Synergistic damage effects of VUV photons/O_2 in SiCOH low-*k* films

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Nov. 9th, 2009

Objectives

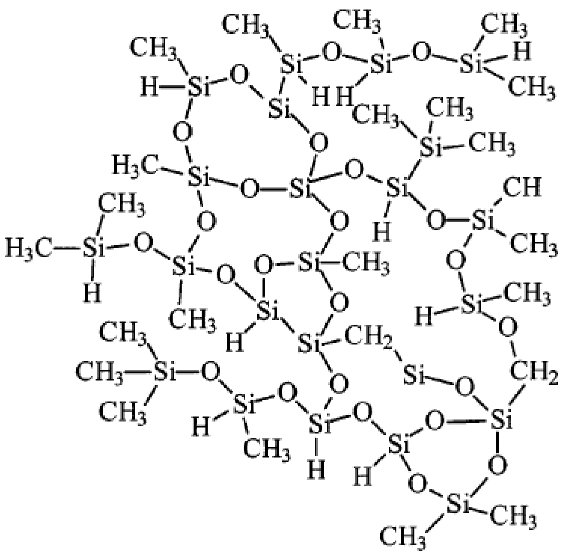
- VUV photons and O_2 molecules interact synergistically to cause major damage in highly porous SiCOH.

- Use of a VUV lamp in a beam system can effectively simulate the VUV damage that occurs to porous SiCOH in plasma studies.
  - Individual species and their combined effect can be analyzed in a highly controlled environment.

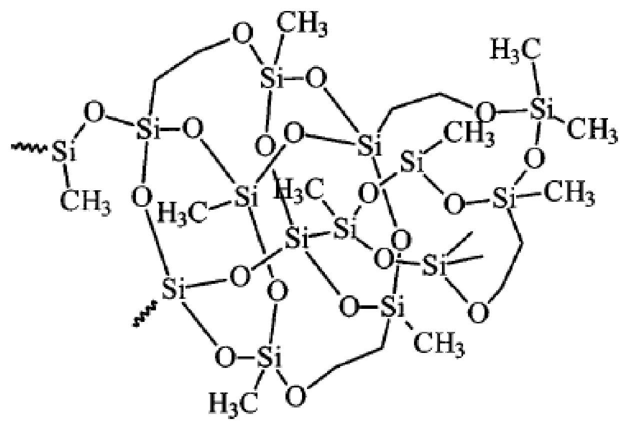
- Manipulation of diffusivity can cut off VUV/O_2 synergistic effects, thereby decreasing damage.

Highly-Porous SiCOH

Si-O-Si network

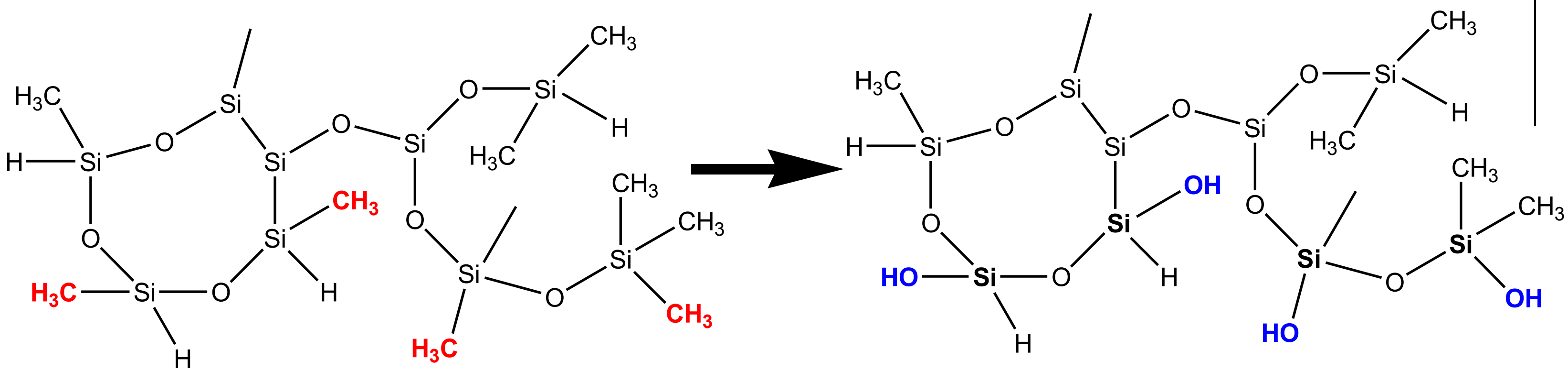


Si-O-Si cage



- Small amounts of porosity inherent due to carbon compounds.
- High pore interconnectivity
  - Porogen used to create highly diffusivity material.
- The material is very susceptable to damage from plasma processing.
  - Changes in film chemistry
  - Dielectric constant increase

Recent Focus



- Changes in dielectric constant have been correlated to the replacement of –CH_3 bonds with –OH bonds due to water vapor reaction.

- Plasma chemistry studies
  - Gas chemistry has an effect
    - Reactive gases cause more damage

- Isolation of plasma components
  - Ions can cause pore collapsing
  - VUV photons and gas radicals potentially change film chemistry.

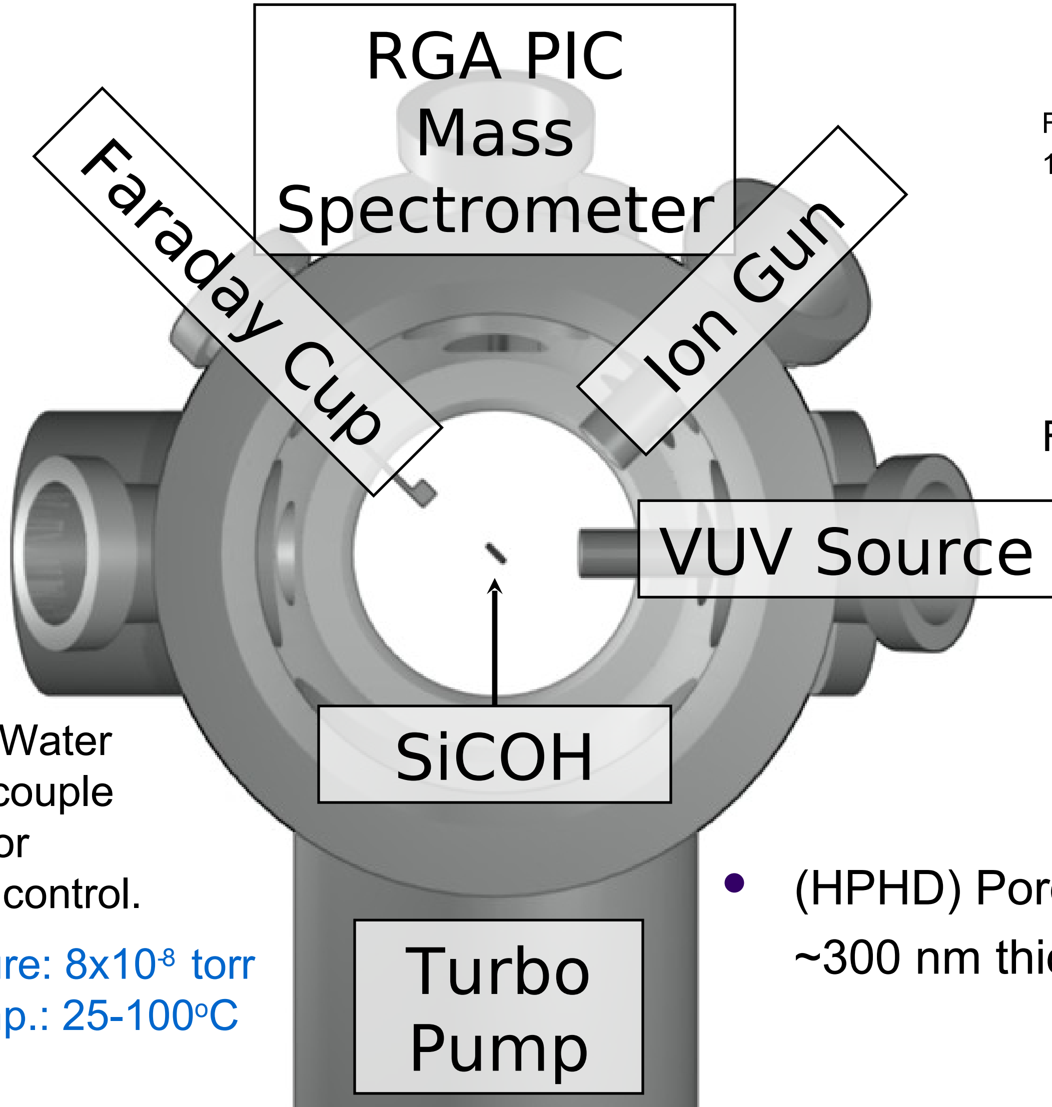
Gas	Flow rate (sccm)	View	Total flux 70–140 nm
C_2F_6	10	Through wafer	11.1
C_2F_6	10	Side view	3.6
CHF_3	10	Through wafer	30.3
CHF_3	10	Side view	9.8
$Ar/C_2F_6/H_2$	10/10/10	Through wafer	176
$Ar/C_2F_6/H_2$	10/10/10	Side view	50.3
Ar	10	Through wafer	350
Ar	10	Side view	22
O_2	10	Through wafer	56.2
O_2	10	Side view	12.7

(10^{14} $cm^{-2}s^{-1}$)

Plasma VUV Emissions

J. R. Woodworth *et al.*, Journal of Vacuum Science & Technology A **19**, 45 (2001).

Experimental Setup



Flux = 2.7×10^{14} ions/(cm^2 s)
150-500 eV Ar+ ions

Flux = 1.3×10^{14} photons/(cm^2 s)

λ= 147 nm

Xe excimer lamp

Not shown: Water bath/thermocouple connection for temperature control.

Base Pressure: 8×10^{-8} torr
Sample Temp.: 25-100°C

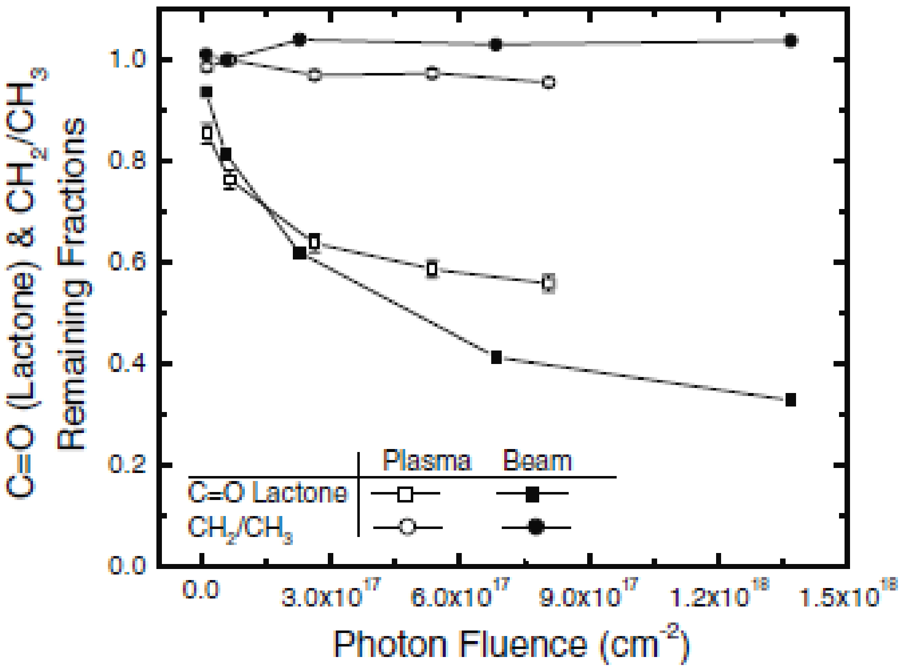
- (HPHD) Porous ULK (k = 2.54)
  ~300 nm thick

NOVELLUS

Plasma vs. Beam System

Plasma		Beam System	
Photons Ions Electrons Radicals Neutrals	Simultaneous	Photons Ions Neutrals	Controllable

- Studies have shown comparable VUV results between Ar plasma and Xe VUV lamp exposures for 193 nm photoresist.
  - Similar chemical changes
  - Different rate of these changes are due to different VUV wavelengths.
    - Ar (104, 106 nm), Xe lamp (147 nm)

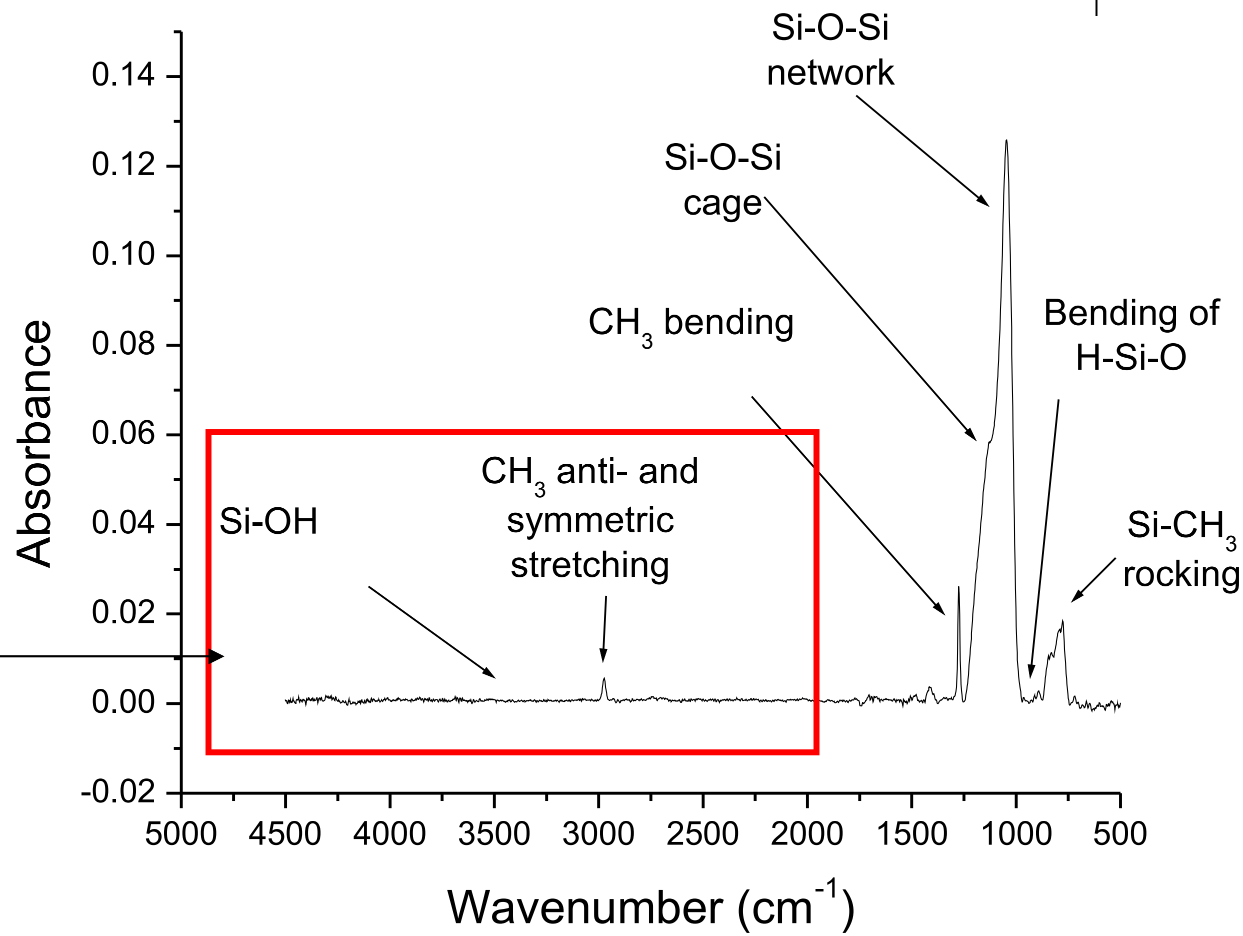


M.J. Titus *et al.*, J. Phys. D: Appl. Phys. **42** (2009).

FTIR of porous ULK

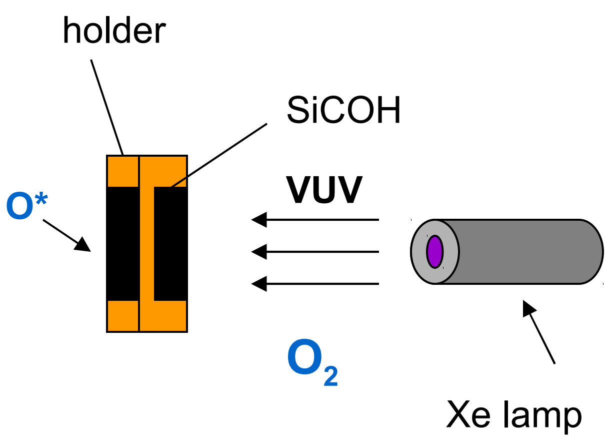
Region of Focus:

3800-2800 cm^{-1}

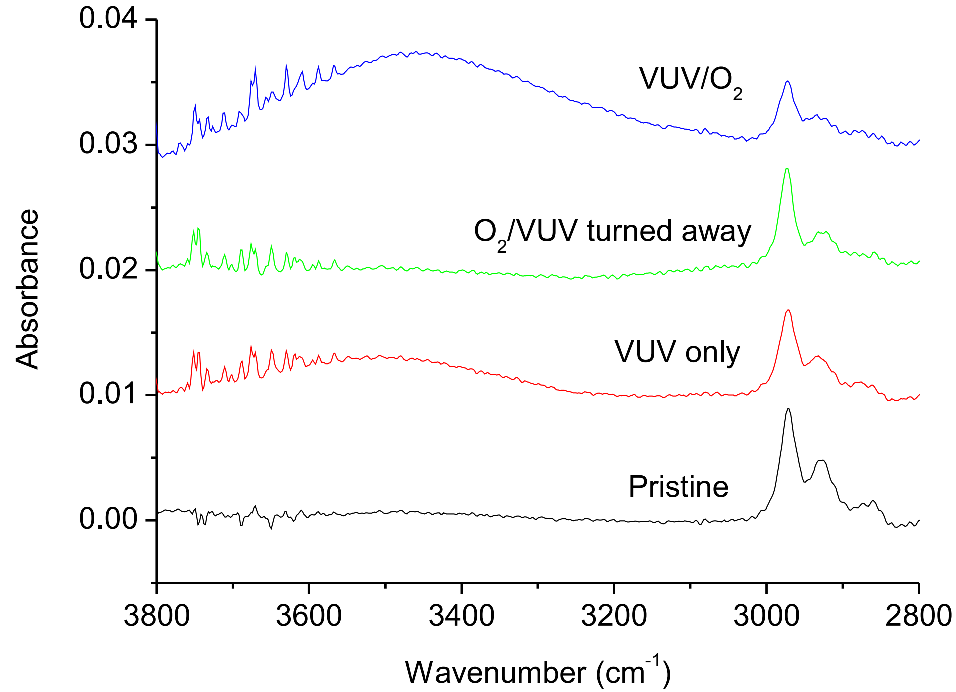


VUV/O_2 exposures

1 hr exposures

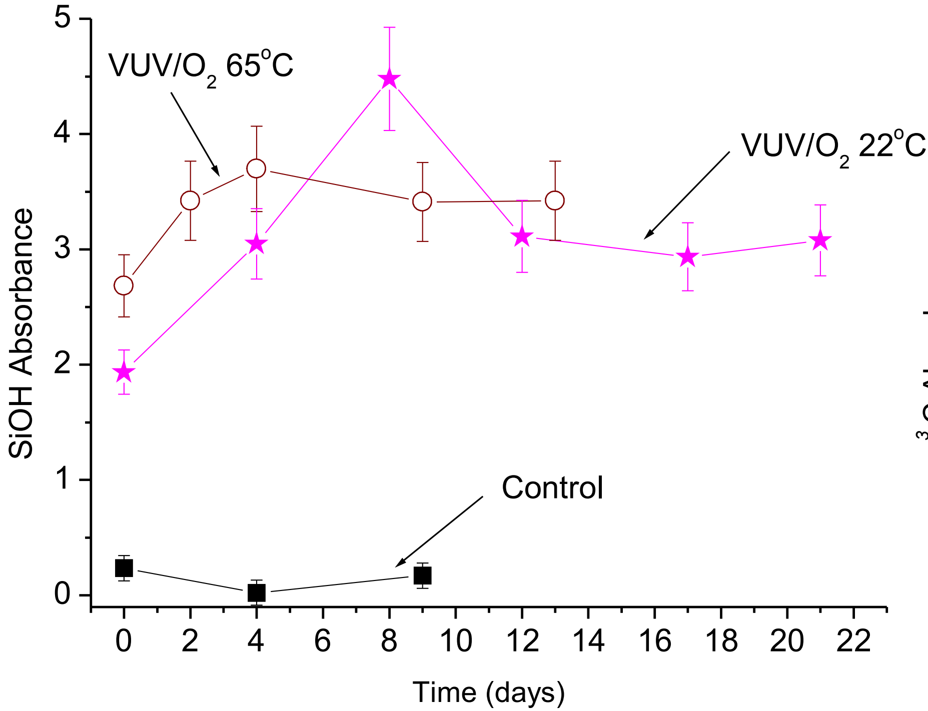


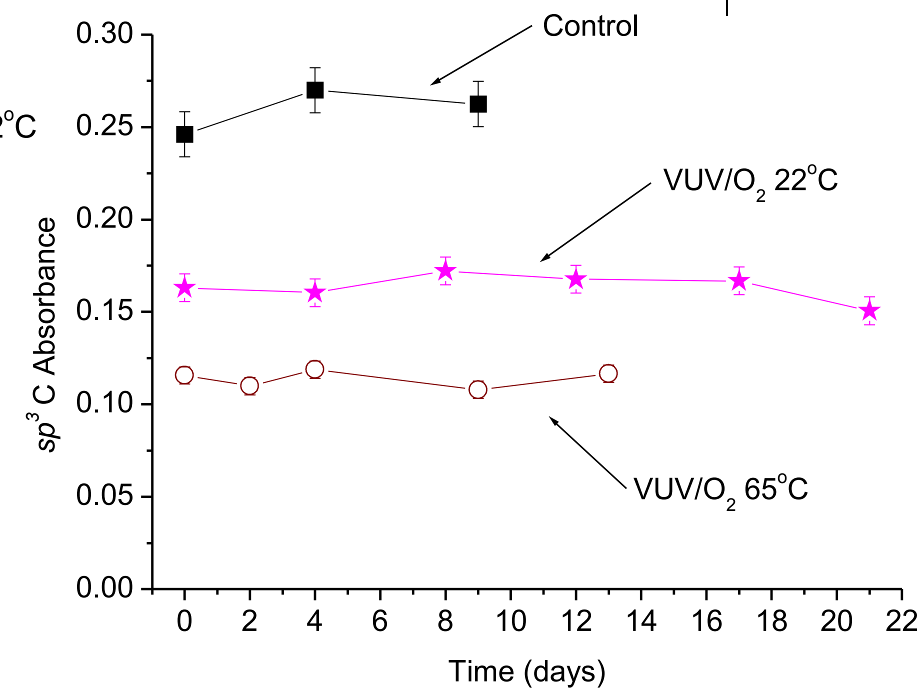
$$O_2 + h\nu \rightarrow 2O$$



- SiOH broad peak and *sp*^{3} carbon loss only seen for VUV exposed samples in *ex situ* FTIR.
- Simultaneous exposure with VUV/O_2 increases level of damage.

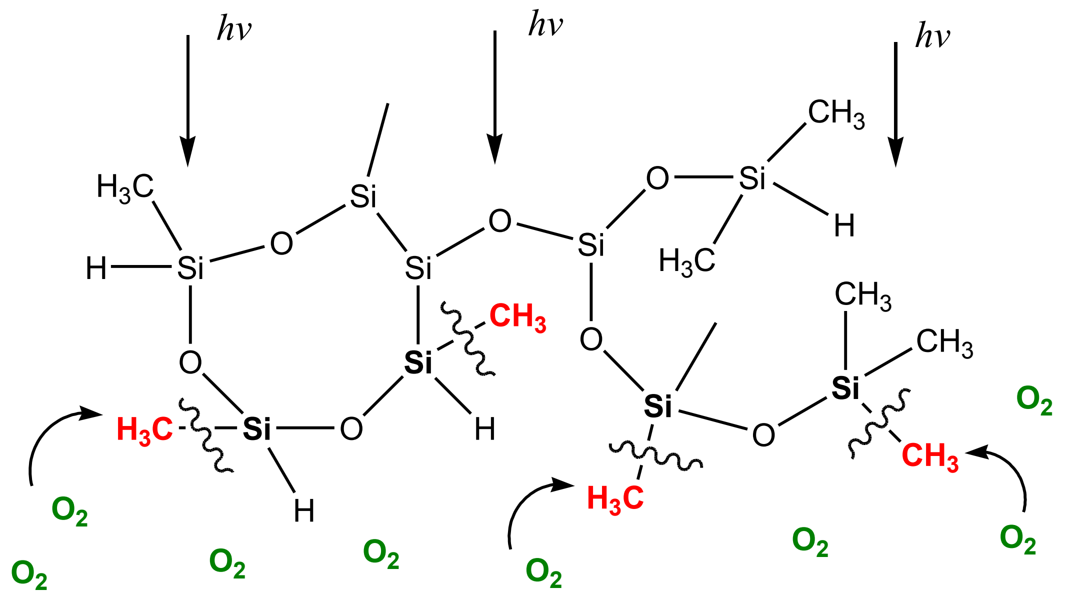
Simultaneous VUV/O_2





- VUV/O_2 simultaneous exposure shows much larger SiOH increases and requires more time to saturate in atmospheric condition.
- *sp^3* C peak remains relatively constant post-exposure.
- Si dangling bonds generated from VUV radiation appear long-lived.

Simultaneous VUV/O_2



- CO_2 and H_2O reaction products are seen from the RGA mass spectra.
- O_2 is interacting with photo-desorbed methyl.
- Generated H_2O can then react with Si dangling bonds to form SiOH.

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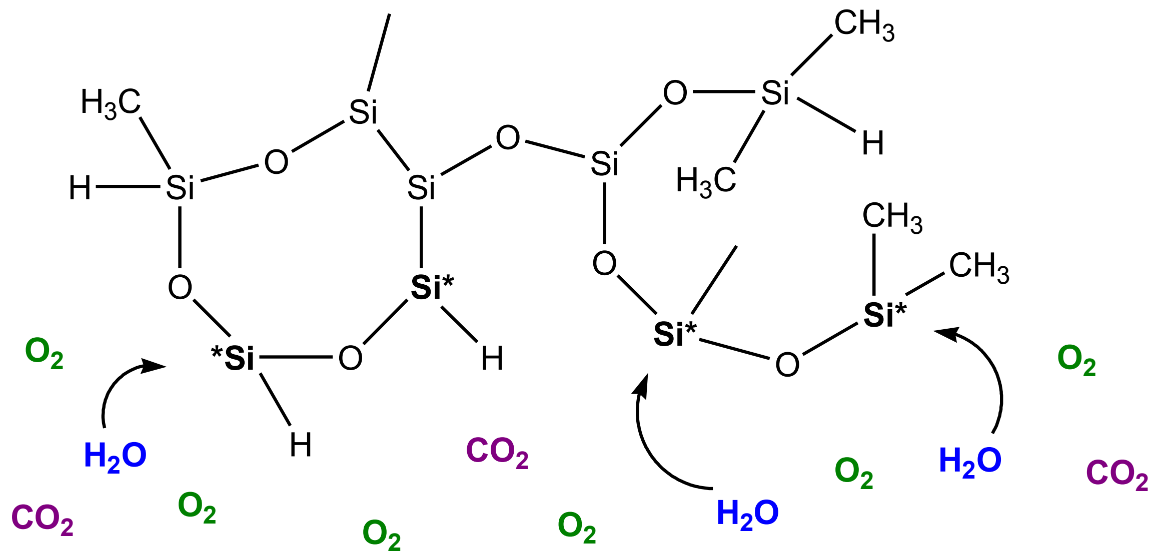
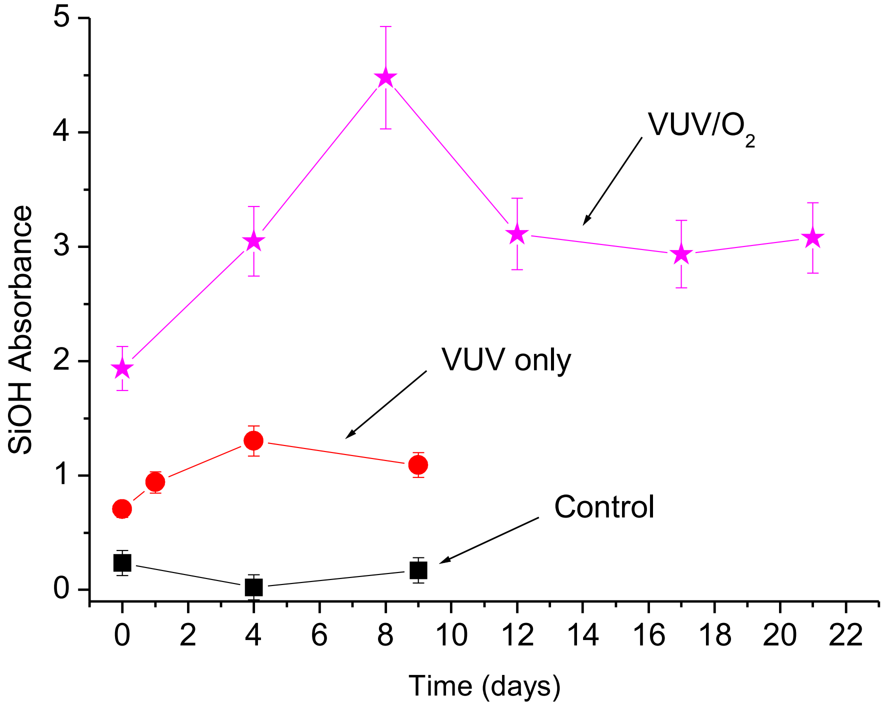
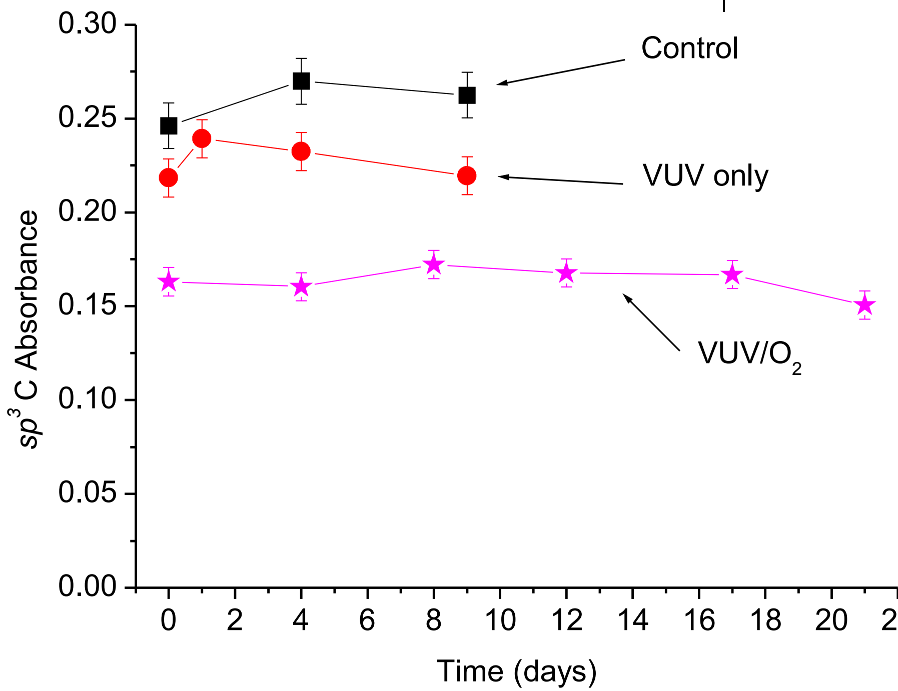


- CO_2 and H_2O reaction products are seen from the RGA mass spectra.
- O_2 is possibly interacting with photo-desorbed methyl.
- Generated H_2O can then react with Si dangling bonds to form SiOH.

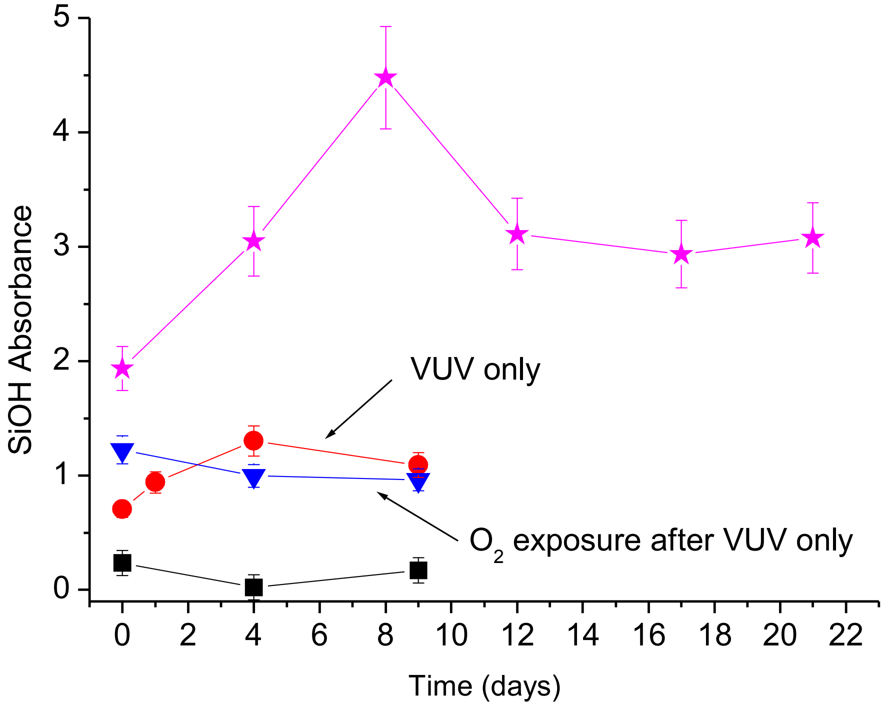
VUV/O_2 effects

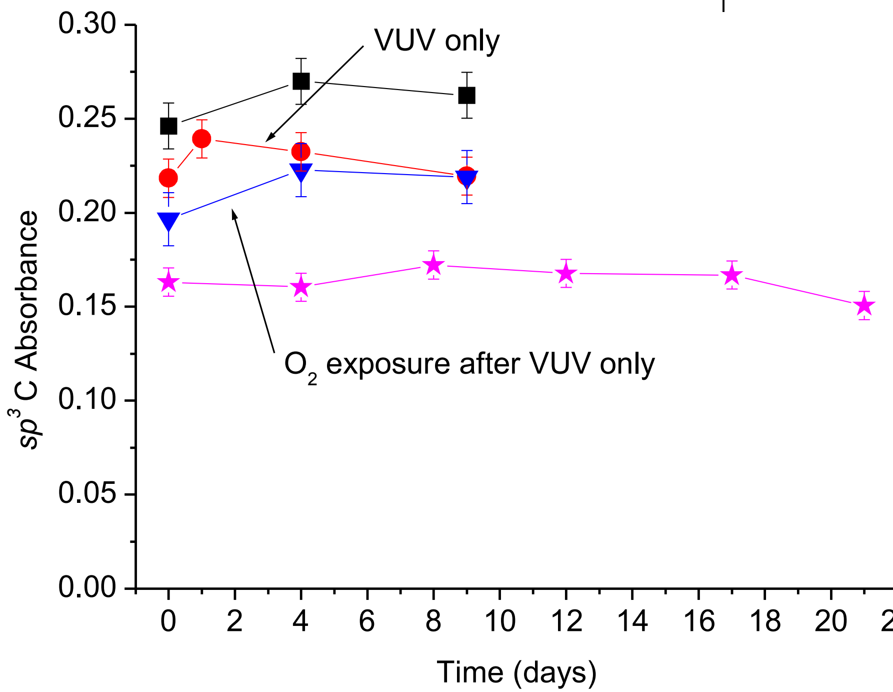




- Damage by VUV photons alone is small.
- Only small amounts of SiOH generation and *sp*^{3} C loss can be seen if the sample is exposed to O_2 immediately after VUV exposure.
- High levels of damage only occur for **simultaneous exposure to VUV and O_2**.

VUV radiation alone





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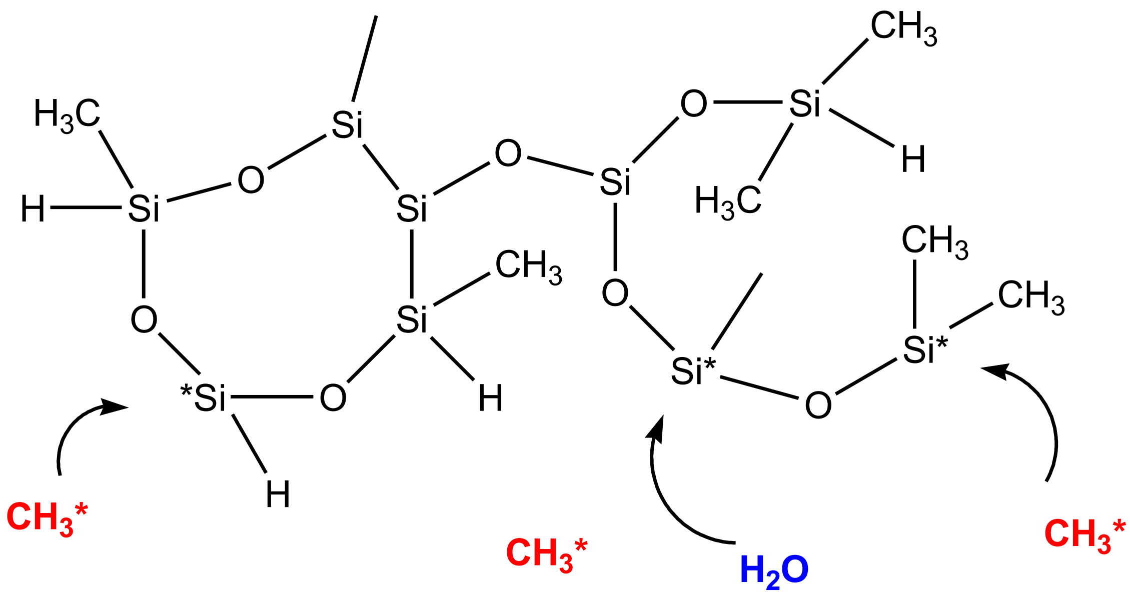


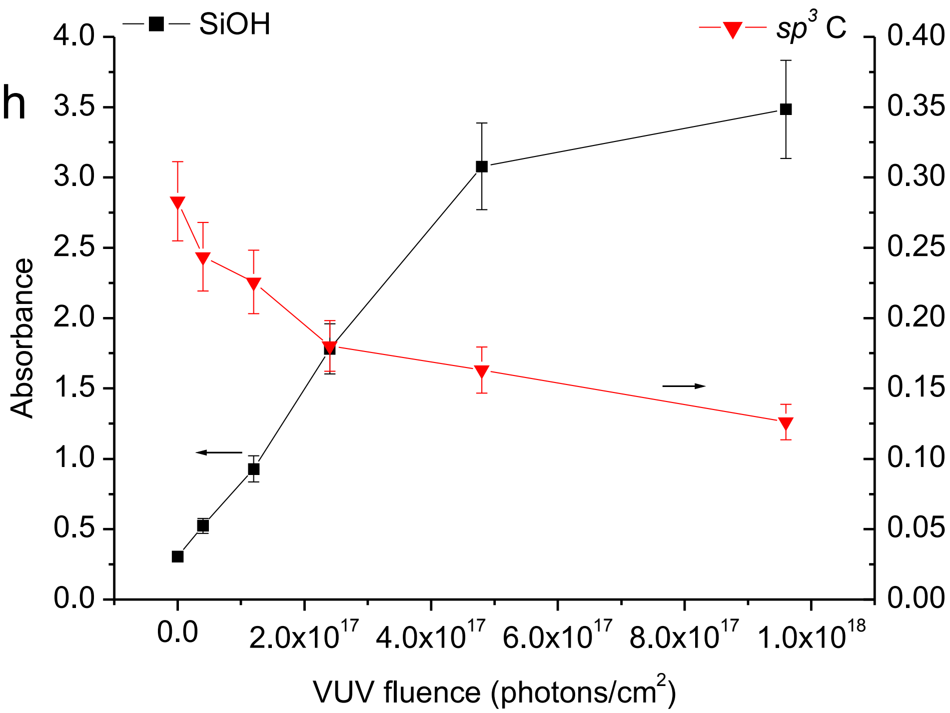
- Due to the lack of oxygen, H_2O and CH_3^* compete for reaction with the Si dangling bond.
- With low amounts of H_2O present, most of the damage is repaired from Si-CH_3 recombination.
- Recombination appears rapid because O_2 did not have large effects without VUV radiation present.

Effects of Exposure Time

- Increasing VUV fluence increases damage.
- Loss of *sp*^{3} carbon and SiOH generation is fairly linear until high fluences.

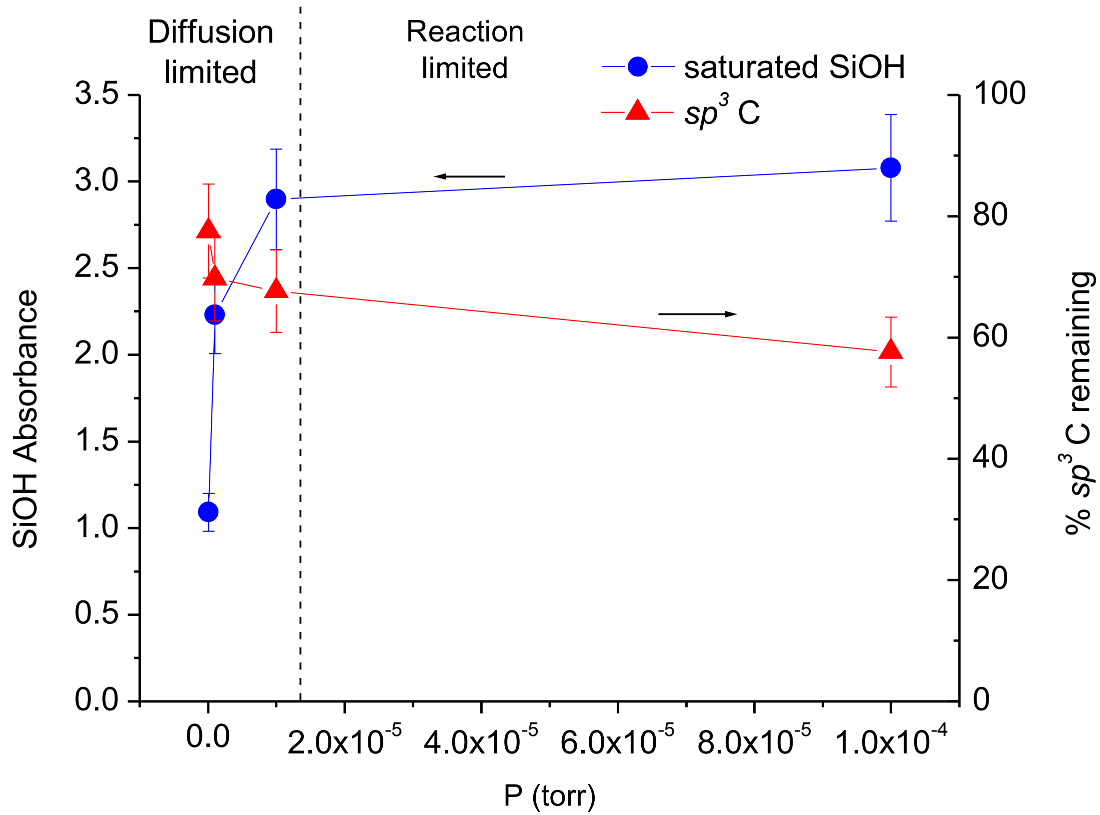
- Typical plasma exposures can reach such fluences in minutes.
  - Ar ICP Plasma (no bias):
    - 70 Watt, 10 mTorr (~10^{10} cm^{-3} density)
    - ~5 min for 10^{18} photons/cm^2

0-2hr exposures



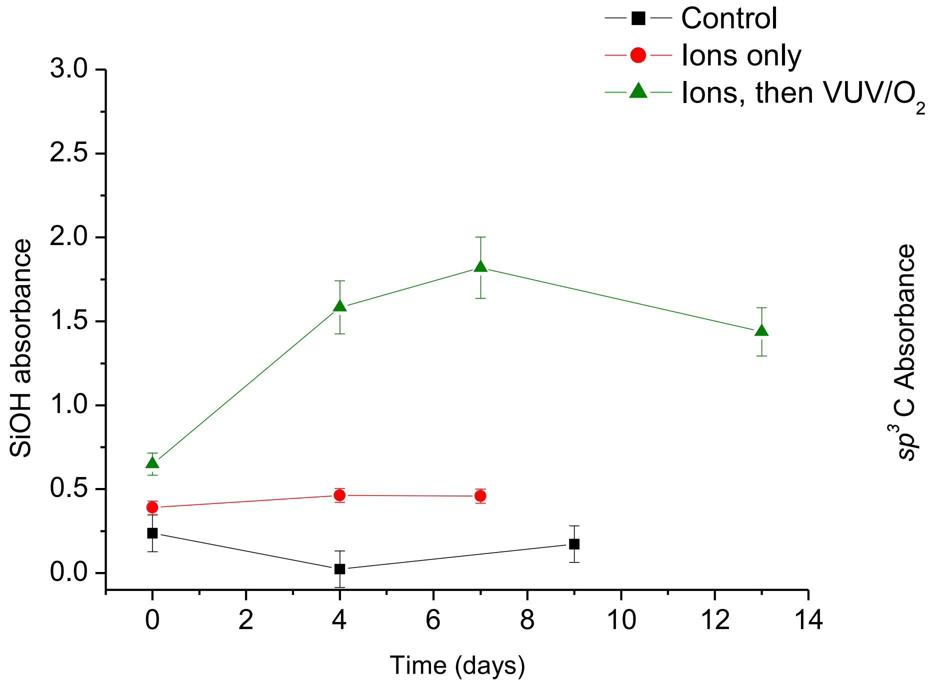
O_2 background pressure

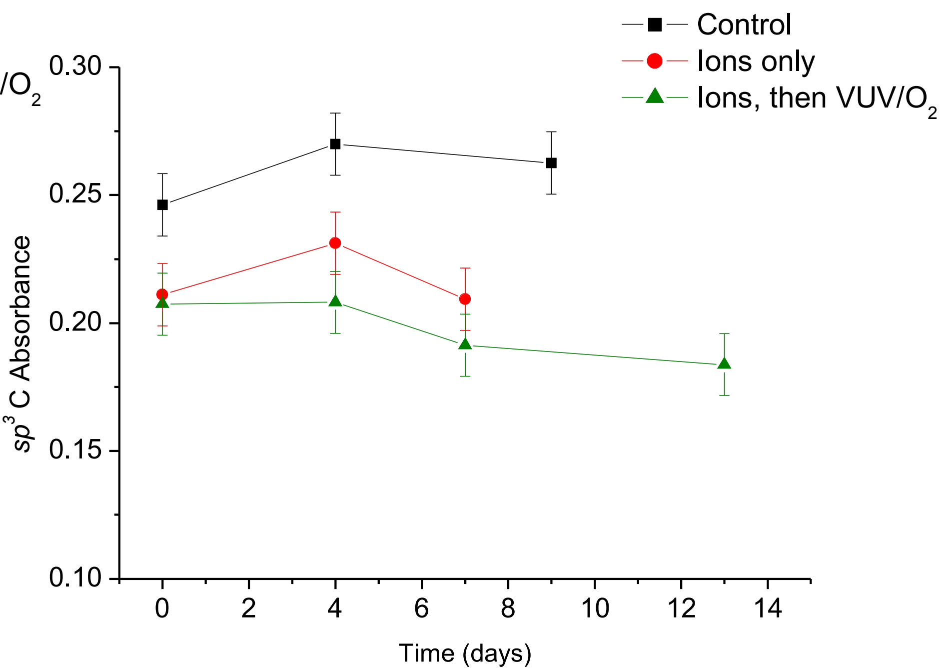
1 hr exposures



- Increased damage at higher pressures of O_2.
- Presence of small amounts of O_2 has detrimental effects.
- Loss in *sp³* carbon and gain in SiOH suggests a diffusion limited and reaction limited region, which implies that O_2 diffusivity is important for damage analysis.

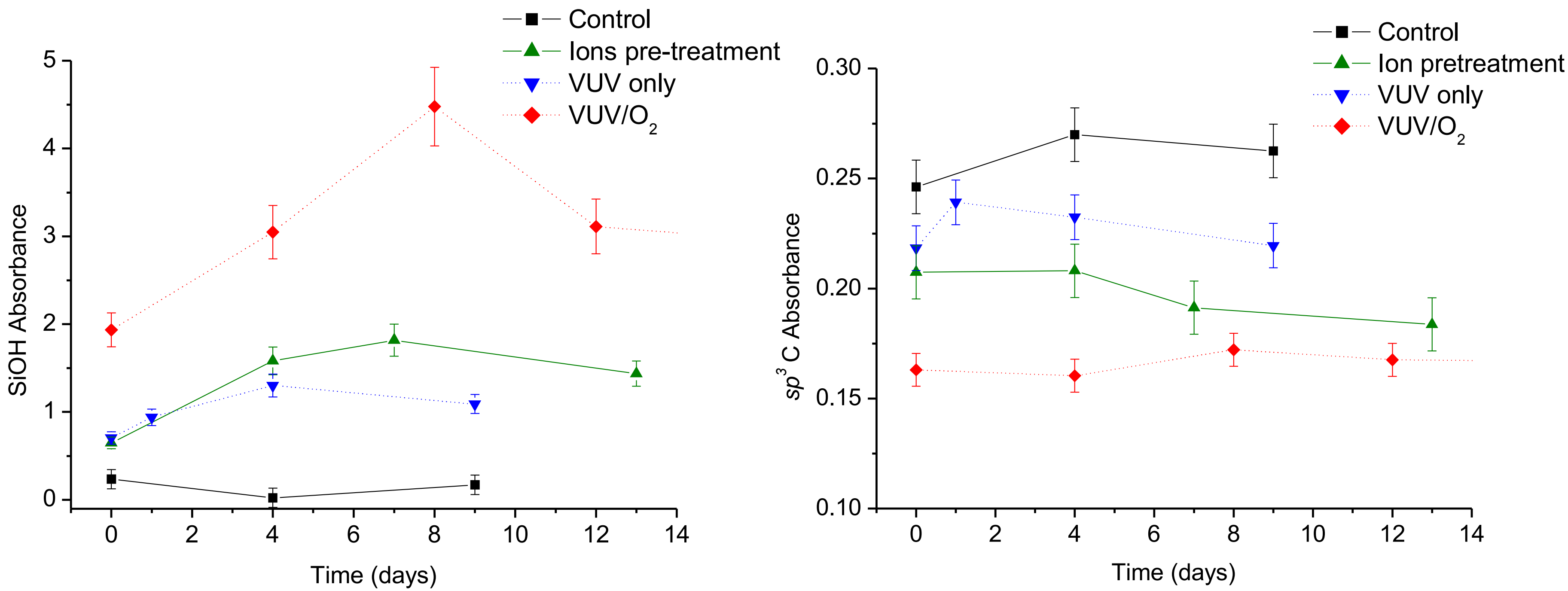
150 eV Ar^+ Ion Bombardment





- Ions have been suspected to cause surface densification.
- While ions decrease the carbon content, little generation of SiOH is seen.

150 eV Ar^+ Ion Bombardment



- Ion pre-treated sample decreases SiOH generation and carbon loss upon VUV/O_2 exposure.
- Densified surface layer appears to have formed, reducing the effect of O_2 exposure to photo-desorbed methyl.

Summary

- VUV photons and O_2 molecules react synergistically to form SiOH, leading to increased dielectric constant 'damage.'
- SiOH generation and carbon loss are functions of photon fluence, oxygen background pressure, and film diffusivity.
- Reduction of film diffusivity can potentially cut off this synergism, decreasing damage.
- Beam system studies performed in a highly controlled environment effectively simulate specific effects that occur in a plasma.

Acknowledgements

- John Coburn, Harold Winters, Dave Fraser
- Dustin Nest, Monica Titus, Ting Ying Cheung
- Semiconductor Research Corporation