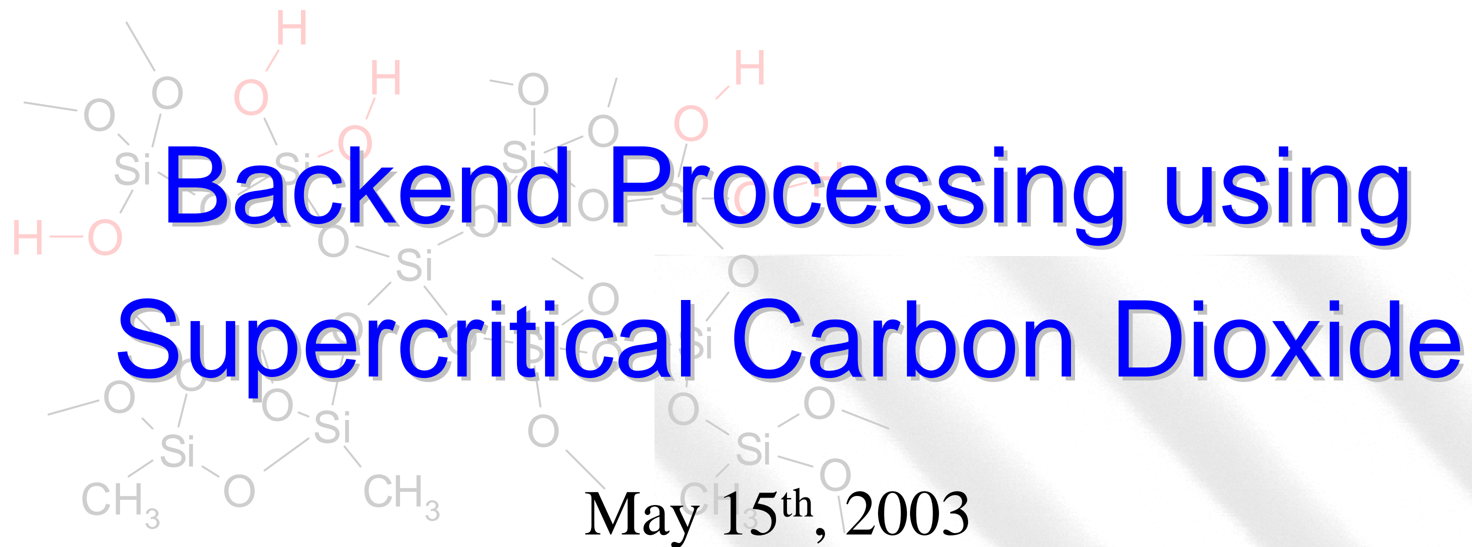


Backend Processing using Supercritical Carbon Dioxide

May 15th, 2003

Bo Xie, Casey Finstad, and Anthony Muscat

Department of Chemical and Environmental Engineering

University of Arizona

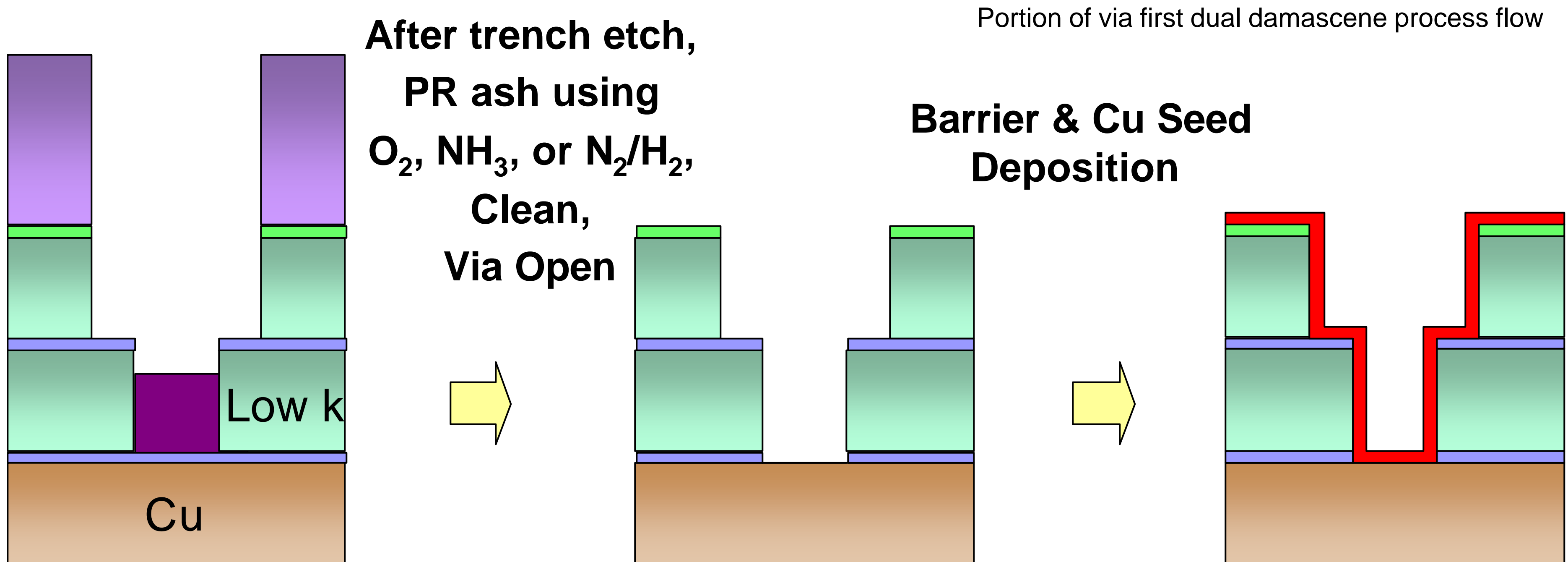
Tucson, AZ 85721

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Outline

- Technical and ESH drivers for ultra-low k (ULK) cleaning
- Properties of supercritical carbon dioxide ($scCO_2$)
- Copper removal from silicon surfaces using $scCO_2$ /chelator
- Water removal from ULK films using $scCO_2$ /cosolvents
- ULK film repair with $scCO_2$ /Si-bearing chemistry
- Conclusions
- Future work
- Acknowledgements

Low-k Cleaning Requirements

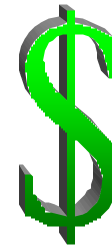


- Residues contain C, H, O, F, Si, Cu, and barrier metal.
- Require good adhesion and device performance.
- Repeat clean for every metal layer present (5-10 times).

- PR removal
- Deveiling
- Cu oxide removal at via bottom
- Contamination trapped in pores
- Pore sealing

Low-k Cleaning Approaches

- Dry
  - Plasma ashing
    - ex. O_2 or N_2/H_2
  - Downstream plasma
- Wet
  - Organic solvent or inorganic acid
  - Surfactants
  - Corrosion inhibitors
  - Complexation agents

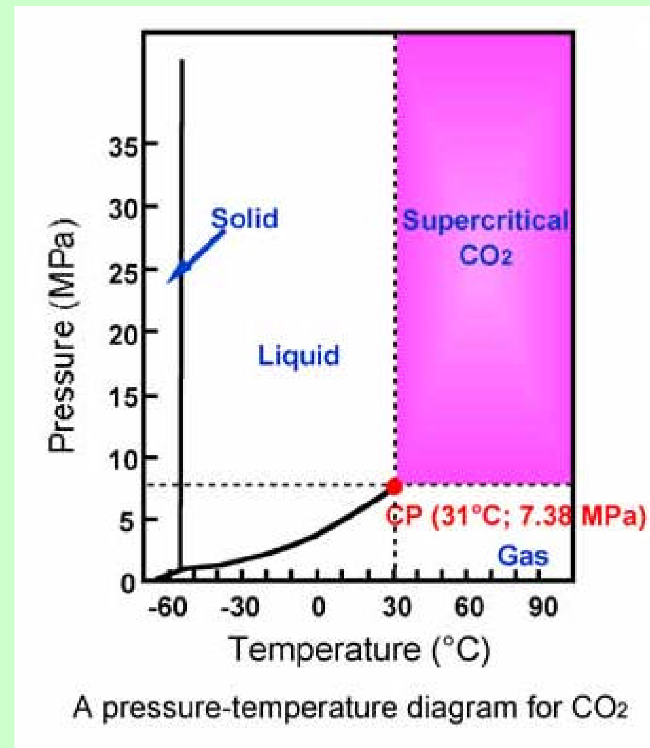


Environmental cost

- Supercritical CO_2
  - Chelators (ppm)
  - Cosolvents < 5-7 vol%

$scCO_2$ Processing Characteristics

- Solvating capability close to a liquid, but mass transfer properties near those of a gas
  - Control density of fluid with pressure
- Inexpensive
- Reusable
- Nonflammable
- Nontoxic
- Nonaqueous
  - Add co-solvent to introduce polarity
- Moderate critical parameters
  - T_c = 31°C and p_c = 72.8 atm

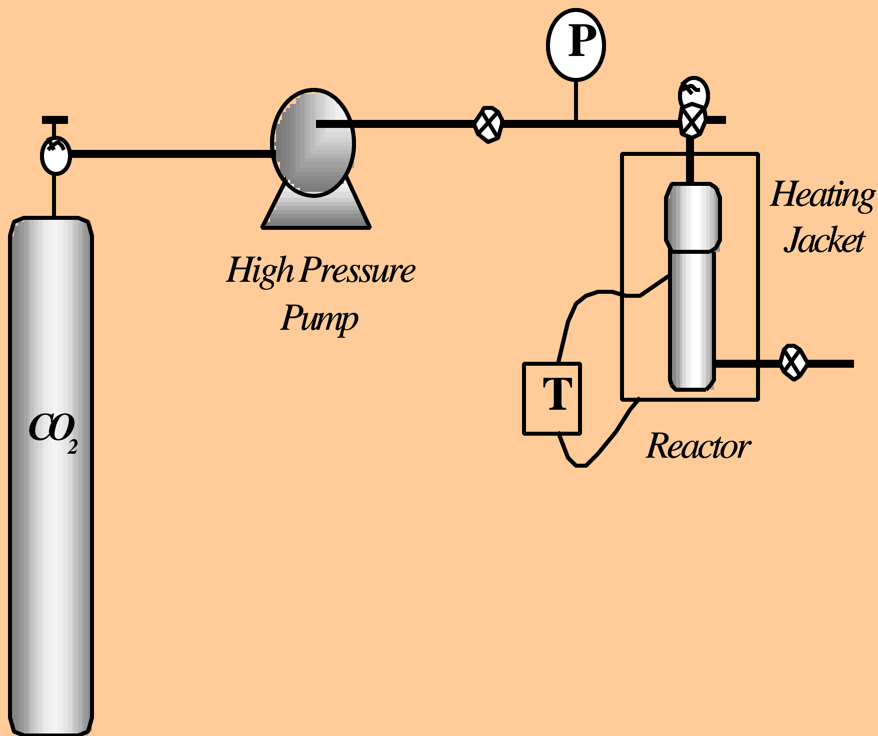


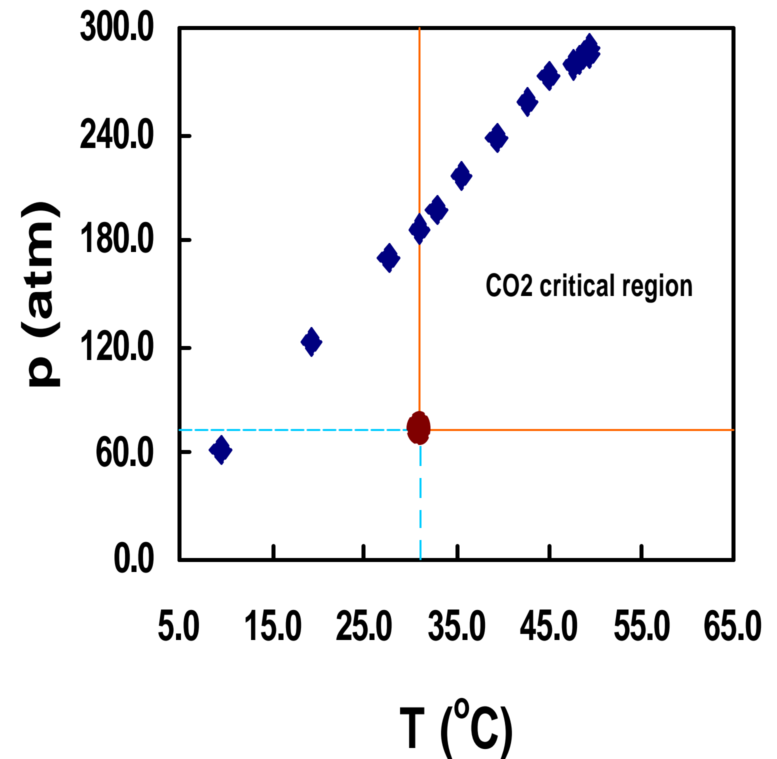
A pressure-temperature diagram for CO_2

Comparison of Fluid Physical Properties

Property	Phase		
	Liquid	Supercritical	Gas
Density (g/cm^3)	1	0.1-1	0.001
Diffusivity (cm^2/s)	10^{-5}	10^{-3}	10^{-1}
Surface Tension (dyne/cm)	20-80	0	0
Viscosity (Pa-s)	10^{-3}	10^{-4}-10^{-5}	10^{-5}

$scCO_2$ Processing Schematic

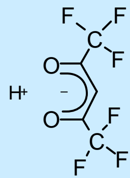




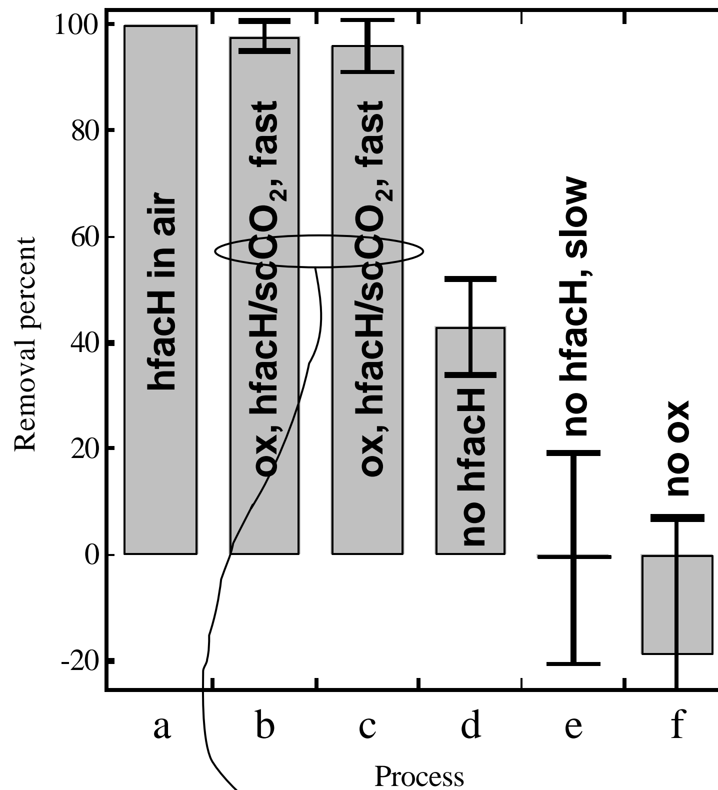
Cu Removal with hfacH/$scCO_2$

Mean change in normalized Cu XPS peak area relative to Si

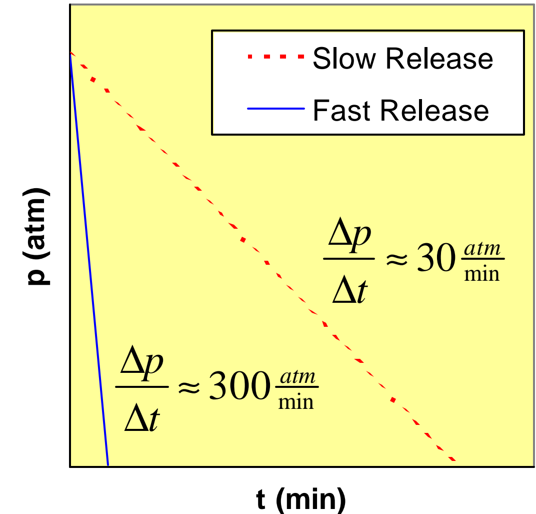
60-100 ppm hfacH



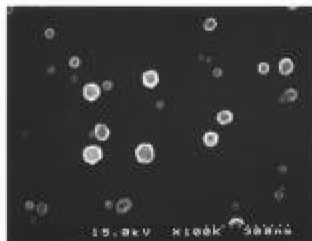
H(hfac) = 1,1,1,5,5,5-hexafluoro-2,4-petanedione

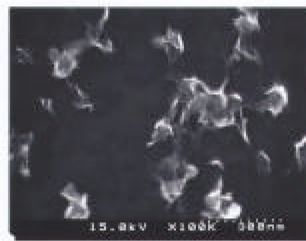


$scCO_2$ reactor pressure release



- Mechanical removal mechanism
- Chemical removal mechanism
- Selectivity between oxidized and nonoxidized Cu



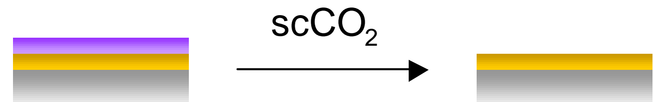


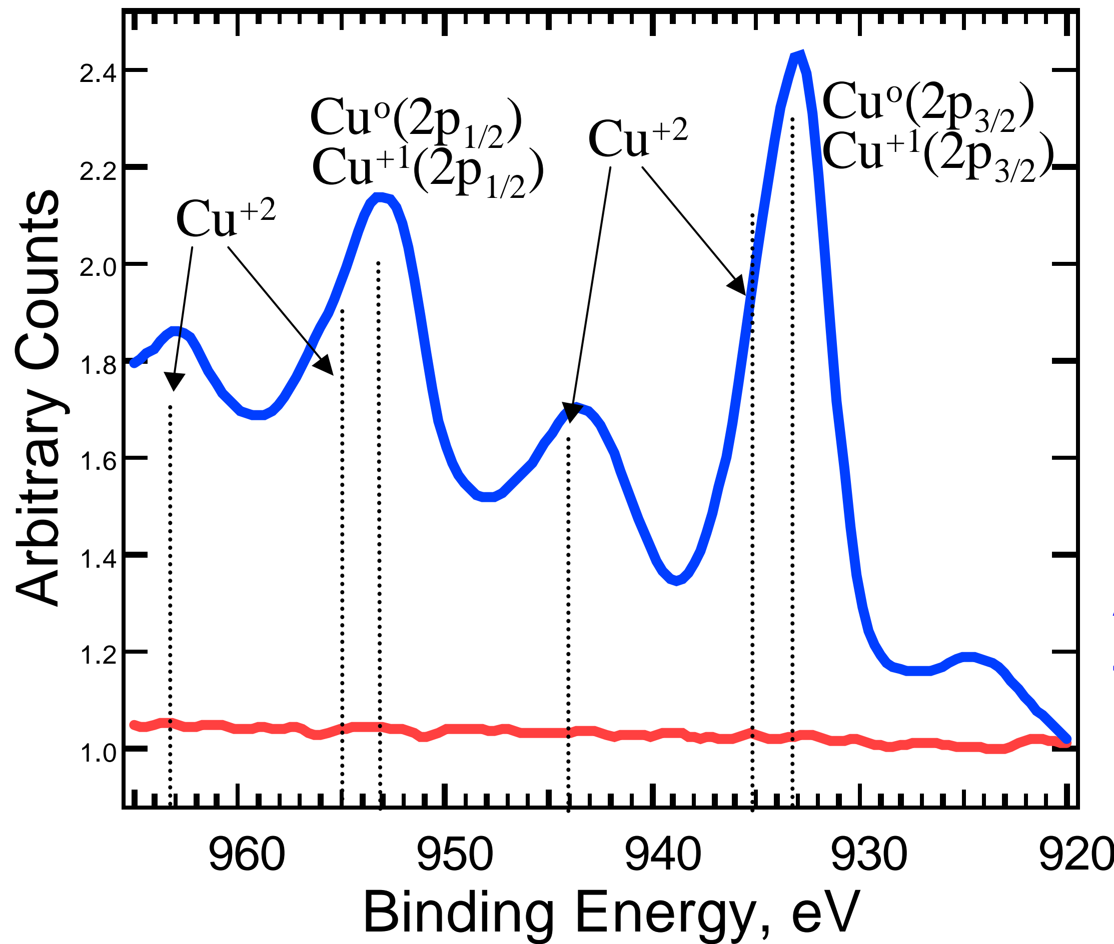
SEM

300 nm

as deposited Cu islands **oxidized** **after hfacH/$scCO_2$**

hfacH/$scCO_2$ Removes Oxidized Copper



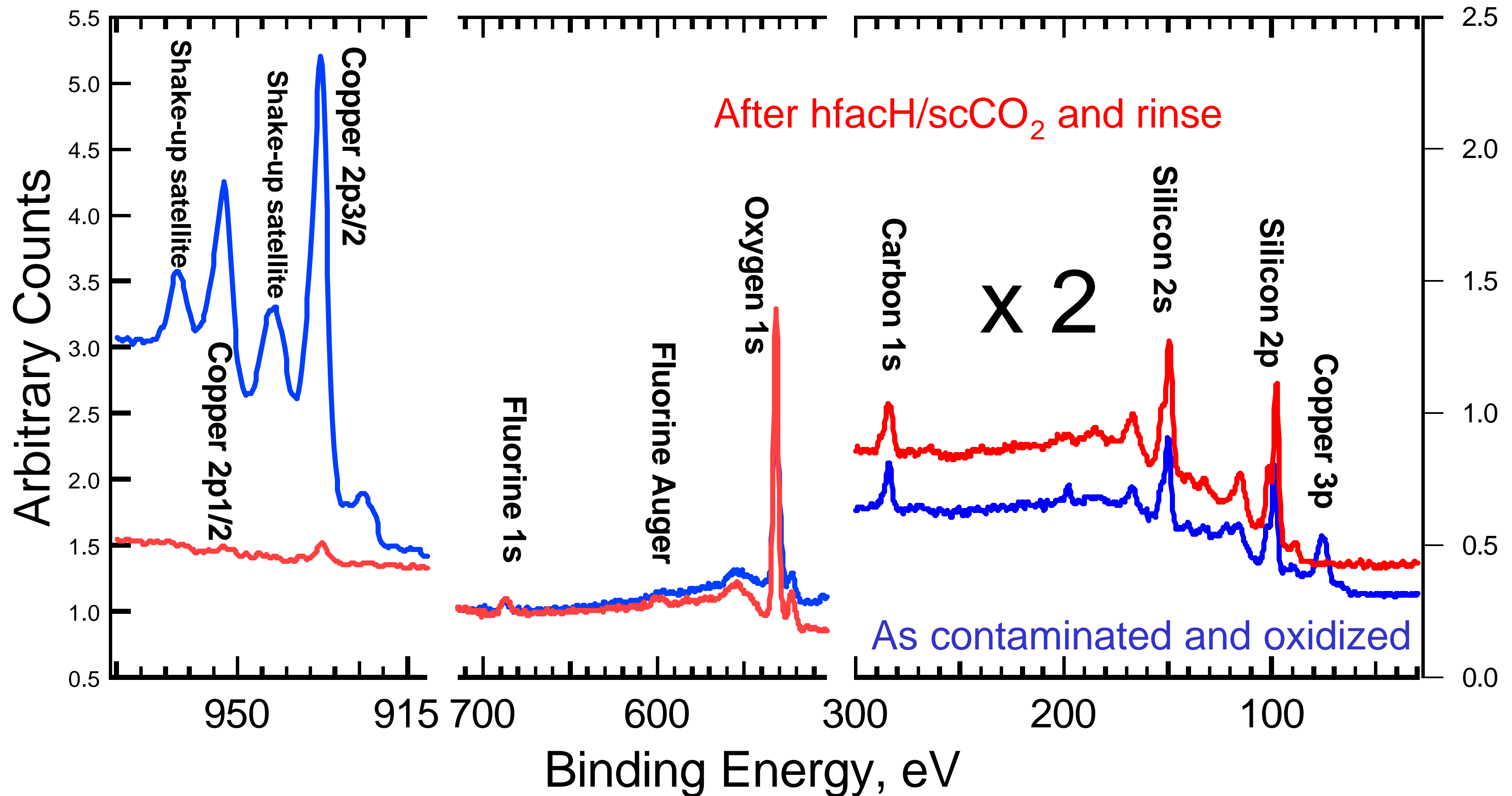


- Chlorinated sample
- < 85 ppm hfac
- Copper removed to XPS detection limit

After 35 min Cl_2 (10 mTorr, 45°C)

After 15 min ramp up and 5 minutes at 180 atm, 58°C (0.67 g/cm^3)

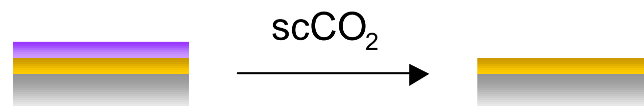
C and F Peaks Unchanged by $scCO_2$ Rinse

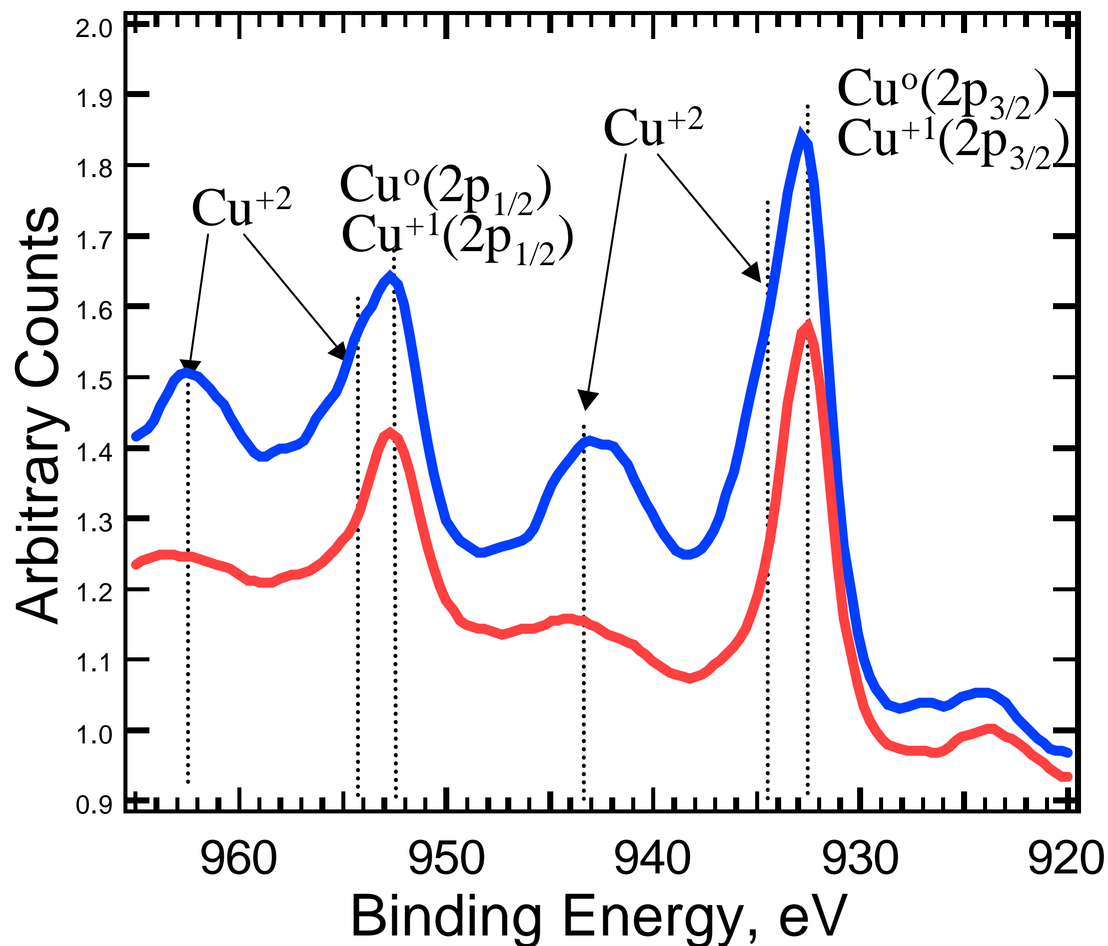


F and C XPS peak areas were constant, indicating no hfacH left on the surface.

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

$scCO_2$ Partially Removes Oxidized Cu



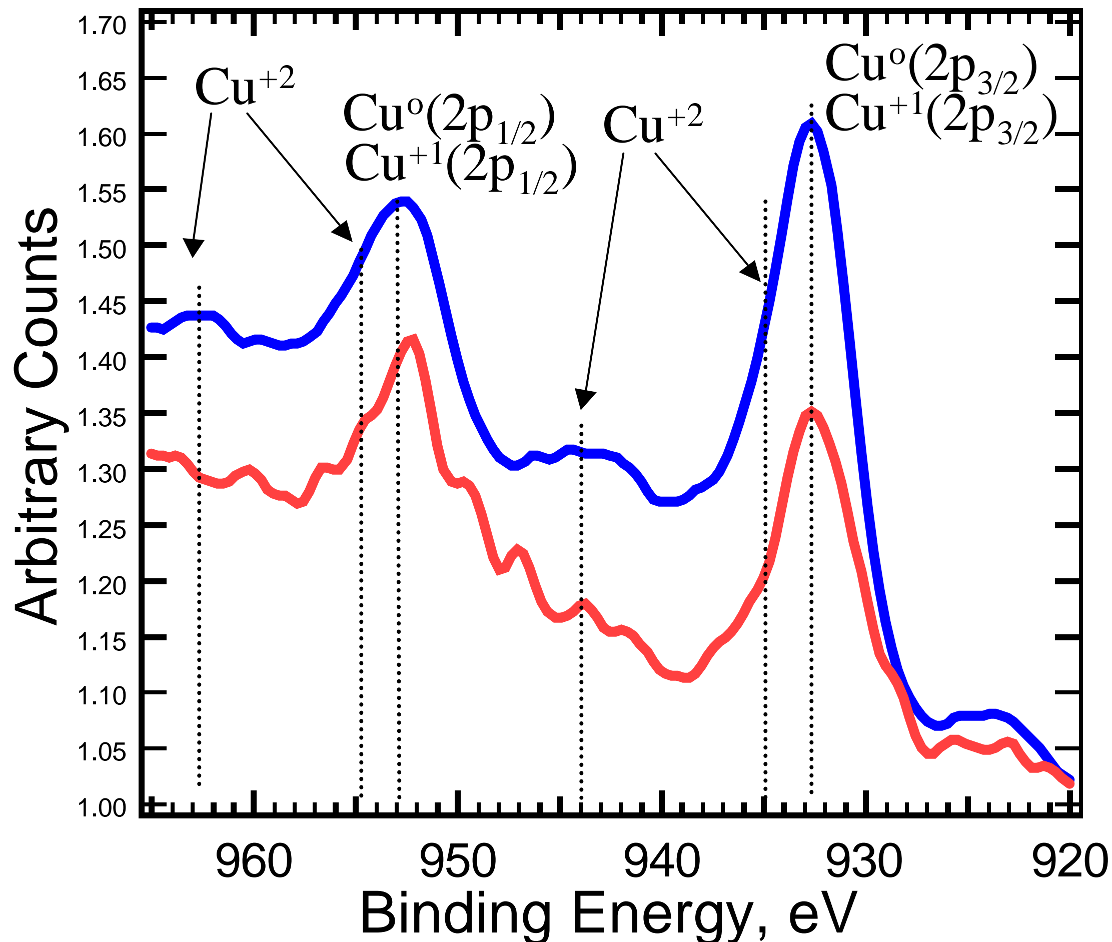


- No hfacH
- Sample oxidized with H_2O_2
- 64% change (decrease) in ref Cu peak area

As Contaminated and oxidized

After 10 minute ramp up, and 5 minutes at 35°C, 90 atm ($0.58\ g/cm^3$)

hfacH/$scCO_2$ Does Not Remove Metallic Cu

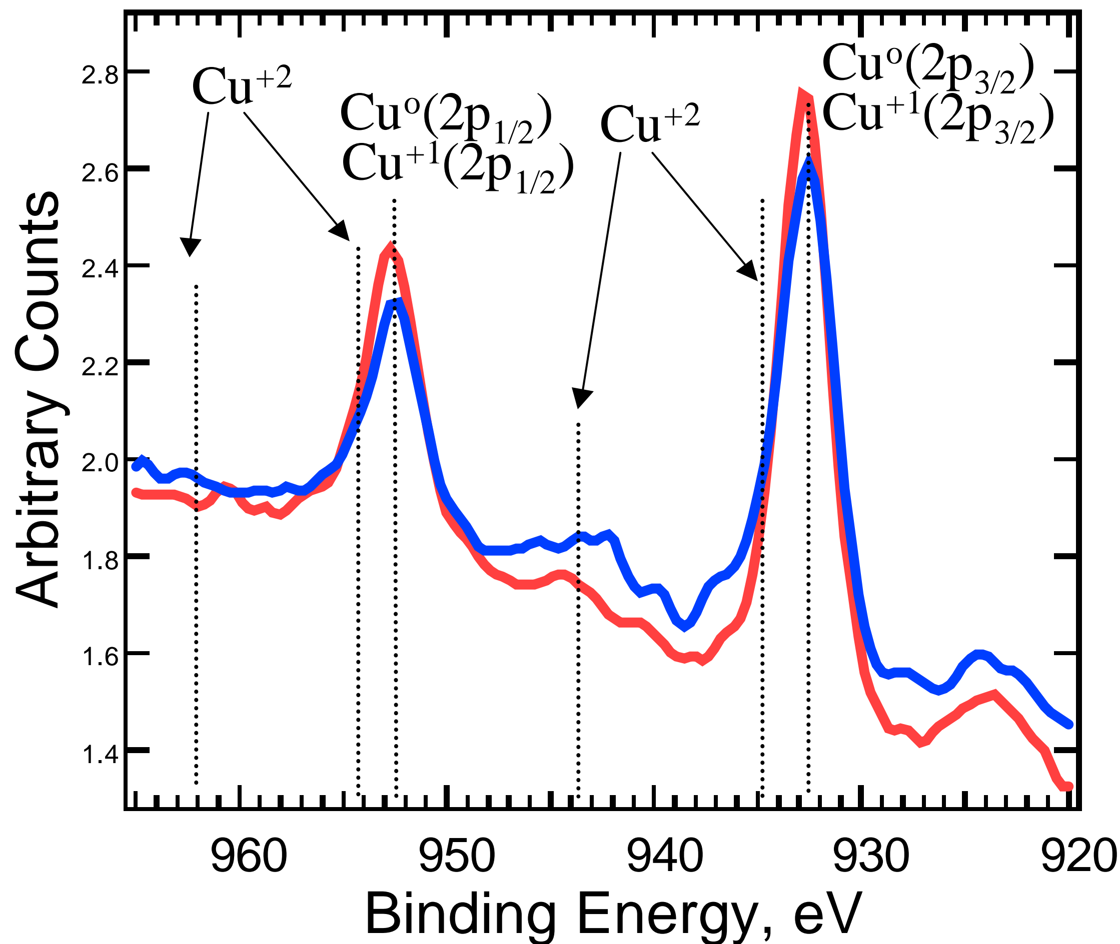


- <100 ppm hfacH dissolved in $scCO_2$
- C and F peaks increased >50%
- No copper removal (-46% change in ref Cu peak area)

As Contaminated

60 min hfac/densified CO_2 (136 atm, 44°C ⇒ 0.68 g/cm^3)

$scCO_2$ Does Not Remove Metallic Cu



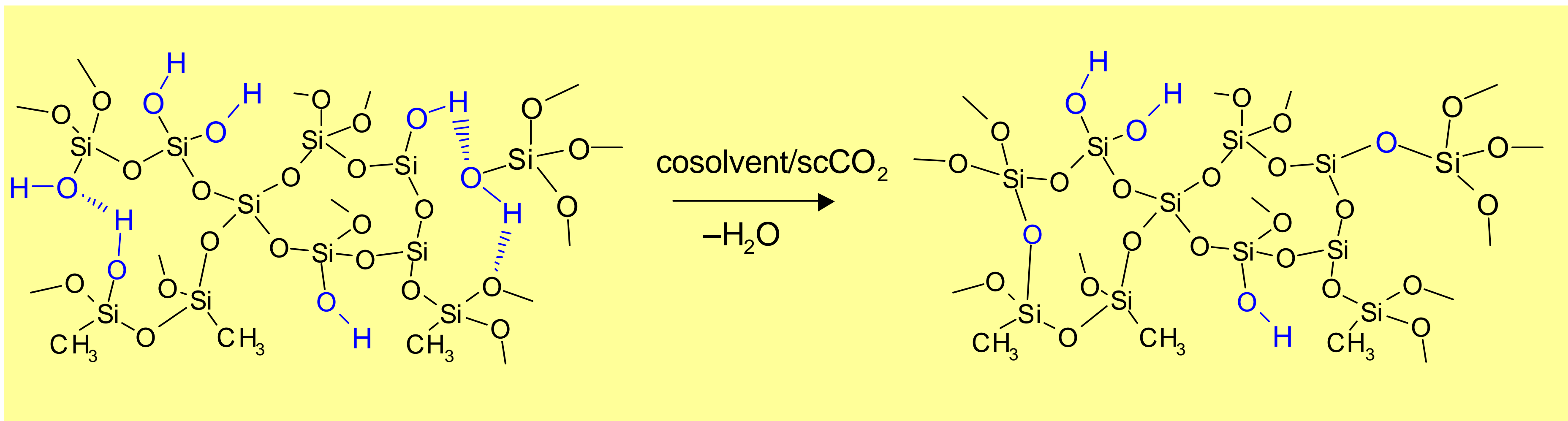
- No hfacH
- Non-oxidized sample
- No Copper Removal (-21% change in ref Cu peak area)

As Contaminated

After 15 minute ramp up, 3 minutes at 55°C, 150 atm (0.60 g/cm³)

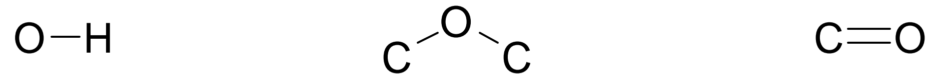
Water Removal from ULK MSQ

- Porous ultra low k MSQ
- Blanket cured, etched, and etched/ashed films
- < 7% cosolvent addition
- $scCO_2$ 45-55°C and 200-300 atm
- 2 min soak, fast release

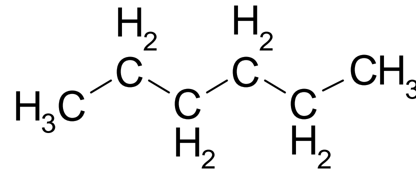


Cosolvent Selection Criteria

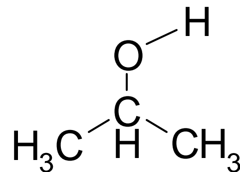
- Dissolve water and post-etching residue ⇒ polar



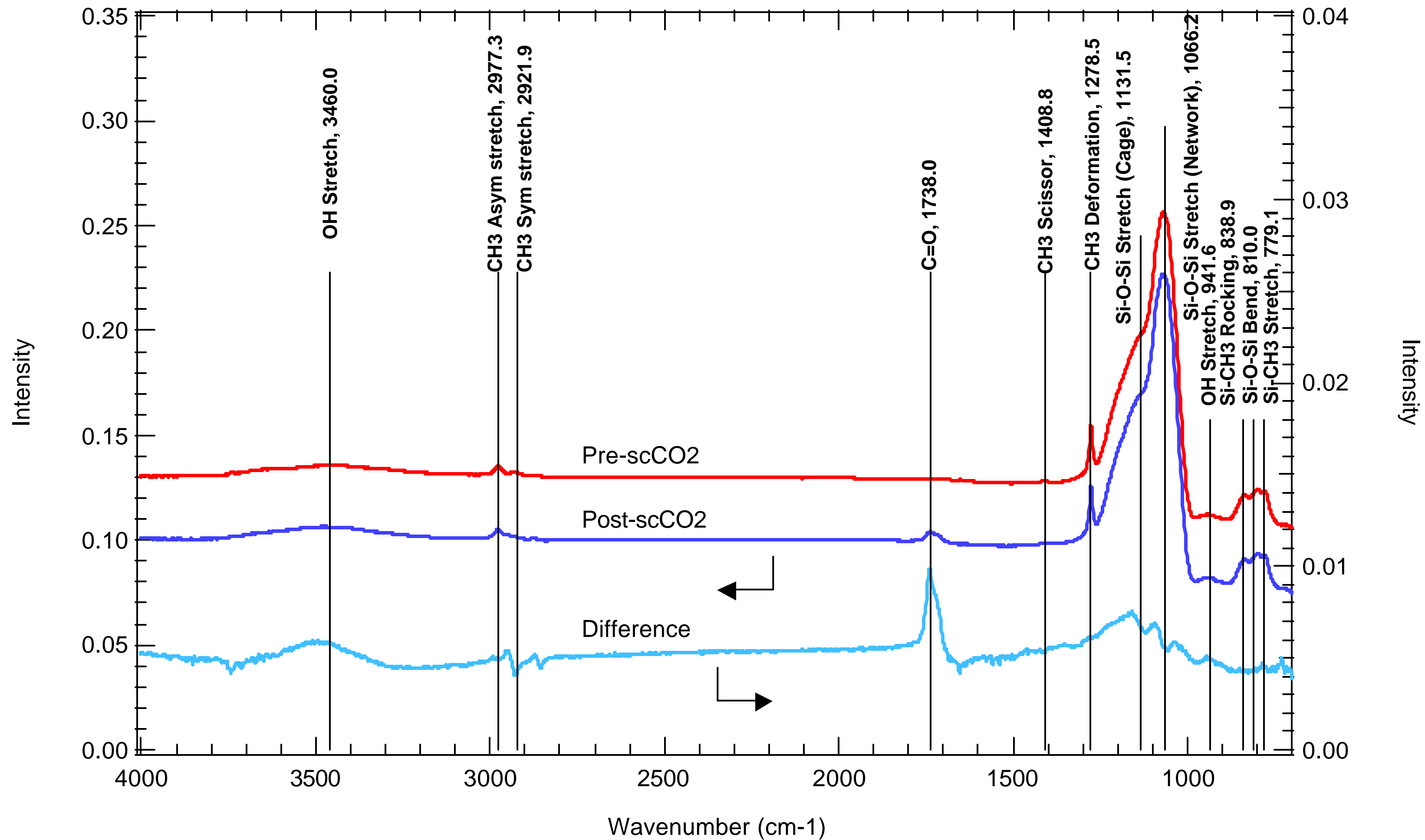
- Complete miscibility with $scCO_2$ ⇒ nonpolar



- Minimize ESH impact ⇒ low vapor p (high boiling pt.)
  - ESH concerns with MeOH CH_3-O-H
  - Longer C-chain

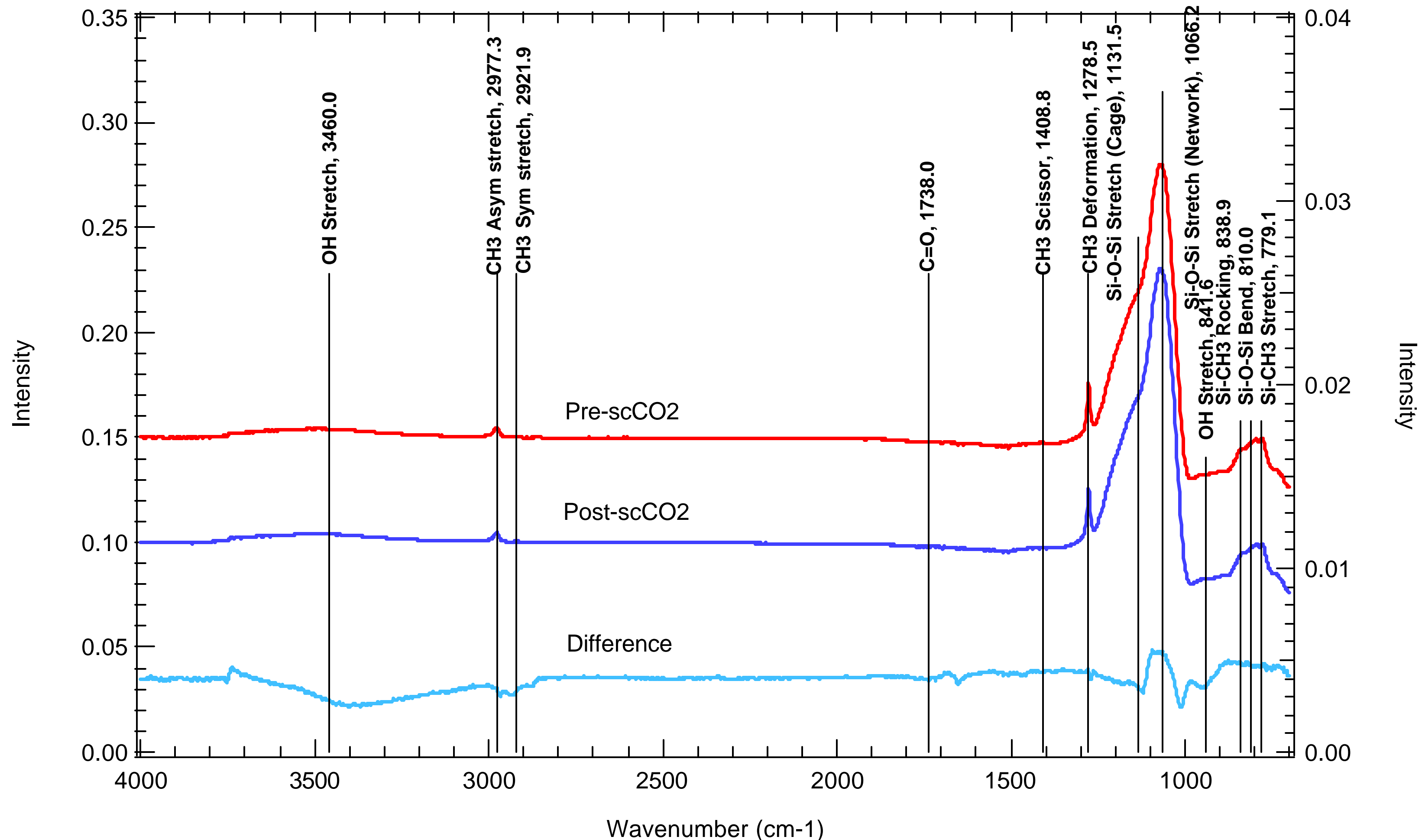


Water Added to ULK MSQ Film



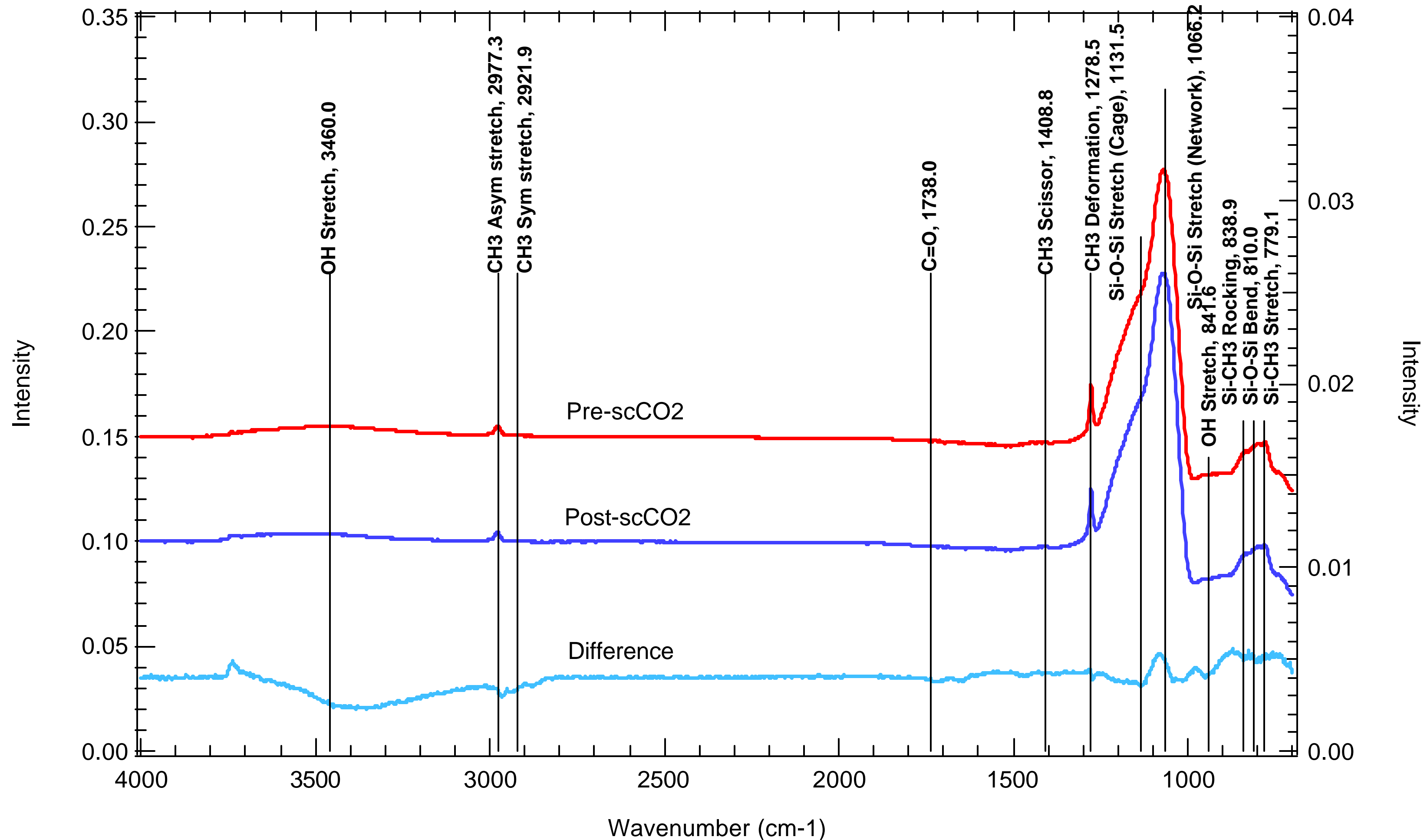
- pure $scCO_2$ at 277 atm and 47°C for 2 min soak
- water added to etched/ashed ULK MSQ film

Water Removed from ULK MSQ Film



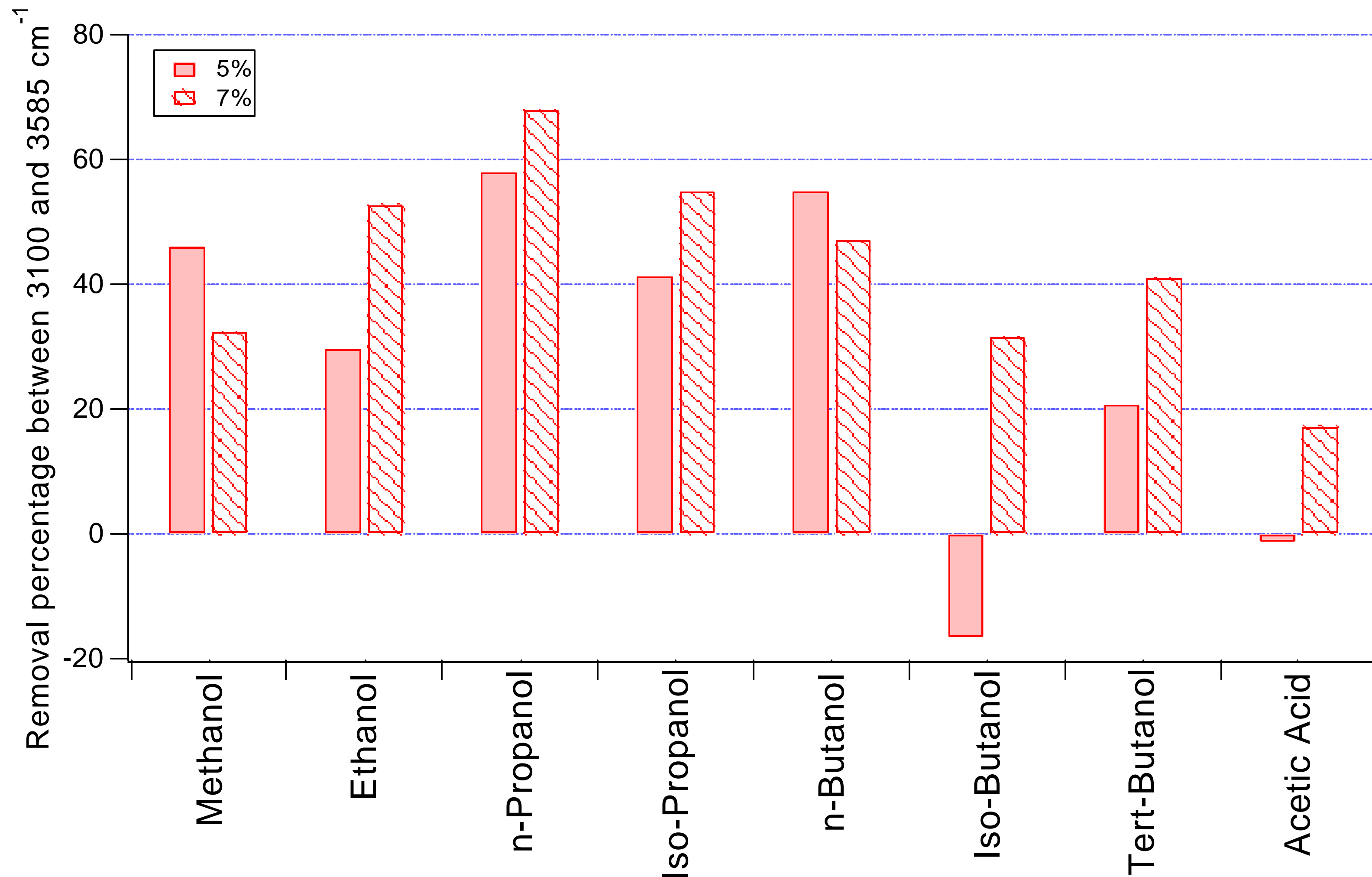
- 5% methanol in $scCO_2$ at 282 atm and 48°C for 2 min soak
- 47% water removed from etched/ashed ULK MSQ film
- Relaxation of Si-O-Si lattice

Water Removed from ULK MSQ Film



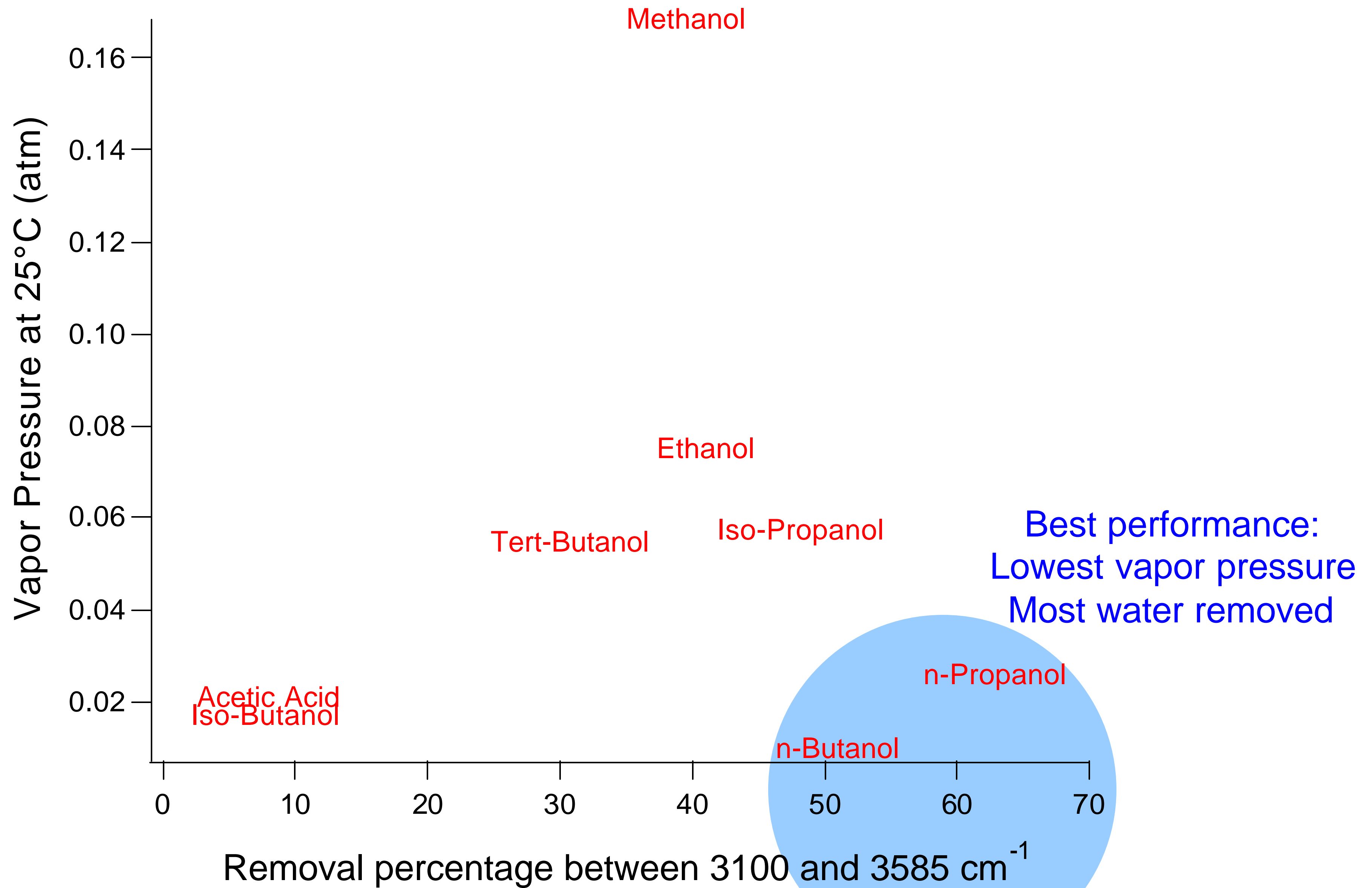
- 7% n-propanol in $scCO_2$ at 289 atm and 49°C for 2 min soak
- 68% water removed from etched/ashed ULK MSQ film
- Relaxation of Si-O-Si lattice

Water Removed by Cosolvent Addition to $scCO_2$



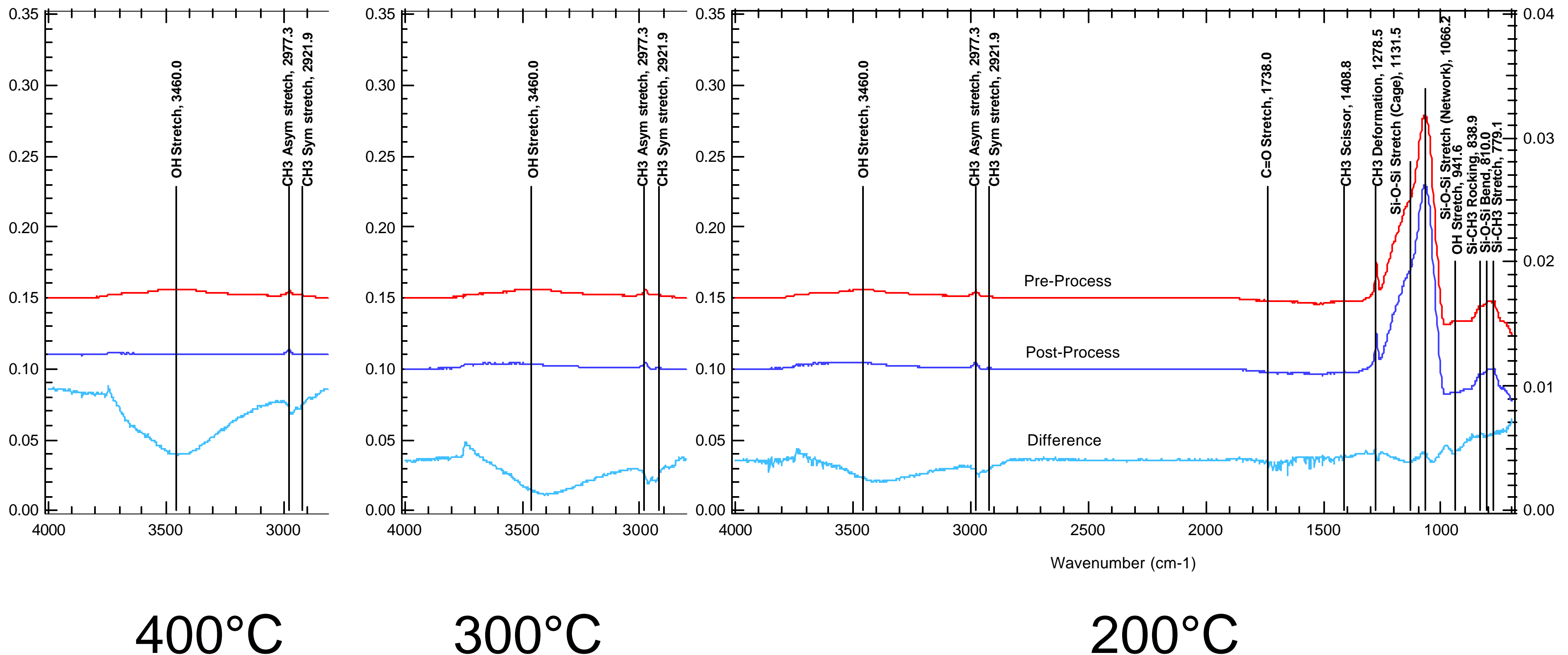
- Pure $scCO_2$ (none) or % cosolvent added to $scCO_2$ at 200-300 atm and 45-55°C for 2 min soak

Performance Evaluation



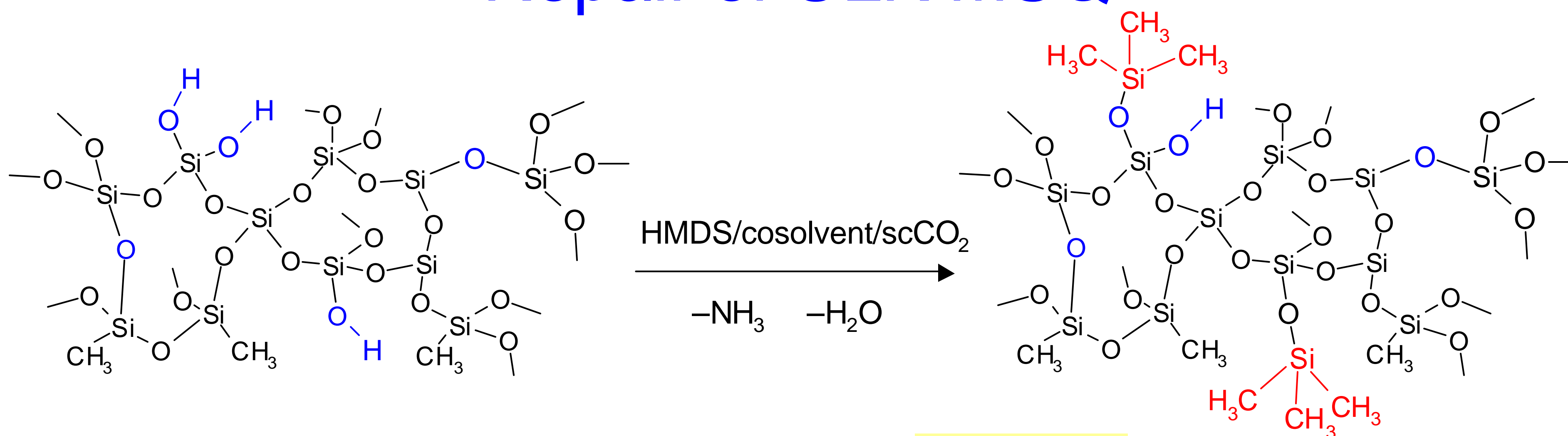
Vacuum Anneal ULK MSQ

- Water removed with 200°C anneal similar to alcohol cosolvent/scCO_2 processes
- 300 and 400°C anneals induce lattice damage

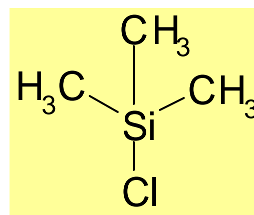


NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

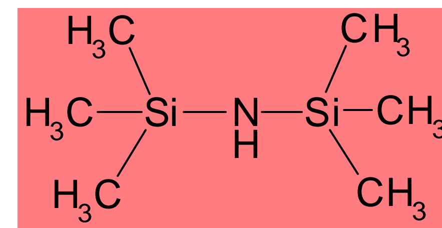
Repair of ULK MSQ



Etched/ashed blanket films



Trimethylchlorosilane
(TMCS)



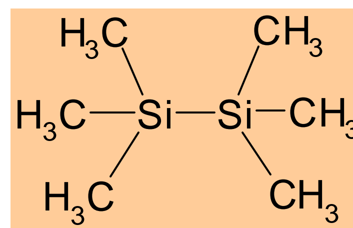
Hexamethyldisilazane
(HMDS)

Cosolvent addition

Si-bearing chemistry

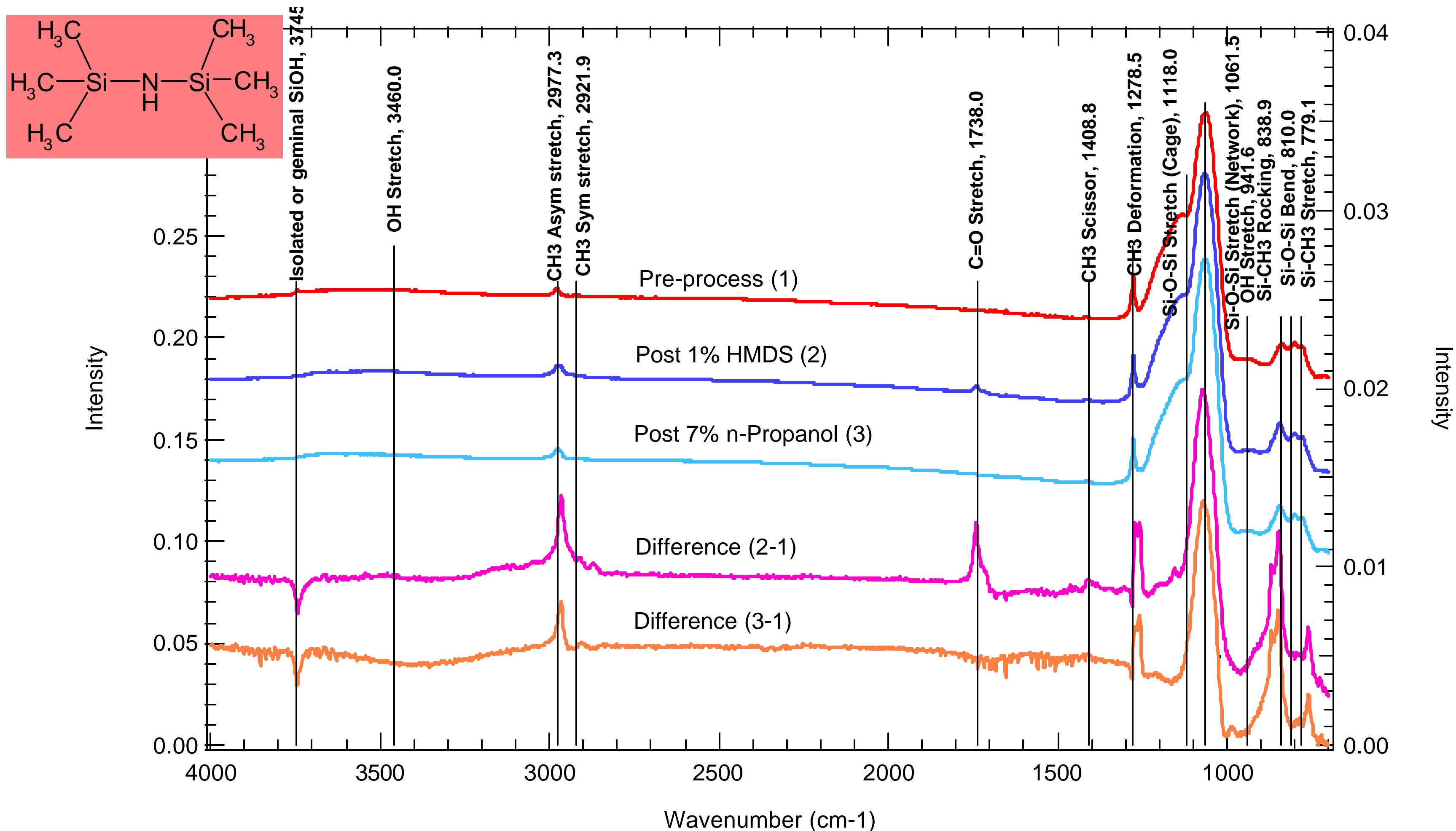
$scCO_2$ 45-55°C and 200-300 atm

2 min soak, fast release



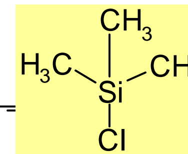
hexamethyldisilane

ULK MSQ Film Repair with HMDS/n-Propanol



- 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

ULK MSQ Film Repair with TMCS



Isolated or geminal SiOH, 3745.1
OH Stretch, 3460.0
CH3 Asym stretch, 2977.3
CH3 Sym stretch, 2921.9
C=O Stretch, 1738.0
CH3 Scissor, 1408.8
CH3 Deformation, 1278.5
Si-O-Si Stretch (Cage), 1118.0
Si-O-Si Stretch (Network), 1061.5
OH Stretch, 941.6
Si-CH3 Rocking, 838.9
Si-O-Si Bend, 810.0
Si-CH3 Stretch, 779.1

Pre-scCO2/TMCS
Post-scCO2/TMCS
Difference

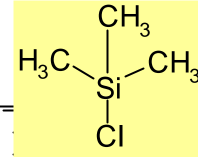
Intensity
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00

Intensity
0.03
0.02
0.01
0.00

4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

- 1% TMCS in $scCO_2$ at 270 atm and 46°C for 2 min soak
- Increased CH_3 and Si-O-Si moieties in different chemical environments
- TMCS preferentially attacks isolated and geminal SiO-H

ULK MSQ Film Repair with TMCS



OH Stretch, 3460.0
CH3 Asym stretch, 2977.3
CH3 Sym stretch, 2921.9
C=O Stretch, 1738.0
CH3 Scissor, 1408.8
CH3 Deformation, 1278.5
Si-O-Si Stretch (Cage), 1118.0
Si-O-Si Stretch (Network), 1061.5
OH Stretch, 941.6
Si-CH3 Rocking, 838.9
Si-O-Si Bend, 810.0
Si-CH3 Stretch, 779.1

Pre-process
Post 1% TMCS
Difference

Intensity
0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35

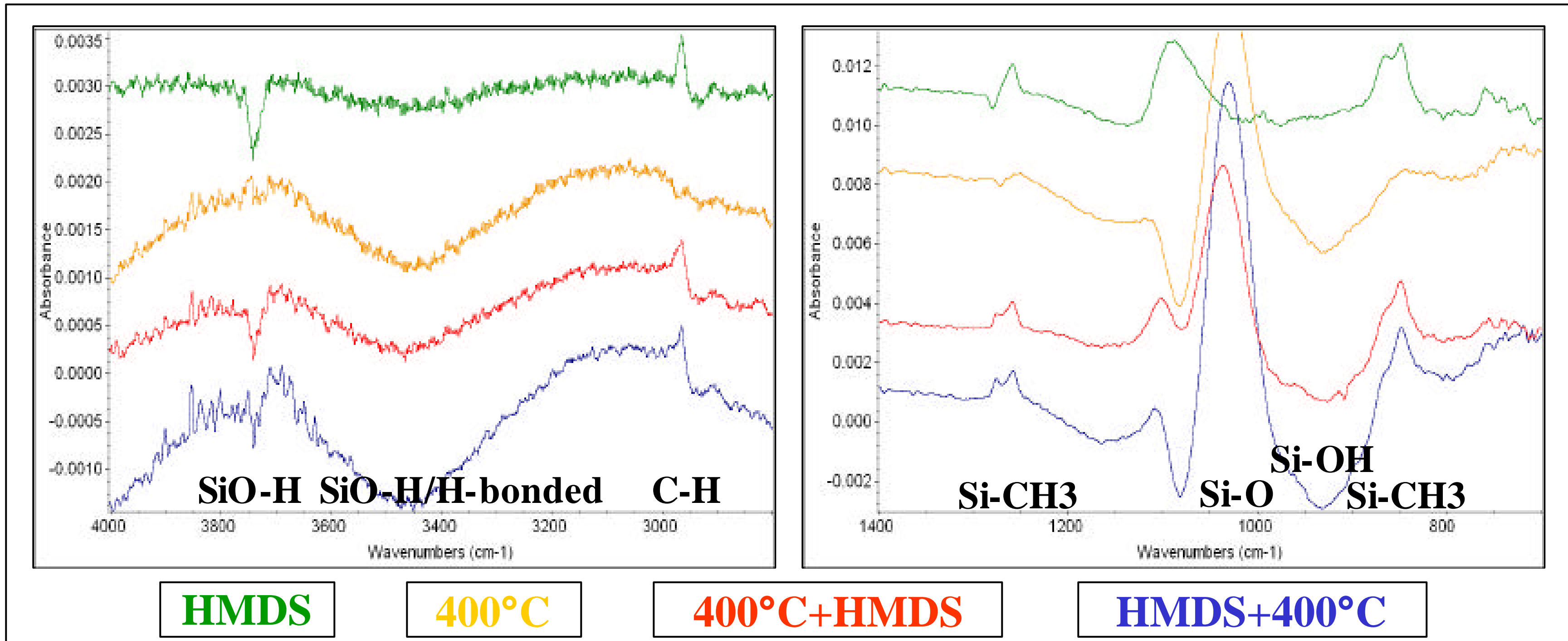
Intensity
0.00 0.01 0.02 0.03

4000 3500 3000 2500 2000 1500 1000
Wavenumber (cm-1)

- 1% TMCS in $scCO_2$ at 299 atm and 50°C for 2 min soak
- *Both* isolated OH groups and H-bonded water reacted

Low k Restoration

Philip Clark, FSI



Process Mechanism

HMDS reacts with isolated silanol groups leaving a hydrophobic surface

- ? SiO-H ? C-H; Si-CH3

400°C facilitates silanol condensation reaction

- ? SiO-H/H-bonded; Si-OH ? Si-O

HMDS + 400°C YIELDS BEST SILANOL REDUCTION

© 2003 FSI International, Inc. All rights reserved.

FSI always thinking // better

Conclusions

- Demonstrated Cu removal using ppm hfacH/$scCO_2$
  - Mechanical removal mechanism
    - Fast release (300 atm/min)
  - Chemical removal mechanism
    - Oxidized Cu to $Cu^{(II)}$
- Demonstrated water removal from ULK MSQ
  - Alcohol cosolvents dissolved in $scCO_2$ at 200-300 atm and 45-55°C
    - n-propanol and n-butanol offered best removal and lowest vapor pressure of additives studied
    - Process compatible with porous structure
    - Results similar to 200°C anneal
  - Removed H-bonded O-H groups
- Repair of ULK MSQ Film
  - TMCS and HMDS
  - Increased CH_3 and Si-O-Si moieties
  - Preferential attack of isolated/geminal SiO-H
    - H-bonded SiO-H reacted at higher p and T
  - Reduced H-bonded SiO-H with cosolvent

Future Work

- Cu Removal
  - Quantify selectivity between Cu and CuO
  - Measure Cu etching rate in hfacH/scCO_2
  - Verify proposed mechanism

- ULK Cleaning
  - Quantify amount of water removed
    - Complete drying possible?
  - Patterned ULK MSQ Films
    - Water removal
    - Post-RIE cleaning
      - New scCO_2 reactor with *in situ* FTIR

- ULK Repair
  - React H-bonded SiO-H's
  - Pore sealing
    - Molecular scaffolding

Acknowledgements

- Texas Instruments
  - Phil Matz, Laura Losey, Trace Hurd, Trish Smith
- International Sematech
  - Josh Wolf (ISMT Etch Program Manager, Intel Assignee)
  - Steve Burnett (ESH Program Manager)
- Motorola
  - Hunter Martinez
- IBM
  - Kenny McCullough
- NSF/SRC EBSM Engineering Research Center
  (EEC-9528813/2001-MC-425)