Supercritical CO_2 in Microelectronics Processing

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Outline

CO_2 Cleaning

CO_2 as a solvent
Modeling cleaning dynamics
Commercial systems

CO_2 Photoresist Technologies

Interactions of CO_2/ polymers
Commercial systems

Other Microelectronics Processing Technologies

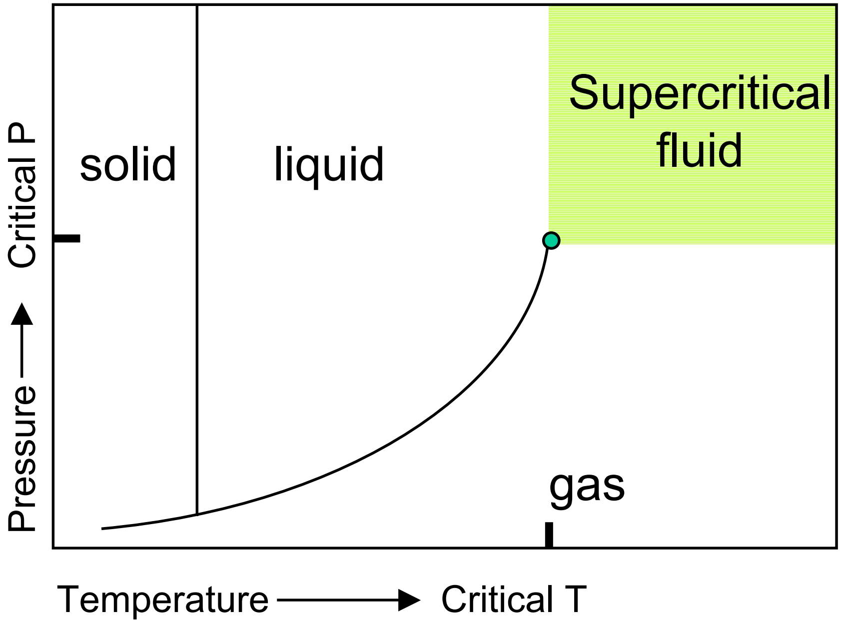
Dielectric materials/ metals/ etching & more

Ober Group Equipment & Capabilities

Co-solvent processing

The Supercritical State

Phase Diagram of CO_2



Supercritical Conditions

- 31 °C or higher
- 73.5 bar (1070 psi to 5000 psi)
- Density 200 to 950 g/l

- High & variable density
  - *Scales with P and T*
- Transport > liquid
  - *Improves contaminant removal*
- Viscosity comparable to gas
  - *Penetrates crevices*
- Tunable solvating power
  - *Varies with T, ρ, cosolvent*
- Low surface tension
  - *Penetrates and flows*

Supercritical Fluid CO_2 Cleaning

Supercritical fluids can:

Dissolve organic compounds with mid to low volatility

- If low MW materials are soluble in hexane, they are likely soluble in CO_2
- Many pure compound solubility studies are available for reference
- Solvent power increases as density increases
- T can increase dissolution (above 350 bar)

  -increase vapor P of solute

  -increase contaminant desorption
- Solubility is affected by other compounds, cosolvents or contaminants

Loosen adhered particles

- Mechanical shear forces are created by CO_2 flow
- Studies on dynamics of particle removal at high P or in SCF are available

Provide better technical results

- Prevent chemical damage to substrate or features
- Prevent pattern collapse or mechanical damage
- Prevent environmental waste

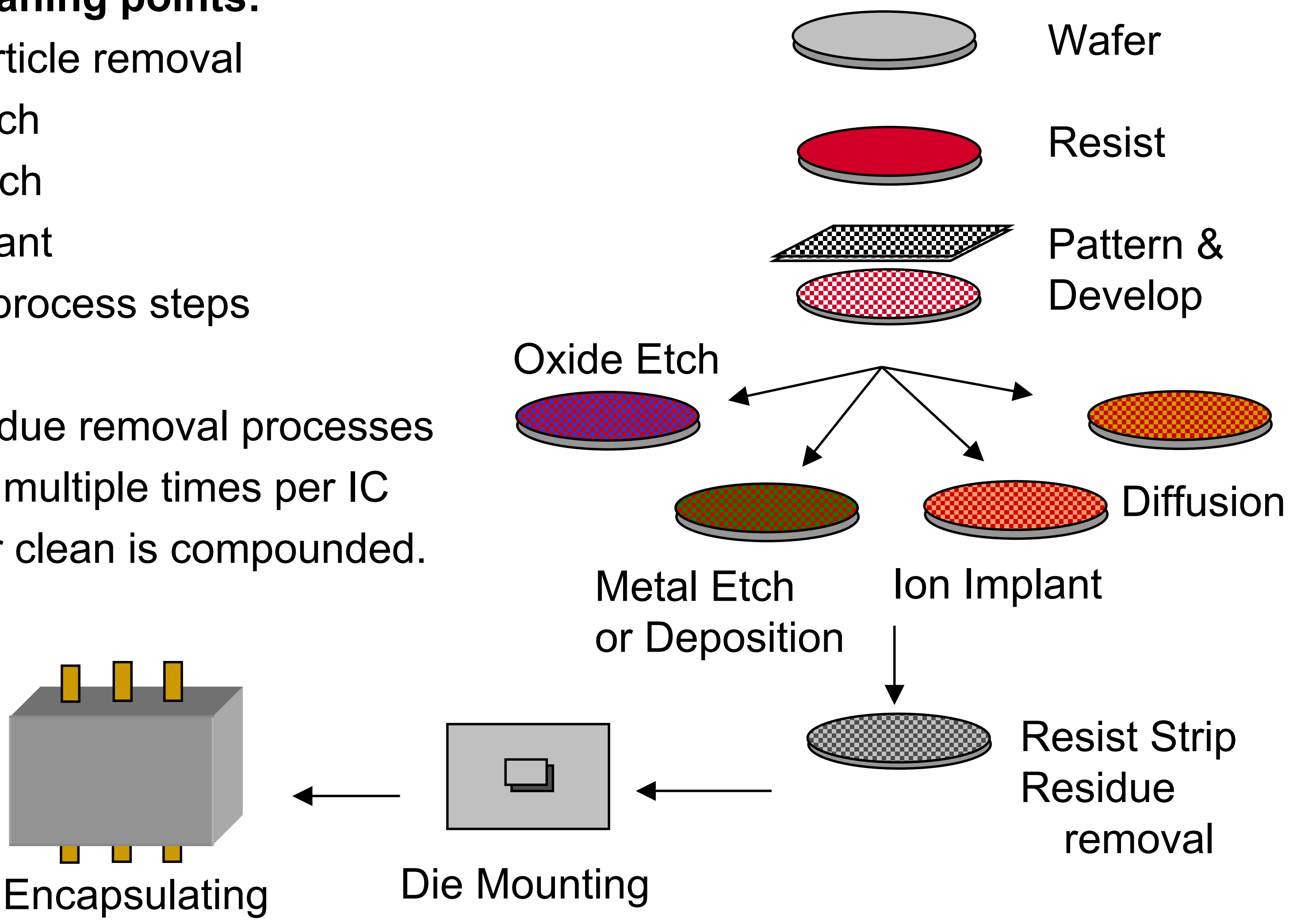
Cleaning at Multiple Points

IC process cleaning points:

- Pre-resist particle removal
- Post oxide etch
- Post metal etch
- Post ion implant
- Damascene process steps

Impact:

- Particle / residue removal processes are repeated multiple times per IC
- Cost/ time for clean is compounded.



Wafer

Resist

Pattern & Develop

Oxide Etch

Metal Etch or Deposition

Ion Implant

Diffusion

Resist Strip Residue removal

Die Mounting

Encapsulating

Traditional Cleaning Methods

Common Methods:

- Ultrasonic clean
- High-pressure jet scrubbing
- Plasma ashing
- Wet chemical stripping

Impact:

- Combination of **chemical/ physical** equipment usually required (& can *damage* material)
- Aqueous methods require long drying, water usage, flash rusting
- Cleaning and waste expenses are high
- Environmental impact is high
- SCF clean can reduce number of process steps

Cosolvent Addition

An excellent way to lower stringent solubility requirements:

- Liquid cosolvent increases density; reduces free volume difference between contaminant (polymer) and SCF
- Cosolvent can provide polar interactions or H-bonding to expand region of miscibility

But:

- Too much cosolvent added can lead to cosolvent-cosolvent bonding that reduces polymer miscibility
- Phase diagrams for mixed -solvent systems are more complex: supercritical and liquid phases coexist or separate liquids and vapors become partially supercritical.

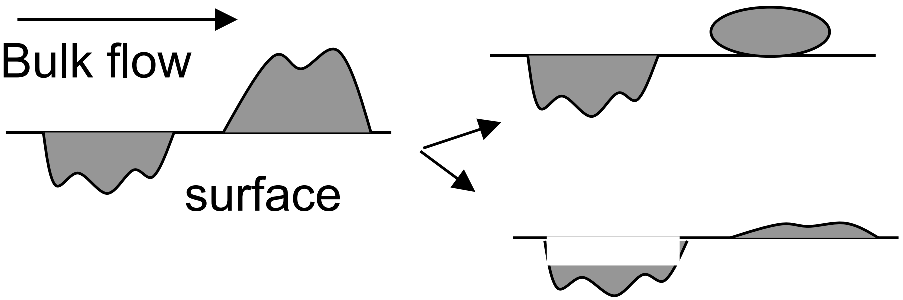
Solvent	**Nonpolar component**	**Polar component**	**Solubility Parameter**
Methanol	7.4	6.0	13.4
IPA	7.7	3.0	10.7
Hexane	7.2	0	7.2
CO_2	7.2	0	7.2

Dynamics of SCF Cleaning

Theory and Experimental Results

- Contaminant removal was modeled based on partitioning phenomena
- SCF can penetrate high aspect ratio vias/trenches
- Boundary layer can be minimized by flow, turbulent mixing, or compression cycles
- Incomplete cleaning may occur when surface interactions dominate.
- It is important to optimize P, T, cosolvent and flow simultaneously
- Small samples may not benefit from effect of mixing
- D_L may be the limiting component and unaided by SCF characteristics

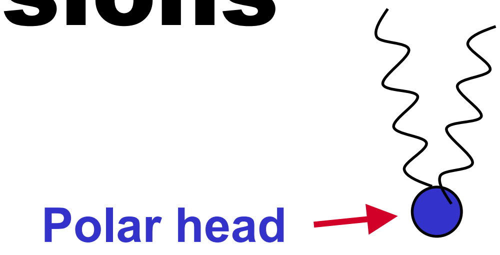
Incomplete Cleaning



High intramolecular attraction, not sufficiently soluble

$P_{SL} > P_{LF}$, sorption to substrate

Reverse Microemulsions

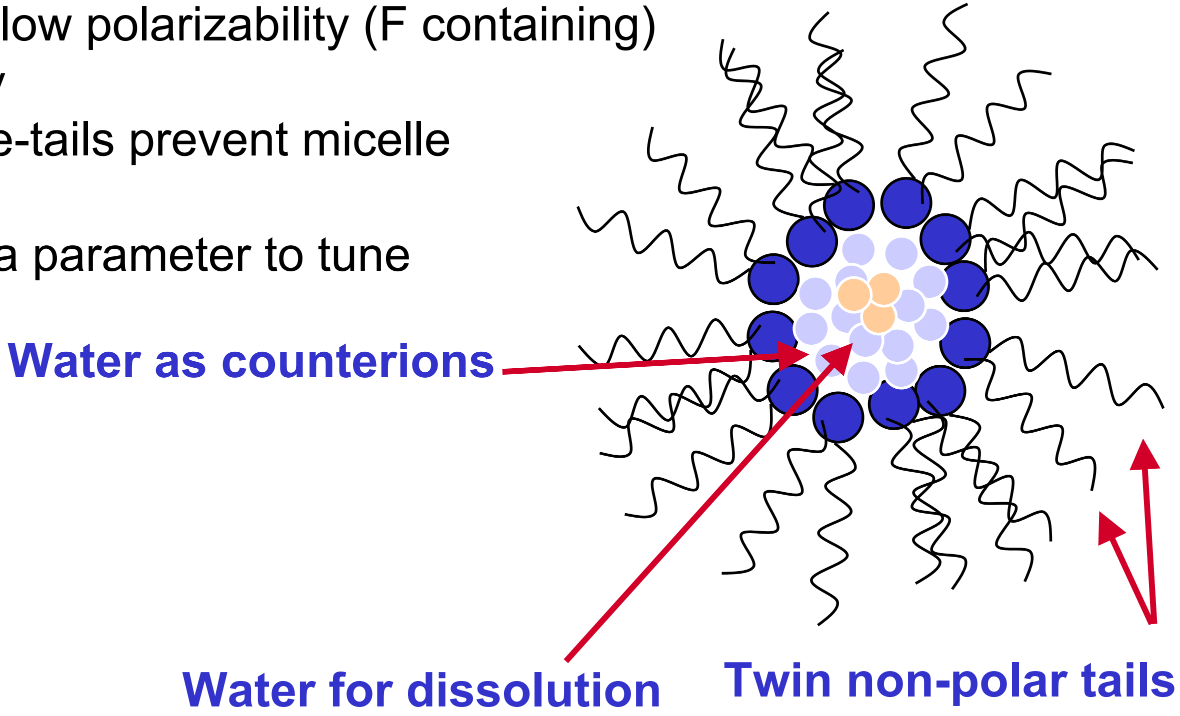


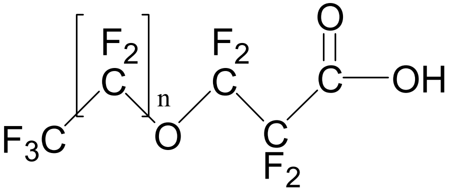
Objectives

- Can dissolve polar or ionic species
- Adds a 2nd solvent environment
- Is an alternative (& lower volatility than) to cosolvents
- Final wash with pure CO_2 removes residues

Accomplishments

- Molecules generally have low polarizability (F containing) & lewis bases for solubility
- Rigid fluoro-chains, double-tails prevent micelle coalescense
- Water : surfactant ratio is a parameter to tune





Fluoroether carboxylate

Supercritical CO_2 Resist Strip

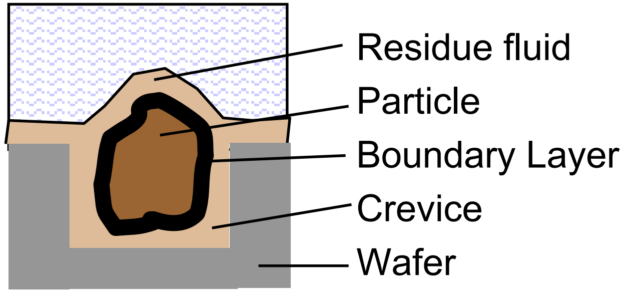
Los Alamos National Lab/ Hewlett Packard - Craig Taylor
Supercritical Systems (Tokyo Electronic) - M. Biberger
SC Fluids, Inc (GT Equipment Tech.) - David Mount
IBM - McCullough

Objectives:

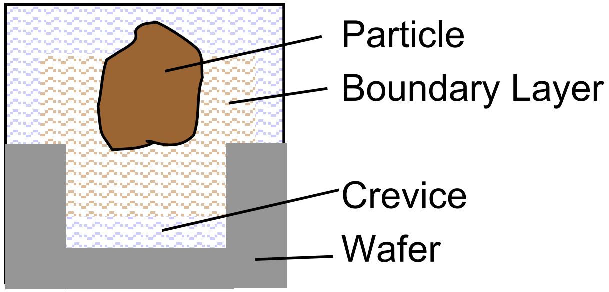
- Eliminate water & waste of wet-stripping
- Shorten strip time, lower costs, *one tool only*
- Provide cleaning alternative for water or temperature sensitive materials

Accomplishments:

- Organic contaminants removed without altering substrate surface (proven successful post oxide or metal etch)
- CO_2 with 0.5% to 1% cosolvent
- Pulsed flow system and/or low viscosity of SCF for effective particle removal
- Final rinsing in pure CO_2 removes any residue
- Dry-in/ dry-out is modular with CVD or etch tools



1200 psi



800 psi

pulse flow particle removal

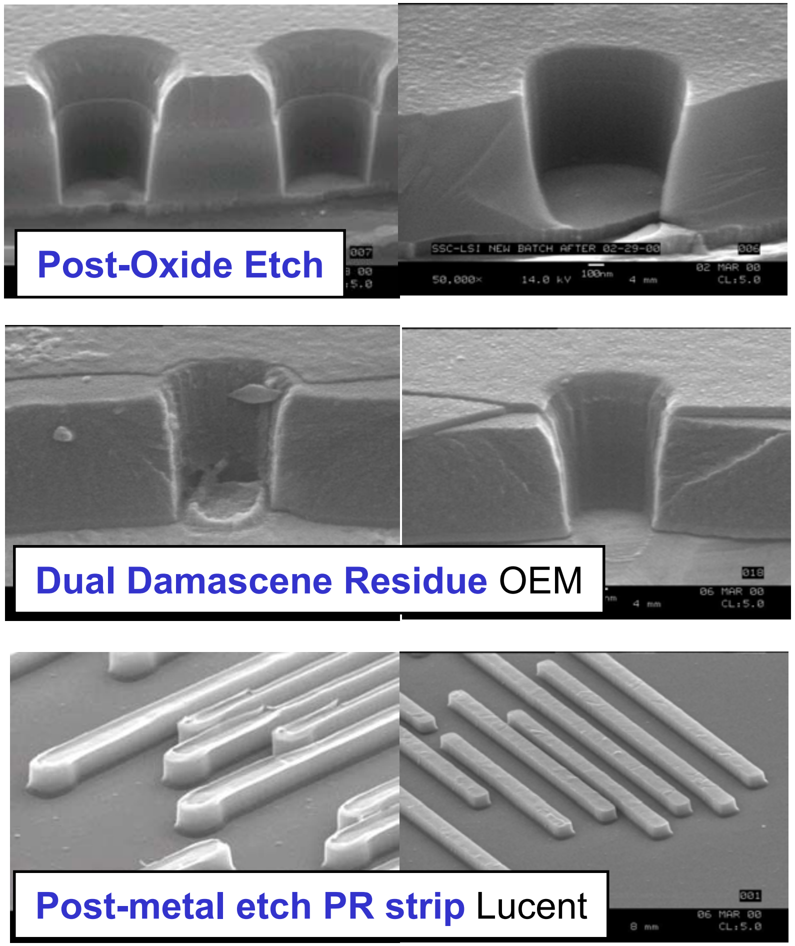
Schumacher, S&K Products

Supercritical CO_2 Resist Strip

Supercritical Systems (Tokyo Electronic) - M. Biberger

Accomplishments:

- Successful resist removal post oxide etch
- Successful residue removal in dual damascene process
- Resist removal post-metal etch does not damage underlying structure
- XPS spectra confirm residue removal
- FTIR/ AFM of low-k materials indicate no structural or chemical changes (except drying) = SiLK
- If diffusion of CO_2 from porous low-k is too slow, surface structure indicates swelling



Post-Oxide Etch

Dual Damascene Residue OEM

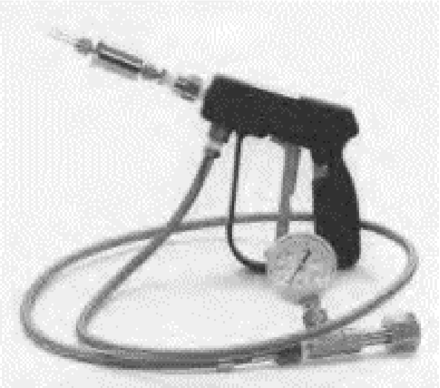
Post-metal etch PR strip Lucent

Before **After**

CO_2 Snow Cleaning

Applied Surface Technologies, Eco-Snow, Va-Tran, Millenium Automation

www.co2clean.com



Objectives:

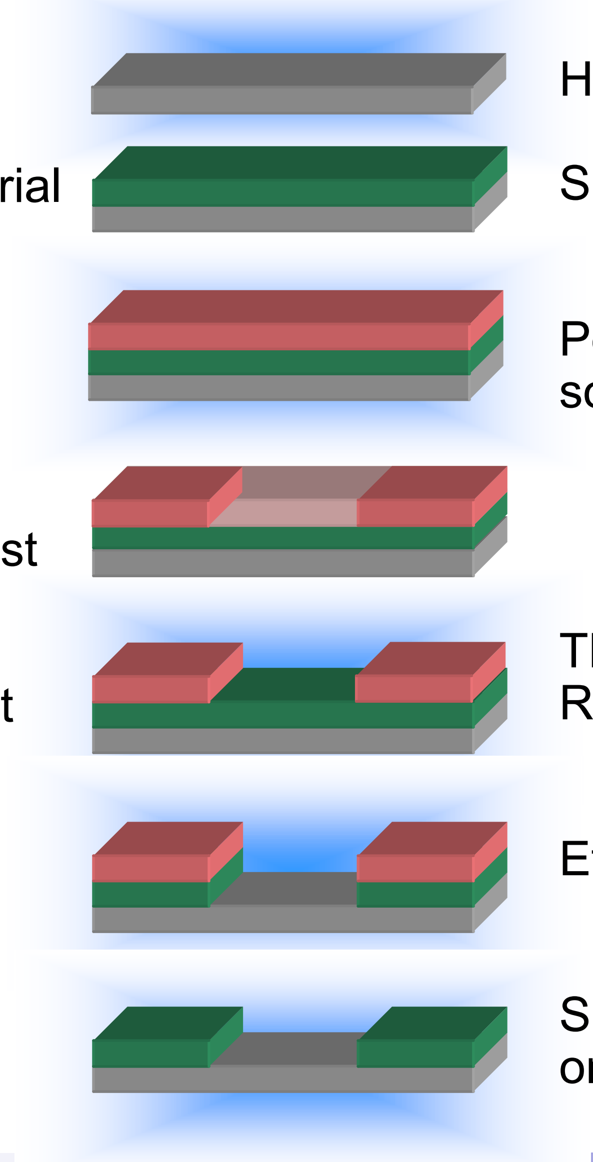
- Based upon the expansion of either liquid or gaseous carbon dioxide through an orifice
- Small dry ice particles and a high velocity gas carrier stream for mechanical particle removal

Accomplishments:

- Nondestructive, nonabrasive, residue-free, no chemical waste
- Micron and submicron particles are removed by momentum transfer
- Hydrocarbon contaminants removed by freeze fracture mechanism or via transient solvent
- Multiple commercially available systems

http://www.ecosnow.com/

Resist Technologies go Green



Prime	HMDS or organic ARC
Deposit dielectric material	Spin-on or CVD
Spin-coat sacrificial photosensitive resist	Polymer dissolved in organic solvents (PGMEA)
Selectively expose resist	
Remove exposed resist (positive-tone)	TMAH Developer Rinse
Etch to transfer pattern	Etch to transfer pattern
Remove resist material	Sulfuric acid + H_2O_2 or organic solvents

CO_2/Polymer Interactions

Polymers undergo CO_2 sorption and swell:

- lowers T_g, plasticizes
- induces crystallization
- increases T_m
- accelerates absorption of small molecules that desorb slower than CO_2

Dissolution *of* and *into* polymers occurs simultaneously:

- Only amorphous regions of polymer dissolve (COOR, CN, Ph-O) in moderation can increase solubility
- Amorphous samples can be impregnated with components
- Crystalline polymers can safely be cleaned
- SCF can dissolve, then form bubbles

NO universal predictive approach exists for solubility

Photoresist Deposition

DeSimone, U. North Carolina

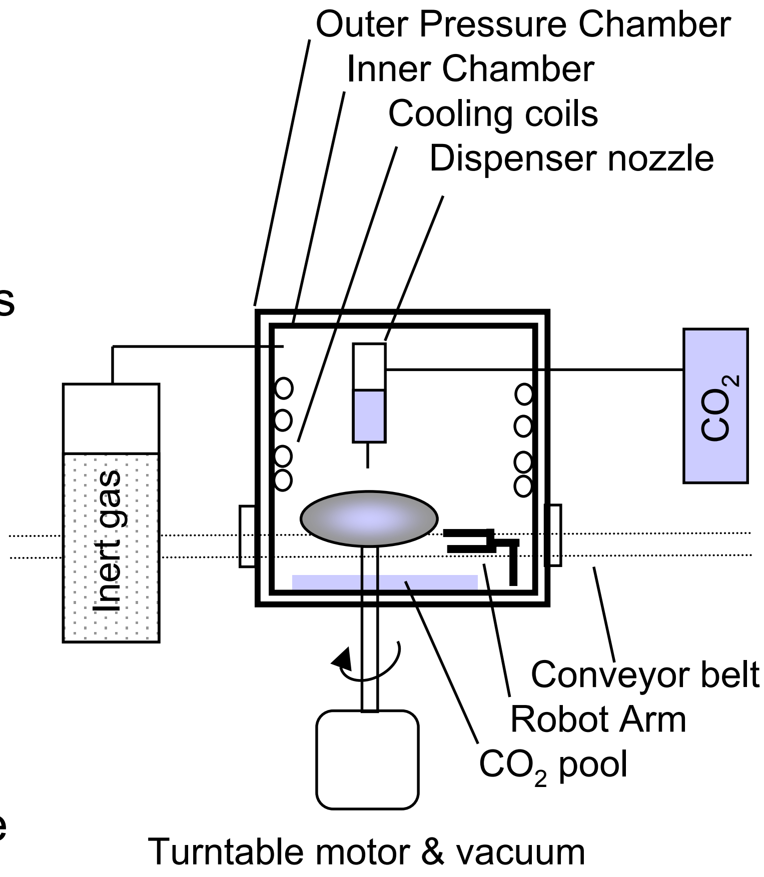
- Traditional spin-coating requires large volumes of VOCs and aqueous solvents

Withdrawal coating (dip-coating):

- Dip-coat from liquid or SCF CO_2
- Application of shear force or surfactants allows deposition of CO_2 insoluble polymers
- First phase may be a liquid melt of a polymer, swollen with CO_2
- Batch or continuous coating can be used

CO_2 Spin coating:

- Deposit possibly: photoresist, antireflective coating, dielectric, adhesion promoter, etc.
- Pressure in chamber 5,000 - 10,000 psi
- Temperature -20°C to -50 °C
- CO_2 may contain viscosity modifier, surface tension modifer, or slower-evaporating cosolvent



Preventing Pattern Collapse

Collapse = bending, fracture or peeling due to capillary forces
Capillary forces = P_A-P_W : arise from difference in surface pressure

Prevention Strategies:

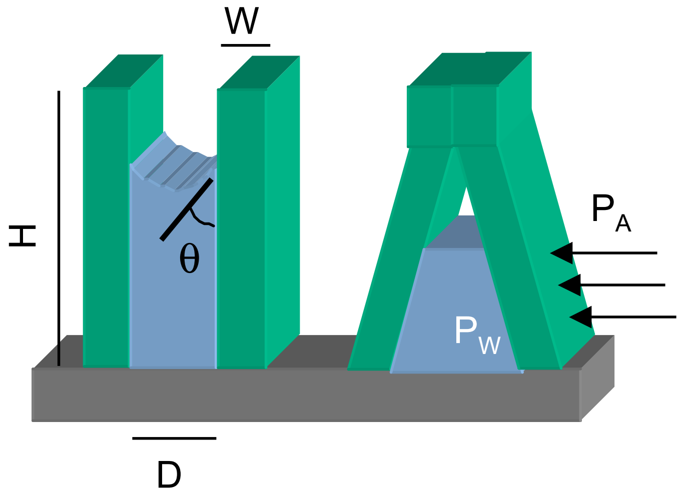
- strengthen resist (post-pattern crosslink)
- lower surface tension (low tension solvent)
- *avoid L/V interface* (use SC Fluid or freeze dry)

$$\sigma_{crit} = 6\gamma\cos\theta / D * (H/W)^2$$

Collapse occurs most frequently at high aspect ratios, narrow spacing

Results:

- Aspect ratios > 6.8 obtained
- EtOH rinsed resists easily $SCCO_2$ dried
- H_2O is not easily replaced directly with CO_2
- H_2O rinsed resists are n-hexane (surfactant) rinsed before CO_2
- H_2O rinsed resists are directly replaced with liq. CO_2 + surfactant



SC CO_2 Resist Drying

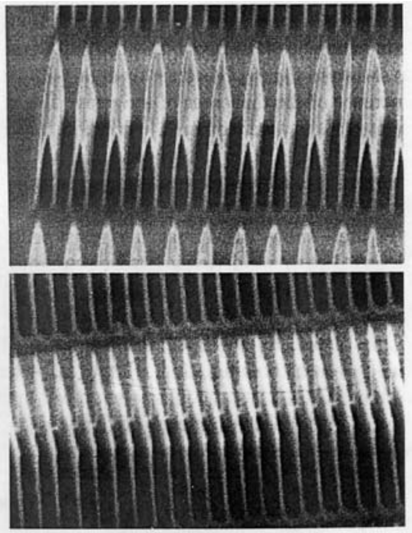
NTT Laboratories - H. Namatsu, H. Ikutsu
U. Wisconsin - D. Goldfarb

Objectives

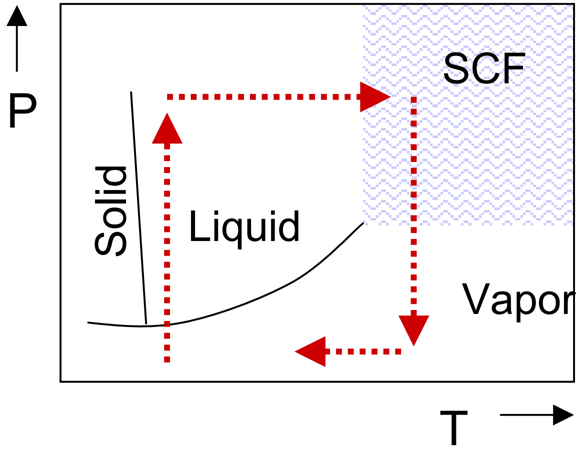
- CO_2 exchange displaces water or polar solvents
- No phase interface - eliminate capillary forces
- Single chamber development & drying of resists
- Prevent distortions of polymer via H_2O sorption

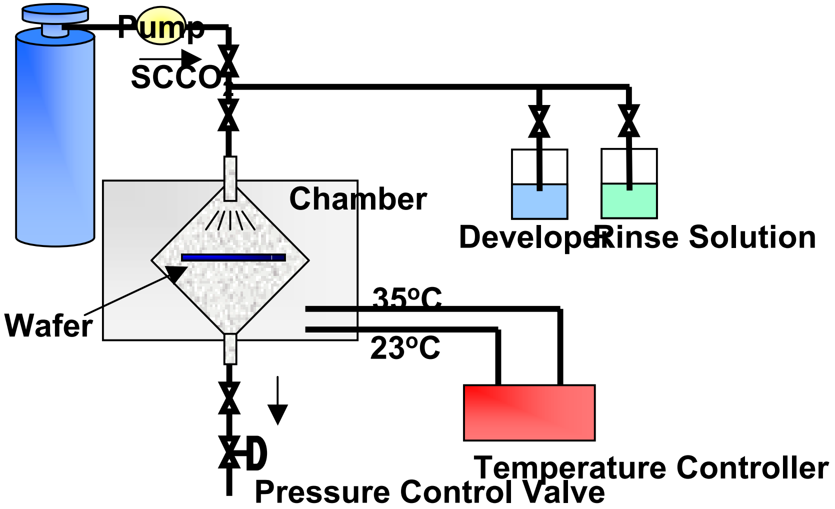
Accomplishments

- N_2/ CO_2 combination used
- Teflon lined chamber to prevent condensation
- Inject SC CO_2 to prevent water vapor



Si structures

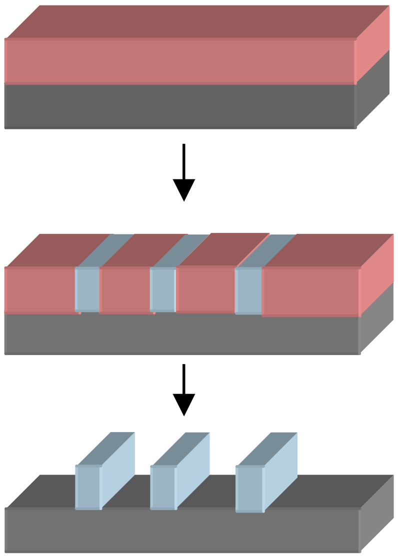




SC CO_2 Resist Development

Cornell University

N. Sundararajan, G. Weibel, V. Pham, C.K. Ober

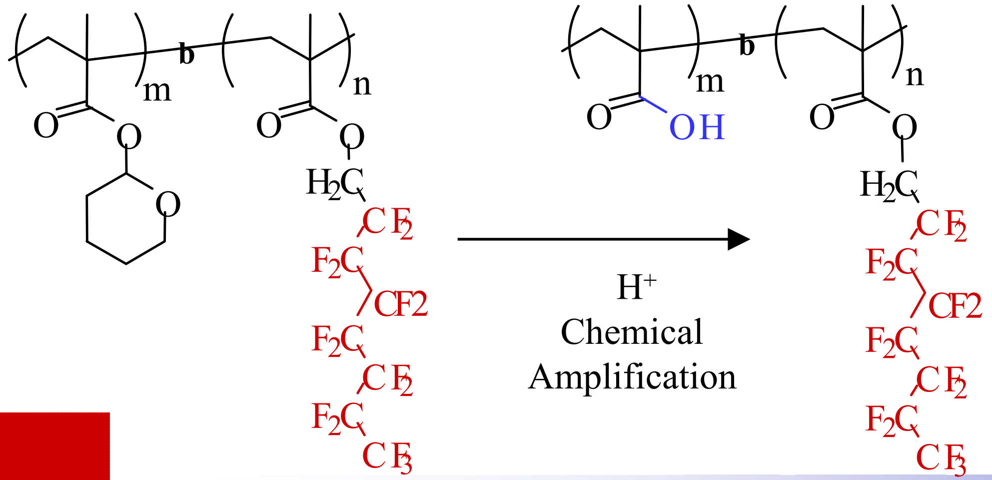


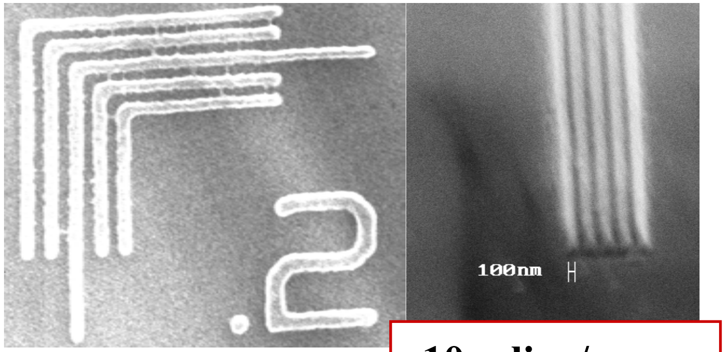
Objectives

- Direct development in SC CO_2 - no cosolvent
- Prevent pattern collapse with **no extra drying steps**

Accomplishments

- Negative-tone fluorinated resists patterned 193 nm & E-beam
- Current work to optimize development conditions and produce **positive-tone imaging**





.10 μ line/space

Microelectronics Processing Technologies

Attributes of SCF are the impetus for novel technologies that invite creation of *replacement* processing steps, rather than *modification* of existing steps.

These may take longer to implement than cleaning or drying

- fewer case studies available
- fundamental studies underway
- few or no commercial manufacturers

These may offer long-term advantages

- lower cost (though high capital cost?)
- less waste/ chemical usage
- environmental compliance
- new technological capabilities

Directly-Patternable Low-κ Dielectric

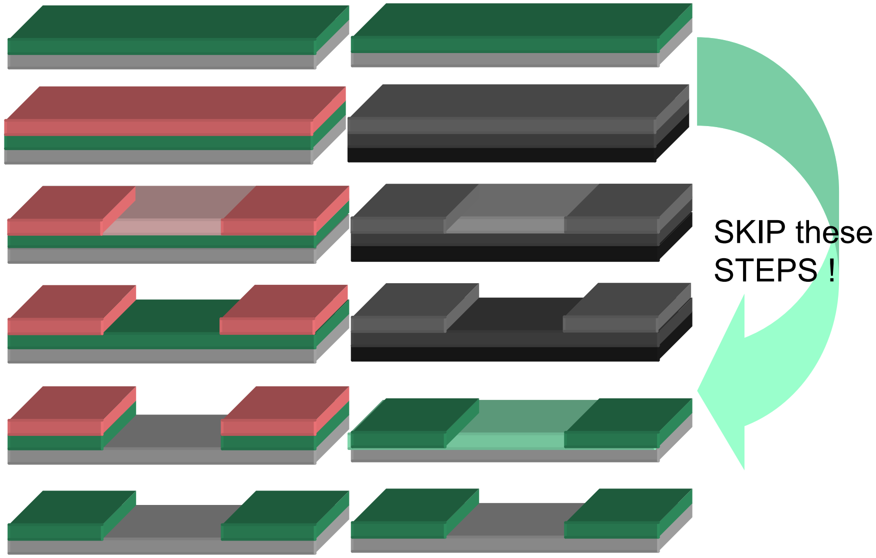
MIT, Cornell University
H. Pryce Lewis, G. Weibel, C. Ober, K. Gleason

Method:

- Fluorinated low-k materials are CVD deposited
- E-beam patterning for small (0.5 μm) features
- Development in SCCO$_2$

Results:

- Directly patternable low-κ material
- Sacrificial photoresist is eliminated
- TMAH developer is eliminated.


•Deposit dielectric material

•Spin-coat sacrificial resist

•Selectively expose resist

•Remove exposed resist

•Etch to transfer pattern

•Remove resist material

SKIP these STEPS !

Formation of Low-κ Materials

Farrar - Micron Technology

Objective:

- Reduce capacitive coupling between metal lines by providing lowest dielectric constant
- Incorporation of air into matrix $\varepsilon_0 = 1.0$
- Silica Xerogel absorbs water, stress & metal-line rupture occur

Foamed Insulating Polymers:

- Dielectric constant 1.2 - 1.8
- Metallization processing steps only are currently low enough for polymer stability
- Polyimides and fluorinated polyimides may withstand high temperatures & foam in CO_2

Metal Contamination Removal

Muscat - ERC- U. Arizona
Douglas - Texas Instruments

Conventional Metal Removal:

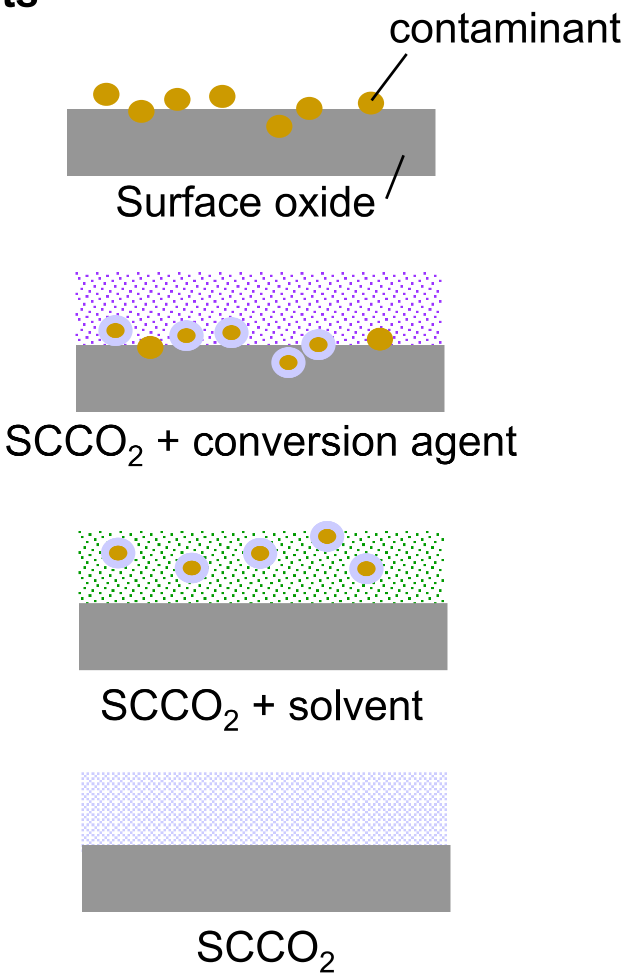
- Wet acidic process may add particles
- Wet oxidant process may add metals
- Wet chemicals are expensive/ unable to clean high aspect ratio features

CO_2 Metal Removal:

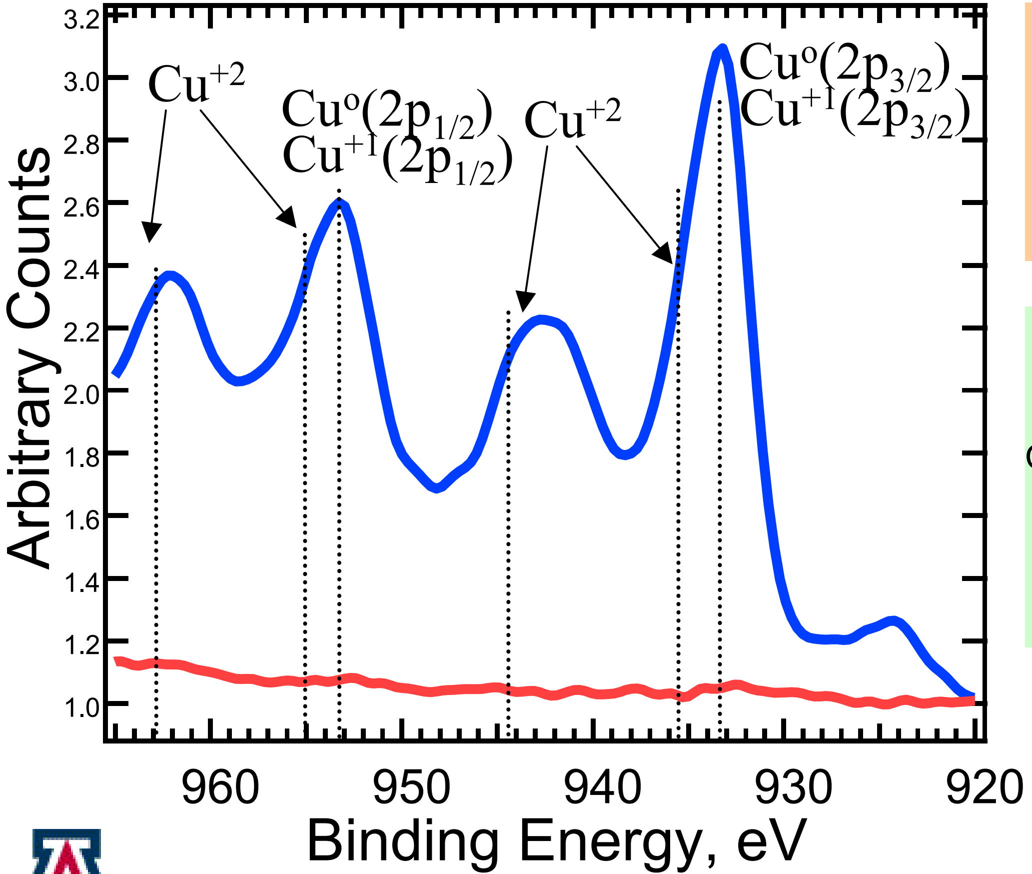
- Metal ions alone are not soluble
- Chelating agents / fluorinated chelating agents
- Modification agents (acid, base, ligand, halogen-containing)
- Solvent agents (polar or non-polar, surfactants, detergent)

Results:

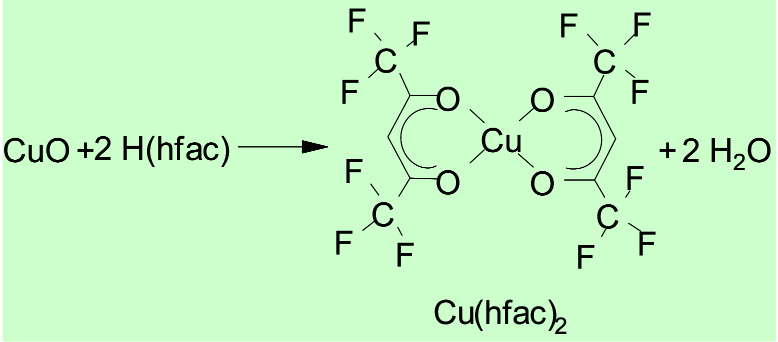
- Cu, when oxidized by Cl to Cu(II) was significantly removed by complexing with H(hfac) in supercritical CO_2



Chelator/$scCO_2$ Removes Oxidized Copper



- H_2O_2 oxidized sample
- < 60 ppm hfac
- 98% copper removed



As contaminated and oxidized

After 15 min ramp up, 2 min at 150 atm, 52°C (0.64 g/cm^3)

Bo Xie, Casey Finstad, and Anthony Muscat/University of Arizona

Supercritical Fluid Etching

Vaarstra- Micron Technology

Wet etchants for inorganic materials:

- High throughput and selectivity
- Isotropic
- Incomplete wetting may occur
- Incomplete removal of etched material
- Harsh chemicals/ requires drying

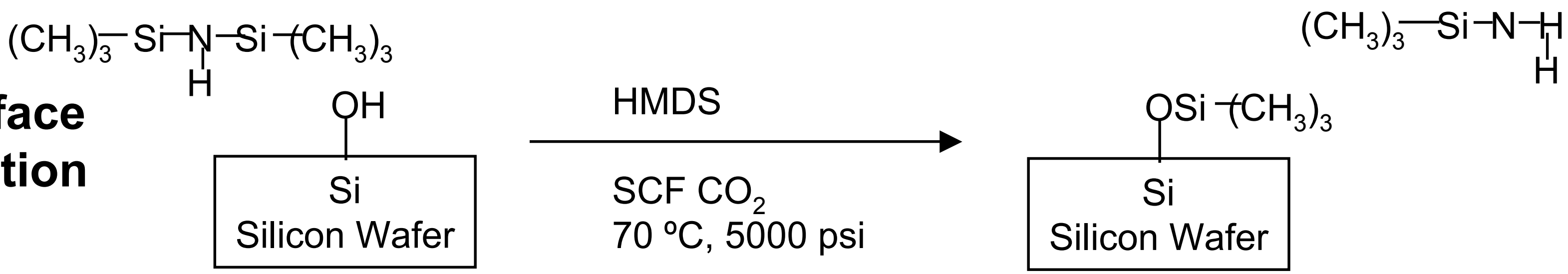
SCF Etching:

- One SC component (CO_2) + one etchant (HNO_3)
- Tailor composition to avoid resist stripping
- A SC component that etches (NH_3)
- Improved uniformity and wetting
- No drying step required

Supercritical Silylation

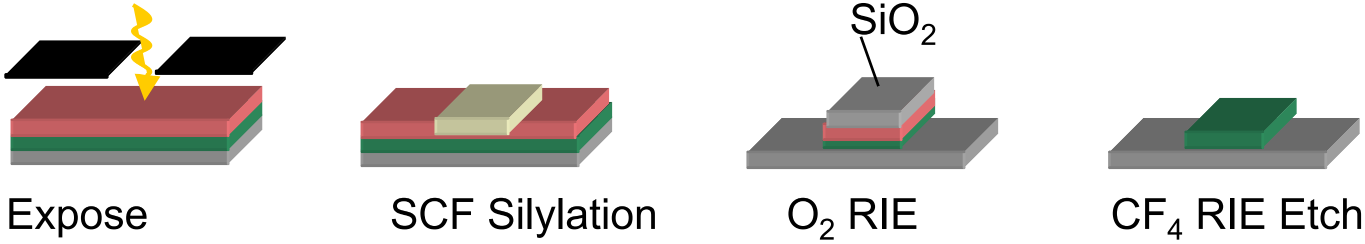
C. Cao, T.J. McCarthy - U. Massachusetts

- **For surface preparation**



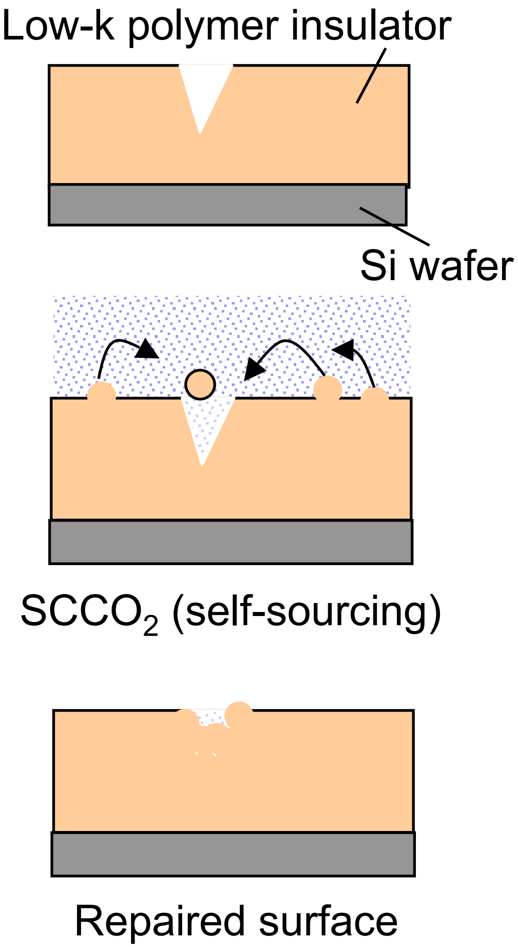
Sample	Contact Angle (water) deg.
Bare Si wafer	26
Si wafer, HMDS in gas phase YES oven	78
Si wafer, HMDS in SCF CO$_2$	87

- **For top surface bilayer imaging**



CO_2 Surface Repair

Boggs - IBM



$SCCO_2$ (self-sourcing)

Repaired surface

CMP or planarization cause scratches:

- Scratches are polished down (ineffective for deep scratches)
- Surface T increased to cause melt & flow (only on insulators with low T_m)

Supercritical Surface Repair:

- Divots, pinholes have high surface energy
- SCF allows polymer mobility to defect sites (polymer insulators)
- Polyimide, F-polymers, parylene, polyamides, polysulfones mobile at supercritical conditions
- SCF ammonia for SiO_2, Si_3N_4 fill materials

Chemical Fluid Deposition

James Watkins, U. Massachusetts

Chemical Vapor Deposition

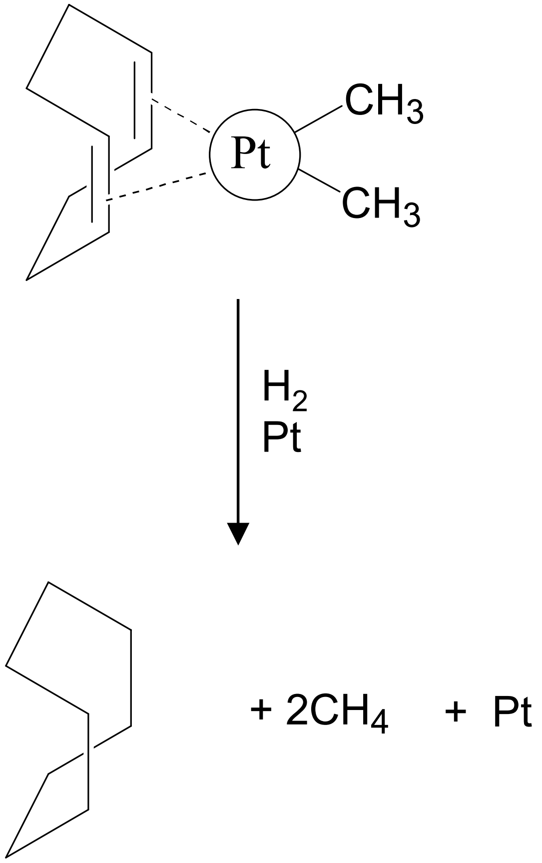
- High purity, conformal coverage
- Limited by precursor vapor P
- Requires high deposition T
- Incompatible with thermally labile substrates

Electroless Deposition/ aqueous plating

- Low T, numerous precursors
- Poor control of deposition, non-uniform
- Immiscible with reducers (H_2)

Chemical Fluid Deposition

- Chemical or thermal reduction of organometallics
- Low-T, higher reagent concentrations at surface
- Conformal coverage, good transport of ligand
- Reduction chemistry must proceed readily at low T
- Pt, Pd, Au, Rh deposited on patterned Si, PTFE, polyimide, microporous aluminum oxide



Pt film for corrosion-resistant contacts

Incorporation Into Processing

Roadblocks:

- Requirement for additives/ cosolvents deter potential users
- Economics of SCF technologies may contribute to slow rate of adoption
- Delay in mass manufacturing of SCF systems keeps prices high
- Batch process is less favorable than continuous process
- Lack of awareness of $SCCO_2$ capabilities

Motivators:

- As industry changes to new wafer size and new dielectric and new Cu process, *this is a natural time to introduce new tools*
- Dry-in, dry-out means the tools can be modular with other tools
- Superior technological results with intricate and water/ heat sensitive samples

Conclusion

- Properties of supercritical fluids have been the impetus for several modifications of and replacements for semiconductor processing steps
- Supercritical CO_2 cleaning is feasible and will likely be the first supercritical technology adopted by semiconductor fabs imminently
- Technological advantages of SCF for photoresist processing will hasten the use of CO_2 in lithography
- Novel research of new microelectronics technologies has introduced a host of new materials capabilities and new processing options to meet the long-term challenges of the industry
- Several companies have been born of new technologies - supercritical fluids have graduated from *academic curiosity* to *commercial applications*

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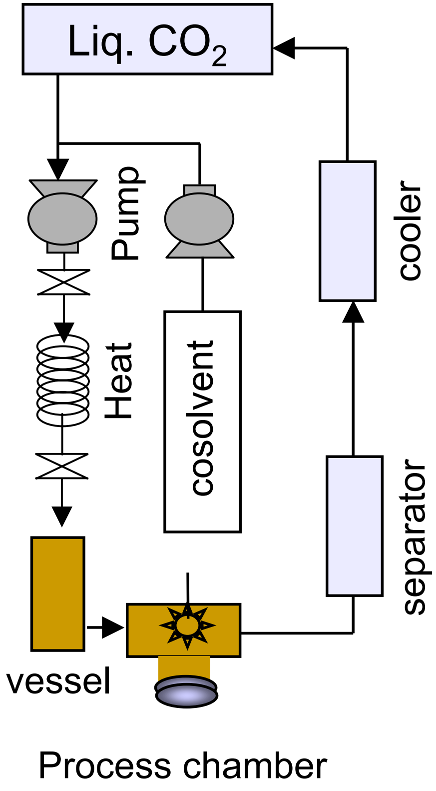
Ober Group Equipment & Capabilities

Co-solvent processing

Equipment/ Instrumentation



CO_2 source: pressurized liquid tank

Pump: Liquid pump - chiller or dip-tubes
HPLC pump and mixing lines for cosolvents

Oven: Digital controller

High pressure vessel(s): Interior Teflon lining
Pressure fluctuating diaphragm
Stir plate or paddle

Window: Cloud-point (solubility) Determination
Dissolution-rate monitoring
Small Angle X-ray Spectroscopy
Light scattering
Raman spectroscopy
Fluorescense spectroscopy

Output: Micrometering flow valves
Gas Chromatography
Mass Spectrometry
Recollection solvents or filters

SC CO_2 Resist Optimization

Cornell University

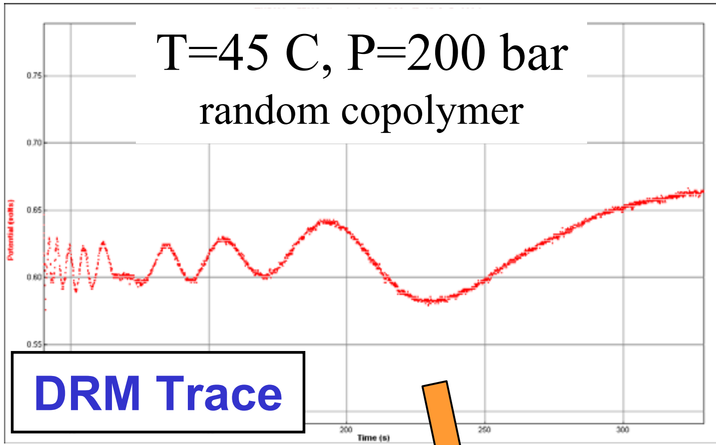
V. Pham, G. Weibel, C.K. Ober

Objectives

- Provide means for optimizing development
- Construct a window to the high-P cell

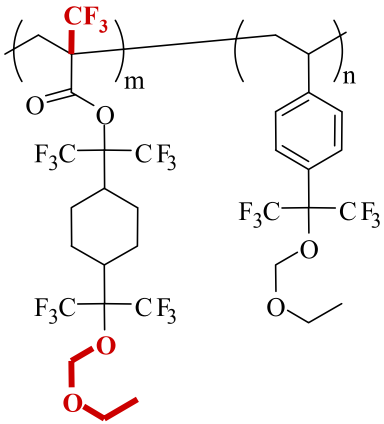
Accomplishments

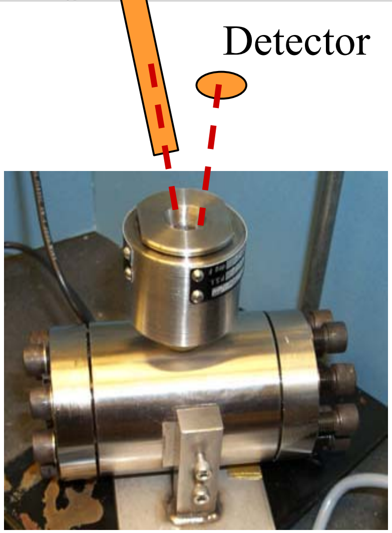
- A laser interferometric DRM was built
- Dissolution behaviors of block vs. random fluorinated copolymers were studied
- DRM will aid in determining optimized conditions for resist development
- 157 nm fluorinated resists slightly modified for SCF CO_2 development



DRM Trace

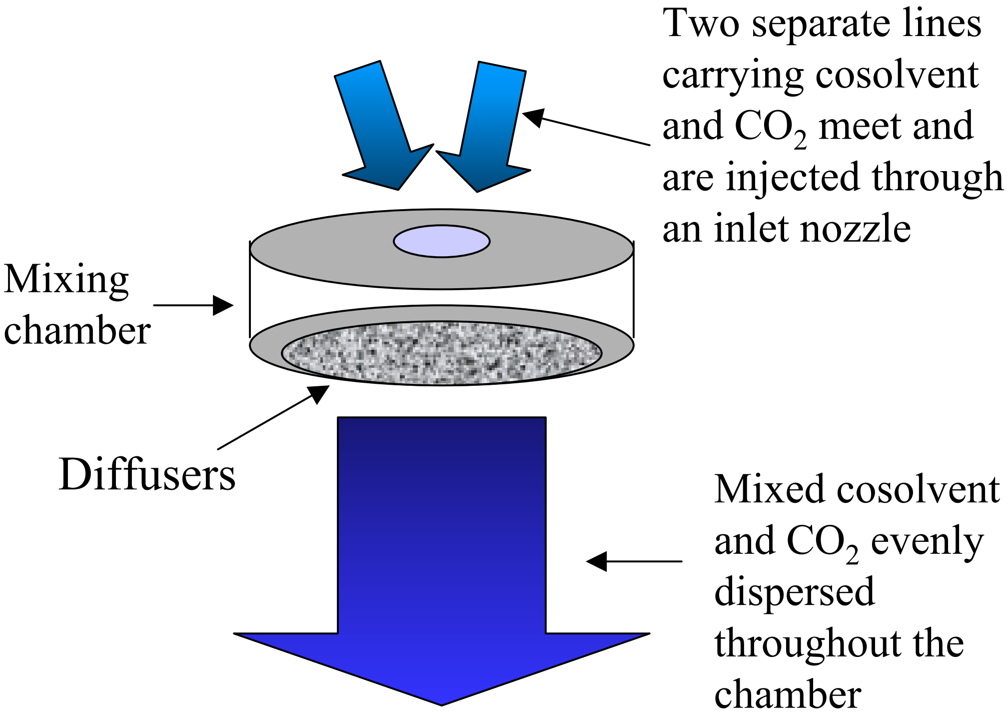
157 nm resist





Mixing of Cosolvents in $SCCO_2$ Vessel

- Total system pressurization (Mayer et al., 2002)
- Two-step addition (Ke et al., 1997)
- Stirrers
- HPLC pump addition (Ober group system)
- Diffusers inside the chamber (Ober group system)



Two separate lines carrying cosolvent and CO_2 meet and are injected through an inlet nozzle

Mixing chamber

Diffusers

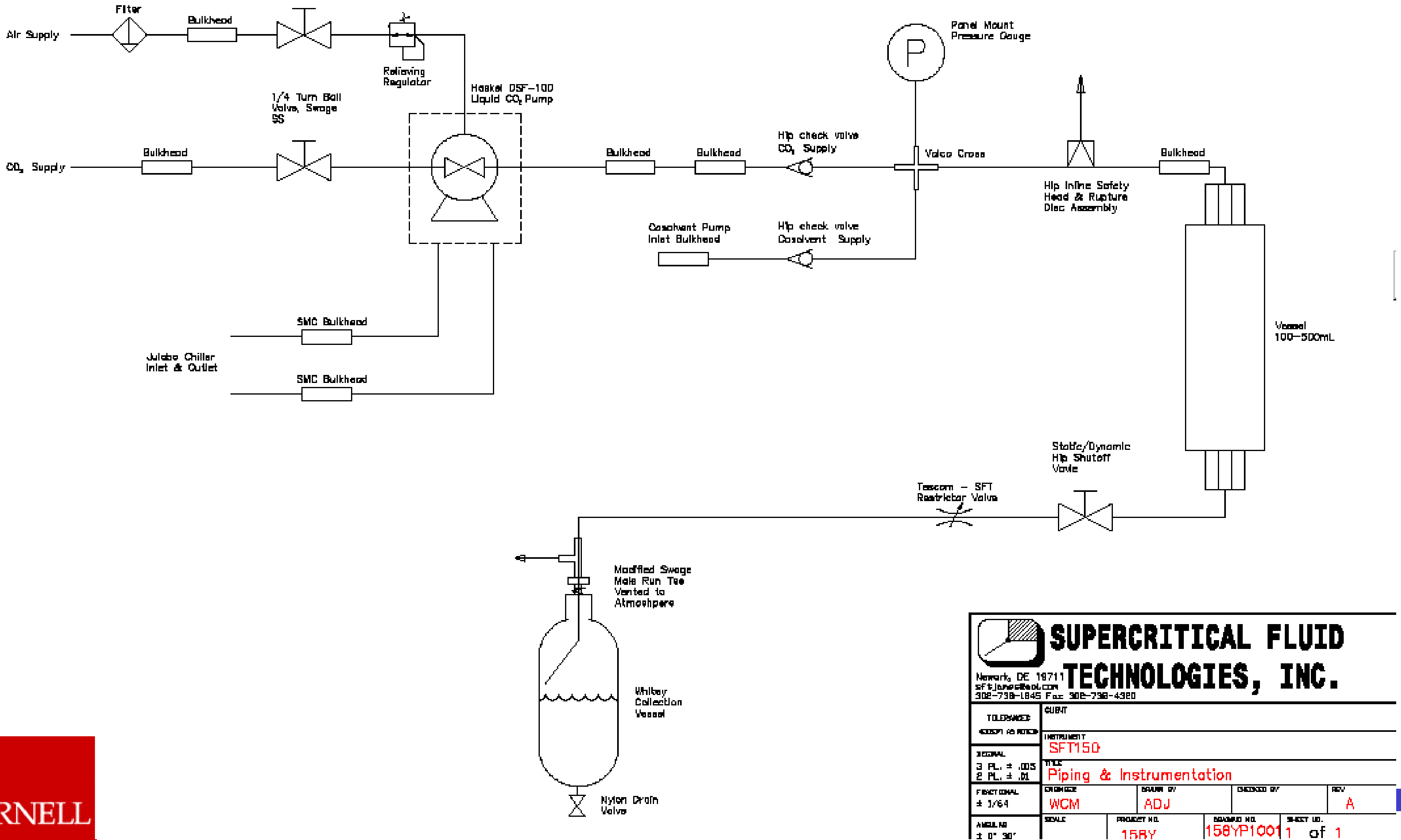
Mixed cosolvent and CO_2 evenly dispersed throughout the chamber

An illustration of the custom SFT-150 inlet diffusion ‘mesh’.

Schematic of the $SCCO_2$ System

Ober Group - Cornell

(Supercritical Fluid Technologies SFT-150)



$SCCO_2$ System Capabilities

System

- Vessel size: **100 mL**
- Maximum operating pressure: **10,000 psi.**
- Flow rates: **1 to 250 grams/min. (2 to 500 mL/min.) liquid CO2 (under standard operating conditions).**
- Temperature range: **Ambient to approximately 573 K. Accuracy within +/- 0.5 K.**

Supercritical Fluid Technologies SFT-150

$SCCO_2$ System Capabilities II

Temperature Control:

- Single resistive temperature device (RTD) located inside the processing chamber for maximum temperature sensitivity.
- An internal temperature controller prevents lags in feedback from heat transfer issues.

Pressure Control:

- An air regulator at the inlet of the system controls the pressure.

Cosolvent Injection

- A micrometer allows precise control over the amount of solvent injected

Expanding Projects at Cornell

- Understand physical/chemical interactions between surface adherents and supercritical fluid carbon dioxide for better cleaning
- Investigate thermodynamics of polymer/cosolvent solubility
- Experiment with new ESH cosolvents to improve the cleaning, development process
- Optimize techniques to reduce processing time, costs
- Determine economics of development with supercritical CO_2

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