# The Effect of Absorbed Moisture on the Etching of Doped Oxide Films

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# Outline

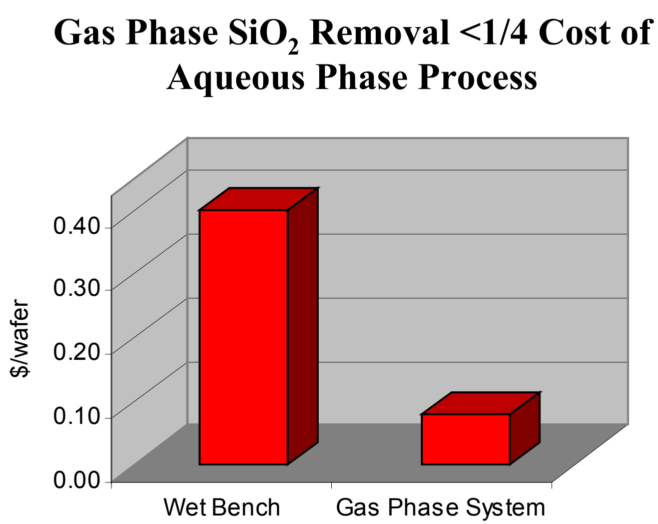
- *Objectives*
- *Experimental*
- *Film Chemistry Before Etching*
- *Film Chemistry After Etching*
  - *Water Soluble P-acid Film Formation*
- *Etching Results*
  - *Induction Time*
- *Conclusions*
- *Future Work*

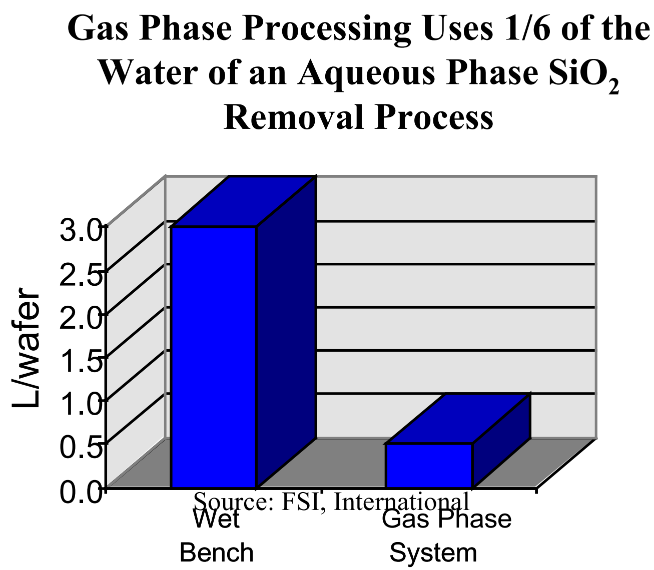
# *Project Objectives*

- *Establish empirical dependencies (etching rate, T, time, and $p_{AHF}$) for AHF etching of doped oxide films.*
- *Assess relative importance of absorbed to product water on etching.*
- *Propose a mechanism for doped oxide etching that explains selectivity.*
- *Identify a process that does not require a water rinse to remove etching by-products.*

# ESH Impact

- *Reduced Resource Use*
  - *Lower water, ultrapure $N_2$, chemical and exhaust (energy) usage.*




Total Cost = Water + Chemicals + Labor + Capital + Cleanroom
Source: C. A. Peterson, Microelectronic Manufacturing and Testing, May, 1988.

  - *Smaller chemical load in waste streams.*
  - *Smaller tool footprint.*
- *Lower Worker Exposure to Chemicals*

# Film Formation

- PECVD Oxide Film Stack
  - 2K Å TEOS
    - 5 wafer batch (Novellus)
    - T = 350°C
    - Gases: $O_2$, TEOS
  - 5K Å BPSG (3.5%B/4.0%P)
    - 5 wafer batch (Novellus)
    - T = 350°C
    - Gases: $N_2$, $SiH_4$, $N_2O$, $PH_3$, $B_2H_6$
- Anneal
  - Batch Furnace
    - Held at temperature for 59 min. in $N_2$
    - As Deposited, 500°C, 750°C, 900°C

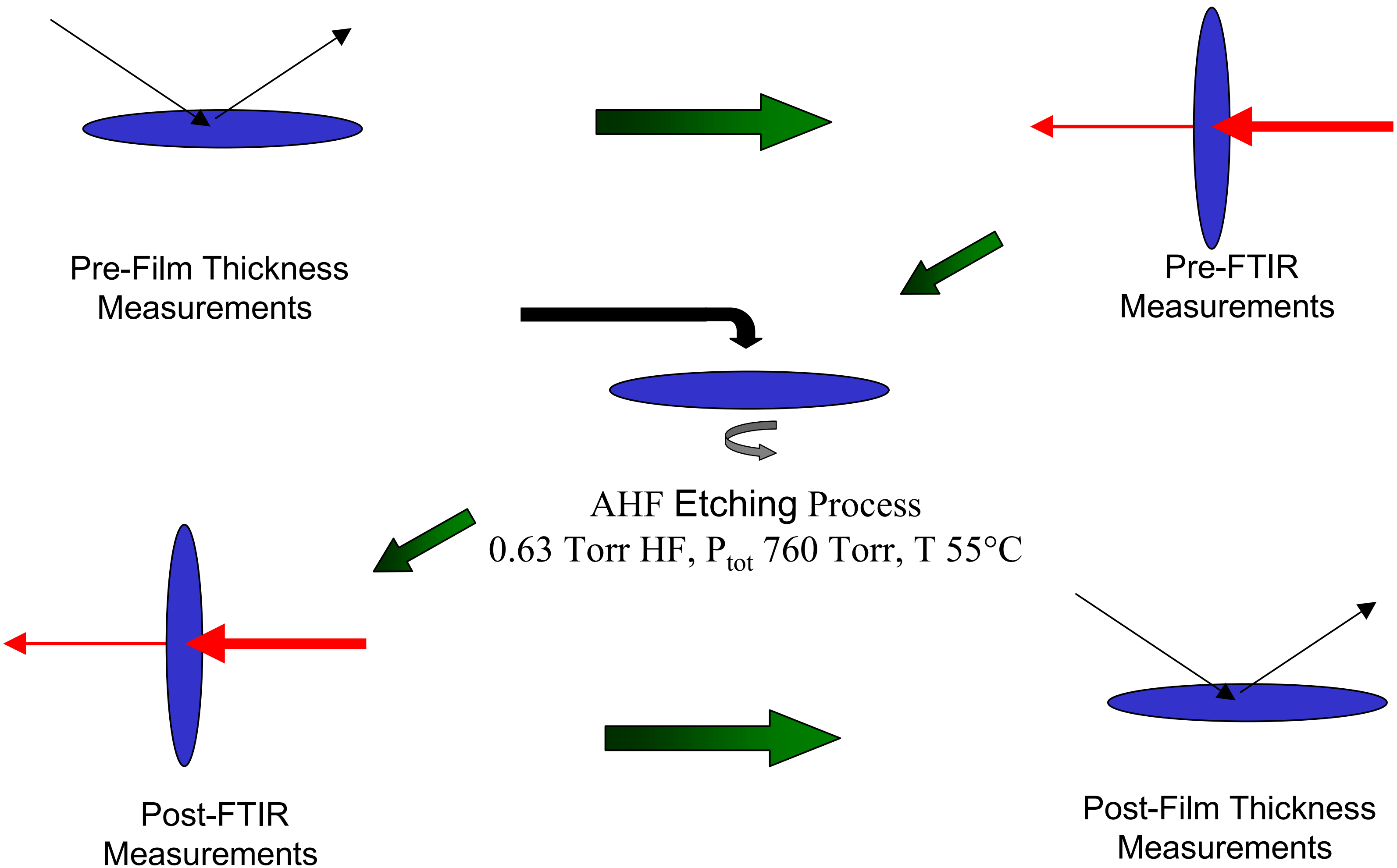
# Film Etching

- FSI Excalibur ISR (In Situ Rinse) Etching Tool
  - Single 8” wafer process
  - Heated using hot $N_2$ and chamber heater
    - All results at 55°C
  - Anhydrous HF process
  - Post-etching rinse

- Film Diagnostics
  - FTIR Spectrometer
  - Ellipsometer

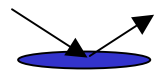
# *Experimental Process and Analysis*

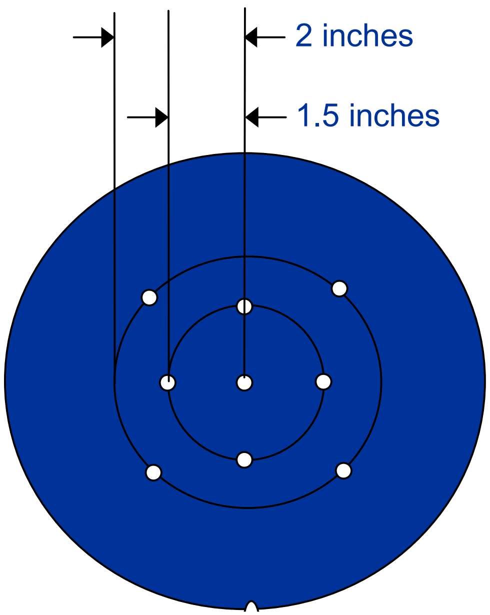
## **5K A BPSG Films on 8 inch Wafers**



# *Experimental Process and Analysis con't*

## **Film Thickness Determination Using Ellipsometry**

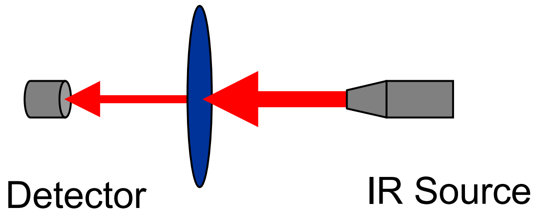




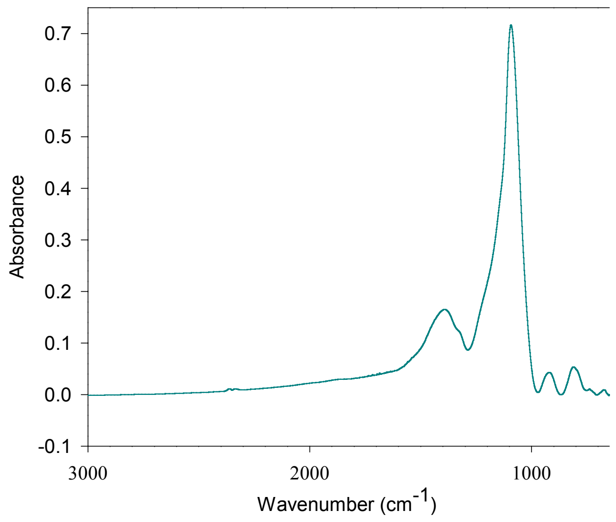

- *200 Wavelengths*
- *Center Fast*
- *95% Confidence Intervals*
  - *Ranged from ± 25 - 45 Å*
- *Standard Deviations* *(Center not Used)*
  - *Pre-Measurements*
    - $E(\sigma)$ = *22.2 Å*
  - *Post-Measurements*
    - $E(\sigma)$ = *56.2 Å*

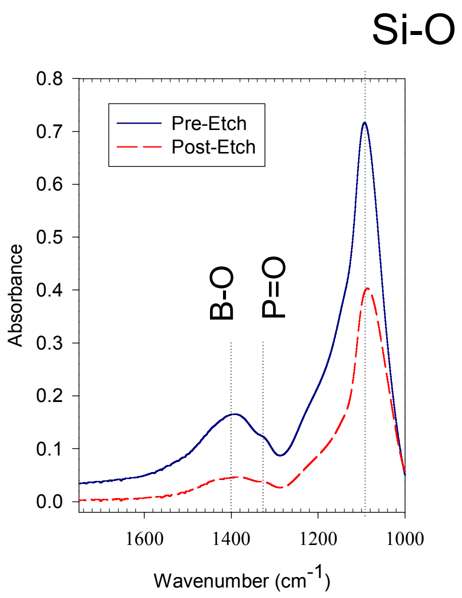
# *Experimental Process and Analysis con't*

## Chemical Species Analysis Using Transmission FTIR




- *Transmission through the wafer.*



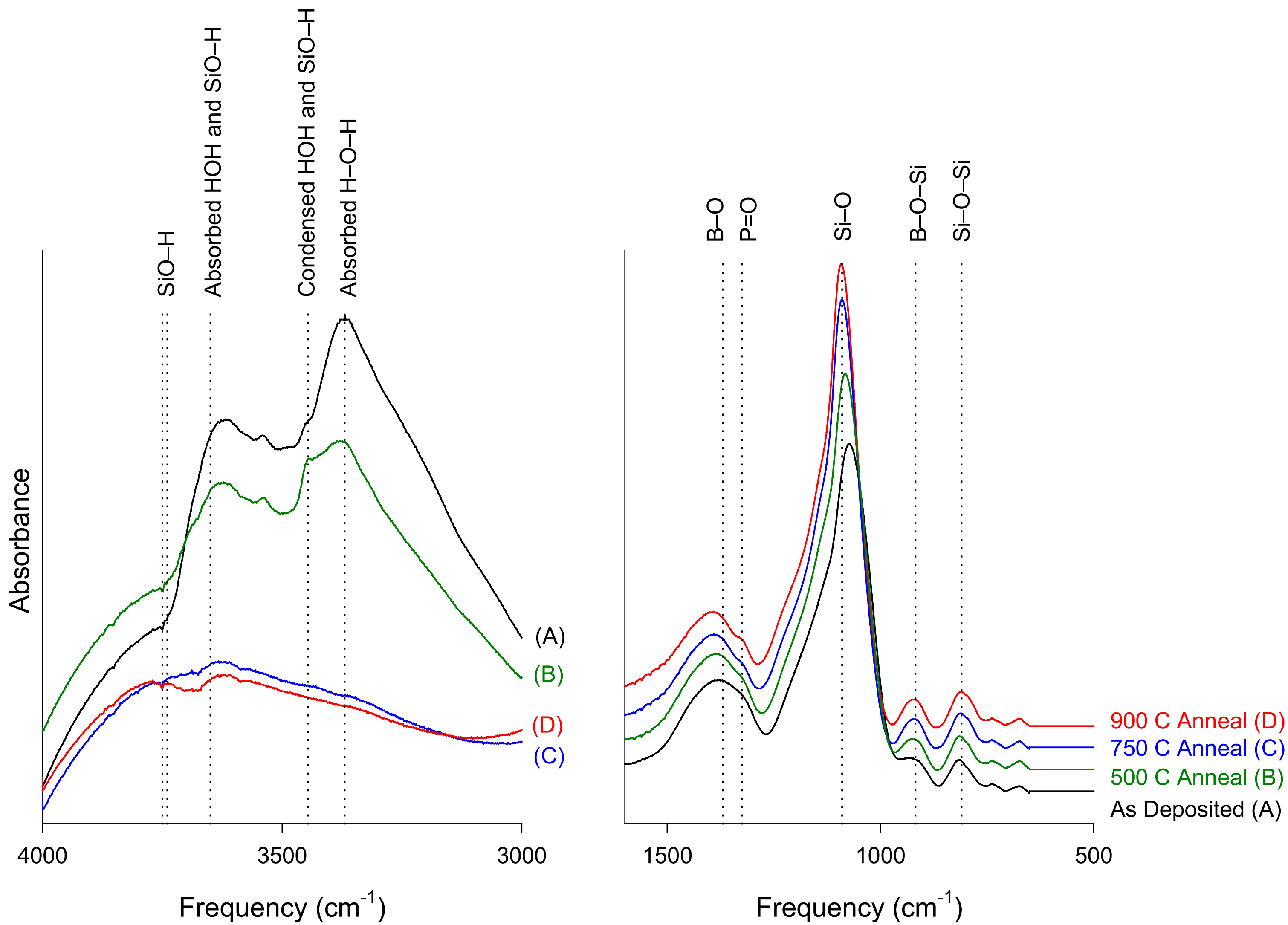

- *Peaks represent specific stretching or bending vibrational modes of a chemical species.*
- *Peak Areas are proportional to the absolute amount.*

# Overview

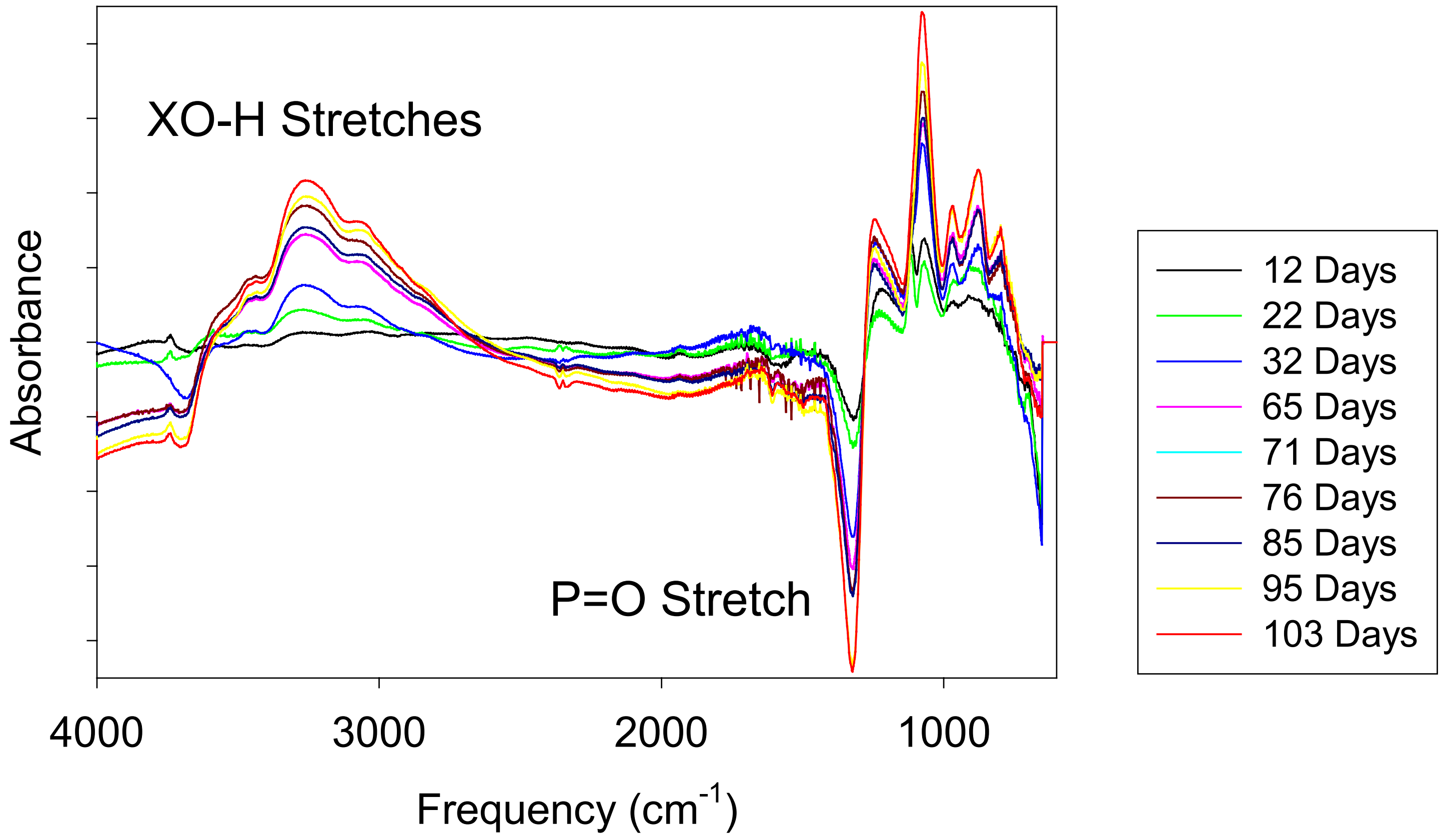
- *First Steps*
  - *Evaluate the initial condition of the films.*
  - *Observe changes in film composition over time using Transmission FTIR.*

- *Pre-Analysis of films*
- *Etching*
  - *AHF at 55°C*
- *Post Analysis of Films and Residue*

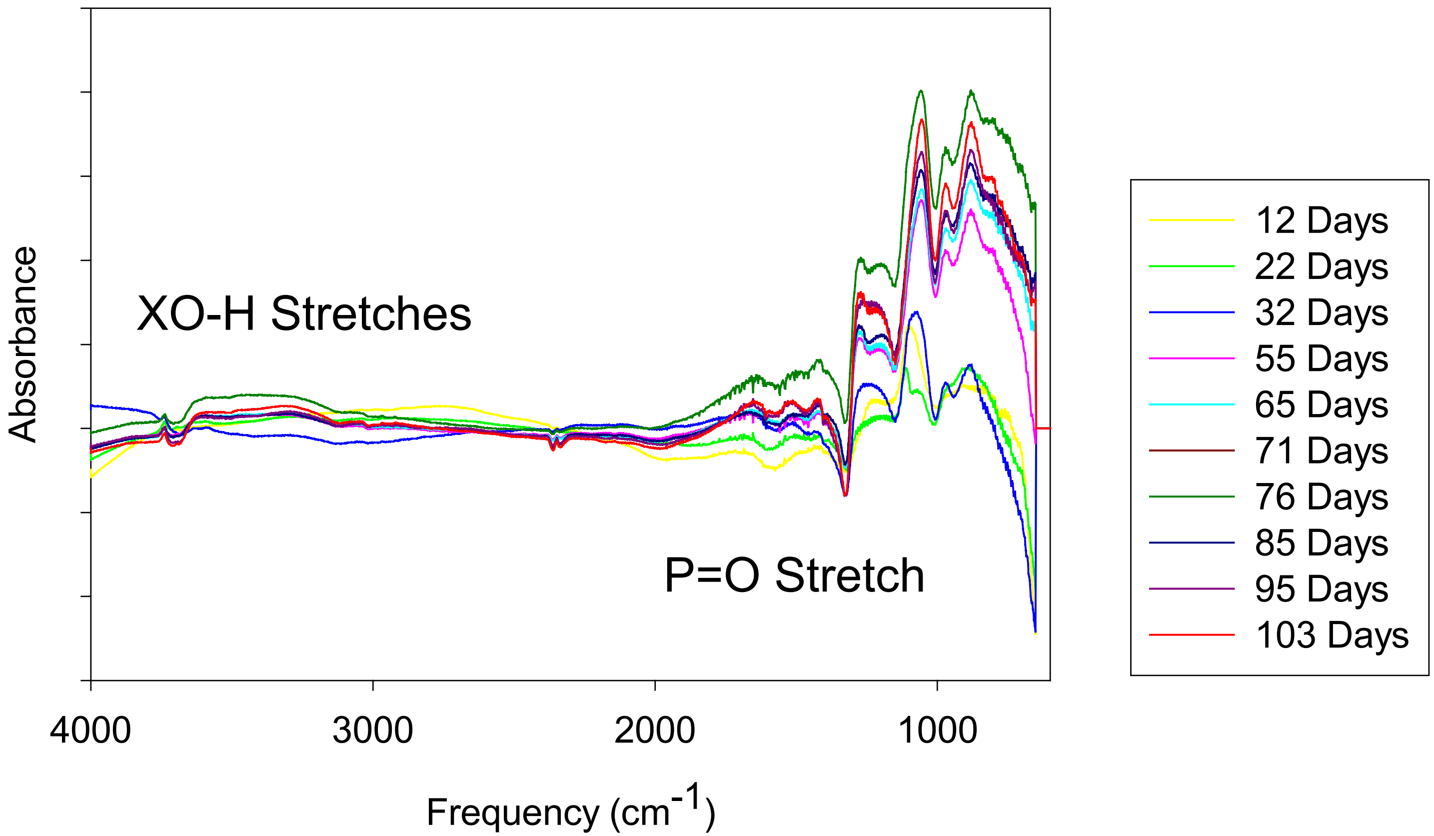
# FTIR of As Received Wafers



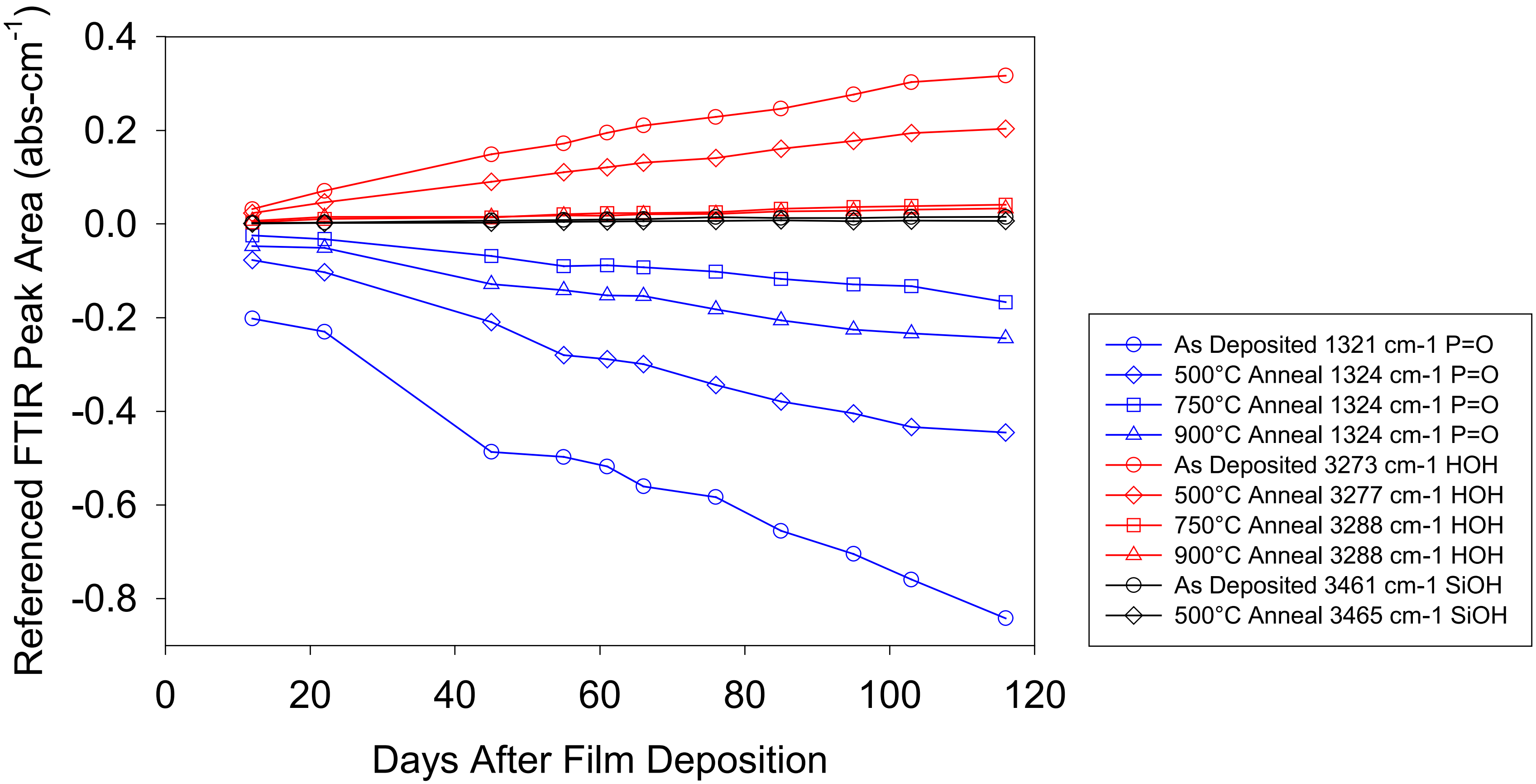
# Referenced FTIR of As Deposited Film as a Function of Time



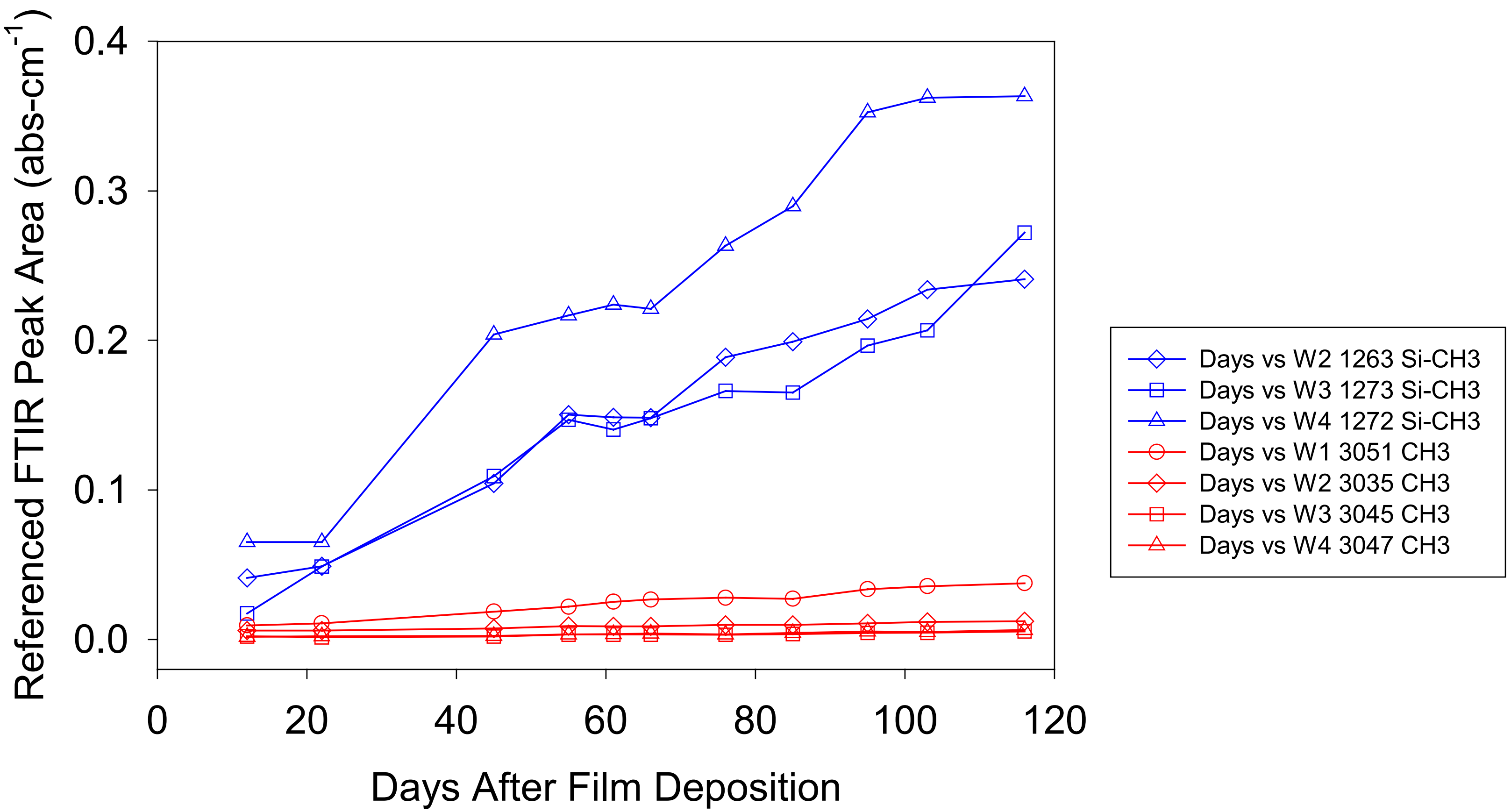
# Referenced FTIR of 900 °C Annealed Film as a Function of Time



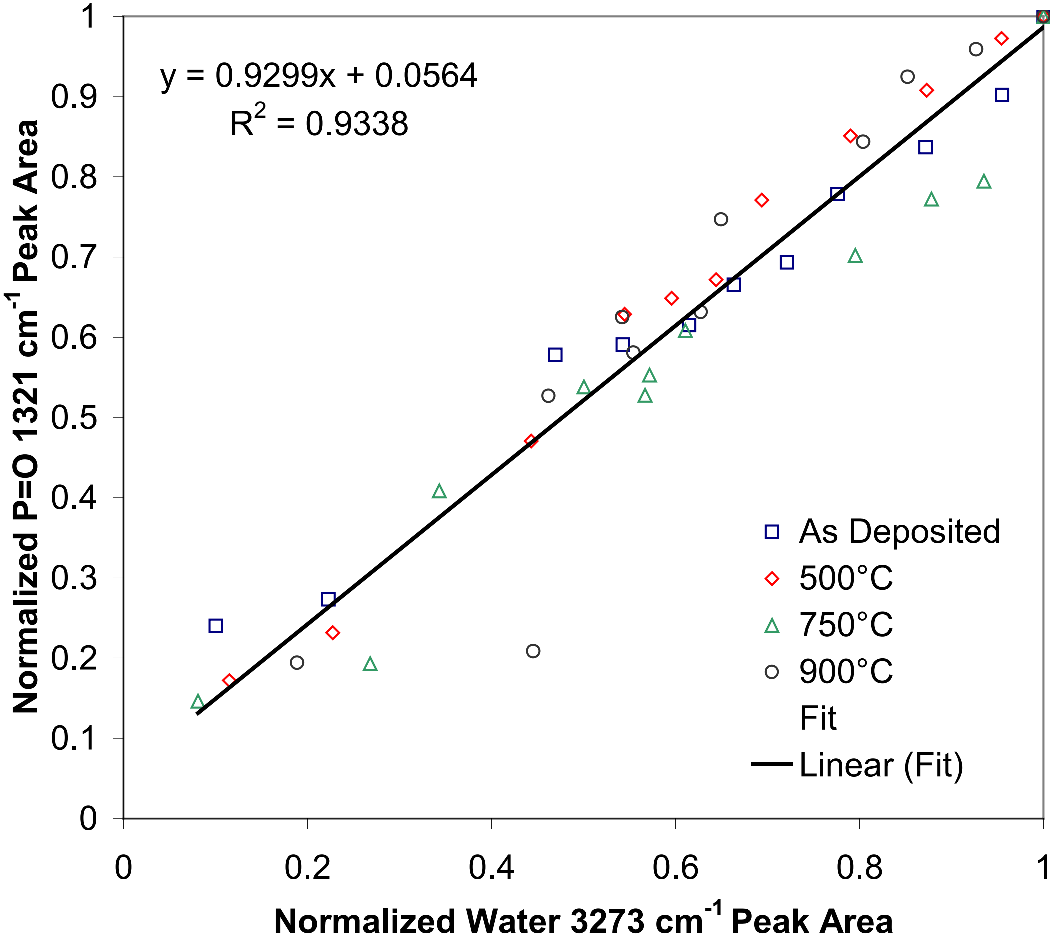
# P=O, Absorbed HO-H, and SiO-H Referenced FTIR Peak Areas



# $SiCH_3$, $CH_3$
# Referenced FTIR Peak Areas



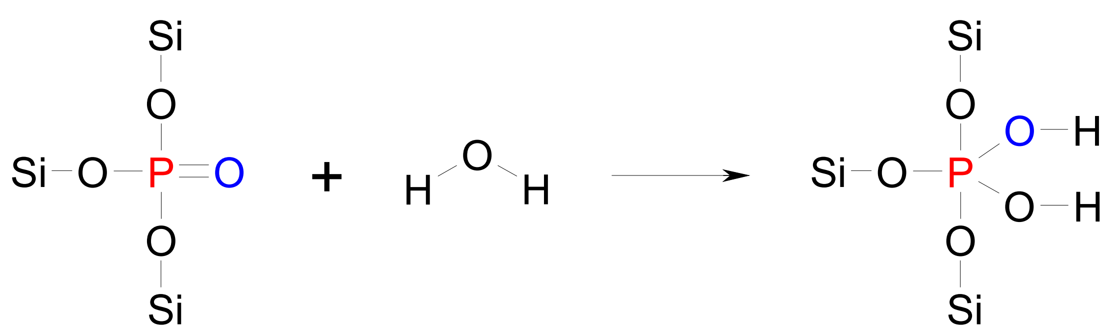
# P=O Reacts with Absorbed Water



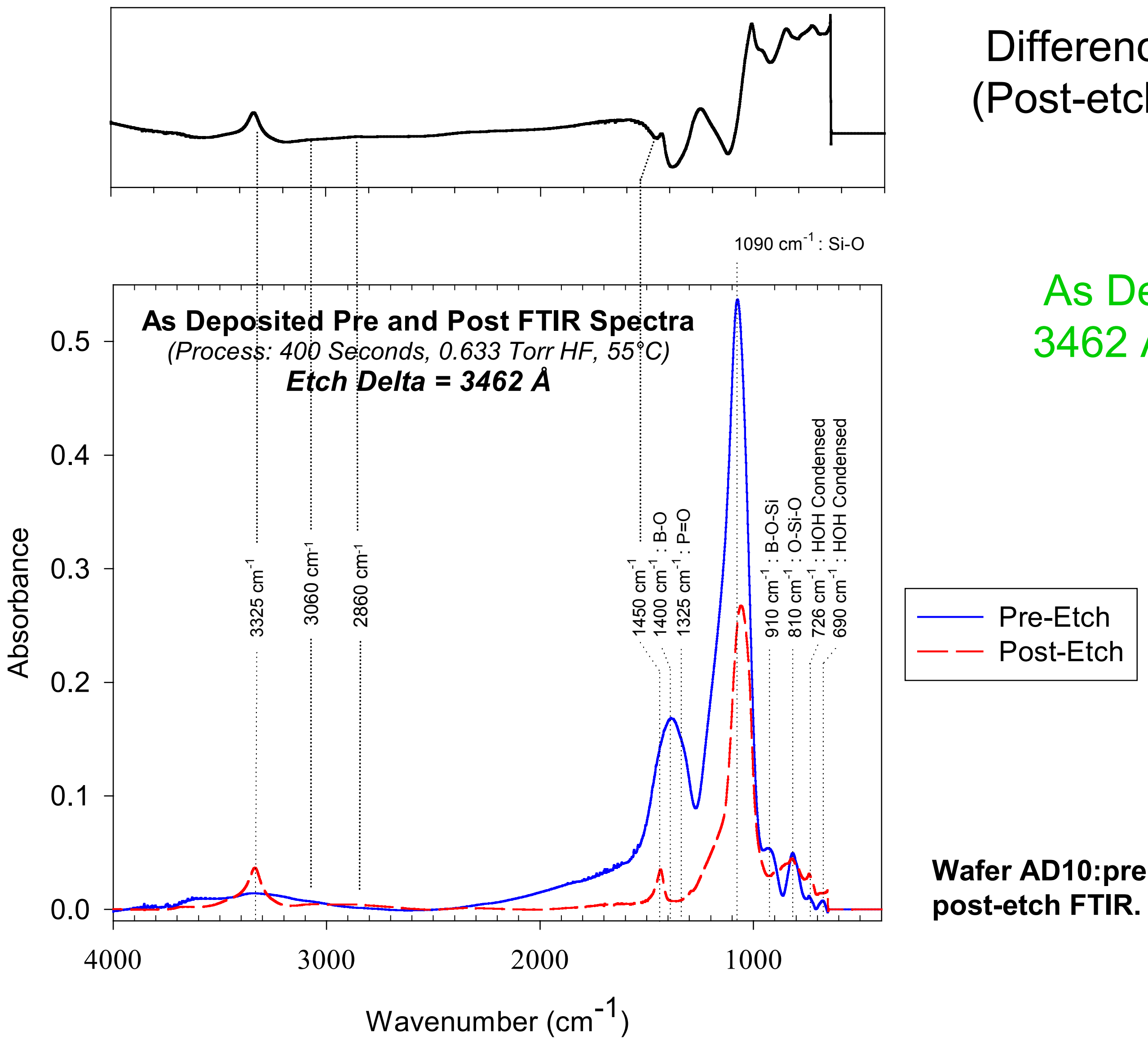

- *Slope ≈ 1 suggests that 1 absorbed HOH reacts with 1 P=O.*

# Chemistry of BPSG Films Before Etching

- *Decrease in P=O peak area indicates that P=O reacts as wafers are aged.*
- *The lower the anneal, the more water absorbed and the larger the decrease in the P=O peak area.*
- *FTIR feature indicative of PO-H could be present in envelope of absorbed water.*
  - *Shoulder near 3300 cm-1 in As Deposited FTIR.*
- *1:1 absorbed HOH to P=O suggests following reaction.*



# New Features Appear in FTIR After AHF Etching

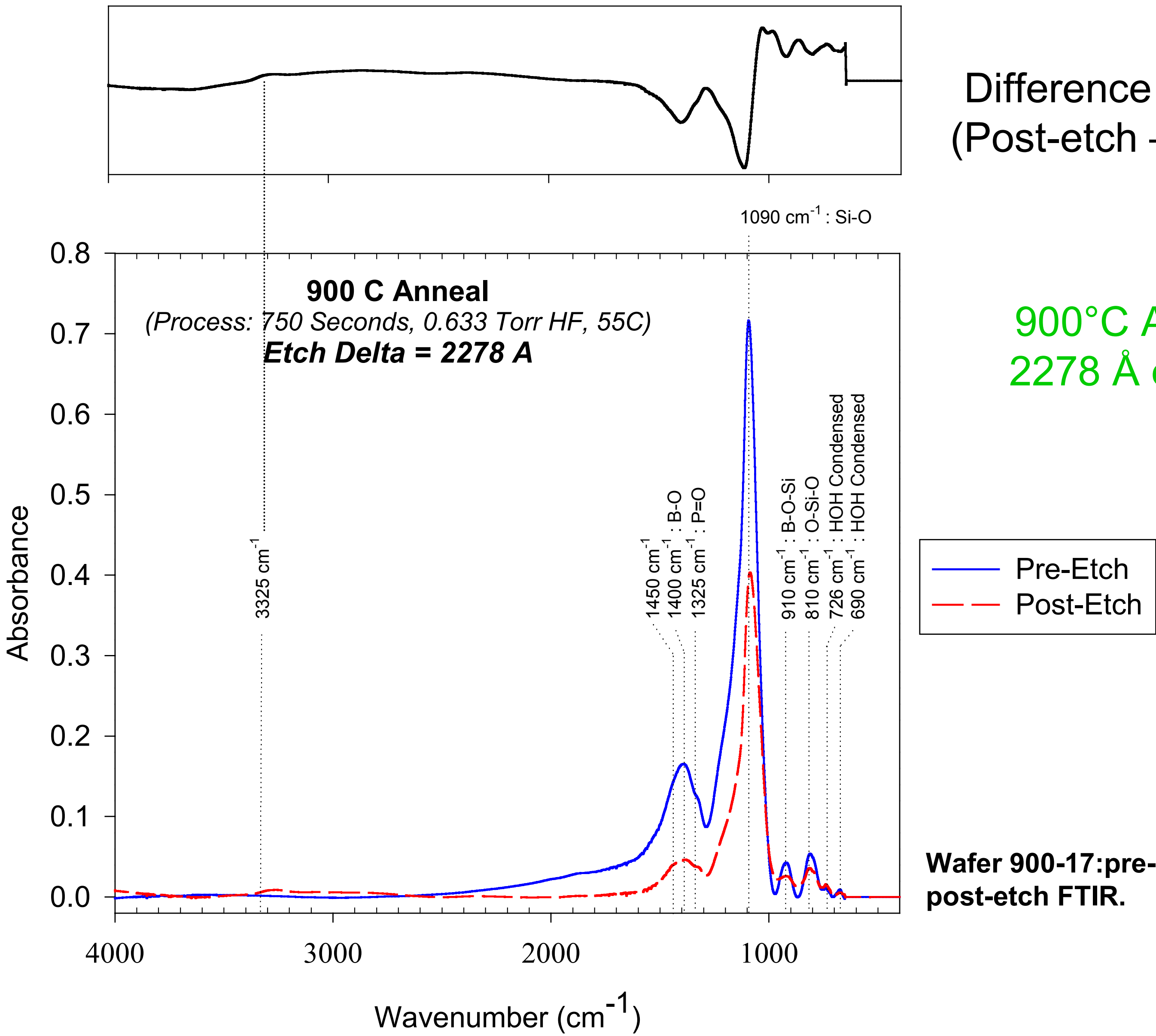



Difference Spectrum (Post-etch – Pre-etch)

As Deposited 3462 Å etched

**Wafer AD10:pre-etch FTIR, etch, post-etch FTIR.**

# The New Features are a Function of Anneal

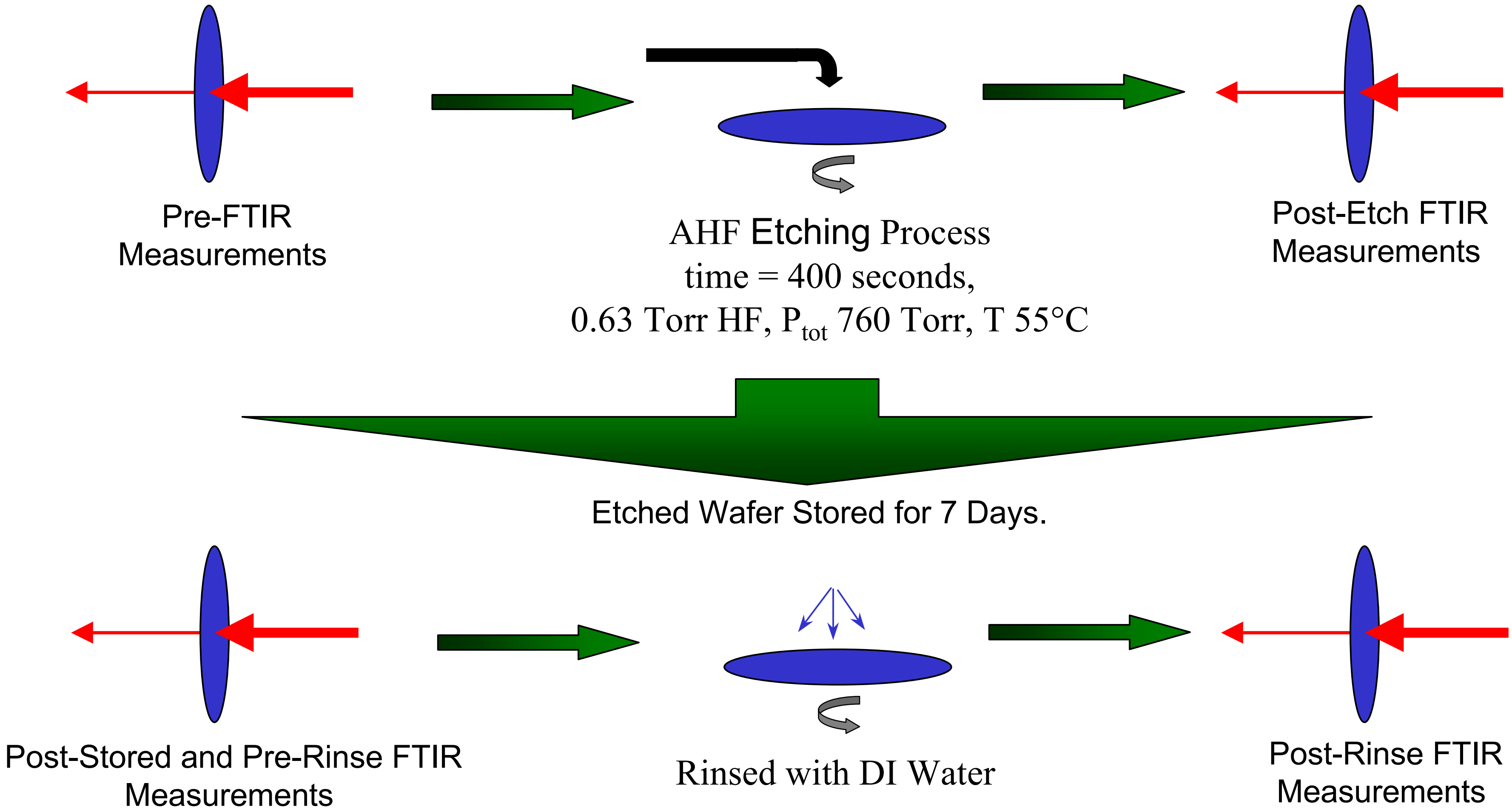



Difference Spectrum (Post-etch – Pre-etch)

900°C Anneal
2278 Å etched

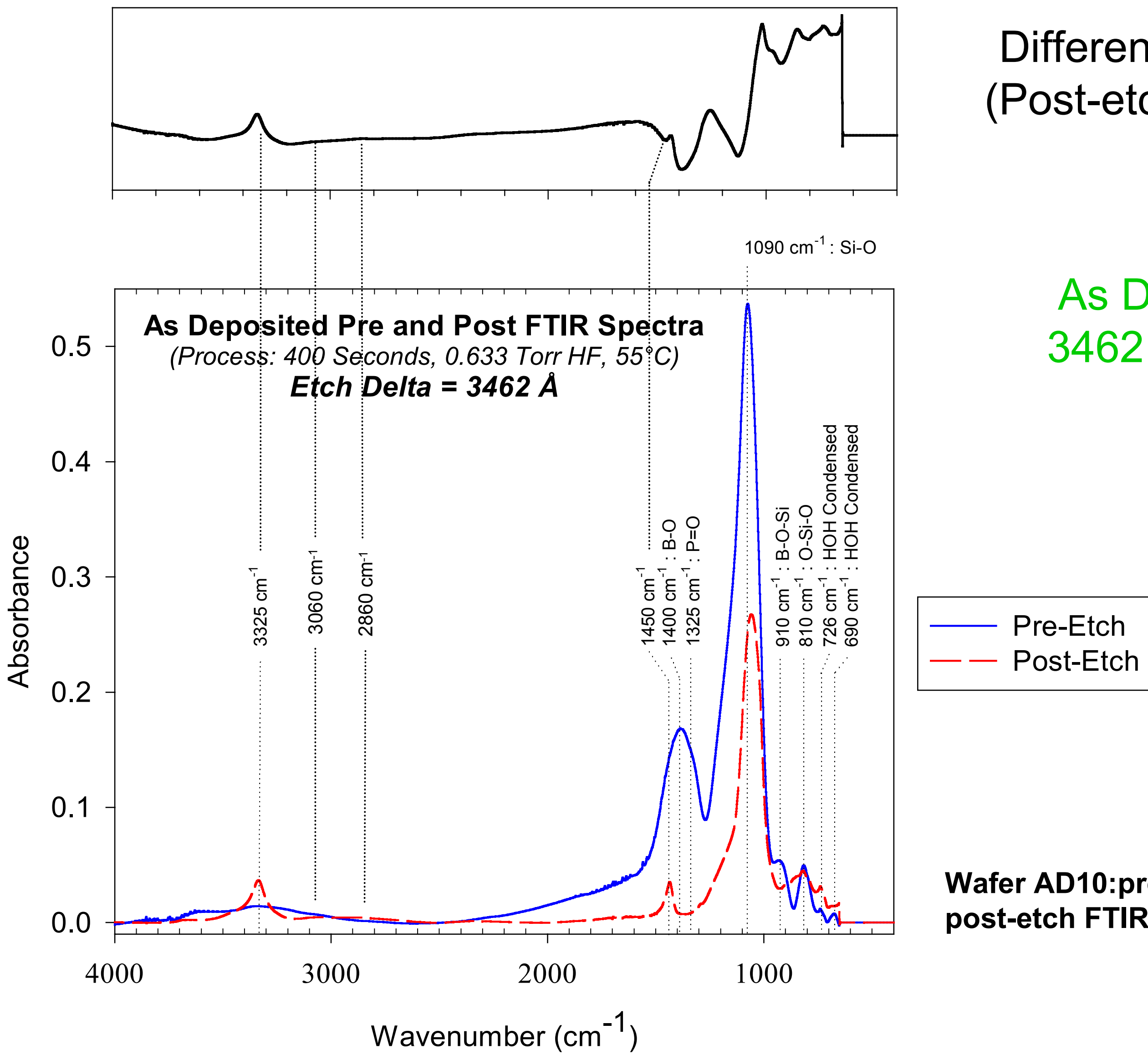
**Wafer 900-17:pre-etch FTIR, etch, post-etch FTIR.**

# Water Soluble Residue on an As Deposited Wafer



# New Features Appear in FTIR After AHF Etching

*Revisited*

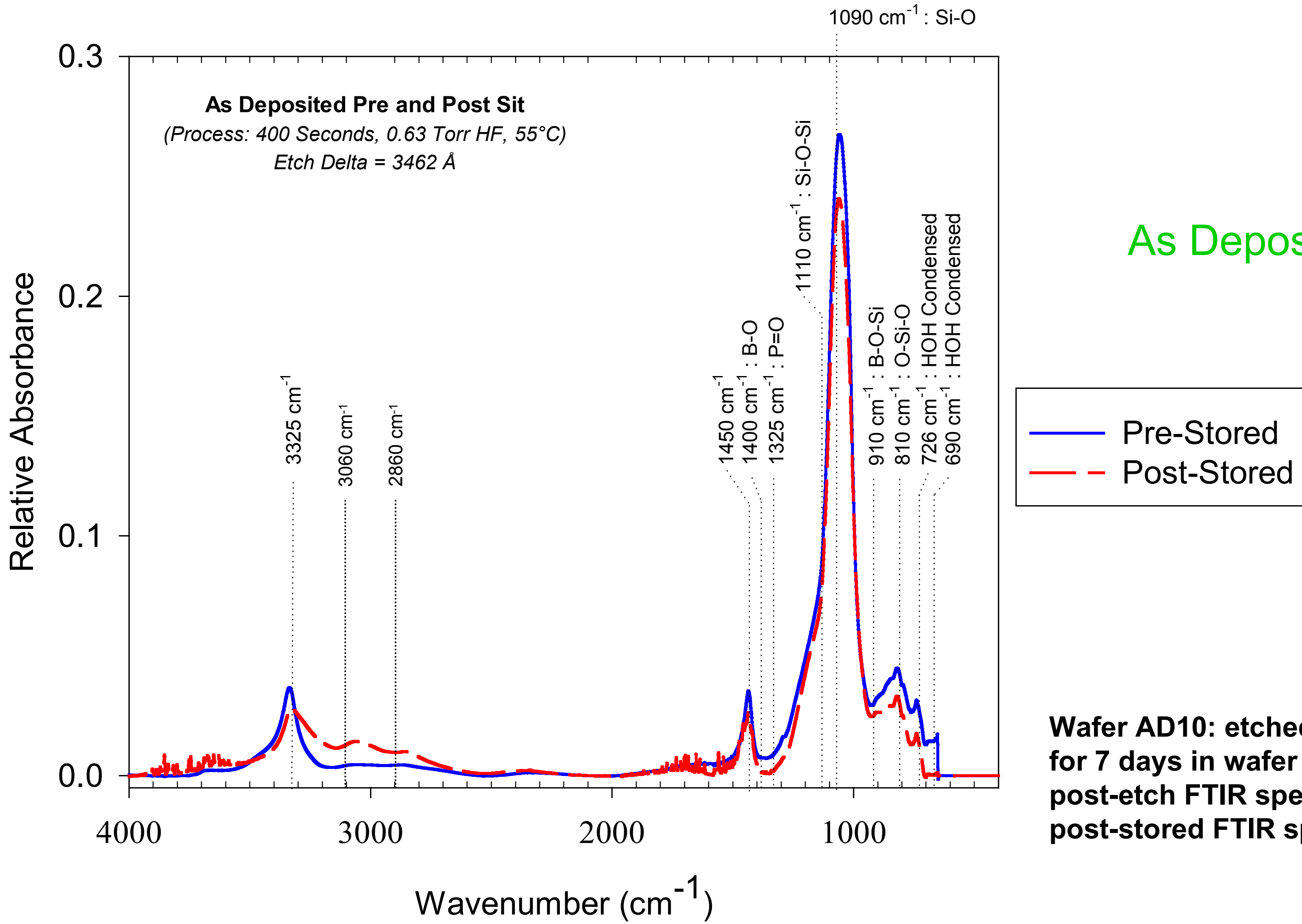



Difference Spectrum (Post-etch – Pre-etch)

As Deposited 3462 Å etched

**Wafer AD10:pre-etch FTIR, etch, post-etch FTIR.**

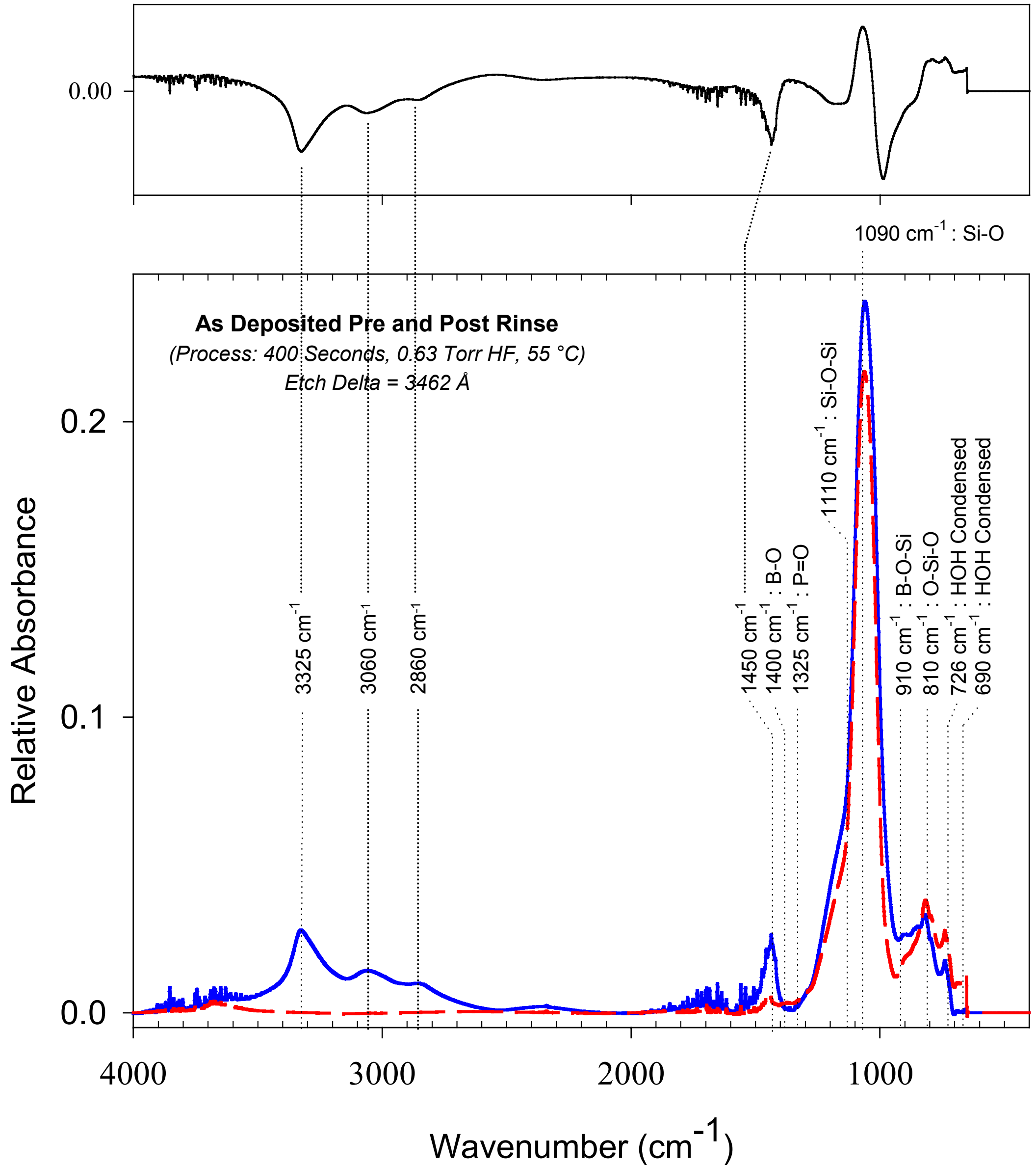
# Residue's Composition Changing With Time




As Deposited

**Wafer AD10: etched then stored for 7 days in wafer box: post-etch FTIR spectrum, post-stored FTIR spectrum.**

# Water Soluble Film Forms on the Wafer Surface

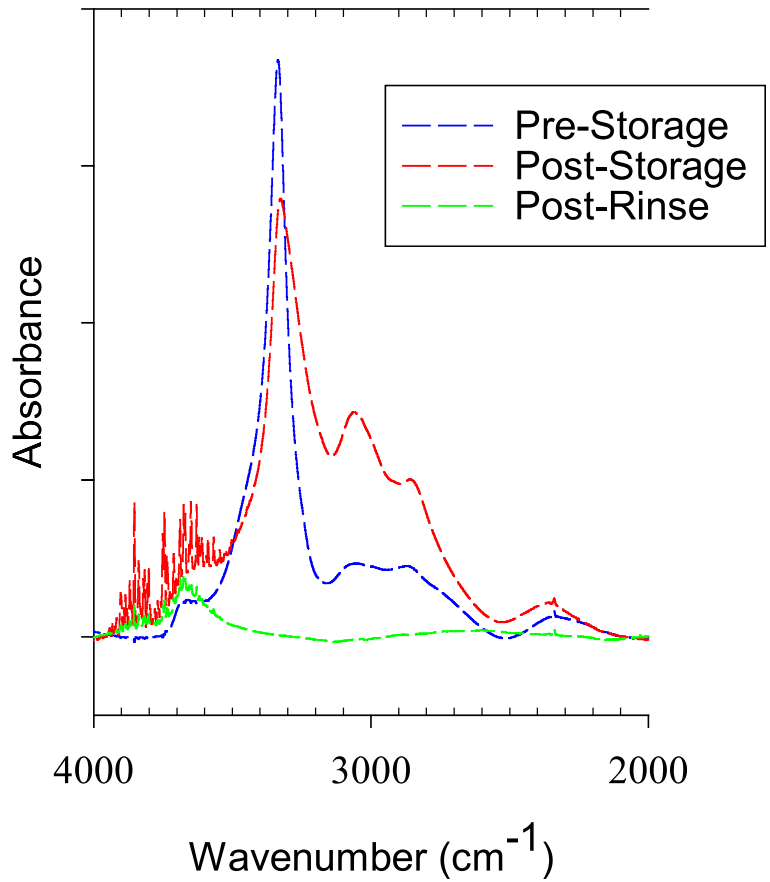



Difference Spectrum
(Post-rinse – Pre-rinse)

As Deposited

**Wafer AD10: etched then stored for 7 days in wafer box; pre-rinse FTIR spectrum, rinse, post-rinse FTIR spectrum.**

# Comparison of an As Deposited Film in O-H Stretching Region

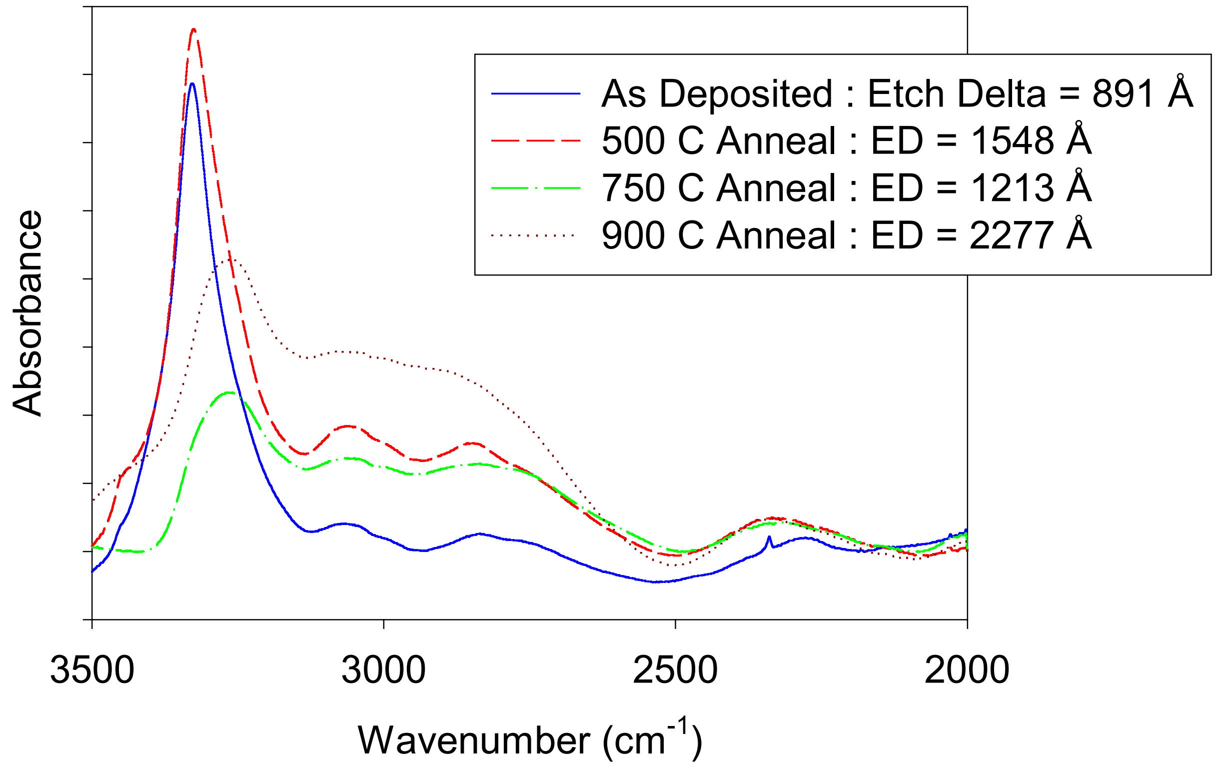



As Deposited

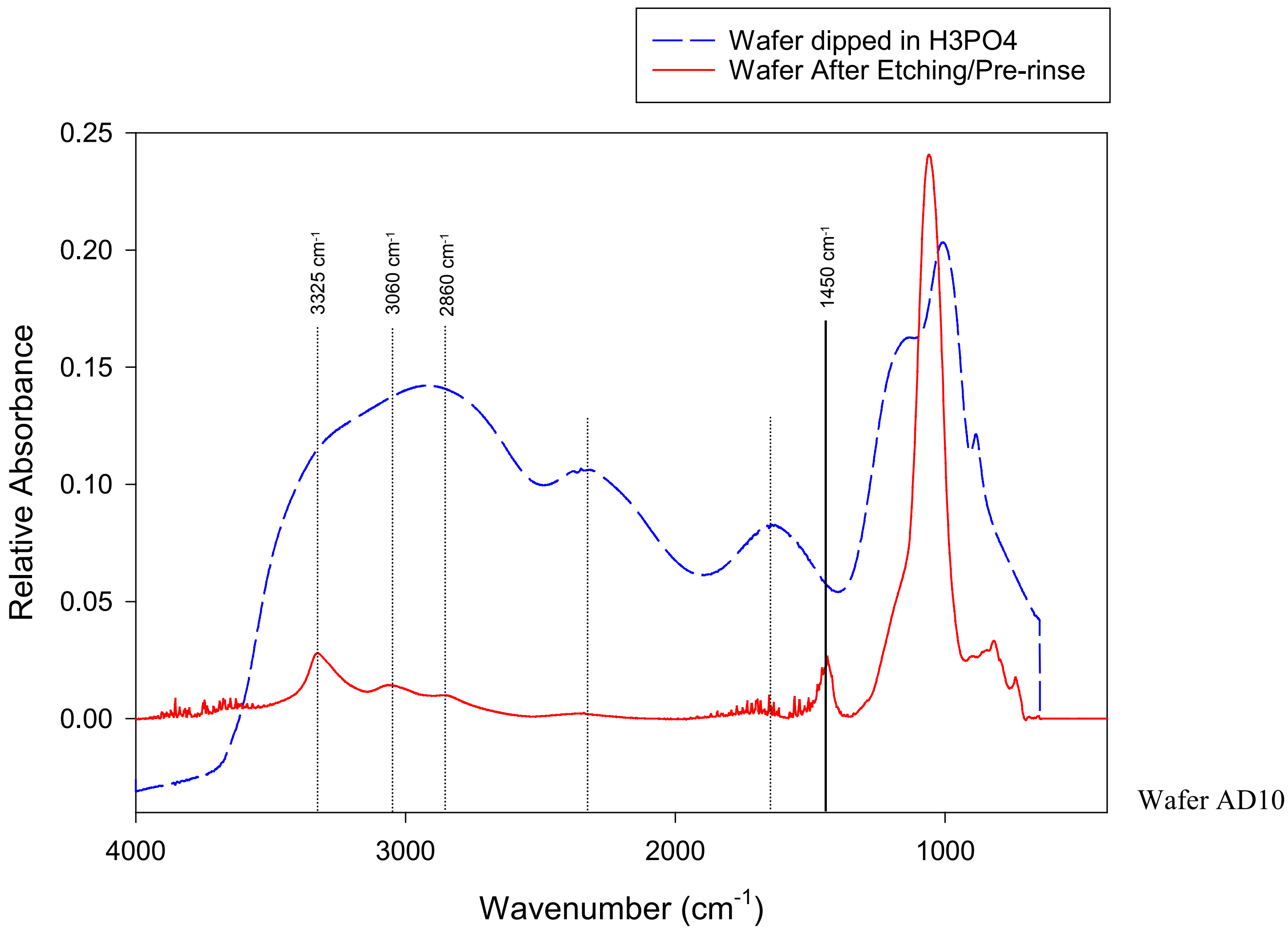
**Wafer AD10: etched then stored for 7 days in wafer box; post-etching FTIR spectrum, pre-rinse FTIR spectrum, post-rinse FTIR spectrum.**

# Comparison of Various Films in O-H Stretching Region

- *Features seem to be related to anneal temperature.*

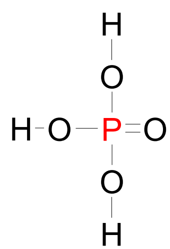


# Comparison of Etched, Rinsed Film to Wafer Dipped in 85% $H_3PO_4$ / 15% HOH Solution

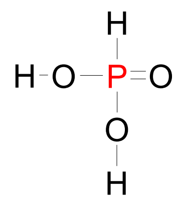


# Chemistry of BPSG Films After Etching

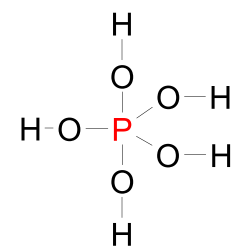
- *FTIR indicates presence of P-containing acid on wafer surface.*

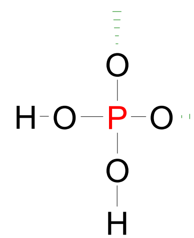


Phosphoric Acid



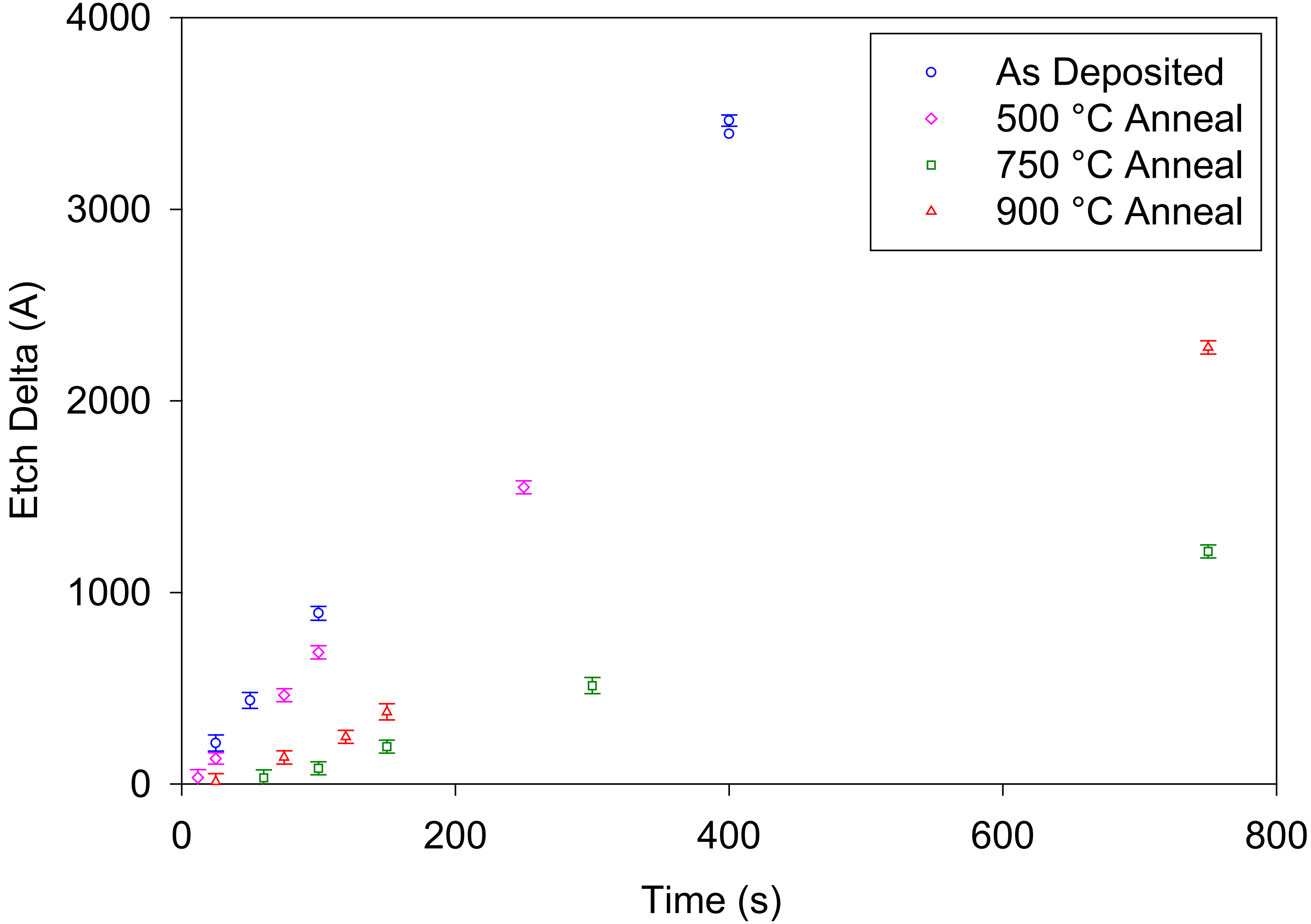
Phosphorous Acid



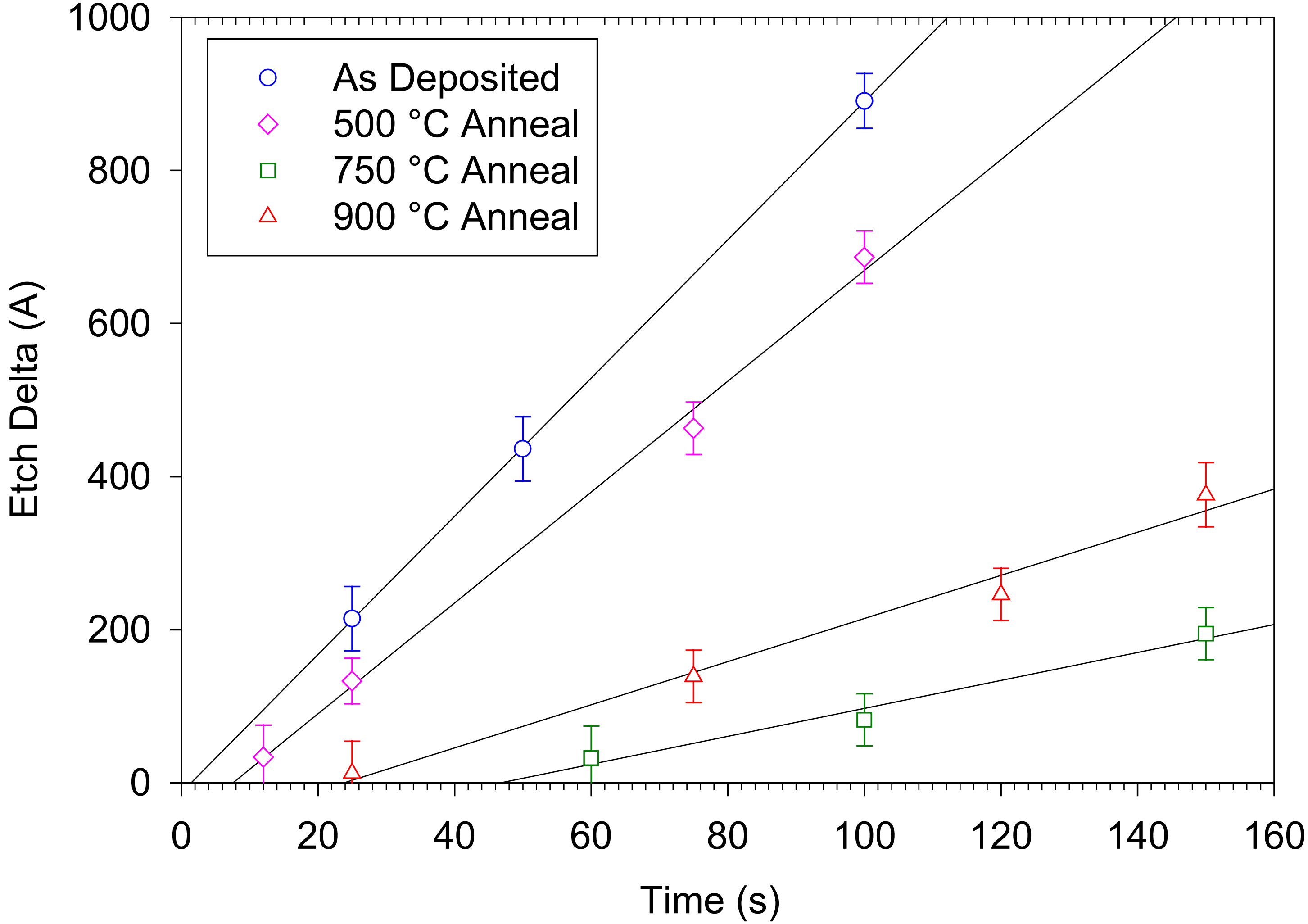


- *Acid film visually present on wafer surface.*
- *OH-bearing components in films on wafer surfaces depend on annealing temperature.*
  - *FTIR (not shown) indicate that wafer characteristics, not etching time determines composition of P-containing film.*

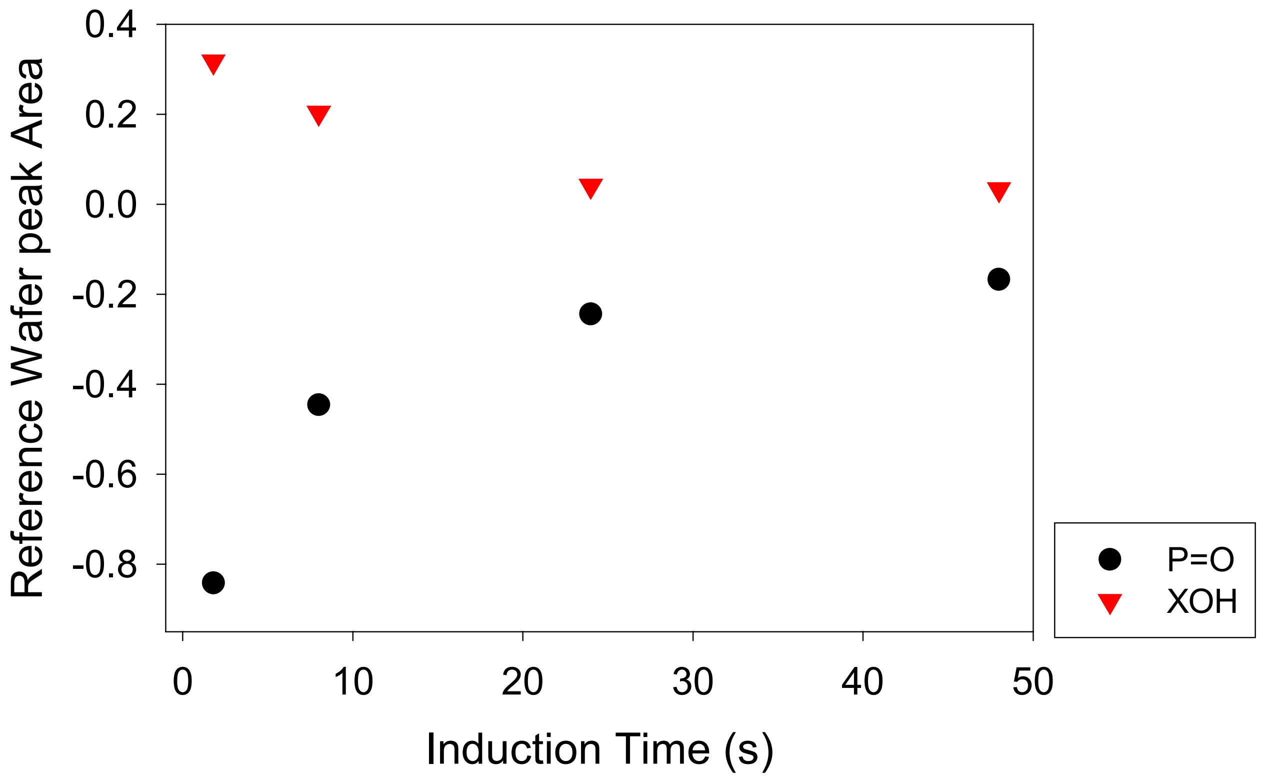
# 55°C AHF Etching Results: No Rinse



# Induction Time Associated with Etching



# *Induction Time Dependence on Peak Areas*




- *Induction time drops when absorbed water is increased and P=O is reacted.*
- *Note 750°C induction t much longer and rate lower than at 900°C, even though 750°C film contains same absorbed HOH and less P=O at start as well as lower anneal T. Other factors?*

# Conclusions

- *Absorbed water reacts with P=O groups in the BPSG film.*
- *Water soluble P-acid products after AHF etching depend on initial film characteristics.*
- *Induction time and AHF etching rate correlate with absorbed water/P=O.*
  - *Sensitive dependence on absorbed HOH and P=O at highest anneal T's.*
  - *Etching behavior depends on initial film character even though ratio of product water to absorbed water large.*
  - *Results suggest that induction is due to attack of HF at weakest X-O bonds in film.*
    - *HF and HOH diffusion through film.*
    - *Film density and stress.*

# Future Work

- *Measure etching activation energies for annealed films.*
  - *Annealing dehydroxylates film producing Si-O-Si.*
  - *Si-O-Si, Si-OH, B-O, P-OH, P=O.*
- *Investigate additives to react P-acid from surface.*
  - *Control product layer thickness.*
  - *Dependence on P-acid product/anneal?*
- *Does B form $B(OH)_3$?*
- *Investigate film chemistry during induction using integrated processing apparatus.*

# *Acknowledgements*

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