Roles of vacuum ultraviolet radiation and ion bombardment in the roughening and degradation of photoresist polymers during plasma processing

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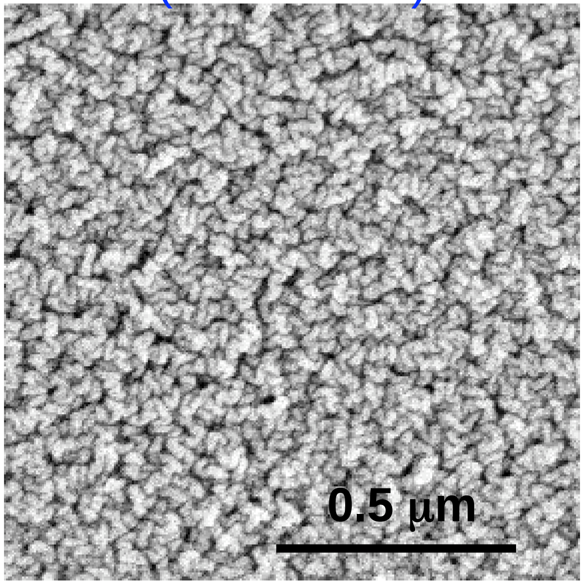
Plasma Applications Group

Introduction

- Motivation
  - Fundamental etching and roughening mechanisms of photoresist (PR) and polymer masking materials are poorly understood.
  - Tolerance for PR roughening is decreased as device dimensions shrink.

- Goals
  - Determine the dominant plasma species responsible for the etching and roughening of PR polymers.

800 W / 20 s Argon plasma (193 nm PR)



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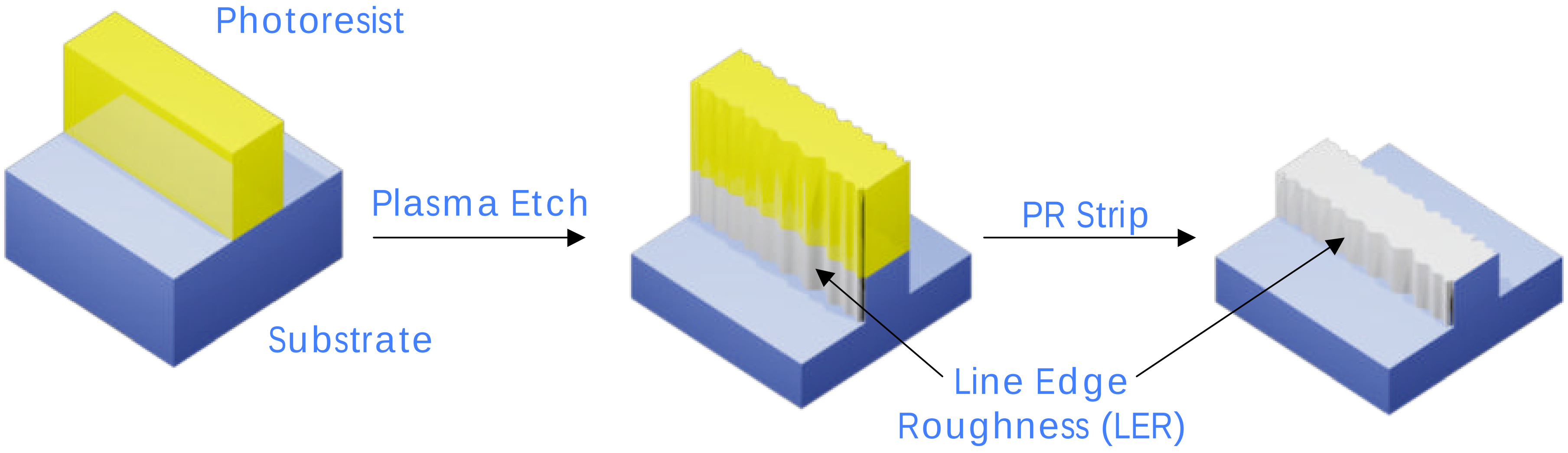

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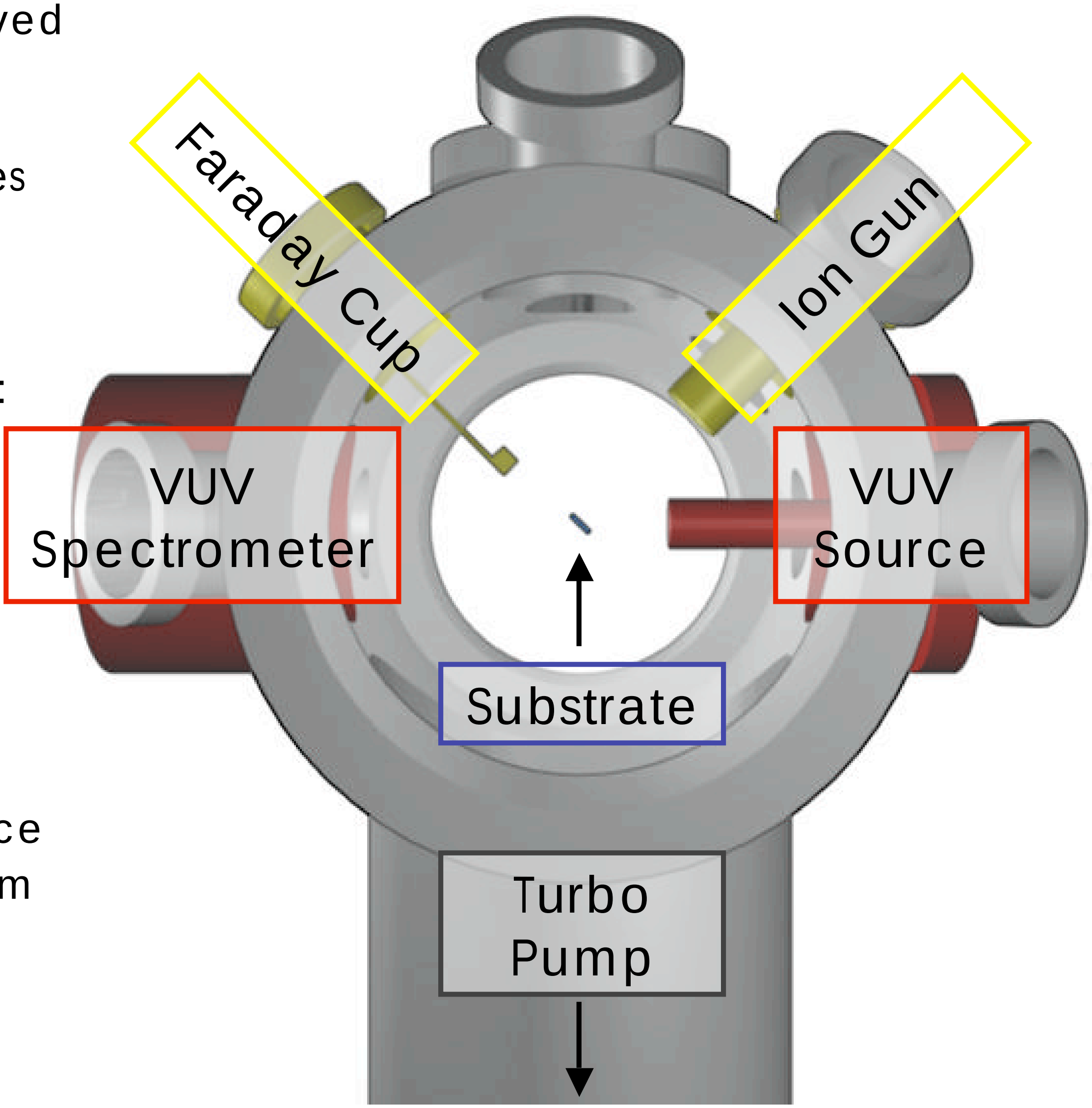
  - Determine the dominant plasma species responsible for the etching and roughening of PR polymers.
  - Investigate model polymers for next generation lithography.

- Outline
  - Beam system approach
  - 193 nm PR and 248 nm PR
  - Model polymers: P4MS and PaMS

Beam System Approach

- Determine which plasma species we believe contribute most to observed effects in the plasma.
- Create well-characterized sources which produce these species.
- Beam system
  - UHV Chamber, Base Pressure: ~5×10^{-8} Torr pumped with a 2000 L•s^{-1} turbo pump, rises to ~3×10^{-5} Torr when ion source is in use
- Commonwealth Ion Source
  - Normal incidence 150 eV Ar^+
- Resonance Xenon VUV Line Source
  - Source of high intensity 147 nm VUV radiation

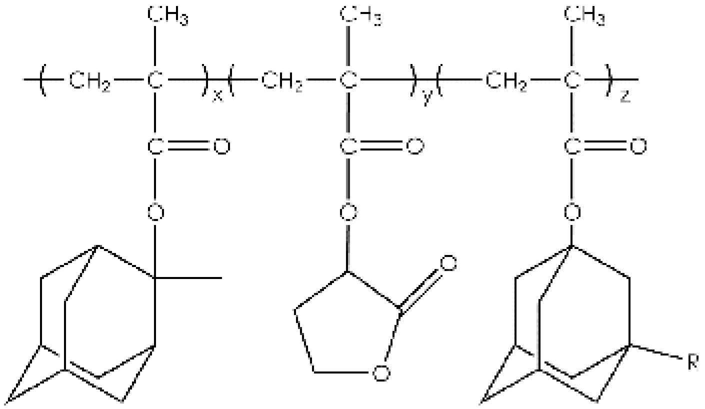


Current Photoresist Materials

» Rohm and Haas PR polymers (w/o PAG or base quencher):

- Sample size: 1 cm^2 (cleaved from 8” wafers coated by R&H)
- 250 nm thick 193 nm PR

193 nm PR



MAMA α-GBLMA RAMA

Bulk modifications observed with
ex situ Transmission FTIR:
C=O and C-O-C bond stretching
$-CH_3$ and $-CH_2-$ stretching

Mass loss observed with
polymer-coated QCMs

Surface roughness: AFM and SEM

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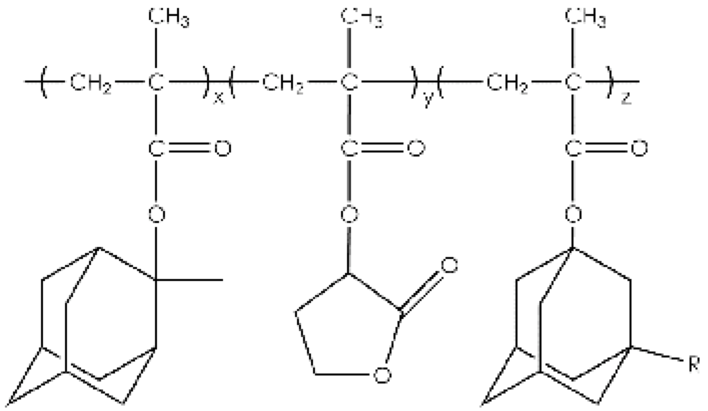
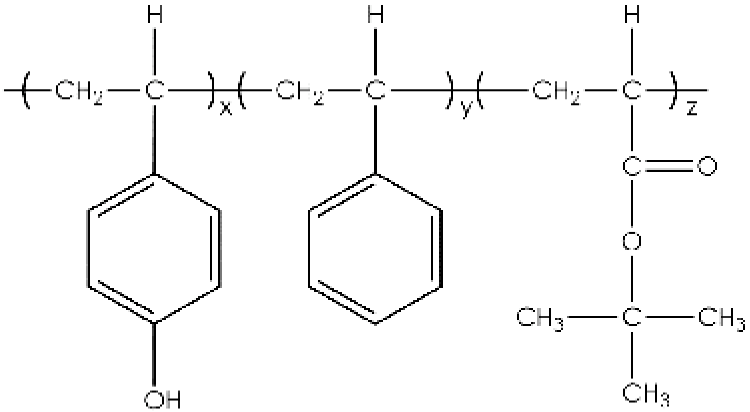


MAMA α-GBLMA RAMA

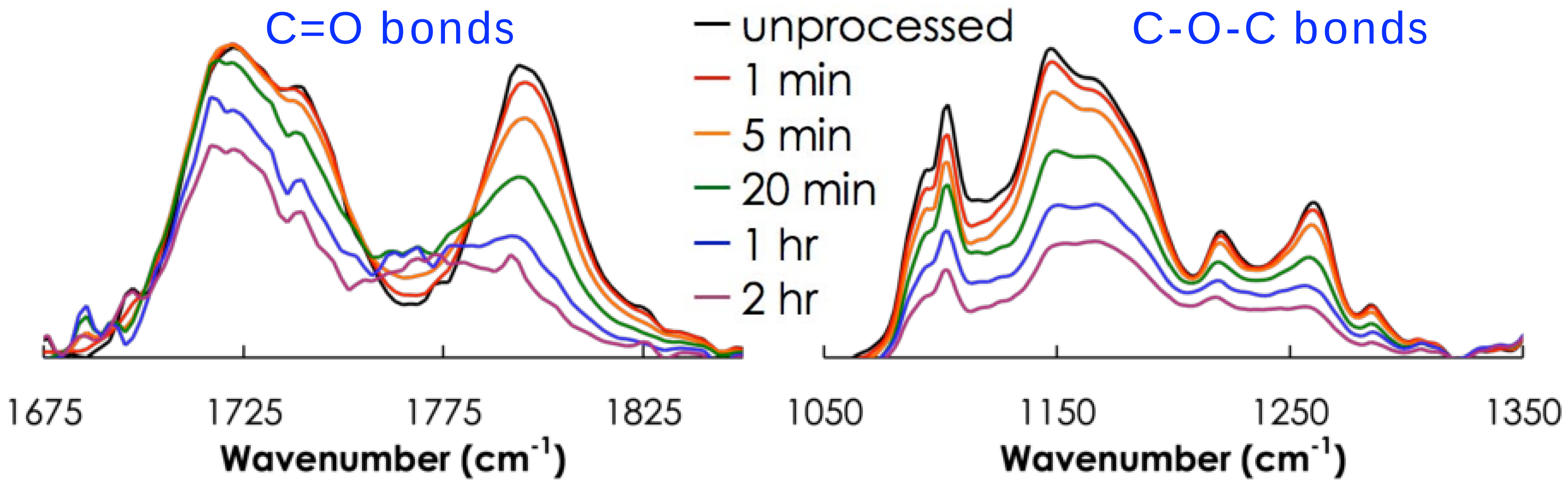
248 nm PR



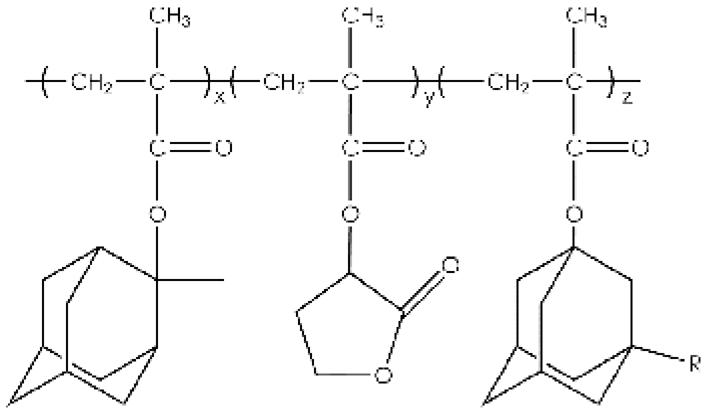
PHOST PS TBA

VUV radiation: bulk modifications

- 193 nm PR exposed to 147 nm VUV (1 min to 2 hrs, 1.9×10^{14} photons/(cm^2•s))
- Bulk chemical modifications observed ex situ with Transmission FTIR



193 nm PR



- Bulk modifications of C=O and C-O-C bonds are observed.
- Very important due to the relatively high oxygen content of 193 nm PR.

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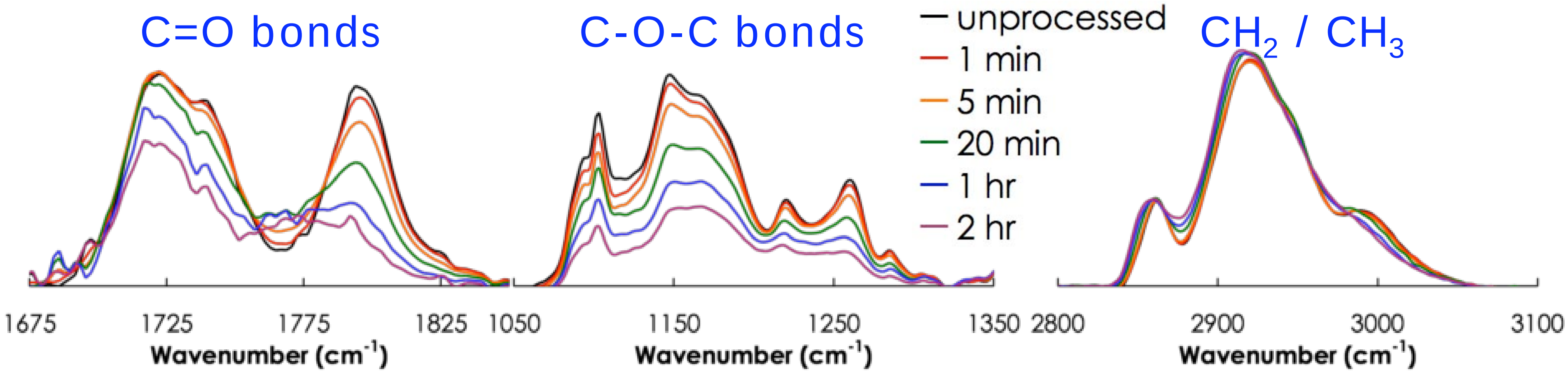
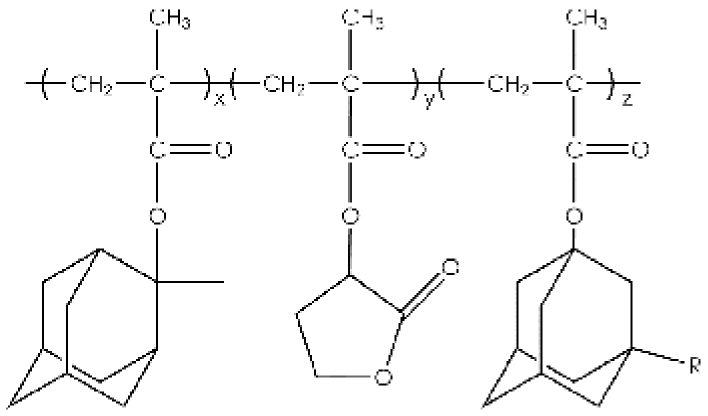
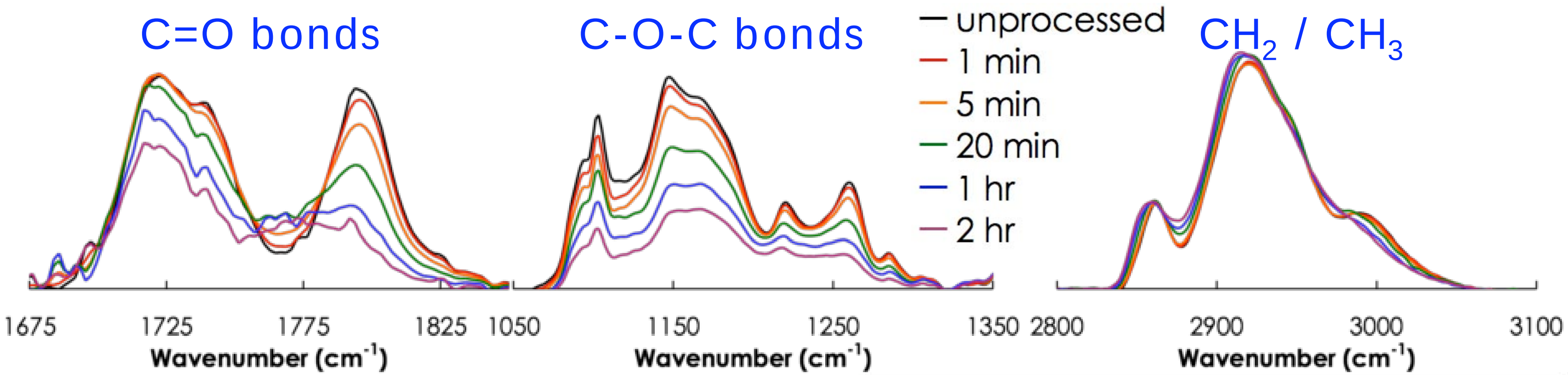
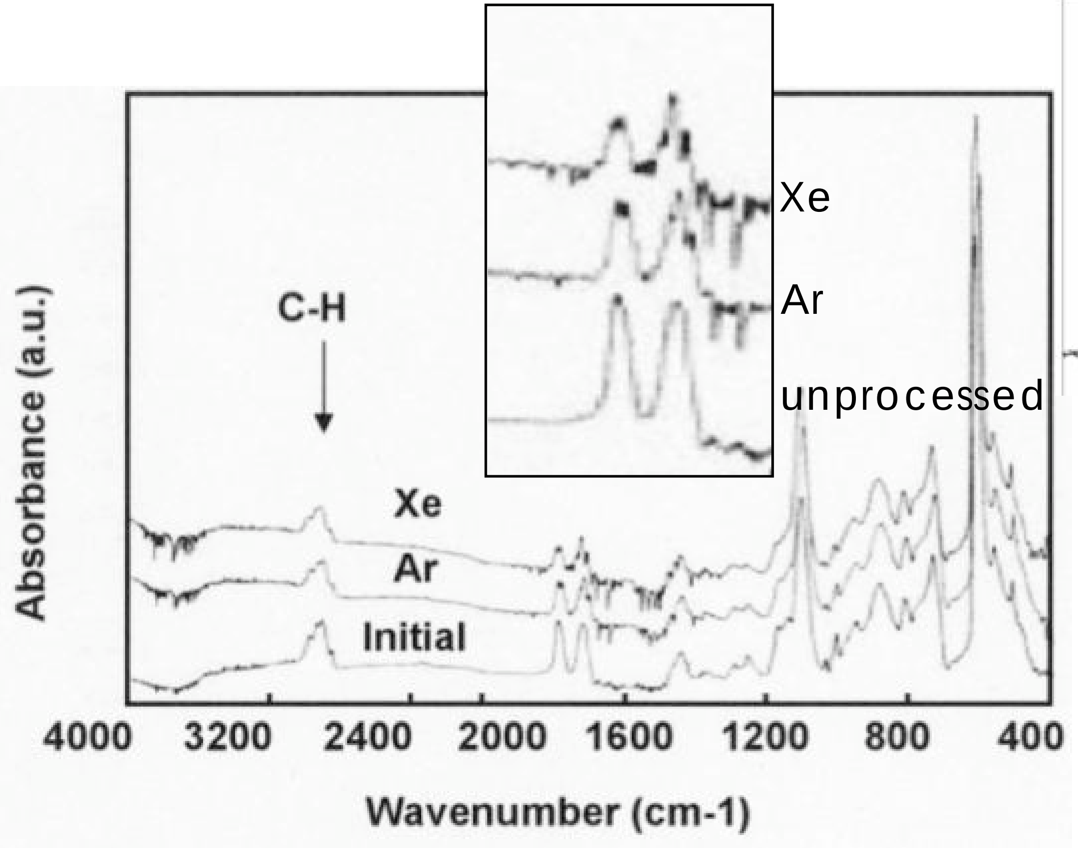


- Bulk modifications of C=O and C-O-C bonds are observed.
- Very important due to the relatively high oxygen content of 193 nm PR.
- -CH_2- / -CH_3 region relatively untouched.
- Note: loss of backbone or adamantyl would require the loss of -CH_2- / CH_3.

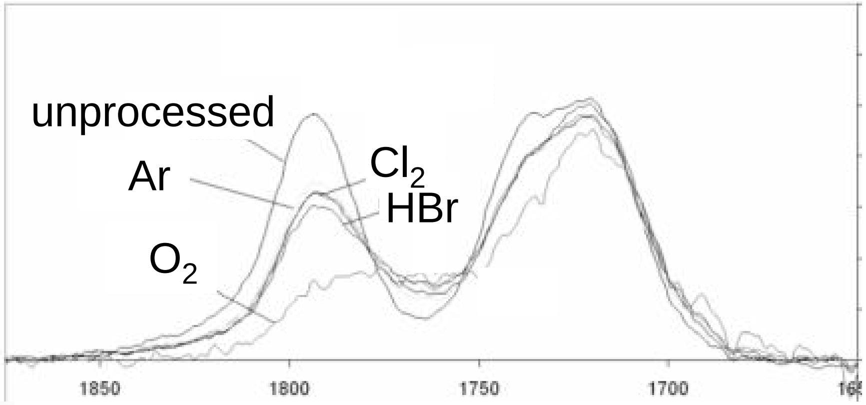
193 nm PR



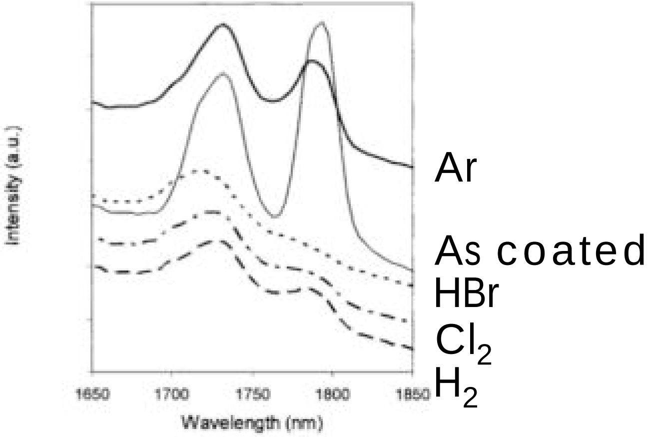




Negishi et al., J. Vac. Sci. Technol B 23, 217 (2005).

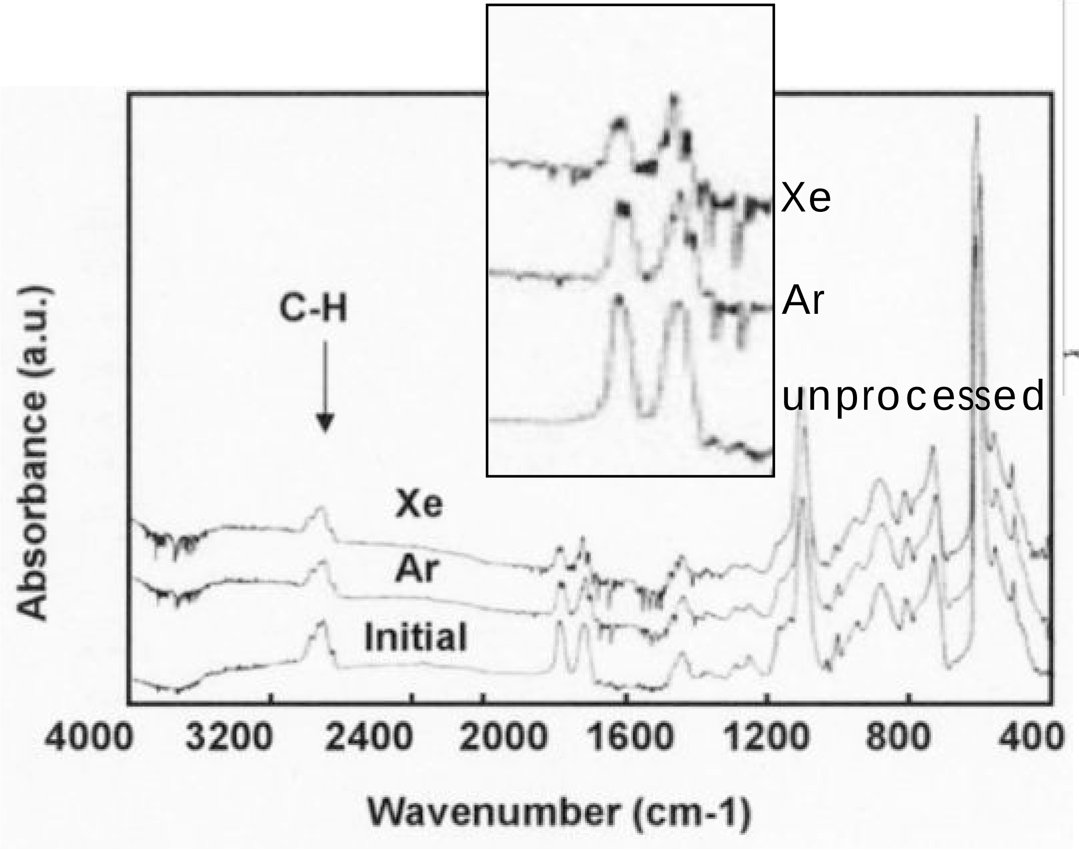


Bazin et al., Proc. SPIE 6519, 65192N (2007).



Kim et al., J. Vac. Sci. Technol. B 24, 2645 (2006).

- None of these authors have previously attributed bulk PR modification to plasma VUV emission.
- The VUV from each plasma (Ar, Xe, O_2, etc.) is different and will likely result in different bulk film modifications.



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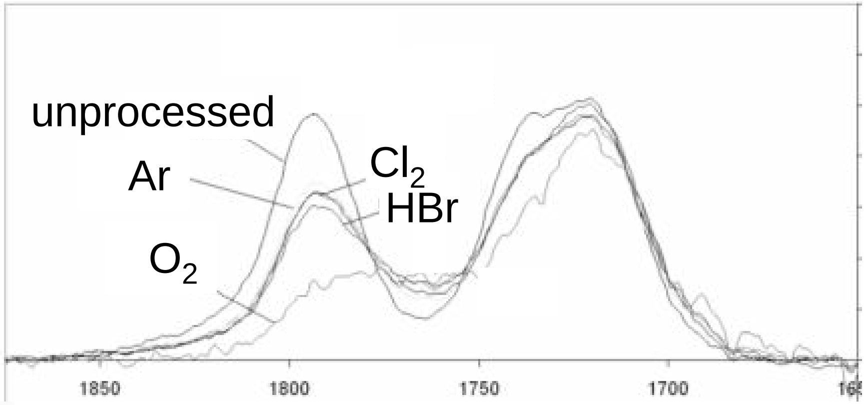

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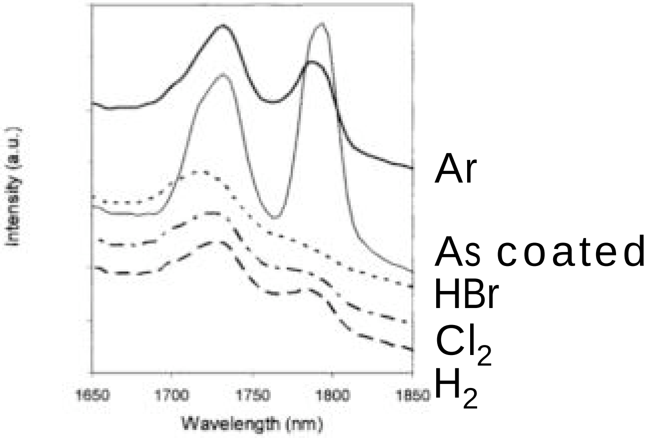
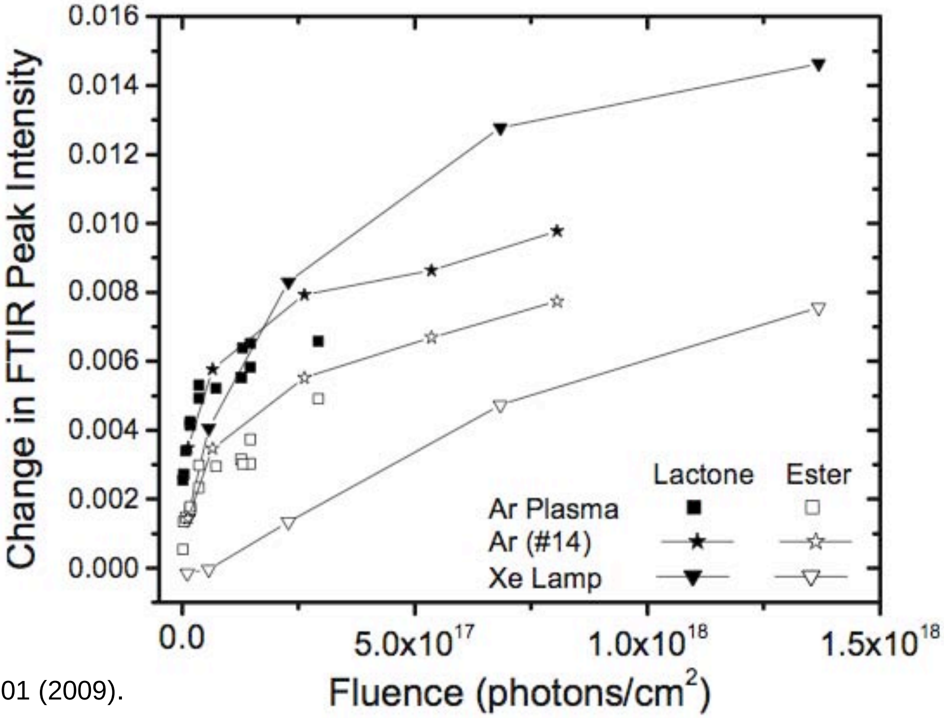


Kim et al., J. Vac. Sci. Technol. B 24, 2645 (2006).

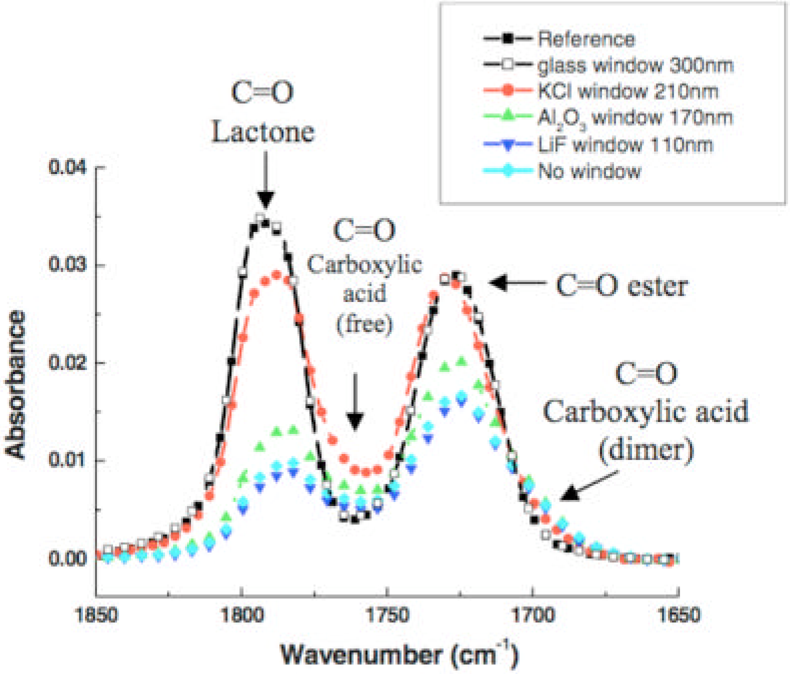
Change in FTIR peak intensity of C=O lactone and ester bonds as a function of VUV fluence.

Comparison of xenon beam system experiments and argon plasma experiments.



Titus et al., Appl. Phys. Lett. 94, 171501 (2009).

FTIR of PR exposed to HBr cure plasma treatments with various VUV transparent windows.



Pargon et al., J. Appl. Phys. 105, 094902 (2009).

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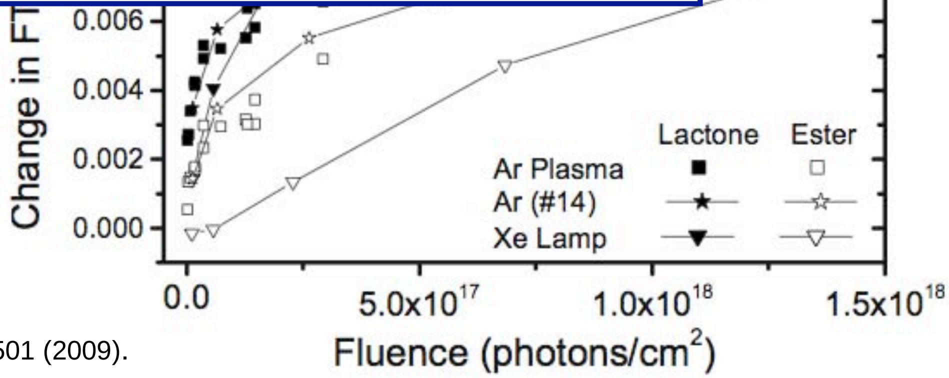

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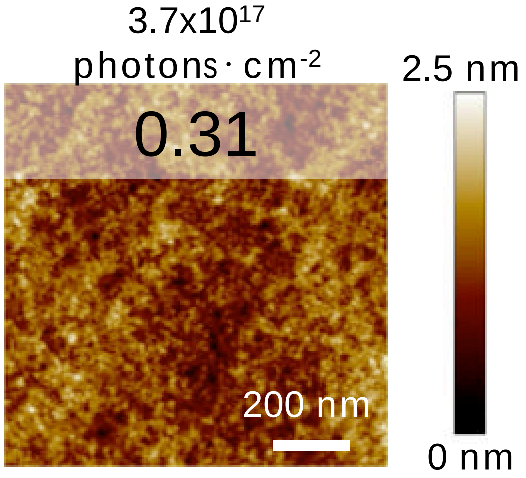
FTIR of PR exposed to HBr cure plasma treatments with various VUV transparent windows.

Bulk modifications are observed after plasma exposure but previously have not been attributed to plasma VUV emission.

VUV exposure results in smooth surfaces, similar to unexposed samples.



Cha
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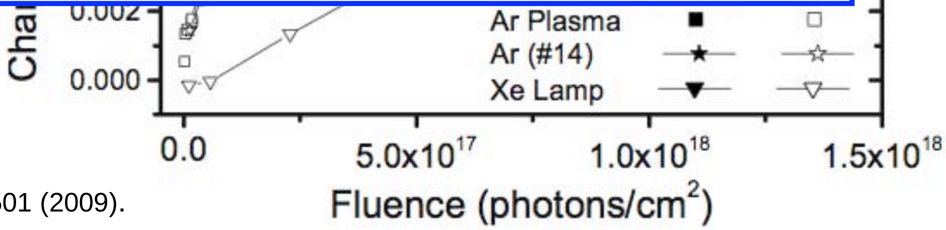
plasma experiments.



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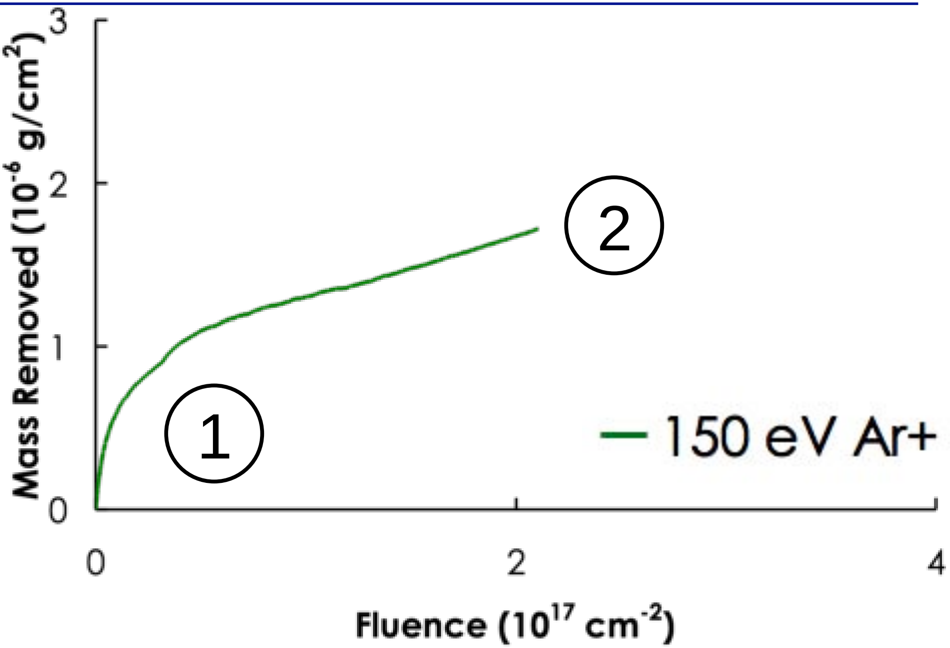
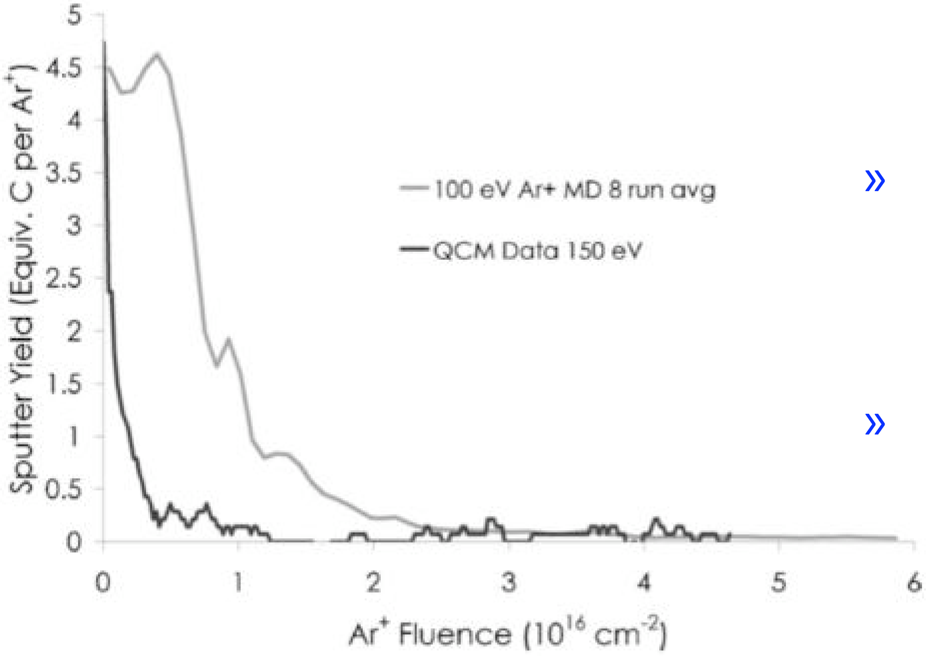
Ion bombardment: mass loss and surface modification

- Observation of mass loss with Quartz Crystal Microbalance (QCM)

① Initial high sputter yield

② Steady-state sputtering





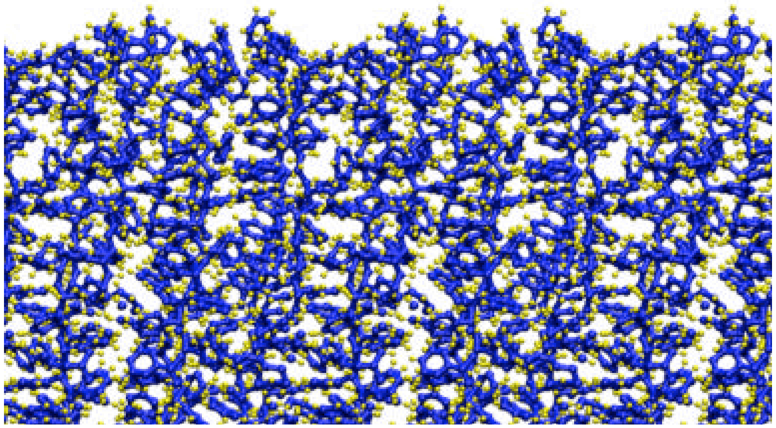
J.J. Vegh, et al., Appl. Phys. Lett., 91, 233113 (2007).

- Molecular Dynamics Simulations of polystyrene (PS) show a similar drop in sputter yield with increasing fluence.
- This is also observed experimentally during ion bombardment of PS.

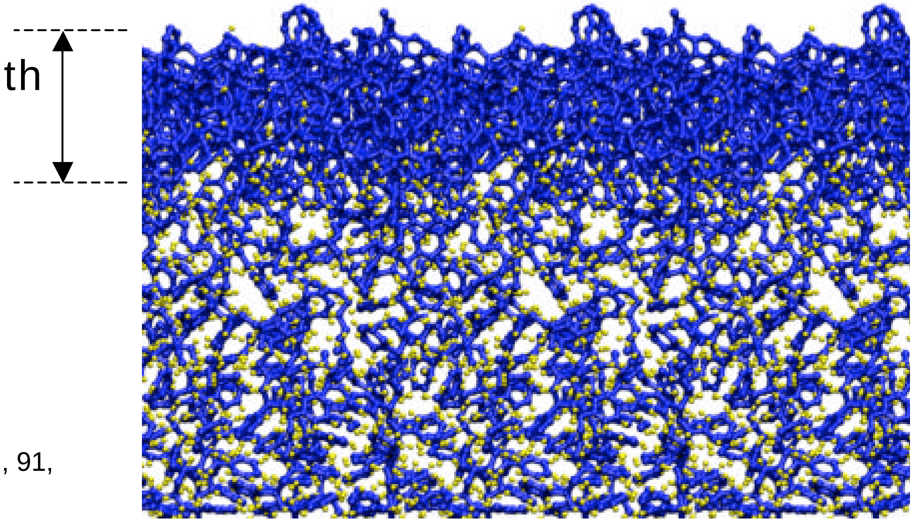
Ion bombardment: mass loss and surface modification

- Molecular Dynamics Simulations of polystyrene (PS) show surface modification on an atomic scale.

Initial film:



Ion-bombarded film:



ion penetration depth (~nm)

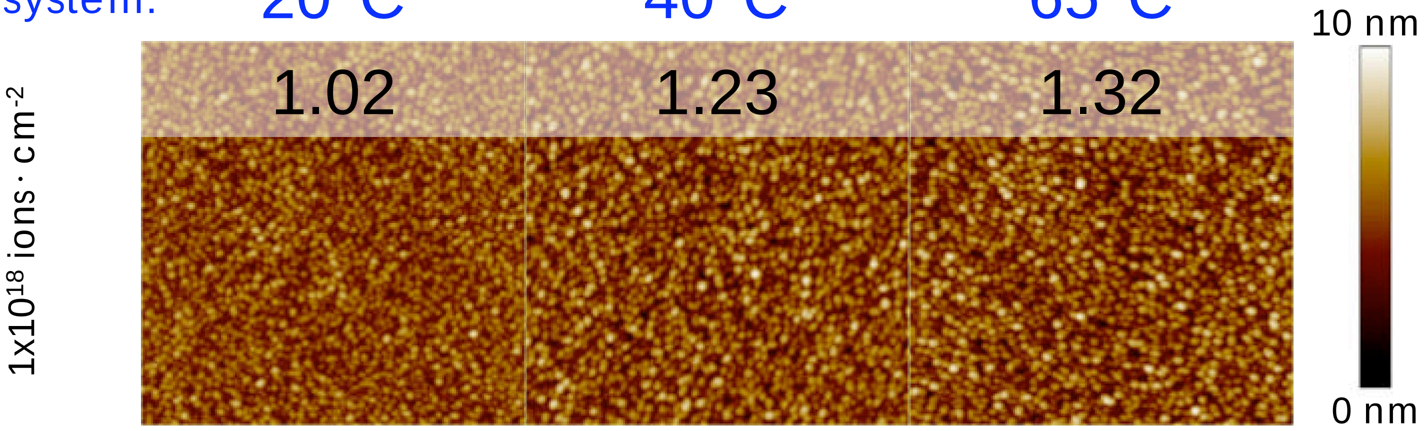
dehydrogenated surface layer

undisturbed polymer

J.J. Vegh, et al., Appl. Phys. Lett., 91, 233113 (2007).

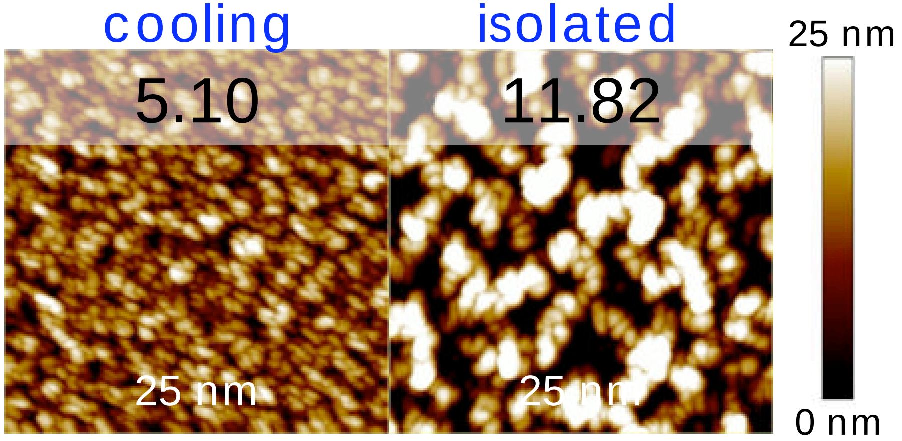
Ion bombardment: surface roughness

Beam system:



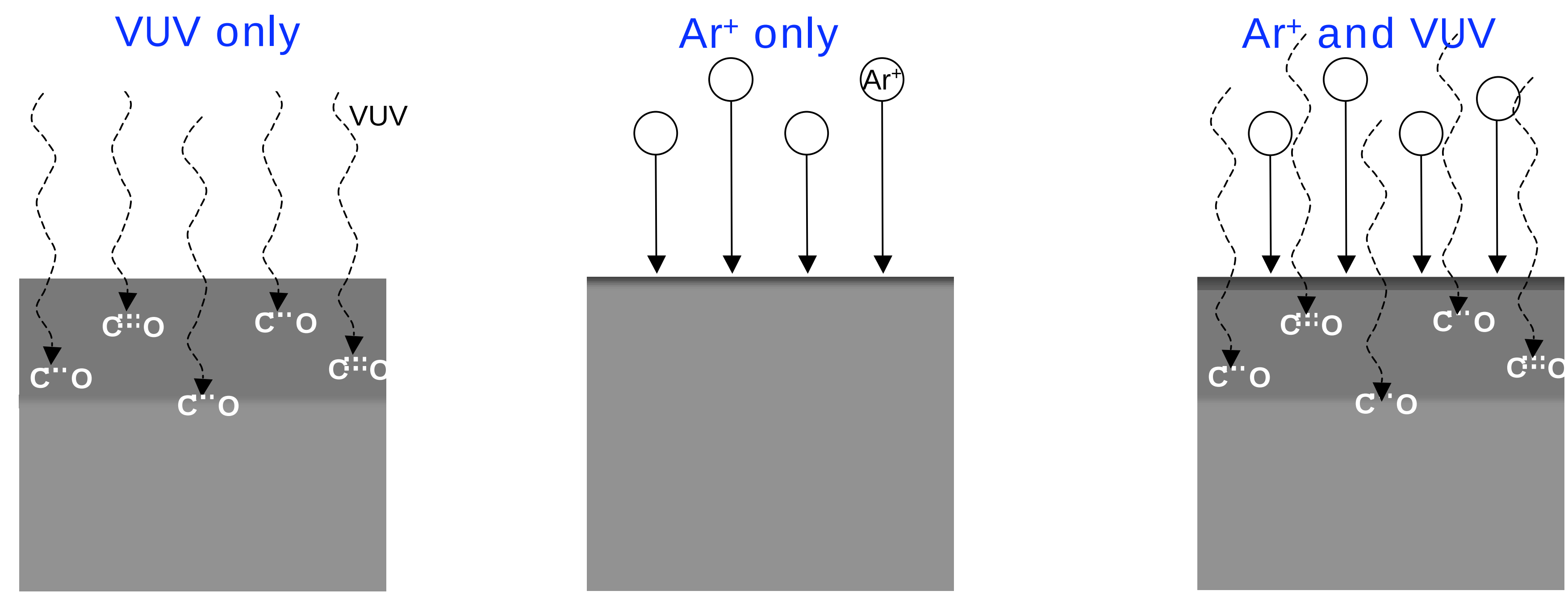
- Beam system ion-only exposure results in slight surface roughening which is nearly independent of temperature.

Argon plasma:



- This is in contrast to high levels of roughness observed during plasma exposure, which is highly temperature dependent.

Simultaneous VUV and Ar^+


VUV only

Ar^+ only

Ar^+ and VUV

No surface roughness
(~0.3 nm)

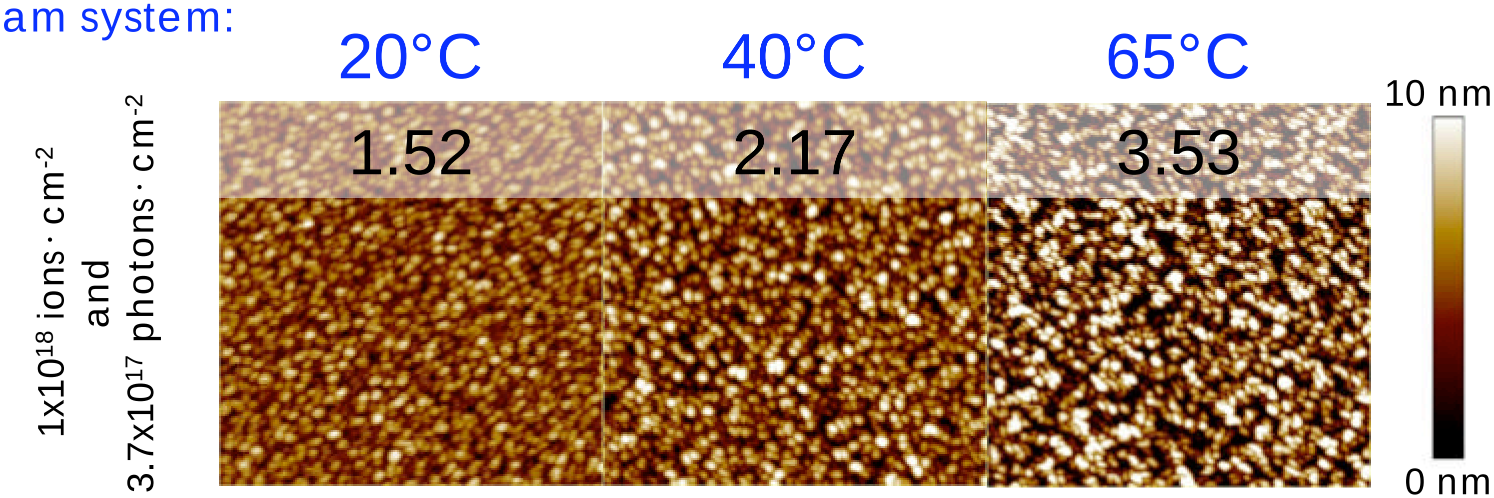
Slight surface roughness
(~1 nm)

VUV photons: Bulk film modification resulting in loss of C=O and C-O-C bonds

Ions: Highly-modified near-surface region

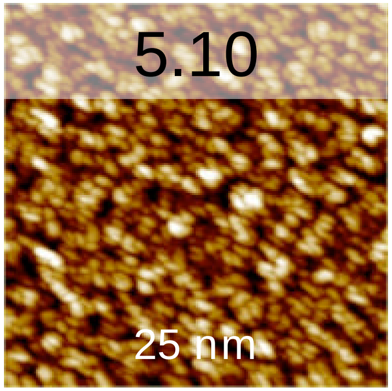
Simultaneous VUV and Ar$^+$

Beam system:



- Surface roughness under simultaneous ion bombardment, VUV radiation, and substrate heating is temperature dependent.
- We now observe the formation of roughness at lower temperatures, even at 20°C.
- The observed level of roughening is similar to plasma exposures.

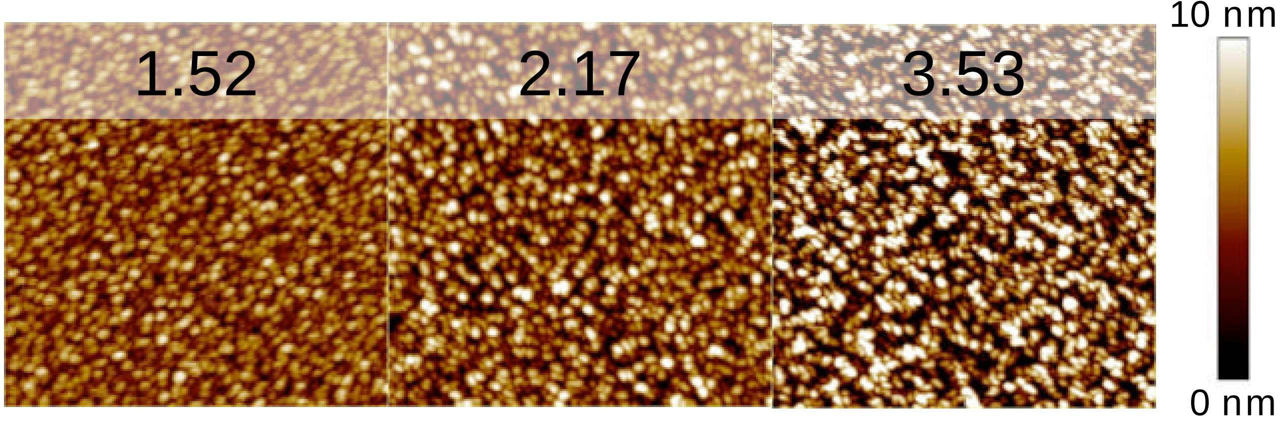
Argon plasma



Simultaneous VUV and Ar^+

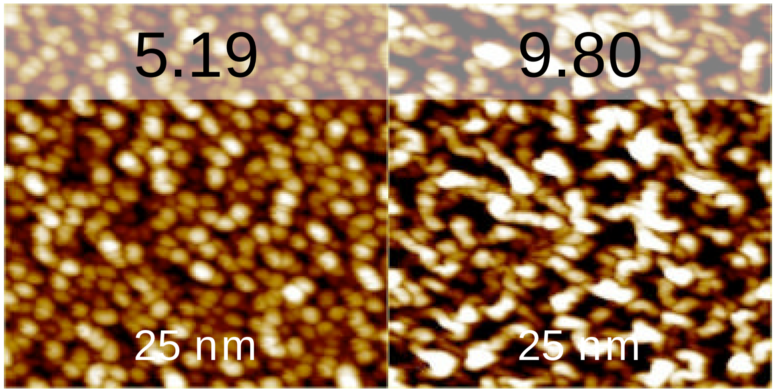
Beam system:

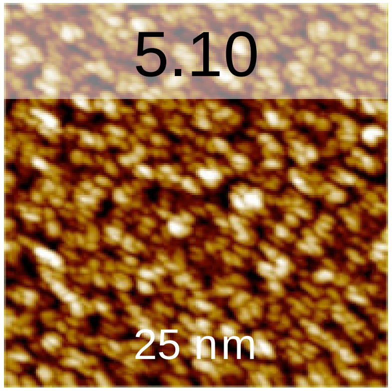
$1\text{x}10^{18}$ ions · cm^{-2}
and
$3.7\text{x}10^{17}$ photons · cm^{-2}

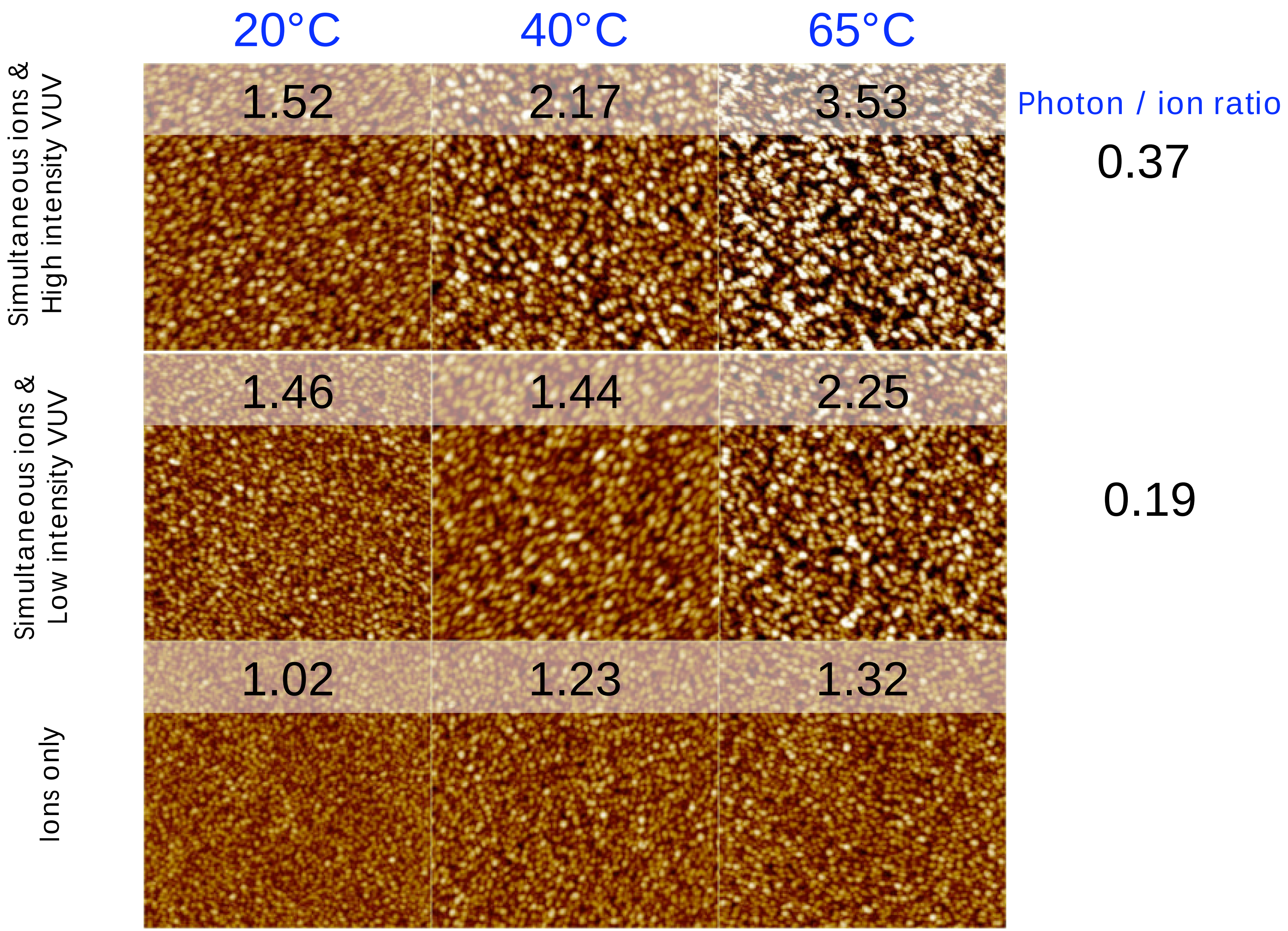

20°C
40°C
65°C

Beam system (uncharacterized
photon source):

$4\text{x}10^{17}$ ions · cm^{-2}
and
photons


75°C
100°C


Argon plasma

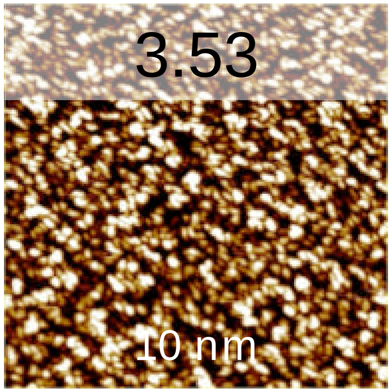


- Surface roughness formation is photon / ion ratio dependent.
- If we went to higher photon / ion ratios, surface roughness could be even higher.

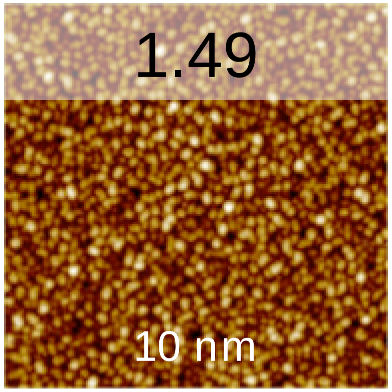
Simulataneous vs. sequential exposure

- All exposures at 65°C

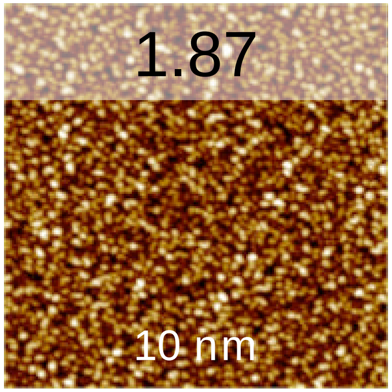
Simultaneous
$1\text{x}10^{18}$ ions·cm^{-2}
and
$3.7\text{x}10^{17}$ photons·cm^{-2}



VUV followed by Ions

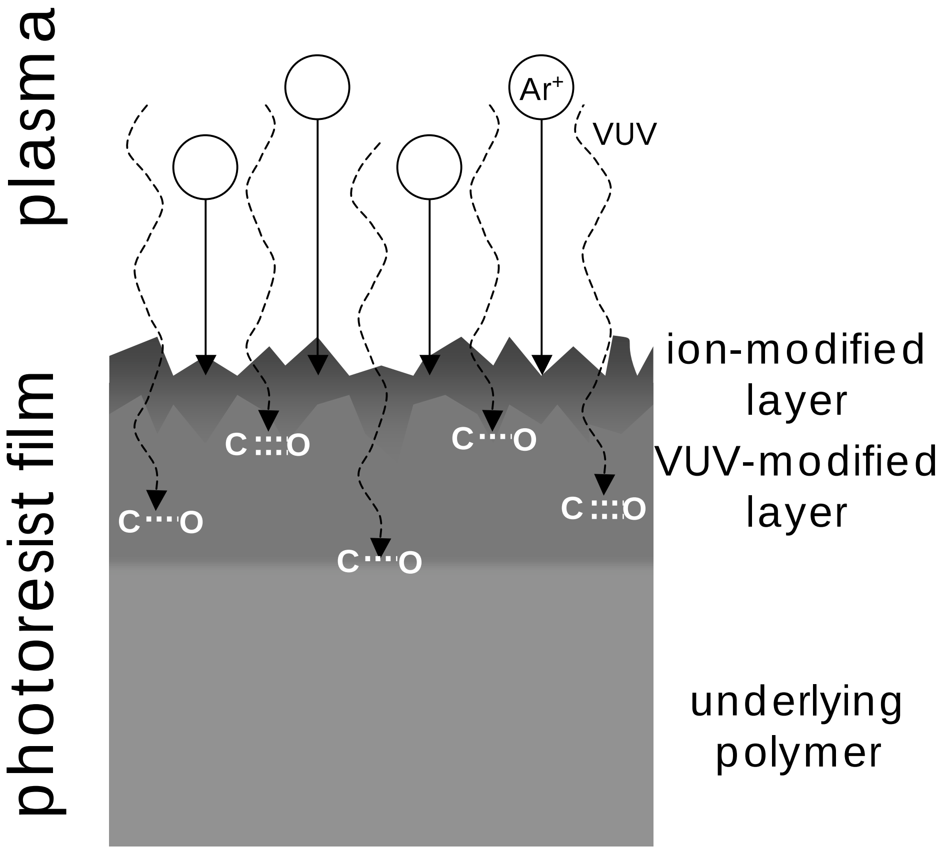


Ions followed by VUV



- The roughnening synergy only occurs for simultaneous VUV and ion bombardment. Sequential exposures do not show the same roughness.

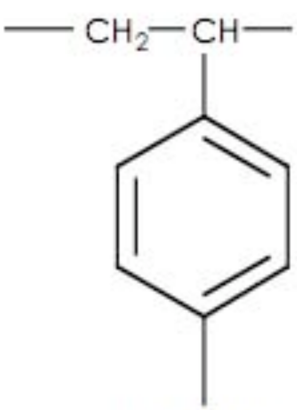
Proposed mechanism:
Ar^+, VUV and heating roughening synergy



- Ion bombardment creates highly modified near-surface region.
- VUV radiation breaks C=O and C-O-C bonds to a depth of ~100 nm.
- We suspect roughness is formed due to large differences in mechanical properties of these two layers which becomes more important at elevated temperatures.

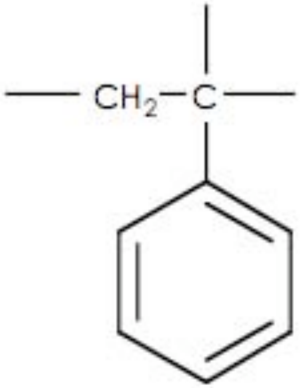
Model Polymers for Next Generation Lithography

- Currently, PR polymer selection is largely guided by requirements for photolithography.
- Next generation lithography techniques (nanoimprint, self-assembly) may remove many of the restrictions currently placed on resist materials.
- Investigate two polymers with identical composition but different structure.



P4MS

T_c ~ 150°C



PαMS

T_c ~ 60°C

- Polymers were chosen for differing responses to radiation.

Model Polymers: VUV Radiation

- 1 hr 147 nm VUV radiation (off-normal 45°, 4.8x10^{17} photons•cm^{-2})

	Temperature (°C)	Thickness Loss (nm)	Roughness (nm)
PαMS	20	2.9	0.30
	45	9.0	0.41
	70	19.0	0.55
P4MS	20	1.7	0.31
	45	1.9	0.28
	70	2.6	0.31

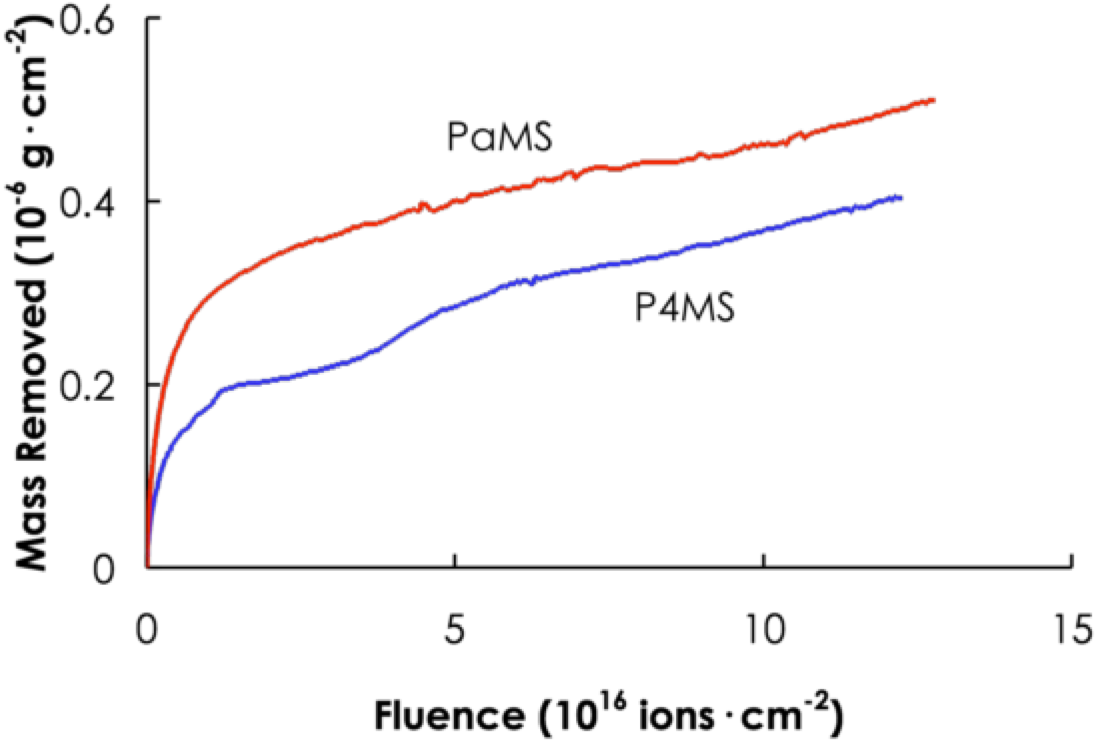
- PαMS thickness change cannot be accounted for from heating only under vacuum and confirms the chain scission behavior PαMS.

- PαMS mass loss continues for at least 4.5 hrs and does not appear to saturate.

- Minimal surface roughness is observed after VUV exposure.

Model Polymers: Ion Bombardment

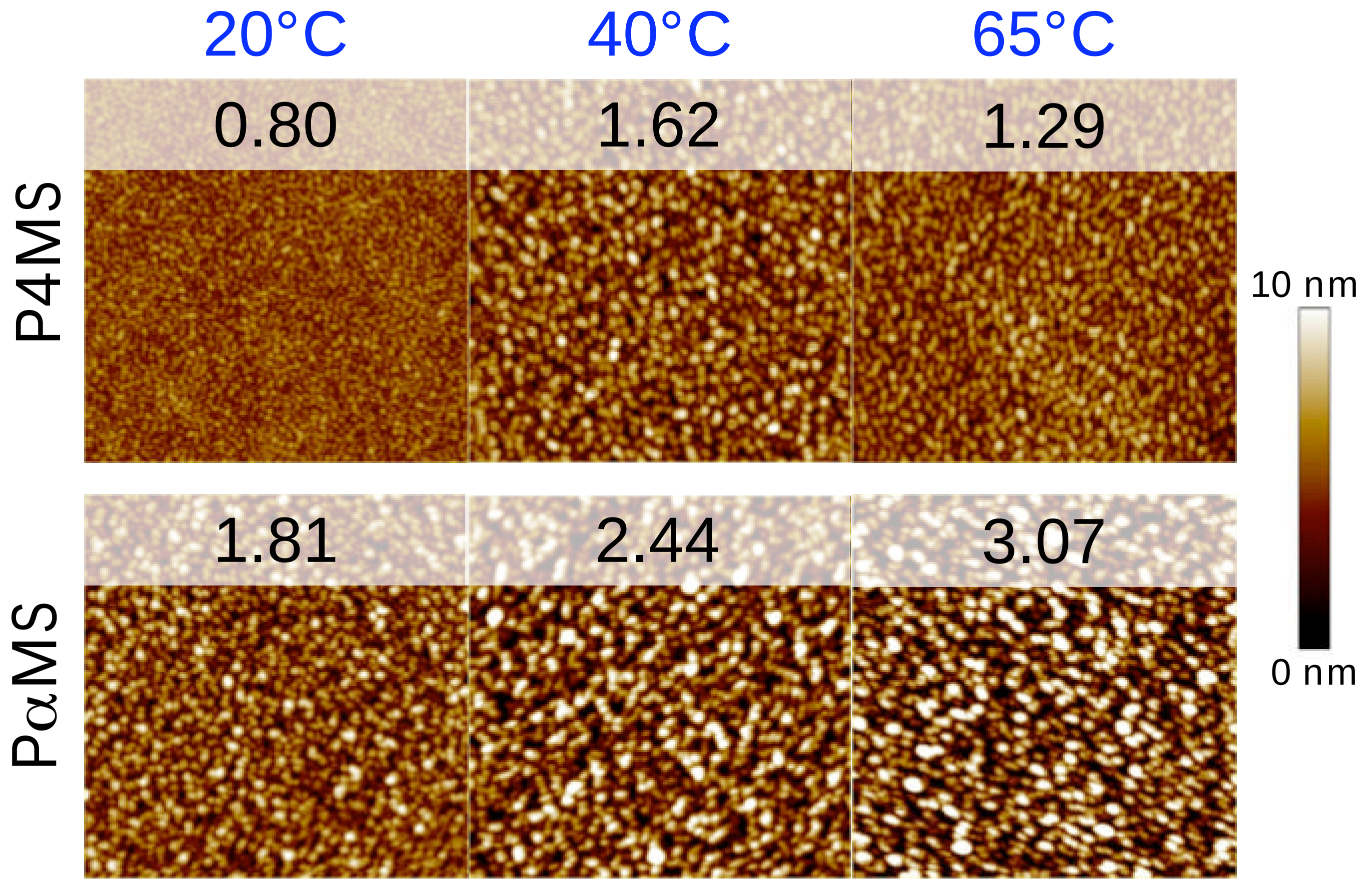
- 150 eV Ar^+ room temperature exposures.



- Steady-state ion etch yields are nearly identical.
- Transmission FTIR demonstrates ion etch yields are not highly temperature dependent.
- Observed mass loss before formation of modified surface layer is structure dependent.

Model Polymers: Ion Bombardment

- 150 eV Ar$^+$ room temperature exposures (1×10^{18} ions•cm^{-2}).

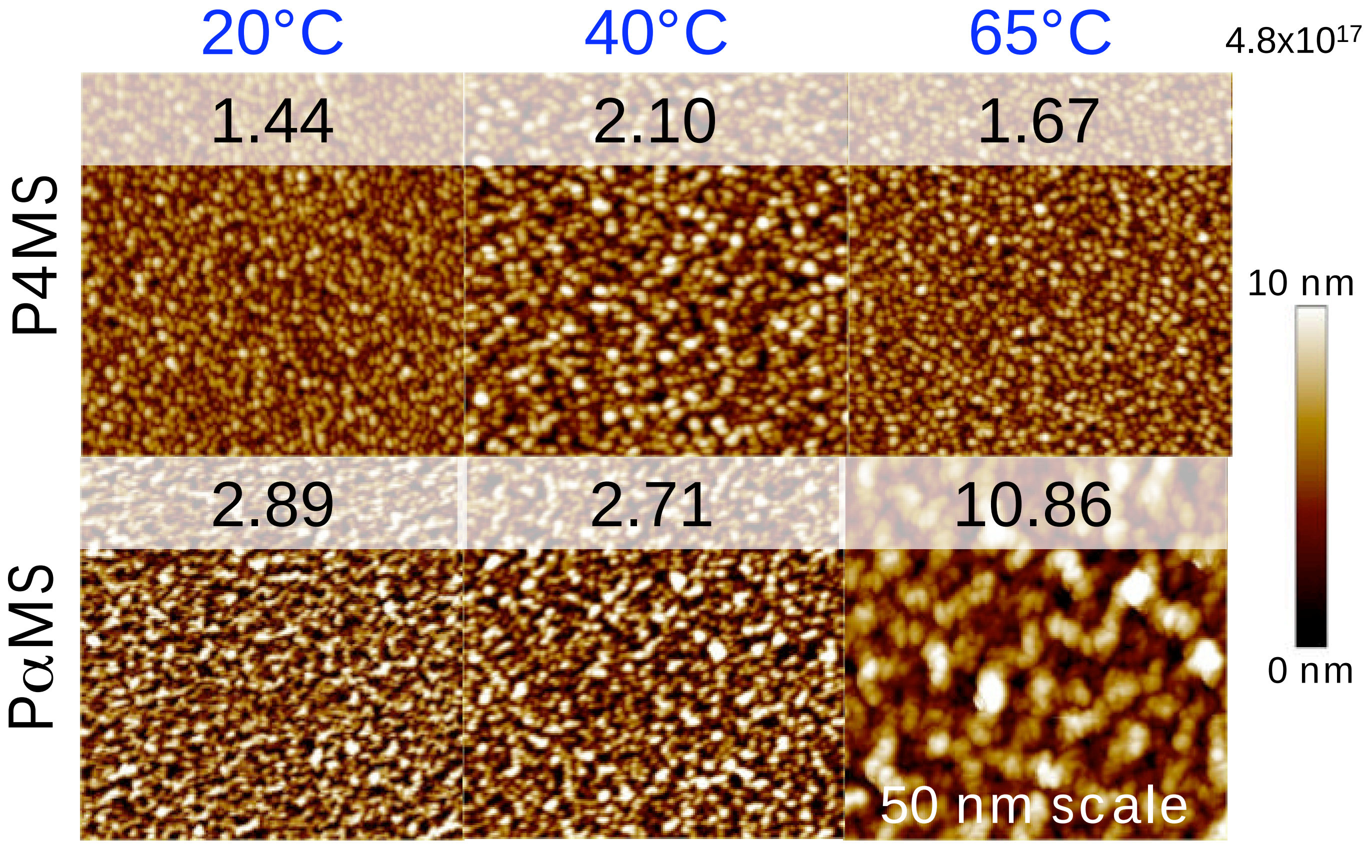


- Higher surface roughness observed for PαMS, where surface roughness increases with increasing temperature.

Model Polymers: Simultaneous VUV and Ar$^+$

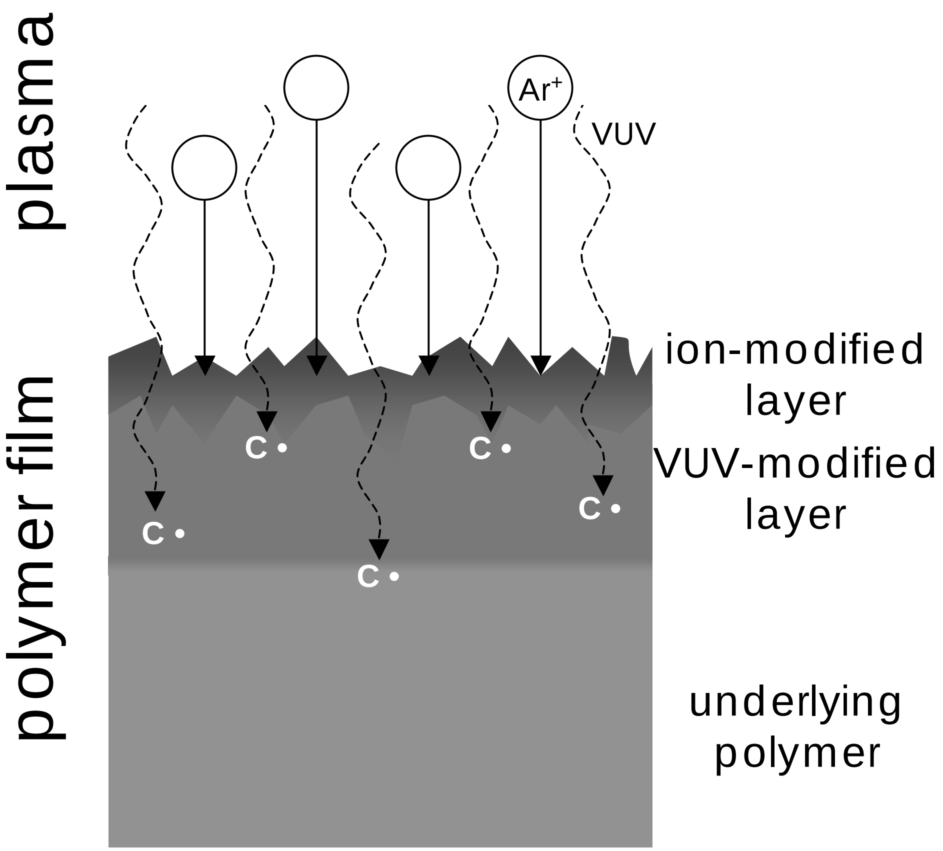
- Simultaneous VUV and Ar$^+$ exposure of P4MS and PαMS

1×10^{18} ions·cm^{-2}
and
4.8×10^{17} photons·cm^{-2}



- Synergistic roughening of PαMS observed at elevated temperatures.
- Simultaneous exposure is again required for formation of elevated surface roughness.
- No synergy is observed with P4MS due to its minimal response to VUV.

Model Polymers: Synergistic Roughening of PαMS



- Role of ions: formation of graphitized surface layer.
- Role of VUV: formation of radicals in bulk polymer. VUV-irradiated polymer decomposes when heated above its ceiling temperature.
- Surface roughening of PαMS again requires simultaneous VUV radiation and ion bombardment.

Conclusions

- Synergistic roughening of 193 nm PR or PαMS requires simultaneous VUV radiation and ion bombardment.
- Role of ions: formation of near-surface graphitized layer.
- Role of VUV
  - 193 nm PR: loss of carbon-oxygen bonds in bulk polymer
  - PαMS: degradation of bulk polymer above the ceiling temperature
- We suspect the roughness forms from differences in mechanical properties of these two layers. Understanding surface roughness requires understanding modifications both on the surface and in the bulk PR.
- The development of sidewall roughness, LER and LWR on patterned samples will require further study.

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