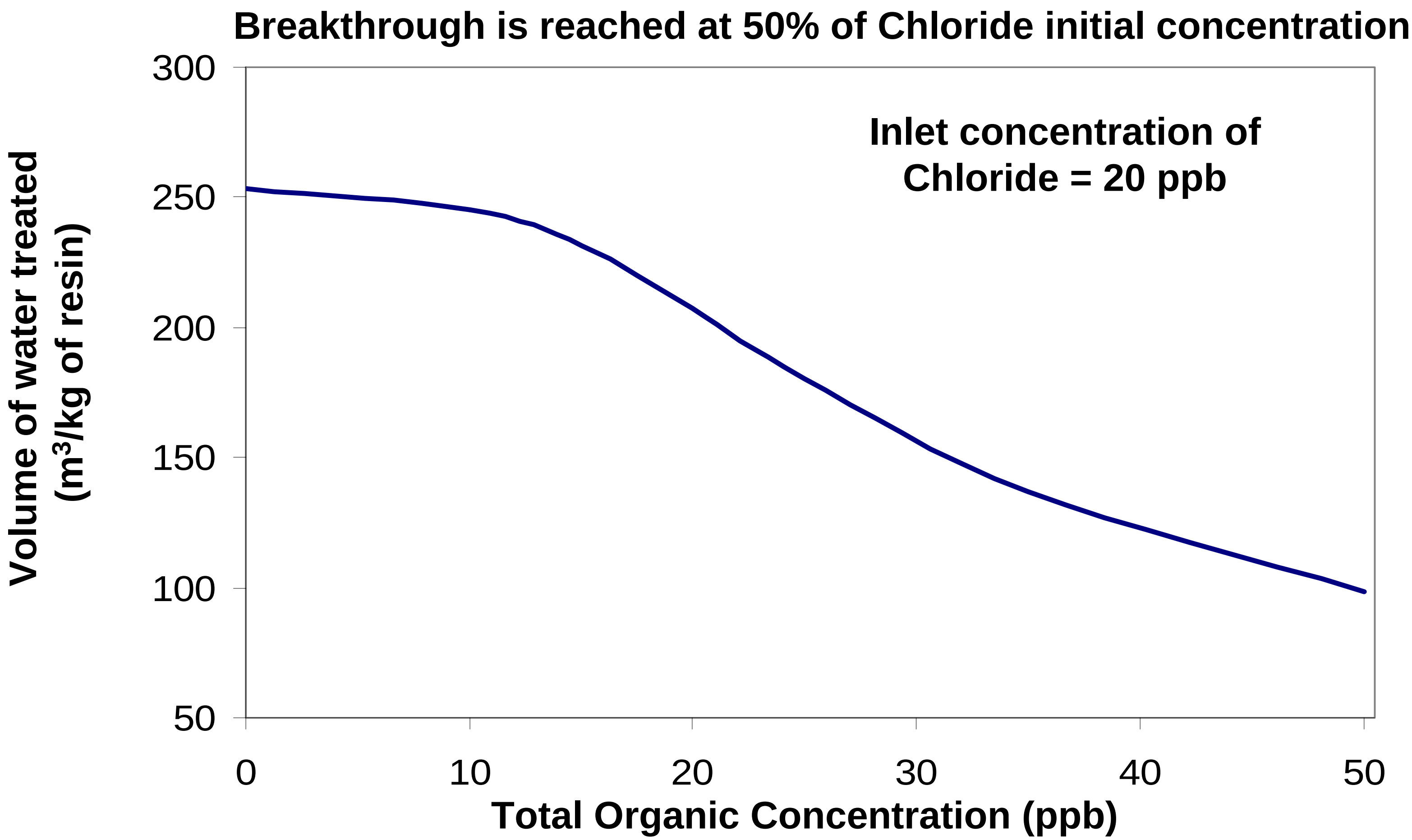
Loss of Ion Exchange Capacity due to Concentration of Organic Impurities

The ion exchange capacity decreases due to the aging effect cause by the presence of organic impurities in water.



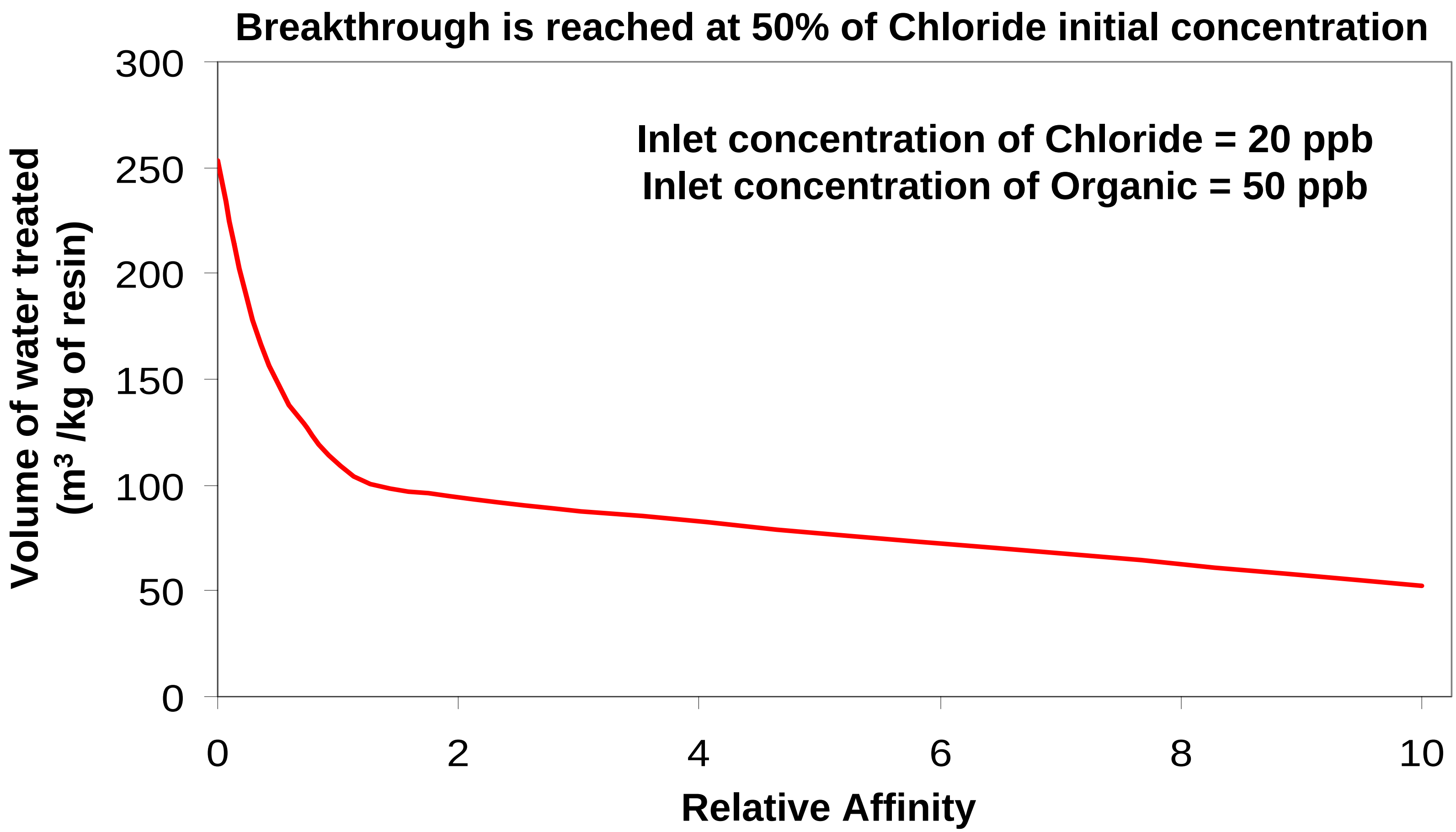
Efficiency of Ion-Exchange Treatment

The volume of water treated before breakthrough is reached increases as the concentration of organic impurities in treated water decreases.



Efficiency of Ion-Exchange Treatment

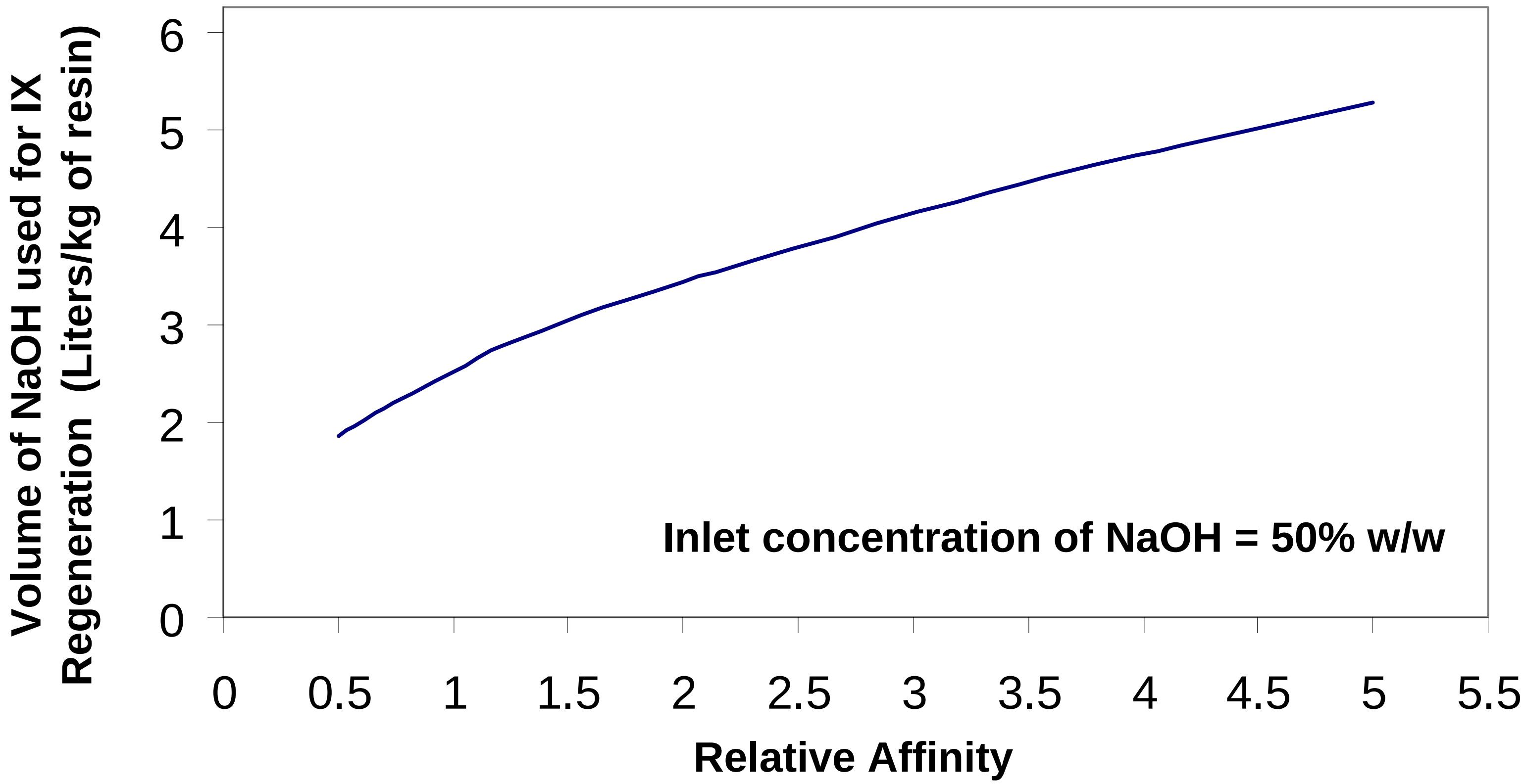
The volume of water treated before breakthrough is reached increases as the relative affinity of organic impurities for the ion-exchange resin decreases.



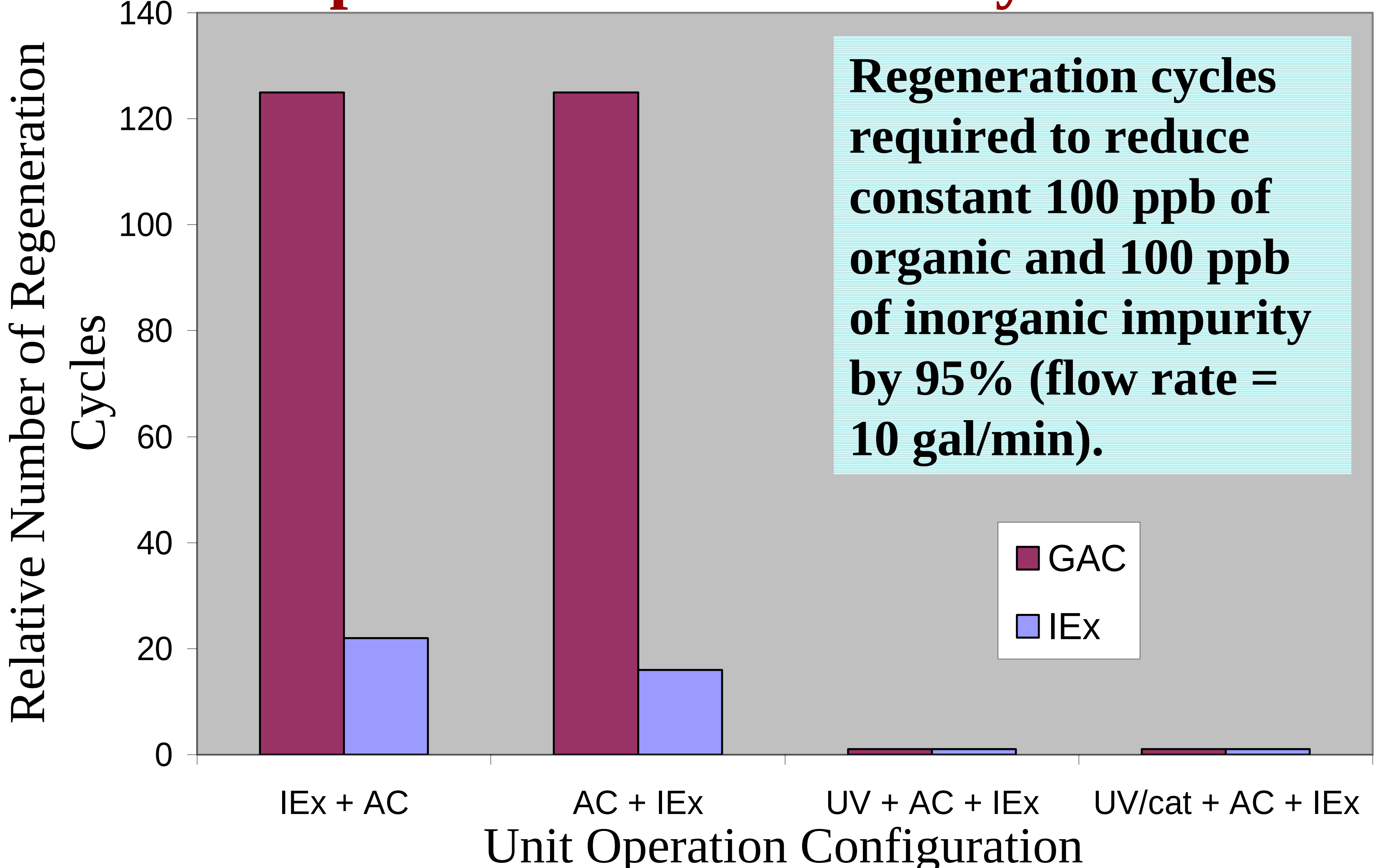
Ion-Exchange Resin Regeneration Treatment

The volume chemical (NaOH) used for regeneration of ion-exchange increases as the relative affinity of organic impurities for the ion-exchange resin increases.

Regeneration is reached when 0.01% of initial capacity for ion is achieved

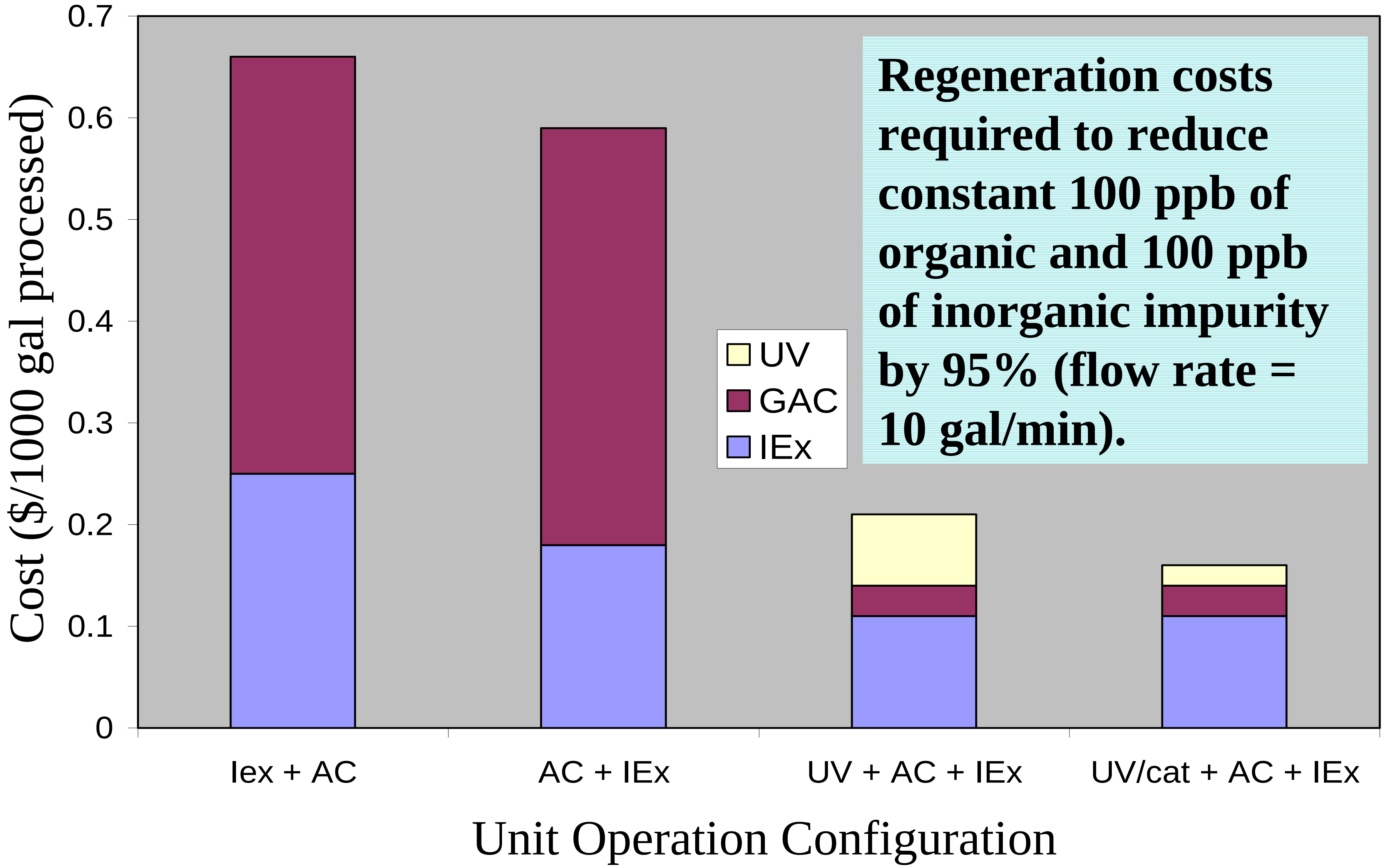


Regeneration/Backwash Cycle Reduction for Optimized Purification System



NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Cost Savings for Optimized Purification System



Conclusions and Highlights:

- **The new integrated, hybrid oxidation/adsorption is an effective technique for the removal of recalcitrant organic impurities such as urea.**
- **The proposed process reduces waste and chemical usage through prolonging the life of ion-exchange and activated carbon units**
- **The catalyst reduces the energy requirement for oxidation.**

Future Plans:

- **Continue to improve the catalyst deposition methodology; emphasize new promoters, based on the mechanism of promoter action found in this study.**
- **Extend the use of promoters to the catalytic membrane degasification process.**
- **Industrial interactions:**
  - **John De Genova (TI); Kon-Tsu Kin (ITRI and TSMC)**

Bio-treatment of Waste Streams Containing Organic Compounds and Copper

(Subtask C-1-2)

Part I: Aerobic Treatment/Chelators

Worawan Maketon and Kimberly Ogden

Chemical and Environmental Engineering, University of Arizona

Objectives

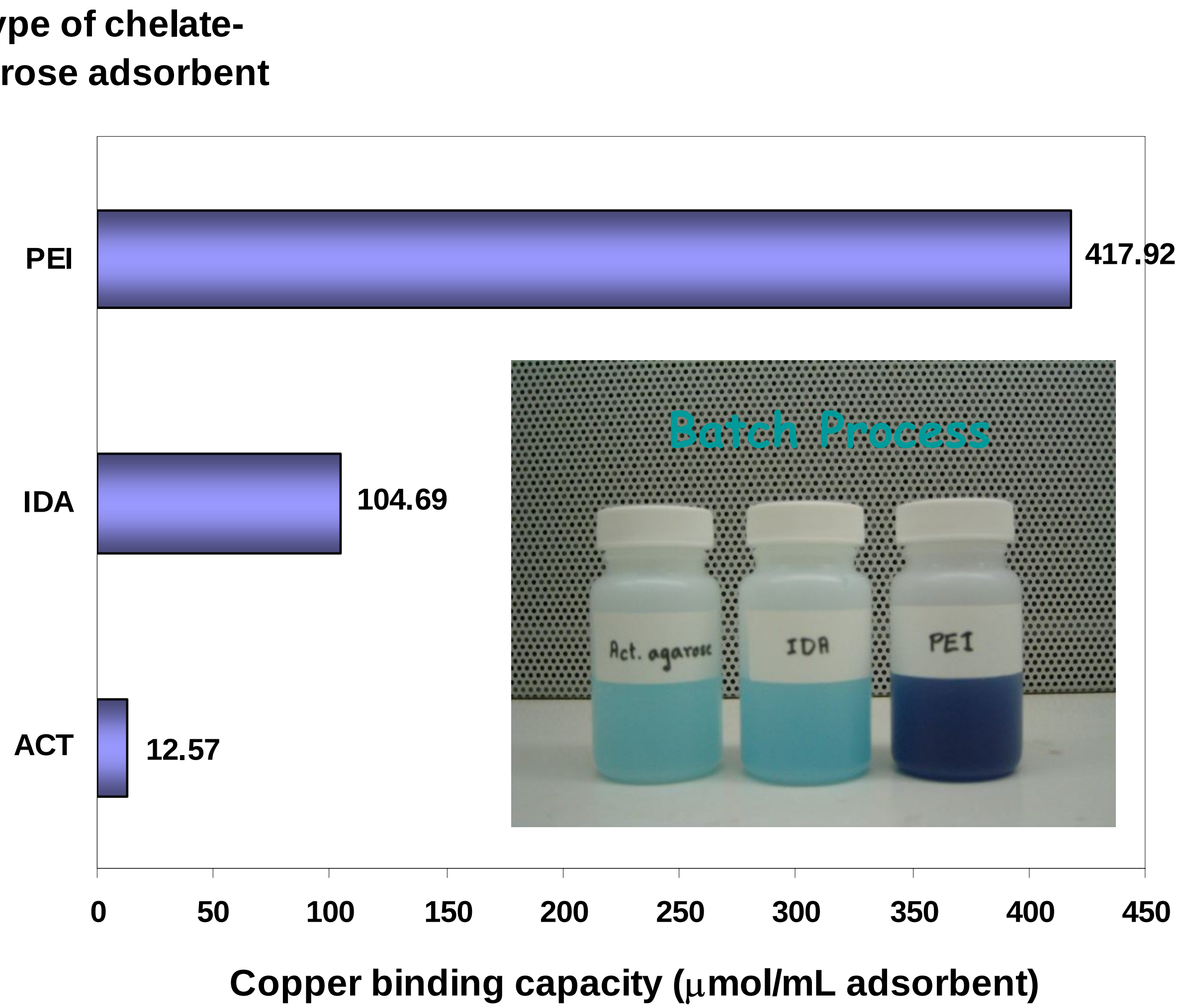
- Investigate the removal of copper (II) using chelators.
- Determine the behavior of a single packed bed column, containing chelated-agarose gel, in treatment process for surrogate Cu-CMP wastes containing copper (II) and organic IPA.
- Investigate the feasibility of chelator binding CMP-pad.

Comparison of Copper binding capacity

PEI – Polyethyleneimine bound activated agarose gel

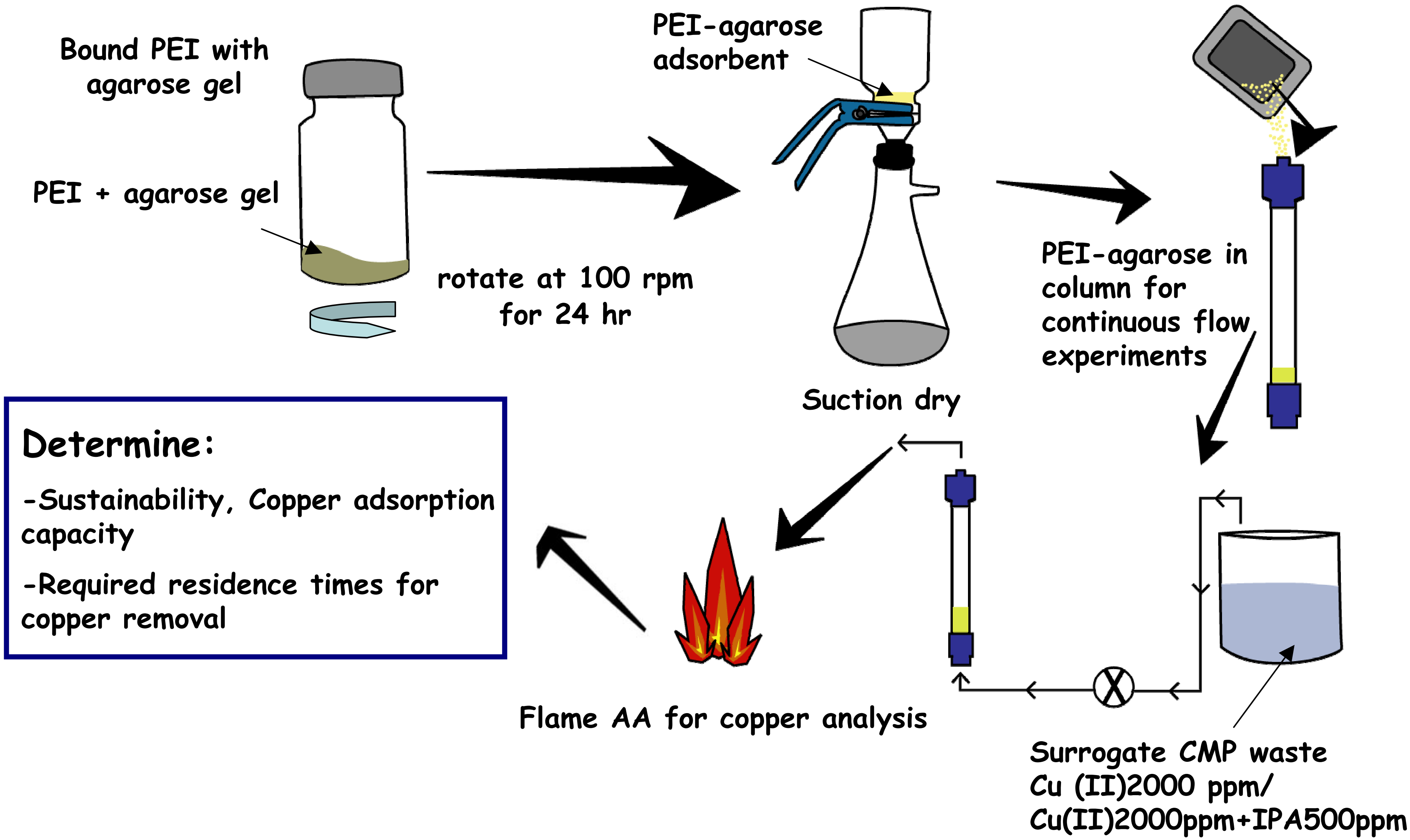
IDA – Iminodiacetic acid bound activated agarose gel

ACT – Activated agarose gel

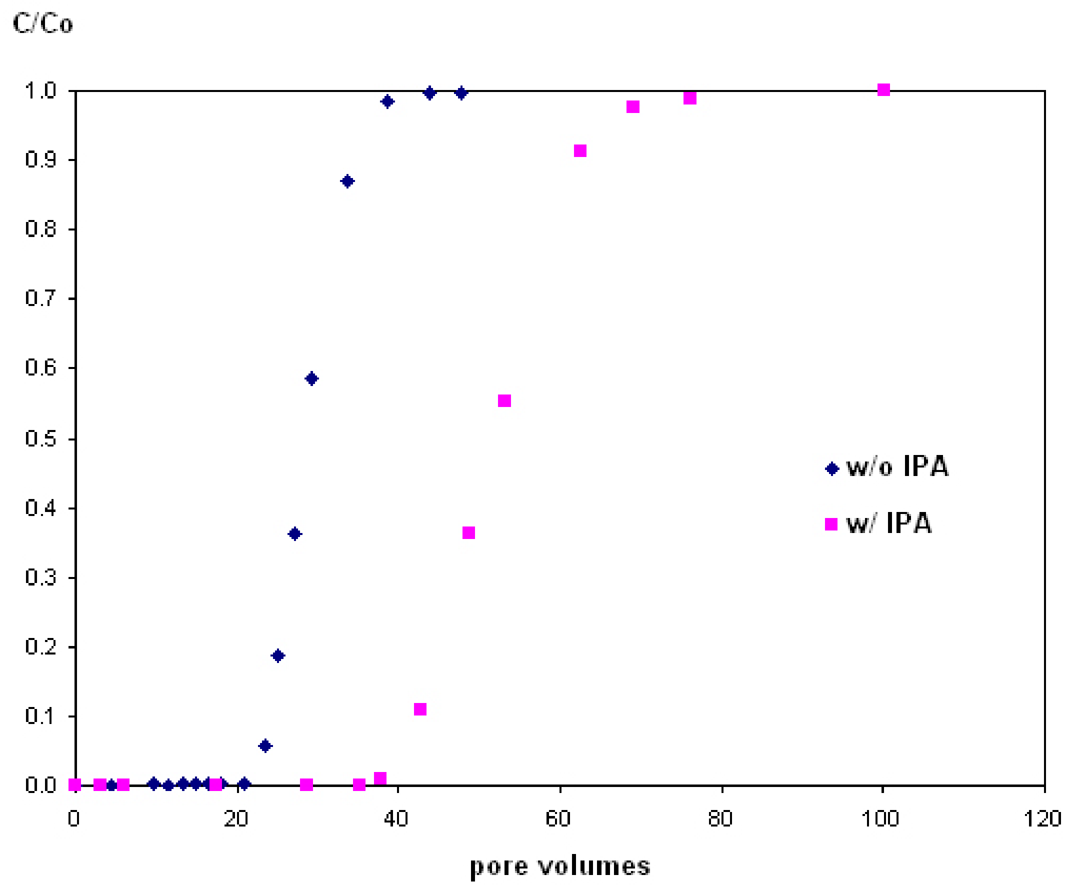


PEI-Agarose was chosen to perform the investigation of the continuous process due to the highest copper binding capacity.

Theory and Method of Approach – Continuous Process



Breakthrough curves of copper adsorption on PEI



Copper binding capacity in a continuous column ($g\ Cu^{2+}/mL$ adsorbent):

- **without IPA 0.028 ± 0.005**
- **with IPA 0.055 ± 0.005**

Results indicate there is a synergistic effect when IPA is present.

Conclusion

- **Initial chelate-agarose adsorbent promising capabilities**
  - **PEI-agarose showed great affinity of binding copper in batch system**
  - **Adsorbent's stability is good**
  - **Performance and reproducibility did not change even after regeneration**
- **Packed bed column performance**
  - **Large volumes of copper contaminated solutions can be concentrated down to much smaller volumes for metal recovery**
  - **A solution containing only copper ions in solution had faster breakthrough than when IPA was present.**
- **Model for breakthrough curve of copper has been partially developed and still in progress of comparing with experimental data**

Biotreatment of Waste Streams Containing Organic Compounds and Copper
(Subtask C-1-2)

Part II: Anaerobic Treatment

Reyes Sierra, Victor M Gamez,
Ryan Kanto and James Field

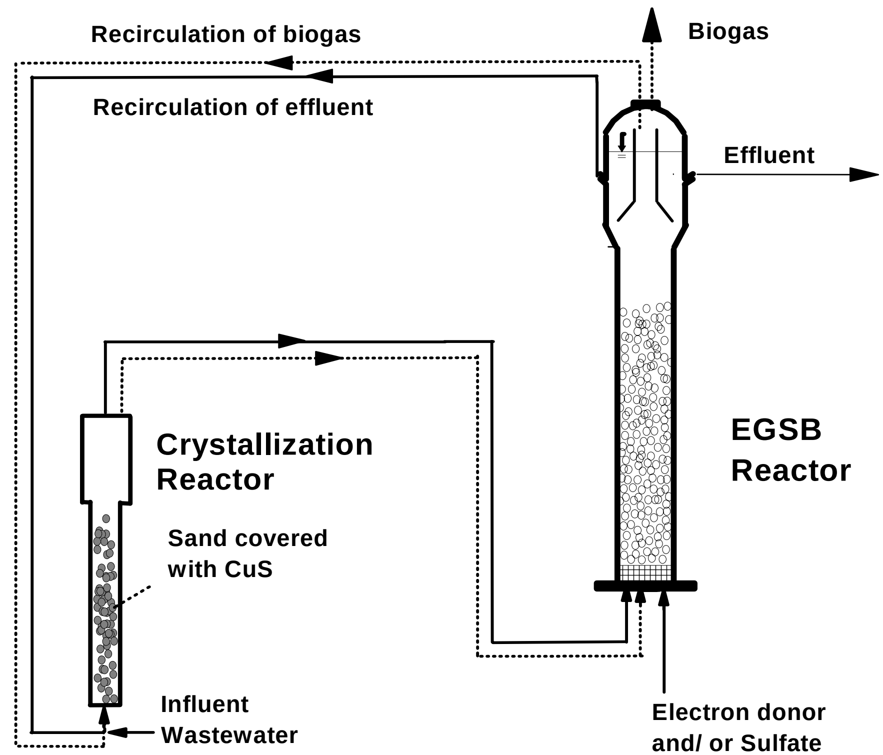
Chemical and Environmental Engineering,
University of Arizona

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Project Objectives

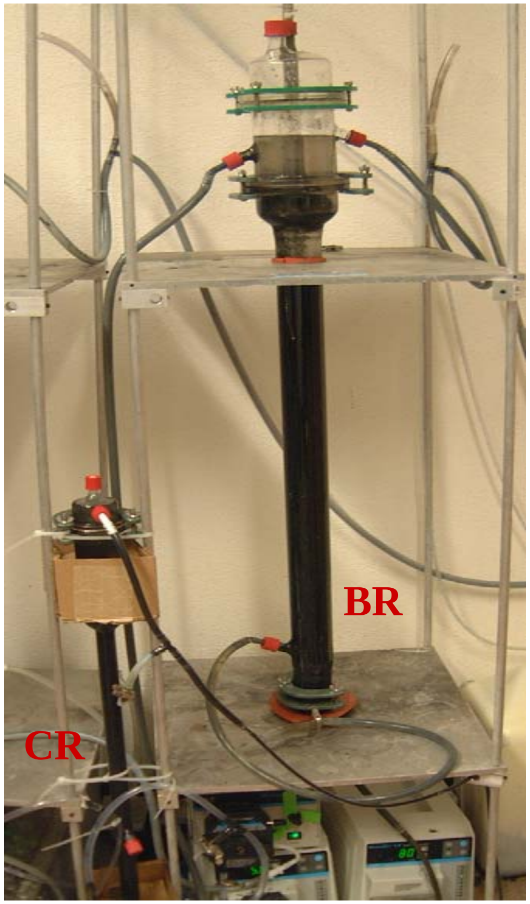
The goal of this research is to investigate the feasibility of anaerobic treatment for the simultaneous removal of copper and organic contaminants in CMP effluents. Removal of Cu will be stimulated by biogenic sulfides produced by sulfate reducing bacteria. The objective of the work presented here is to assess the anaerobic treatability of CMP effluents, *i.e.*,

- assess the susceptibility of key wastewater components to biodegradation by anaerobic microorganisms under batch and continuous-flow bioreactor conditions
- evaluate the treatment of simulated Cu-CMP effluents in a continuous flow bioreactor in conjunction with a crystallization reactor



Schematic representation of the anaerobic bioreactor - crystallization reactor utilized in the simultaneous treatment of copper and organics from CMP wastewaters

Bioreactor Study



Photograph of the two reactor system used in this research. (BR) Anaerobic bioreactor; (CR) Crystallization reactor packed with sand

Bioreactor (BR) & Crystallization Reactor (CR):

Period I

Ethanol (3000 mg COD/L)

Period II

Simulated Organic CMP Waste [Isopropyl alcohol (IPA)/poly(ethylene glycol) (PEG)/citric acid] (1000 mg COD/L each)

Period III

Simulated CMP Waste (5 mg Cu/L)

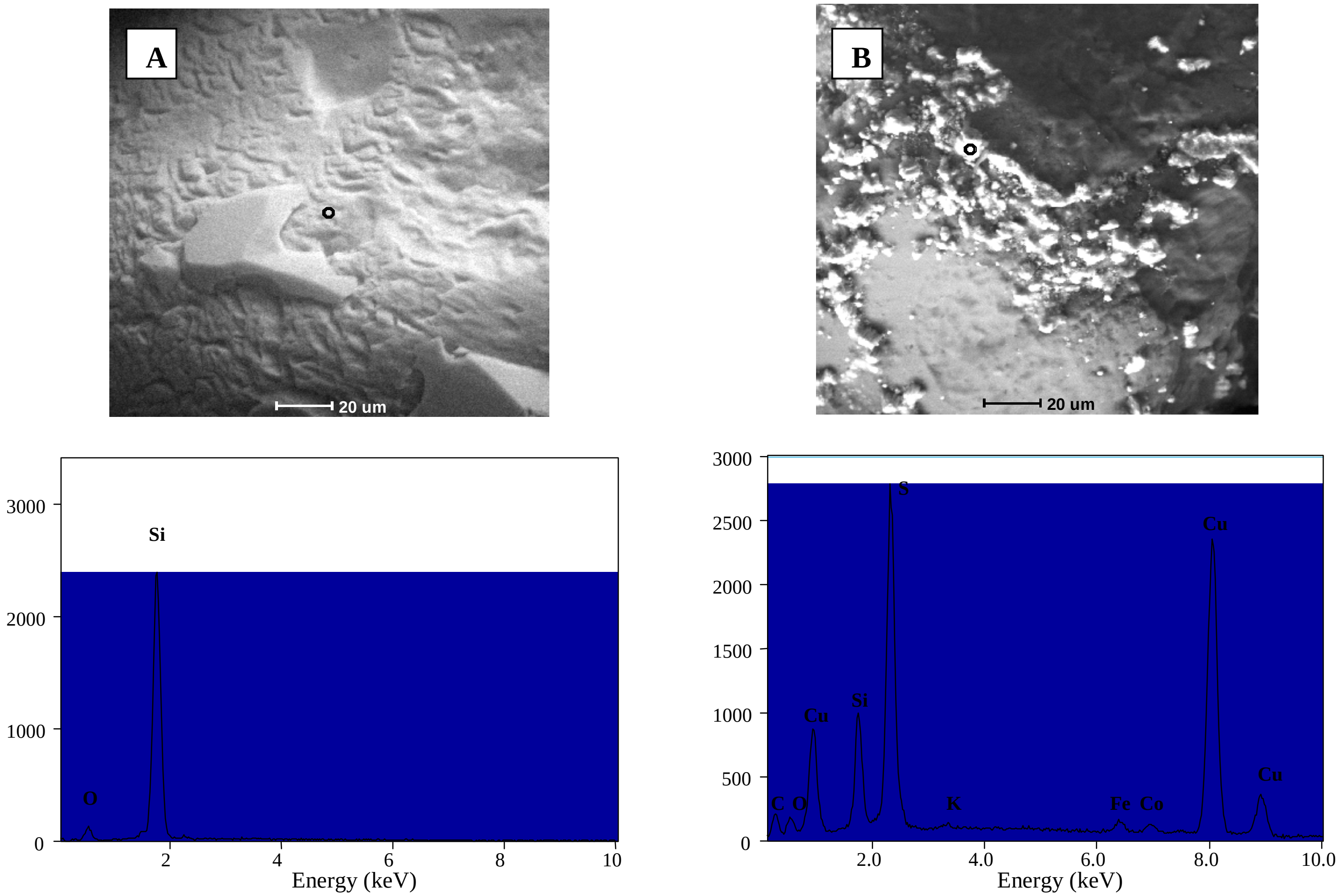
Period IV

Simulated CMP Waste (25 mg Cu/L)

Period V

Simulated CMP Waste (65 mg Cu/L)

Bioreactor/CR - EDS Analysis of Sand



Energy dispersive spectrometry (EDS) results showing (A) the clean sand (B) CuS crystal growth on sand obtained from crystallization following copper (25 mg/l) removal

System Performance:

Removal of Soluble Copper

Period	Cu^{2+} -in (μg/l)	Cu^{2+} -out (μg/l)	Cu removal (%)	Cu Removal (%) CR only
III	5,000	16 (+/- 19)	99.4 (+/-1.3)	99.3 (+/-0.6)
IV	25,000	162 (+/-84)	99.3 (+/-0.5)	99.3 (+/- 0.2)
V	65,000	104 (+/- 45)	99.9 (+/-0.2)	99.8 (+/- 0.1)

Conclusions

- Soluble Cu was successfully removed (>99% removal) from a simulated CMP wastewater containing with 65 mg/L $Cu^{2+}$by means of precipitation in the combined bioreactor-crystallization reactor system
- Optimization of the removal of total Cu in the crystallization reactor should improve reactor removal efficiency and help meet regulatory requirements

Future Work

- Complete the study of the treatment of simulated Cu-CMP effluents in continuous laboratory experiments (anaerobic reactor combined with crystallization reactor) using increasing concentrations of copper
- Test the anaerobic treatment system using effluents from a CMP pilot plant
- Develop a feasible and effective biological treatment system for the simultaneous removal of metals and organics in CMP effluents

Acknowledgements. This project is partially supported by the ERC and by an NSF Advance grant (BES 0137368).

Fundamentals of Rinse and Chemicals Carry-Over

Electrochemical Residue Sensor for In-Situ and Real-Time Rinse Monitoring

Subtask C-2-1

Jun Yan[1]

Bert Vermeire[2] and Farhang Shadman[1]

[1]Chemical and Environmental Engineering, UA
[2]Environmental Metrology Corporation, Tucson, AZ

Objective and Approach

Objectives:

Determine mechanisms by which water usage in rinse processes can be reduced without sacrificing overall wafer cleanliness

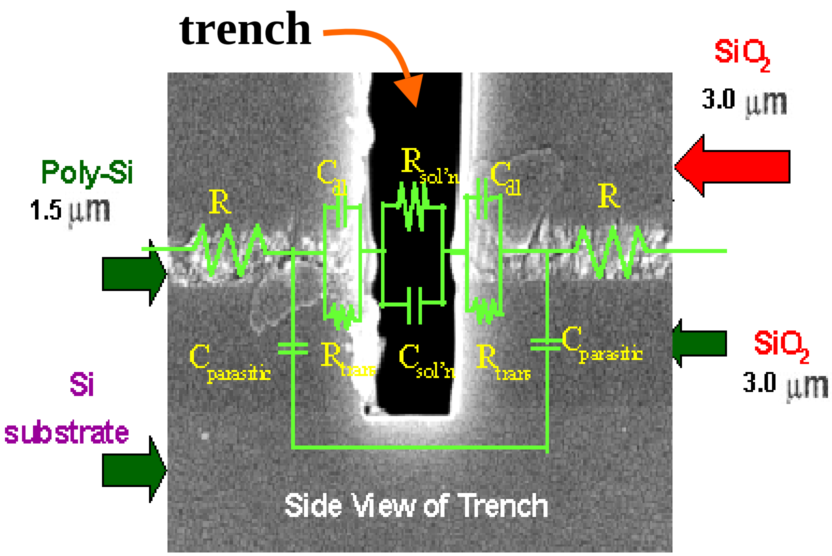
ESH Impact:

Conserve resources, reduce processing time, increase manufacturing productivity, and reduce cost.

Approach:

- **Develop a sensor for in-situ and real-time measurement of residual contamination on plane and patterned wafers, microstructures, and porous films during rinsing.**
- **Understand process bottlenecks by experiments and process modeling**

Principle of Operation



Trench solution impedance

measured trench interface impedance (see slide 5)

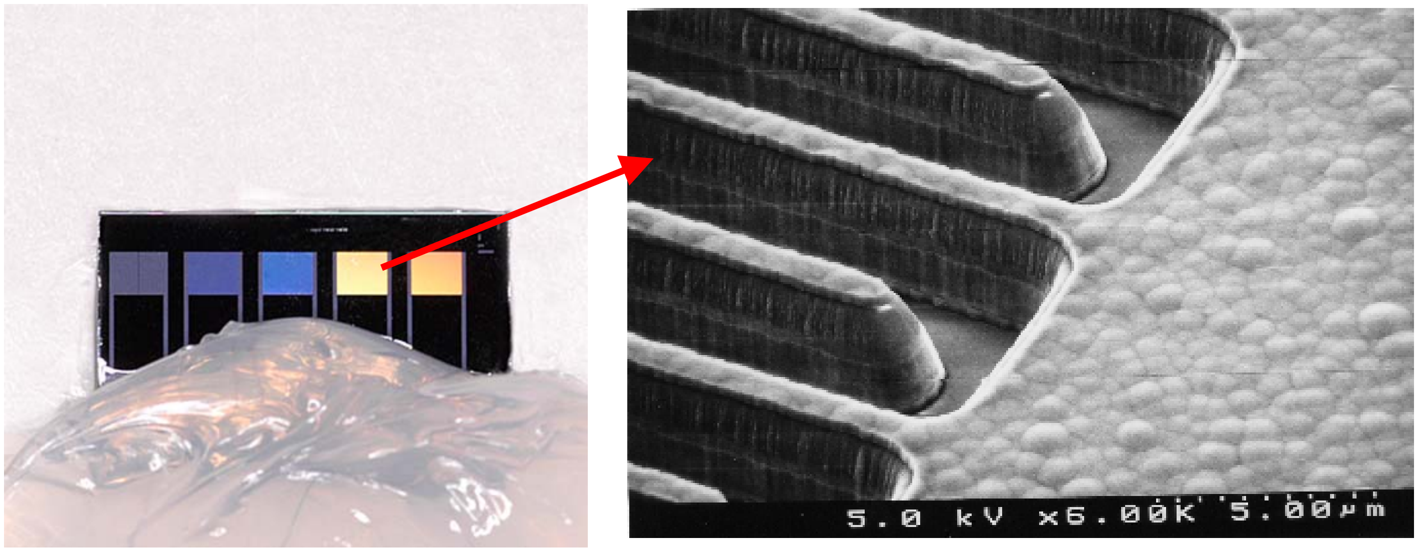
$$Z_{T.D.} = \frac{1}{\dfrac{1}{Z_{total} - 2 \times Z_1} - \dfrac{1}{Z_3}} - 2 \times Z_2$$

measured with impedance analyzer

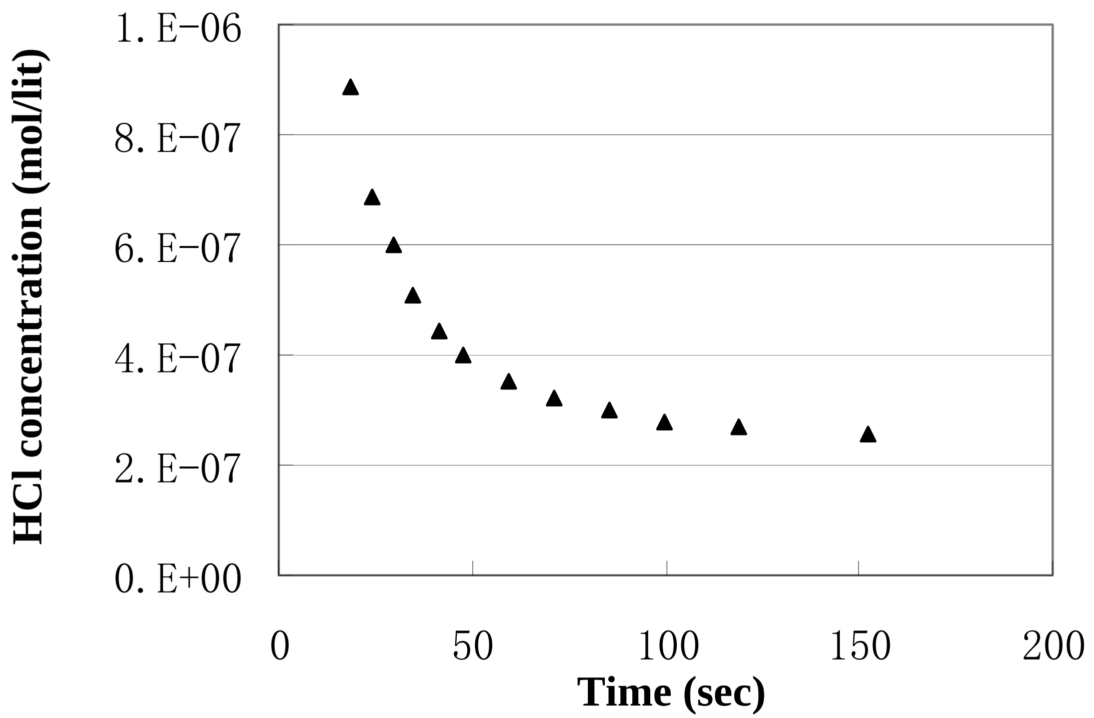
calculated from material properties

$Z_{T.D.}$ is related to the concentration of ions in the solution during rinsing process

Sensor Structure and Prototype



Concentration and Sensitivity



Solution (pH)	UPW (pH=7)	H_2SO_4 (pH=6)	H_2SO_4 (pH=5)
Resistivity (MΩ)	18.26	2.32	0.232
Resolution	5 ppt	30 ppt	420 ppt

Highlights and Future Plans

Highlights:

- Novel Electrochemical Residue Sensor (ESR) has good sensitivity for in-situ and on-line monitoring of rinse process in the fabs.
- A method for equivalent circuit analysis, design and fabrication of sensor is developed; optimum test frequency is determined; prototype is fabricated and tested.

Future Plans:

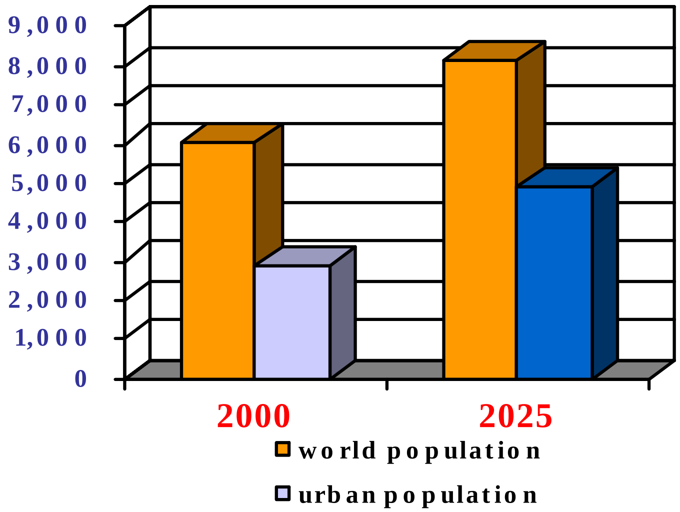
- Develop a packaging methodology for a sealed device.
- Design the specific structure used for low-k materials cleaning studies.
- Evaluate the effect of additives and temperature on rinse times using TXRF.
- Work with industry for testing the prototype and commercialization

Water Reuse Planning: Manufacturing Sustainability under Resource Constraints

Paul Blowers, Umur Yenal, and Katherine Nierva

Department of Chemical and Environmental Engineering

The University of Arizona



- Growing worldwide population
- Most of that population growth is concentrated in urban centers, especially in smaller cities

• Populations are growing rapidly in states such as Nevada, Arizona, and California - There are no readily available sources of new water supplies in many many of these areas

•Alternative sources of supply such as desalination are currently more expensive than water reuse.

Project Objectives for Industrial Water Reuse Modeling

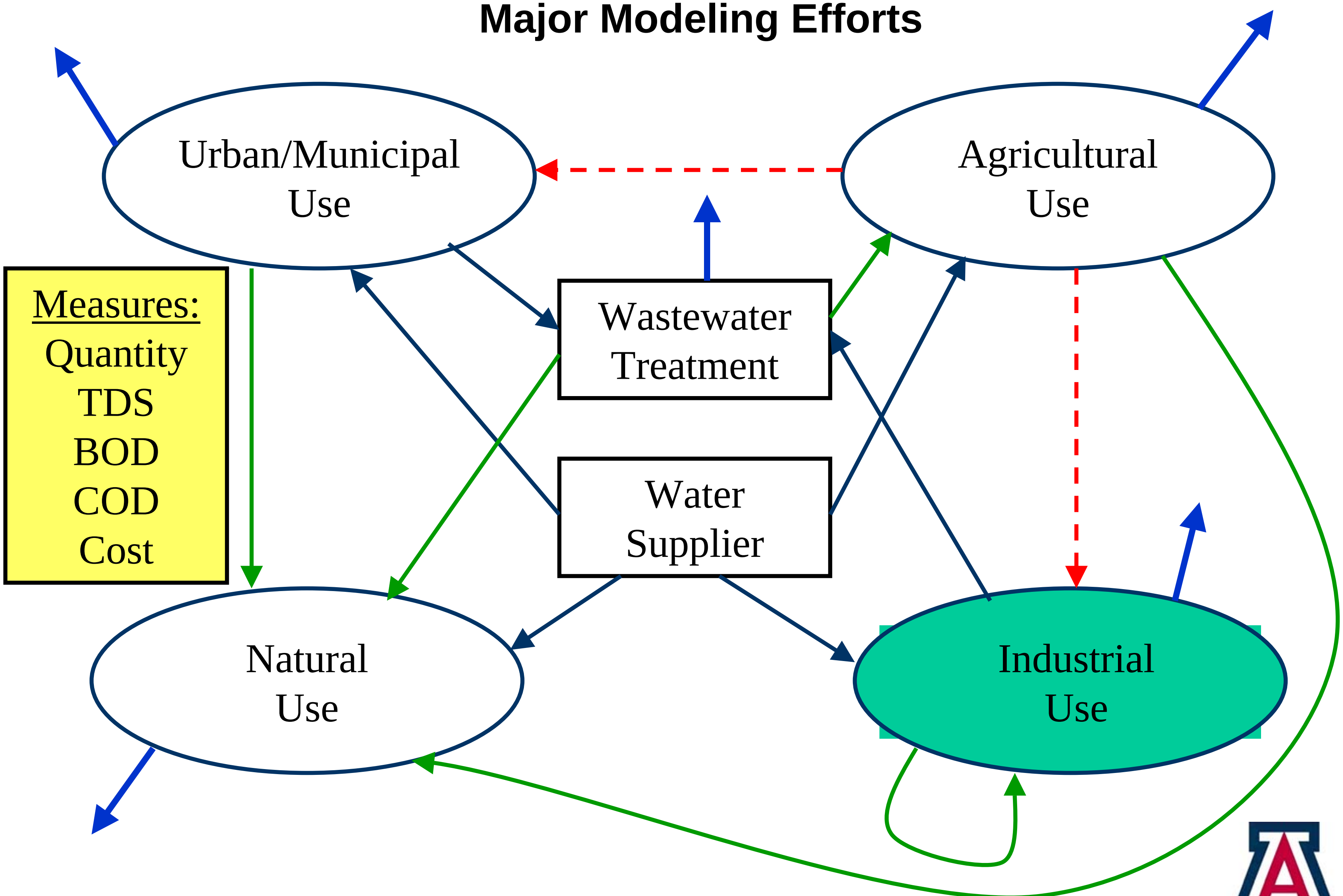
•Comprehensive tools for impact of management alternatives on water quantity, quality and cost are not available. This is particularly true of water issues related to introduction of **nanotechnology!**

•Answer - develop an integrated water management tool. Specifically, this research will develop a comprehensive decision support simulation model to aid management decisions, analyze trends, and perform "what if?" analyses.

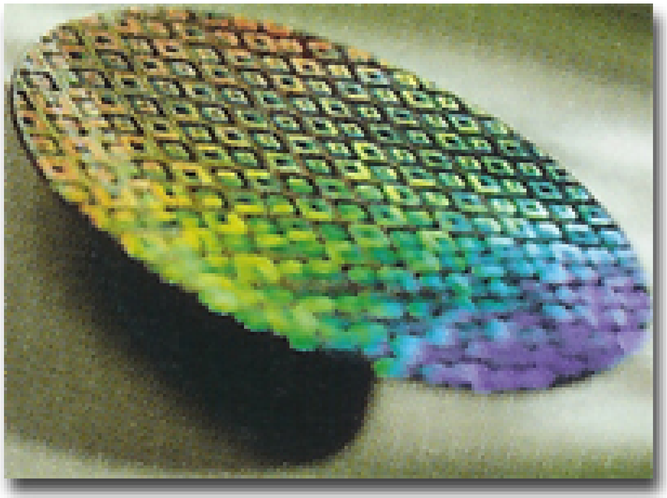
•Premise- Water users affect water quality to different degrees, and have varying requirements on their supply.

For example, irrigation can employ lower quality water than is acceptable to residential consumers for some quality measures. In the future, residential point of use water treatment may alter this balance. Industrial water users are of particular importance when water quality is a water-use criterion. Their demand for high quality water often requires in-house treatment before or after use. Optimizing industrial operations can reduce their overall costs and produce a potential new water resource.

Major Modeling Efforts



ESH Impacts of Industrial Water Modeling



Semiconductor Manufacturers:

large amounts of water
some internal recycle, but issues
metals
organics
need high quality inlet

Nanotechnology:

unknown issues at this time

Issues Related to Measures:

TDS, BOD, COD are not the only important measures of quality
Semiconductor manufacturing technologies change rapidly, leading to price and water use variability
Few industries use little to no water

Water is an economic lynchpin for sustainability!

Treatment Modeling Subset

Treatment Unit	*Scale of Use*	*Water Quality Effect*	*Cost*
Reverse Osmosis	Large/Small	TDS/Hardness/Heavy Metals	$$$
Ion Exchange Resin	Small	Hardness/Heavy Metals	$$
Activated Sludge	Large/Medium	BOD	$$
RBC[1]	Small/Medium	BOD	$
Trickling Filters	Large/Small	BOD	$
USBR[2]	Large/Medium	BOD	$$
CAD[3]	Large	BOD	$$

[1]RBC : Rotating Biological Contractors
[2]USBR : Upflow Sludge Blanket Reactor
[3]CAD : Conventional Anaerobic Digester

What Does This All Mean Again?

Water reuse opportunities externally: between other industries and other sectors

- Use the recycled water after some treatment to match with a wider selection or opportunities that will provide better a match for water reuse.
- This will minimize the technological and economic intensity for each treatment

Acknowledgments

Funding for this work was provided by the NSF/SCR Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Collaboration and funding from Arizona TRIF Programs is greatly appreciated

Tools for Integrated Technology Assessment Under Uncertainty (TITAU)

Yue (Nina) Chen, Greg McRae

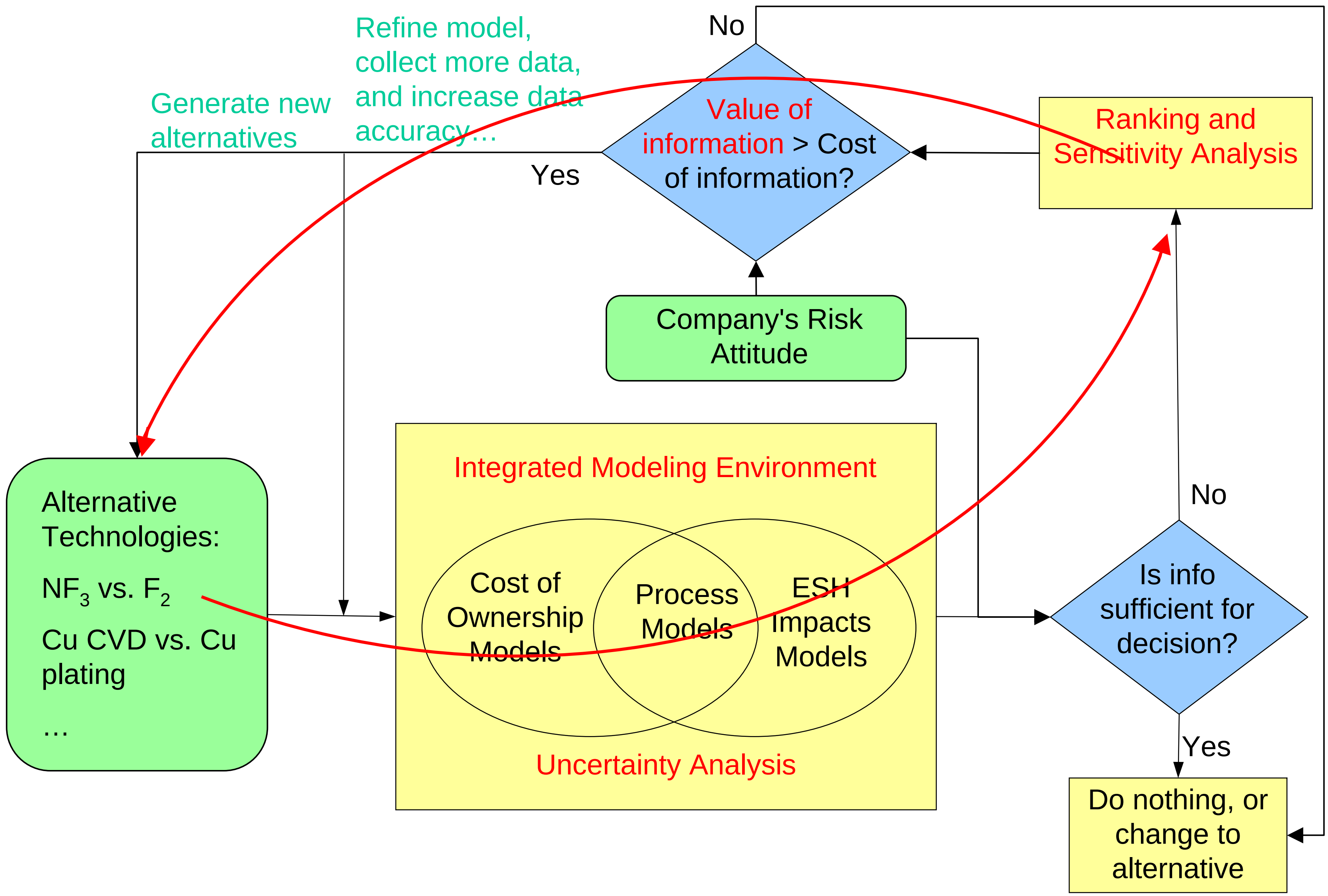
Task C-4-2

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

NSF/SRC Engineering Research Center

Environmentally Benign Semiconductor Manufacturing

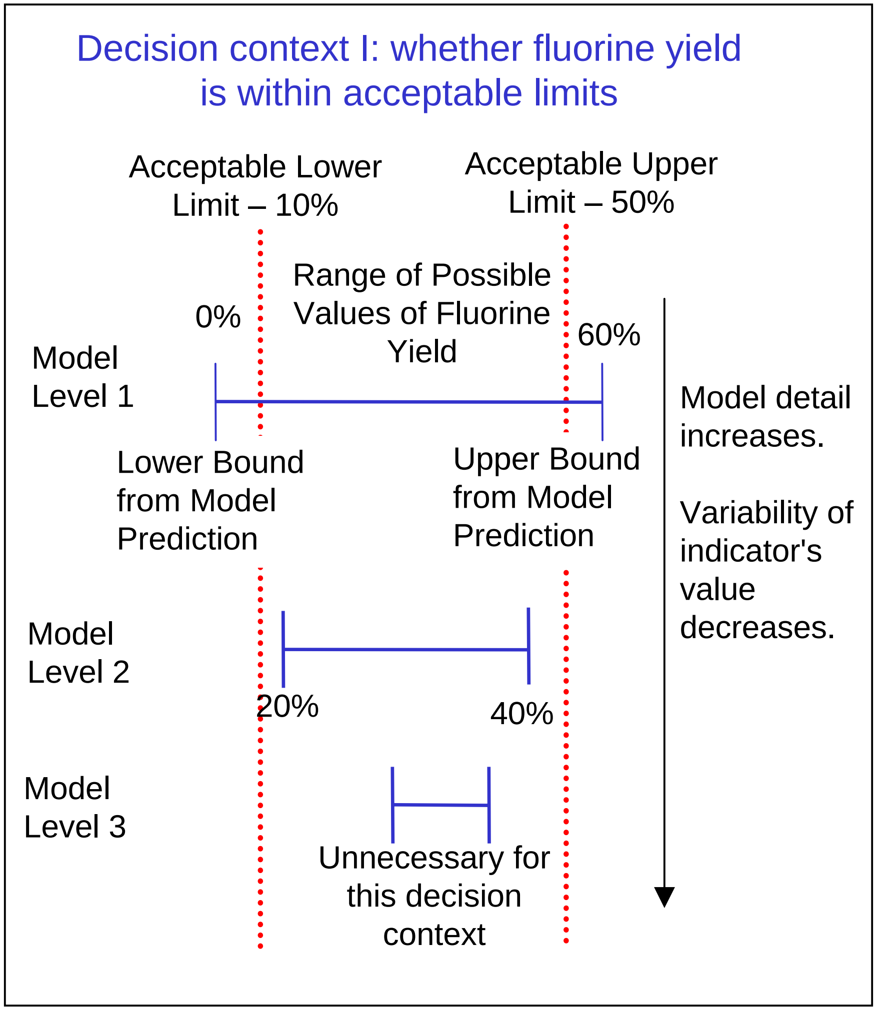
Tools for Integrated Technology Assessment under Uncertainty (TITAU)

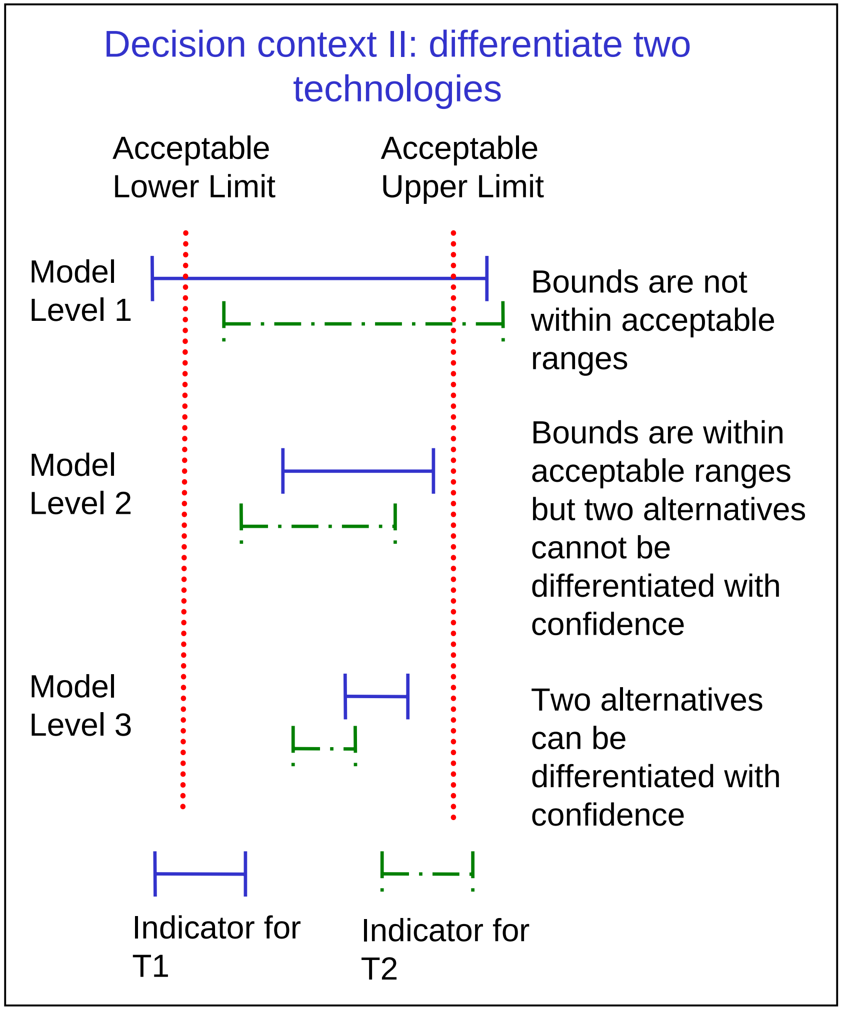


It is a generic framework and can be used for other analyses.

Hierarchical Modeling

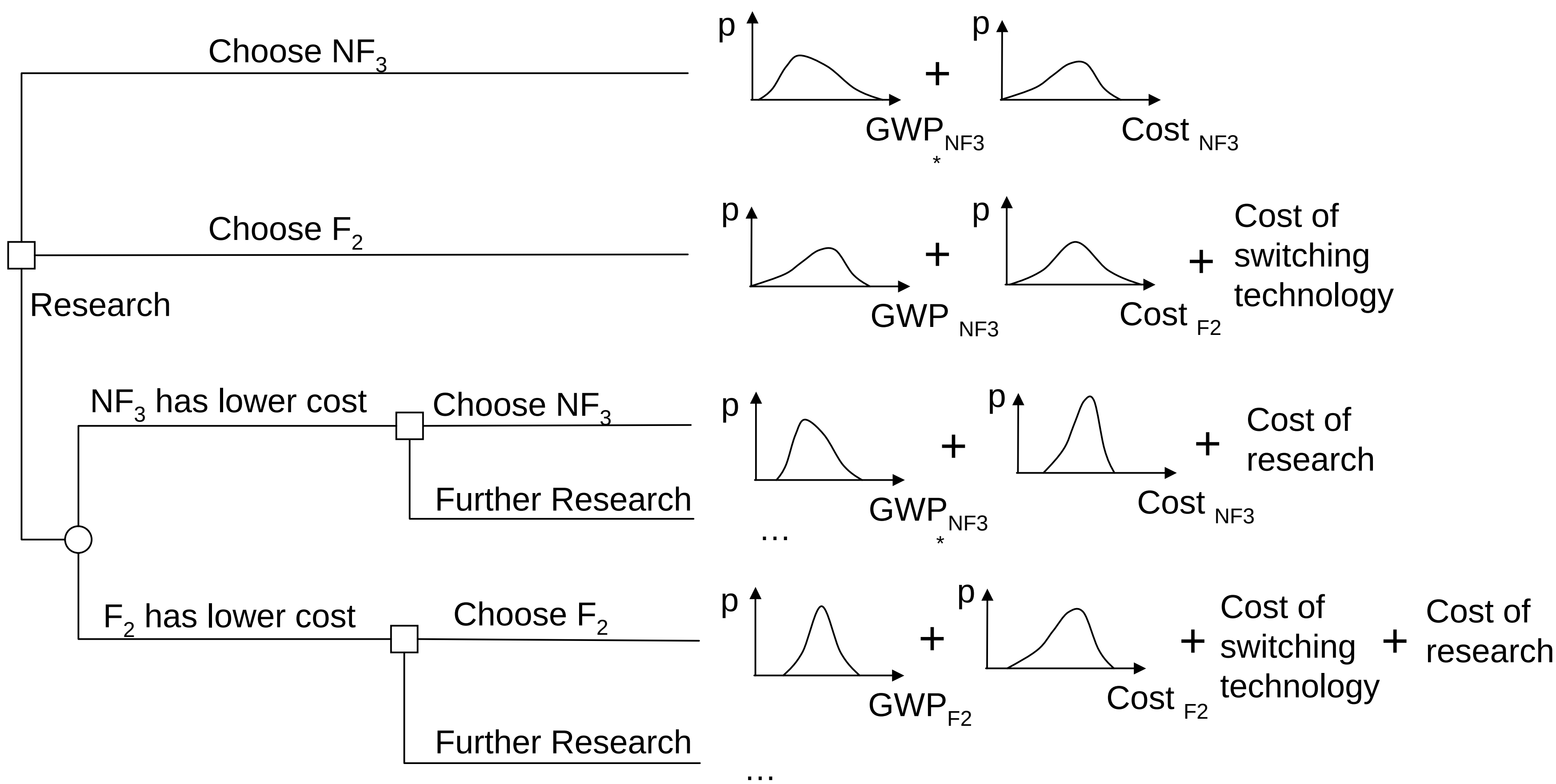
Hierarchical Modeling – Start from simple models and rough estimations, carry out analysis, and based on whether results are satisfactory or not to determine whether next level of detail is required.





Value of Information (VOI)

Net VOI – additional value (or reduced cost) of a project that new information brings compared to value (or cost) of project without the new information, minus cost of obtaining the new information.



*GWP: Global Warming Potential

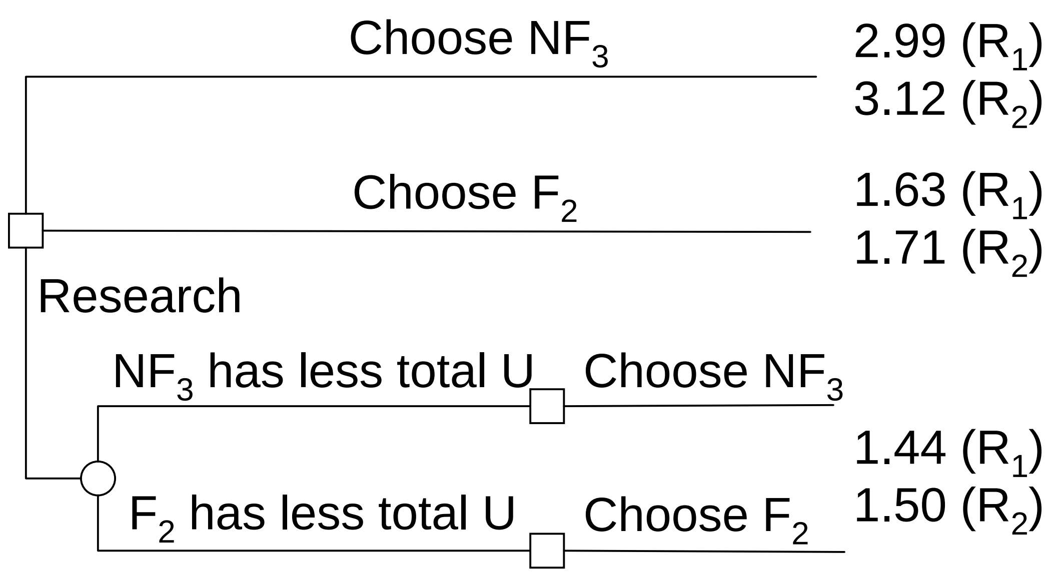
VOI of Further Research

- Monte Carlo simulations recalculate GWP and COO. In each simulation, if

$$U_{GWP\_F2} + U_{swith\_F2} + U_{COO\_F2} < U_{GWP\_NF3} + U_{COO\_NF3},$$

then choose F_2. Otherwise, choose NF_3.

- Overall outcome is aggregated.



- $VOI_1 = 1.63 - 1.44 = 0.19 > 0 \ (R_1)$
- $VOI_2 = 1.71 - 1.50 = 0.21 > 0 \ (R_2)$

It is worthy to carry out further research!

Conclusions

- TITAU is a comprehensive multi-criteria technology assessment tool.
- Large uncertainty in the inputs does not necessarily lead to low confidence in decisions.
- The combination of hierarchical modeling, VOI, and uncertainty analysis effectively allocate resources on information collection and prevent unnecessary spending.

UNCERTAINTY ≠ IGNORANCE

Acknowledgement

- Laura Losey
- David Bouldin, Mike Kasner, Tim Yeakley, and Tina Gilliland **– Texas Instruments**
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- Alejandro Cano-Ruiz and Pauline Ho **– Reaction Design**
- Daren Dance **– WWK**
- Joe Van Gompel **– BOC Edwards**
- Holly Ho **– TSMC, Taiwan**

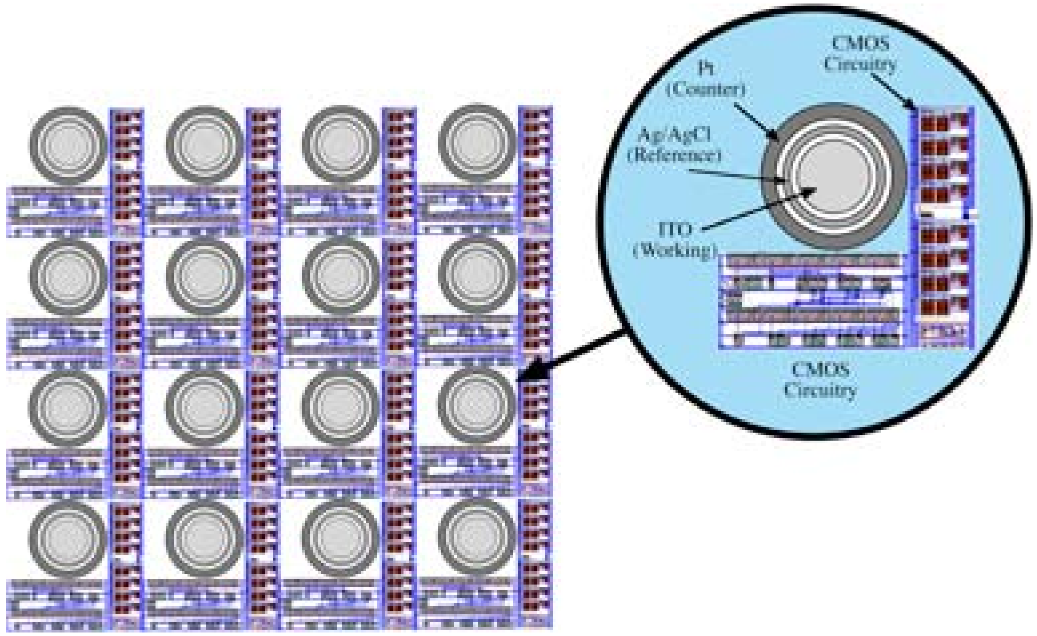
CMOS Biochips for Rapid Assessment of New Chemicals

Subtask C-4-3

David Mathine[1,2], Lee Ann Mathine [1], Seth Ginter[3], Gabriel Gray[3], Daniel J. O'Connell[4], Joseph J. Bahl[4], Matt Scholz[5] , and Raymond B. Runyan[5]

[1]Optical Sciences, [2]Electrical Engineering, [3]Optical Engineering, [4]Sarver Heart Center, and [5]Cell Biology and Anatomy, University of Arizona, Tucson

Project Objectives

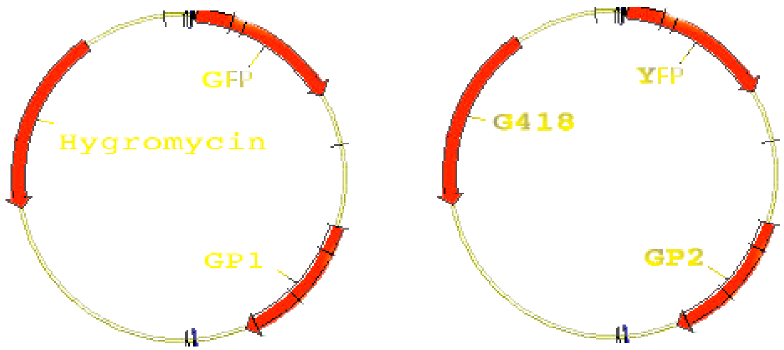


Traditional means of determining chemical toxicity, which typically involve expensive and laborious animal studies, cannot keep pace with the demand for new chemicals by industry. The advent of biochip technology promises to yield a high-throughput means of screening even complex mixtures of chemicals for toxicity. By monitoring the exposure response of reporter cells/tissues, investigators can identify signature reactions that indicate toxic insult.

Cell health will be monitored in real time using a CMOS based sensor where each pixel is capable of optical, chemical, and electrical measurements.

Approach to a Toxicity Assay

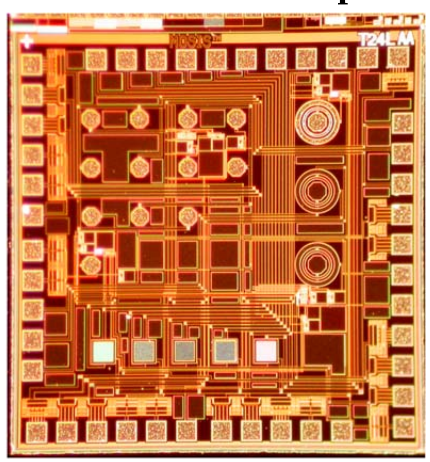
1.



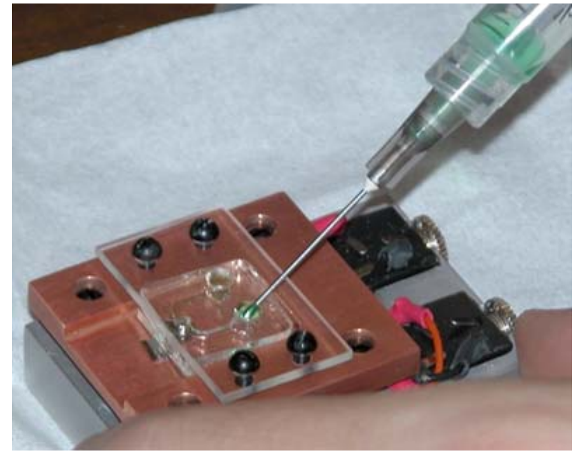
Human cells are cotransfected with plasmids coding for proteins (GP1 and GP2) linked to the fluorescently labeled proteins (GFP and YFP, respectively). By design, the expression level of one protein (GP1) responds to toxic insult and that of the other protein (GP2) does not.

2.

Cells are arrayed onto biochip electrodes, which double as photodetectors



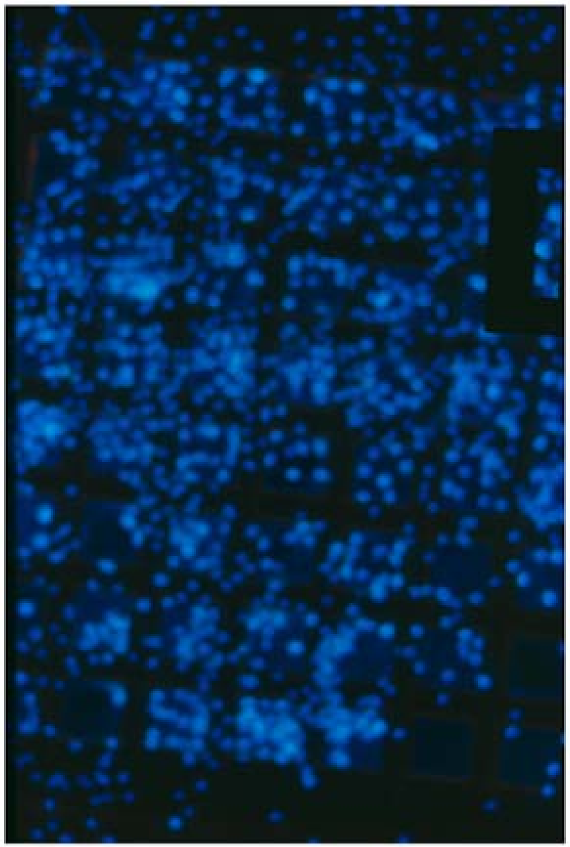
3.



Biochip is exposed to test chemical of interest. Many forms of data relating to cell health are being developed, including:

- **GP1 Protein expression normalized to a housekeeping protein (GP2)**
- **Cellular action potentials**
- **Cell spreading and cell death**
- **Electroactive analyte concentrations**
- **Autoluminescent and fluorescent reporters**

Cell Attachment Studies



The biosensor surface is foreign to cells. Therefore, the attachment to the SiO_2 and ITO surfaces was studied. We found that COS-7 cells derived from monkey kidney cells, attached and grew well on ITO and SiO_2 coated silicon substrates without patterned biomolecules. COS-7 cells attached better to ITO coated substrates and we were able to obtain confluent cell layers.

The above figure shows DAPI stained COS-7 cells attached to a CMOS chip. An electrode grid pattern can be seen in the image.

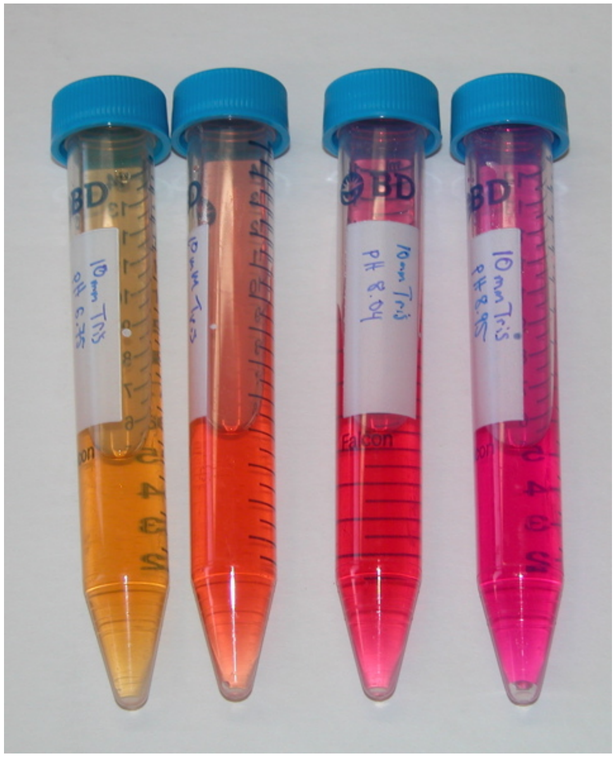
EHS Metrics

I) Basis of Comparison - Current best technology involves animal studies to determine toxicity of new chemicals. Approaches to solve this problem center around reduced usage of toxic materials.

II) Manufacturing Metrics - The new approach aims to increase the through put of chemical toxicity testing so that new chemicals will not be introduced into the manufacturing line before the toxicity effects of these chemicals is known.

III) ESH Metrics

The goals of this work are to determine the toxicity of new chemicals. This work hopes to define the standards for toxicity.



Future Plans

<u>Next year plan:</u>

•Perform attachment studies on COS-7 cell line
•Integrate cells with optical detectors
•Test electrochemical sensors within biochamber
•Monitor cellular responses to chemicals in real time

<u>Future Plans</u>:

The CMOS biochip promises to deliver a new generation of highly selective and inexpensive sensors for real-time and online monitoring at the manufacturing site. Future plans include building low-cost sensors for use by chemical suppliers (responsible for starting feed materials) and process engineers and ESH professionals (responsible for evaluation of new chemistries during and after the processing cycle).

IPA Tool Cleaning Effectiveness

Task ID : C-4-4

Srini Raghavan (PI)
Farhang Shadman (PI)
Hrishikesh Shende (Graduate Student)
Department of Material Science and Engineering,
Department of Chemical and Environmental Engineering
University of Arizona

Mentors
Bob Leet
Stephen Wagner
Michael Mcswiney
Intel

Objective

- To understand the mechanism of removal of nitride and oxide films deposited on chamber walls of PECVD reactors by IPA-water solutions

Goal

- To reduce the amount of IPA used for cleaning deposition and etch tools

Motivation

2003 ITRS roadmap states

- "Equipment Cleaning--Critical Needs relate to understanding solvent usage, emission of HAPs and VOCs, hazardous waste disposal, and required personal protective equipment. It will also be important to understand the proper selection of cleaners and cleaning methodologies."
- Environmental, Safety and Health hazards of IPA
- Stringent *OSHA/NIOSH* standards

  (29 CFR 1910.1000 Z-1) Table

  General Industry PEL: 400 ppm, 980 mg/m^3 TWA
- Use of IPA in many places in a fab

IPA Usage in semiconductor manufacturing

IPA is used

- To clean inside of CVD/ Sputtering/Etch tools
- To wipe down equipments, sample boxes and notebooks taken into the clean room
- To clean fab walls
- To dry wafers
- For Intermediate rinses in BEOL cleaning

IPA Concentration in Wipes

The following IPA concentrations are used for optimum cleaning efficiency

- In fab, outside of tool : 6% IPA polyester wipe
- In fab, inside tool , 100% IPA
- Gowning room, wipes 6% IPA

Research in Progress

- Aluminum metal wafers (8” diameter) used as substrate for experiments
- Nitride film deposition carried out in a PECVD tool at Intel’s Ocotillo fab; Source: silane and ammonia; Deposition Temperature: 400^0C

  Post-deposition Treatment: NF_3 etch
- Characterization of films (SEM/EDX)
- Removal of films:

  Mechanical scrubbing with wipes saturated IPA/water solutions of different composition
- Analyze for any relationships between IPA content of solutions and removal efficiency

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Future Work

- Investigate the desorption of water and IPA from cleaned surfaces using APMIS

- Extend the work to the removal of films deposited on etch tool chamber walls

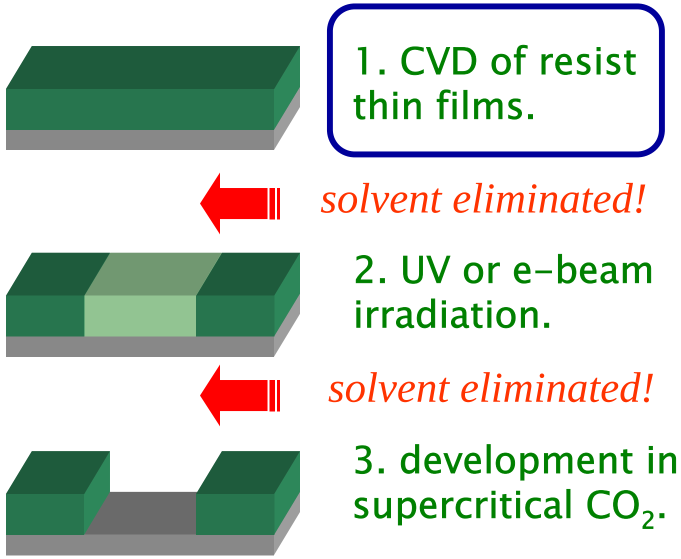
Thrust D, Task D.1
Chemical Vapor Deposition of Resist Thin Films for Solventless Lithography

NSF/SRC ERC EBSM Annual Retreat
February 24th-25th, 2005

Yu (Jessie) Mao
Prof. Karen K. Gleason

Nelson M. Felix
Prof. Christopher K. Ober

Objective: Solventless Lithography



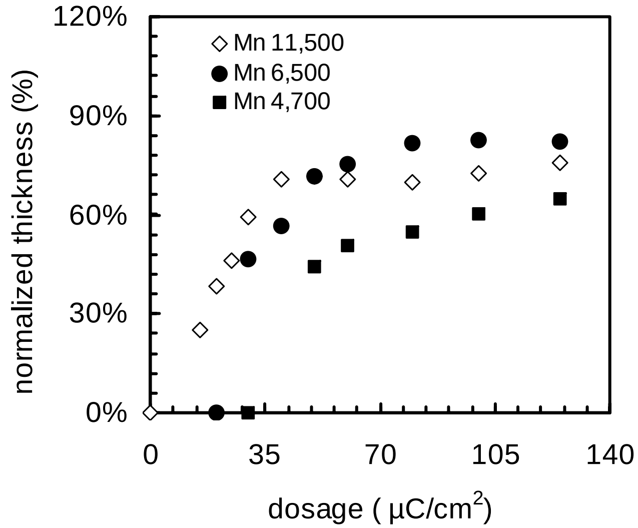
Vapor deposition process

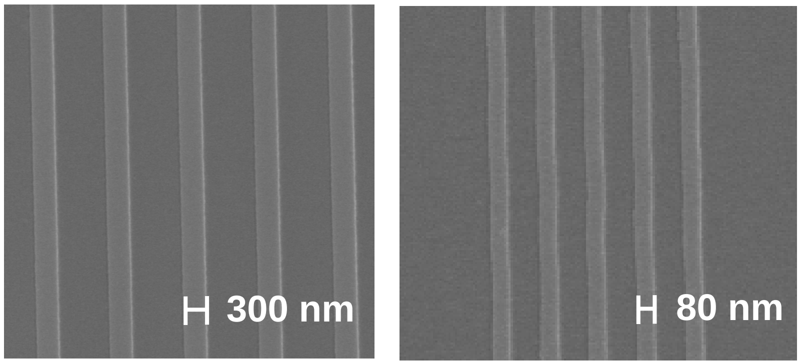
- ❑ low energy (1-3 W).
- ❑ low temperature (< 200°C).
- ❑ fast deposition rate (> 200 nm/min).
- ❑ systematic control over film composition.

- ⌦ Retain chemical functionality.
- ⌦ Achieve good sensitivity & resolution.
- ⌦ Enhance $scCO_2$ solubility.

CVD PGMA Sensitivity and Resolution

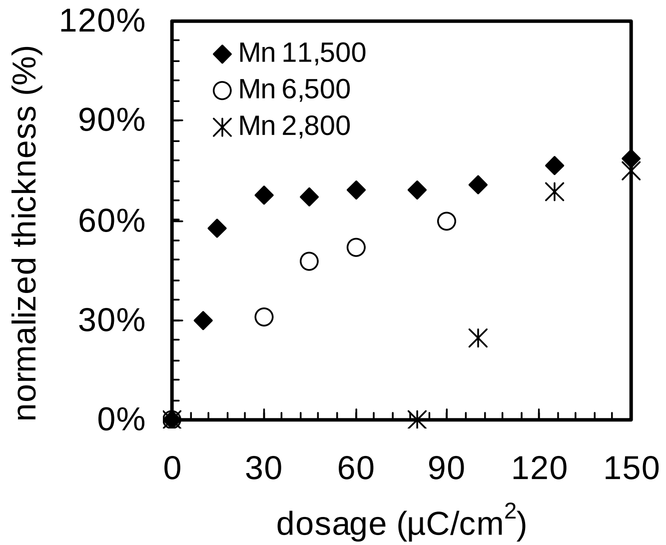
wet development

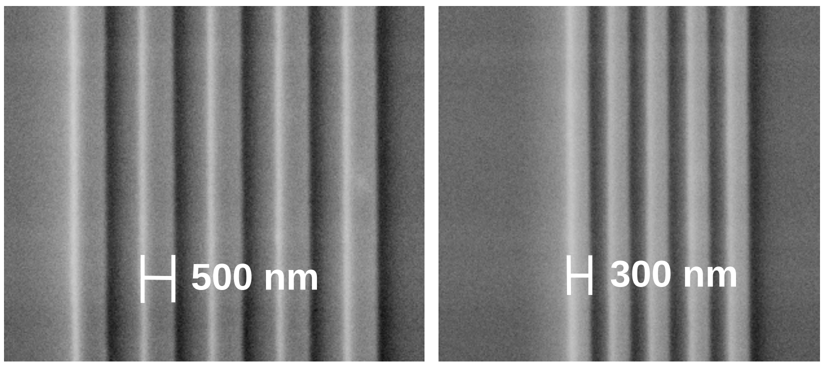




e-beam 70 μC/cm^2, 70/30 wt% IPA/acetone mixture.

$scCO_2$ development

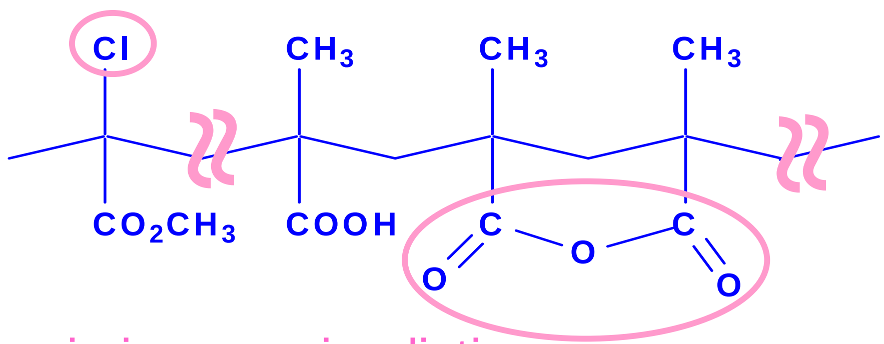




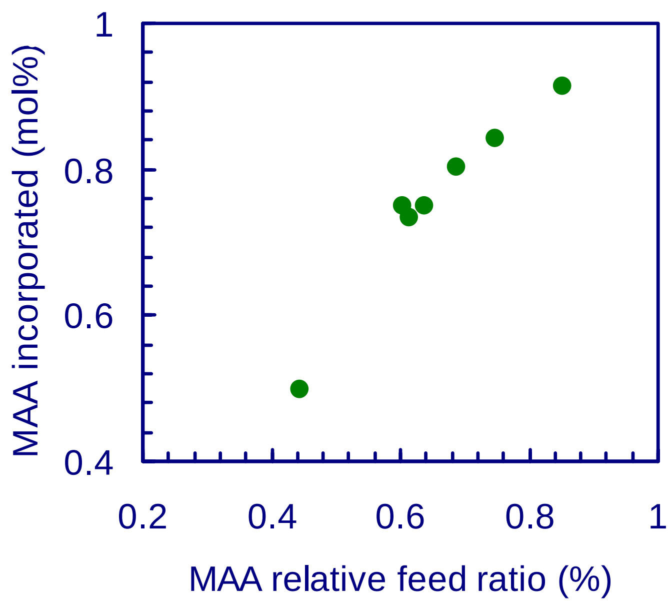
e-beam 140 μC/cm^2, $scCO_2$ 4500 psi, 45°C, 2 vol% acetone.

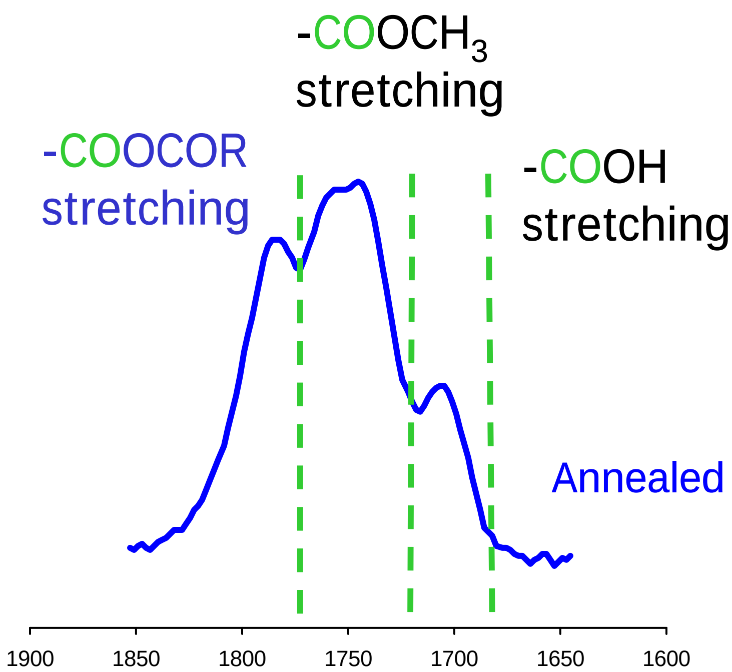
Positive-tone CVD Resist

P(MCA-MAA-MAH)



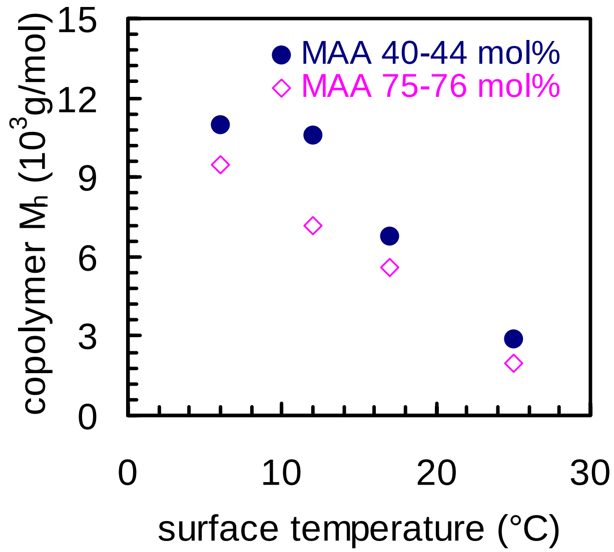
chain scission upon irradiation.

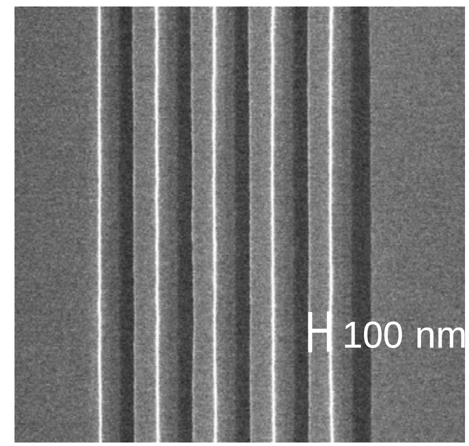


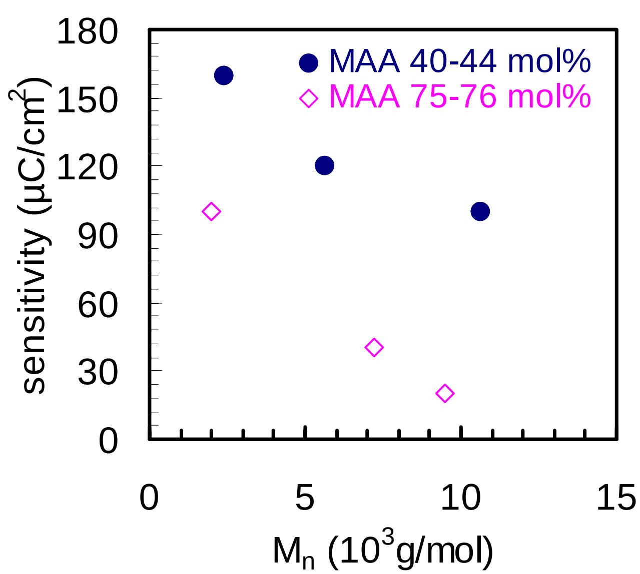


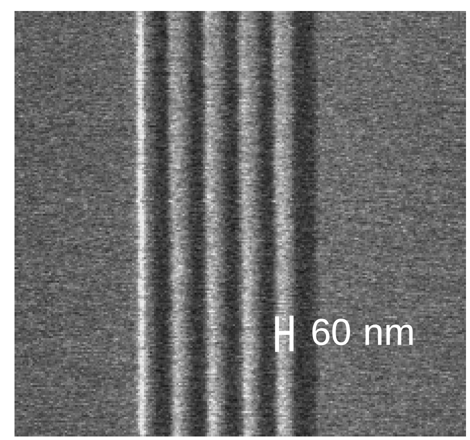
❑ CVD provides systematic engineering of film composition *in-situ*.

Sensitivity and Resolution









M_n 7.2k, MAA 76 mol%

70 μC/cm^2, 50 kV, IPA solution 20 secs.

Summary

- Negative-tone CVD resist.
  - -- Retention of irradiation-sensitive functionality, control of film MW.
  - -- 80 nm features achieved using wet development.
  - -- 300 nm features achieved using scCO_2 development.
  - -- Low-energy vapor deposition process for resist deposition.

- Positive-tone CVD resist.
  - -- Improved image quality.
  - -- 60 nm features achieved using wet development.
  - -- Fluorine-containing moiety improves CO_2 solubility.
  - -- 300 nm features achieved using scCO_2 development.

Solventless Lithography: Supercritical CO_2 for Resist Development

Thrust D, Subtask D-1

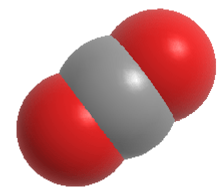
Nelson Felix*, Kristie Grammatikos†, Jessie Mao**, Karen Gleason**, Christopher Ober***

ERC Retreat, August 2004

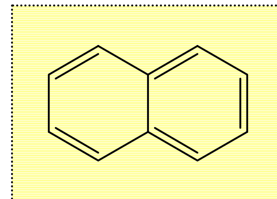
*School of Chemical and Biomolecular Engineering, Cornell University
**Department of Chemical Engineering, MIT
***Department of Materials Science and Engineering, Cornell University
†Department of Chemical Engineering, University of Delaware

Supercritical CO_2 and Solubility

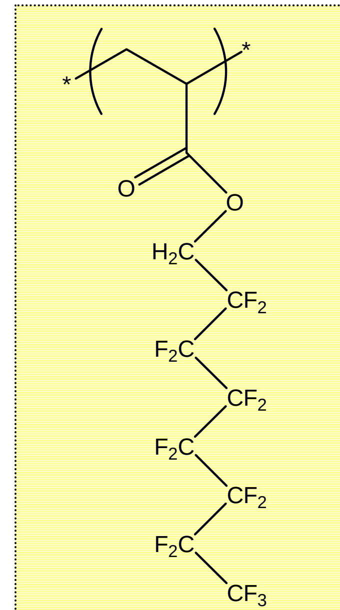
- One phase exists above the critical point
  - CO_2: T_c=31C, P_c=1070 psi (74 bar)
- Gas-like diffusivity and viscosity, but liquid-like density.
- No phase boundary – zero surface tension.



- CO_2 is non-polar, though has a large quadrupole moment
  - Non-polar repeat units: solvent-solvent interactions dominate
  - Polar repeat units: polymer-polymer interactions dominate

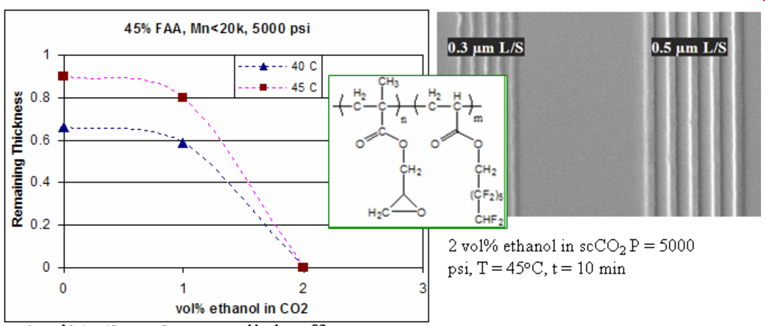


naphthalene



Poly(1,1-dihydroperfluorooctyl acrylate)

Cosolvents to extend the dissolving power of $scCO_2$



2 vol% ethanol in $scCO_2$ P = 5000 psi, T = 45°C, t = 10 min

- 1vol% **ethanol**….very little effect
- 2vol% **ethanol**….100% removal

Properties that affect polymer solubility:

–Chain stiffness (***entropy***)

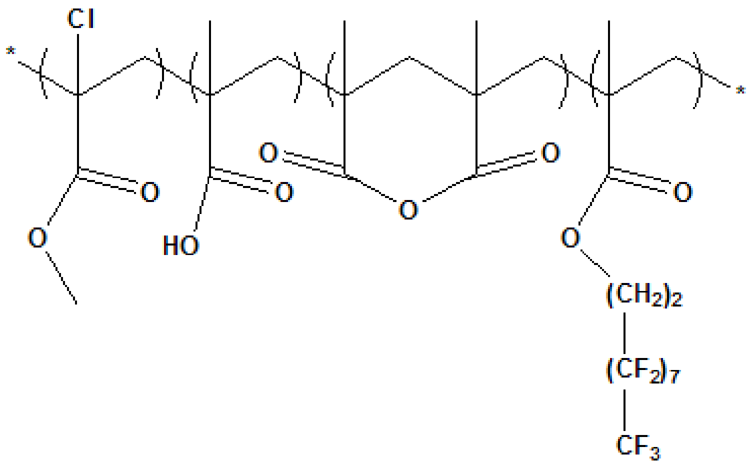
–Molecular weight (***size***)

–Existence of electron-dense groups (***enthalpy***)

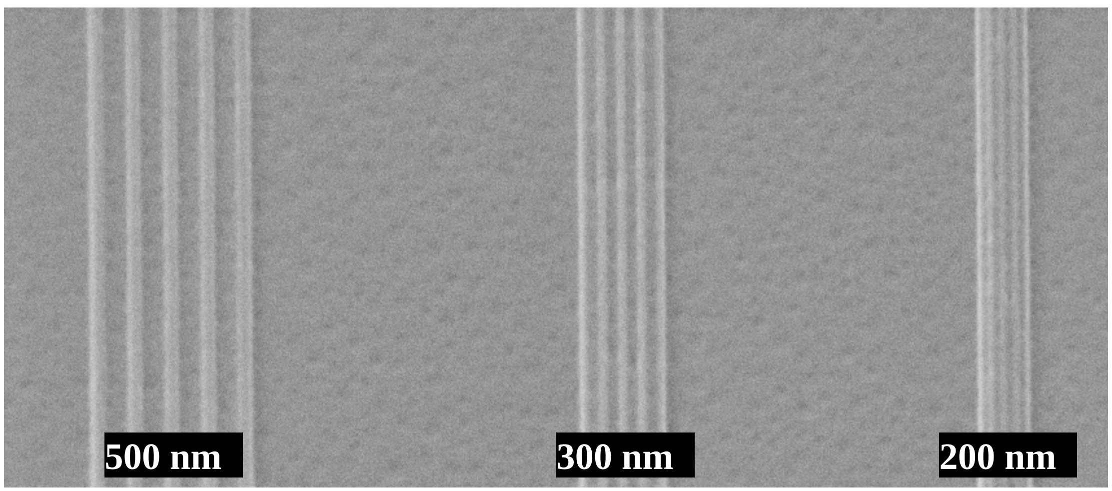
•Acrylate groups

•Fluorine substituted moieties

Positive Tone E-beam resist developable in $scCO_2$



- Chain scission mechanism
- 40% fluorinated monomer incorporated
- Positive tone features once developed in pure supercritical CO_2

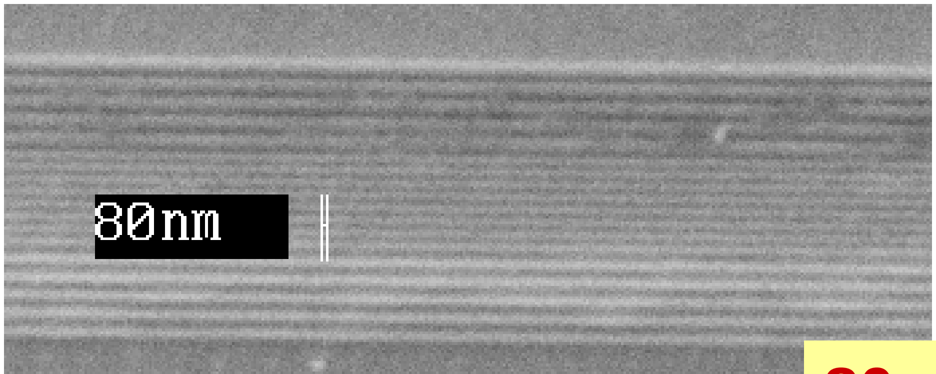


Film deposited by HFCVD (MIT, Gleason Group):

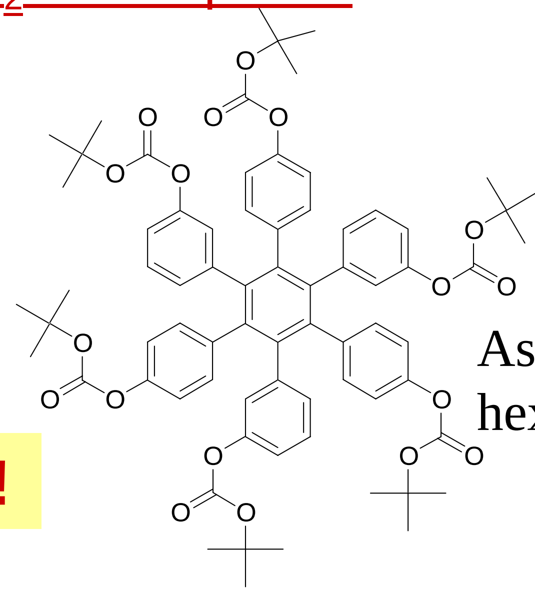
All dry lithography process!

High Contrast Negative-tone Molecular Glass Resist System

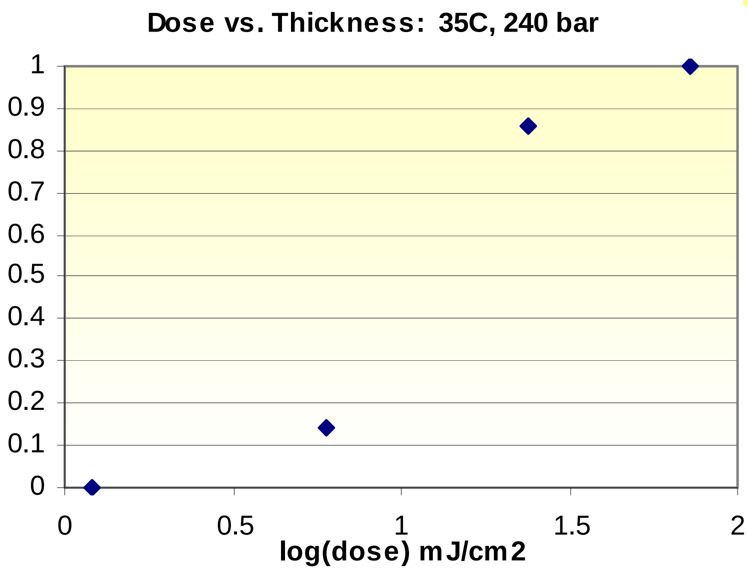
for Supercritical CO_2 Development

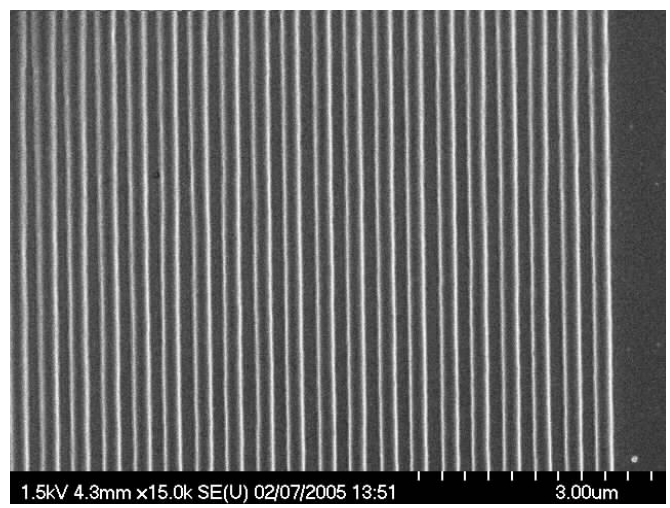


80 nm!



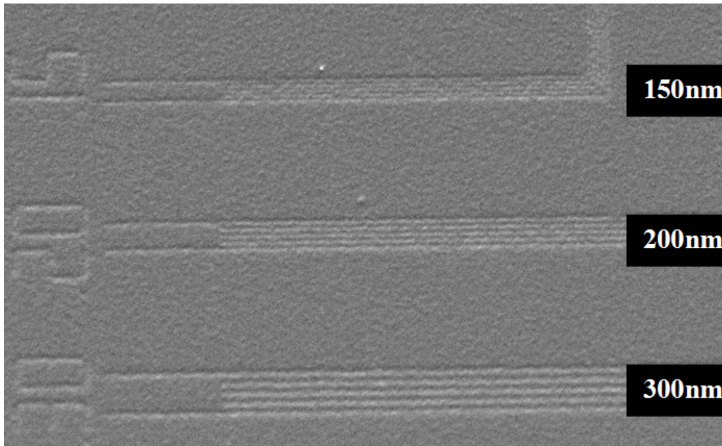
Asymmetric hexaphenol-tBoc

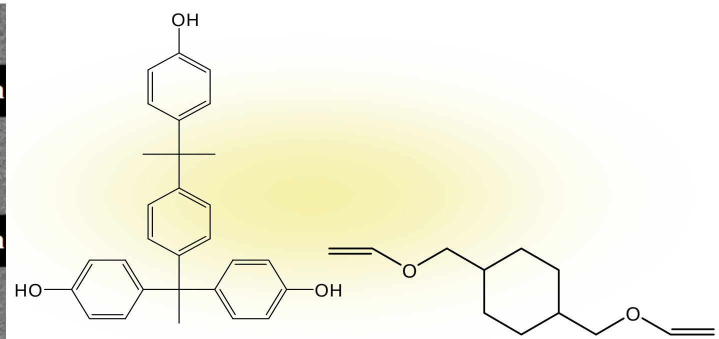


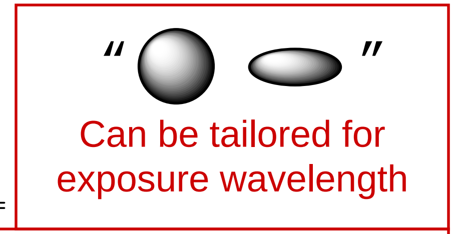


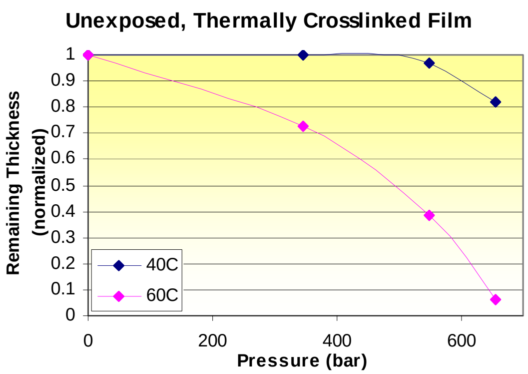
Positive-tone Molecular Glass Resist System

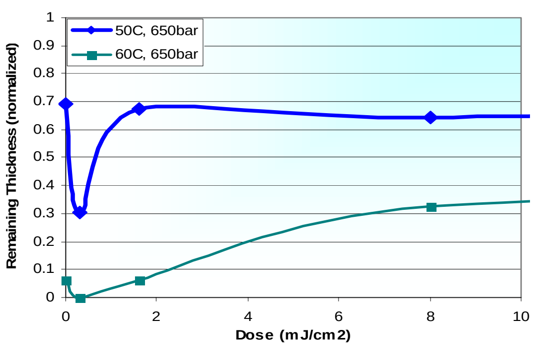
for Supercritical CO_2 Development

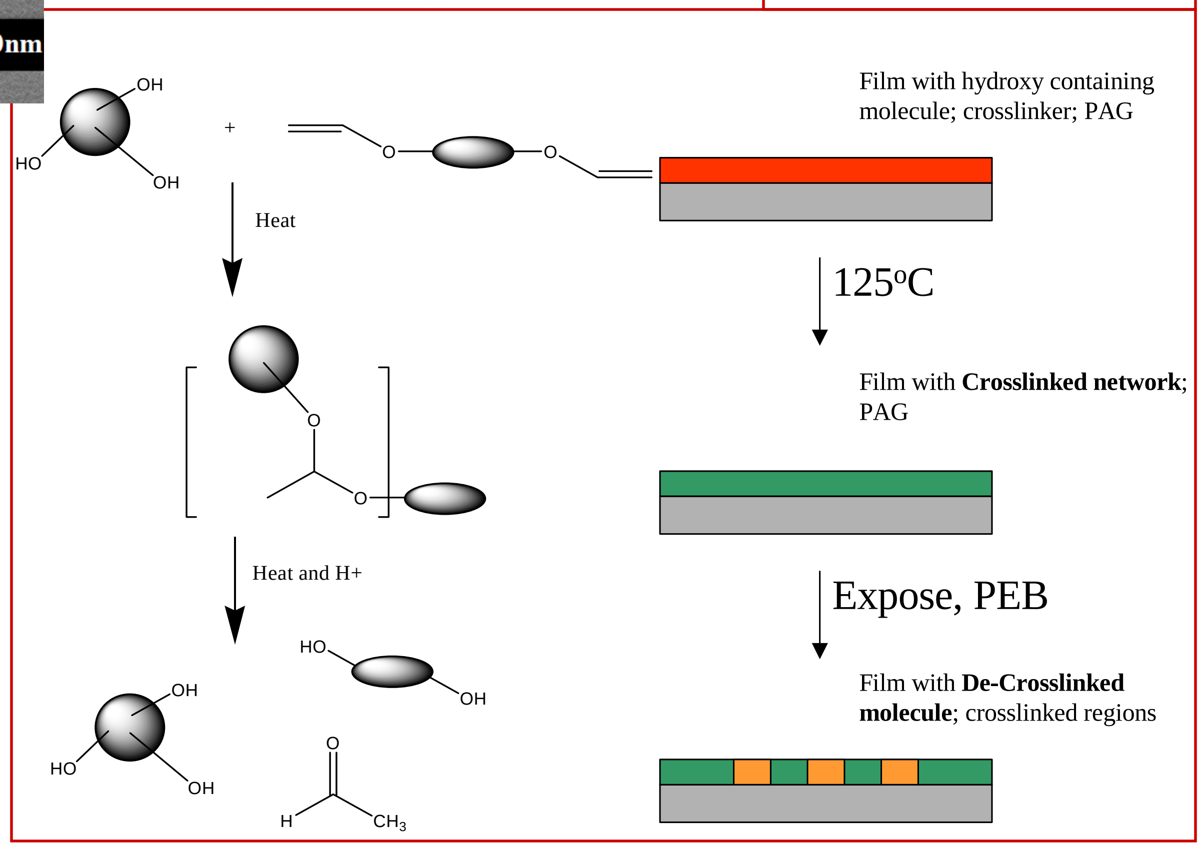












Conclusions & Future Plans

- Improvement in performance of all-dry lithography
- **<u>80 nm</u>** negative tone L/S patterns developed in $scCO_2$
- Demonstrated chemistries for positive tone CO_2-developable DUV photoresists: polymers and molecular glasses
  - <200 nm features achieved
  - First of its kind!
- Synergy between molecular glass resists and CO_2 development

- Study $scCO_2$ development of new molecular glass resists
  - Investigate LER smoothing and pattern collapse inhibition in new high resolution resists
- Fundamental studies of solubility
  - To find optimal cosolvents/conditions/materials
  - To understand effect of resist architecture

Environmentally Benign Deposition of Photoresist and Low-k Dielectrics

Goksen G. Yaralioglu

B. (Pierre) T. Khuri-Yakub

Stanford University

E. L. Ginzton Laboratory

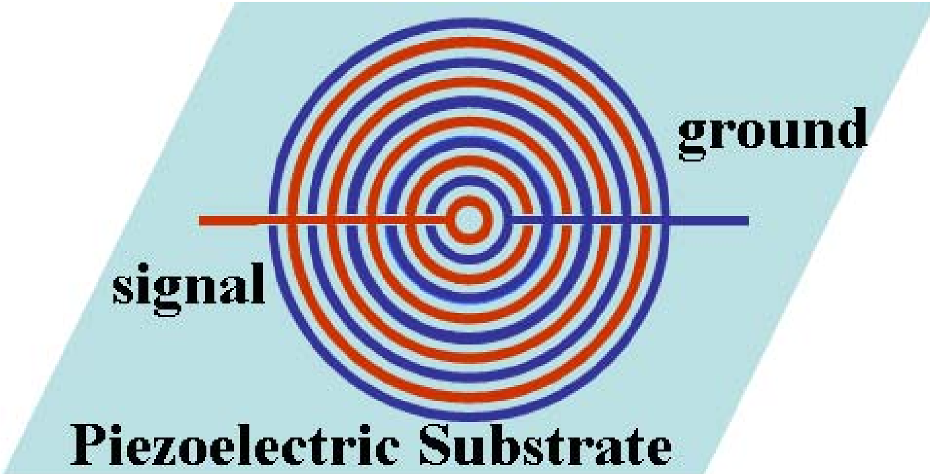
Stanford, CA 94305-4088

Task D   ID# 425.006

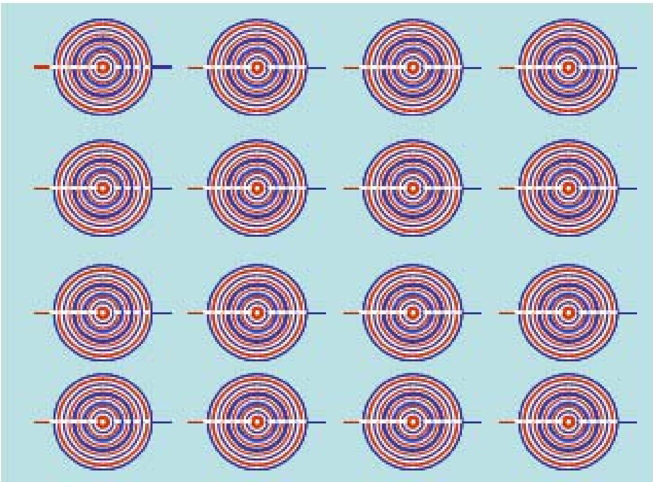
http://piezo.stanford.edu

khuri-yakub@stanford.edu, goksenin@stanford.edu

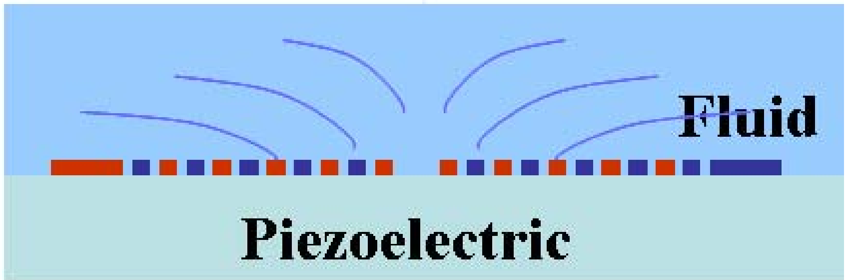
Interdigital Ring Ejectors



Top View

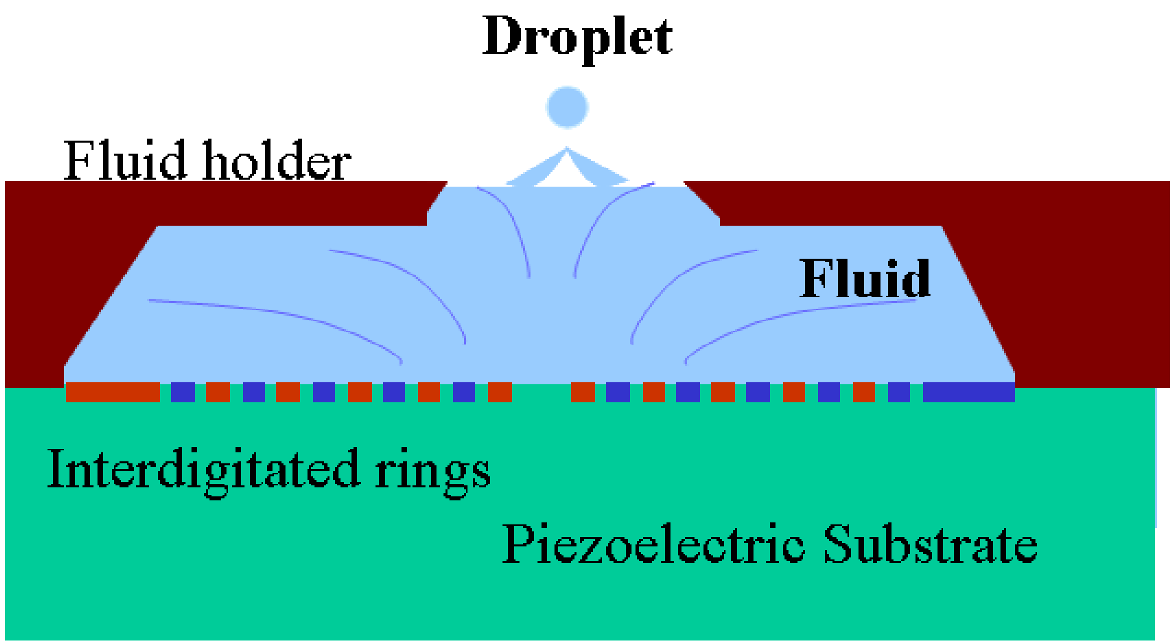


Droplet size:
28 µm

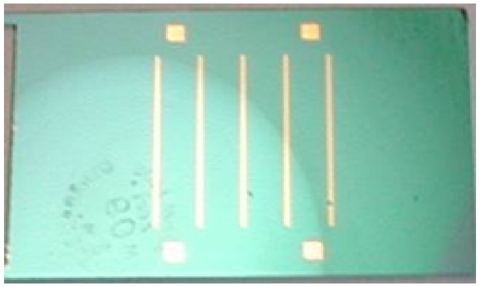


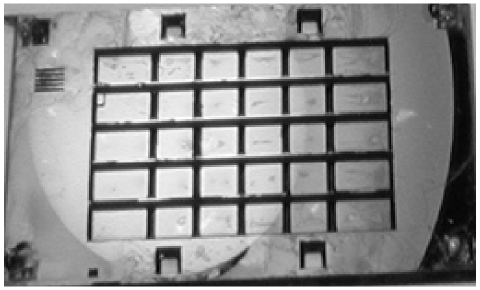
Side View

Fabricated Spacers

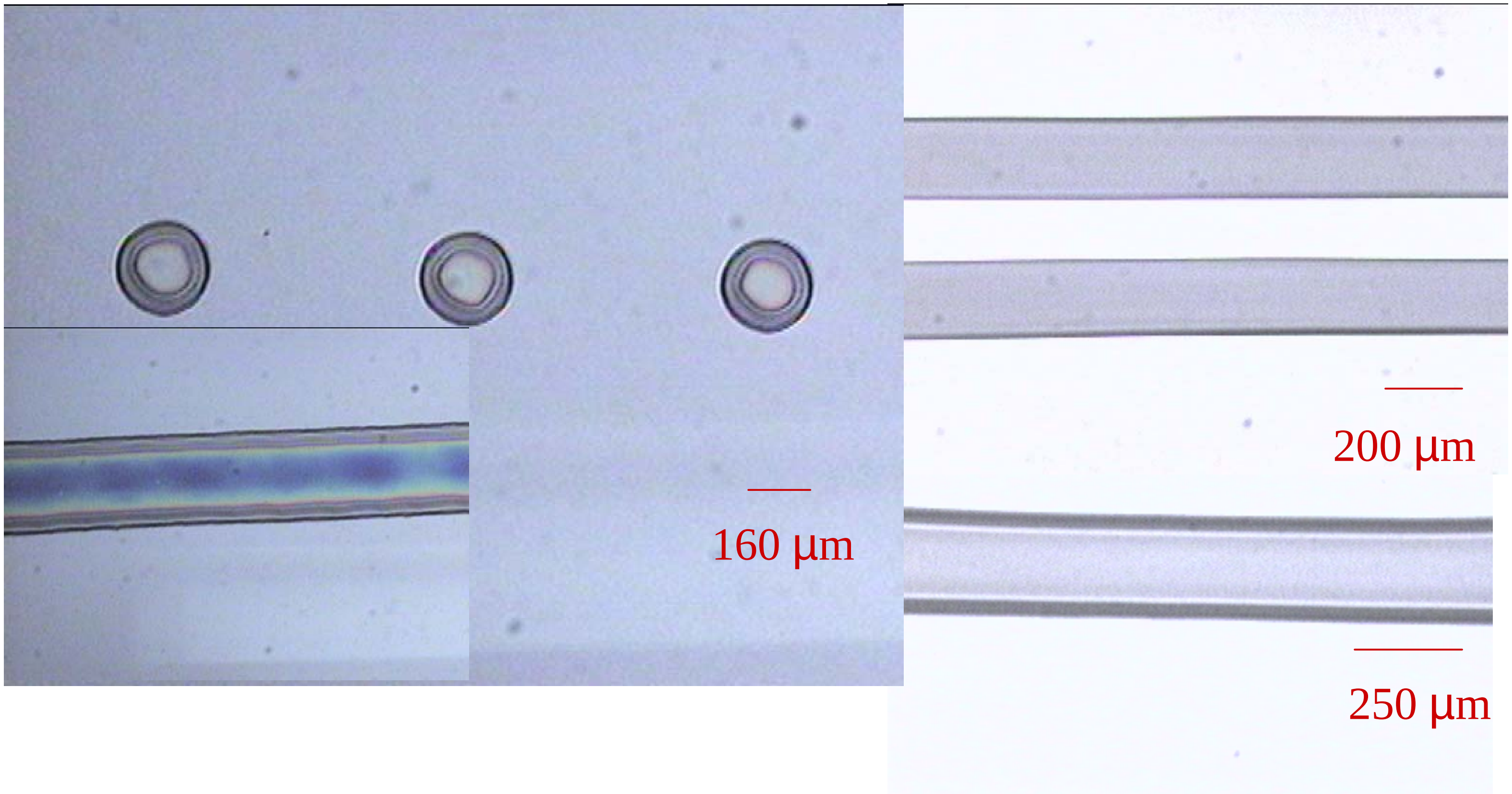


We have two micromachined spacers aligned on top of each other.
300 µm and 500 µm thick wafers; 50,100,200 µm wide ejection pools





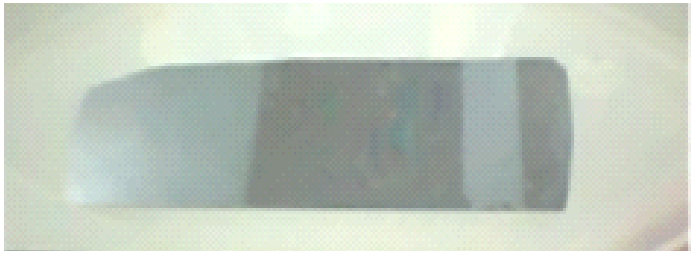
Picoliter Photoresist Drops Deposited onto the Wafer



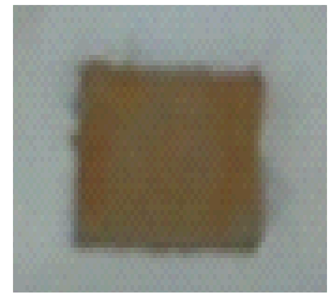
Single droplets of photoresist can be written on the silicon wafer surface.
A photoresist line can be drawn, and a wafer can be covered.
Two photoresist lines written simultaneously: non-overlapping and overlapping with each other.

Coverage Experiments

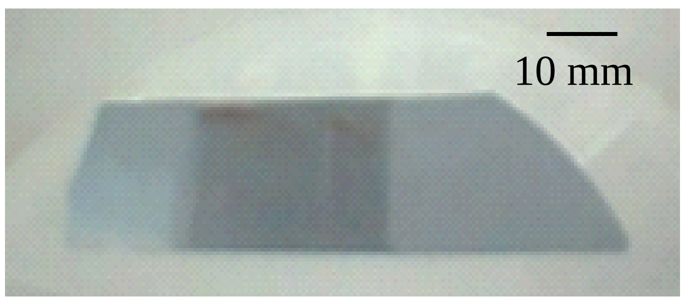
(a)



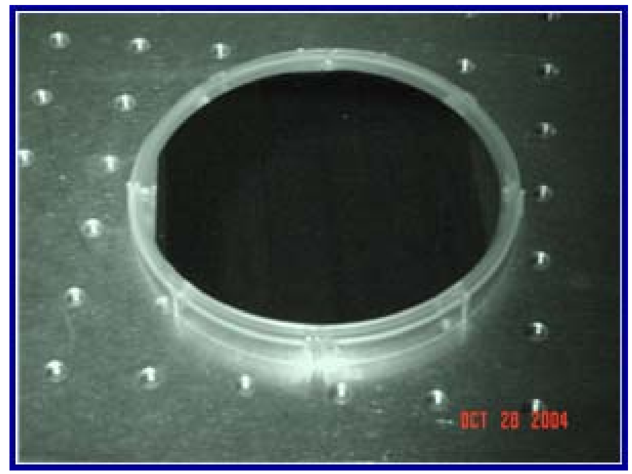
(c)



(b)



(d)



Coverage experiments:

(a) Selective photoresist coverage of a wafer pieces 20 mm x 30 mm in area,

(b) 20 mm x 20 mm in area,

(c) Coverage of a 10 mm x 10 mm in area on a silicon wafer.

(d) Coverage of a full wafer with uniformity 2.8 ± 0.02 µm.

Summary and Future Research

- Ejected high viscosity fluids.

Ejected Fluids	Water	Isopropanol	Photoresist	Ethylene glycol
Viscosity (cP)	1	5	5-8	16

- Drop on demand and Continuous mode of operation.
- Each element is easily addressable.
- Easily cover surfaces with fluids and reduce waste.
- Single lithography step. Easy to fabricate as arrays.
- Easy to make the each array element eject.
- Cross-talk is no longer a serious problem, does not impede ejection.
- FEA predicts device characteristics.
- All the 2D array elements ejected droplets.

- Future Research: Demonstrate Photolithography

Thrust D: Patterning

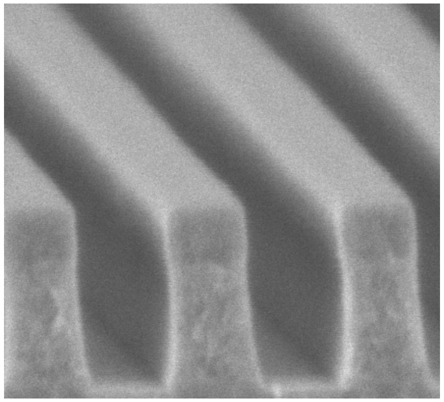
Project 5: Supercritical CO_2 Processing of Wafer Surfaces

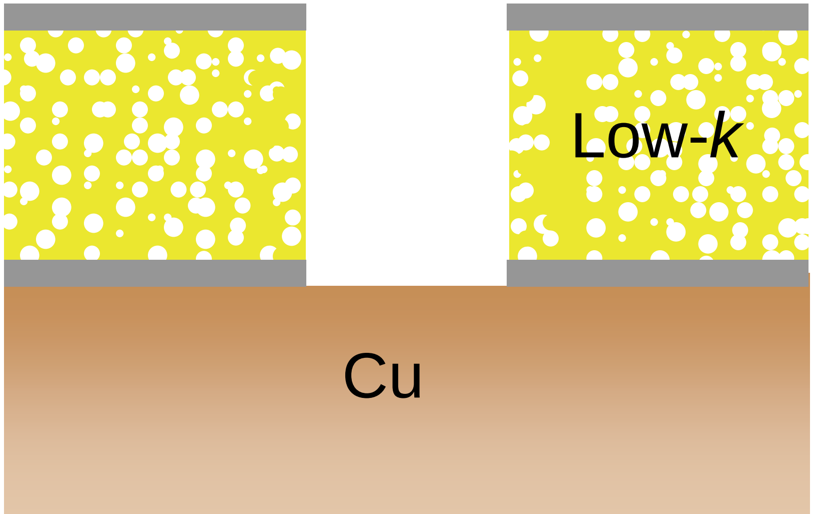
Bo Xie, Lieschen Choate, Rachel Morrish,
Michael Durando, and Anthony Muscat
Department of Chemical and Environmental Engineering
University of Arizona
Tucson, AZ 85721

NSF/SRC EBSM ERC Review
February 24-25, 2005

Cu/Low-*k* Cleaning Process Integration

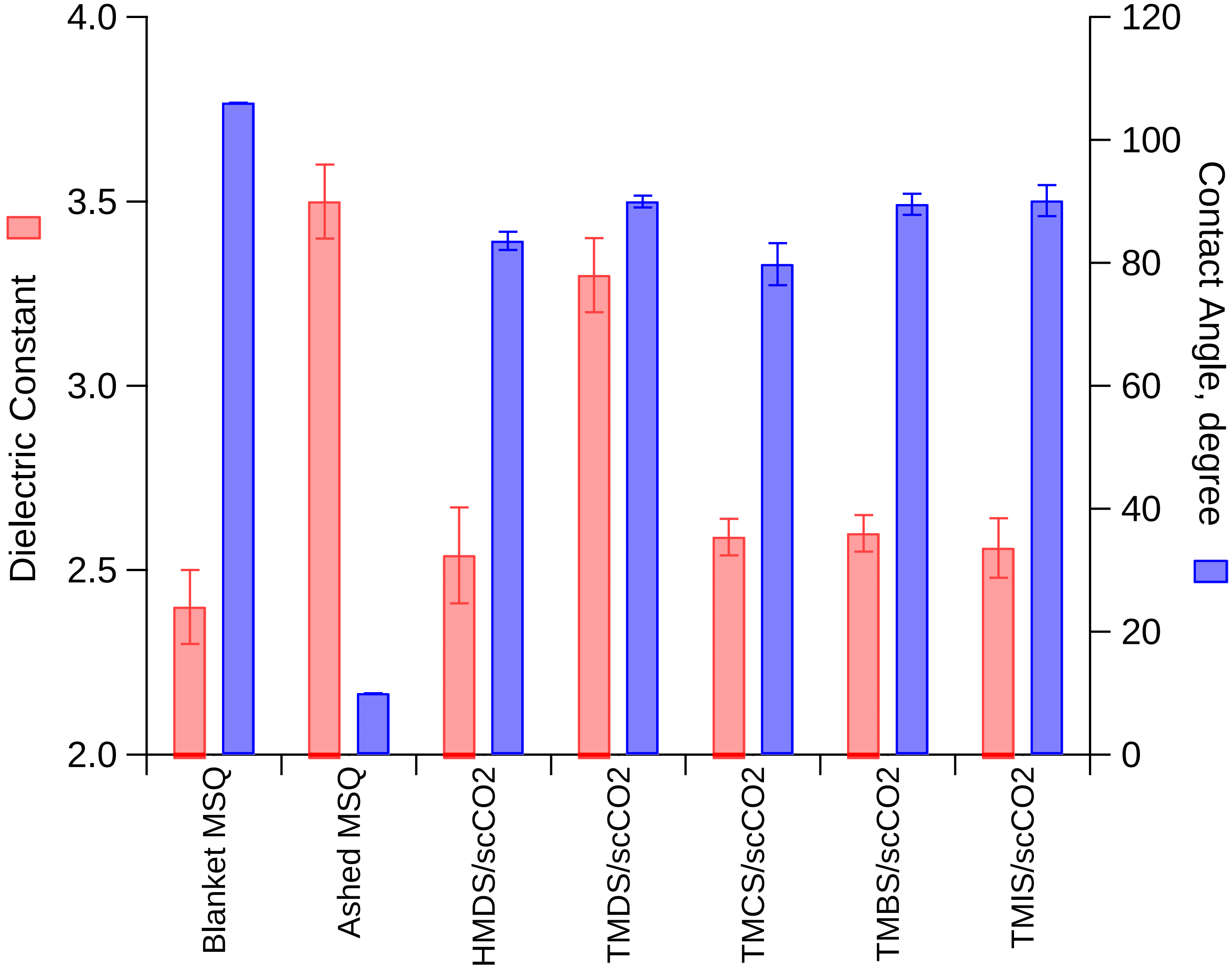
- Contamination
  - Etching and ashing residue
  - PR, Cu, Cu oxides, and barrier metal
- Preserve film properties
  - Dielectric constant
  - Hydrophobicity
- Practical issues
  - Pore sealing
  - Cu barrier
- Maintain device structure
  - Critical dimension
  - Etching profile
  - Remove Cu oxides without removing Cu



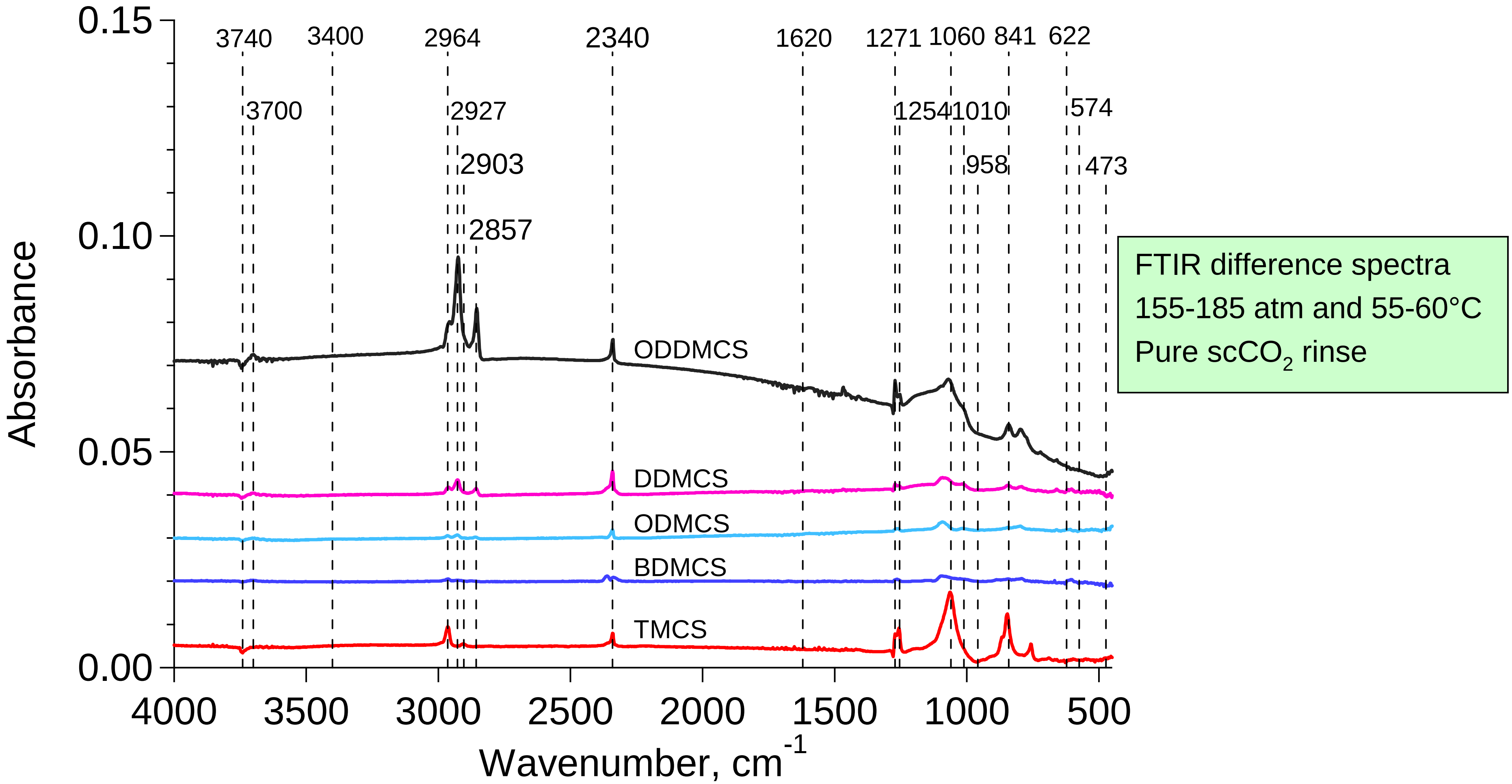


- Veils
- Contamination trapped in pores
- Damage
  - CH_3 depletion
  - Si-OH groups
- Materials compatibility
  - low-*k* film
  - Cu interconnects
  - TiN or TaN diff. barriers
  - Si_3N_4 or SiC etch stops

Contact Angle and Dielectric Constant on p-MSQ for Short Chain Molecules in $scCO_2$

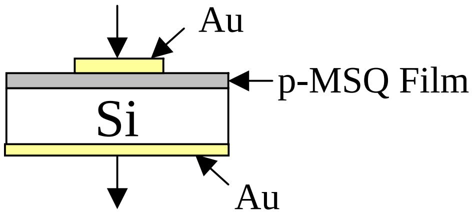


p-MSQ Processed with Monochlorosilanes + $scCO_2$

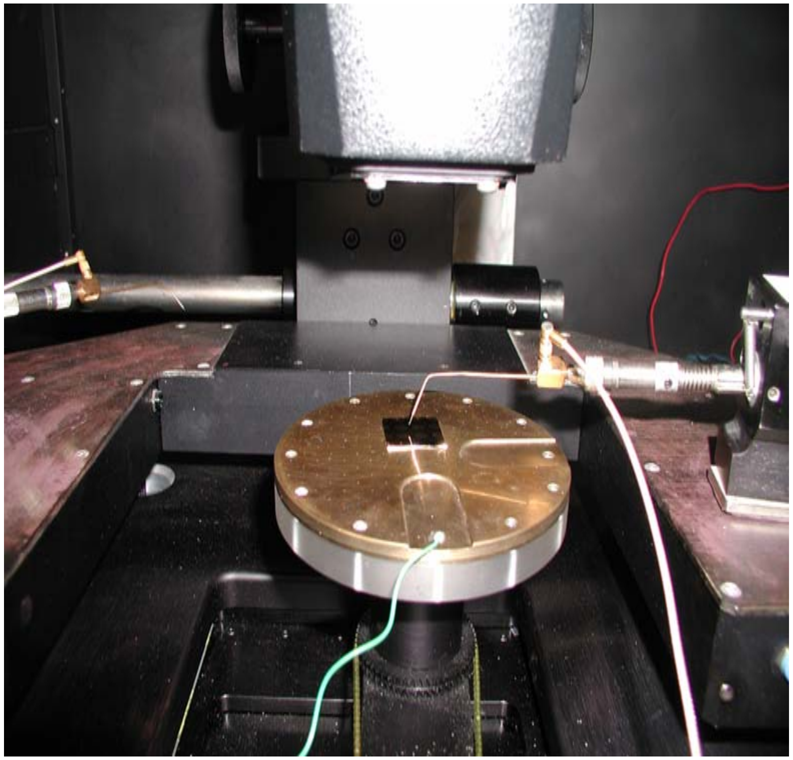


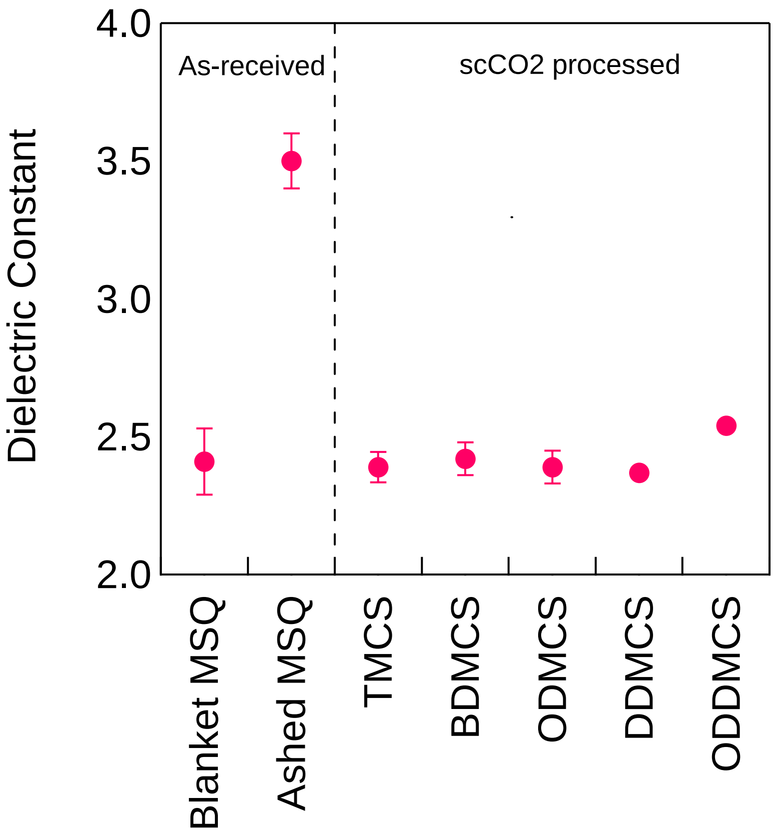
- Heterogeneous and homogeneous chlorosilane condensation reactions
  - 1060 cm^{-1} $R_3Si–O–Si≡$
  - 1010 + 1120 cm^{-1} $R_3Si–O–SiR_3$
- No Cl left on the surface, confirmed by XPS
- 2340 cm^{-1} peak due to physisorbed CO_2 which is removed with time/heating

Electrical Testing



- 4284A Agilent Precision LCR Meter
- 1MHz, -40V to +40V sweep
- 100nm thick, 0.1cm diameter Au gate, 100nm thick Au on the wafer backside
- Capacitance in accumulation is used to determine dielectric constant





Conclusions

- Repair of p-MSQ Film
  - Increased CH_3 and Si-O-Si moieties
  - Both isolated/geminal SiO-H and H-bonded SiO-H reacted
  - Recovery of hydrophobicity with HMDS, TMDS, TMCS, TMBS, and TMIS
  - Restoration of dielectric constant with HMDS, TMCS, TMBS, and TMIS

- Capping of p-MSQ Film
  - Increased CH_3, CH_2, and Si-O-Si moieties
  - Both isolated/geminal SiO-H and H-bonded SiO-H reacted
  - Recovered hydrophobicity of starting surface
  - Restored dielectric constant of starting material

Education Thrust

Kimberly L. Ogden

Thrust Leader

Mission

Establish the ERC as a key resource for providing **Continuing Education** and training in ERC related areas.

Educate a **New Breed of Engineers and Scientists** who integrate ESH into process design and development

Leverage ERC programs to **Attract Outstanding/Diverse Students** into academic disciplines critical to semiconductor industry

Increasing Diversity

- Developed relationship with UPR-Mayaguez
  - Ogden and Muscat are PIs
  - Two joint advised PhD students from UPRM
  - Students recently passed PhD exams, will spend summer and fall 2005 in Tucson
- Developed relationship Navajo Nation
  - REU TCUP summer program for community college students

Continued Funding

- NSF
  - Teachers, diversity, undergraduates
- Water Sustainability Program
  - U of A
  - Funding for short courses related to water sustainability for industry available

Surveys on Industry's Continuing Education Needs

- ERC IAB Survey 2001(our members)
- 2001 Survey of Phoenix area semiconductor mangers and engineers (broader-based)
- 2004 survey – Completed in June and reviewed on teleconference

What are the Next Steps for the ERC's Continuing Education Program?

- Does industry need the ERC to supply continuing ed courses?
- Is the time right now? Is industry funding training?
- Is the ERC the right supplier?
- Faculty instructors? Or combination of faculty and industrial instructors?

Biological Molecules (Microtubules) as Templates for Copper Interconnects

Kim Leung Valenzuela

SRC Master's Scholar

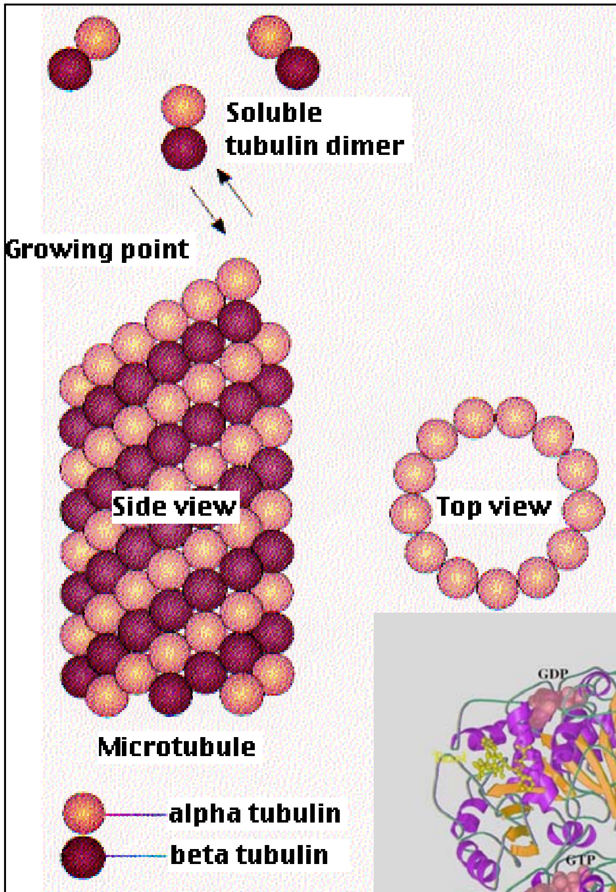
Dr. Srini Raghavan (PI)

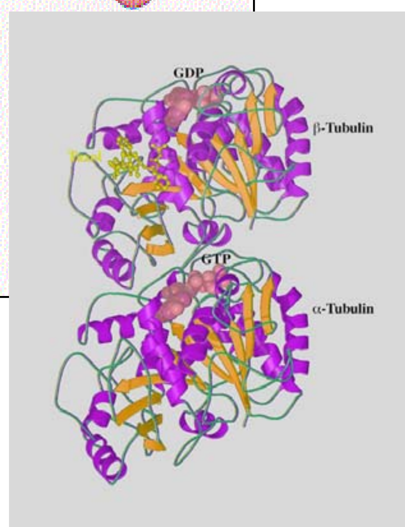
Materials Science and Engineering Department

Nanotechnology Interdisciplinary Research Team (NIRT)

University of Arizona

Microtubules





- Proteinaceous structures of the cytoskeleton of eukaryotic cells
- <u>Components</u>: Alpha and beta tubulin dimers
- <u>Functions</u>: Cell structure, Transportation, Cell Divison
- <u>Properties</u>: 25 µm in diameter, several micrometers in length, tubular structure, reproducible

Project Objectives

- Feasibility of using microtubules (MTs) as templates for forming copper lines
- Copper metallization of MTs with biologically benign chemistries
- Orientation of MTs to form interconnects

Copper Plating Using Biological Redox Agents

- Electroless copper plating is typically carried out using reducing agents such as formaldehyde which are toxic to biological molecules
- This research uses ascorbic acid (vitamin C) and NADH

Copper

$Cu^{+2} + 2e = Cu$ $E° = 0.34V$

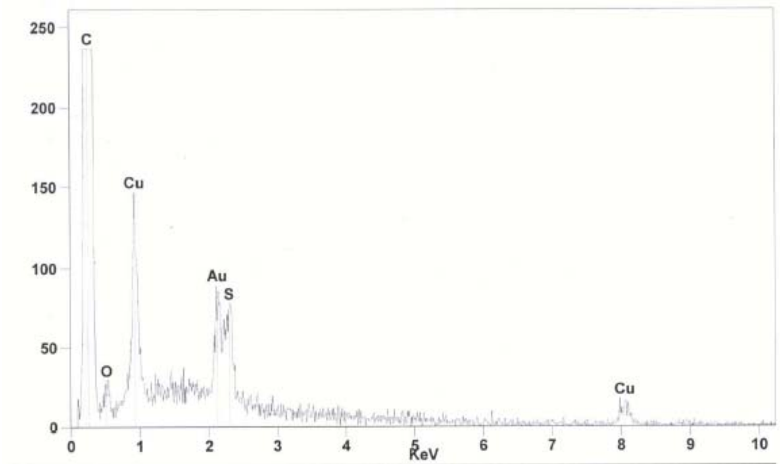
Ascorbic acid

E° = -0.127 to -0.34V for pH = 4 and 7, respectively

NAD^{+}/NADH (Nicotinamide adenine dinucleotide)

$NAD^{+} + H^{+} + 2e = NADH$ $E° = -0.32\ V$

Copper Coated Microtubules



- MTs metallized with copper were imaged using scanning electron microscopy (SEM). The presence of copper particles on the microtubule surface was confirmed using energy-dispersive spectroscopy (EDS). The thickness of the copper coating ranges from 5 to 45nm.
- Morphology of MTs and copper coating presently being investigated using Atomic Force Microscopy (AFM)

Future Plans

- Orient the microtubules with an electric field
- Use the biologically compatible agent NADH to reduce copper
- Strategies to coat the inside of microtubules
- Electroless plating of microtubules with other metals such as gold

Conclusions

- Developed a method to copper plate microtubules