$scCO_2$ Processing Methods for ESH Friendly Lithography

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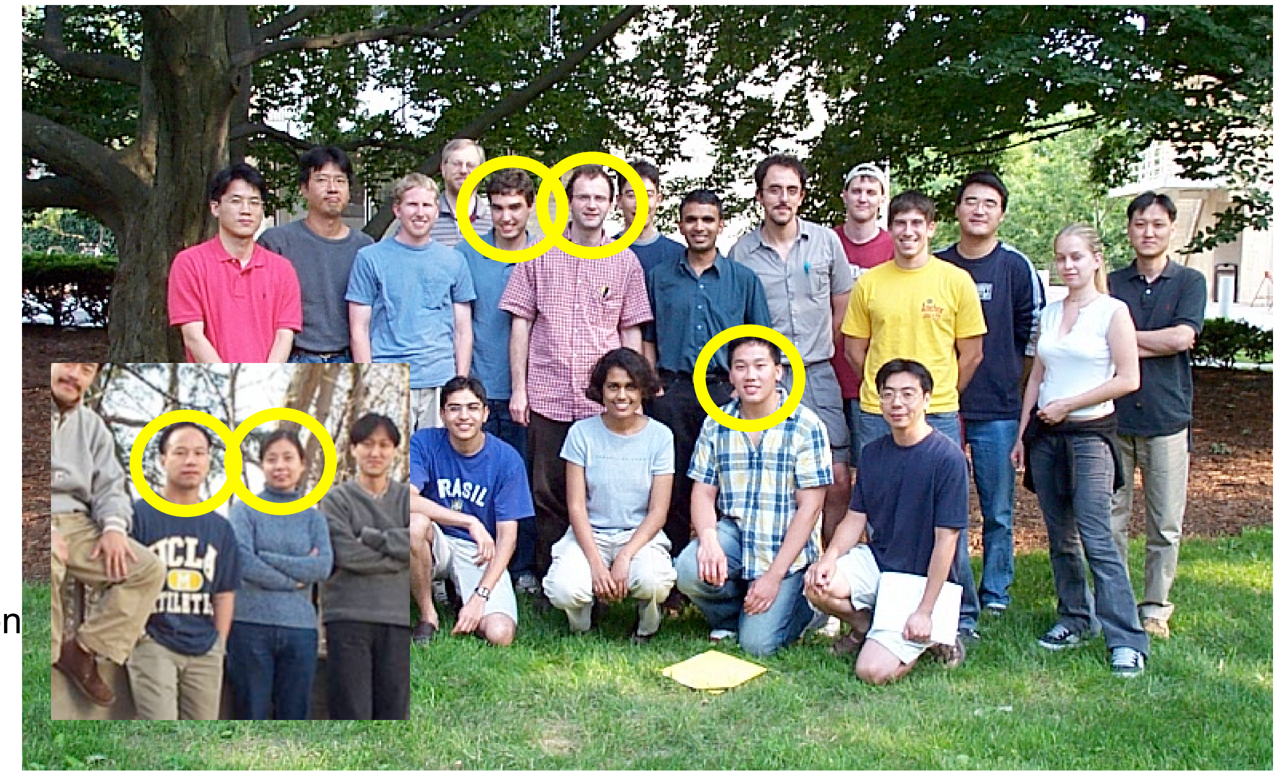
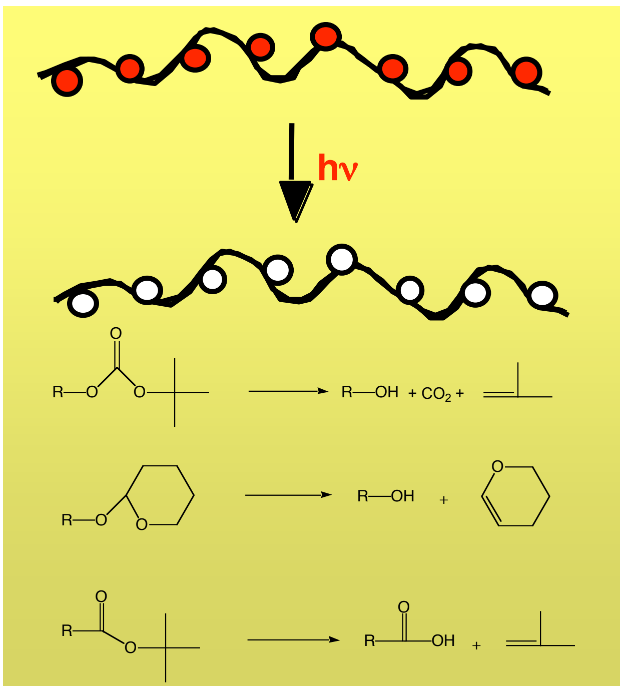
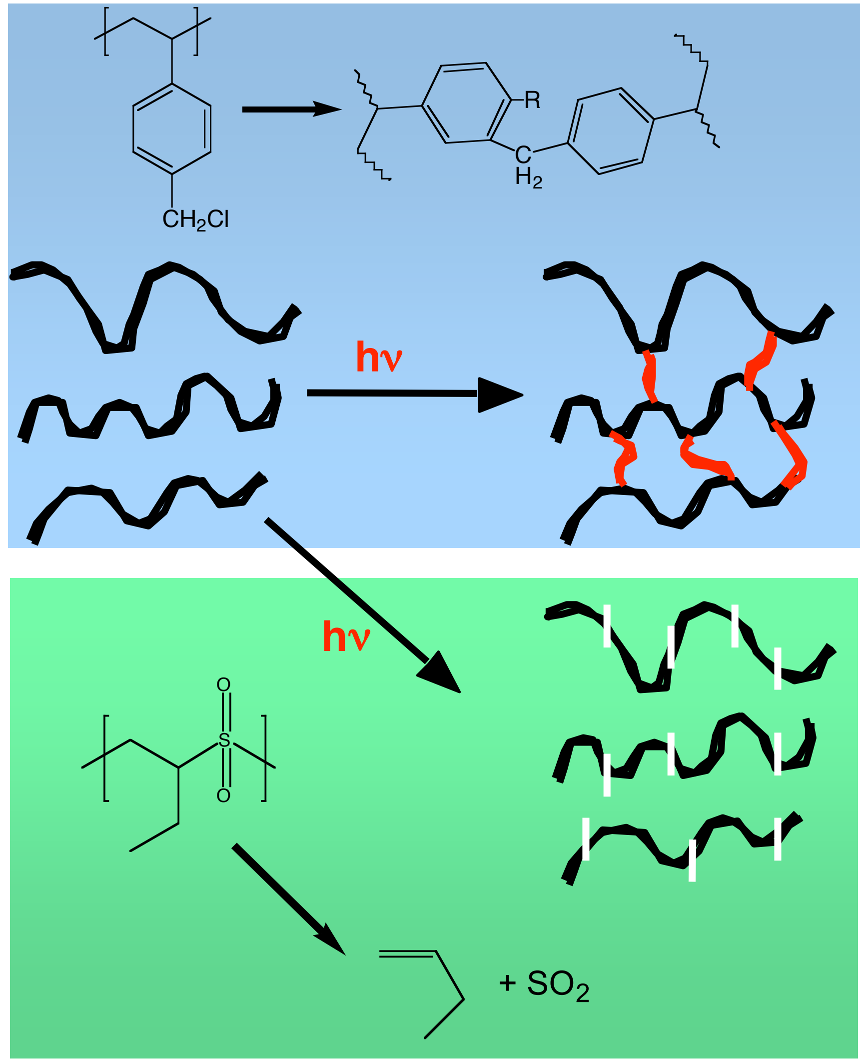


Making the Pattern

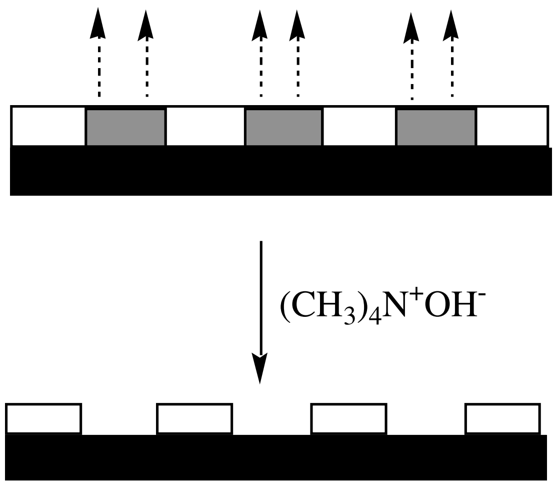
- Crosslinking
- Chain scission
- Polarity change

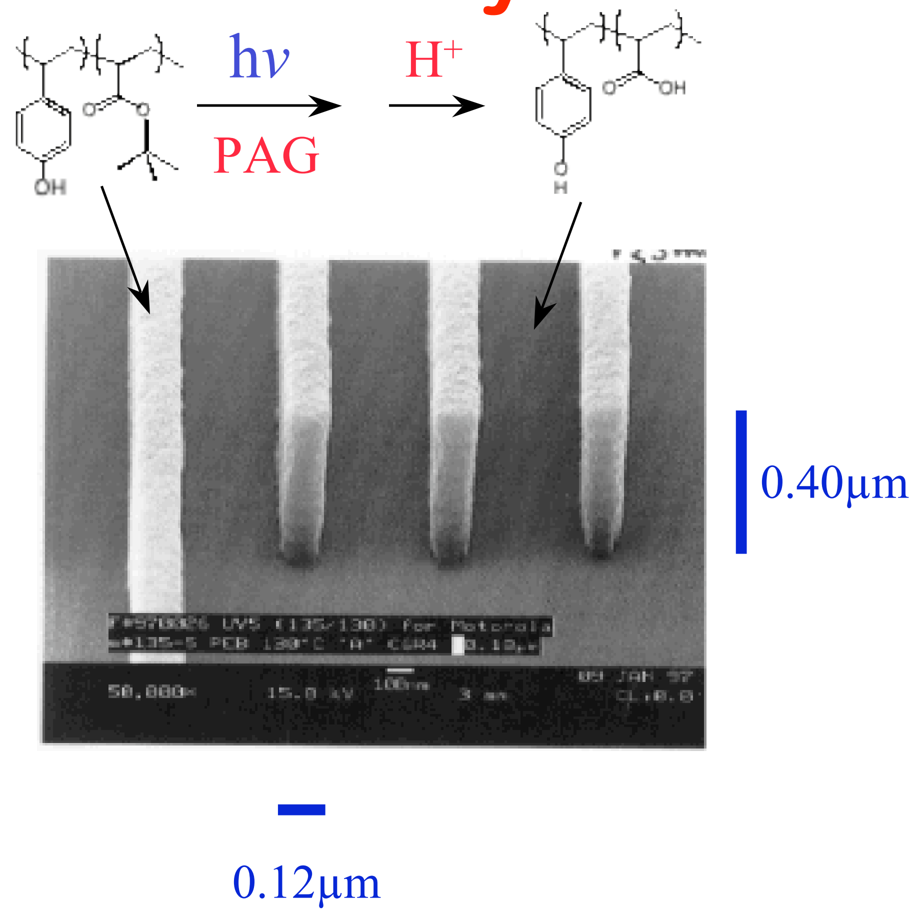




Positive Chemically Amplified Photoresist Chemistry

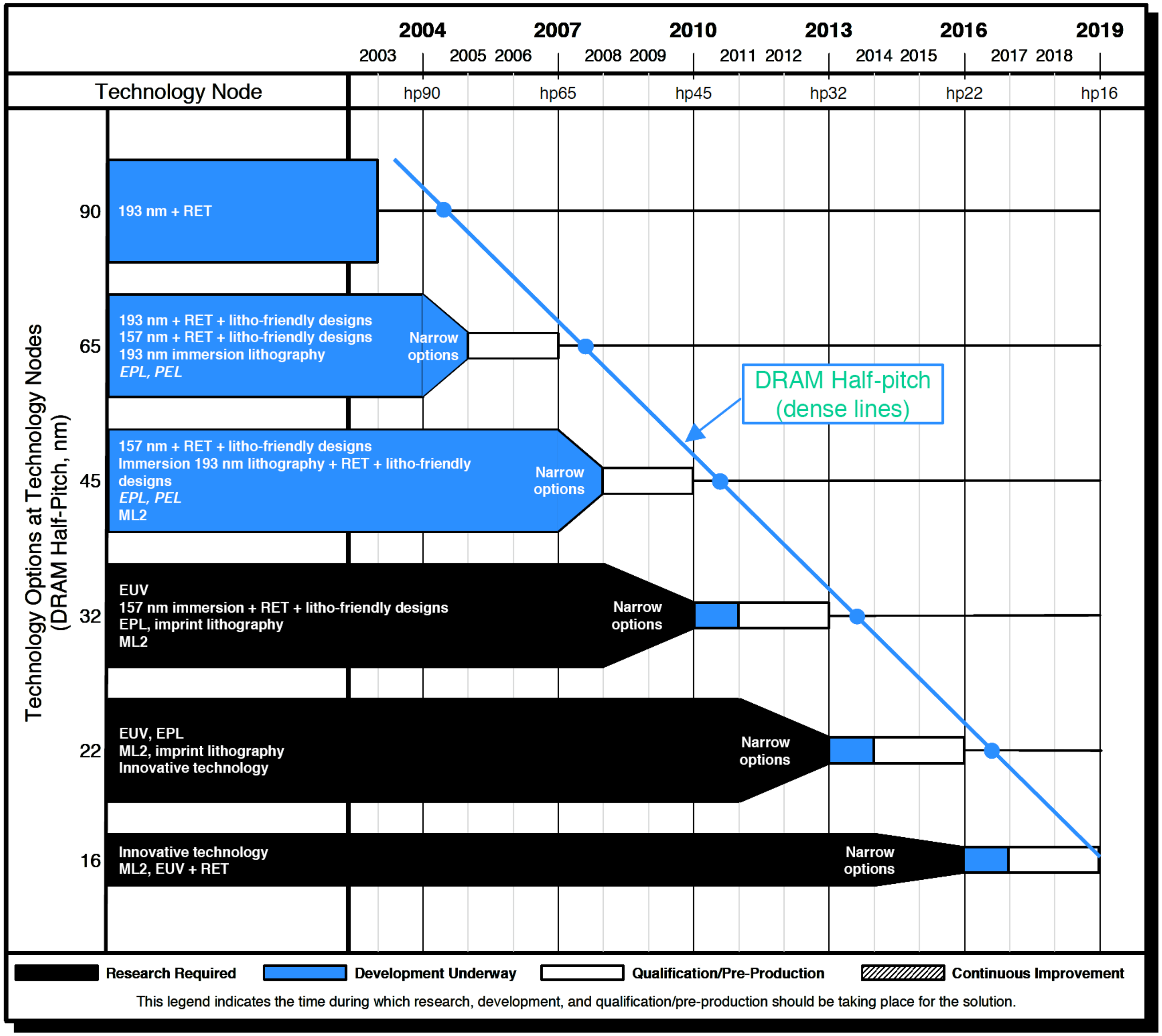
Aqueous Base Dissolution





*Courtesy George Barclay (Shipley)

International Technology Roadmap for Semiconductors



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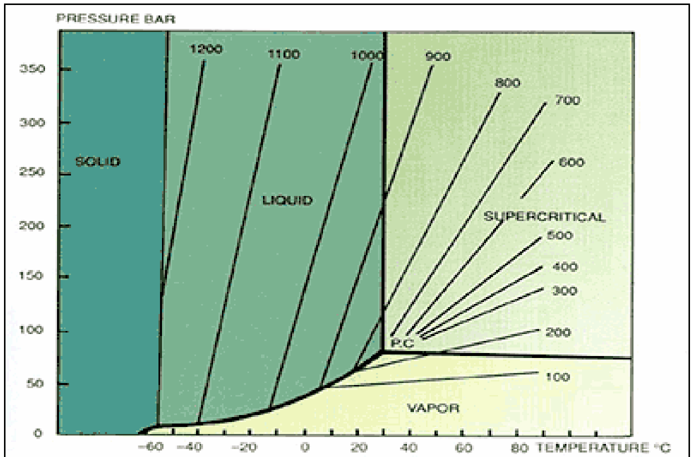
Performance Issues for NGL Lithography

- Possible increased role of fluoropolymers
  - Transparency at 193 nm and 157 nm
  - Effect of aqueous developers on pattern collapse
  - Pattern profiles demand low viscosity, low surface energy developer
- Non-polar resists for EUV lithography
- High resolution development
- Environmental issues
  - Release of TMAH
  - Water reuse
  - PAG use

Supercritical CO_2 as a Developer



Phase diagram of CO_2. Constant density lines (g/l)

	GAS	Supercritical Fluid		Liquid
	P=0.1 MPa T= 15 °C	Tc, Pc	Tc, 4Pc	P=0.1 MPa T= 15 °C
Density ρ (g/cm^2)	0.0006 – 0.002	0.2-0.5	0.4-0.9	0.6-1.6
Viscosity μPa-s	10-30	10-30	30-90	200-3000
Diffusion cm^2/s	0.1-0.4	0.7×10^{-3}	0.2×10^{-3}	0.2×10^{-5} 2.0×10^{-5}

High and variable density

- Dissolution selectivity can be manipulated
- Tunable solvating power

Higher diffusion coefficient than liquid

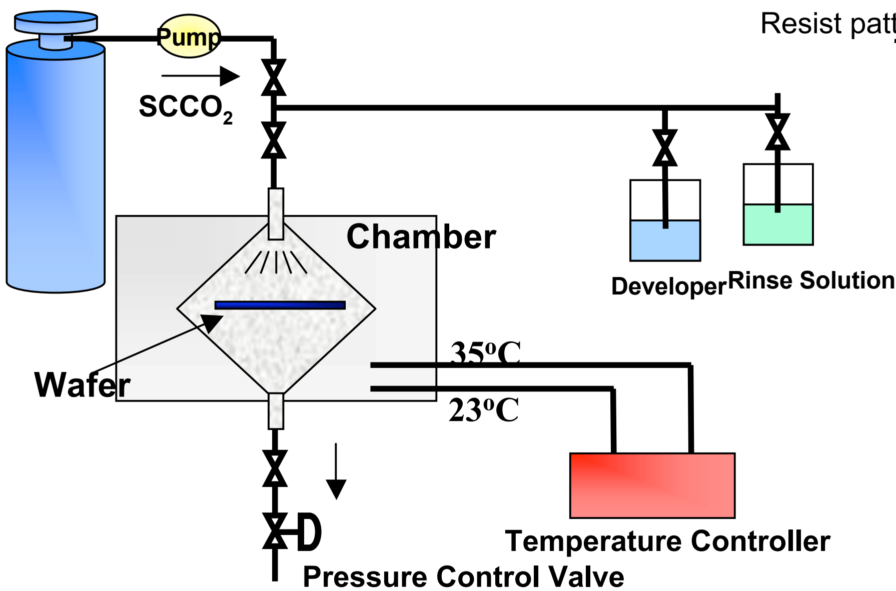
- Accurate and rapid development

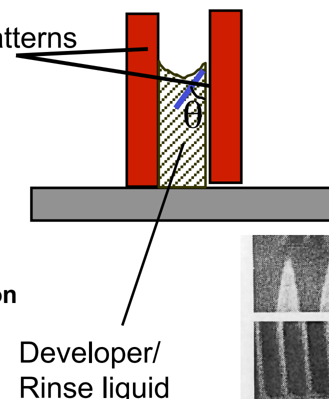
Low viscosity: comparable to gas

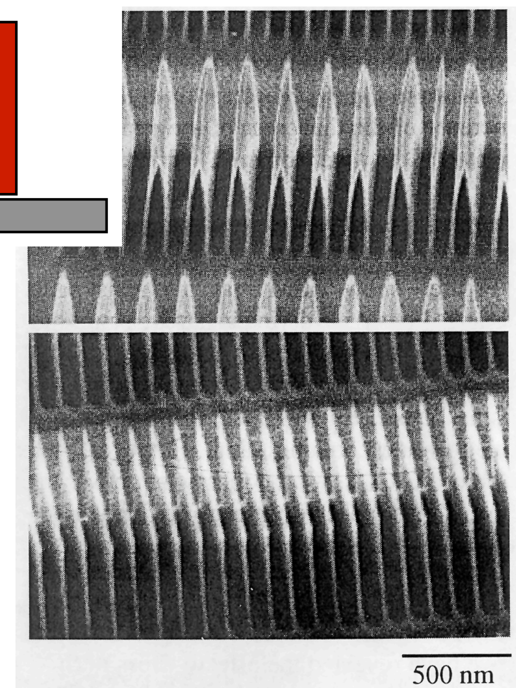
- No surface tension
- Pattern collapse of features avoidable

NTT Process - Avoiding Pattern Collapse

- Use CO_2 to replace water or polar solvents
- Reduce/ eliminate capillary forces that lead to pattern collapse
- Combinations of N_2 and CO_2 used in successful processing
- Remarkably fine features possible



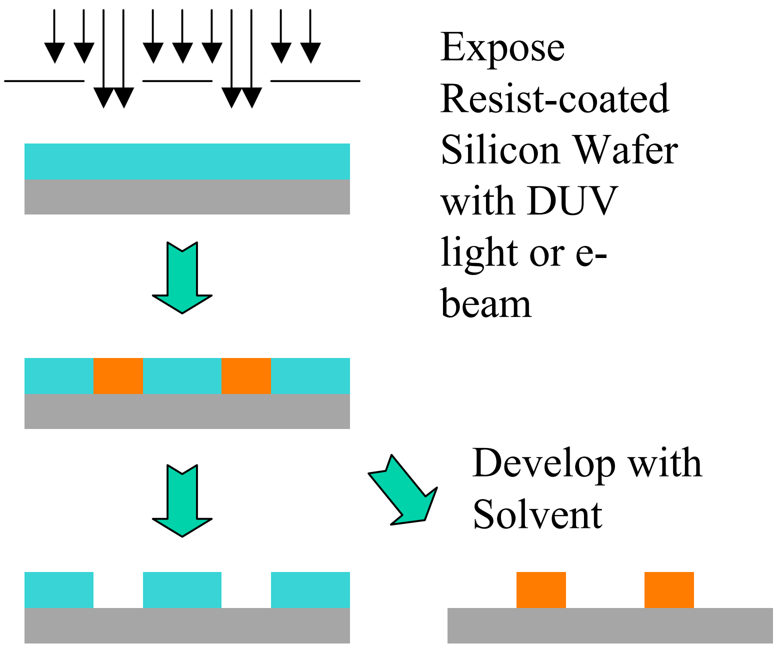




H. Namatsu et al., NTT Basic Research Laboratories, Kanagawa, Japan

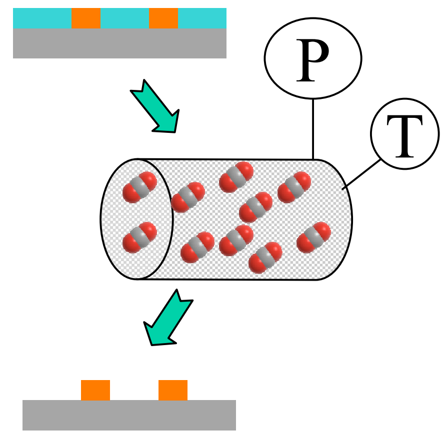
Photoresist Development

Traditional Development



Supercritical CO_2 Development

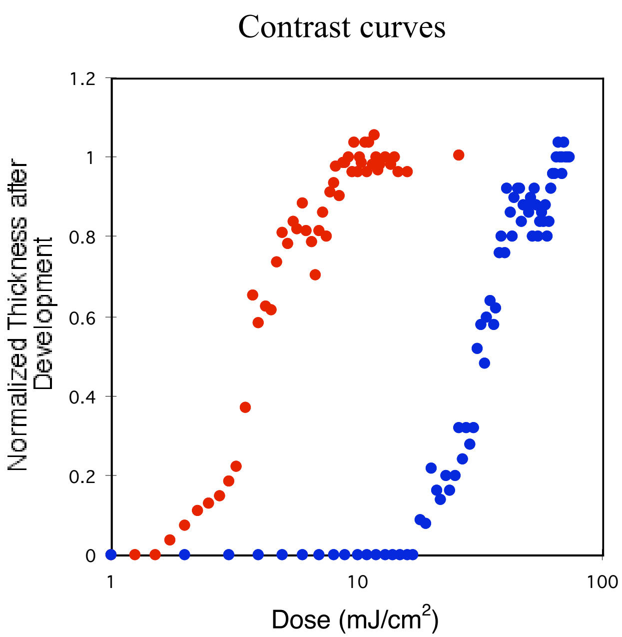
Use Supercritical CO_2 as a development solvent!

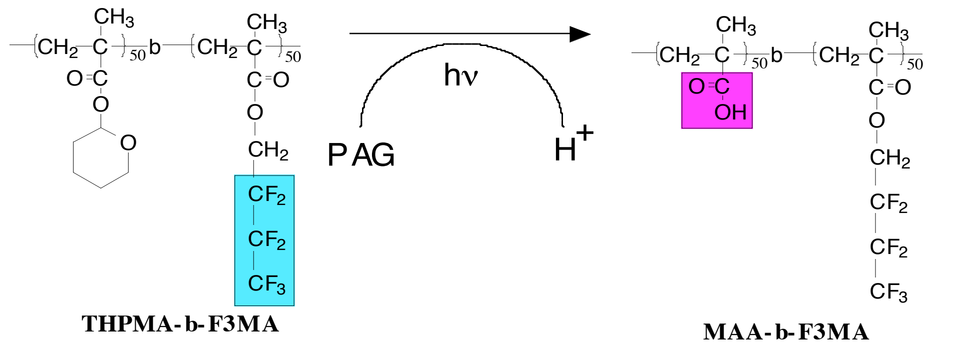


Questions about $scCO_2$ in Lithography

- Where can it be used?
- Process time - how does pressurization impact cycle time?
- Costs - are they comparable to solvent/water process costs?
- Recycling vs disposal?
- Is it really an ESH improvement?
  - Cosolvents
- Positive tone vs. negative tone?
- New “disruptive” ideas?

Patterning Fluoropolymers in SCF CO_2

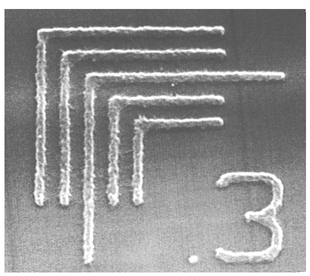




soluble in supercritical CO_2 insoluble in supercritical CO_2

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

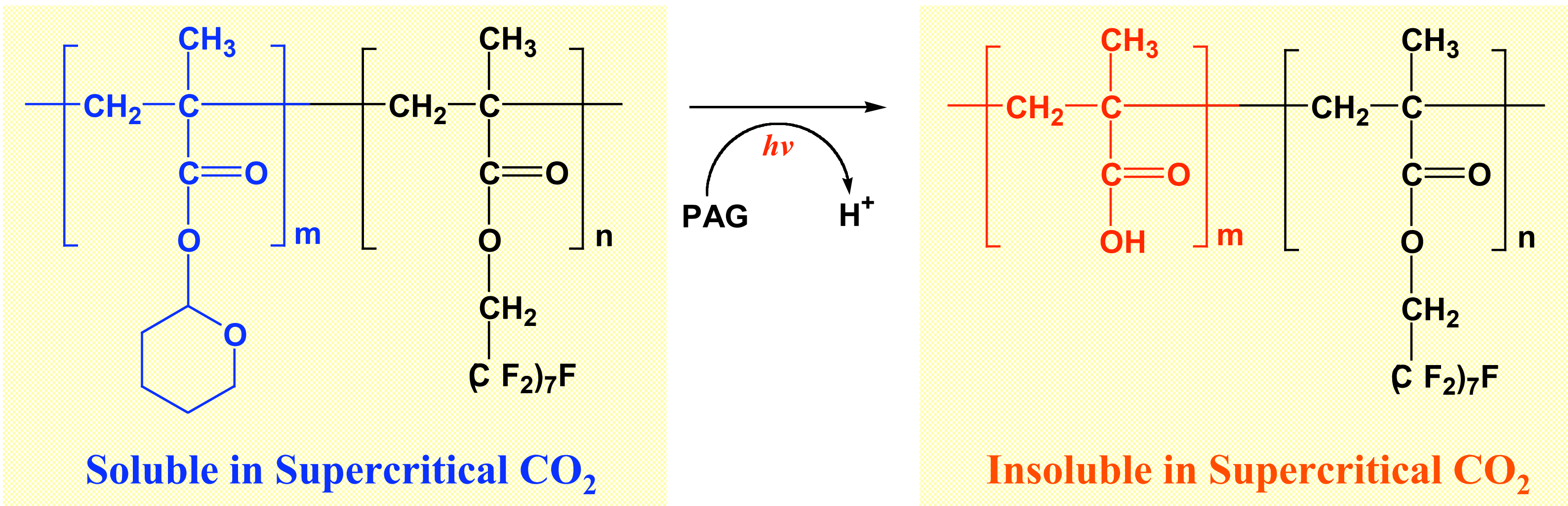
Thickness ~ 2700 Å
Halo alkyl Iodonium PAG ~ 1 wt %
Post-apply bake - 120C/60s
Post-Exposure bake - 120C/60s
Develop in SCF CO_2 at 45C, 4500 psi



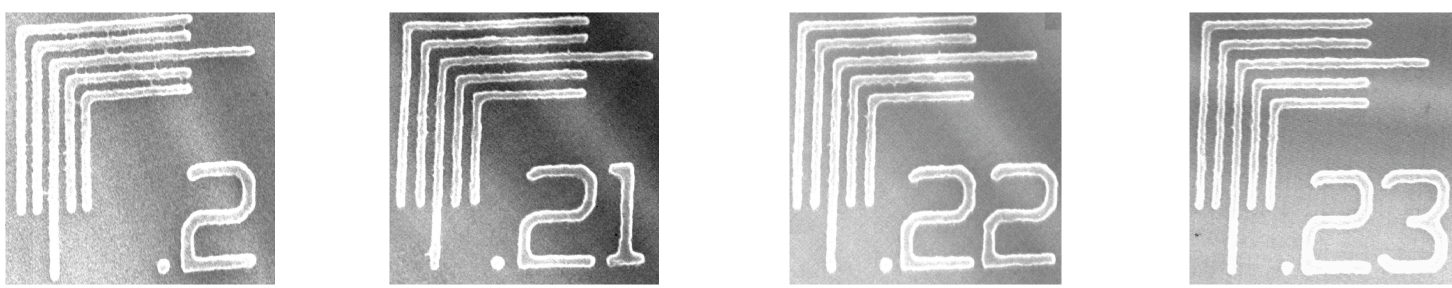
N. Sundararajan, S. Yang, J. Wang, K. Ogino, S. Valiyaveettil, C. K. Ober, S. K. Obendorf and R. D. Allen, "Supercritical CO_2 Processing for Sub-micron Imaging of Fluoropolymers", *Chem. Mater.*, 2000, **12**, 41-48.

Supercritical CO_2 Developable Photoresist

- **Imaging Mechanism: negative-tone image**



- **Resist preparation and SC CO_2 development at Cornell**
- **193 nm Exposure at IBM Almaden**



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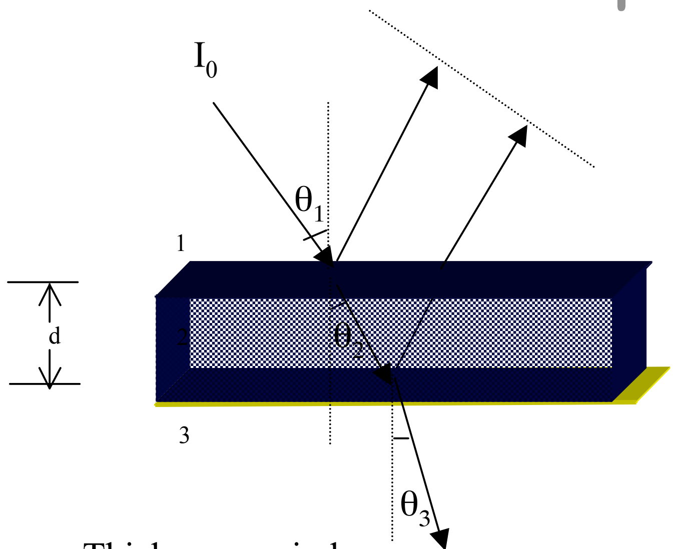
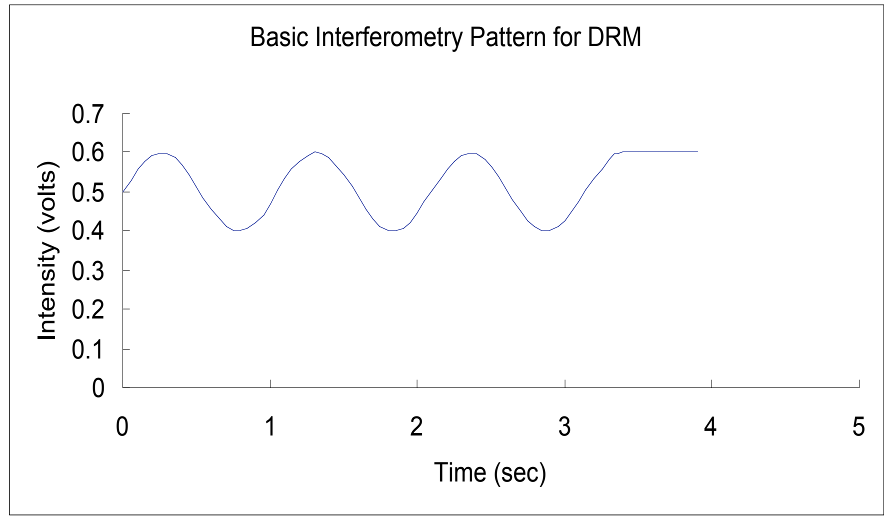
Measurement of Film Dissolution

Principles of Interferometry



Thickness period

$$d_p = \frac{\lambda}{2\left[n_2^2 - n_1^2 \sin^2\theta_1\right]^{1/2}}$$



Assumptions:

•Non-swelling

•One optically distinct moving boundary

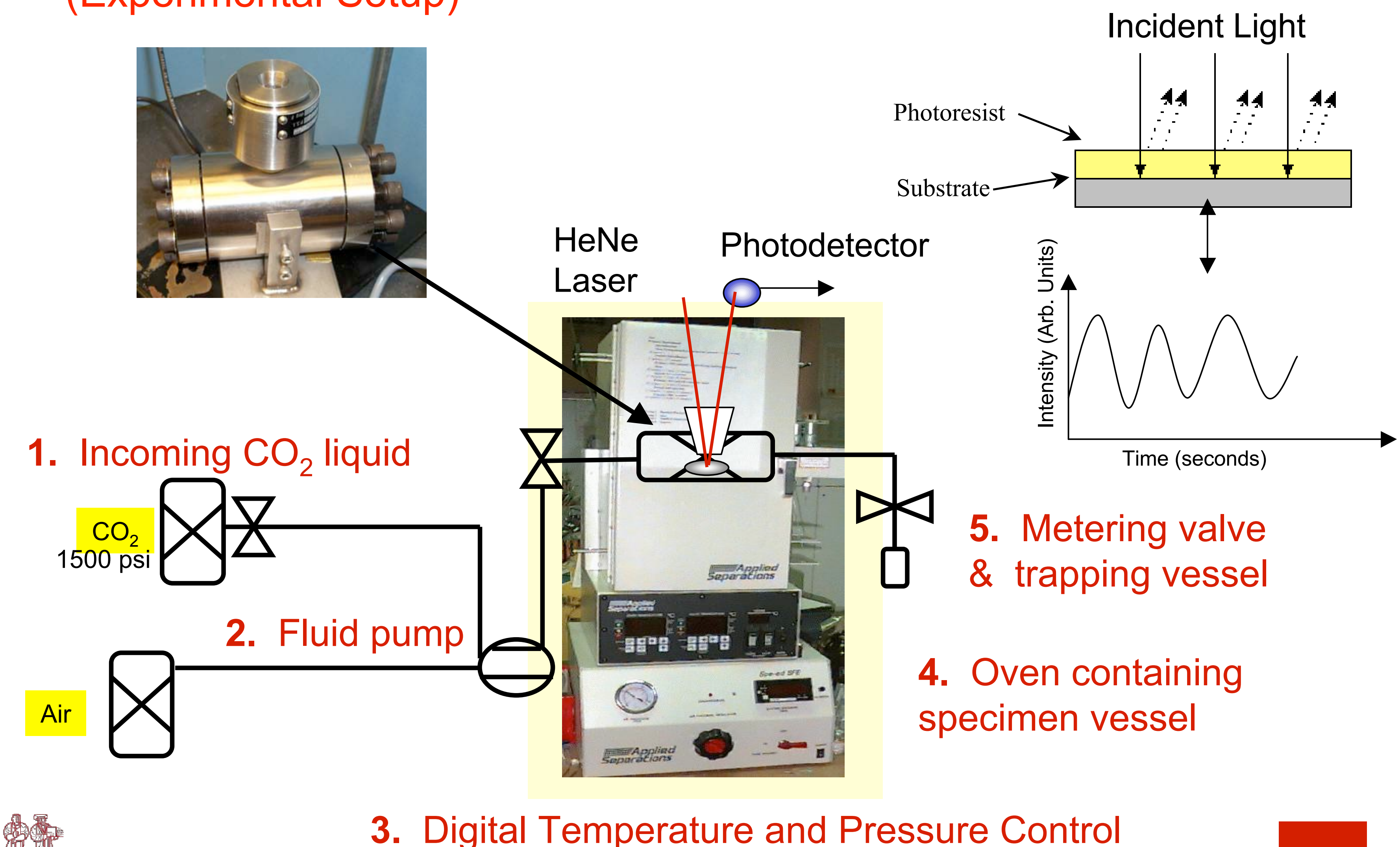
•Film dissolves at constant rate

$scCO_2$ development

- Swelling is expected
- Fluid equilibration, swelling, and dissolution occur simultaneously
- Density and refractive index of solvent vary with P, T
- 7/8” thick quartz glass window

Dissolution Studies with $SCFCO_2$

(Experimental Setup)



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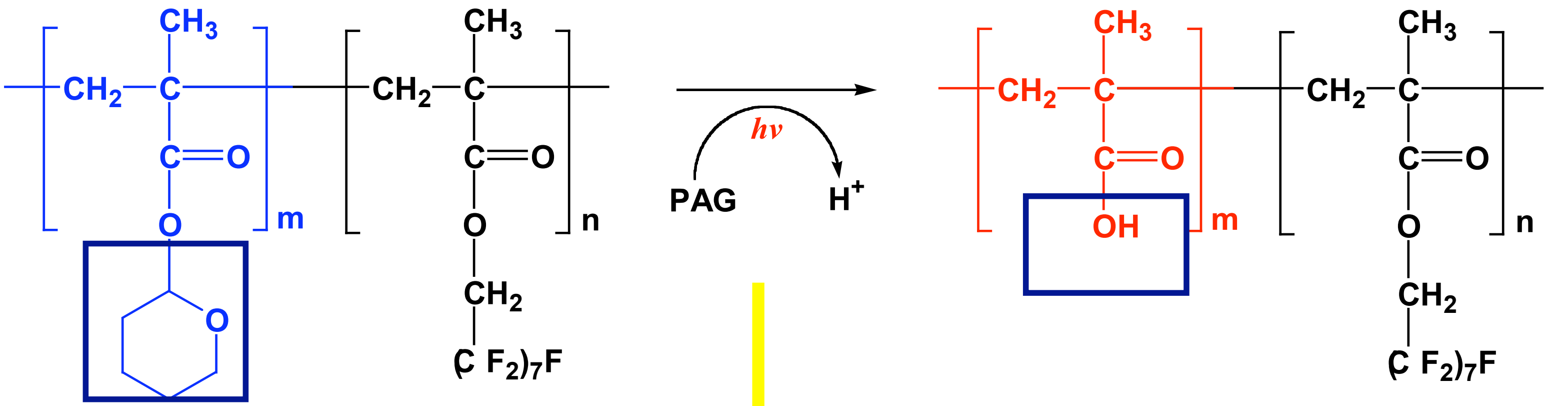
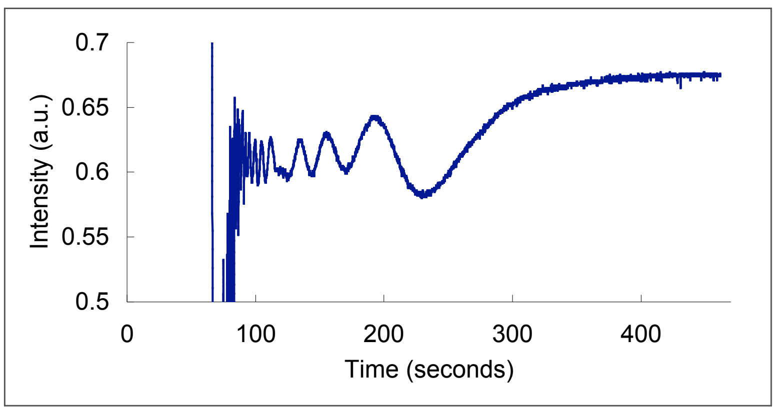
Pham, Rao, Ober, *J. Supercritical Fluids,* (2004) in press.

Random Copolymer Dissolution Selectivity

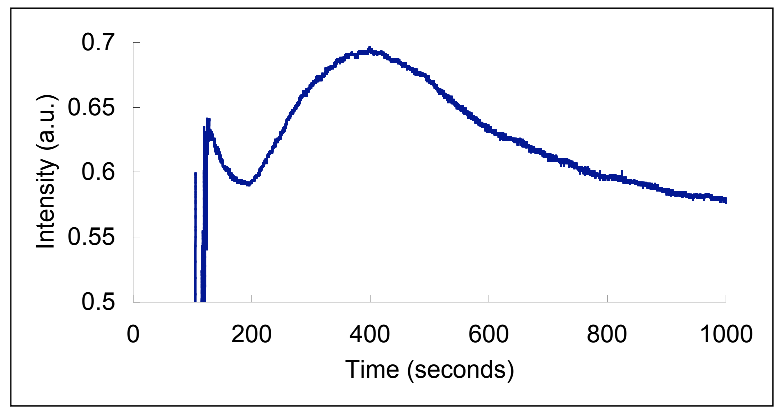


High solubility in CO_2



- Time varying rates
- Complete development of film

Low solubility in $scCO_2$



- Very slow rate of dissolution
- Incomplete development

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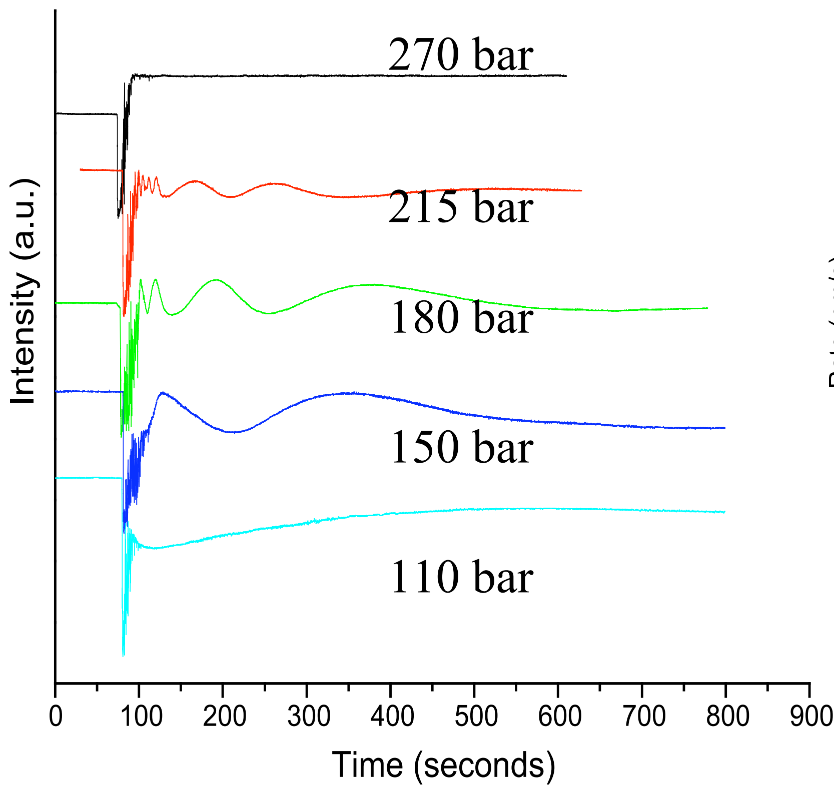
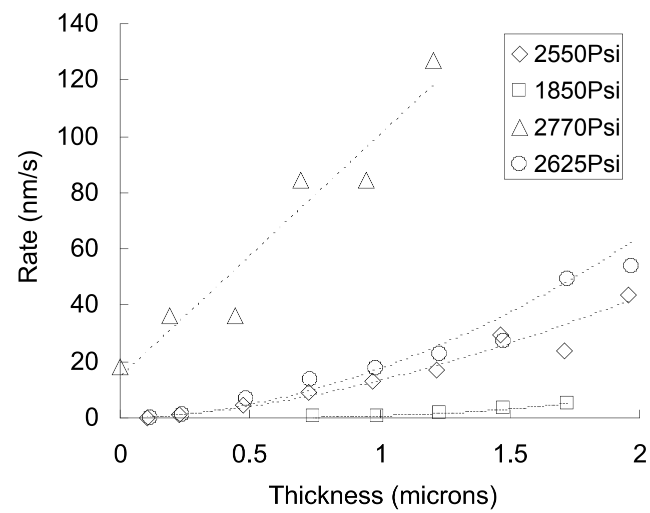
Dissolution Rate, Completeness

Dissolution Rate vs. Pressure



Dissolution Rate vs. Thickness



Victor Q. Pham, Nagesh Rao, Christopher K. Ober, "Swelling and dissolution rate measurements of polymer thin films in supercritical carbon dioxide", *J. Supercritical Fluids*, in press.

- DRM can also be used for cloud-point detection in solubility studies

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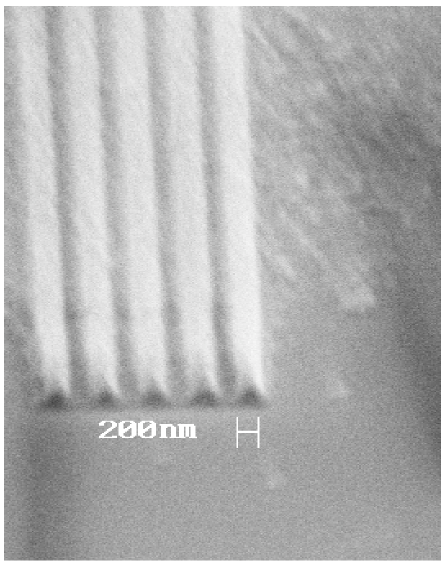
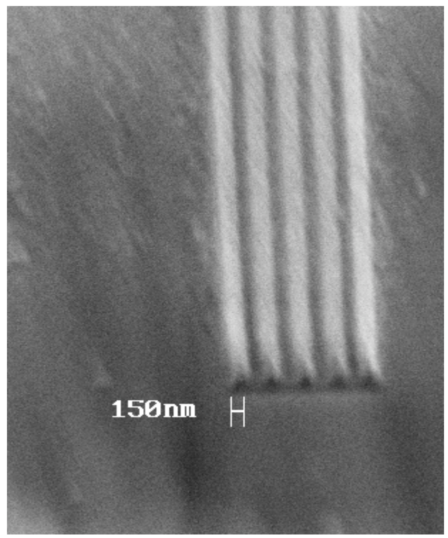
Developing/ Drying Combined

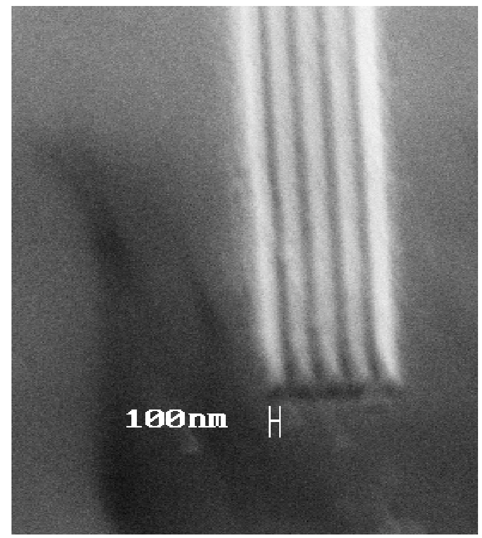
- Use CO_2 to replace water or polar solvents
- Reduce/ eliminate capillary forces that lead to pattern collapse
- Projected improvement for developing fine features



.2 μm lines and spaces



.15 μm lines and spaces



.1 μm lines and spaces

SEM images of THPMA-F7MA polymer patterned with E-Beam.

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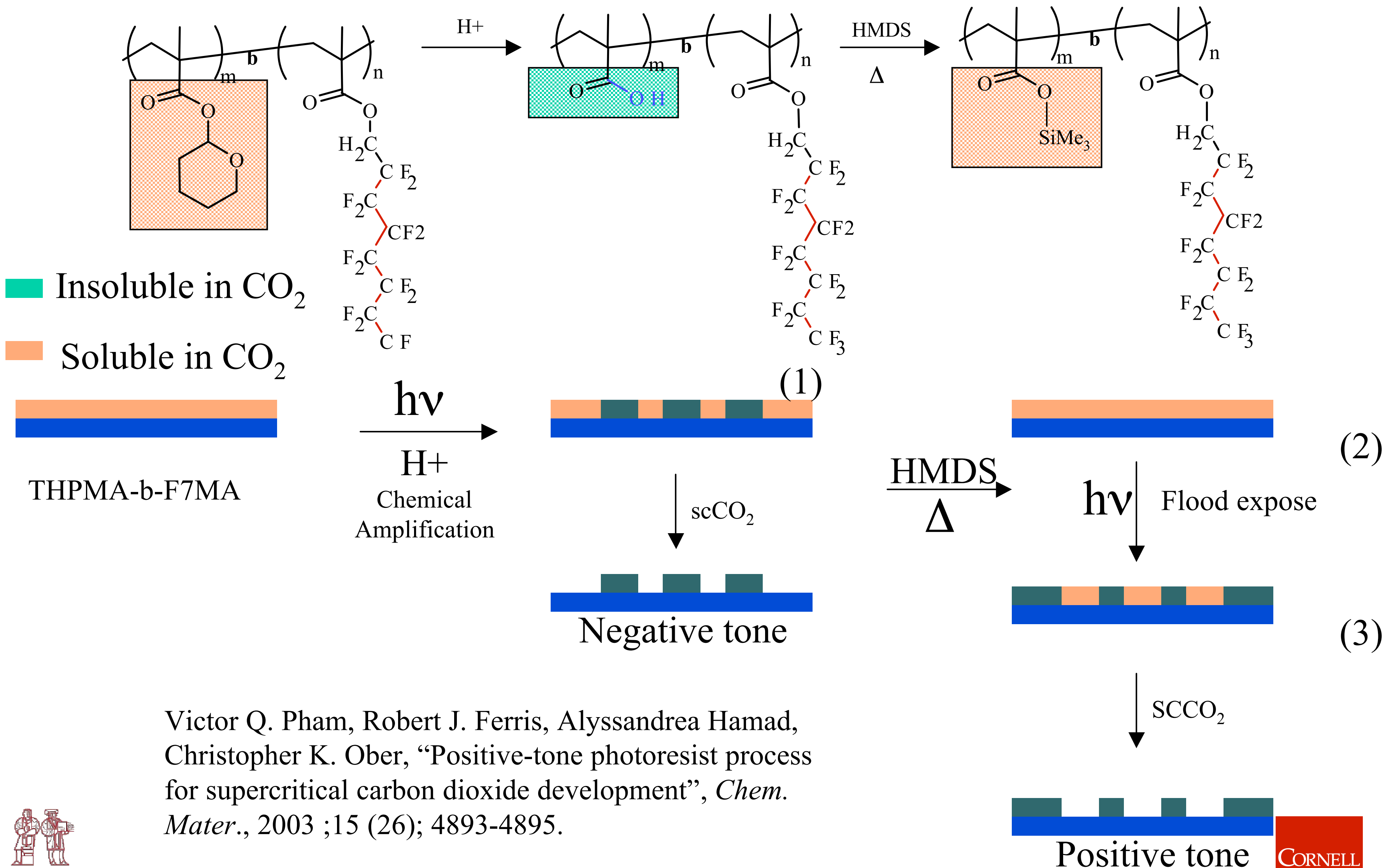
DESIRE for Positive-tone CO_2 Development



Victor Q. Pham, Robert J. Ferris, Alyssandrea Hamad, Christopher K. Ober, "Positive-tone photoresist process for supercritical carbon dioxide development", *Chem. Mater.*, 2003 ;15 (26); 4893-4895.

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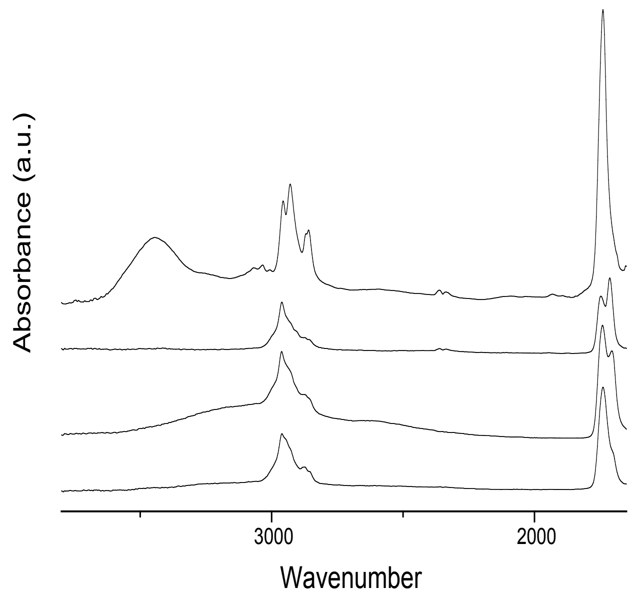
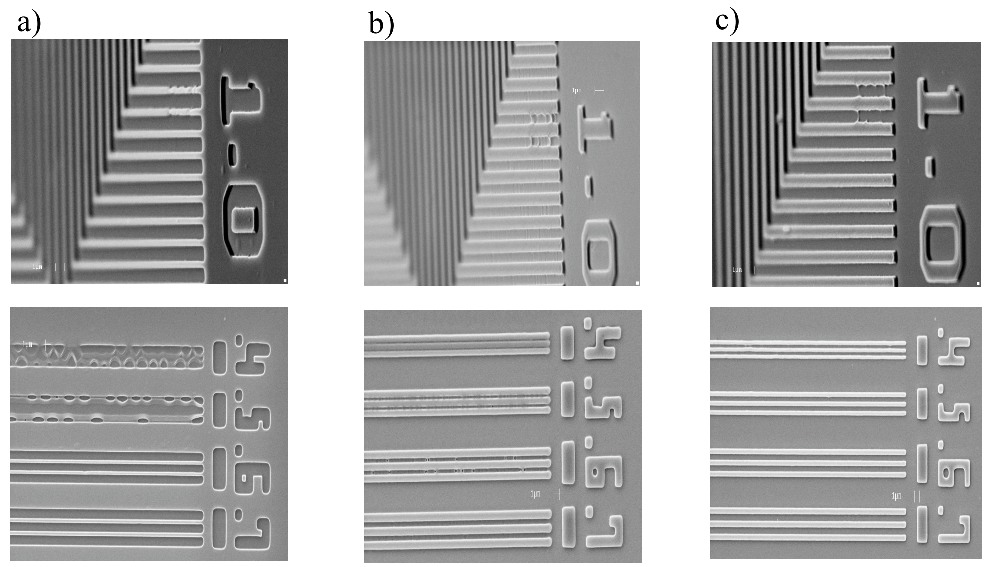
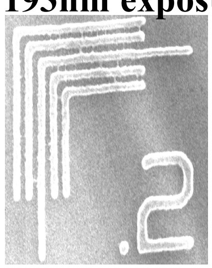
Silylated Positive-tone $scCO_2$ Developed Resist



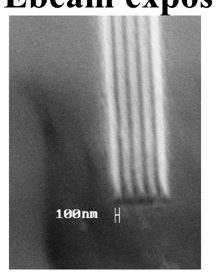


193nm exposure



Sundararajan, Ph.D.

Ebeam exposure



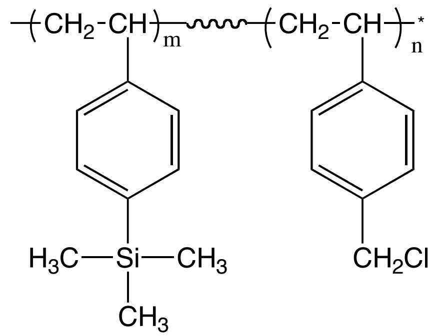
V. Pham

Negative-tone features ~100nm
Can we achieve positive-tone for block copolymers?

NGL EUV Resists with $scCO_2$

- Negative tone EUV resist
- Insoluble in pure supercritical CO_2
- Soluble in $scCO_2$ when cosolvents are added to supercritical fluid.

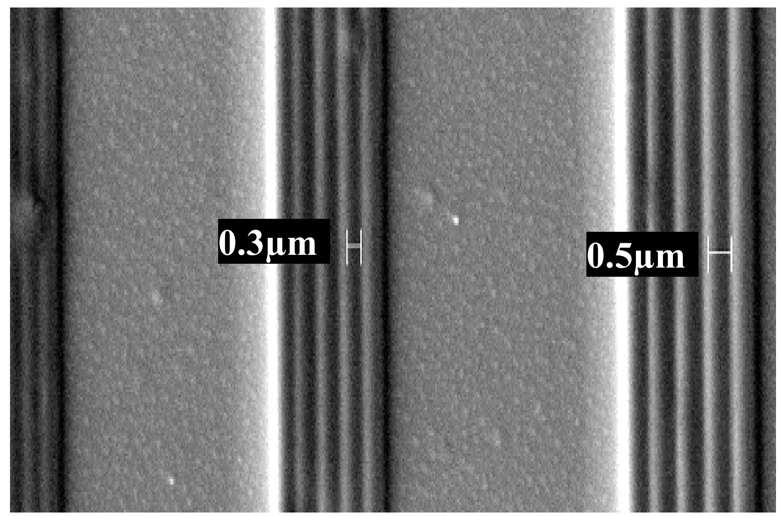
Poly(trimethylsilylstyrene-co-chloromethylstyrene)



m = 90, n = 10

P = 5000 psi, T = 45 ^oC, t = 10 mins

SCCO2 / EUV RESIST / ORGANIC SOLVENT		
Organic Solvent	**Amount Added**	**Effect**
Tetrahydrofuran (THF) (10 min)	**2 vol%**	**Film removed**
Tetrahydrofuran (THF) (5 min)	**2 vol%**	**Film removed**
Tetrahydrofuran (THF) (1 min)	**2 vol%**	**Film removed**
Isopropanol (IPA) (10 min)	**6 vol%**	**Film removed**
Isopropanol (IPA) (10 min)	2 vol%	Clouding of film
Ethanol (EtOH) (10 min)	2 vol%	No effect
Methanol (MeOH) (10 min)	2 vol%	No effect



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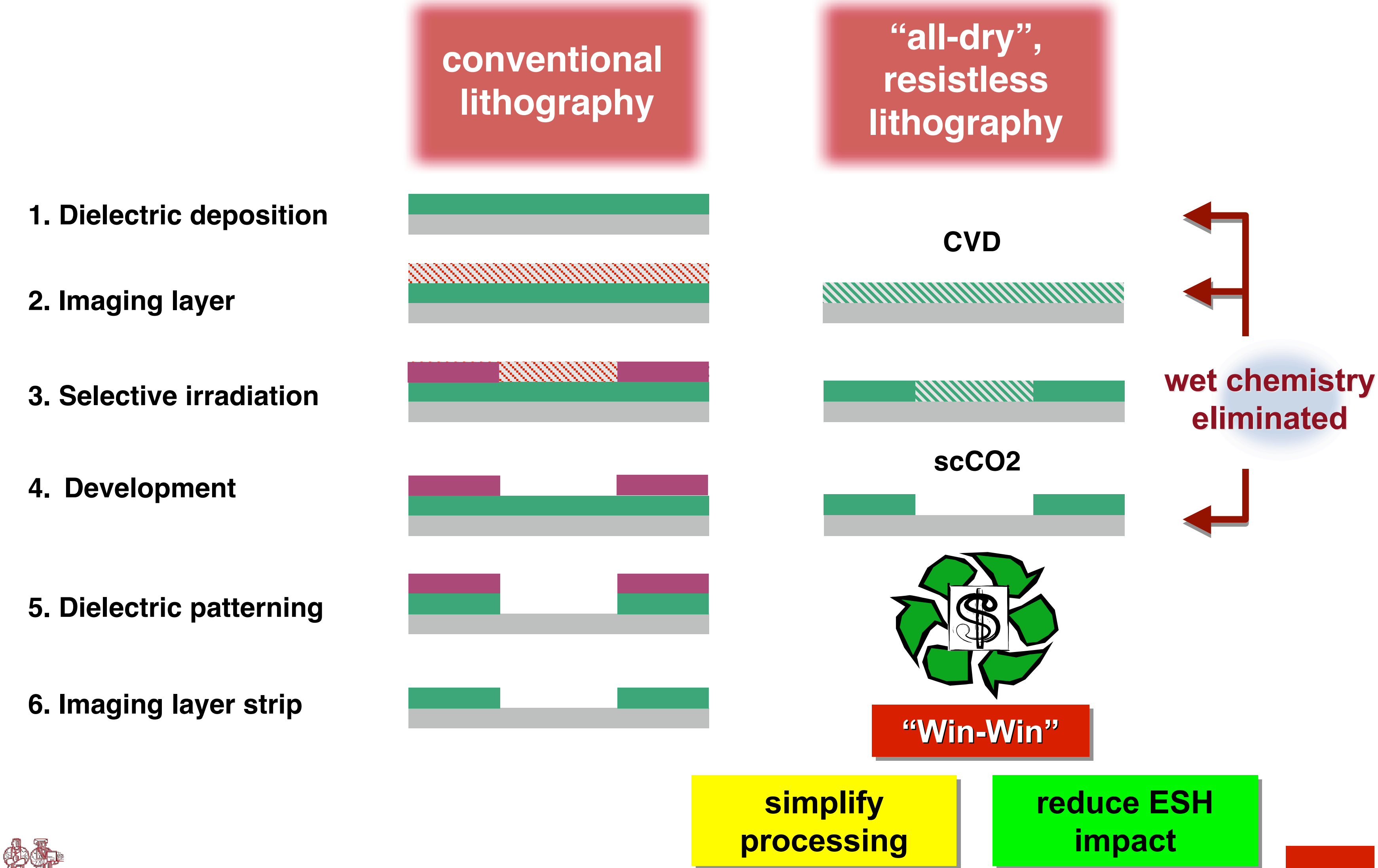
Goal: Simplified Lithographic Processing



Low- κ Strategy

- **Low- κ candidates**
  - **doped oxides.**
  - **fluorinated glasses.**
  - **porous films.**
  - **air gaps.**
- **Must be compatible with Damascene.**

	% porosity to reach κ ~ 2
SiO_2	55 – 65
hydrocarbon polymer	40 – 50
fluorocarbon polymer	0

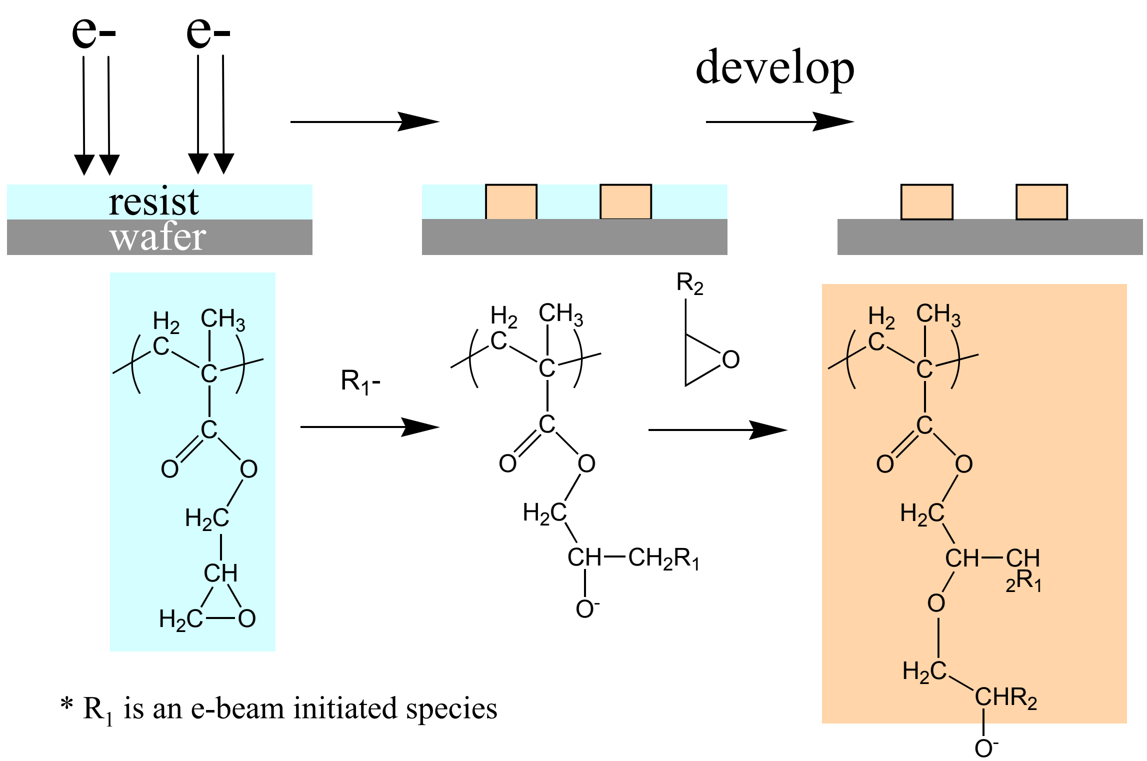
SiO_2:

hydrocarbon polymer:

fluorocarbon polymer:

FC Material	κ
Bulk PTFE $(CF_2CF_2)_n$	2.1
a-C:F (Endo, NEC)	2.1-2.5
a-C:F,H (Theil, HP)	2.2-3.3
FLAC (Mountsier, Novellus)	2.0-2.5
FDLC (Grill, IBM)	2.5-2.7
CF_x (Akahori, TEL)	2.5
SPEEDFILM (Rosenmayer, Gore)	1.7-2.0

E-beam Resist Developable in $scCO_2$



* R_1 is an e-beam initiated species

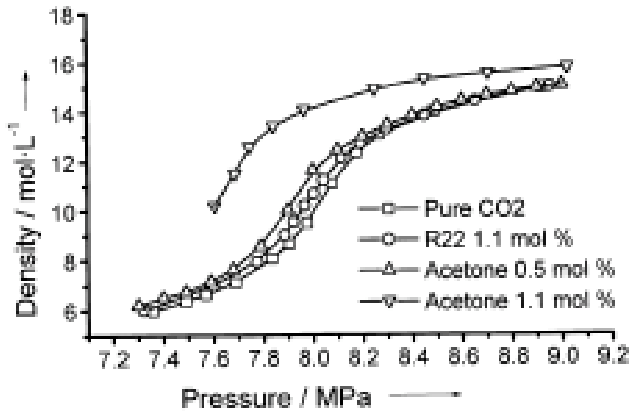
Film deposited by HFCVD (MIT, Gleason Group):

All dry lithography process!

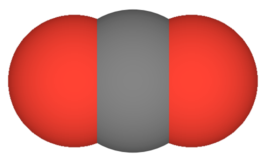
Images courtesy CNF

Addition of Modifiers to $scCO_2$

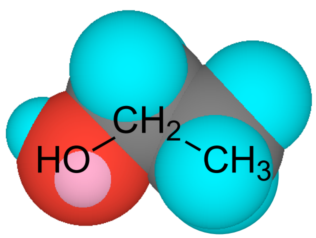
- Small amounts of cosolvents added to supercritical fluid drastically change solvating power
  - Increases solvent density (liquids at R.T.)
  - May increase polarity of fluid
  - Specific interaction with a comonomer



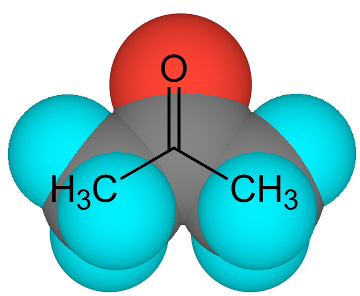
Zhang, et al. *Chem. Eur. J.* 2002, **8**(22). 5107-11.



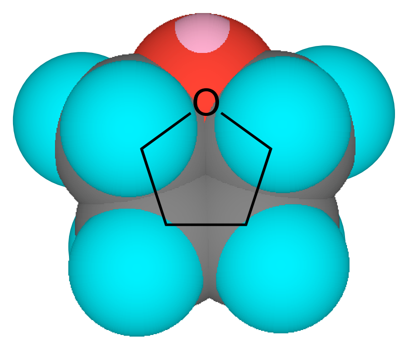
CO_2



Ethanol



Acetone



Tetrahydrofuran

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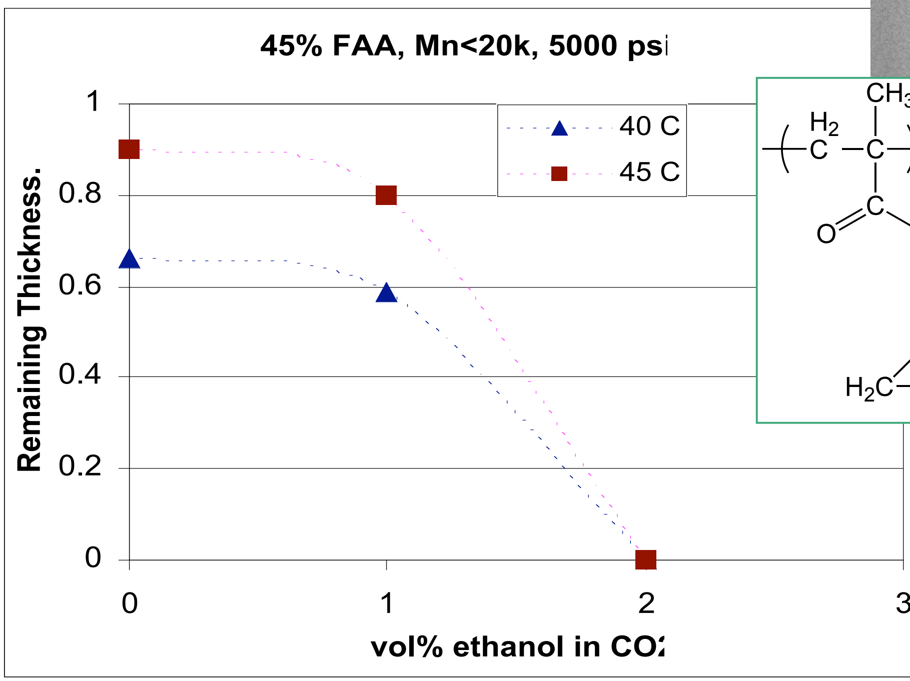
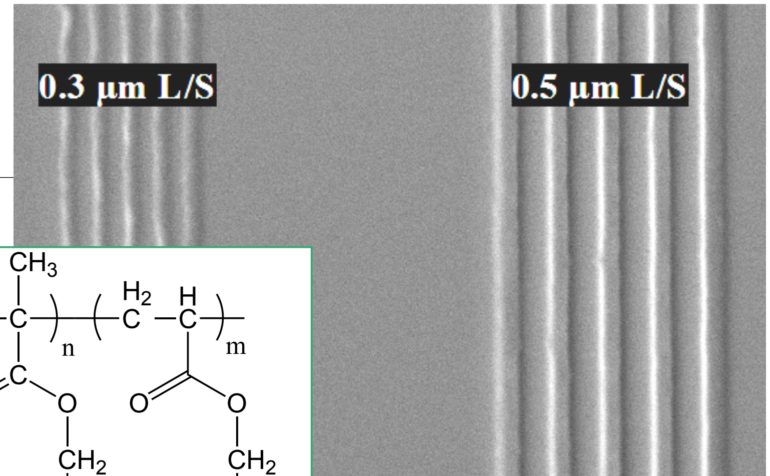
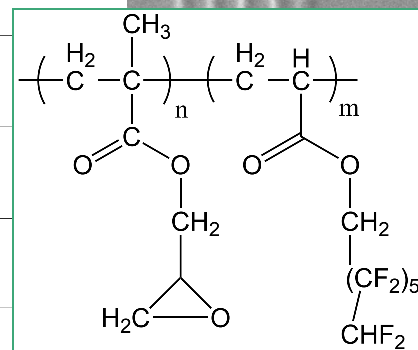
The Cosolvent Effect

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



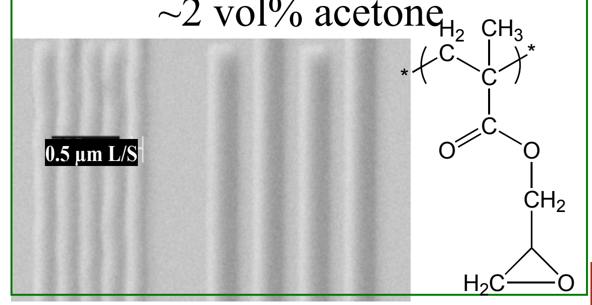




2 vol% ethanol (1.5mol%, 1.6wt%) in $scCO_2$

P = 5000 psi, T = 45°C, t = 10 min

~2 vol% acetone



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

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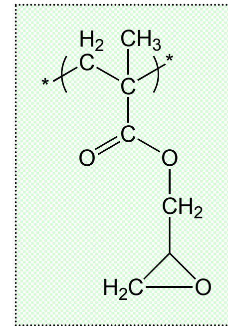
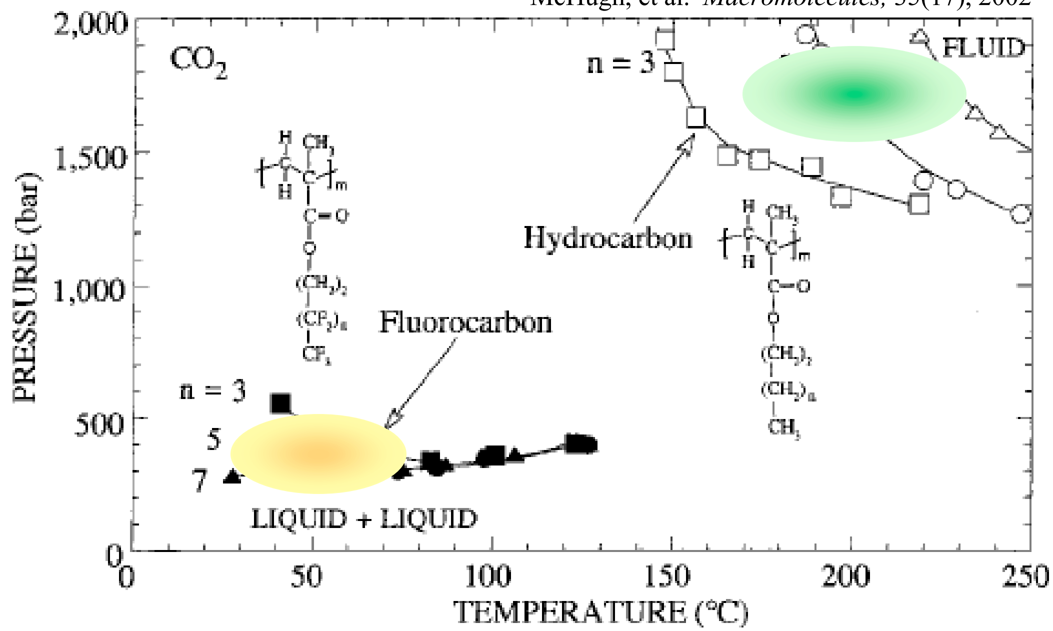
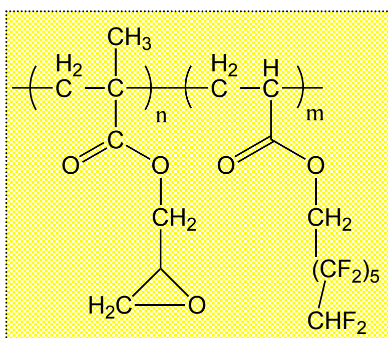
Questions Being Addressed

- Fundamental relationships between resist architecture and solubility in $scCO_2$.
  - Groups
  - Copolymers
- Regions of cosolvent miscibility
- Cosolvent mixing times
- Behavior in cosolvents



McHugh, et al. *Macromolecules,* 35(17), 2002





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Summary

- $scCO_2$ is excellent high resolution developer
  - Avoids pattern collapse
  - Environmental benefit
  - Costs/process time/performance all promising
- $scCO_2$ optimized resists CAN produce sub-100 nm patterns
  - Architecture matters
  - Blocks more effective than random polymers
    - Adhesion & development
- Positive tone resists demonstrated
- All dry lithography (CVD/$scCO_2$) demonstrated