Supercritical Drying and Repair of Ultra Low-k Films

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

Temperature (ºC) vs Pressure (psi)

- CO2
- EtOH
- CO2+7m%EtOH
- MeOH
- 1-PrOH
- 2-PrOH
- 1-hexanol
- hexane
- acetone
- 1,4dioxane
- chlorofom
- water

Region of interest
# Experimental Ultra Low-k (ULK) Materials

<table>
<thead>
<tr>
<th></th>
<th>MSQ</th>
<th>TEFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric Constant</td>
<td>~2.3</td>
<td>~2.3</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>Other properties</td>
<td>Hydrophobic; loses CH$_3$ in H$_2$ and O$_2$ plasma</td>
<td>Absorbs some water; after 400°C, water lost, but $k=2.1 \rightarrow 2.3$</td>
</tr>
</tbody>
</table>
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

TEFS: 50% porosity
SC: 45°C 1500 psi

- TEFS before
- SC CO2 30min
- SC-CO2_EtOH 2hr

water
Liquid CO₂ Drying of dense TEFS Films

TEFS 25% porosity
conditions: 31°C 1100psi 1 hour

- no treatment
- SC CO₂
- 1m/o EtOH+Scco₂

water
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
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 H₂ Ashed MSQ
(after 48 hours in 90% humidity)
Effects of SC-processing on TEFS

increased transmittance decreased dielectric constant

- Si transmission
- TEFS no treatment
- SC CO2 30min 35C 1200psi
- SC CO2 EtOH 30min 35C 1400psi
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: $n = 1.19$
Possible Causes for IR Transmittance Behavior

• Change in porosity and/or electronic structure  
  – ellipsometry experiments \(\rightarrow\) 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
- → ellipsometry of MSQ samples
### SC-treated MSQ: Ellipsometry

<table>
<thead>
<tr>
<th></th>
<th>Film thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before SC treatment</td>
<td>526</td>
<td>1.280</td>
</tr>
<tr>
<td>After 1 hr SC-CO₂</td>
<td>525</td>
<td>1.279</td>
</tr>
<tr>
<td>After 1 hr SC-CO₂ +</td>
<td>529</td>
<td>1.277</td>
</tr>
</tbody>
</table>
Effects of SC-treatments on MSQ

- ellipsometry: very small changes in $n$
- \( \rightarrow \) changes in dielectric constant may be due to ionic polarizations, not electronic (porosity)
- \( \rightarrow \) 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
- Enlargement of pores through removal of adsorbed species
- Expansion of film
- Chemical changes in pores or surfaces
Supercritical Functionalization of ULK films

- In situ functionalization of low-k materials
  - ambient conditions $\rightarrow$ 12-24 hours
  - supercritical conditions $\rightarrow$ $\ll 1$ hour
- Goals:
  - TEFS $\rightarrow$ improve hydrophobicity
  - MSQ $\rightarrow$ dry and repair post ash damage
Supercritical Functionalization

![Graph showing absorbance vs wavenumber for TEFS after methylation for 1 hr]
Surface Modification: Drying

![Graph showing absorbance vs. wavenumber (cm⁻¹) before and after treatment.]
Determination of MSQ repair: contact angle measurements

- Plasma removes methyl groups $\rightarrow$ loss of hydrophobicity
- Ashing also causes some densification
- Functionalization may return hydrophobicity and expand collapsed region
## Contact Angle Measurements

<table>
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<tr>
<th>TEFS</th>
<th>Contact Angle</th>
</tr>
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<tbody>
<tr>
<td>As deposited</td>
<td>30</td>
</tr>
<tr>
<td>Treatment 1 10% 15 min</td>
<td>63</td>
</tr>
<tr>
<td>Treatment 1 10% 30 min</td>
<td>101</td>
</tr>
<tr>
<td>Treatment 2 5% 5 min</td>
<td>76</td>
</tr>
<tr>
<td>Treatment 2 10% 5 min</td>
<td>96</td>
</tr>
<tr>
<td>Treatment 2 10% 15 min</td>
<td>105</td>
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<td>As deposited</td>
<td>103</td>
</tr>
<tr>
<td>H₂ ashed</td>
<td>7</td>
</tr>
<tr>
<td>Treatment 1 5% 5 min</td>
<td>100</td>
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Effectiveness of liquid and SC-CO$_2$-based fluids etchants

- Comparison between liquid and SC-CO$_2$ based solutions
- Determination of ambient etchants solubilities in SC-CO$_2$
- Viability of combinations of etchants
FTIR of MSQ Etching

Absorbance

- no treatment
- liq CO2 + HF + organic 1min 10C
- SC CO2 + HF + organic 1min 35C

Wavenumber (cm$^{-1}$)

SC sample picked up some water

Loss of SiO$_2$
Summary of FTIR of films after exposure:

- Liquid CO$_2$ 2000:1 ETOH:HF/Organic acid $\rightarrow$ no change in wafer or significant water adsorption
- SC-CO$_2$+ 2000:1 ETOH:HF $\rightarrow$ stripped wafer
- SC-CO$_2$+ 2000:1 ETOH:HF/Organic acid strips wafer $\rightarrow$ 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 $\rightarrow$ apparent full solubility of etchant in liquid and SC-CO$_2$
- Same etchant concentration in both solutions
- Liquid CO$_2$/etchant $\rightarrow$ no significant material removal
- SC-CO$_2$/etchant $\rightarrow$ aggressive removal
- Transport and/or chemical effect?
Proposed Mechanism for SC Etching of MSQ

surface attack

penetrating attack

spallation

delamination
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
# Supercritical Research Efforts

<table>
<thead>
<tr>
<th>Activity</th>
<th>Status</th>
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<tbody>
<tr>
<td>Dielectric and mechanical effects due to SC-processing</td>
<td>On-going work: FTIR, ellipsometry, capacitance measurements, nanoindentation</td>
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<tr>
<td>SC-repair of plasma damaged ULK films</td>
<td>On-going work: FTIR, ellipsometry, contact angle, NRA, RBS</td>
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<tr>
<td>Effect of rapid pressure changes on cleaning and water removal</td>
<td>On-going work: FTIR, ellipsometry, nanoindentation</td>
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### Supercritical Research Directions

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<td><em>in situ</em> observation of drying, cleans, and possibly etch processes</td>
<td><strong>Building SC- FTIR cell</strong> (completion: July 2002)</td>
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<td>Studies of SC processing on patterned wafers</td>
<td><strong>Building SC reactor for 200mm wafers, designing reactor for 300mm wafers (July 2002)</strong></td>
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<tr>
<td>ultra low-k film synthesis</td>
<td><strong>Developed and characterized SC-CO$_2$ soluble templates, preliminary synthesis experiments</strong></td>
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