SUPERCRITICAL CO_2 CLEANING

An Overview

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What is a Supercritical Fluid?

A supercritical fluid can be considered
as a fourth state of matter with combined properties of both,
gas and liquid.

solid
liquid
gas

supercritical

"supersolvent"

Solubility power can be modified and adapted.
Can dissolve nonpolar solids.
Is superior to conventional solvents for certain classes of chemicals.

Candidates for Supercritical Fluids

	Critical Temperature [^{o}C]	Critical Pressure [psi]
Methane (CH_4)	-82.4	667.2
Propane (C_2H_6)	96.8	616.4
Methanol (CH_3-OH)	240.1	1173.4
Isopropanol (CH_3-CHOH-CH_3)	235.8	690.4
Carbon Dioxide (CO_2)	31.1	1070.4
Ammonia (NH_3)	132.4	1646.2
Water (H_2O)	374.4	3208.2

Why Supercritical CO_2?

CO_2 has a low critical point.

CO_2 dissolves readily many substances.

CO_2's solubility power can be enhanced.

CO_2 is environmentally friendly and not rated.

Acetal
Acetaldehyd
Acetic acid
Acetic anhzdride
Acetone
Acetonitrile
Acetophenone
Acetyl chloride
Acrolein

Acrylonitrile
t-Amyl alcohol
Anisole
Benzaldehyde
Benzene
Benzonitrile
Benzoyl chloride
n-Butane
sec-Butyl alcohol
t-Butyl alcohol

2-Butanone
n-Butyl ether
Butyl oxalate
n-Butyraldehyde
Camphor
Caproic acid
Caprylic acid
Carbitol

Carbon disulfide
Carbon tetrachloride
Cellosolve
Chlorex
Chloroacetone
Chlorobenzene
Beta-Chloroethyl acetate
Chloroform
Chloromaleic anhzdride
o-Chlorophenol
Crotonaldehyde

Cyclohexane
Cyclohexanone
Diacetone alcohol
Di-sec-butylbenzene
p-Dichlorobenzene
2,4-Dichlorophenol
N,N-Dethylaniline
N,N-Diethylformamide
p-Dimethoxybenzene

N,N-Dimethylacetamide
Kerosene
N,N-Dimethylaniline
N,N-Dimethylformamide
2,2-Dimethylpentane
p-Dioxane
n-Dodecane
Ethane
Ethyl acetate

Ethyl acetoacetate
Ethyl alcohol
Ethyl benzoate
Ethyl carbonate
Ethyl chloroacetate
Ethyl chloroformate
Ethylene bromide
Ethylene diformate

Ethyl ether
Ethyl formate
Ethyl lactate
Ethyl maleate
Ethyl oxalate
Ethyl phenylacetate
Ethyl salicylate
Ethyl succinate
Ethyl sulfate
Formic acid
Gasoline

1-Heptaldehyde
n-Heptane
2,5-Hexanedione
Hexyl Alcohol
Hydrogen sulfide
4-Hydroxy-4-methyl-2-pentanone
Beta-Hydroxypropionitrile
Isopropyl alcohol

Isopropyl ether
Isocaproic acid
Limonene
Mesityl oxide
Methanol
Beta-Methoxyethanol
Methyl acetate
Methylal
Methyl benzoate
Methylcyclohexane

Methyl ethyl ketone
Methyl formate
Methyl salicylate
Methyl sulfate
Nitrobenzene
Nitroethane
Nitromethane
o-Nitrophenol
1-Nitropropane
o-Nitrotoluene

2-Octanone
p-Oxathiane (thioxane)
Paraldehyde
Phenyl isocyanide
Phosphorus trichloride
2-Picoline
Pinene
Propane
Propionaldeyde

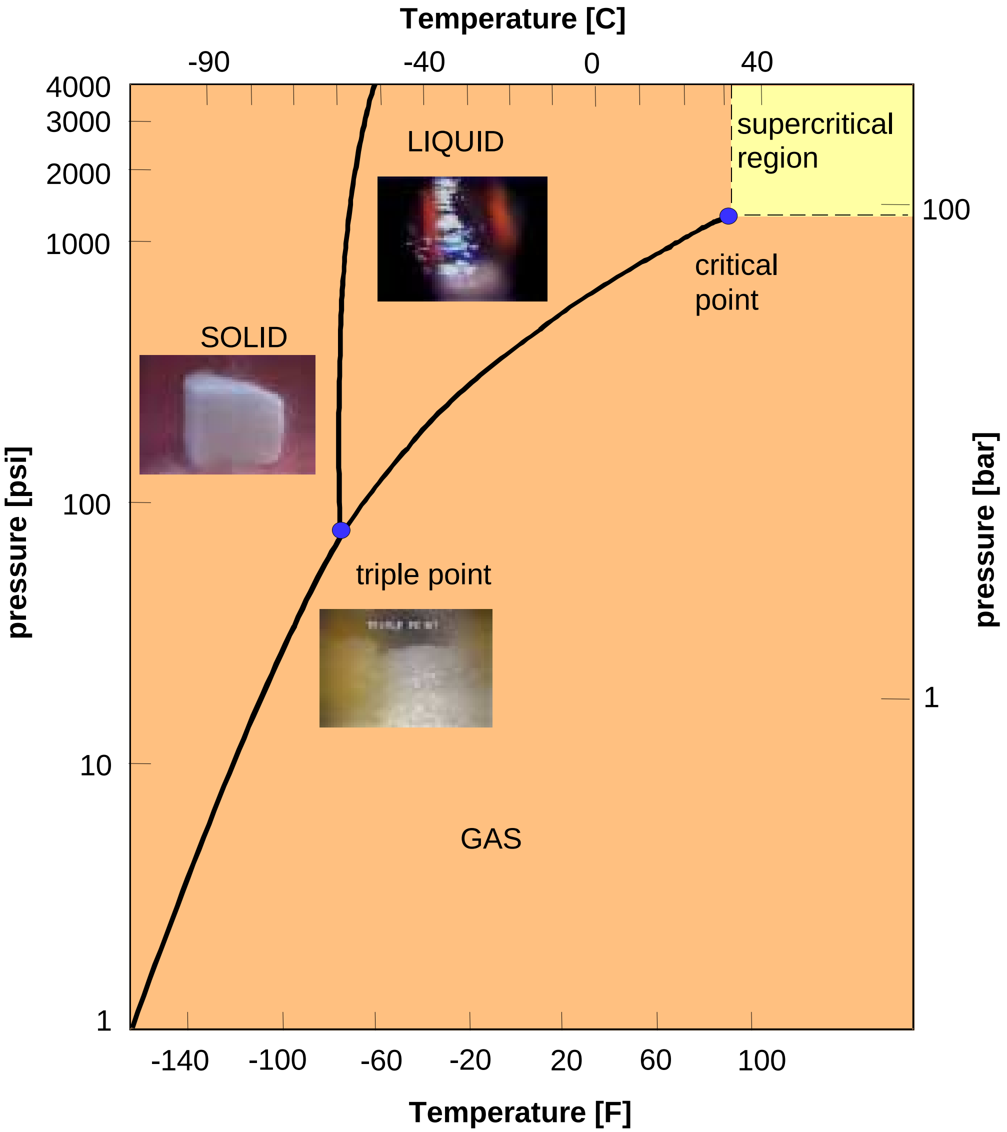
Propylene
Pyridine
Salicylaldehyde
Stannic chloride
Sulfur dioxide
Sulfuryl chloride

Thiophene
Thioxane
Toluene
Tolunitriles
Triacetin
Tri-sec-Butylbenzene
2,2,3-Trimethylbutane
Valeraldehyde

Advantages of $SCCO_2$

- ✓ Approved by EPA as an ODC alternative (SNAP list, 1995)
- ✓ Zero ODP
- ✓ No hazardous waste generated
- ✓ Low toxicity
- ✓ Non-flammable
- ✓ Non-corrosive
- ✓ Very inexpensive
- ✓ Low viscosity
- ✓ Low surface tension

Phase Diagram of CO_2



Carbon Dioxide

- Critical Values
    - Critical temperature = 31°C (85°F)
    - Critical Pressure = 73.8 atm (1070psi)
- No dipole moment
- Large Quadrupole moment
- CO_2 has both acidic and basic sites

Supercritical Fluid Technology Applications

Particle Removal
Post-CMP
Cleans

Photoresist
Strip/
Residue Removal

Dry Resist
Develop

Deposition

MEMS

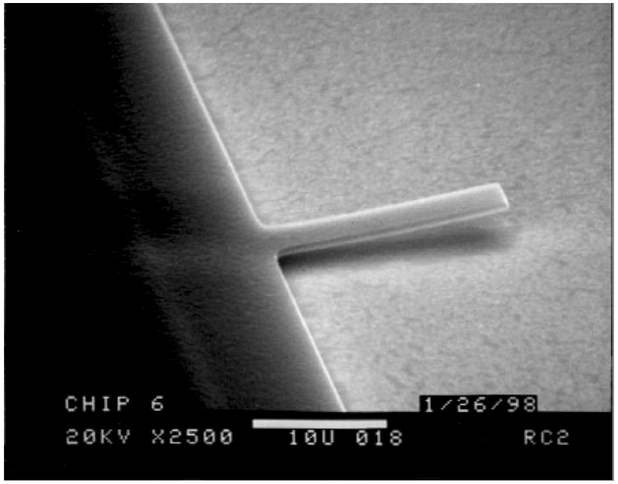
Current Application: MEMS Drying

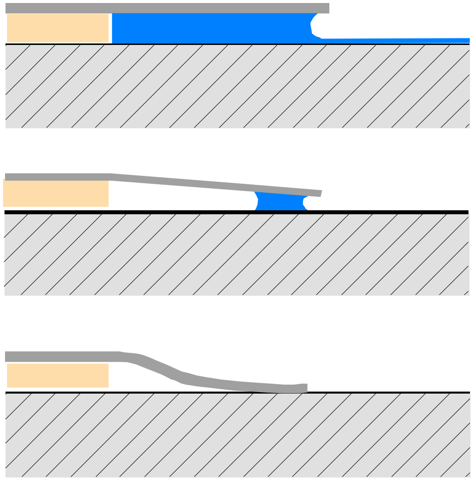
MEMS = Micro Electro Mechanical Structures

Problem: **Liquid Bridging** or **STICTION**

Stiction is due to the surface tension effects of trapped capillary liquids upon drying.

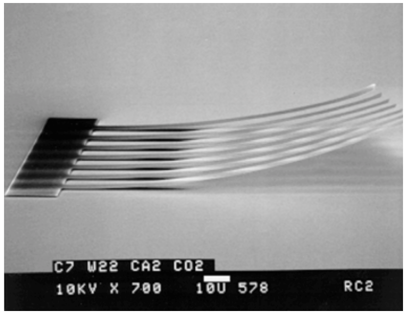
$$F_m = \frac{\gamma A}{h}\left(\cos\Theta_1 + \cos\Theta_2\right), \quad \gamma(H_2O) = 72\ dynes/cm, \quad \gamma(SCCO_2) = 0$$

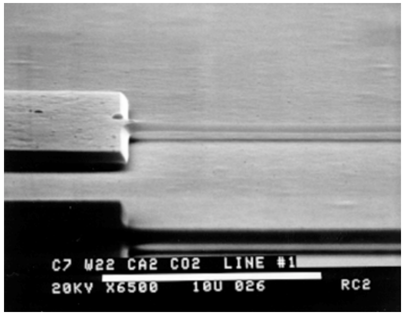


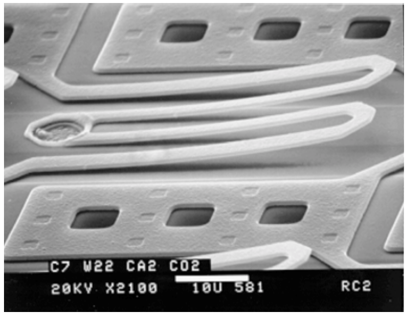


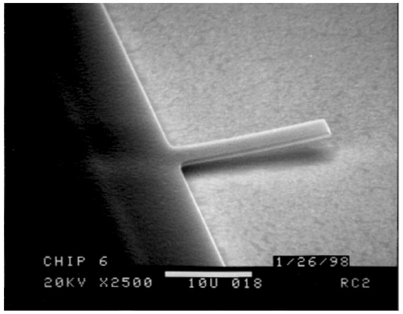
Development of stiction upon evaporation of the rinsing liquid.

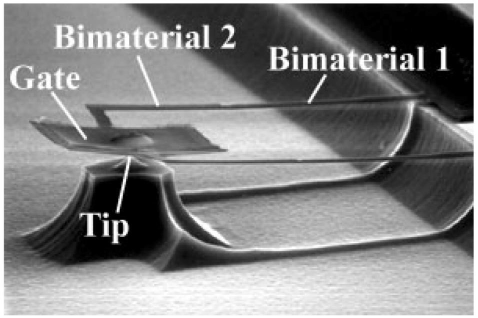
MEMS: Process Results

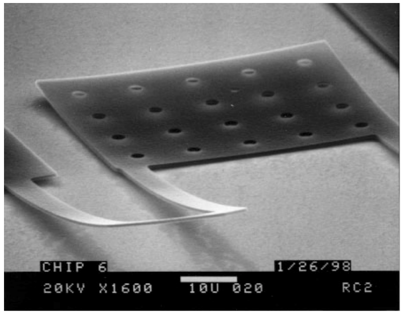


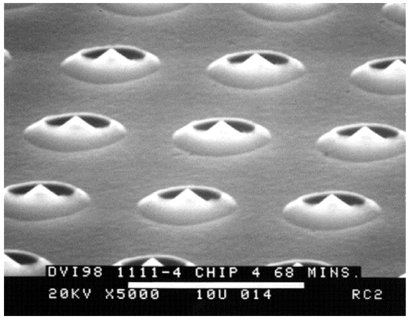


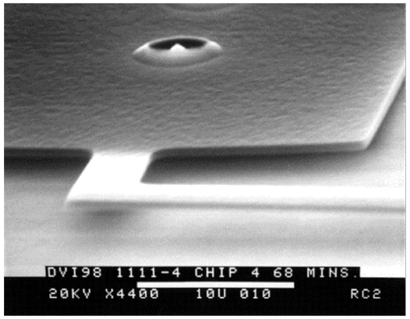


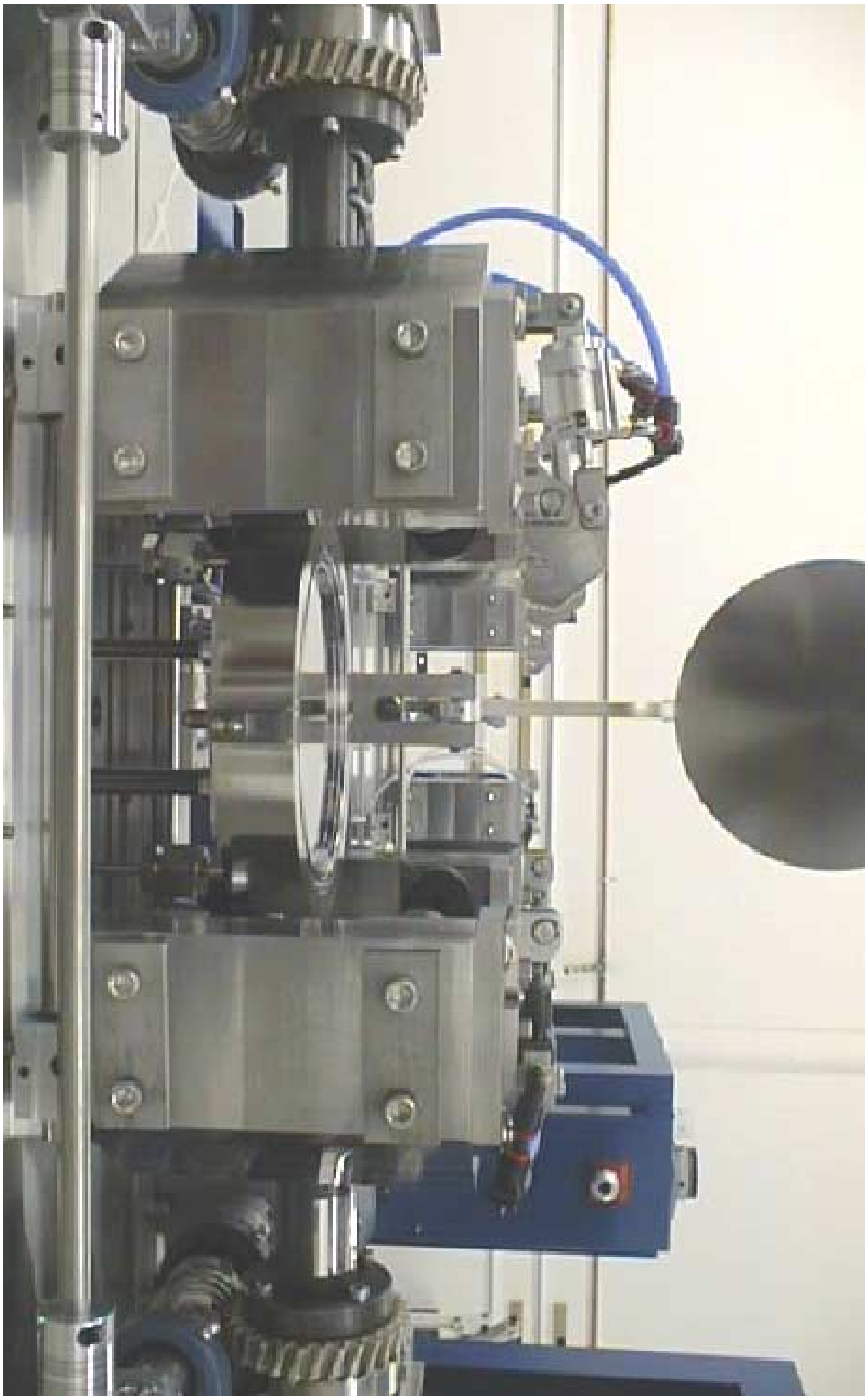






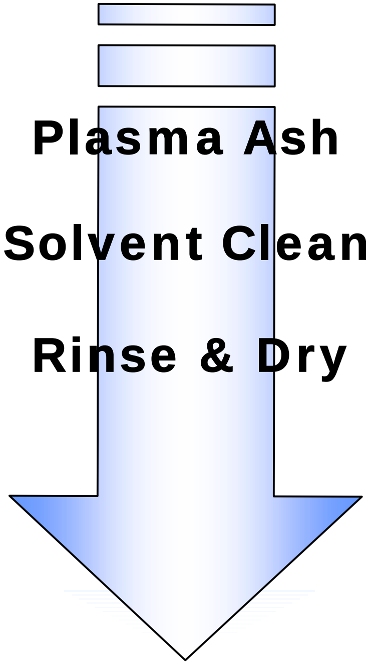






Photoresist/Residue Removal

State-of-the-art Stripping Technology and Residue Removal



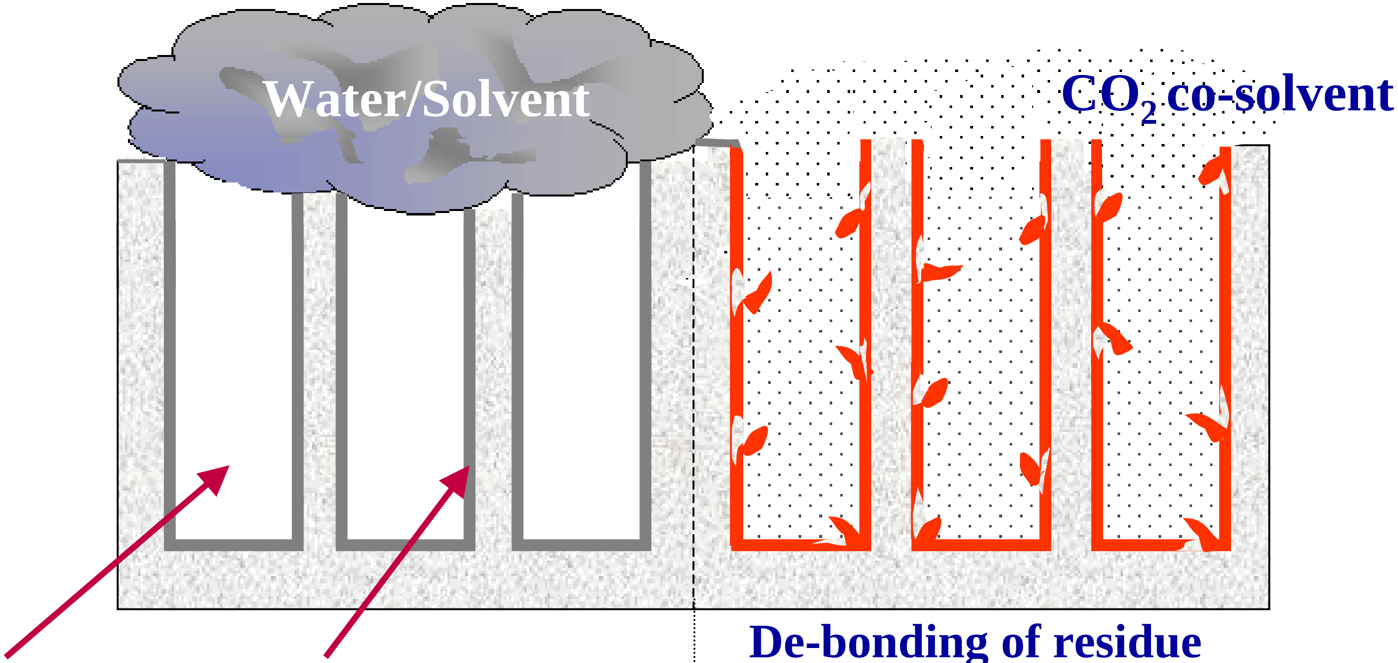
Plasma Ash

Solvent Clean

Rinse & Dry

Enabling Technology ~ Why? Part 1

Photoresist Removal in a One-Step Process for 150nm Technology



Water/Solvent

CO_2 co-solvent

Via hole/trench

Sidewall Polymer

De-bonding of residue

Wet Process

CO_2 Process

Road Block to Cleaning

<0.18 Features with Liquids

- Surface Tension
- Capillary Force

Side-Wall Polymer/Residue Removal

(Compositions)

- **Fluorinated Hydrocarbons**
- **Siloxanes**

$CF_{(N)}$ - M_X Si O_y ?

- **Elemental Al or Refractory Metal or Cu**

Side-Wall Polymer/Residue Removal

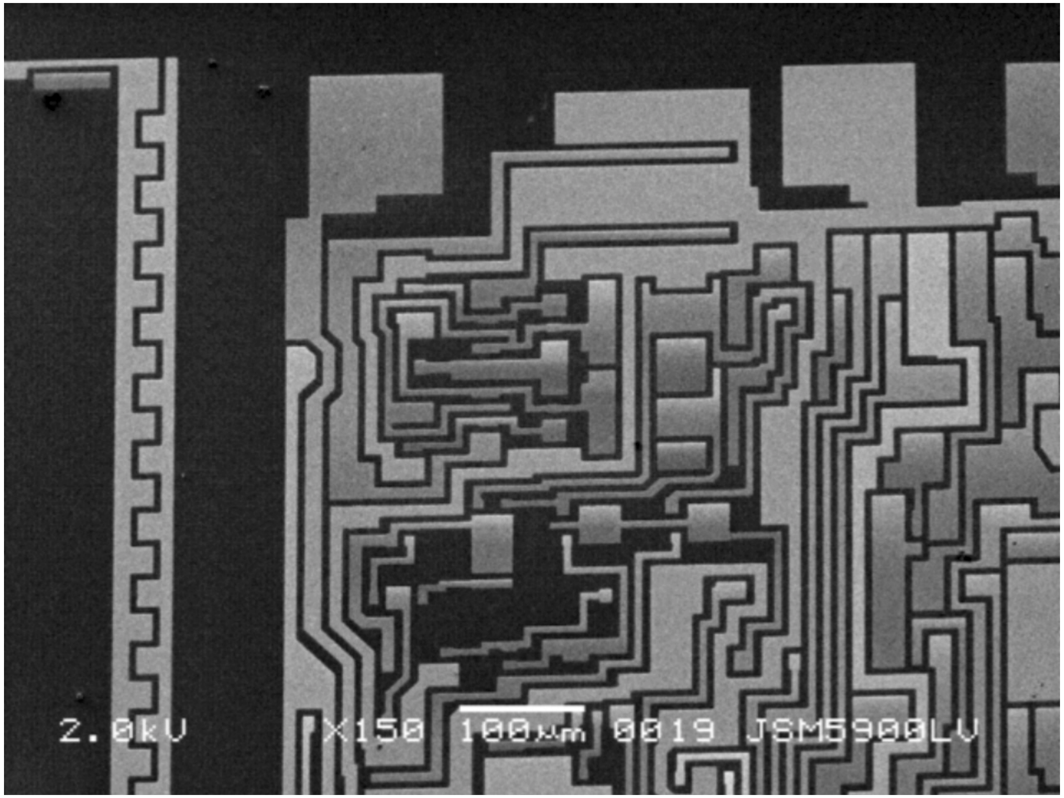
(Chemistries)

- $SCCO_2$ + Co-Solvent
- $SCCO_2$ + Co-Solvent + Chelating Agent(s)

Decompression Techniques

Process Results: Metal Pattern (TiW)

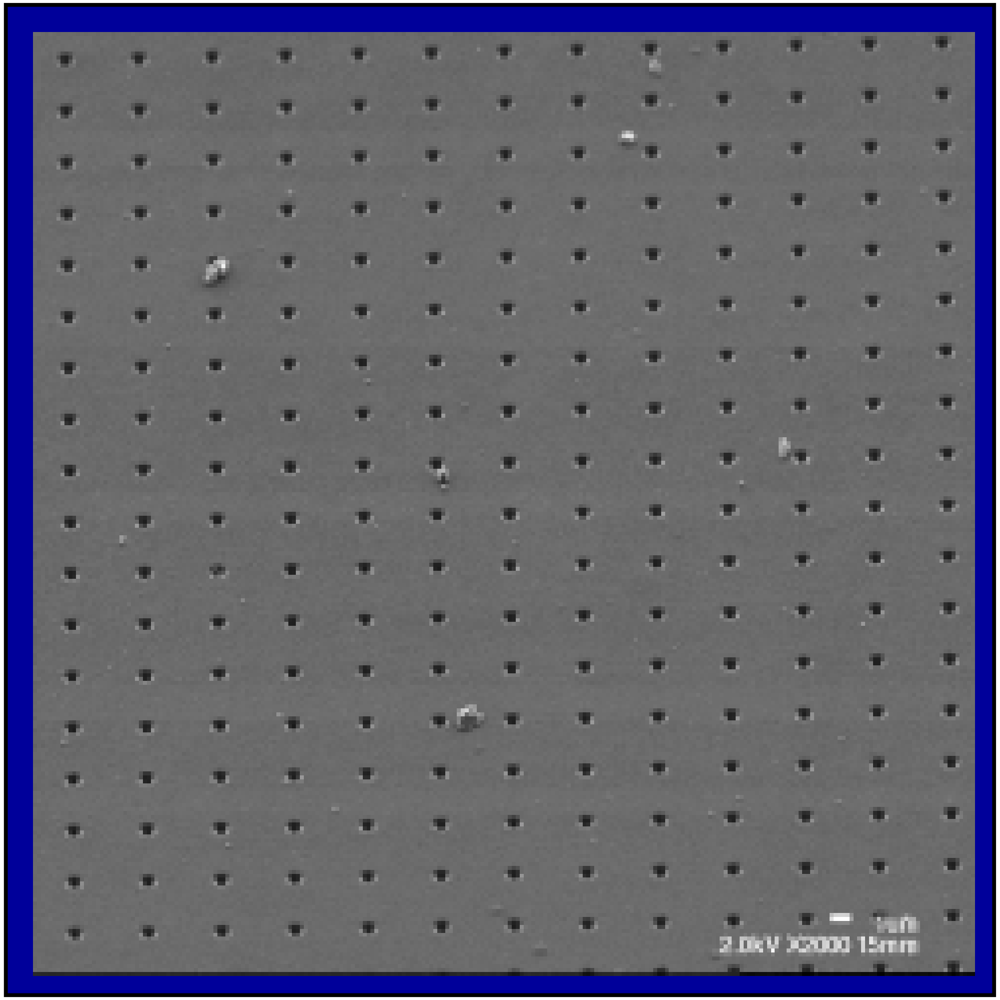
Prestrip: 5000 Å of resist
Result: Photoresist and sidewalls removed, no loading effect



processed with CO_2

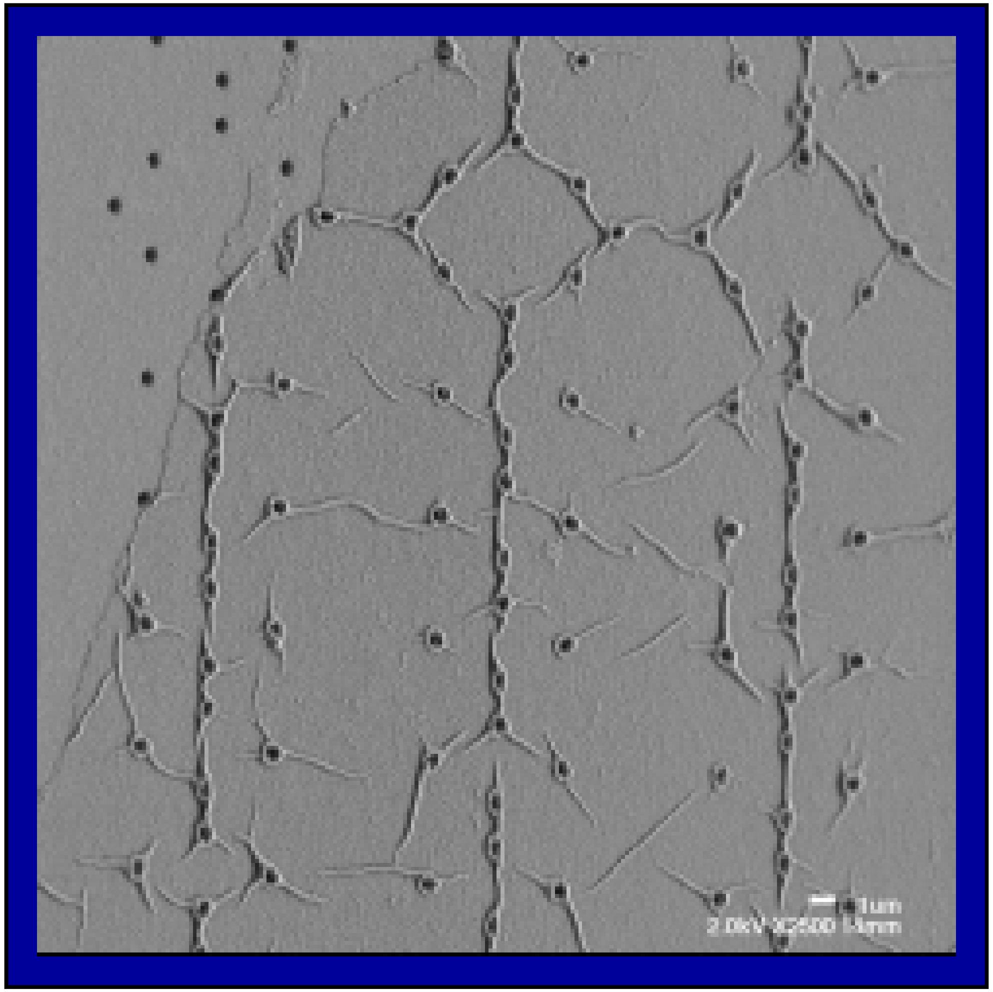
Oxide Via Field

4K Å Photo Resist
Pre-Strip



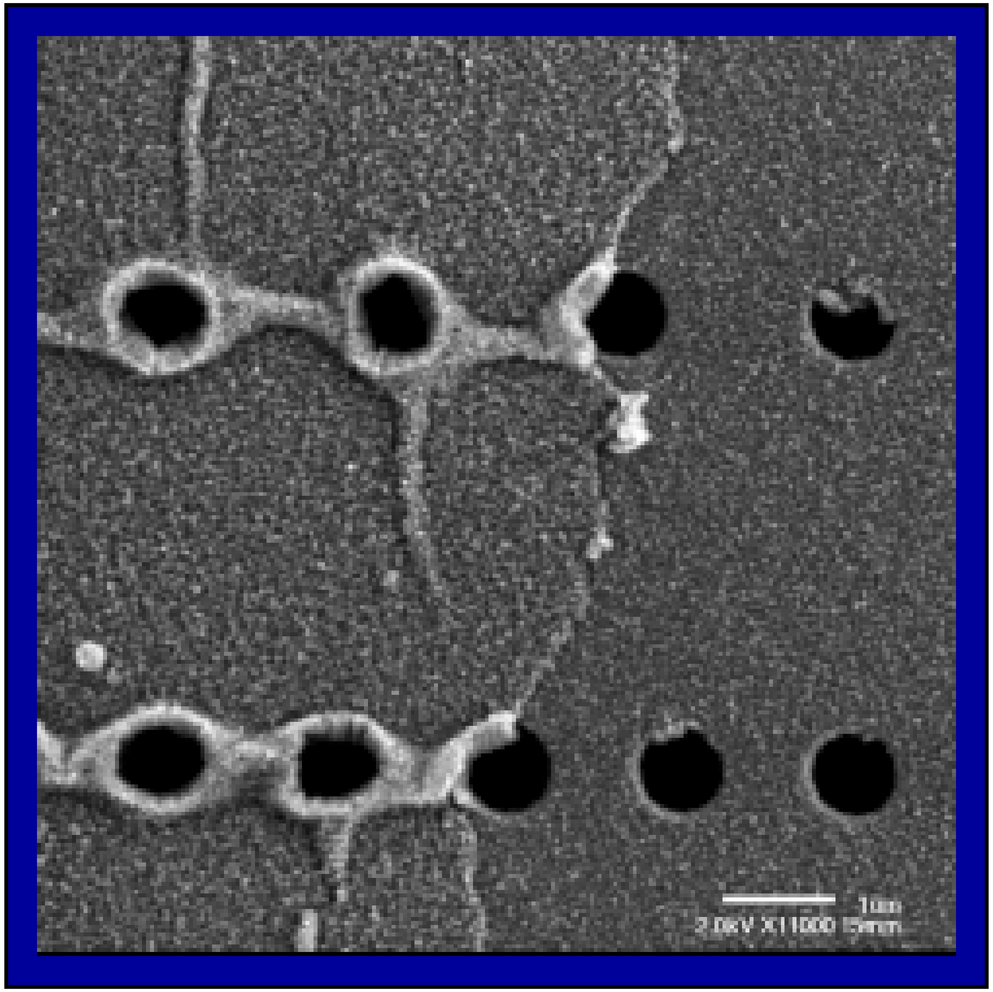
Oxide Via Field

Partial Strip



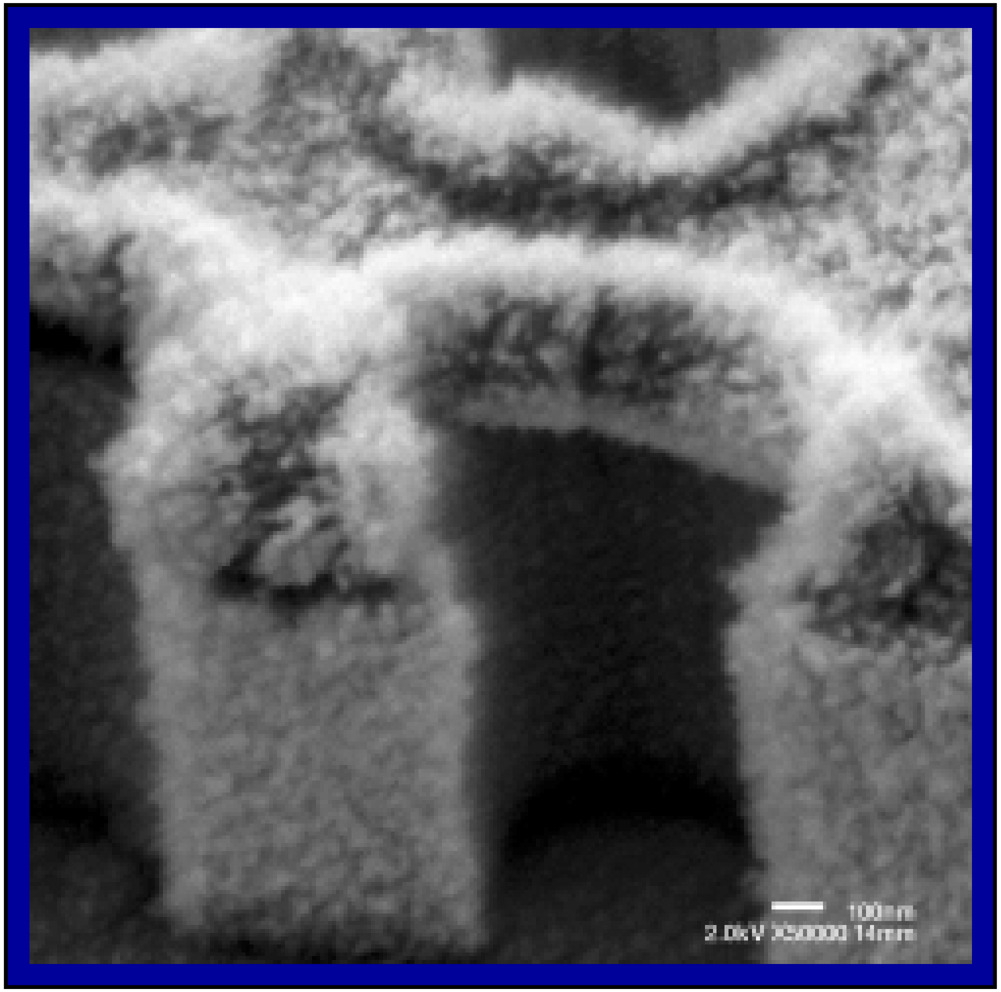
Oxide Via Field

Partial Strip



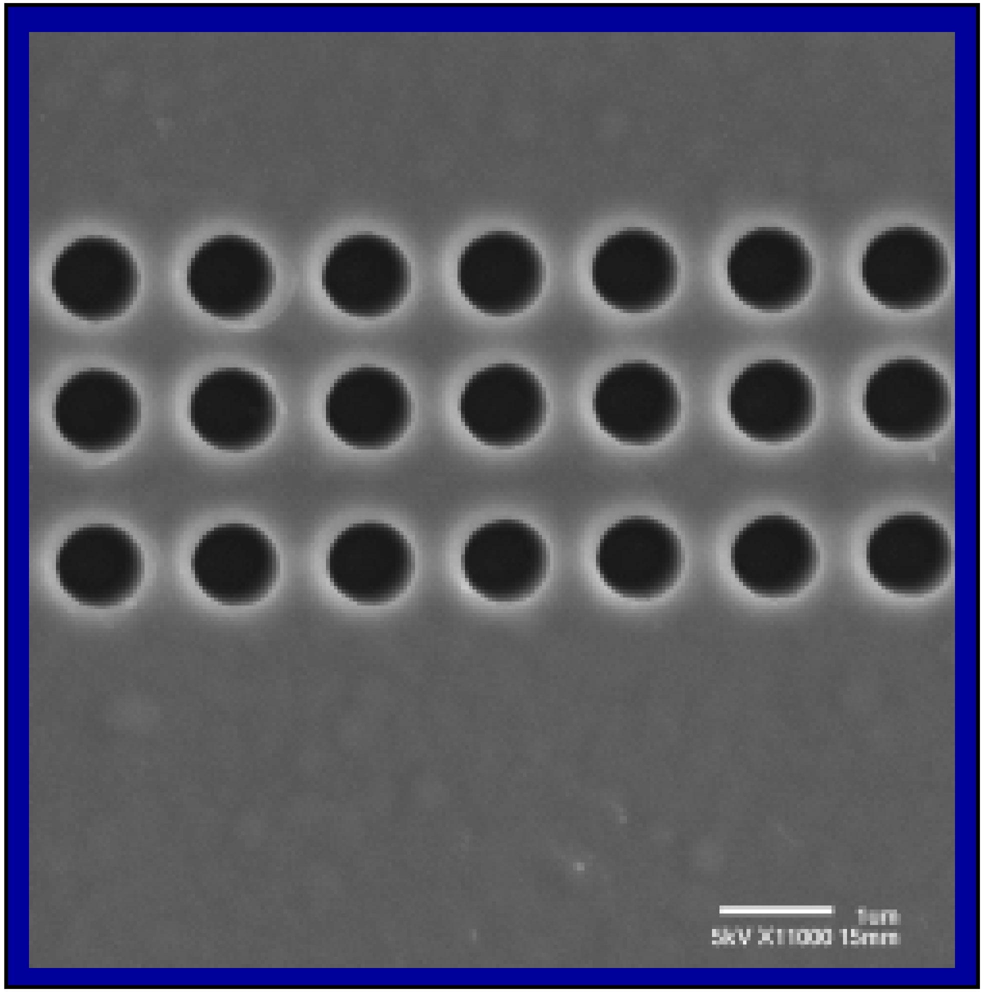
Oxide Via

Partial Strip



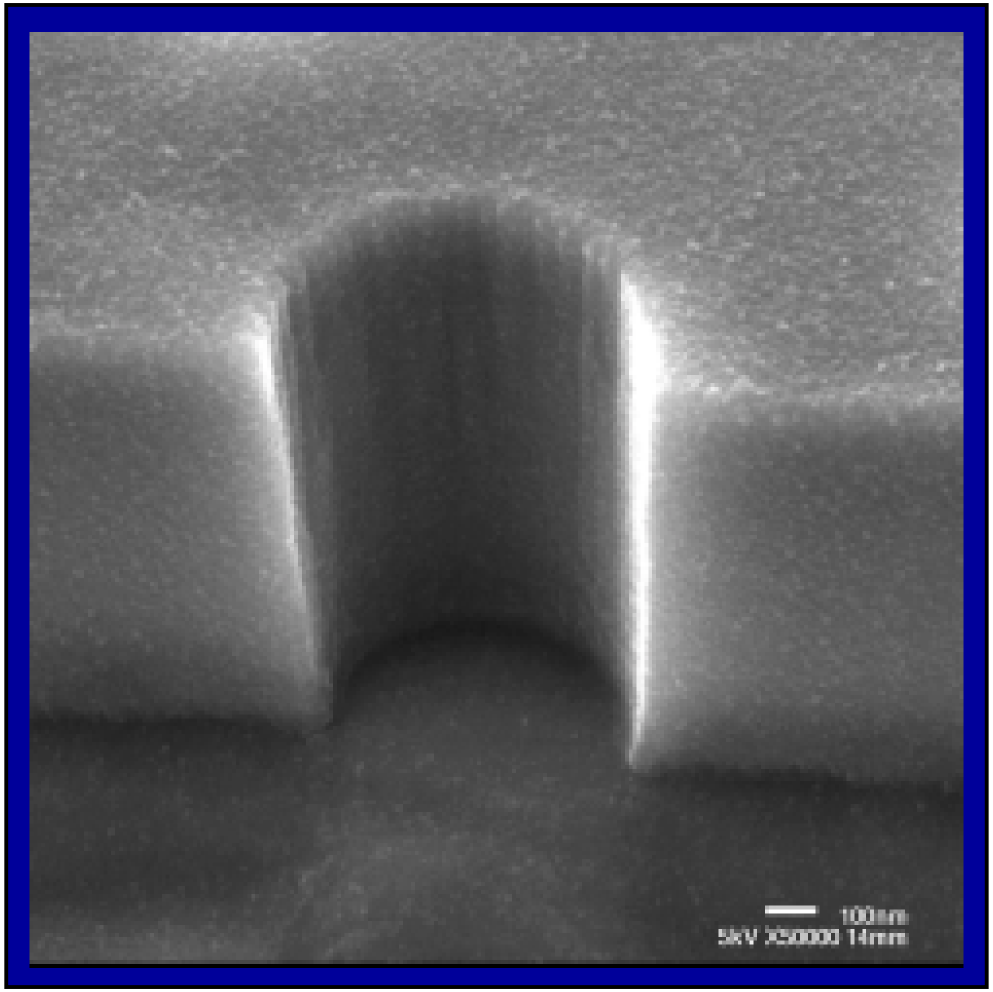
Oxide Via Field

Complete Strip



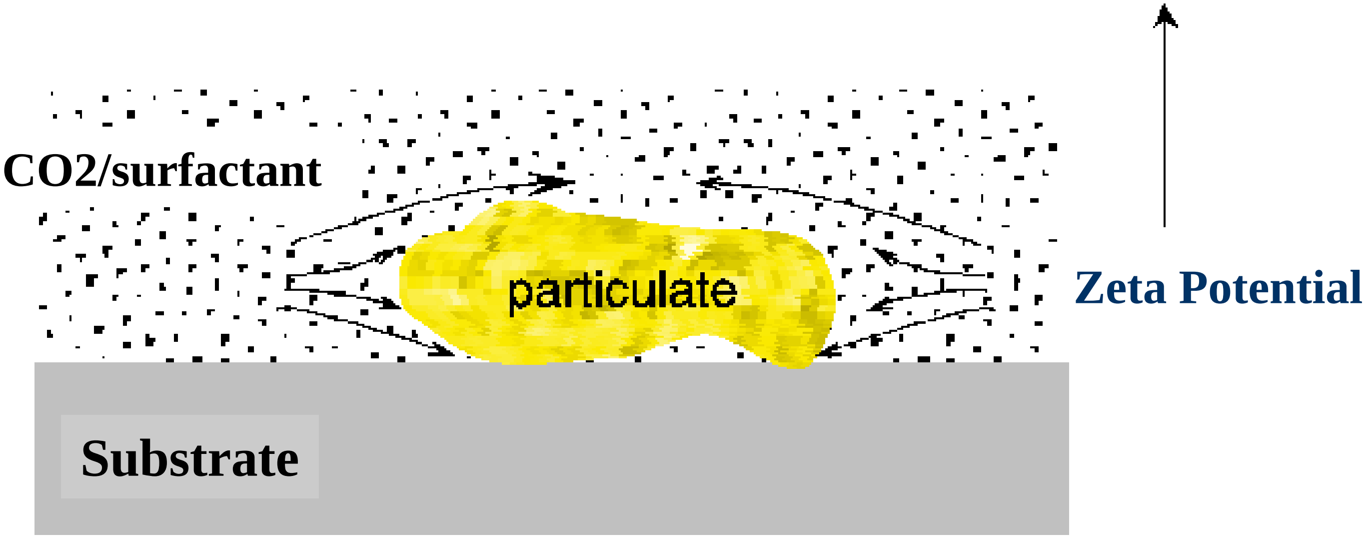
Oxide Via

- Resist Strip 4K Å
- Side-Wall Polymer Removed
- No Residue



Enabling Technology - Why? Part II

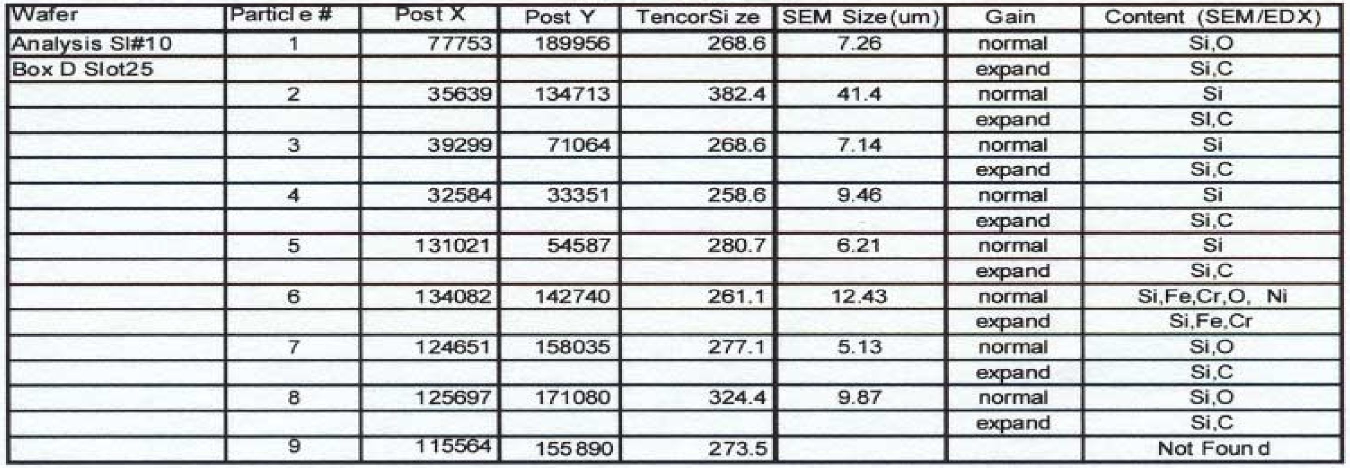
Particulate Removal



Changing Zeta Potential

Examples of Particle Morphology

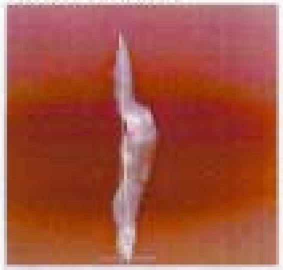
Wafer Slot #25



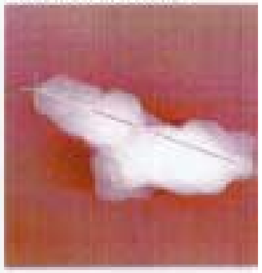
Wafer	Particle #	Post X	Post Y	TencorSize	SEM Size(um)	Gain	Content (SEM/EDX)
Analysis SI#10	1	77753	189956	268.6	7.26	normal	Si,O
Box D Slot25						expand	Si,C
	2	35639	134713	382.4	41.4	normal	Si
						expand	SI,C
	3	39299	71064	268.6	7.14	normal	Si
						expand	Si,C
	4	32584	33351	258.6	9.46	normal	Si
						expand	Si,C
	5	131021	54587	280.7	6.21	normal	Si
						expand	Si,C
	6	134082	142740	261.1	12.43	normal	Si,Fe,Cr,O, Ni
						expand	Si,Fe,Cr
	7	124651	158035	277.1	5.13	normal	Si,O
						expand	Si,C
	8	125697	171080	324.4	9.87	normal	Si,O
						expand	Si,C
	9	115564	155890	273.5			Not Found

Slot#25 Particle #1

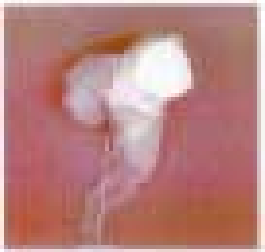
Slot#25 Particle #2



Slot#25 Particle #3



Slot#25 Particle #4



Slot#25 Particle #5

Slot#25 Particle #6

Slot#25 Particle #7

Slot#25 Particle #8

Particle Removal

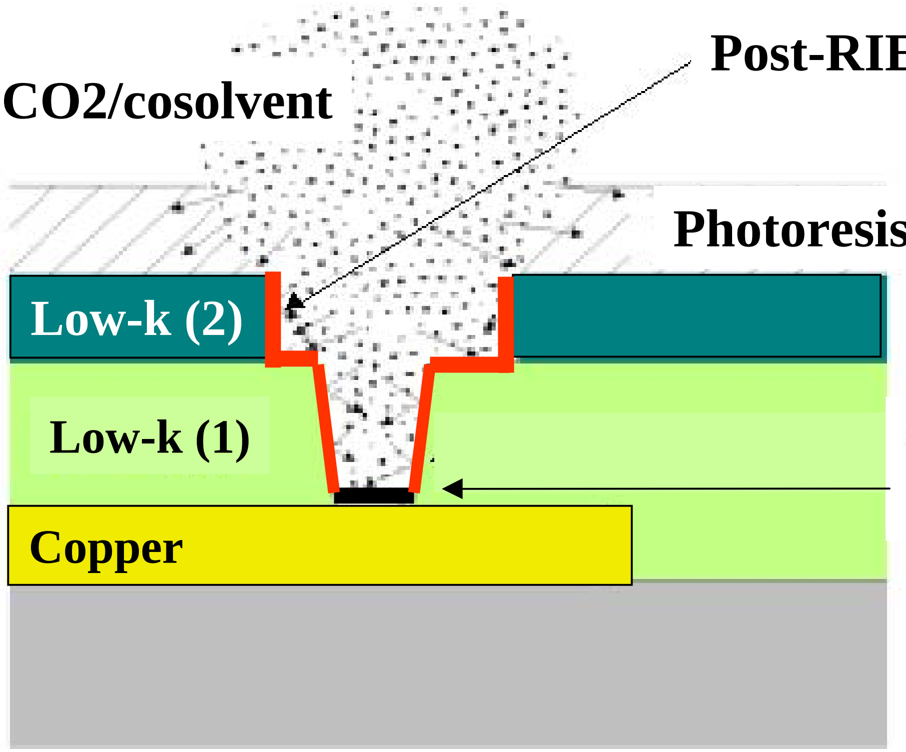
- ◆ “Engineered” Surfactants to Change Zeta Potential

R & D Required

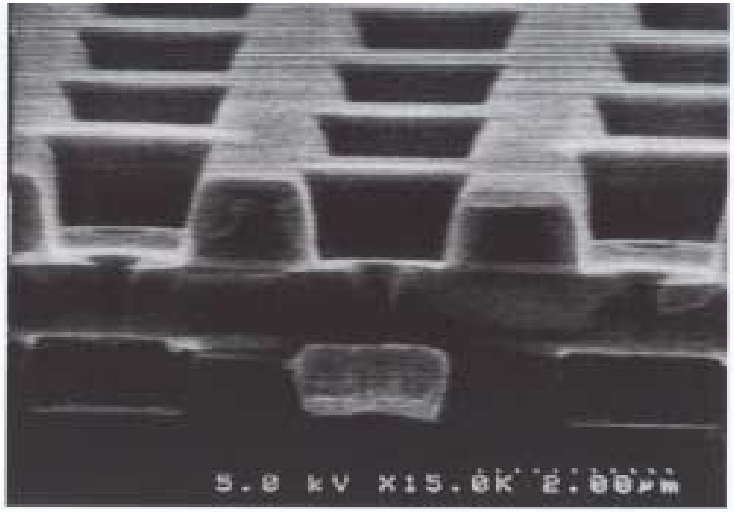
- ◆ Screen and Select Cationic and Amphoteric Surfactants
- ◆ Study Surface Forces
- ◆ Electro Kinetics and Colloid Behaviors of Surfactants

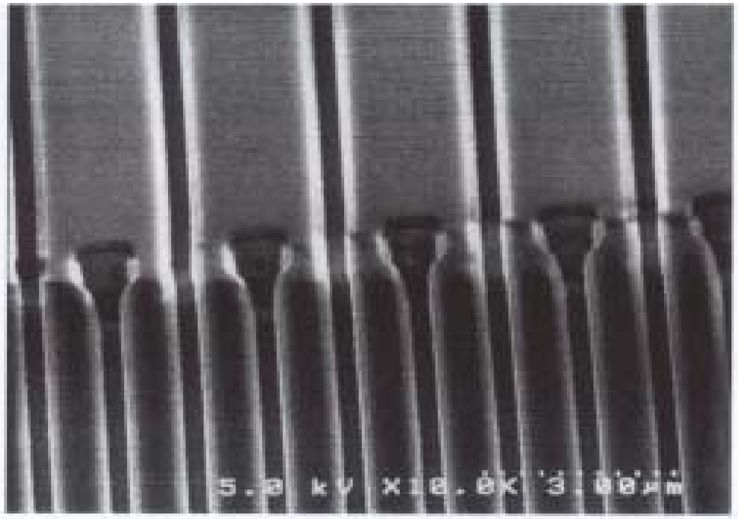
Enabling Technology - Why? Part III

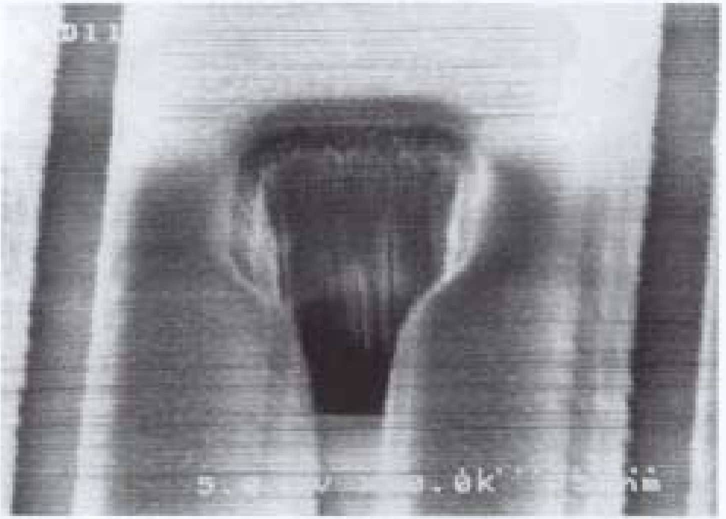
Compatibility/Selectivity With Low-k Technology



Side Wall Removal - Process Matrix







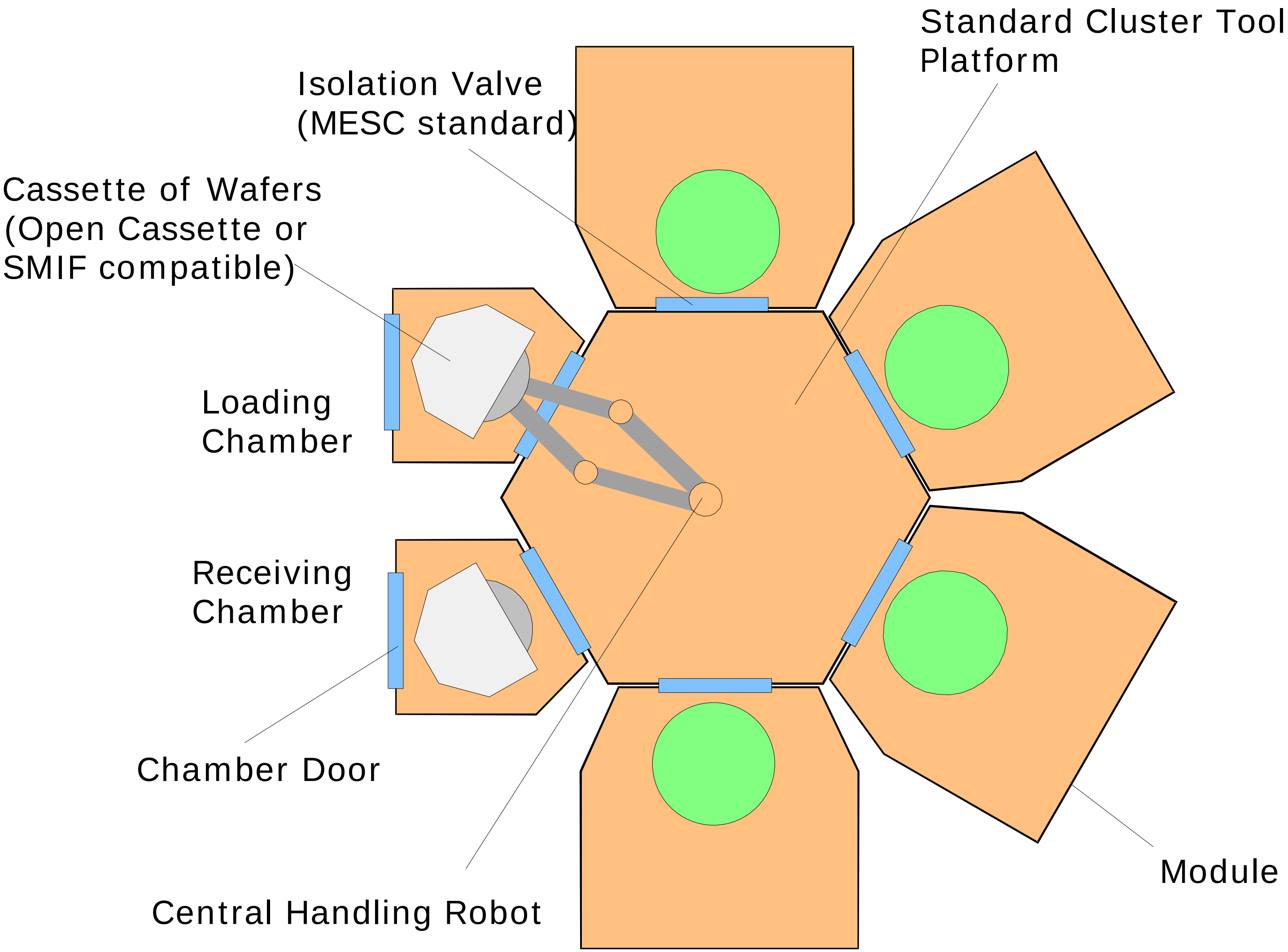
processed with CO_2

Co-Solvent and Surfactant Mixture in $SCCO_2$

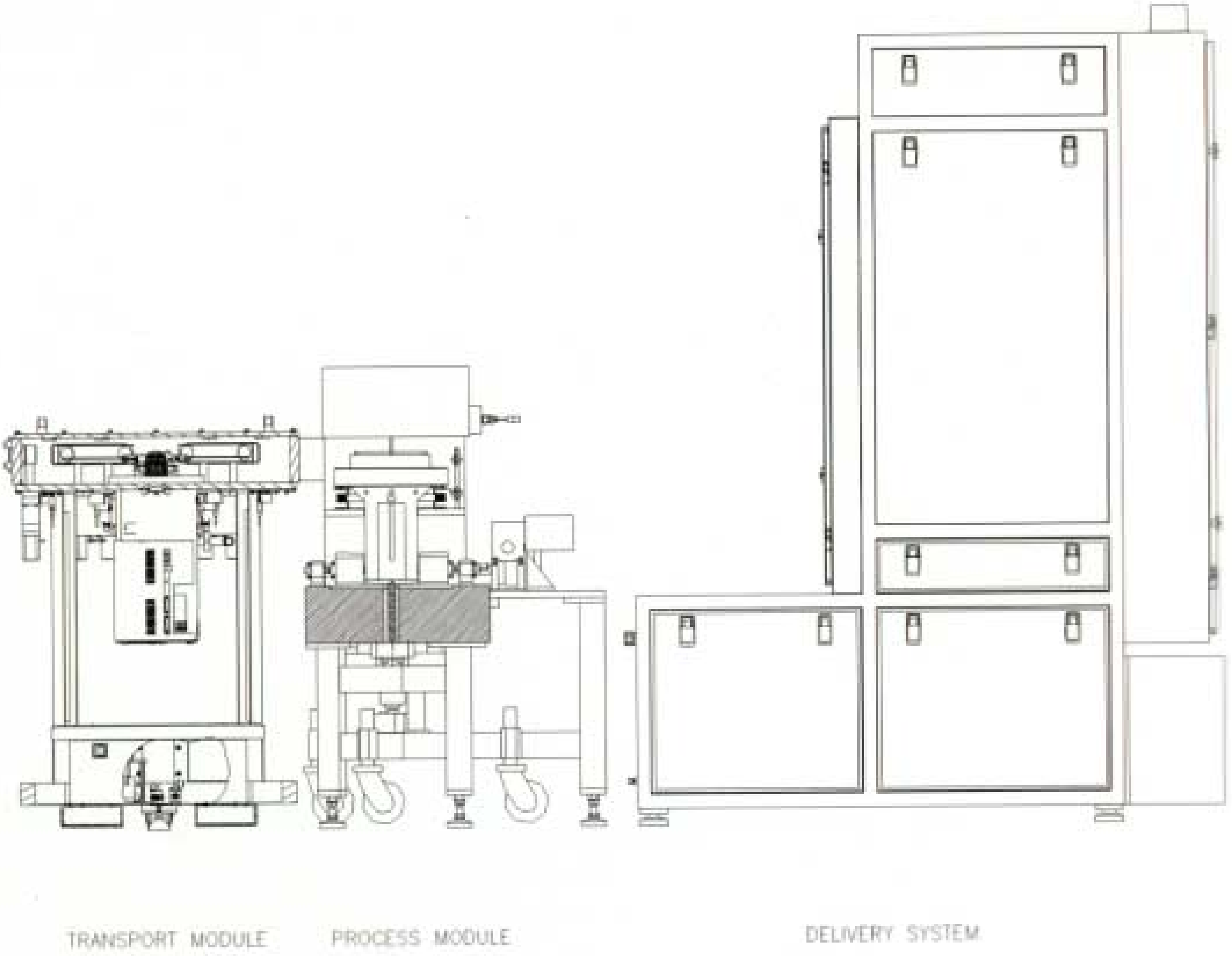
General Comments:

- Many substances dissolve in $SCCO_2$ (principally organic)
- Both organic acid and bases are soluble in $SCCO_2$
- Mixtures can be made with “other” supercritical fluids and organic and metal-organic compounds, in combination(s)
- Solubility of these compounds (parameters) are generally 1 - 8%
- Mixtures move the “critical values”, or the critical point of CO_2, (T crit and P crit), to higher values.

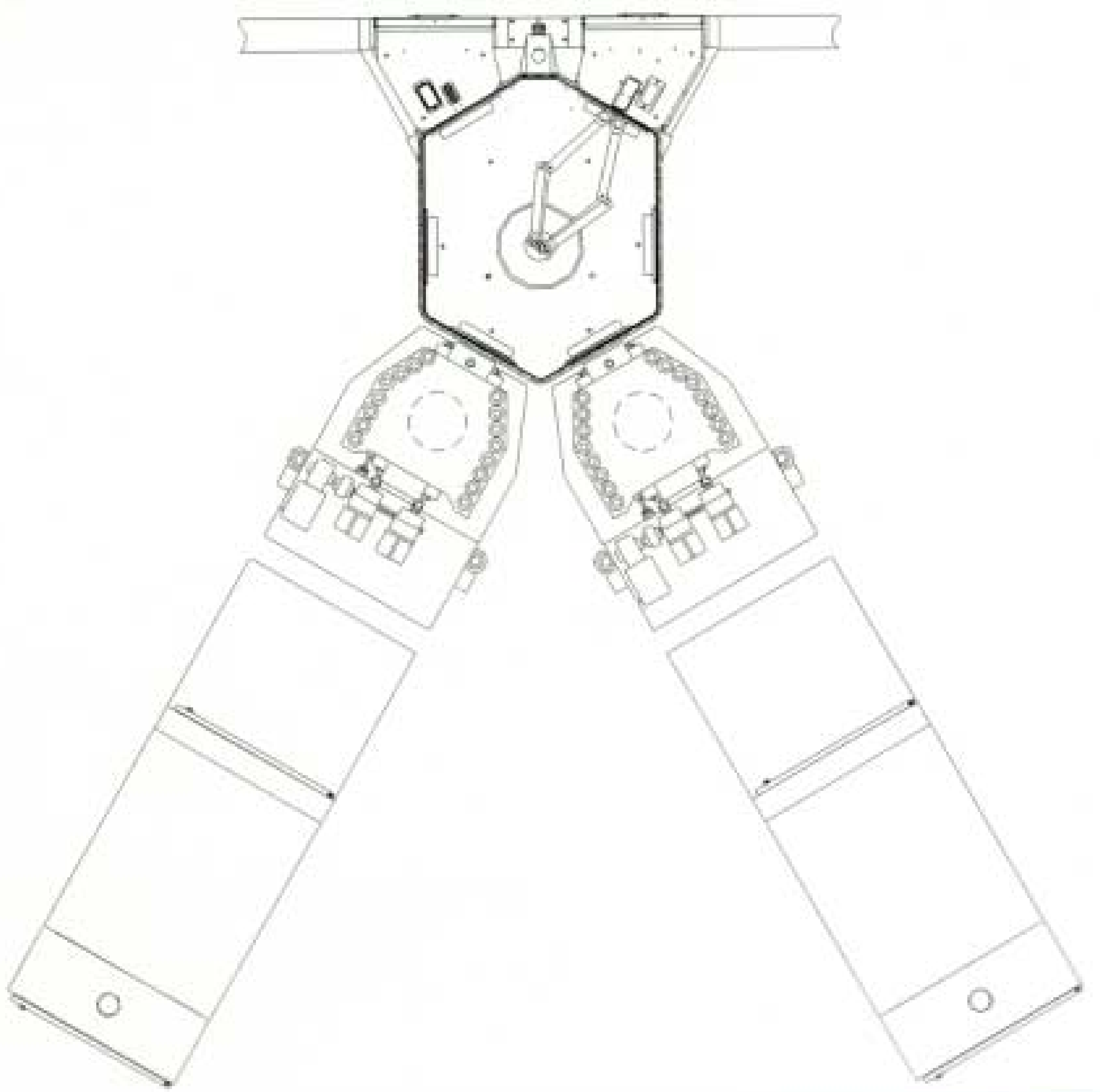
Manufacturing Tool Concept

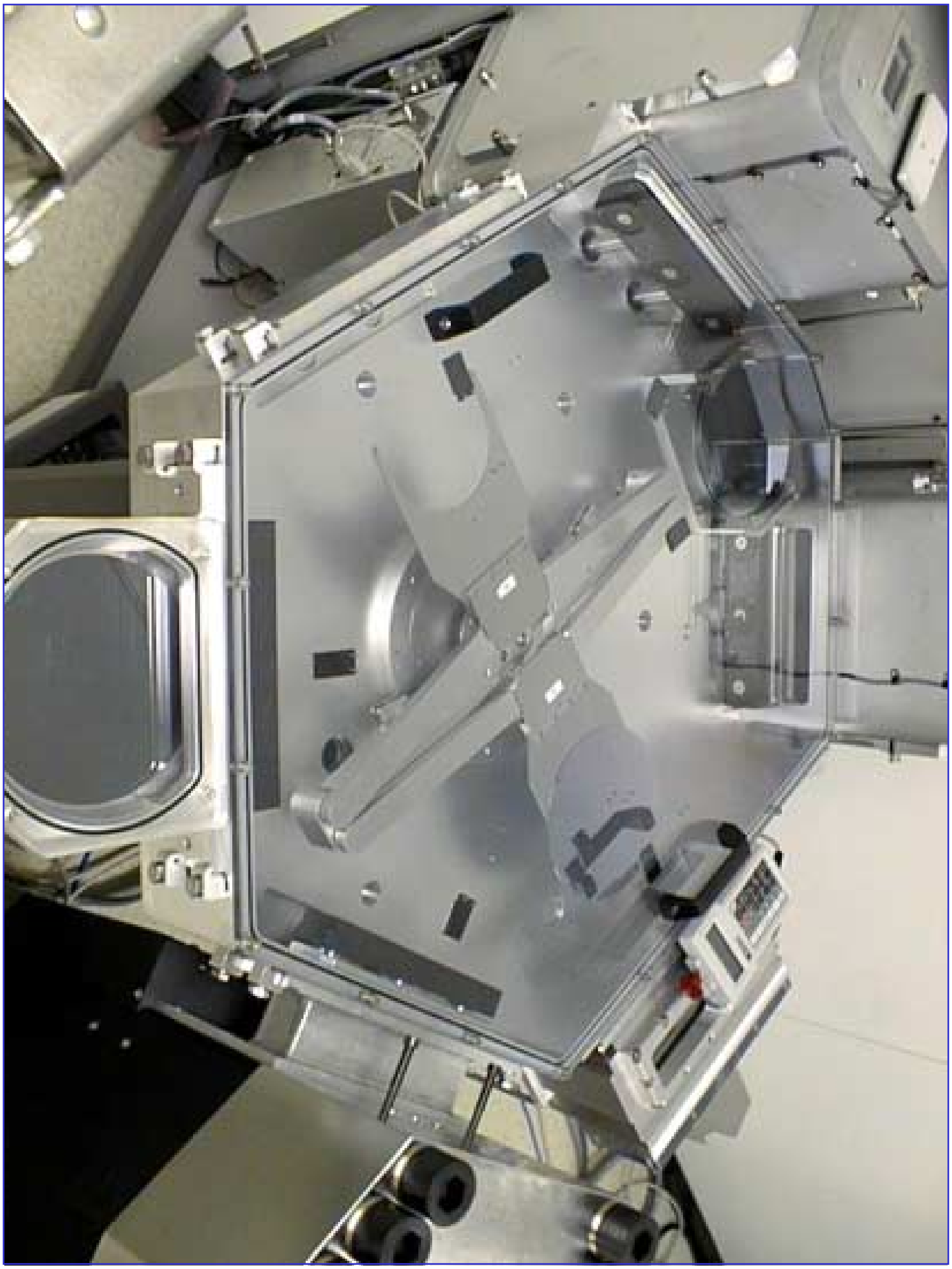


Side View of ARROYO™ System

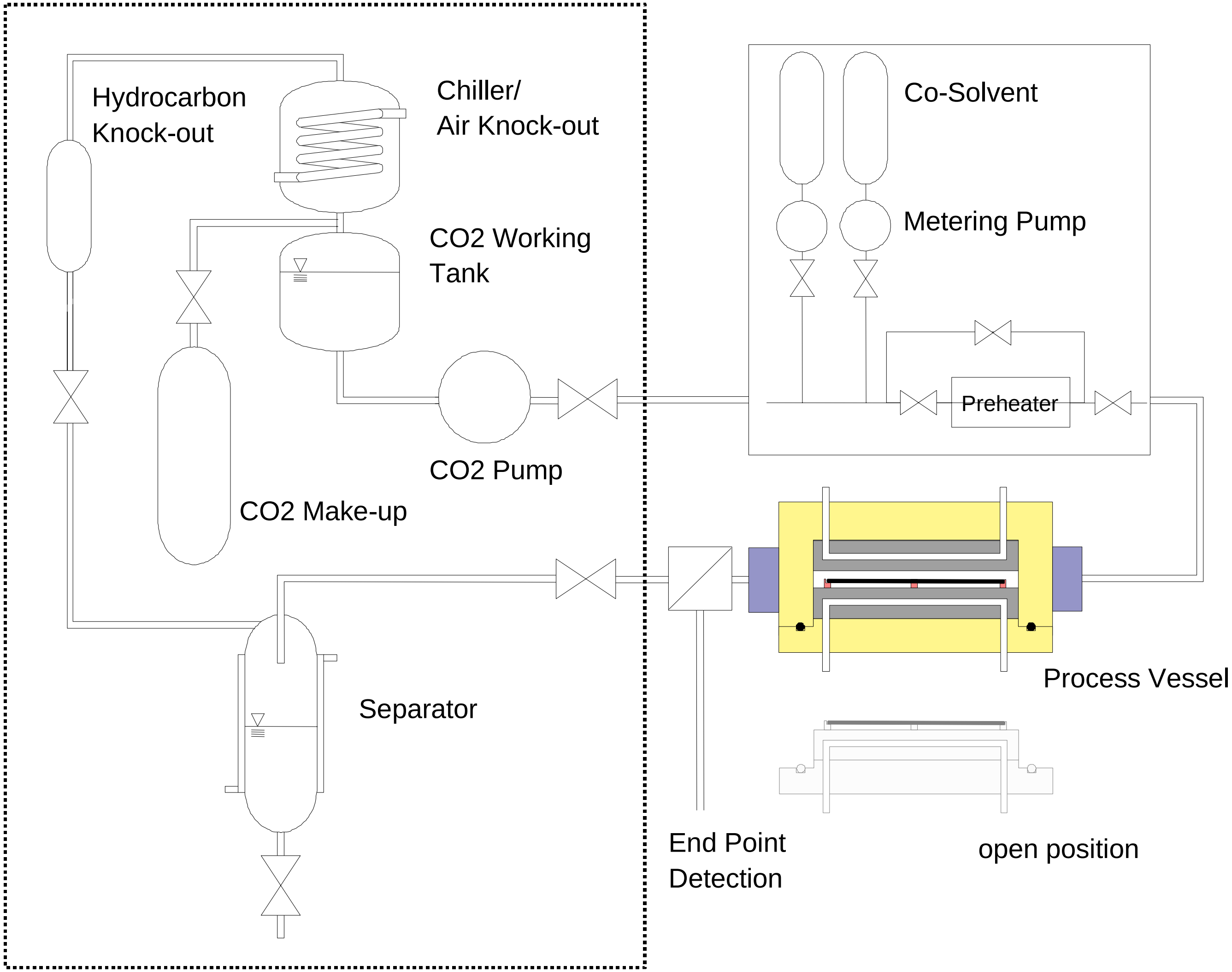


Top View of ARROYO™ System





Process & Instrumentation Diagram



APPLICABILITY

APPLICABILITY OF SC FLUIDS FOR 300mm WAFER:

Since SCCO$_2$ Technology is NOT Plasma or Vacuum-Based:

- Isostatic Pressure (No ΔP on Wafer)
- No RIE Lag
- No Loading Effects
- No Uniformity Gradients
- No Mass Transport Issues

Benefits of $SCCO_2$ Technology

- Benign Process Temperature (50-150°C)
- Non-toxic/non-flammable process media
- No environmental or employee health hazard
- No hazardous waste disposal
- No water consumption
- Small footprint
- Extendable to 300 mm wafers
- Dry-to-dry process
- Applicable to photoresist stripping, side wall polymer, particle removal,and deposition (future work)
- Viable for low-k dielectrics (no change in “k” value)
- Enabling technology for <0.18µm structures

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