Microelectronic Device Manufacturing with CO_2

April 2003

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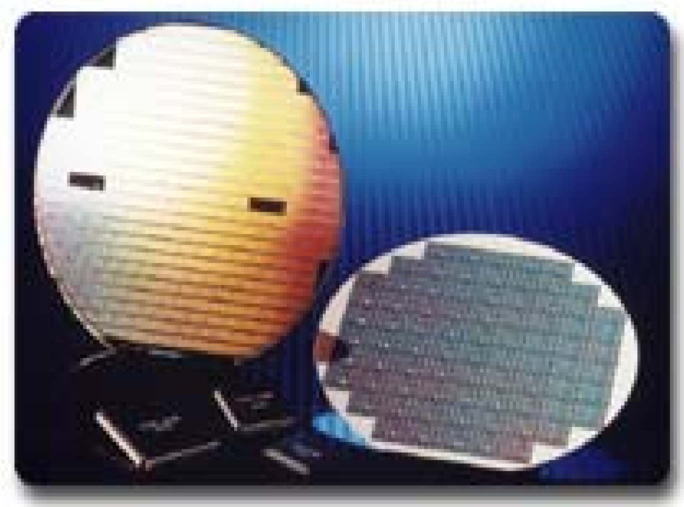


Agenda

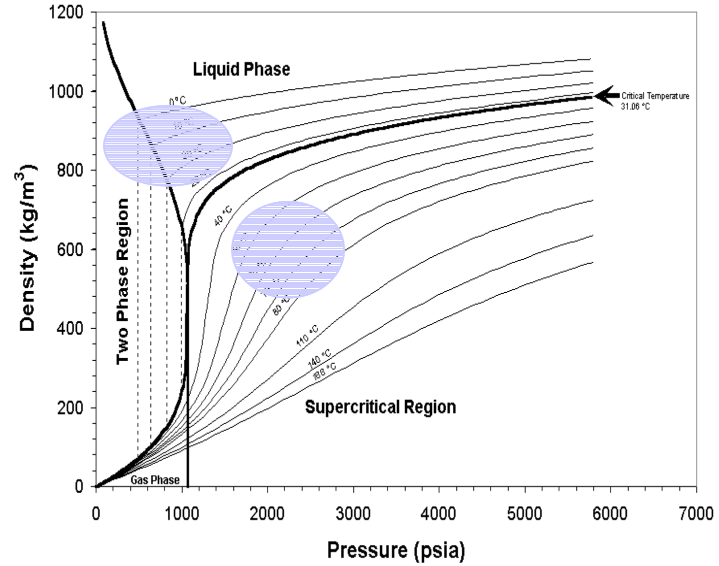
- Industry Challenges
- MIS Background
- The Broad Process Opportunities
- Execution

Challenges Industry Faces

- Device Yield vs. Device Performance
  - Shrinking device features (practical limits of water-based processes)
  - Smaller devices require new materials (incompatibility)

- Escalating Operating Costs
  - Excessive materials/chemistry usage
  - EH&S - challenging abatement/recycle

Why CO_2-based Processing?



- Low viscosity and surface energy
  - Wets any surface
  - Will not damage structures
  - Reduced boundary layer
- High density
  - Improves solvent properties
- Active micelle chemistry
  - Surfactants for carrying reactive and active chemicals in to the wafer structure
- Dry process platform
  - Cluster tools
  - High throughput

Micell Integrated Systems - Intellectual Property

- Patents
  - Access to 64 patents issued in US
  - 3 additional filings recently allowed
  - Licensed patent rights account for 27 of the 64 issued
  - 34 additional patent applications pending with USPTO
- Internal Expertise
  - 7 Ph.D. Research Scientists
  - 2 Senior Process Engineers
  - 2 Research Scientists, 1 Process Engineer
- Long-term Relationships
  - Prof. Joseph DeSimone (Chairman) and Prof. Ruben Carbonell (Advisor)
  - Kenan Center for the Utilization of CO_2 in Manufacturing (NCSU & UNC-CH)
  - cutting edge scientists, engineers, and national labs

Required Technology Components

- Chemistry Formulations
  - Ubiquitous capabilities - micro -domains, active chemistries...
  - Application specific formulations based on generic and optimized with process and hardware
- Process
  - Ubiquitous methods - rapid mix, rapid fill/vent, physical action...
  - Process of record - specific chemistry formulations and process recipe optimized for chamber configuration
- Hardware
  - infrastructure
  - process specific chamber configurations
  - tool platform

Cleaning - Why CO_2

- Performance/Yield
  - New Materials such as porous low-k dielectrics
    - Removal of bulk water/chemistry from porous structure
    - Presence of chem-sorbed and physi-sorbed water impacts dielectric value
    - Increase in k due to Si-OH formation (post etch/ash + H_2O)
  - Feature size / aspect ratios
    - $ScCO_2$ -zero surface tension, ultra-low viscosity, lead to
    - Excellent wetting
  - Other structurally challenging features (air-bridges, cantilevers, MEM's, Masks)
    - Avoid collapse, stiction
- Environmental, Health, and Safety
  - Reduced solvents, water, byproducts, recyclable

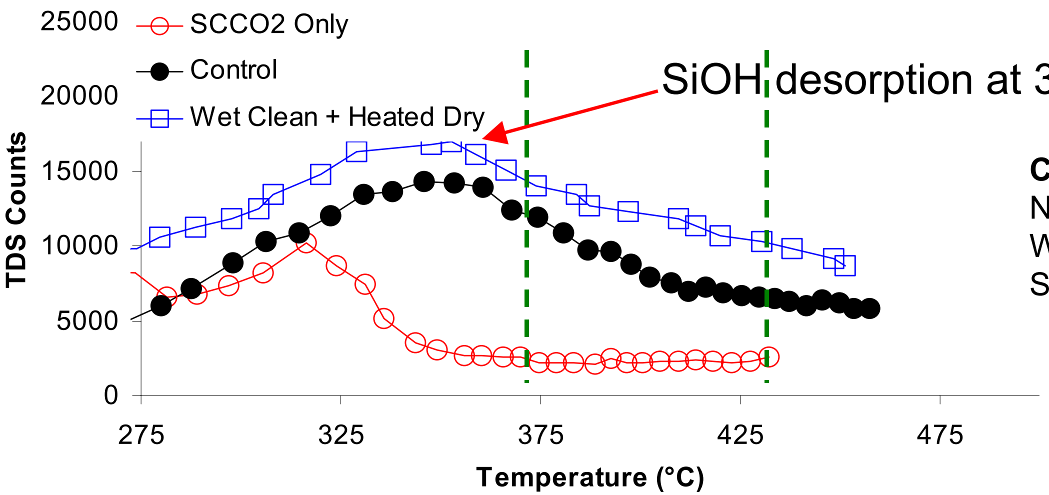
$scCO_2$ Cleaning Applications

- Drying (cleaning water)
- Post-etch/ash residue
- Copper - Post barrier breakthrough
- Specialty apps
- Masks
- Generic process capabilities

Porous Low k Materials
Effects of Etch/Ash plus Wet on k Value

- Etch/Ash process followed by wet clean raises dielectric value due to film damage (creation of SiOH groups)
- SiOH groups lead to higher k values
- CO_2 cleaning process avoids creation of SiOH groups

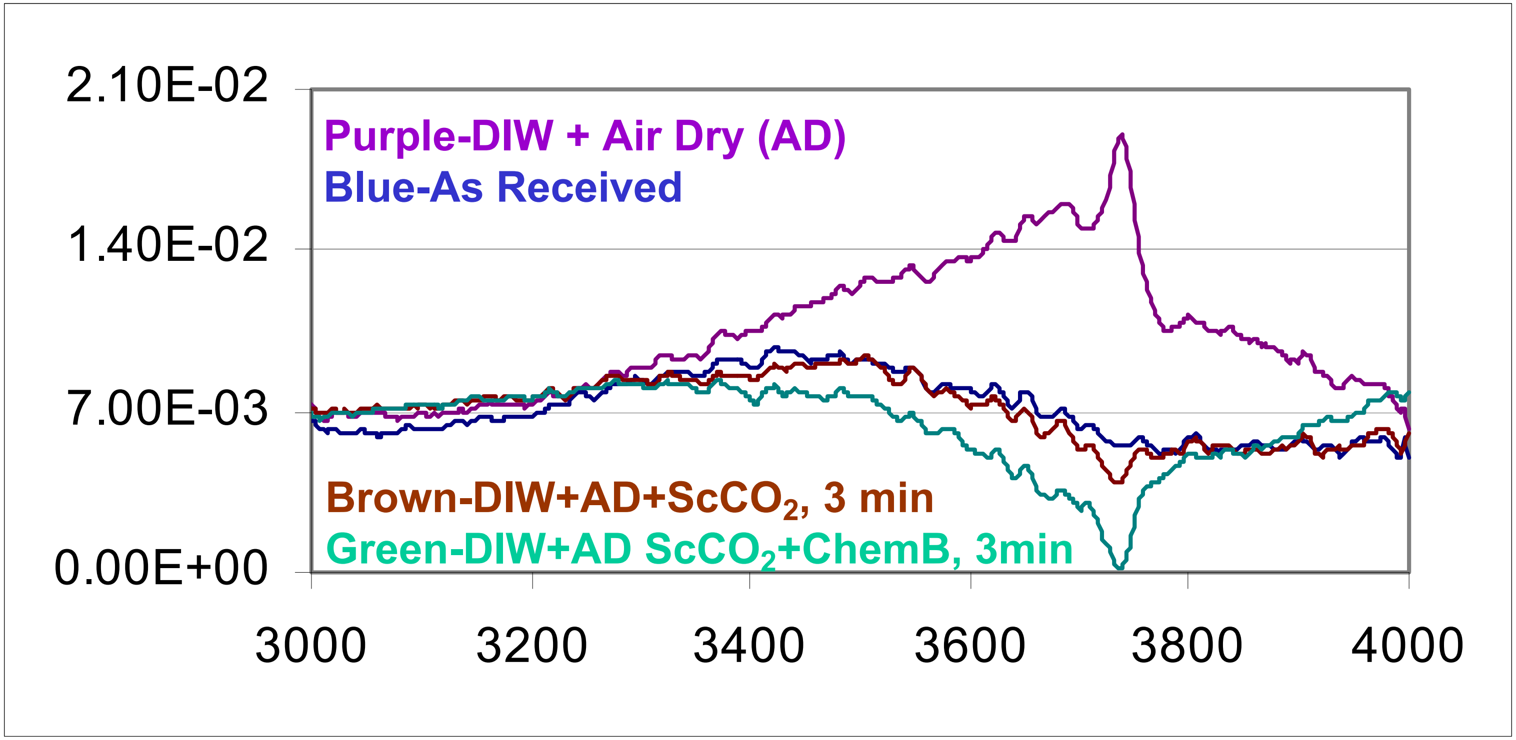
Thermal Desorption Spectroscopy



Cleaning Conditions	**κ-value (25°C)**
None-ash only (control)	2.57
Wet clean + Heated dry	2.69
$SCCO_2$ clean	2.39

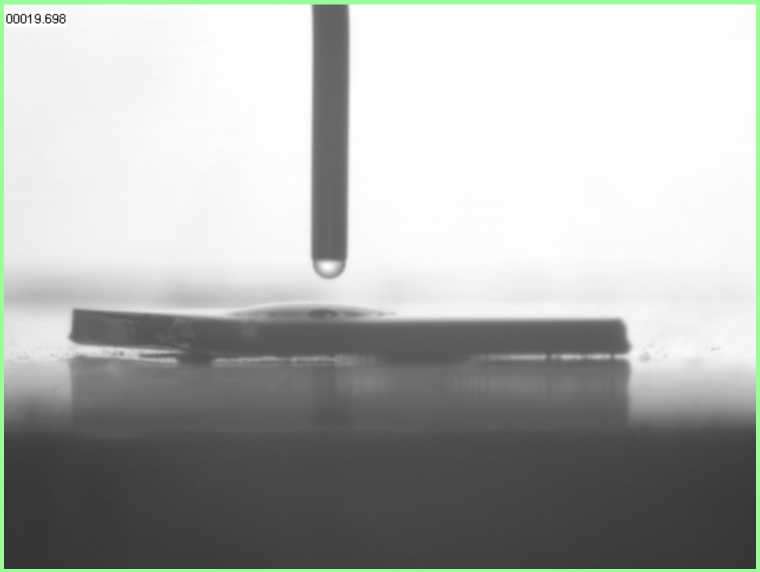
Drying of Etch/Ash Exposed Porous MSQ with $scCO_2$ Formulations

- Etch exposure/damage of MSQ rendered the film hydrophilic
- CO_2 rapidly removes adsorbed water from the film
- CO_2 formulation rapidly dries MSQ film and reduces the SiOH content with additive chemistry

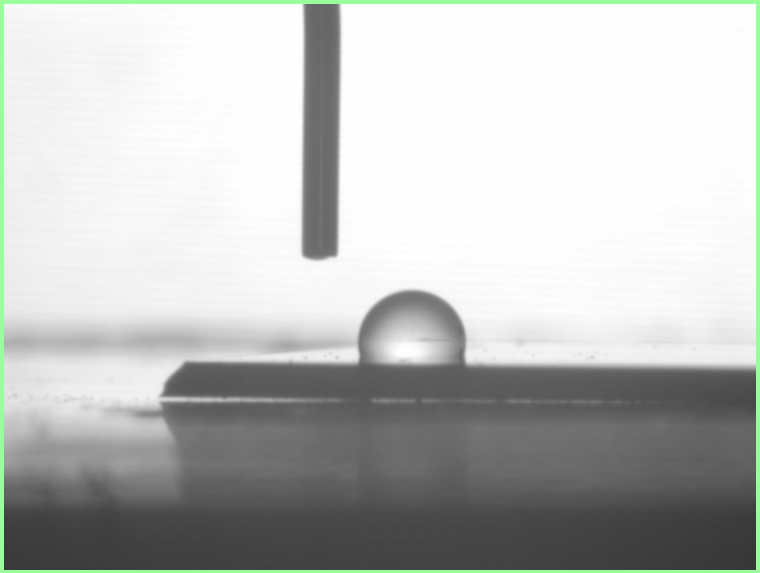


Repair of Plasma Damaged Porous MSQ ($\text{Formulated } scCO_2$)

As Received



Post CO_2 Repair Process



- Etch/Ash exposed porous MSQ
- Increased surface silanol content
- Contact angle of 13º

- Supercritical CO_2 based formulation repair of etch damaged film
- Contact angle of 106º

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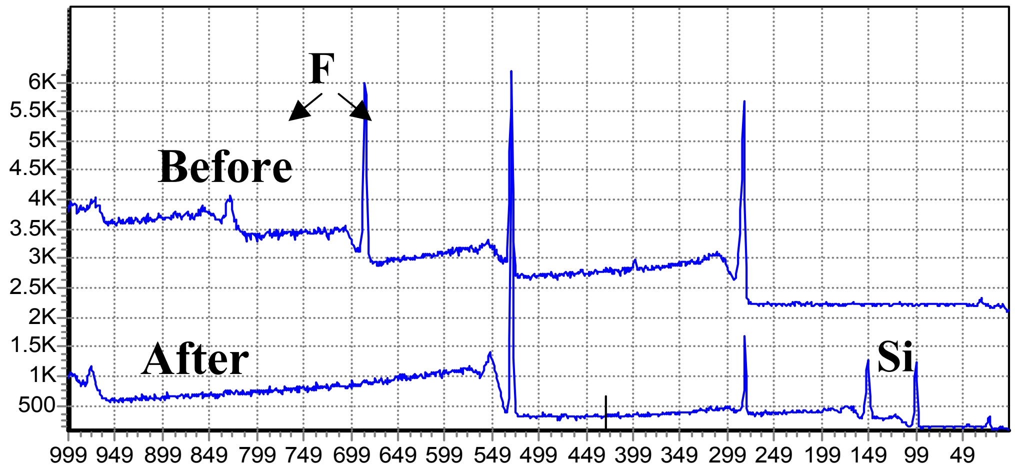
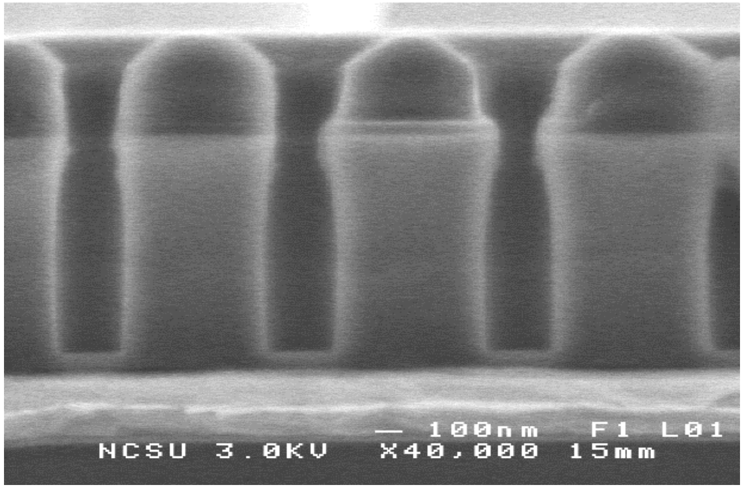
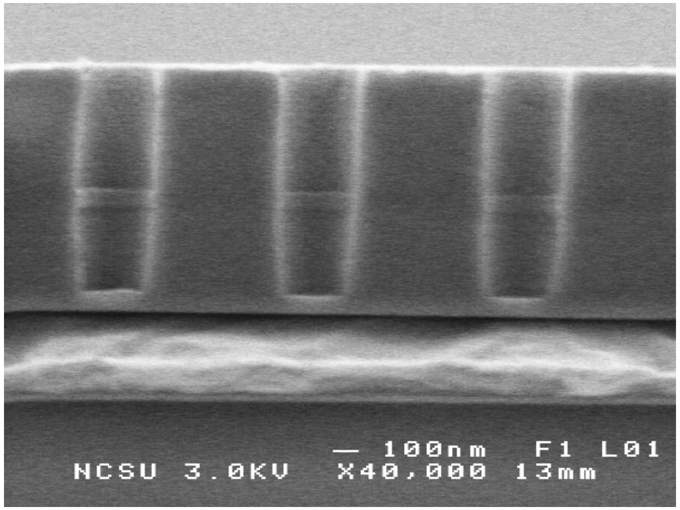
Post Dielectric Etch Cleaning with $scCO_2$

Photoresist Strip and etch residue removal



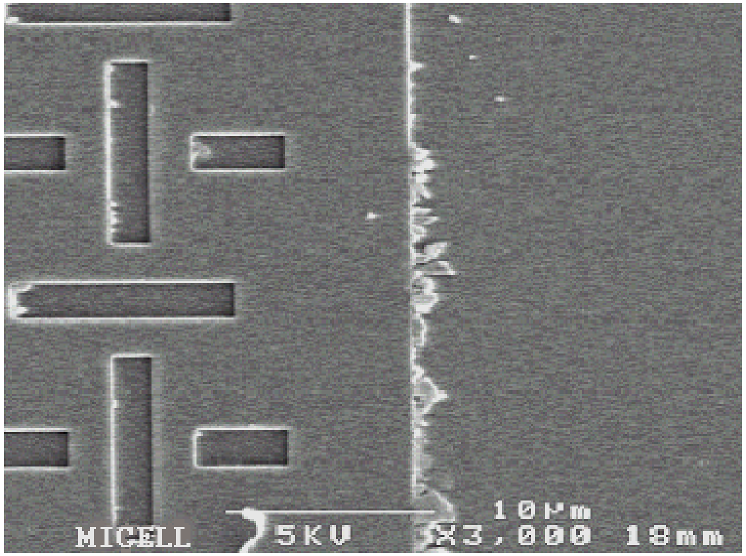
XPS data on a post-etch pre barrier breakthrough sample before and after CO_2 based cleaning.



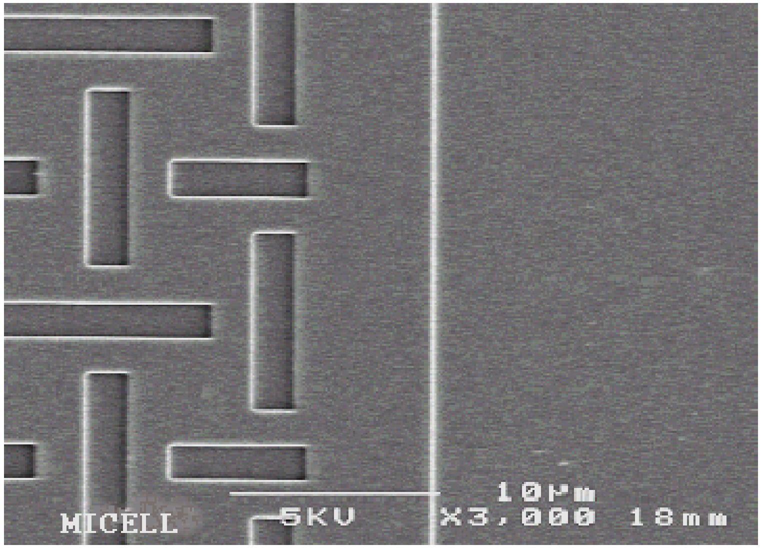


Post MSQ Etch (post-ash) $scCO_2$ Cleans Lab-scale Results

MSQ wafer - as received



MSQ wafer - processed

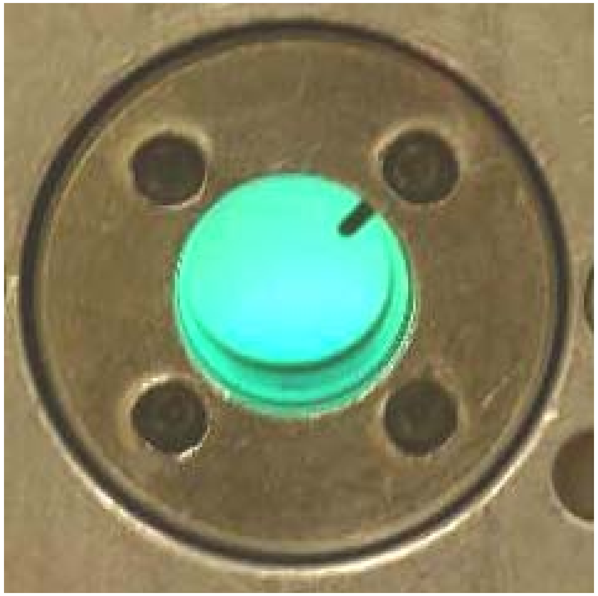


- Active chemistry developed for MSQ etch/ash residue cleaning
- Incorporates 'CO_2-philic' active ionic component
- Excess etch residue produced from MSQ low k etch at pre-metal 1 process stage; visible at left
- CO_2-philic active removes etch/ash residues from MSQ structures with no measurable CD loss; visible at right.

Specialty Cleaning Formulations for Copper Ion Removal for Semiconductor Substrates

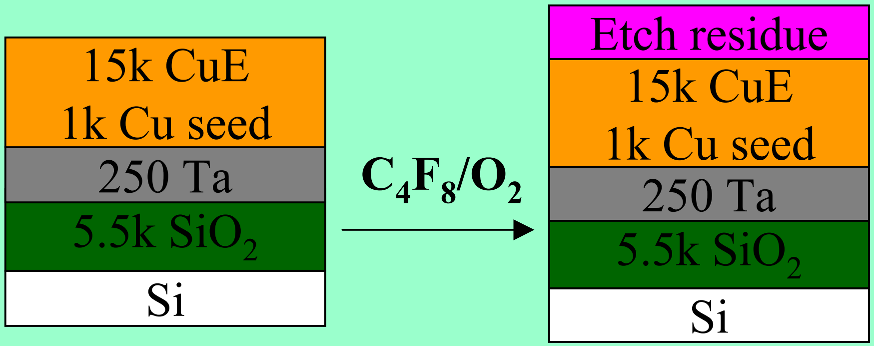
- Dense CO_2 is the ultimate non-polar solvent. No net dipole. Solubility characteristics toward ionic materials similar to hexane.
- Oxidized metal species (ca. CuF_2, CuO, $CuCl_2$, CuF, Cu_2O, $Cu(OF)_2$) only removed by charge dissociation
  CuF_2 ----- $Cu^{2+} + 2F^-$
- Ion dissociation (dissolution of ionic species) facilitated in polar, protic media such as water.
- Co-solvents added to CO_2 in small quantities, <15% are ineffective in changing non-polar nature of dense CO_2
- Additives are needed that in small quantities can enhance the ionic potential of the fluid medium. Water-in-CO_2 microemulsions!

Copper Ions in water-in-CO_2 Microemulsion



- Approximately 2 mg/mL of Copper in CO_2
- 170 bar at 40^{o}C
- 2% surfactant concentration, 17:1 mole ratio of water to surfactant
- Ionic surfactant with non-alkali counter ion

Copper Challenge Wafer Cleaning



Sematech Challenge Wafer

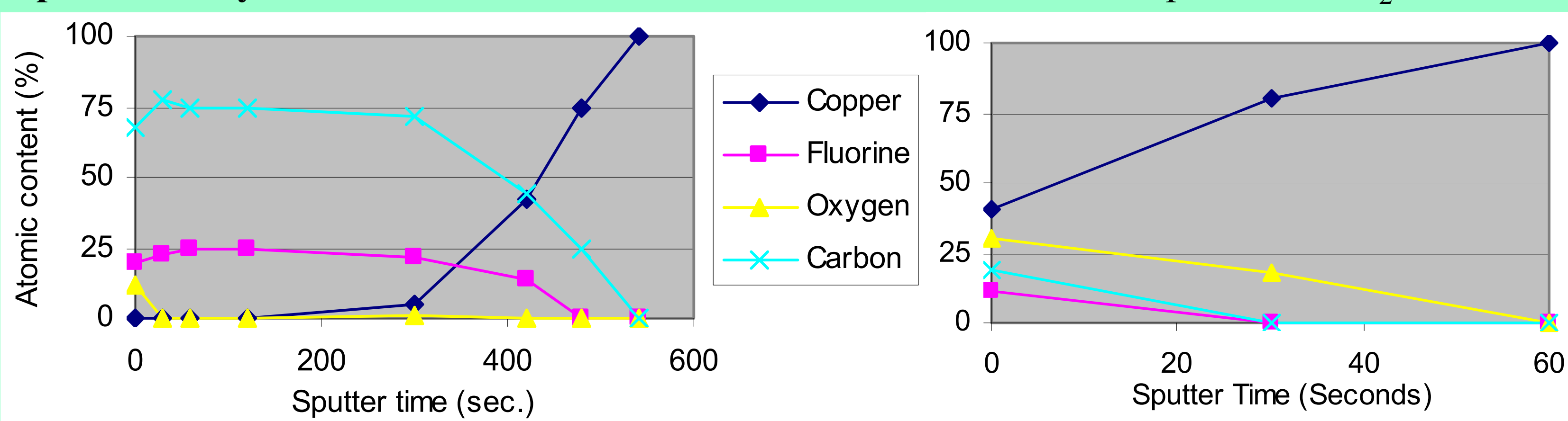
- Clean copper surface exposed to etch stop break through gas

Sample	Cu	F	O	C
As Received	0	22	13	65
EKC 525 Cu	16	9	23	52
CO_2: Form. 25	41	11	30	19
CO_2: Form. 27	34	4	14	37

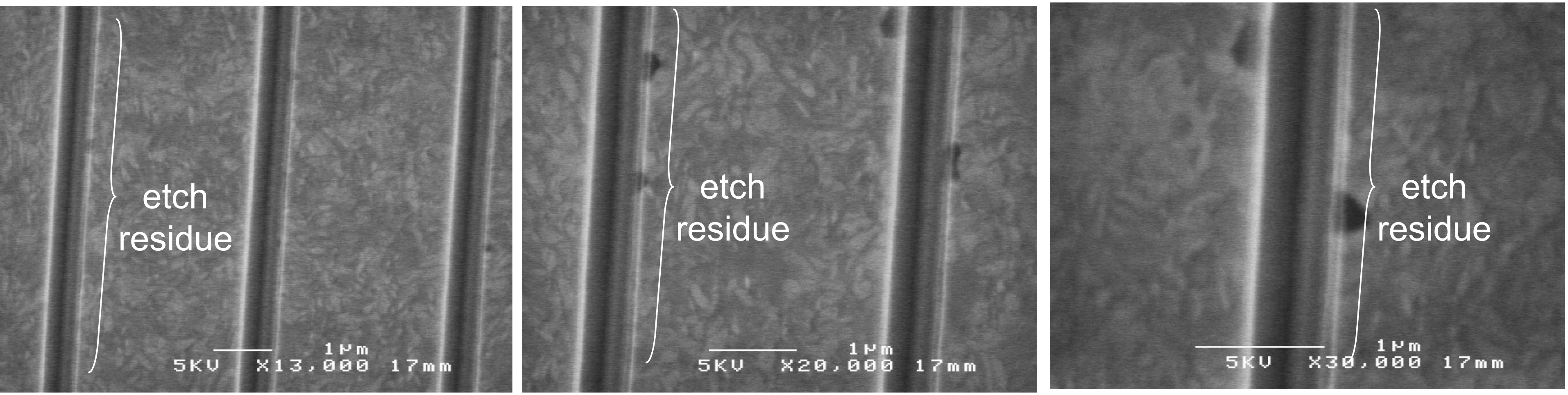
XPS Analysis

- Surface content of an as received wafer
- Comparison of commercial wet cleaned and scCO_2 cleaned samples

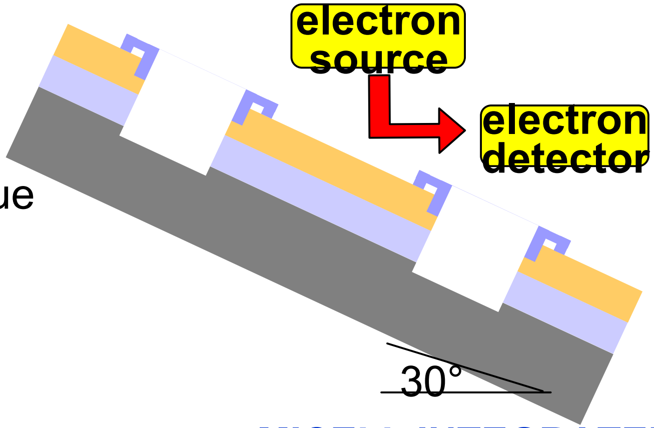
XPS Sputter Analysis: Surface content versus time for the as received sample and a CO_2 cleaned sample



Specialty Cleaning Applications
CO_2 Enabling Technologies

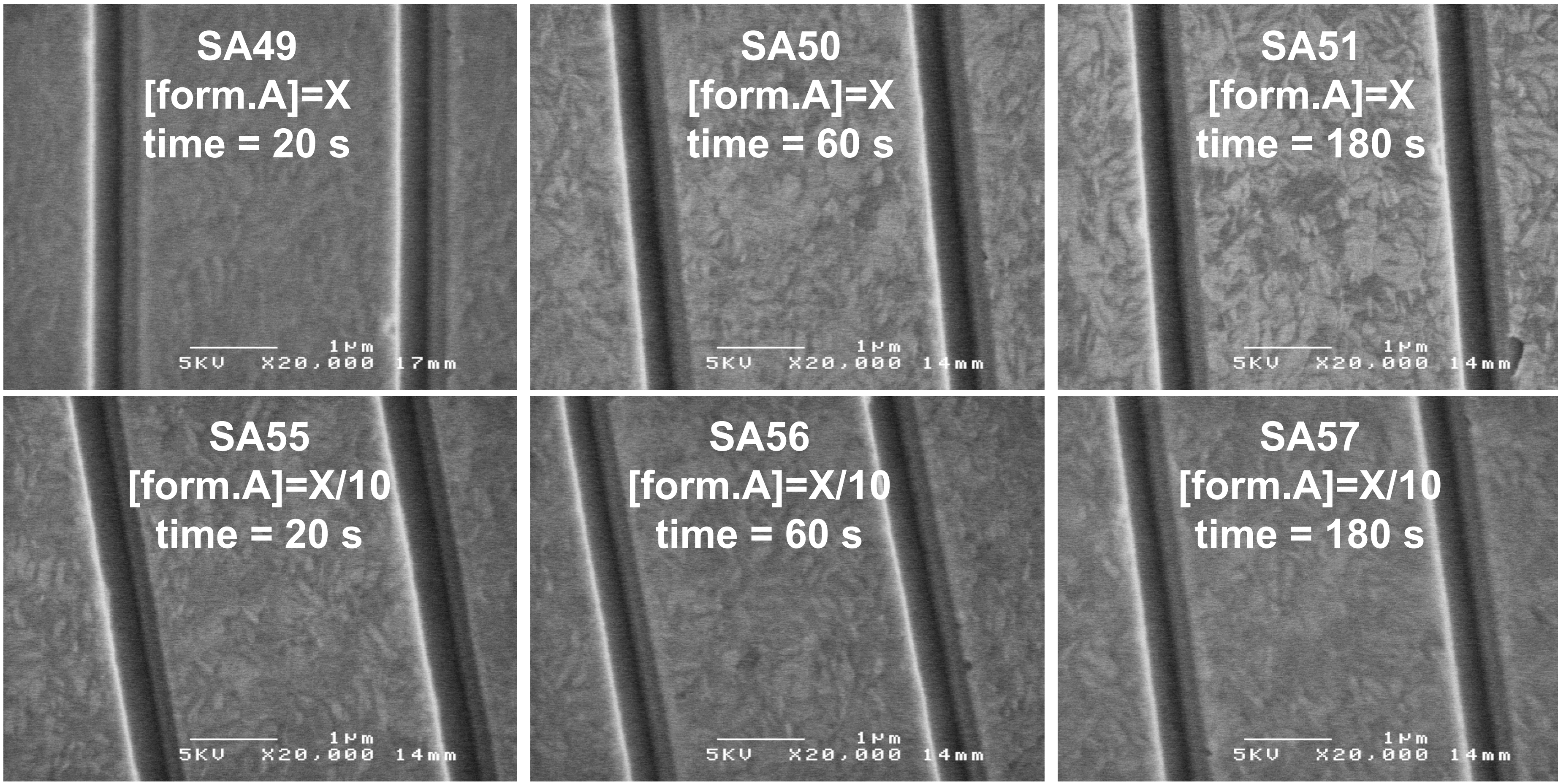


- Post metal etch (Aluminum)
- Etch residue on right side of trench is visible by SEM as a thin, white, translucent strip along trench edge
- Etch residue is not visible along left side of trench edge due to viewing angle



Post-etch Residue Removal using formulated $scCO_2$

Surfactant-based active chemistry for etch residue removal



Specific Needs for EUVL Mask Cleaning

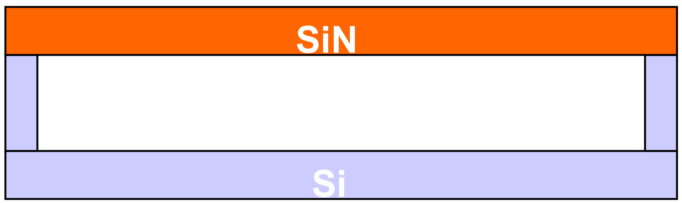
- More Frequent Cleaning Expected (No Pellicle)
- Present Cleaning Technology Not Adequate
  - New Mask Materials
  - No Change To Mask Topography. No Surface Roughening, Etching Or Swelling Permitted
- Water And Organic Contamination Is Detrimental Even At Mono Layer Level
- Stringent Particle Specifications
- Fluorine EUV Resists Are Highly Soluble In $scCO_2$ - Ease Of Cleaning

Mask Cleaning and Rework

- Chemical ‘Aggressiveness” can be Adjusted as Needed
- CO_2 Fluid Properties Enhance Particle Removal with Superior Processing Technology
  - Ideal wetting properties (low viscosity, negligible/no surface tension, liquid/scCO_2) contribute to thinner boundary layer versus water
  - ‘Water-like’ density provides comparable momentum transfer
  - Fluid compressibility, phase modulation, enhances particle removal from within features
  - Megasonic energy useful in reducing boundary layer, smaller particle removal
  - Proprietary processing steps enhance particle control and prevent particle redeposition.

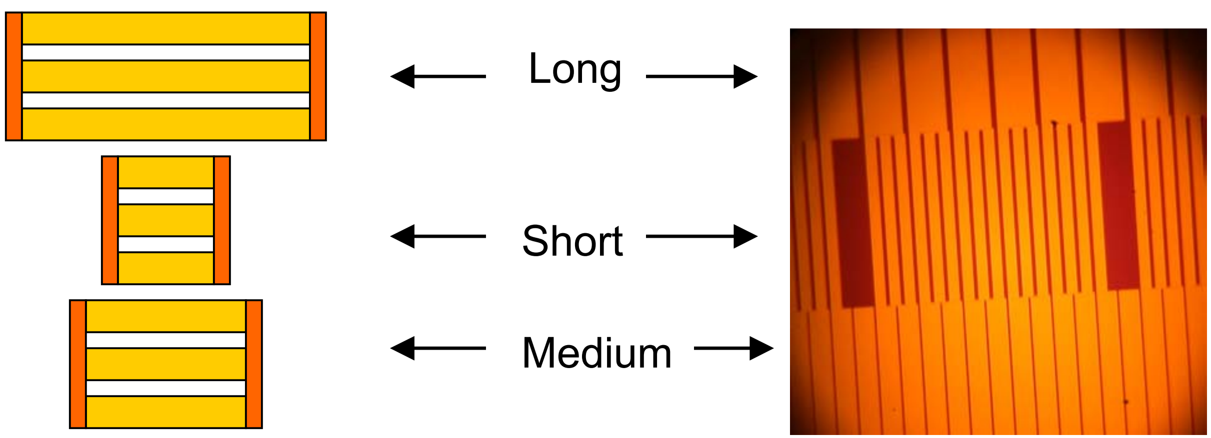
$scCO_2$ Processing Advantages: Proprietary Fluid Handling Processes

$scCO_2$ Technology for Geometrically Challenging Structures



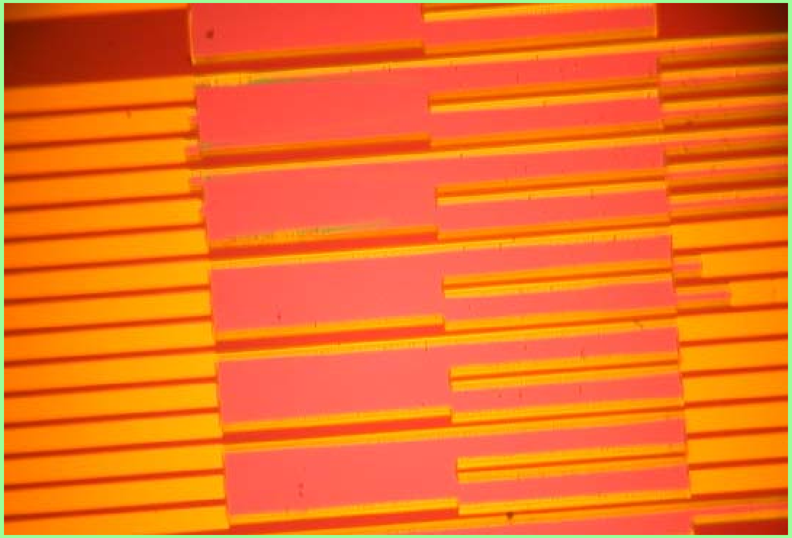
Air-Bridge Structure
for MEM's Cleans Evaluations

Top Down View: 3 different lengths (Optical Scope, 100 x)

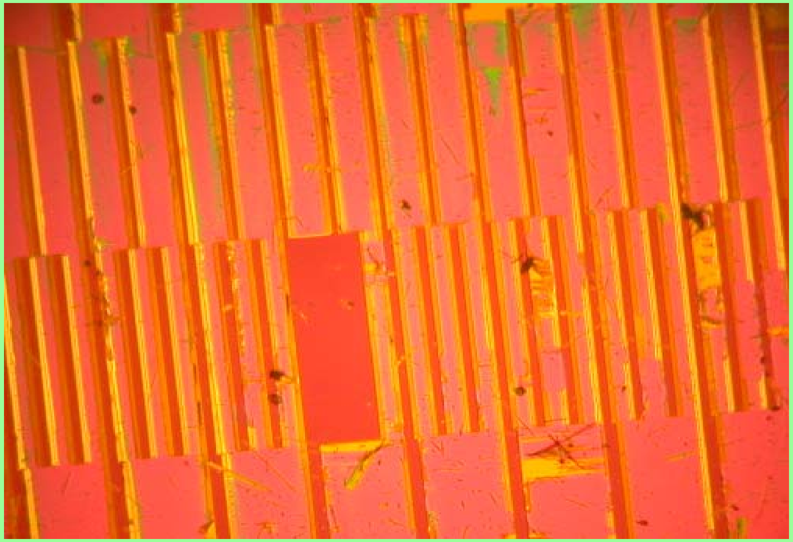


Air Bridge Structure Samples: Bulk Solvent Soak Experiments

Bulk Hexane



Bulk Water



<u>Percent Structure Damage</u>

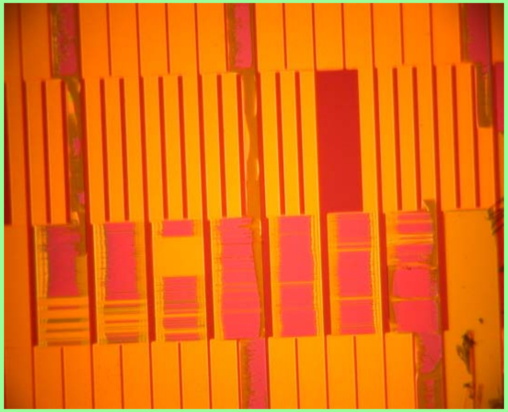
Short bridges:	25
Medium bridges:	100
Long bridges:	100

<u>Percent Structure Damage</u>

Short bridges:	100
Medium bridges:	100
Long bridges:	100

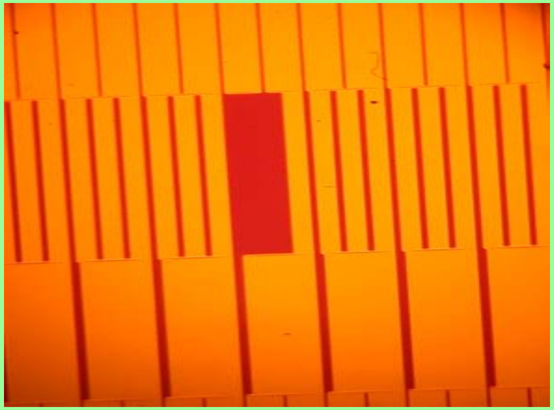
Air Bridge Structure Samples: Delivery and Rinsing of Formulation A in CO_2

CO_2 with formulation A: Slow rinse, fast vent



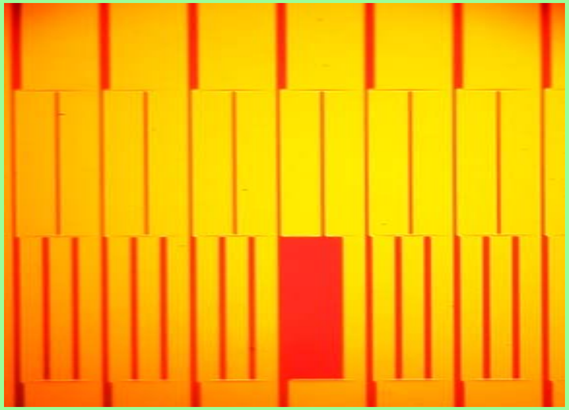
Vent 3000 to atmosphere in 20 sec.
0.63L/sec. @ STP

CO_2 with formulation A: Slow Rinse, Slow Vent



Vent 3000 to atmosphere in 4 min.
0.053L/sec. @ STP

CO_2 with formulation A: MIS Proprietary Fast Rinse/Vent Process



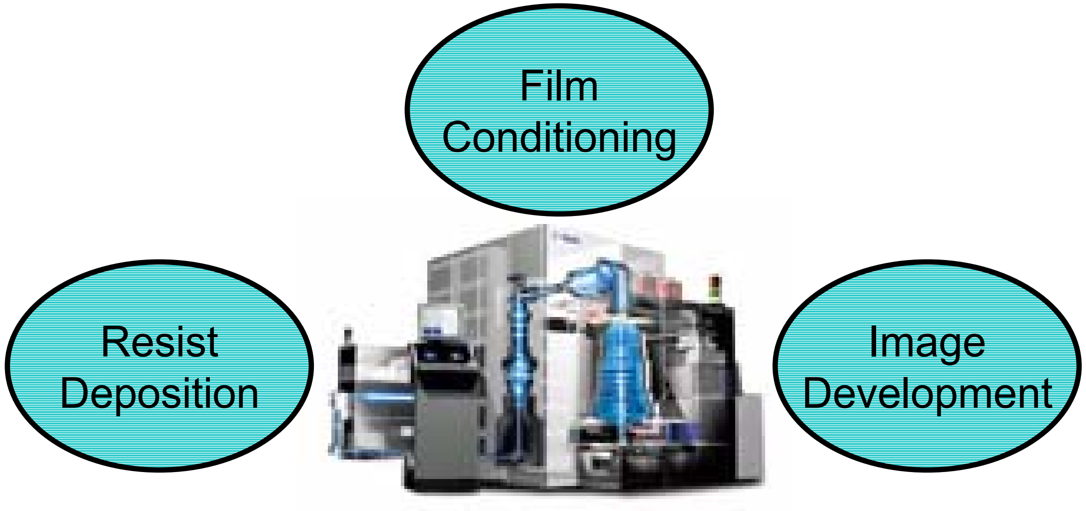
Vent 3000 to atmosphere in 10 sec.

Percent Structure Damage	
Short bridges:	15
Medium bridges:	20
Long bridges:	90

Percent Structure Damage	
Short bridges:	0
Medium bridges:	0
Long bridges:	0

Percent Structure Damage	
Short bridges:	0
Medium bridges:	0
Long bridges:	0

Pattern Transfer Applications for CO_2-based Process Technology



Imaging Tool

Dense CO_2 enables each capability without the typical sacrifice or tradeoff in benefits

Capability	**Benefit**
‘Dry’ film deposition “no outgassing”	CD control and defects
Control of physical uniformity	CD control and defects
Control of film composition and homogeneity	CD control and defects
‘Dry’ low temperature film treatment/ densification	CD control and etch resistance
CO_2-philic resist	Transparency and etch resistance
Zero surface tension drying	High aspect ratio patterns

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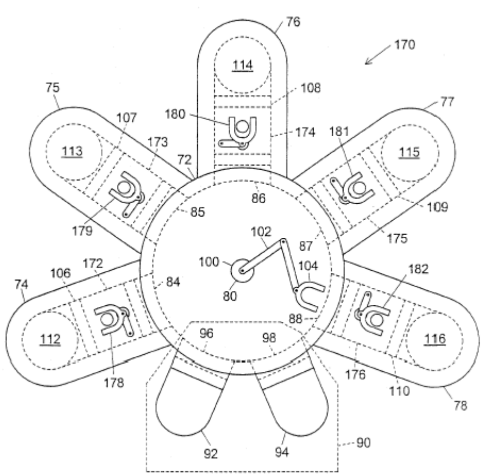
Integrated CO_2-based Processes

- "Totally dry" process technology
  - Wide range of compositions and CO_2 densities combine for unparalleled processing window
  - Formulated CO_2 solution provides performance-led process solution

- Pattern transfer applications coupled directly to etching and stripping/cleaning processes
  - Enables complete processing of structures without exposure to aqueous solutions.

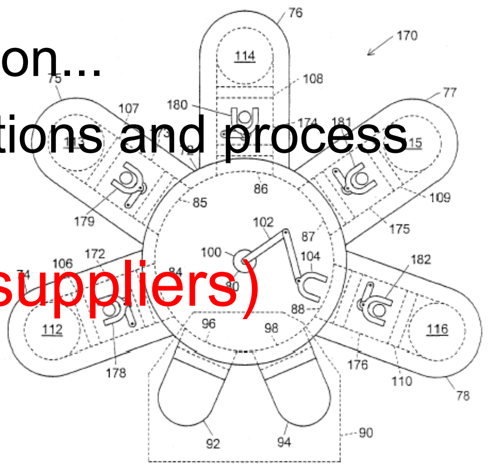
Other Applications for the Technology Platform

- Ultra Low-k Dielectric Material Processing
  - applicable IP
- MEMS Manufacturing
  - applicable IP
- Read-Write Heads
  - applicable IP
- CMP
  - applicable IP

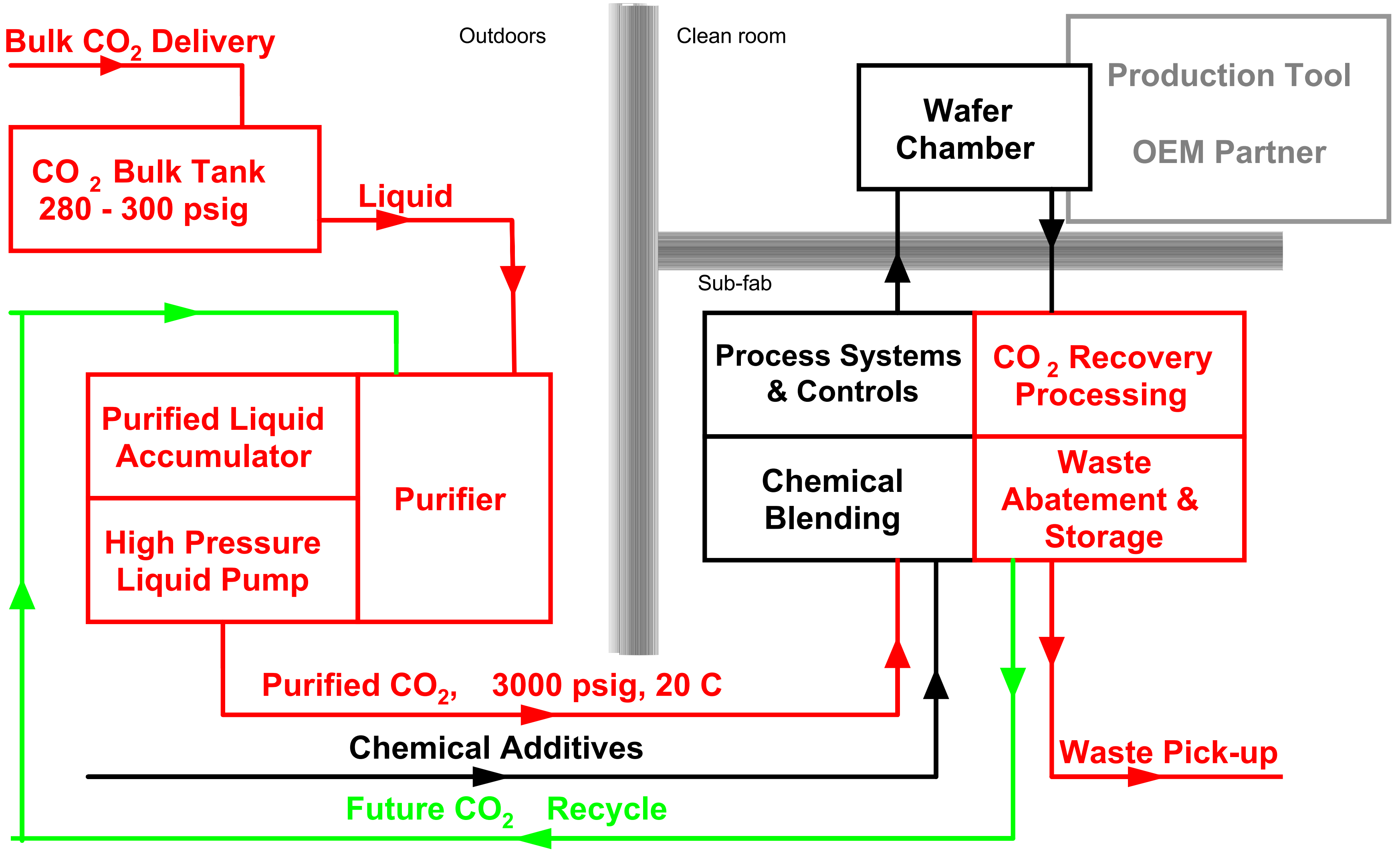


Execution

- Strategic, Developmental and Commercial Alliances
  - Chemistry Formulations (Specialty Chemistry Providers)
    - generic capabilities - micro -domains, active chemistries...
    - application specific formulations based on generic and optimized with process and hardware
  - Process (End Users and OEMs)
    - generic - rapid mix, rapid fill/vent, physical action...
    - Process of record - specific chemistry formulations and process recipe optimized for chamber configuration
  - Hardware (BOCE, OEMs, other industry suppliers)
    - infrastructure
    - process specific chamber configurations

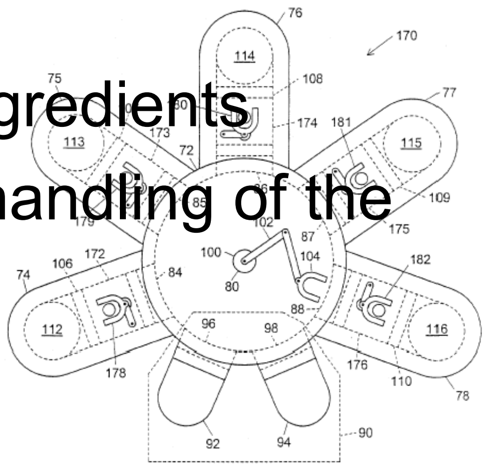


$scCO_2$ Process System, Supply & Support

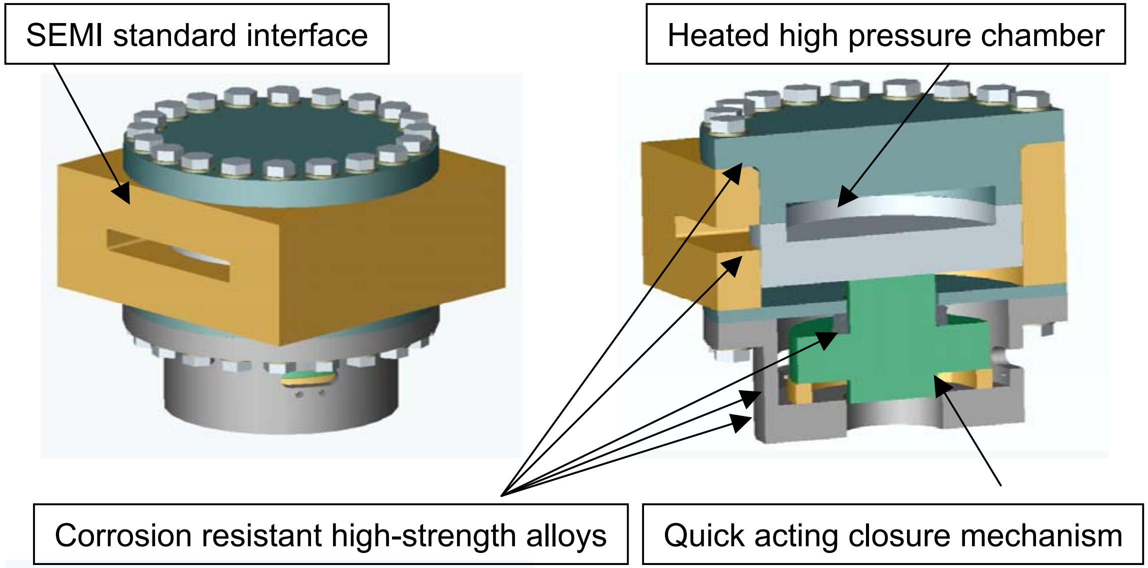


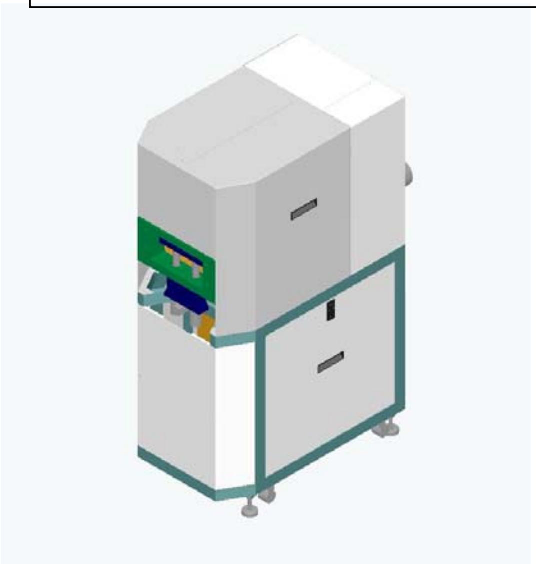
Infrastructure
BOC - $scCO_2$ Supply Solutions

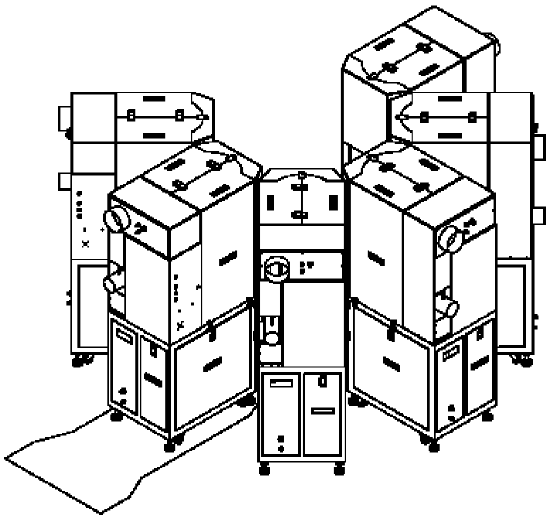
- Integrated approach to supply ***supercritical CO_2 ($scCO_2$)***
- CO_2 from BOC's extensive supply network
  - Designated quality control processes
  - Flexible and consistent supply
- Unique purification and pressurization equipment
  - Further tightens $scCO_2$ control
  - Reduces variability
- Unique $scCO_2$ chemistry provides active ingredients
- Accurate control of the inputs and reliable handling of the outputs to your process



Micell / BOC Edwards Technology







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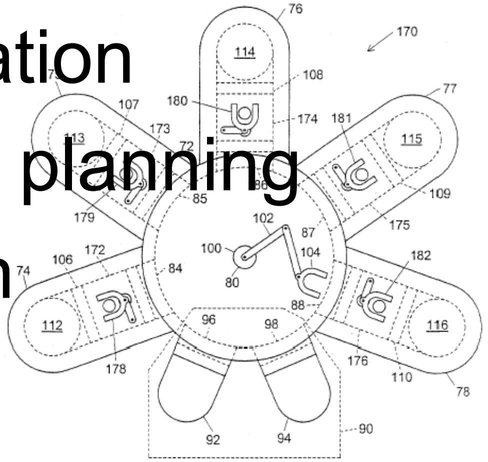
Summary - Current Projects

- Cleaning (Direct Funding)
  - Development on-going
  - Commercial approach evolving
- Metal Deposition (Direct Funding)
  - C&F (12/02 - 05/03)
  - Shift to development Summer 03
- Mask Cleaning - opportunity evaluation
- Lithography - consortium approach planning
- Ultra Low-k - early stage evaluation
- MEMS - early stage evaluation



Questions and Discussion

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- More Information

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