Supercritical Carbon Dioxide Compatible Additives:

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

(Task Number: 425.030)

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

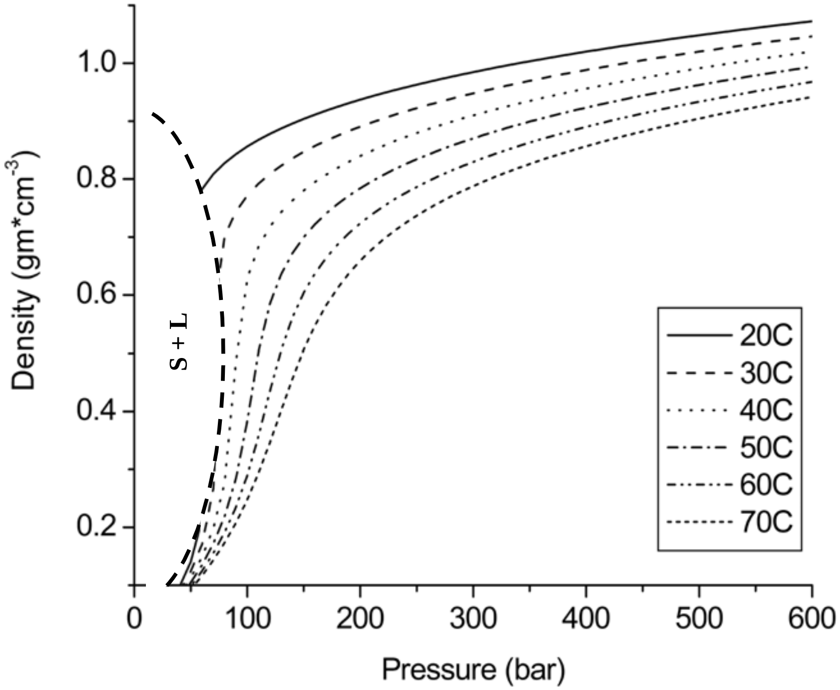
4. Reduction in the use of chemicals

Minimal use of organic solvents

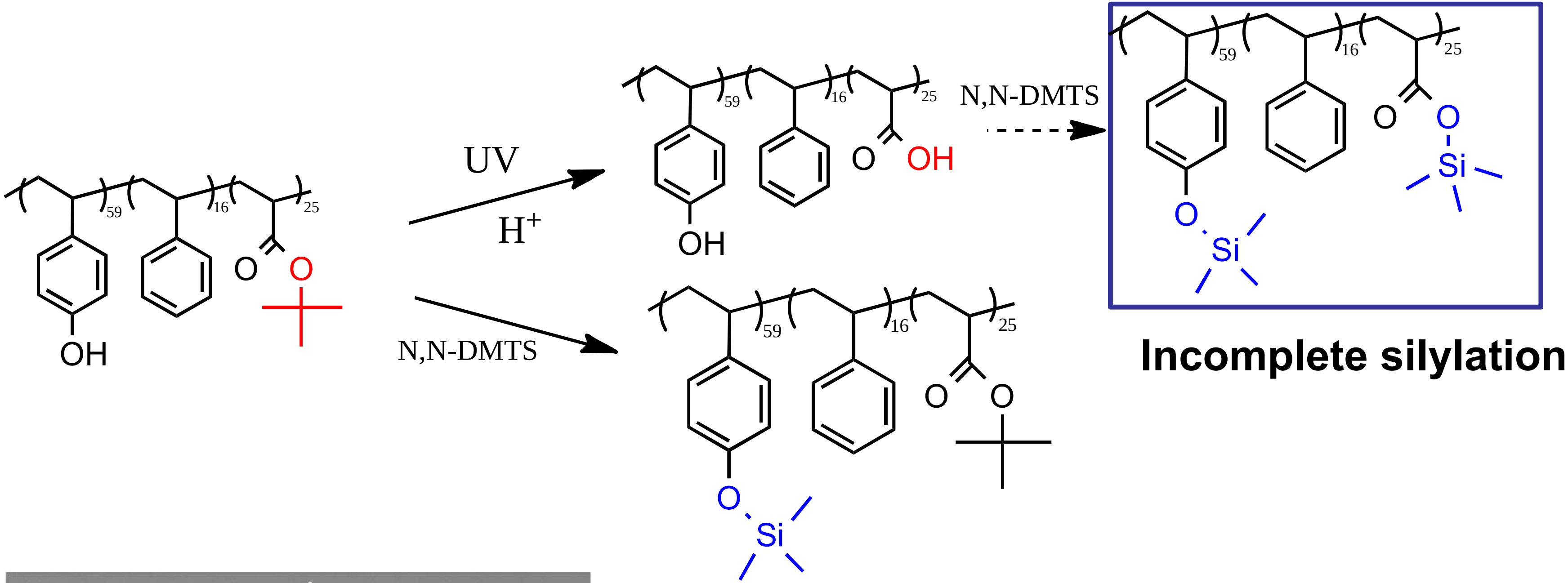
Why a Non-Aqueous Developer Solvent?

Environmental and Performance Advantages of $scCO_2$

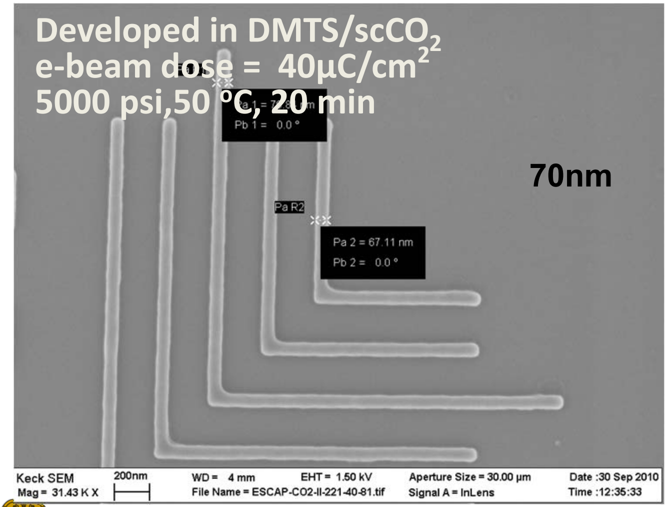
- Environmentally friendly, zero VOC solvent
- Highly tunable solvating power
  - $\rho(T,P)$
  - Leaves no residue
  - Clean separations
- One-phase fluid
  - Zero surface tension
  - Transport, viscosity between that of liquid and gas
- Nonpolar, inert character
- Potential to reduce LER and eliminate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



scCO$_2$ Development of ESCAP

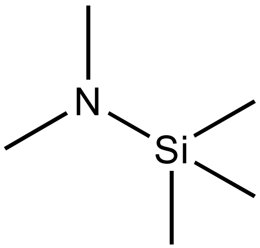


Incomplete silylation


Developed in DMTS/scCO$_2$
e-beam dose = 40µC/cm^2
5000 psi, 50 °C, 20 min

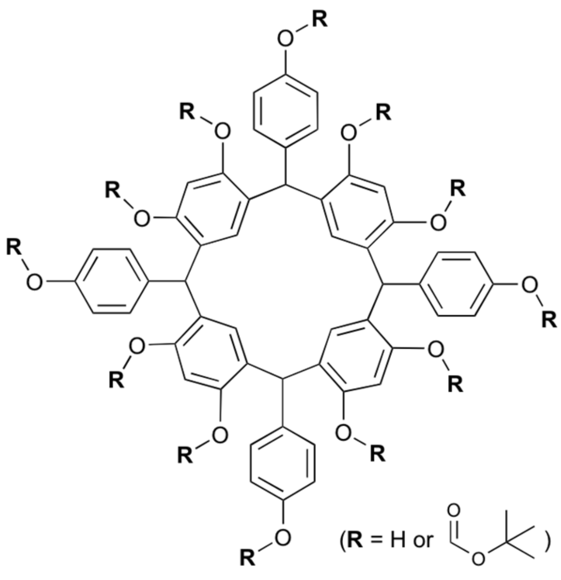
70nm

- **Silicone-containing additive**

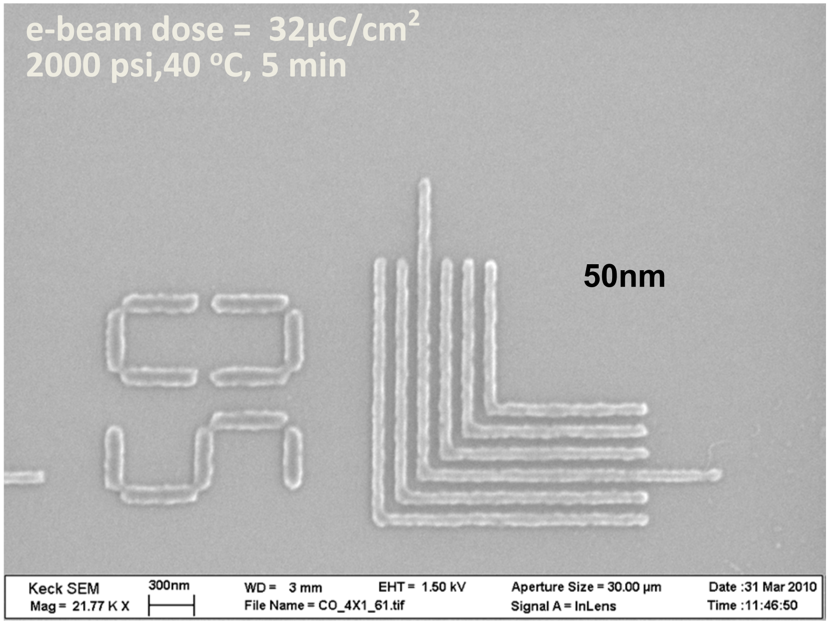


(N,N-Dimethyl)trimethyl silane (N,N-DMTS)

$scCO_2$ Development of Calixarene Resist



CHPB-boc



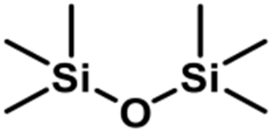
e-beam dose = 32μC/cm^2
2000 psi,40 °C, 5 min

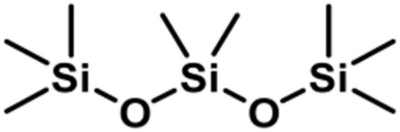
- **Soluble in $scCO_2$ due to small size**
- **Potential to reduce LER and achieve higher resolution**

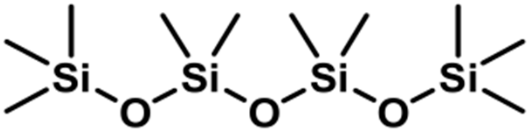
Silicone Fluids-Linear Methyl Siloxanes

- 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

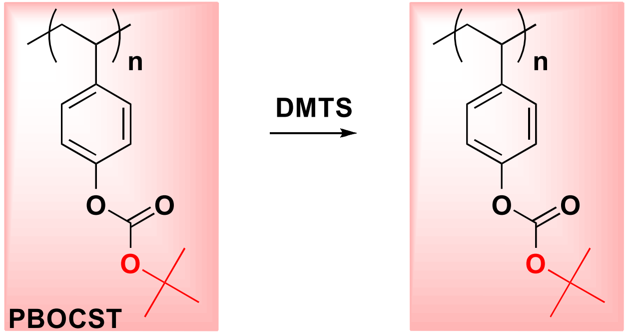

Hexamethyldisiloxane


Octamethyltrisiloxane

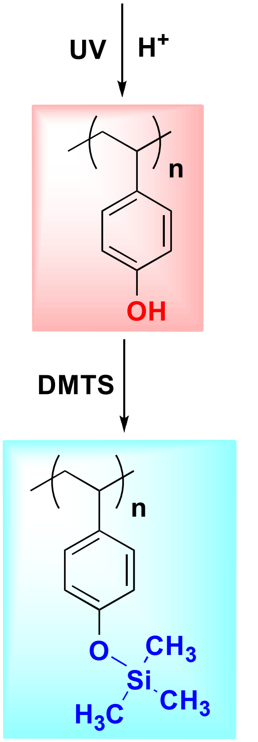

Decamethyltetrasiloxane

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

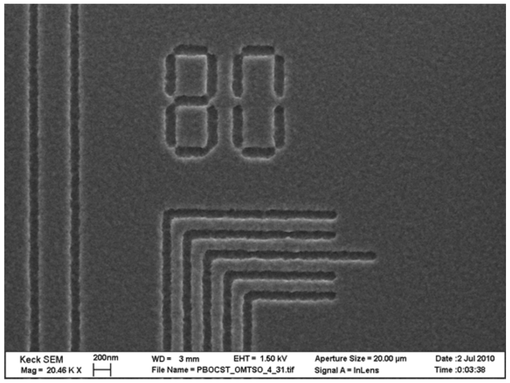
Development of PBOCST in Silicone Fluids



insoluble in silicone-fluids

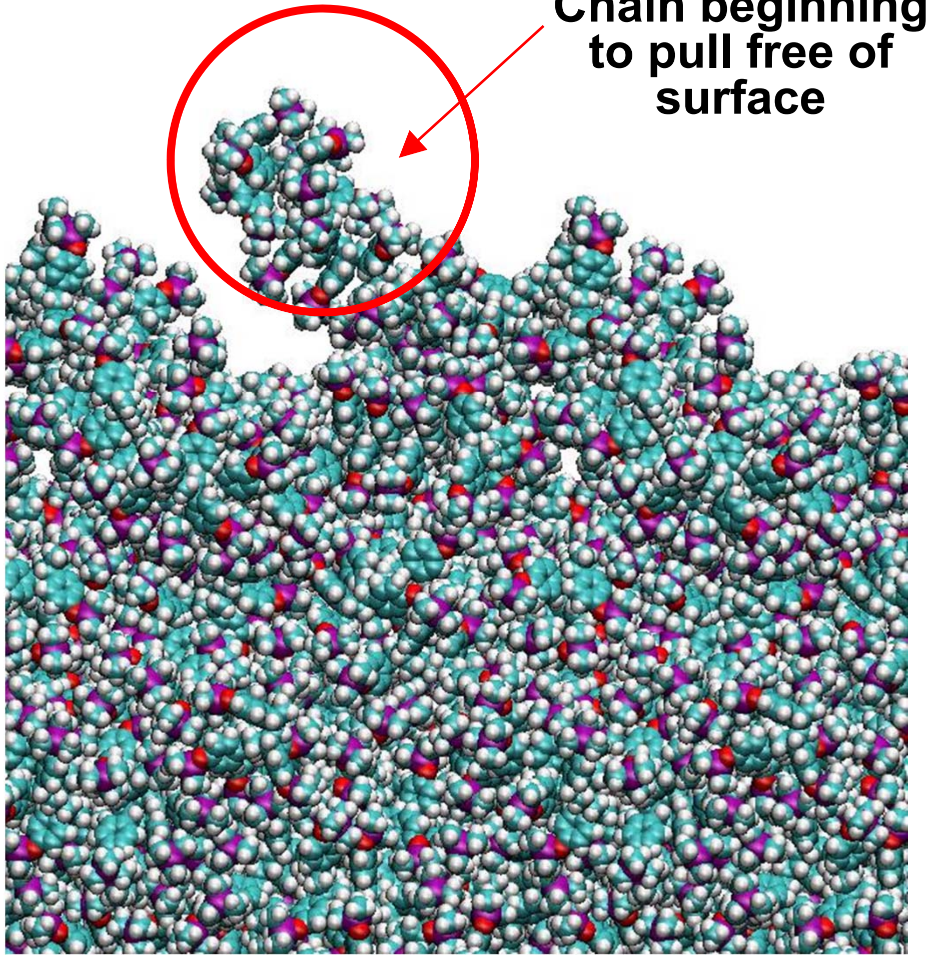


soluble in silicone-fluids

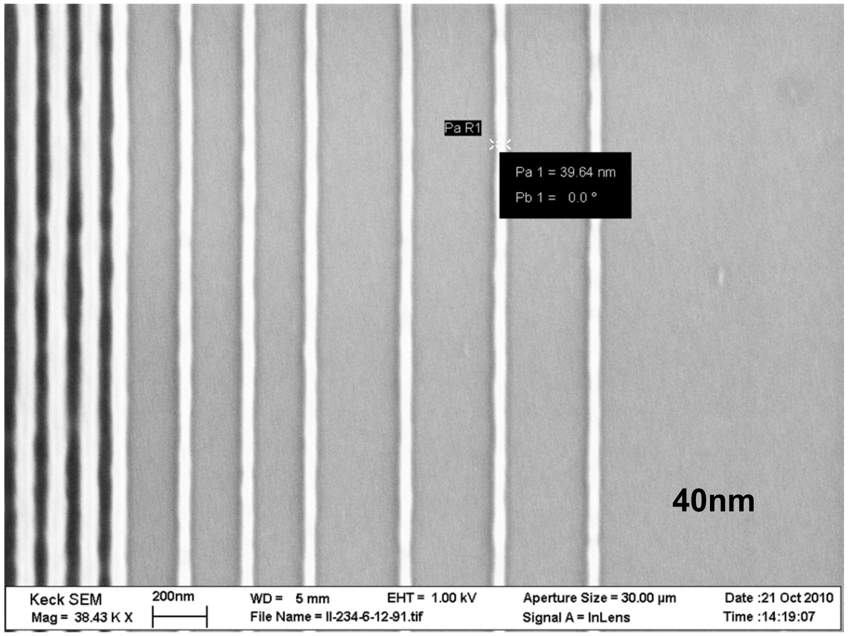


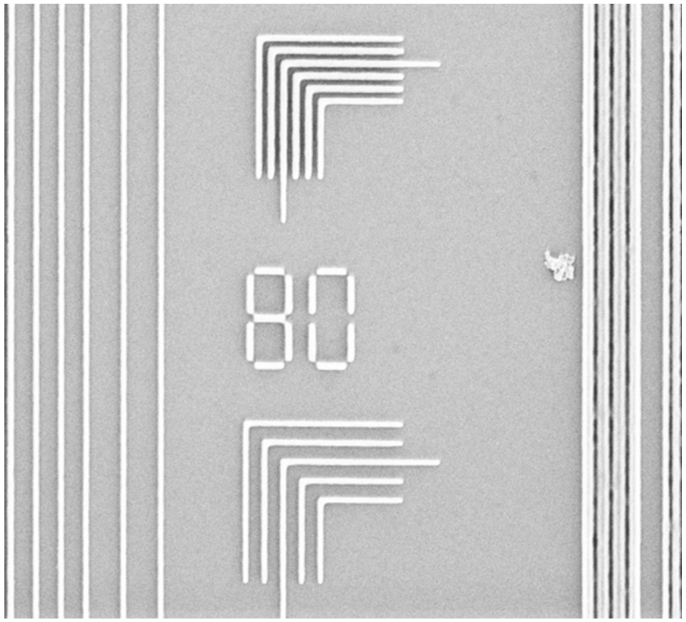
Solvent: DMTS/Octamethyltrisiloxane
e-beam dose = 100μC/cm^2

Chain beginning to pull free of surface



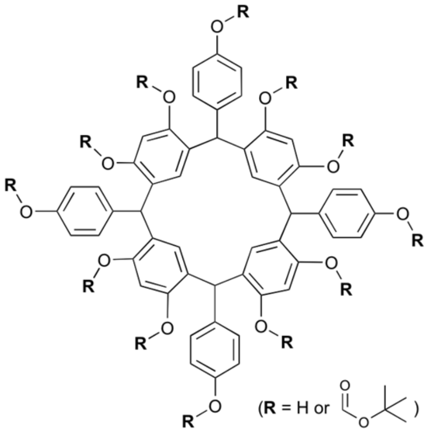
Electron-Beam Patterning and Silicone Fluid Development of Conventional Photoresists





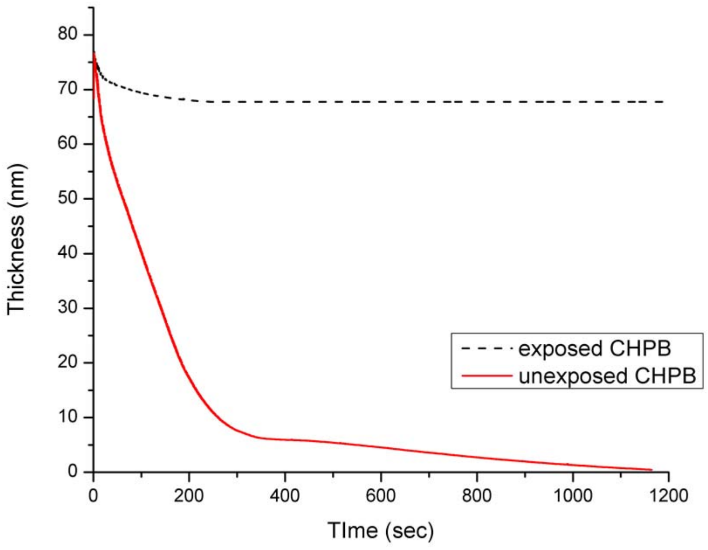
TOK photoresist
DMTS: HMDSO=1:20 at 40^{o}C for 40 minutes
Resist film thickness ~350 nm

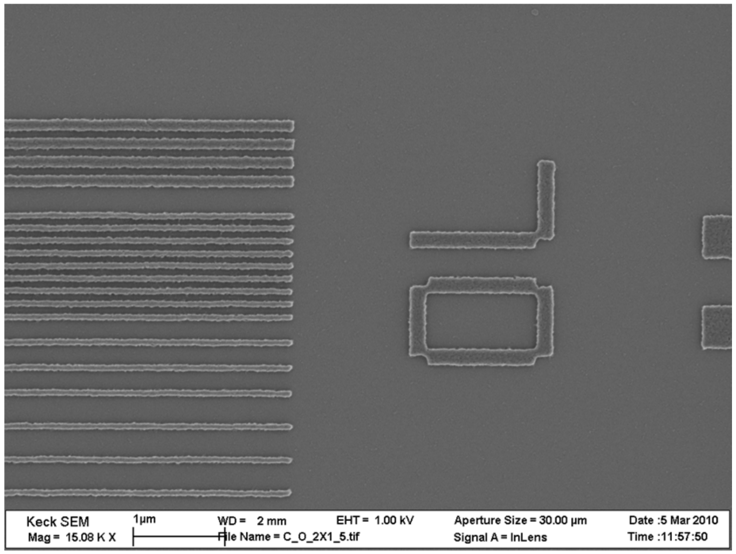
Electron-Beam Patterning and Silicone Fluid Development of Calixarene Resist



CHPB-boc

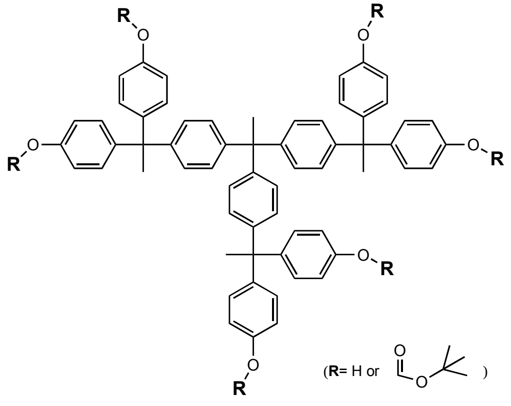
QCM of CHPB in hexamethyldisiloxane



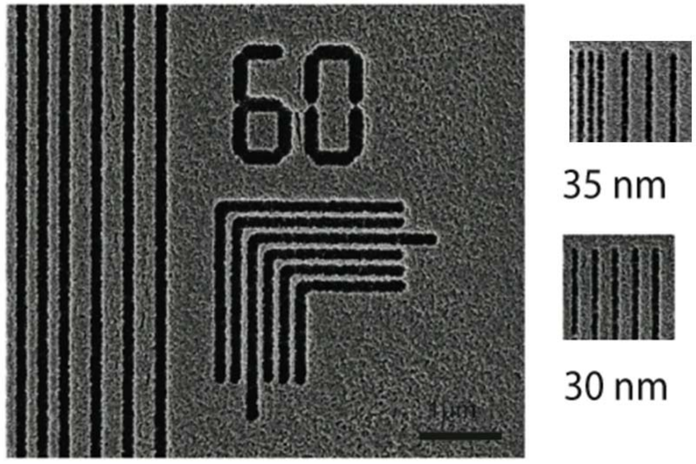


Solvent:Octamethyltrisiloxane
e-beam dose = 32μC/cm^2

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



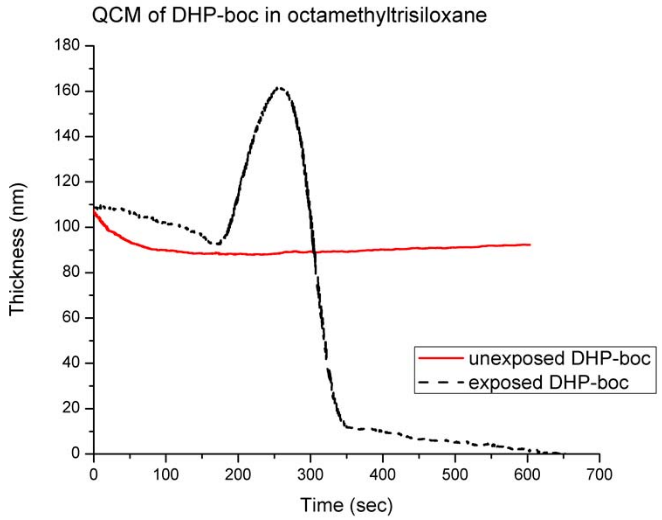
DHP-boc



35 nm

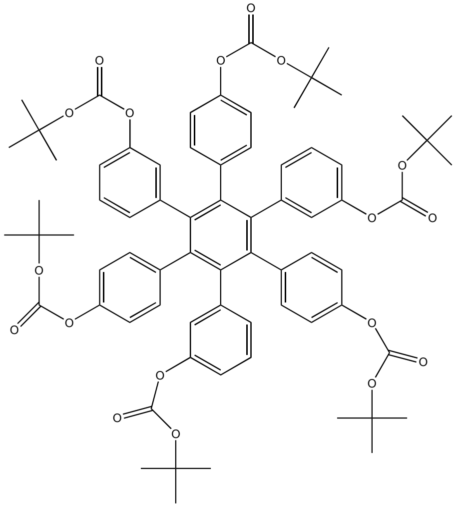
30 nm

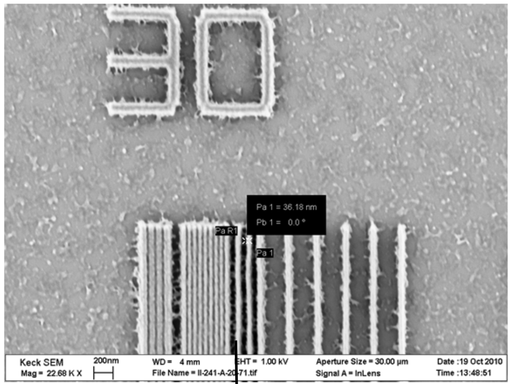
60 nm



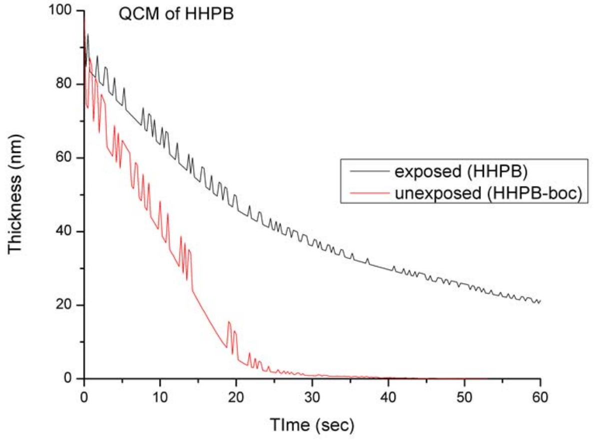
Solvent: DMTS/octamethyltetrasiloxane
e-beam dose: 40μC/cm^2
Aspect ratio~5:1

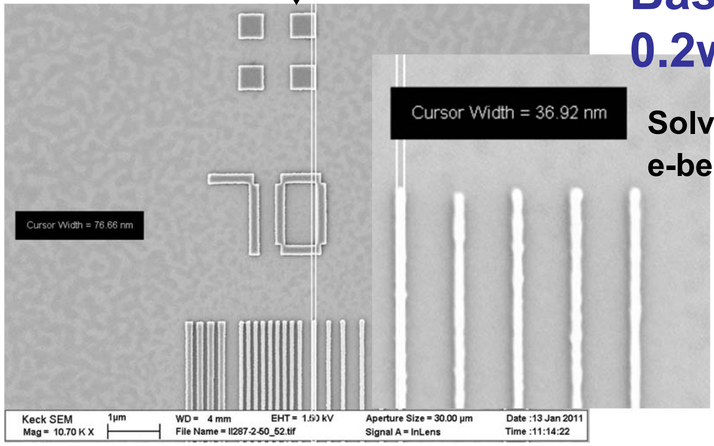
Electron-Beam Patterning and Silicone Fluid Development of Molecular Glass Photoresist





Solvent:Octamethyltrisiloxane
e-beam dose = $20 \mu C/cm^2$
microbridging

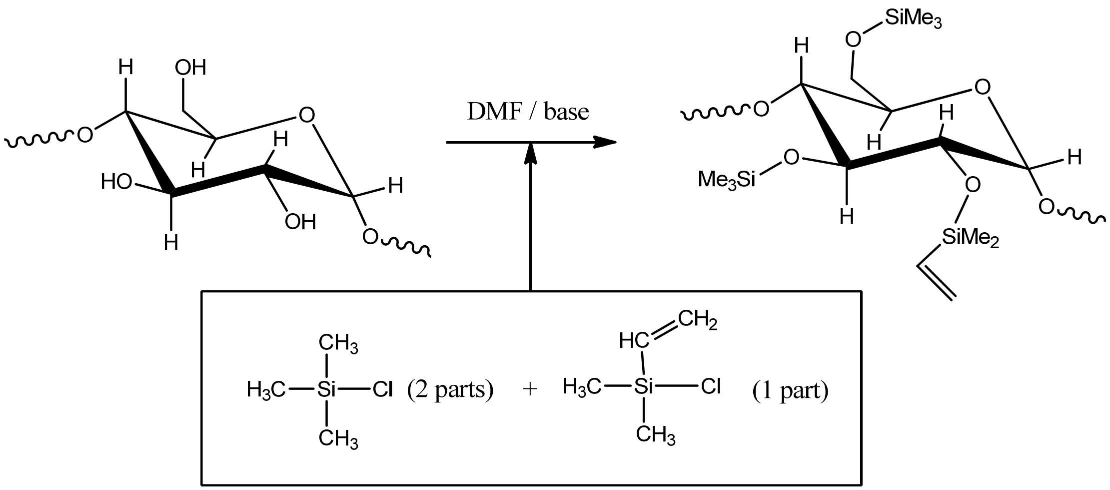


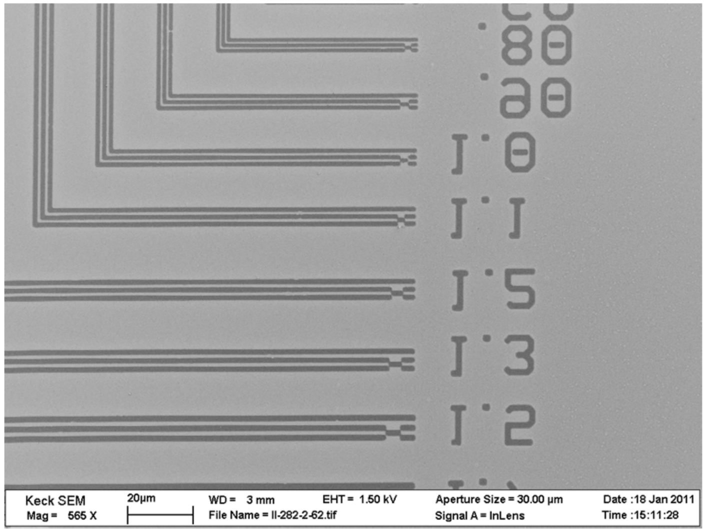


Base quencher
0.2wt %trioctylamine

Solvent:octamethyltrisiloxane
e-beam dose = $50 \mu C/cm^2$

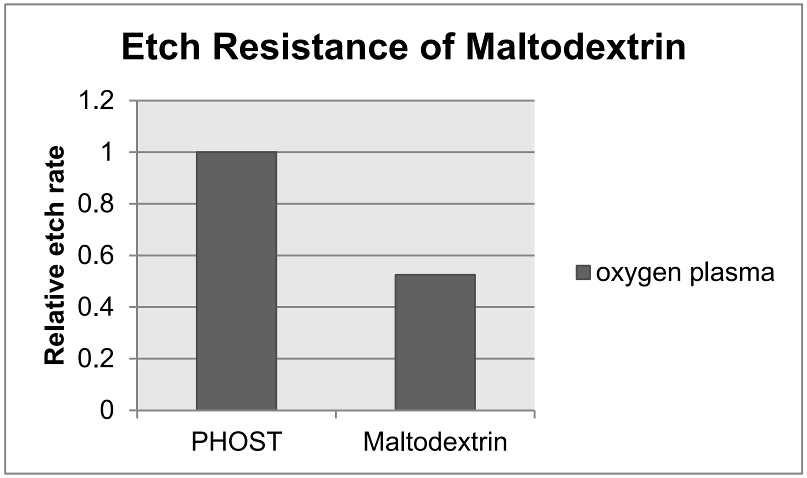
Development of Maltodextrin Photoresists



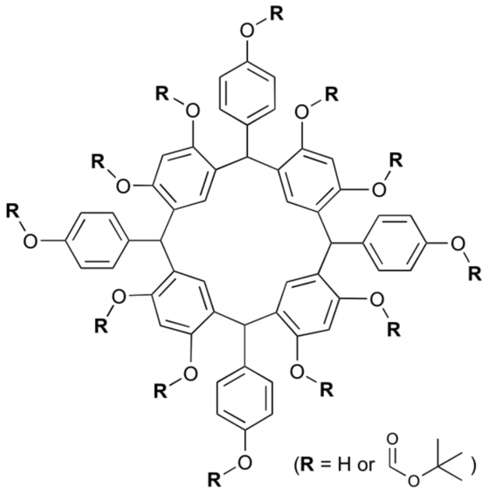


Solvent:Octamethyltrisiloxane
254 nm UV light
Dose: 10.2 mJ/cm^2

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

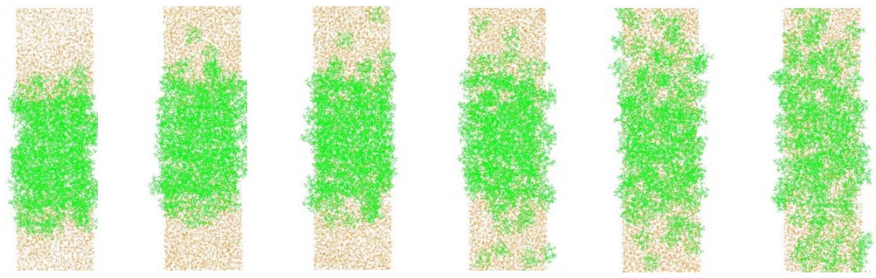


Interactions with de Pablo Group



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 Foundry**
- **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

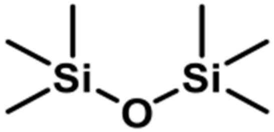
- C. Y. Ouyang, J.-K. Lee, J. Sha, C. K. Ober, "*Environmentally Friendly Processing of Photoresists in scCO_2 and decamethyltetrasiloxanes*", *Proceedings of SPIE* (2010), 7639
- C. K. Ober, C. Y. Ouyang, J.-K. Lee, J. Sha, "*Green Processing of Photoresists in non-polar fluids for high resolution patterning*", ACS preprtins (2010)
- J. Sha and C. K. Ober, "*Fluorine- and Siloxane-Containing Polymers for Supercritical Carbon Dioxide Lithography*", *Polymer International* (2009), 58(3), 302-306.
- 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.
- J. Sha, J-K Lee, C. K. Ober, "*Molecular Glass Resists Developable in Supercritical CO_2 for 193-nm Lithography*", *Proceedings of SPIE* (2009), 7273, 72732T.

Presentations

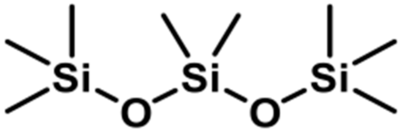
- Advances in Resist Materials and Processing Technology XXVI conference (part of the SPIE Symposium on Advanced Lithography) (Feb 2010). "*Environmentally Friendly Processing of Photoresists in scCO_2 and decamethyltetrasiloxane*"
- ERC Teleseminar (Mar 2010). "*Green Processing in Lithography*"
- 240th ACS National Meeting (Aug 2010). *"Green Processing of Photoresists in Non-Polar Fluids for High-Resolution Patterning"*

Objectives

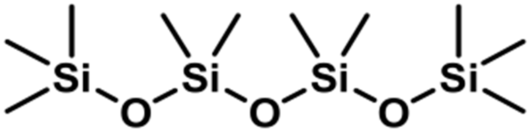
- Develop environmentally benign chemistry platforms for traditional photoresists using alternative solvents: Siloxanes and $scCO_2$



Hexamethyldisiloxane



Octamethyltrisiloxane



Decamethyltetrasiloxane

- Generate the definitive molecular model for siloxane solvents
  - Complete parameterization of all bonds, torsions, charges, etc.
  - Reproduction of experimentally-obtained chemical properties (density, heat of vaporization, etc.)

- Study behavior of traditional photoresists in new solvents and supercritical carbon dioxide

CO_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:

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

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

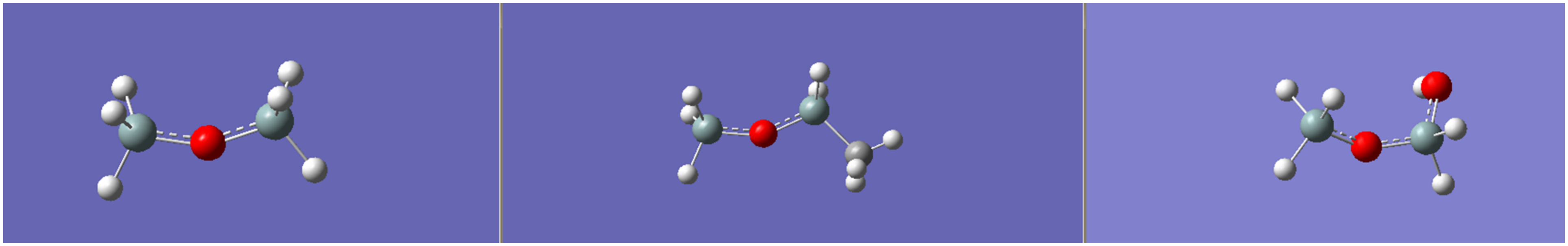
$$V_{Bond} = \frac{1}{2}k_{Bond}\left(r - r_0\right)^2$$

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

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

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

Sample elementary building blocks:

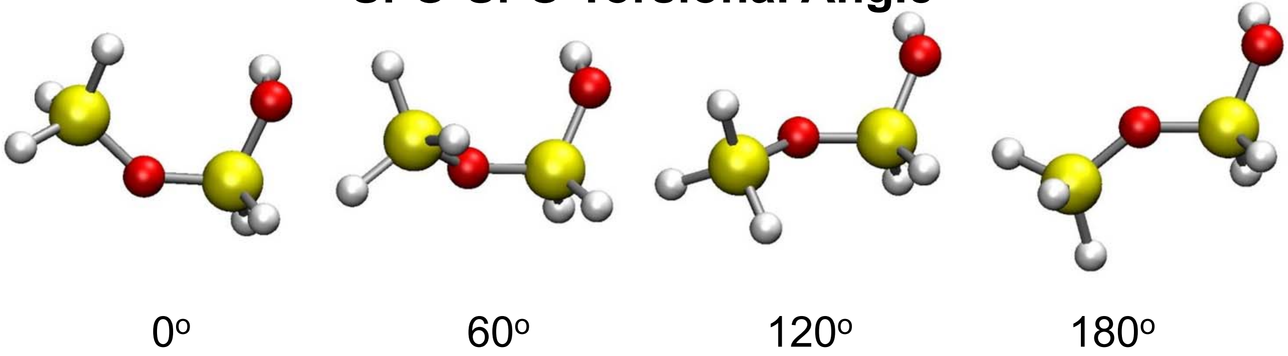


Si-O-Si-H **Si-O-Si-C** **Si-O-Si-O**

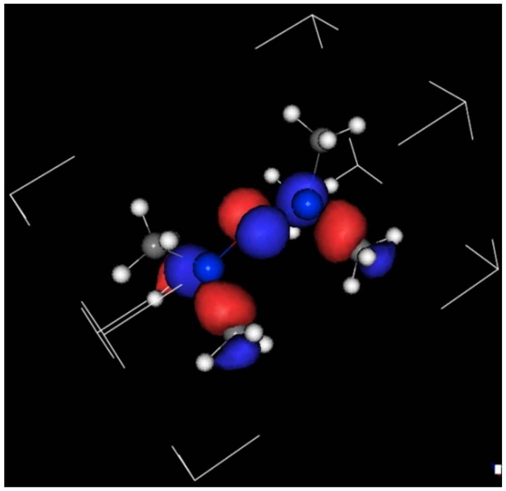
Quantum Mechanics

- Provides a detailed description of electron position as we probe different configurations
  - Can determine charges (q_i) directly
  - Map energy as a function torsion angle, etc.
  - rb3lyp model with 6-311+g(2d,p) basis set

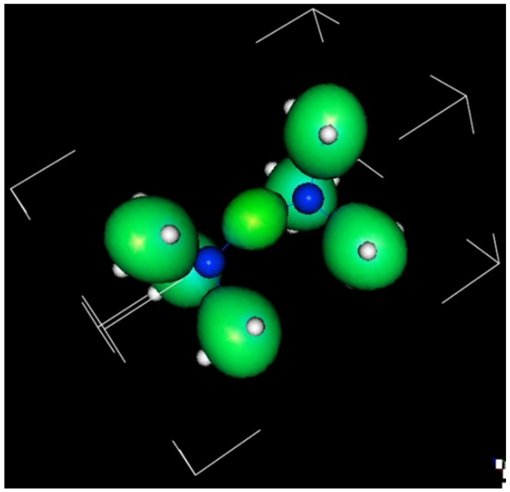
Si-O-Si-O Torsional Angle



HMD Siloxane



HOMO



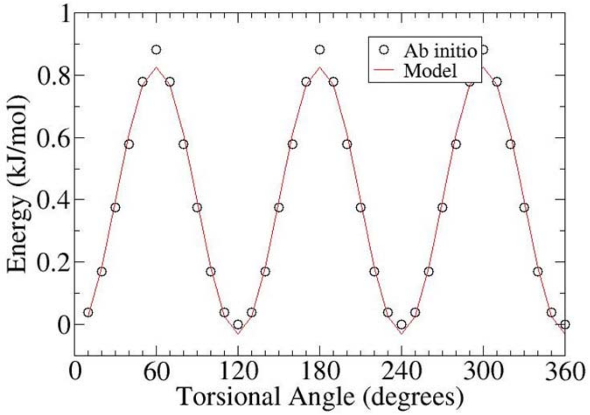
LUMO

Potential Fitting – Torsional Sample

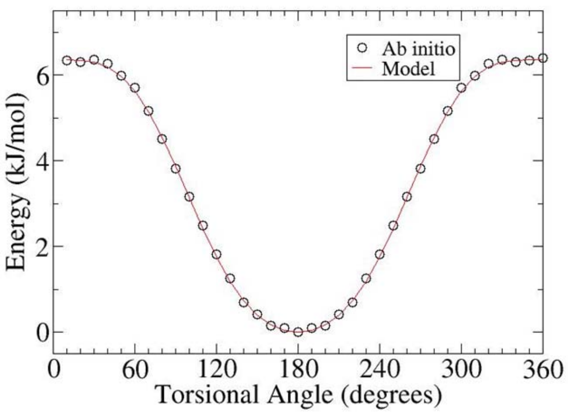
- **Si-O-Si-C and Si-O-Si-O torsions most important parameters in determining shape of the solvents**

- **Torsional parameters fit to capture difference between quantum mechanical results and non-bonded interactions**

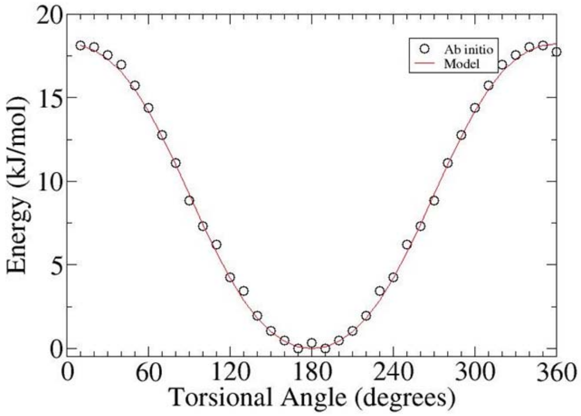
Si-O-Si-H



Si-O-Si-C

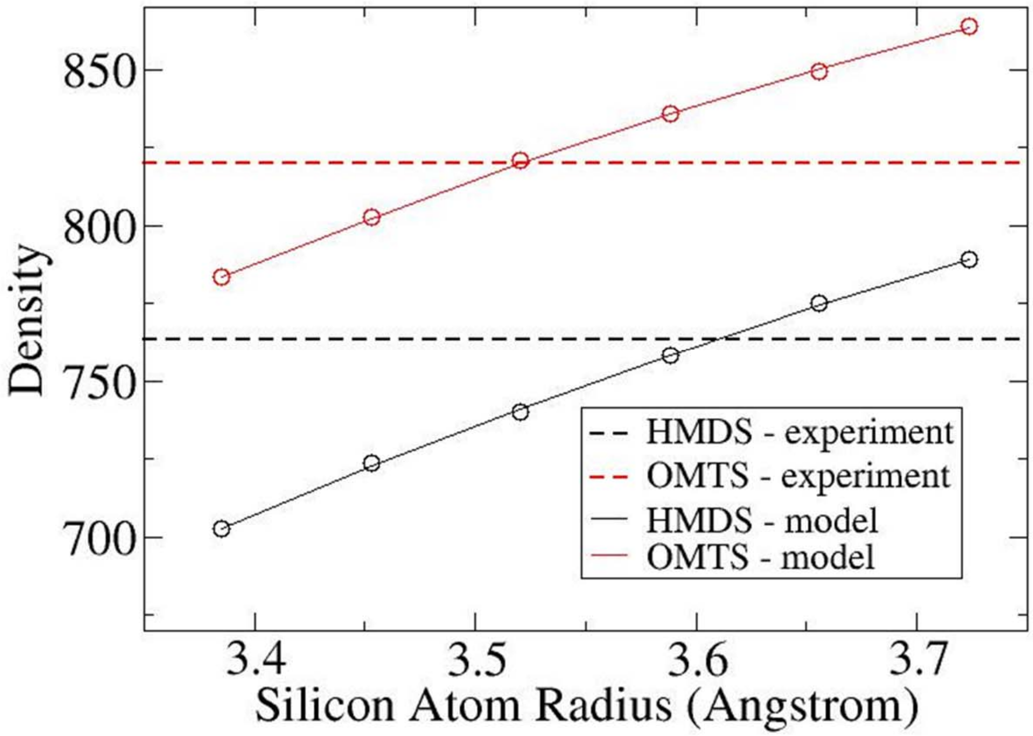


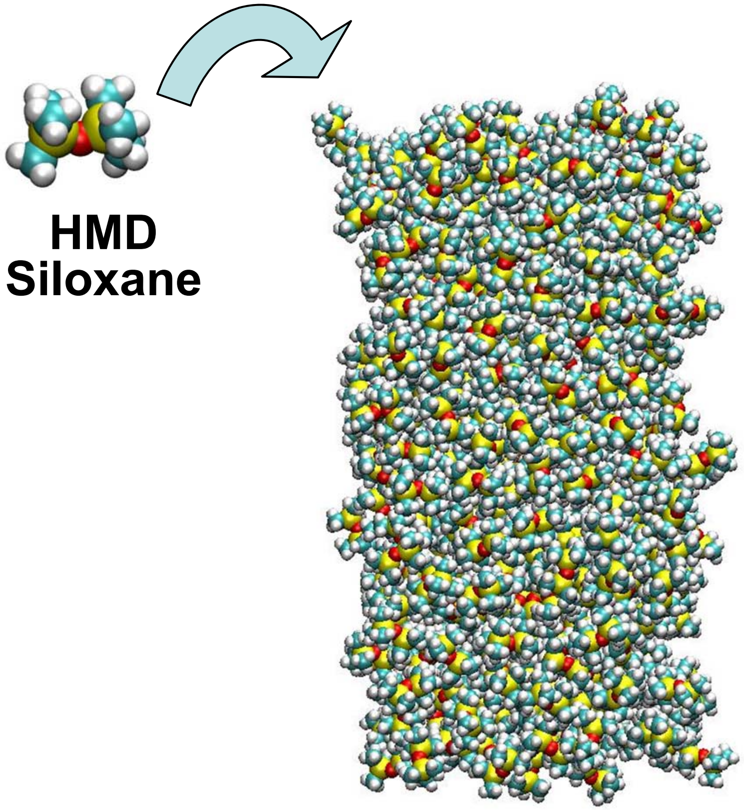
Si-O-Si-O



Intermolecular Interactions

- **Having built a complete intramolecular model from quantum mechanics, we now tune intermolecular many-body interactions to match experiment**





Experimental Measurables

	HMD Siloxane		**OMT Siloxane**		**DMT Siloxane**	
	Experimental	Model	Experimental	Model	Experimental	Model
Heat of Vaporization (kcal/mol)	7.2	7.1	~~40.4~~ **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**

Energy Use

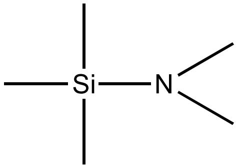
- Waste treatment is a major cost
  - Must separate solvent from dissolved polymer
- Siloxane solvents require less heat to distill
  - Half of the heat capacity
  - Order of magnitude lower heat of vaporization
- Approximately 1/8th heating cost incurred

Solvent	TMAH	HMD Siloxane
C_p	3.2 - 4.18 J/g K	1.92 J/g K
T_{boil}	383K	373K
ΔH_{vap}	>2260 J/g	186 J/g

Application of Siloxane Model: ESCAP

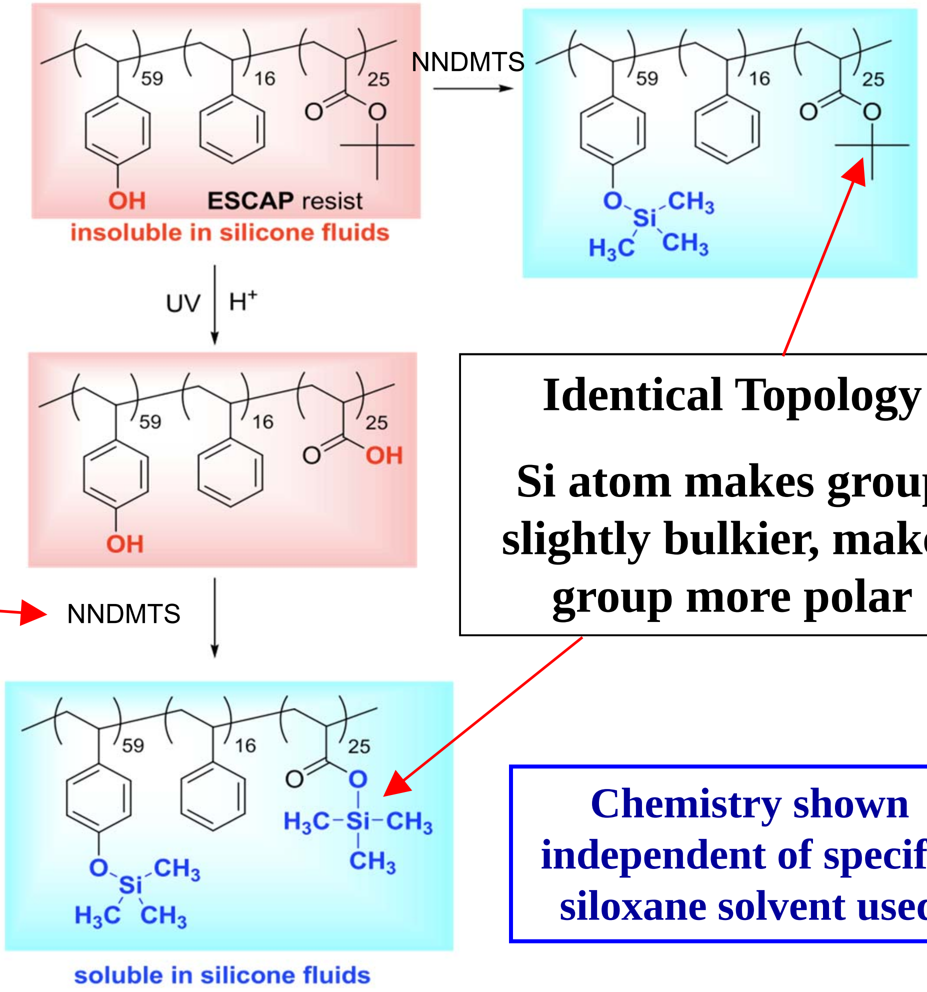
- ESCAP is our model EUV photoresist
  - Model previously developed and tested for $scCO_2$

- In experiment, chemically modified by NNDMTS:



(N,N-Dimethyl)trimethyl silane

- Similarity between exposed and unexposed form makes ESCAP a serious test of model sensitivity



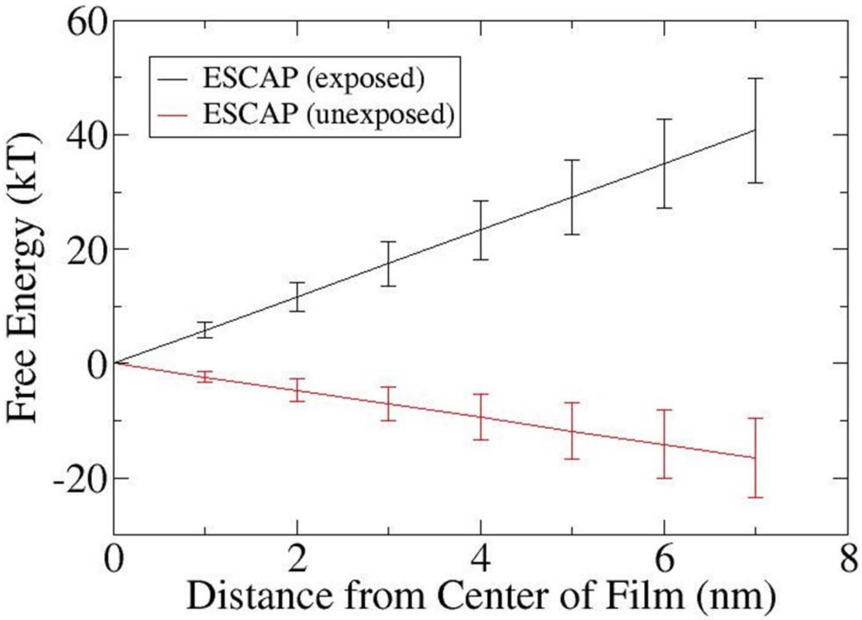
Identical Topology

Si atom makes group slightly bulkier, makes group more polar

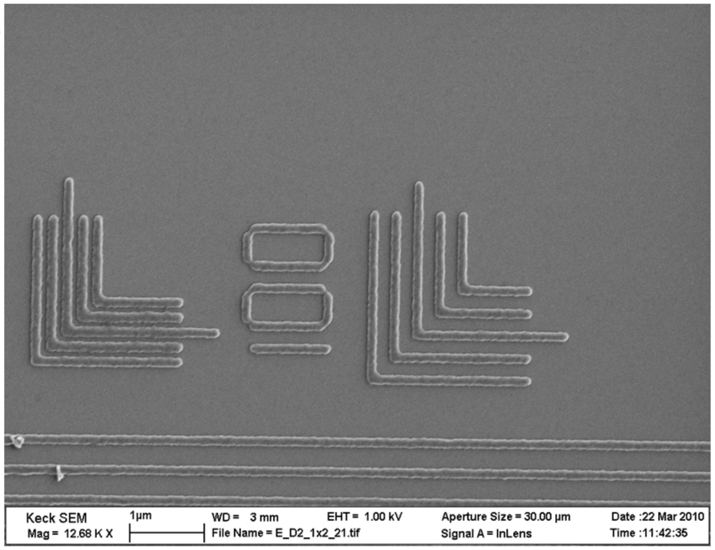
Chemistry shown independent of specific siloxane solvent used

ESCAP Result

- **Model predicts only unexposed films to be unstable:**
    - **Negative Tone**
- **Results from experimental collaborator corroborate result**



Solvent: Hexamethyldisiloxane



Solvent: DMTS/Decamethyltetrasiloxane

e-beam dose = 20 µC/cm^2

Photoresist:ESCAP

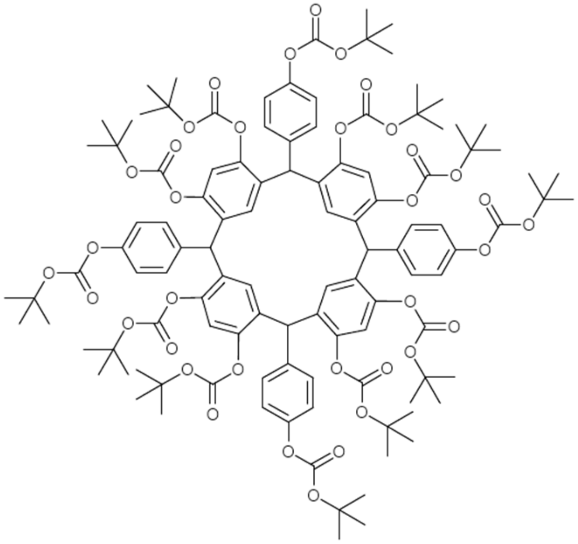
Chemical modifier: NNDMTS

Solvent: Decamethyltetrasiloxane

Dose = 20 µC/cm^2

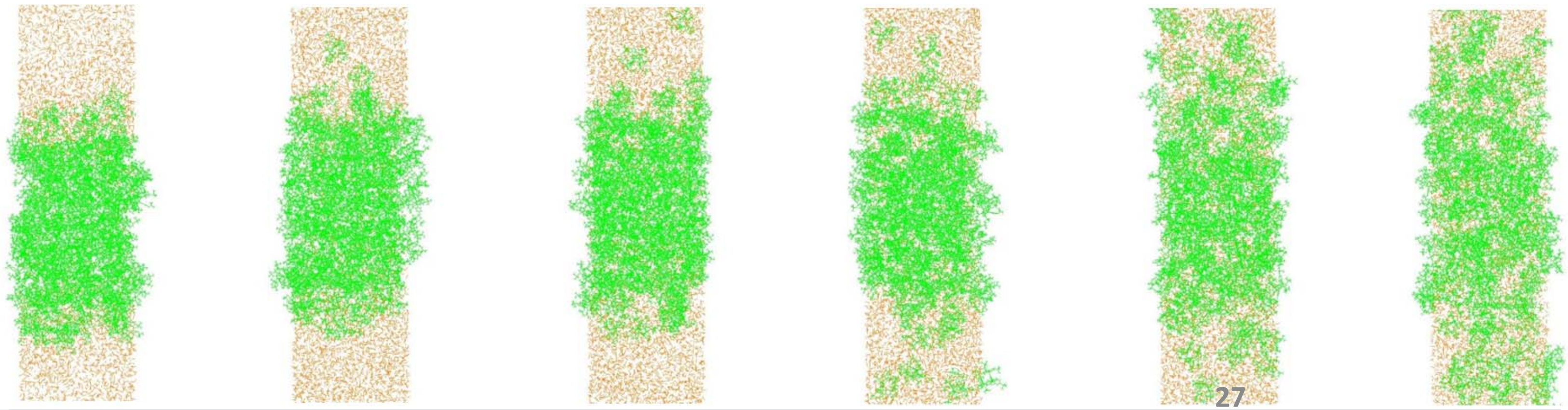
PEB: 115 °C, 60 sec

Predictive Power of Simulation: Calixarene



- **Molecular glass photoresist capable of high-resolution patterns (low LER)**
- **Last January we demonstrated potential of this 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**

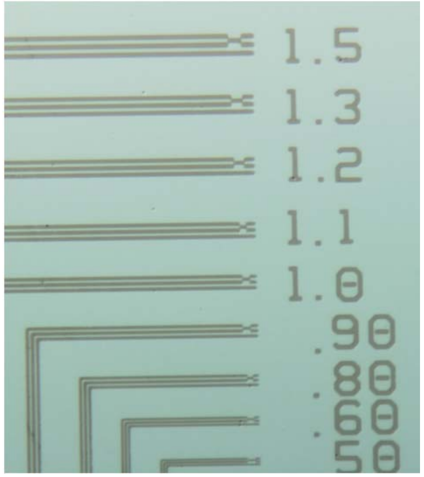
Time (1-2 ns between images)



in CO_2

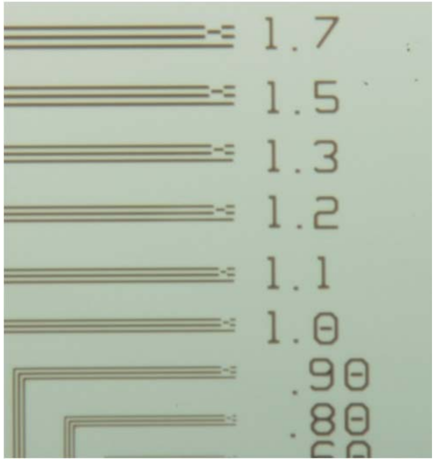
Calixarene Experimental Results

- Collaborators have demonstrated true potential of this compound in siloxane solvents
- Negative tone resist



HMD Siloxane
Dose:350 mJ/cm^2
PEB:90°C, 30 sec

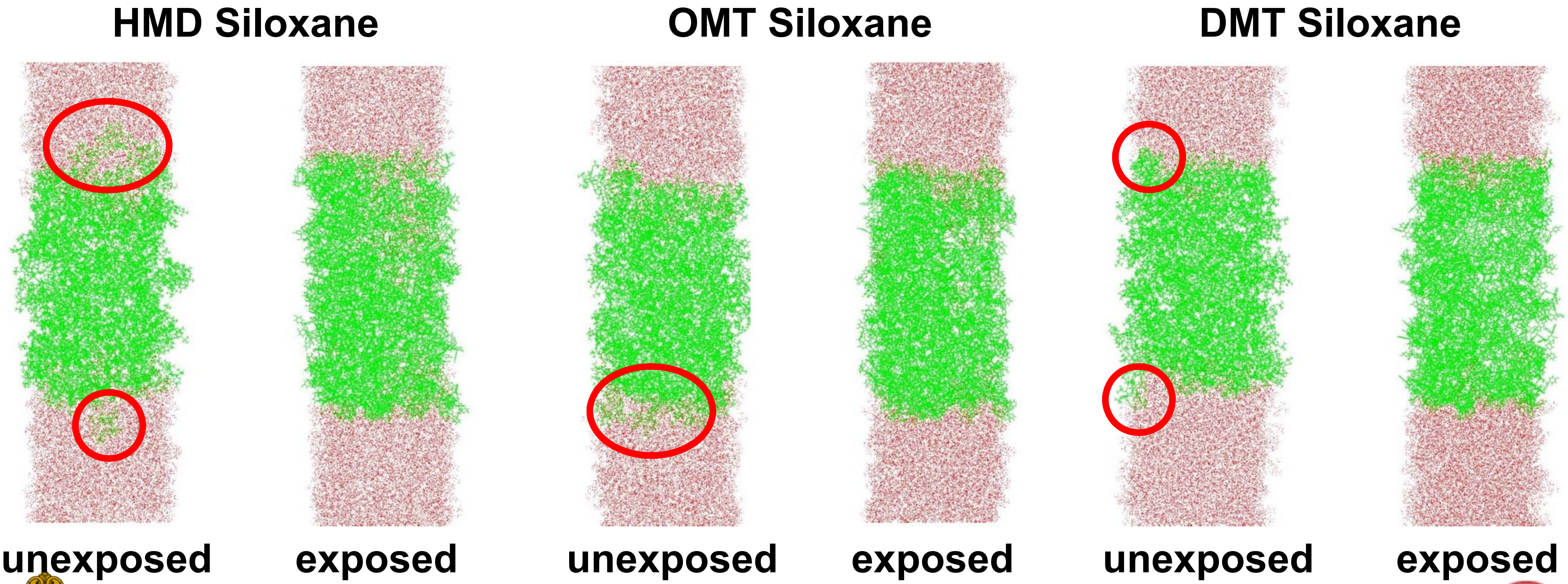
OMT Siloxane
Dose:250 mJ/cm^2
PEB:90°C, 30 sec



DMT Siloxane
Dose:300 mJ/cm^2
PEB:90°C, 30 sec

Calixarene Simulation Results

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



Industrial Interactions and Technology Transfer

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

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

Publications, Presentations, and Recognitions/Awards

Publications

- 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)
- J. Sha and C. K. Ober, "*Fluorine- and Siloxane-Containing Polymers for Supercritical Carbon Dioxide Lithography*", *Polymer International* (2009), 58(3), 302-306.
- 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.
- J. Sha, J-K Lee, C. K. Ober, "*Molecular Glass Resists Developable in Supercritical* CO_2 *for 193-nm Lithography*", *Proceedings of SPIE* (2009), 7273, 72732T.

Presentations

- Advances in Resist Materials and Processing Technology XXVI conference (part of the SPIE Symposium on Advanced Lithography) (Feb 2010). "*Environmentally Friendly Processing of Photoresists in* $scCO_2$ *and decamethyltetrasiloxane*"
- ERC Teleseminar (Mar 2010). "*Green Processing in Lithography*"
- 240th ACS National Meeting (Aug 2010). *"Green Processing of Photoresists in Non-Polar Fluids for High-Resolution Patterning"*