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Title: SCORR - Supercritical Carbon Dioxide Resist Removal

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SCORR - Supercritical Carbon Dioxide Resist Removal

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SCORR, short for supercritical carbon dioxide resist removal, is a new technology that could continue to enable the technological development of photolithography processes in industry. SCORR is based upon the physical properties of supercritical fluids (SCFs). These special properties enable SCFs to remove coatings, residues, and particles from high-aspect-ratio structures in integrated circuits (ICs). SCORR also eliminates rinsing and drying steps presently used in IC manufacture, thereby eliminating the generation of millions of gallons of water per fab per day.

Fabricating integrated circuits relies heavily on photolithography to define the shape and pattern of individual components. Once a single stage of a silicon wafer's topography has been completed, the hardened resist must be removed. Conventional processes generates more waste than any single step in the IC manufacturing process, and the production of a complete IC can involve many photolithography iterations. The cost associated with the treatment and disposal of this waste, as well as employee health and safety considerations, are driving a search for alternative, environmentally benign, cost-effective solutions.

In addition, photoresist stripping is confronting finer architectures and higher aspect ratios, as well as new low-k materials that are highly sensitive to post-etch residue. Low-k dielectrics and low-resistivity conductors such as copper are necessary for meeting industry's need for faster and smaller chips. Further, each low-k choice requires different plasma-etching processes, or chemistries, to etch structures into the low-k material; therefore, the nature of the residues can be different. No one product can meet all copper/low-k applications, and existing chemistries are not tunable—or even desirable—for the new processes.

We have developed a new process—known as SCORR—that removes photoresist and post-ash, -etch, and -CMP (particulate) residue from semiconductor wafers. As IC feature sizes become smaller, the need for ensuring particle removal will increase. With feature sizes of less than $0.18\mu m$, it will become imperative that all particles greater than about 0.1 micron be removed from the semiconductor wafer. Existing cleaning technologies (such as liquid or high-pressure jet scrubbing) cannot remove particles on the order of 0.1 micron because of surface boundary layer constraints. Because of the low viscosities of supercritical fluids (SCFs), these constraints are virtually eliminated.

The key to the effectiveness of SCORR is the use of SFCs, specifically supercritical carbon dioxide (CO_2). The physical properties (e.g.. density, viscosity, diffusivity) of a supercritical fluid often lie between those of gases

and liquids, and can be varied by small changes in temperature and/or pressure.[1]
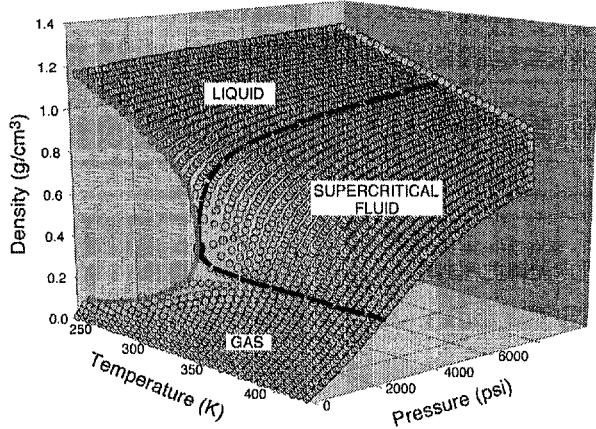

Fig. 1. Carbon dioxide density as a function of temperature and pressure.

The possibility to obtain a wide range of physical properties without changing the chemical composition and by using a fluid than becomes gaseous at atmospheric pressure, makes these fluid attractive for a wide range of applications.[2] Carbon dioxide is generally chemically inert with respect to inorganic materials and is therefore compatible with existing semiconductor materials and metallization systems. Supercritical fluids have, by definition, no surface tension which offers the possibility for the removal of very small (sub-micron) particles from substrate surfaces.[3] They are therefore ideal candidates for the removal of photoresist from fabricated surface structures having high aspect ratios. Carbon dioxide is noncombustible, readily available in high purity, environmentally friendly (not ozone depleting), and has a low human toxicity.

Pure supercritical CO_2 is limited in its ability to dissolve most polymers (photoresists).[4] Rather, it is the absorption of supercritical CO_2 into the polymer and the resulting swelling of the polymer that can be utilized to achieve various desirable interactions. By "tuning" the CO_2/polymer interaction with pressure and temperature adjustments, supercritical CO_2 is absorbed into the polymer-based photoresist, thus plasticizing the polymer and lowering its glass transition temperature significantly below that observed at atmospheric pressure. Lowering the polymer's glass transition temperature softens it, thereby enhancing penetration and speeding the diffusion of the supercritical fluid into the polymer/substrate interface.[5] The principle is to swell the polymer with the dense gas, allowing the supercritical CO_2 to diffuse throughout the polymer matrix and then suddenly release the pressure, forcing a rapid volume change that ruptures the polymer from the substrate.[6]

To further enhance solubility or overcome bonding effects, a second compound, or co-solvent, is added to the supercritical CO_2. The high densities achievable in the SCF region provide the necessary solvating power to solubilize small amounts of co-solvent (less than 5% by volume), which then can diffuse throughout the polymer matrix and to the polymer/substrate interface. This diffusion provides for significant chemical interaction, which promotes the photoresist and residue removal.

Supercritical CO_2 is also attractive from the viewpoint of waste minimization. After the cleaning step, CO_2 is easily separated from the extracted or dissolved compounds, resulting in streams of concentrated compounds and pure, recyclable CO_2. Because SCORR uses pure CO_2 for its

final rinse step, it does not deplete critical water reserves. SCORR's solvent system is not only nontoxic but also recyclable, and thus the only waste generated is the spent solubilized photoresist, which is itself non-regulated. And finally, instead of using alcohol for the drying process, we merely lower the pressure and temperature of the superctricial CO_2, and thus the supercritical fluid returns to its gaseous phase, leaving the silicon wafer dry and virtually free of any residue.

The SCORR system is a technology based on sound green chemistry principles while enabling the industry to meet its development goals, such as the introduction of low-k dielectric materials, which are sensitive to the established chemistries, plus copper and smaller line widths. The SCORR system chemistry and instrumentation will be presented in detail. Advantages of the SCORR system to the industry and the environment will also be discussed.

[1] a) Squires, T. G.; Venier, C. G.; Aida, T. *Fluid Phase Equilibria,* **1983**, 10, 261-268. b) Tiltscher, H.; Hofmann, H. *Chem. Eng. Sci.***1987**, 42, 959-977.

[2] Clifford, T. Fundamentals of Supercritical Fluids, Oxford University Press, Inc., New York, 1999.

[3] Manivan, G.; Sawan, S. P., Supercritical Fluid Cleaning: Fundamentals, Technology, and Applications, McHardy, J., editor, Noyes Publications, Westwood, New Jersey, 1998.

[4] DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science*, **1992**, 257, 945-947.

[5] Chiou, J. S.; Barlow, J. W.; Paul, D. R. *J. Appl.Polym. Sci.*, **1985**, 30, 2633-2642.

[6] Barton, J. U.S. Patent 6 085 762, 2000.

SCORR
Supercritical CO_2 Resist Removal

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Science Serving Society
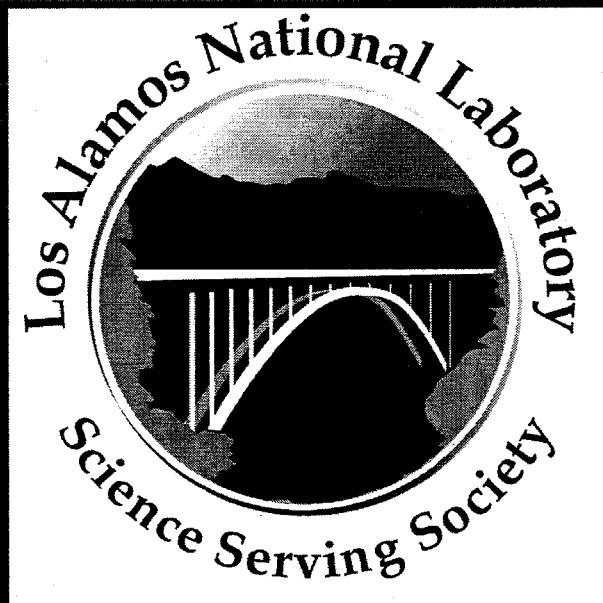
SCORR

Cleaning Fluid:

CO_2 + 1-3 wt% cosolvent at supercritical conditions.

Benefits

- Compatible with higher aspects ratios (<0.10 μm)
- Compatible with low-k materials
- Removes photoresist, post-ash, -etch and CMP residues
- Eliminates DI water rinse step
- Eliminated IPA dry step
- Reduces hazardous chemiclas
- Recycle CO_2

Future Applications in IC Manufacturing

Wafer cleaning

Film deposition

Film etching

Photoresist developing

Photoresist stripping

Residue removal

Drying (MEMS)

Particulate removal

Waste treatment

Supercritical Fluids

Fluid	T_c (°C)	P_c (psi)
Ne	-229	400
N_2	-147	492
Ar	-122	706
Xe	17	858
CO_2	31	1072
SF_6	46	545
C_3H_8	97	617
NH_4	**133**	**1654**
H_2O	374	3209
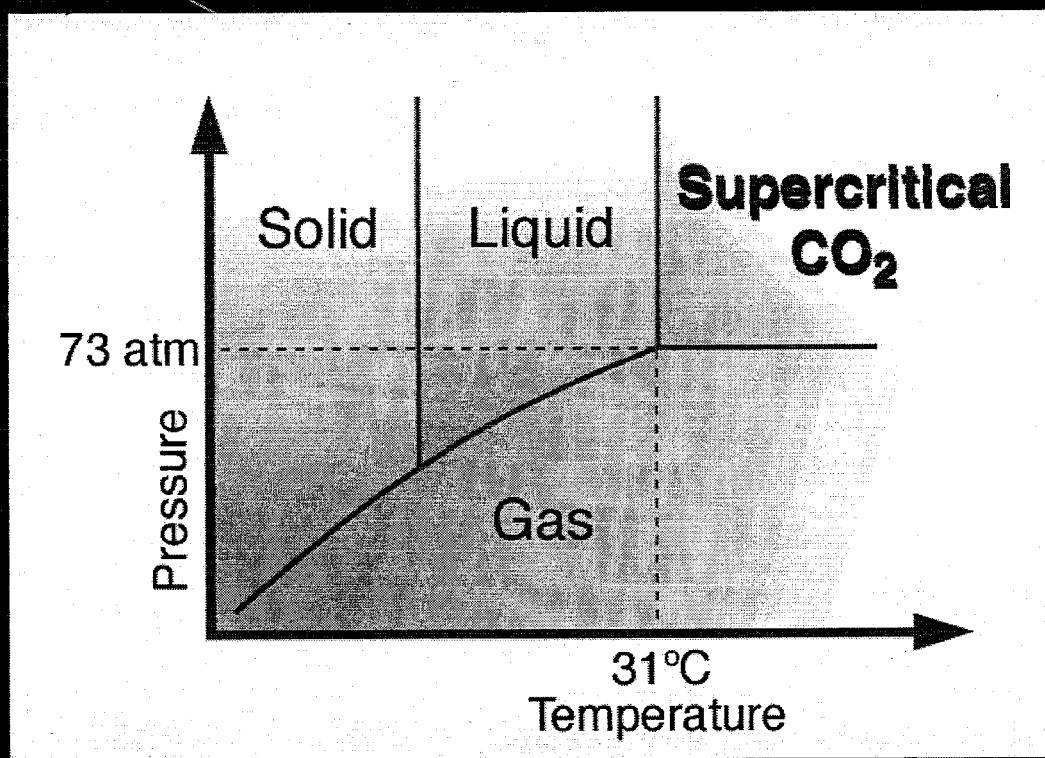
	Liquid	SCF	Gas
Density (g/cm^3)	1	0.1-0.5	10^{-3}
Viscosity (Pa-s)	10^{-3}	$10^{-4} - 10^{-5}$	10^{-5}
Diffusivity (cm^{-2}/s)	10^{-5}	10^{-3}	10^{-1}

Pure Fluid PVT Surface

Supercritical fluids are attractive solvents because of

- **high diffusivity**
- **low viscosity**
- **zero surface tension**
- **tunable solvent strength**
- **nontoxic**
- **recyclable**
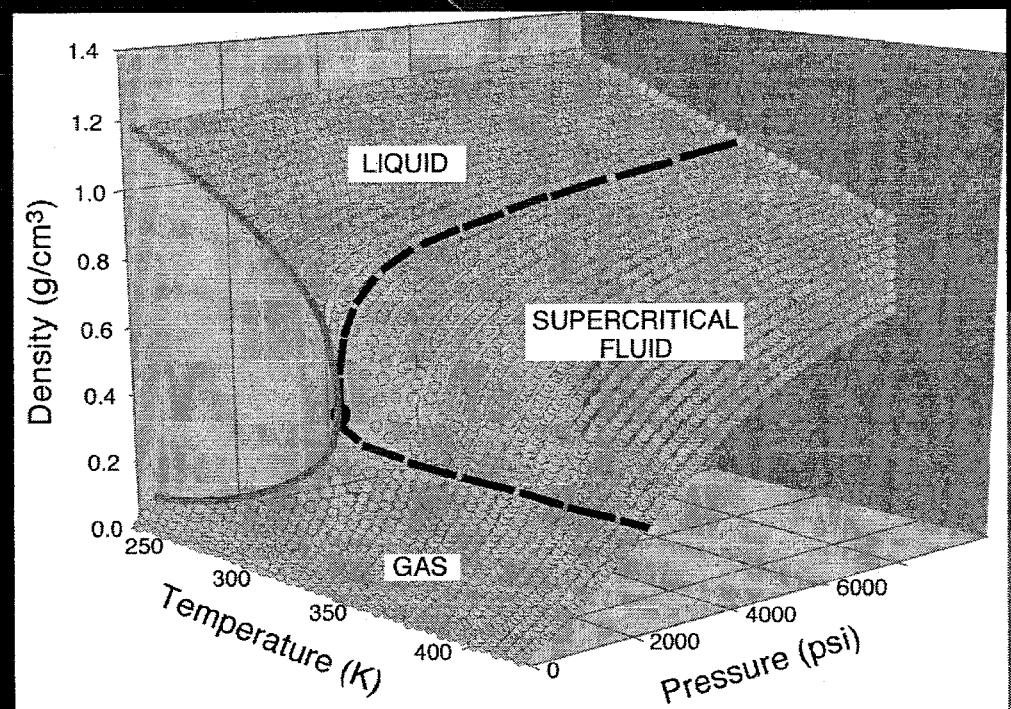
Supercritical Fluid Facility at LANL

Open user facility for applied research

Bench scale to production scale pressure vessels (5 mL – 60 L)

Applications: Weapon parts cleaning
Dry cleaning (Drywash)
Materials modification
Synthesis
Biotechnology
Extraction / separation
Alternative / replacement solvents

Supercritical Fluid Process
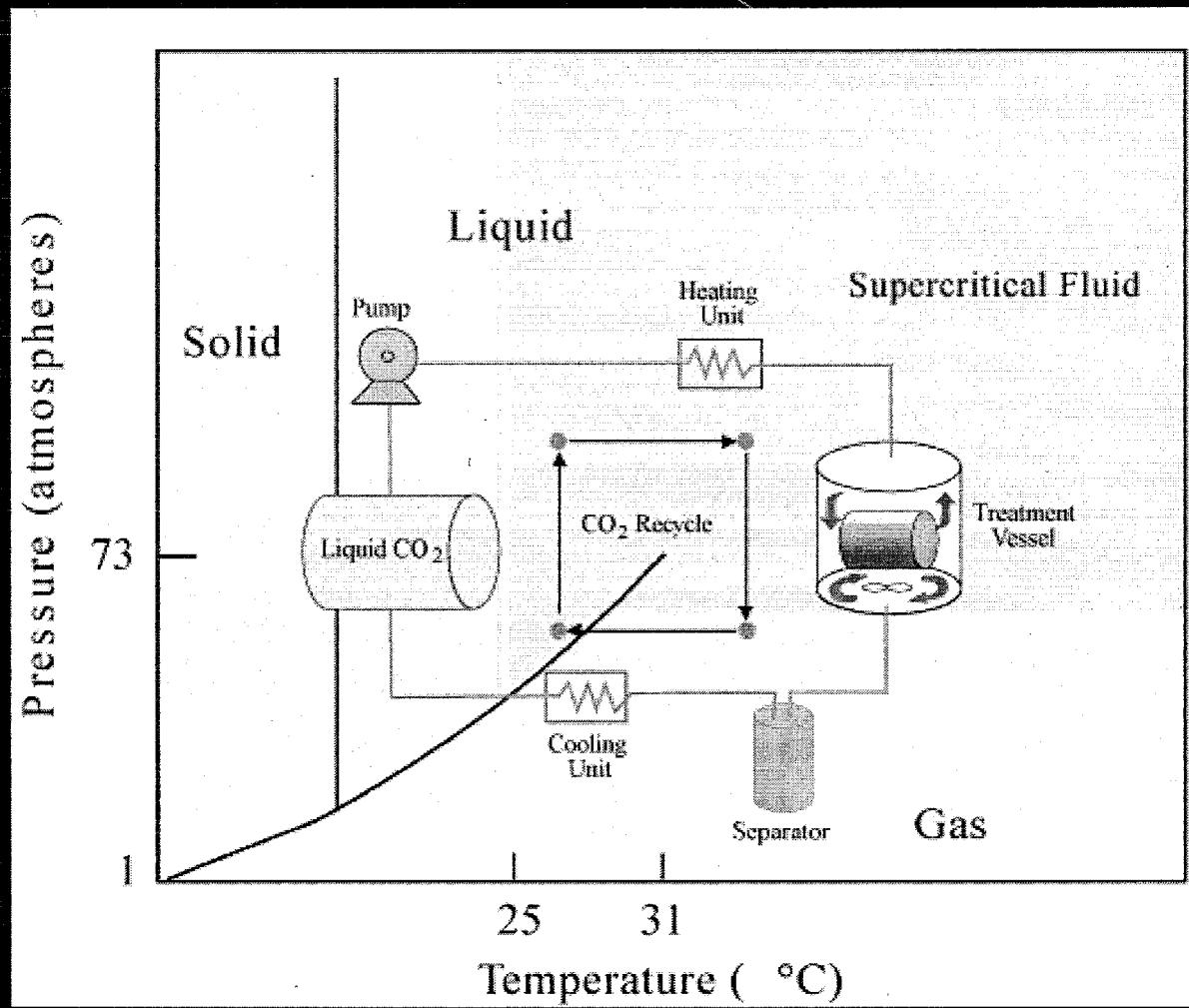
Supercritical Fluid Facility at LANL

High-Pressure Equipment Bay
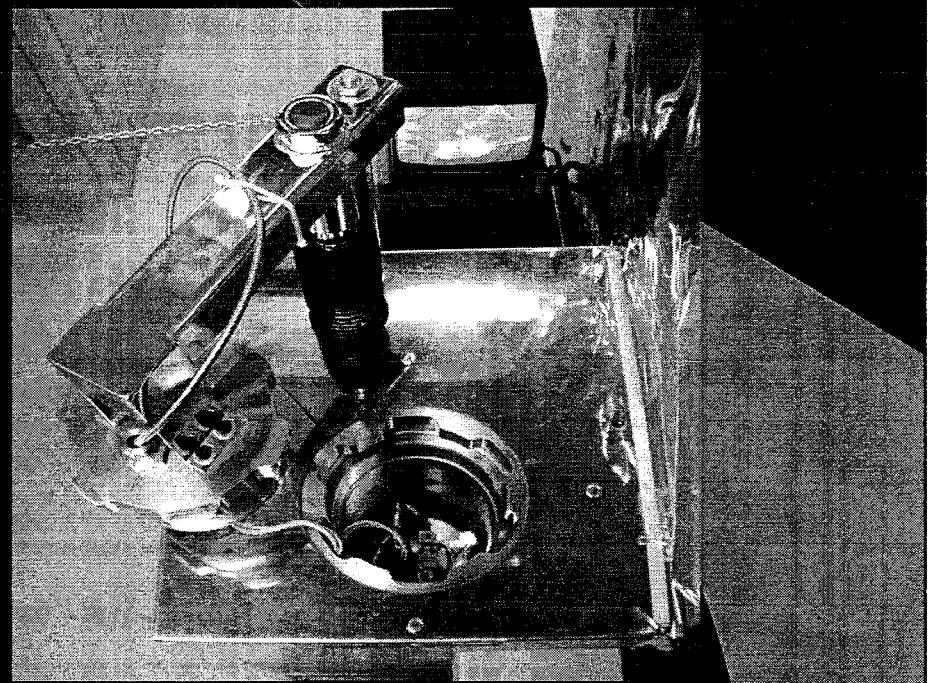
10-Liter High-Pressure Vessel

Commercial Applications

- The concept of SCF's as an industrial solvent has grown out of commercial SCF extraction and purification applications

  - Decaffeinating coffee
  - Production of hops extracts
  - Food processing
  - Various processes in the petrochemical industry (ROSE process, tertiary oil recovery)
  - Dyeing fibers
  - SCWO

Photoresist Removal

- Few polymers are soluble in CO_2

- CO_2 is absorbed into many polymers at high pressures

Therefore, unlike wet chemical cleaning,
coatings removal with SCF's does not rely on the dissolution of the polymer coating in the solvent, but rather the dissolution of the SCF solvent in the polymer, and the resulting swelling, to effect its removal.

Polymer – SCF Interactions

Applications requiring polymer solubility in the SCF

- Polymerization
- Fractionation
- Selective Extraction

Applications requiring SCF solubility in the polymer

- Plasticization
- Crystallization
- Selective Extraction
- *Coatings Removal*

Polymer – CO_2 Interactions

Factors which affect polymers ability to solubilize CO_2:

- chemical structure
- polymer crystallinity
- amount of crosslinking
- solubility paramater (δ) match

How do you calculate δ?
How do they change with T and P?
How do they change when adding cosolvent?

Solubility Parameters

The Hildebrand solubility parameter, δ, is defined as

$$\delta^2 = \left(\frac{\Delta E}{V} \right)$$

where E is energy of vaporization to the gas at zero pressure, *i.e.* infinite separation of the molecules, V is the molar volume, and

$\left(\dfrac{\Delta E}{V} \right)$ is the cohesive energy density.

Solubility Parameters for SCF

δ can also be expressed as a function of P_c

Giddings approximation:

$$\delta = 0.47 P_c^{1/2} \rho_r^{SCF}$$

CO_2 Equation of State (Huang, F.E., Li, M.H., Lee, L.L., and Starling, F.T., J. of Chemical Eng. of Japan, 1984)

$$P = \rho RT \left[\begin{array}{l} 1 + b_2 \rho' + b_3 \rho'^2 + b_4 \rho'^3 + b_5 \rho'^4 + b_6 \rho'^5 + b_7 \rho'^2 \exp\left(-c_{21}\rho'^2\right) + b_8 \rho'^4 \exp\left(-c_{21}\rho'^2\right) \\ + c_{22} \rho'^2 \exp\left(-c_{27}(\Delta T)^2\right) + c_{23} \dfrac{\Delta \rho}{\rho'} \exp\left(-c_{25}(\Delta\rho)^2 - c_{27}(\Delta T)^2\right) \\ + c_{24} \dfrac{\Delta \rho}{\rho'} \exp\left(-c_{26}(\Delta\rho)^2 - c_{27}(\Delta T)^2\right) \end{array} \right]$$

1-Parameter Solubility Values CO$_2$
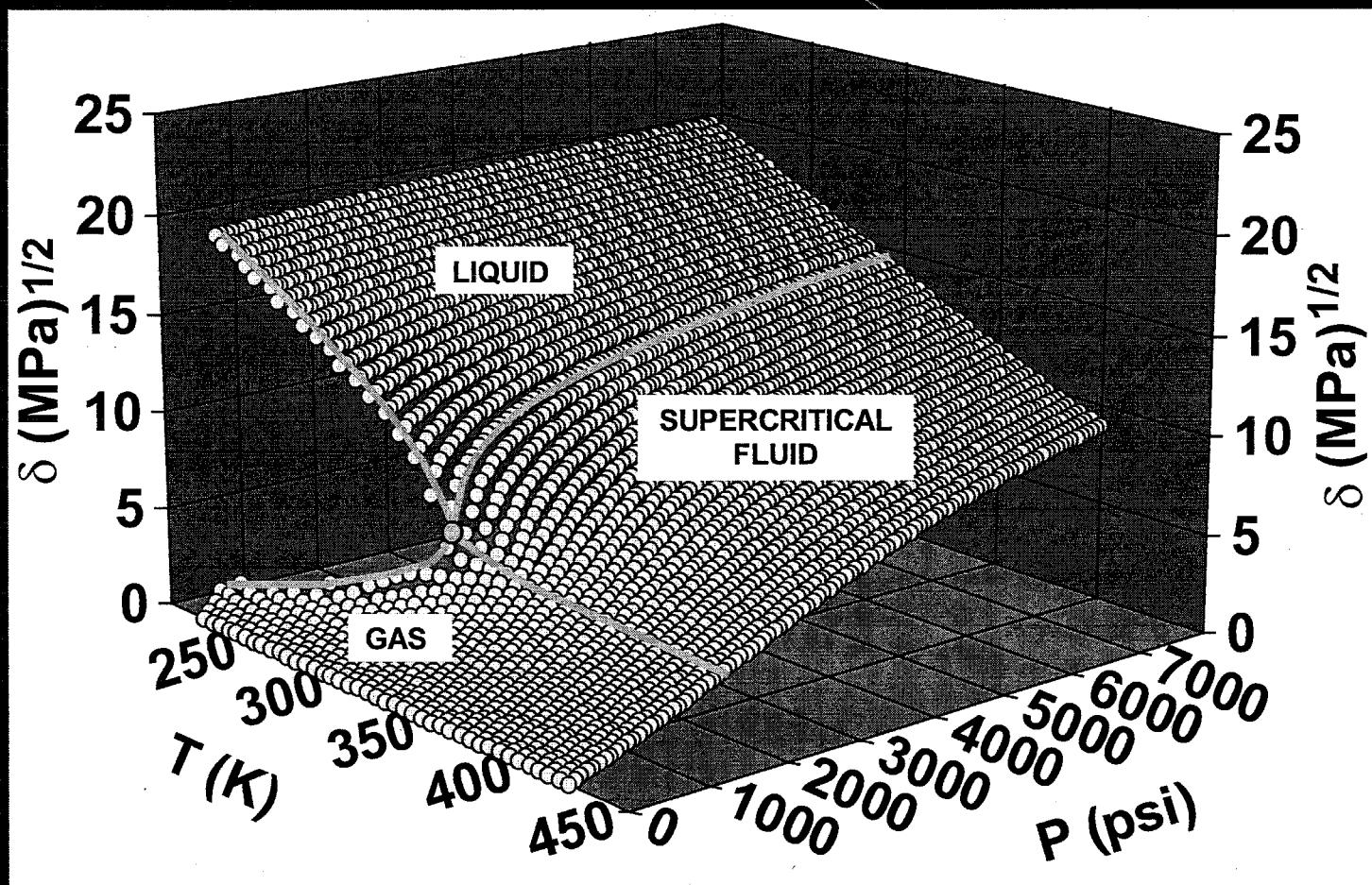
Hansen Solubility Parameters HSP

- Improved 3 parameter model

$$E = E_d + E_p + E_h$$

- Assumes the total cohesive energy density (E) is made up of

E_d nonpolar (dispersion) interactions

E_p polar (dipole-dipole, dipole-induced dipole) interactions

E_h hydrogen bonding (also Lewis acid-base) interactions

$$\therefore \ \delta_T^2 = \left(\frac{E_d}{V_m}\right) + \left(\frac{E_p}{V_m}\right) + \left(\frac{E_h}{V_m}\right) = \delta_d^2 + \delta_p^2 + \delta_h^2$$

HSP's

HSP for CO_2

HSP values for CO_2 calculated at 25°C

$$\delta_d = 15.6 \text{ MPa}^{1/2}$$
$$\delta_p = 5.2 \text{ MPa}^{1/2}$$
$$\delta_h = 5.8 \text{ MPa}^{1/2}$$

Values change with T and P

Finding Solubility Parameters

Fig 5-11

Binary Interactions

- If CO_2 HSP cannot match polymer HSP then add a cosolvent

- Calculate solvent-cosolvent HSP using a volume average model

$|solvent/cosolvent/polymer| \rightarrow$

solvent/ solvent	solvent/ cosolvent	solvent/ polymer
cosolvent/ solvent	cosolvent/ cosolvent	cosolvent/ polymer
polymer/ solvent	polymer/ cosolvent	polymer/ polymer

Polymer Swelling in CO_2

CO_2 sorption into polymer lowers T_g

Swelling is increased if T_g is exceeded

Swelling decreases polymer/polymer interactions and therefore reduce the δ

Additional polymer/polymer interactions can be reduced by a cosolvent

Depressurization cracks polymer before Polymer/polymer interactions are reestablished.

Fig. 2-8
Swelling above and below Tg

Photoresist Removal

- Photoresists usually has higher HSP than CO_2

- Increase CO_2 HSP by
    - adding cosolvent
    - increasing P
    - lower T

- Find T condition above T_g but below T_{mp} to increase polymer swelling.

CO$_2$ soluble surfactans

- **PFPE (anionic)**

$$CF_3\!\!-\!\!(OCF_2CF)_3\text{-}OCF_2\!\!-\!\!\overset{\overset{\displaystyle O}{\|}}{C}O^-NH_4^+$$
$$|$$
$$CF_3$$
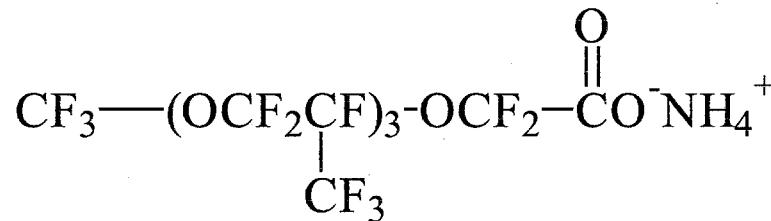
Johnston et.al. *Science*, 1996, 271, 624

- **PBO-PEO (nonionic)**

$$HO\!\!-\!\!(CH_2CHO)_{12}\!\!-\!\!(CH_2CH_2O)_{15}\text{-}H$$
$$|$$
$$CH_2CH_3$$

- **Lodyne 106A (cationic)**

$$C_6F_{13}\diagup\!\!\diagup\!\!S\diagup\!\!\diagup\overset{\overset{\displaystyle OH}{|}}{}\diagdown\!\!N^+(CH_3)_3Cl^-$$

Interfacial Tension

CO$_2$-water-PFPE

T = 45 °C

P = 276 bar

Interfacial Tension (mN/m)

Surfactant Concentration (wt. fraction)

cμc
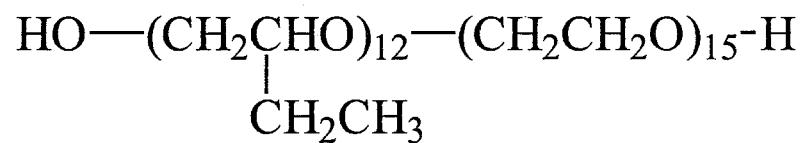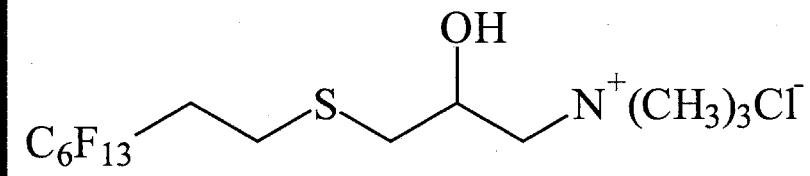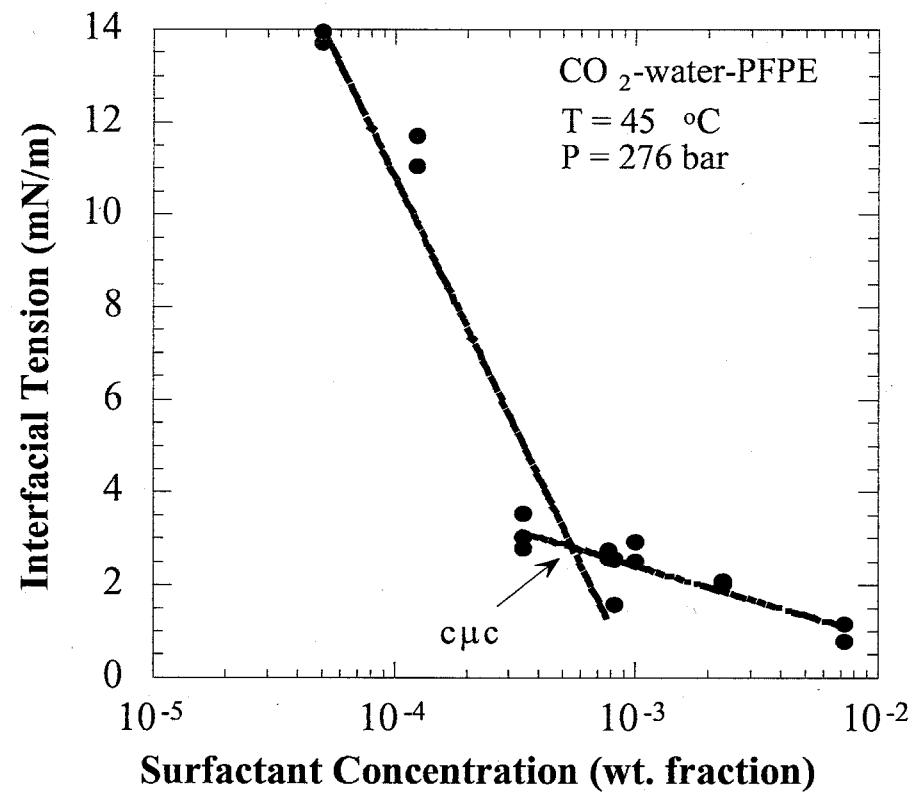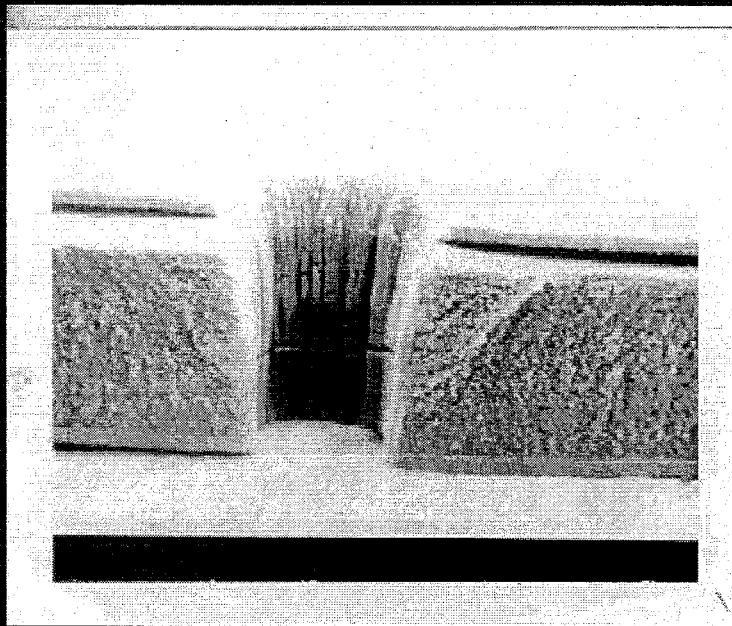
Residue Removal

Exact sidewall polymer composition
Unknown, "fluorinated residue"

3,7 % v/v Butylene carbonate
2900 psi, 85 ºC

Dual Damascene Test Structure

Via-veil

Cap
low-k
Barrier
SiOx
Si
Cu
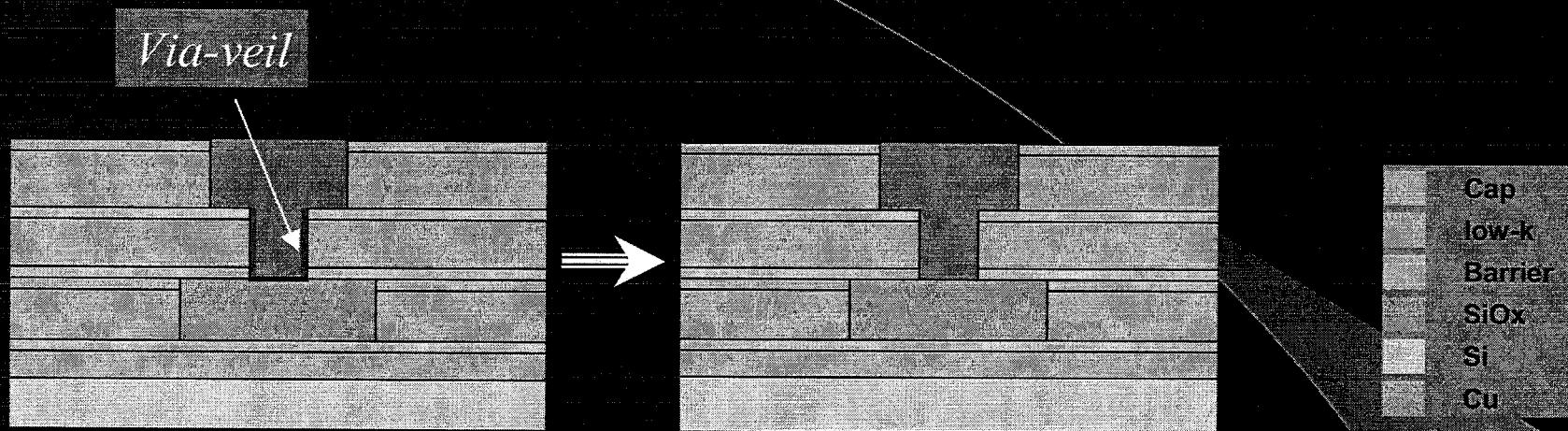
⇨ Remove via veil and clean the Cu contact surface (CuO_x, F, C)
⇨ Low-k material is SiO_2
⇨ Via size is 0.25 μm, depth of via is ~ 0.5 μm
⇨ Static conditions in CO_2-NH_3 (95/5 V%),
   30 min, 40°C.
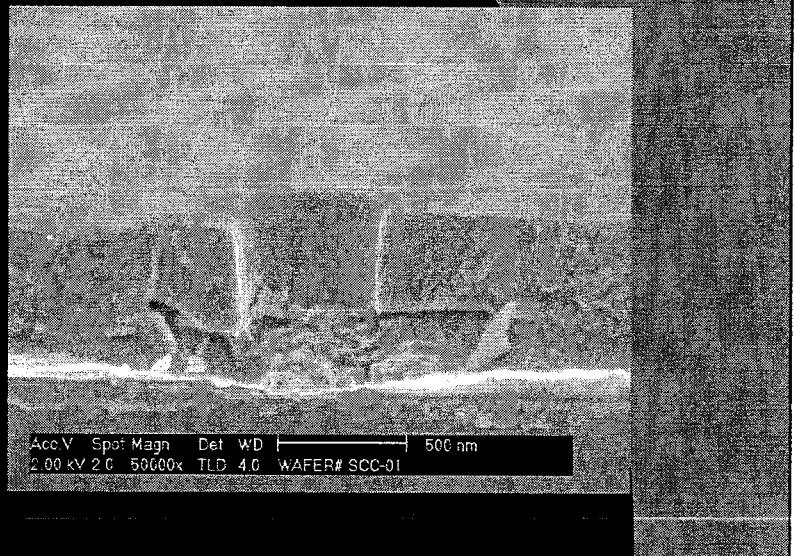
FTIR spectra blanket low-k film

Conditions: Co-solvent: Butylene Carbonate, 2900psi, 90°C, 7min
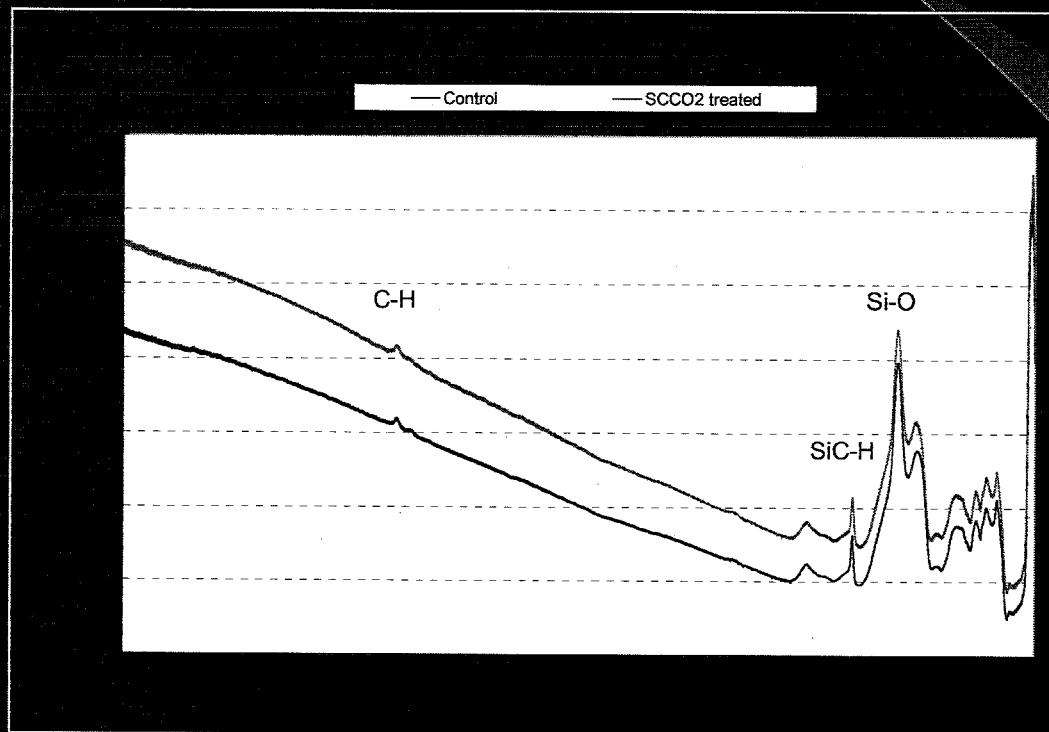
Conclusion: Treatment does not change low-k film

The Arroyo® System
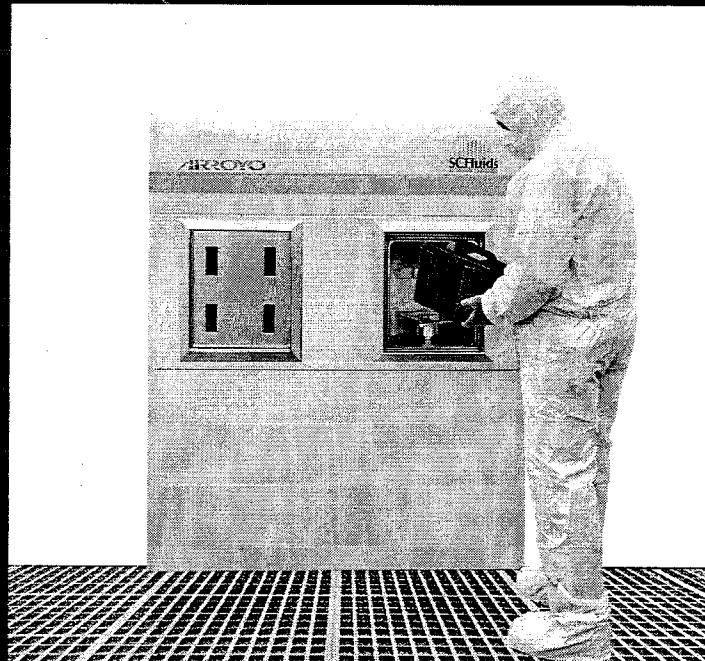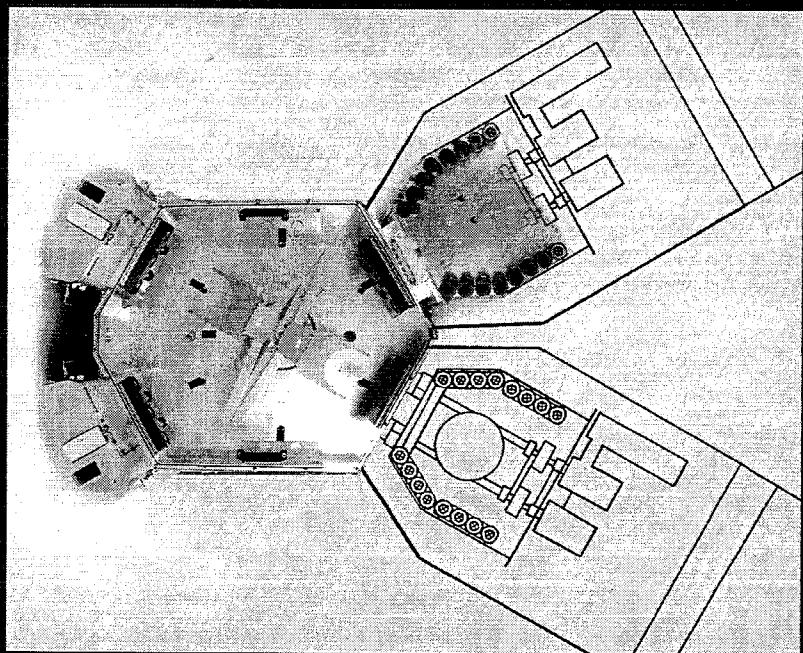
- **Cluster tool configuration**
- **Sold by SC Fluids / GT Equipment**

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