Positive and Negative Tone Resists for Supercritical CO_2 Development

Nelson Felix[1], Anthony Spizuoco[2], Camille Luk[3], Christopher K. Ober[3]

1.School of Chemical and Biomolecular Engineering, Cornell University
2.Department of Chemical Engineering, UMass Amherst
3.Department of Materials Science and Engineering, Cornell University

Task 425.008

ERC Teleseminar

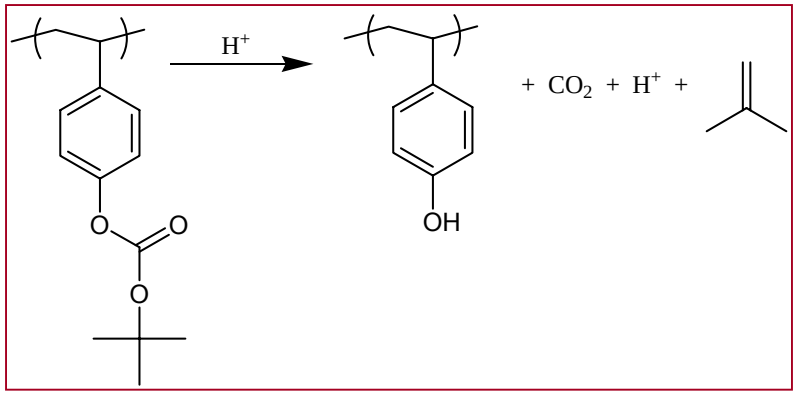
November 3, 2005

Outline

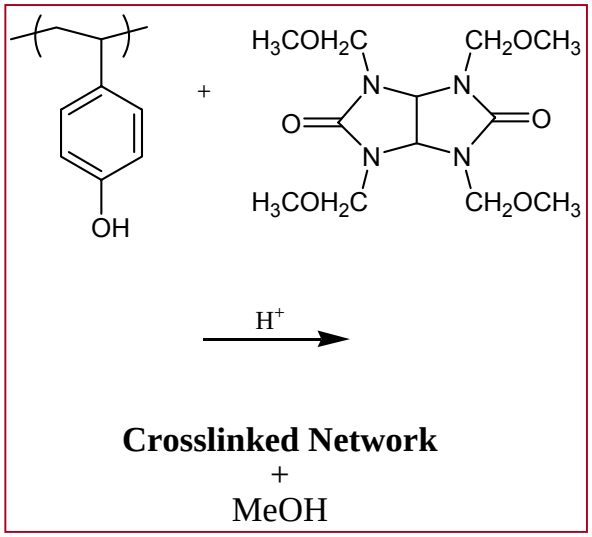
- Conventional photolithography
  - Background
  - Issues
- Supercritical carbon dioxide
  - Properties
  - Challenges
  - Results with polymers, cosolvents
- Changing the photoresist: Molecular Glasses
  - Solubility
  - Results

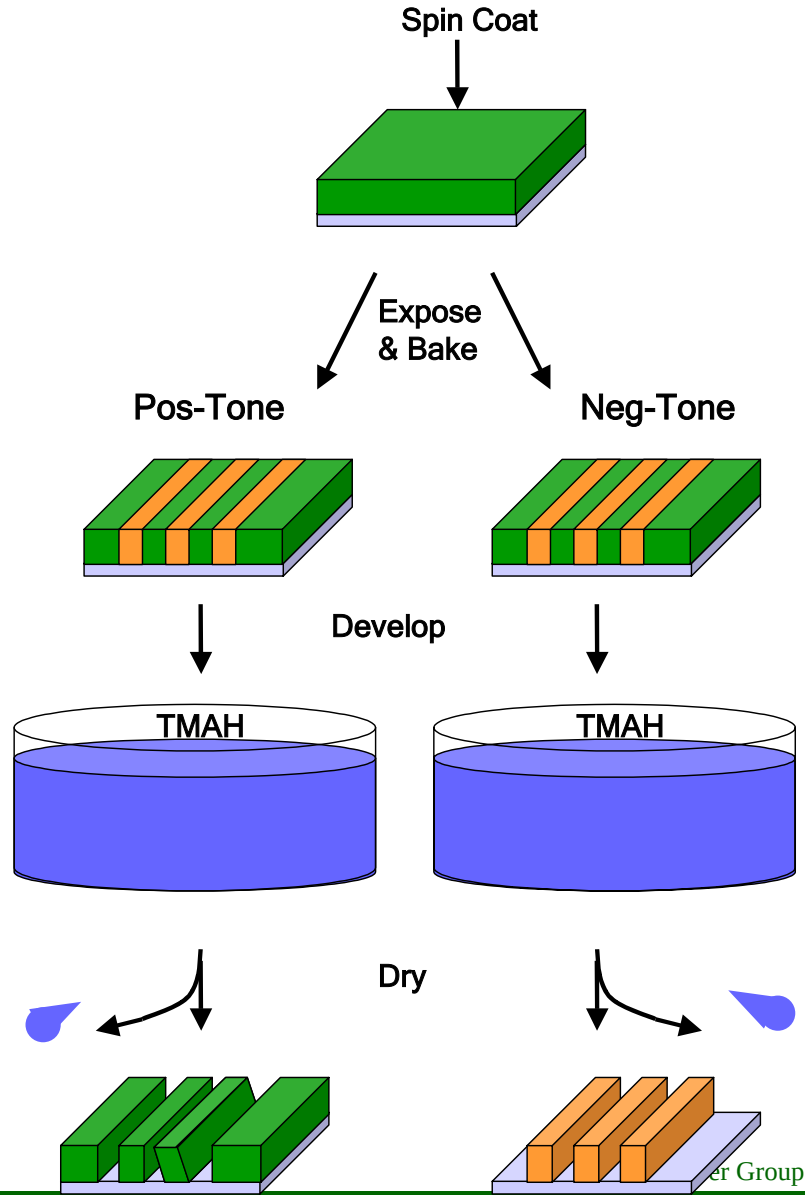
Photoresist Chemistry / Pattern Development

Polarity Change



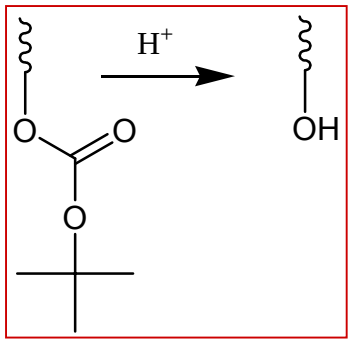
Crosslinking

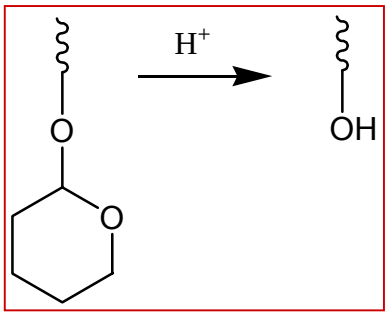


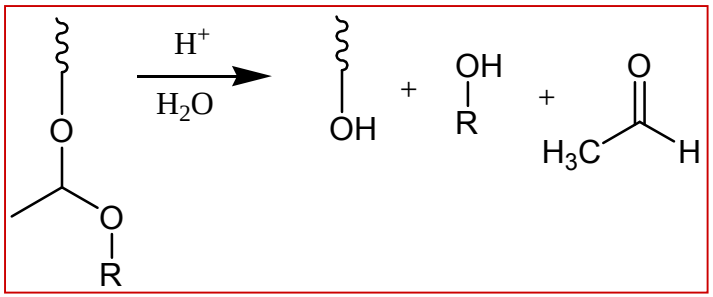


Photoresist Chemistry / Other examples

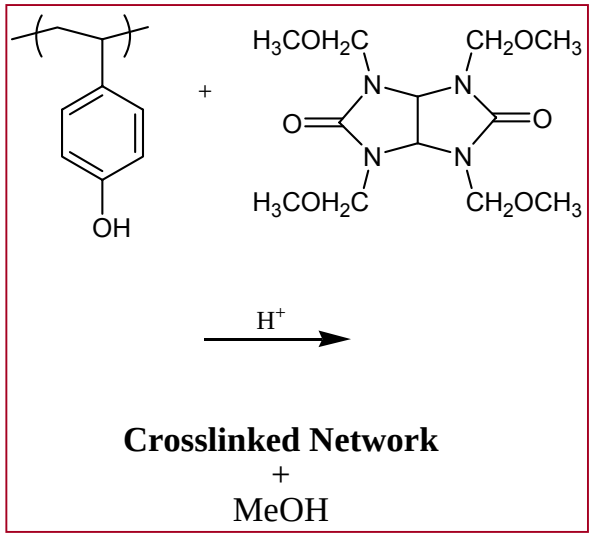
‘Positive Tone’

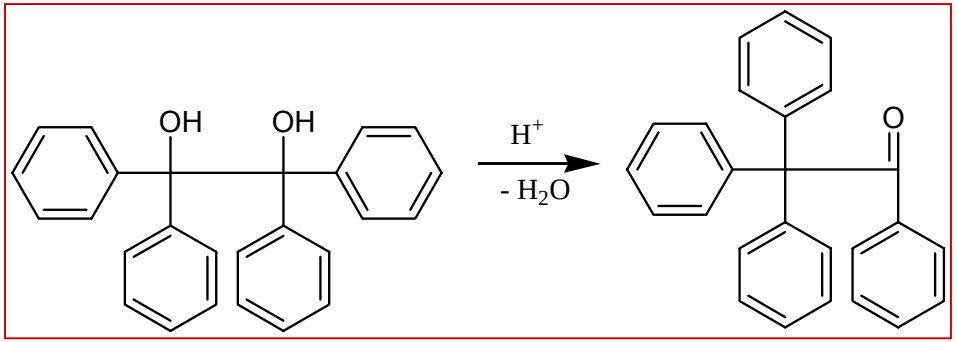






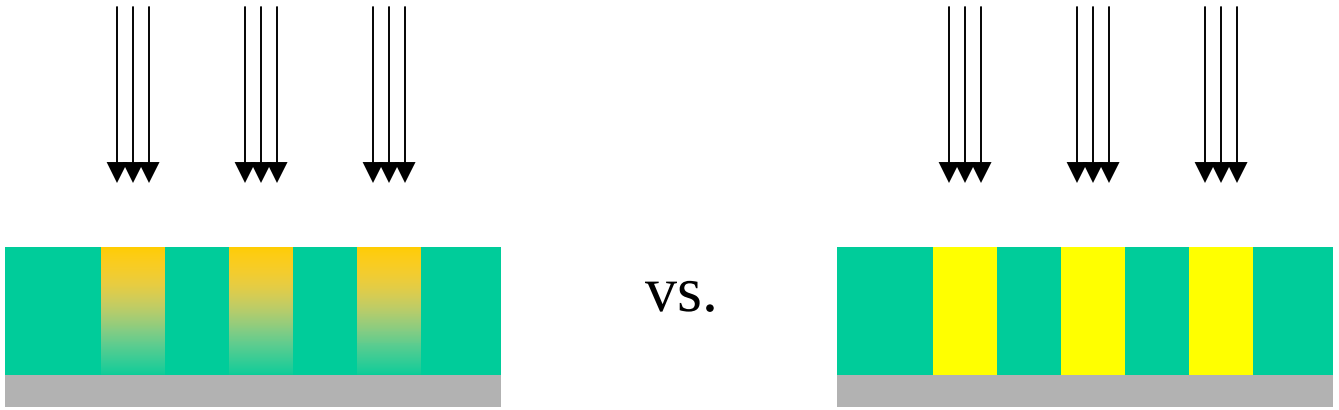
‘Negative Tone’





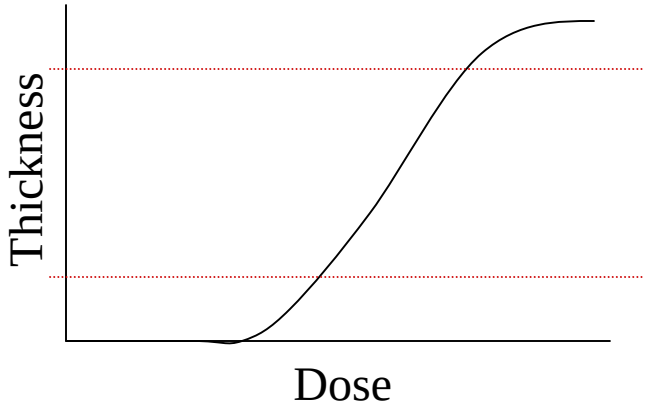
Issue: Materials

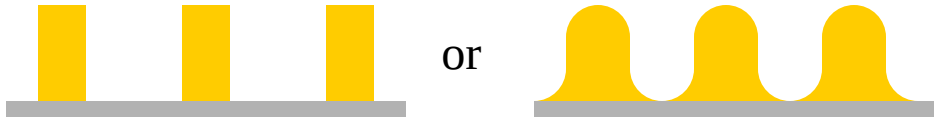
- Exposure wavelength
  - Photoresist material must be transparent at exposure wavelength
  - **248nm**, 13.4nm: aromatic rings acceptable
  - 193nm: acrylate, aliphatic groups acceptable
  - 157nm: fluorinated moieties acceptable

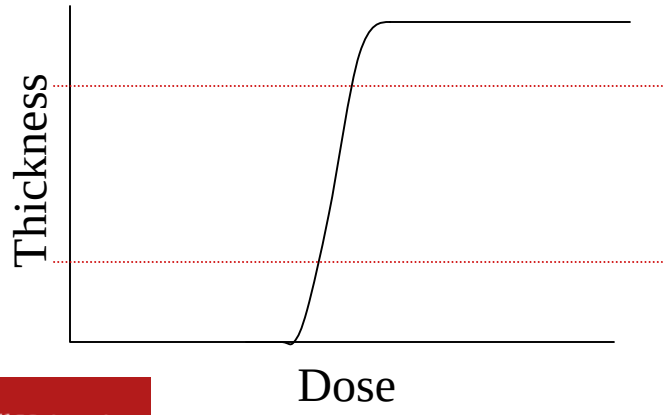


Issue: Contrast

- Chemical / Solubility Contrast



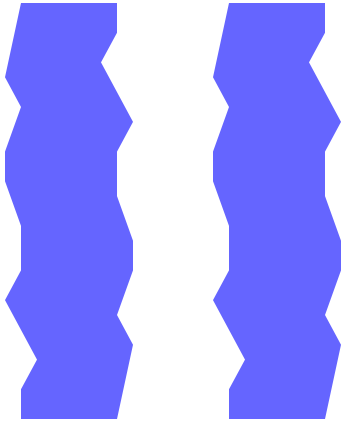




Next Generation Lithography: Key Problems

- Pattern variations are of increased concern

(Top view)



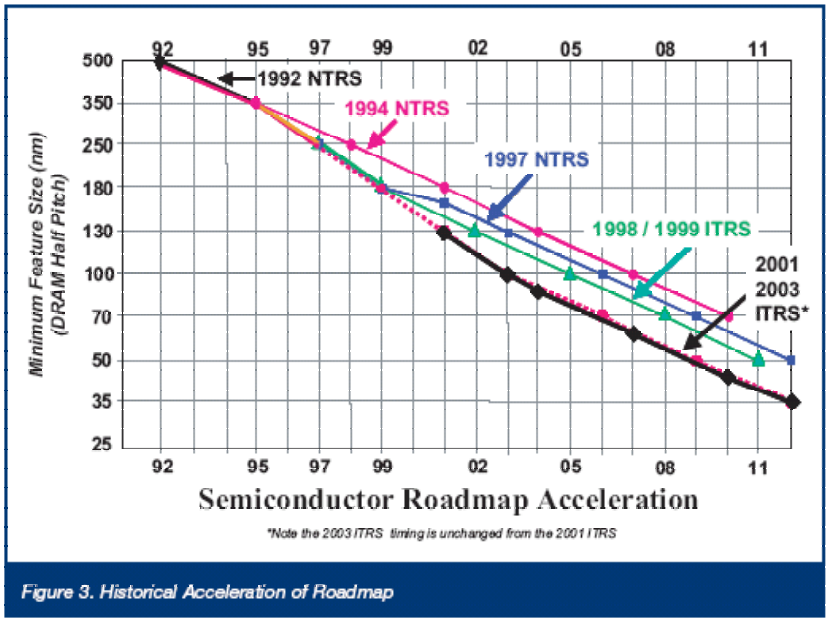
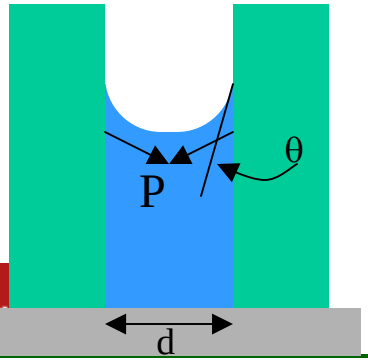
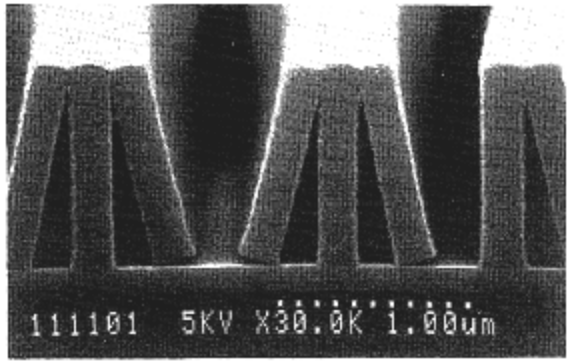


Figure 3. Historical Acceleration of Roadmap

- Pattern collapse becomes more of an issue
  - @ 100 nm line/space, aspect ratios > 3.5:1



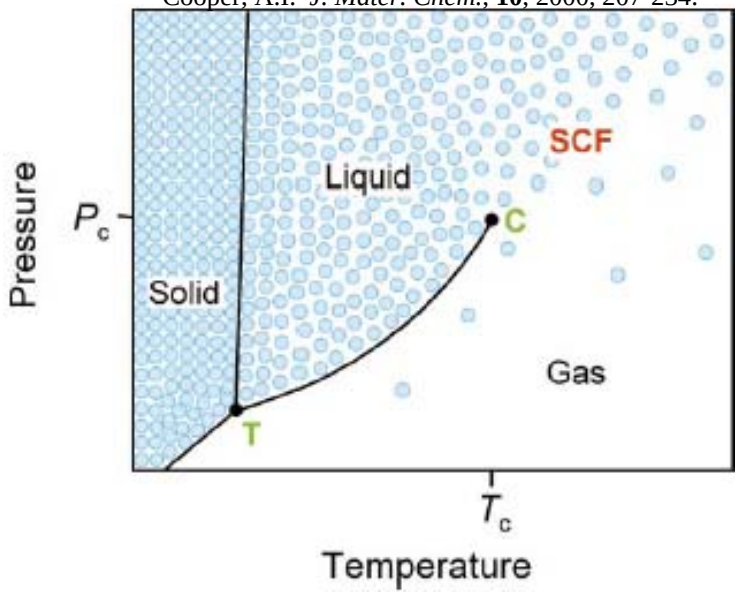
$$P = \frac{\sigma}{R} = \frac{2\sigma\cos\theta}{d}$$



T. Tanaka, M. Morigami, N. Atoda, *JJAP*, **32**(pt1, 12B) 6059 (1993).

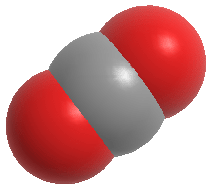
Supercritical CO_2

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



CO_2 is non-polar, though has a large quadrupole moment

- Non-polar functionalities: solvent-solvent interactions dominate
- Polar repeat functionalities: solute-solute interactions dominate



- One phase exists above the critical point
  - CO_2: T_c=31 °C, P_c=1070 psia (74 bar)
- CO_2: Non-flammable, non-toxic, abundant, recyclable. Environmentally Benign.
- Modest operating condition

Other Fluids:

Water: T_c=374 °C, P_c=3212 psia

Acetone: T_c=235 °C, P_c=682 psia

Isopropanol: T_c=235 °C, P_c=691 psia

Advantages of Supercritical Fluids

Environmental benefits

- Potential to eliminate need for organic solvents and ultra-pure water during processing
  - For a typical semiconductor process producing 5000 wafers a day, 8000 liters of waste solvent and contaminated rinse water exit the process[1]

- Harmful solutes are very easily separated from exit streams via depressurization

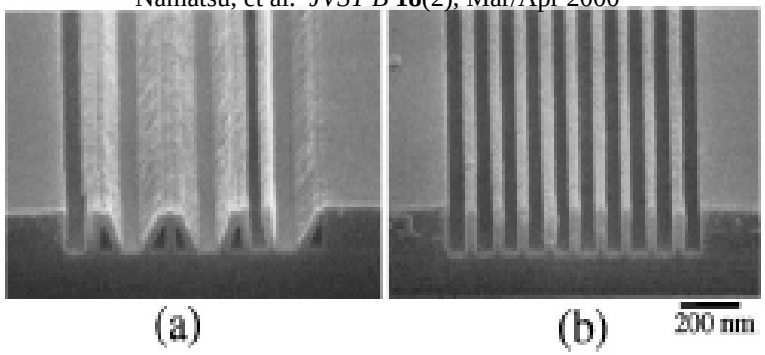
Performance Benefits

- Liquid-like and variable density
  Tunable solvating power

- Gas-like diffusivity & viscosity
  Penetrates crevices
  High rate of development
  No residue

- No surface tension
  Eliminates pattern collapse in dense, high aspect ratio features

Namatsu, et al. *JVST B* **18**(2), Mar/Apr 2000



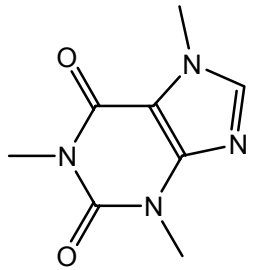
[1]J. M. DeSimone, S. L. Wells, *Angew. Chem. Int. Ed.* **40**, 518 (2001).

Supercritical CO_2 in Industry

- Extraction of essential oils from organic matter
  - Cinnamon, ginger, sandalwood, etc
  - Pharmaceutical applications

Flavex®

- Decaffeination of coffee
  - CO_2 replaced CH_2Cl_2 as solvent, removed only caffeine

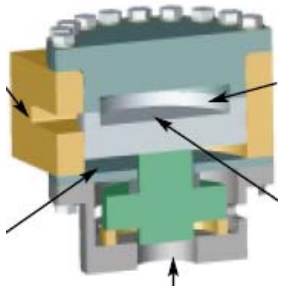


- Dry Cleaning
  - Addition of surfactants

Hangers CLEANERS

- **Wafer cleaning**
  - BOC Edwards DFP-200
  - Critical Point Dryer

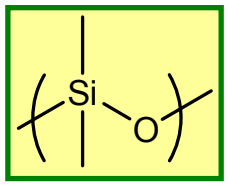
BOC Edwards



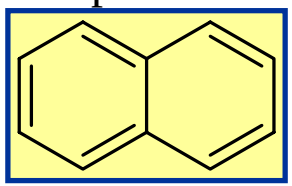
Supercritical CO_2 and Solubility

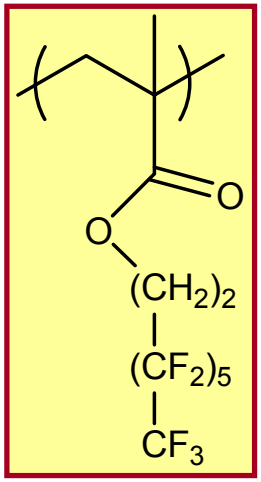
- Solvating power is related to fluid density – tunable solvent strength
  - Selective dissolution
  - Solutes can easily be separated

PDMS



Naphthalene





Properties that affect solubility:

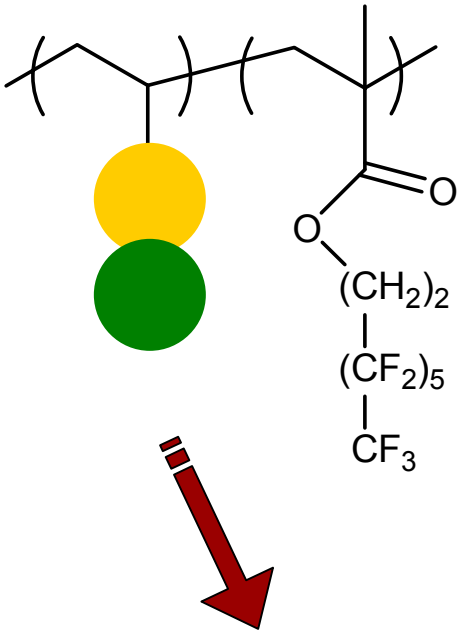
–Stiffness (***entropy***)

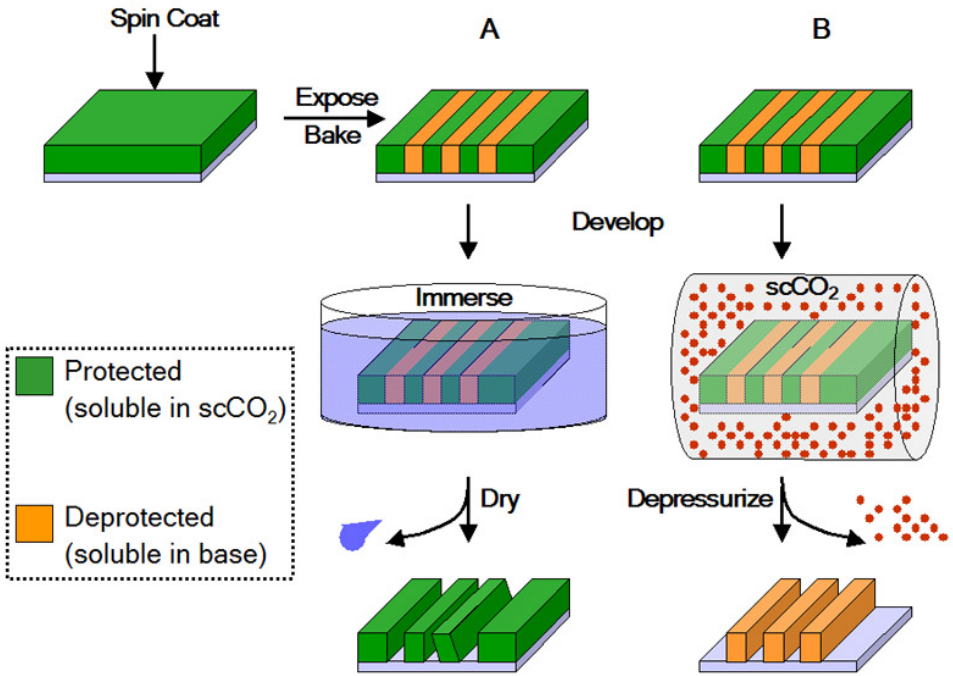
–Molecular weight (***size***)

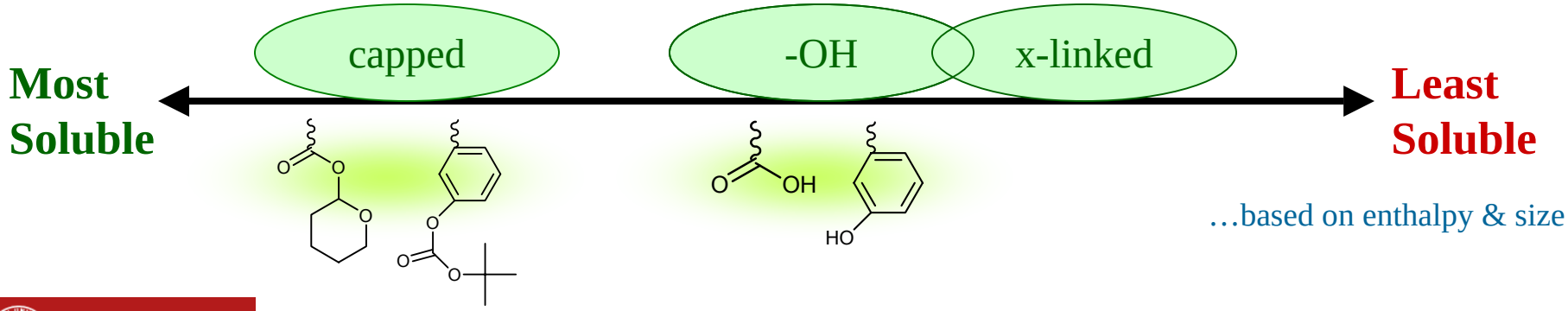
–Existence of electron-dense groups (***enthalpy***)

- Acrylate groups, aromatics
- Fluorine substituted moieties

Supercritical CO_2 and Solubility



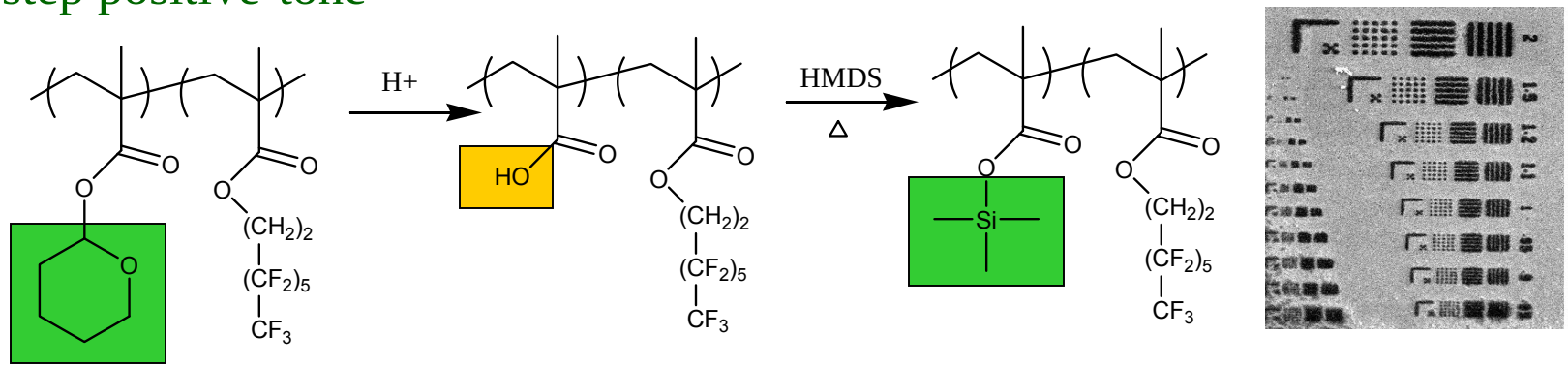




…based on enthalpy & size

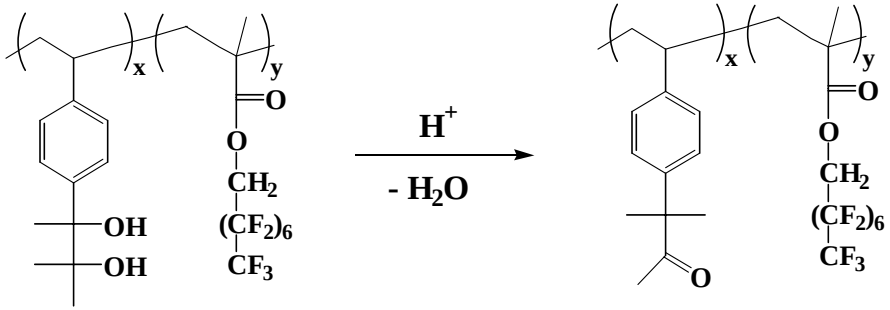
Previous Positive Tone Resists Developable in $scCO_2$

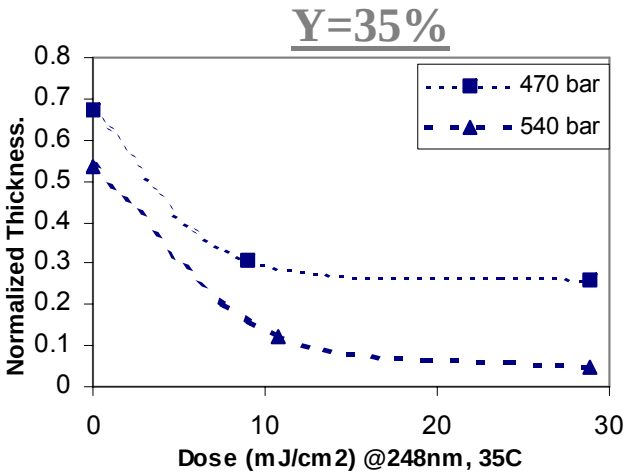
Two-step positive-tone



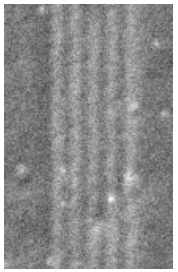
Pham, V Q.. et al., *Chem. Mater.* 15(26), 2003, 4893-5.

Intrinsic positive-tone!





200 nm

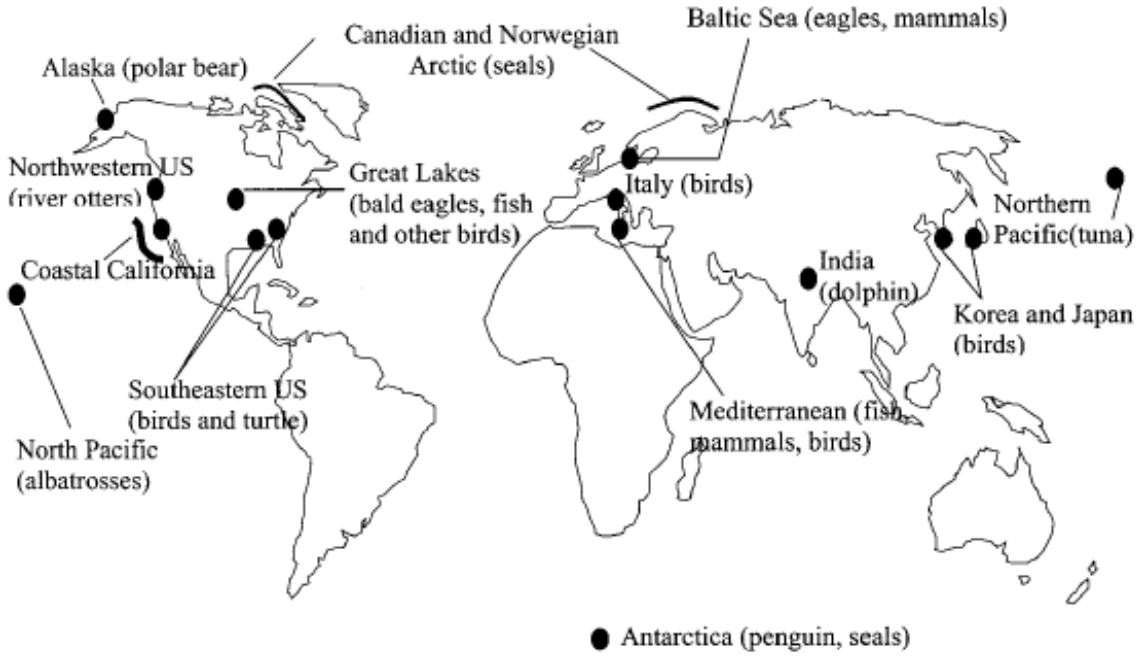


Reduce Fluorination

Perfluorinated octyl compounds have been shown to bioaccumulate and disrupt cellular functions

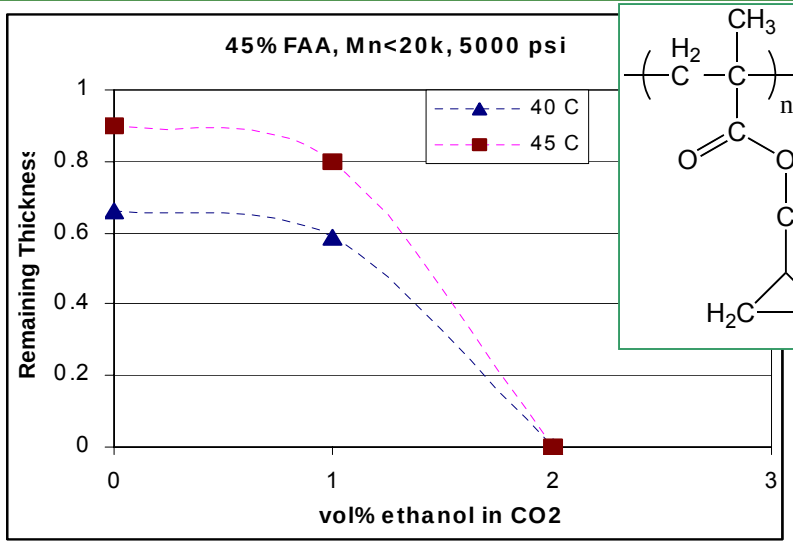
Environmentally friendly? → reduce need for fluorination

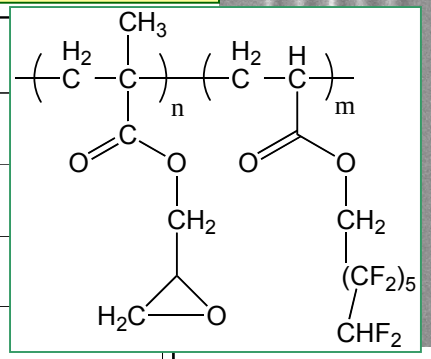
Giesy J P; Kannan K, Environ. Sci. & Tech. (2001), 35(7), 1339-42

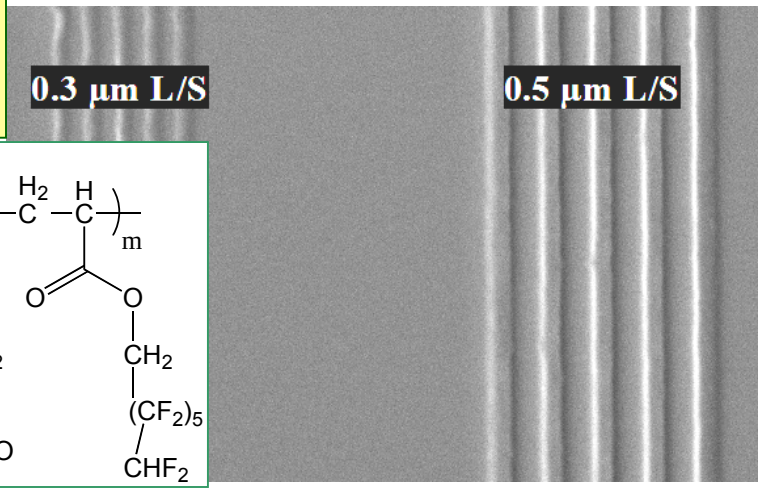


Reduce Fluorination: The Cosolvent Effect

- Increase solvent density
- Tune polarity of fluid
- Specific interaction with a comonomer



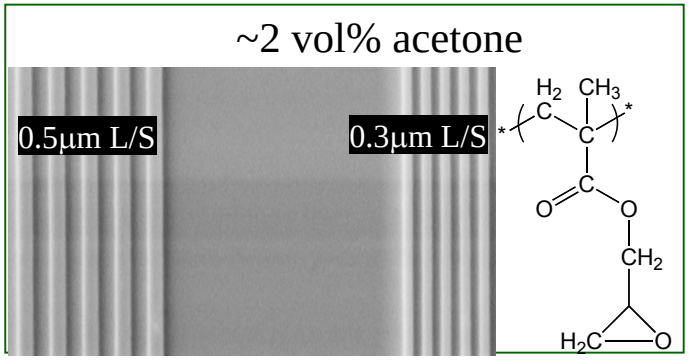




2 vol% ethanol (1.5mol%, 1.6wt%) in $scCO_2$

P = 5000 psi, T = 45°C, t = 10 min

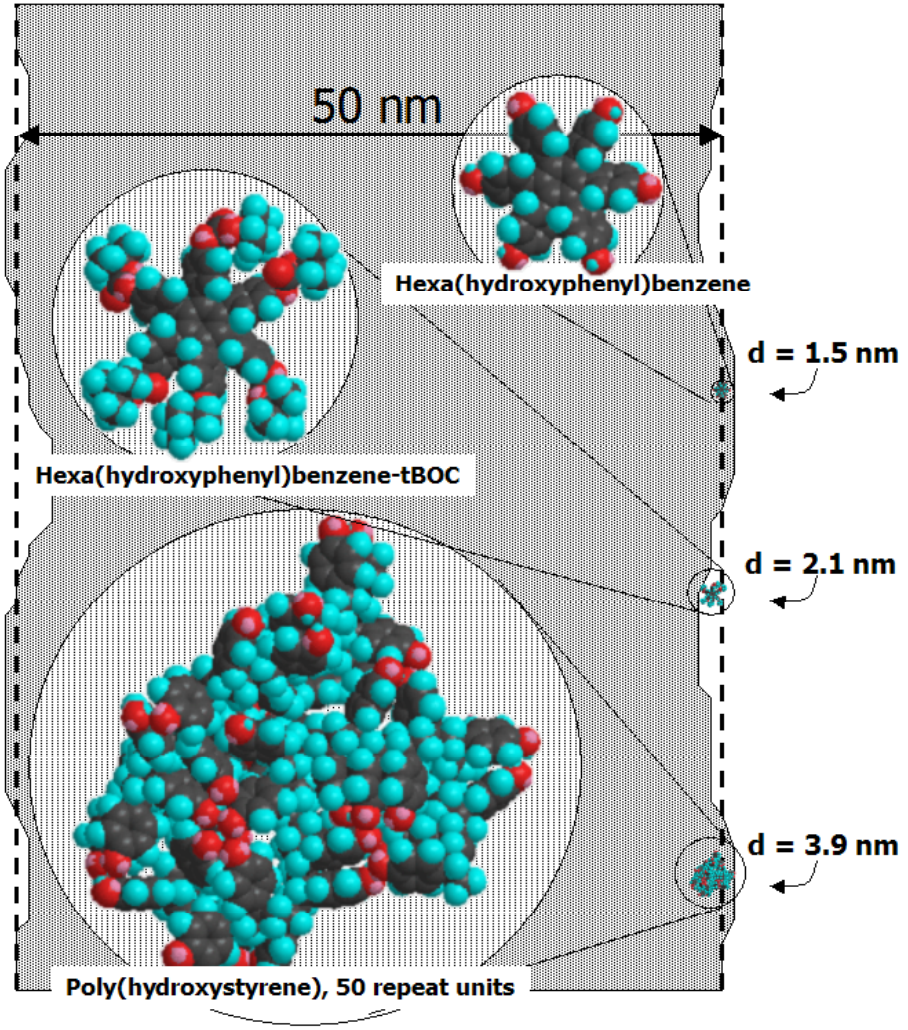
- 1vol% **ethanol**….very little effect
- 2vol% **ethanol**….100% removal



Mao, Yu; Felix, N. et al., *JVST B.*, **22**(5), 2004, 2473-8.

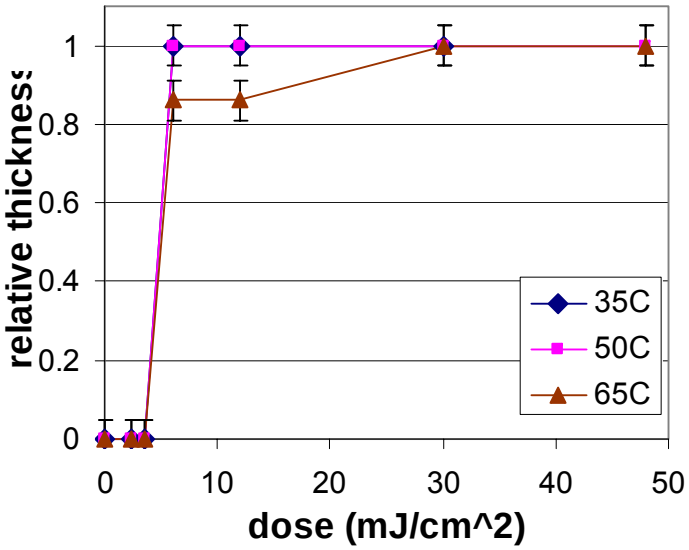
Reducing LER: Molecular Glass Photoresists

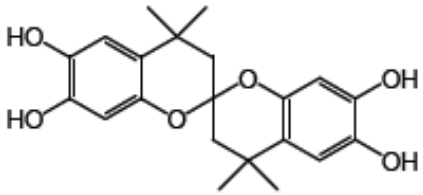
- Small molecule size ~1-2nm
- Well defined molecular structures
  - No distribution of mass
- Low tendency towards crystallization
  - bulky irregular shape or different conformation states
- Strong intermolecular attractive forces for high Tg
  - Specific interactions such as H-bonding
- Better miscibility of resist components

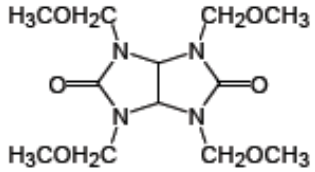


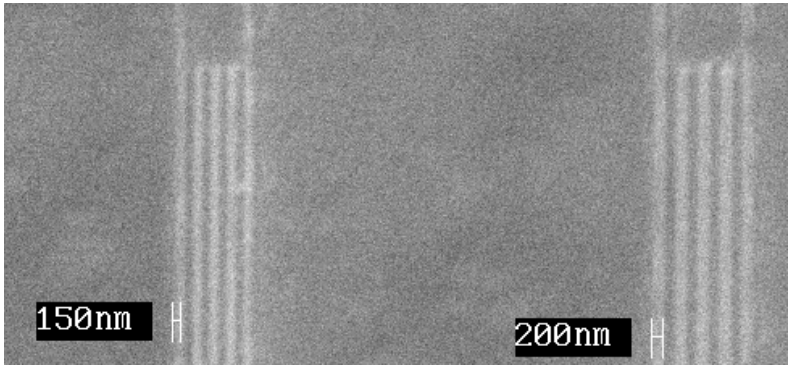
Molecular Glasses and $scCO_2$

- Due to their small size, molecular glass resists of all types have **potential for CO_2 solubility…no fluorine needed**!
  - Nonpolar molecules with aromatic rings are most soluble
  - Crosslinking chemistries offer better contrasts, processing windows
- Example:



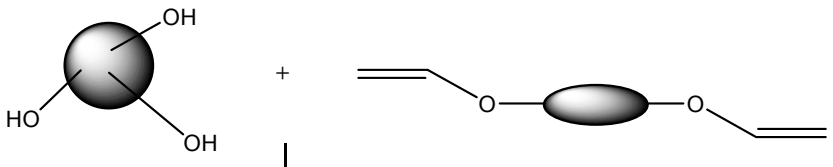




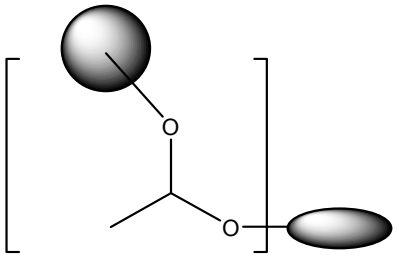


Developed at 50C, 300 bar

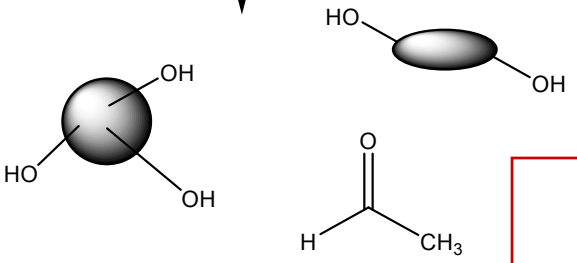
Positive Tone Molecular Glass Resists for $scCO_2$ Development



Heat



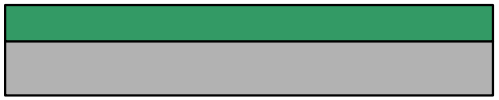
Heat and H+



Film with hydroxy containing molecule; crosslinker; PAG

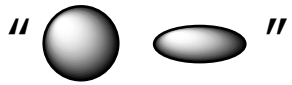
125°C

Film with **Crosslinked network**; PAG



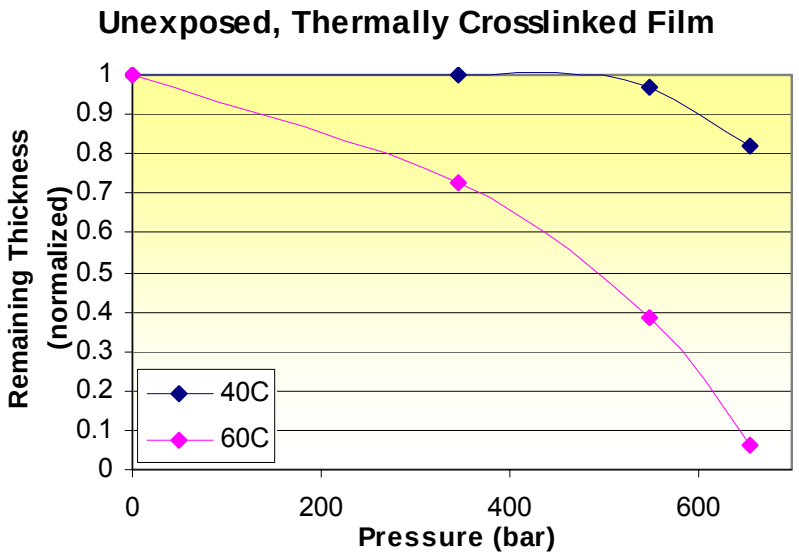
Expose, PEB

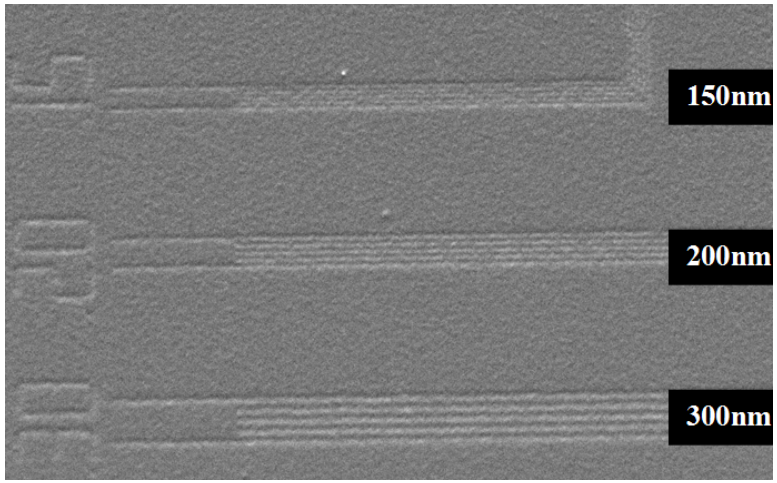
Film with **De-Crosslinked molecule**; crosslinked regions

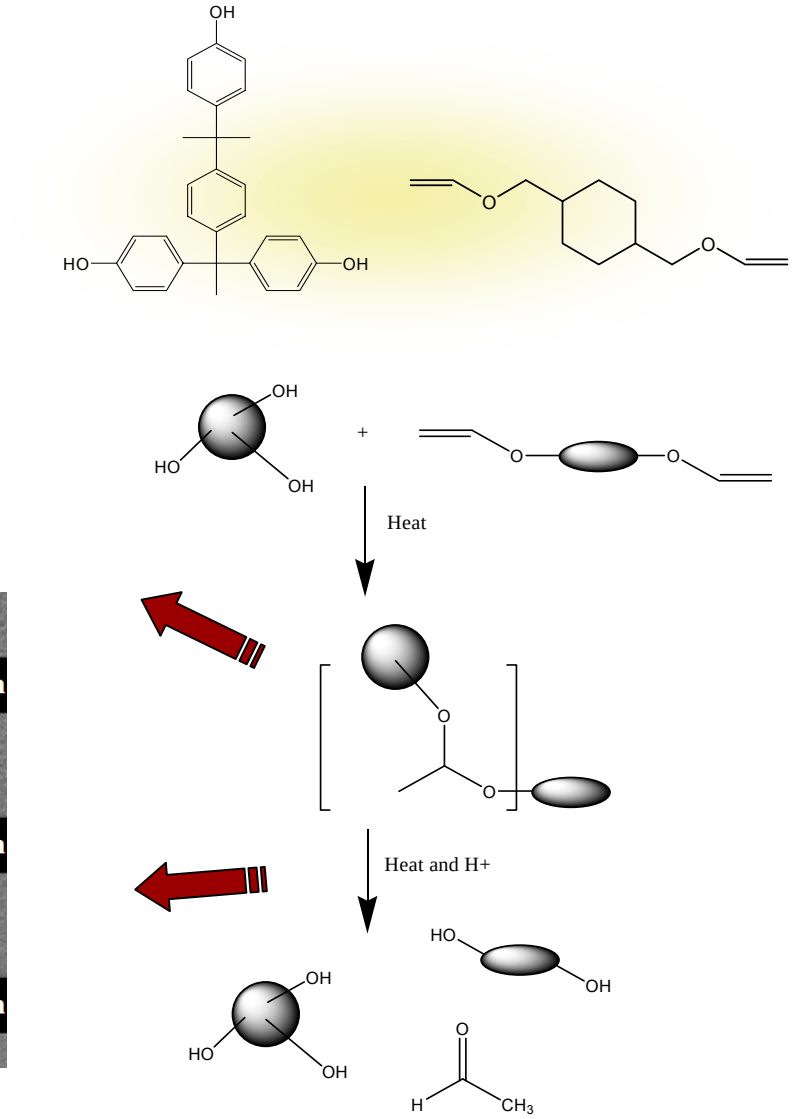


Can be tailored for exposure wavelength

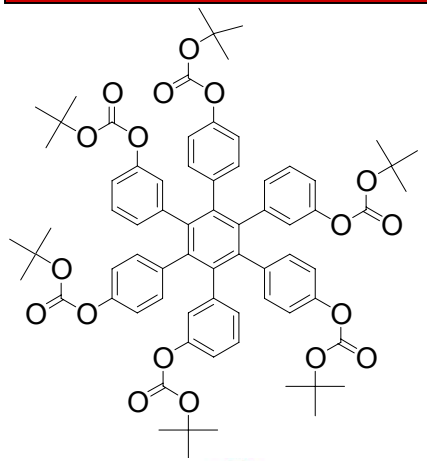
Positive Tone Molecular Glass Resists for $scCO_2$ Development

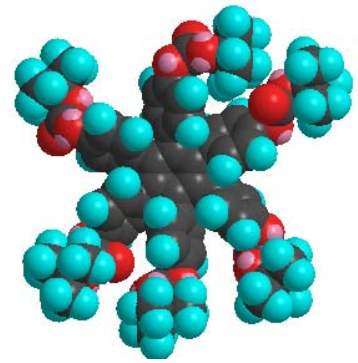


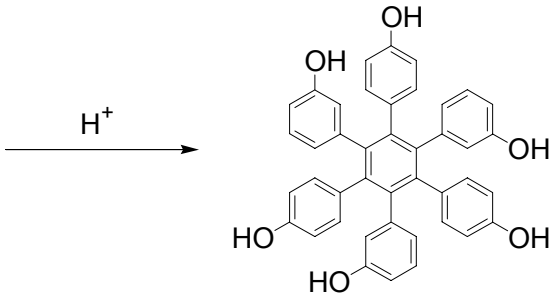


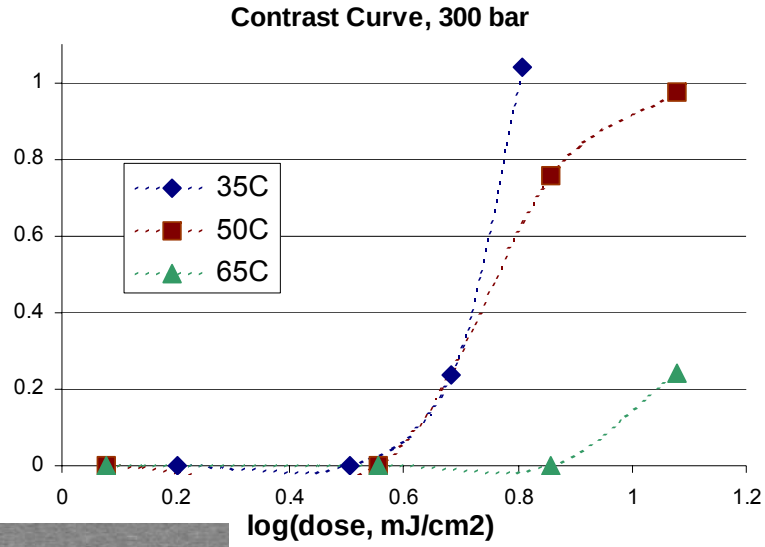


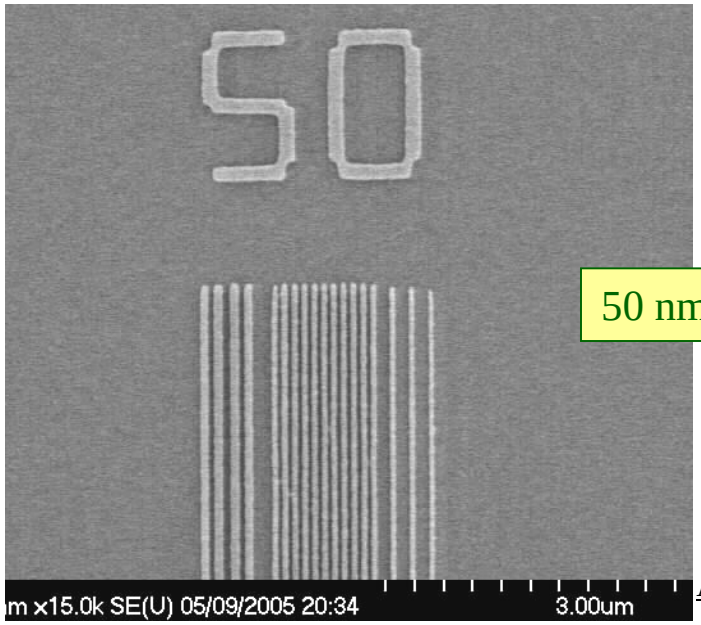
High Contrast Negative-tone Molecular Glass Resist for $scCO_2$









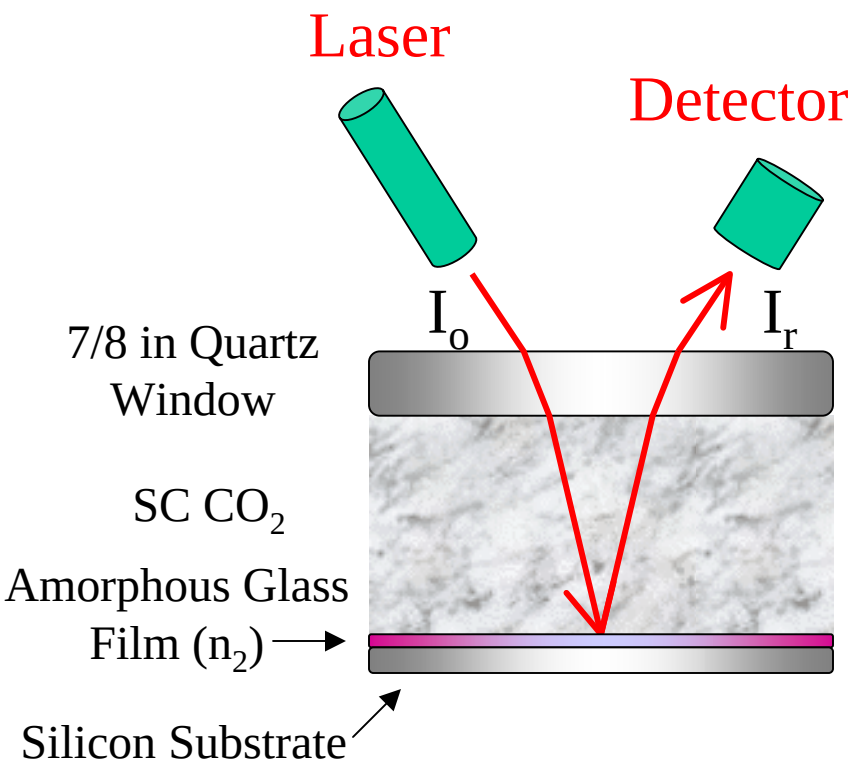


50 nm!

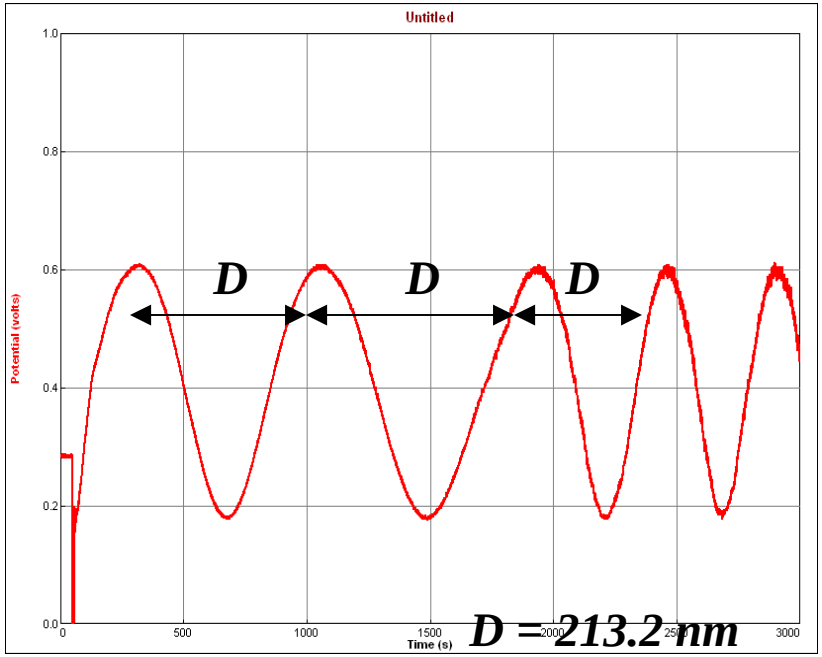
35C, 300 bar

Advanced Materials, *submitted, under revision*

Future Direction: Dissolution Rate Monitor



Graph of T-Shape + X-Linker
Unexposed, 65 °C, 4300 psia

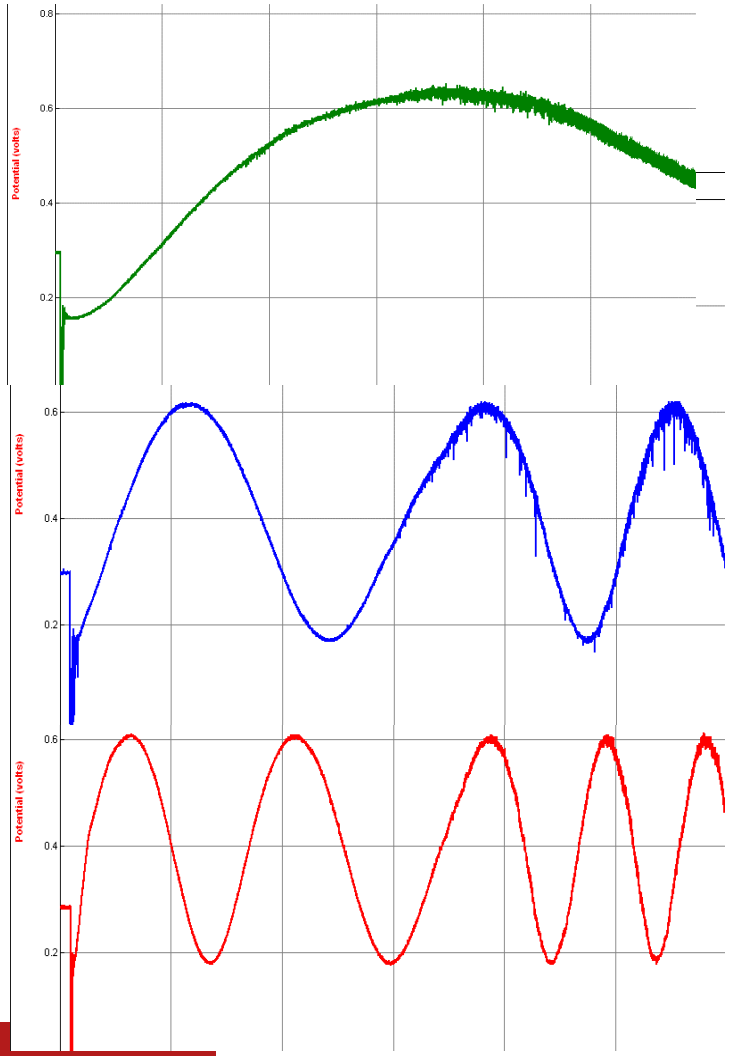


Thickness Period:

$$D = \frac{\lambda}{2\sqrt{n_2^2 - n_1^2 \sin^2 \theta_1}}$$

As anticipated, the film dissolves according to a sinusoidal wave

Effect of Pressure on Dissolution Rate



T-Shape + X-Linker Unexposed

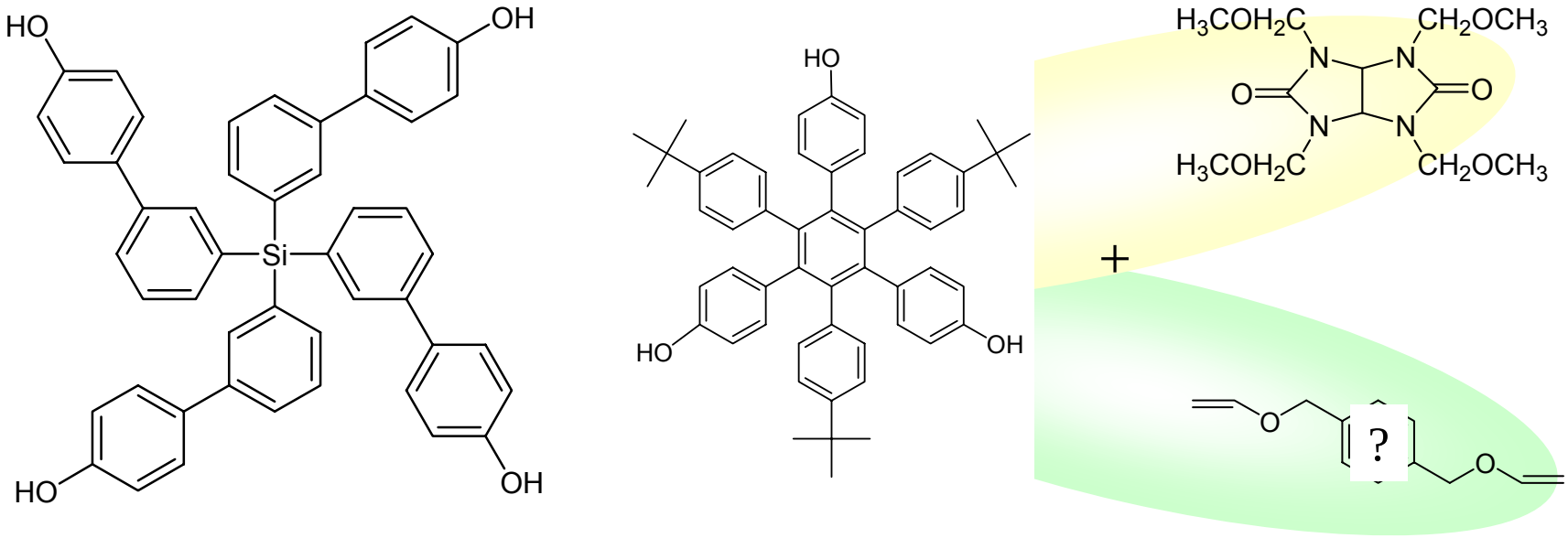
← 65 °C, ≈ 2300 psia

← 65 °C, ≈ 3400 psia

← 65 °C, ≈ 4300 psia

Future Directions

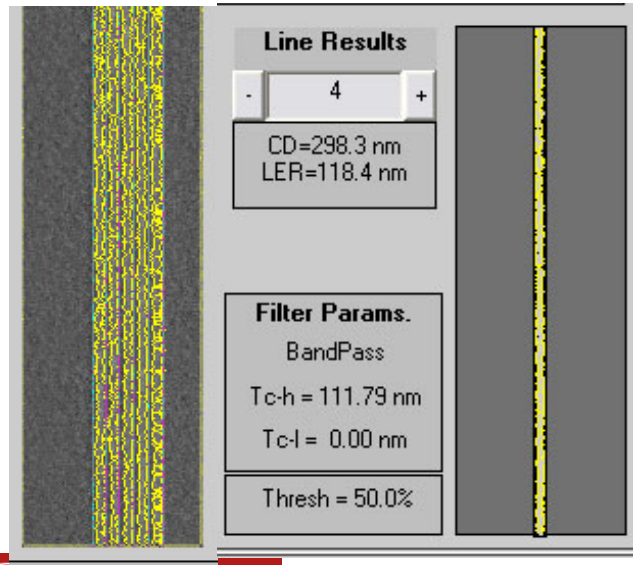
- Continue study of molecular glass resist systems developable in $scCO_2$.



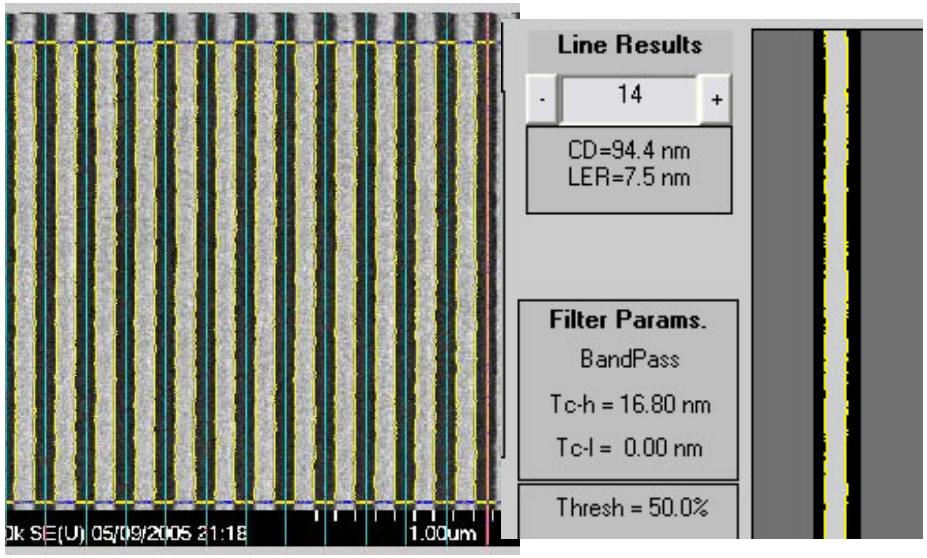
Future Directions

- Investigate properties affecting resolution and LER
  - Contrast
  - Tg

Tg ~ 46°C
Processed at 52°C
→ LER > 100 nm ☹



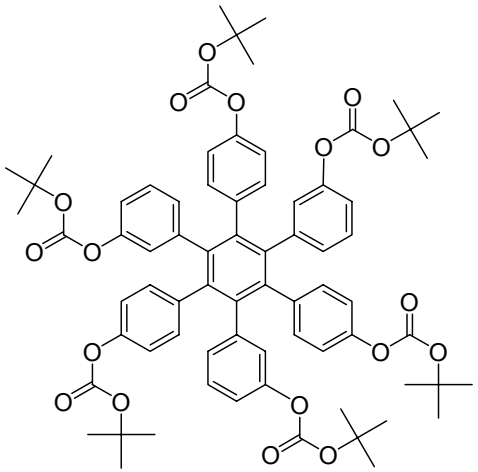
Tg ~ 100°C
Processed at 35°C
→LER ~ 7.5 nm



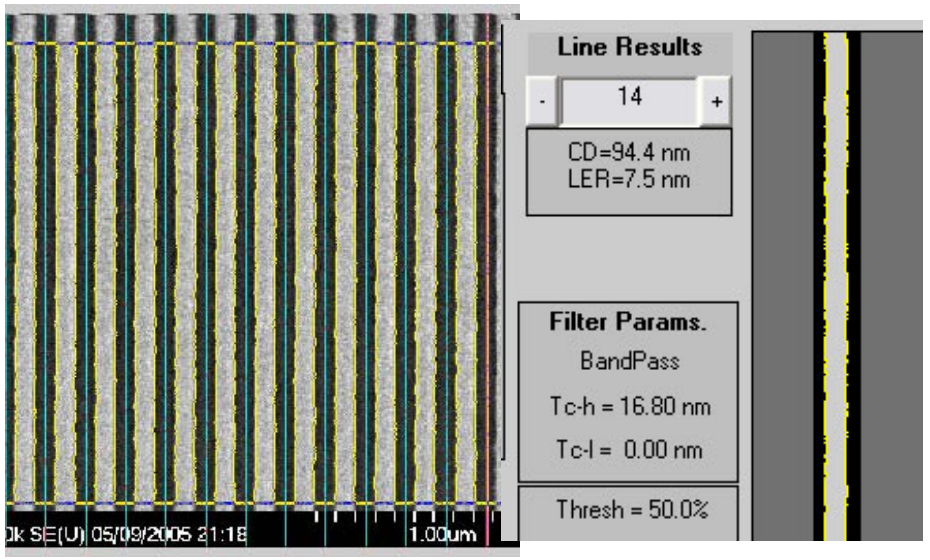
Conclusions

- A green process can also be made industrially attractive by optimizing materials and conditions.
  - New materials
  - Inherent performance advantages

- Impressive synergy between molecular resists and $scCO_2$ development.



LER ~ 7.5 nm



Acknowledgments

- **NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing**

- Cornell Center for Materials Research (CCMR)
- Cornell Nanoscale Facility (CNF)

- Ober Group
  - Kosuke Tsuchiya
  - Camille Luk
  - Anuja De Silva
  - Seung Wook Chang
  - Da Yang
  - Dan Bratton
  - Prof. Chris Ober