Supercritical Carbon Dioxide Compatible Additives:

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

(*Task Number: 425.030)*

PI:

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Collaborator:

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Graduate Student:

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Objectives

- To demonstrate high-resolution patterning capabilities and $scCO_2$ development of molecular glass resists based on environmentally benign cores
- To synthesize and characterize fluorinated quaternary ammonium salts (QAS) as CO_2 compatible additives to develop conventional photoresists in $scCO_2$
- To demonstrate environmentally benign development of conventional photoresists using $scCO_2$ and silicone fluids using silicon-containing additives

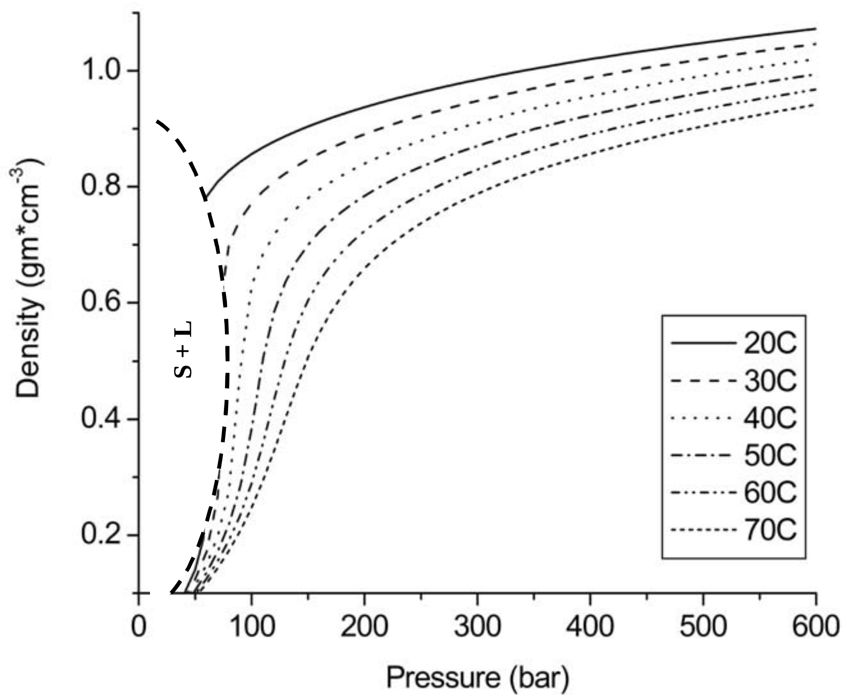
ESH Metrics and Impact

	Usage Reduction			Emmision Reduction			
Goals/Possibilities	Energy	Water	Chemicals	PFCs	VOCs	HAPs	Other
Reduce organic solvents used in processing materials	No energy used to purify and treat water	Eliminate need for water usage	Up to 100% reduction of organic solvents used	N/A	Minimal use of organic solvents	Up to 100% reduction of HAPs	N/A
Reduce processing time / temperature	Reduce anneal process costs	N/A	N/A	N/A	N/A	N/A	N/A
Additive processing	N/A	N/A	Eliminate waste of costly material	N/A	Minimal use of organic solvents	N/A	N/A

Why a Non-Aqueous Developer Solvent?

Environmental and Performance Advantages of $scCO_2$

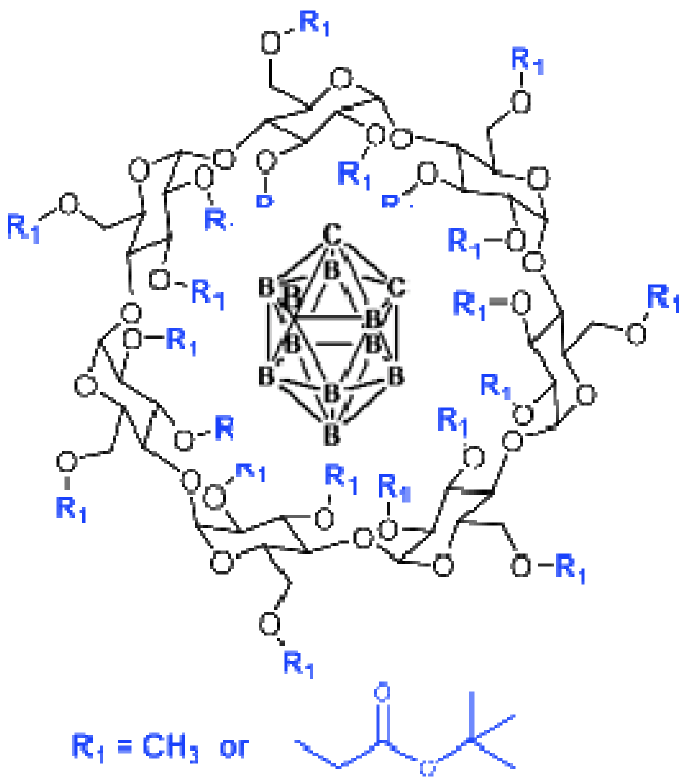
- Environmentally friendly, zero VOC solvent
- Highly tunable solvating power
  - ρ(T,P)
  - Leaves no residue
  - Clean separations
- One-phase fluid
  - Zero surface tension
  - Transport, viscosity between that of liquid and gas
- Nonpolar, inert character



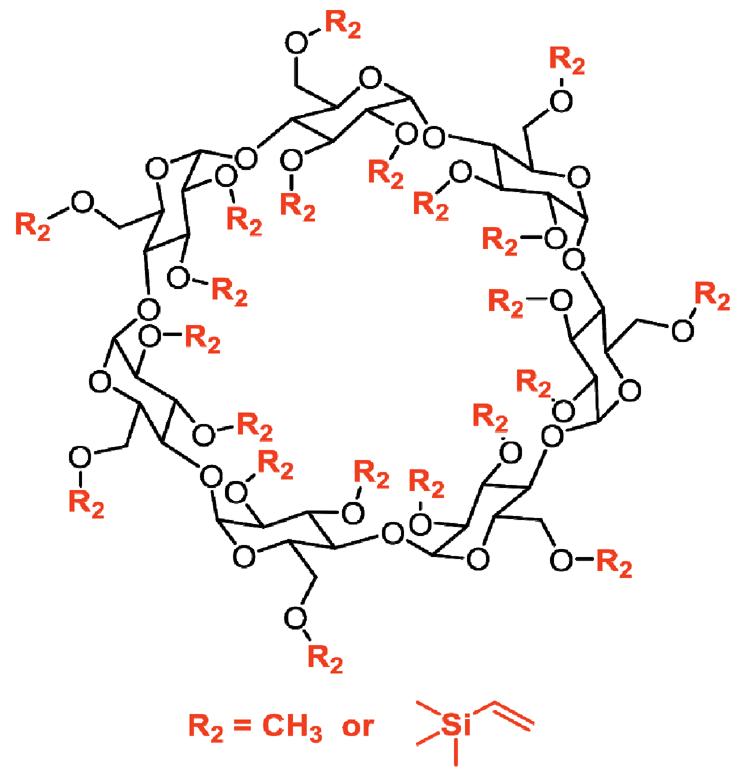
- Potential to reduce LER and eliminate pattern collapse

Molecular Glass Resists with Alicyclic Cores

Environmental friendliness and $scCO_2$ solubility



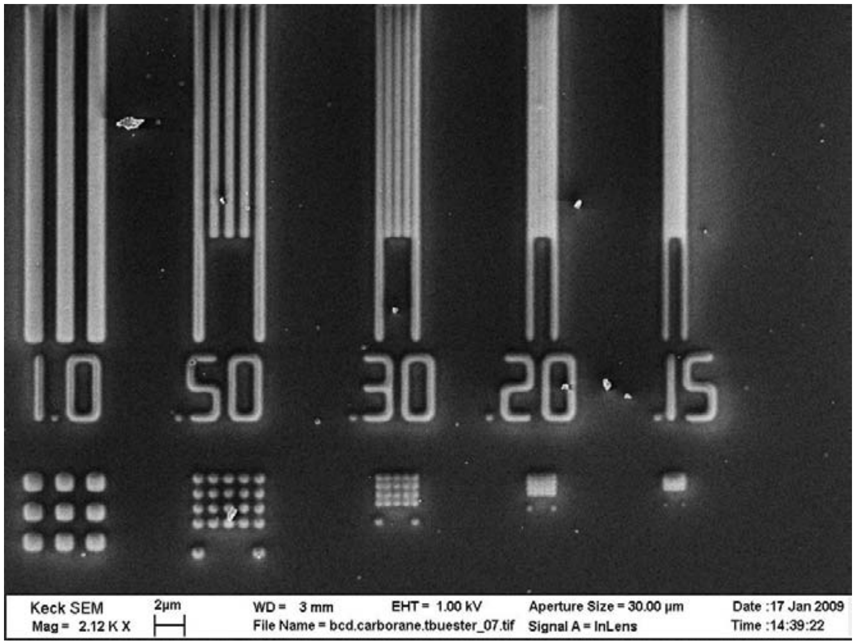
Cyclodextrin-carborane complex

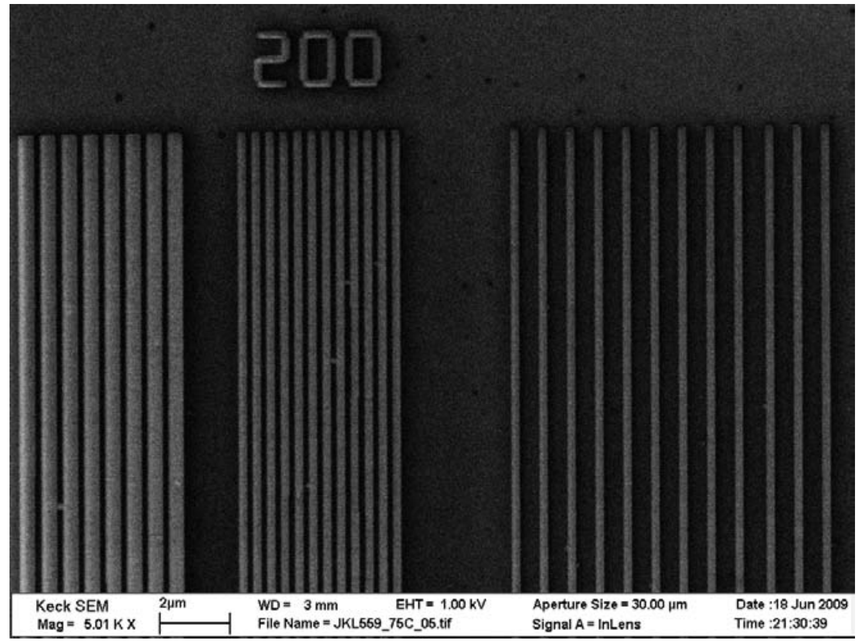


Vinyl silane cyclodextrin

Cyclodextrins are good hosts for inclusion complexes and have potential as molecular resists to hold functional moieties on their periphery

Electron Beam Patterning and $scCO_2$ Development of Cyclodextrin Resists





Cyclodextrin-Carborane complex

E-beam dose = μC/cm^2

PEB: 115 ^oC, 60 sec

$scCO_2$: 5000 psi, 5 min

Vinyl silane cyclodextrin

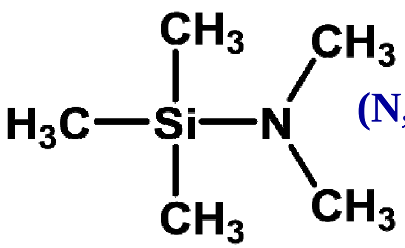
E-beam dose = 44 μC/cm^2

PEB: 75 ^oC, 60 sec

$scCO_2$: 2000 psi, 2 min

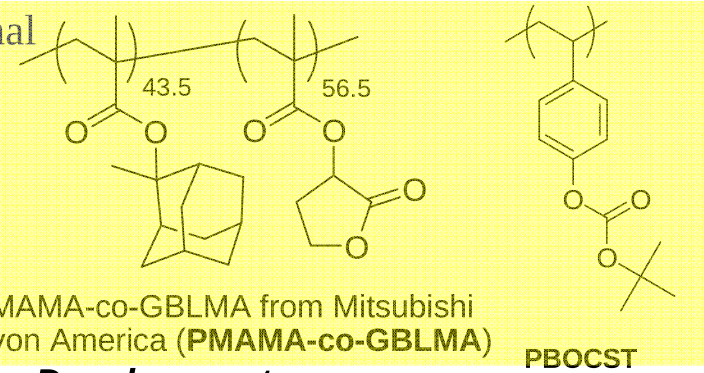
Additives for $scCO_2$ to Develop Conventional Resists

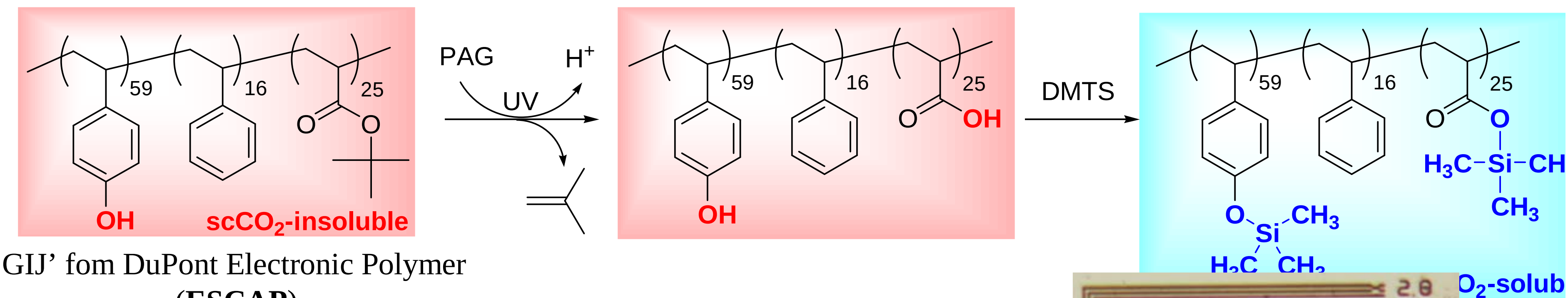
•Silicon-containing Additive



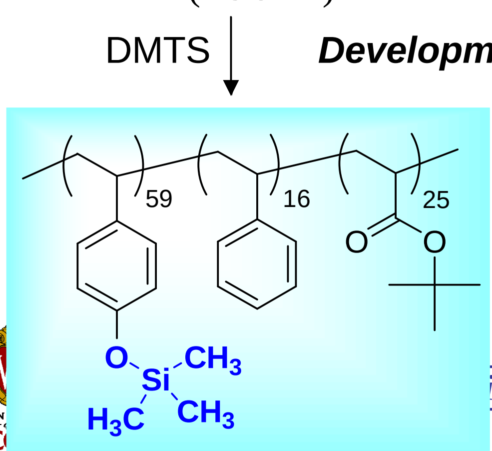
(N,N-Dimethyl)trimethyl silane (DMTS)

Other conventional resists tested

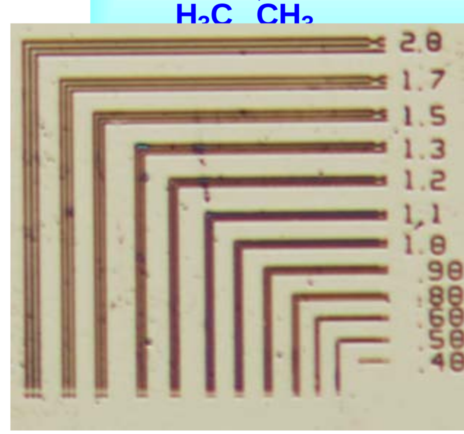




‘GIJ’ fom DuPont Electronic Polymer (**ESCAP**)



-According to resist materials and lithographic conditions, both positive and negative-tone imaging is possible

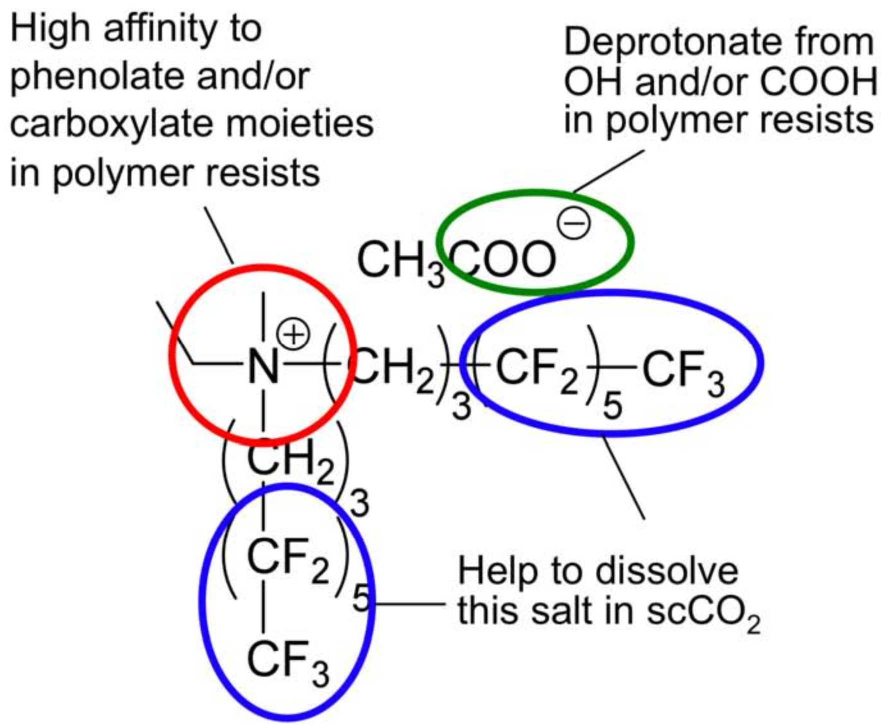


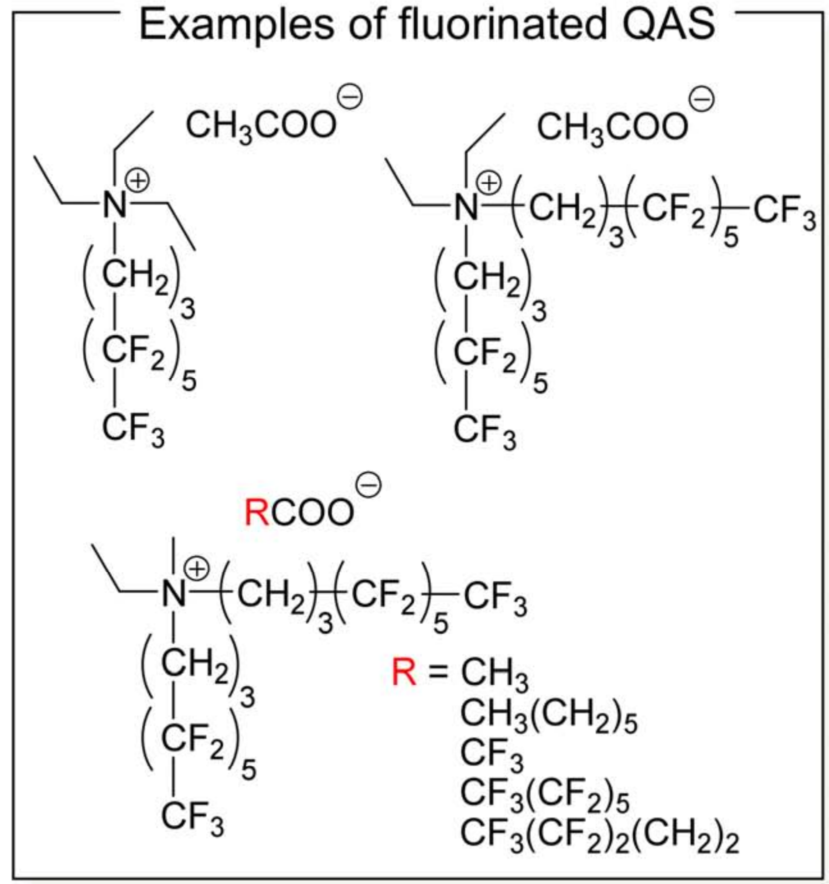
Negative image

Quaternary Ammonium Salts (QAS)

$scCO_2$ Compatible Additives:

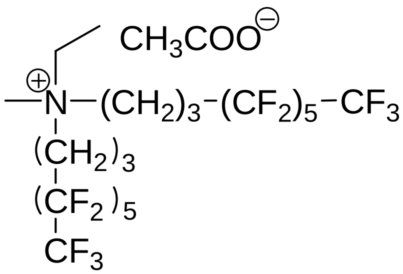
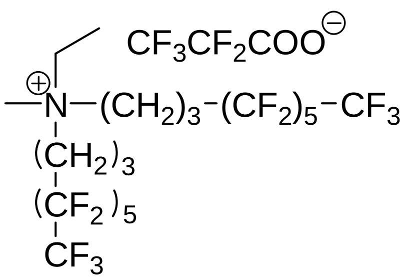
Fluorinated Quaternary Ammonium Salts (QAS)





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

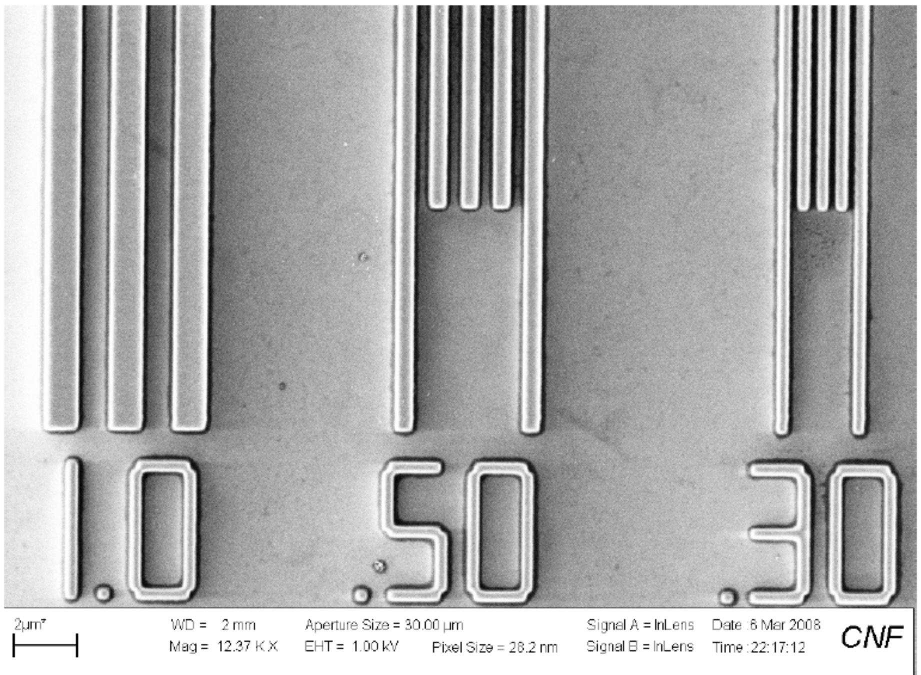
Initial Dissolution Results of Resists with QAS

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

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

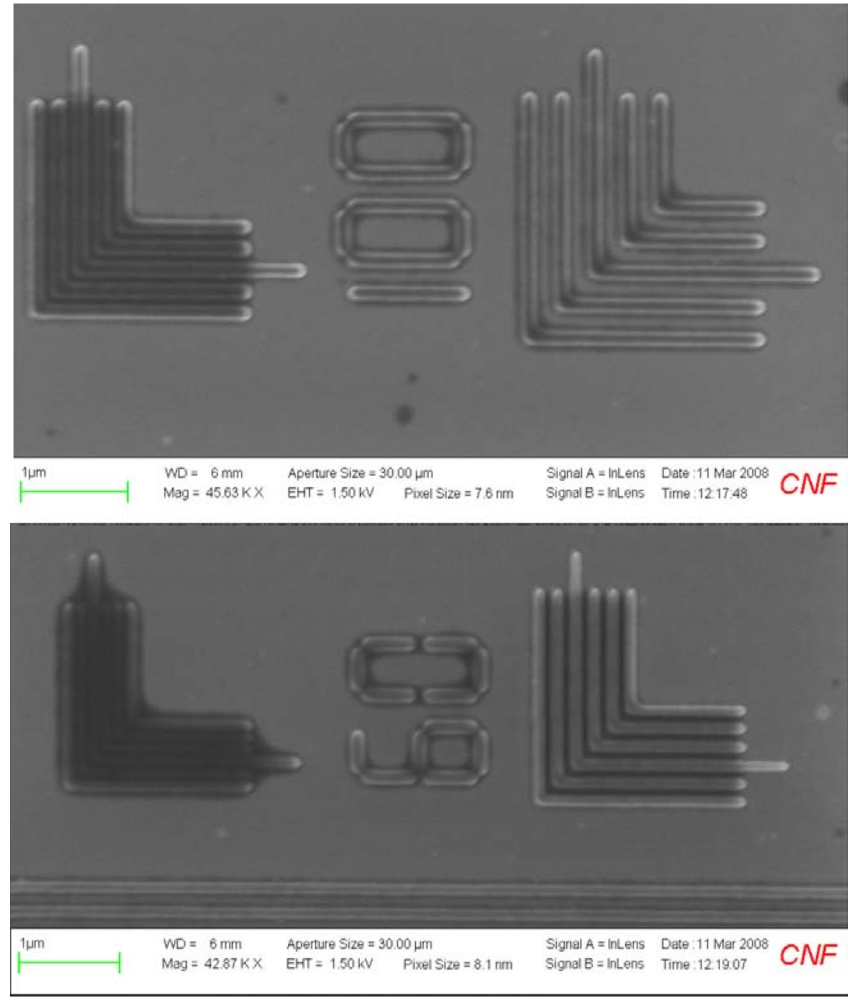
Electron Beam Patterning

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



Dose: 107 uC/cm^2, QAS-4 (1.25 mM), dev. for 60 min at 50ºC, 5000 psi, flow 30 min

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

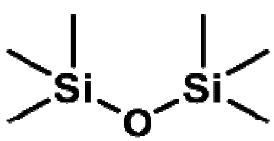


Dose: 20 uC/cm^2, QAS-7 (1.25 mM), dev. for 60 min at 50ºC, 5000 psi, flow 30 min

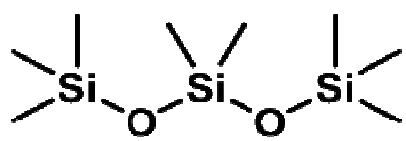
Silicone Fluids-Linear Methyl Siloxanes

- **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**

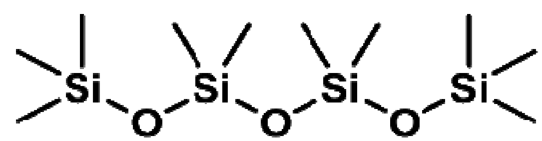
-degrade to naturally occurring chemical species



Hexamethyldisiloxane



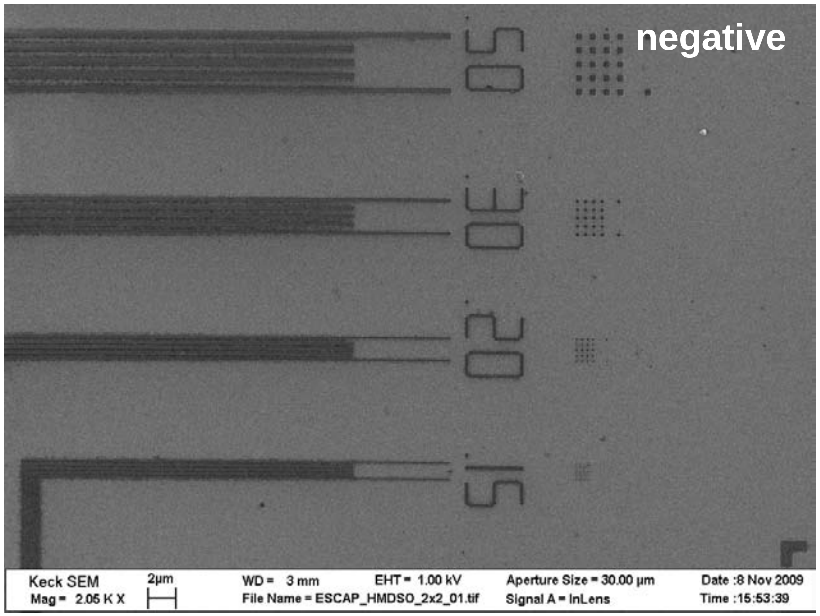
Octamethyltrisiloxane



Decamethyltetrasiloxane

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

Electron Beam Patterning and Silicone Fluid Development of Conventional Photoresists



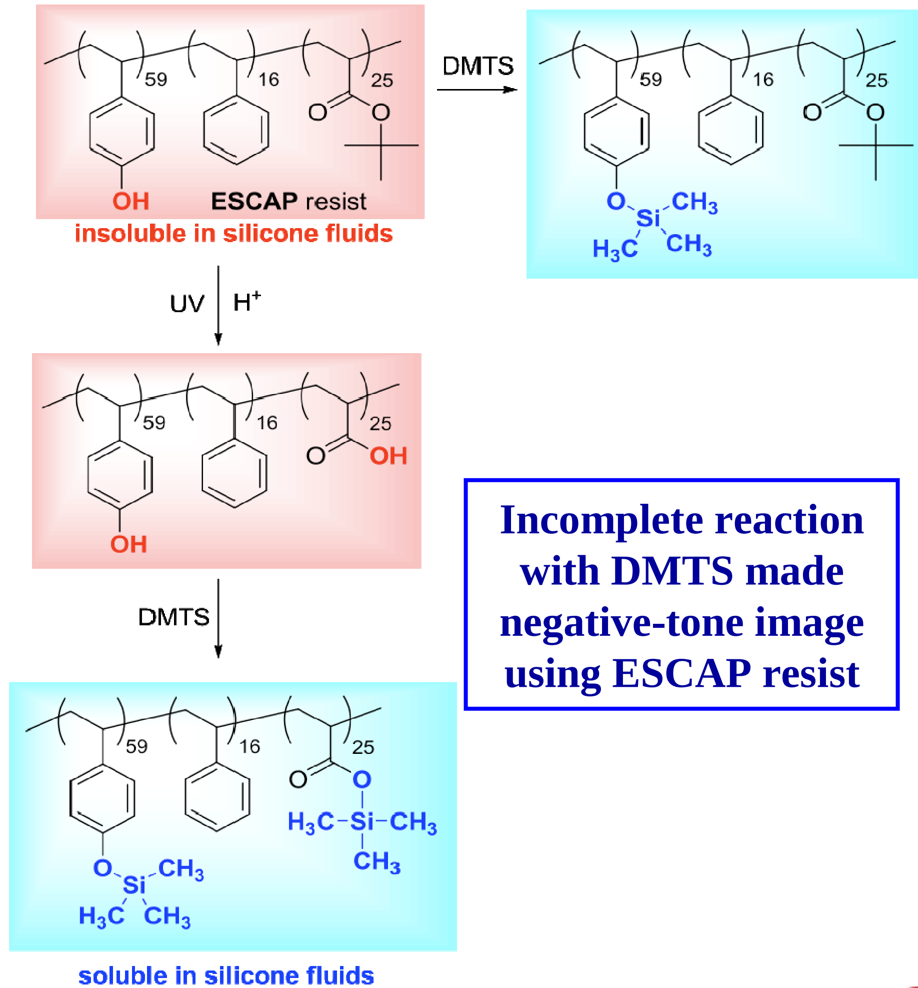
Photoresist:ESCAP

Chemical modifier: DMTS

Solvent:Hexamethyldisiloxane

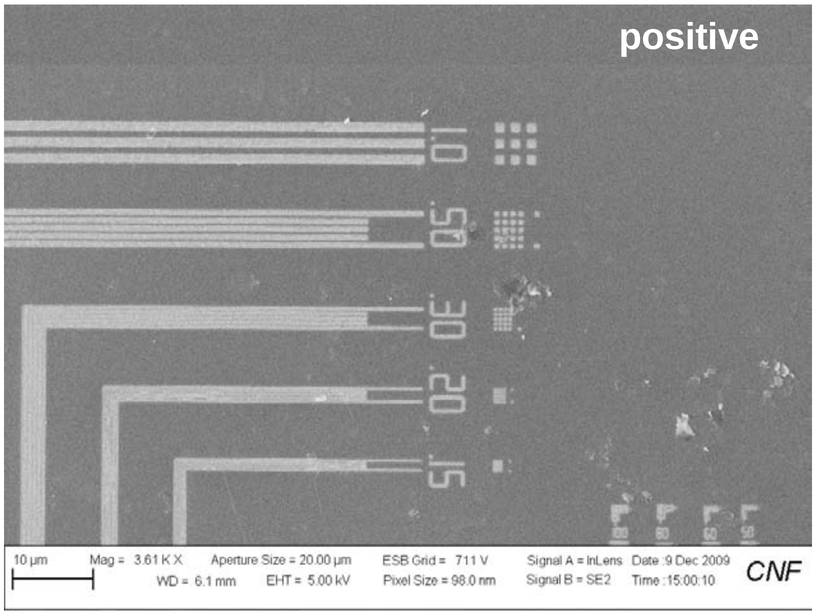
E-beam dose = μC/cm^2

PEB: 115 ^{o}C, 60 sec



Incomplete reaction with DMTS made negative-tone image using ESCAP resist

Electron Beam Patterning and Silicone Fluid Development of Conventional Photoresists



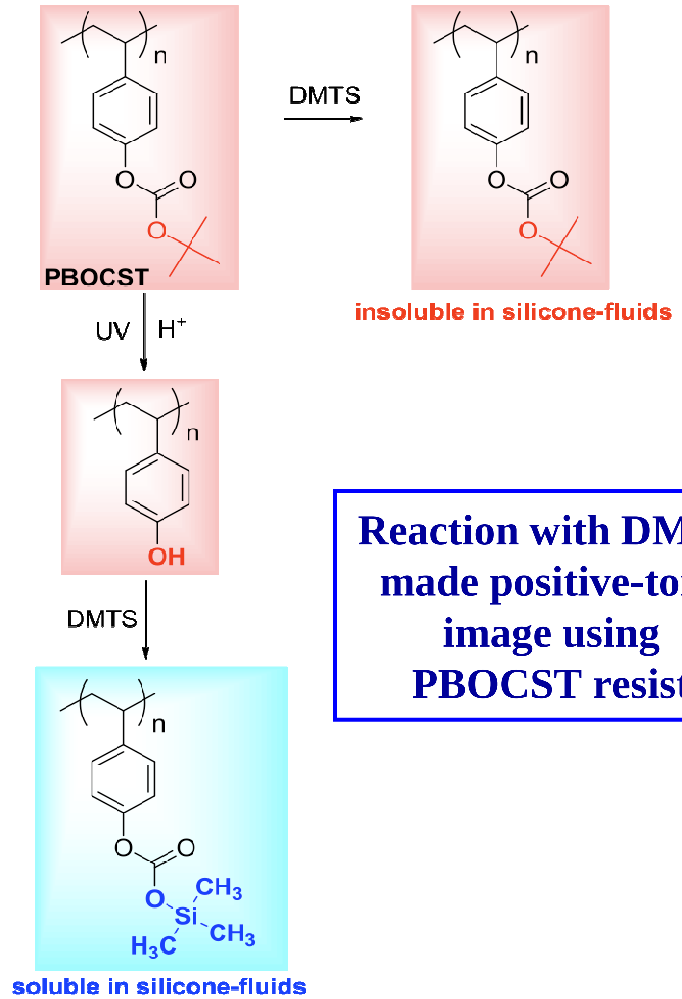
Photoresist:PBOCST

Chemical modifier: DMTS

Solvent:Octamethydisiloxane

E-beam dose = μC/cm^2

PEB: 90 ^{o}C, 60 sec



Reaction with DMTS made positive-tone image using PBOCST resist

THE UNIVERSITY of WISCONSIN MADISON

Industrial Interactions and Technology Transfer

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

Task Deliverables

- **Report on the preparation of a series of quaternary ammonium salts for resist development (6/30/2009)**

  -completed

Future Plans

Next Year Plans (seed effort)

- **To explore more organosilanes and non-fluorinated quaternary ammonium salts (QAS) for faster dissolution of photoresists in silicone fluids and $scCO_2$ with the help of simulation data from Prof. Juan J de Pablo Group in Univ. of Wisconsin, Madison**
- **To continue synthesis efforts for $scCO_2$ processable molecular glass resists with environmentally benign, naturally occurring cores for next generation high-resolution lithography**

Long-Term Plans

- **To expand use of additives for $scCO_2$ and environmentally friendly silicone fluids to develop positive tone resists**
- **To create new chemistries for patterning and functionalizing small, non-polar molecules in $scCO_2$**

Publications, Presentations, and Recognitions/Awards

Publications

- M. Tanaka, A. Rastogi, N. M. Felix, C. K. Ober, "*Supercritical Carbon Dioxide Compatible Salts: Synthesis and Application to Next Generation Lithography*", *J. Photopolym. Sci. Technol.* (2008), 21(3), 393-396.
- 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

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