# Supercritical Drying and Repair of Ultra Low-k Films

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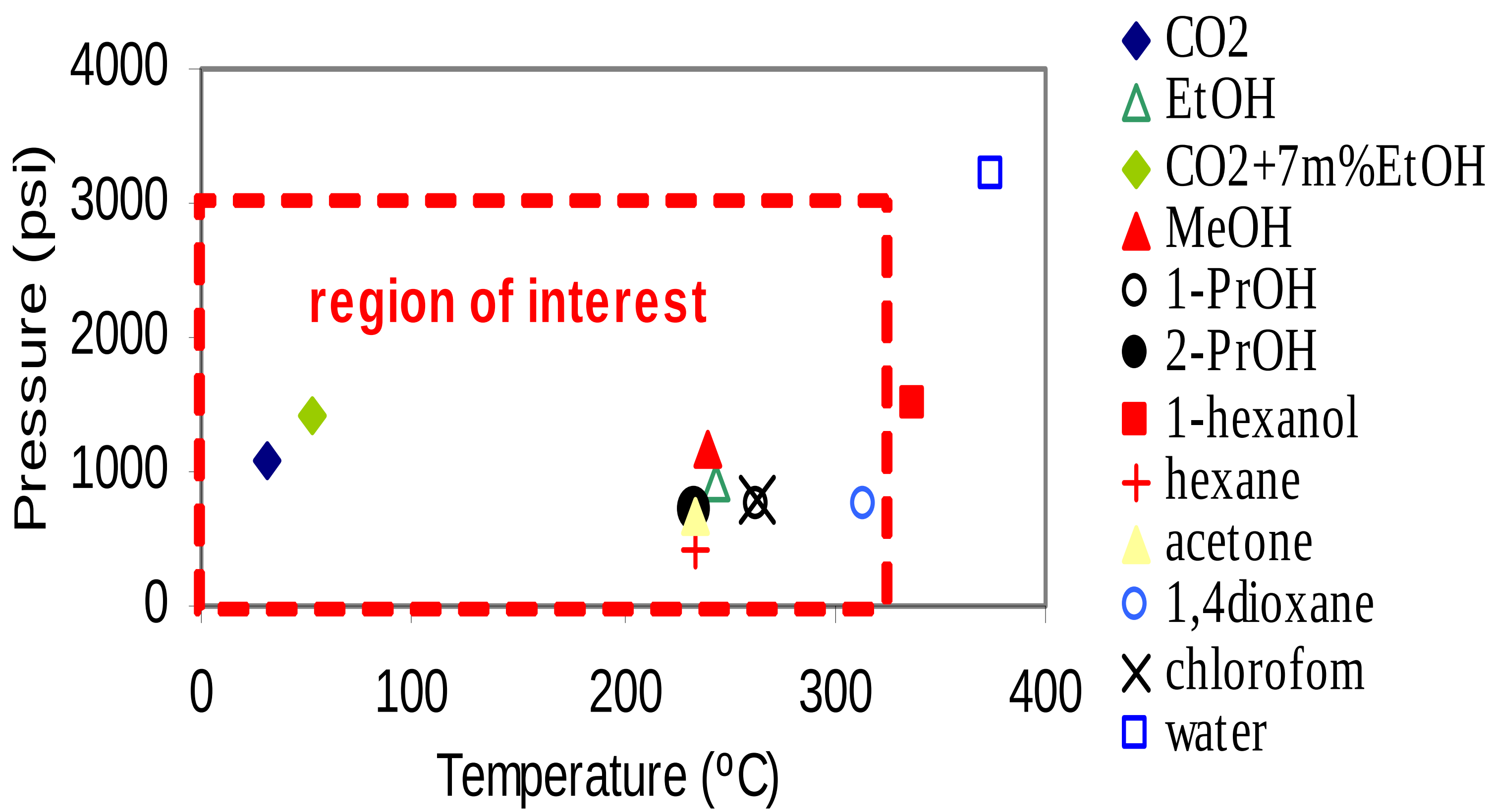
# Questions to be addressed

- Can SC-$CO_2$/co-solvent systems effectively remove water from porous ULK's without diminishing key properties?
  - What changes are introduced?
- Does supercritical processing change ULK dielectric behavior?
  - What are the mechanisms?
- Can ULK's be functionalized in SC-$CO_2$?
  - Is this an viable means of introducing hydrophobicity?
  - Can plasma damaged MSQ be repaired in supercritical media?
- Are etchants effective on ULK's in SC-$CO_2$?

# Critical Points for Solvents

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# Experimental Ultra Low-k (ULK) Materials

| | MSQ | TEFS |
|---|---|---|
| **Dielectric Constant** | ~2.3 | ~2.3 |
| **Elastic modulus (GPa)** | 4 | 12 |
| **Other properties** | Hydrophobic; loses $CH_3$in $H_2$ and $O_2$ plasma | Absorbs some water; after 400C, water lost, but k=2.1→ 2.3 |

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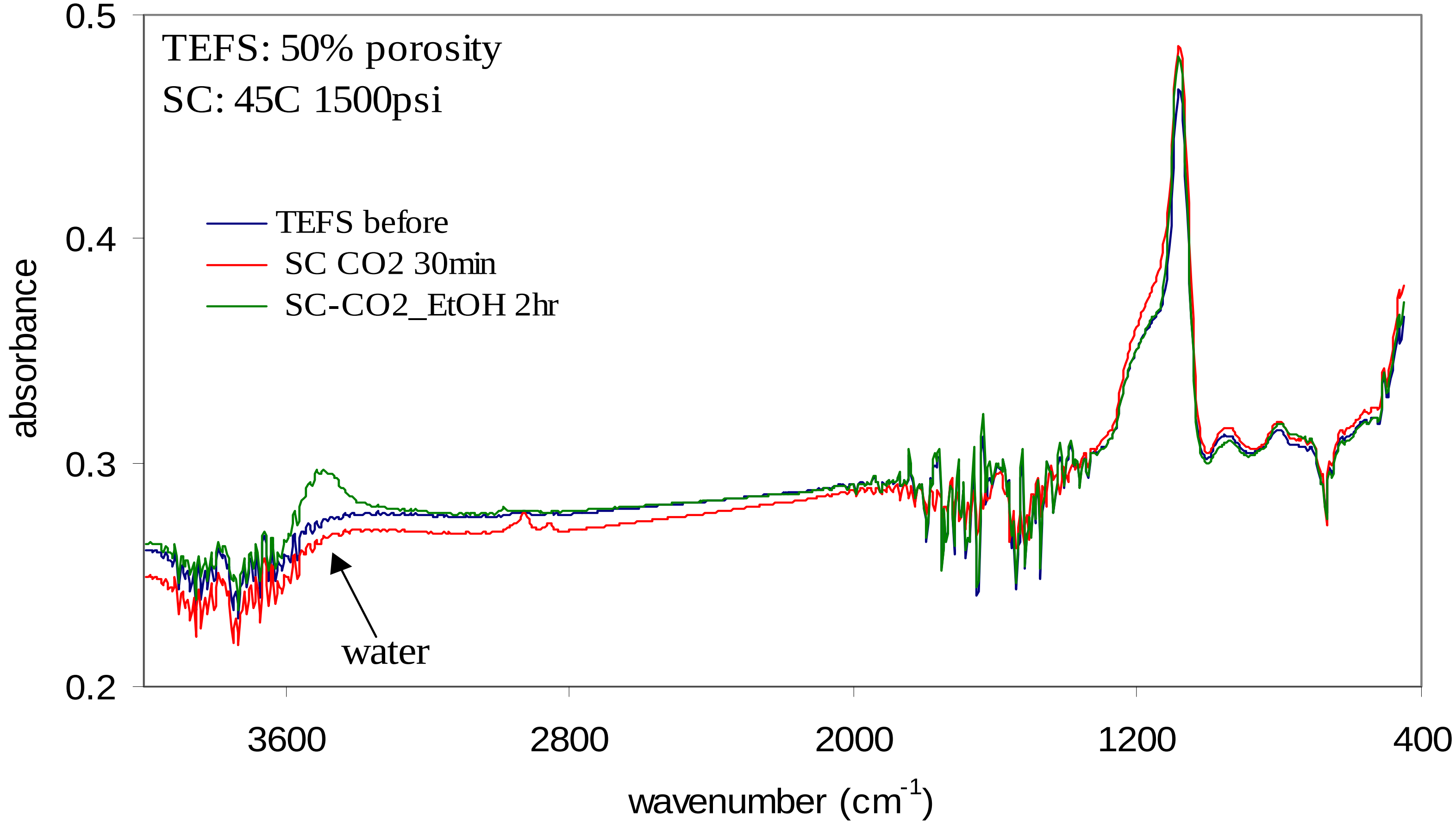
# Drying of ULK Films

- Determine the effects on TEFS of:
  - liquid and SC-$CO_2$ based solutions
  - SC-$CO_2$ vs SC-$CO_2$ + EtOH
  - films with different porosities
- Drying of ashed MSQ
  - liquid and SC-$CO_2$ based solutions
  - SC-$CO_2$ vs SC-$CO_2$ + EtOH

# TEFS Drying Experiments

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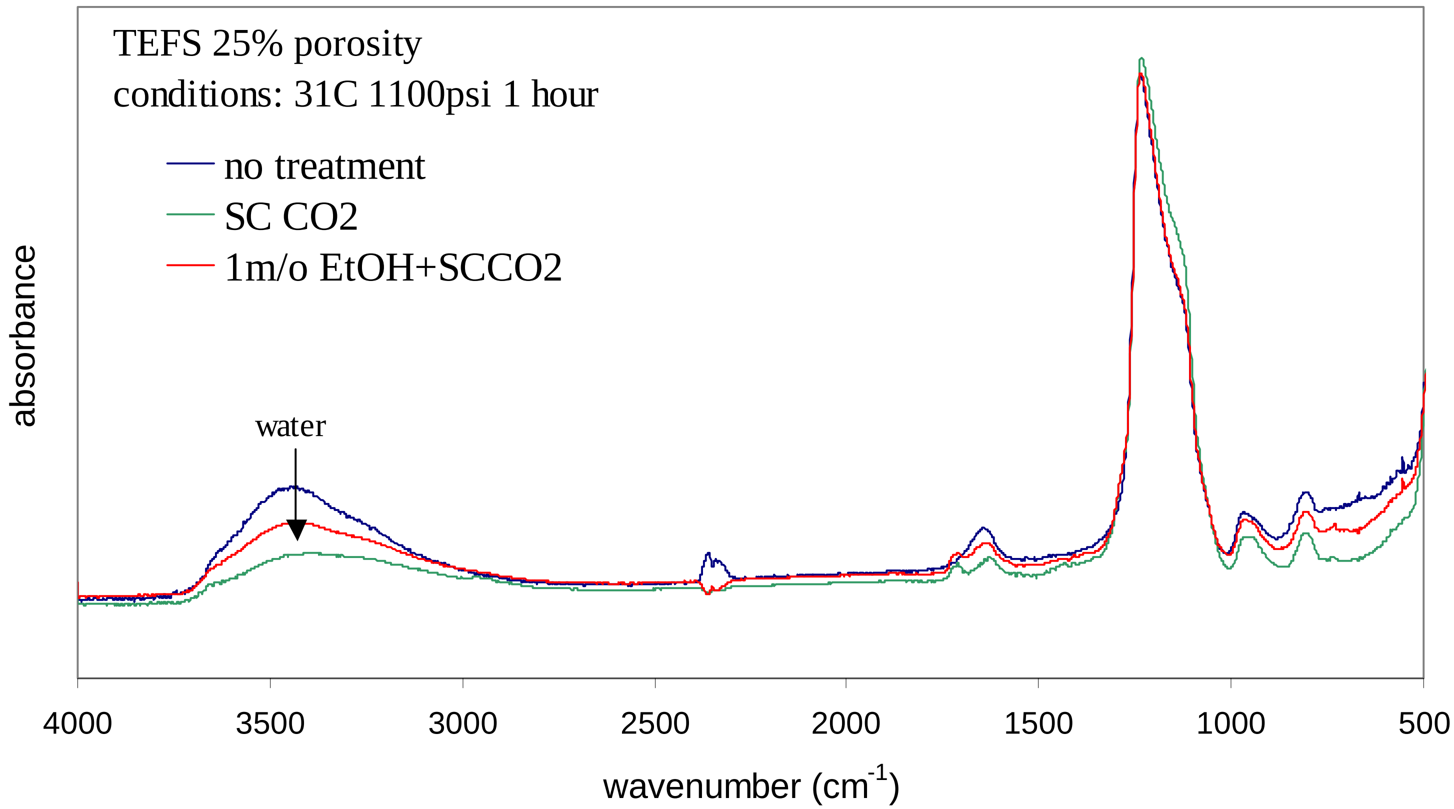
# Liquid $CO_2$ Drying of dense TEFS Films



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# Drying of TEFS

- SC-$CO_2$ removed some water
- SC-$CO_2$ + 1m%EtOH gained water (50% sample)
- → liquid and SC-$CO_2$ a better drying agent than liquid and SC-$CO_2$ + EtOH

# Why do SC-$CO_2$+EtOH treated films gain water?

- Hypothesis:
  - – TEFS films are highly porous and may have trapped moieties absorbed into pores
    - → removal of these species may expose surfaces that can absorb water when exposed to ambient lab conditions
    - → removal may induce structural changes in film



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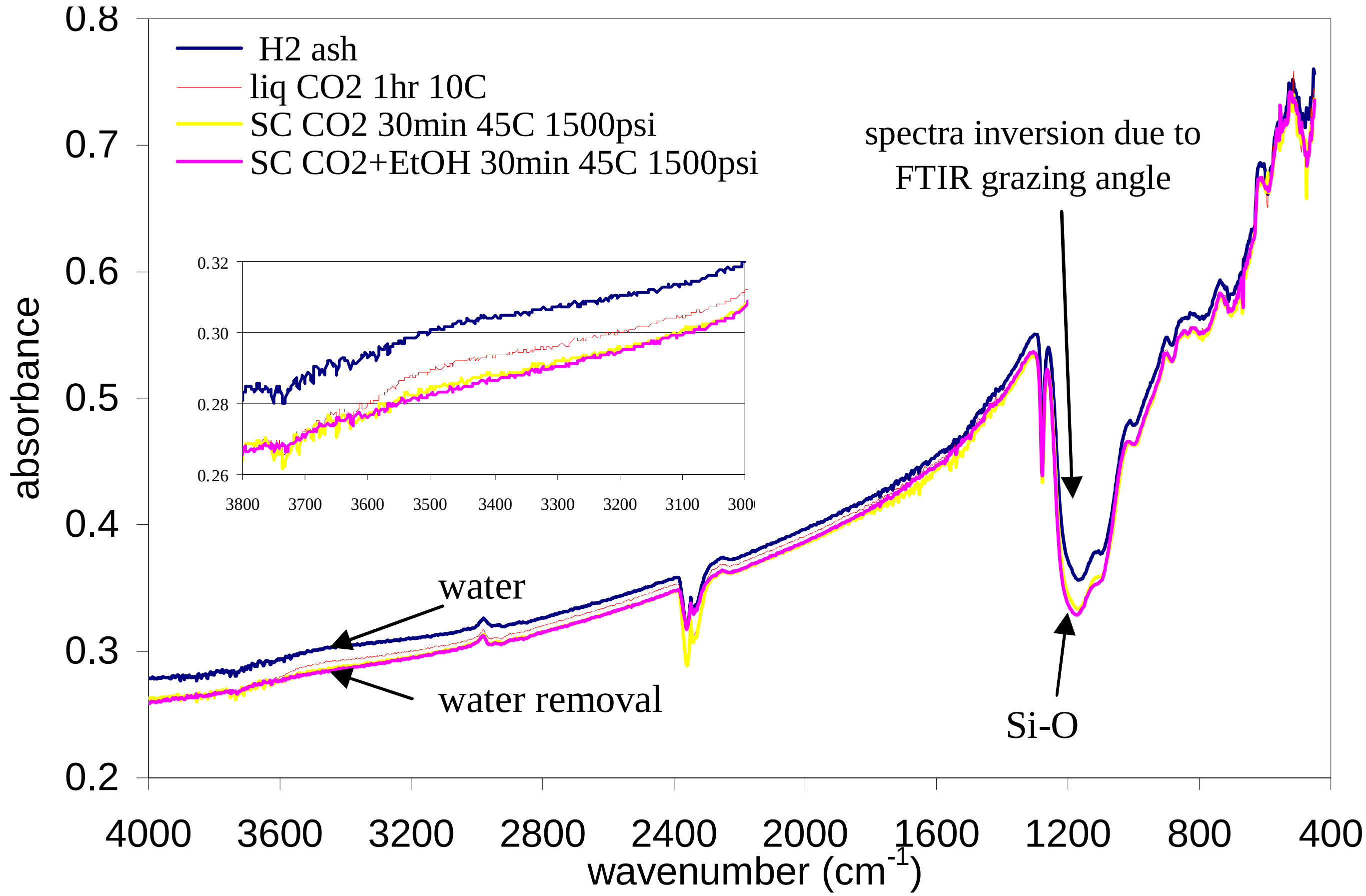
# Ashed-MSQ Drying

- Films exposed to 90% humidity for 48 hours
- Dried with:
  - liquid $CO_2$
  - SC-$CO_2$
  - SC-$CO_2$ + ETOH

# Drying of $H_2$ Ashed MSQ
## (after 48 hours in 90% humidity)



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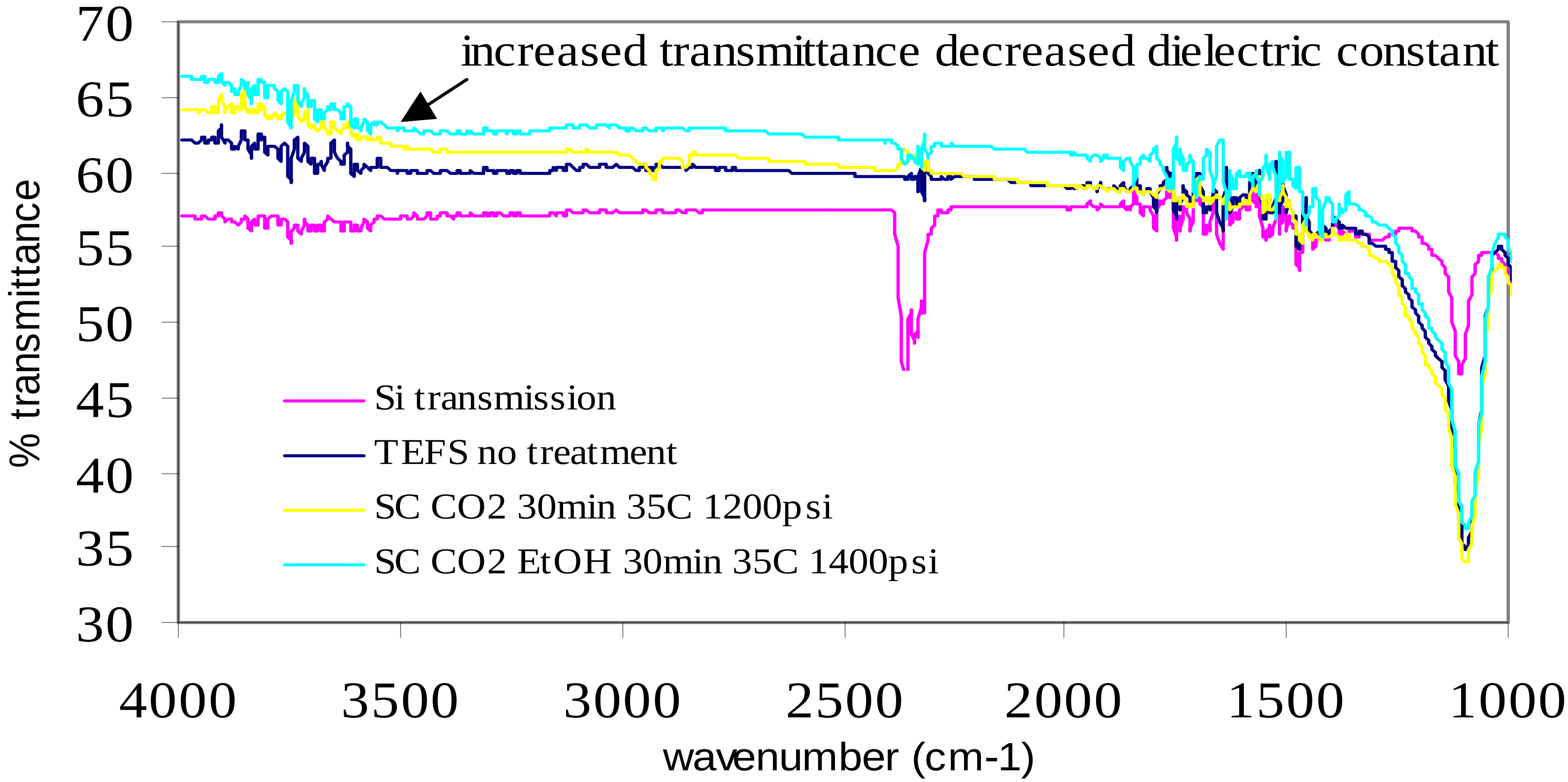
# Effects of SC-processing on TEFS



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# TEFS: IR Transmittance Changes after SC-$CO_2$

- How did we do the calculations?

  Changes in refractive index were calculated from the transmission spectra using standard Fresnel equations, including the reflections from the back of the substrate
- Before treatment: n = 1.21
- After treatment: n = 1.19



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# Possible Causes for IR Transmittance Behavior

- Change in porosity and/or electronic structure
  - ellipsometry experiments → changes in visible refractive index
- Change in film chemistry
  - detailed FTIR experiments

# Similar behavior in MSQ?

- TEFS IR were conducted with double polished wafers in transmission
- Double polished MSQ were unavailable
- $\rightarrow$ ellipsometry of MSQ samples

# SC-treated MSQ: Ellipsometry

| | Film thickness (nm) | Refractive index |
|---|---|---|
| **Before SC treatment** | 526 | 1.280 |
| **After 1 hr SC-$CO_2$** | 525 | 1.279 |
| **After 1 hr SC-$CO_2$ + EtOH** | 529 | 1.277 |

# Effects of SC-treatments on MSQ

- ellipsometry: very small changes in n
- → changes in dielectric constant may be due to ionic polarizations, not electronic (porosity)
- → cleaning out of pores (trapped solvents and/or ash products?)

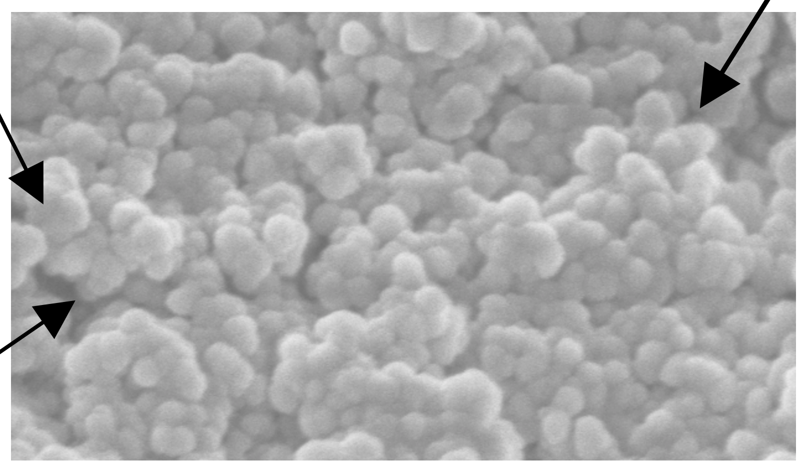
# Why study changes in k after SC processing?

- Confirm reports of lower k post SC drying
- Need to study mechanism to develop process
- Goal $\rightarrow$ reproducible lowering of k without diminishing other properties

# What could be happening to ULK films during SC processing?

changes to skeletal structure

chemical changes in pores or surfaces



expansion of film

enlargement of pores through removal of adsorbed species



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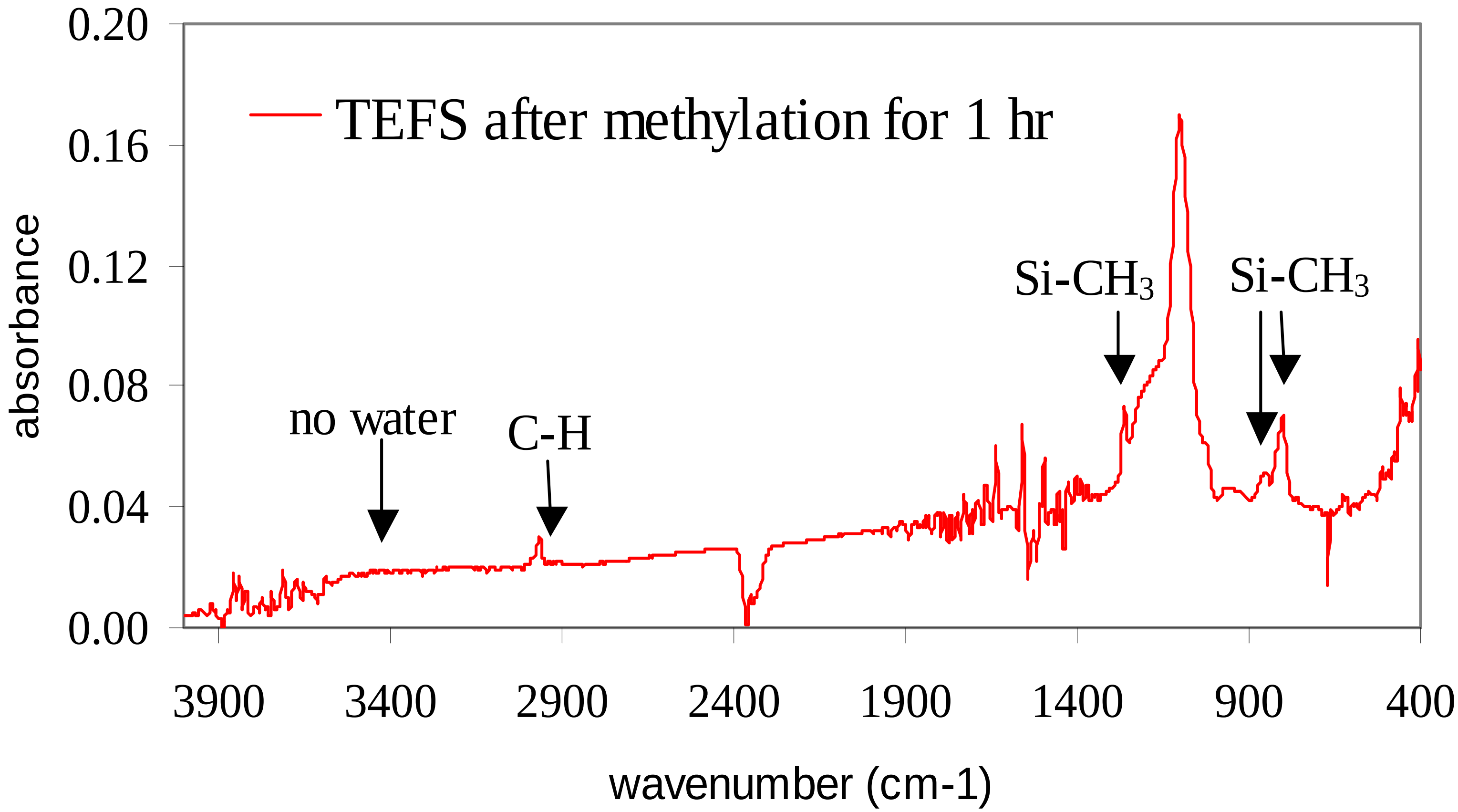
# Supercritical Functionalization of ULK films

- In situ functionalization of low-k materials
  - ambient conditions → 12-24 hours
  - supercritical conditions → «1 hour
- Goals:
  - TEFS → improve hydrophobicity
  - MSQ → dry and repair post ash damage

# Supercritical Functionalization



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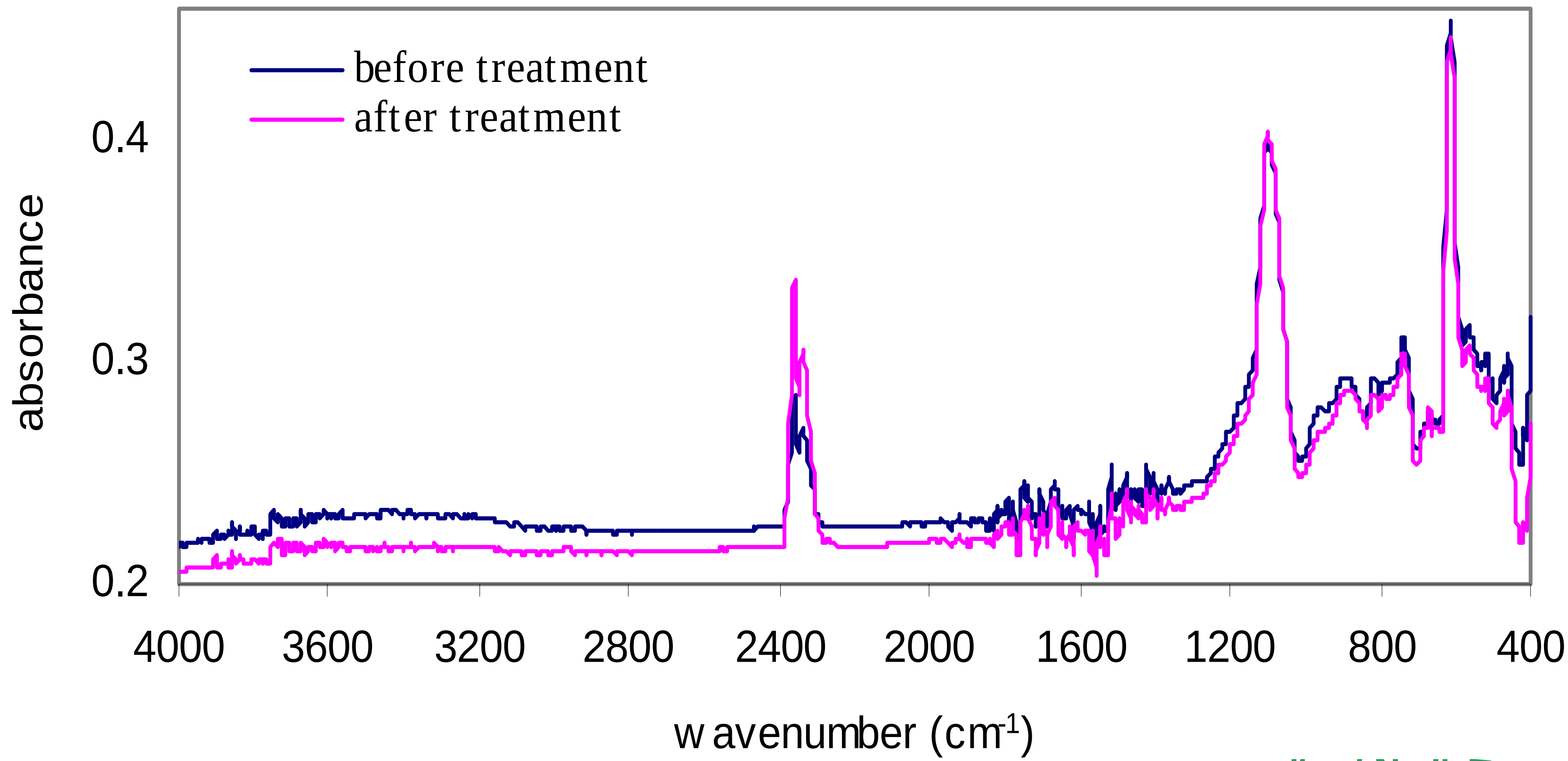
# Surface Modification: Drying



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# Determination of MSQ repair: contact angle measurements

- Plasma removes methyl groups → loss of hydrophobicity
- Ashing also causes some densification
- Functionalization may return hydrophobicity and expand collapsed region

# Contact Angle Measurements

| TEFS | Contact Angle |
|---|---|
| As deposited | 30 |
| Treatment 1 10% 15 min | 63 |
| Treatment 1 10% 30 min | 101 |
| Treatment 2 5% 5 min | 76 |
| Treatment 2 10% 5 min | 96 |
| Treatment 2 10% 15 min | 105 |
| **MSQ** | |
| As deposited | 103 |
| $H_2$ ashed | 7 |
| Treatment 1 5% 5 min | 100 |

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# Effectiveness of liquid and $SC\text{-}CO_2$-based fluids etchants

- Comparison between liquid and $SC\text{-}CO_2$ based solutions
- Determination of ambient etchants solubilities in $SC\text{-}CO_2$
- Viability of combinations of etchants



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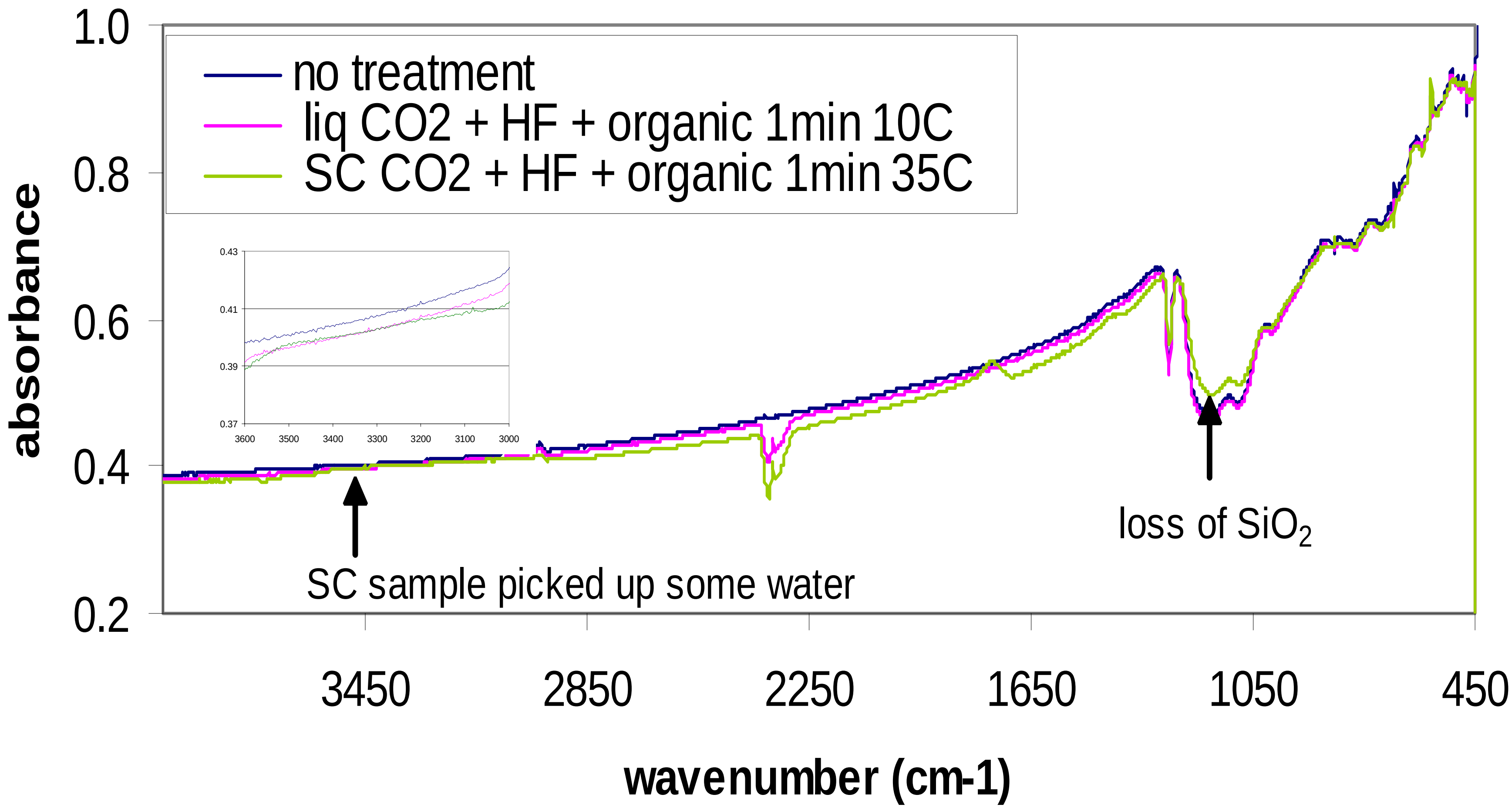
# FTIR of MSQ Etching



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# MSQ SC-Etching Results

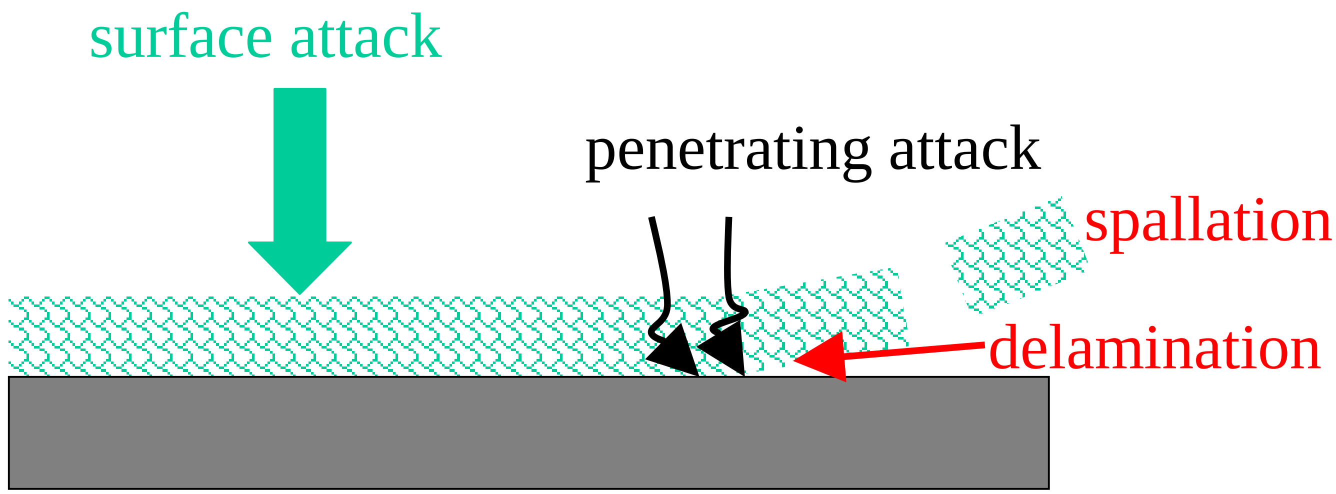
Summary of FTIR of films after exposure:

- Liquid $CO_2$ 2000:1 ETOH:HF/Organic acid → no change in wafer or significant water adsorption
- SC-$CO_2$+ 2000:1 ETOH:HF→ stripped wafer
- SC-$CO_2$+ 2000:1 ETOH:HF/Organic acid strips wafer→ within 1$^{st}$ minute MSQ begins to flake off wafer
  - ***Attack is both on MSQ and at MSQ-Si interface***

# Liquid vs SC-$CO_2$ as Etch Solvent

- SC reactor has sight glass → apparent full solubility of etchant in liquid and SC-$CO_2$
- Same etchant concentration in both solutions
- Liquid $CO_2$/etchant → no significant material removal
- SC-$CO_2$/etchant → aggressive removal
- Transport and/or chemical effect?

# Proposed Mechanism for SC Etching of MSQ



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# Summary

- Drying of TEFS with SC-$CO_2$ appears more effective than SC-$CO_2$ +EtOH
- SC drying/cleans → some changes in ULK films, mechanisms still unknown
- SC drying removes water from ashed MSQ
- SC functionalization → very rapid and effective → efficient drying agent



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# Supercritical Research Efforts

| Activity | Status |
|---|---|
| Dielectric and mechanical effects due to SC-processing | *On-going work: FTIR, ellipsometry, capacitance measurements, nanoindentation* |
| SC-repair of plasma damaged ULK films | *On-going work: FTIR, ellipsometry, contact angle, NRA, RBS* |
| Effect of rapid pressure changes on cleaning and water removal | *On-going work: FTIR, ellipsometry, nanoindentation* |

# Supercritical Research Directions

| Activity | Status |
|---|---|
| *in situ* observation of drying, cleans, and possibly etch processes | *Building SC- FTIR cell (completion: July 2002)* |
| Studies of SC processing on patterned wafers | *Building SC reactor for 200mm wafers, designing reactor for 300mm wafers (July 2002)* |
| ultra low-k film synthesis | *Developed and characterized SC-$CO_2$ soluble templates, preliminary synthesis experiments* |