Using $scCO_2$ and Cosolvents for Microelectronics Processing

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CORNELL

Outline

- Review of Supercritical Fluids (SCF)
  - Supercritical CO_2 ($scCO_2$) and SCF properties
  - Reasons for interest in semiconductors (2 examples)
- Adding organic solvents to $scCO_2$ solutions
  - Effects
- Ober Group CO_2 System with Cosolvent Capabilities
  - Specifications
- Using $scCO_2$ and $scCO_2$ + cosolvent to develop photoresists
  - MIT/Cornell chemical vapor deposition (CVD) resist project

Outline (Continued)

- Difficulties / Concerns
  - Effects
  - Rationale for choosing cosolvent
- Conclusions / Outlook
  - Closing remarks
  - Acknowledgements

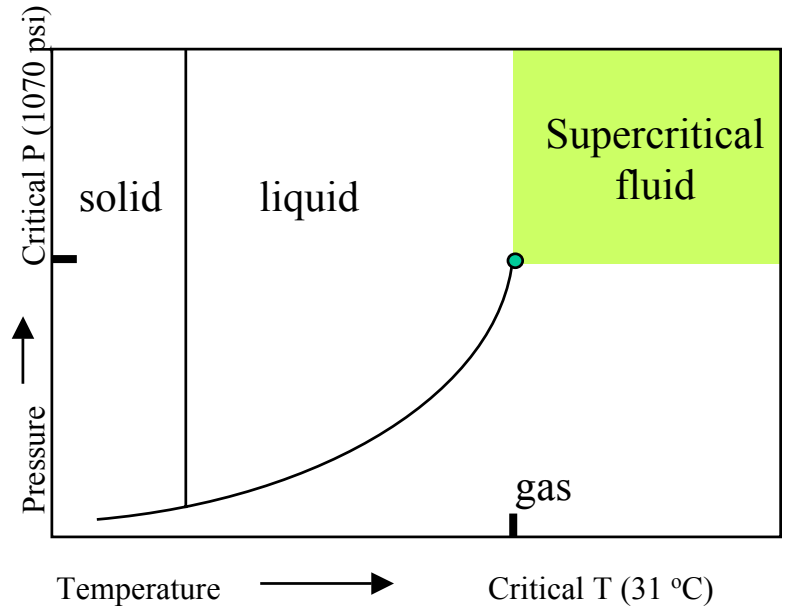
Why Consider Alternative to Organic Solvents?

- The semiconductor industry has been growing at an annual rate of about 15% over the last thirty years.
- Typically, a semiconductor processing line that produces 5000 wafers per day will generate 8000 liters of waste solvent and 8000 liters of contaminated rinse water per day.*
- These contaminated organic and aqueous solvents are environmentally unfriendly and costly to recover and dispose of.

* S. Wells, J. Desimone, *Angew. Chem. Int. Ed.* **2001**, *40*, 518-527.

Supercritical CO_2 ($scCO_2$)

- CO_2 is inexpensive and it has a moderate critical point: T_c (31.1 ^oC) and P_c (1070 psi). Non-flammable and non-corrosive.
- Gas-like diffusivity and viscosity, but liquid-like density.



- Low viscosity and near zero surface tension.
- No dipole moment, but a very large quadrupole moment.

Supercritical Fluids vs. Gases and Liquids

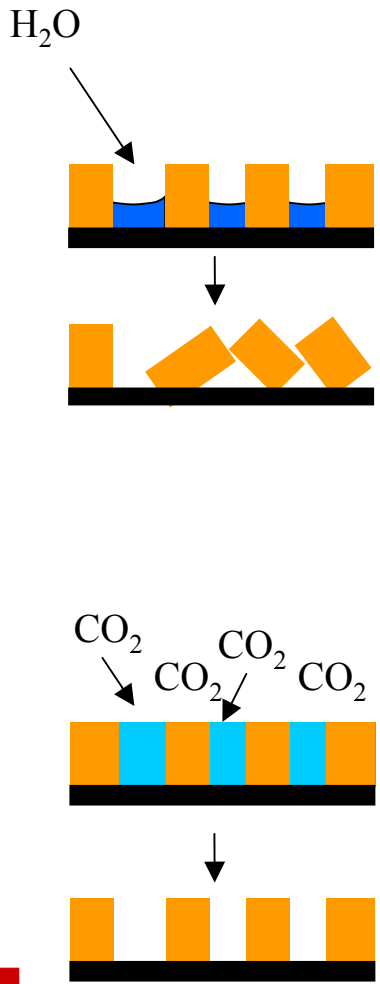
- Order-of-magnitude comparison of physicochemical properties of a typical gas, liquid, and a supercritical fluid (SCF)

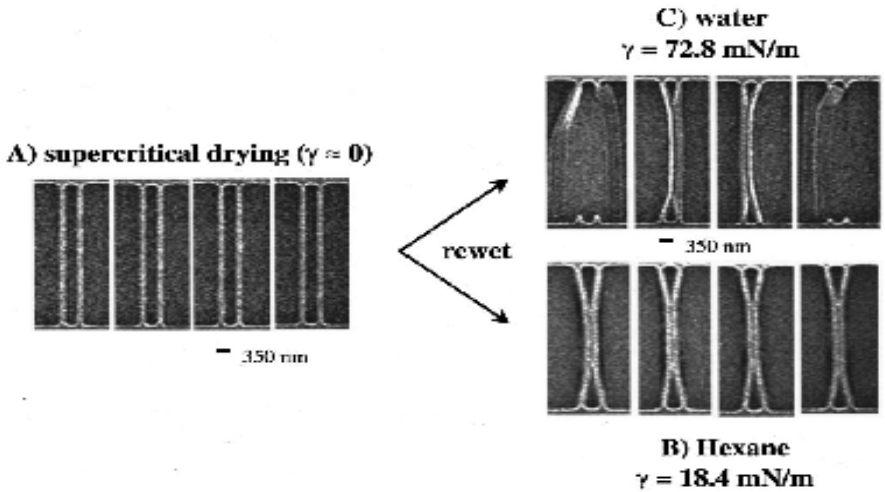
Property	Gas	SCF	Liquid
Density (kg/m^3)	1	700	1000
Viscosity (g/cm s)	10^{-5}	10^{-4}	10^{-3}
Diffusion Coefficient (cm^2/s)	10^{-1}	10^{-4}	10^{-5}

Environmental Benefits of $scCO_2$

- CO_2 is naturally occurring and readily available (as a by-product from the production of other compounds.)
- When released into the atmosphere, liquid CO_2 leaves no residue to contaminate the environment or personnel.
- Processes that use CO_2 do not add directly to the green-house effect.
- CO_2-based processes can be more energy efficient than those based on water or conventional solvents since CO_2 has a low heat of vaporization.
- Approved by the EPA as a non-ozone-depleting chemical alternative.

Processing Benefits: Preventing Pattern Collapse

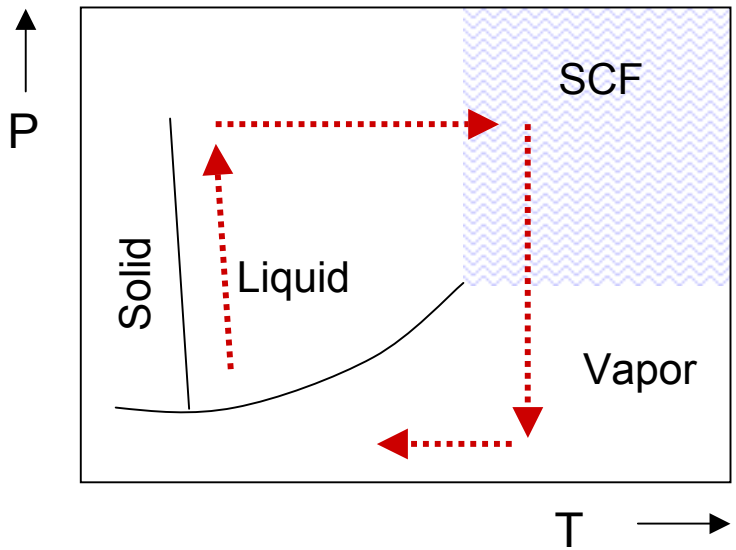




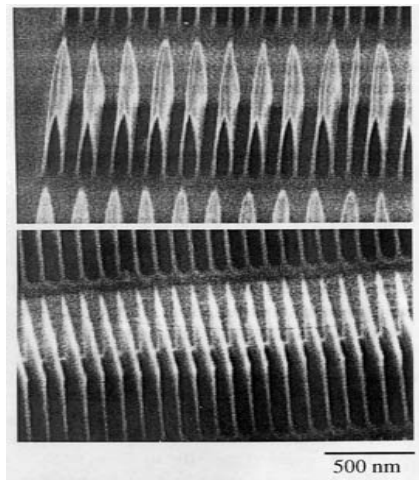
Goldfarb, D., de Pablo, J., Nealey, P., Simons, P., Moreau, W., Angelopoulos, M. Journal of Vacuum Science & Technology, B: Microelectronics and Nanometer Structures (2000), 18(6)

$scCO_2$ MEMS Drying Device

- CO_2 exchange displaces water or polar solvents
- Elimination of capillary forces



Si structures



H. Namatsu, K. Yamakazi, K. Kurihara
Microelectronics Engineering, 46 (1999)

Effect of Cosolvents on Supercritical CO_2 Mixture

- Since CO_2 is not polar, polar solutes do not dissolve in $scCO_2$.
- Adding a small volume of a polar cosolvent can dramatically improve the solubility of a polar solute in $scCO_2$ thanks to interactions between the cosolvent and the solute.
- By adding cosolvents, we are affecting the thermodynamics of the mixture. Generally, these thermodynamic interactions are complicated.

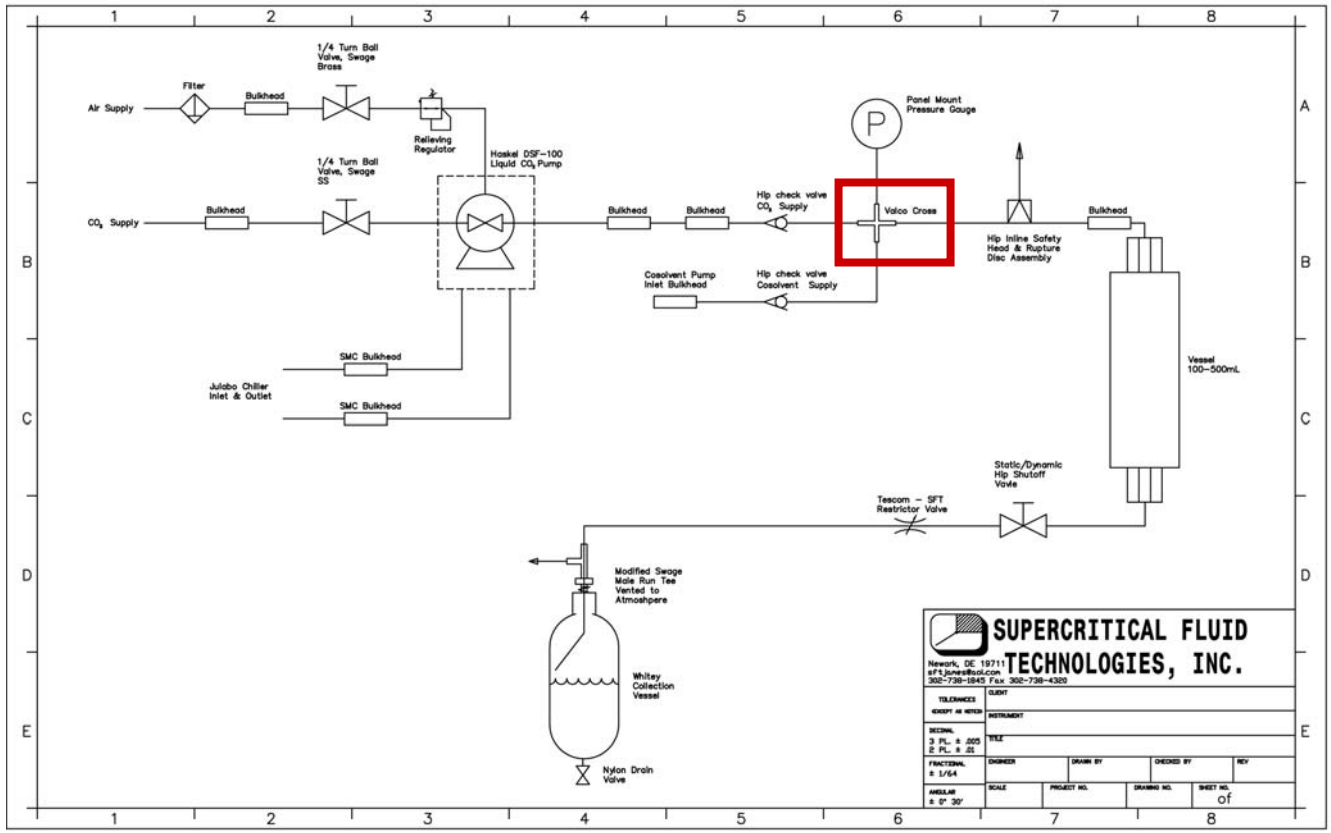
Mixed Solvent Processing

Solvent Pump

$scCO_2$ System

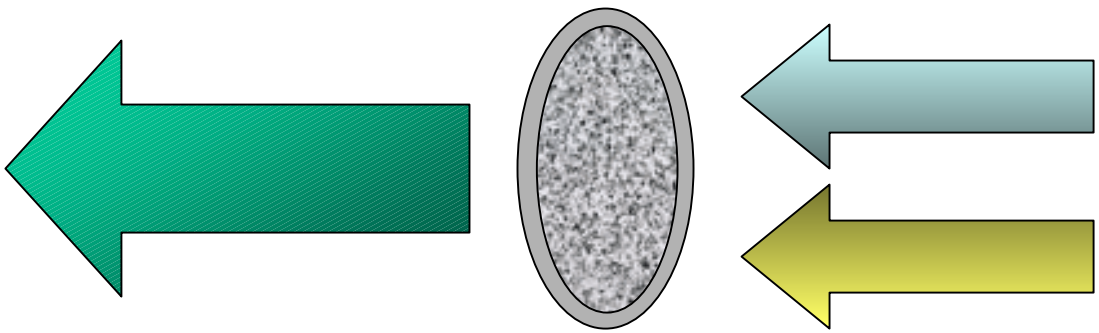
SCF Processing Vessel at Cornell

- Manufactured by Supercritical Fluid Technologies (Newark, DE)



Introducing Cosolvents:
The Ober Group Supercritical Fluid Technologies SFT-150

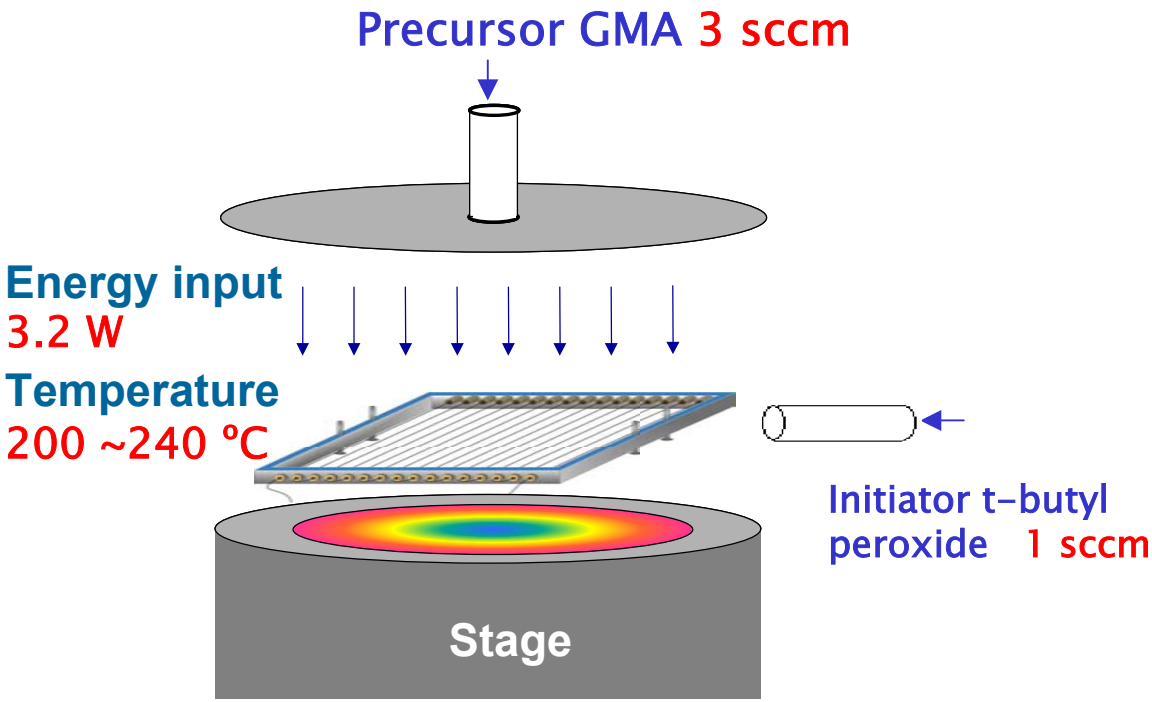
- Cosolvents are pumped into the system using a HPLC pump.
- CO_2 mixes with the cosolvent before passing through diffuser plates and into the processing vessel.



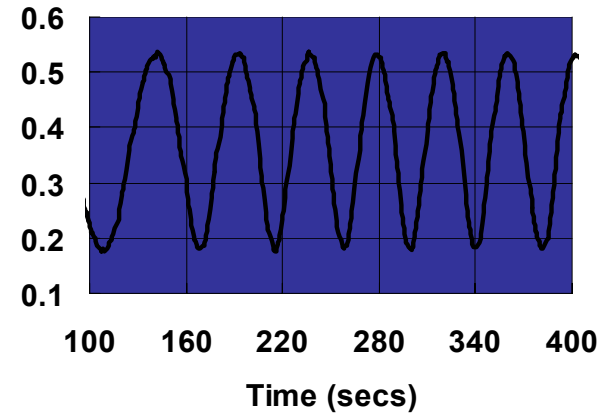
MIT / Cornell
Chemical Vapor Deposition (CVD) Photoresist

- The Gleason group at MIT has been working on a system of *hot filament CVD* that can deposit uniform polymer films onto Si wafers.
- The polymer used in this collaboration is poly(glycidyl methacrylate) – a known high-speed electron-beam (e-beam) resist.
- Incident electrons induce a crosslinking reaction in the polymer film.
- As is, poly(glycidyl methacrylate) is a negative-tone (exposed area remains after developing) resist system.

Hot Filament CVD of GMA



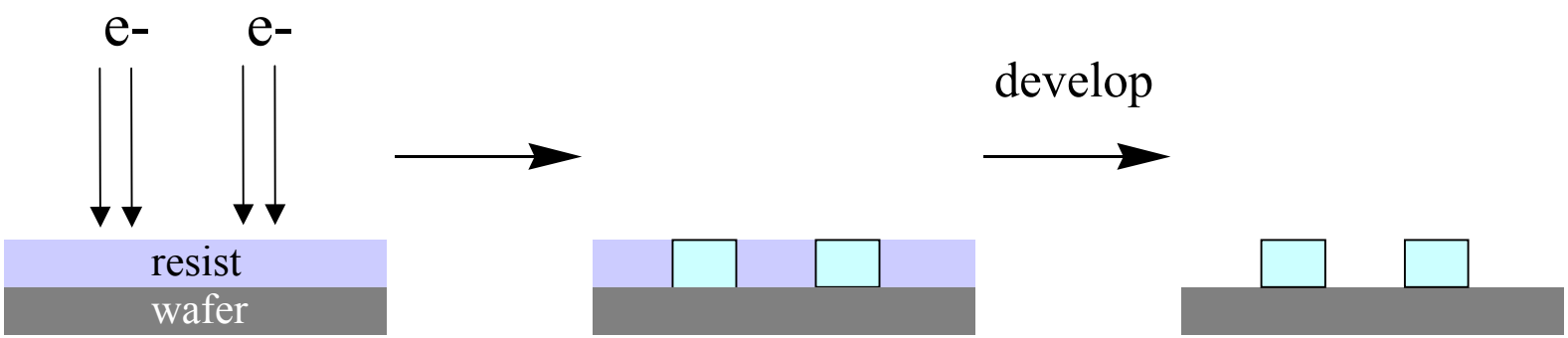
In-situ growth rate monitor

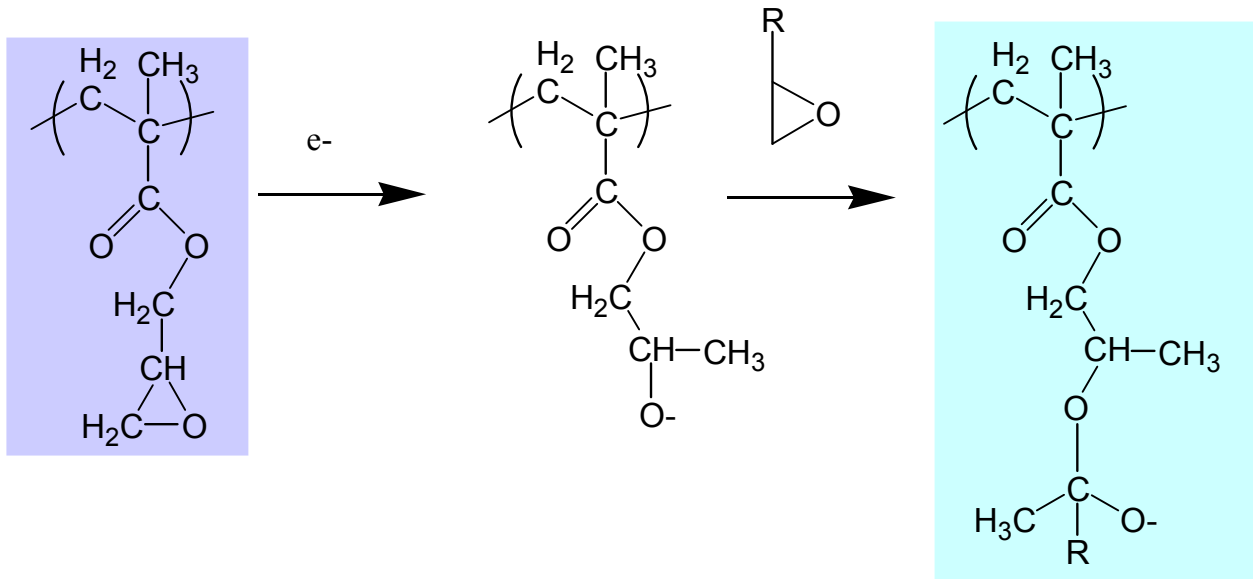


- Rapid deposition rate >3,000 Å/min
- RMS roughness <2 nm
- Thickness variation <2 %
- MW range 20K-120K

- thermal generation of growth species.
- low-energy process, low filament temperature.
- no UV irradiation and ion bombardment.
- control over reaction pathways.
- material utilization efficiency ~10%.

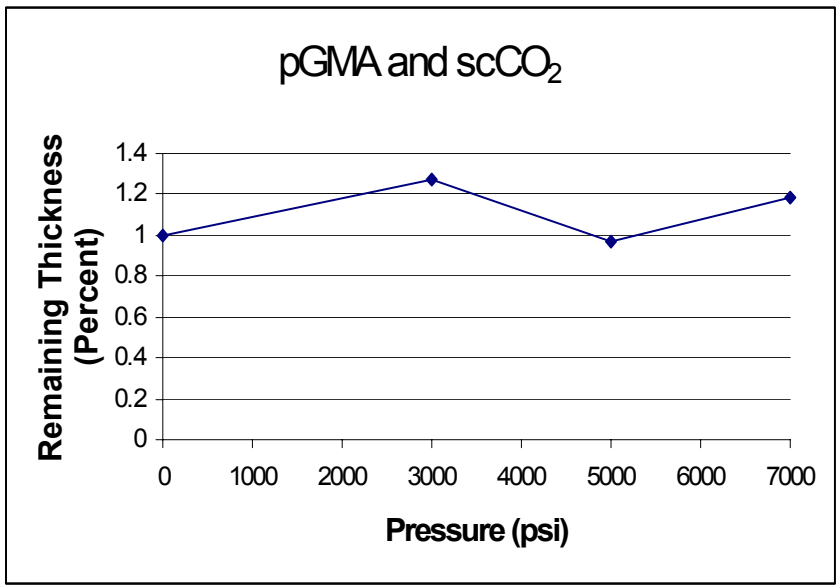
Crosslinking pGMA

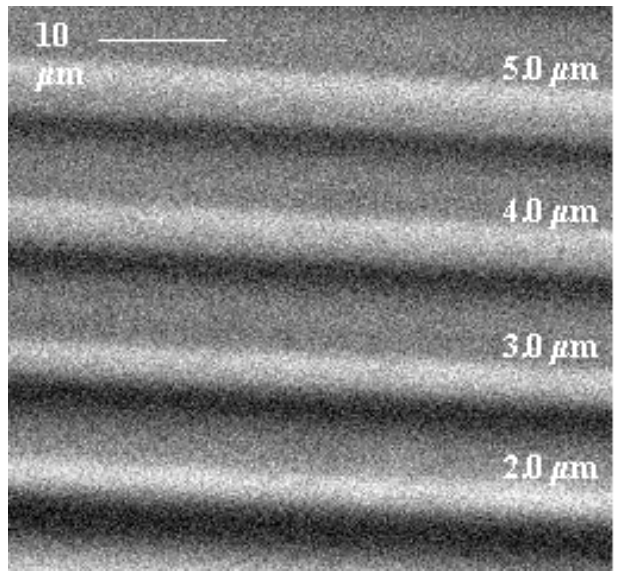




Results with pGMA

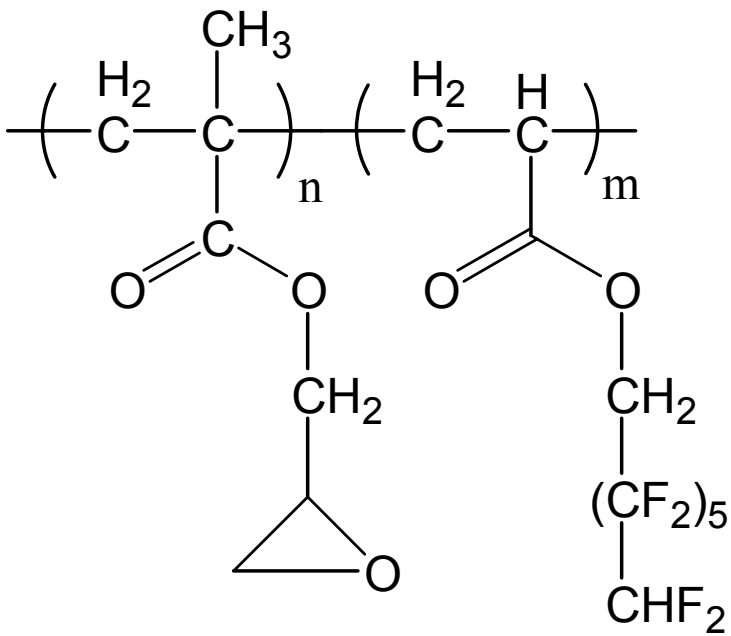
- As expected, the polymer is insoluble in $scCO_2$.
- Adding 2 vol% CH_2Cl_2 allows for some patterns to be developed.



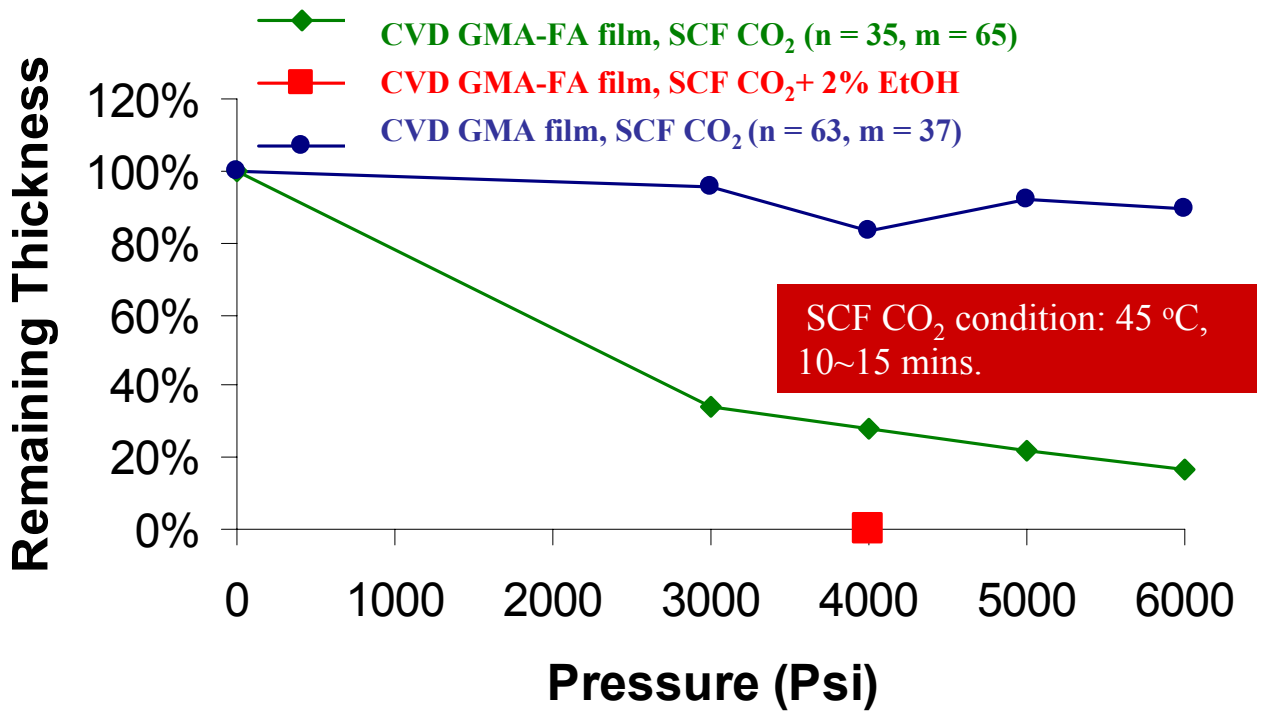


Methods of Improving the Resist

- Adding fluorine containing groups to the polymer has the potential of dramatically improve the solubility in CO_2.



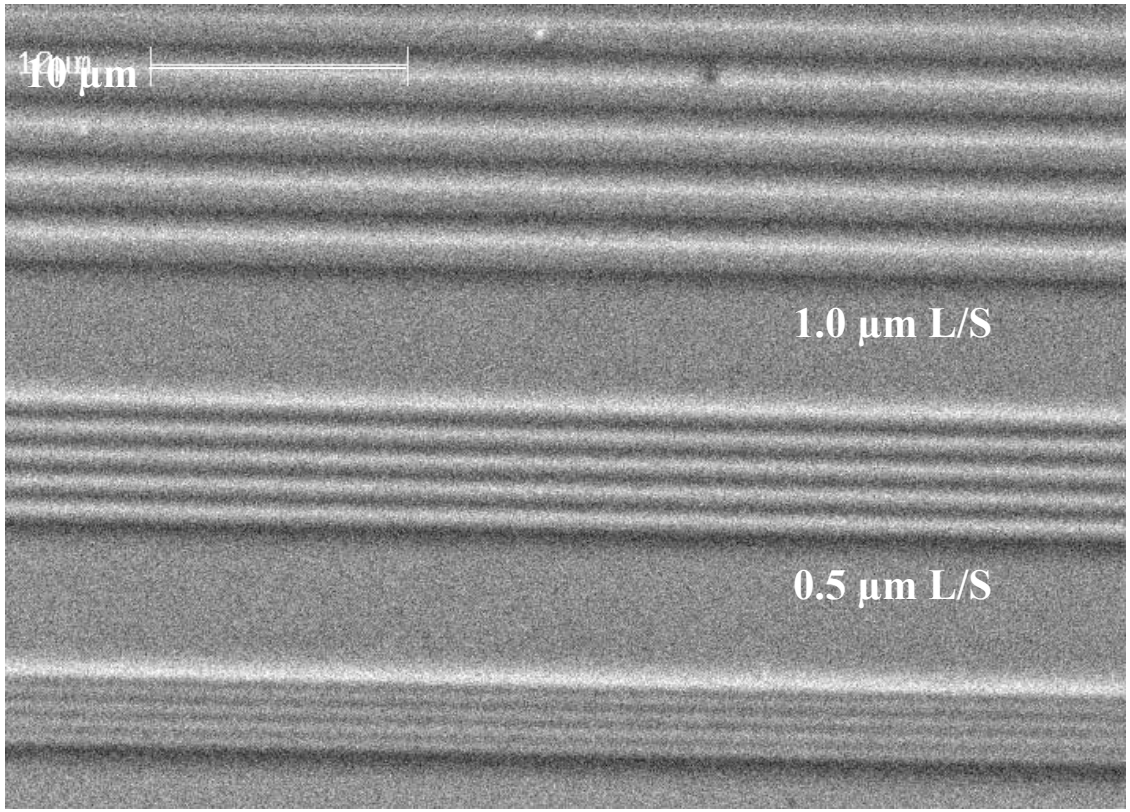
FA-GMA Copolymer



FA-GMA Copolymer (continued)

P = 6000 psi, T = 45 °C, t = 10 min

n = 35, m = 65



How We Chose the Cosolvent

- Choosing cosolvents is sometimes complicated……..

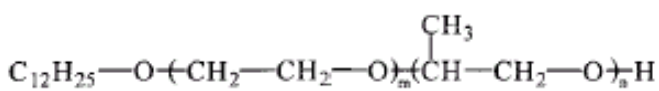
$scCO_2$ / pGMA / 2 vol% Organic Solvent	
Cosolvent	**Effect**
Tetrahydrofuran	*Film Removed*
Methylene Chloride	*Film Removed*
Isopropanol	No Effect
Acetone	No Effect
Ethanol	No Effect
Methanol	No Effect

This leads us to the next point…

An Alternative to Cosolvents: Specific Surfactants

- Specifically designed organic surfactants have been used as additives to $scCO_2$. For example:

Chart 1. The Structures of Ls-36 and Ls-45 Surfactants



Ls-36: m = 3, n = 6

Ls-45: m = 4, n = 5

J. Liu, B. Han, Z. Wang, J. Zhang, G. Li, and G. Yang. *Langmuir* **2002**, 18

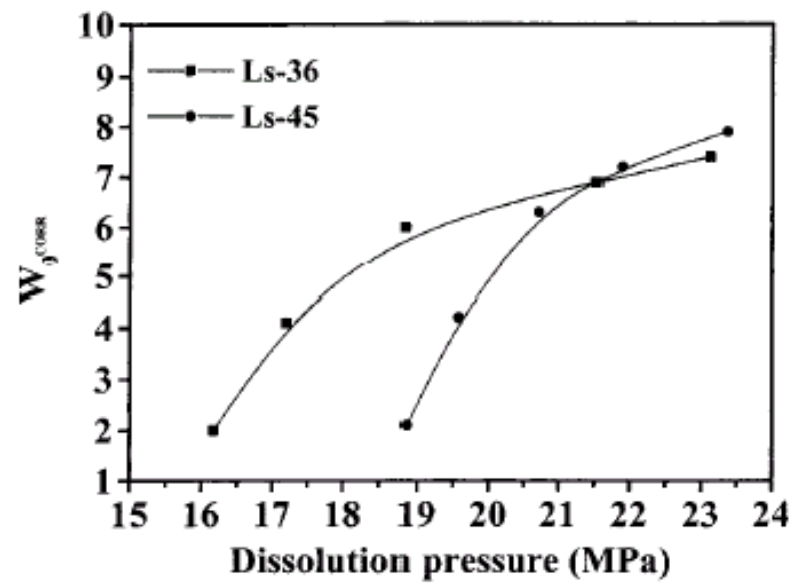


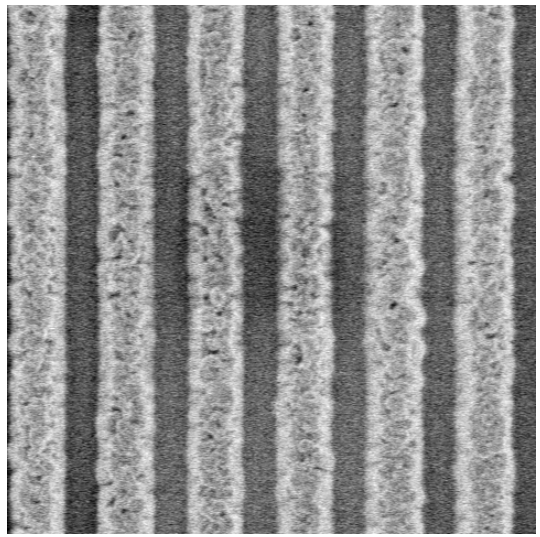
Figure 3. Loading water of 0.02 M Ls-36/H_2O/SC CO_2 and 0.02 M Ls-45/H_2O/SC CO_2 systems at 308.2 K and different pressures.

Difficulties / Concerns

- Although there do exist methods of calculating solute solubility in SCFs, these methods may be cumbersome and impractical to apply to polymers.
- Qualitative methods do exist (GC column, solubility triangle, etc.) but they have limitations of their own.
- A rapid screening technique / predictive tool would be a great boon to the art of supercritical fluid processing / extraction.
- Some of the cosolvents that are being used are still not optimal. Cosolvents that are truly environmentally benign may not be effective.

A Look at an Ongoing Project: Replacing the Ashing Step with $scCO_2$

- The ashing step in a semiconductor plant is required to remove residual resist, barc, etc. from the wafer after etching.
- Is it possible to replace this ashing step with CO_2 and a cosolvent / surfactant?



Sample pattern that has been etched, but not ashed. Magnification of 100X Image courtesy of Phil Matz, Texas Instruments.

Outlook and Conclusions

- $scCO_2$ is a unique solvent that embodies many of the qualities that manufacturing may be interested in.
- By adding small volumes of cosolvents, the thermodynamic properties of a SCF mixture can dramatically change.
- We has shown that $scCO_2$ and cosolvents can be used together in order to develop a negative-tone photoresist.
- Conditions have yet to be optimized, and an improvement in resolution is expected in the near future.

Acknowledgements

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Cornell Center for Materials Research (CCMR)

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The entire Ober Group (Cornell University)

Prof. Karen Gleason and Jessie Mao (MIT)