Green Processing in Photolithography

ERC TeleSeminar
March 25th, 2010

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Outline

- Introduction

  -Lithographic Process

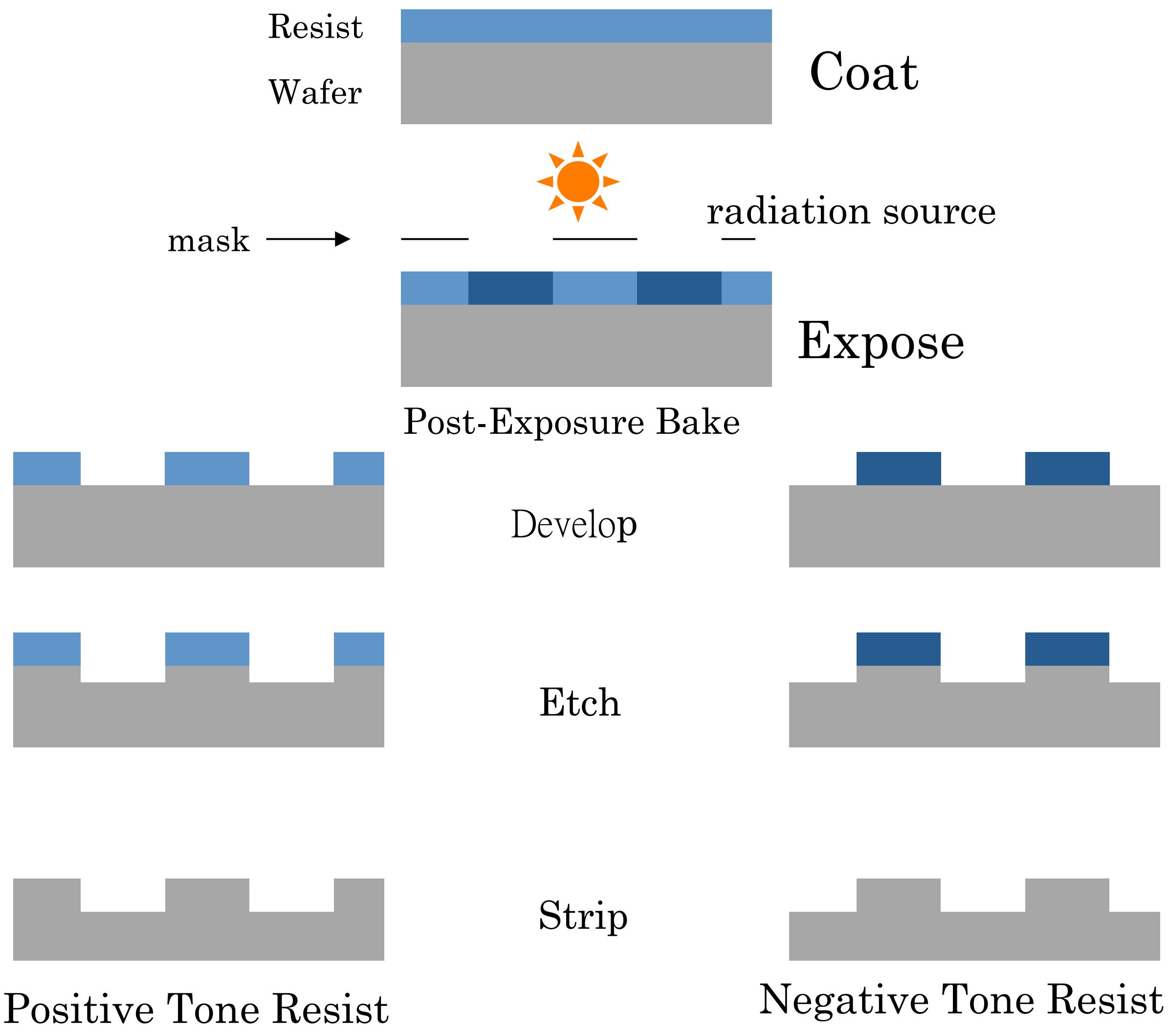
  -Environmental Issues
- Approaches

  -Environmentally Benign Developing Solvents

  -Photoresists

  -Sugar-Based “Sweet” PAG
- Conclusions

Lithographic Process



Resist

Wafer

Coat

radiation source

mask

Expose

Post-Exposure Bake

Develop

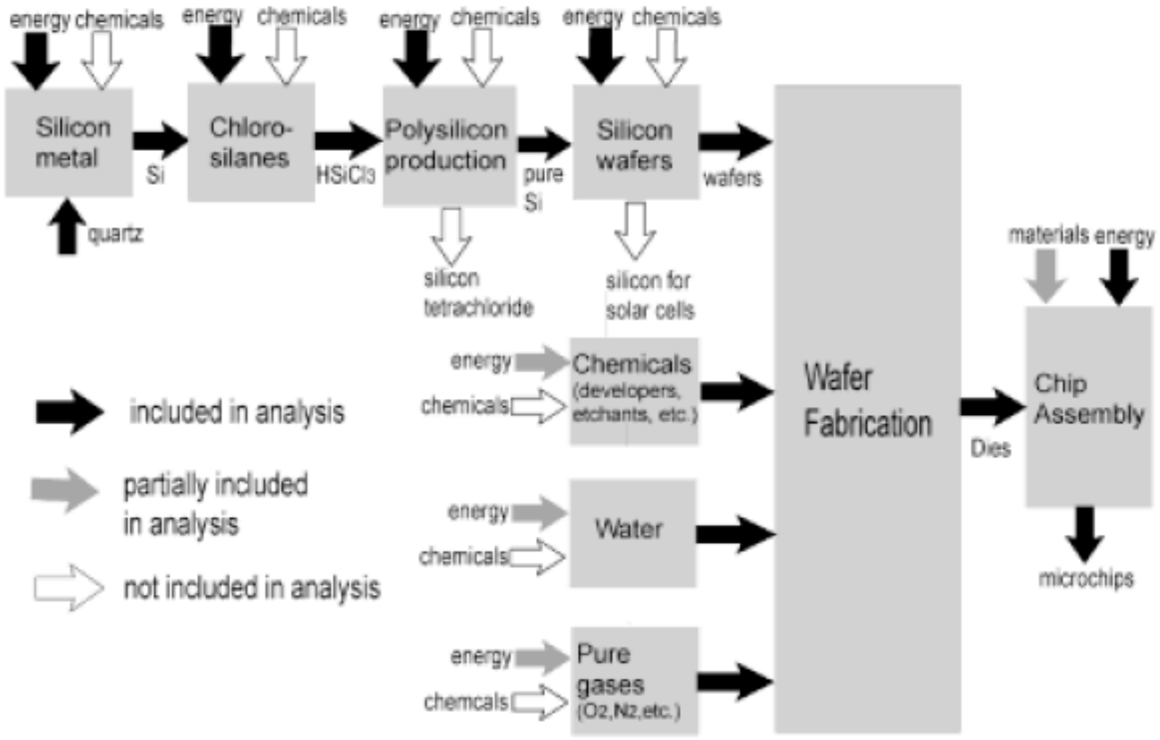
Etch

Strip

Positive Tone Resist

Negative Tone Resist

Environmental Issues



E.D. Williams, R.U. Ayres, M. Heller, *Environ. Sci. Technol*. **2002,** 36, 5504-5510

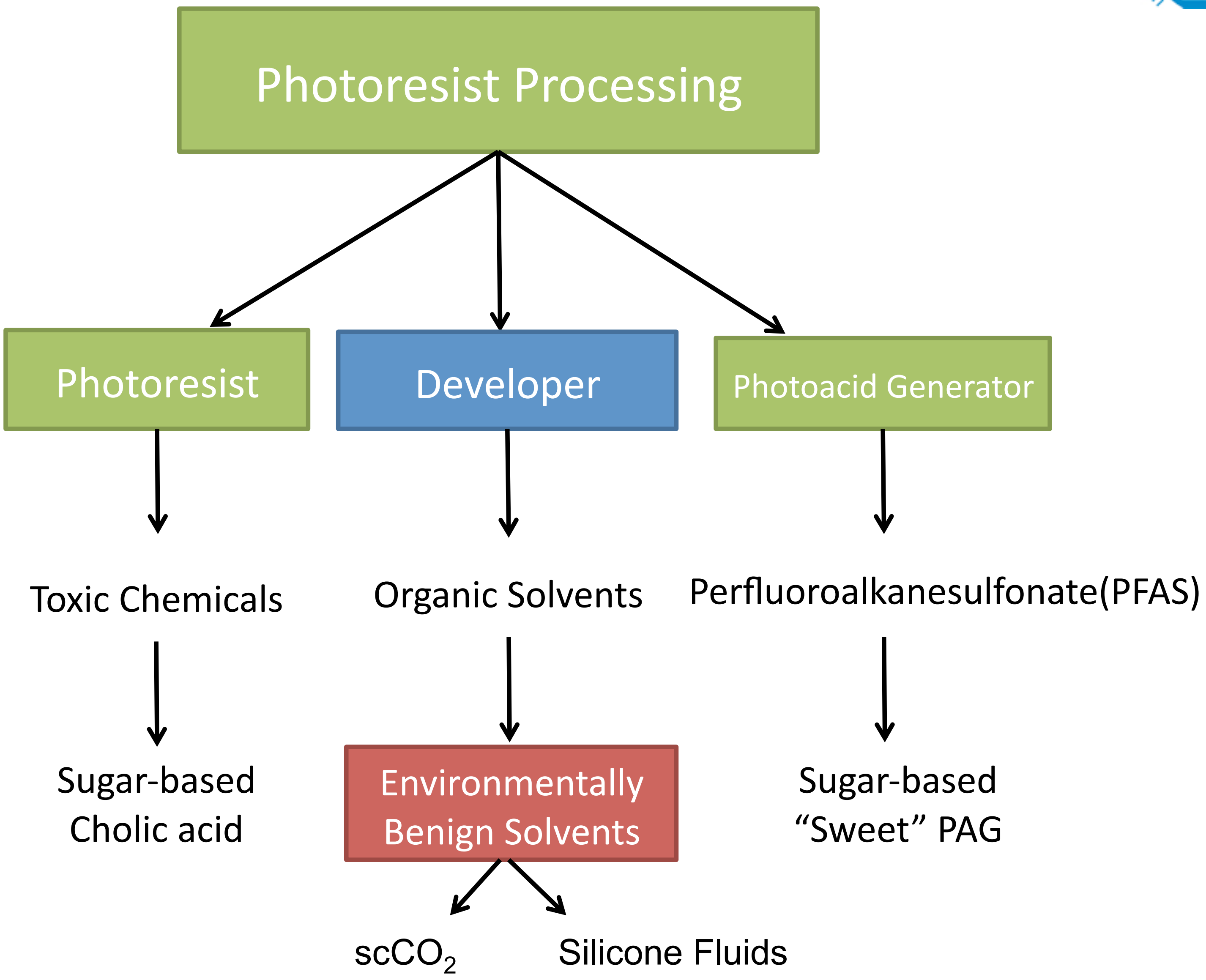
- Use of Toxic chemicals

-potential impacts of emissions on air, water, and ground systems

- Water consumption

-2-3 millions gallons of water per day for a typical 6-inch wafer plant

Approaches



Photoresist Processing

Photoresist

Developer

Photoacid Generator

Toxic Chemicals

Organic Solvents

Perfluoroalkanesulfonate(PFAS)

Sugar-based Cholic acid

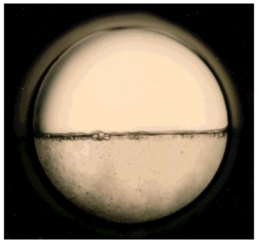
Environmentally Benign Solvents

Sugar-based “Sweet” PAG

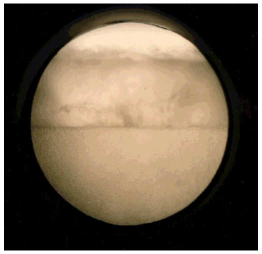
$scCO_2$

Silicone Fluids

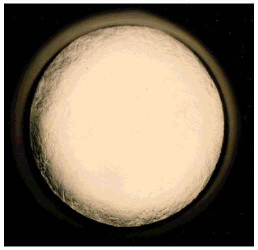
“Green” Solvent-Supercritical CO_2



Below critical point
– separate liquid and gas phases

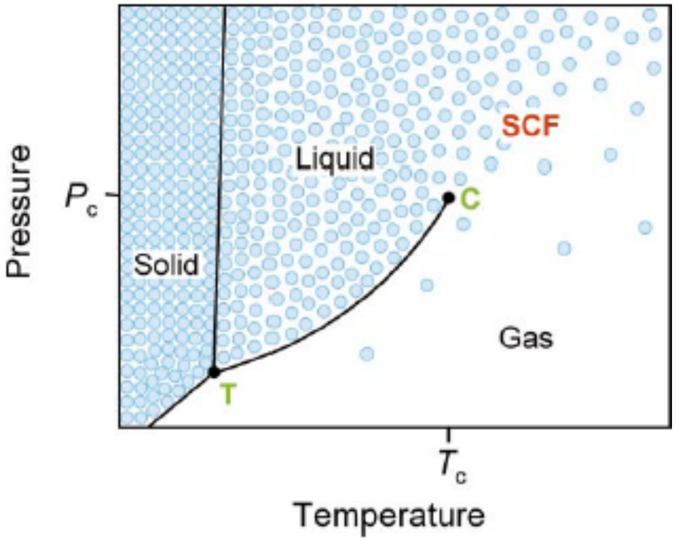


Near critical point
– meniscus begins to fade



Above critical point
– no meniscus, homogeneous phase

R. S. Oakes, A. A. Clifford and C. M. Rayner, *J. Chem. Soc., Perkin Trans. 1* **2001**, 917



A. I. Cooper, *J. Mater. Chem.* **2000**, 10, 207-234.

•Supercritical state of carbon dioxide
-T_c = 31.1 °C, P_c = 72.8 bar
•Non-toxic
•Environmentally benign
• Pressure adjustible solvating power
• Low viscosity
• Zero surface tension

Existing "Green" Lithographic Process Using $scCO_2$

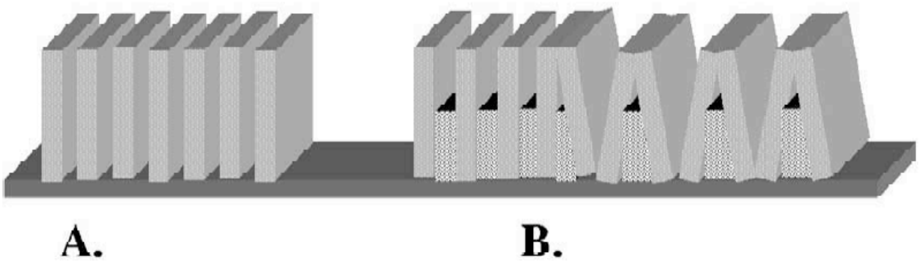
- Substrate cleaning

-Solubility of non-polar organic compounds is high in $scCO_2$

-Leave no organic residues

- Thin film deposition
- Resist stripping
- Etching
- Drying

-Prevent pattern collapse



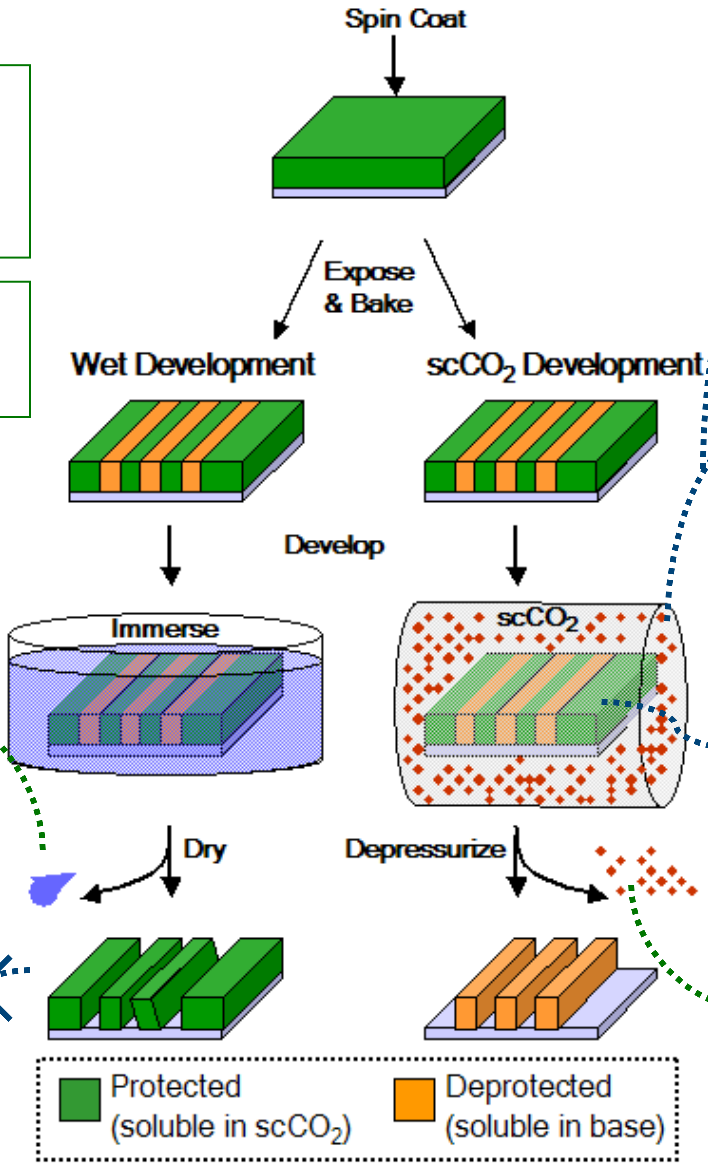
G.L. Weibel, C.K. Ober, *Microelectronic Engineering* **2003,**65, 145-152

Supercritical CO_2 as a Developer

Elimination of organic solvents and ultra-pure water during processing

2 gram DRAM chip → 32 kg of water

Williams, et al., *Environ. Sci. Tech.*, **36**, 5504, (2002).



Liquid-like density, Tunable Solvating Power

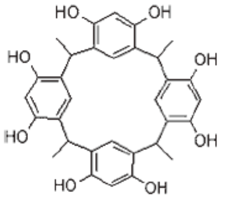
Gas-like transport

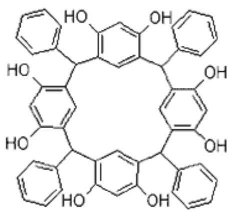
Penetrates crevices, no residue

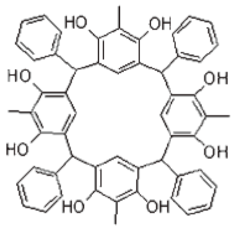
Solvent is cleanly separated from resist residues via depressurization

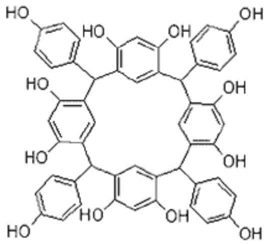
No surface tension, eliminates pattern collapse

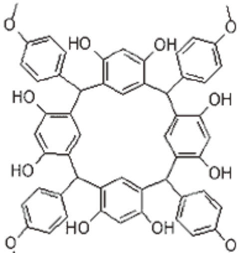
Molecular Glass Resists- Calix[4]resorcinarene Derivatives

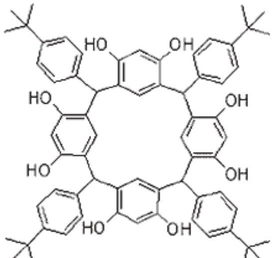

C-M-4-R

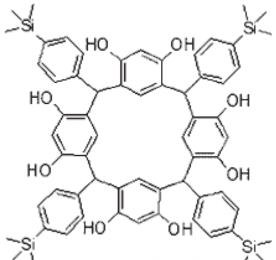

C-B-4-R


C-2M-B-4-R


C-HPB-4-R


C-MOB-4-R


C-TBB-4-R

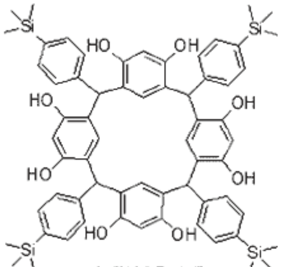

C-TMSB-4-R

- High Tg
- High Thermal stability
- Excellent film forming characteristics
- Ability to tune chemical structure through minor synthetic modifications
- Uniform dissolution rates leads to sharp solubility contrast and lower roughness

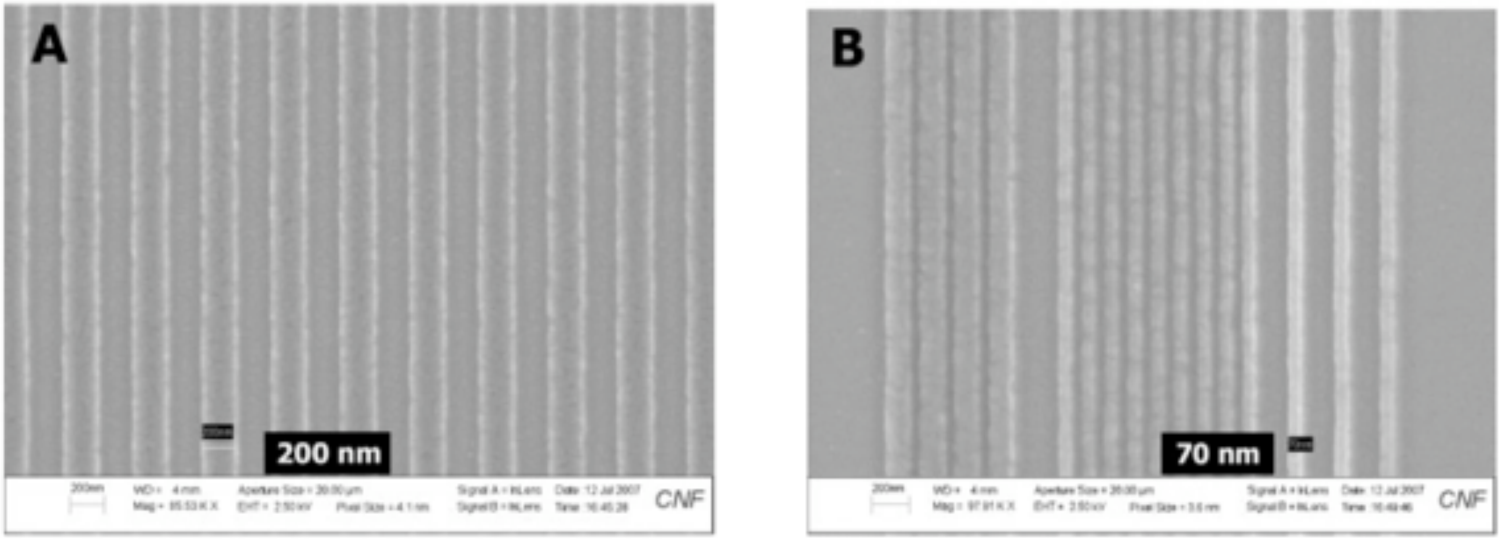
N.M. Felix, A. De Silva, C.K. Ober, *Adv. Mater*. **2008**, 20, 1303-1309

Lithographic Results of Calix[4]resorcinarene Derivatives

C-TMSB-4-R-100tBOC
Developed in $scCO_2$

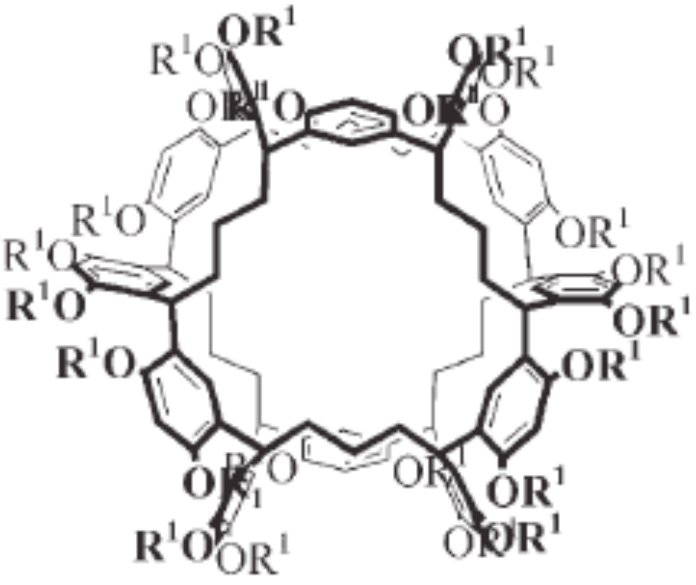


C-TMSB-4-R



N.M. Felix, A. De Silva, C.K. Ober, *Adv. Mater*. **2008**, 20, 1303-1309

“Noria-Boc” Molecular Glass Resists



noria-Boc

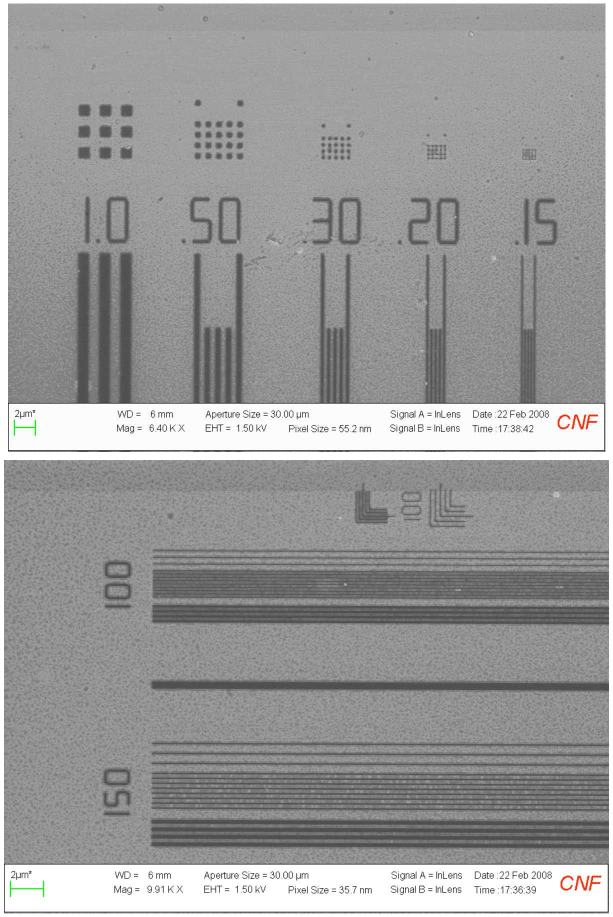
R^1 = $-COOC(CH_3)_3$

High molecular weight molecular glass

$M_{w\ Noria\text{-}boc}$ = 4108.3 g/mol

$M_{w\ Noria}$ = 1705.9 g/mol

M.Tanaka, A. Rastogi, H. Kudo, D.Watanabe, T.Nishikubo, C. K. Ober, *J. Mater. Chem.* **2009**, 19, 4622 - 4626



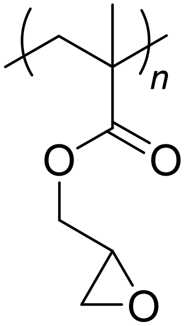
E-beam Dose: 107 uC/cm^2(top), 77uC/cm^2(bottom)

PEB:120^{o}C

scCO$_2$: 50^{o}C, 5000 psi, 30 min

Processing of Conventional Photoresists in $scCO_2$

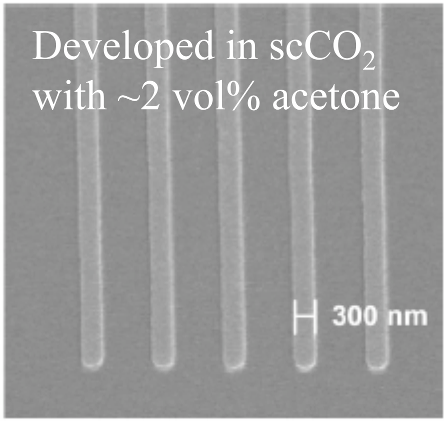
- **Co-solvents**



Addition of acetone as a co-solvent

Non-fluorine polymer was dissolved in $scCO_2$.

- Increase solvent density
- Tune polarity of fluid



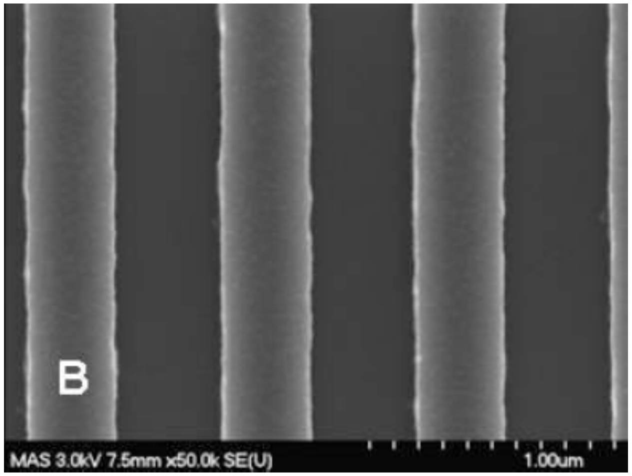
C. K. Ober, K. K. Gleason, et al., *JVST B.* **2004**, 22, 2473-8.

- **$scCO_2$ Compatible Salts**

Micell Integrated Systems developed a new additive for $scCO_2$.

$$(R)_a(R')_bN^+X^-$$

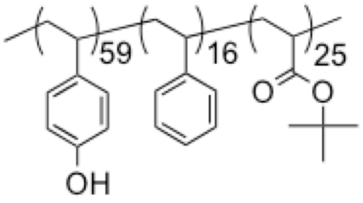
where a + b = 4, and R' is a partially fluorinated alkyl or aryl group, and X- is the counter anion



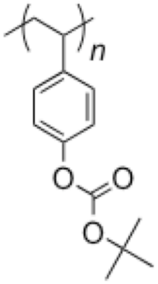
M. Wagner, et al., *Proc. of SPIE* **2006**, 6153, 61531I, *Proc. of SPIE* **2006**, 6153, 615345, *Proc. of SPIE* **2006**, 6153, 615346, *Proc. of SPIE* **2006**, 6153, 61533W, *Proc. of SPIE* **2007**, 6519, 651948.

Processing of Conventional Photoresists in scCO$_2$

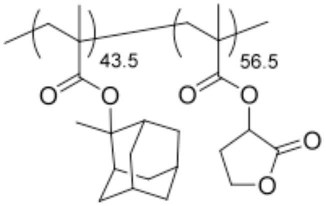
Structures of Conventional Photoresists



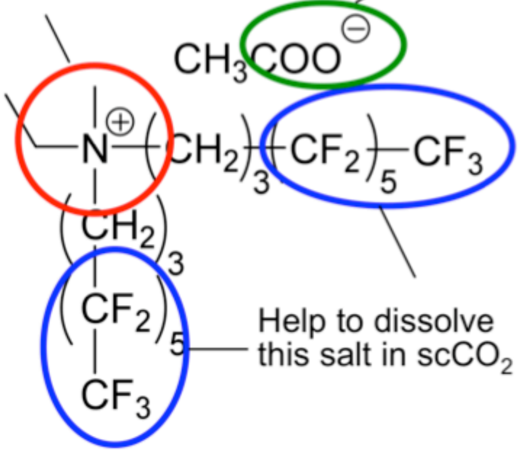
ESCAP



PBOCST



193nm resist



High affinity to phenolate and/or carboxylate moieties in polymer resists

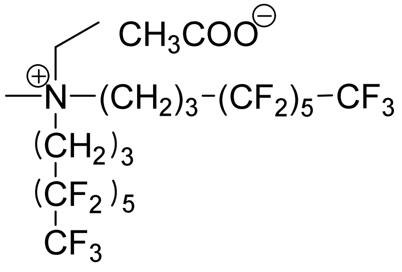
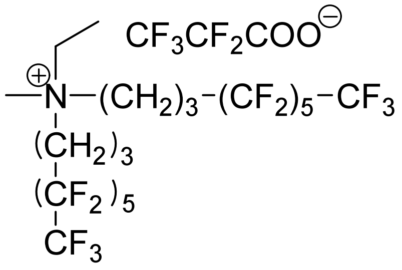
Deprotonate from OH and/or COOH in polymer resists

Help to dissolve this salt in scCO$_2$

- Conventional photoresists are not soluble in scCO$_2$ before or after exposure
- Could interact with QAS and become soluble
- Negative-tone images with sub-100 nm features

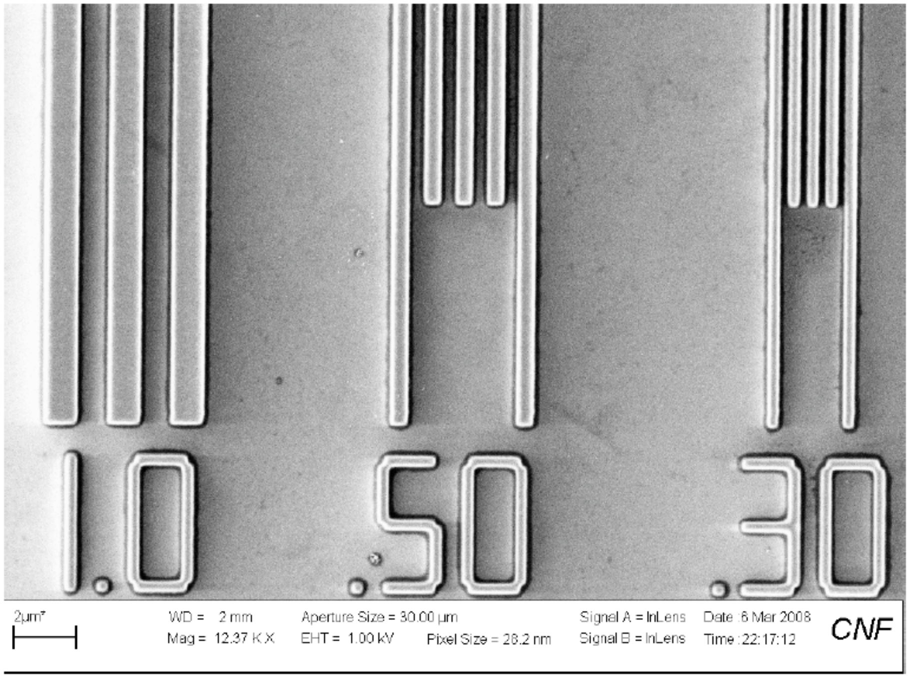
M. Tanaka, A. Rastogi, G. N. Toepperwein, R. A. Riggleman, N. M. Felix, J. J. de Pablo and C. K. Ober, *Chem. Mater* **2009**, 21, 3125-3135

Dissolution of Conventional Photoresists/QAS in $scCO_2$

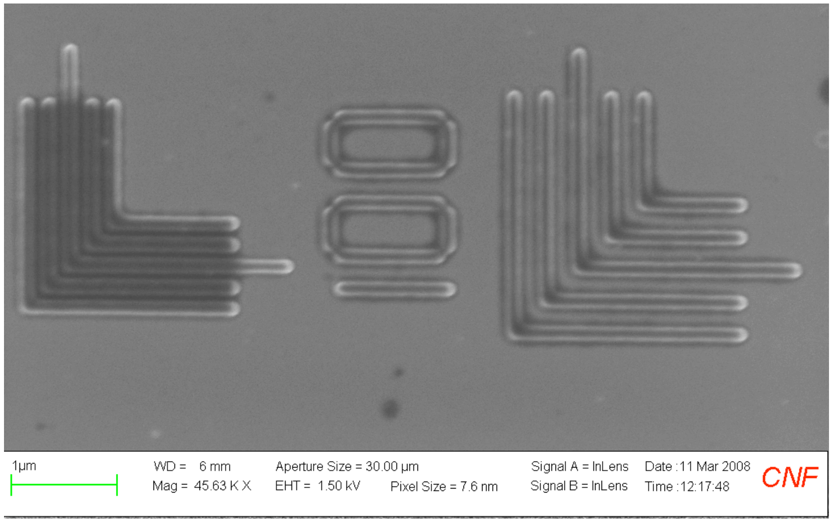
QAS	Resist	Unexposed	Exposed	note
 **QAS-4** (1.25 mM)	PBOCST	**Dissolution** (40 nm/min)	**Slow dissolution** (1-4 nm/min)	*Negative tone resist*
	ESCAP (Du Pont)	**Dissolution** (25 nm/min)	**No dissolution**	*Negative tone resist*
	PMAMA-co-GBLMA (Mitsubishi Rayon)	No dissolution	No dissolution	
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

E-beam Patterned Conventional Photoresists Developed in $scCO_2$

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



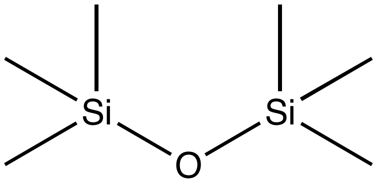
Dose: 107 uC/cm^2, QAS-4 (1.25 mM), dev. for 60 min at 50^{o}C, 5000 psi, flow 30 min



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

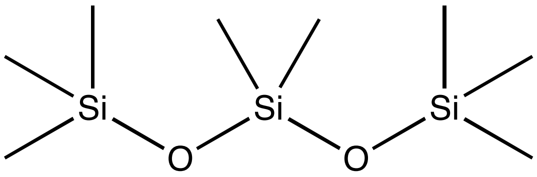
“Green” Solvent-Silicone Fluids

- Linear Methyl Siloxanes
- Low molecular weight
- Contain only silicon, carbon, hydrogen, and oxygen
- Non-polar solvent
- Solvent power can be enhanced by adding additives
- Low in toxicity, VOC exempt
- Non-ozone depleting
- Degrade to naturally occurring compounds
- Low surface tension



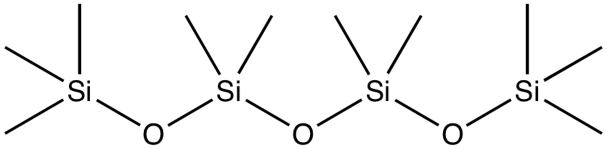
Hexamethyldisiloxane

HMDSO



octamethyltrisiloxane

OMTSO

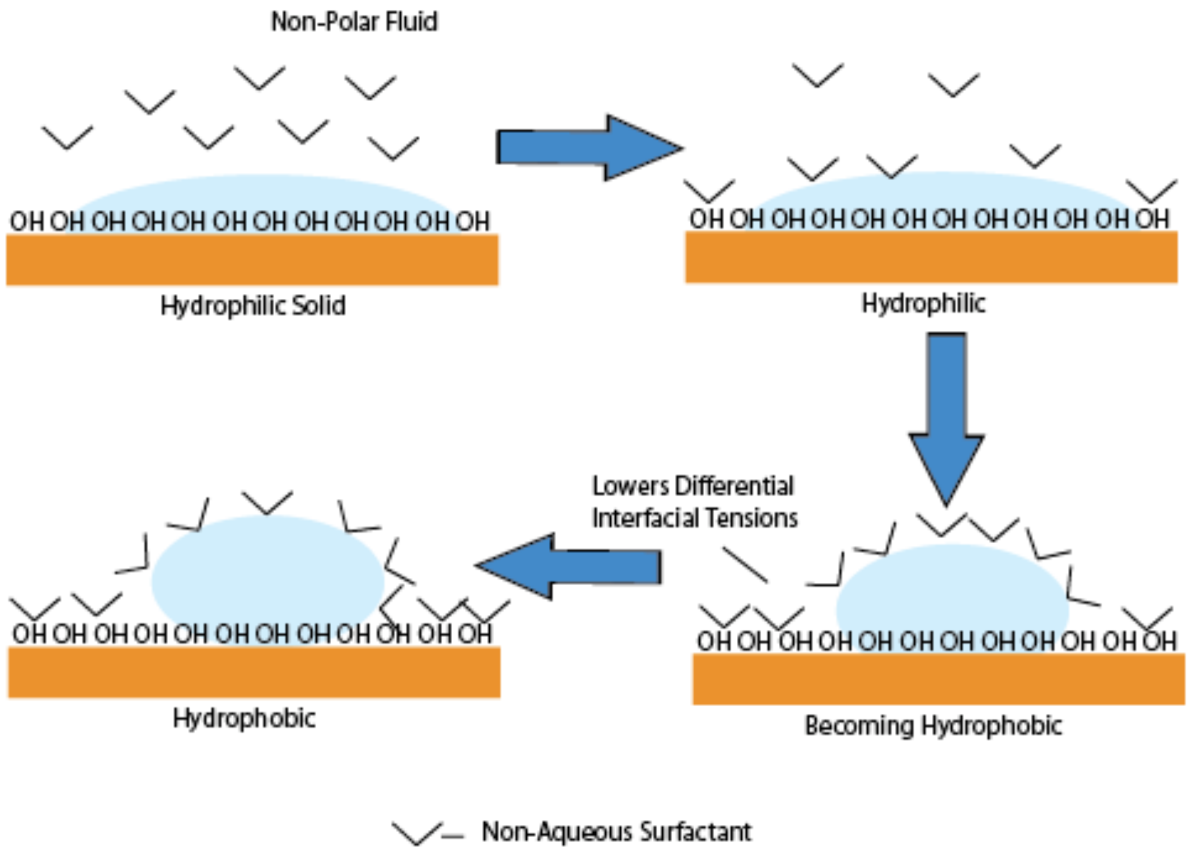


decamethyltetrasiloxane

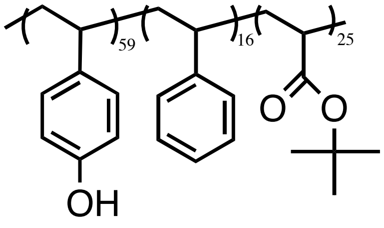
DMTSO

Existing “Green” Lithographic Process Using Silicone Fluids

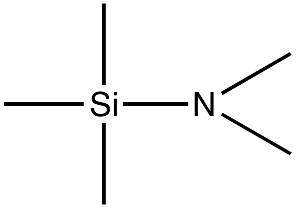
- Precision water removal-Immiscible fluid water displacement drying



Development of ESCAP in Silicone Fluids



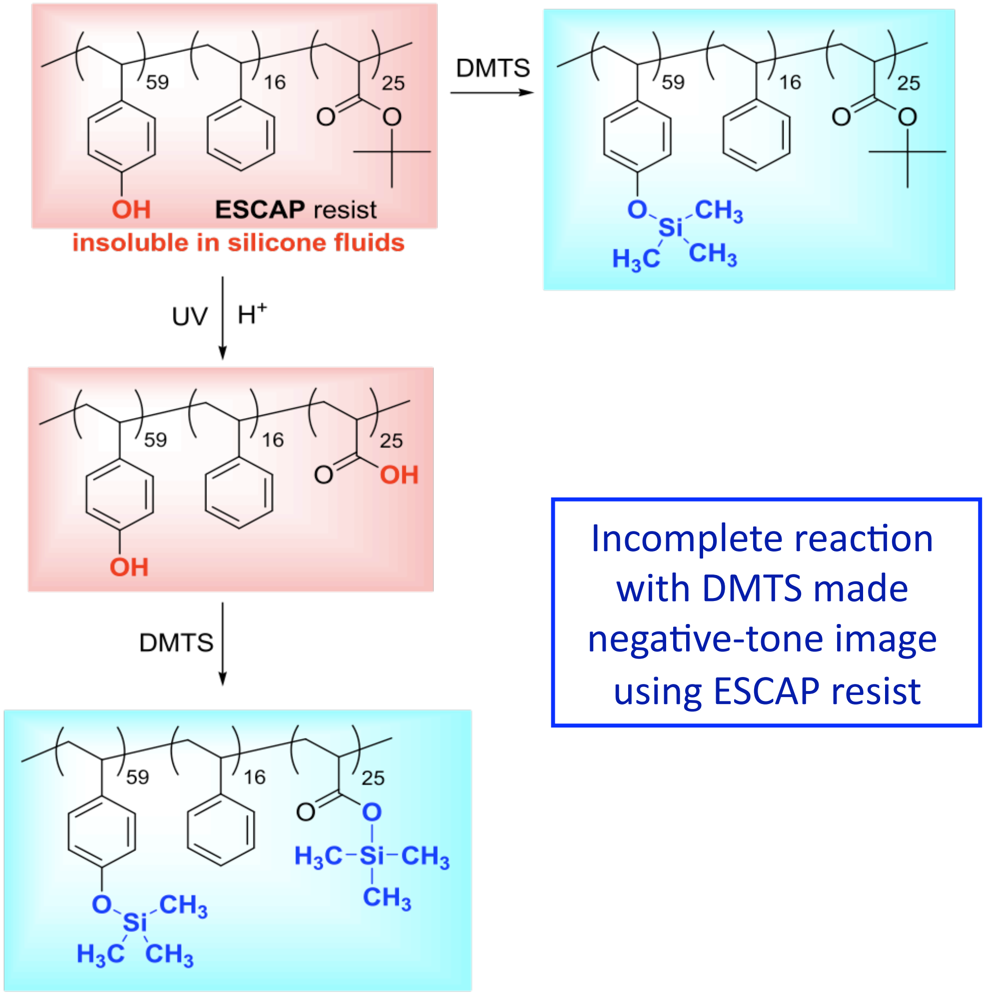
ESCAP



(N,N-Dimethyl)trimethyl silane

DMTS

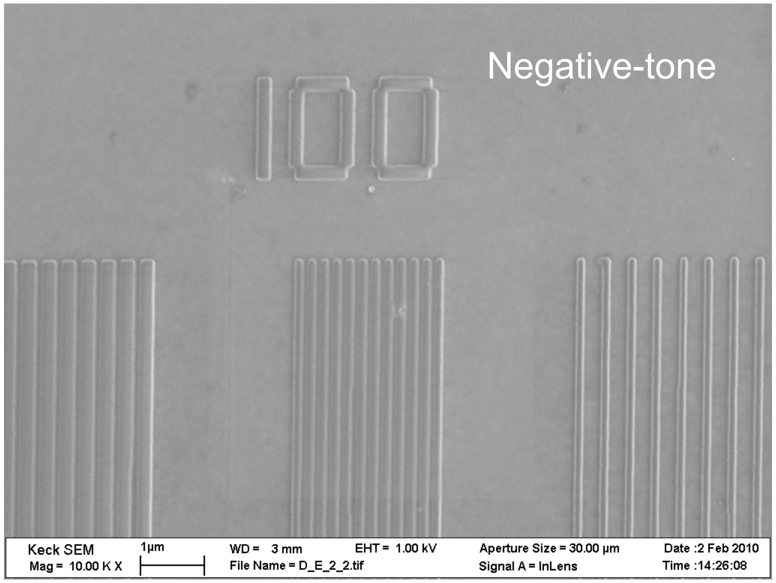
Structure modifier to incorporate trimethylsilyl(TMS) group



soluble in silicone fluids

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

Patterned ESCAP Developed in Silicone Fluids



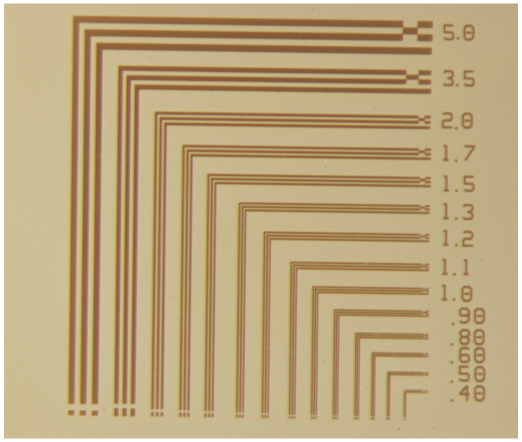
Photoresist:ESCAP

Chemical modifier: DMTS

Solvent: Decamethyltetrasiloxane

E-beam dose = 24 µC/cm^2

PEB: 115 ^{o}C, 60 sec



Photoresist:ESCAP

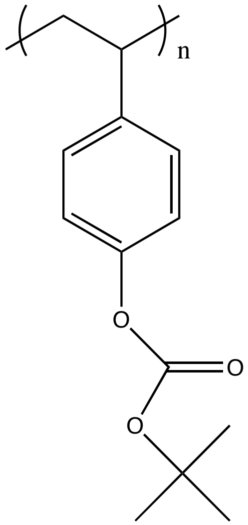
Chemical modifier: DMTS

Solvent: Octamethyltrisiloxane

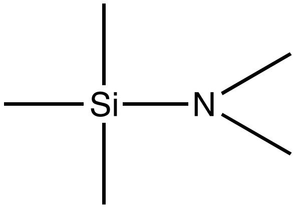
Dose = 50mJ/cm^2

PEB: 115 ^{o}C, 60 sec

Development of PBOCST in Silicone Fluids



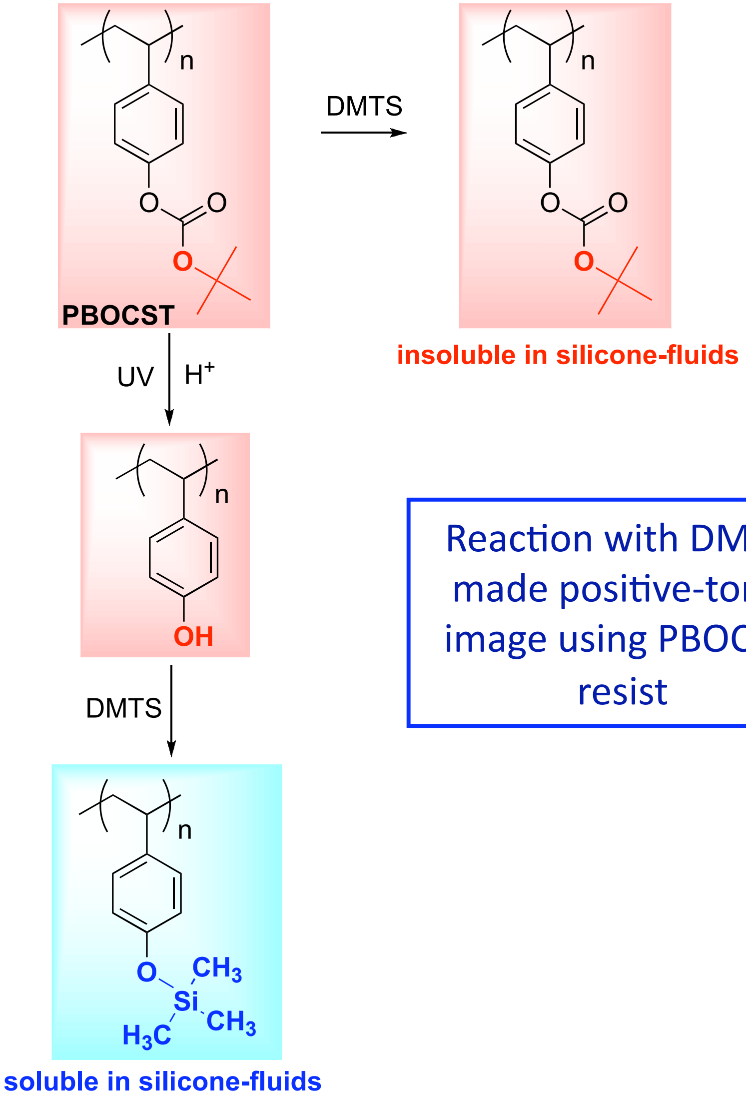
PBOCST



(N,N-Dimethyl)trimethyl silane

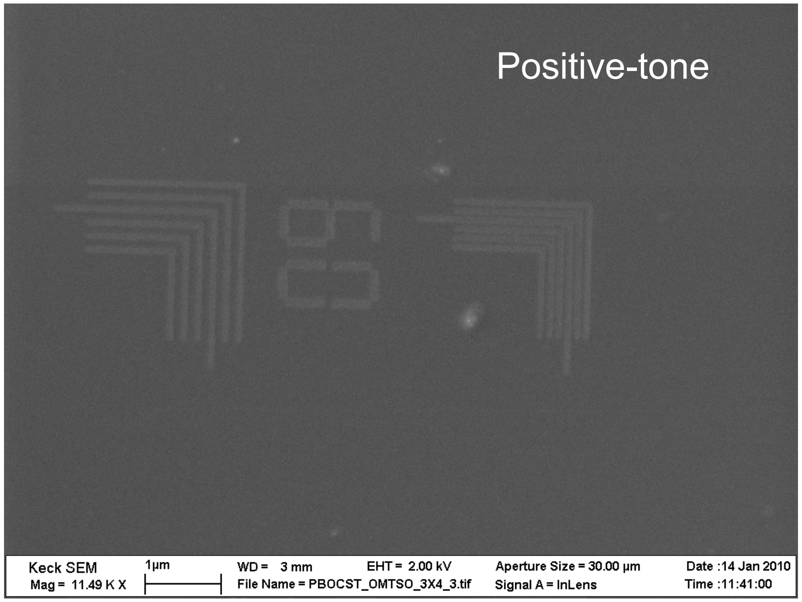
DMTS

Structure modifier to incorporate trimethylsilyl(TMS) group



Reaction with DMTS made positive-tone image using PBOCST resist

Patterned PBOCST Developed in Silicone Fluids



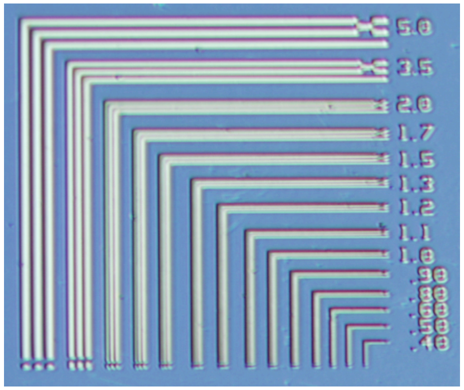
Photoresist:PBOCST

Chemical modifier: DMTS

Solvent:Octamethydisiloxane

E-beam dose = 150µC/cm^2

PEB: 90 ^{o}C, 60 sec



Photoresist:PBOCST

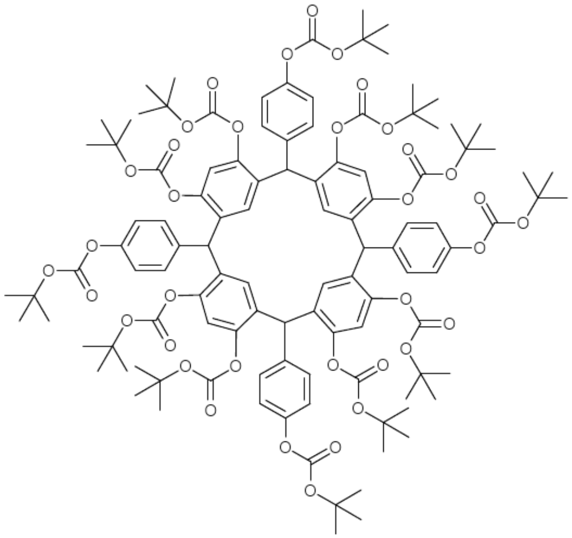
Chemical modifier: DMTS

Solvent: Hexamethyldisiloxane

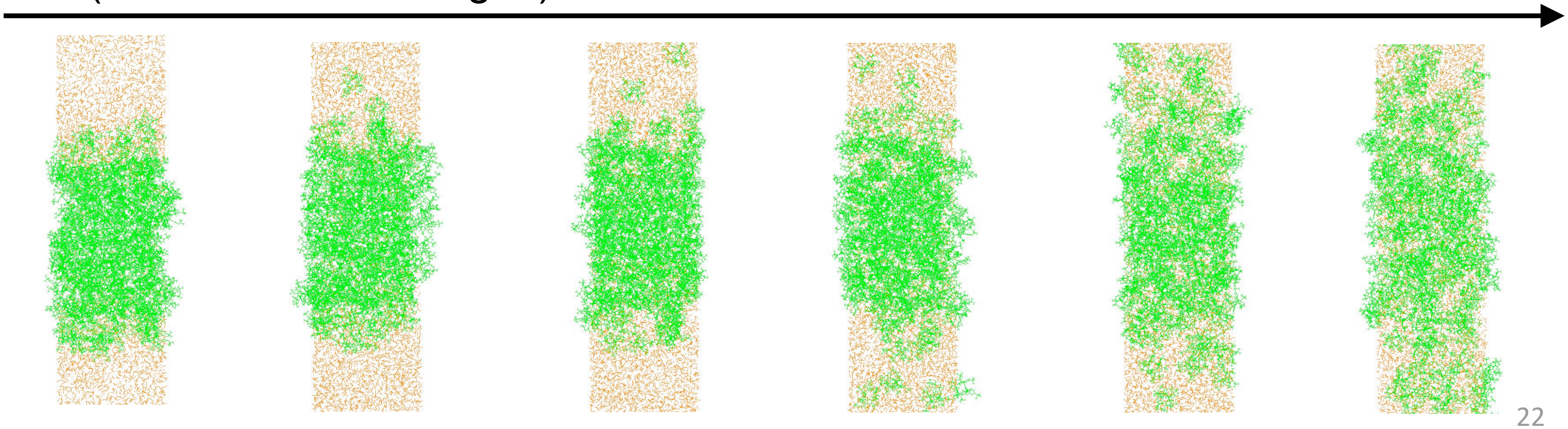
Dose = 550 mJ/cm^2

PEB: 90 ^{o}C, 60 sec

Molecular Glass Resists-Calixarene



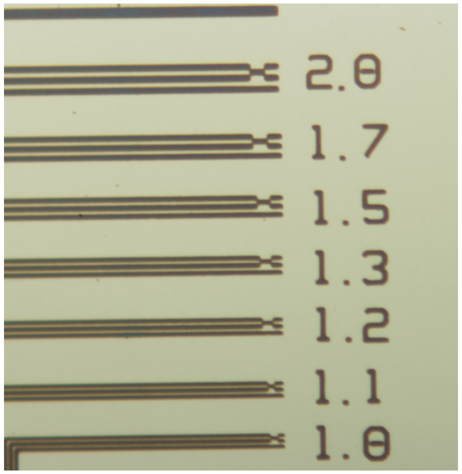
- Potential to produce high-resolution patterns
- Ring structure imparts high Tg
- Soluble in silicone fluids and $scCO_2$ without any additives
- Negative-tone images
- Computer simulation done by the de Pablo group at UW-Madison



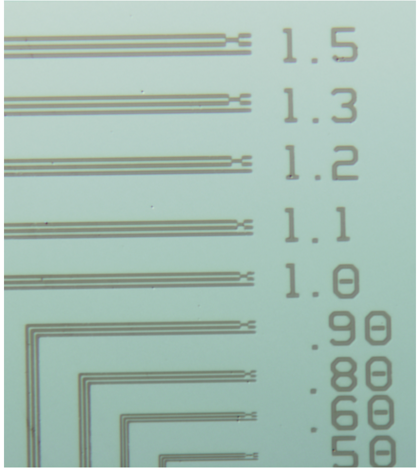
Time (1-2ns between images)

Calixarene Develoed in Silicone Fluids

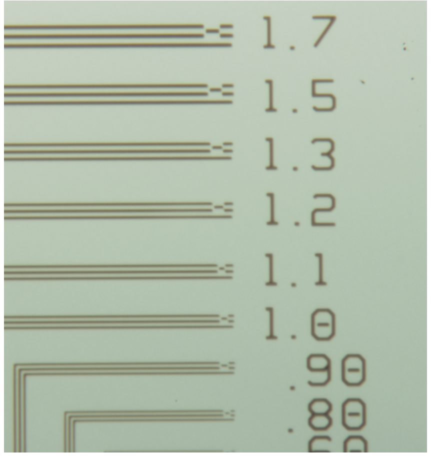
Negative-tone



OMTSO
Dose:250 mJ/cm^2
PEB:90^{o}C, 30 sec



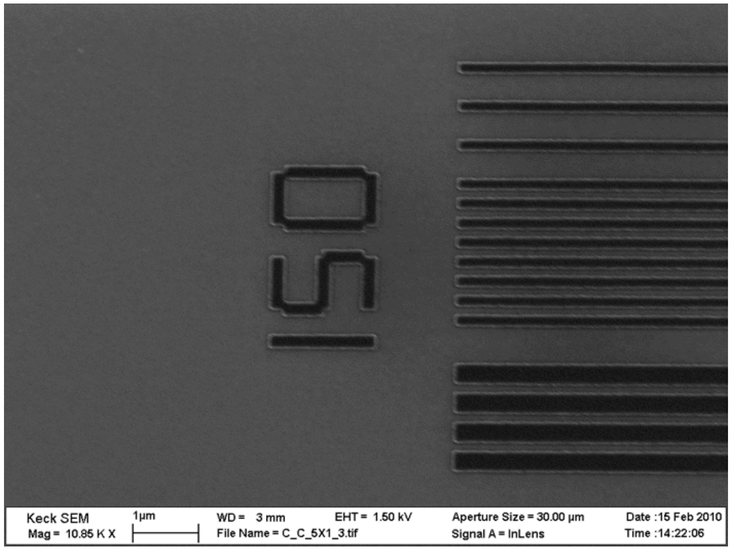
HMDSO
Dose:350 mJ/cm^2
PEB:90^{o}C, 30 sec



DMTSO
Dose:300 mJ/cm^2
PEB:90^{o}C, 30 sec

E-beam Patterned Calixarene

scCO$_2$

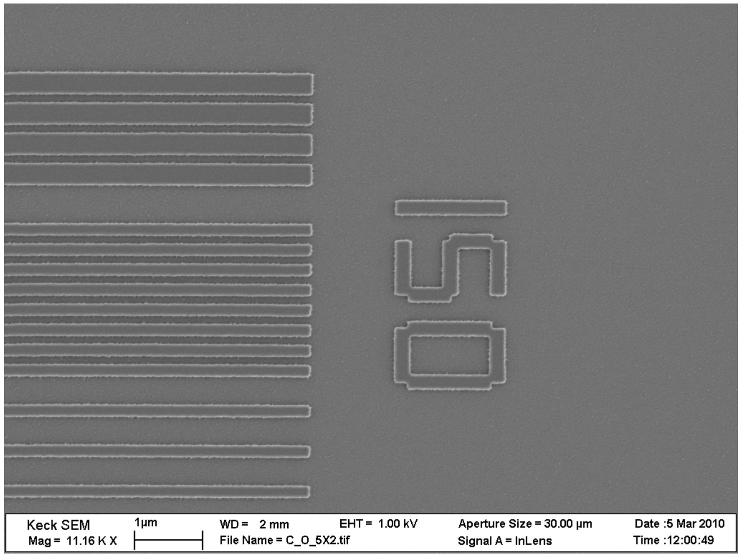


E-beam dose = 112µC/cm^2

PEB: 90 ^{o}C, 60 sec

2000 psi,40 ^{o}C, 5 min

Silicone Fluids

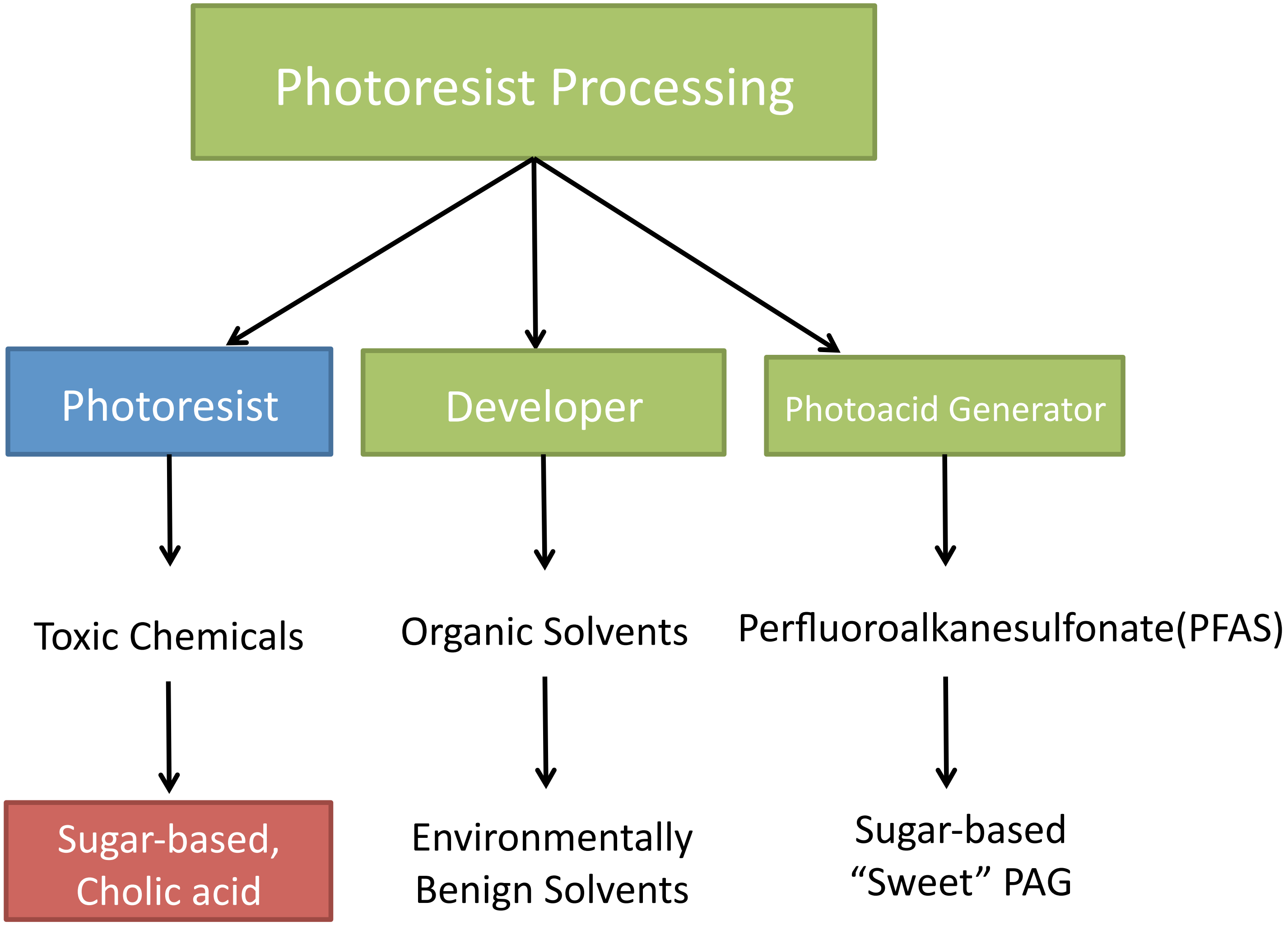


E-beam dose = 96µC/cm^2

PEB: 90 ^{o}C, 60 sec

Solvent:OMTS

Approaches



Photoresist Processing

Photoresist

Developer

Photoacid Generator

Toxic Chemicals

Organic Solvents

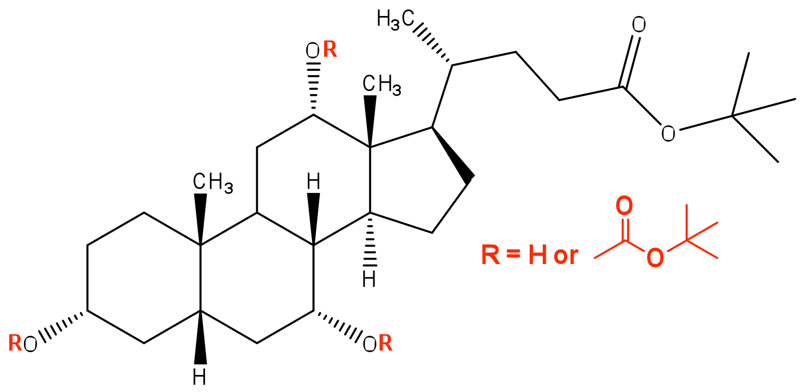
Perfluoroalkanesulfonate(PFAS)

Sugar-based,
Cholic acid

Environmentally
Benign Solvents

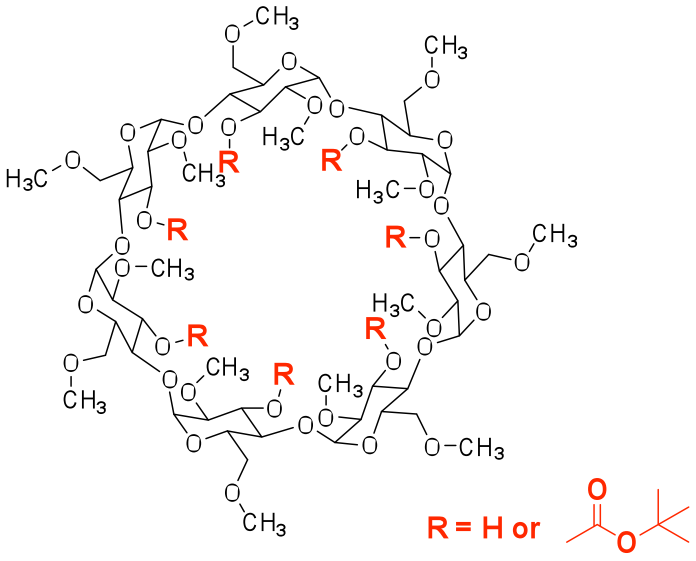
Sugar-based
“Sweet” PAG

MG Resists with Alicyclic Cores and *t*Boc Groups



*t*BOC-protected *tert*-butyl cholate

Tg = ~100 °C



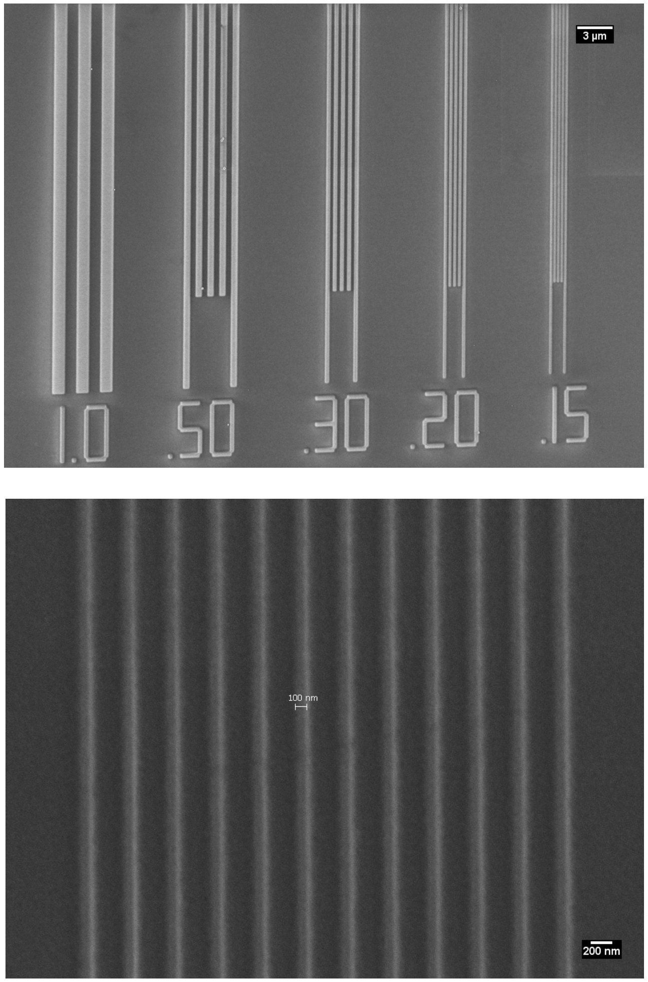
*t*BOC-protected methylated β-cyclodextrin

Tg = ~125 °C

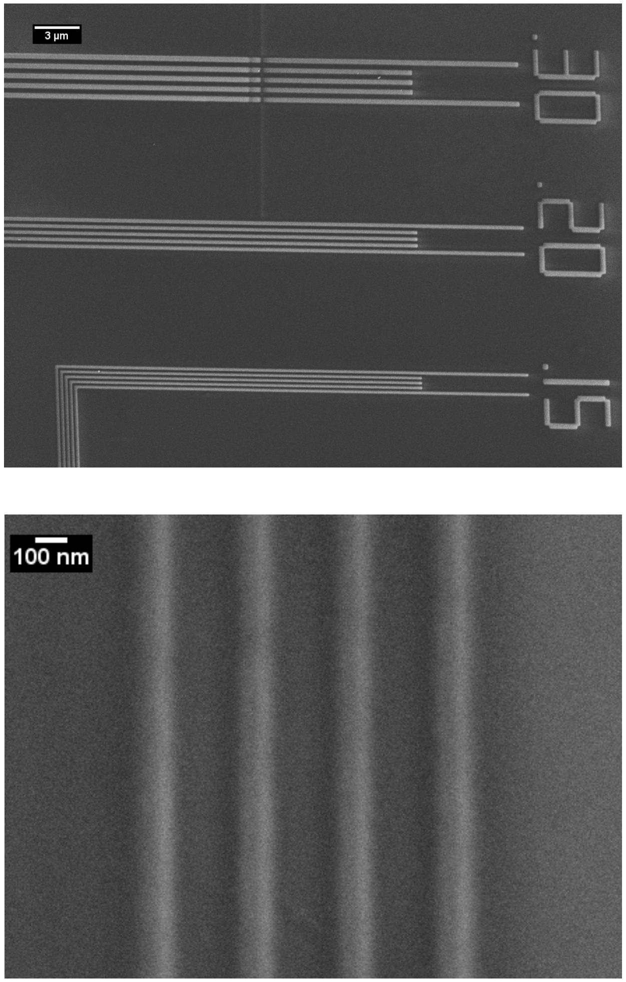
- Cholic acid cores are etch-resistant and have strong intermolecular interactions which can contribute to the relatively high glass transition temperatures of cholates.
- Cyclodextrins are good hosts for inclusion complexes.

Lithographic Performance of Cholate and Cyclodextrin

*t*Boc-protected *tert*-butyl cholate

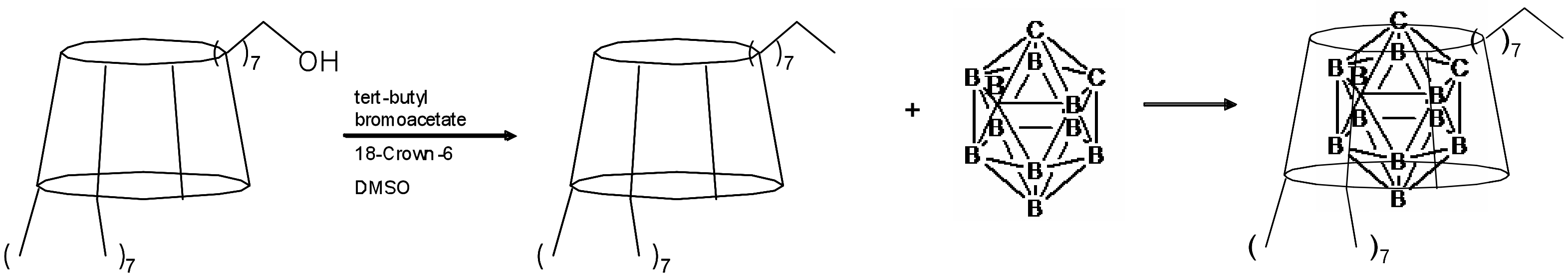


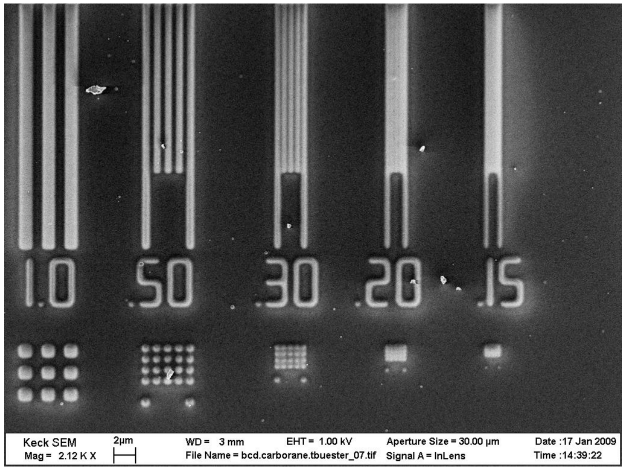
*t*Boc-protected methylated β-CD

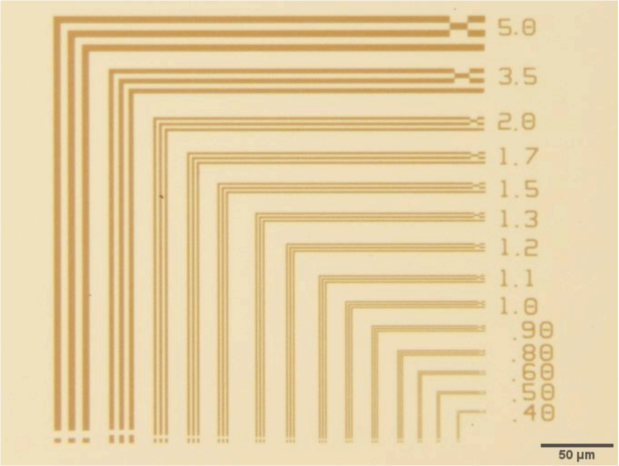


J. Sha, J.-K. Lee, C. K. Ober, *Proc. of SPIE* **2009**, 7273, 72732T

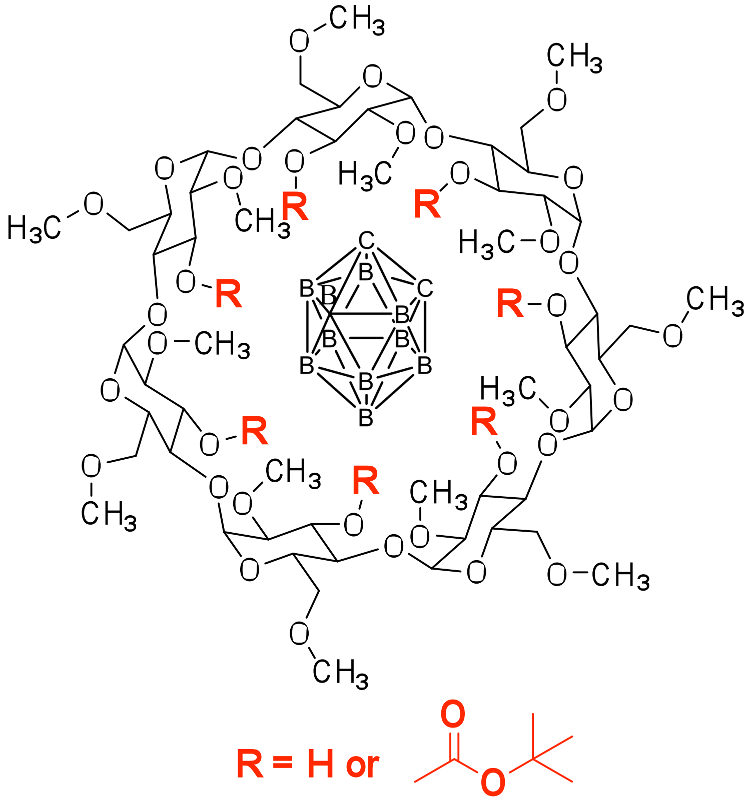
Cyclodextrin - Carborane Inclusion Complex



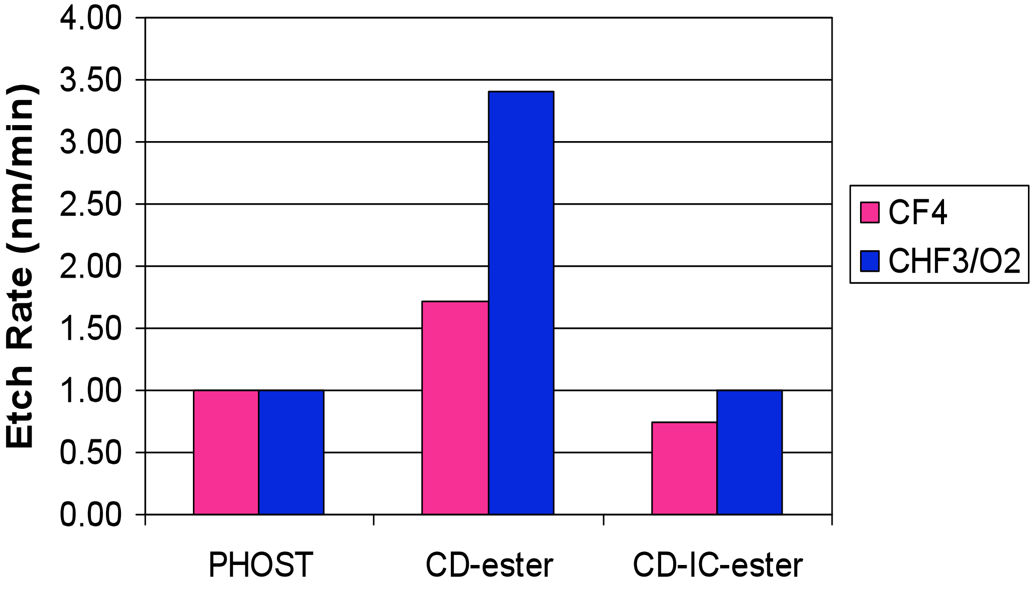




Incorporating Carborane for Inclusion Complex to Increase Etch Resistance of Cyclodextrin



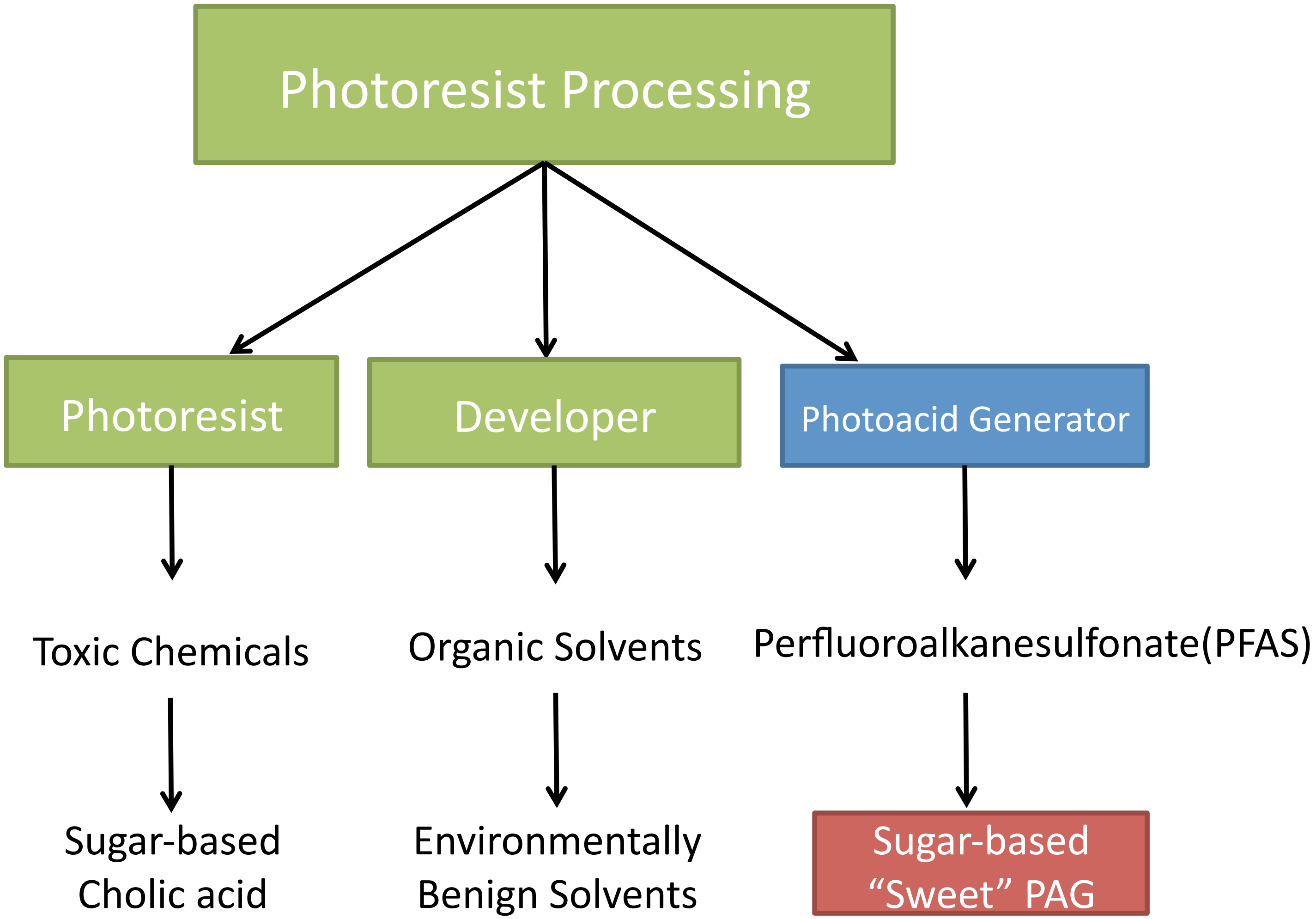
Etch Rates of mβCD and mβCD-IC
In Comparison with PHOST



Etch Rates of CD-IC comparable to PHOST

M. Krysak, A. De Silva, J. Sha, J.-K. Lee, C. K. Ober**,** *Proc. of SPIE* **2009**, 7273, 72732N

Approaches



Photoresist Processing

Photoresist

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Photoacid Generator

Toxic Chemicals

Organic Solvents

Perfluoroalkanesulfonate(PFAS)

Sugar-based
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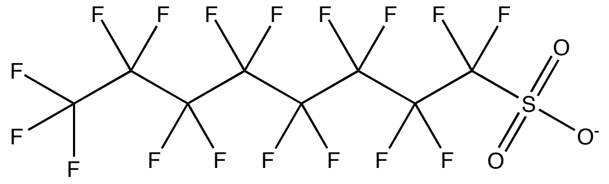
Environmentally
Benign Solvents

Sugar-based
“Sweet” PAG

PFOS-Based PAG



- PFOS($C_8F_{17}SO_3^-$)-based PAGs

-high quantum yield for acid generation

-excellent resist miscibility

-good thermal and storage stability in resist films

-suitable diffusion length

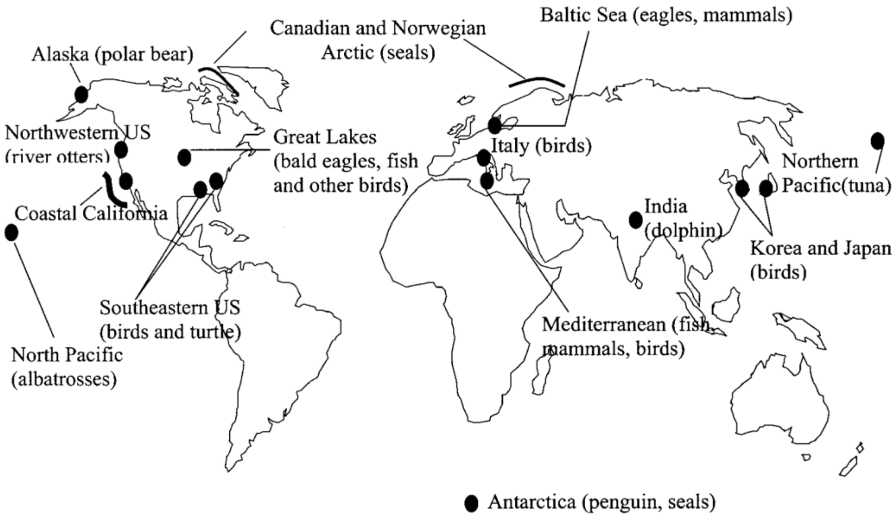
- Perfluoroalkanesulfonate (PFAS) groups with more than four CF_2 are environmental hazards

-bioaccumulation

-toxic

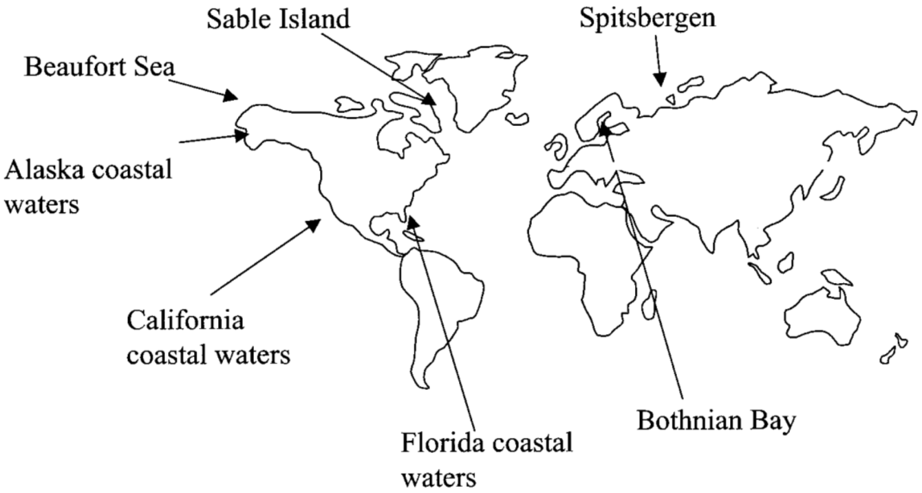
PFOS Problems

Global Distribution of PFOS in Wildlife



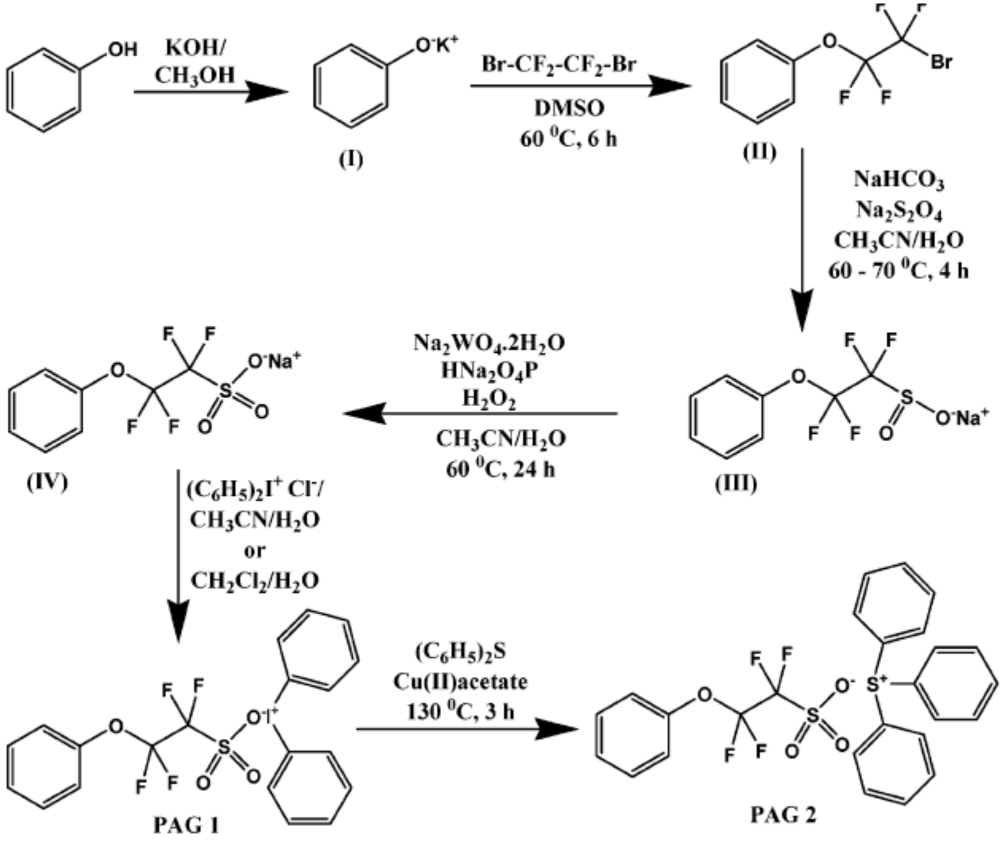
Environ. Sci. Technol. 2001, *35*, 1339.

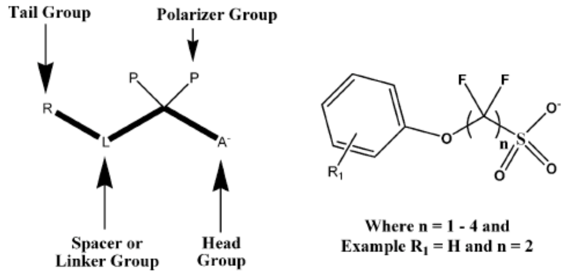
Accumulation of PFOS in Marine Mammals



Environ. Sci. Technol. 2001, *35*, 1593.

PFOS-Free PAG

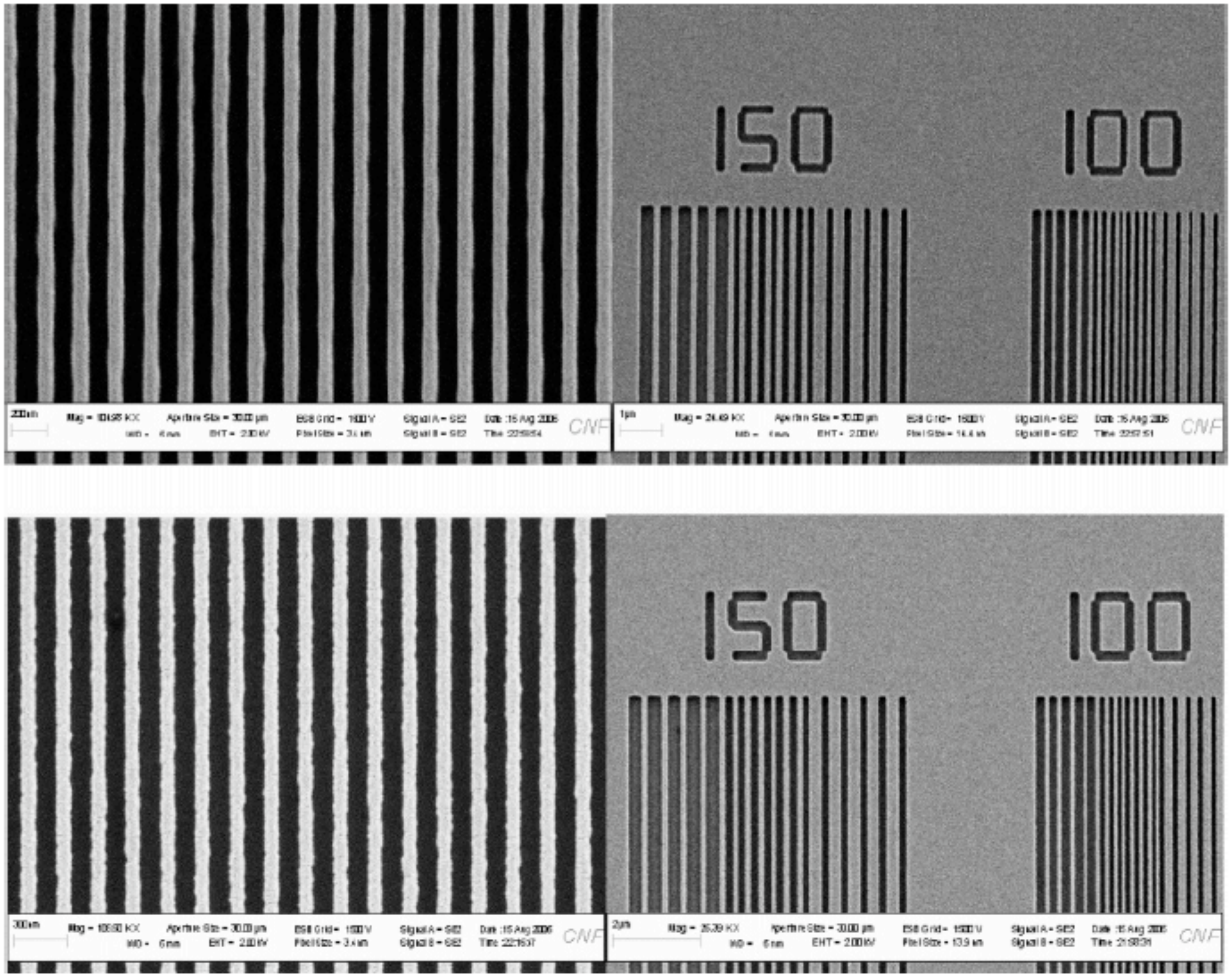




- Sulfonate as acid head group
- Perfluorinated unit to enhance acid strength
- Spacer to link tail and core
- Tail group may be used to vary acid strength, size , miscibility, and transparency

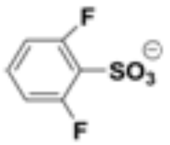
R.Ayothi, Y. Yi, H. B. Cao, W. Yueh, S. Putna, C. K. Ober, *Chem. Mater*. **2007**, 19, 1434-1444

E-beam Patterns Using PFOS-Free PAG



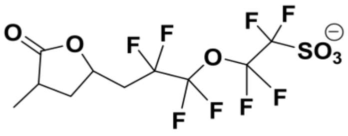
R.Ayothi, Y. Yi, H. B. Cao, W. Yueh, S. Putna, C. K. Ober, *Chem. Mater*. **2007**, 19, 1434-1444

Environmental Compatibility of New PFOS-Free PAG Anions



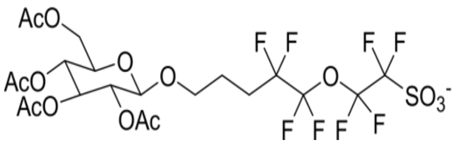
1st generation

(Aromatic structure)



2nd generation

(Aliphatic structure)

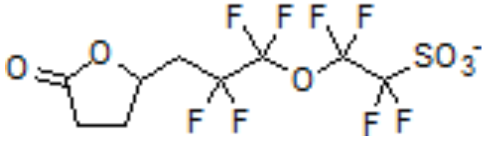


3rd generation

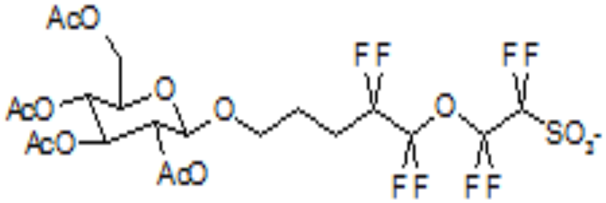
(Sugar structure)

- 1st Generation Non-PFOS PAGs: Low toxicity and low bioaccumulation potential but relatively persistent to microbial degradation.
- 2nd Generation Non-PFOS PAGs: Preliminary results show that replacing the phenyl group with a UV-transparent alicyclic moiety increases the susceptibility of the PAG compound to biodegradation.
- 3rd Generation Non-PFOS PAGs: Replacing with sugar and natural groups is expected to increase biodegradation.

Chemical Degradation of New PAGs



Lactone



Sweet PAG (Sweet)

Compounds	Degradation	PAG Removed (%)	Fluoride Released (%)
Lactone PAG	YES	100	5.7
Sweet PAG	YES	100	8.7
PFOS	NO	0.8	0.6
PFBS	NO	0.5	0.4

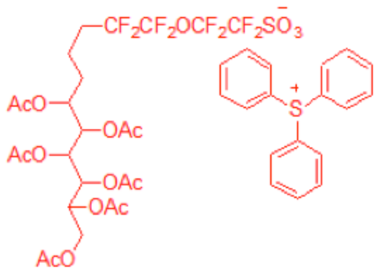
<u>Fenton's reaction:</u>

$Fe^{2+} + H_2O_2 \dashrightarrow Fe^{3+} + \cdot OH + OH^-$
$Fe^{3+} + H_2O_2 \dashrightarrow Fe^{2+} + \cdot OOH + H^+$
PAG + radicals → Oxidized products

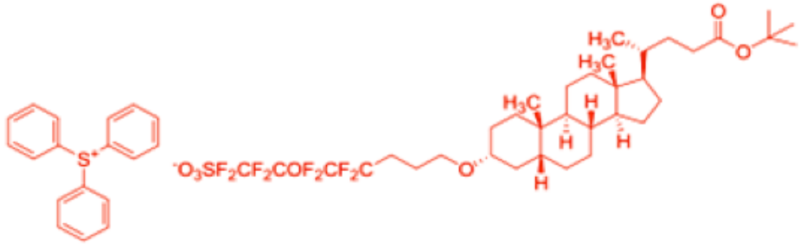
- Non-PFOS PAG compounds were effectively degraded by advanced oxidation using the Fenton's reaction
- Perfluorinated PAGs such as PFOS and PFBS were resistant to attack.

Sugar-Based "Sweet" PAG

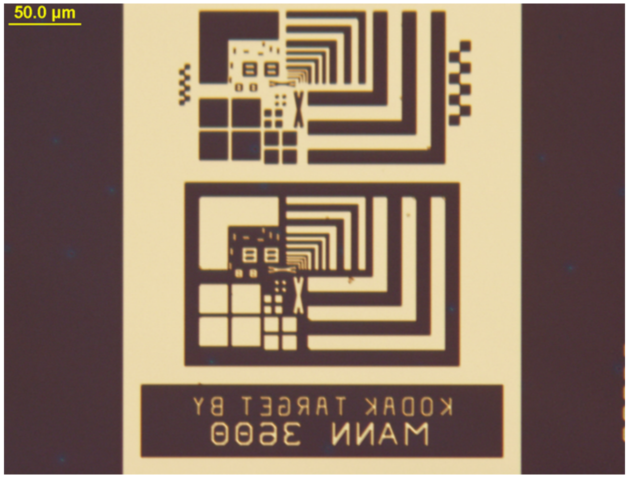
- Linear type

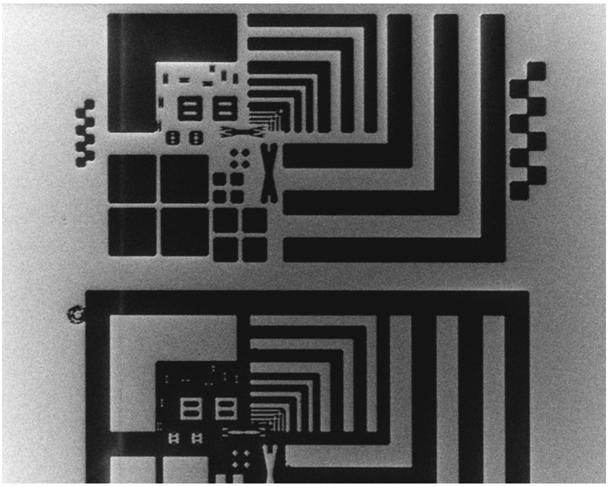


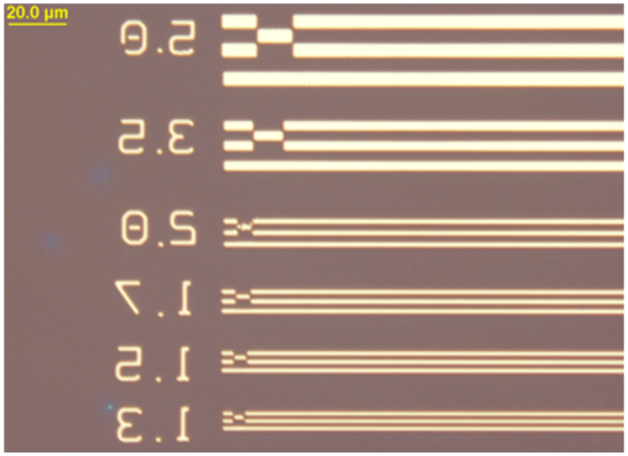
- PAG Based on steroids and their analogs

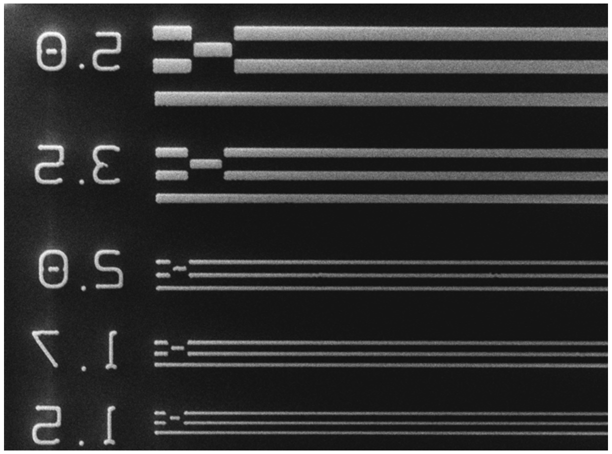


Lithographic Evaluation of Linear "Sweet" PAG









Conclusions

- We have demonstrated the use of two environmentally benign solvents to develop conventional photoresists and molecular glass resists
- Both $scCO_2$ and silicone fluids have the potential to eliminate pattern collapse because of their low surface tension
- Sugar-based “Sweet” PAGs present significant ESH advantages compared to PFOS-based PAGs

Acknowledgements

- Ober group
- de Pablo Group at University of Wisconsin
- SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
- Cornell Center for Materials Research(CCMR)
- Cornell NanoScale Science and Technology Facility(CNF)