High Temperature Water Clean and Etch Reactions with Low-k and SiO$_2$ Films: Experiments and Simulations

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Rationale

• High temperature water (HTW) has demonstrated some interesting capabilities etching SiN (SPCC 2015)

• Given HTW’s enhanced reactivity, is HTW selective for hydrophilic (SiO$_2$) or hydrophobic (low-k) films?
Outline

• Experimental Apparatus and Conditions
• Low k (k=2.3 porosity ~35%)
• Silica (thermal oxide)
• Low-k and SiO$_2$ characterization following exposure to HTW
  • Ellipsometry—thickness changes
  • FTIR—changes in the chemistry and thickness
  • Profilometry—define boundaries
• Simulations of HTW reactions with porous low-k films
Experimental Conditions

- Samples placed in the reactor with 98°C DI water
- Heated to 120, 140, 160, and 180°C for 5, 10, and 20 minutes (heat up takes ~11-38 minutes)
- Reactor removed from heat and quenched in water for 2 min
- Samples rinsed with DI water and allowed to dry.

Heating mantle and reactor (600ml)  Reactor can be easily removed from mantle  Sample holder
Previous work on SiO$_2$ in HTW

- Solubility increases ~6x at 160°C (vs RT)
- solubility at 160°C sufficient to remove >1000 nm of oxide (much greater than current sample)

RO Fournier and JJ Rowe, Amer. Miner, 62 1052-1056 1977
Ionization of Silica in HTW

- Ionization of silica- ~10x than room temperature
- First ionization (formation of silicic acid) maxes at ~160°C
- Second ionization (formation of silicic acid) maxes at ~120°C
## Ellipsometry Results and Etch Rates

<table>
<thead>
<tr>
<th>Type</th>
<th>Unetched Thickness (Å)</th>
<th>0 Minutes Thickness (Å)</th>
<th>5 Minutes Thickness (Å)</th>
<th>10 Minutes Thickness (Å)</th>
<th>20 Minutes Thickness (Å)</th>
<th>Etch Rate (Å/min)</th>
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</thead>
<tbody>
<tr>
<td>Low K 160°C</td>
<td>4123</td>
<td>3969</td>
<td>3955</td>
<td>3977</td>
<td>3941</td>
<td>Negligible</td>
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<tr>
<td>Low K 180°C</td>
<td>4123</td>
<td>3979</td>
<td>3956</td>
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<tr>
<td>SiO$_2$ 120°C</td>
<td>322</td>
<td>300</td>
<td>202</td>
<td>58</td>
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<tr>
<td>SiO$_2$ 140°C</td>
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<td>149</td>
<td>59</td>
<td>0</td>
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<tr>
<td>SiO$_2$ 160°C</td>
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<td>0</td>
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<tr>
<td>SiO$_2$ 160°C</td>
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<td>2408</td>
<td>1864</td>
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<tr>
<td>SiO$_2$ 180°C</td>
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<td>1817</td>
<td>938</td>
<td>355</td>
<td>162</td>
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</table>
Etch Rates: low-k vs SiO$_2$

- SiO$_2$ etch rate quickly increases around 160°C
- low k showed a negligible etch rate at temperatures where SiO$_2$ was significantly etched
Profilometry Profile SiO$_2$: from Protected to Exposed to 160°C Water

- Region exposed to HTW showed etching
- Etching increased with time
GATR FTIR of SiO$_2$

- Shows SiO$_2$ thickness decreasing with time
GATR FTIR of low-k

- This is interesting because?
Contact Angle: low-k

- Contact angle decreases with time at elevated temperatures
Simulations of nanoporous low-k and water system using Reactive Force Field (ReaxFF) based MD

- Nanoporous silica was generated with 35% porosity (J. Am. Ceram. Soc. 97(2015)2772).
- Surface is formed and water added to the surface and forms an interface
- Water/silica system studied using Reactive Force Field (ReaxFF) (J. Phys. Chem. C 120 (2016) 24803)
- Equilibration at different temperatures for 1 nano-seconds (4x10^6 steps)
- Monitored reactions such as Si-O-Si dissociation via hydrolysis and Si-CH₃ breakage
Reaction steps in Si-O-Si breakage

H₂O+Si-O-Si - → Si-OH + HO-Si  Via a hydronium ion.
Summary (Experimental)

• HTW SiO$_2$ etch rate increases dramatically around 160°C
• Low K samples were not measurably etched
• Decreasing hydrophobicity of Low K with treatment time → some changes in film surface

Future work
• Confirm etching mechanism
• Etching of other films
• Use HTW to remove particles from low-k films
Summary (Simulations)

- Reactive force field based MD simulations generated nanoporous organosilicate glass structures with 35% porosity and 10% carbon.
- Water/OSG interface formed and reaction studied at different temperatures.
- Si-O-Si hydrolysis reactions due to hydronium ions. HO-SiO$_3$ and SiO$_4$ are more vulnerable than CH$_3$-SiO$_3$ (concurs with experiments)
- Source of hydronium ions: enhanced dissociation of water and subsequent silicic acid formation.
- Future work:
  - to analyze reactions as a function of temperature and time to obtain statistical data.
  - Compare reactivity of OSG and nanoporous silica with similar porosity.
Acknowledgements

• Sematech (wafers)
• Center of Advanced Research and Technology (CART)