Mechanisms of Plasma-Induced 193 nm Photoresist Roughening

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IMPACT – UC Discovery
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Acknowledgements

Plasma-Surface Interactions in Nanoscale Feature Shape Evolution
2008-present; IMPACT: UC Discovery
J. Chang (UCLA), M. Lieberman (UCB), D. Graves (UCB)
M. Titus, M. Morimoto (Hitachi visitor)

Plasma Etching and Surface Modification of Dielectrics
2008-present; SRC (1862)
J. Kelber (UNT), D. Graves (UCB)
S. Behera, J. Lee

John Coburn (UCB)
Dave Fraser (UCB)
Harold Winters (UCB)

Nanotechnological Manufacturing: Nanostructured Polymers Designed for Plasma/Energetic Beam Templating of Materials
2005-2009; NSF NIRT (DMR-0506988)
G. Oehrlein (UMd), R. Phaneuf (U Md); A. Alizadeh (GE); G. Willson (UT); D. Graves (UCB)
B. Long, R. Bruce, T. Kwon, D. Nest, J. Végh, G. Choudhary, H. Kan, F. Weilnboeck, T. Lin

Interaction of Plasma/Energetic Beams with Organic Masking Materials
2005-present; NSF GOALI (DMR-0406120; -0705953)
G. Oehrlein (UMd), D. Graves (UCB), E. Hudson (Lam Research), C. Andes/D. Wang (Rohm & Haas; Dow)
D. Nest, T. Chung, J. Végh, M. Titus, F. Weilnboeck, S. Engelmann, R. Bruce
Recent Focus on 193 nm PR

193 nm Photoresist (Dow Chemical)

Pattern Transfer and Etching Complications

193 nm Photoresist (Dow Chemical)

MAMA

α-GBLMA

RAMA

Plasma-Induced Roughness in 193 nm Photoresists

Dense Features

Isolated Features

Sidewall striations post-etch
Additional Examples

After Development

ARC (Plasma)

Oxide (Plasma)

Ash (Plasma)

Final Feature

Spansion (unpublished)
PR Roughness: Device Performance Implications

What role can/does plasma play in improving or worsening this?
PR Roughness: Exposure and Development

Plasma impact on 193 nm photoresist linewidth roughness: Role of plasma vacuum ultraviolet light

E. Pargon, M. Martin, K. Menguelti, L. Azarnouche, J. Foucher, and O. Joubert

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FIG. 1. (Color online) LWR variation ($\text{LWR}_{\text{final}} - \text{LWR}_{\text{initial}}$) measured by CD-AFM on isolated patterned resist line after Cl$_2$/O$_2$ plasma exposure under LiF, Al$_2$O$_3$, and KCl windows as well as when no window is in place
Plasma-**Polymer** Interactions: Ions and Radicals

1. Ion-surface interactions – ion impact profoundly alters the near-surface polymer region.
   - dramatic example of ion-neutral synergy


3. How do these effects manifest themselves in plasma-polymer interactions?
Classic Ion-Neutral Synergy for INORGANIC Materials

FIG. 1. Schematic diagram of the apparatus used to study ion-assisted gas-surface chemistry. The gas injection tube is 1.6 mm inside diameter and is about 3 mm from the quartz crystal microbalance. The gas flow is determined from the rate of pressure increase in the reservoir when the shut-off valve is closed.

FIG. 2. Ion-assisted gas-surface chemistry using Ar⁺ and XeF₂ on silicon (volatile reaction product). Ar⁺ energy = 450 eV, Ar⁺ current = 0 (t < 200 sec), Ar⁺ current = 2.5 μA (t > 200 sec), XeF₂ flow = 2 x 10⁻¹¹ mol/sec (t < 660 sec), and XeF₂ flow = 0 (t > 660 sec). (The Ar⁺ current density and the XeF₂ flux are not uniform over the Si surface. The effective area for the Ar⁺ current and the XeF₂ flux are estimated at 0.1 and 0.3 cm², respectively.)

Ion- and electron-assisted gas-surface chemistry—An important effect in plasma etching
J. W. Coburn and Harold F. Winters
Can There be *Other* Important Plasma-Induced Effects?

Well known that polymers are susceptible to scissioning and/or cross-linking by *electrons* and *photons*

- Electron beam and optical lithography are based on this!

Even well known that plasma-generated UV/VUV can strongly alter polymers....

- Earliest paper: may be from Martin Hudis, 1972

*Look for photon and electron synergies in plasma-organic material interactions*
193 nm PR Roughness Observed: 

Ar-only plasma

ICP system: 10 mtorr; $V_{dc} \sim -150$ V; 100% Ar

G.S. Oehrlein et al., UMd

800 W / 20 s Argon plasma-exposed 193 nm PR

What explains this extreme roughness??
Strategy to Identify Plasma-Surface Alteration Mechanisms

Beam Experiments

Plasma Experiments

MD Simulations
Molecular Dynamics (MD) Simulation

Interatomic Potential $\Phi(r)$

Interatomic Forces

$F_i = -\nabla \Phi(r) = m_i \frac{d^2 r}{dt^2}$

typical MD time step:

initial configuration

update positions

update velocities

evaluate forces

$Ions assumed to neutralize before impact: fast neutral interacting with surface$

$\Phi(r)$ is assumed to model all reactive and non-reactive interactions
Interatomic Potentials

- Tersoff-Brenner style, many body REBO potential for short range covalent bonds like Si-C-F-O-H systems*

- Repulsive pair potential (Molière) for Ar ‘ion’ interactions

- No van der Waals forces

MD Setup for Polymers

- C-H-O REBO Potential*
- $\text{Ar}^+$ at 100 eV (normal incidence) from top
- Sample polymer simulation cell ($\sim$20 Å in x and y)
  - 9 chains of 20 monomers each
  - Bottom two fixed
- Periodic boundary conditions in X and Y
- Additional material added to the bottom
- Minimum # of atoms maintained
- Cell cooled back to 300K
- **Polymers simulated (C/H/O)**
  1. PS, PMMA, PVN, PBN, P4MS, PMAMA
  2. HDPE, Teflon

* Ni B, Lee H K and Sinnott B S 2004
Periodic boundary conditions

- Mimics an infinite surface
PMMA ($\text{C}_5\text{H}_8\text{O}_2$) simulation

- C (red); O (green); H (black)
Sputter yield v. fluence
Depth Profile: Steady State
**MD vs. experiment**

- Ion beam data
  - Initial sputter yield matches well.
- Sharp drop observed
- Initial sputter yield
  - MD ~14 C/Ar
  - Experiment ~ 12 C/Ar

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D. Nest

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- pMAMA MD simulation
- 193nm OR QCM

Yield (Eqv. C per Ar\(^+\)) vs. Ar\(^+\) Fluence (10\(^{16}\) cm\(^{-2}\))
Propose 3 Effects to Generate PR Roughening in Ar Plasma

• Ion bombardment (Ar⁺)
• VUV photons
• Substrate temperature (50°C -100°C)

Compare plasma (Ar) and vacuum beam exposures
Vacuum Beam Setup

Vacuum Beam (VB) System: Side View

Faraday Cup

Ion Source

VUV Spec.

H₂O In

Sample

H₂O Out

To Turbo Pump

Base Pressure: 5 x 10⁻⁸ Torr
Sample Temperature: 20 – 100°C
Ion Source: 150 eV Ar⁺ (Commonwealth)
VUV Source: Xe & Ar VUV Source
Ion bombardment only: Not enough roughening

150 eV Ar$^+$, $4.0 \times 10^{17}$ ions$\cdot$cm$^{-2}$

(D. Nest et al, 2007)
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Only VUV: surface observation

Surface roughness quantified with 1x1 \( \mu m^2 \) AFM images. (D. Nest et al, 2007)

Minimal surface roughness forms with remote UV/VUV exposure.
Simultaneous Ions and Photons: *agreement!*

**Ar⁺ & VUV (Ar) Beam**
- 75°C: 5.19 nm, 9.80 nm
- 100°C: 5.10 nm, 11.82 nm

**Argon plasma “floating”**
- 75°C: 2.30 nm, 1.59 nm
- 100°C: 1.17 nm, 2.03 nm

(D. Nest et al, 2007)
Ar ICP Comparison

ICP Chamber: Top-Down View
10 mT Ar, \( J_+ \sim 1 \text{ mA.cm}^2 \)

Ar 104.8 and 106.7 nm
Total VUV Flux

VUV Spec.

Plasma Stability
Plasma Chemistry

250 nm thick
PR Sample
1 cm\(^2\)

To Neutral
Mass Spec.

To Roughing
Pump

\( \text{H}_2\text{O In} \)
\( \text{H}_2\text{O Out} \)

RF Bias

Ion Current

Probe

Load-Lock
Port

H. Singh, (UC Berkeley, 2000)

Langmuir Probe:
\( n_e, T_e, \Phi_p \)
Elevated Temperature Necessary for Enhanced Roughening

(M. Titus et al, 2009)

**Conditions:**
- Vacuum Beam System
- 150 eV Ar⁺, Ar VUV
- 40 min Exposures
- $4 \times 10^{17}$ ions/cm²

**Results:**
- Monotonic increase in roughening
- No variation in C = O and CH₂/CH₃ loss i.e. bulk modification is independent of temperature.
‘Damaged’ Layer Necessary for Enhanced Roughening: \textit{Energetic Ions + VUV + T_{\text{dental}}}

(M. Titus et al, 2009)

\begin{align*}
J_+ . t \approx 10^{17} \text{ cm}^{-2} \\
J_{hv} . t \approx 10^{17} \text{ cm}^{-2} \\
T \approx 60^\circ\text{C}
\end{align*}

Beam vs. plasma: remarkable agreement overall
Patterned Sample: Beam Measurements

M. Morimoto (Hitachi visitor); C. Gabriel (Spansion 193 nm immersion samples)

<table>
<thead>
<tr>
<th></th>
<th>Unprocessed</th>
<th>Heat Only</th>
<th>Ion Only</th>
<th>VUV Only</th>
<th>Simultaneous</th>
</tr>
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<tbody>
<tr>
<td>Dense</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
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<tr>
<td>Isolated</td>
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<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- **Dense**: 100nm, 65degC
- **Isolated**: 65degC
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**PαMS vs. P4MS**

(D. Nest et al., accepted J. Phys. D, 2009)

Beam exposure

<table>
<thead>
<tr>
<th>Temperature</th>
<th>P4MS</th>
<th>PαMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>1.44</td>
<td>2.89</td>
</tr>
<tr>
<td>45°C</td>
<td>2.10</td>
<td>2.71</td>
</tr>
<tr>
<td>70°C</td>
<td>1.67</td>
<td>10.86</td>
</tr>
</tbody>
</table>

4.8x10^17 147 nm photons·cm⁻²
10^18 0.15 keV Ar⁺·cm⁻²

Deep scissioning *necessary* for enhanced roughness with Ar⁺
Electrons: *Scissioning Amplifies Roughening; Cross-Linking Suppresses Roughening*

- Elevated substrate temperature increases surface roughness.
- Low fluence electrons (1 mC/cm²) enhance surface roughness.
- Electron-induced cross-linking changes surface morphology.
- High fluence electrons (8 mC/cm²) reduce surface roughness

(T. Chung et al, 2009)
PMMA-Based 193 nm PR Roughening Mechanism?

• Ion bombardment alters near-surface (1-2 nm), creating a heavily H-, O-depleted, C-rich region
  - probably *compressively stressed*

• There is a 1-to-1 correspondence between ion-induced C-rich surface layer and enhanced roughening

• VUV photon penetrate ~ 50-100 nm, breaking C-O bonds; this is known to increase polymer mobility or relaxation dynamics (cf. E. Pargon, LETI)

• Heating increases polymer mobility or relaxation dynamics
PMMA-Based 193 nm PR Roughening Mechanism?

Huang model: wrinkling

Fig. 1. A schematic of the model structure: (a) reference state; (b) wrinkled state.

Our model of PR in plasma

Conclusions

• Ion bombardment, VUV photons, (and substrate heating) act synergistically to give observed roughening.

• Comparisons of beam and plasma exposure experiments show similar roughening when ion fluence and energy, VUV fluence and wavelength and surface temperature are the same – even though fluxes and therefore experiment duration differ by $\sim 10^2$!

• Similar results for patterned 193 nm PR: ion/VUV/heating synergy in enhanced roughening.
Conclusions, continued

• Pα methyl styrene vs. P4 methyl styrene experiments showed same pattern for these homopolymers: deep scissioning + ion bombardment and elevated T results in enhanced roughening

• 1 keV electron beams on 193 nm PR act like VUV photons in enhanced roughening synergy if they remain in low fluence scissioning mode; cross-linking electrons suppress roughening