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.

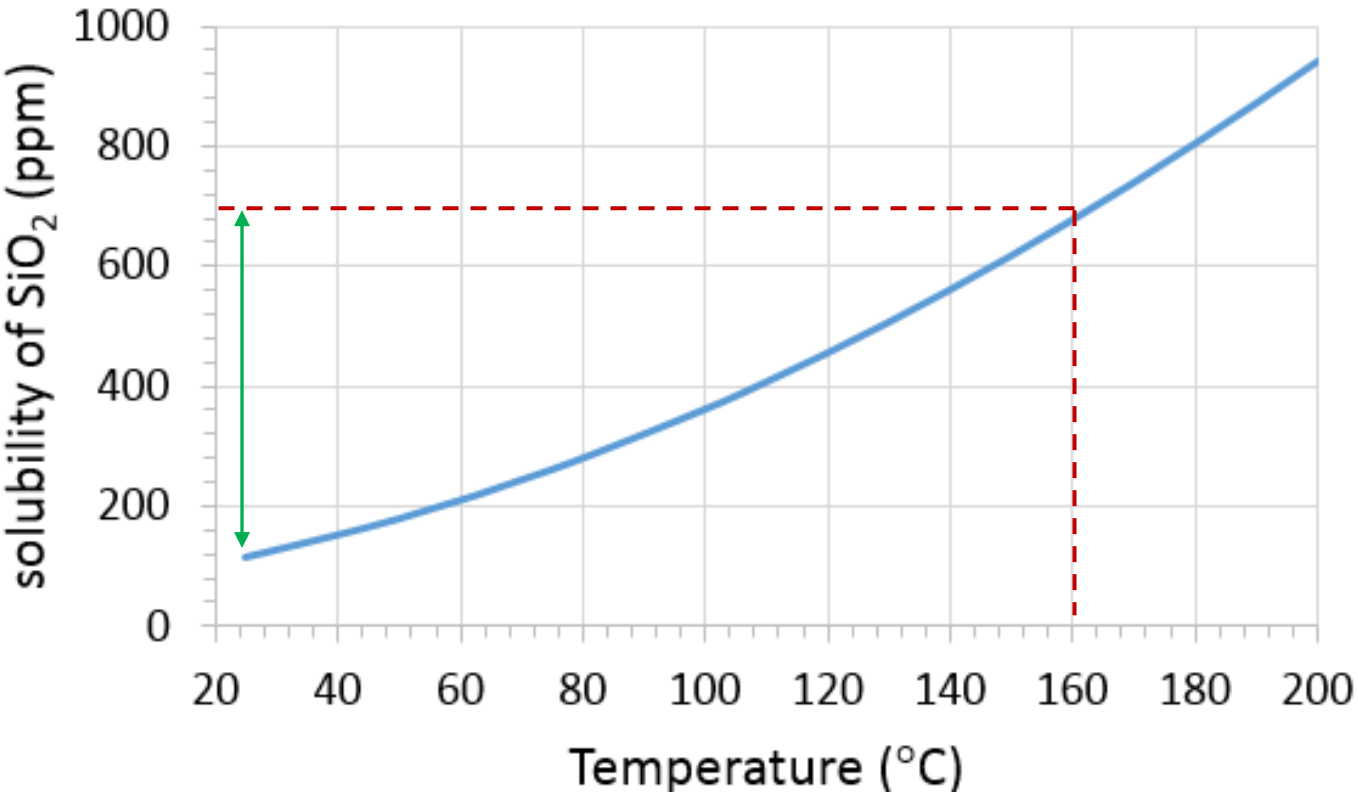
Heating mantle and reactor (600ml)

Reactor can be easily removed from mantle

Sample holder

Previous work on SiO_2 in HTW

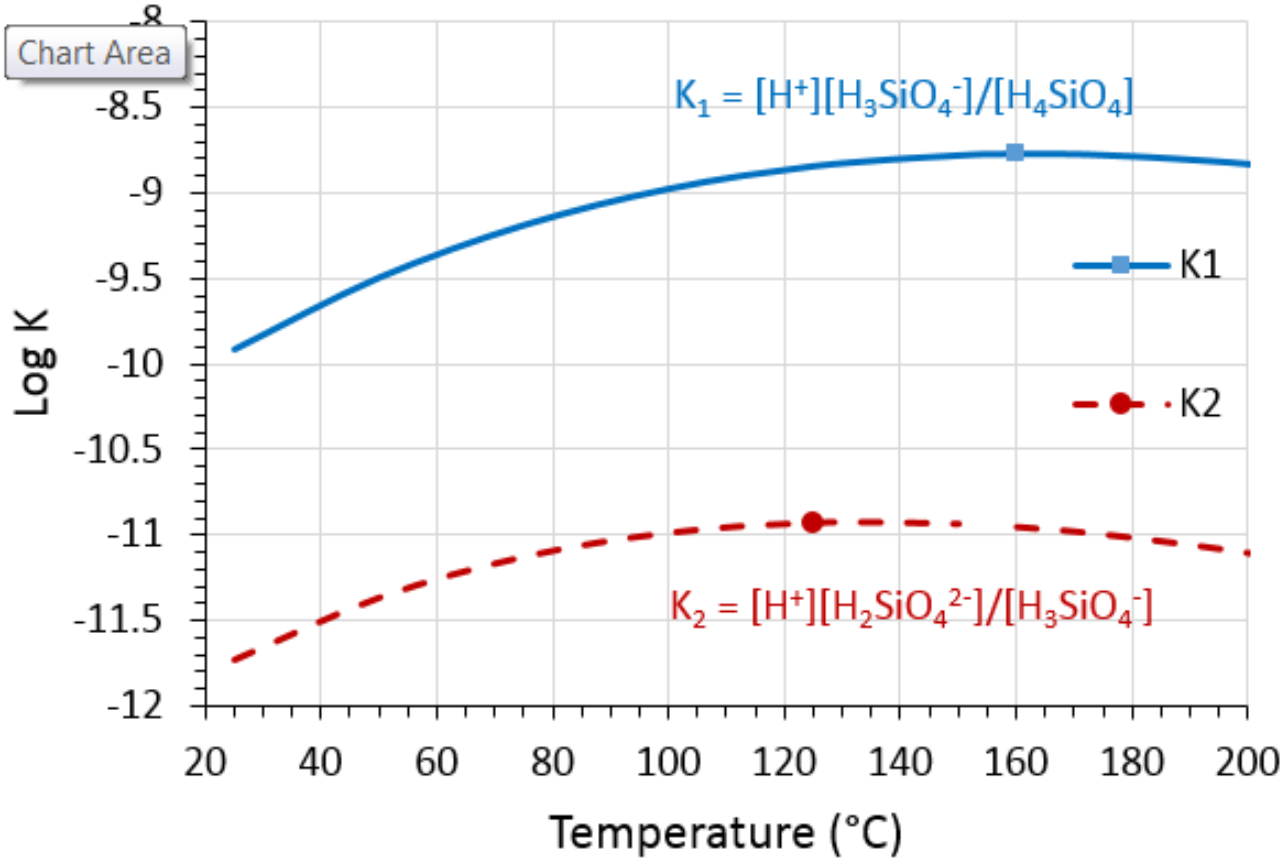
- Solubility increases **~6x** at 160°C (vs RT)
- solubility at 160°C sufficient to remove >1000 nm of oxide (much greater than current sample)



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

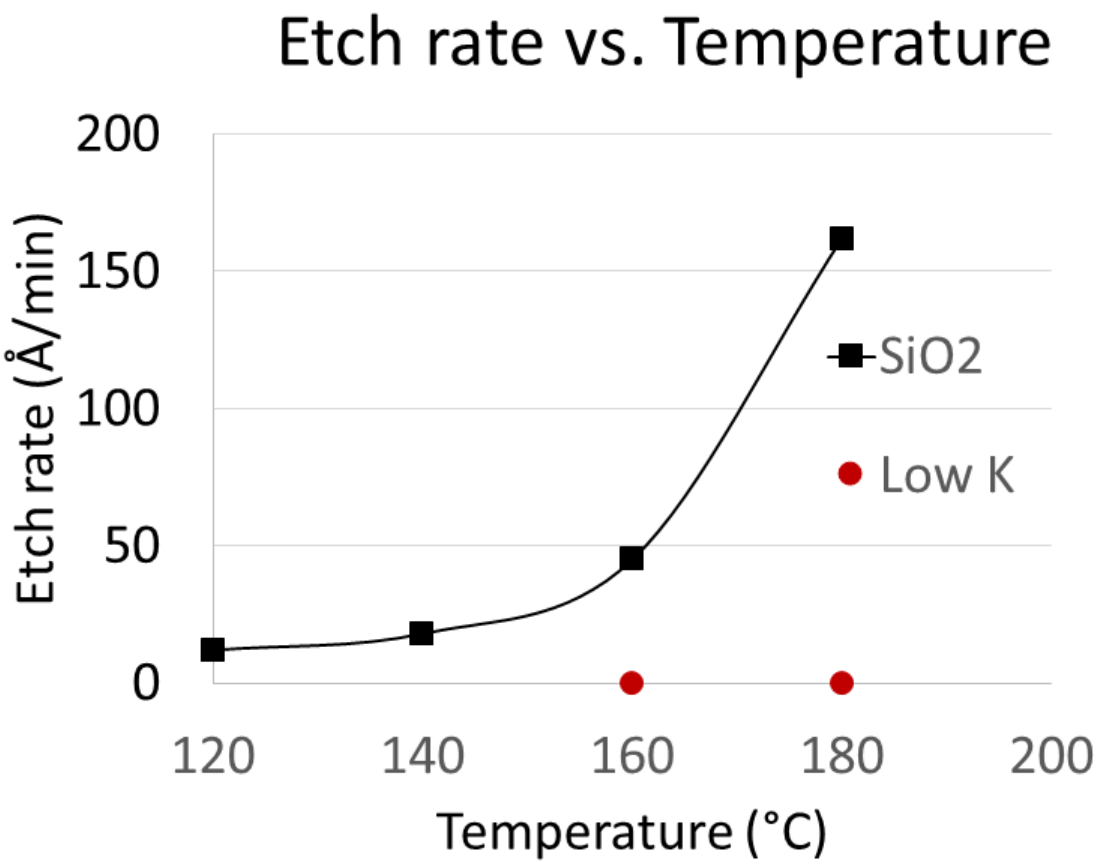


Ellipsometry Results and Etch Rates

Type	Unetched Thickness (Å)	0 Minutes Thickness (Å)	5 Minutes Thickness (Å)	10 Minutes Thickness (Å)	20 Minutes Thickness (Å)	Etch Rate (Å/min)
Low K 160°C	4123	3969	3955	3977	3941	Negligible
Low K 180°C	4123	3979	3956	3939	3856	Negligible
SiO_2 120°C	322	300		202	58	12
SiO_2 140°C	322	149	59	0		18
SiO_2 160°C	322	0			0	
SiO_2 160°C	3098	2828		2408	1864	57
SiO_2 180°C	3098	1817	938	355	0	162

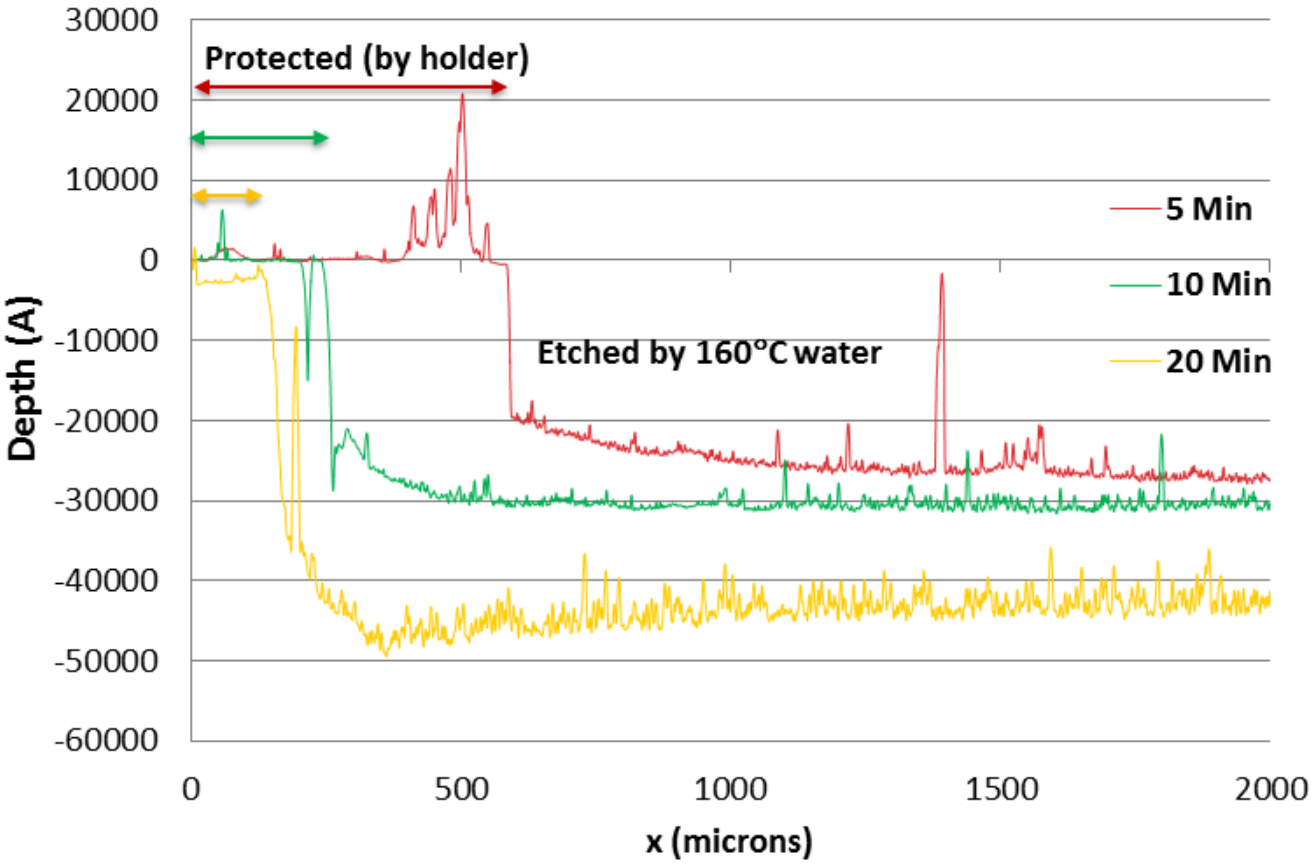
Etch Rates: low-k vs SiO_2

- SiO_2 etch rate quickly increases around 160°C
- low k showed a negligible etch rate at temperatures where SiO_2 was significantly etched

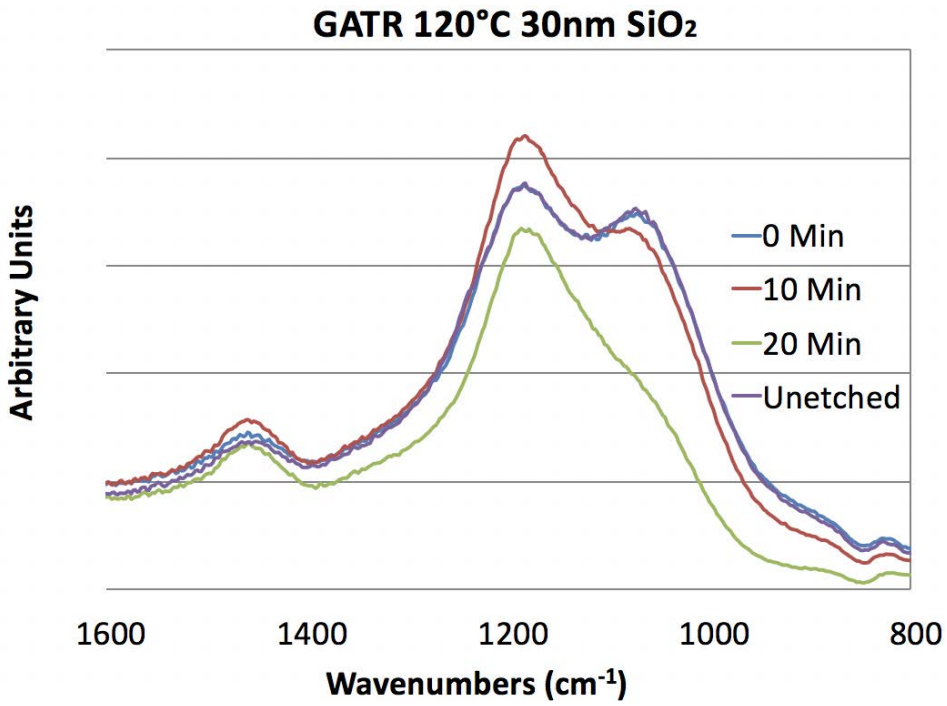


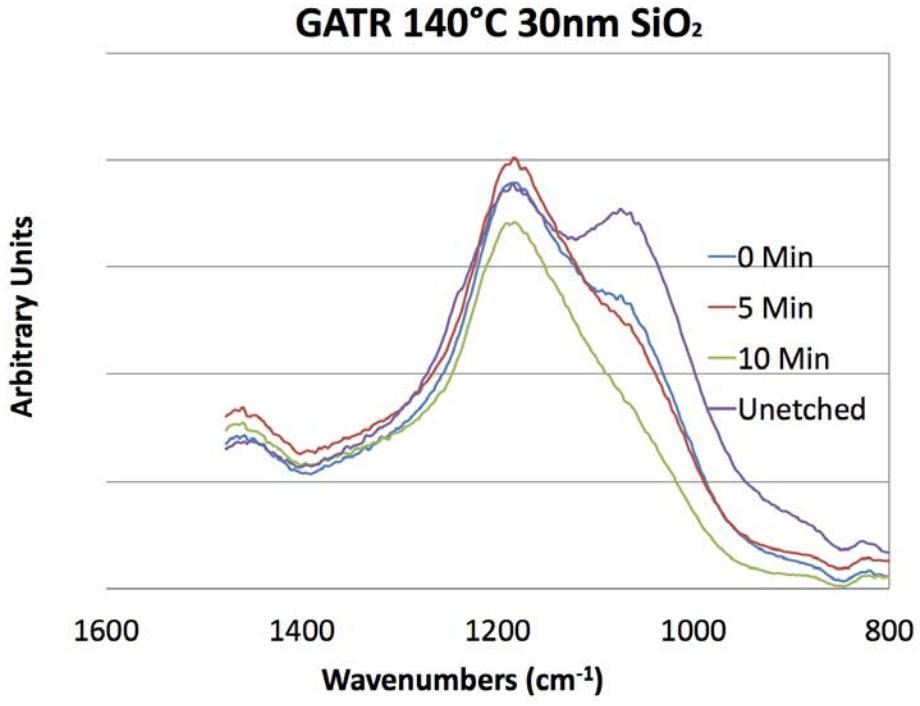
Profilometry Profile SiO_2: from Protected to Exposed to 160°C Water

- Region exposed to HTW showed etching
- Etching increased with time



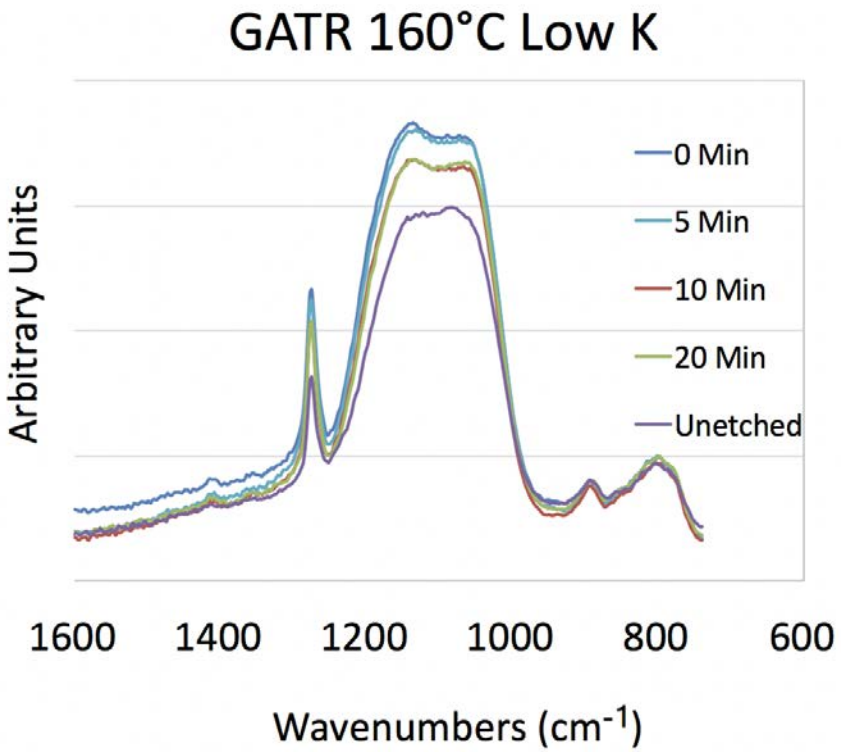
GATR FTIR of SiO_2

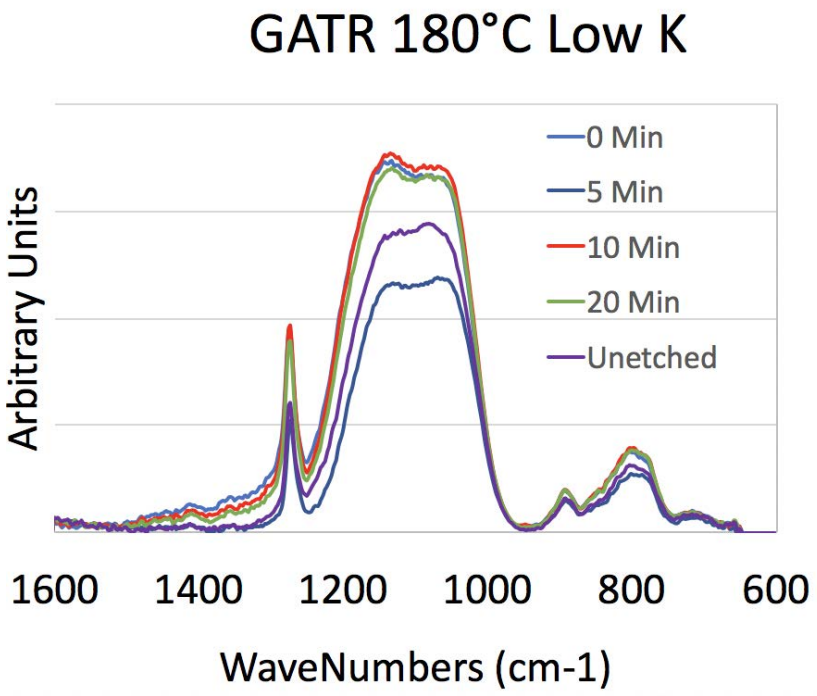




- Shows SiO_2 thickness decreasing with time

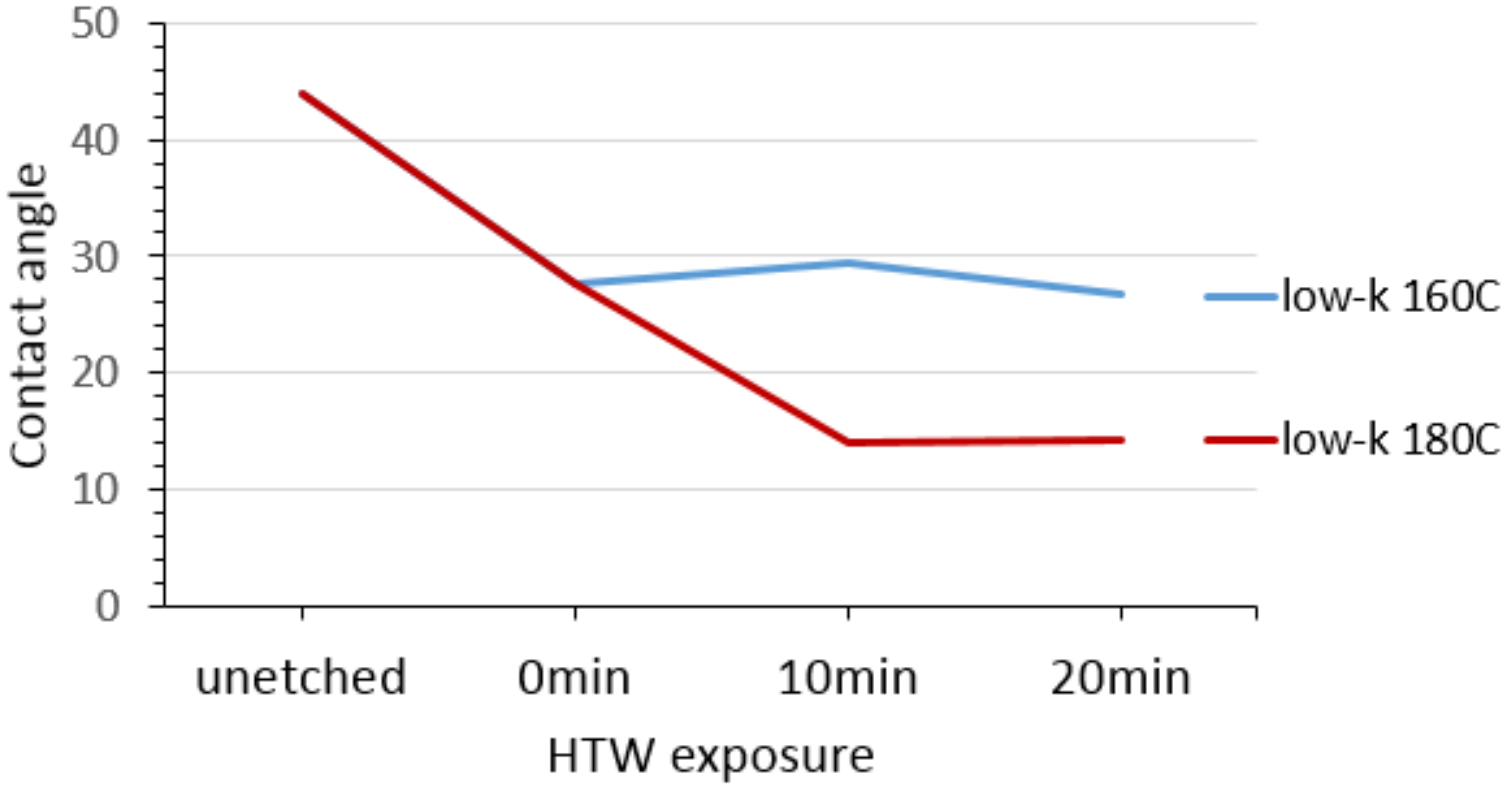
GATR FTIR of low-k





- This is interesting because?

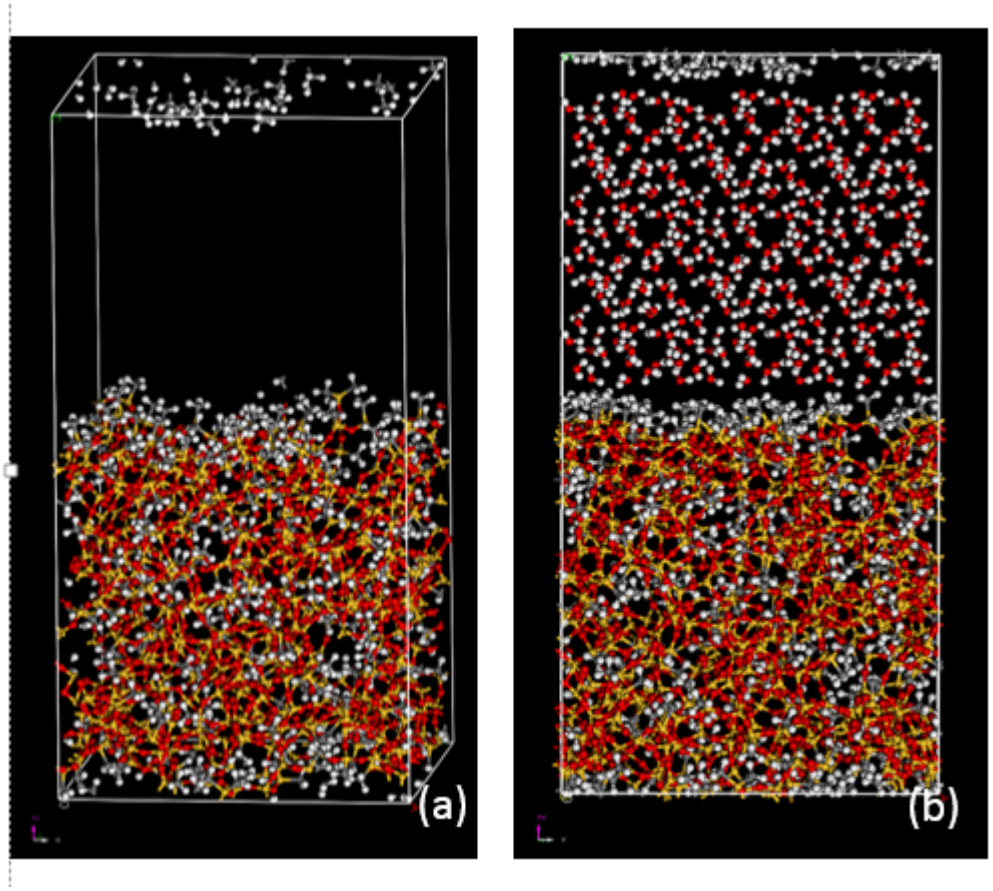
Contact Angle: low-k



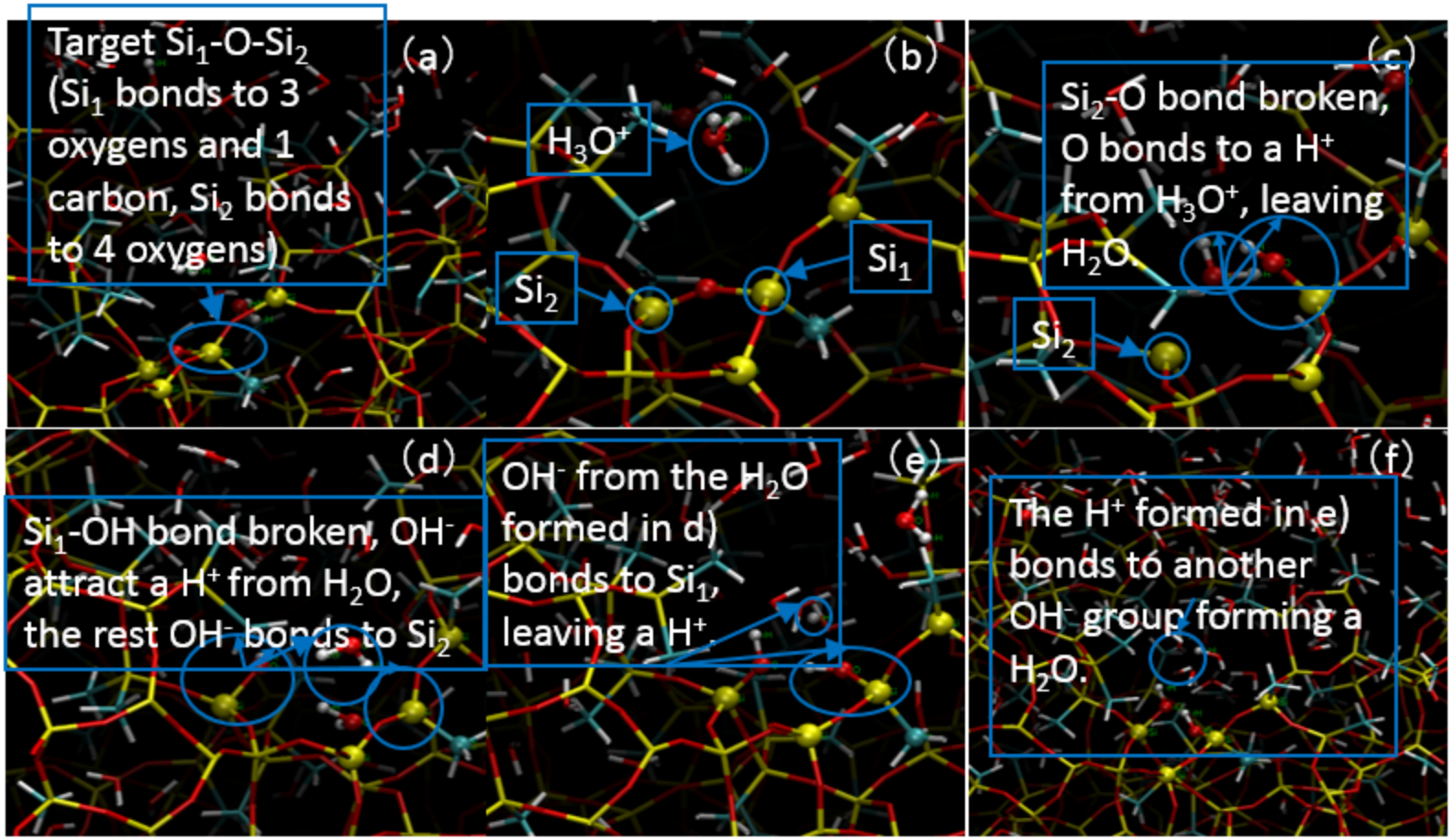
- Contact angle decreases with time at elevated temperatures

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).
- Organic component introduced to nanoporous silica to form OSG (*J. Non-Cryst. Solids*, 431(2016)103).
- 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-CH_3 breakage



Reaction steps in Si-O-Si breakage



H_2O+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)
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