New Photoresists and Processing Methods for $scCO_2$ Development

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NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

MIT

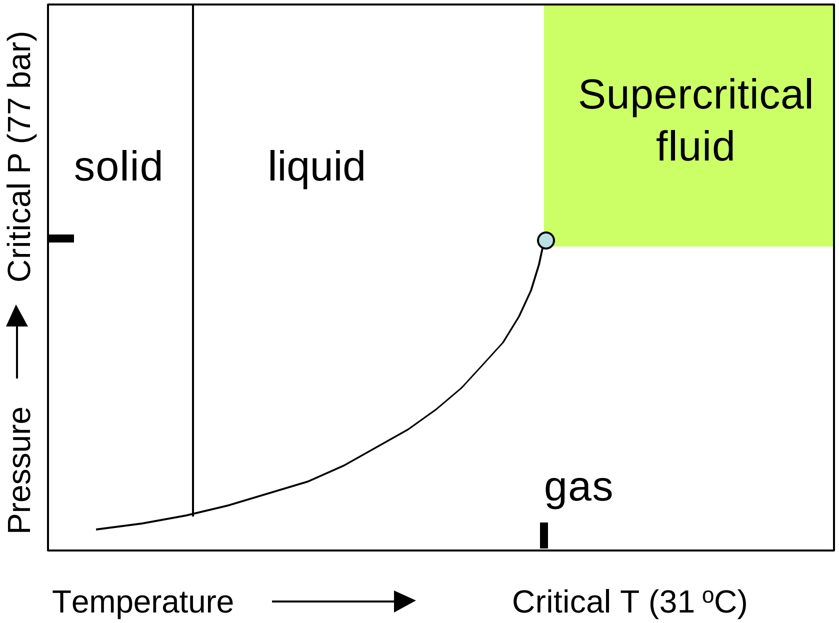
Outline

- Background on $scCO_2$ processing
  - Equipment for dissolution studies

Overview

- Positive-tone resist development
  - Silylation
  - ***Intrinsic positive-tone***
- Cosolvent addition for enhanced solubility of novel resist materials
  - $scCO_2$ development of EUV resist
  - HFCVD patterning and processing (MIT collaboration)
- *Non-fluorinated $scCO_2$ developable resist*

Advantages of $scCO_2$ and Industrial Applications



- **Photoresist and etch residue removal**
  - ▪ **Post metal etch**
  - ▪ **Post oxide etch**
- **Post-ash cleaning**
- **FEOL residue removal**
- **K-value restoration**
- **MEMs non-stiction drying**
- **Post CMP cleaning**

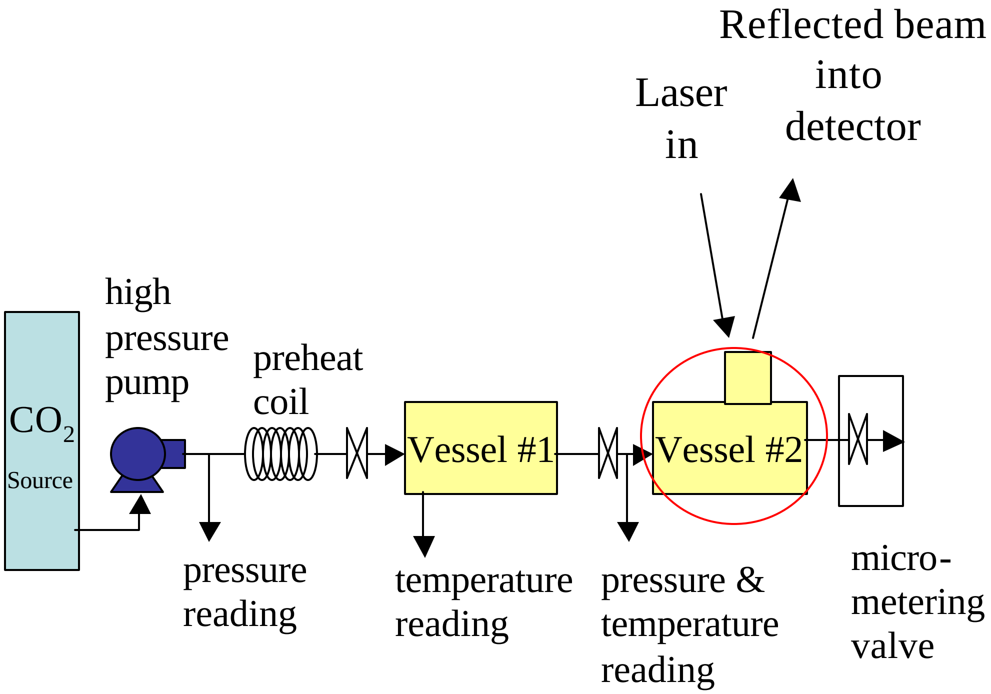
Desirable Properties

- **Liquid-like and variable density**
  Tunable solvating power
- **Gas-like diffusivity & viscosity**
  Penetrates crevices
  High rate of development
- **Strong quadrupole moment**
  Dissolves fluorinated polymers (193nm, 157nm)
- **No surface tension**
  Eliminates pattern collapse in dense, high aspect ratio features

Environmental benefits

- Gas collected and purified from industrial effluents and not generated
- Reduce water consumption and replace hazardous chemical developers
- Non-flammable, non-toxic, abundant, recyclable
- Modest operating condition

DRM Equipment



Reflected beam into detector

Laser in

high pressure pump

preheat coil

CO_2 Source

Vessel #1

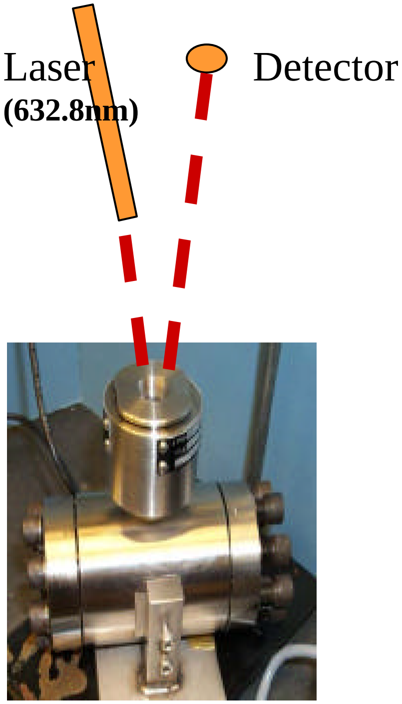
Vessel #2

pressure reading

temperature reading

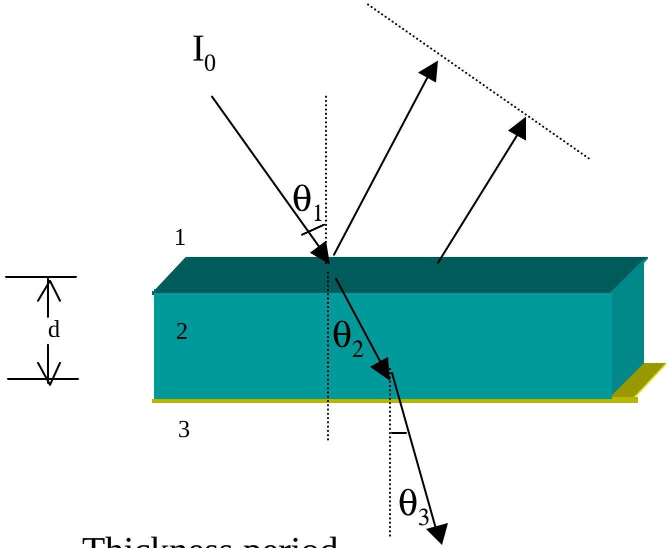
pressure & temperature reading

micro-metering valve



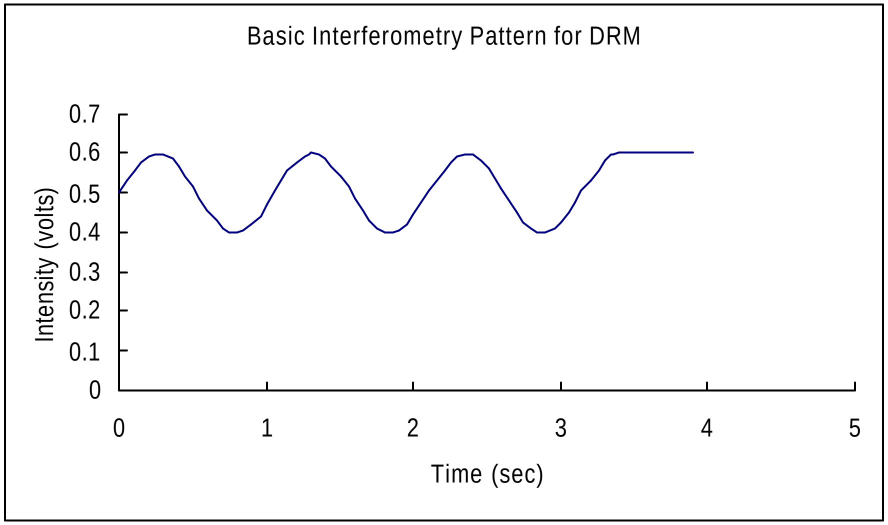
Measurement of Film Dissolution

Principles of Interferometry



Thickness period

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



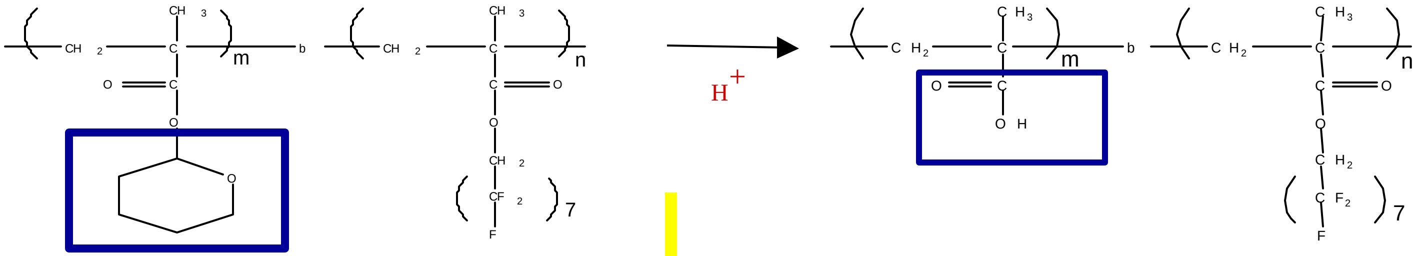
<u>Assumptions</u>:

- Non-swelling
- One optically distinct moving boundary
- Film dissolves at constant rate

scCO$_2$ development

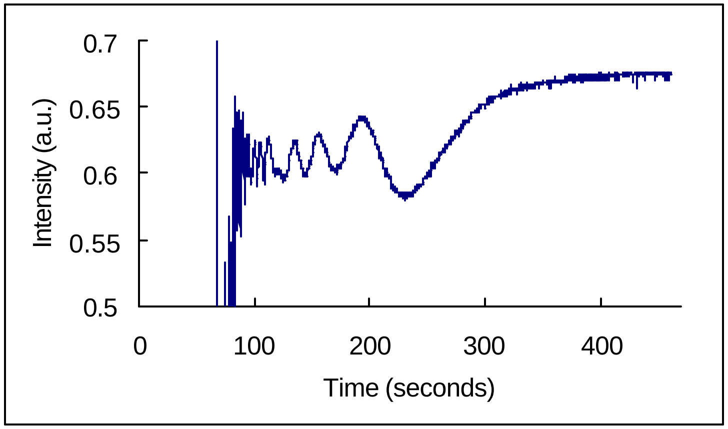
- Swelling is expected
- Fluid equilibration, swelling, and dissolution occur simultaneously
- Density and refractive index of solvent vary with P, T
- 7/8” thick quartz glass window

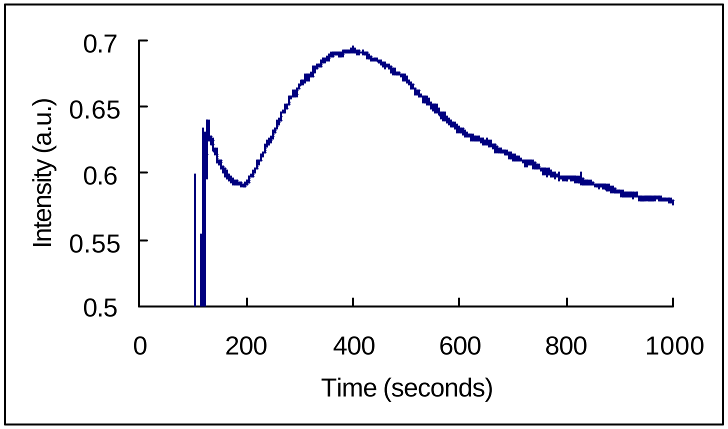
Random Copolymer Dissolution Selectivity



High solubility in CO_2

Low solubility in $scCO_2$

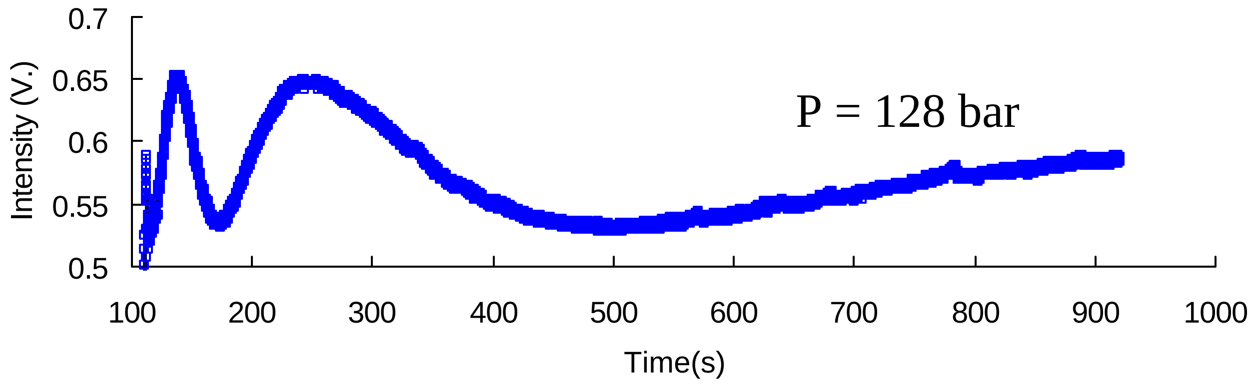


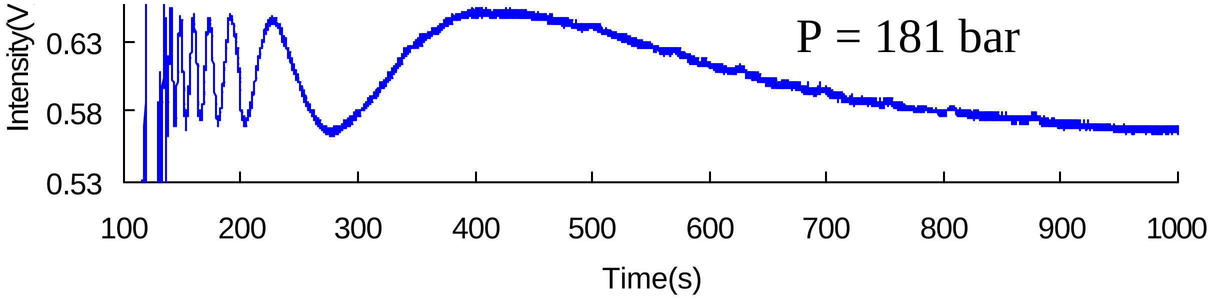


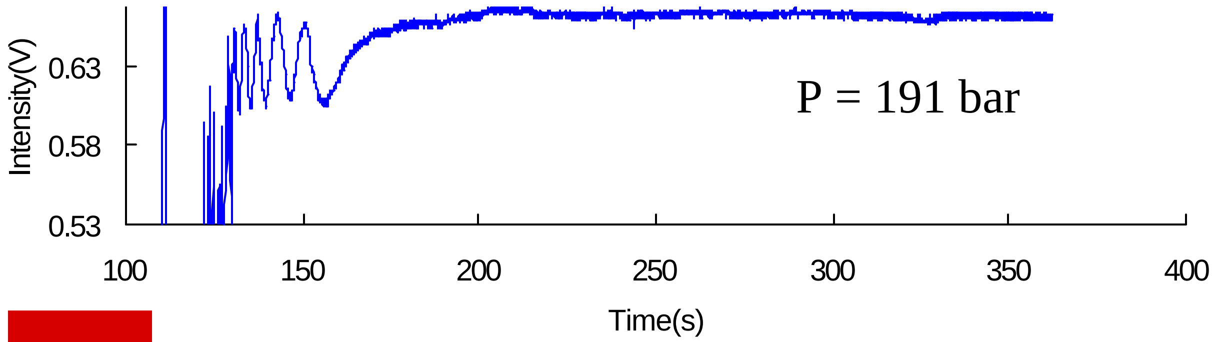
- **Time varying rates**
- **Complete development of film**

- **Very slow rate of dissolution**
- **Incomplete development**

Dissolution Rate and Completeness for THPMA-F_7MA







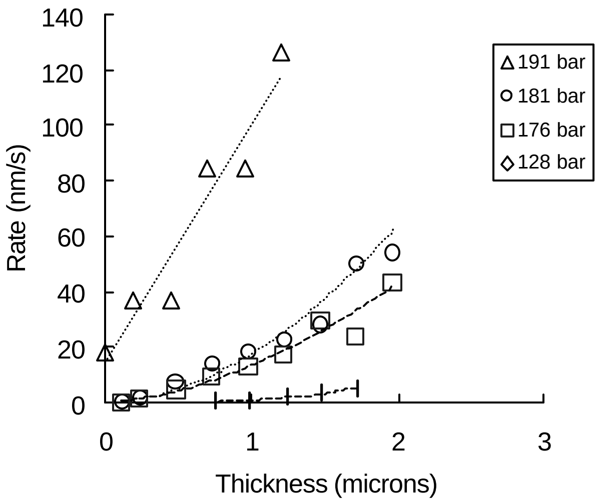
Amplitude of oscillation

$R_+^o=[(n_1-n_3)/(n_1+n_3)]^2$

$R_-^o=[(n_1n_3-n_2^2)/(n_1n_3+n_2^2)]^2$

Thickness period

$$d_p = \frac{l}{2\left[n_2^2 - n_1^2 \sin^2 q_1\right]^{1/2}}$$

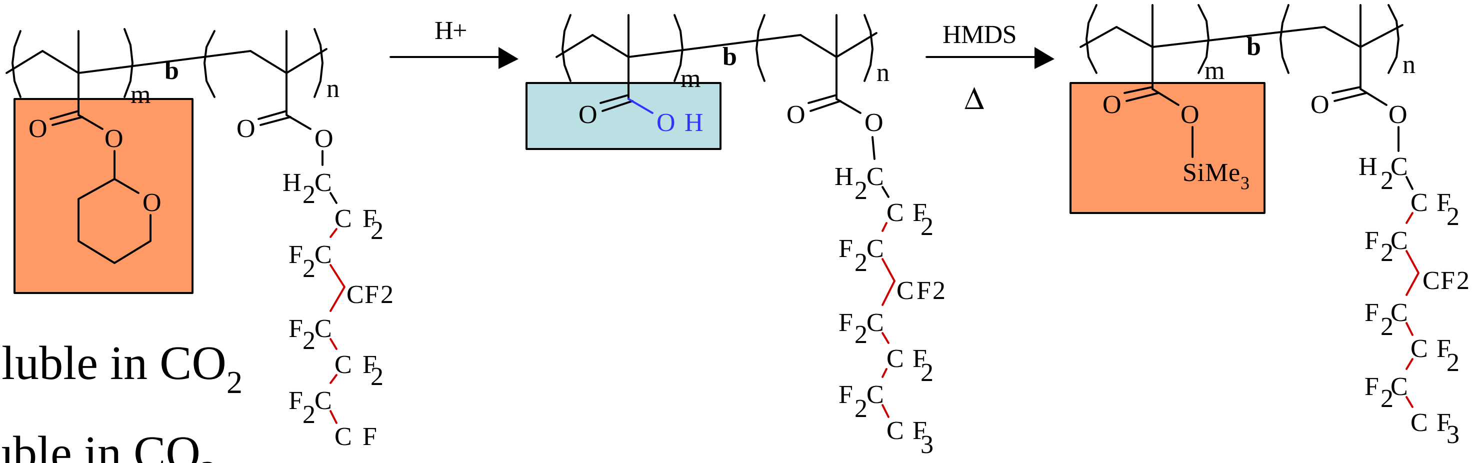


Positive-tone $scCO_2$ Developable Resists

I. Put a non-polar group on - Silylation

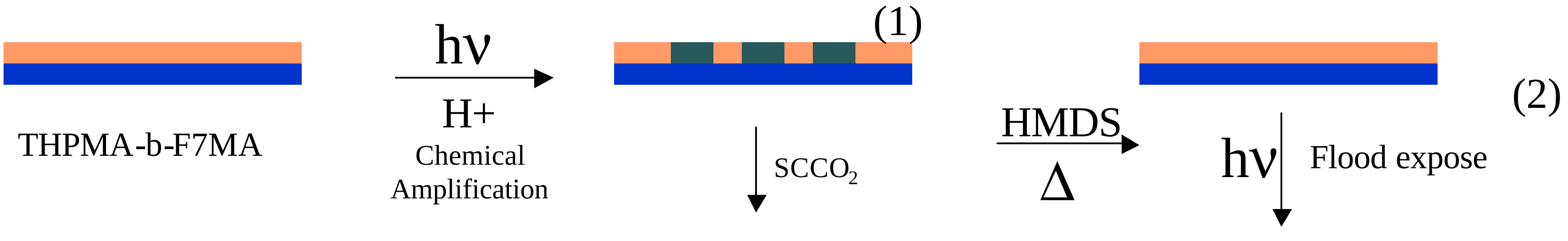
II. Take a polar group off – Enthalpic, entropic manipulations

DESIRE for Positive-tone CO_2 Development



🟦 Insoluble in CO_2

🟧 Soluble in CO_2



THPMA-b-F7MA

hν

H+

Chemical Amplification

(1)

$SCCO_2$

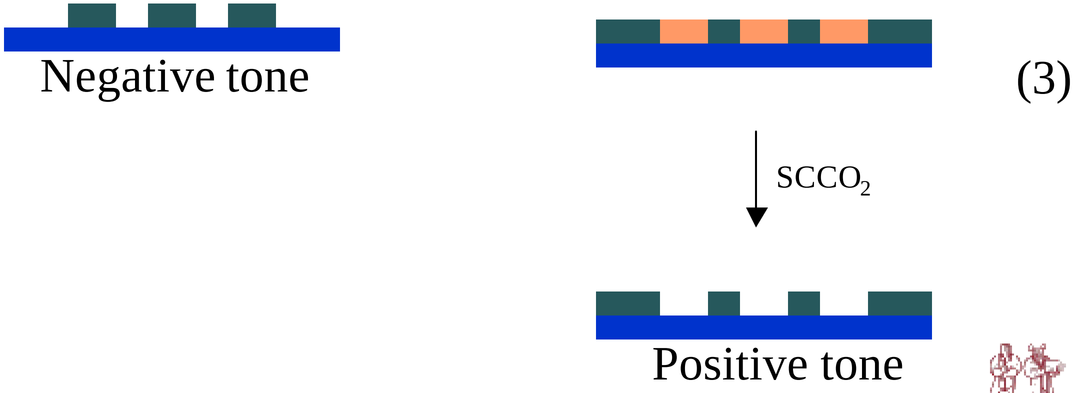
HMDS

Δ

(2)

hν

Flood expose

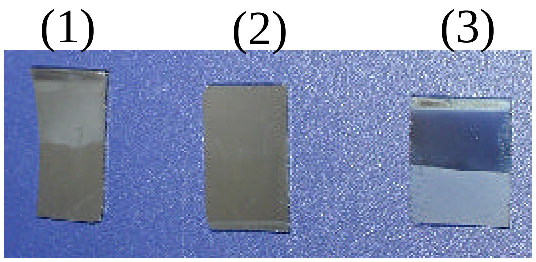


Negative tone

(3)

$SCCO_2$

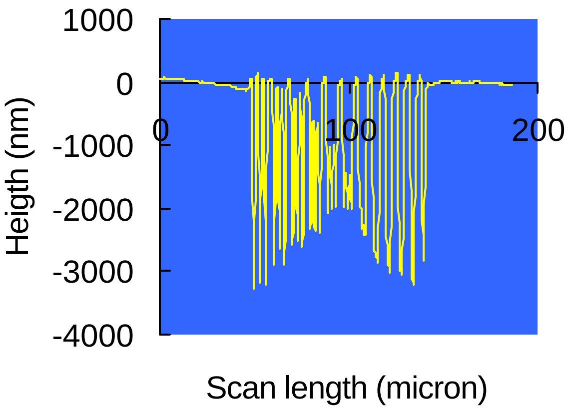
Positive tone



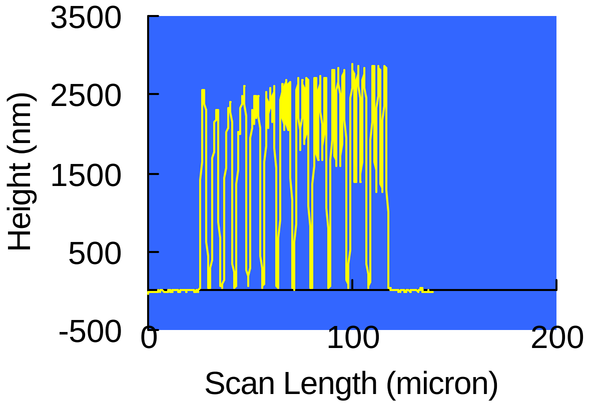
Contrasting Feature Profiles – from Negative-tone to Positive

Profilometer Plots of Patterns

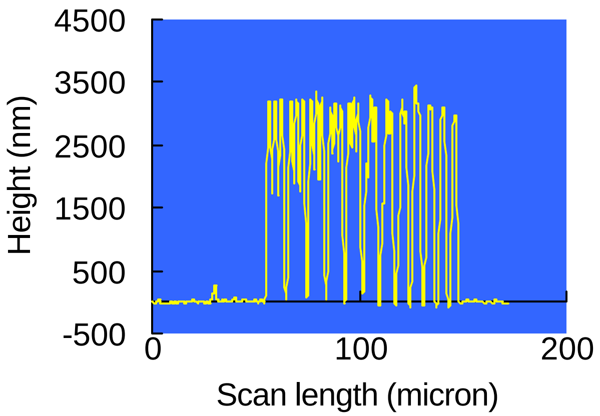
Negative-tone

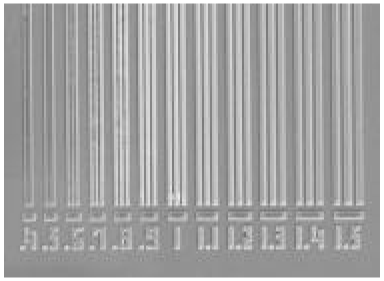


HMDS60



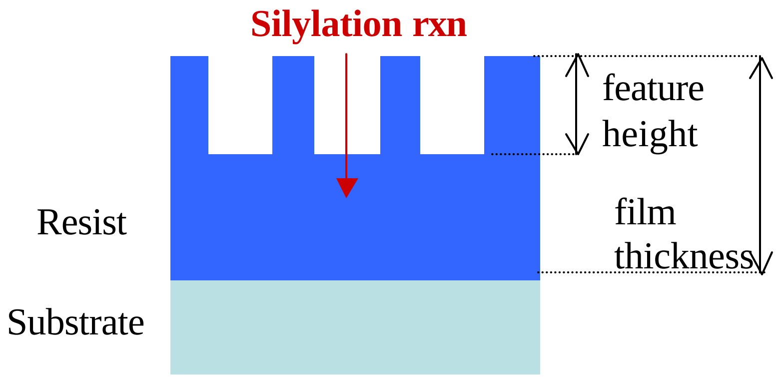
TMDS40

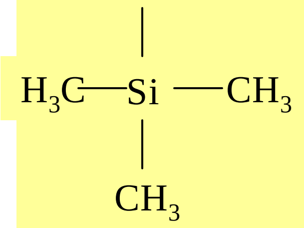




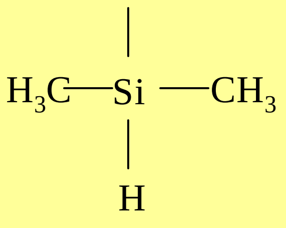
*TMDS – Tetramethyl disilazane

Depth of Silylation Reaction



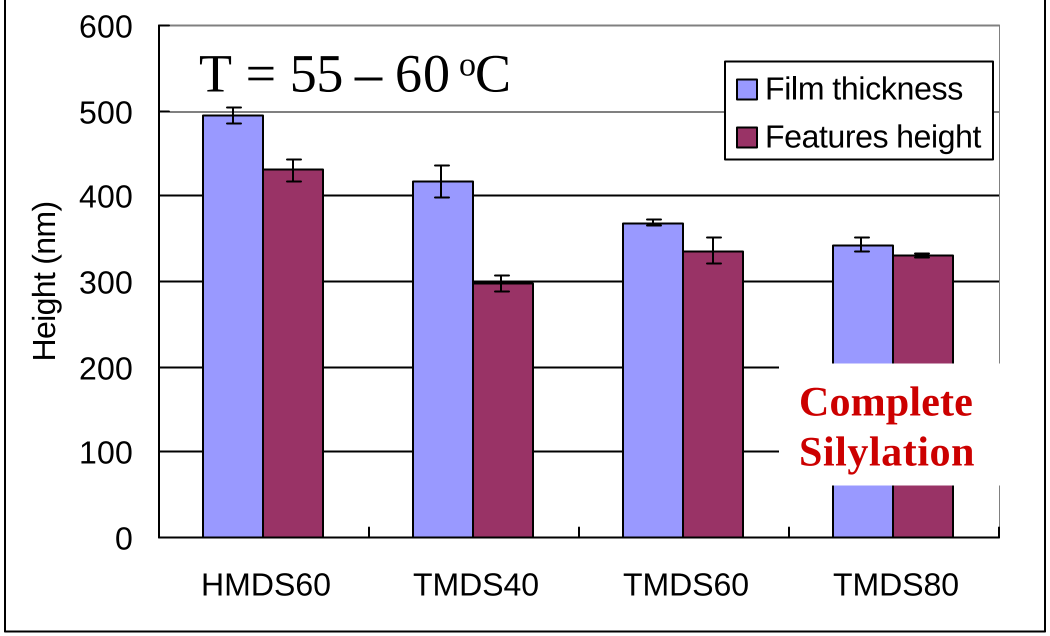

$H_3C-\underset{CH_3}{\overset{|}{Si}}-CH_3$

TMS


$H_3C-\underset{H}{\overset{|}{Si}}-CH_3$

DMS

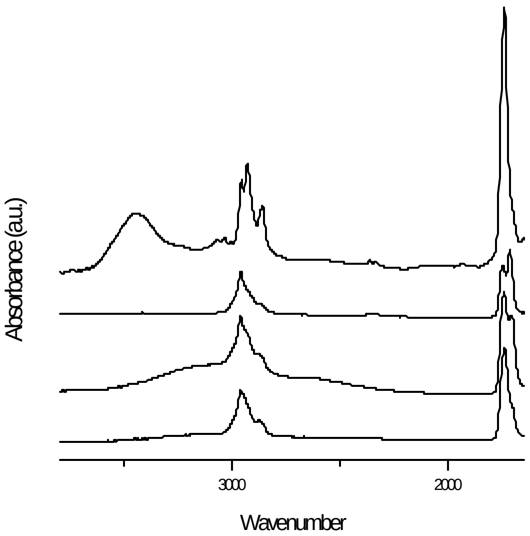
Comparison of film vs. feature heights with HMDS, TMDS silylation

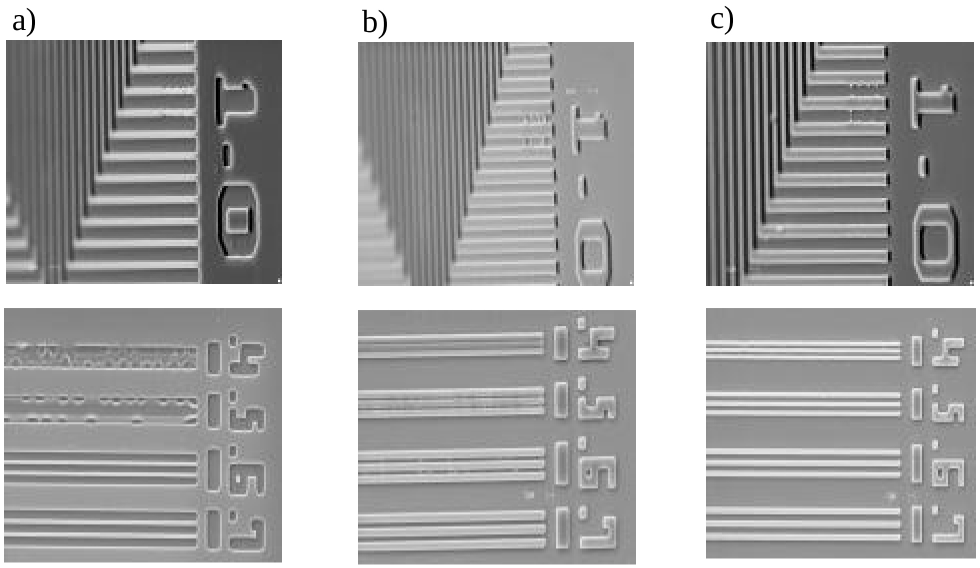


Complete Silylation

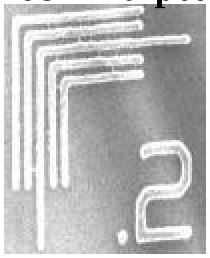
- TMDS, more mobile and more polar than HMDS, offers greater vertical diffusion in more polar exposed regions

Silylated Positive-tone $scCO_2$ Developed Resist



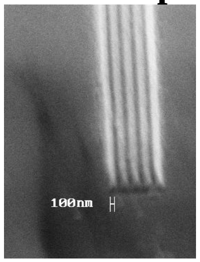


193nm exposure



Sundararajan, Ph.D.

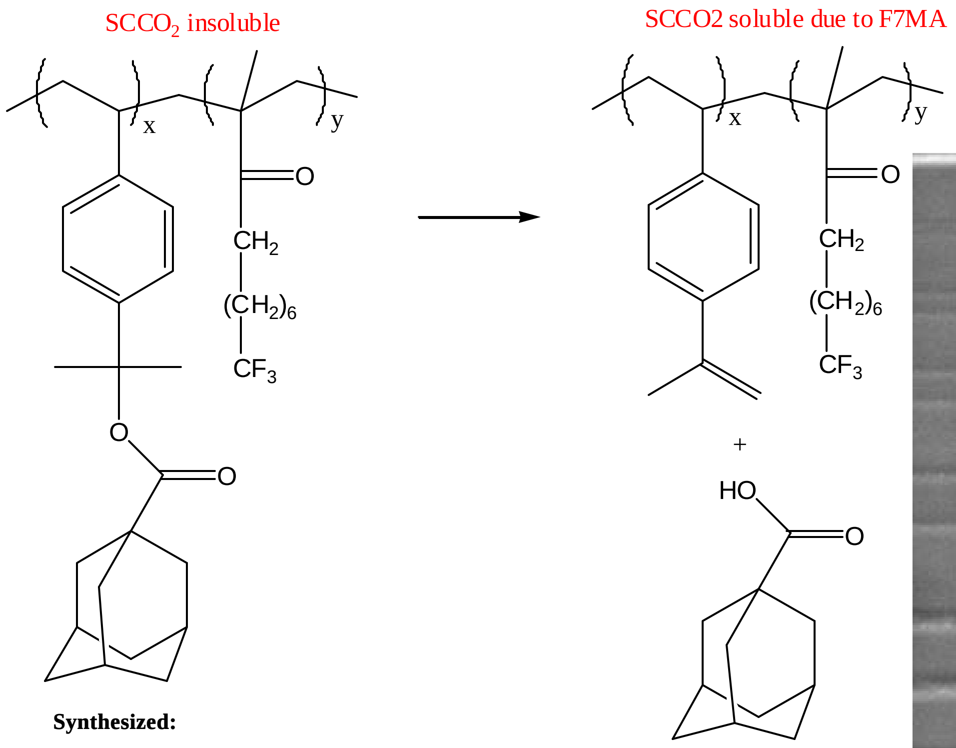
Ebeam exposure



V. Pham

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

Intrinsic Positive-tone Resist for $scCO_2$

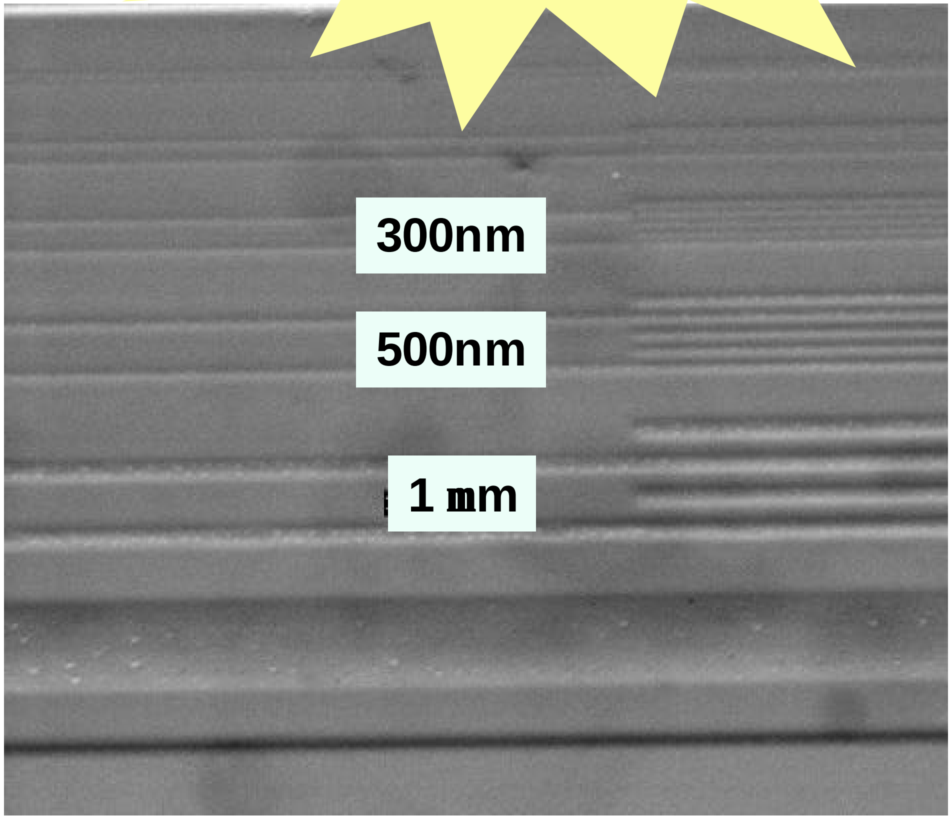


Synthesized:

Polymer A191 (x = 40, y = 60, feed ratio)

Polymer A192 (x = 60, y = 40, feed ratio)

Patterning with 248nm and E-beam demonstrated



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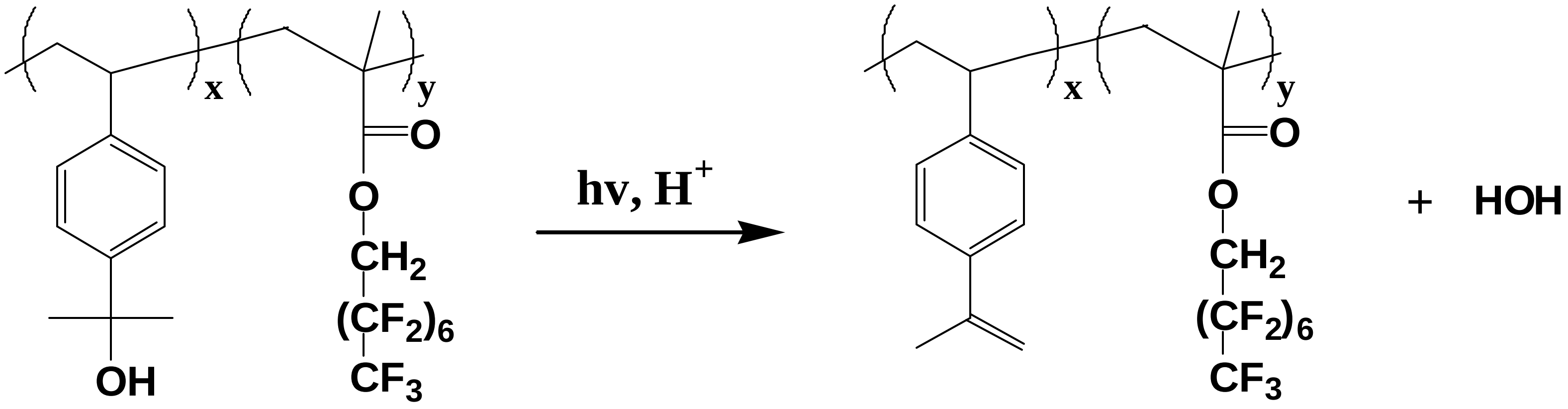
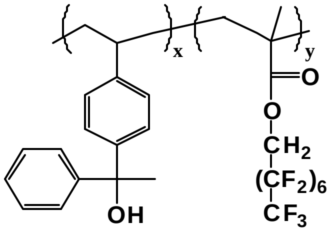
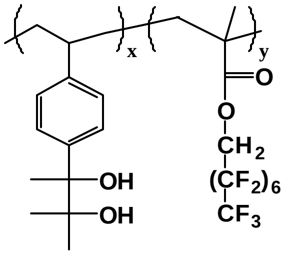
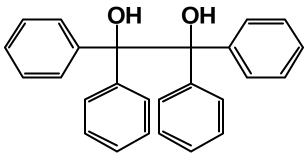
Positive Tone $scCO_2$ Photoresist Systems



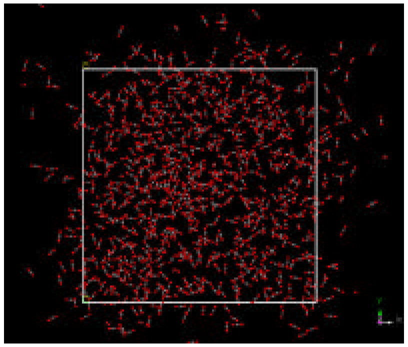




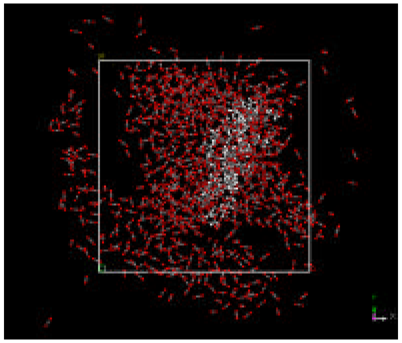


CO_2 – Cosolvent – Polymer Interactions

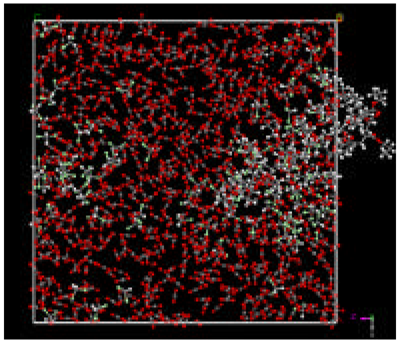
Peter Nguyen
Nelson Felix
Victor Pham



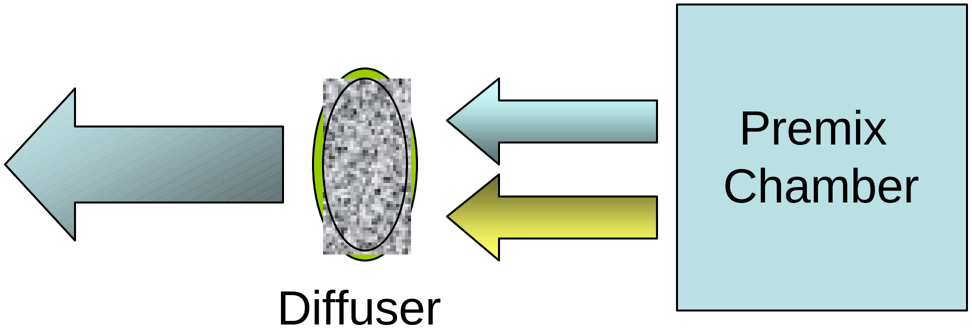
$scCO_2$



$scCO_2$
+ PPA



$scCO_2$
+ PPA
+ CH_2Cl_2



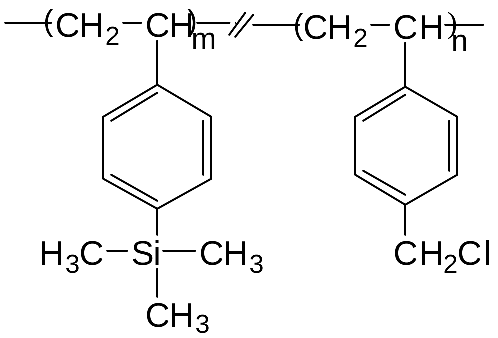
Premix Chamber

Diffuser

Effect of Cosolvents with $scCO_2$

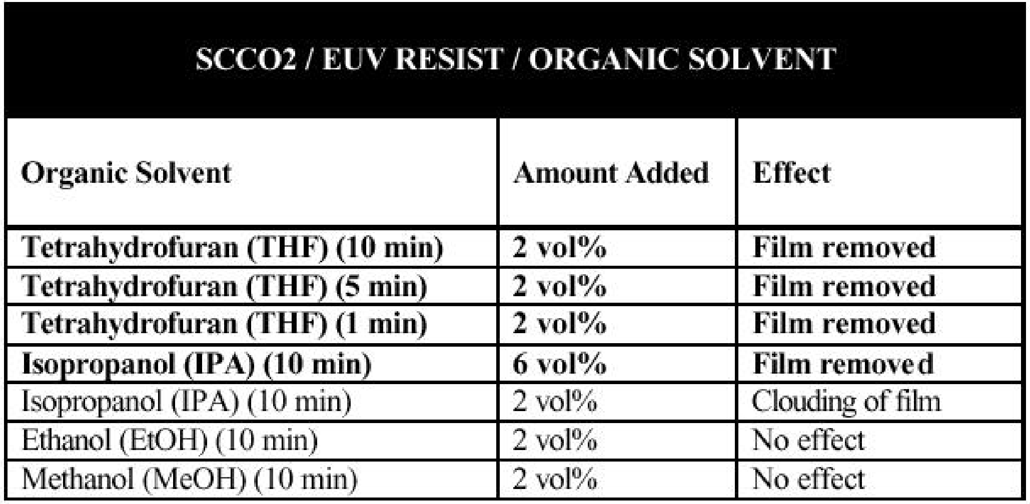
- Negative tone EUV resist
- Insoluble in pure supercritical CO_2
- Soluble in $scCO_2$ when cosolvents are added to supercritical fluid.

Poly(chloromethylstyrene-co-trimethylsilylstyrene)

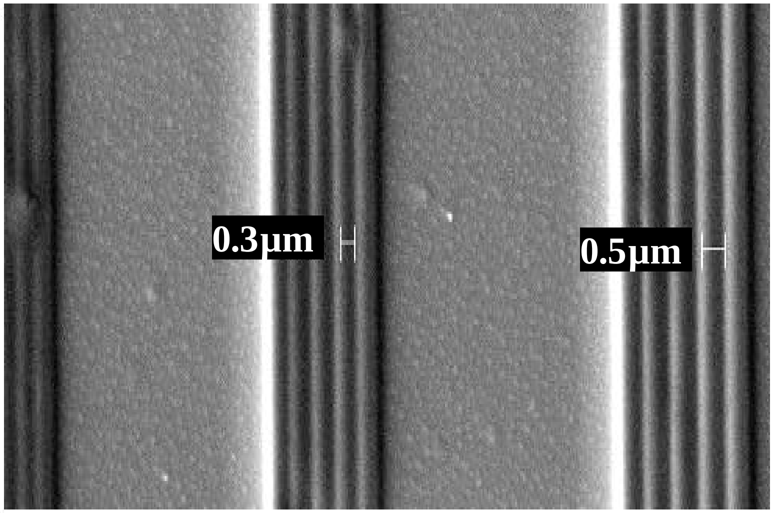


m = 90, n = 10

P = 5000 psi, T = 45 °C, t = 10 mins

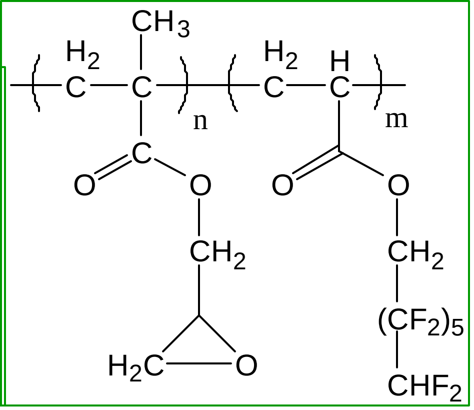


SCCO2 / EUV RESIST / ORGANIC SOLVENT		
Organic Solvent	**Amount Added**	**Effect**
Tetrahydrofuran (THF) (10 min)	**2 vol%**	**Film removed**
Tetrahydrofuran (THF) (5 min)	**2 vol%**	**Film removed**
Tetrahydrofuran (THF) (1 min)	**2 vol%**	**Film removed**
Isopropanol (IPA) (10 min)	**6 vol%**	**Film 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

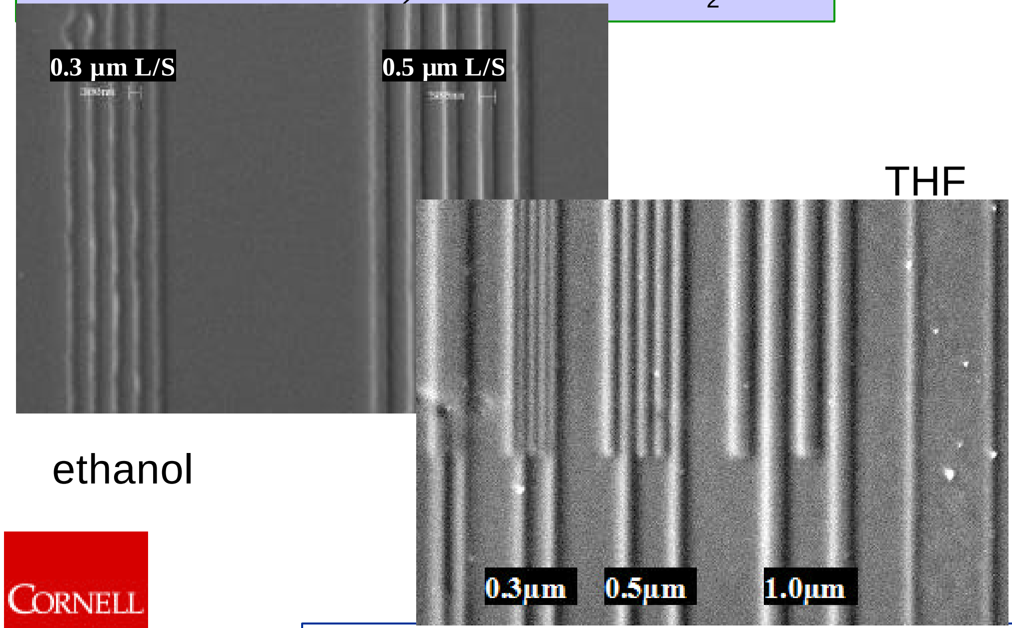


E-beam resists deposited by CVD

- A negative-tone e-beam resist, glycidyl methacrylate (GMA), deposited by hot filament CVD at MIT (Gleason Group).
- GMA block insoluble in $scCO_2$,fluorinated repeat unit (FAA) added to form a block copolymer soluble in $scCO_2$.



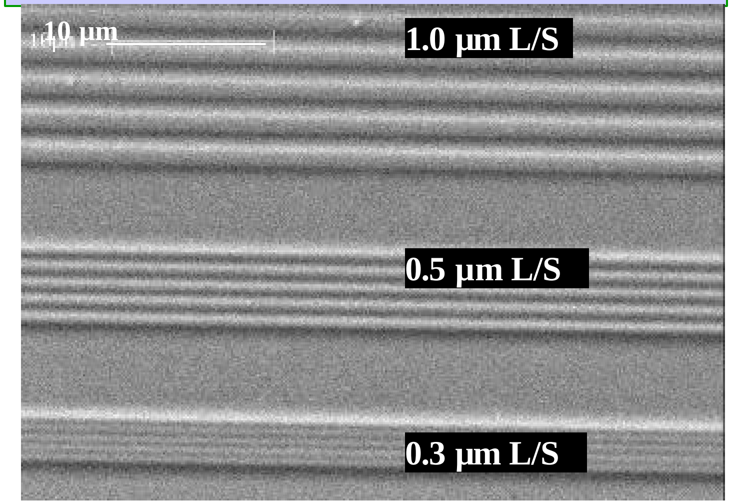
Low FAA content (37%): soluble in 2%ethanol/ $scCO_2$ or 2%THF/ $scCO_2$



THF

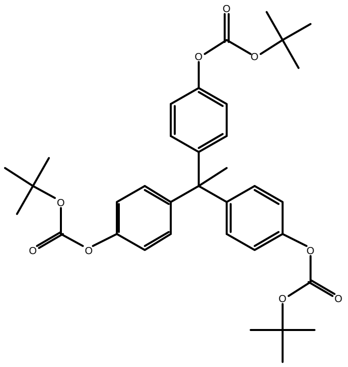
ethanol

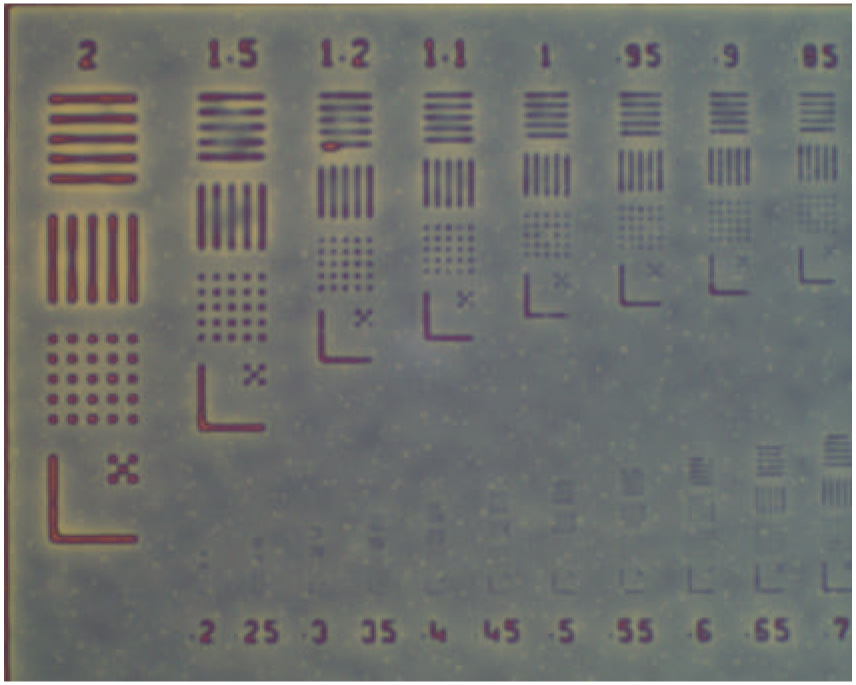
High FAA content (65%): $scCO_2$ soluble



Non-fluorinated Resist for $scCO_2$

Molecular glass as resist for low LER





248 nm exposure
Developed in CO_2 at ~1000 psi, 40°C

Summary

- Dissolution rate measurement
- Positive-tone resist development
  - Silylation
  - Intrinsic positive-tone
- Experimental and theoretical work on cosolvent addition for development and cleaning
  - $scCO_2$ development of EUV resist
  - HFCVD patterning and processing
- Non-fluorinated resist systems

Acknowledgement

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- Cornell Center for Materials Research (CCMR)
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- Praxair

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