Supercritical Carbon Dioxide Compatible Additives:

Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography

(*Task Number: 425.030 – 425.031)*

PI:

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

Collaborator:

- **Juan de Pablo, Chemical and Biological Engineering, University of Wisconsin-Madison**

Graduate Student:

- **Christine Ouyang: PhD candidate, Materials Science and Engineering, Cornell University**
- **Gregory Toepperwein, PhD candidate, Chemical Engineering, University of Wisconsin**

Objectives

- **To reduce the use of organic solvents and water in the development process by using environmentally benign solvents**
- **To reduce pattern collapse by using low surface tension fluids**
- **To demonstrate environmentally benign development of conventional photoresists using $scCO_2$ and silicone fluids**
- **To achieve high resolution and high aspect-ratio patterning with molecular glass photoresists**

ESH Metrics and Impact

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

100% reduction in the use of aqueous base TMAH developer

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

Up to 100% reduction in VOCs and HAPs emission

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

Eliminate water usage

Reduction in energy for water treatment and purification

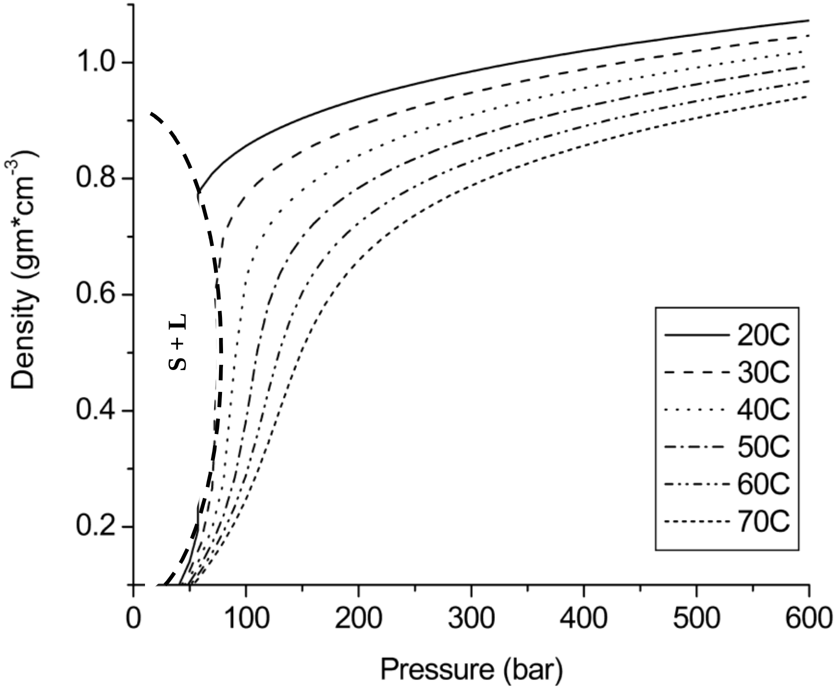
4. Reduction in the use of chemicals

Minimal use of organic solvents

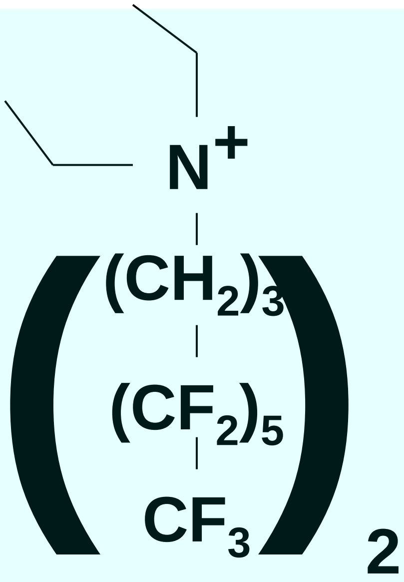
Why a Non-Aqueous Developer Solvent?

Environmental and Performance Advantages of $scCO_2$

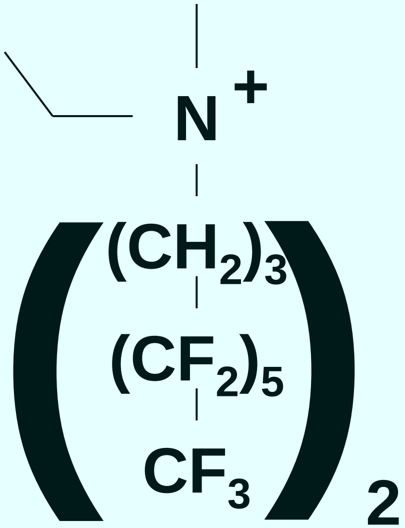
- **Environmentally friendly, zero VOC solvent**
- **Highly tunable solvating power**
  - **$\rho(T,P)$**
  - **Leaves no residue**
  - **Clean separations**
- **One-phase fluid**
  - **Zero surface tension**
  - **Transport, viscosity between that of liquid and gas**
- **Nonpolar, inert character**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



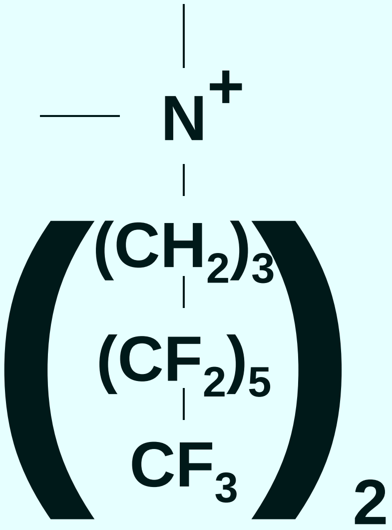
QAS Salts



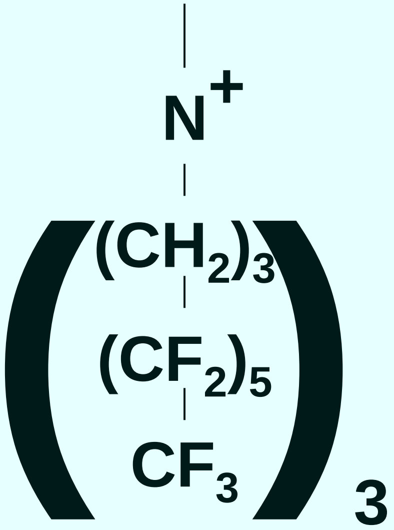
Diethyl



Ethyl-Methyl



Dimethyl



Monomethyl

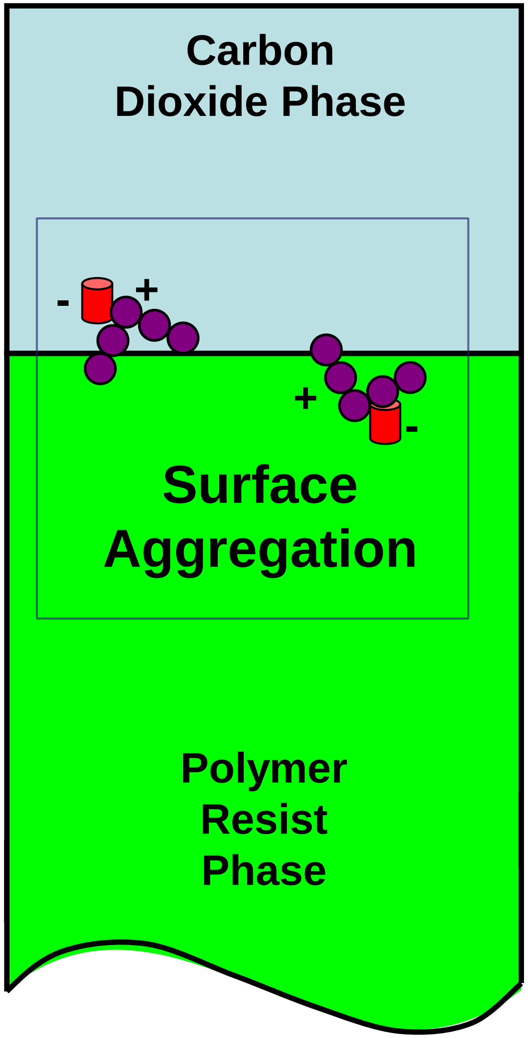
Cations

Anions

$CF_3(CF_2)_1COO^-$ $CF_3(CF_2)_5COO^-$

CH_3COO^- CF_3COO^- $CF_3(CF_2)_2COO^-$

QAS Mechanisms – Example 1

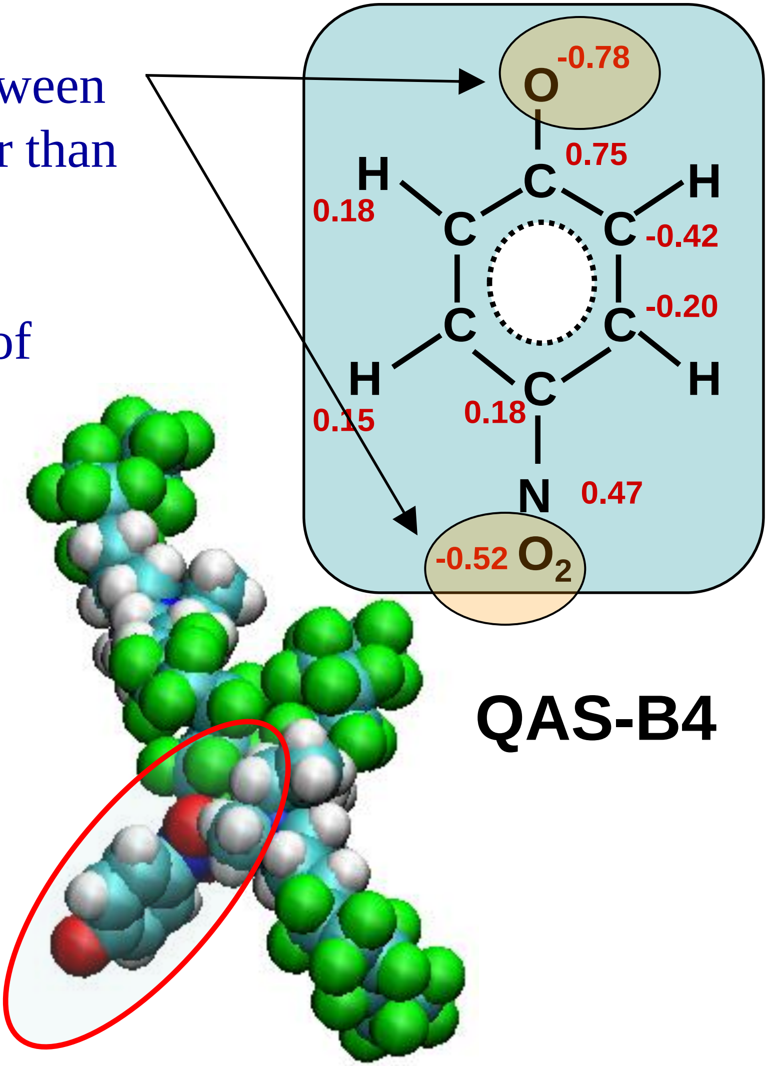


Carbon Dioxide Phase

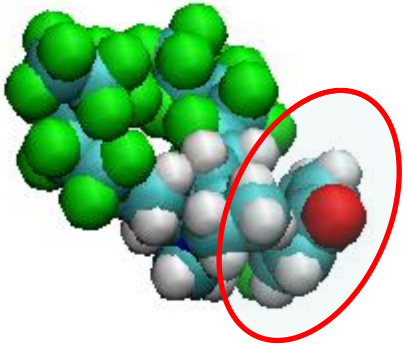
Surface Aggregation

Polymer Resist Phase

- Charge delocalization enables interaction between anion and species other than cation
- Effective despite lack of film penetration



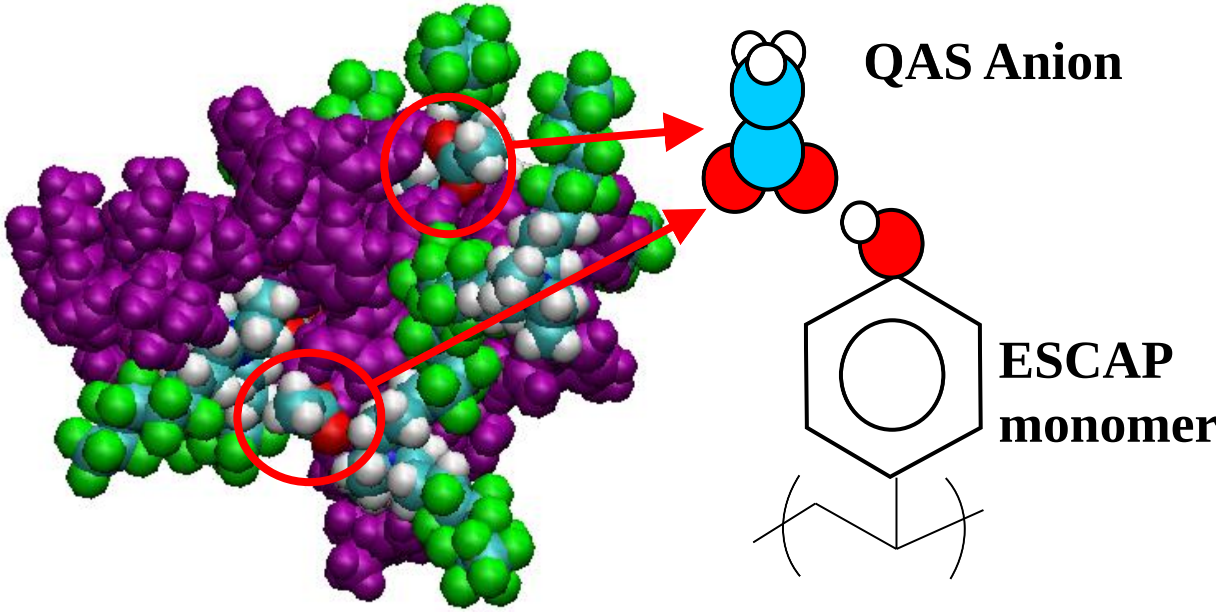
QAS-B4

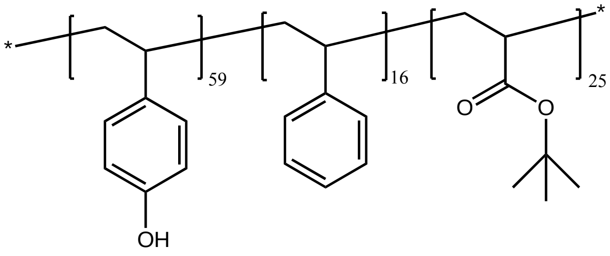


Other QAS-B

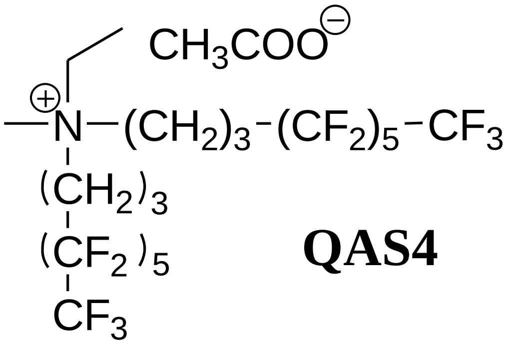
QAS Mechanisms – Example 2

- Soluble with QAS4 additive
- Experimental confirmation
- Forms micelle due to hydrogen bonding with small anion



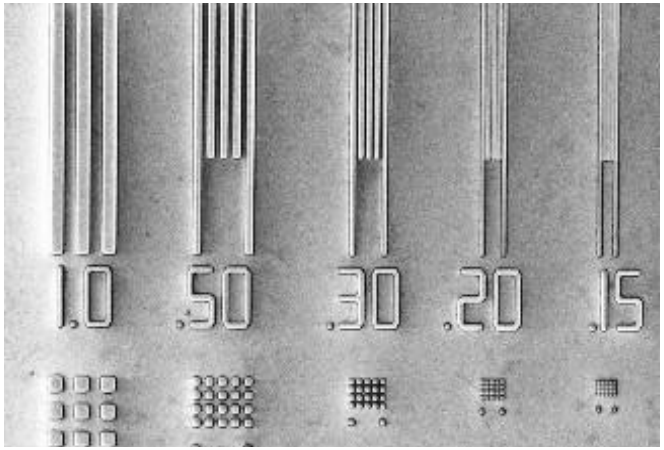


ESCAP



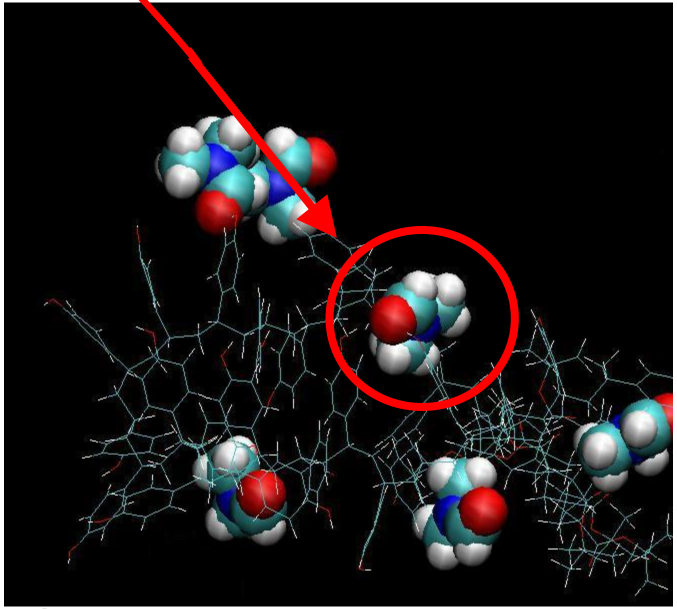
$$\mathrm{CH_3COO}^{\ominus}\qquad -\overset{\oplus}{\underset{\substack{|\\(\mathrm{CH_2})_3\\|\\(\mathrm{CF_2})_5\\|\\\mathrm{CF_3}}}{\mathrm{N}}}-(\mathrm{CH_2})_3-(\mathrm{CF_2})_5-\mathrm{CF_3}$$

QAS4

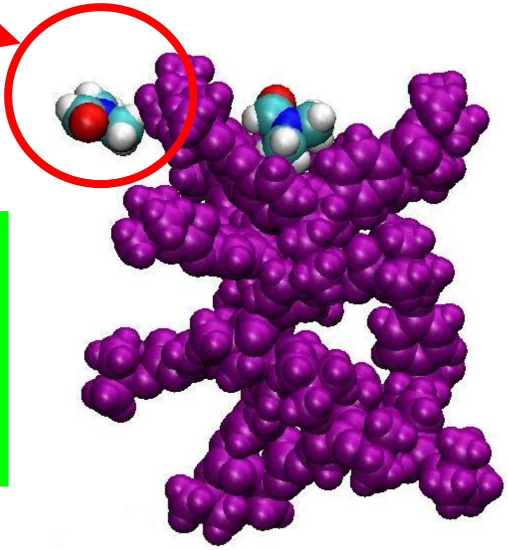


Mechanisms of Non-fluorinated Additves

- Additive was based on applying our understanding of QAS4 effectiveness on ESCAP
- DMAA demonstrates similar hydrogen bonding
- Ineffective with PHOST; obstructs terminal t-butyl group, instead exposing polar region, reducing scCO_2 solubility



Can develop non-fluorinated additives, but they are more resist-specific



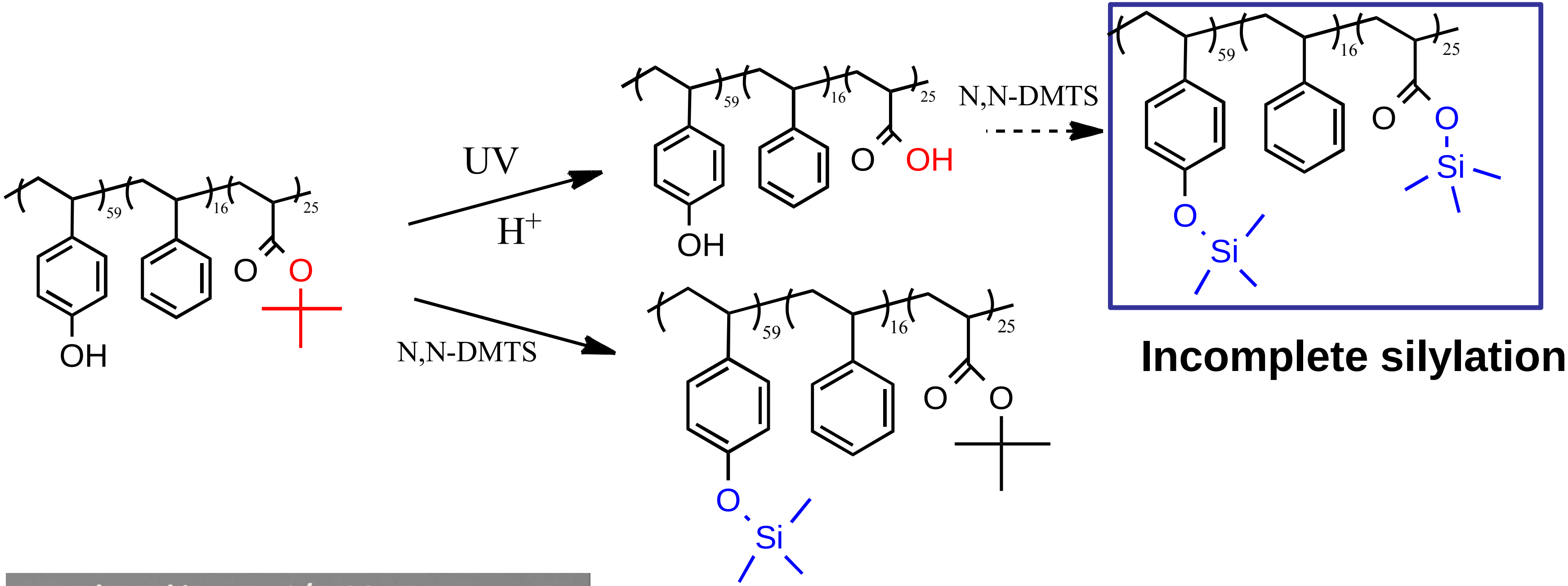
Summary of Simulated Additves with Traditional Photoresits

- Examined polymer resist dissolution enhancement for both protected and unprotected resist
- Developed mechanistic understanding

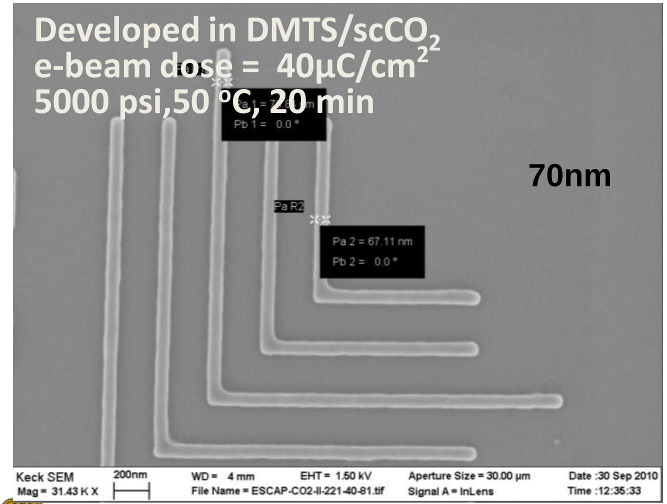
PASS	Possible Pass	FAIL	Untested
🟩	🟨	🟥	⬜

	Additive														
Photoresist	QAS4	QAS6	QAS7	QAS11	QAS12	QAS13	QAS14	Isocyanate	TMDS	HMDS	DMAA	PGMEA	Silane	DMTS	none
ESCAP	🟩	🟩	🟥	⬜	⬜	⬜	⬜	🟨	🟨	🟨	🟩	🟨	🟨	🟩	🟥
193nm	⬜	⬜	⬜	🟥	🟥	🟥	🟩	🟩	🟩	🟩	🟨	🟨	🟩	⬜	🟥
PHOST	🟩	⬜	⬜	⬜	⬜	⬜	⬜	🟨	🟩	🟩	🟥	🟨	⬜	🟩	🟥

$scCO_2$ Development of ESCAP

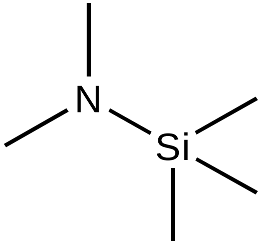


Incomplete silylation


Developed in DMTS/$scCO_2$
e-beam dose = 40µC/cm^2
5000 psi,50 °C, 20 min

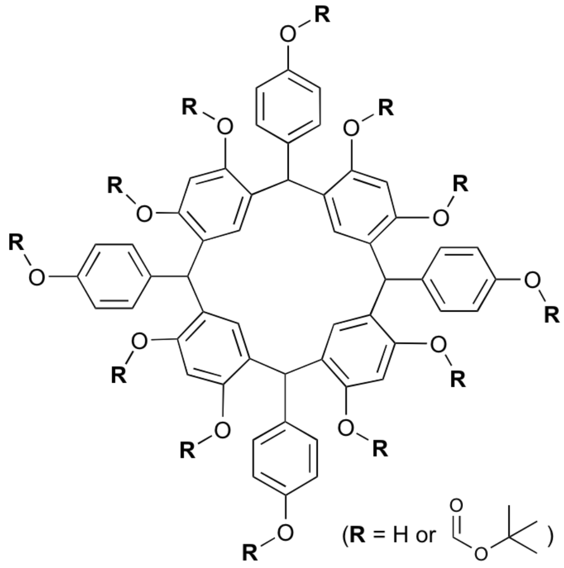
70nm

- **Silicone-containing additive**

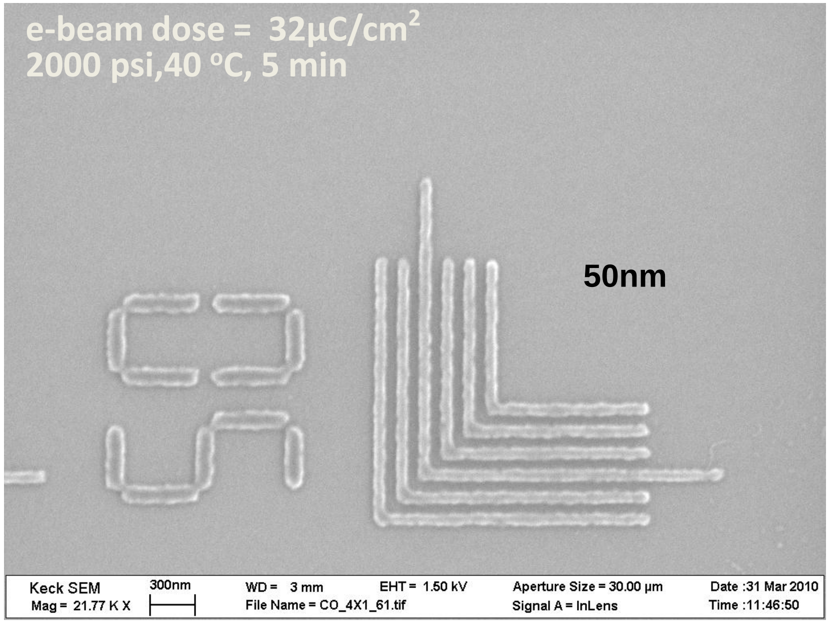


(N,N-Dimethyl)trimethyl silane (N,N-DMTS)

$scCO_2$ Development of Calixarene Resist

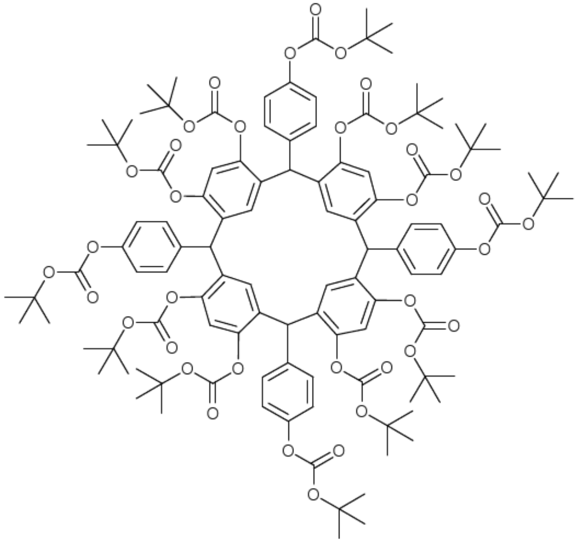


CHPB-boc



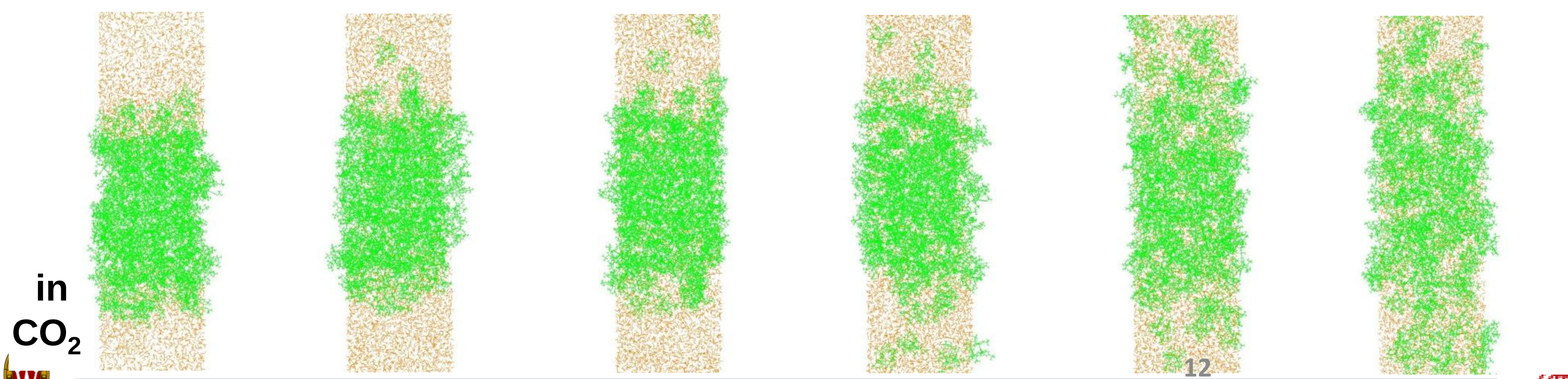
- **Soluble in $scCO_2$ due to small size**
- **Potential to reduce LER and achieve higher resolution**

Predictive Power of Simulation: Calixarene



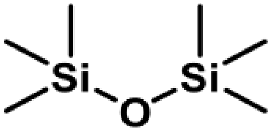
- Molecular glass photoresist capable of high-resolution patterns (low LER)
- Previously we demonstrated its potential via simulation (before experiment)
- Capable of dissolution in $scCO_2$ without any additive (first material to show this property, shown below)
- Viable in siloxane-based solvents also

Time (1-2 ns between images)

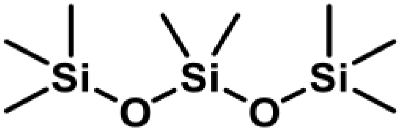


Silicone Fluids-Linear Methyl Siloxanes

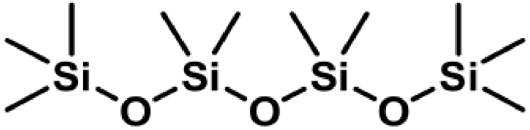
- Low in toxicity
  - Environmentally friendly
  - VOC exempt
- Contribute little to global warming
- Non-ozone depleting
  - replacement for Ozone Depleting Substances
- Low surface tension
  - potential to eliminate patterns collapse
- Can be recycled
  - degrade to naturally occurring chemical species



Hexamethyldisiloxane



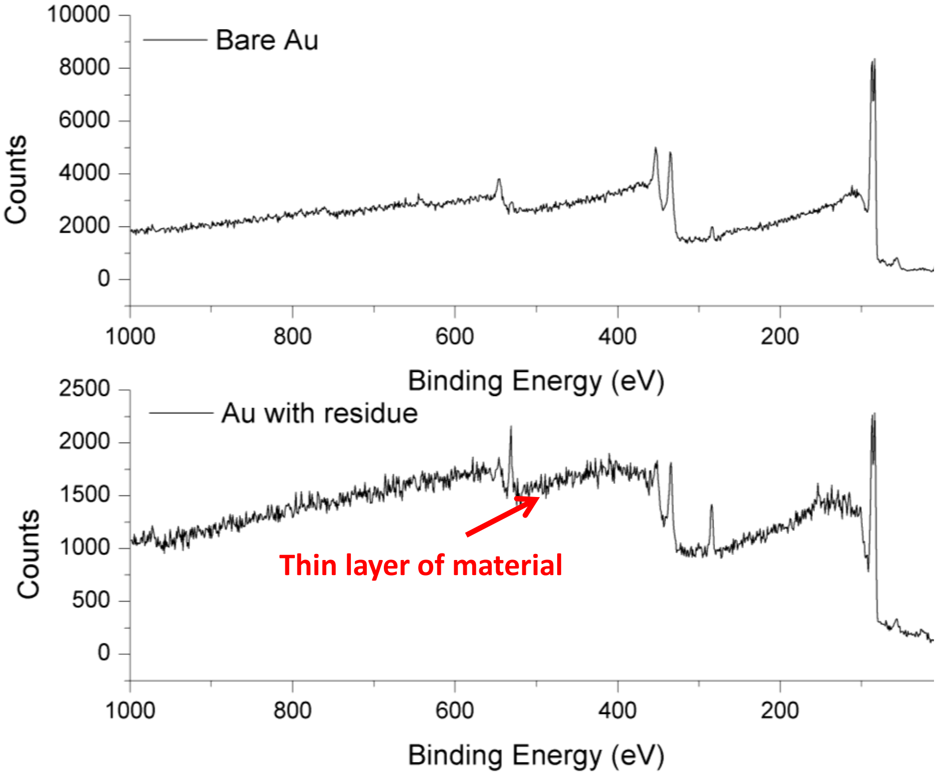
Octamethyltrisiloxane



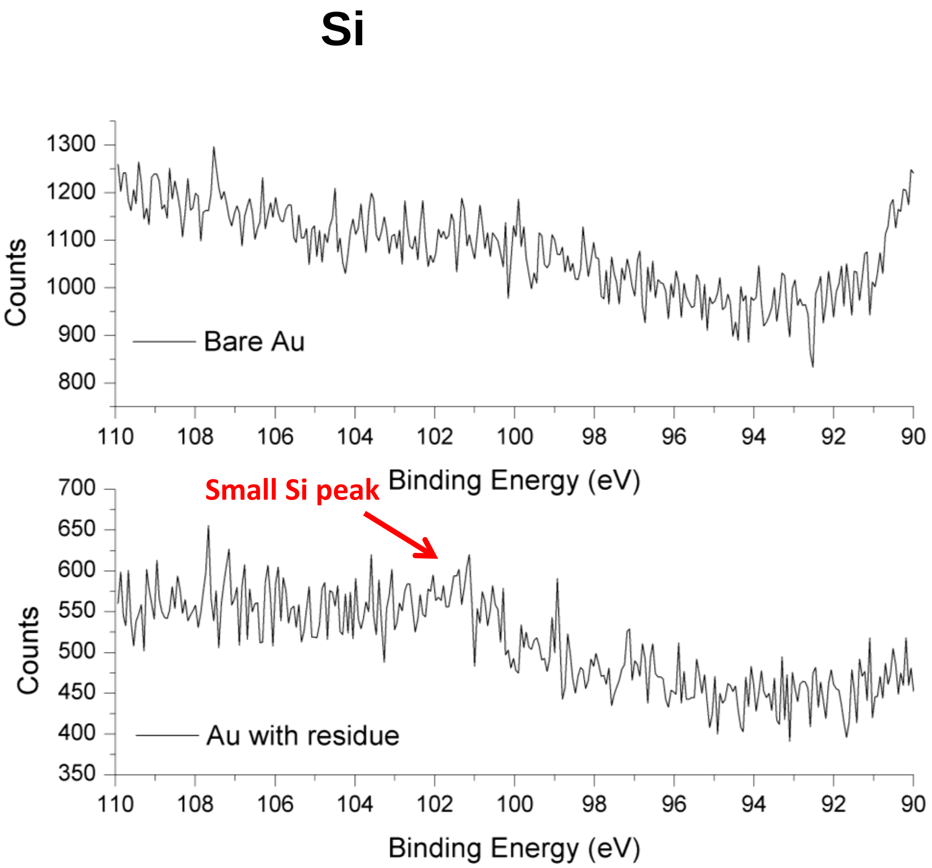
Decamethyltetrasiloxane

D. E. Williams, *ACS Symposium Series*, 2000, 767, 244-257.

XPS Study of Residual Solvent



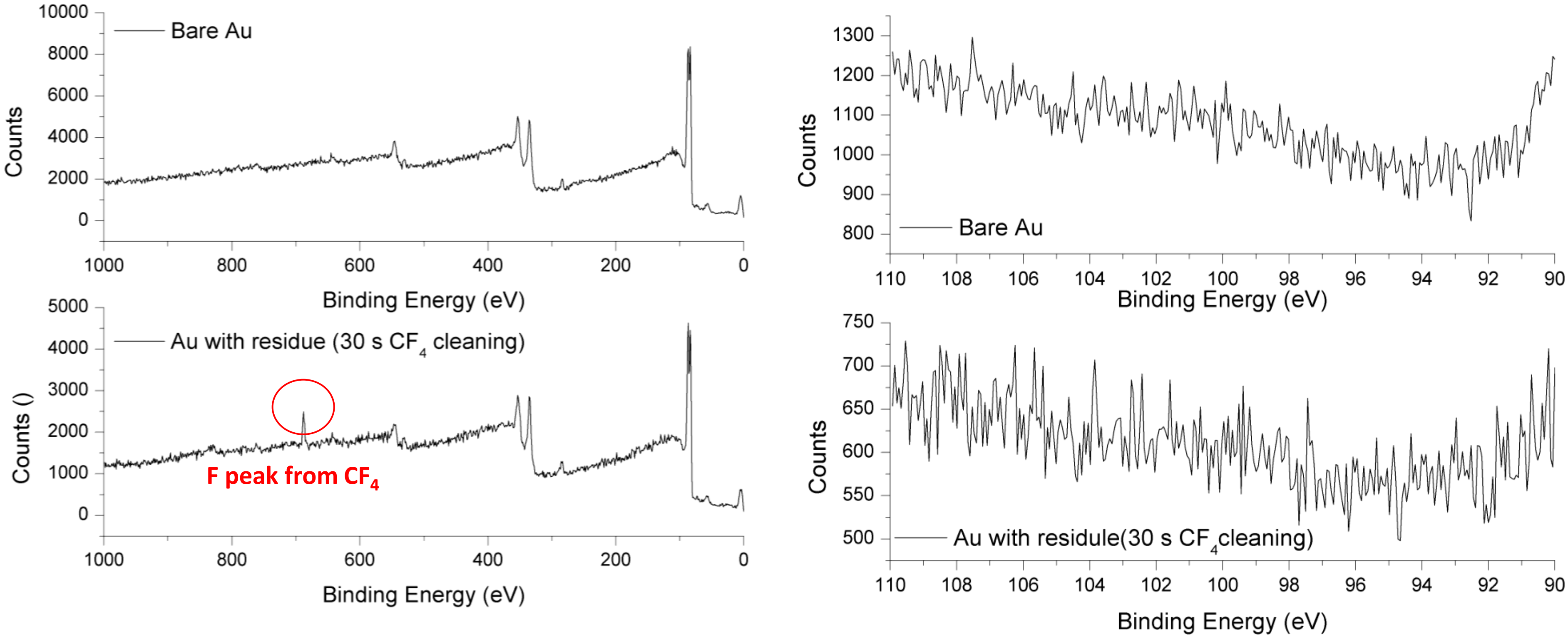
Thin layer of material



Small Si peak

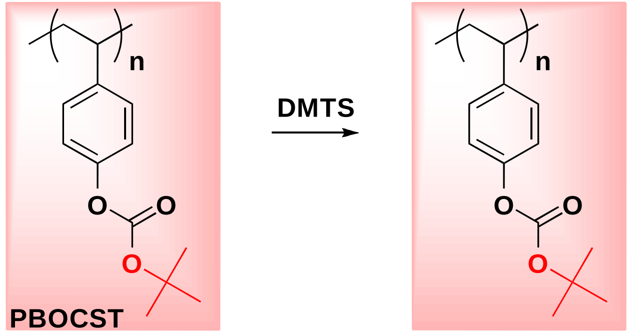
Negligible Si was detected on surface

XPS Study of Residual Solvent

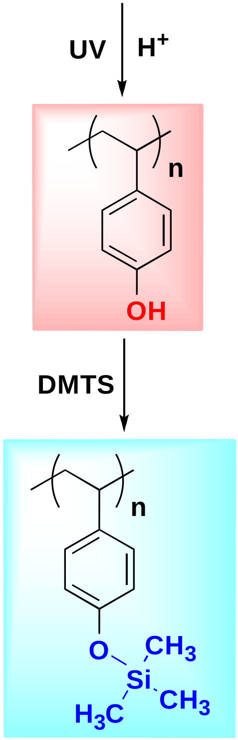


Residue can be easily removed

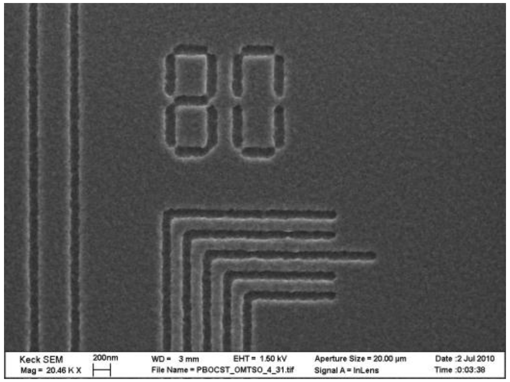
Development of PBOCST in Silicone Fluids



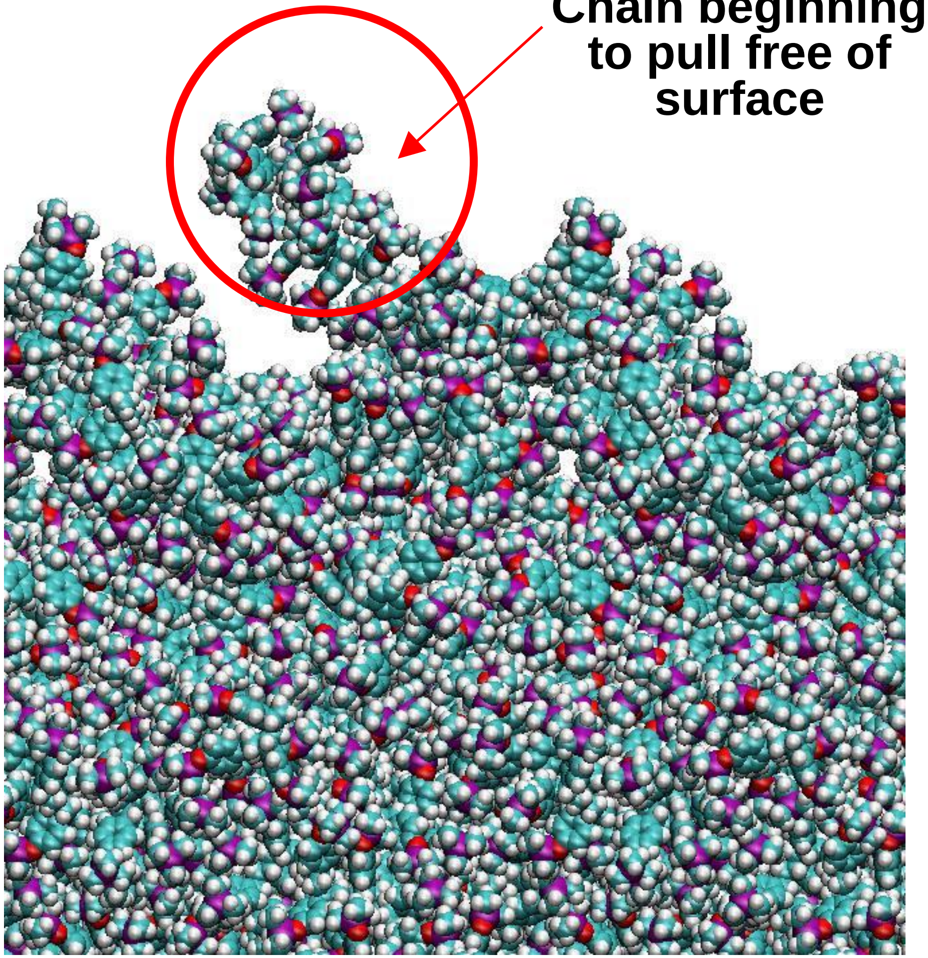
insoluble in silicone-fluids



soluble in silicone-fluids

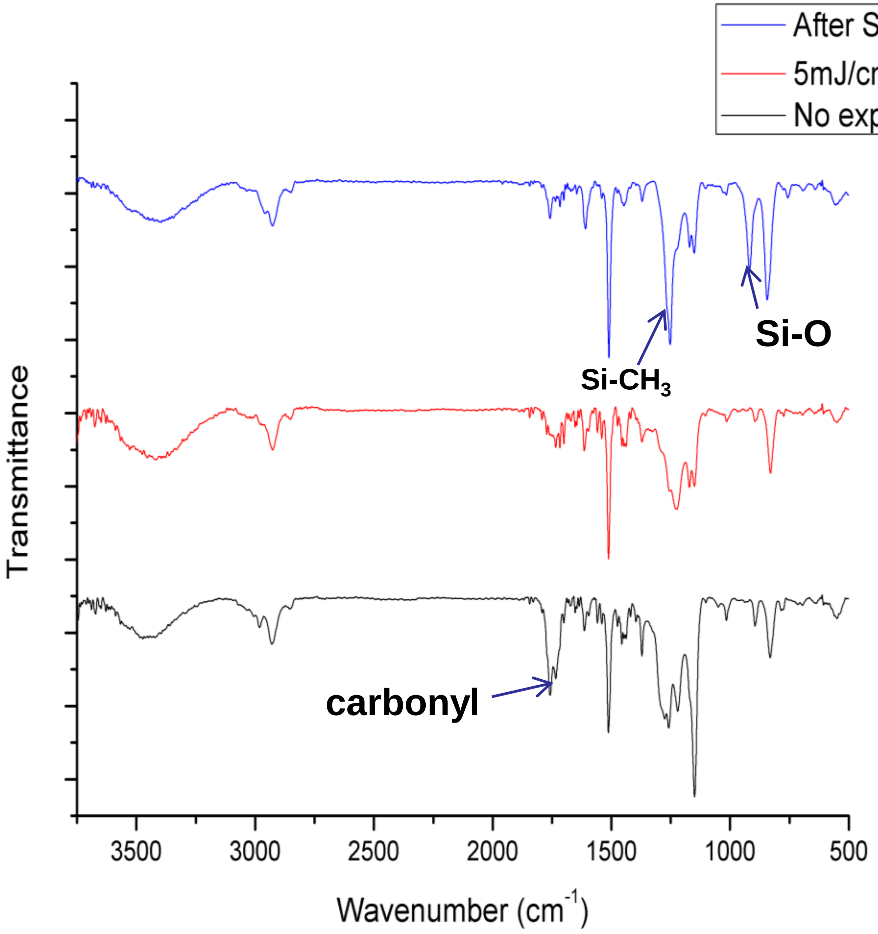


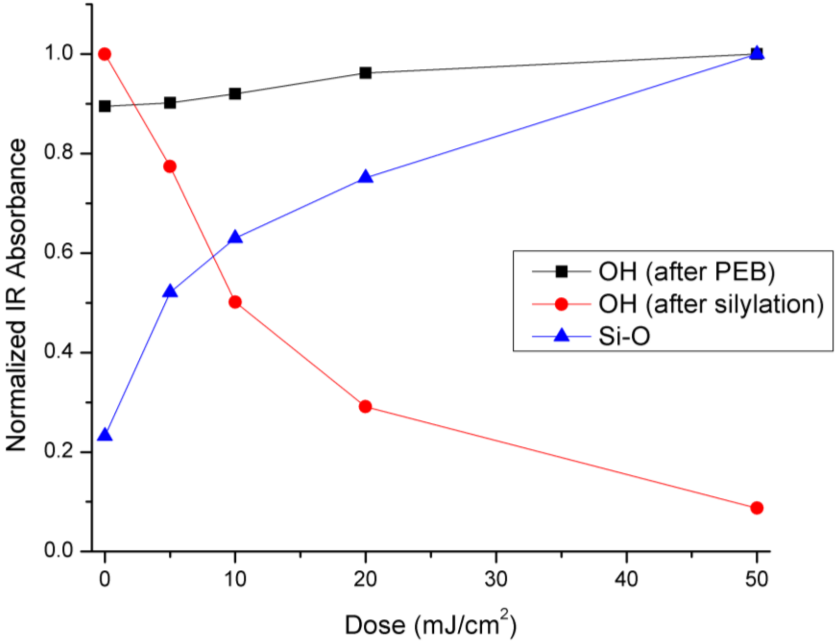
Solvent: DMTS/Octamethyltrisiloxane
e-beam dose = 100µC/cm^2



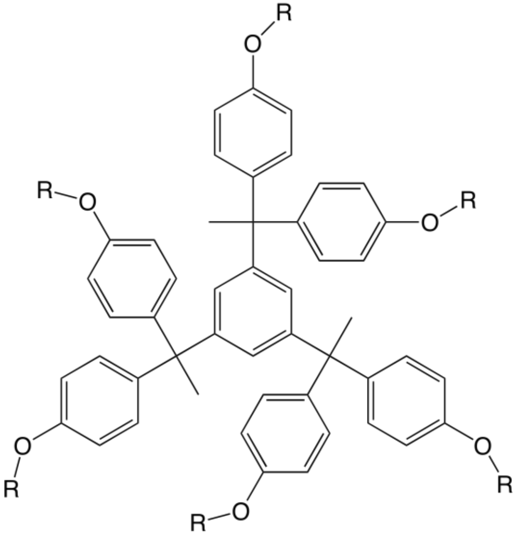
Chain beginning to pull free of surface

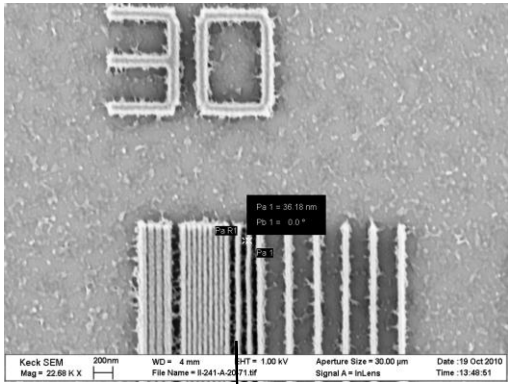
Chemical Contrast of Silylation Process



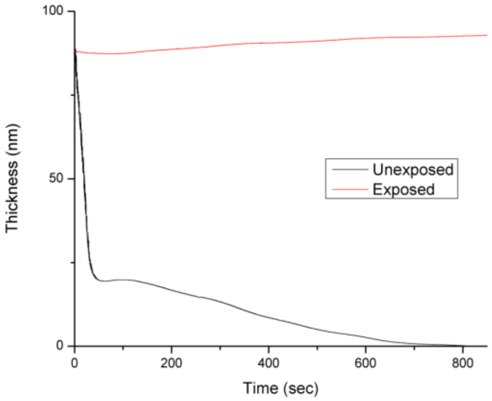


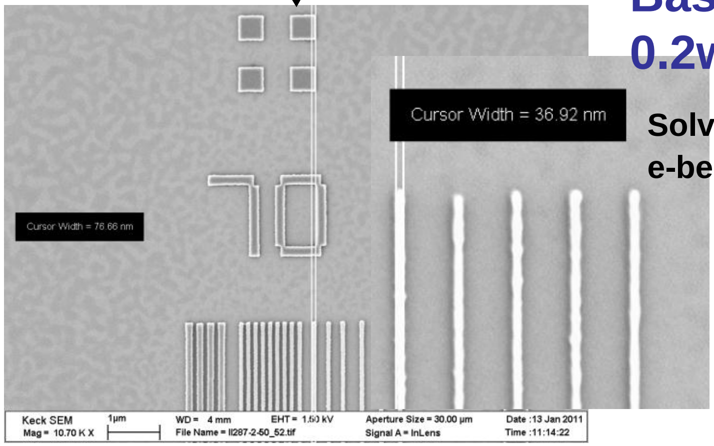
Electron-Beam Patterning and Silicone Fluid Development of Molecular Glass Photoresist





Solvent:Octamethyltrisiloxane
e-beam dose = 20µC/cm^2
microbridging

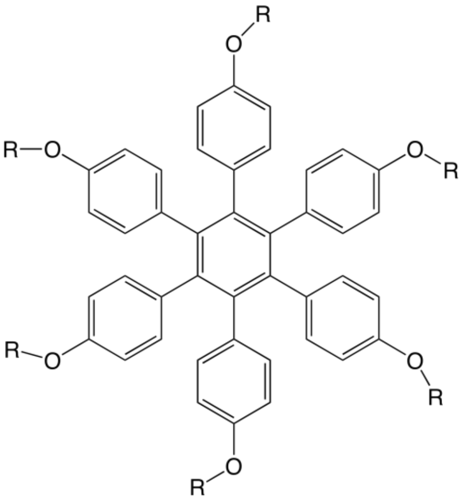


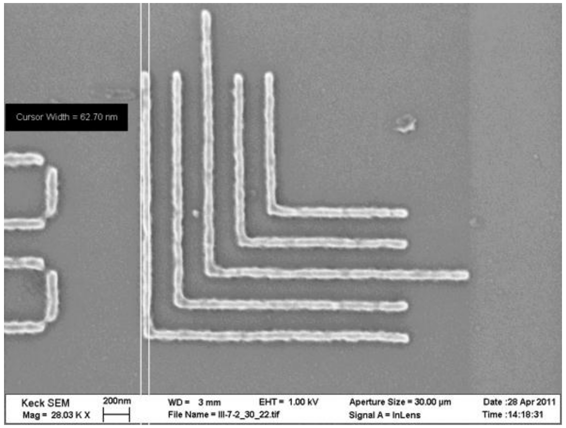


Base quencher
0.2wt %trioctylamine

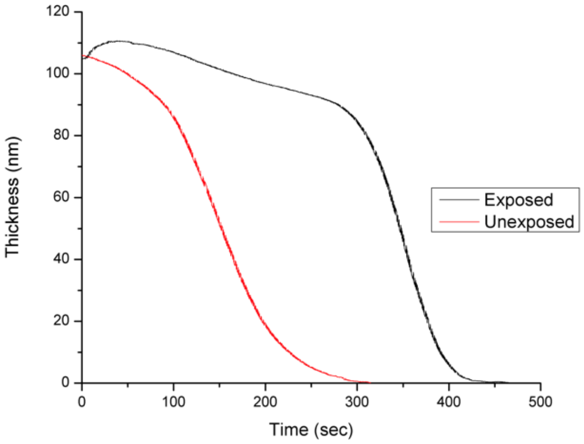
Solvent:octamethyltrisiloxane
e-beam dose = 50µC/cm^2

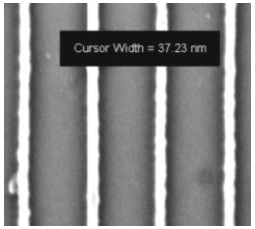
Electron-Beam Patterning and Silicone Fluid Development of Molecular Glass Photoresist





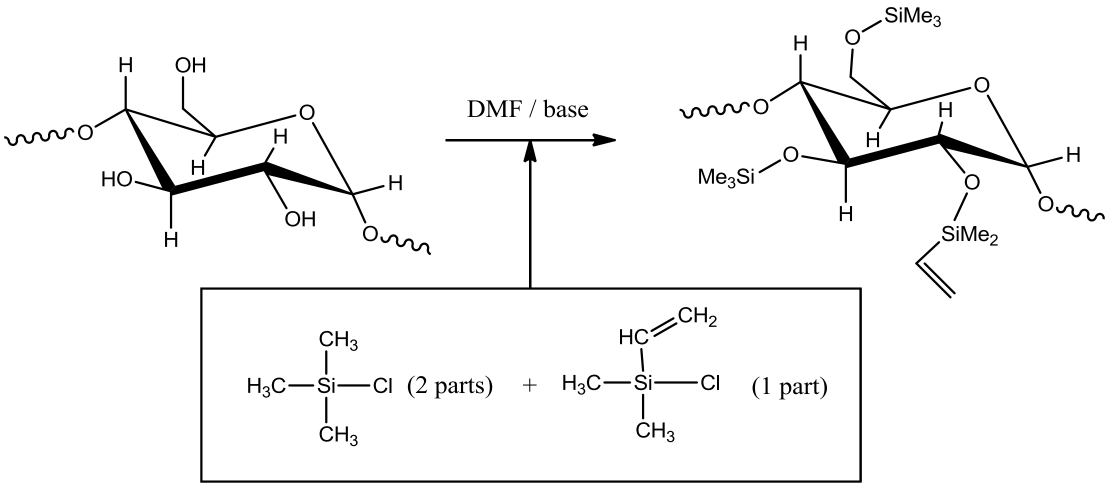
0.25wt% trioctylamine
Solvent:Hexamethyldisiloxane
e-beam dose = 30μC/cm^2

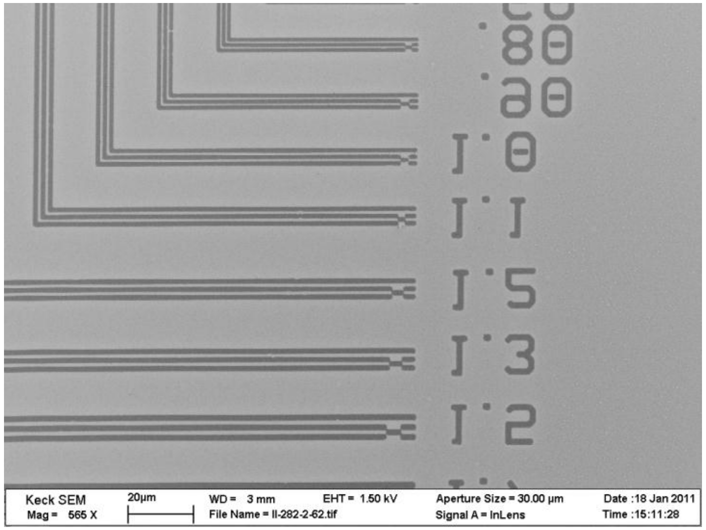




0.3wt% trioctylamine
Solvent:Octamethyltrisiloxane
e-beam dose = 70μC/cm^2

Development of Maltodextrin Photoresists





- Based on natural materials
- Si-containing groups to increase etch resistance and solubility in silicone fluid
- Unexposed form soluble in silicone fluids

Solvent:Octamethyltrisiloxane
254 nm UV light
Dose: 10.2 mJ/cm^2

Model

- **Chose functional form consistent with generic formalism to enable transferability**
- **Parameters derived from quantum mechanical calculation and experimental analysis**
- **Modeled six elementary building blocks from which an arbitrary structure can be created**

Model Formalism:

$$V_{Total} = \underbrace{V_{LJ} + V_{Coul}}_{\text{Intermolecular}} + \underbrace{V_{Bond} + V_{Ang} + V_{Tors}}_{\text{Intramolecular}}$$

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

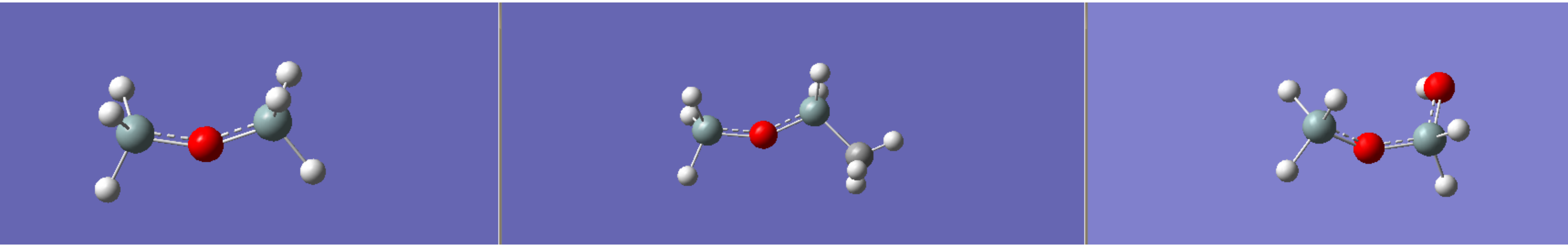
$$V_{Coul} = \frac{q_i q_j}{4\epsilon_0 \epsilon r}$$

$$V_{Bond} = \frac{1}{2} k_{Bond} \left(r - r_0\right)^2$$

$$V_{Ang} = \frac{1}{2} k_{Ang} \left(\theta - \theta_0\right)^2$$

$$V_{Tors} = \sum_{n=0}^{5} c_n \cdot cos(\phi)^n$$

Sample elementary building blocks:



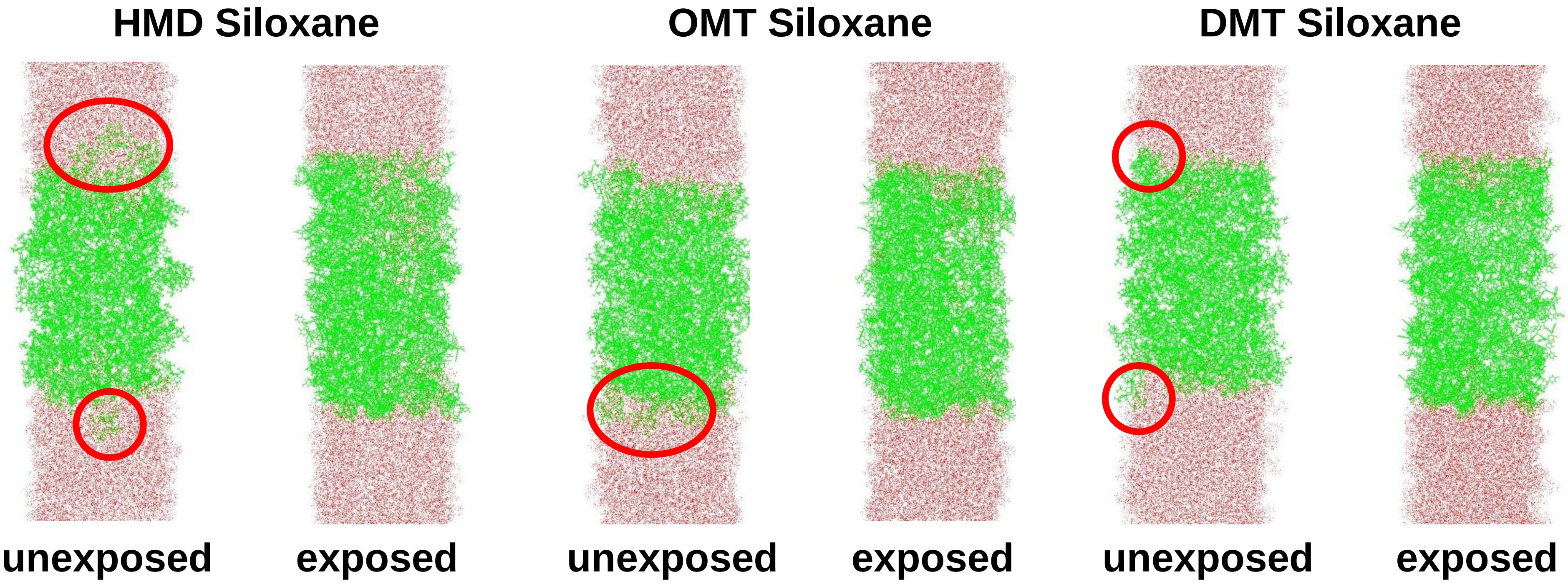
Experimental Measurables

	HMD Siloxane		OMT Siloxane		DMT Siloxane	
	Experimental	Model	Experimental	Model	Experimental	Model
Heat of Vaporization (kcal/mol)	7.2	7.1	8.5	10.1	12.0	13.2
Specific Heat (cal/g*K)	0.46	0.21	0.29	0.42	0.41	0.65
Density (g/ml)	0.764	0.758	0.820	0.836	0.854	0.875
Dipole Moment (Debye)	Unknown	1.016	Unknown	1.203	Unknown	2.0553
Dielectric Constant	Unknown	1.339	Unknown	1.400	Unknown	1.875

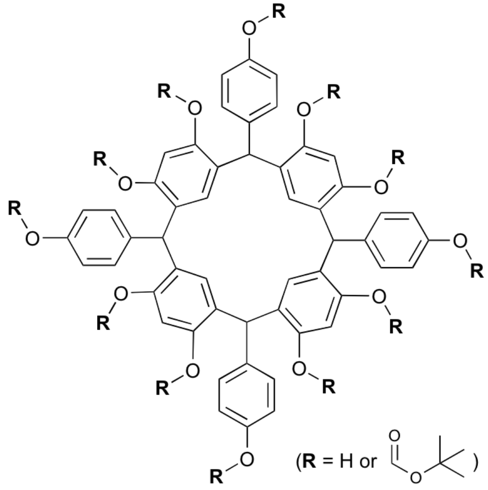
- **Good agreement with known properties**
- **Model suggested error in literature of OMTSiloxane heat of vaporization, repeat of measurement confirmed model was correct**

Calixarene Simulation Results

- **Calixarene after 10ns in Siloxane solvents:**
  - **Unexposed photoresist molecules breaking away from surface**
  - **Exposed photoresist makes smooth interface with solvent**
  - **Negative tone resist**
  - **Excellent experimental agreement**

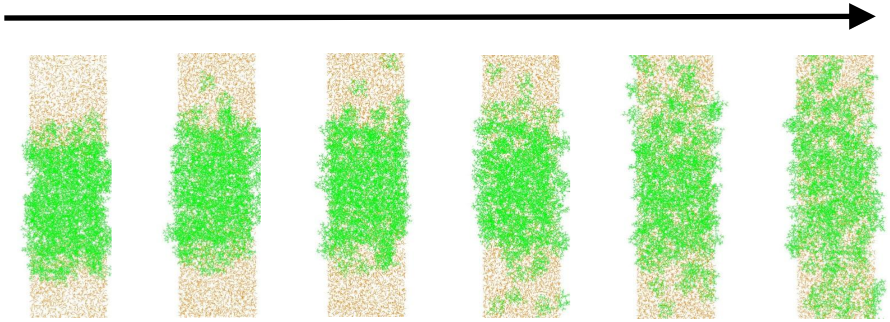


Interactions with de Pablo Group



CHPB-boc

Time (1-2ns between images)



Ober Group

- Provide experimental results
- Development process
- Synthesize photoresists

monthly teleconference

- Computer Simulations
- Pre-screening of possible photoresist structures
- Provide information on dissolution mechanism at a molecular level

de Pablo Group

Future Plans

Next Year Plans (seed effort)

- Continue successful studies of $scCO_2$ and silicone fluid processable photoresists with computational studies as a guide for new photoresist structures
- Expand range of environmentally friendly solvents with excellent performance
- Examine unique solubility characteristics of molecular glasses as photoresists for non-polar solvent development
- Explore environmentally benign, naturally occurring cores (e.g. cyclodextrin) for next generation high-resolution molecular glass photoresists

Long-Term Plans

- Identify additional additives for $scCO_2$ and environmentally friendly silicone fluids to develop other conventional photoresists
- Create new chemistries for patterning and functionalizing small, non-polar molecules in $scCO_2$ and silicone fluids

Industrial Interactions and Technology Transfer

- **Discussions with Dow electronics on non-polar solvent development**
- **Interactions with Robert Allen from IBM**
- **Interactions with Kenji Yoshimoto from Global Foundries**
- **Former student (N. Felix) hired by IBM Fishkill Research Center**
- **Jing Sha hired by Intel**
- **Collaboration with Albany Nanotech for EUV exposures**

Publications, Presentations, and Recognitions/Awards

Publications

- C. Y. Ouyang, J.-K. Lee, M. E. Krysak, J. Sha, C. K. Ober, "*Environmentally Friendly Patterning of Thin Films in Linear Methyl Siloxanes, " Journal of Materials Chemistry* (2012)
- C. Y. Ouyang, J.-K. Lee, C. K. Ober, *"Studies of Environmentally Friendly Solvent-based Developers," Journal of Photopolymer Science and Technology*(2011), 24(2), 239-240
- C. Y. Ouyang, J.-K. Lee, M. E. Krysak, C. K. Ober, *"Environmentally Friendly Patterning of Conventional Photoresists in Silicone Fluids, " Proceedings of SPIE*(2011),79720O
- C. Y. Ouyang, J.-K. Lee, C. K. Ober, "*Environmentally Friendly Development of Conventional Polymeric Photoresists Using Non-Polar Silicone Fluids, " ACS Preprints (2011)*
- C. Y. Ouyang, J.-K. Lee, J. Sha, C. K. Ober, "*Environmentally Friendly Processing of Photoresists in scCO*$_2$ *and decamethyltetrasiloxanes", Proceedings of SPIE* (2010), 7639
- C. K. Ober, C. Y. Ouyang, J.-K. Lee, J. Sha, "*Green Processing of Photoresists in non-polar fluids for high resolution patterning*", ACS preprtins (2010)
- A. Rastogi, M. Tanaka, G. N. Toepperwein, R. A. Riggleman, J. J. dePablo, C. K. Ober, "*Fluorinated Quaternary Ammonium Salts as Dissolution Aids for Polar Polymers in Environmentally Benign Supercritical Carbon Dioxide*", *Chem. Mater.* (2009), 21(14), 3121-3135.

Presentations

- Advances in Resist Materials and Processing Technology XXVI conference (part of the SPIE Symposium on Advanced Lithography) (Feb 2011). "*Environmentally Friendly Patterning of Conventional Photoresists in Silicone Fluids*"
- ERC Teleseminar (Aug2011). "Environmentally Friendly Non-Aqueous Development"
- 28th International Conference of Photopolymer Science and Technology(Jun 2011). *"Studies of Environmentally Friendly Solvent-based Developers"*
- *241st ACS National Meeting* (Mar 2011). "*Environmentally Friendly Development of Conventional Polymeric Photoresists Using Non-Polar Silicone Fluids."*