CO_2 Microemulsions for Rapid Removal of Etch Residues of Porous Low k Materials

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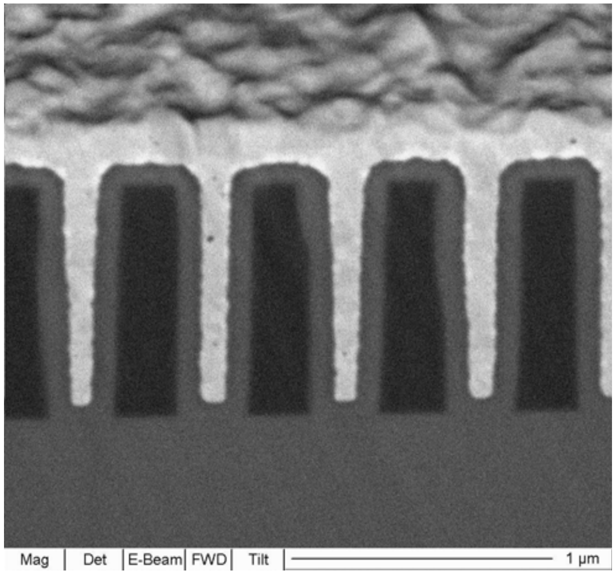
CO_2 motivation: environmentally benign, high performance

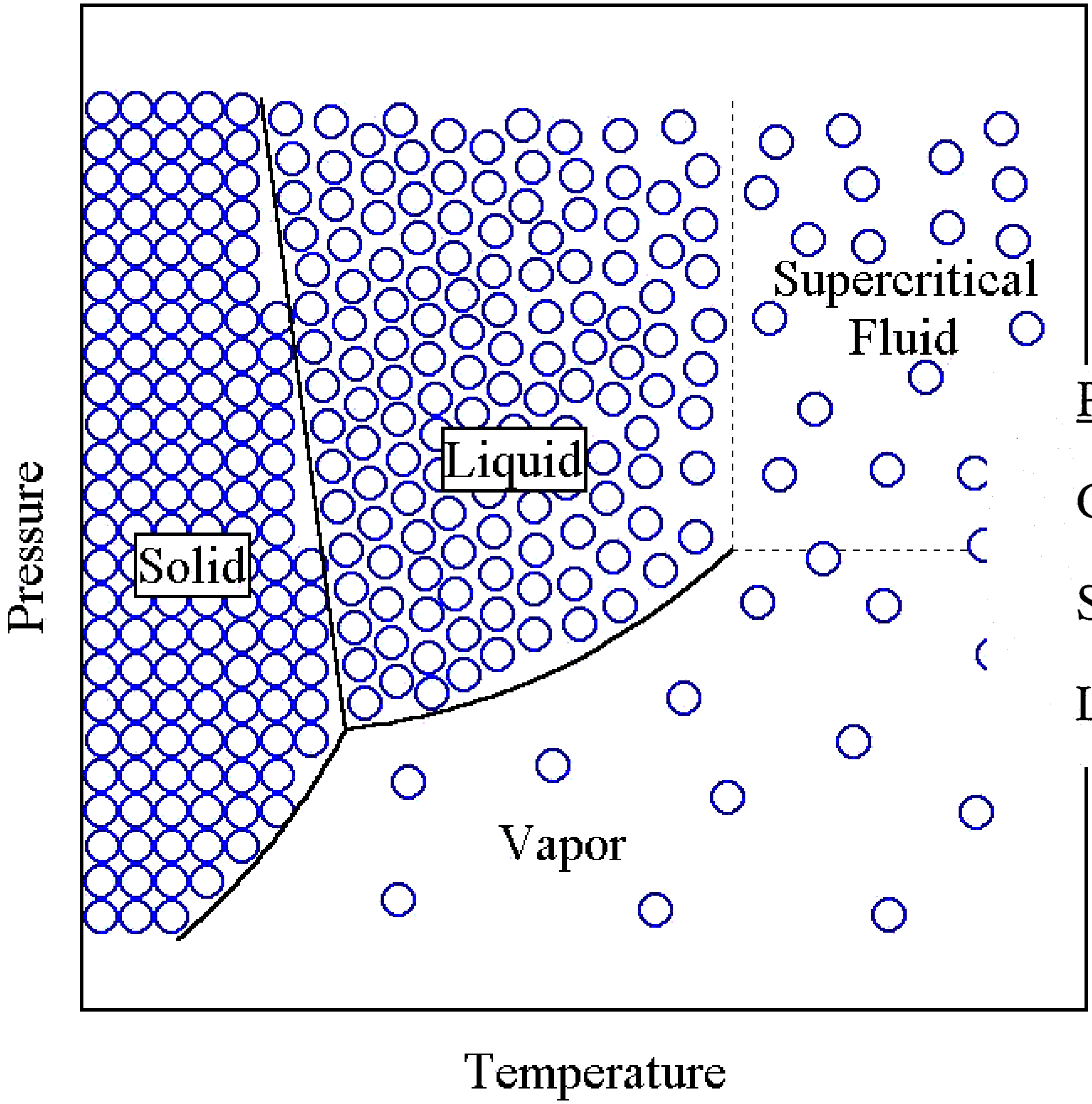
- non-toxic, nonflammable, relatively inert, no solvent residues, benign solvent emissions, inexpensive
- micro-and macro-emulsions of water and CO_2 to solubilize both hydrophilic and CO_2-philic materials
- tunable solvent strength, low viscosity and interfacial tension
  - phase equilibria, reactions, crystallization, colloid stability
  - penetration into nanoporous materials
  - avoid capillary collapse during drying
  - avoid defects (rings) due to dewetting



Cu Chem. Fluid Deposition for interconnects

Watkins et al Science, 294, 141, 2001)

CO_2: Environmentally Benign, Non-toxic, Non-flammable; low interfacial tension and viscosity aid penetration



- Highly compressible
- C.P. 31 C, 73 atm

Property	D (cm^2/sec)	μ (g/cm/s)
Gases	10^{-1}	10^{-4}
SCF	10^{-3}	10^{-3}
Liquids	10^{-5}	10^{-2}

Advantages of CO2 Processing

- Environ. benign, nontoxic, nonflammable
- Favorable transport rates
  - Low viscosity
  - High diffusion coefficients
- Low interfacial tension
  - Wetting of small pores- removal of impurities
  - Prevention of capillary collapse
- Avoid swelling and voiding of films- ellipsometry versus organic solvents

Key Advances in Supercritical Fluid Based Colloidal Dispersions

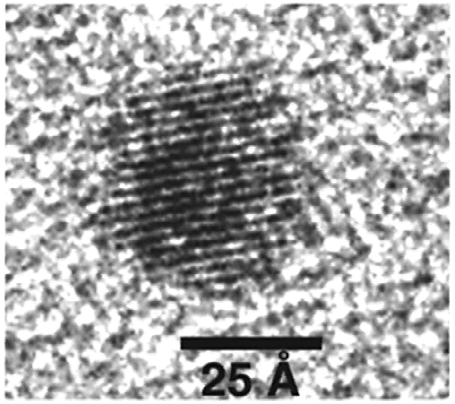
Colloid and Supercritical Fluid	**Stabilizing group**
Water-in-alkane microemulsion (1988)	Alkane[122]
Water-in-CO_2 microemulsion (1994)	a. alkane/fluoroalkane hybrid[21,22] b. perfluoropolypropylene oxide (<1000 molar mass) [23,24]
Polymer latex in CO_2 (1994)	Polymeric flouroacrylates and siloxanes (high molar mass) [53]
Metal and semiconductor nanocrystals in water/CO_2 microemulsion(1999)	a. perfluoropolypropylene oxide and alkane [25] b. perfluoropolypropylene oxide [26]
Metal nanoparticle dispersion in water (2000)	a. Without stabilizer [106] b. Alkane thiols [14]
Metal nanocrystal dispersion in CO_2 (2000)	Fluoroalkane thiol [27]
Gold nanocrystals for synthesis of Si nanowires in alkanes and octanol at high temperature (2000)	Alkane thiol[19]
Si nanocrystal dispersion in alkanes and octanol (high T) (2001)	Octanol [13]

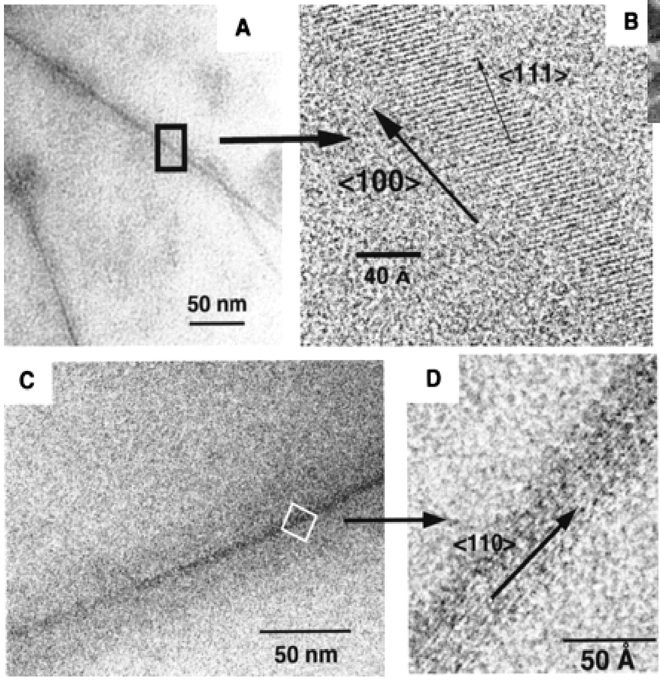
Synthesis of Group IV Semiconductor Nanocrystals in Supercritical Fluid

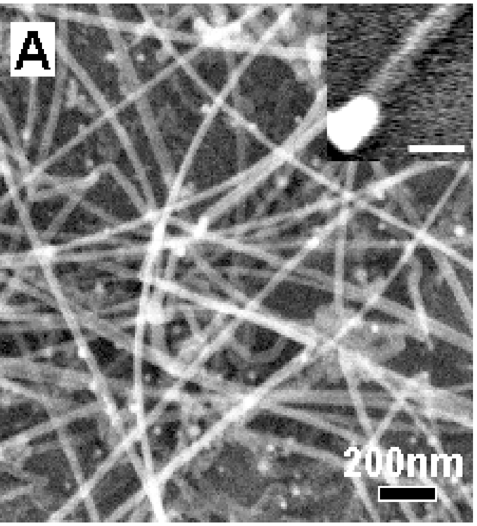
- Si Nanocrystals (1.5-4 nm)
- Holmes et al., *J. Am. Chem. Soc.*, **2001**,3743
- Ding et al., *Science*, **2002**, 1296.

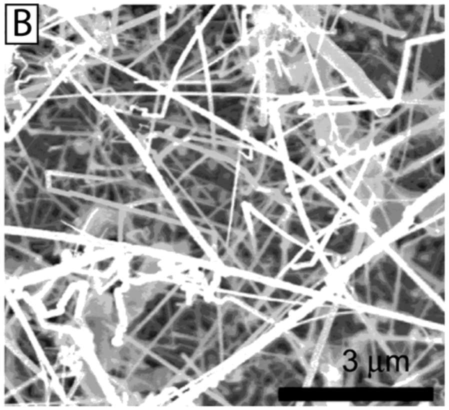
- Si Nanowires (4-5 nm dia.)
- Holmes *et al.*, *Science*, **2000**, 1471
- Lu *et al.*, *Nano Lett.*, **2003**, 93

- Ge Nanowires (10-150 nm)
- Hanrath *et al.*, *J. Am. Chem. Soc.*, **2002**,*124*, 1424









Why Liquid and Supercritical CO_2?

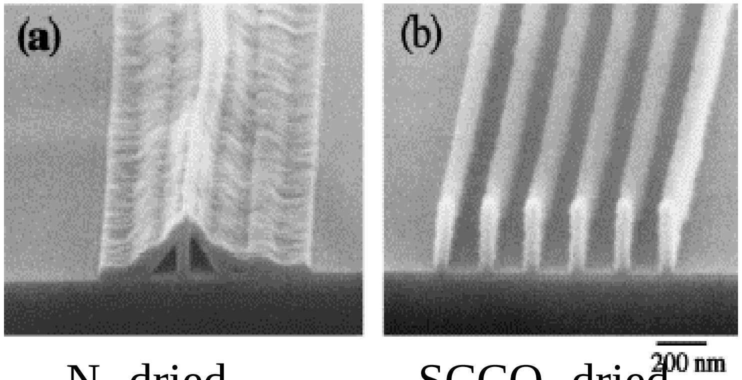
Used extensively in many polymer processes:

- *Foaming*
- *Impregnation*
- *Separations*
- *Synthesis*
- *Microelectronic processing*

Advantages

- *Non-flammable, non-toxic, abundant*
- *Mild critical conditions (T_c = 31 ℃, P_c = 73.8 bar)*
- *Tunable properties*
- *Low surface tension*

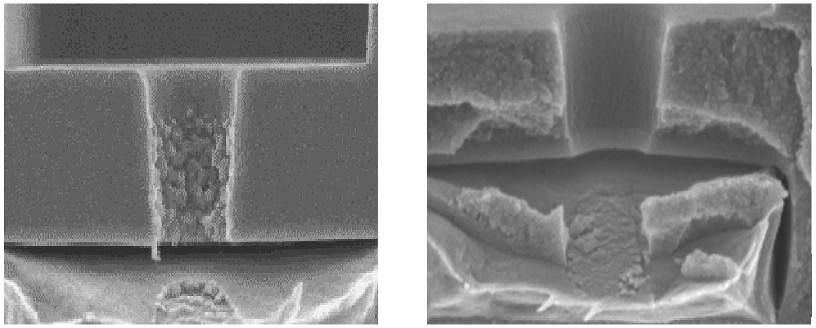
Drying Photoresist



N_2 dried SCCO$_2$ dried

Namatsu, *J. Vac. Sci. Tech. B*, 2000.

Low dielectric constants cleaning



No treatment SCCO$_2$+H_2O+Surf.

Zhang et al., *J. Vac. Sci. Tech. B*, 2004.

CO_2 plasticization plays a critical role in these processes

Avoid dissolution and collapse of low k material

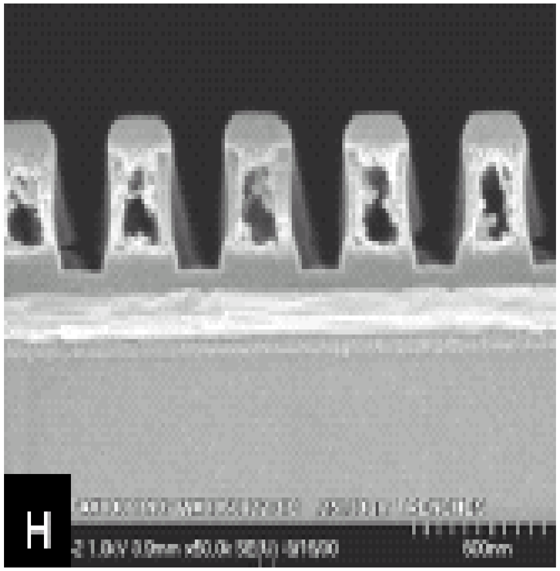
*Use surfactants to avoid dissolution by organic solvents or organic cosolvents in CO_2

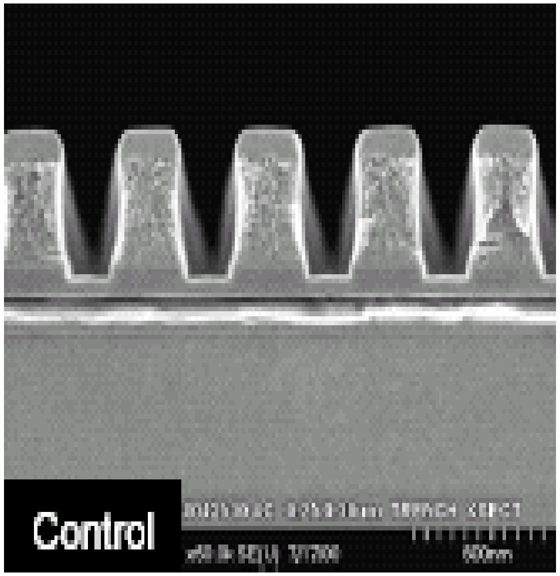
*Avoid side-wall degradation

*Remove organic, organometallic, inorganic

*Maintain low k values

*Avoid attack of copper



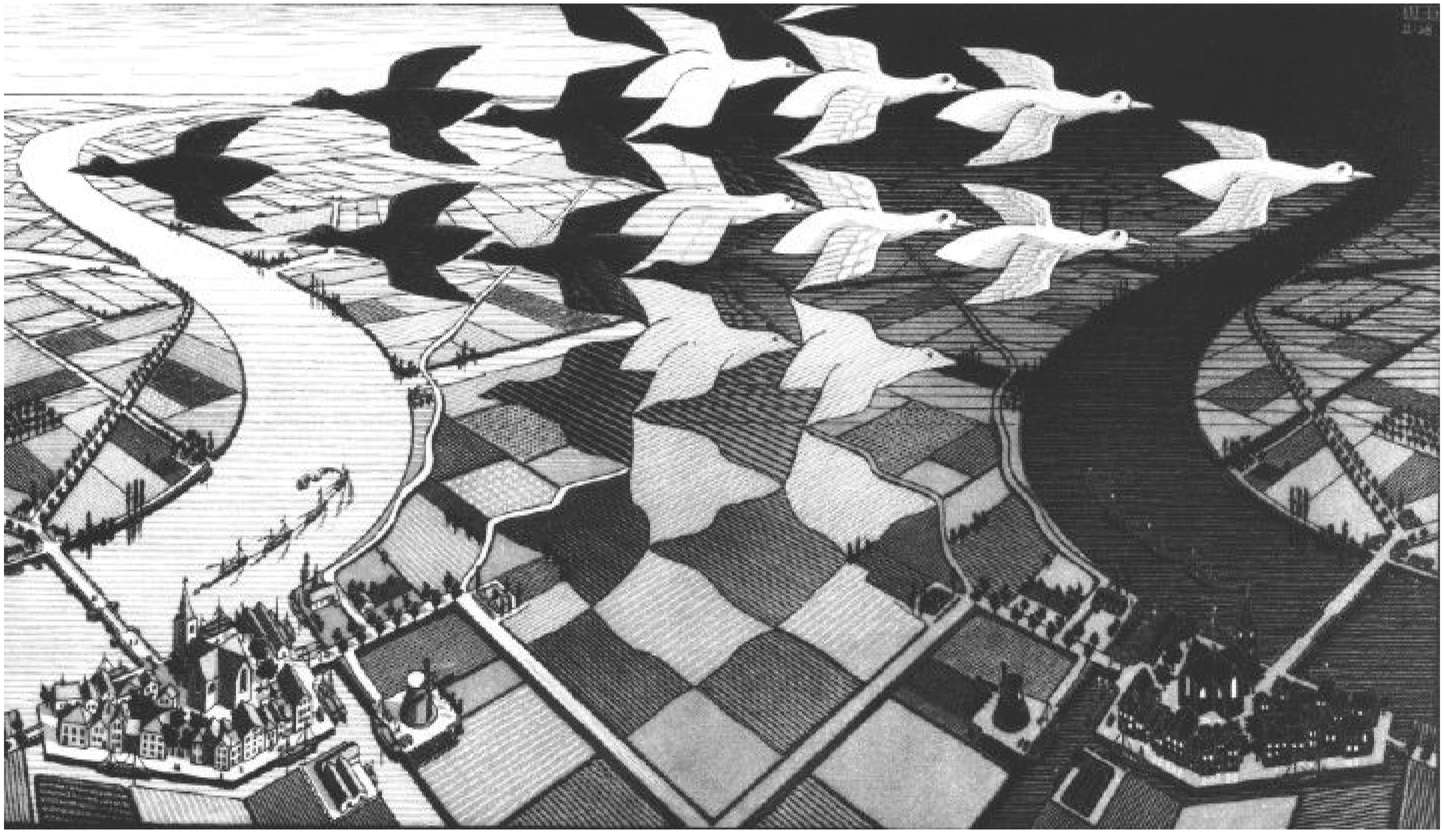


Applications of W-C Micro- and Macroemulsions

- ***Separations/cleaning***
  - extraction of hydrophilic substances (proteins, amino acids, heavy metals)
  - Cu, Europium Yates et al. (2001)
  - enhanced oil recovery (viscosity)
  - dry cleaning (commercialized process)
- ***Microelectronic devices : high diffusion rates, low surface tension***
  - lithography, cleaning low k dielectrics
- ***Reactions- phase transfer***
  - $C_6H_5Cl + KBr \rightarrow C_6H_5Br + KCl$
    Jacobson et al.; *J.Org.Chem* (1999)
- ***Liposomes-drug delivery***
  - Otake et al., *Langmuir* (2001)
- ***Nanoparticle Templates***
  - Ag, $R_p = 3 - 8$ nm
    Ji et al.; *JACS* (1999)
  - CdS, $R_p = 1 - 2$ nm
    Holmes et al., *Langmuir* (1999)
  - Cu
    Cason and Roberts, *JPC B* (2000)
- ***Latexes (dispersion-emulsion polymerization, coatings)***
  - Fascile drying versus water
  - Impregnation, Liu andYates, 2003
- ***Bio-solubilization / conversions***
  - **BSA-AC solubilized in μ–emulsions**
  - Johnston et al.; *Science* (1996)
  - lipase-catalyzed hydrolysis
    Holmes et al.;*Langmuir* (1998)

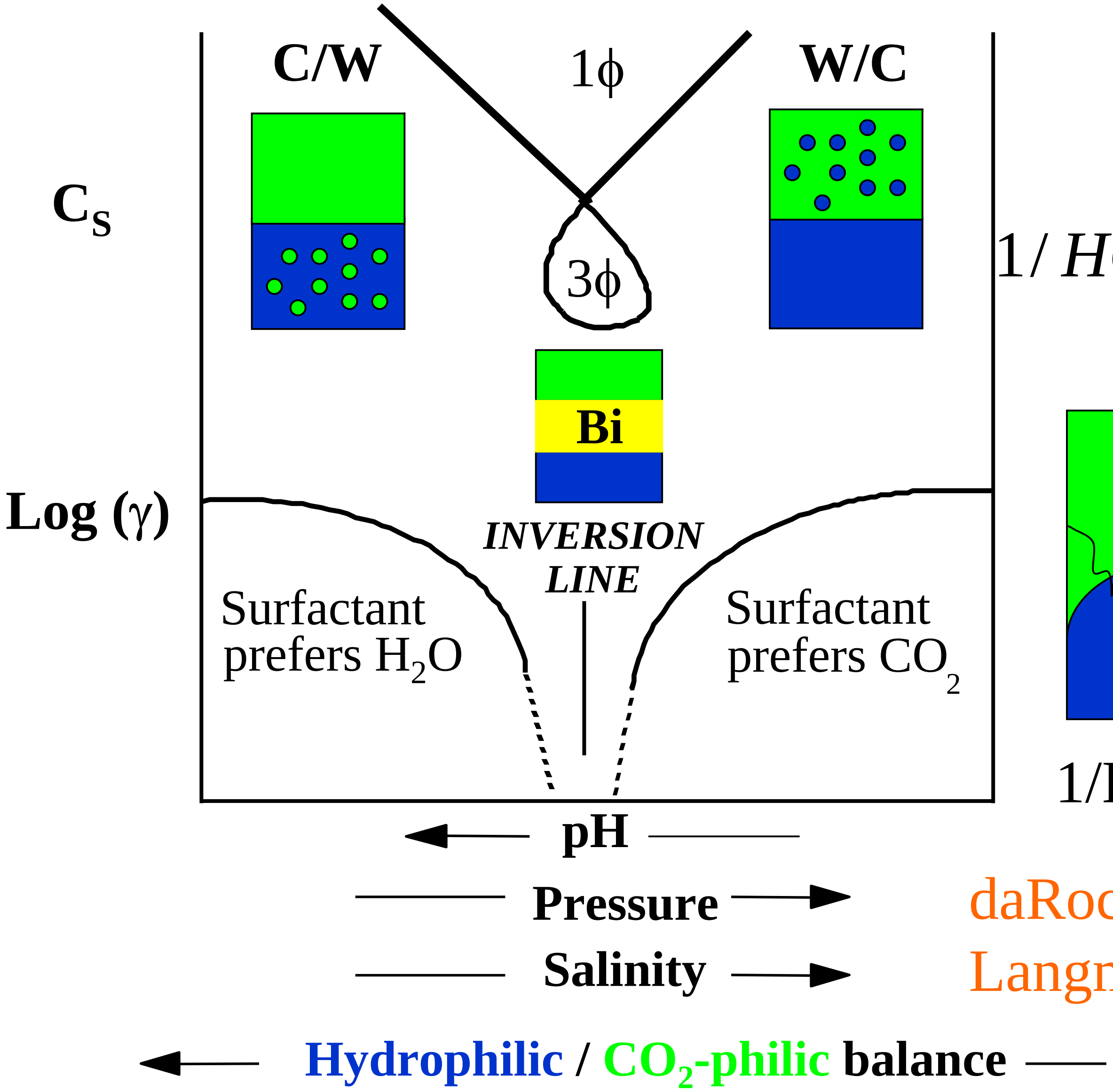
Surfactants in CO2- From Art to Science

Day and Night ***M.C. Escher***



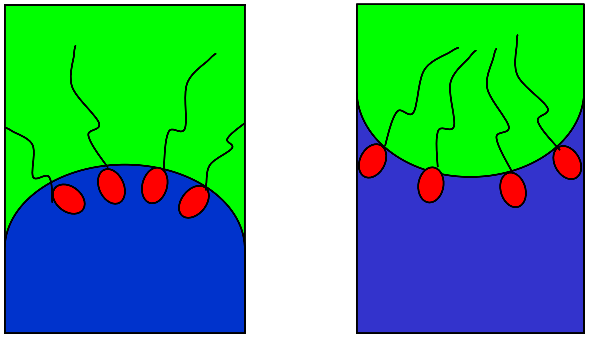
Formulation Variable: Amount of Light

Roadmap for emulsion and microemulsion formation and stability: Surfactant adsorption and partitioning



$$dG = \gamma dA$$

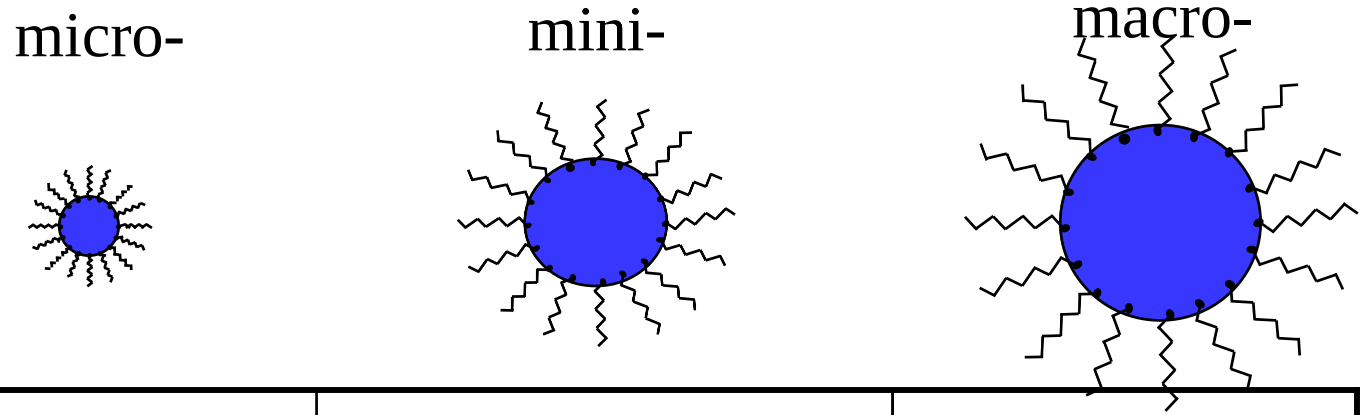
$$1/HCB = \frac{A_{TC} - A_{TT} - A_{CC}}{A_{HW} - A_{HH} - A_{WW}}$$



1/HCB > 1 1/HCB < 1

daRocha, S.R.P. et al. Langmuir, 1999.

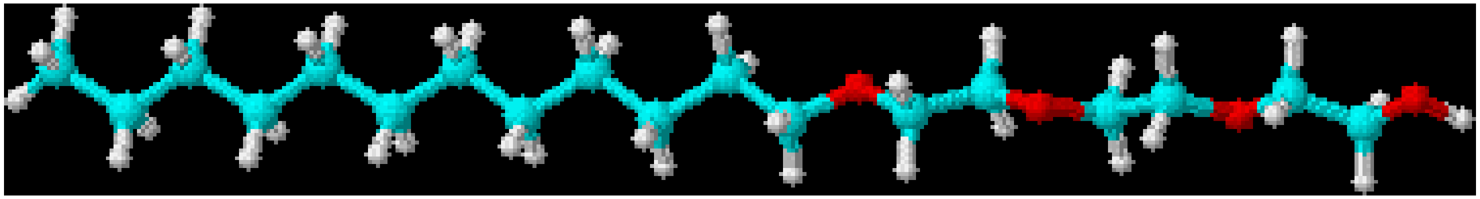
W/CO_2 Emulsion Classifications



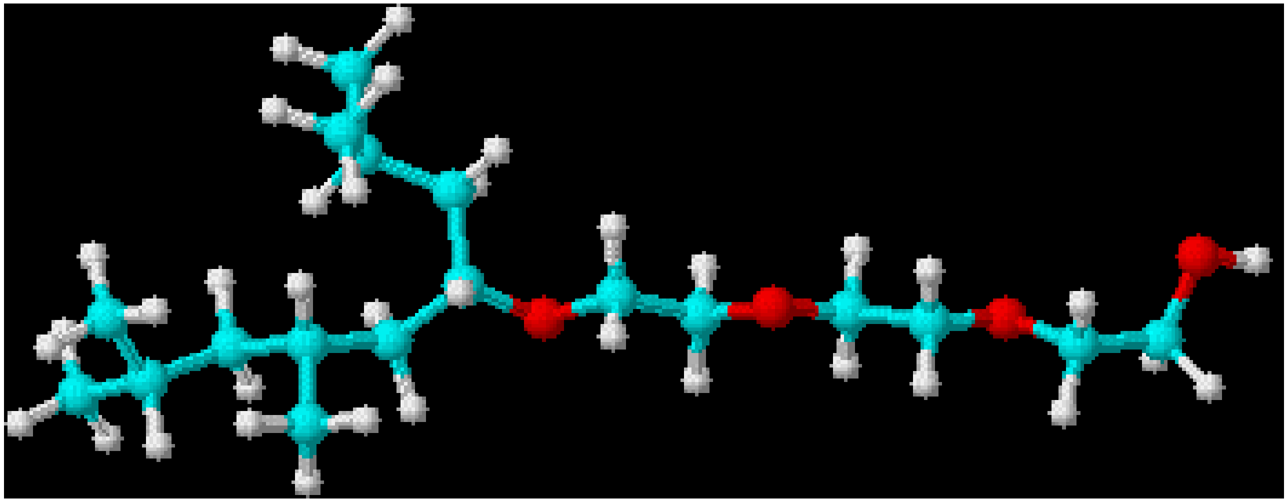
* - at 35ºC, 300 bar

Appearance	transparent	opaque	opaque
Radius (nm)	<10	50-500	>500
Area/vol (cm^{-1}) (surfactant amount)	10^7	10^6	10^5
γ (mN/m)	< 2	< 2	< 10
Settling Rate* (cm/hr)	Thermo. stable	0.5×10^{-3}	0.5
H_20/surf (mol/mol)	5-60	>1000	> 1000

Tergitol TMN Series with Methylated and Branched Tail



$n\text{-C}_{12}\text{E}_X$



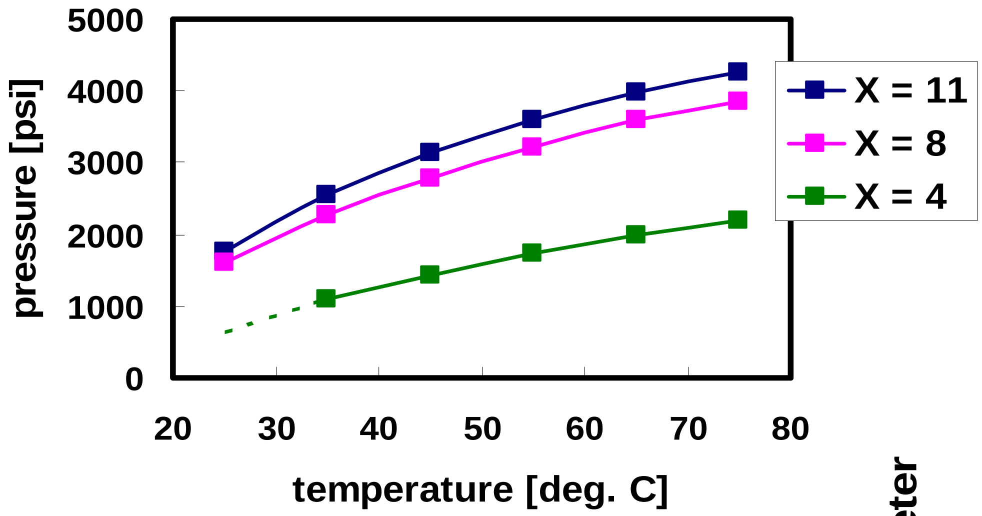
$5b\text{-C}_{12}\text{E}_X$

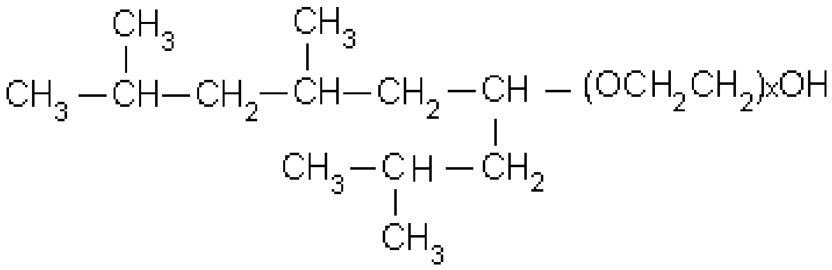
Weaken A_{TT}

$$1/HCB = \frac{A_{TC} - A_{TT} - A_{CC}}{A_{HW} - A_{HH} - A_{WW}}$$

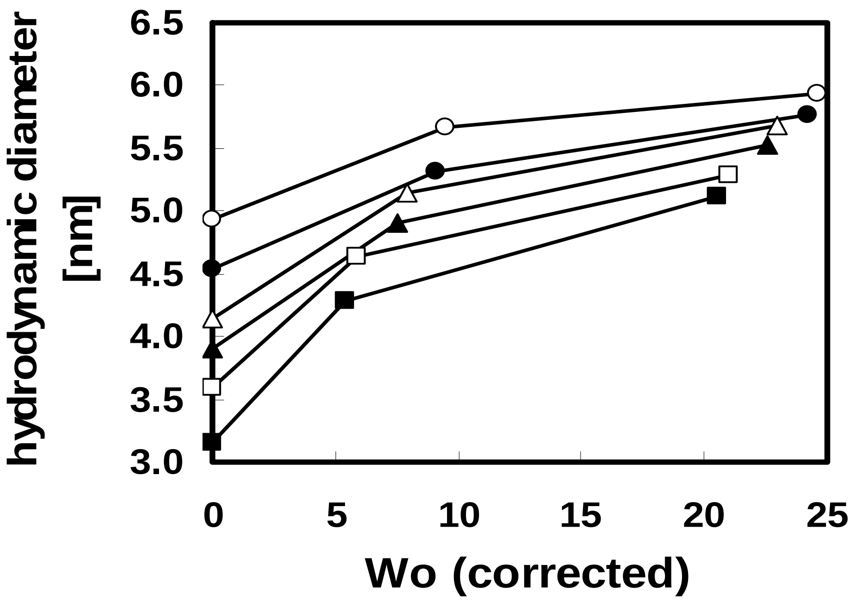
Hydrocarbon Surfactants for W/C microemulsion

Solubility of 1 wt.% surfactant in CO2





Dynamic light scattering result

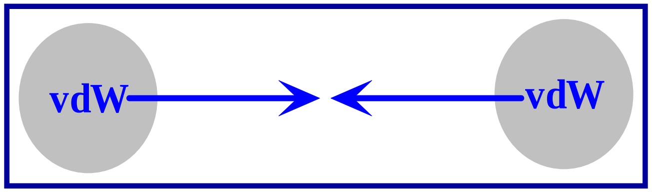


Ryoo, Won et al. Ind. & Eng Chem Research, 2003. **42**(25): 6348-6358.

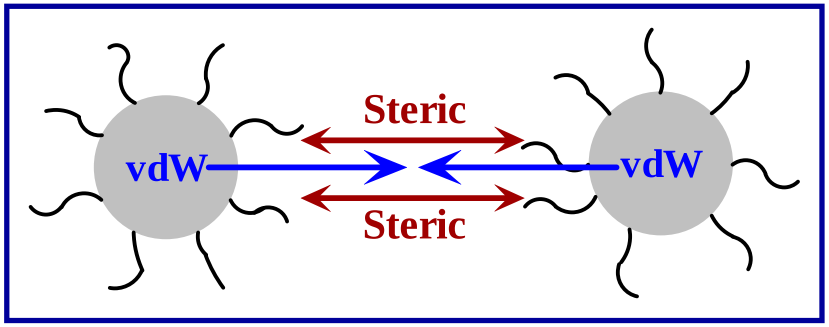
Colloid Stabilization

- Total Interaction (Φ_{total}) Definition

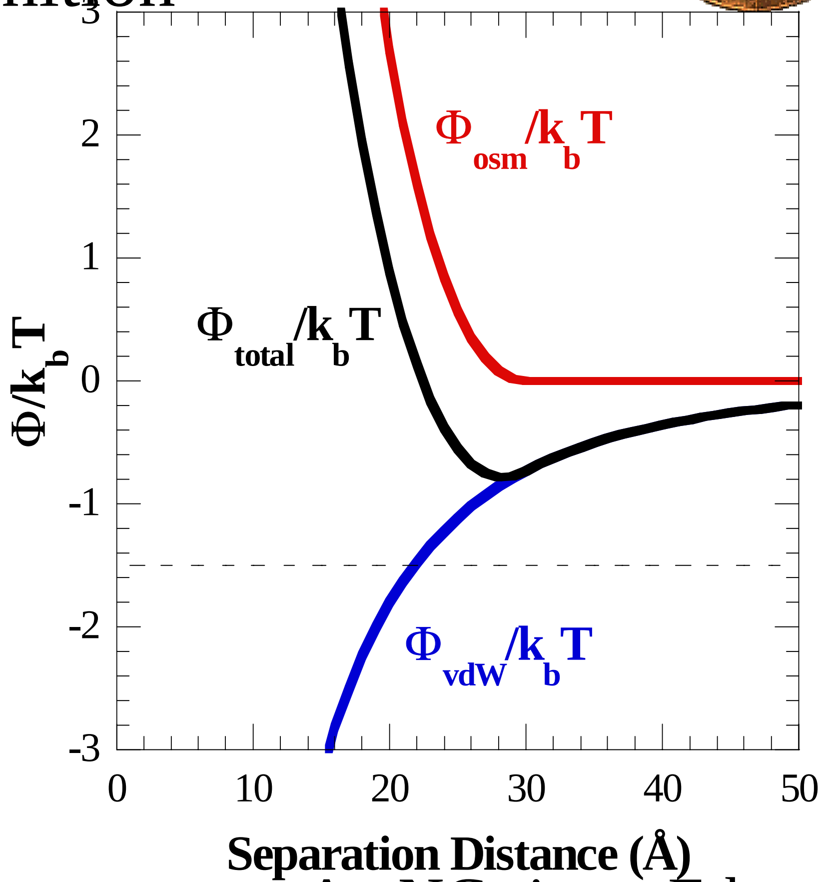
$$\Phi_{total} = \Phi_{vdW} + \Phi_{osm}$$



$$\Phi_{vdW} = -\frac{A}{6}\left[\frac{2R^2}{d^2-4R^2} + \frac{2R^2}{d^2} + \ln\left(\frac{d^2-4R^2}{d^2}\right)\right]$$



$$\Phi_{osm} = \frac{4\pi R_p k_b T}{v_{solv}}\phi^2\left(\frac{1}{2}-\chi\right)\left[l^2\left(\frac{d-2R_p}{2l} - \frac{1}{4} - \ln\left(\frac{d-2R_p}{l}\right)\right)\right]$$



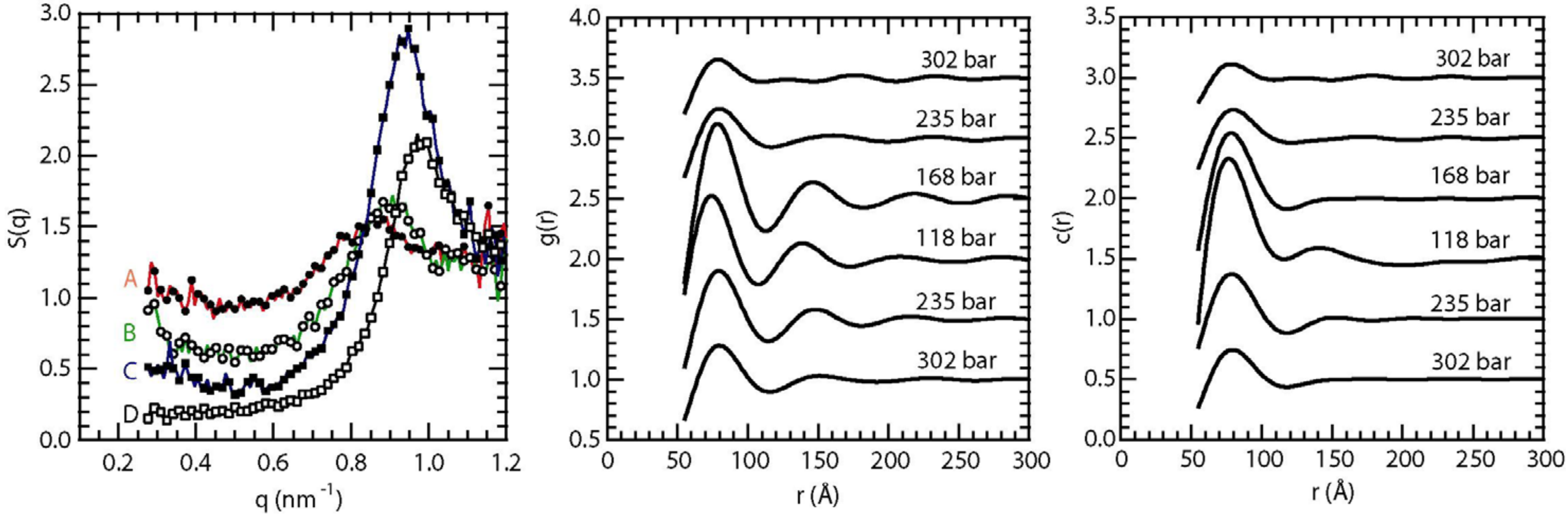
Ag NCs in sc-Ethane

276 bar, 35°C

$\chi = 0.485$

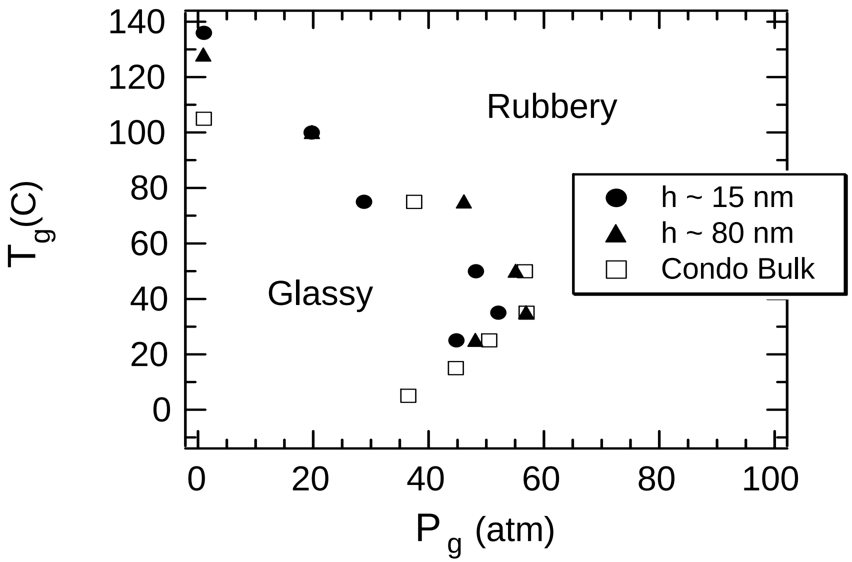
SAXS of interactions of 5 nm gold nanocrystals coated with PFPE ligands in CO2

- S(q) used to calculate *g*(*r*) and *c*(*r*)
- Interactions relatively strong at highest ρ and grow with a decrease in ρ – similar to PFPE w/c microemulsions (Lee et al)

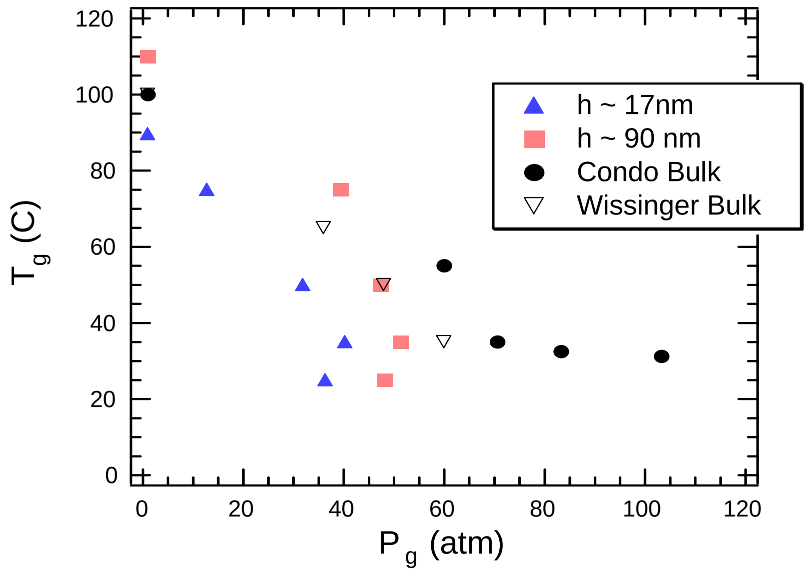


Retrograde Vitrification of PMMA and PS Thin Films

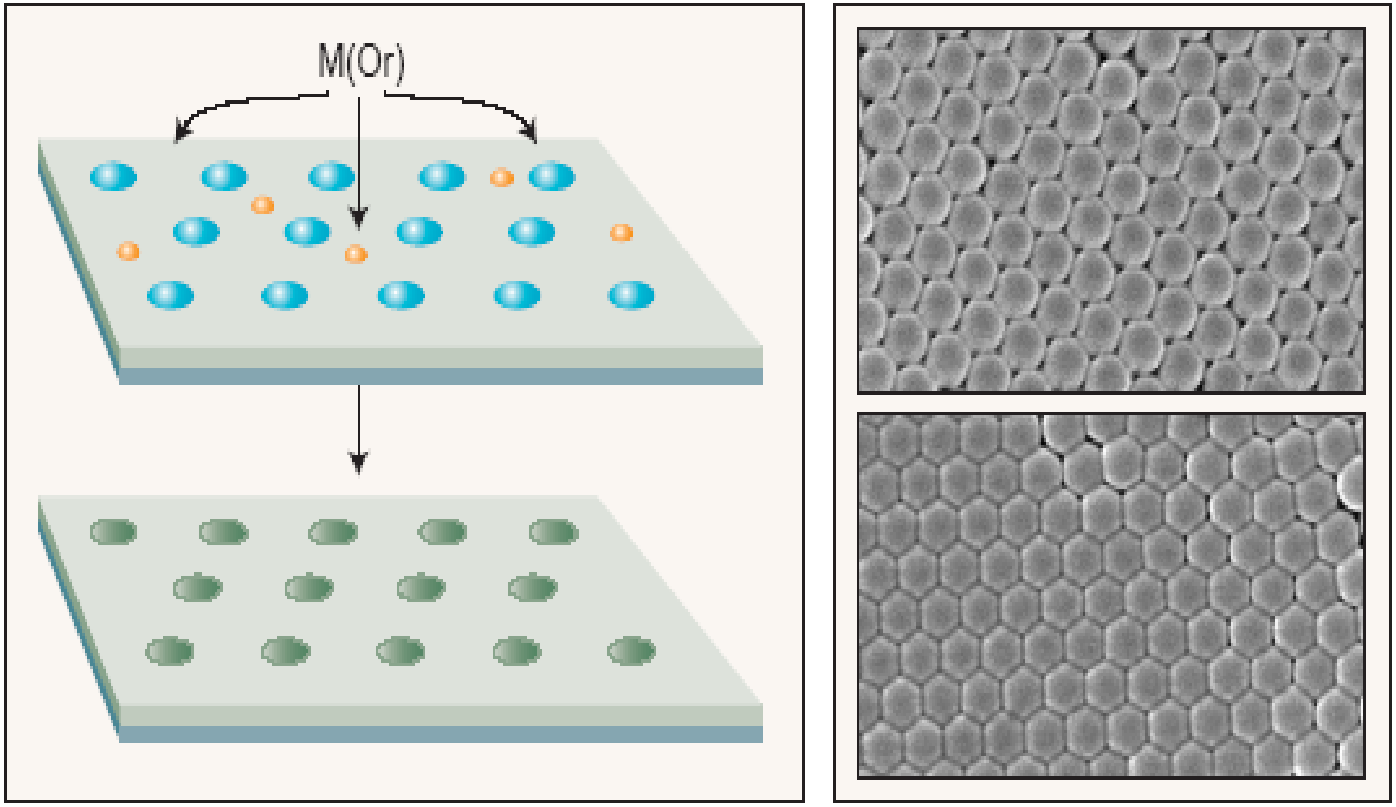
CO_2/PMMA/SiOx/Si



CO_2/PS/SiOx/Si



- *Retrograde vitrification phenonmenon observed in both PMMA and PS thin films*
- *At constant pressure, a rubbery-to-glassy transition at high temperatures and a glassy-to-rubbery transition at low temperature*
- *Retrograde vitrification envelope of thin films shift to the left lower pressures*

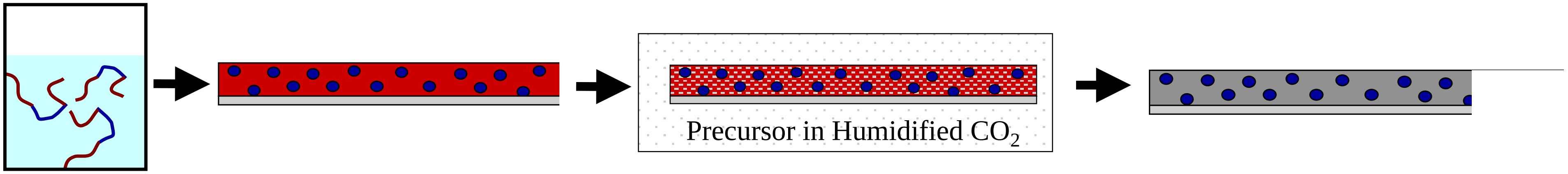


Template for future chips. Block copolymer micelles provide a rigid preordered template that is swollen by supercritical carbon dioxide to allow the metal organic precursor to diffuse in.

ynthesis of Mesoporous Metal Oxides by 3-D Replication of Block Copolymer Templates in CO

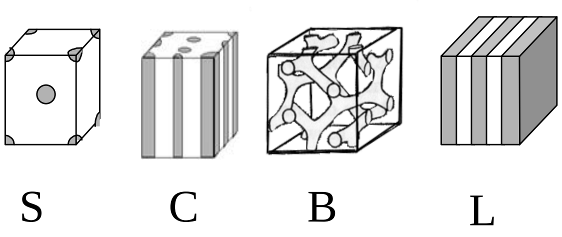
Watkins et al., U. Mass.

1. Prepare BCP Template 2. Modify by Phase Selective Chemistry

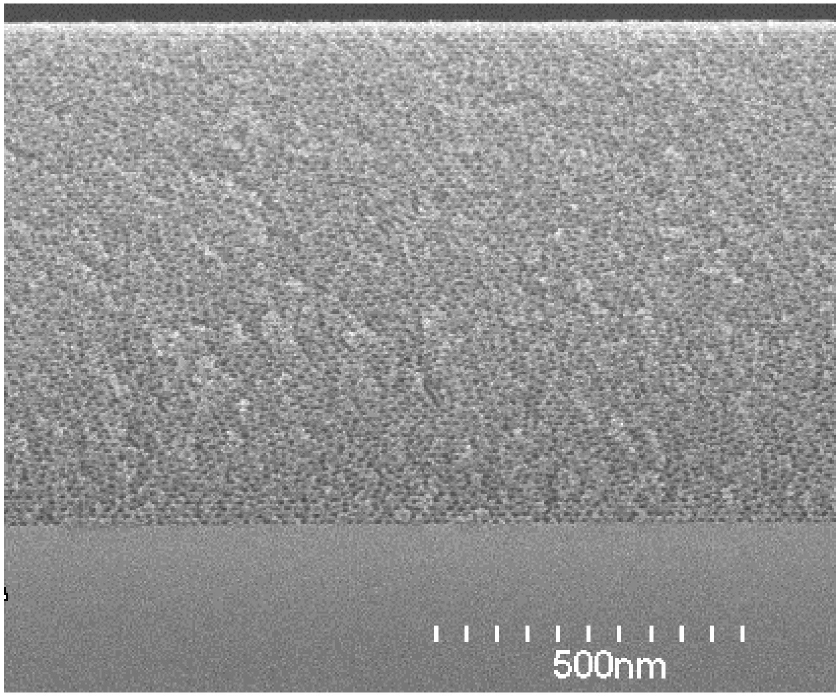

Precursor in Humidified CO_2

- Localize Catalyst in Hydrophilic Domain of Copolymer Template
- Condense Alkoxide to Yield Metal Oxide

  e.g. TEOS + H_2O → SiO_2
- Heterogeneous Approach Preserves Template Morphology!

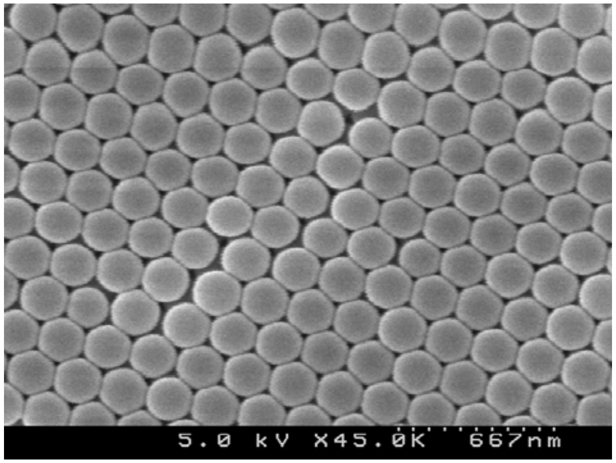


Spherical Pore Morphology →

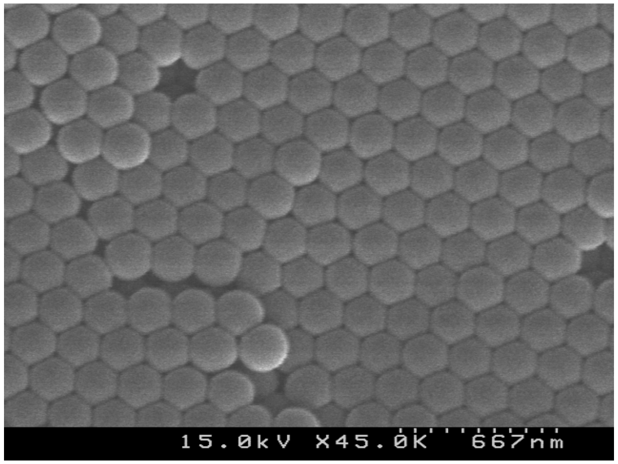


CO2 welding: Change in Photonic Crystal with time-PS

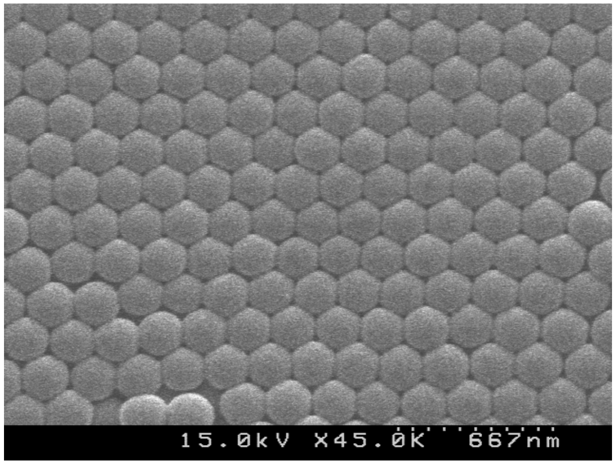
32°C 3715 PSI



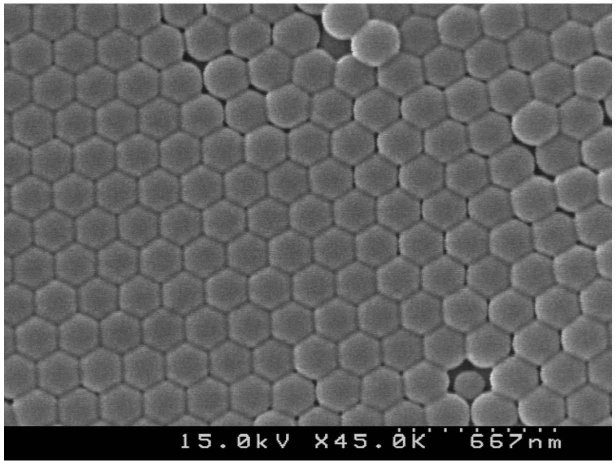
0 min



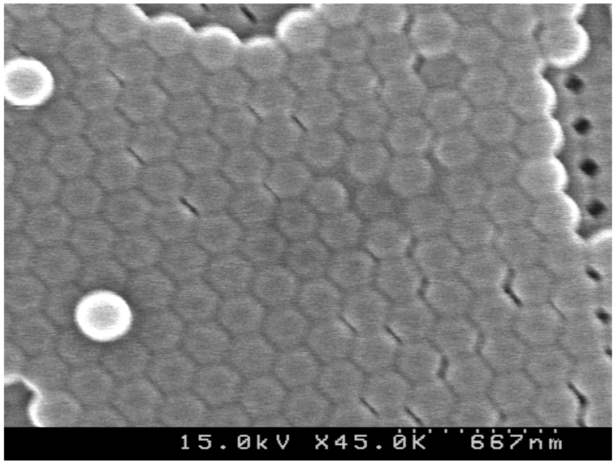
6 min



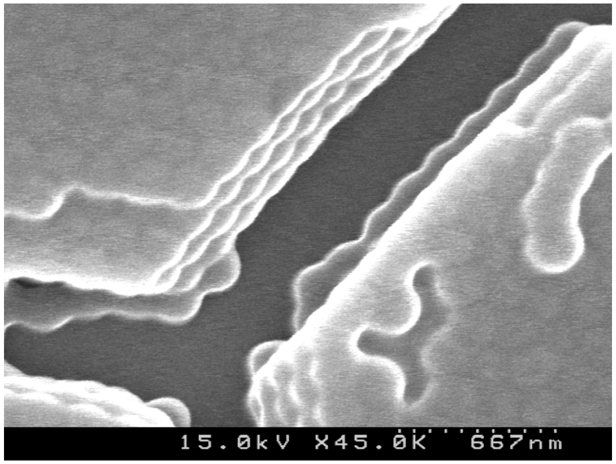
15 min



70 min



180 min

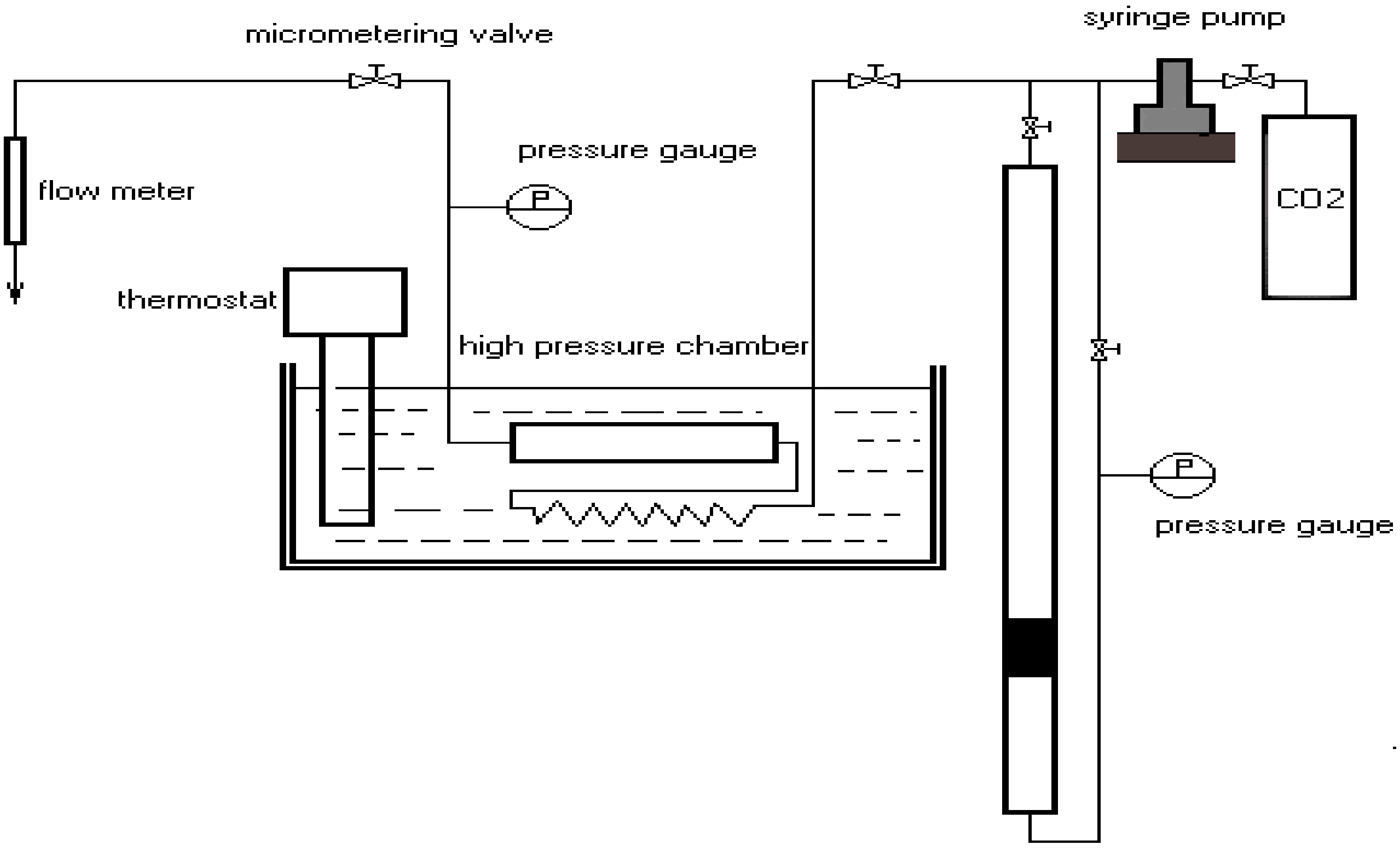


3600 min

Objectives

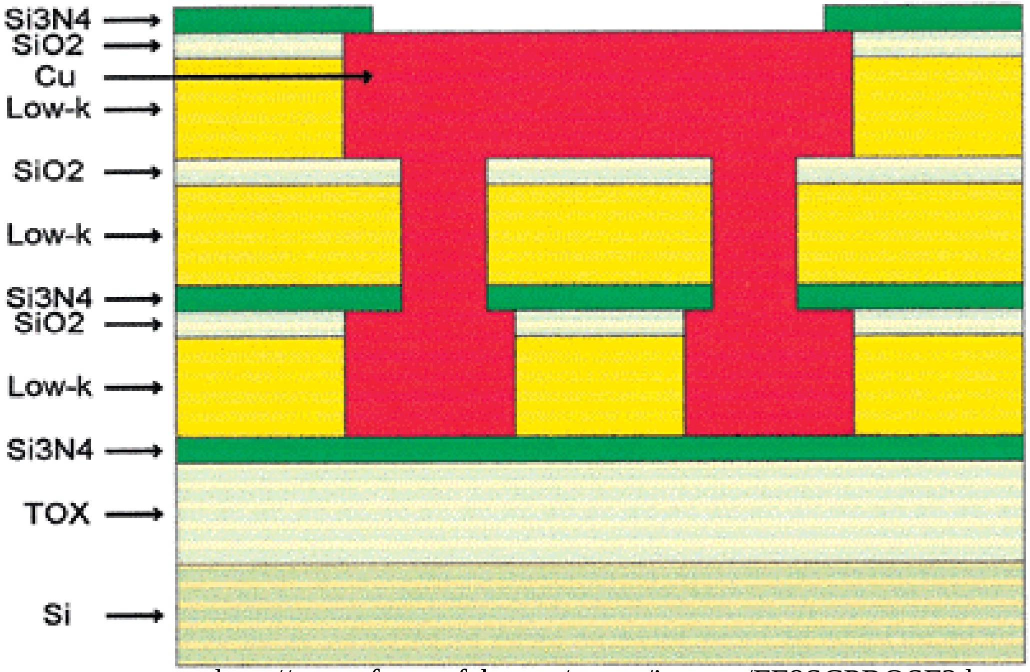
- Cleaning (residue removal) (JSR 5109 pMSQ)
  - Novel cleaning technique using TMN-6, H_2O and $scCO_2$ microemulsion optimized at 40 ^oC and 2000 psi, 15-40 ml/min (30 s residence time)
  - Cleaning time reduced to 2 minutes
- HMDS repair in $scCO_2$ of etched and ashed wafers (lit.- Muscat, Reidy)
  - 1% HMDS by weight for 1 minute
  - Ellipsometry, contact angle and FTIR show repair
- Ellipsometry: films return to values near initial conditions after two sorptions- no damage

Supercritical CO2 apparatus for cleaning wafer pieces



Chemical-Mechanical Cleaning method

- Clean with surfactant, water and CO_2
- Invert during CO_2 rinse
- Possible further decrease using ultrasonic actuator

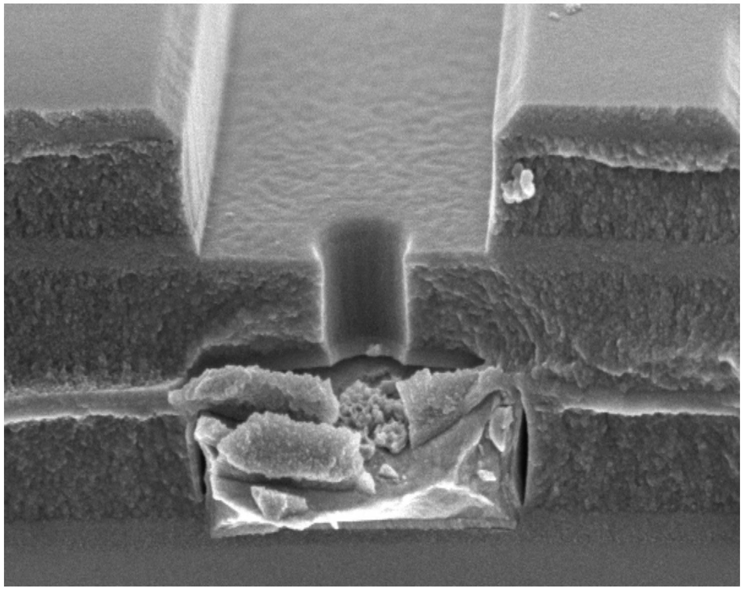


http://www.future-fab.com/assets/images/FF8SCPROSF2.htm

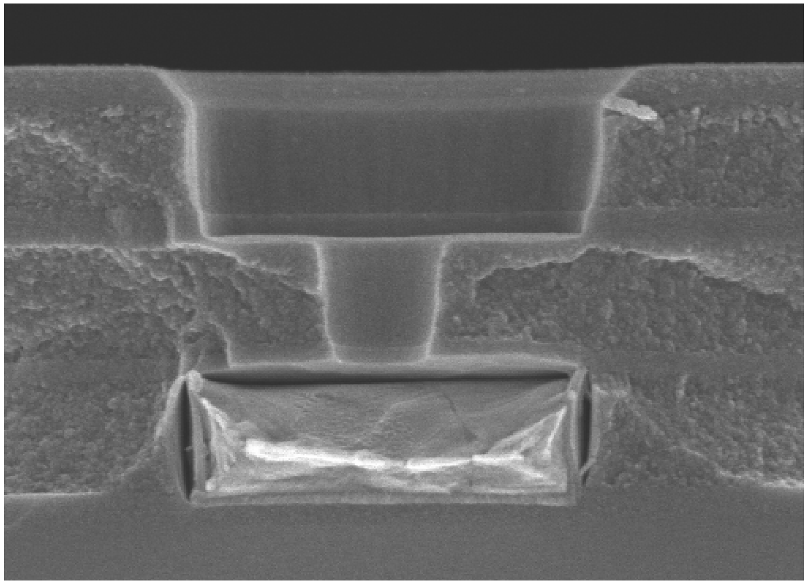
Dual-damascene structure

Optimization of cleaning time

Cleaning method	**Clean time (min)**	**Rinse time (min)**	**Total time (min)**
Chemical	30	30	60
Chem/mech	1.4	1.1	2.5



Chemical dissolution clean only– residue remains

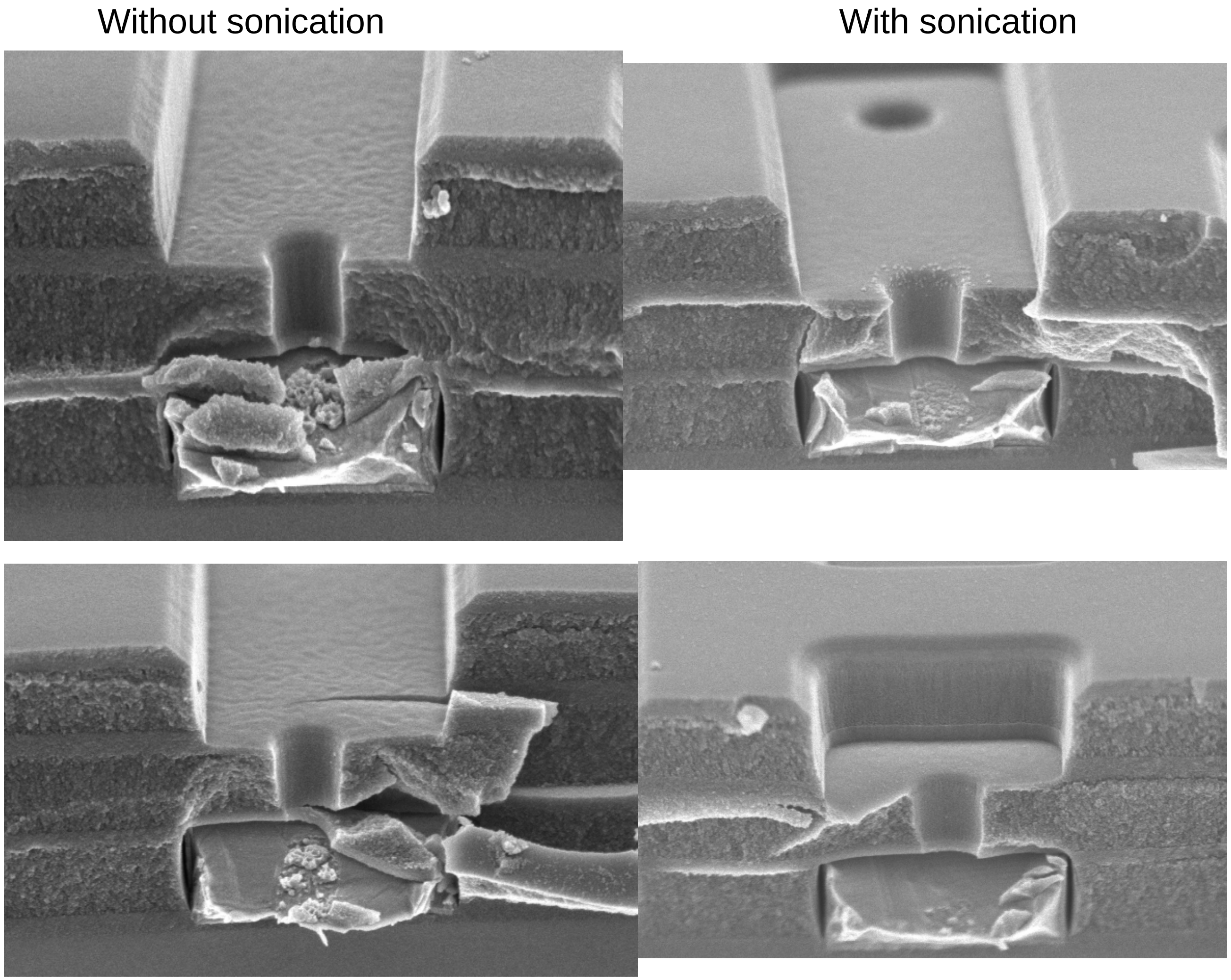


Chemical/mechanical clean– all the residue is removed

Ultrasonic cleaning using microemulsion

40°C and 3000 psia

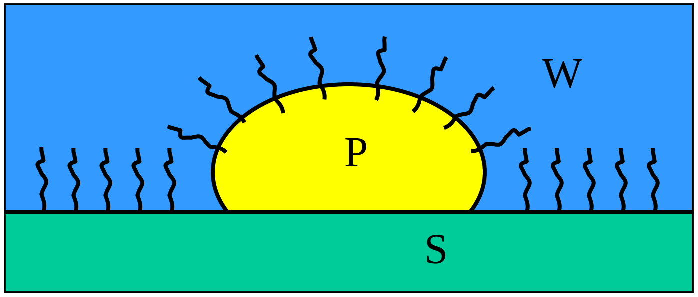
- **TMN-6 (8EO)**
  - without sonication - residues remain
  - with sonication - little residue remains
- **TMN-3 (4EO)**
  - without sonication - residues remain
  - with sonication - some residue remains



TMN-6 surfactant cleaning

Chemistry	**Clean model**	**Clean time (min)**	**Rinse time (min)**	**Cleaning result**
Pure CO2		30	30	residues remain
TMN-6 (1%)	chemical	30	30	residues remain
TMN-6 + IPA	chemical	30	30	residues remain
TMN-6 With ultrasonic	chemical	30	30	mostly clean
TMN-6 (1%)	chem/mech	5	5	clean
TMN-6 (0.5%)	chem/mech	5	5	clean
TMN-6 (0.4%)	chem/mech	5	5	some residues remain

Particle disengagement from surface (water in trench)

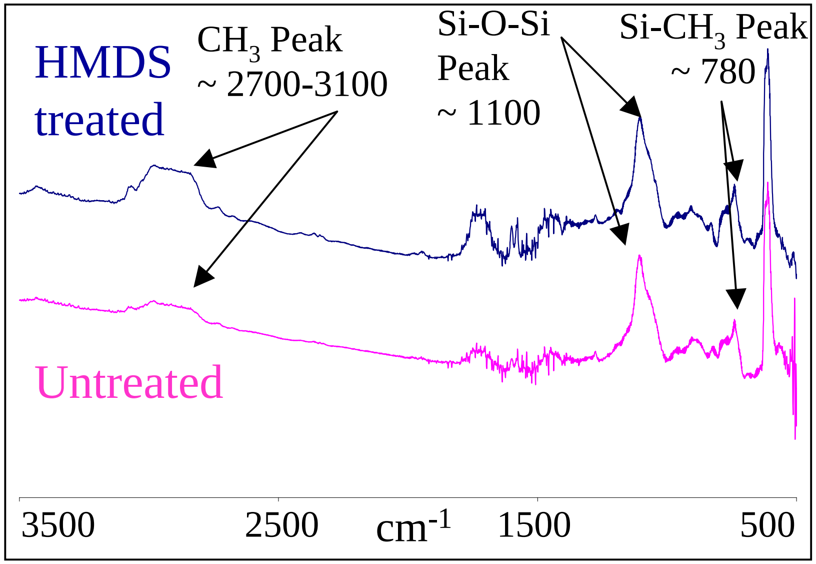


- Detergency mechanism: $\gamma_{SP} > \gamma_{PW} + \gamma_{SW}$
- The surfactant lowers both values on rhs favoring particle disengagement
- Particles sterically stabilized in water phase
- Water droplets may be emulsified in CO_2

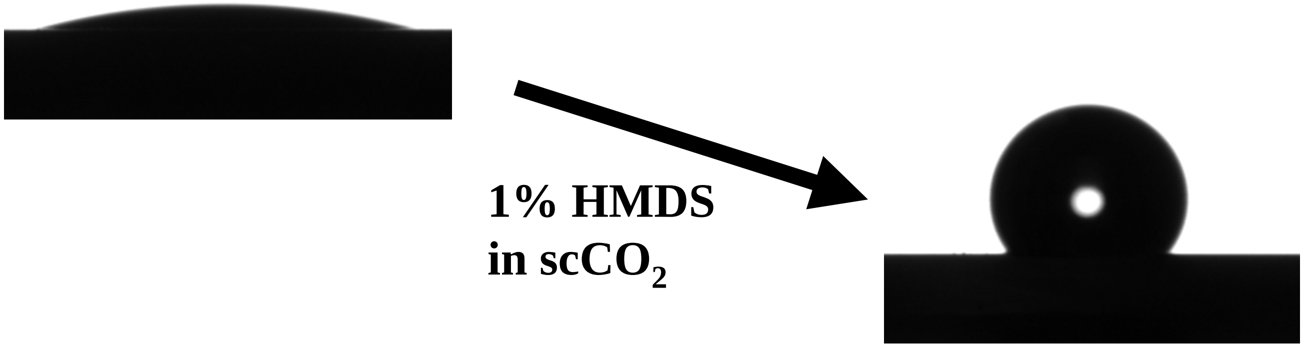
HMDS repair of blanket partially etched/ashed JSR

HMDS (wt%)	**Temp (˚C)**	**Pressure (psig)**	**Time (min)**	**CH_3 Area**	**Thickness (Å)**
Untreated	n/a	n/a	n/a	18.18	2371.3±31
1	50	2200	10	22.38	2424.8±5
1	50	1500	10	26.45	2513.4±44
1	50	1500	1	23.12	2560.8±25

HMDS capping experiments to determine optimal conditions

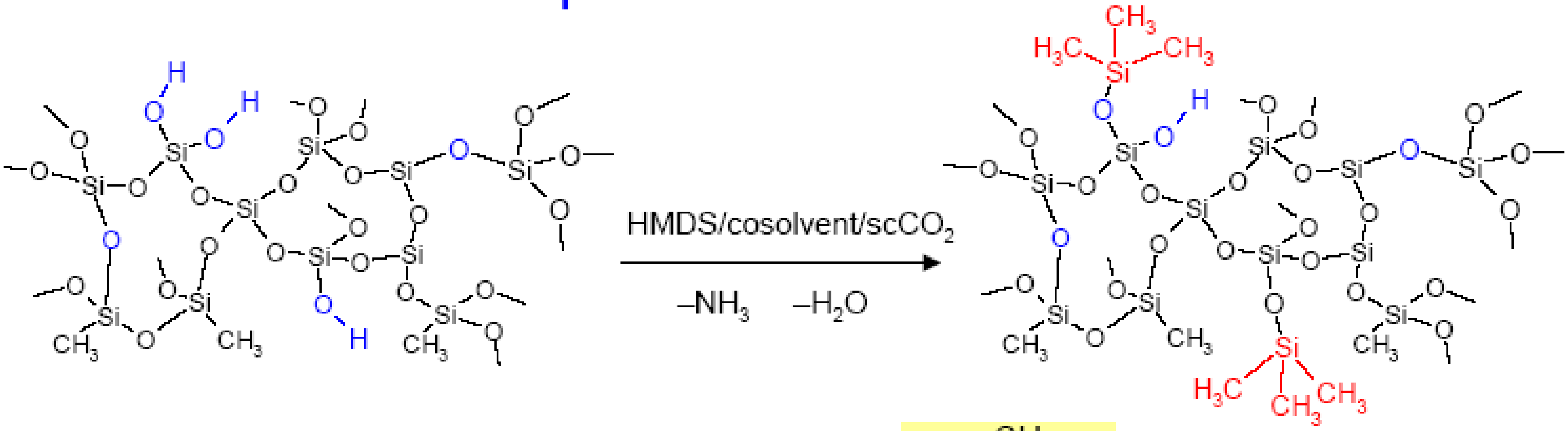


FTIR spectra shows effect of HMDS repair

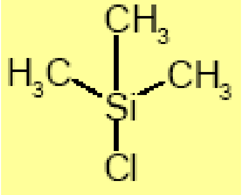


Contact angle before and after HMDS repair

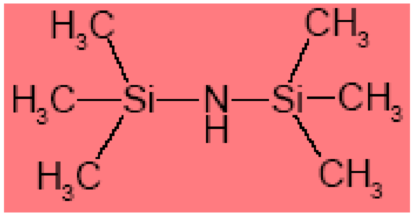
Repair of low k film (Muscat et al, Wafer Clean Workshop, 2003, Austin, TX)



Etched/ashed blanket films



Trimethylchlorosilane
(TMCS)



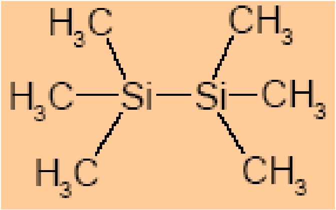
Hexamethyldisilazane
(HMDS)

Cosolvent addition

Si-bearing chemistry

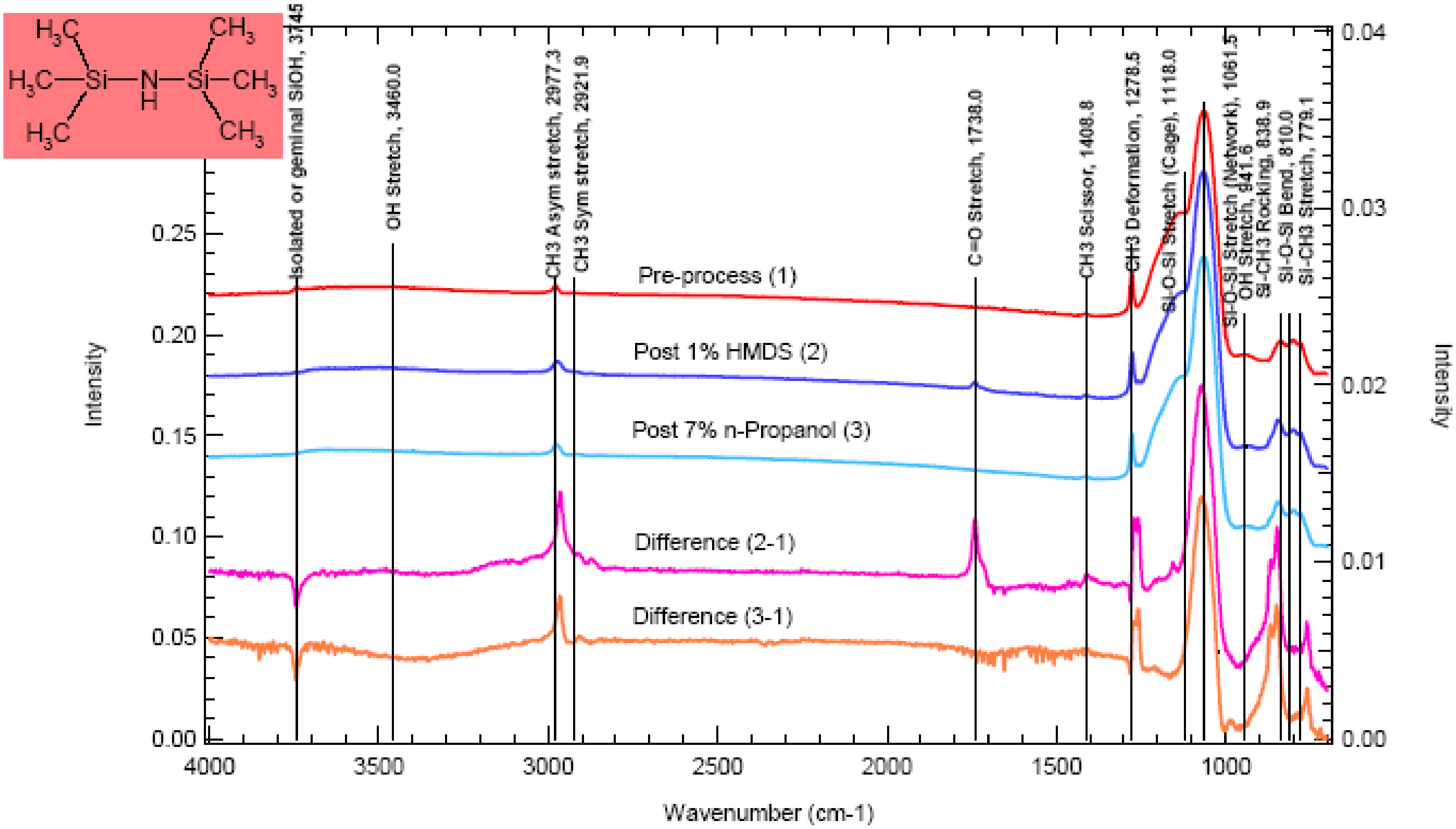
scCO$_2$ 45-55°C and 200-300 atm

2 min soak, fast release



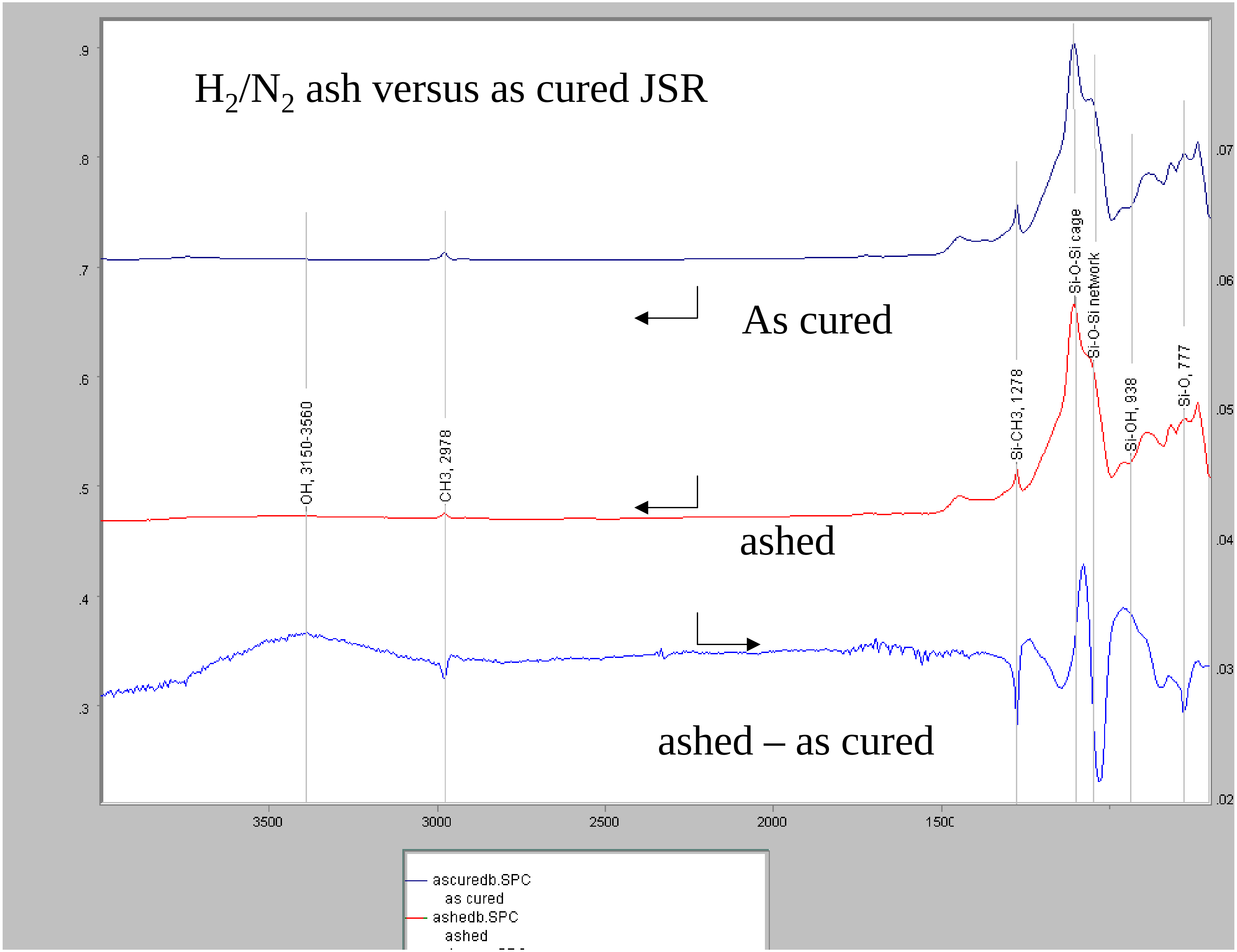
hexamethyldisilane

Low k Repair (Muscat et al. Muscat et al, Wafer Clean Workshop, 2003, Austin, TX)



- 1% HMDS in $scCO_2$ at 209 atm and 54°C for 2 min soak
- 7% n-Propanol in $scCO_2$ at 174 atm and 53°C for 2 min soak
- ↑ CH_3, Si-O-Si ↓ iso/gem SiO-H ↓ H-bonded SiO-H

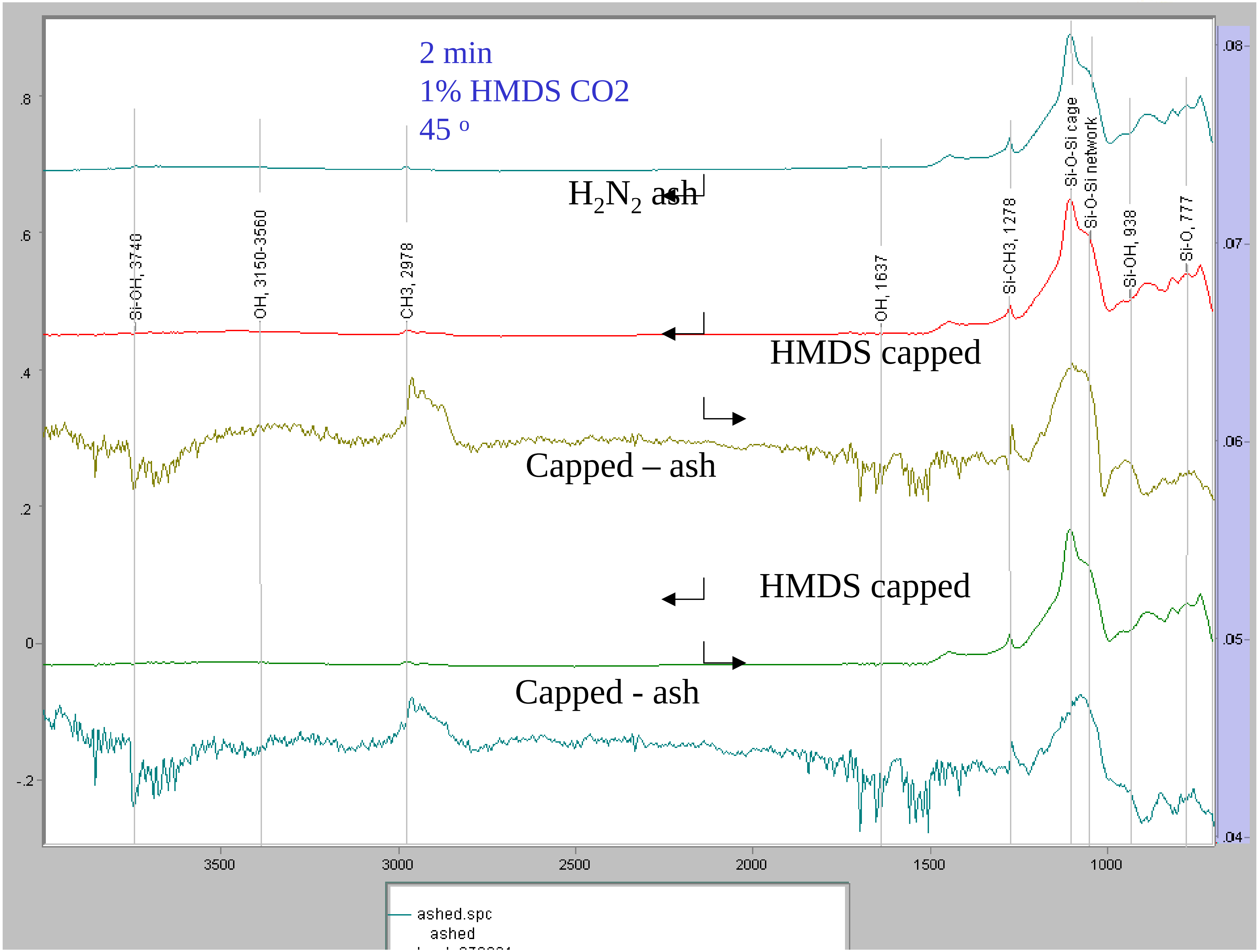
H_2/N_2 ash versus as cured JSR



As cured

ashed

ashed – as cured



2 min
1% HMDS CO2
45 ^{o}

H_2N_2 ash

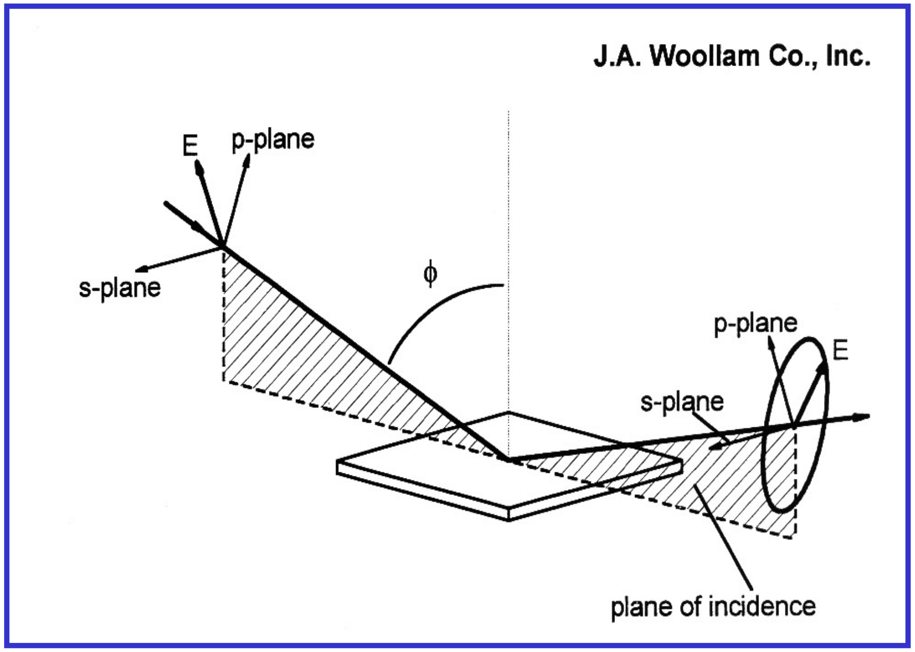
HMDS capped

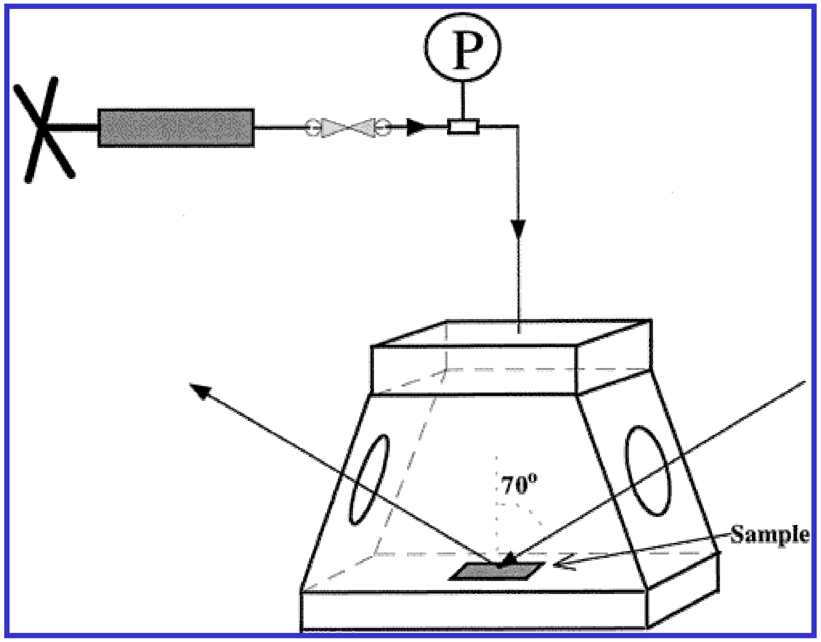
Capped – ash

HMDS capped

Capped - ash

Spectroscopic Ellipsometry



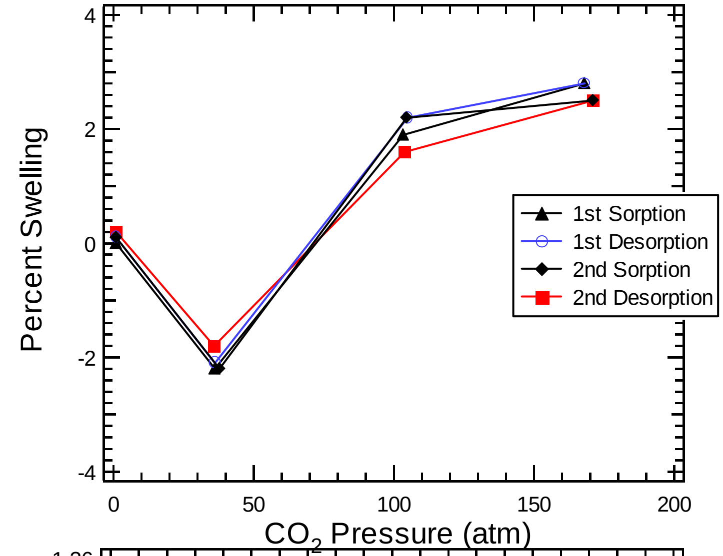


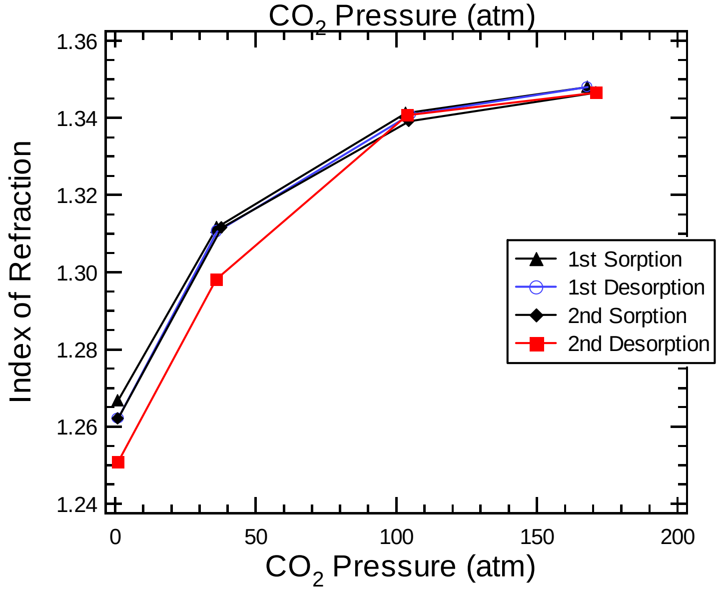
- *Measure change in polazition state upon reflection (ψ and Δ)*
- *Ellipsometric angles are collected (ψ and Δ)*
- *Ellipsometric angles are modeled to obtain film thickness and optical constants*
- *Has been used to measure Tg, swelling of films in presence of solvents, surface roughness, monolayer formation*

Partially Etched/Ashed Porous MSQ

- At higher pressures, CO_2 sorption expands films
- Increase in the index of refraction indicates that CO_2 replaces air in the voids
- Same effect over 2 sorptions
- CO_2 does not damage the films

35°C





Summary

- Chemical/mechanical method
  - Clean using TMN-6, H_2O and $scCO_2$ for 2 minutes
- HMDS repair in $scCO_2$
  - Ellipsometry, contact angle and FTIR show repair
- Ellipsometry shows $scCO_2$ does not harm JSR during processing