Photoresist Development Using Supercritical CO_2: Achieving Small Dimensions with an Environmentally Friendly Solvent

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Task 425.008, 425.017

ERC Teleseminar

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Outline

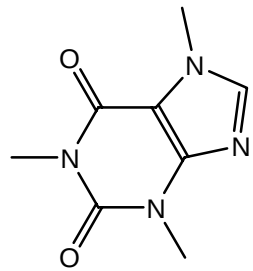
- Challenges of next generation lithography
- Supercritical carbon dioxide
  - Properties
  - Solubility
- Development of polymeric photoresists
  - Resist fluorination
  - Fluid additives
- Molecular glass photoresists
  - Inherent solubility
  - Sub-65nm resolution

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

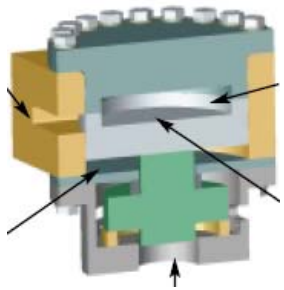


- Dry Cleaning
  - Addition of surfactants

Hangers CLEANERS

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

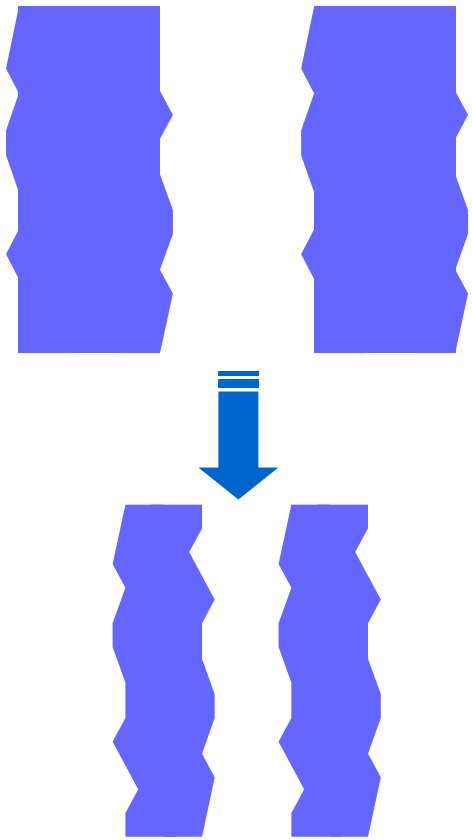
BOC Edwards



Next Generation Lithography: Key Problems

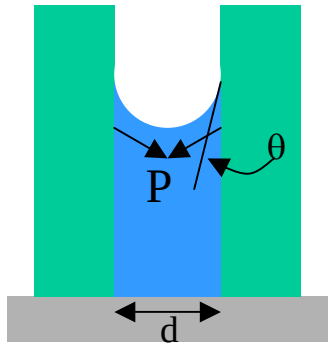
Pattern Variations

< 3nm for 32nm node



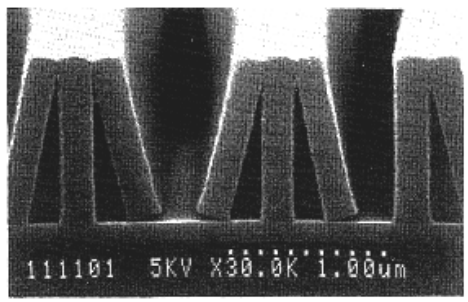
Pattern Collapse

Reduce surface tension



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

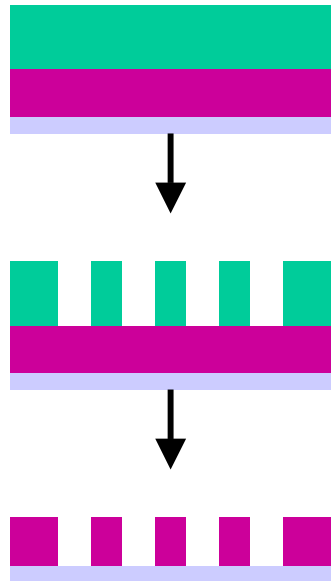
@ 50nm L/S, aspect ratios >2:1 collapse w/water



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

Non-polar Materials

Low-κ applications



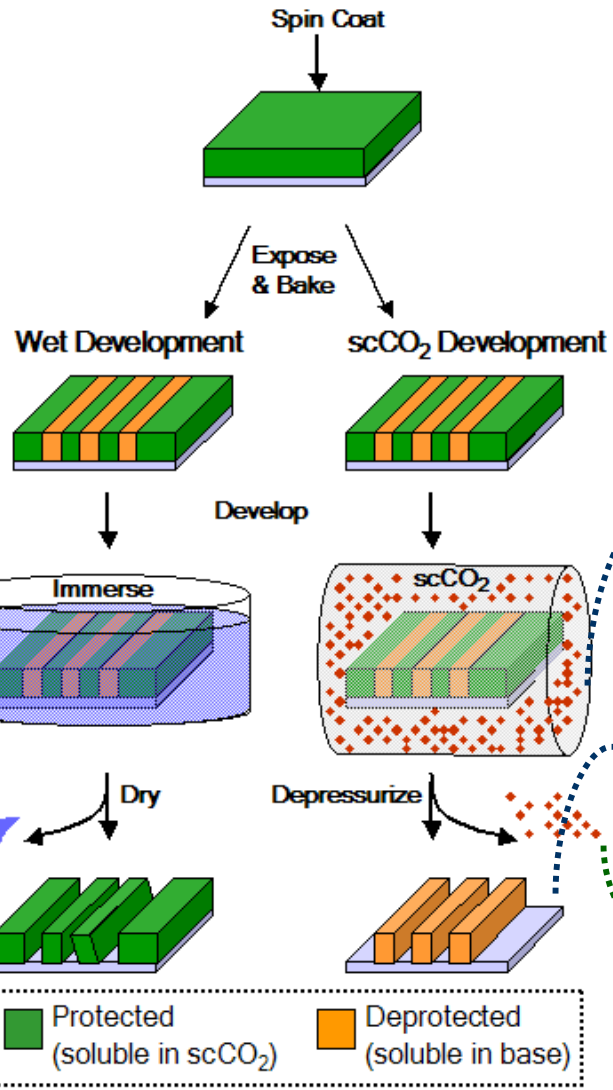
Lack of appropriate non-polar developers → Must use mulitple subtractive steps

Advantages of Supercritical CO_2 Development

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

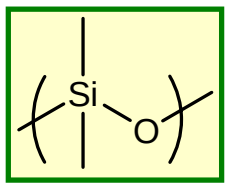
Harmful solvents are cleanly separated via depressurization

No surface tension, eliminates pattern collapse

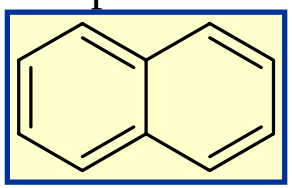
Supercritical CO_2 and Solubility

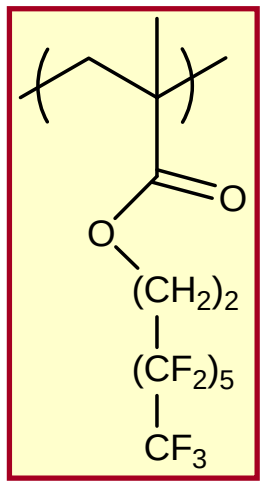
- Solvating power is related to fluid density – tunable solvent strength
  - Selective dissolution
  - Solutes can easily be separated

PDMS



Naphthalene





Fluid Phase Equilibria 146 (1998) 325–337

Properties that affect solubility:

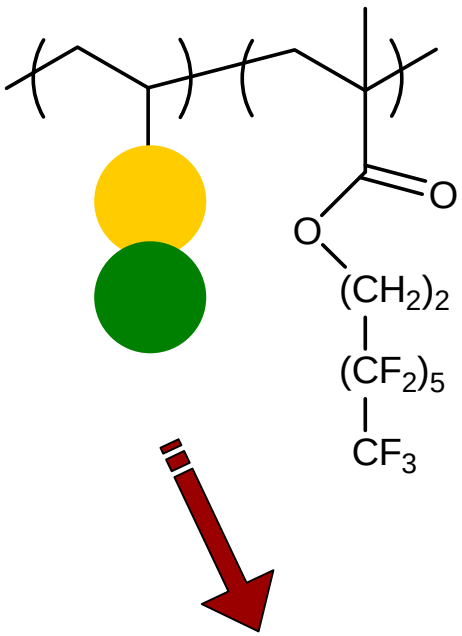
–Stiffness (***entropy***)

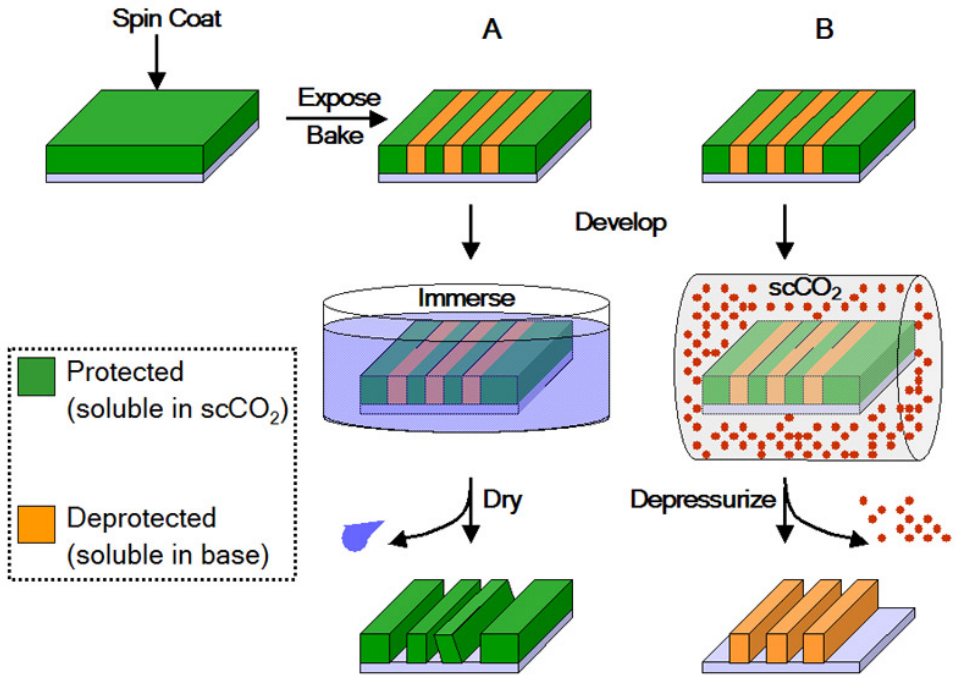
–Molecular weight (***size***)

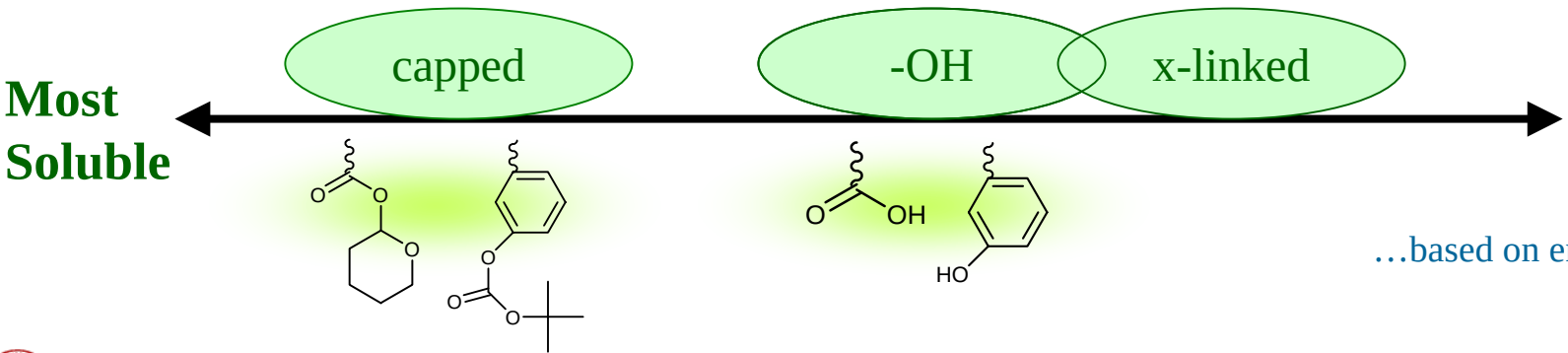
–Existence of electron-dense groups (***enthalpy***)

- Acrylate groups, aromatics
- Fluorine substituted moieties

Supercritical CO_2 and Solubility



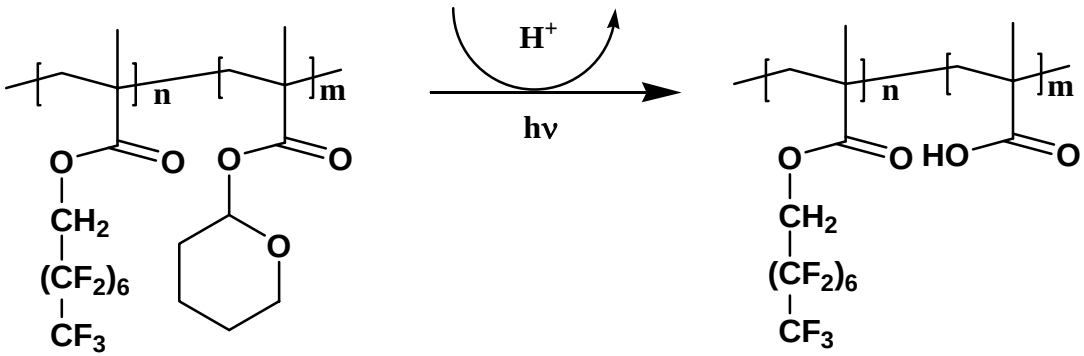




…based on enthalpy & size

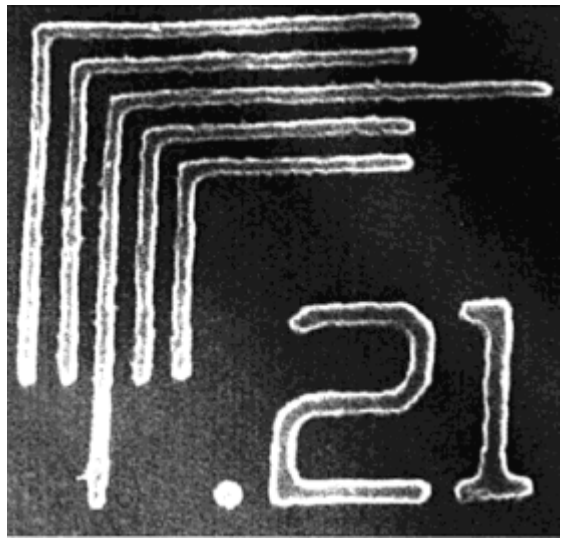
Fluorinated scCO2 Soluble Photoresists

- First platform for soluble polymeric photoresists
  - Copolymerize traditional photoresist monomers with fluorinated monomers
- Negative tone



Soluble

Insoluble



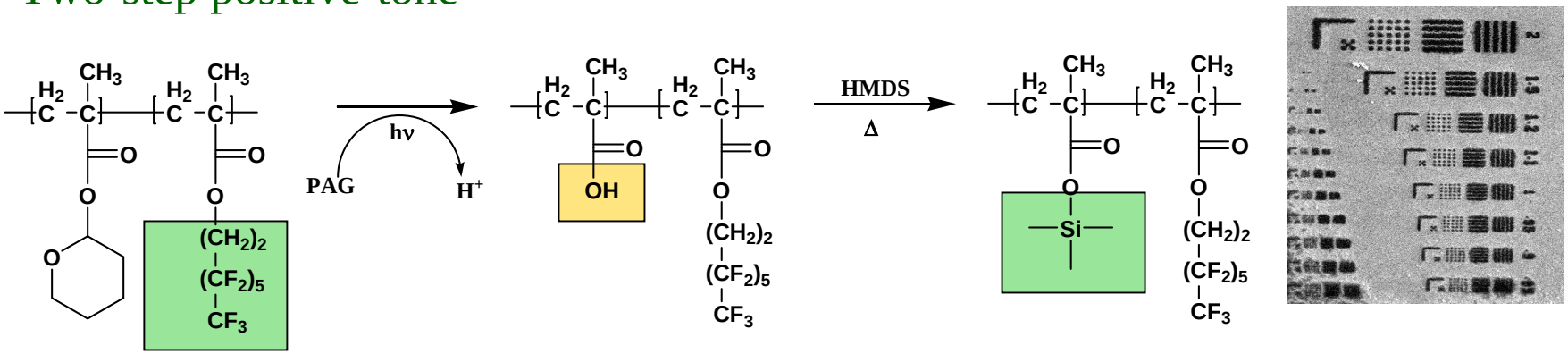
Sundararajan, et al. 193 nm exposure.

- Block copolymer (Cornell) and random copolymer (UNC) versions demonstrated.

N. Sundararajan, S Yang, K Oglno, S Vallyaveettfl, J Wang, X Zhou, C. K. Ober, S. K. Obendorf, and R. D. Allen, *Chem. Mater*. 12, 41 (2000).
D. Flowers, E N Hogan, R Carbonell, mad J. M. DeSlmone, in Proceedings of SPIE, 4690, 419 (2002).

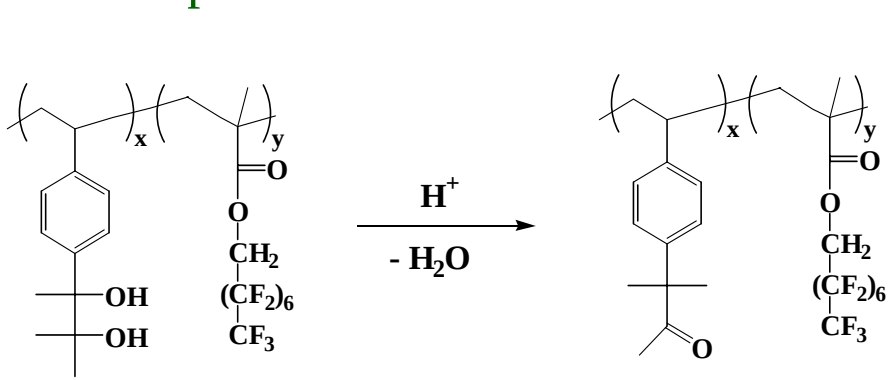
Positive Tone Resists for $scCO_2$ Development

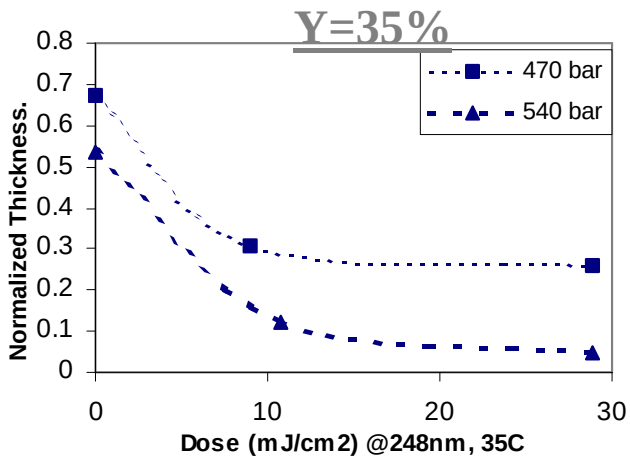
Two-step positive-tone

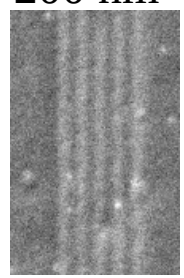


Pham, V Q.. et al., *Chem. Mater*. 15(26), 2003, 4893-5.

Intrinsic positive-tone!







Resist Fluorination

- Advantages
  - High transparency at 193 nm, 157 nm exposure wavelengths
    - Library of fluorinated monomers
  - Simple to increase scCO2 solubility with monomer inclusion

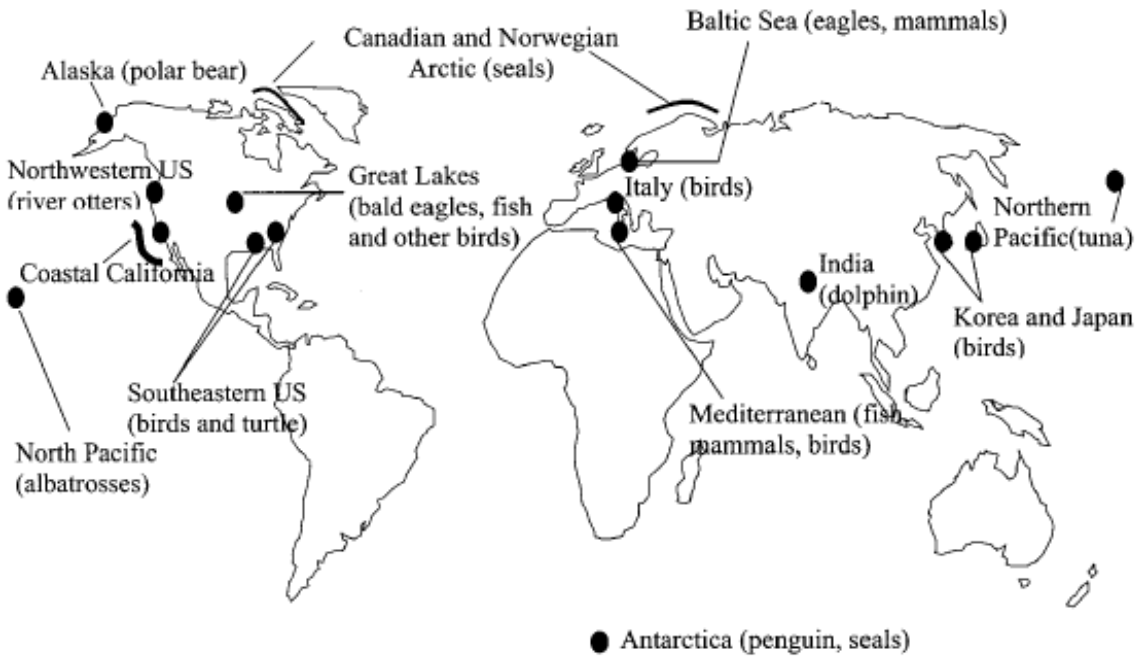
- Disadvantages
  - Low plasma etch resistance of F-containing structures
  - Surface compatibility: low surface energy
  - Low glass transition temperatures (Tg)
    - Difficult to keep sharp pattern shape
    - Low contrast

Reduce Fluorination

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

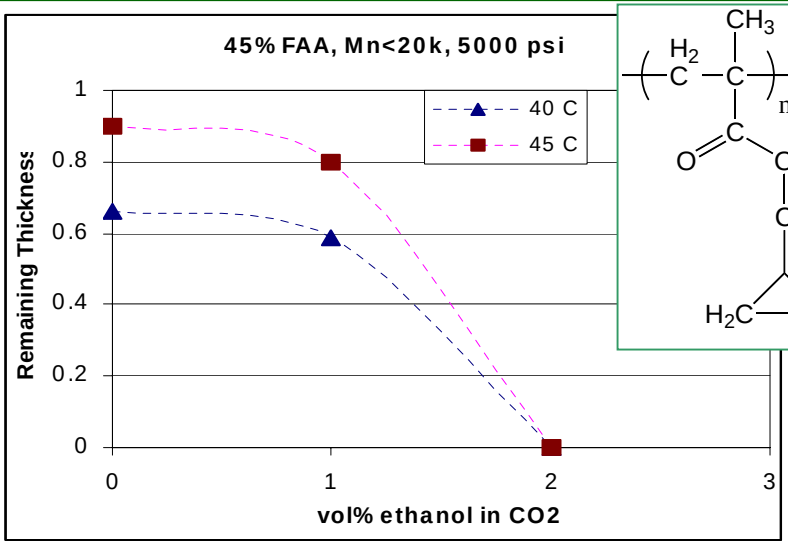
Environmentally friendly? → reduce need for fluorination

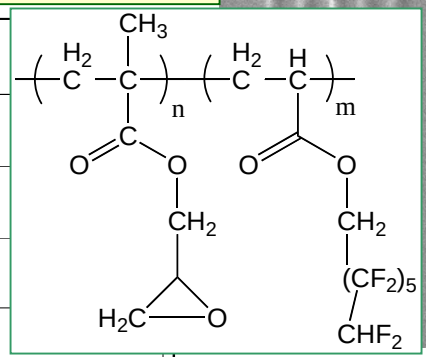
Giesy J P; Kannan K, Environ. Sci. & Tech. (2001), 35(7), 1339-42

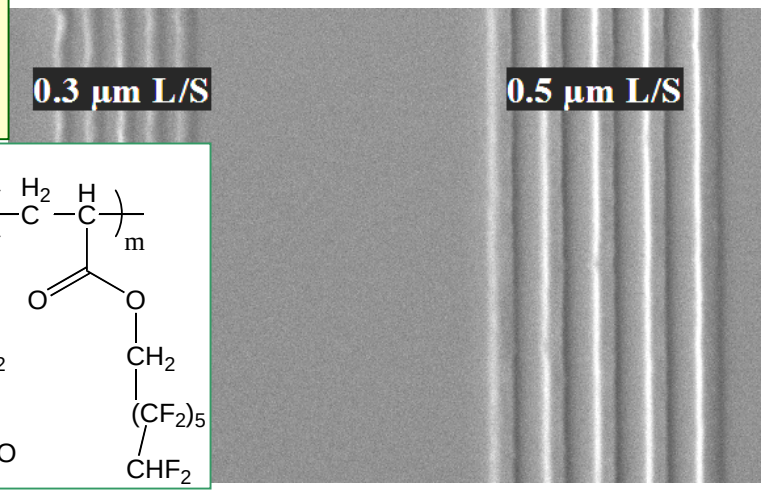


Reducing Fluorination: Using Cosolvents

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





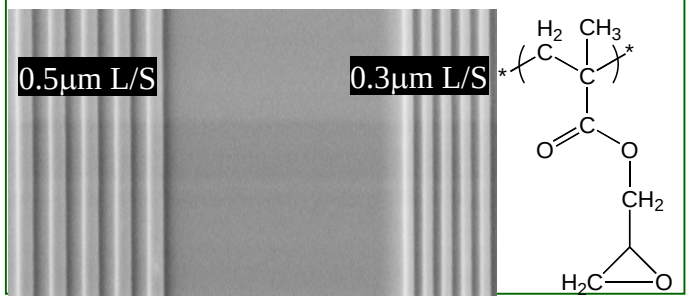


2 vol% ethanol (1.5mol%, 1.6wt%) in $scCO_2$

P = 5000 psi, T = 45°C, t = 10 min

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

~2 vol% acetone



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

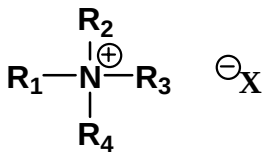
Additives for Processing Conventional Resists

- Patent literature full of examples of surfactant libraries used for scCO2 dissolution of photoresists
  - Fluorinated or hydrocarbon tails
  - Polar or carboxylate heads
  - Mostly seen for pattern cleaning/drying

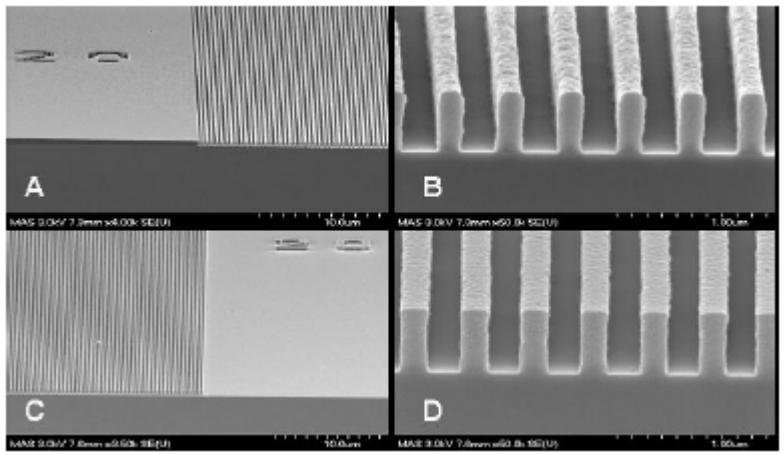
- Recent work by Micell Technologies on reactive ionic additives to impart scCO2 solubility to conventional photoresists

'CO_2 Compatible Salts'

- Rather than ionic surfactants, reactive fluorinated salts added to solution
  - Interact with weak acidic groups of photoresist to impart solubility
  - Due to lower amounts of acidic groups, unexposed regions gain sufficient solubility first
  - Presence of generated acid in exposed regions inhibits reaction with photoresist



R: fluorinated alkyl or aryl group
X: halide or carboxylate group



Aqueous TMAH develop

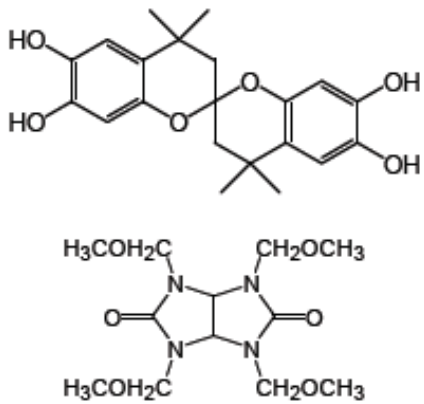
CO_2/CCS develop

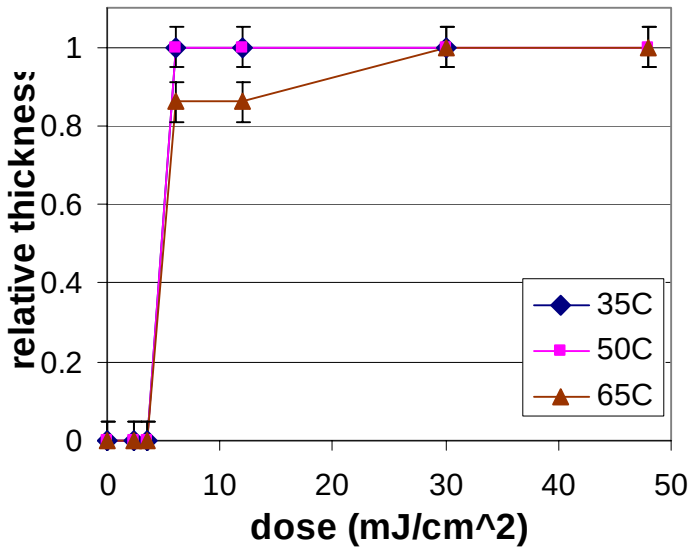
Wagner, M., DeYoung, J., and C. Harbinson, SPIE v 6153 I 2006, p 61531.

DeYoung, J., et al., SPIE v 6153 I 2006, p 615345.

Inherent scCO2 Solubility w/o Fluorine

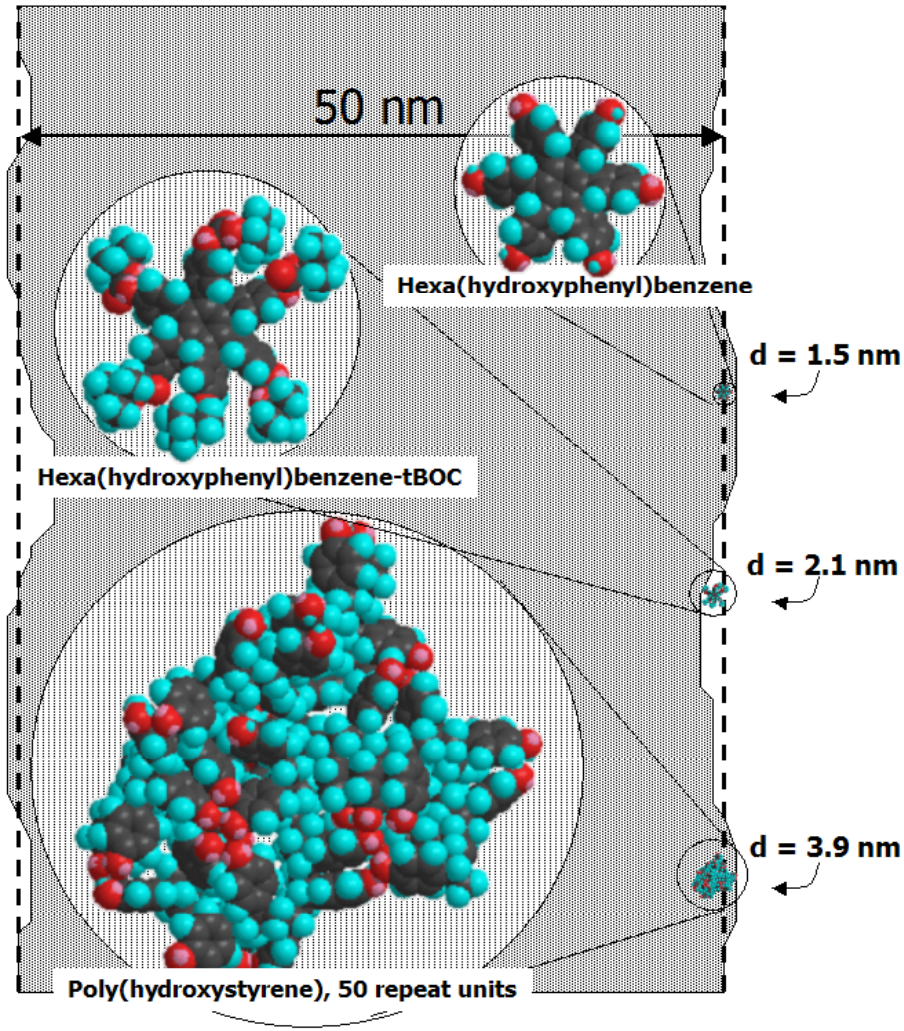
- Molecular Glass Resists
  - Due to their small size, molecular glass resists of all types have potential for CO_2 solubility…no fluorine needed!
    - Nonpolar molecules with aromatic rings are most soluble
    - Crosslinking chemistries offer better contrasts, processing windows



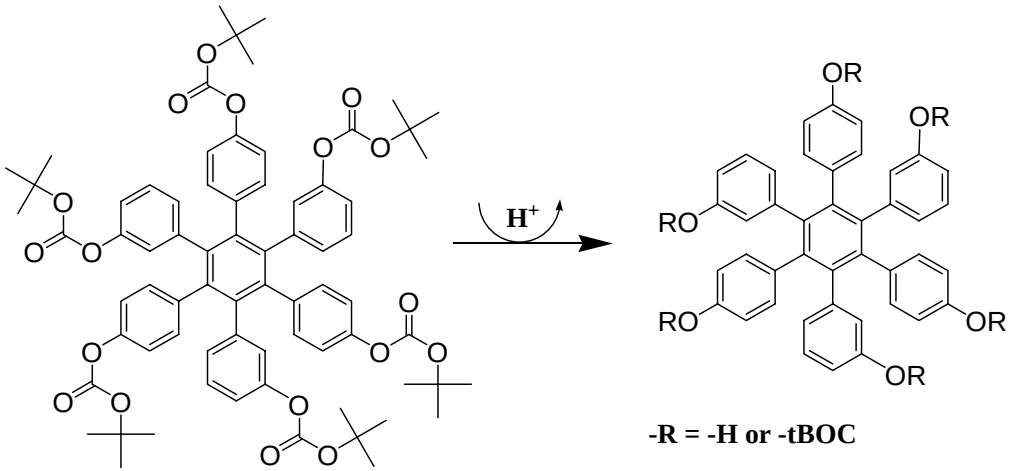


Molecular Glass Photoresists

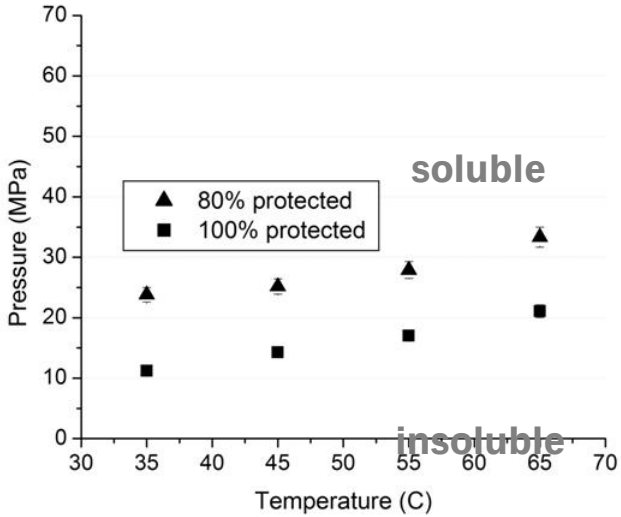
- Small molecule size ~1-2nm
- Well defined molecular structures
  - No distribution of mass
- Low tendency towards crystallization
  - bulky irregular shape or different conformation states
- Strong intermolecular attractive forces for high Tg
  - Specific interactions such as H-bonding
- Better miscibility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

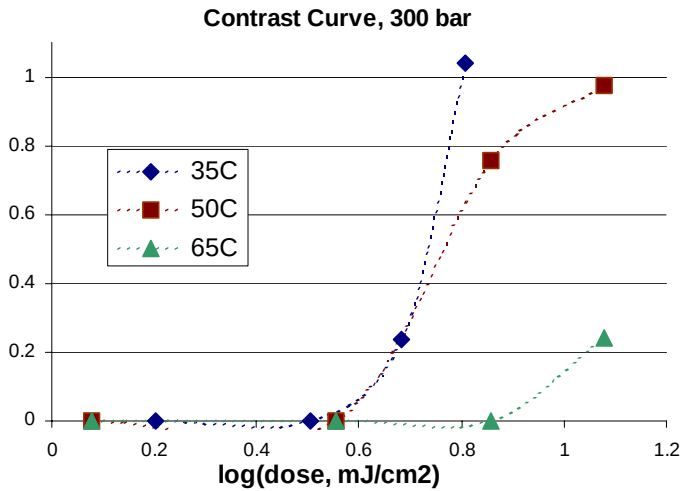


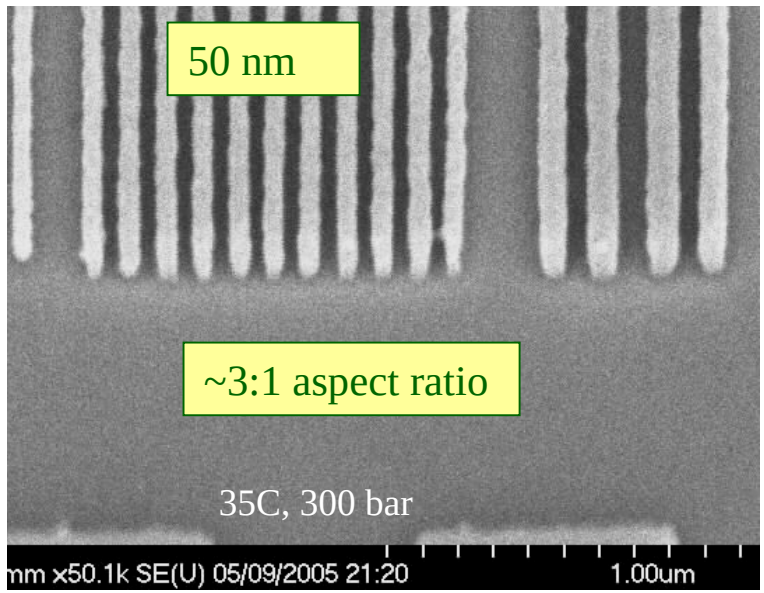
High Resolution MG Resist for Supercritical CO_2



-R = -H or -tBOC

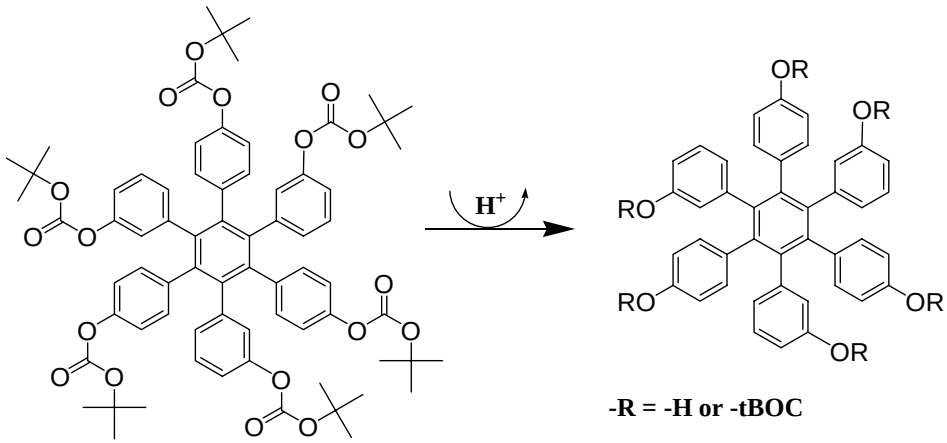


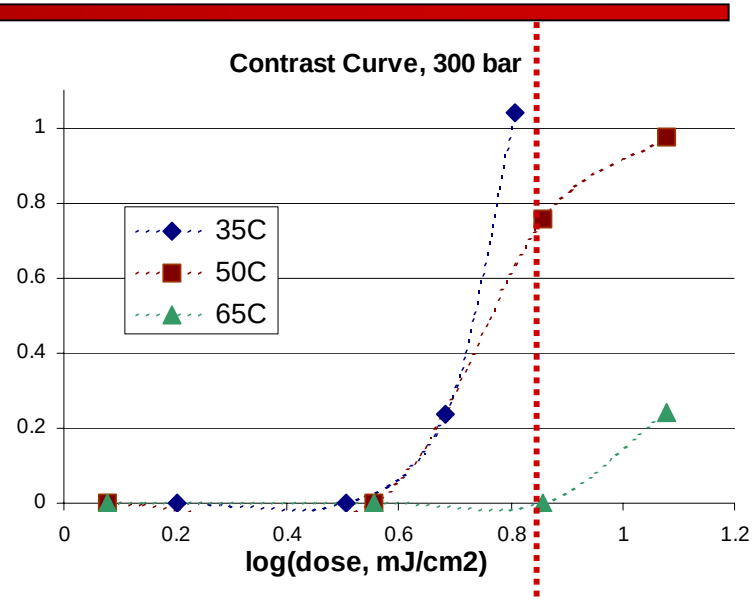




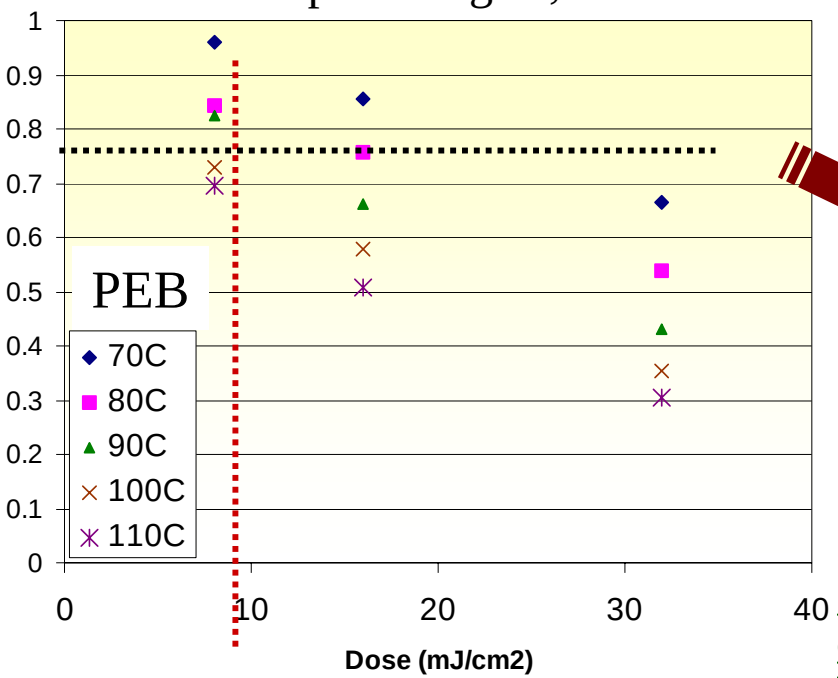
Felix, N. M, Tsuchiya, K., and C. K. Ober, *Adv. Mater.*, 18(4), 2006, p 442-446.

Solubility Switching



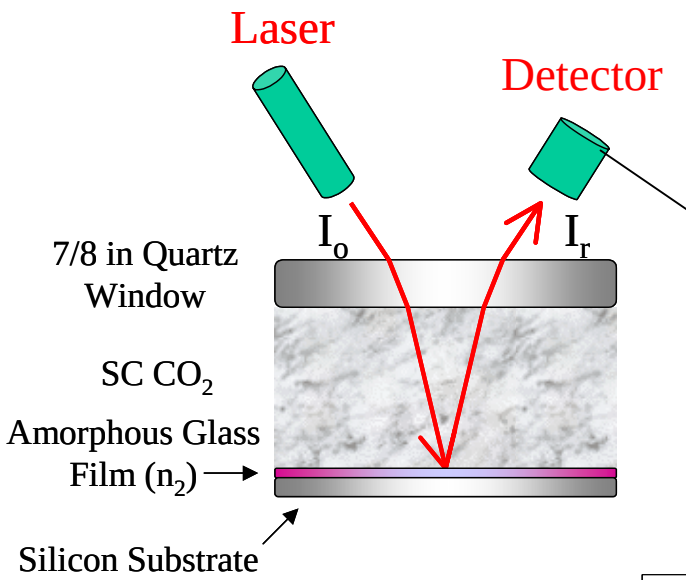


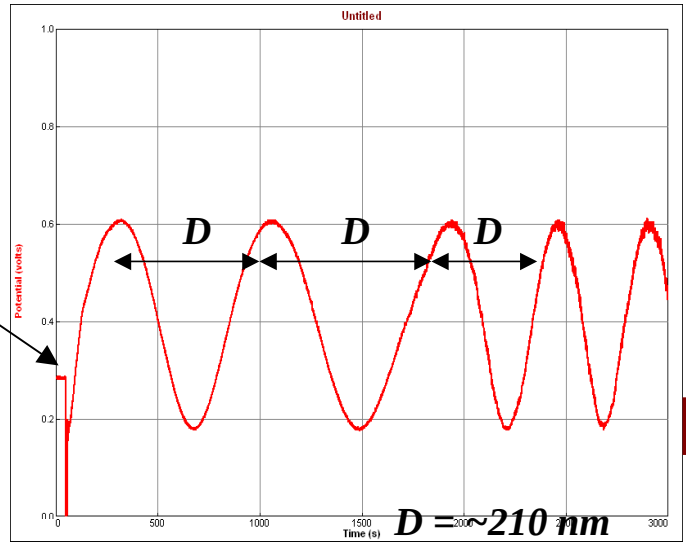
FTIR peak heights, C=O



From FTIR data, solubility switch happens below <80% tBOC protection

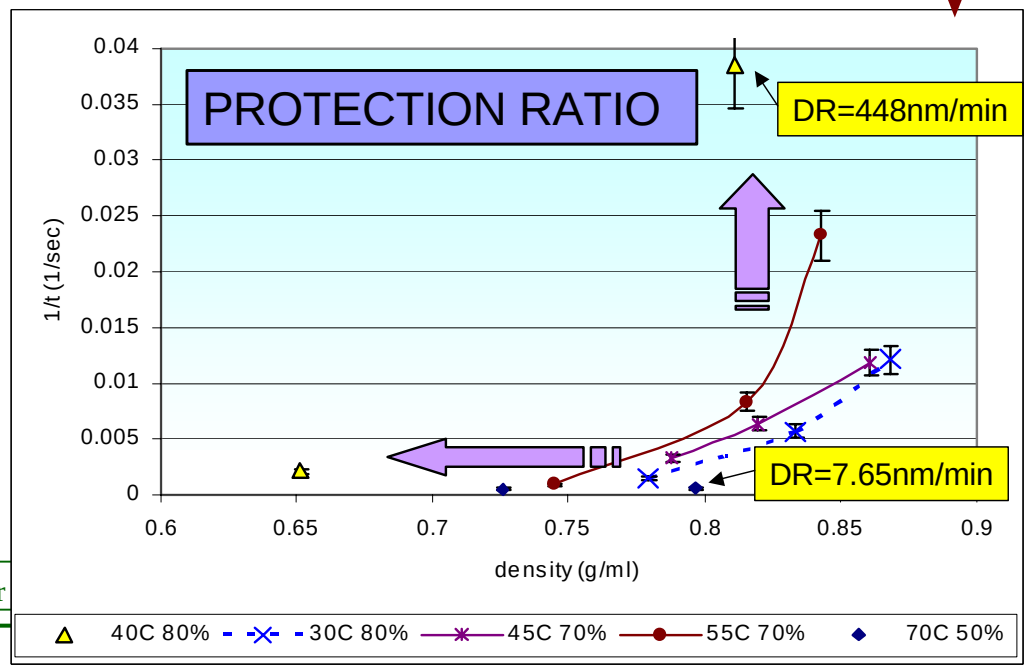
Dissolution Rate Measurments





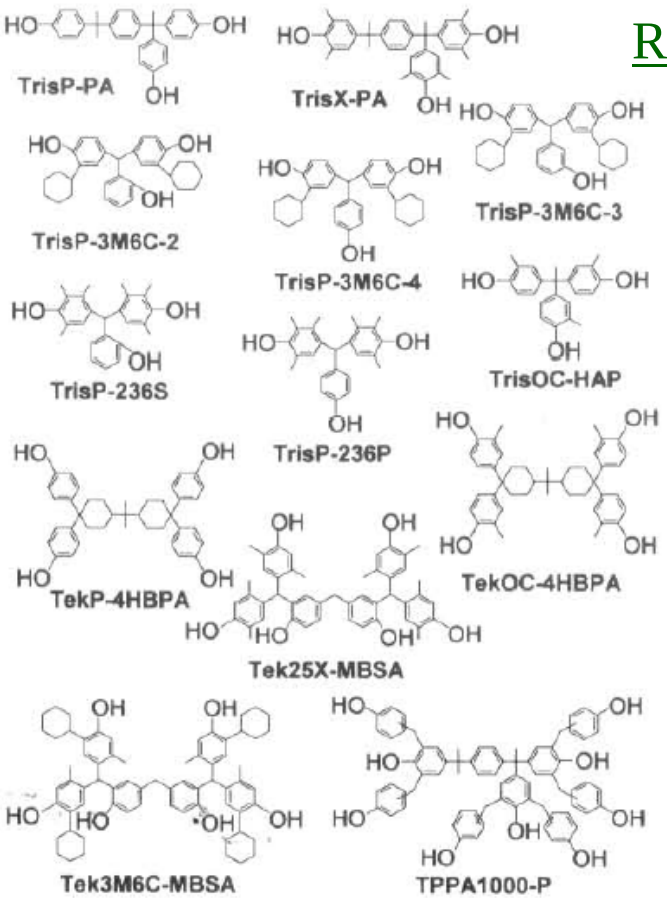
DR >400nm/min
above 80% protection

DR <10nm/min
below 80% protection

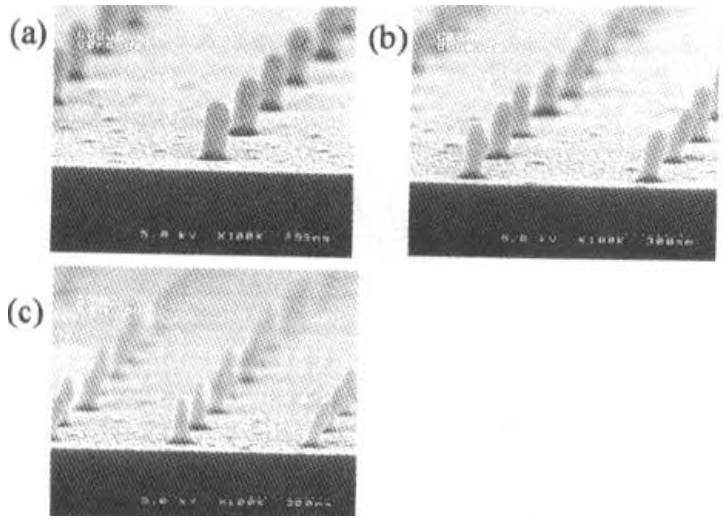


Molecular Glass Resist Solubility

- Wide range of resist cores can be used
- Balance between size and polar functionality



Recent example

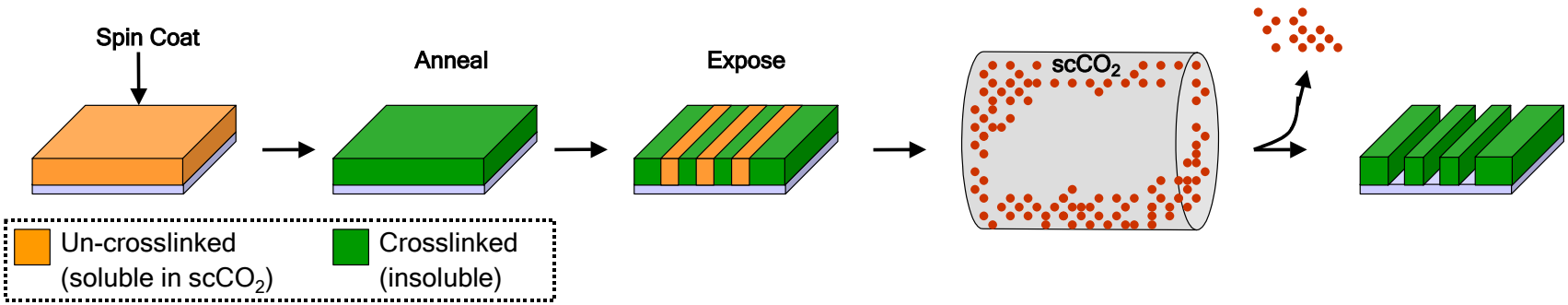


H. Shiraishi, J. Yamamoto, T. Sakamizu, *J. Photopolym. Sci. Technol.* **19**(3) (2006), 367-372.

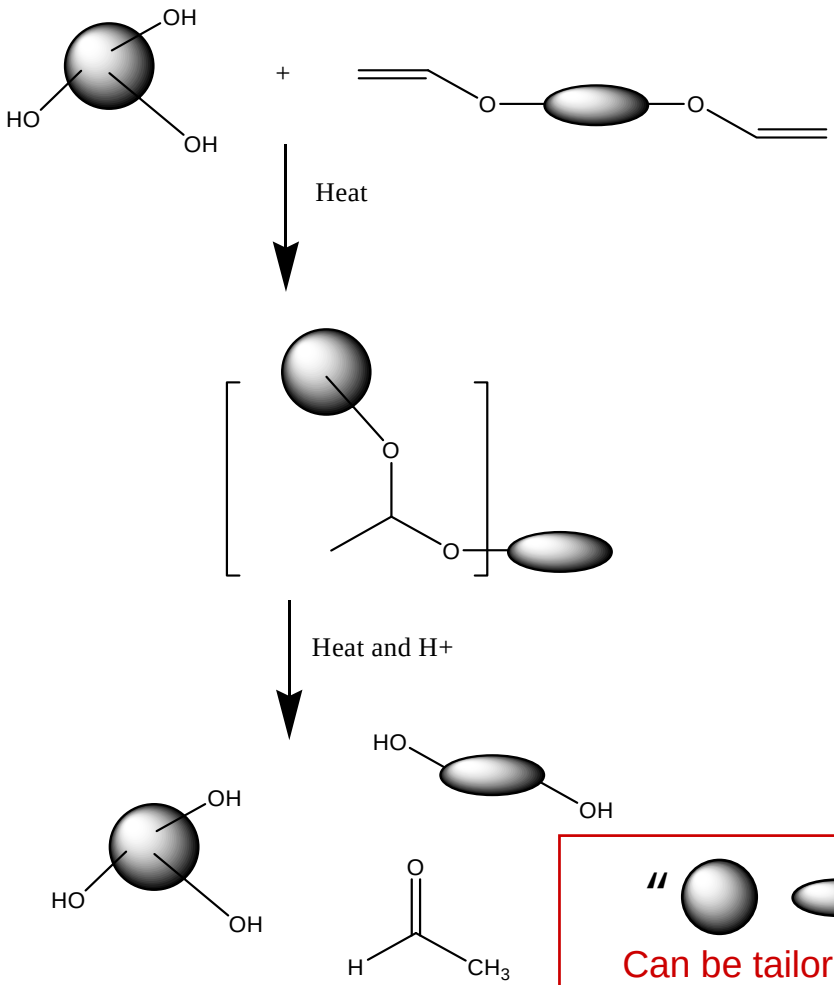
De-crosslinking Resists for Positive Tone

- PMMA is classic example
  - High resolution e-beam, EUV resist with low LER
  - Problem: low sensitivity

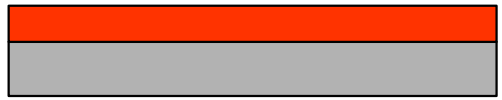
- Acid catalyzed de-crosslinking
  - Improved sensitivity
  - Use acetal bonds to crosslink otherwise $scCO_2$ soluble species



Positive Tone Molecular Glass Resists for $scCO_2$ Development



Film with hydroxy containing molecule; crosslinker; PAG

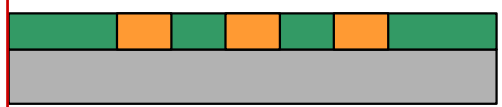


125°C

Film with **Crosslinked network**; PAG

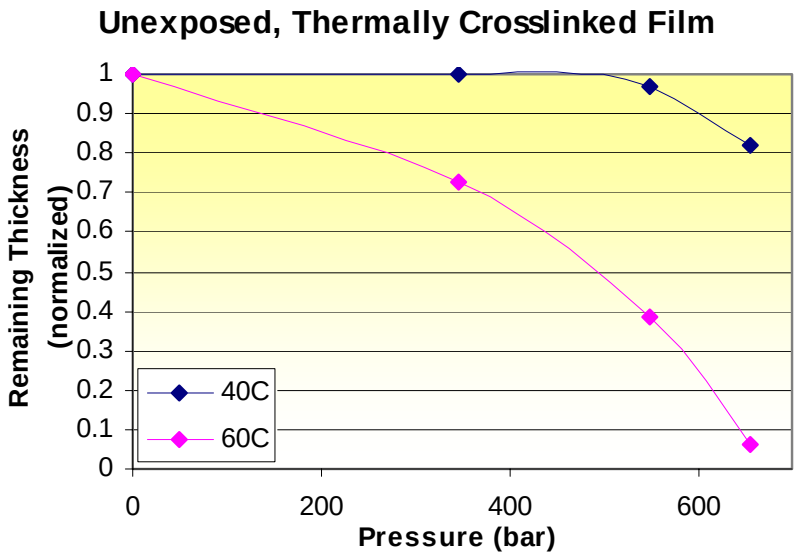
Expose, PEB

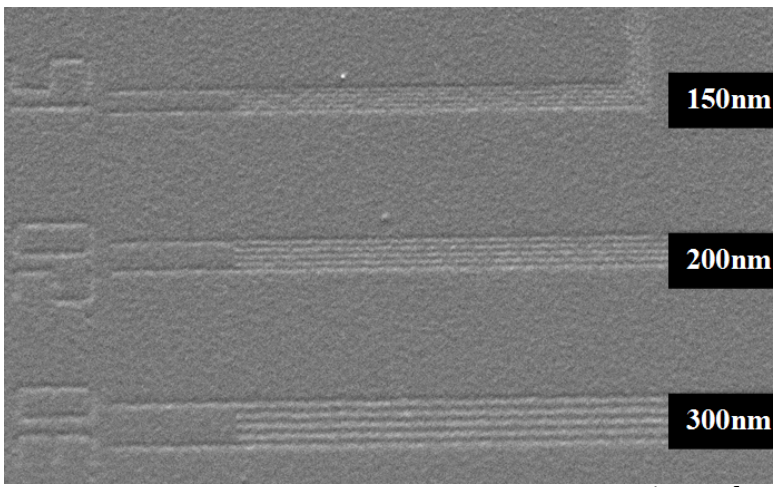
Film with **De-Crosslinked molecule**; crosslinked regions

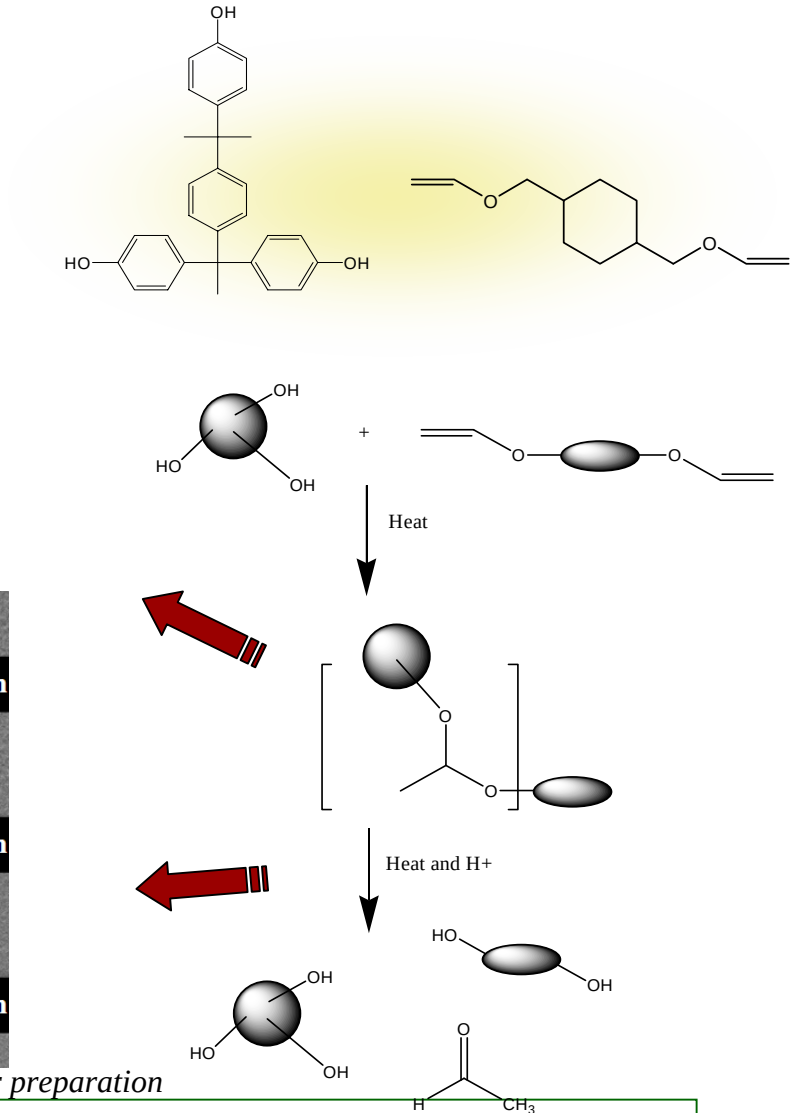


" " Can be tailored for exposure wavelength

Positive Tone Molecular Glass Resists for $scCO_2$ Development







Manuscript under preparation

Conclusions

- Many inherent benefits to using supercritical fluid processes
- Potential benefits can be realized with breakthrough in materials
  - Fluorinated resists
  - Cosolvents
  - Fluorinated or solubilizing additives
  - Molecular glass resists
- Sub-65 nm features with high aspect ratios can be achieved

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