A Surface Chemistry Approach to the Development of Gas Phase Wafer Cleaning Processes

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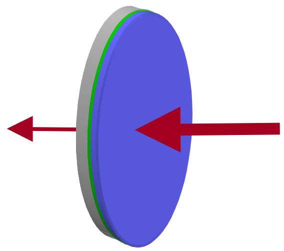
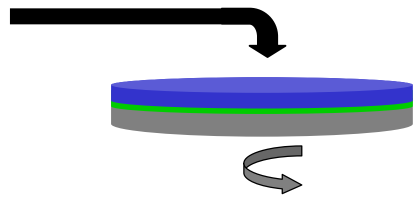
Outline

- Gas phase removal of doped oxide etching residues using UV-Cl_2 processes
- Mechanism of thermal oxide removal using low pressure gas phase HF/H_2O mixtures
- Future work

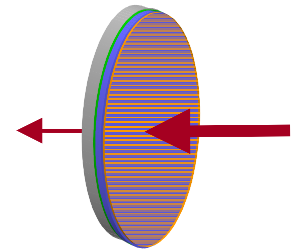
Residue Removal Process Flow



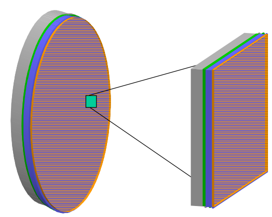
Pre-Etch
Transmission FTIR 30°
5K Å, 500°C, 4/3.5% BPSG Films
On 8" Wafers



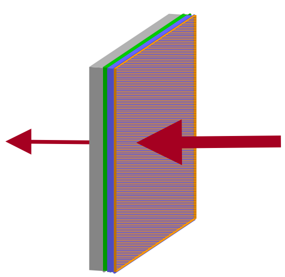
FSI Excalibur ISR
AHF Etching Process
0.1% HF, 99.9% N_2
760 Torr, 55°C



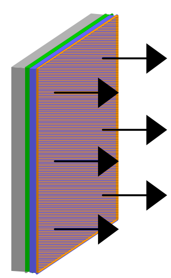
Post-Etch
Transmission FTIR 30°
3000 Å of BPSG Etched
Residue Formation



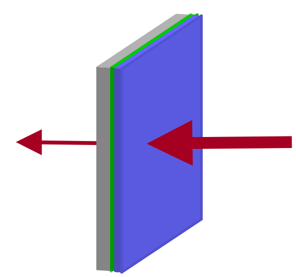
Dice 8" wafer into 1 x 1 cm pieces



Pre-Residue Removal
Transmission FTIR 30°

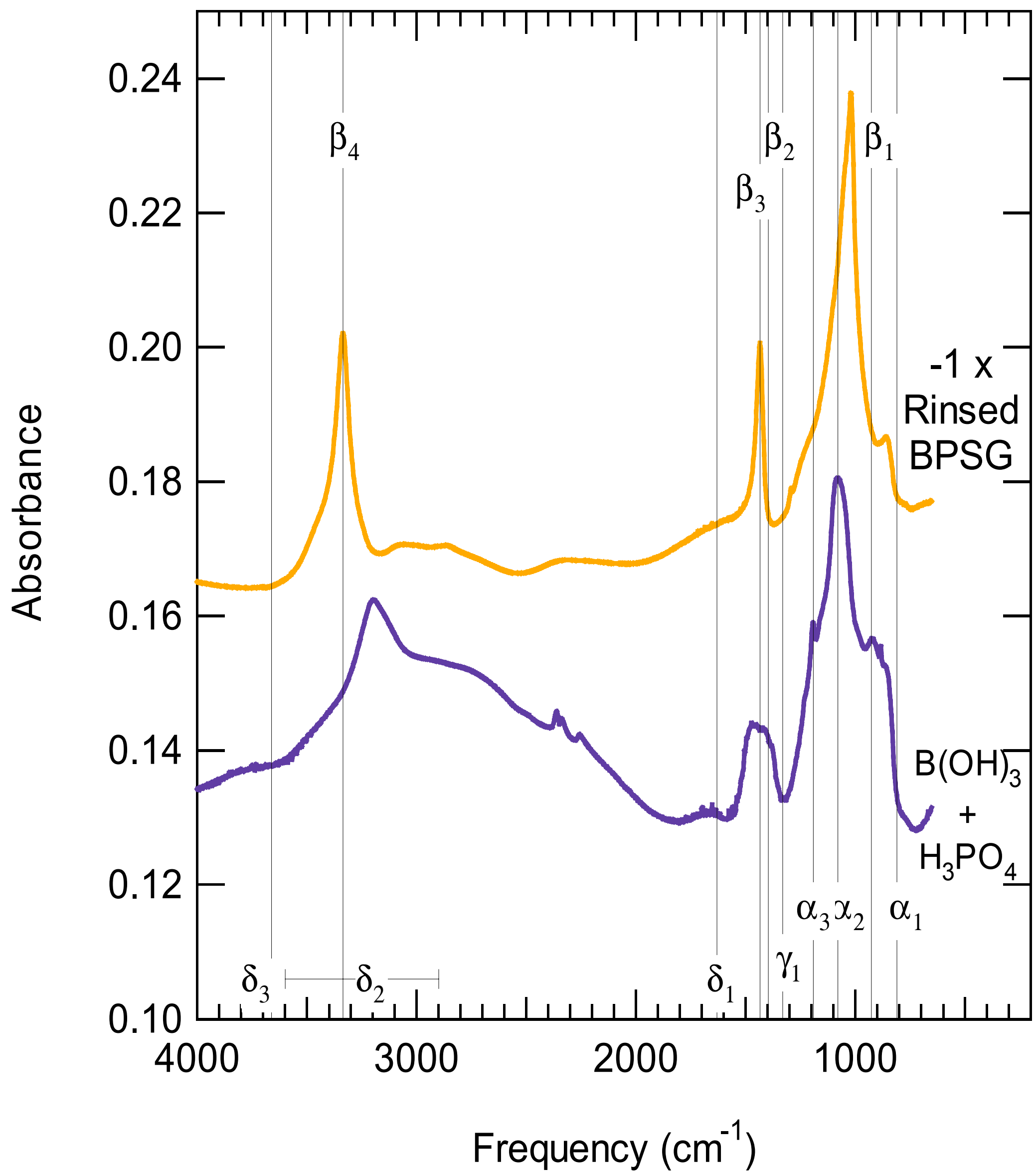


Residue Removal
in Research Cluster Apparatus



Post-Residue Removal
Transmission FTIR 30°

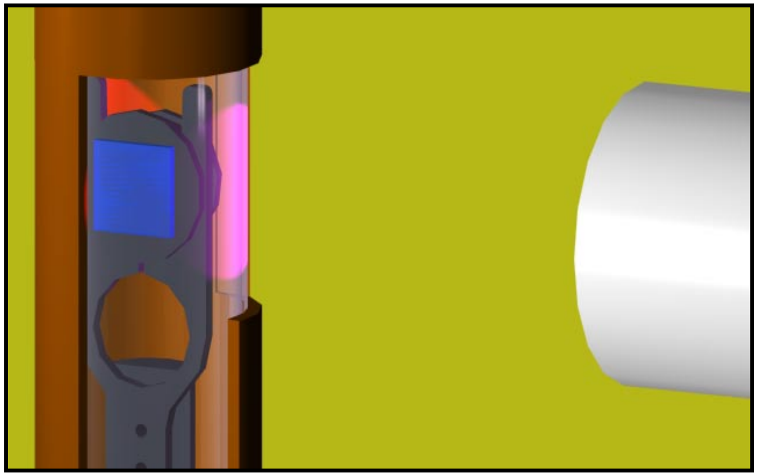
Mixed Acid on Etched BPSG

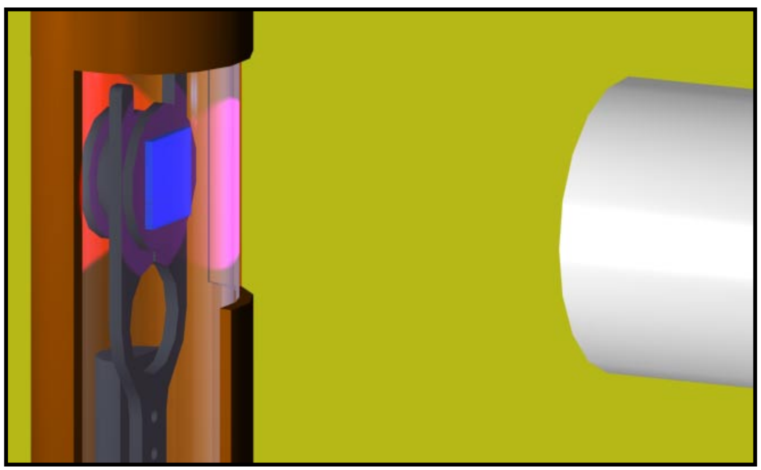


Muscat et al., JVSTA 19(4), 1854 (2001)

- Residue after etching and rinsing BPSG film compares closely with $B(OH)_3 + H_3PO_4$ mixture
- Peak Shift β_4
- Chemistry
  - $P_2O_5+3H_2O(l) = 2H_3PO_4(l)$
  - $B_2O_3+3H_2O(l) = 2B(OH)_3(a)$

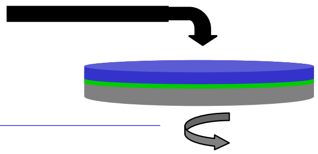
UV / Cl_2 Reactor

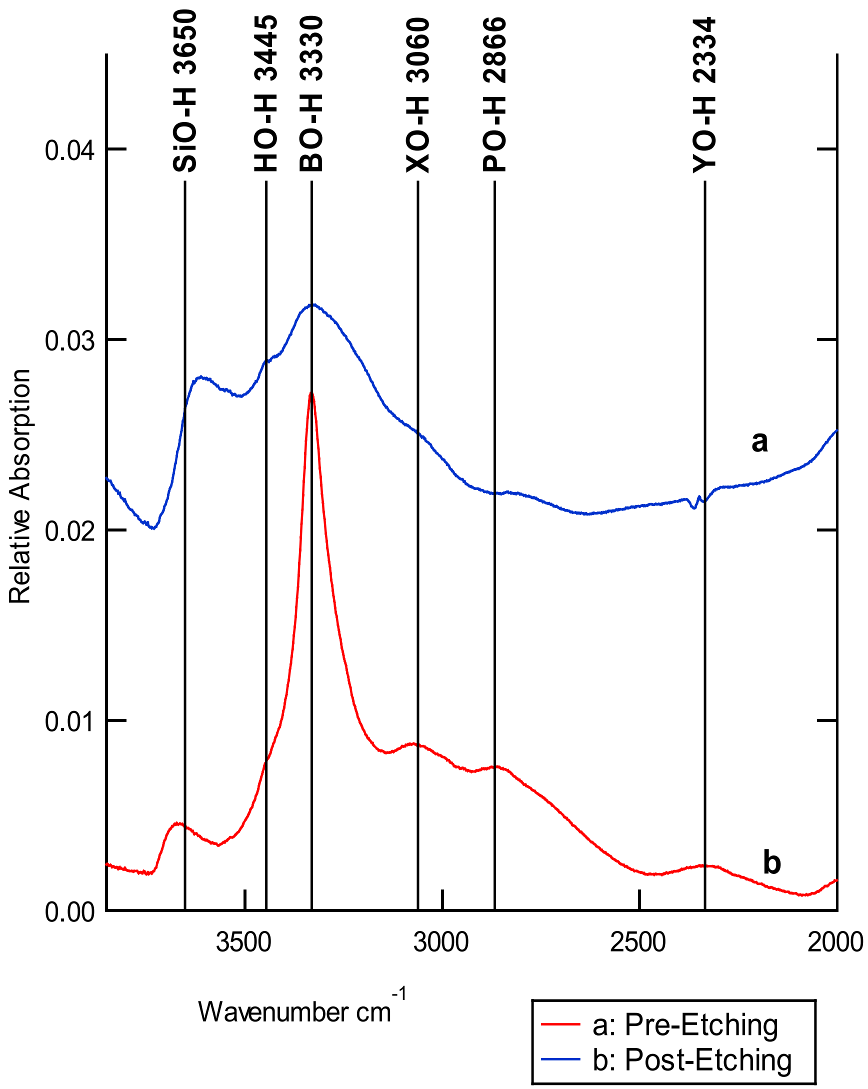




- Quartz Tube
  - ID = 33 mm
- Thermally Insulated
- Processing Parameters
  - 750 mTorr
  - 100 sccm
    - 10 – 35 mol% Cl_2
    - τ = 1 s
  - 20 – 350°C
- 1000 watt high-pressure Xe Arc Lamp

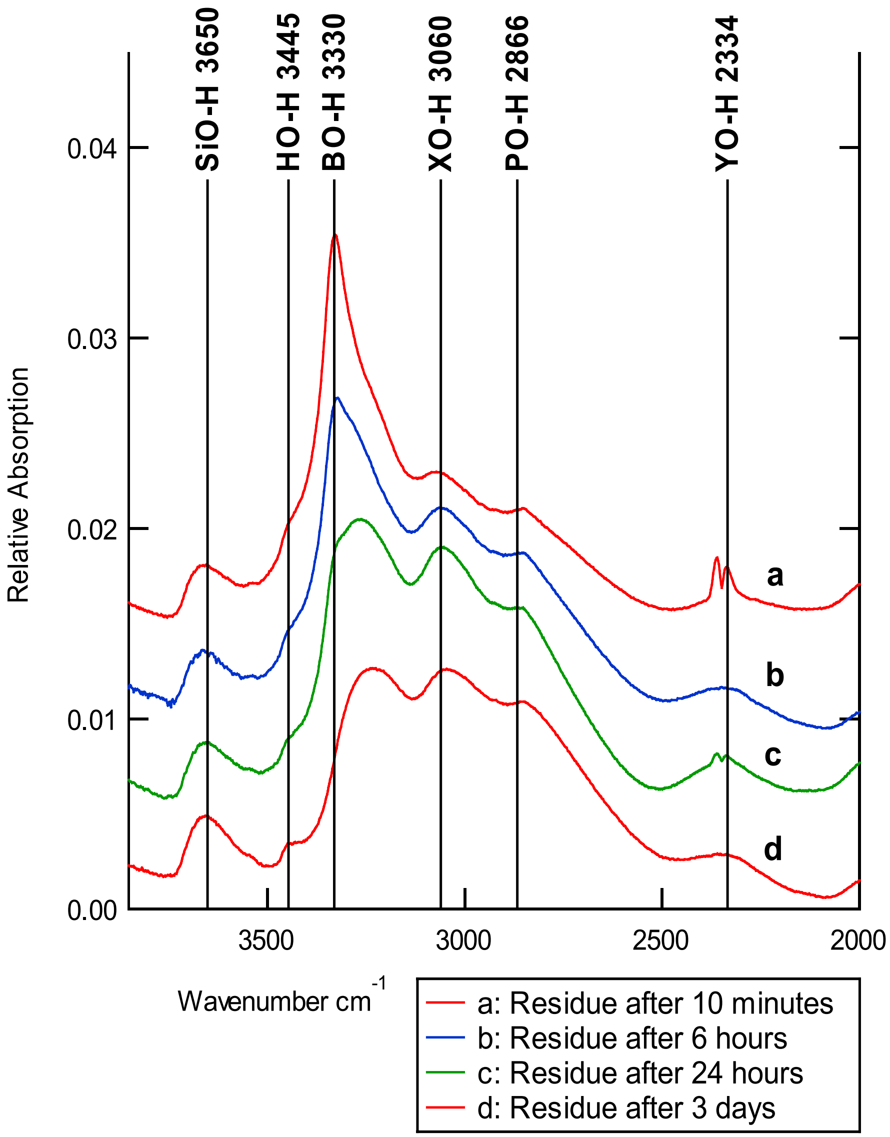
Residue Formation





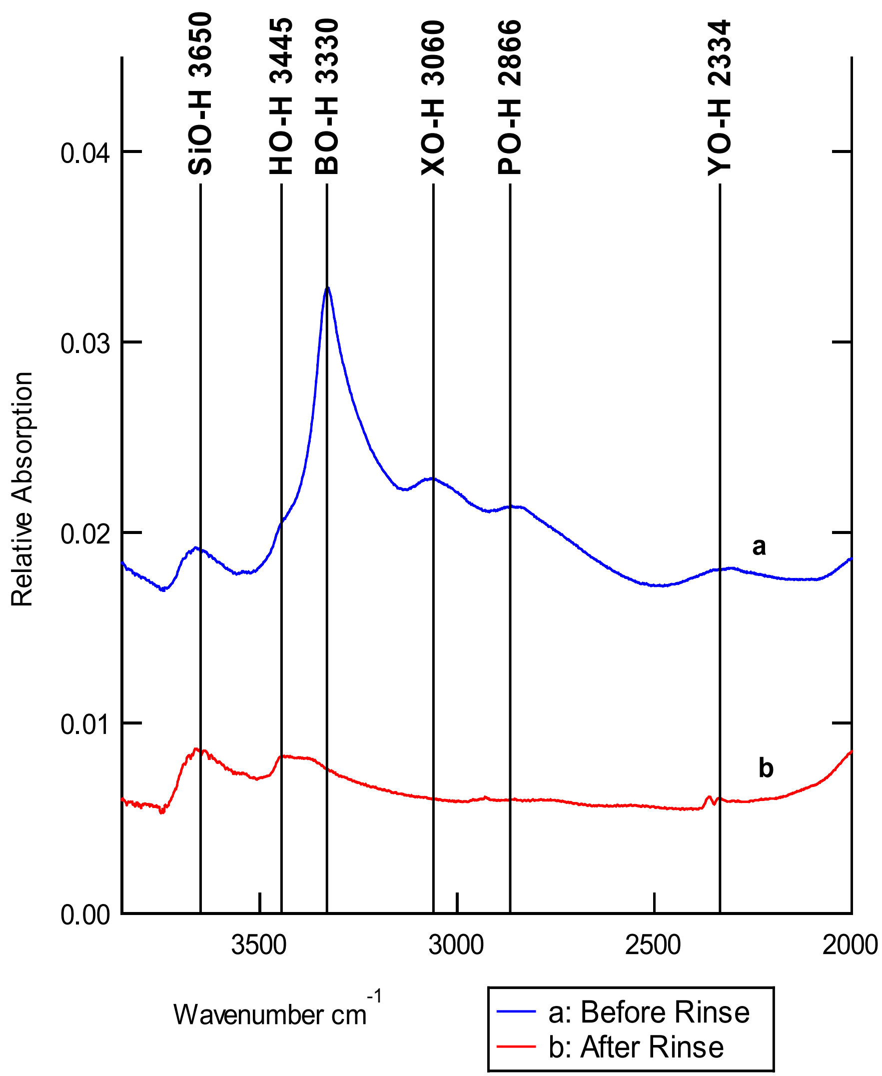
- 500°C Annealed BPSG
- FSI Excalibur ISR
  - AHF Etching Process
  - 760 Torr
    - 0.1% HF
    - 99.9% N_2
  - 55°C
- ~ 3000 Å oxide etched
- ~ 1000 Å thick mixed acid residue

Residue Change Over Time



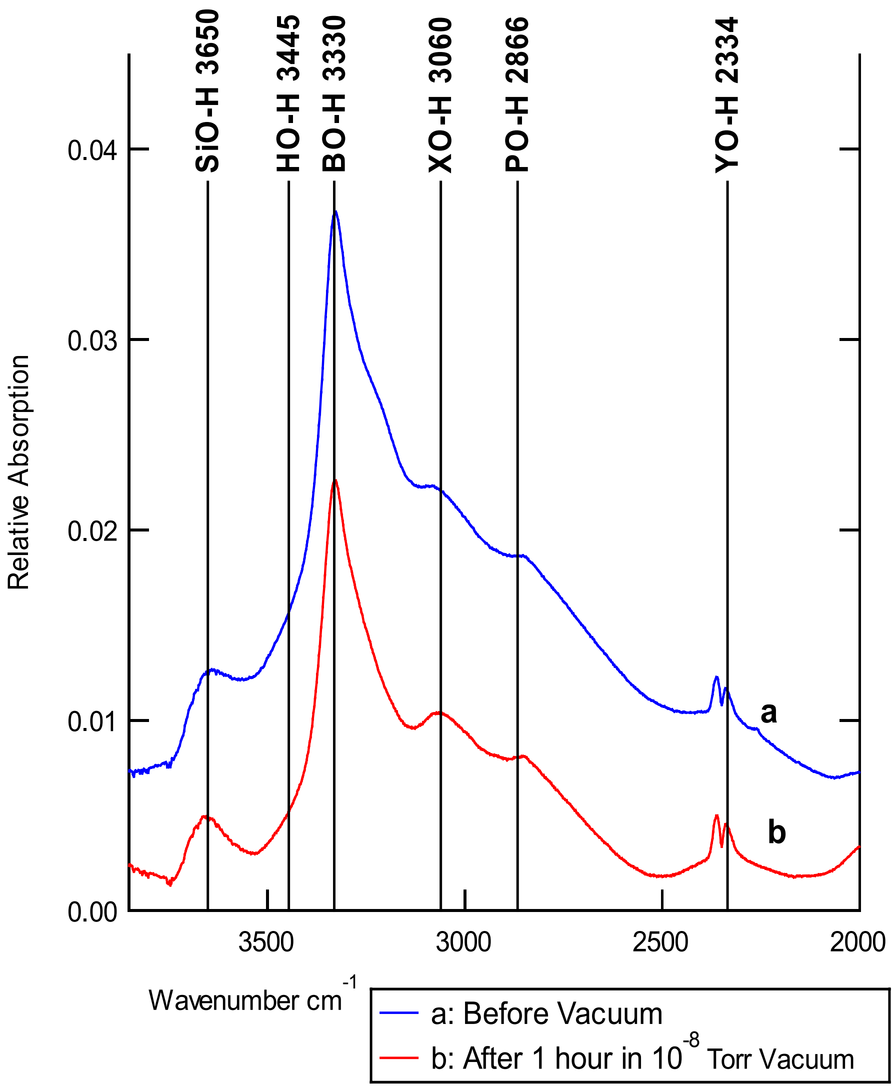
- Time
  - 10 minutes
  - 6 hours
  - 24 hours
  - 3 days
- Cleanroom
  - 760 Torr
  - 23°C

Rinsing The Residue



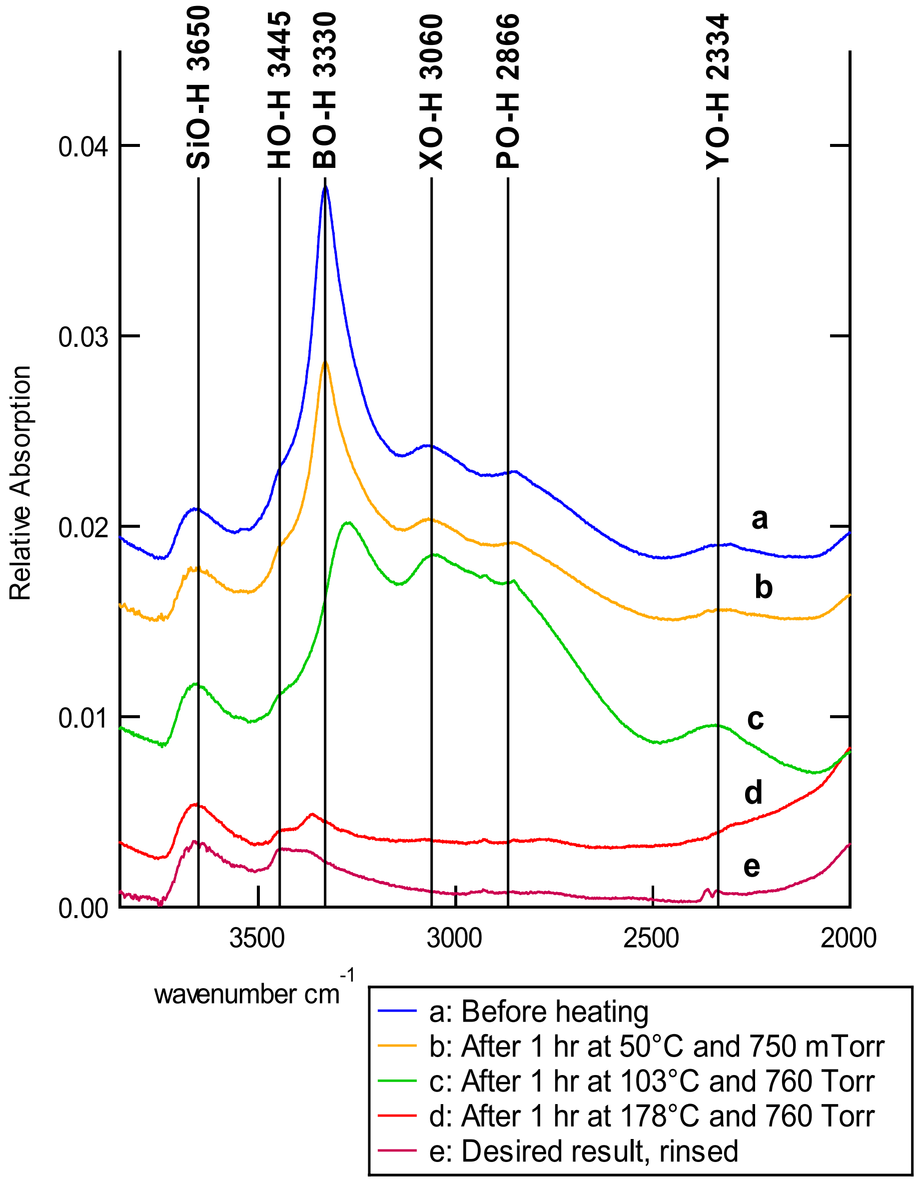
- Current industrial residue removal process
  - UPW rinse
  - UPW displacement with alcohol and super critical CO_2
- Rinsed with UPW
- No cloudy residue remains after process

Effect of Vacuum Alone

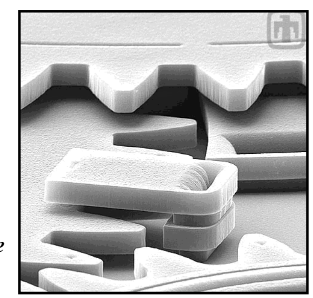


- Vacuum
  - 1 hour
  - 10^{-8} Torr
  - 22°C
- Cloudy residue remains after vacuum exposure

Removal By Heating

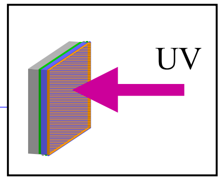


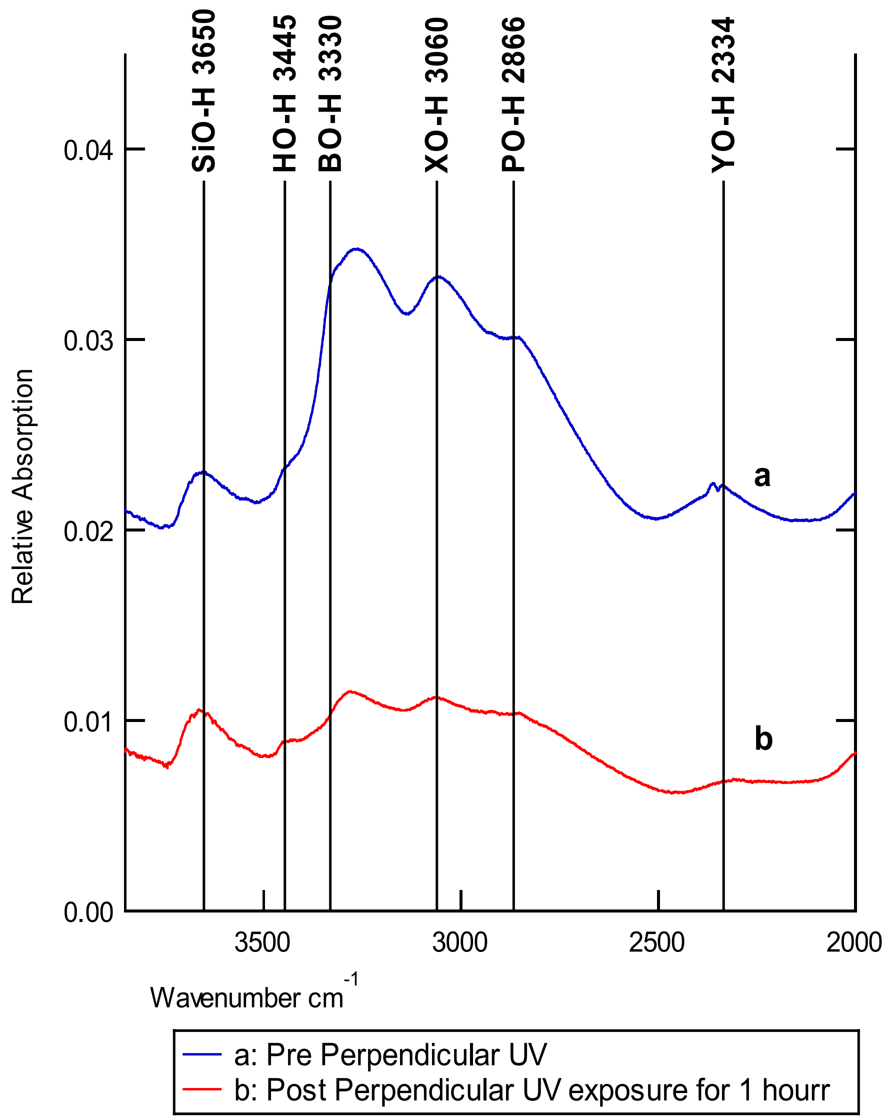
- Process
  - 1 hour
  - a → b : 50°C, 750 mTorr N_2
  - a → c : 103°C, 760 Torr
  - a → d : 178°C, 760 Torr
- Physical properties
  - Phosphoric acid
    - 85% b135°C, Pure d70°C
  - Boric acid
    - m165°C, d185°C
- Cloudy residue remains after the heating process
- Evaporation of residue creates stiction
  - (A. Witvrouw *et al.*, 2001)



Courtesy of:
Sandia National Laboratories
Intelligent Micromachine initiative
www.mdl.sandia.gov

Perpendicular UV

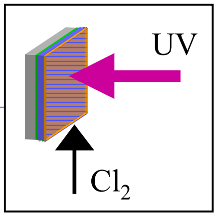


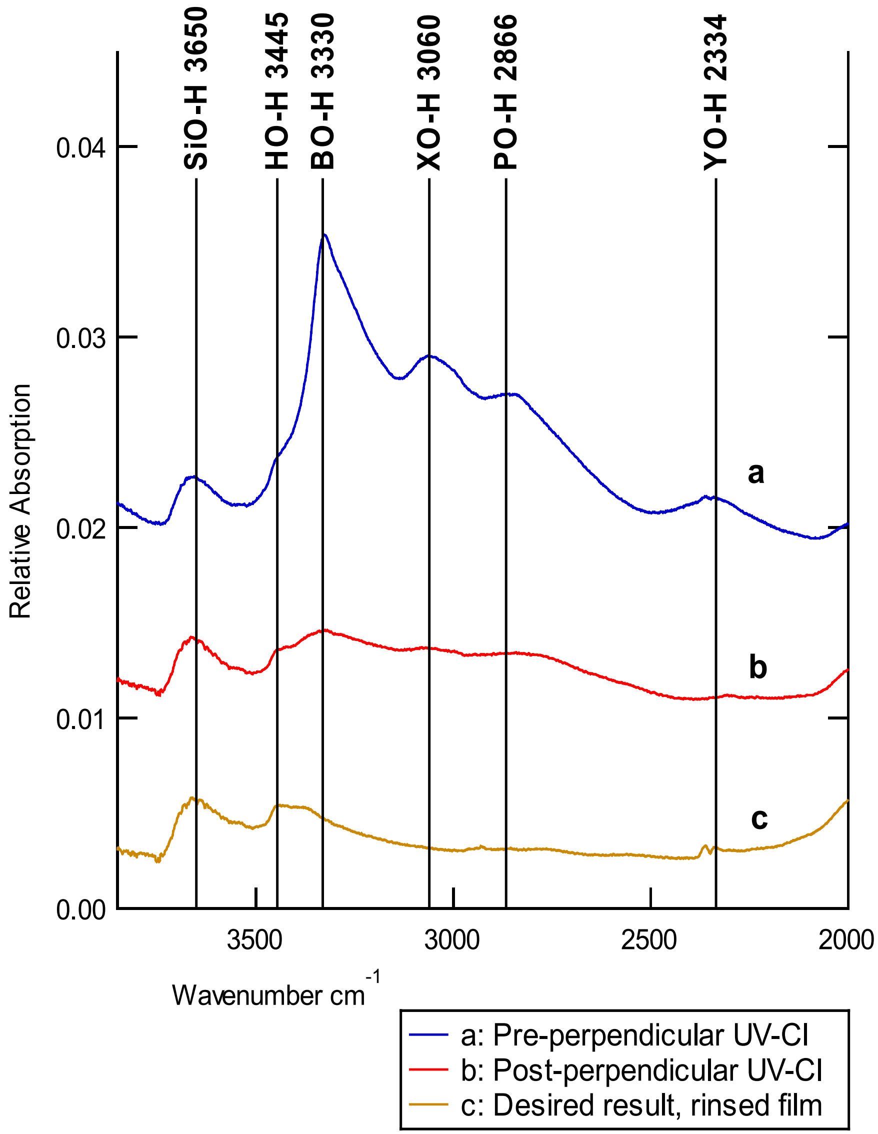


- UV Only Process
  - 1 hour
  - 750 mTorr
    - 100% N_2
  - 100°C

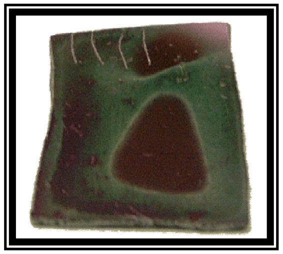
- Cloudy residue remains after UV only process

Perpendicular UV-Cl_2 Process

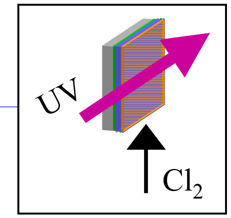


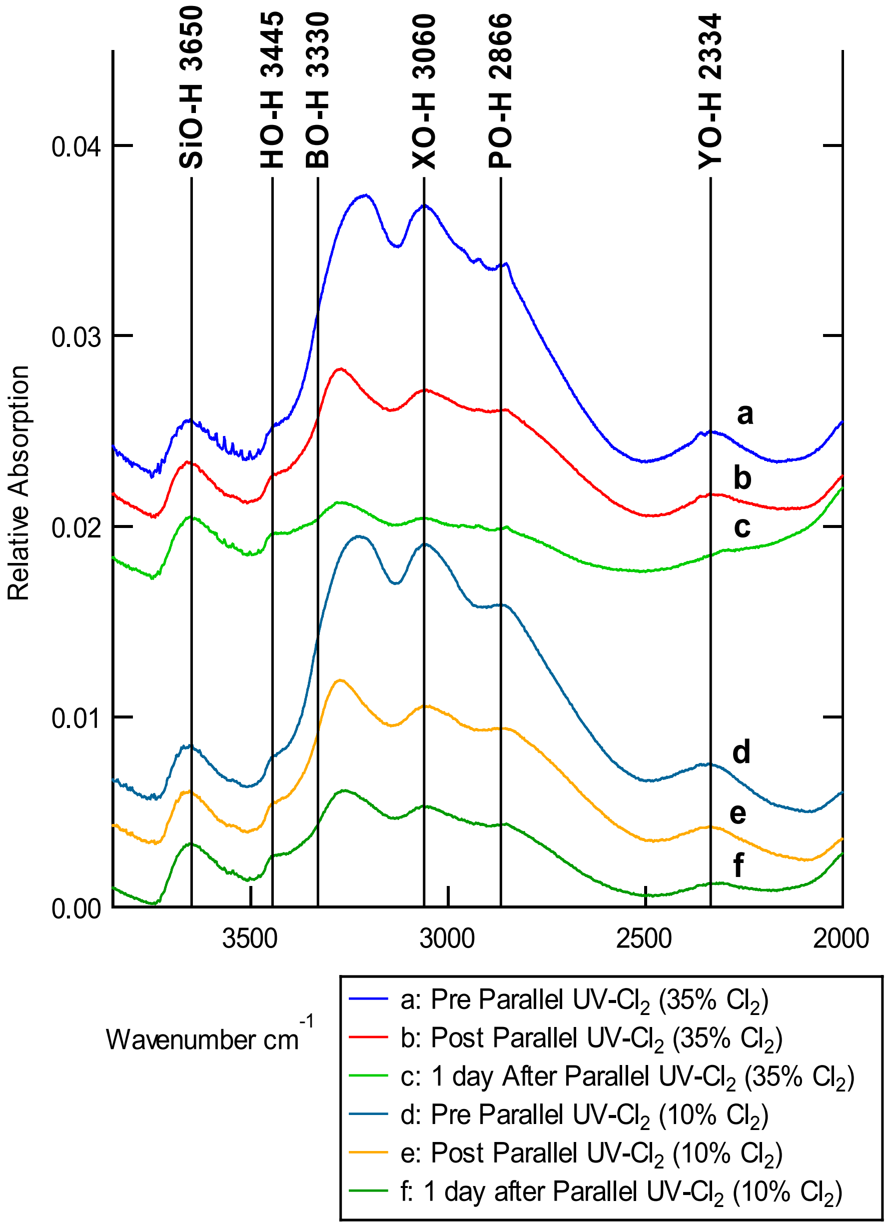


- UV-Cl_2 Process
  - 1 hour
  - 750 mTorr
    - 90% N_2, 10% Cl_2
  - 150°C
- Unrinsable opaque residue remains after process

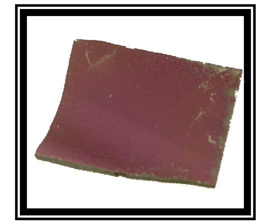


Parallel UV-Cl_2 Processes

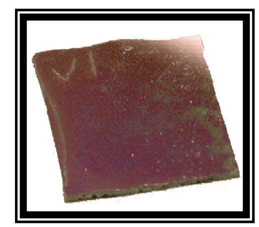




- Process
  - 1 hour, 50°C, 750 mTorr
- a → b (35% Cl_2)
  - 47.5% reduction in peak envelope
- b → c (35% Cl_2)
  - 1 day in cleanroom
  - 80% reduction in peak envelope
- d → e (10% Cl_2)
  - 38.4% reduction in peak envelope
- e → f (10% Cl_2)
  - 1 day in cleanroom
  - 63.5% reduction in peak envelope

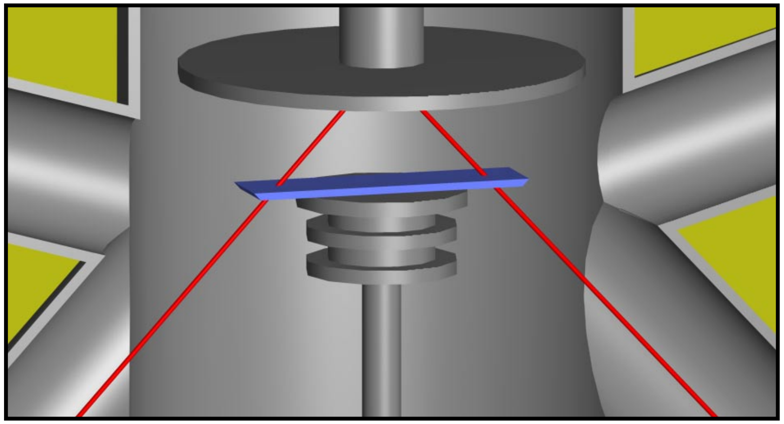


After b

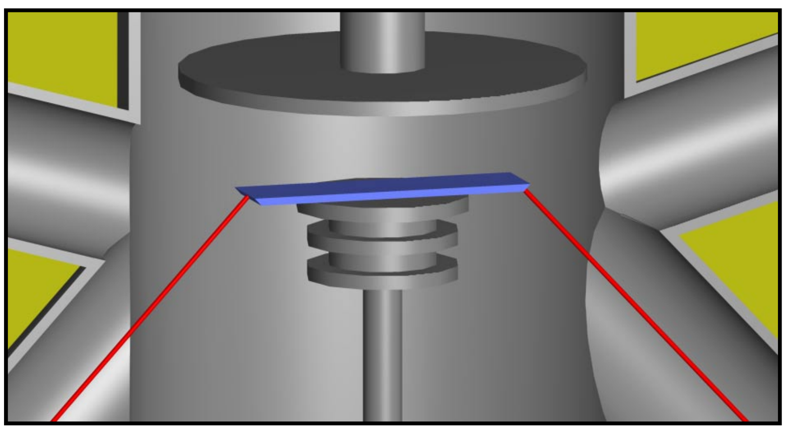


After e

HF/Vapor Etching Reactor



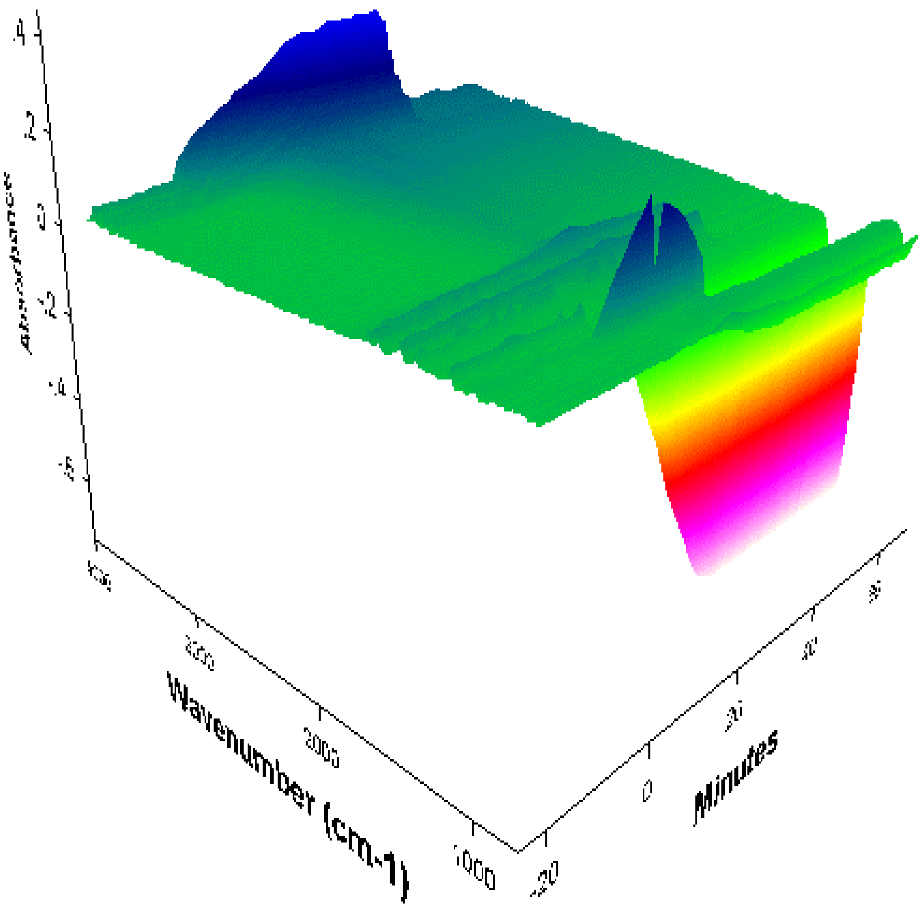
45° Transmission Mode



ATR Mode

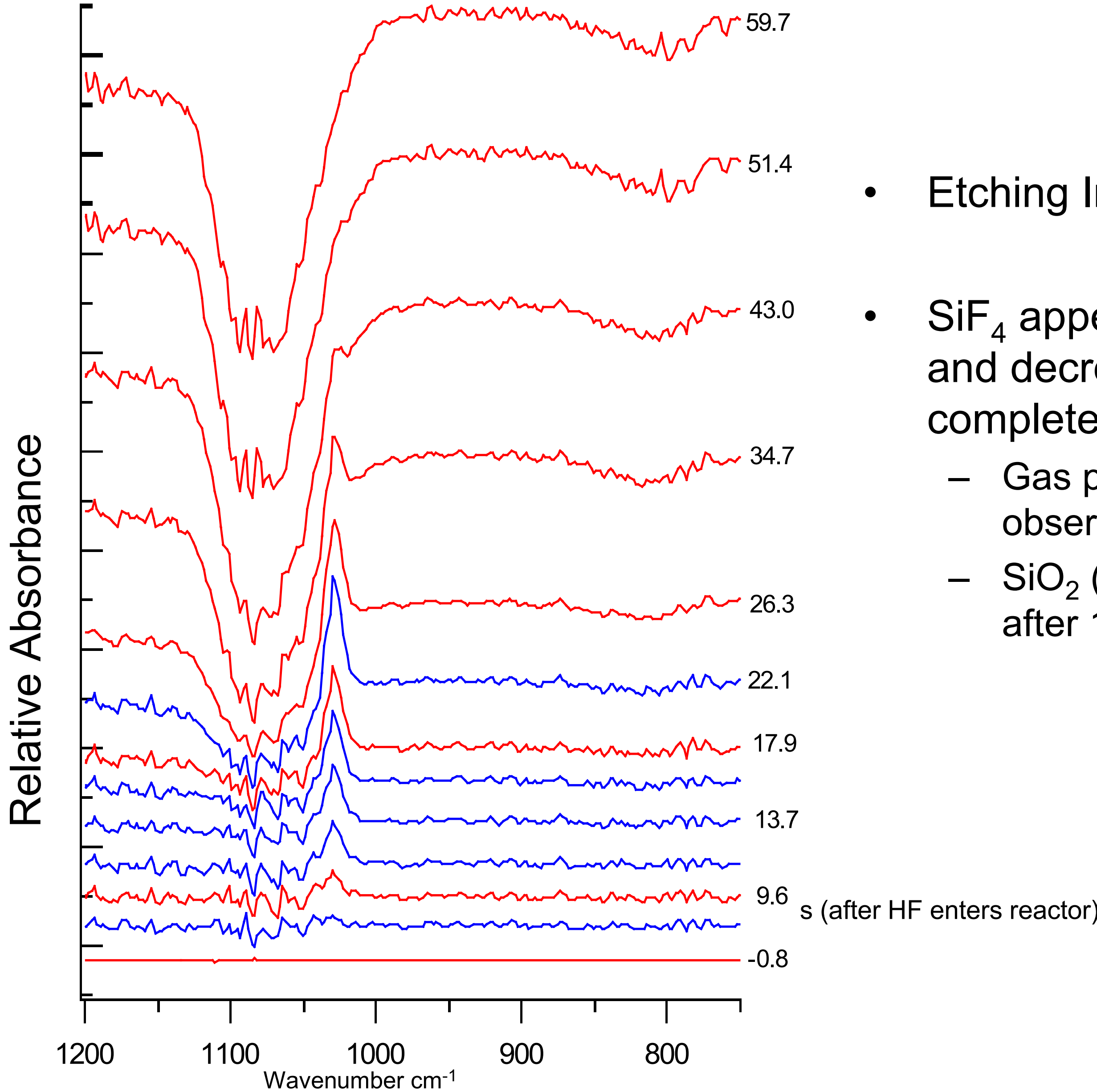
- Process Parameters
  - 50 - 800 Torr
  - 20 - 100°C
  - Broad range of HF and vapor partial pressures
- Direct introduction of vapor
  - Water and alcohols
- *In situ* Ellipsometry
- *In situ* FTIR
  - ATR and Transmission
- $\Delta P < 0.2$ Torr, transient < 1 s when HF or vapor introduced
- LabView computer control

Time Resolved FTIR of HF Vapor Process



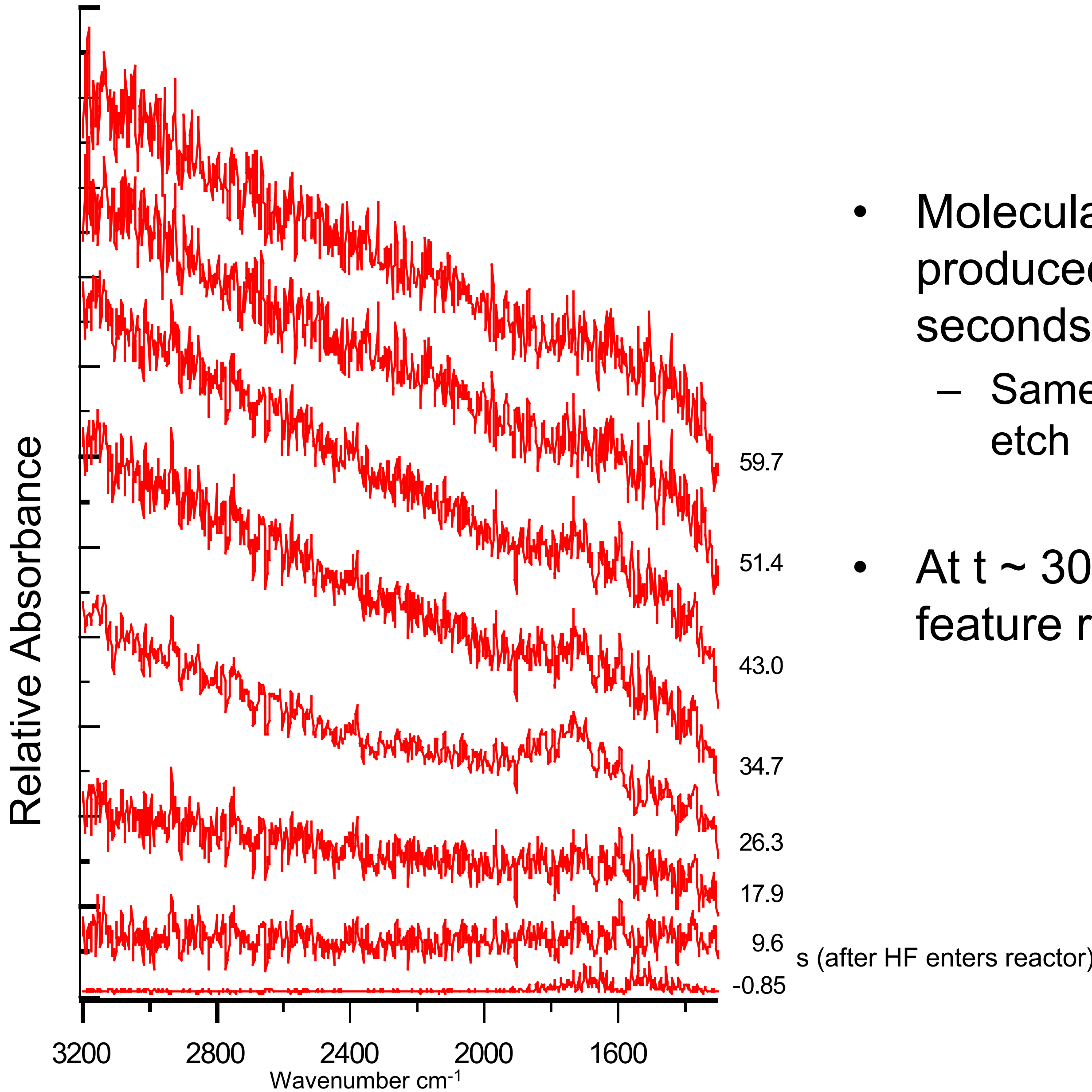
- Process parameters
  - 40°C
  - 250 Torr
  - Gas Flow
    - 400 sccm of N_2, 34 sccm of H_2O, 73 sccm of HF
- 2000 Å film was stripped in 36 s (56 Å/s)
- HF introduced into the reactor at time ≡ 0
- Reaction quenched with N_2 after 63 s

Low Frequency IR Vibrations



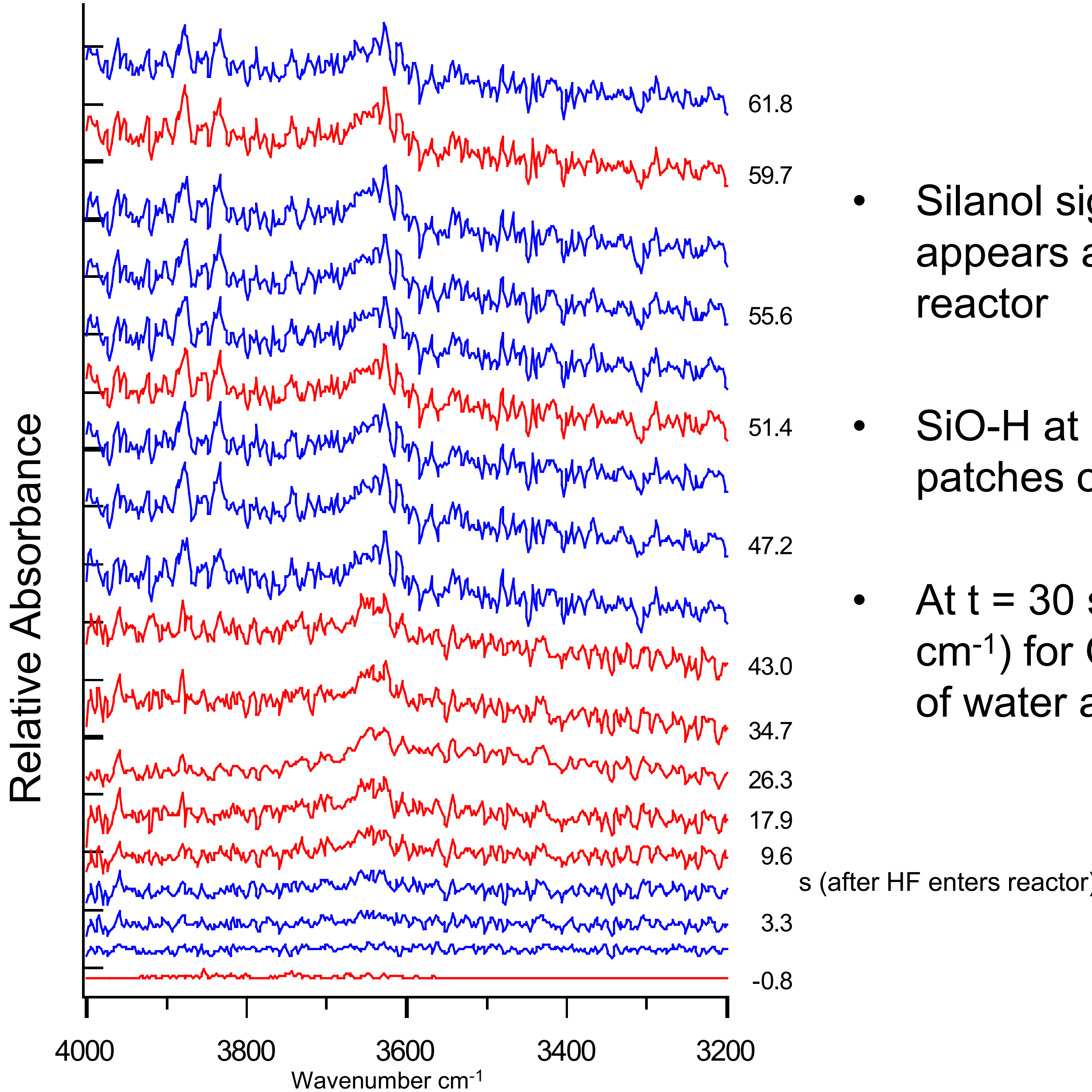
- Etching Induction Time
- SiF_4 appears before SiO_2 etches and decreases before etching is complete
  – Gas phase SiF_4 (1026 cm^{-1}) observed after 7 s
  – SiO_2 (1080 cm^{-1}) starts to etch after 14 s

Mid Frequency IR Vibrations



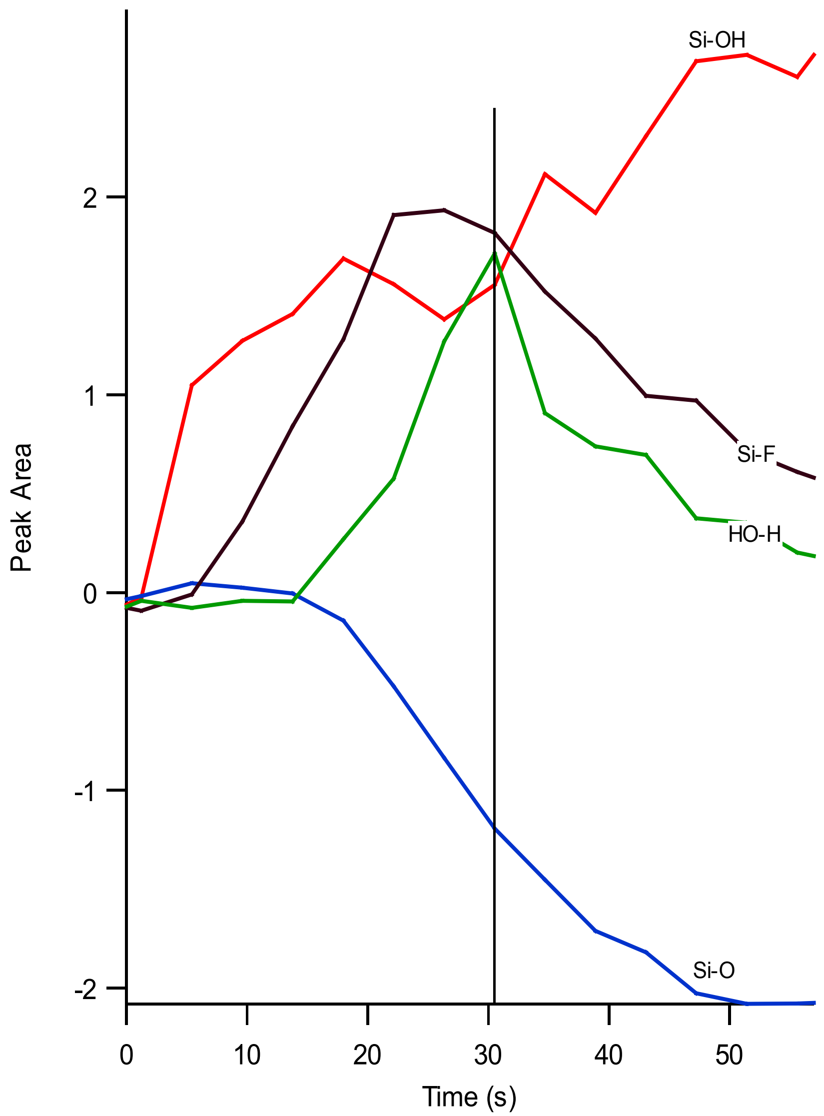
- Molecular water (1620 cm^{-1}) produced by reaction after 14 seconds.
  - Same time as SiO_2 starts to etch
- At t ~ 30 s the 1620 cm^{-1} feature reaches its maximum

High Frequency IR Vibrations



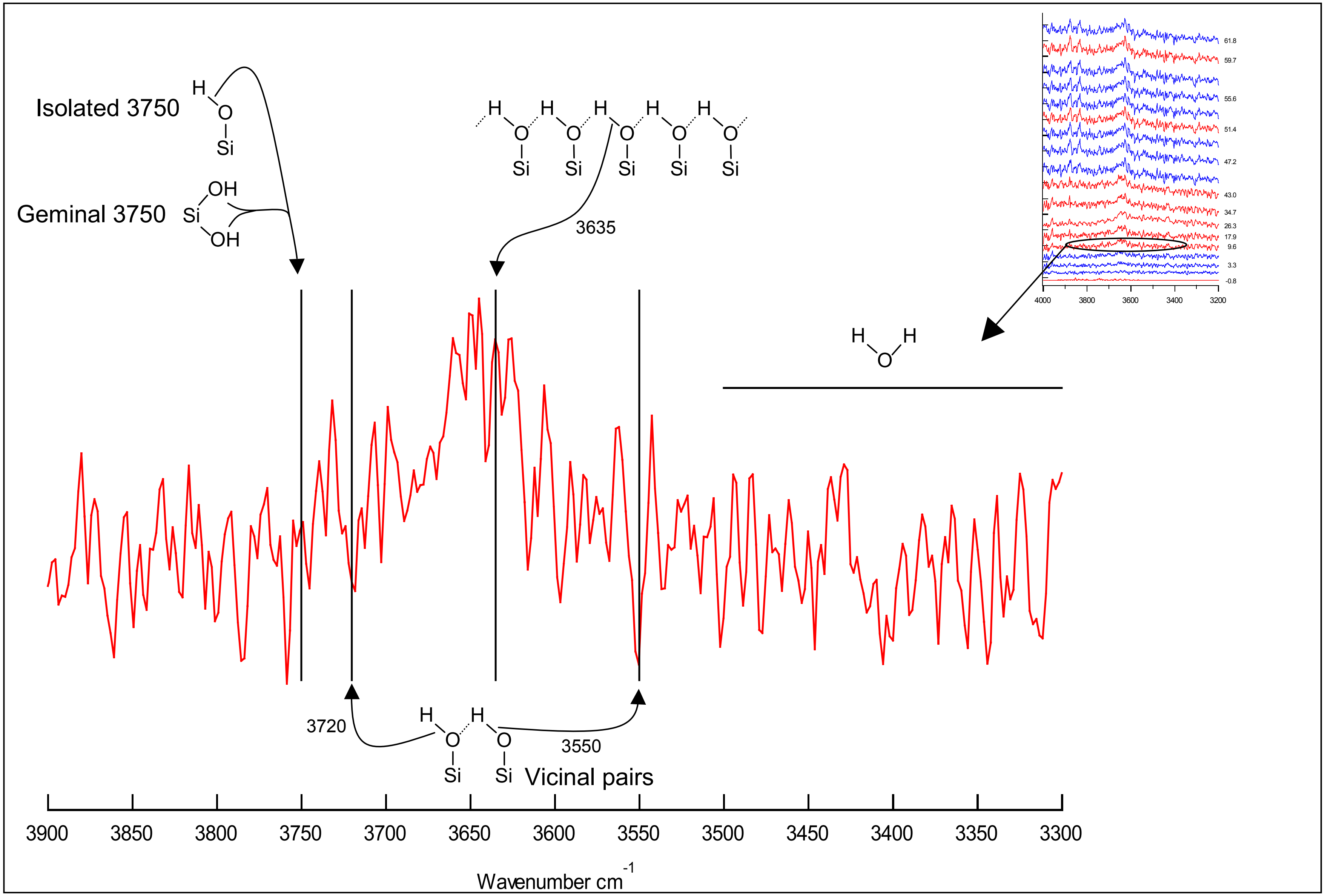
- Silanol signature (3650 cm^{-1}) appears as soon as HF enters reactor
- SiO-H at 3650 cm^{-1} indicative of patches of H-bonded silanols
- At t = 30 s, envelope (at 3500 cm^{-1}) for O-H stretching modes of water apparent

Integrated FTIR Peak Areas



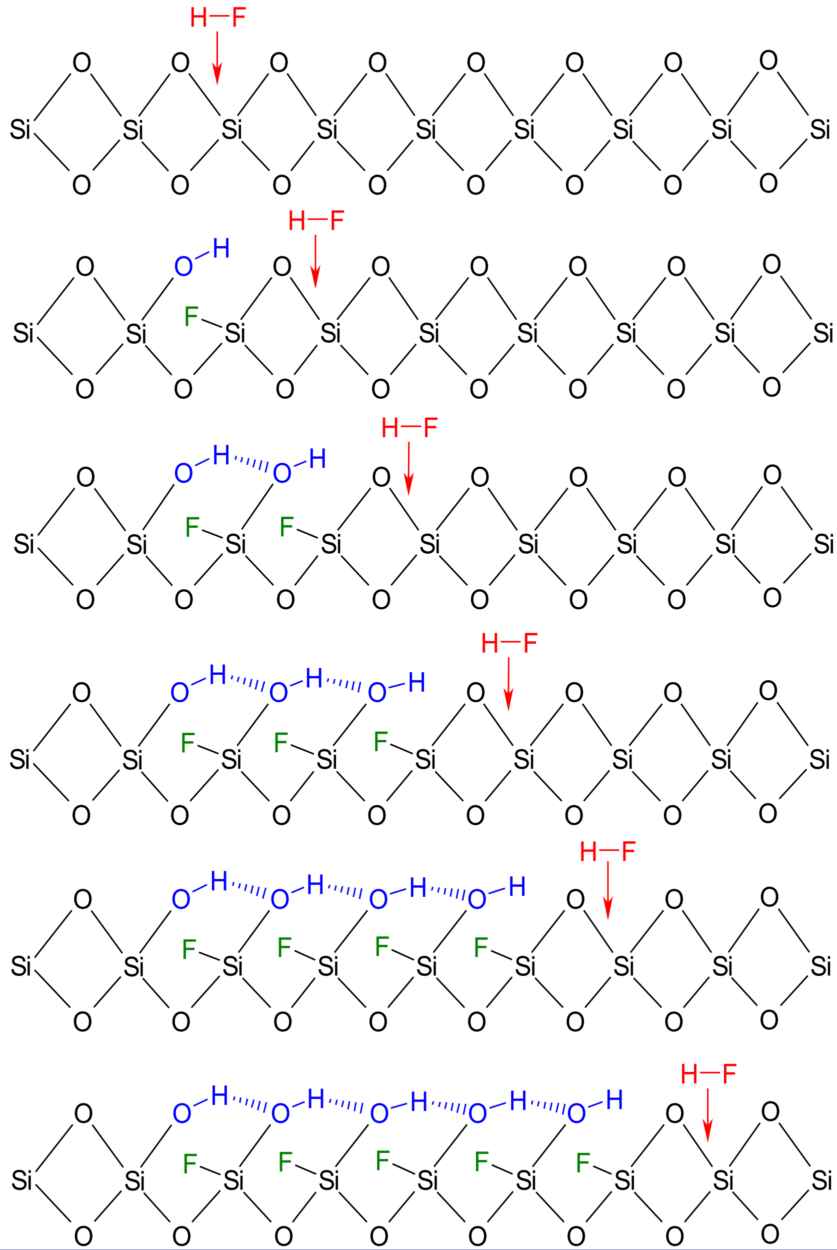
- SiO-H appears when HF enters reactor
- The SiF_4 signature appears 7 s after HF is introduced but before SiO_2 etching is apparent
- SiO_2 etching starts 14 s after HF enters reactor
- Max. in SiO_2 etching rate and surface HOH correspond
  - Occurs at ~ ½ initial oxide film thickness

Silanol FTIR Peak Identification



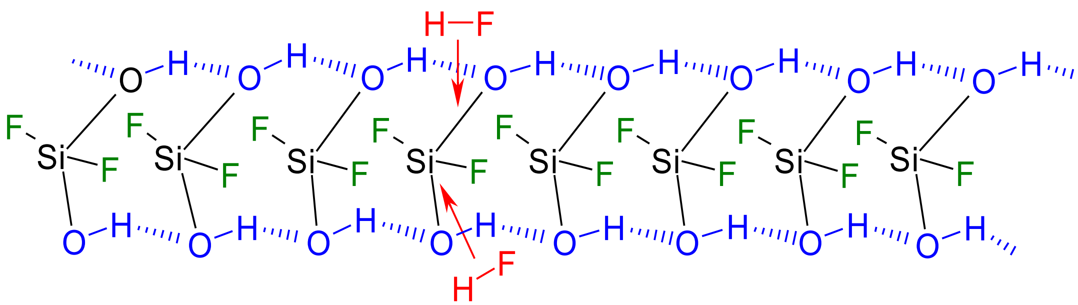
H. E. Bergna 1990

Proposed HF/H_2O Initiation Mechanism

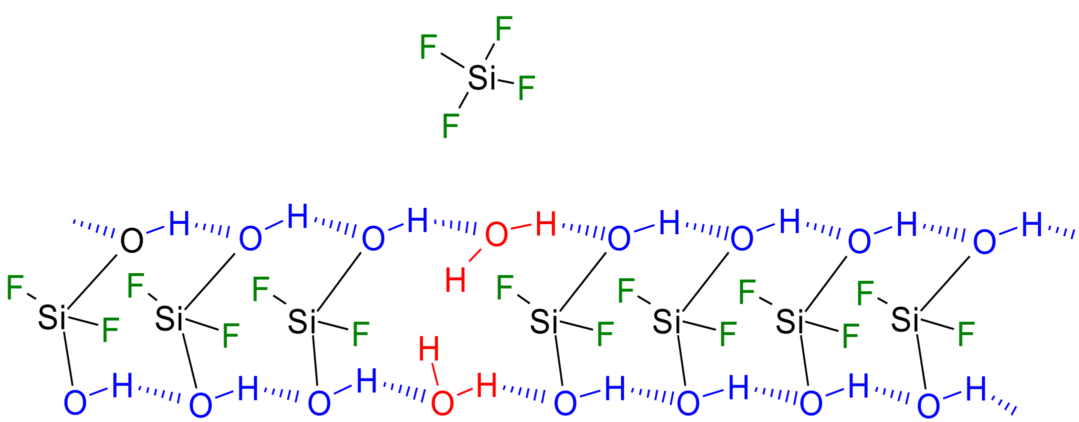


- HF attacks Si-O bond
  - Random
  - Activated
- SiO-H and Si-F produced
  - Si-F in FTIR?
- Succeeding HF molecules unzip oxide lattice
- Groups of H-bonded SiO-H produced during induction t

Proposed HF/vapor Bulk Etching Mechanism



- Hydroxylated Si-O surface
- HF attacks remaining Si-O bonds



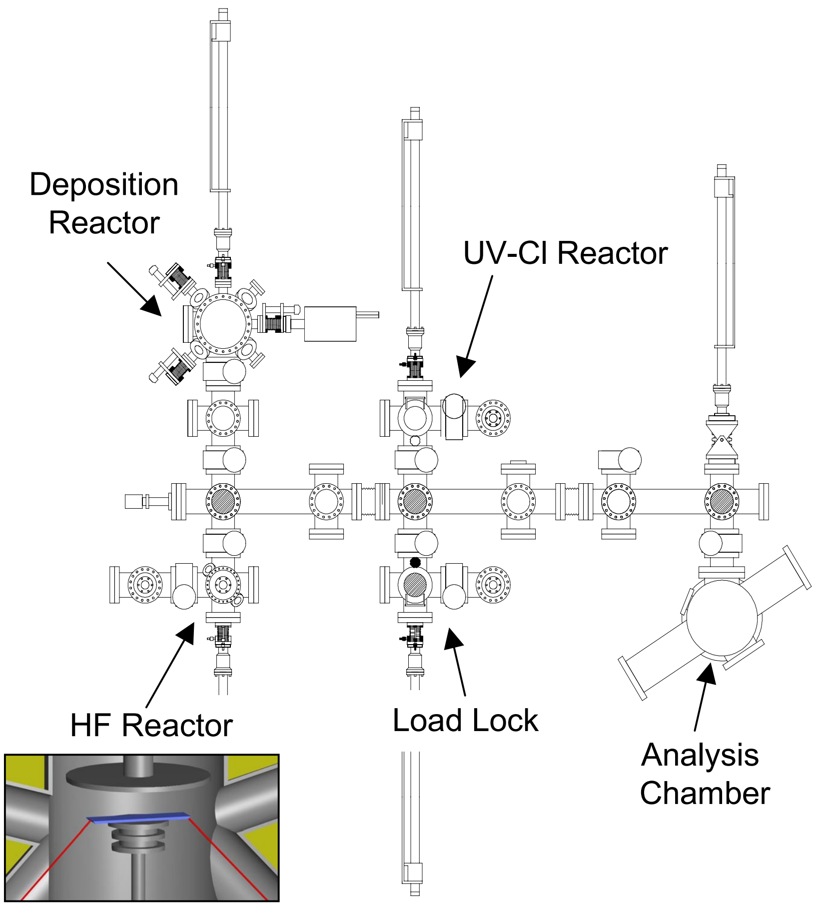
- SiF_4 produced
- Molecular water production and Si-O etching coincide

Summary

- Mixed acid residue formed on BPSG after AHF etching
- UV-Cl_2 process effective in removing residue
  - High temperature perpendicular UV exposure
    - Unrinsable residue
  - Low temperature parallel UV exposure
    - Eliminates water rinse
    - Process optimization/time

- HF/vapor Etching Mechanism
  - H-bonded silanols produced during induction time
  - Molecular water produced by HF attack of Si-OH bonds in F_xSi-OH groups
  - Liberate Si and etch film
  - Etching rate decreases before oxide film is stripped

Future Plans



- Determine details of the initial stages of HF/vapor etching
- Process doped oxide films in cluster apparatus
  - Develop UV-Cl_2 removal process
- Clean/prepare surfaces for Cu barrier and high-κ film deposition
- Develop metal removal mechanism with UV-Cl_2

Acknowledgements

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