Cornell University

Environmentally Friendly Non-Aqueous Development

ERC TeleSeminar
August 11th, 2011

Christine Y. Ouyang[1], Gregory N. Toepperwein[2], Juan J. de Pablo[2] and Christopher K. Ober[1]

[1]Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853

[2]Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706

Outline

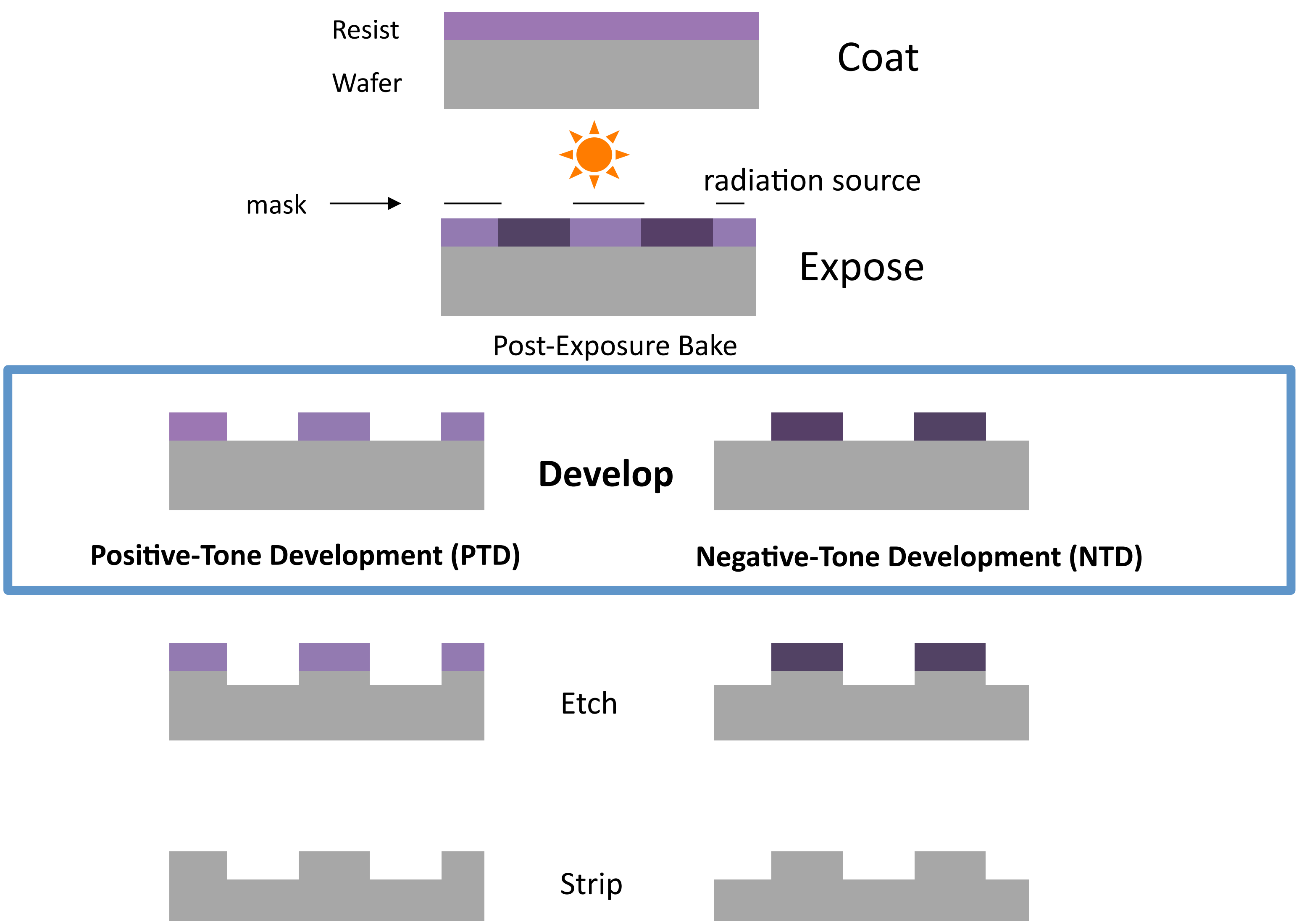
- Lithographic Process
- Solvent-based development
- Key Issues related to development process
- Development in ESH friendly, non-polar solvents

-Supercritical CO_2

-Silicone Fluids

- Summary
- Acknowledgements

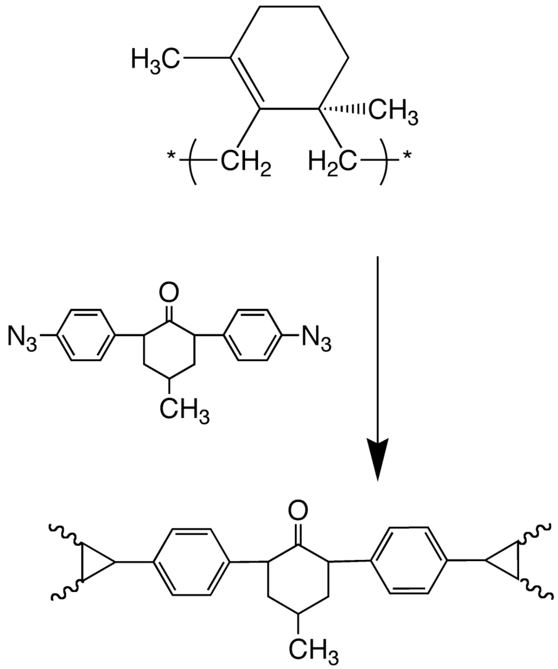
Lithographic Process



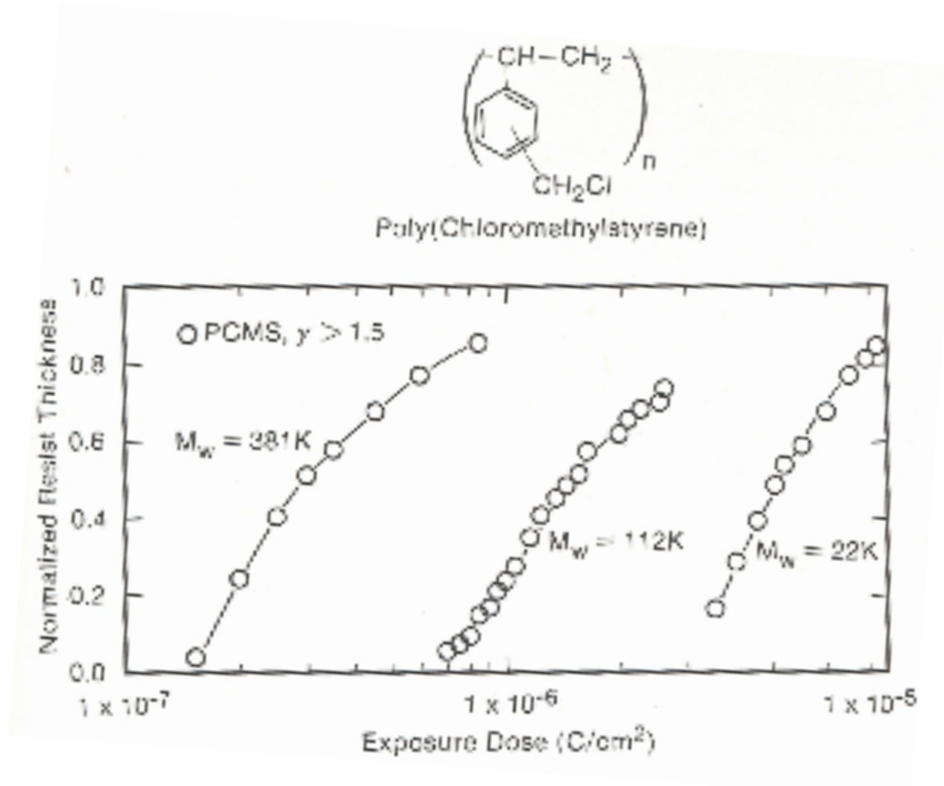
Solvent-based Development

- Classical solvent based patterning materials
- Flory-Huggins theory and development
- The special case of chemical amplification
- Issues related to development process
- Development in ESH friendly, non-polar solvents
  - Supercritical CO_2
  - Silicone fluids

Solvent Development: A Retrospective Look



Cyclized Polyisoprene
365 nm DUV



Poly(chloromethyl styrene)
E-beam

L. Thompson, C.G. Willson, M. Bowden, "Introduction to Microlithography, 2nd Ed.", ACS, Washington, DC 1994.

Solvating Polymers and Blending Mixtures

$$\frac{\Delta G}{RT} = \boxed{\phi_1 \ln \phi_1 + \frac{\phi_2}{x} \ln \phi_2} + \boxed{\chi \phi_1 \phi_2}$$

Entropic Enthalpic

Key Points

- Big is important (chain size)
  - Can be basis for solubility change
  - Limits entropic drive for solution formation
- Polymer solubility driven by enthalpic effects - how well solvent interacts with polymer

Flory-Huggins

$$\chi = V_{seg}(\delta_1 - \delta_2)^2 / RT$$

- Many ways to calculate χ
- Simple conceptually to use solubility parameter - related to energy needed to completely separate individual units
- Intermolecular forces and enthalpic factors (H-bond, ionic bond, etc.) are stronger than van der Waals interactions

An Issue with Solvent Development

- By F-H theory, if no chemical change, then solvent good for both regions
- Leads to swelling and "snaking"
- Attached to surface - stresses give unrepairable deformation

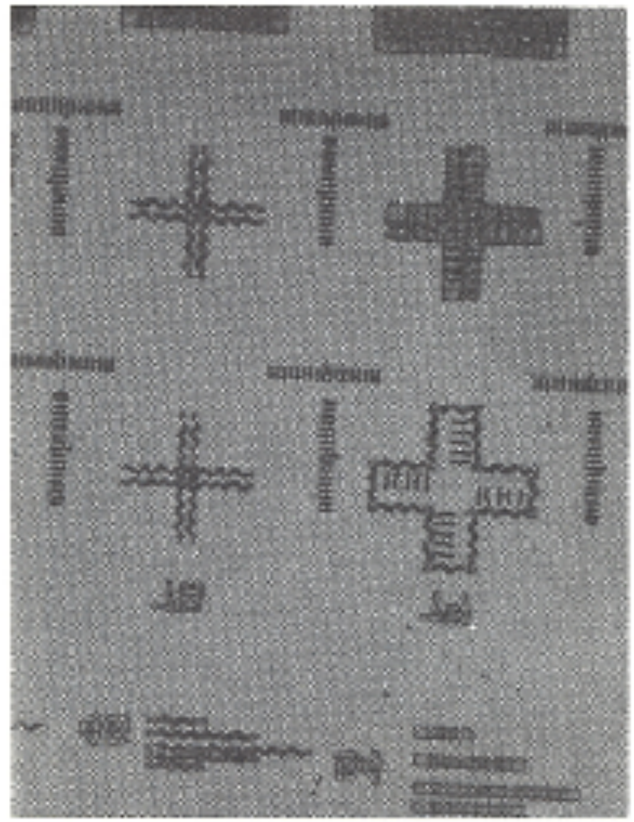
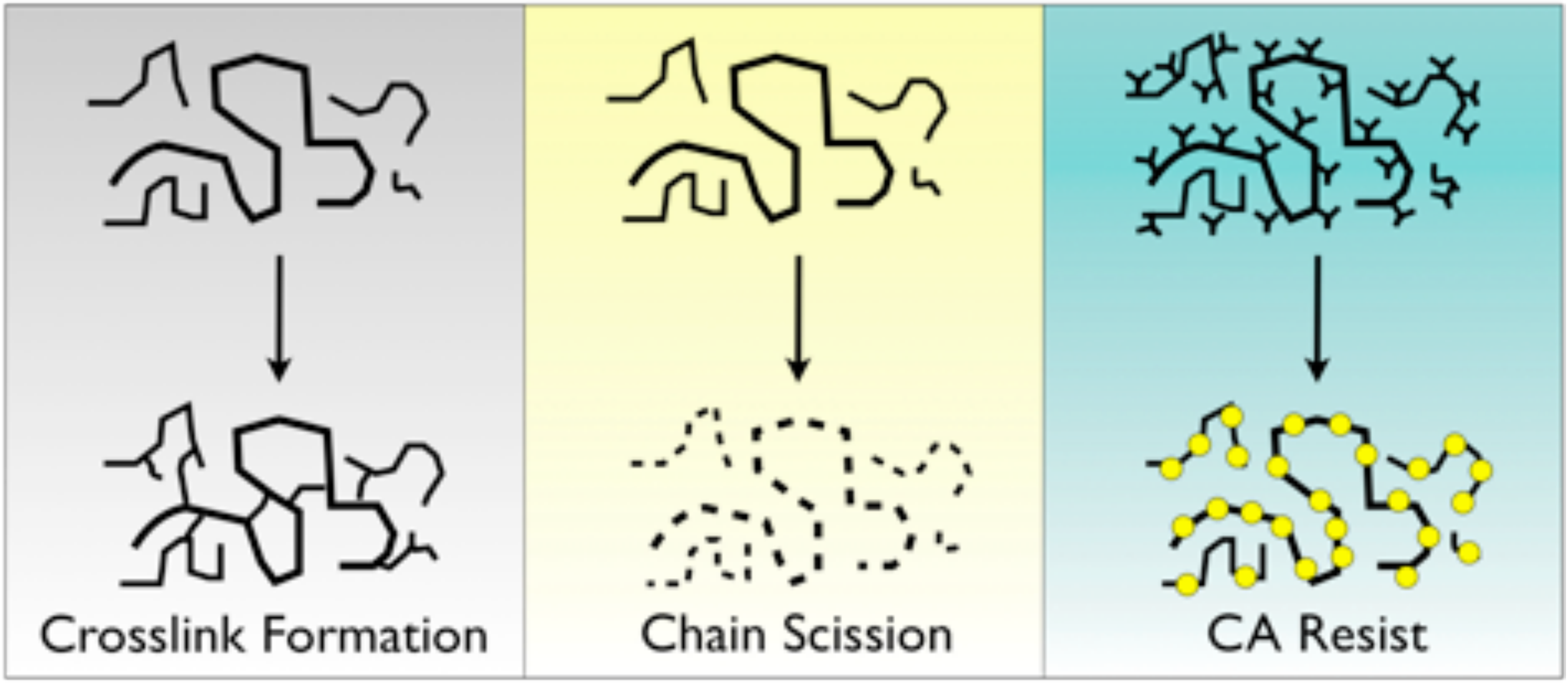


Figure 38. Optical photomicrograph of swollen images in an experimental, negative optical resist demonstrating the "snaking" phenomenon. Stress relief in long, narrow resist lines is achieved by the obvious, oscillatory distortion.

Reference: L. Thompson, C.G. Willson, M. Bowden, "Introduction to Microlithography, 2nd Ed.", ACS, Washington, DC 1994.

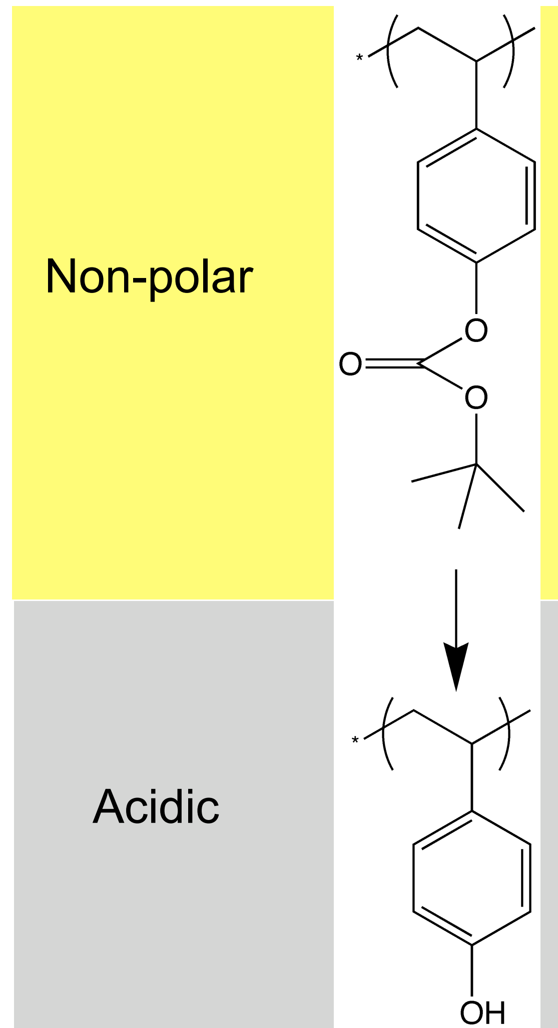
Driving Forces in Solubility Change



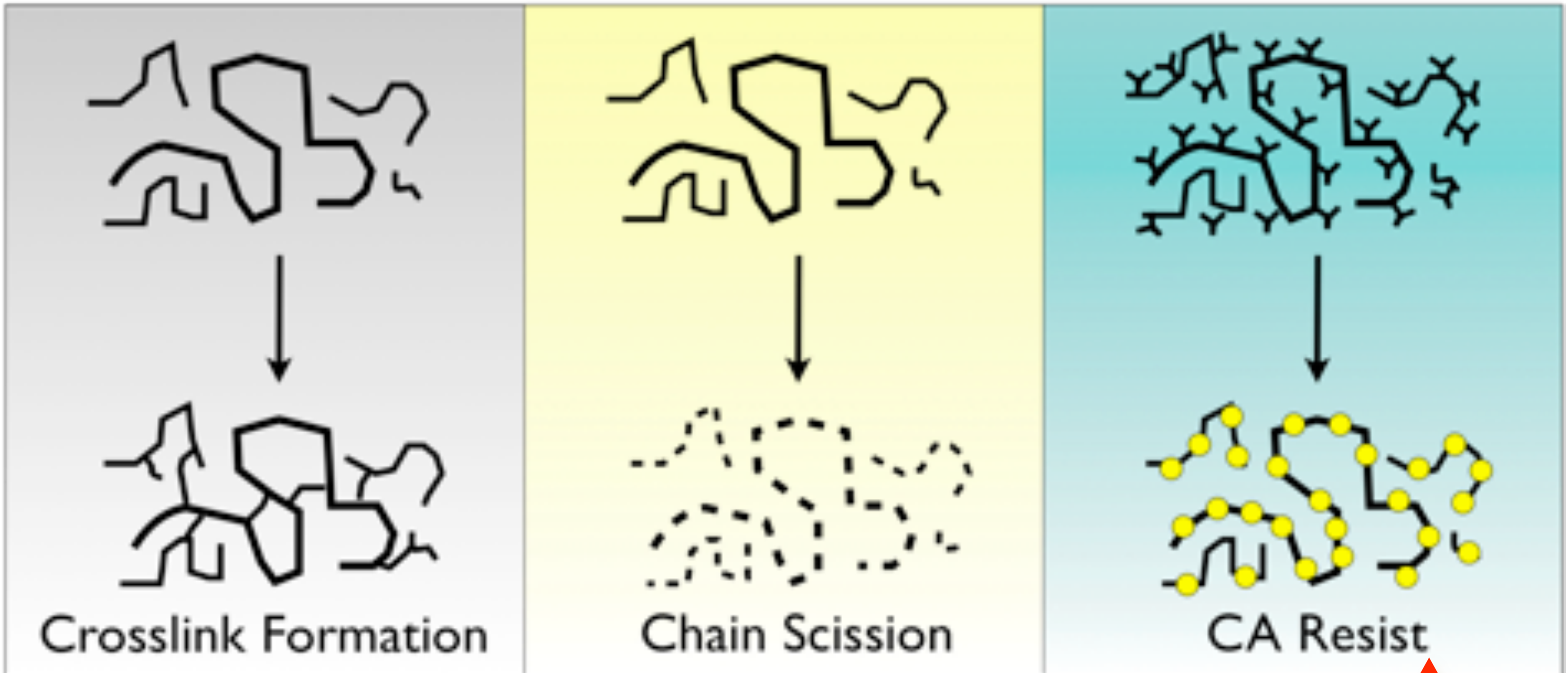
- Each approach is capable of changing dissolution behavior between exposed and unexposed regions

Solvent Develop - CA Resists

- Why is it different?
  - strong H-bonds hold together exposed regions - phenolic and acid groups
  - requires solvent strong enough to break up H-bonds in exposed region
- Charge and polarity - affecting χ
- Bigger difference in δ_1 and δ_2
- Non-polar solvents can more easily dissolve unexposed resist, due to weaker intermolecular bonding



Driving Forces in Solubility Change

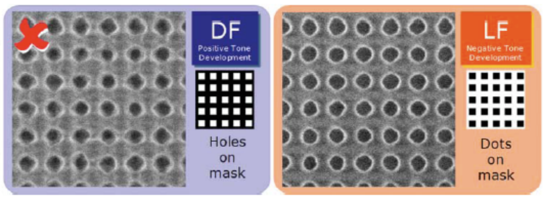


DP_n ↑ DP_n ↓ χ ↕

- Polarity change has more dramatic effect on solubility contrast than DPn

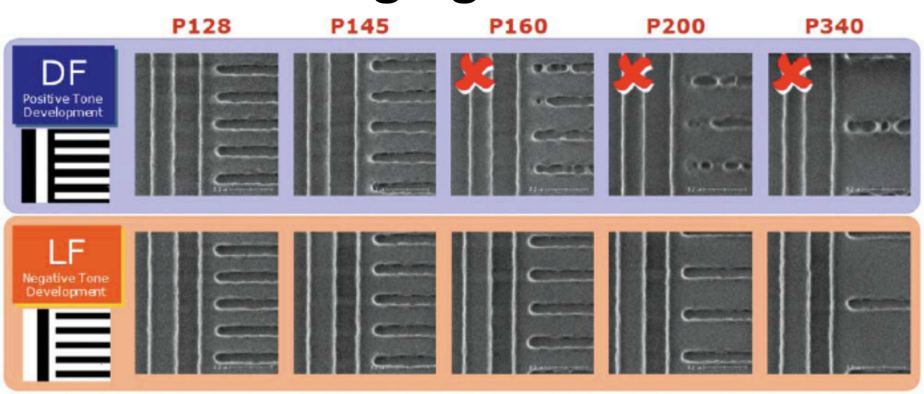
Recent Negative-Tone Solvent-based Development

- Contact hole patterning



45 nm contact holes

- Trench imaging

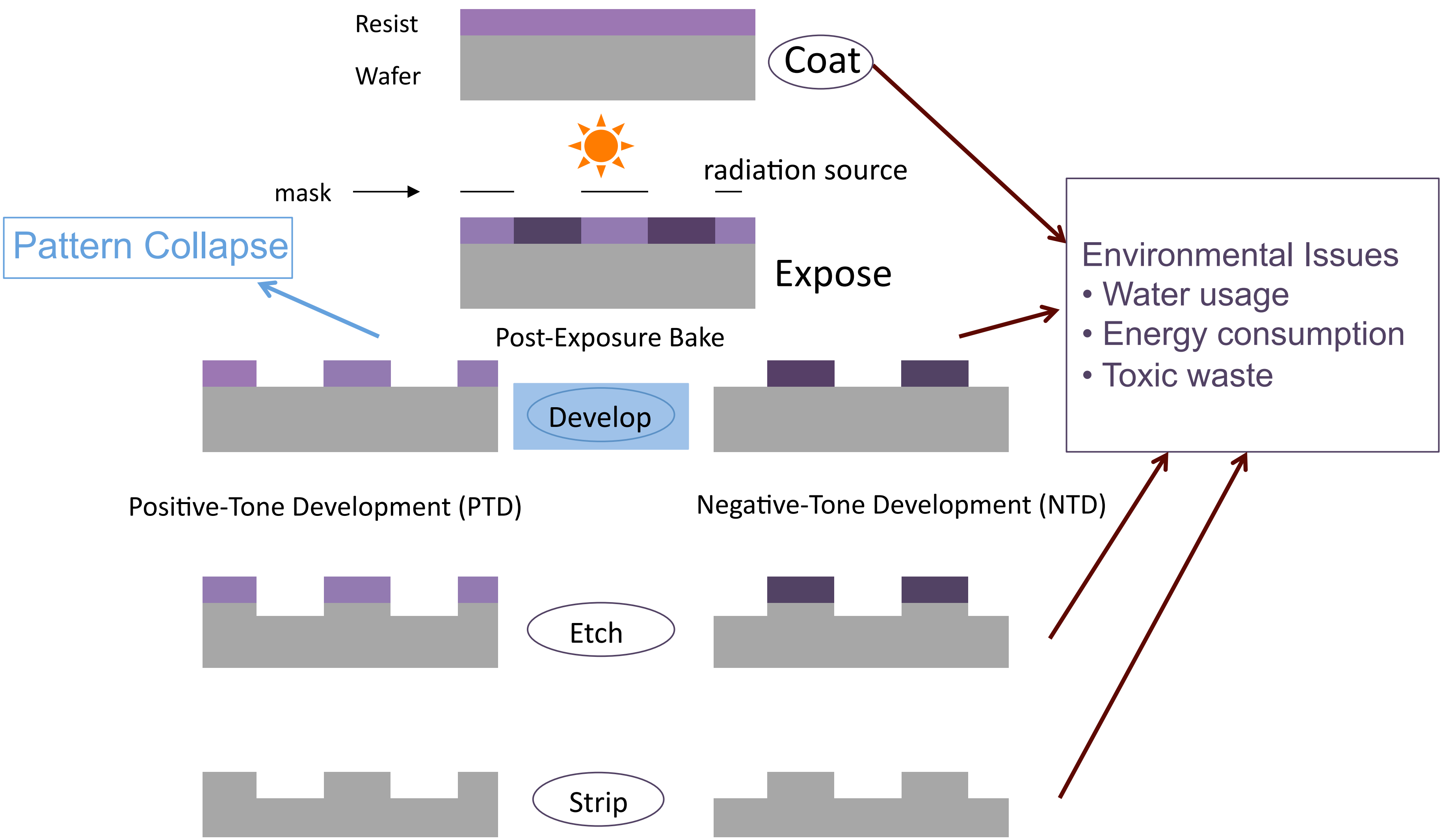


40 nm trenches with varying trench pitch

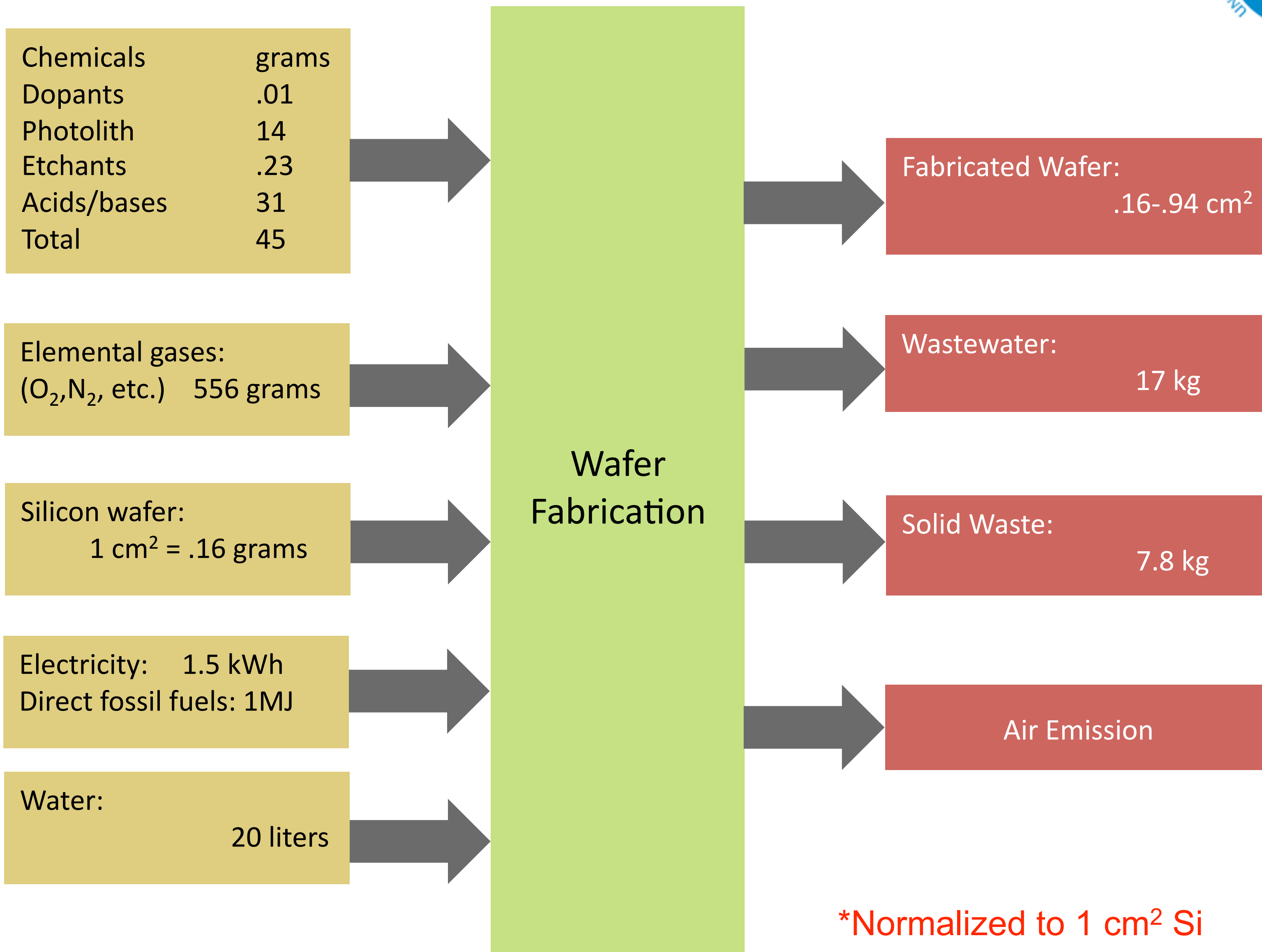
- NTD has better performance for contact hole and trench imaging due to better aerial images from bright field masks
- Choice of solvents is important for NTD performance
- Ketone- and ester or acetate-based developers

L. Van Look, J. Bekaert, V. Truffert, V. Wiaux, F. Lazzarino, M. Maenhoudt, G. Vandenberghe, M. Reybrouck, S. Tarutani, SPIE, 2010, 764011
Y. C. Bae, S. Lee, R. Bell, L. Joesten, G. G. Barclay, SPIE, 2011, 797207,

Lithographic Process & Key Issues



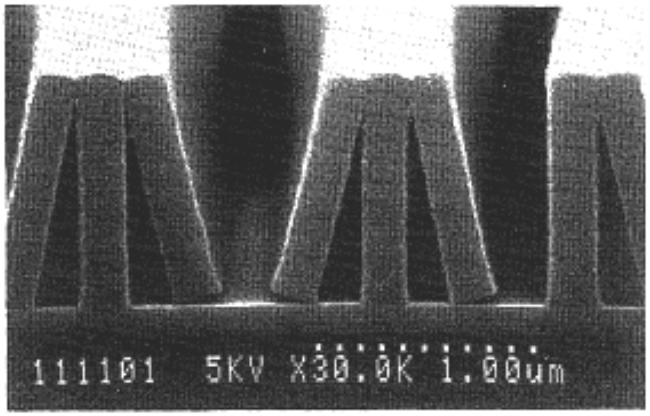
Environmental Issues



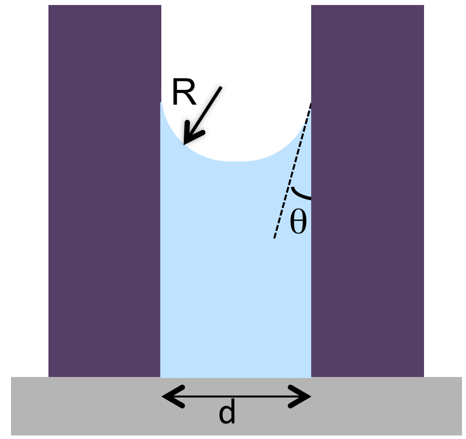
*Normalized to 1 cm^2 Si

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

Pattern Collapse



Aspect ratio=5:1



$$P = \frac{\sigma}{R}$$

$$R = \frac{d}{2\cos\theta}$$

$$F = P \times A = \frac{\sigma}{R} \times A$$

$$= \frac{2\sigma\cos\theta}{d} A$$

- Due to surface tension of rinse liquid
- Important for high aspect ratio (A>5) patterns and fine patterns (small d)

P: pressure in rinse liquid
σ: surface tension
θ: contact angle at resist surface
F: pattern peeling force
A: aspect ratio of resist pattern
d: space width
R: radius of curvature of rinse liquid

T.Tanaka, M. Morigami and N. Atoda, *Jpn. J. Appl. Phys.* **1993,** 6059-6064

Approaches and Challenges

Environmental Issues

- Photoresists based on natural materials, e.g. cyclodextrin
- Sugar-based photo acid generators (PAGs)
- Environmentally benign developers, e.g. water

-Supercritical CO_2

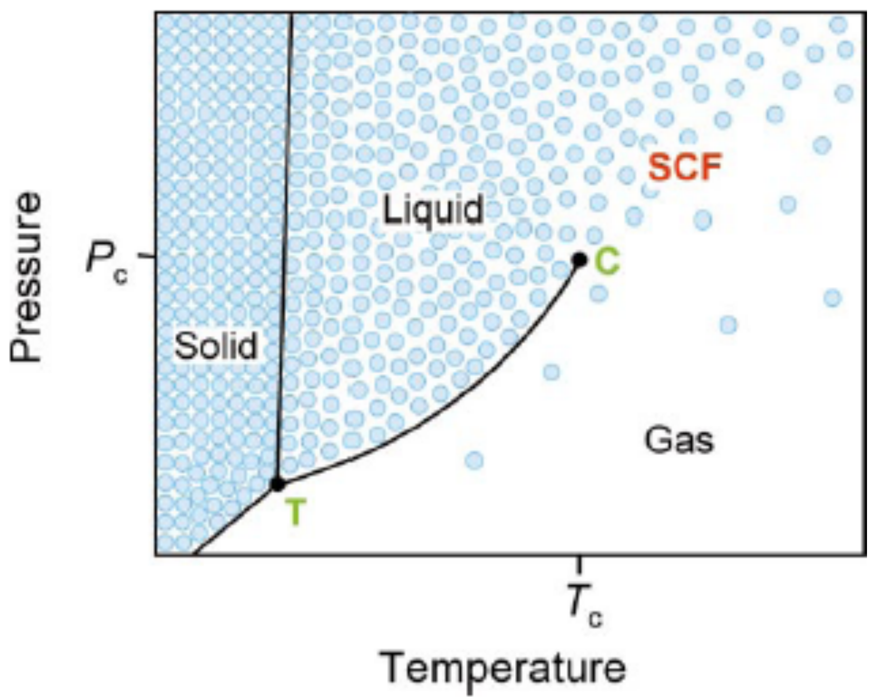
-Silicone Fluids

Pattern Collapse

- Increase resist hardness
- Introduction of surfactants during rinse stage
- Resist heating during rinsing
- Supercritical drying
- Use of low surface tension(< 30 dynes/cm) rinse liquid, e.g. perfluorohexane (10 dynes/cm)

Solvent	Surface tension @ 20°C
acetone	25.2
water	72.8
hexane	18.4
isopropanol	23.0
hexamethyldisiloxane	15.9
octamethyltrisiloxane	17.4
decamethyltetrasiloxane	18.0

Supercritical Carbon Dioxide



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

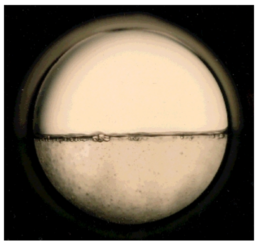
Properties

- T_c=31.1°C, P_c=73.8 bar
- Non-toxic, Non-flammable
- Environmentally benign
- Pressure adjustable solvent power
- Low viscosity
- Zero surface tension

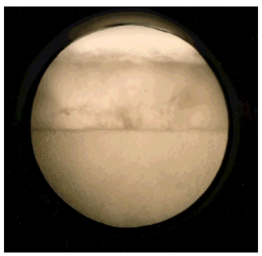
Solvent Characteristics

- Non-polar solvent
- Good solvent for low-molecular weight compounds
- Poor solvent for polar, high-molecular weight materials

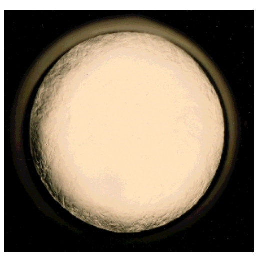
Supercritical CO_2 as a Solvent



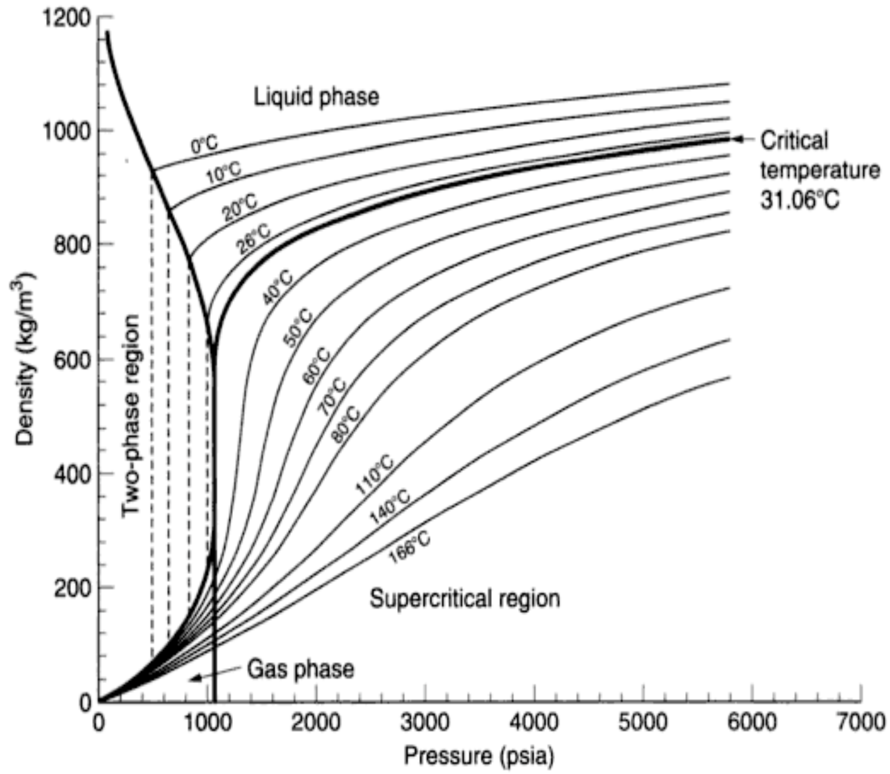
Below critical point – separate liquid and gas phases



Near critical point – meniscus begins to fade



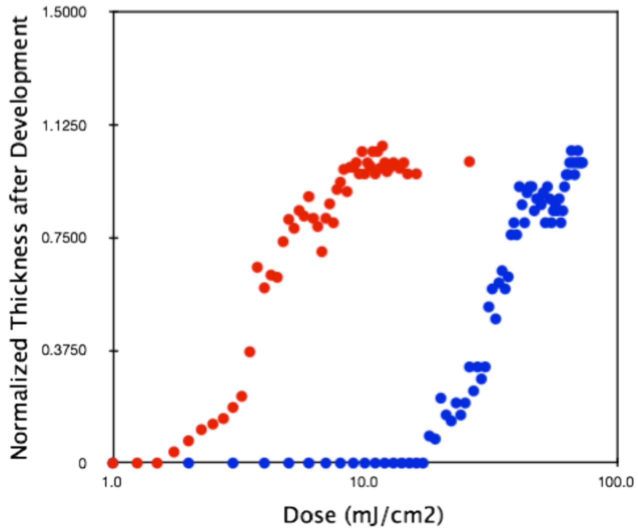
Above critical point – no meniscus, homogeneous phase

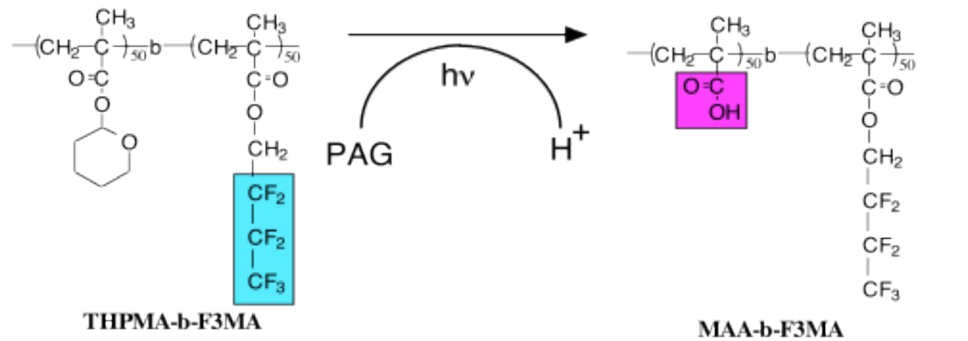


R. S. Oakes, A. A. Clifford and C. M. Rayner, *J. Chem. Soc., Perkin Trans. 1* **2001**, 917

Patterning Fluoropolymers in $scCO_2$

Contrast curves





soluble in supercritical CO_2 insoluble in supercritical CO_2

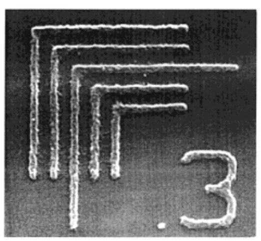


Figure 6. Features resolved using THPMA−F3MA copolymers using 193 nm exposure and SC CO_2 development.

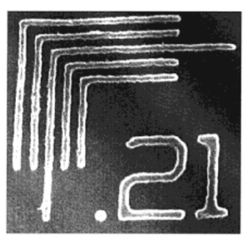


Figure 7. Features resolved using THPMA−F7MA copolymers using 193 nm exposure and SC CO_2 development.

Polymer	Vol. fraction (%) of fluorocomponent	Pressure (psi)	Temperature (°C)
THPMA-b-F3MA	22	Insoluble at conditions tried	
THPMA-b-F3MA	32	Insoluble at conditions tried	
THPMA-b-F3MA	46	Insoluble at conditions tried	
THPMA-b-F3MA	51	4500	45
THPMA-b-F3MA	56	*6500*	*65*
THPMA-b-F3MA	62	2800	45

N. Sundararajan, S. Yang, J. Wang, K. Ogino, S. Valiyaveettil, C. K. Ober, S. K. Obendorf and R. D. Allen, "Supercritical CO_2 Processing for Sub-micron Imaging of Fluoropolymers", *Chem. Mater.*, 2000, **12**, 41-48.

Positive-Tone Development in $scCO_2$

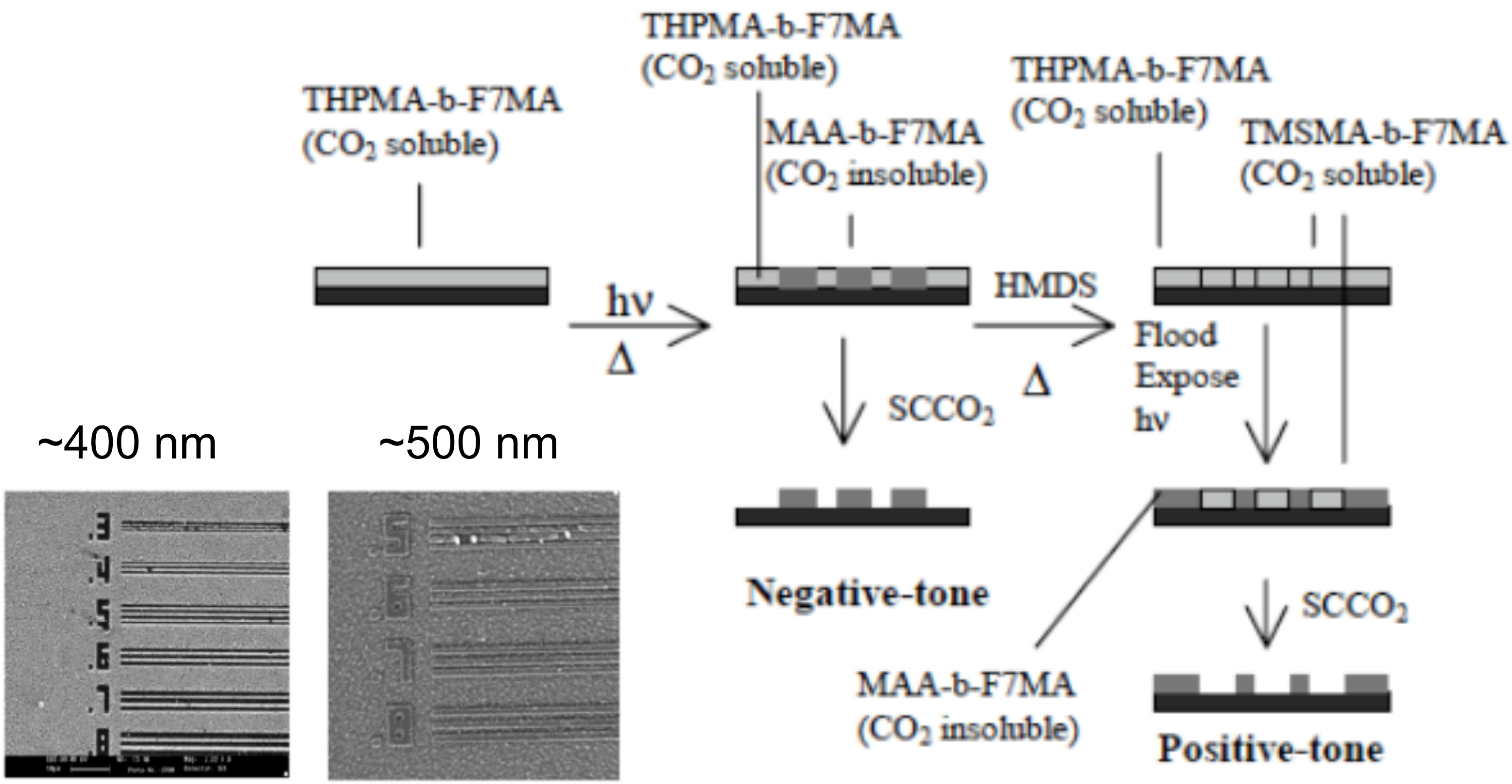


Figure 2. (a) THPMA-F7MA block copolymer resist exposed with 248-nm Nikon stepper and developed in $scCO_2$; (b) sample processed after silylation, showing positive-tone patterns.

V.Q. Pham, P.T. Nguyen, G.L. Weibel, R. J. Ferris, C.K. Ober, *Polymer Preprints,* **2002**

Development of non-Fluorinated Resists in $scCO_2$

- Problems with fluoropolymers

-Degrade plasma-etch resistance

-Expensive

-No features smaller than 100nm

- Patterning of conventional photoresists

-Fluorinated quaternary ammonium salts

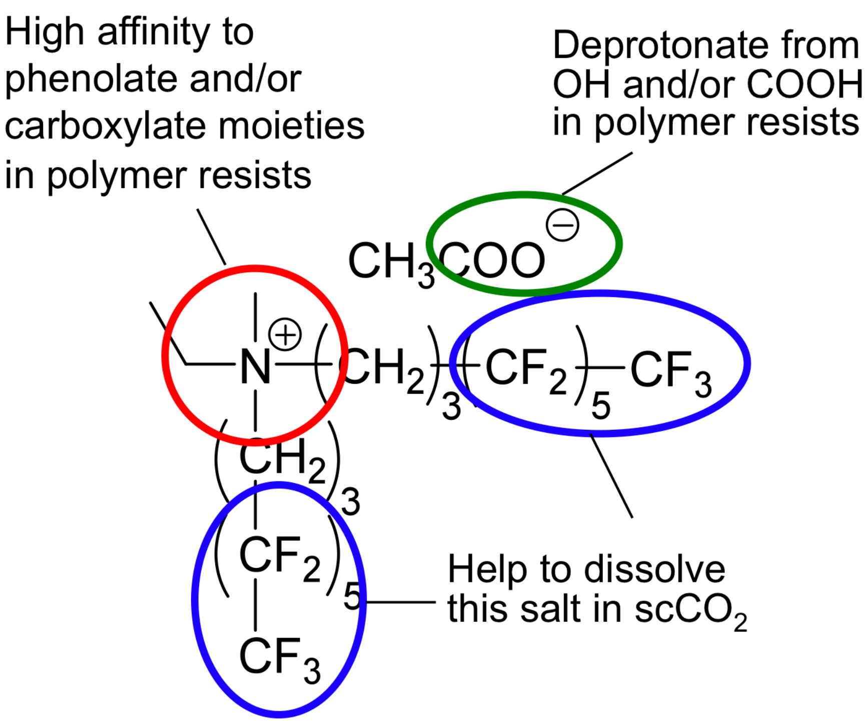
-Other non-fluorinated additives

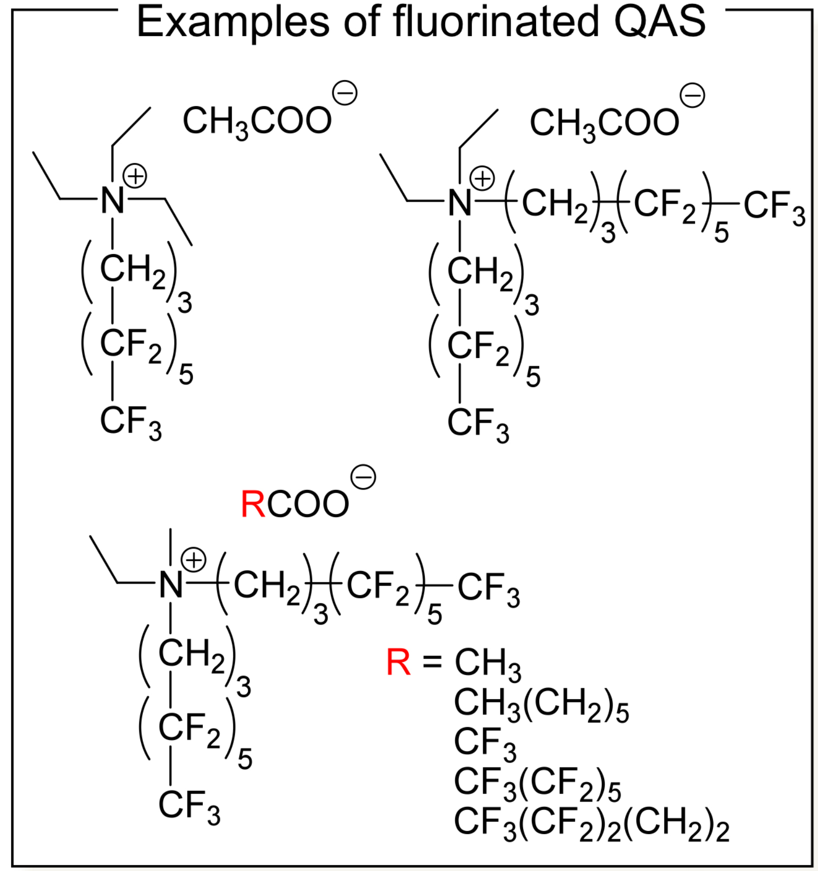
- Molecular glass resists

Patterning Conventional Photoresists in $scCO_2$

$scCO_2$ Compatible Additives:

Fluorinated Quaternary Ammonium Salts (QAS)



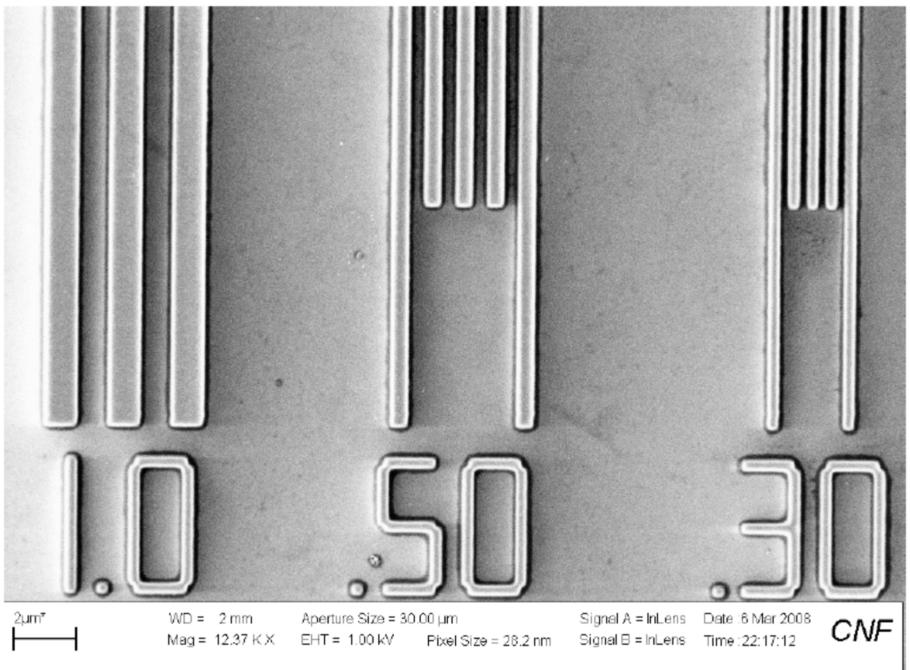


Some of the fluorinated ammonium salts form ***Micelle*** in $scCO_2$.

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.

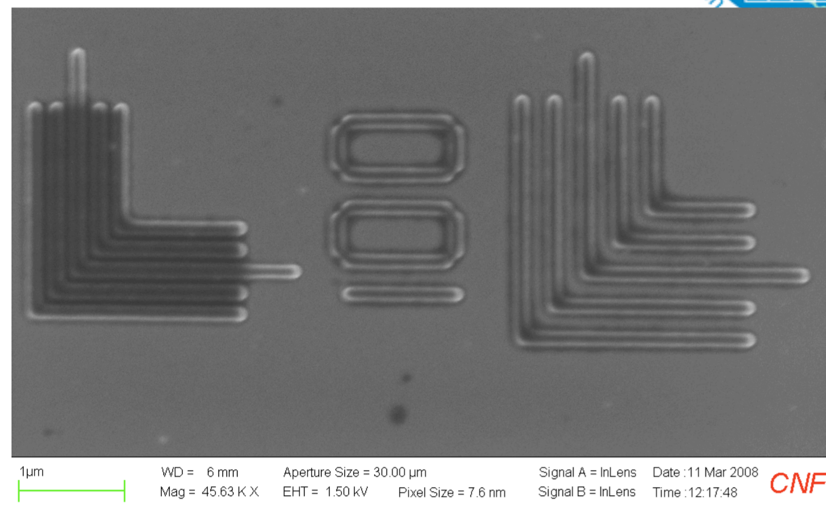
Patterning Conventional Photoresists in $scCO_2$

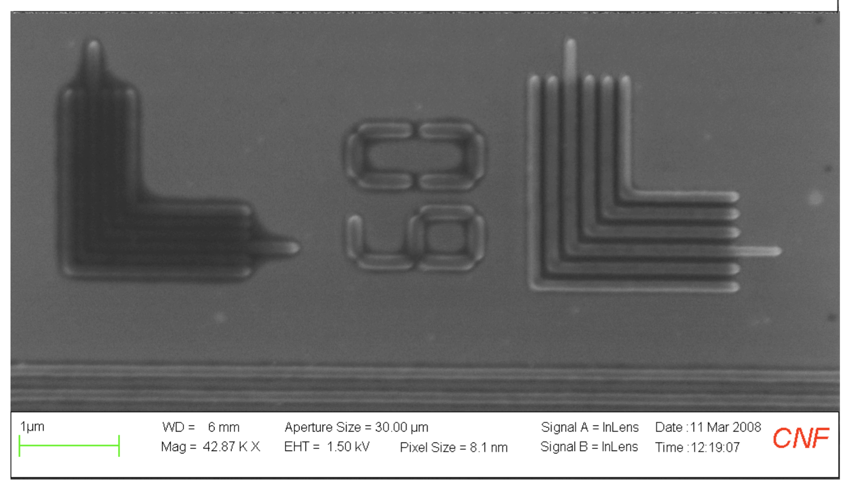
Development test of EB-patterned TOK resist (EUV-P568) with QAS-4 or QAS-7



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

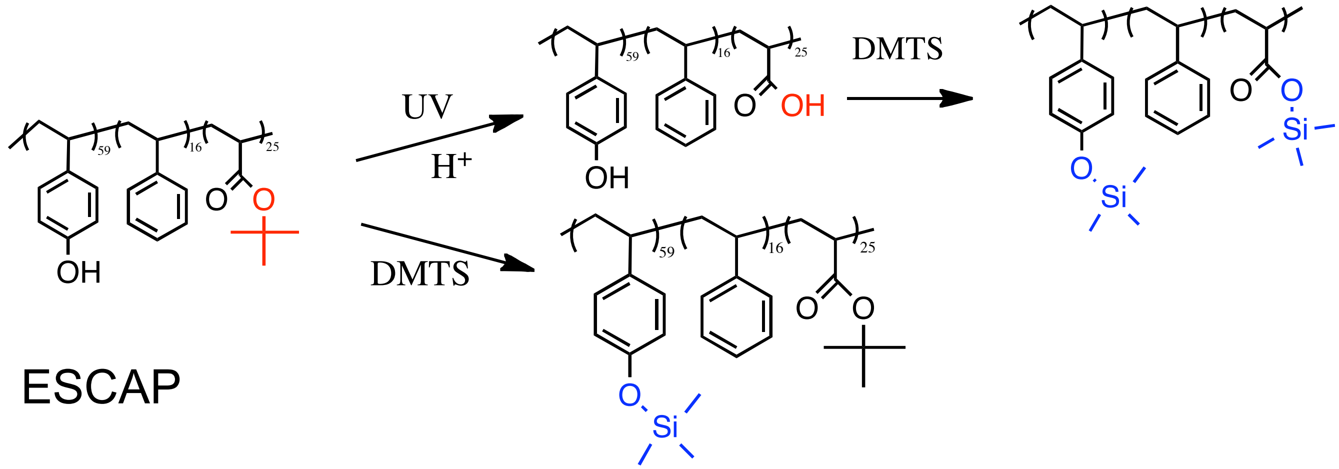
Negative tone patterns with sub-100 nm feature sizes were obtained.

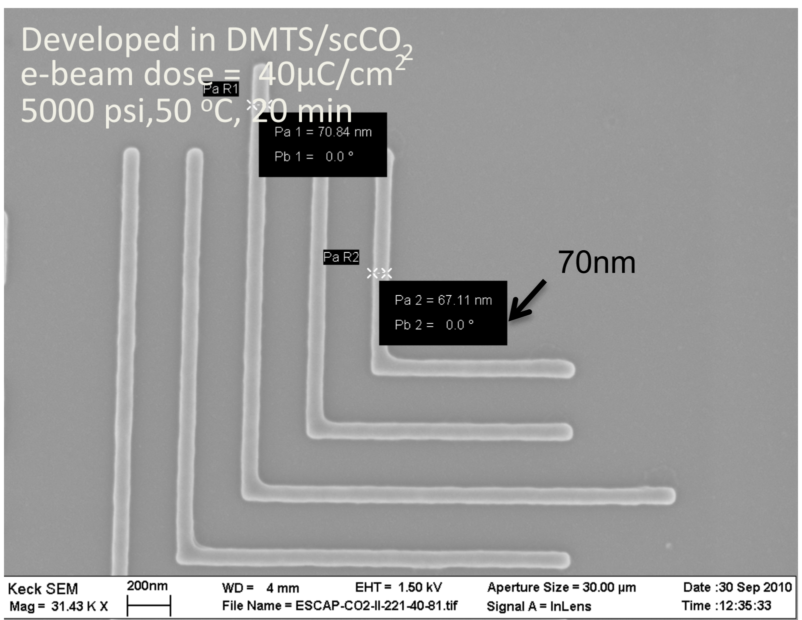




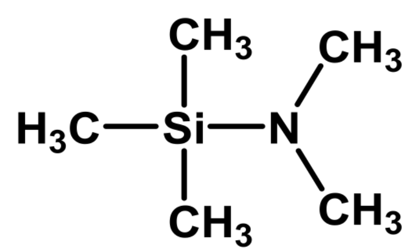
Dose: 20 uC/cm^2, QAS-7 (1.25 mM),
dev. for 60 min at 50^{o}C, 5000 psi, flow 30 min

Fluorine-Free Additives for Conventional Photoresists



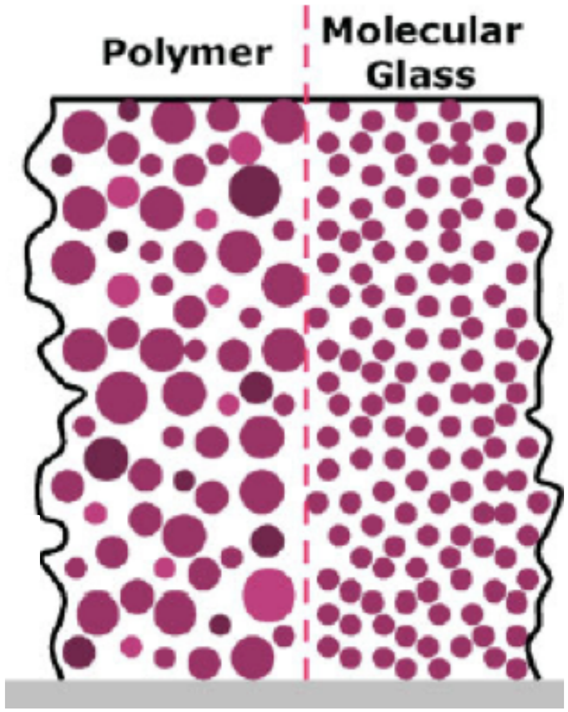


- Silicon-containing Additive



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

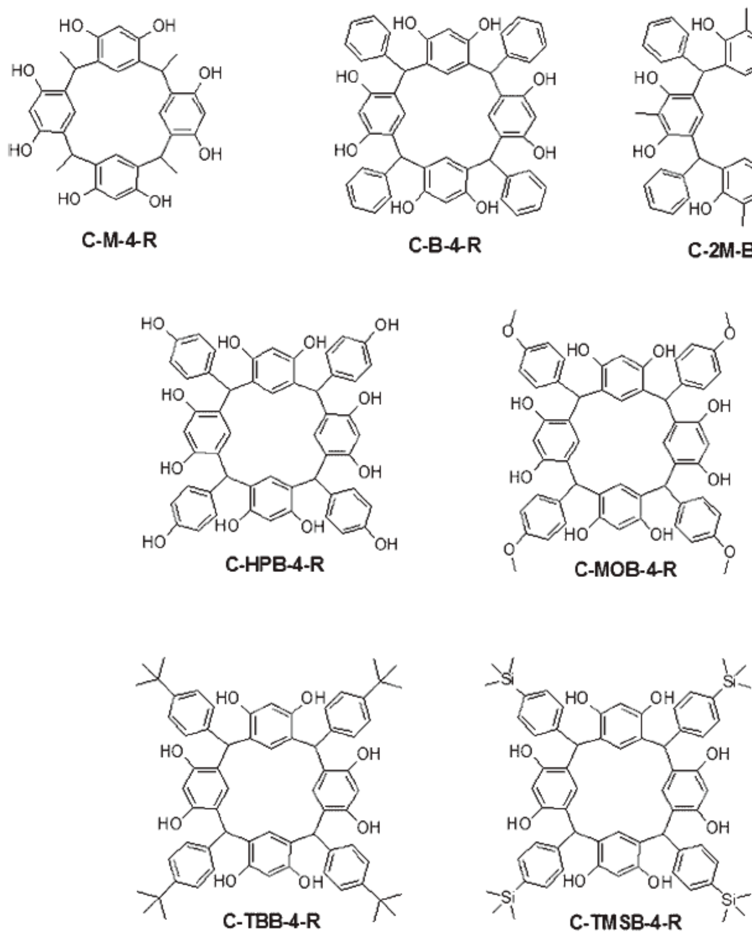
Molecular Glass Resists for High Resolution Patterning



- Small and amorphous materials
- Small "pixel" size leads to high-resolution patterns
- Potential to reduce line edge roughness (LER)
- Small free volume units to limit acid diffusion
- High Tg required for lithographic processes

A. De Silva, N. M. Felix and C. K. Ober, *Advanced Materials*, **2008**, 20, 3355-3361.

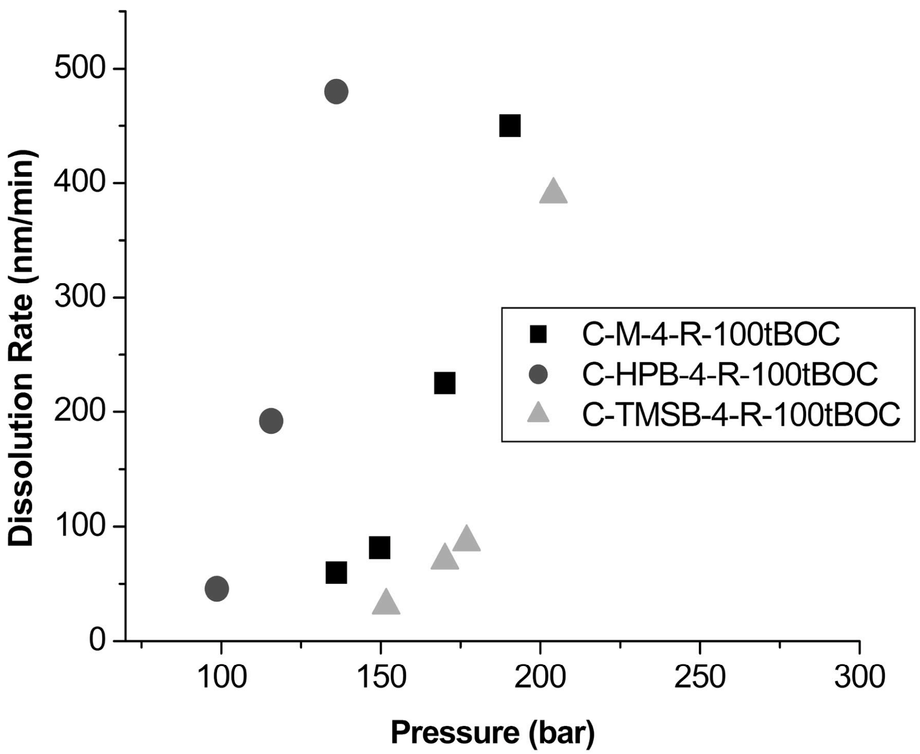
Molecular Glass Resists- Calix[4]resorcinarene Derivatives

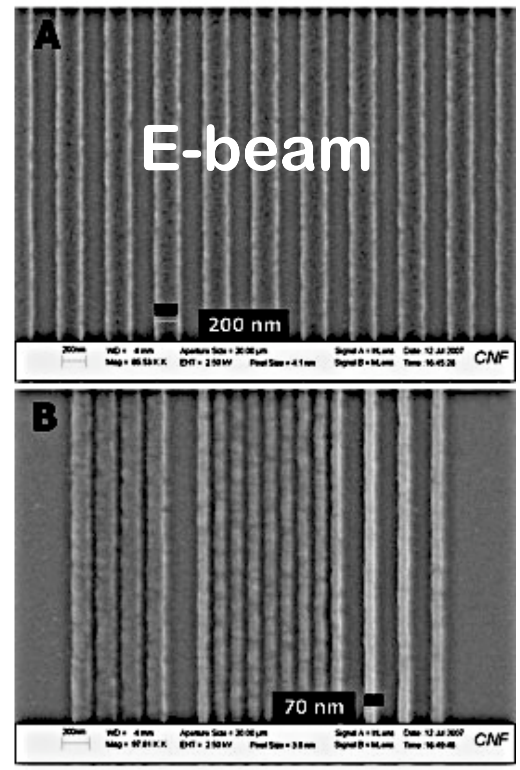


- High Tg
- High thermal stability
- Excellent film forming characteristics
- Ability to tune chemical structure through minor synthetic modifications
- Uniform dissolution rates leads to sharp solubility contrast and lower roughness

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

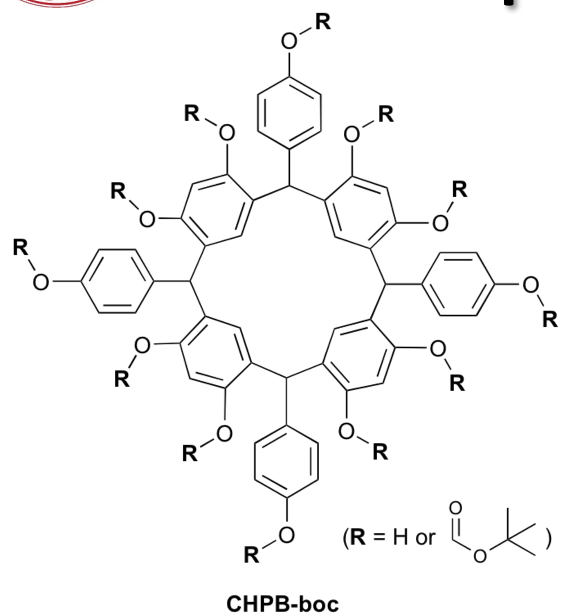
Development in $scCO_2$

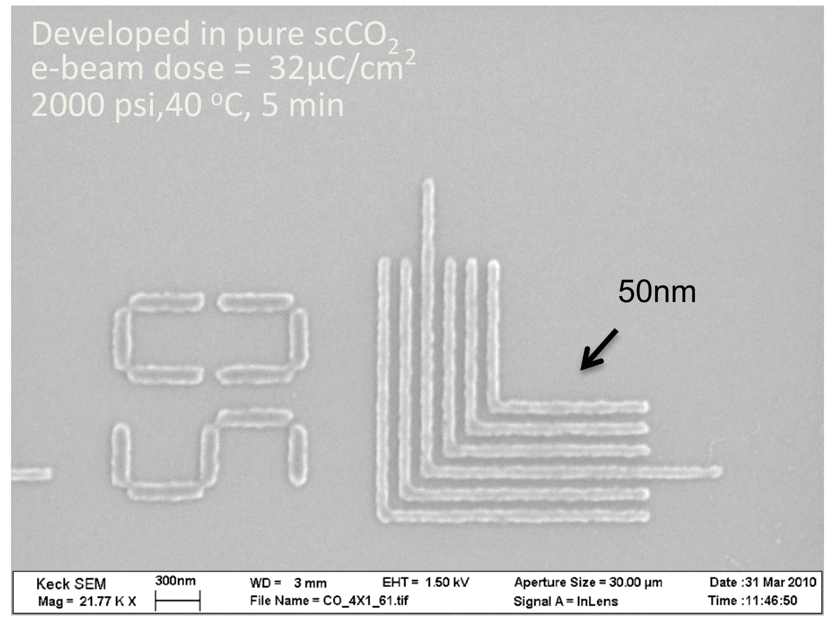




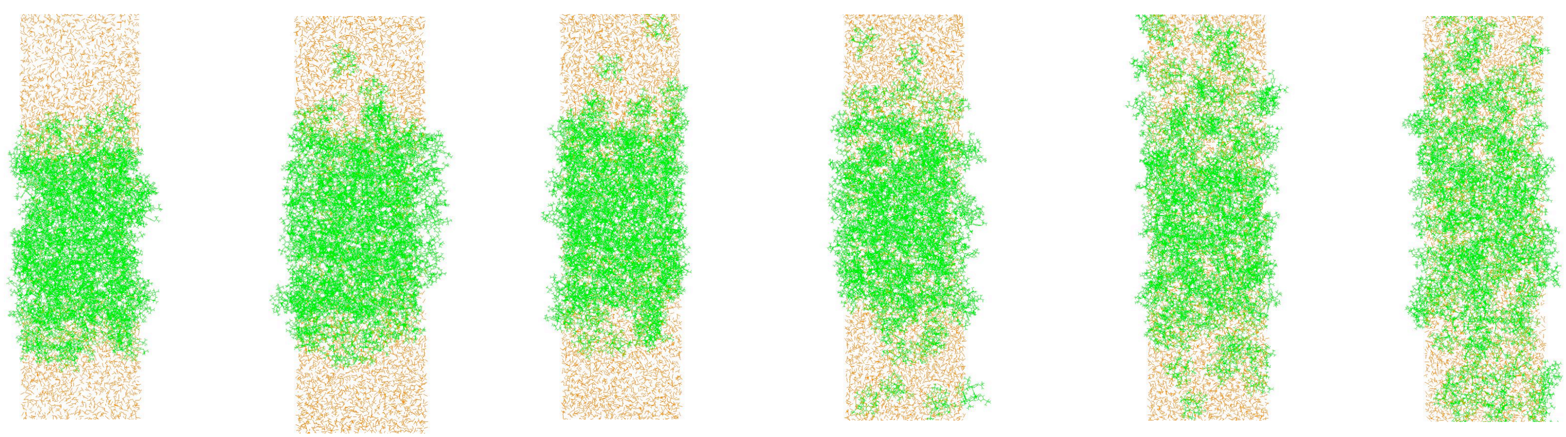
- t-BOC groups aid solubility in $scCO_2$
- Leads to fluorine free development

Computational Simulations





Time (1-2ns between images)



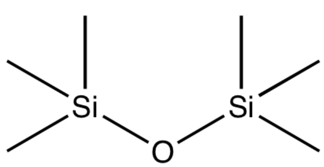
Silicone Fluids-Linear Methyl Siloxanes

Properties

- Low molecular weights
- Low surface tension
- Low in toxicity
- Non-ozone depleting
- Degrade to naturally occurring compounds
- Adjustable solvent power

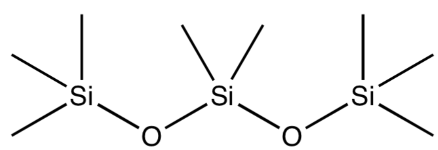
Solvent Characteristics

- Non-polar
- Good solvents for non-polar, non-ionic materials, e.g. oils, grease, silicones



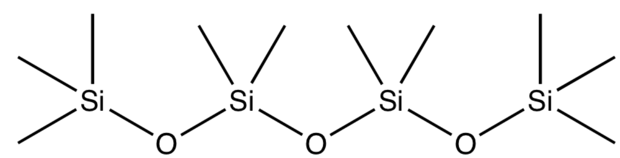
Hexamethyldisiloxane

MW=162.38 g/mol
b.p.=101^{p}C
Surface tension=15.9 dynes/cm



octamethyltrisiloxane

MW=234 g/mol
b.p.=151^{o}C
Surface tension=17.4 dynes/cm



decamethyltetrasiloxane

MW=340 g/mol
b.p.=194^{o}C
Surface tension=18 dynes/cm

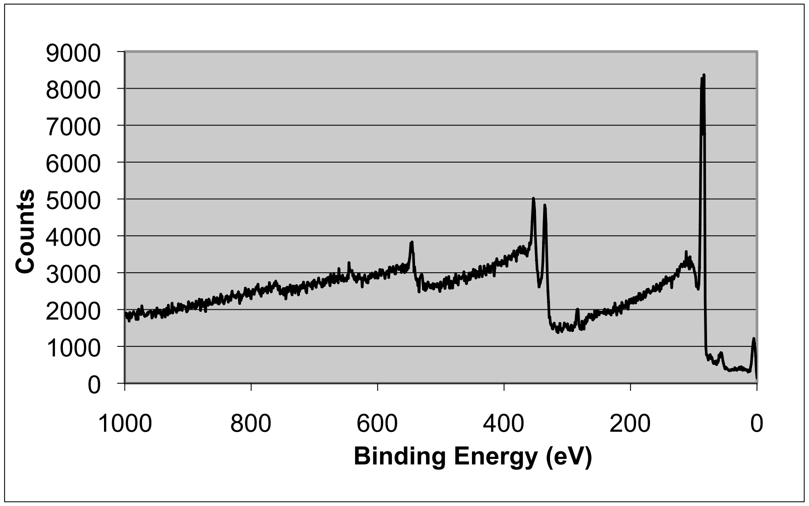
XPS Study of Residual Solvent

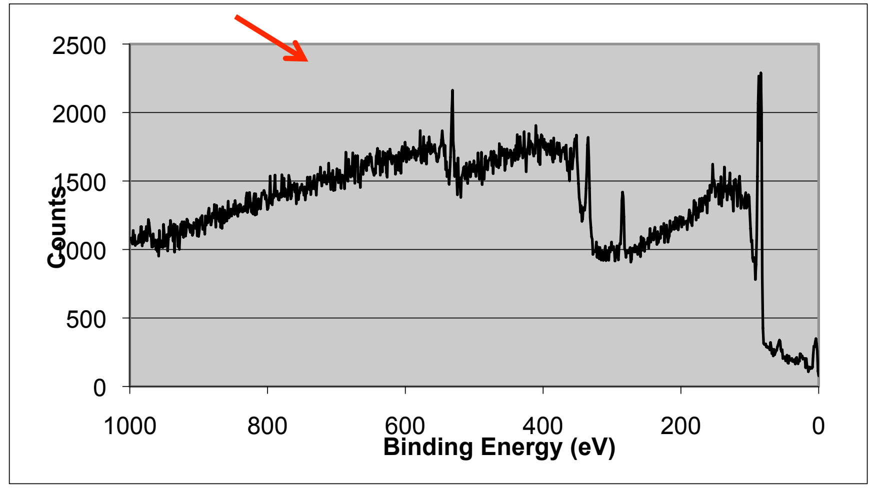
Bare Au

Au with residue

Thin layer on top of gold

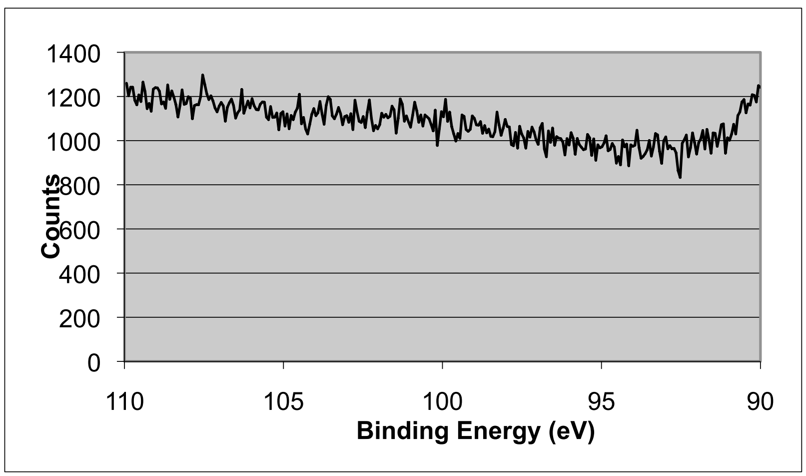
Au

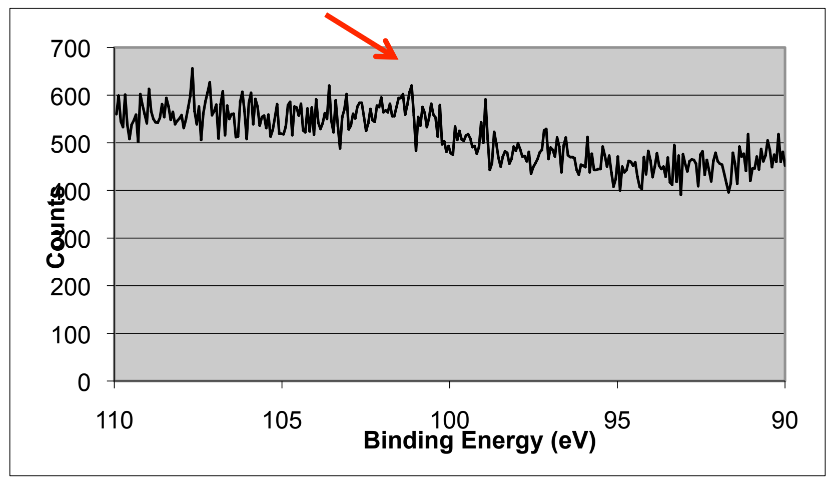




Small Si peak

Si





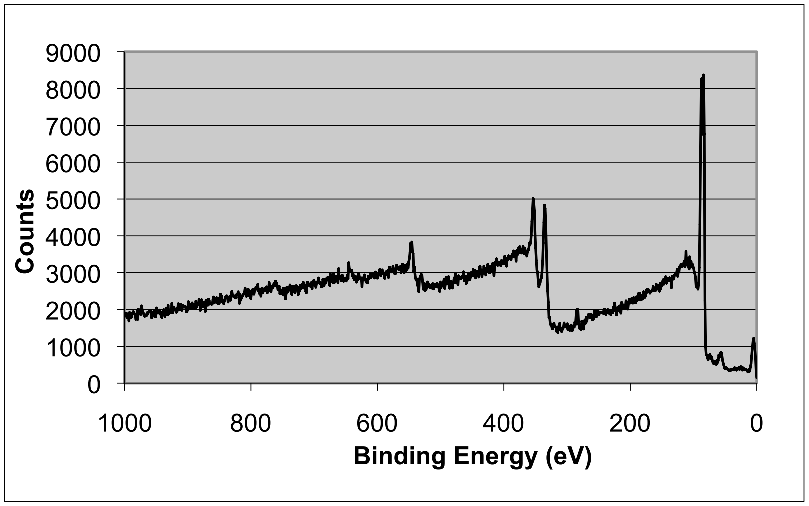
Negligible Si was detected on surface

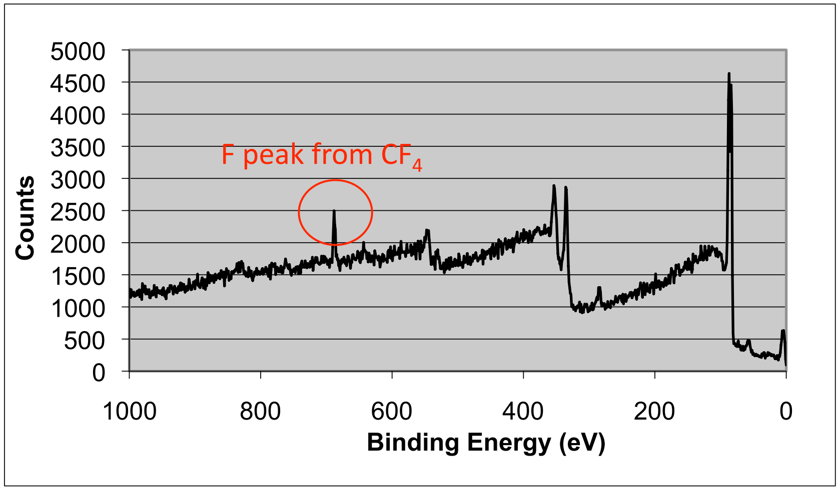
XPS Study of Residual Solvent

Bare Au

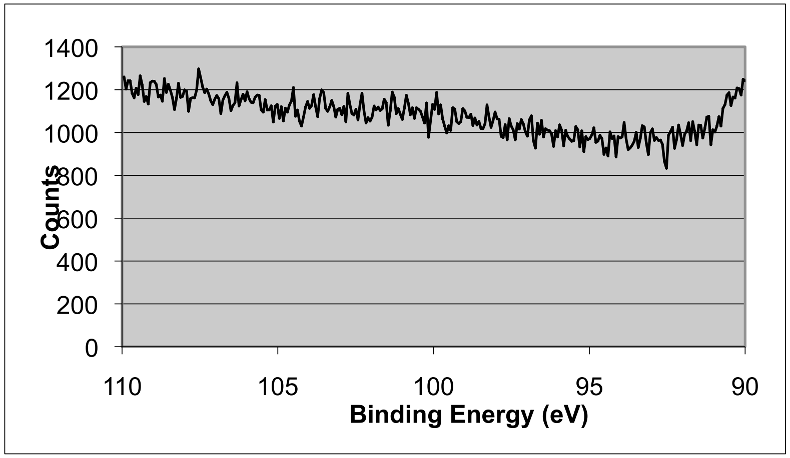
Au with residue-cleaned under CF_4 for 30 s

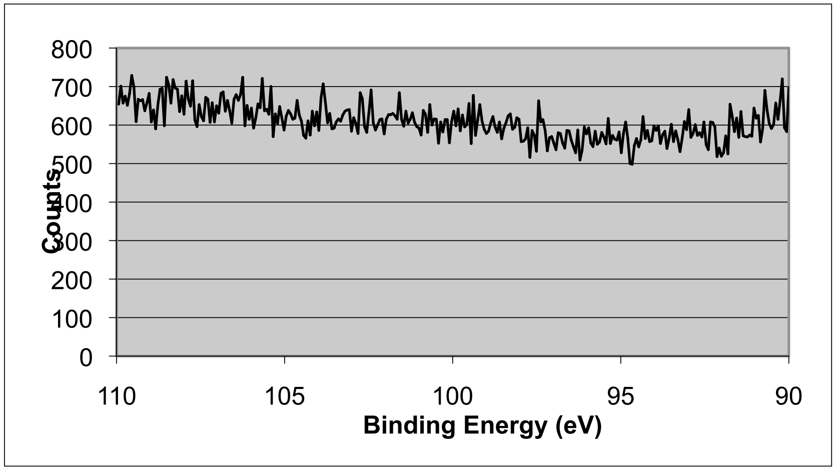
Au





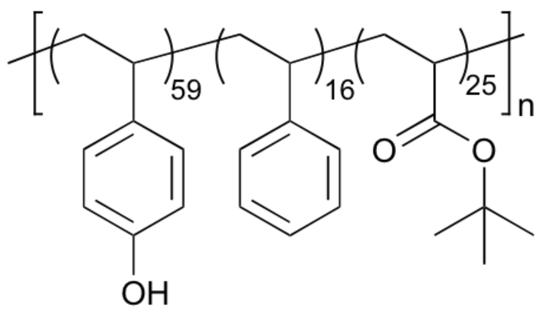
Si



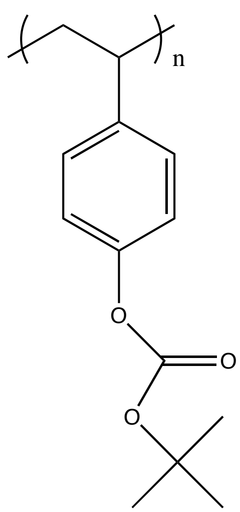


Residue can be easily removed

Developing Conventional Photoresists



ESCAP



PBOCST

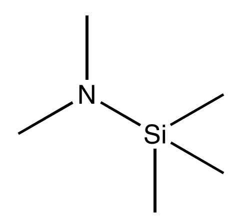
- **Acid-labile protecting groups**

-ESCAP: *tert*-butyl groups

-PBOCST: *tert*-butoxycarbonyl(*t*-boc) groups

- Both polymers are insoluble in silicone fluids before and after exposure
- Hydroxyl groups formed after exposure can be silylated
- Silicon-containing trimethylsilyl (TMS) groups can increase solubility in silicone fluids

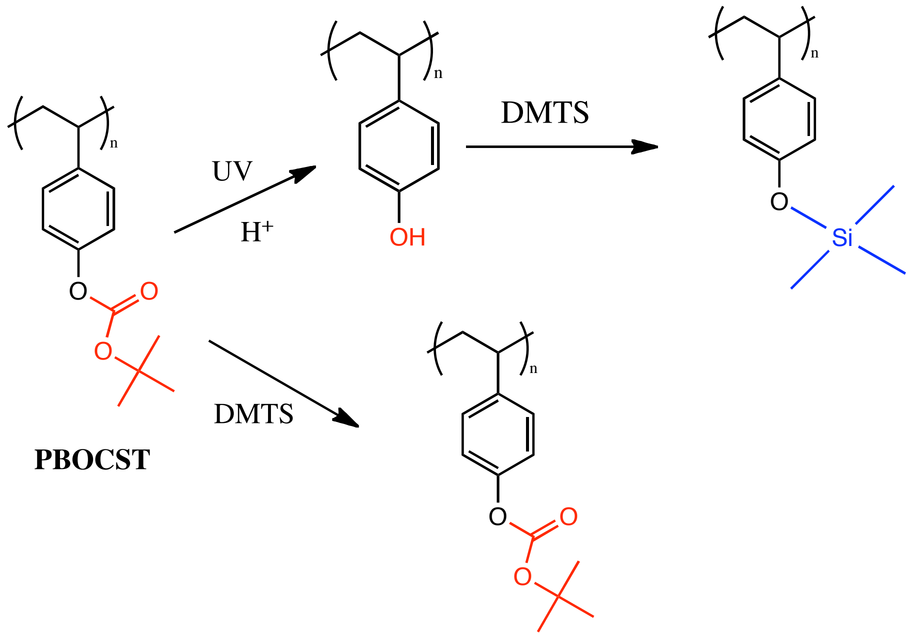
•Silylating reagent:



(N,N-dimethylamino)trimethylsilane (DMTS)

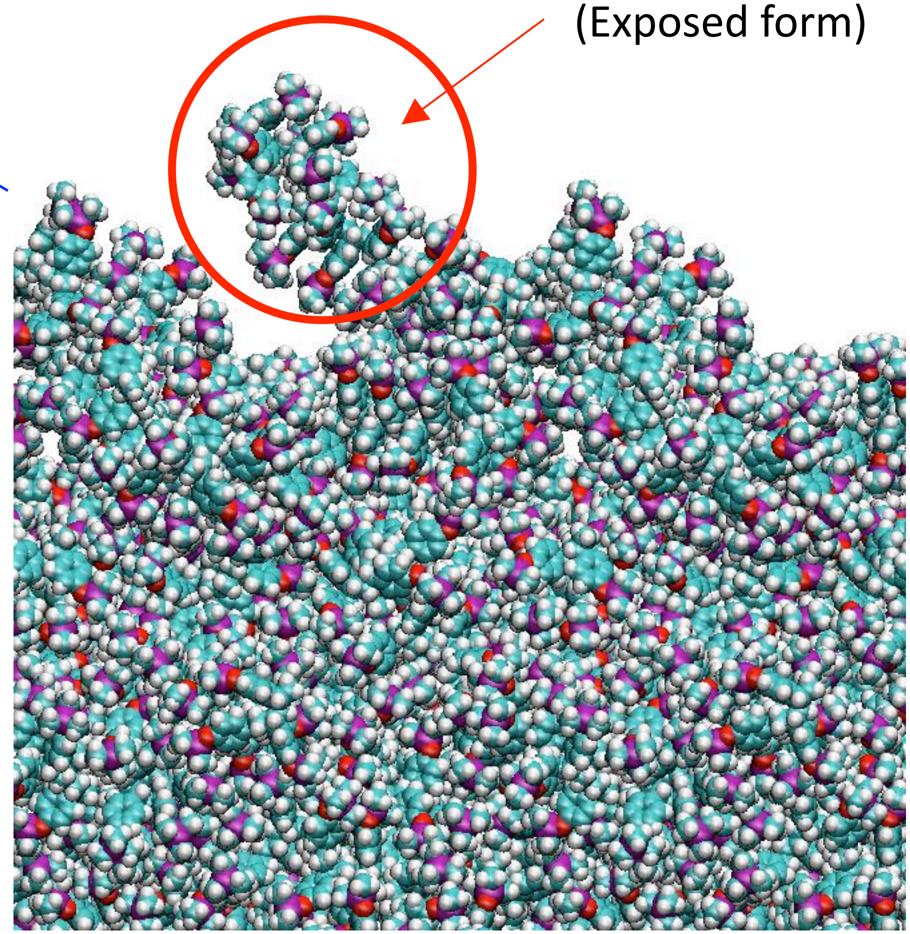
*ESCAP: poly(hydroxystyrene-*co*-styrene-*co*-*tert*-butylacrylate)
PBOCST:poly(4-*tert*-butoxycarbonyloxystyrene)

Positive-Tone: PBOCST



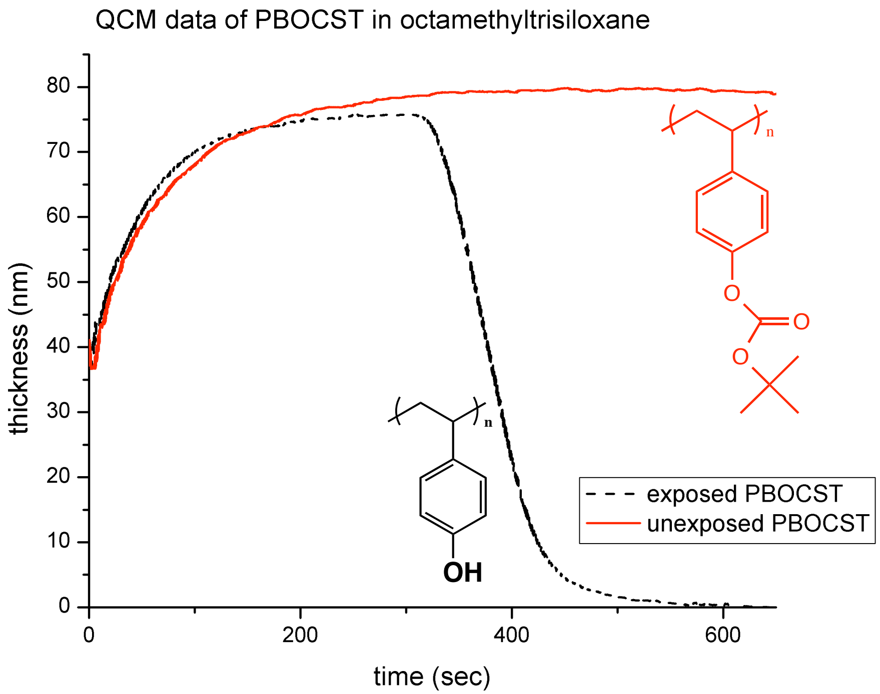
Chain beginning to pull free of surface

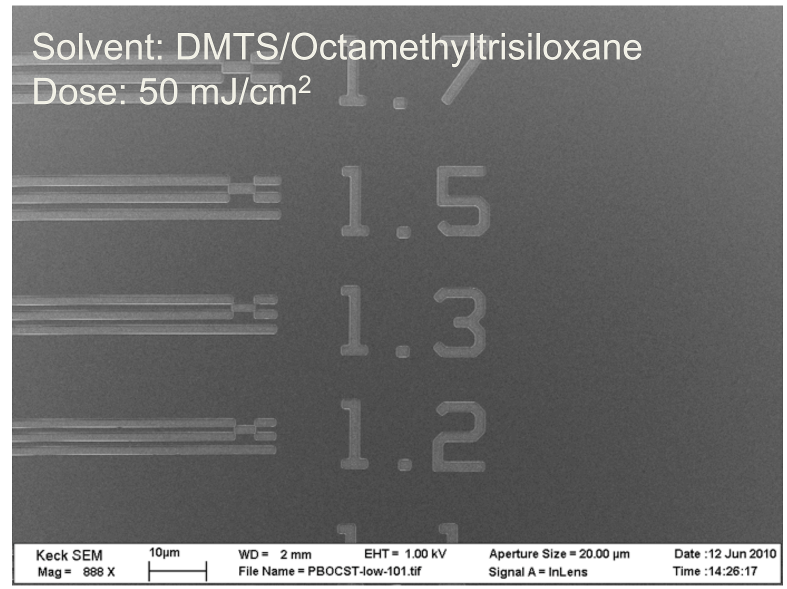
(Exposed form)

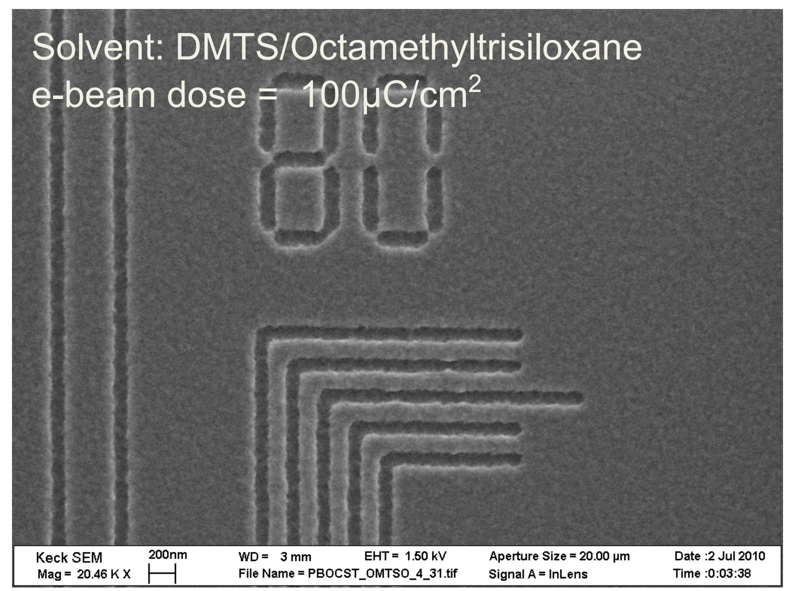


- Not soluble in pure silicone fluids
- Developed in DMTS: silicone fluids=1:10 (by vol.) mixed solvents at 40°C for 5 minutes

Positive-Tone: PBOCST

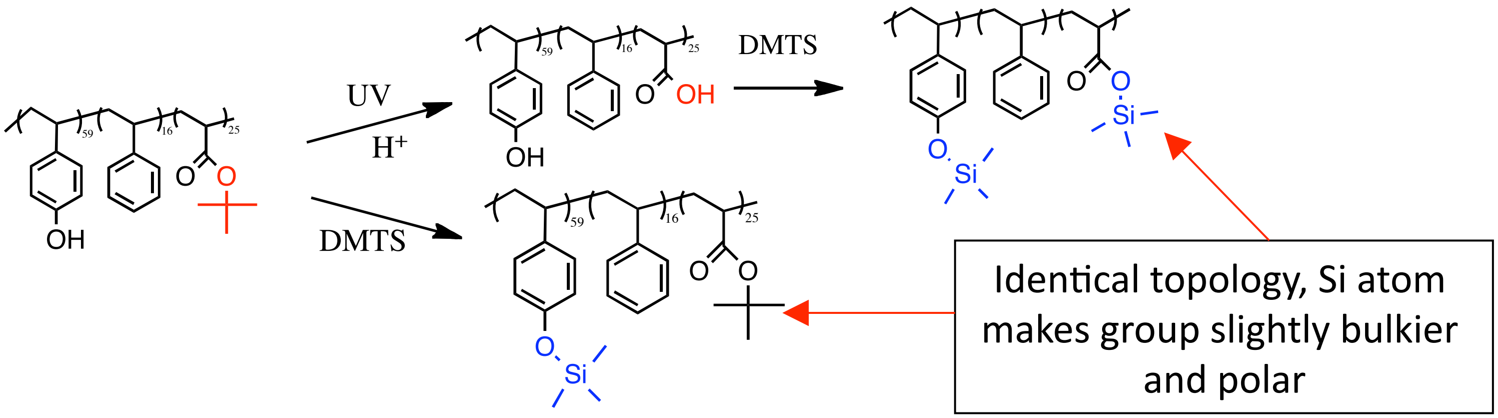


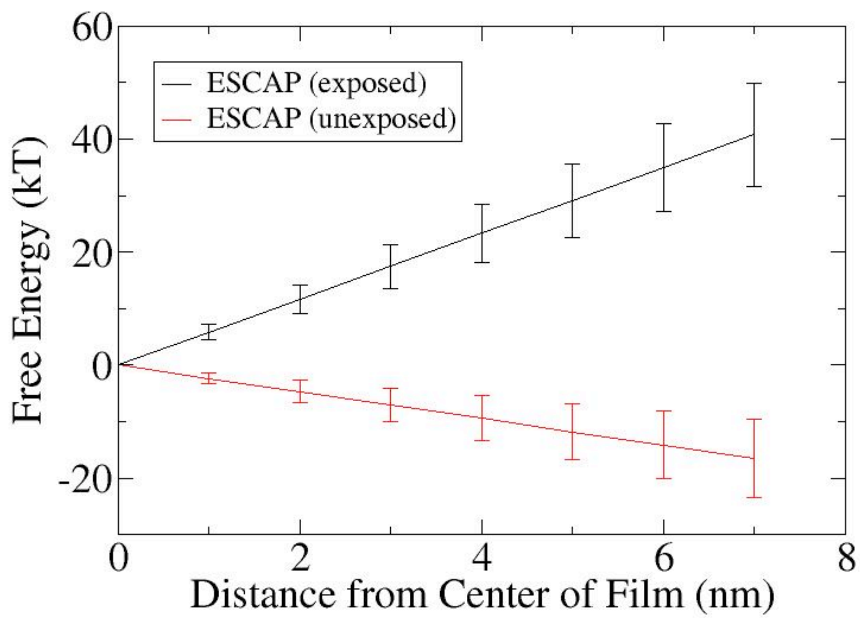




- Not soluble in pure silicone fluids
- Developed in DMTS: silicone fluids=1:10 (by vol.) mixed solvents at 40^{o}C for 5 minutes
- Swelling stage due to incorporation of bulky trimethylsilyl (TMS) groups

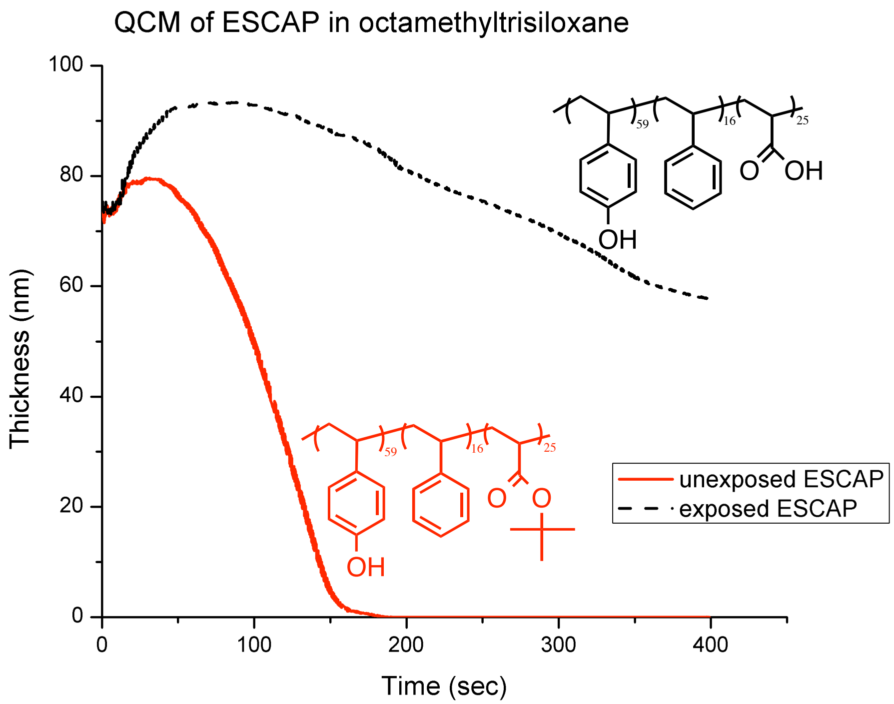
Negative-Tone: ESCAP

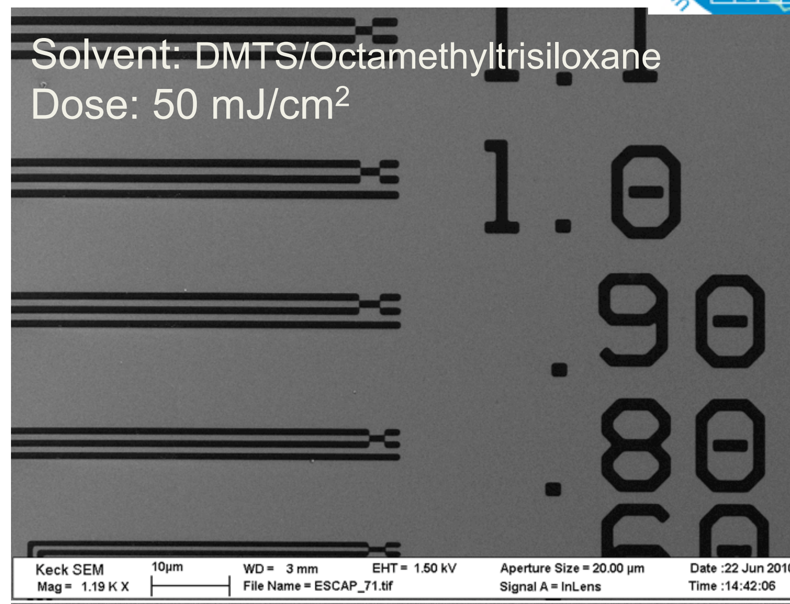


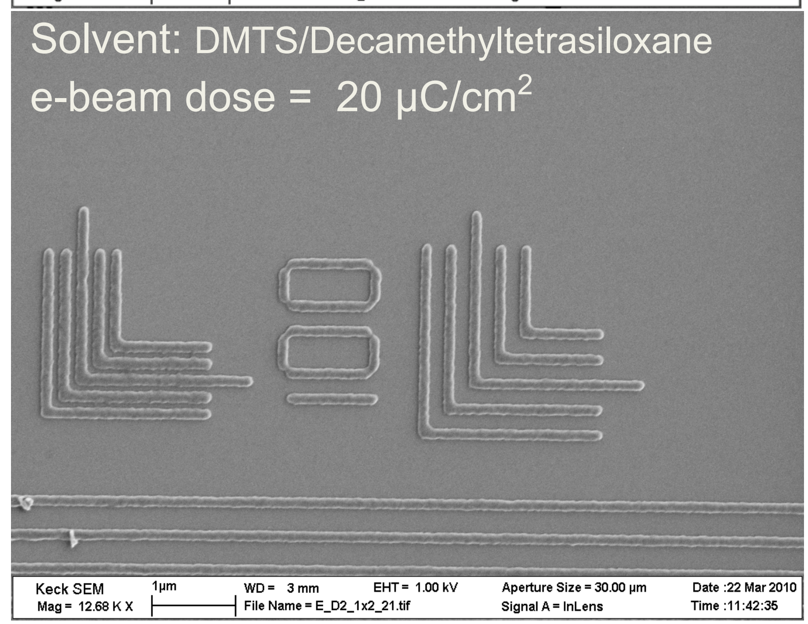


- Not soluble in pure silicone fluids
- Developed in DMTS: silicone fluids=1:10 (by vol.) mixed solvents at 40^{o}C for 5 minute

Negative-Tone: ESCAP

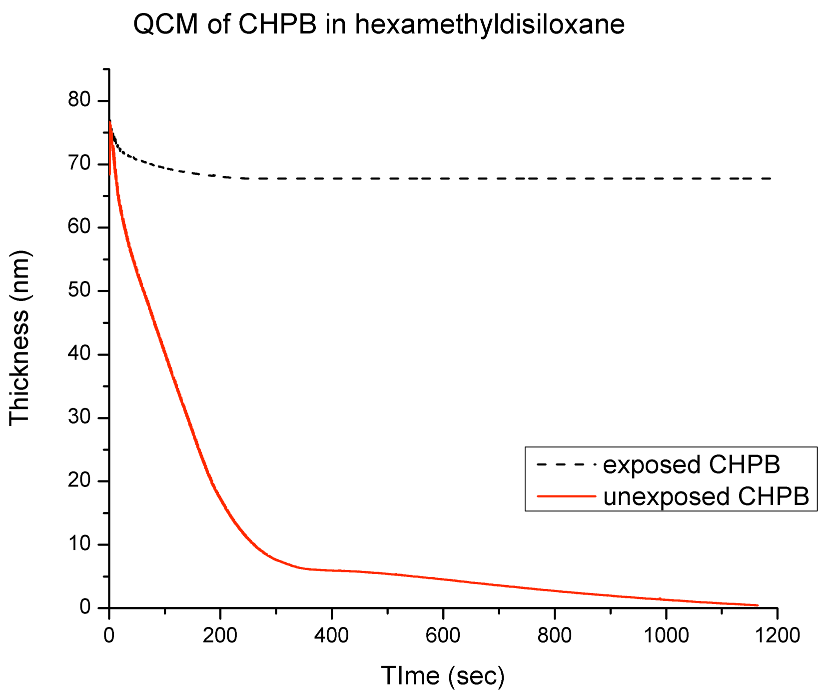


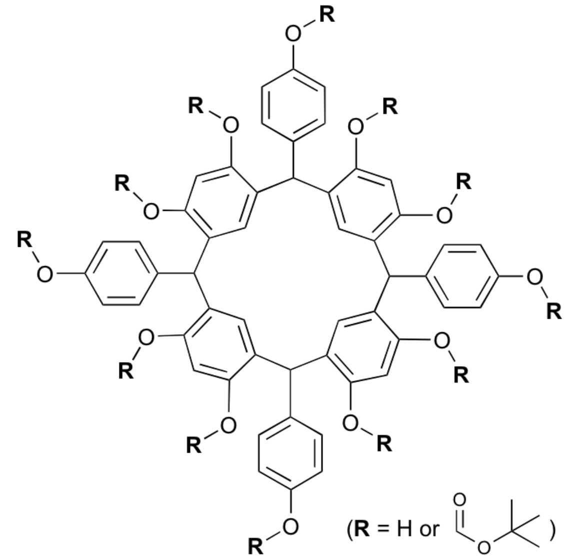




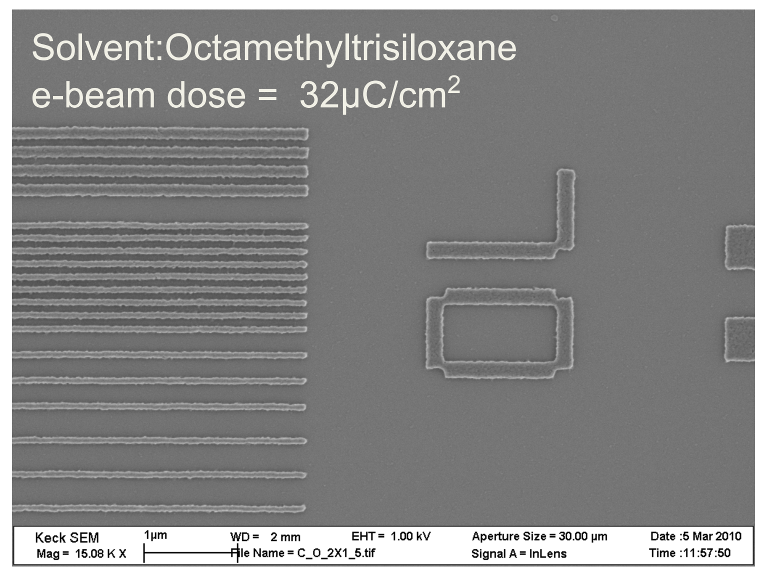
- Not soluble in pure silicone fluids
- Developed in DMTS: silicone fluids=1:10 (by vol.) mixed solvents at 40^{o}C for 5 minutes
- Unexposed resist showed higher solubility compared to exposed resist

Negative-Tone: Calixarene Resist



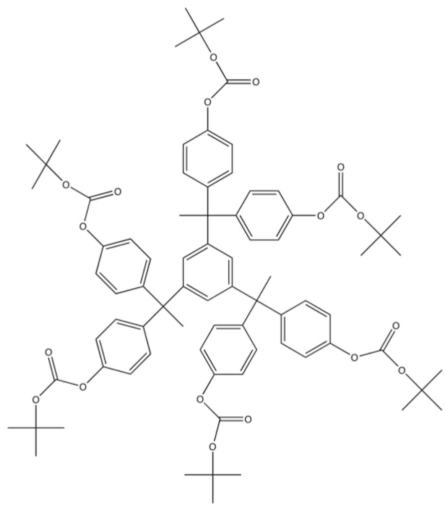


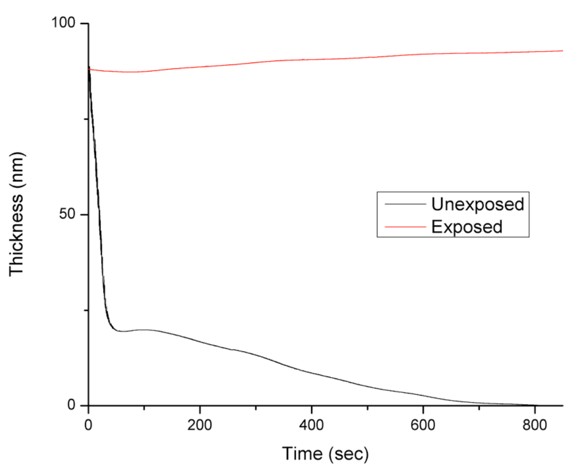
CHPB-boc

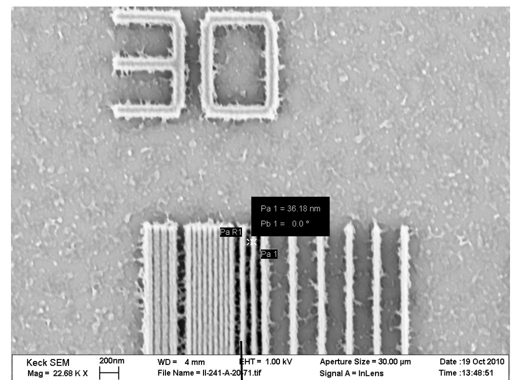


- Ring structure to impart high Tg
- Soluble in silicone fluids without any additives due to small size
- Polarity change after exposure

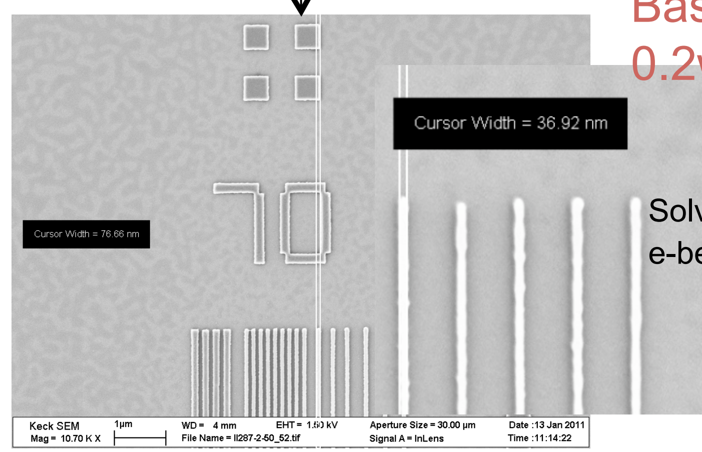
Negative-Tone: CR-15 Resist







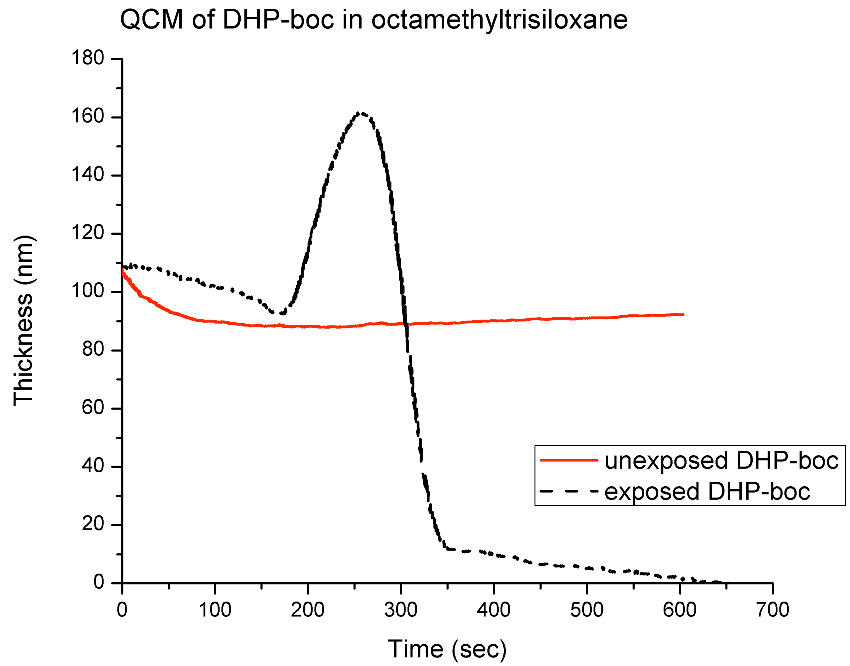
Solvent:Octamethyltrisiloxane
e-beam dose = 20μC/cm^2
microbridging

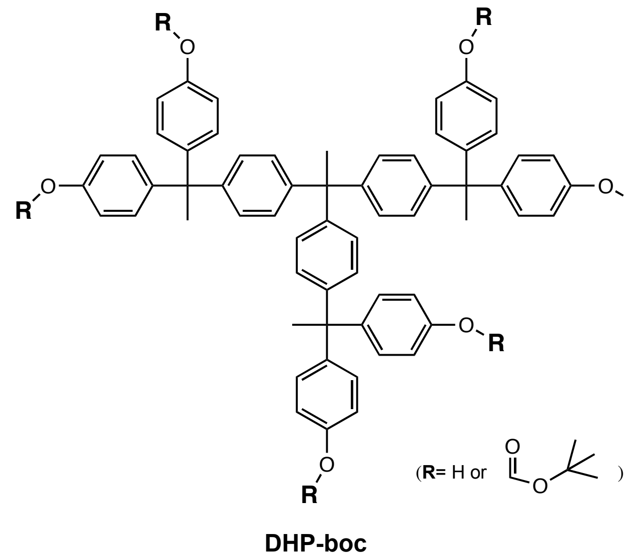


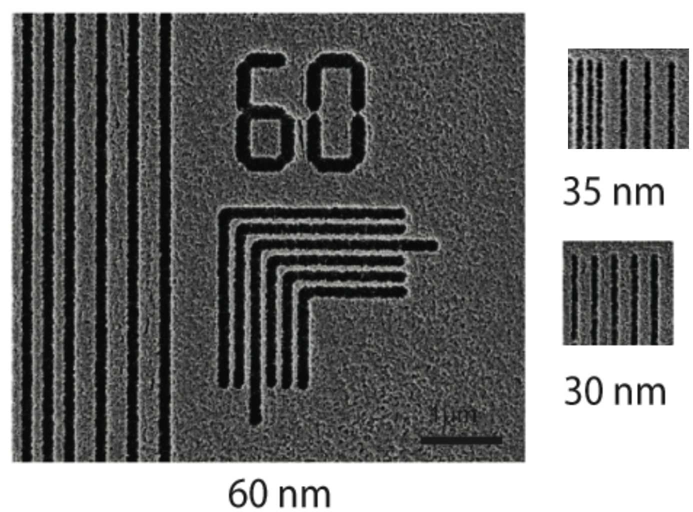
Base quencher
0.2wt %trioctylamine

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

Positive-Tone: Dendritic Hexaphenol Resist







- Not soluble in pure silicone fluids
- Developed in DMTS: silicone fluids=1:10 (by vol.) mixed solvents at 40°C for 5 minutes
- Film thickness after development~173 nm
- Aspect ratio ~5:1

Solvent: DMTS/octamethyltetrasiloxane
e-beam dose: 40μC/cm^2

Summary

- The development contrast of CA resists provides new opportunities with non-polar solvent development
- Protecting groups determine development potential
- Additives may be key in accessing top performance
- Extreme non-polar solvents such as $scCO_2$ and silicone fluids can exploit this behavior
- Both polymeric and molecular glass resists were successfully developed in both solvents

Acknowledgements

- Ober Group
- De Pablo Group
- SRC/Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
- GRC/Applied Materials
- Cornell NanoScale Science and Technology Facility
- Cornell Center for Materials Research