

Recent Advances in Photoresist Processing Using Supercritical CO₂

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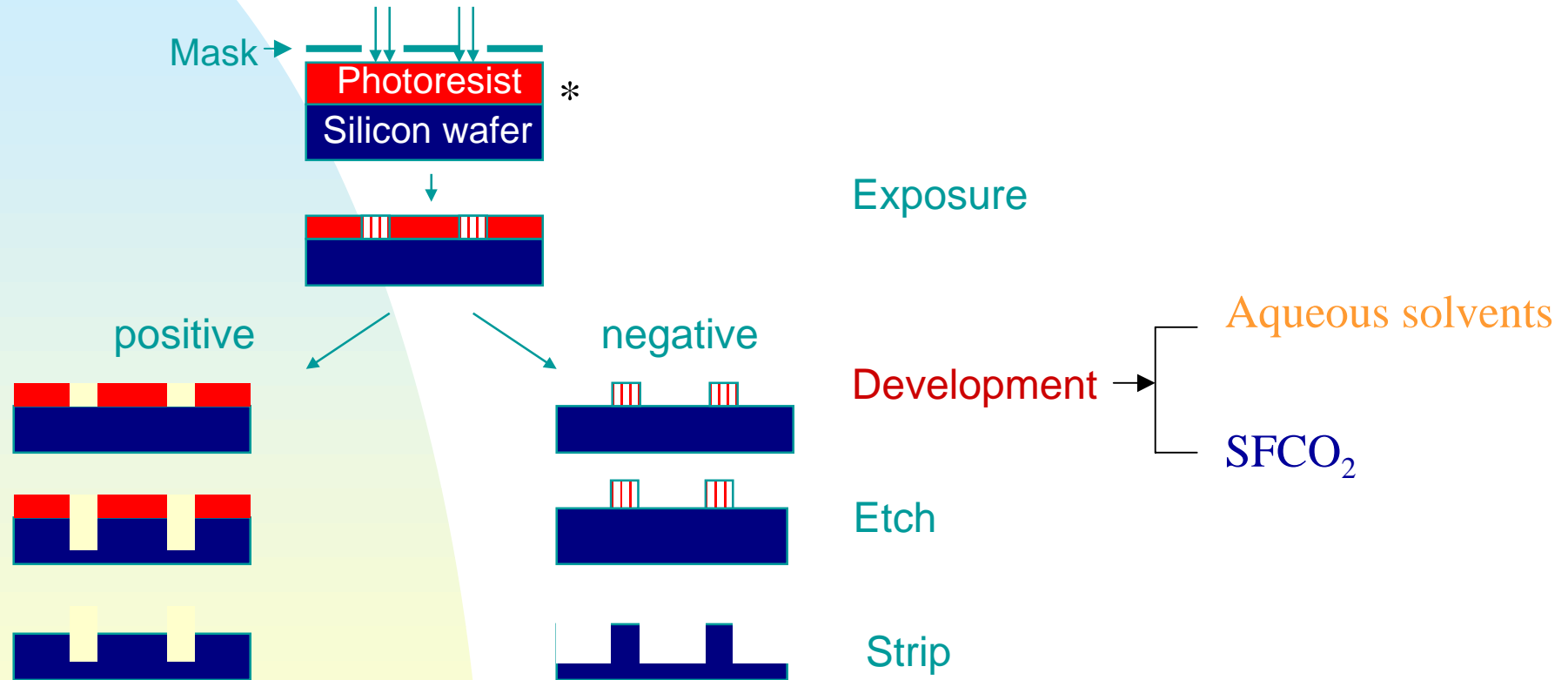
Uniqueness of Our Research

- Our Research Interests:
 - ❖ Completely solventless processing with SFCO_2
 - ❖ All dry, resistless, solventless lithography for low- κ dielectric patterning

Topics of Presentation

- General Overview of Lithographic Process
- Recent Achievements:
 - ◆ Fluorinated Resists
 - ◆ Patternable Low- κ Dielectrics
(Gina L. Weibel (Cornell), Hilton Pryce Lewis (MIT))
- Dissolution Rate Measurements in SFCO_2
 - ◆ Equipment design
 - ◆ Issues anticipated
 - ◆ Early results
- Summary

General Overview of the Lithographic Process



* **Chemically amplified resists** contain Photoacid Generators, Dissolution Inhibitors, Base Additives, Surfactants ... to aid sensitivity and performance

Advantages of SFCO₂ Processing

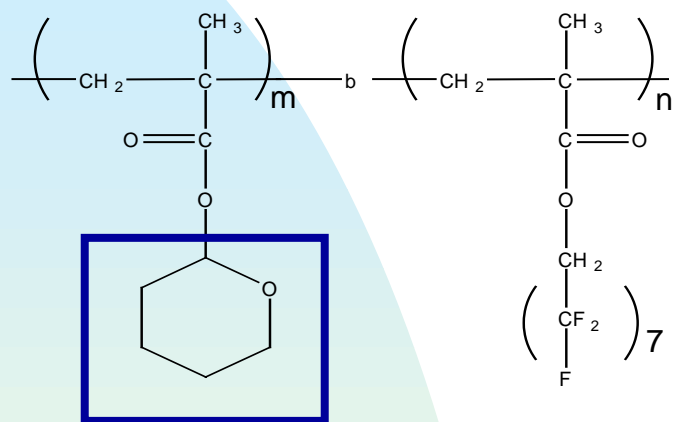
Desirable Properties of Fluorinated Resists

- ✓ E-beam Patternable (NGL)
- ✓ Transparent at 157nm
- ✓ Chemically Amplified
- ✓ CO₂ Developable

Benefits of Fluorinated Resist Processing with SFCO₂

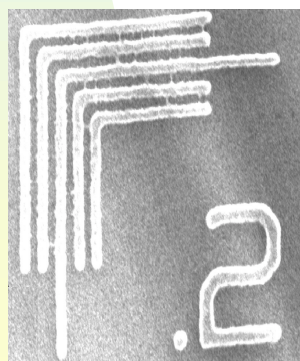
- ✓ No Solvents
 - ✦ Environmental considerations
 - ✦ Worker health and safety
- ✓ Greater Feature Properties
 - ✦ Tunable solvating power
 - Facile processing optimization
 - ✦ Low surface tension of CO₂
 - Avoid feature collapse
 - High aspect ratio
- ✓ Save Money
 - ✦ CO₂ is abundant
 - ✦ CO₂ can be recycled
 - ✦ No hazardous waste storage, disposal

Chemically Amplified, E-beam Patternable, CO₂ Developable, Negative Tone Resist



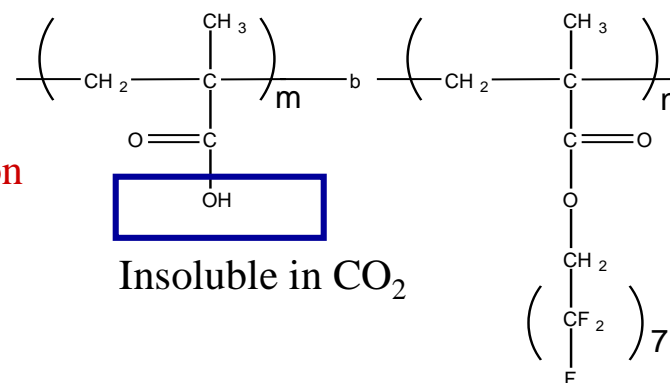
Soluble in CO₂

193nm exposure



Sundararajan, Ph.D.

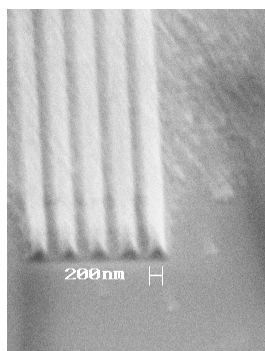
$\xrightarrow{\text{H}^+}$
Chemical
Amplification



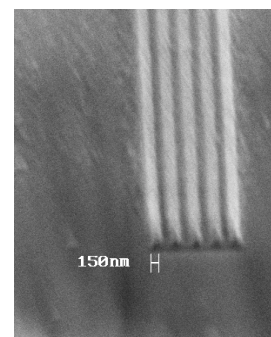
Insoluble in CO₂

* Synthesized by Sandi Hamad (Cornell Ober group)

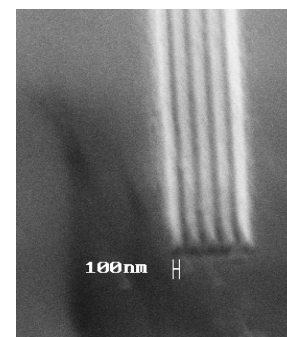
E-beam exposures



.2μ line/space

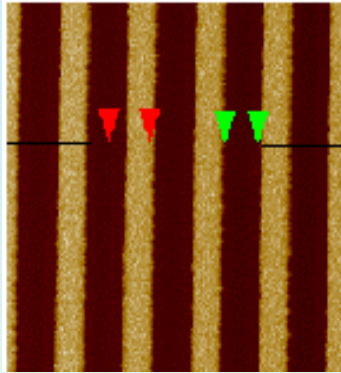


.15μ line/space

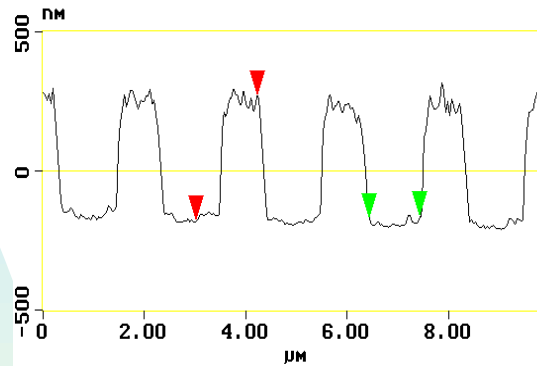


.1μ line/space !!!

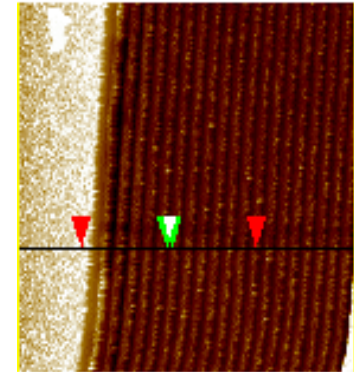
CO₂ Processing of CVD Deposited, E-beam Exposed, Low- κ Dielectric for Interconnects



1.0 μ Lines/ spaces



Cross section

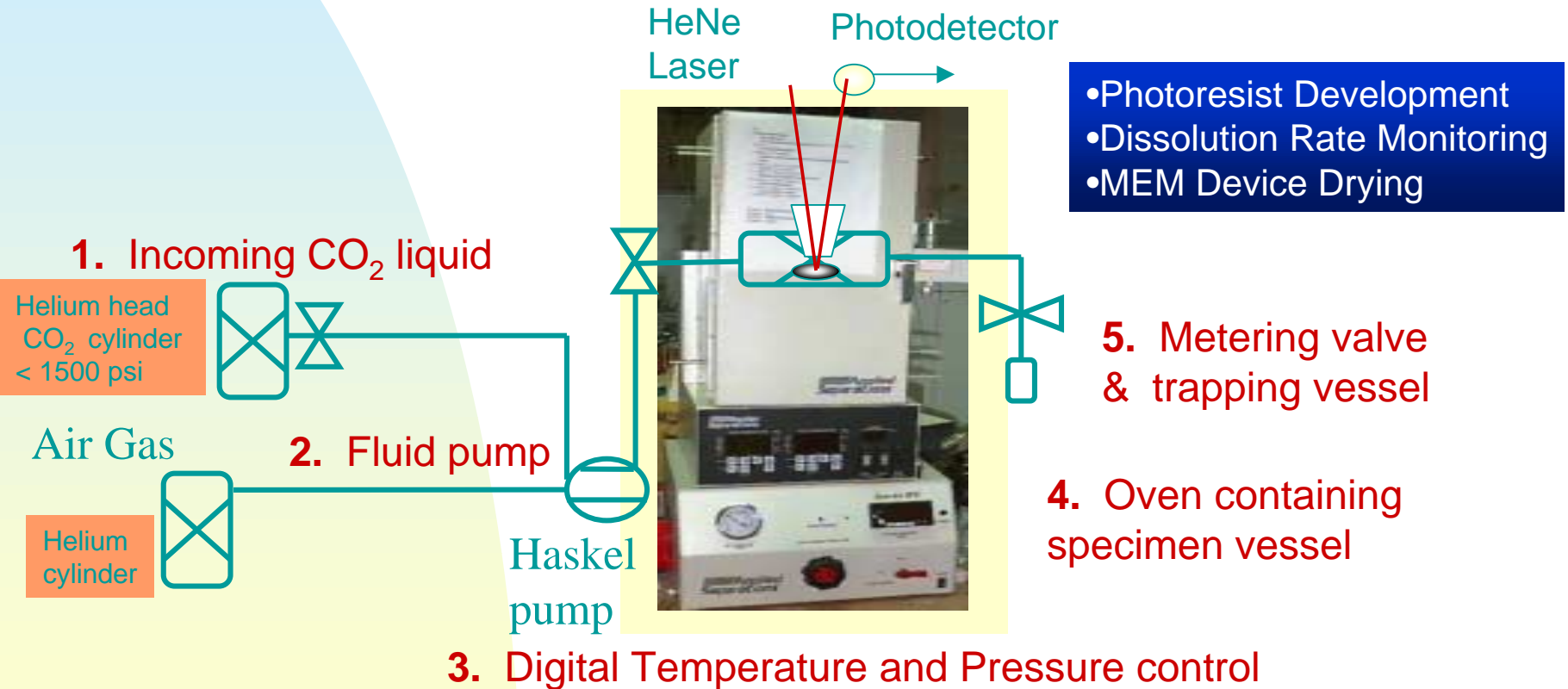


0.25 μ Lines/ spaces

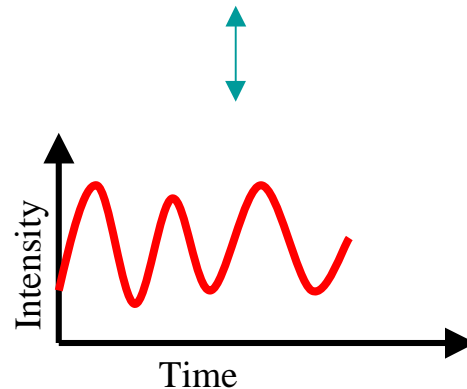
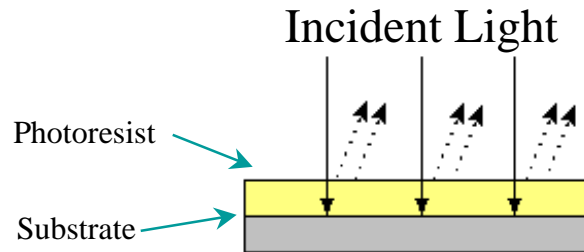
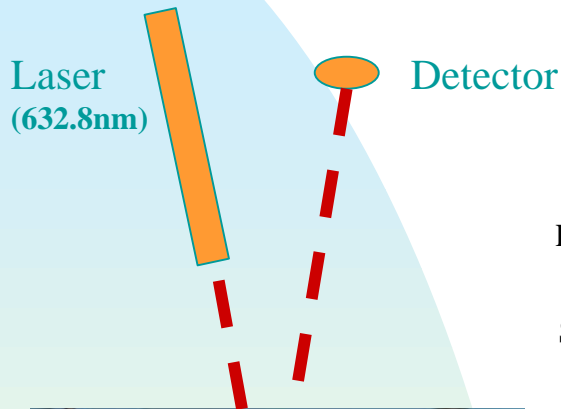
–Demonstrated patternable hot-filament CVD fluorocarbon films (HFPO)

- Film composition can be tailored
- E-beam used to effect solubility change

CO₂ Processing - Experimental Equipment



Dissolution Rate Monitor (DRM)



Interferometer

Laser reflects off
- photoresist surface
- silicon surface

Interference gives
sinusoidal pattern

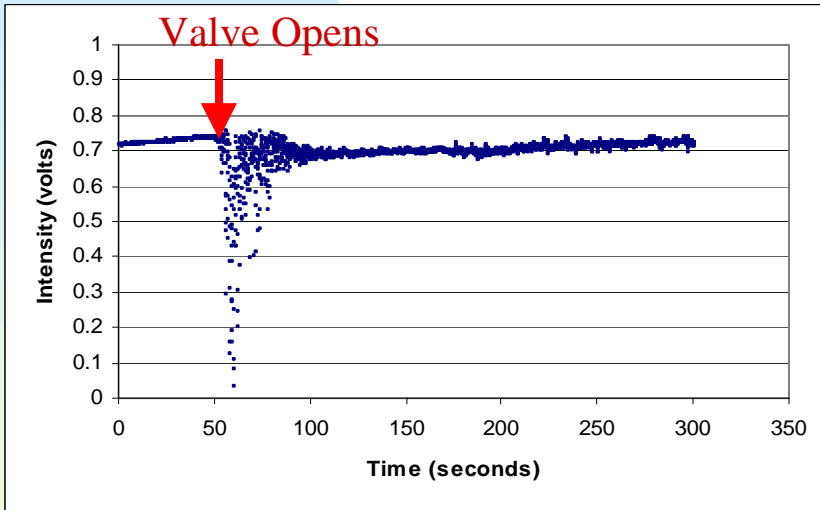
Period of oscillation
provide details on rate
of thickness change

* Dissolution rate measurement techniques in supercritical fluids
not yet firmly established

Early Results from Dissolution Rate Monitor

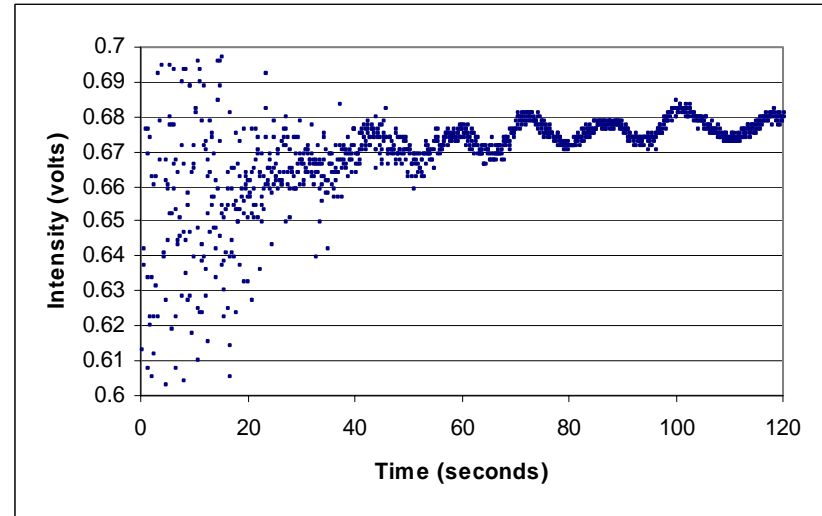
Pressure ~ 1100 psi (too low ?)

Temperature ~ 55 °C

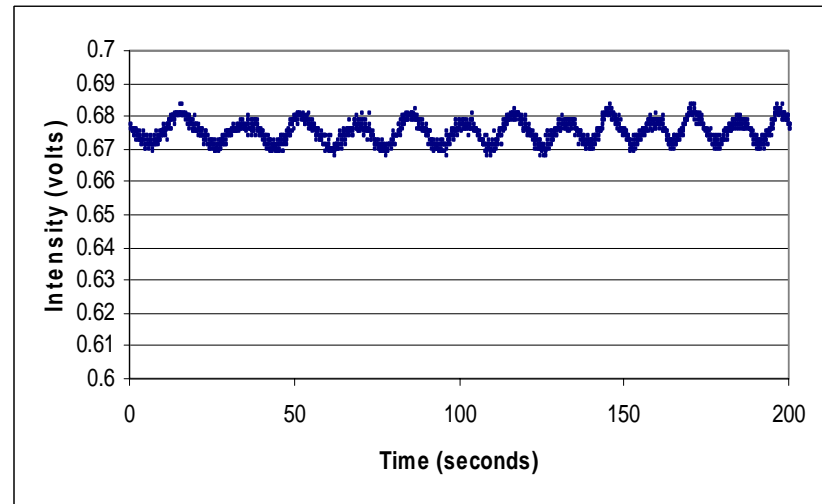


Blank silicon wafer.

Entering CO₂ scatters light
Equilibration time ~ 50 sec
Is film shrinking or swelling?



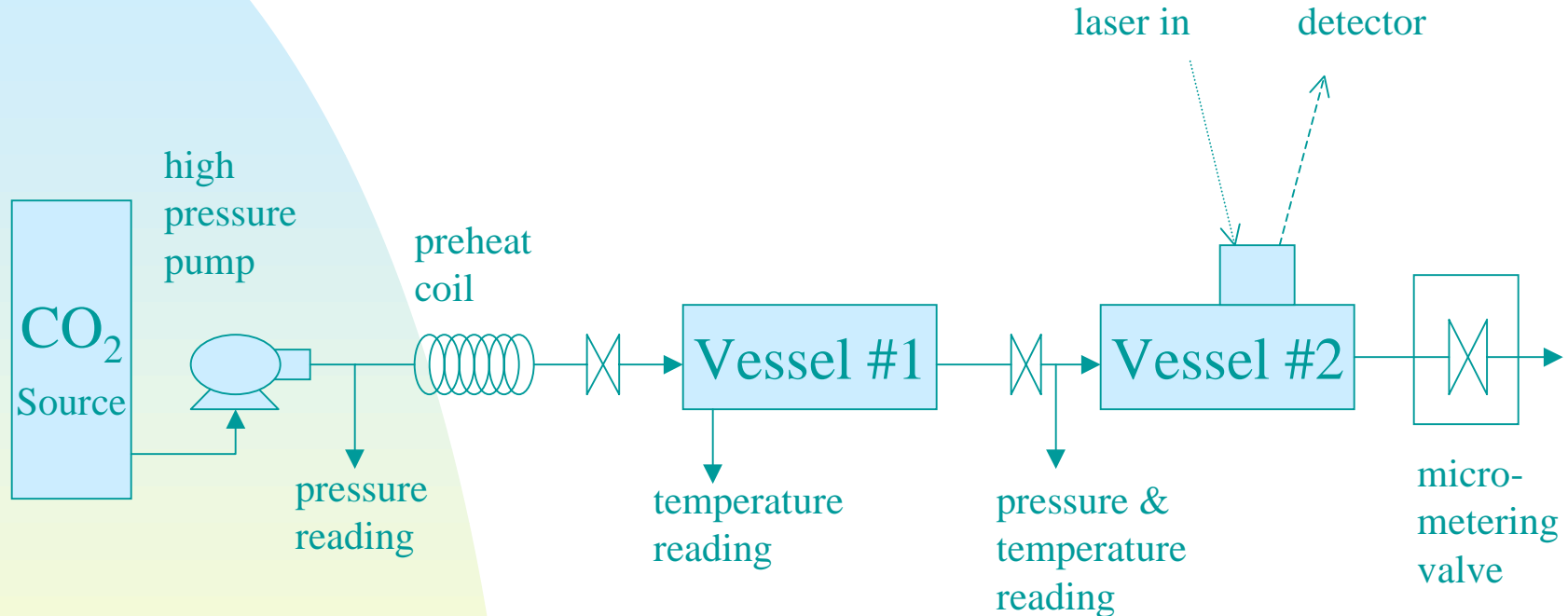
Silicon wafer coated with THPMA-F₇MA



Issues to Be Addressed

- Achieving High Pressures in Short Times
 - ◆ Currently only ~ 1100 psi under 60 seconds
 - ◆ Need a better pump system (?)
- Rapid CO₂ Equilibration
 - ◆ Pre-chamber equilibration
 - ◆ More efficient heat transfer in inlet tubes
- Impurities in CO₂ Affecting Dissolution Behavior
 - ◆ Helium head cylinder
- Understanding Physical Properties of SFCO₂ (e.g., RI as a function of pressure/temperature)

Equipment Design



- No need for Helium
- Equilibration to supercritical conditions before entering processing vessel
- Eliminate scattering by solid or liquid CO₂

Summary

- Continue to Achieve Higher Resolution Limits for Fluorinated Resist with SFCO₂
 - ◆ **E-beam exposed features of ~ 100nm**
- Demonstrated Patternable Hot-filament CVD Fluorocarbon Films
 - ◆ **Film composition can be tailored**
 - ◆ **E-beam used to effect solubility change**
- Successfully Developed CVD Polymer with SFCO₂
 - ◆ **Density/solvating power of CO₂ can be controlled**
 - ◆ **Promise of EHS benefits for semiconductor processing**
- Dissolution Rate Monitor to Provide Insights to Development Process
 - ◆ **Early results indicate potential usefulness**
 - **Phase behavior/properties of CO₂ in supercritical phase**
 - **Rate of dissolution to optimize processing conditions**
- Challenges and Issues
 - ◆ **Decouple factors that affect film thickness changes**

Acknowledgement

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