Plasma-Surface Interactions at the Nanometer Scale

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We are already in nano feature era

*Courtesy Dr. Ying Zhang, IBM Research Division*

- Nano features are no longer only for ‘exploratory’ research any more

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K. Gopalakrishnan, et. al., IEDM 2005

A MNAB device showing very thin (~10nm) Si nanofins with floating poly-Si regions in between them

A ‘traditional’ FET device with an ~8nm gate on ultra-thin SOI (~4nm)
Etch Pattern Transfer for Nanoscale Features

What are the limits of defining a feature by patterning an etch mask followed by etching to transfer the pattern to an underlying film?

Even if etch mask has perfect fidelity, transferring to underlying film is not trivial for features ≤ 10-20 nm.

How to control mask erosion and roughness? This is especially problematic for polymer etch masks.

The more general question: How does plasma alter near-surface topography (rough/smooth textures)?
How Do Plasmas *Roughen* (or Smooth) 193 nm Photoresist?

<table>
<thead>
<tr>
<th></th>
<th>DARC Etch</th>
<th>Oxide Etch 1</th>
<th>MSL Etch</th>
<th>Oxide Etch 2</th>
<th>Ash</th>
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<tbody>
<tr>
<td><strong>Dense Features</strong></td>
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<td><strong>Isolated Features</strong></td>
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Sidewall striations post-etch
193 nm PR Roughness Observed in ICP

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

*G.S. Oehrlein et al., UMd
Vacuum Beam Setup

Vacuum Beam (VB) System: Side View

Faraday Cup

Ion Source

VUV Spec.

Sample

VUV Source

H₂O In

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
MD-Experiment Ar⁺/PS Yield Comparison (150 eV)

Initial sputtering yield:
MD/Exp: 4.8/4.6

Final sputtering yield:
MD/Exp: 0.02/0.07

Molecular Dynamics (MD) Simulation

Interatomic Potential

\[ \Phi(r) \]

Interatomic Forces

\[ F_i = -\text{grad}(\Phi) = m_i d^2r/dt^2 \]

typical MD time step:

- initial configuration
- update positions
- evaluate forces
- update velocities

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

\( \Phi(r) \) is assumed to model all reactive and non-reactive interactions
Polystyrene Starting Cell: MD Cell Sideview

\[ \text{~ 20 Å x 28 Å x 52 Å} \]
\[ \text{(depth x width x height)} \]
\[ \rho \sim 1 \text{ g/cm}^3 \]
\[ \text{H:C Ratio} = 1 \]
Polystyrene Surface Before and After $10^{17}$ cm$^{-2}$ Ar$^+$ Fluence (100 eV)

Near-surface alterations consistent with separate XPS and ellipsometry measurements of beam-processed samples
MD: ‘Snapshot’ Images (100 eV Ar⁺)
MD-Experiment Ar\textsuperscript{+}/PS Yield Comparison (150 eV)

Initial sputtering yield:
MD/Exp: 4.8/4.6

Final sputtering yield:
MD/Exp: 0.02/0.07

PMMA MD Simulation: Steady State

initial → steady state

Species Density (Arb)

Note C density
Materials

• **Model 193 nm photoresist**
  - Random terpolymer, supplied by Dow Electronic Materials with a film thickness ~250 nm. Tg ~ 180°C, Mw = 10,000 g/mol
  - Without photoacid generator and base quencher

• **Homo-polymer**
  - Supplied by Dow Electronic Materials with a film thickness ~240 nm
  - Without photoacid generator and base quencher

![Chemical structures](image)

Methyl adamantyl methacrylate (MAMA)
α- gamma butyrolactone methacrylate (α-GBLMA)
R-functionalized adamantyl methacrylate (RAMA)
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

Base Pressure: 5 x 10⁻⁸ Torr
Sample Temperature: 20 – 100°C
Ion Source: 150 eV Ar⁺ (Commonwealth)
VUV Source: Xe & Ar VUV Source

Faraday Cup
Ion Source
VUV Spec.
Sample
H₂O In
H₂O Out
To Turbo Pump

VUV Source

(a)
(b)
Vacuum Beam System: Xe VUV Characterization

- Ar VUV source also used, however, not fully characterized.
- 147 nm Xe VUV emission
- Photon flux $\sim 1.9 \times 10^{14}$ cm$^{-2}$s$^{-1}$
- VUV intensity is varied by translating line source (to/from sample).
Ion bombardment *only*: Not enough roughening

- 150 eV Ar\(^+\), 4.0 \(\times\) 10\(^{17}\) ions\(\cdot\)cm\(^{-2}\) (D. Nest et al, 2007)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>193 nm PR</th>
<th>248 nm PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>0.86 nm</td>
<td>0.45 nm</td>
</tr>
<tr>
<td>60°C</td>
<td>0.95 nm</td>
<td>0.34 nm</td>
</tr>
<tr>
<td>75°C</td>
<td>0.88 nm</td>
<td>0.64 nm</td>
</tr>
<tr>
<td>100°C</td>
<td>2.62 nm</td>
<td>0.78 nm</td>
</tr>
</tbody>
</table>

- (D. Nest et al, 2007)
Only VUV: Surface smoothing

Surface roughness quantified with 1x1 $\mu^2$ AFM images.

(D. Nest et al, 2007)
Simultaneous Ions and Photons: agreement!

$\text{Ar}^+ \ & \ VUV \ (\text{Ar}) \ Beam$

75°C

193 nm PR

5.19 nm

2.30 nm

248 nm PR

9.80 nm

1.59 nm

100°C

Argon plasma

“floating”

5.10 nm

1.17 nm

11.82 nm

2.03 nm

(D. Nest et al, 2007)
Patterned Sample: Beam Measurements
M. Morimoto (Hitachi visitor); C. Gabriel (Spansion 193 nm immersion samples)
ICP Chamber: Top-Down View
10 mT Ar, $J_+ \sim 1$ mA.cm$^{-2}$

Ar 104.8 and 106.7 nm
Total VUV Flux

Plasma Stability
Plasma Chemistry

Ion Flux

To Neutral
Mass Spec

250 nm thick
PR Sample
1 cm$^2$

OES

To Ion
Mass Spec.

Ion Current
Probe

To Roughing
Pump

RF Bias

Ion Energy

Langmuir Probe:
$n_e, T_e, \Phi_p$

H$_2$O In

H$_2$O Out

(M. Titus et al, 2009)
Ar ICP – VUV Characterization

110 W Ar Plasma VUV spectra

- 104.8 nm and 106.7 nm VUV emissions monitored.
- Double peaks observed at 210 nm. Verified with MgF₂ window.
- CO emissions (140 – 210 nm) minimized at 10 mT.
- Ar emission decrease at higher pressures due to radiative trapping and quenching.
## Ar ICP – Experimental Conditions

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>$\Phi_p$ (eV)</th>
<th>Temp (°C)</th>
<th>Average Bias Voltage (V)</th>
<th>VUV Flux ($\times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$)</th>
<th>Ion Flux ($\times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$)</th>
<th>Photon to Ion Flux Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>16.2</td>
<td>50</td>
<td>~105</td>
<td>0.45 ± 0.02</td>
<td>1.44 ± 0.06</td>
<td>0.31</td>
</tr>
<tr>
<td>70</td>
<td>15.8</td>
<td>20 – 100</td>
<td>0 - 220</td>
<td>2.87 ± 0.25</td>
<td>5.51 ± 0.34</td>
<td>0.52</td>
</tr>
<tr>
<td>150</td>
<td>15.8</td>
<td>50</td>
<td>~105</td>
<td>7.87 ± 0.64</td>
<td>12.7 ± 0.48</td>
<td>0.62</td>
</tr>
</tbody>
</table>

- Compare plasma conditions with beam experiments: PR roughening comparable?
  - Ion/photon fluence (flux x time)
  - Bias voltage (ion energy)
  - Substrate temperature
Elevated Temperature Necessary for Enhanced Roughening

**Conditions:**
- Vacuum Beam System
- 150 eV Ar\(^+\), Ar VUV
- 40 min Exposures
- 4 \(\times 10^{17}\) ions/cm\(^2\)

**Results:**
- Monotonic increase in roughening
- No variation in C = O and CH\(_2\)/CH\(_3\) loss i.e. bulk modification is independent of temperature.

(M. Titus et al, 2009)
Ar ICP Roughening: *Energetic Ions + VUV + $T_{elevated}$*

![Graph showing RMS roughness vs. ion energy for different crosslinking levels: No Crosslinking, Little Crosslinking, Crosslinked.]

$J_+ . t \sim 10^{17} \text{ cm}^{-2}$

$J_{hv} . t \sim 10^{17} \text{ cm}^{-2}$

$T \sim 60^\circ \text{C}$

**Beam vs. plasma: remarkable agreement overall**

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

• Ion bombardment alters near-surface (1-2 nm), creating a heavily cross-linked, C-rich region
  – probably *compressively stressed*

• Subsequent experiments showed 1 to 1 correspondence between cross-linked surface layer and enhanced roughening

• VUV photon effects penetrate ~ 50-100 nm, breaking C-O bonds; this is known to increase polymer mobility or relaxation dynamics

• More recent results (Chung et al.) show that the roughening correlates with the photolysis of the adamantyl leaving group in the P-MAMA component; temperature dependence of roughness follows adamantane vapor pressure
PMMA-Based 193 nm PR Roughening Mechanism?

Huang model: wrinkling

Compressively stressed

Cross-linked Layer (Carbon-rich)

2 nm

~100 nm

Scissioned (C-O depleted)

Pristine PR

Si

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

Our model of PR in plasma

Surface roughness vs. loss of adamantane

Chung et al., 2011

[Graph showing surface roughness and temperature relationship]
Conclusions: PMMA-Based 193 nm PR Roughening

• Ion bombardment, VUV photons, and substrate heating act synergistically to give observed roughening in beam system; may be due in part to wrinkling instability

• Roughening in Ar plasma very similar to beam result if ion and VUV photon fluences (flux x time), ion energy and substrate temperature similar

Effects of electrons and vuv/uv photons may be related to existing ‘knobs’;
Can we exploit these effects further??
Use Molecular Dynamics to Simulate Nanoscale Feature Etch: What Can Be Learned?

- Although computationally expensive, gain insights not possible from traditional feature profile modeling

- MD for feature scale evolution in its early stages – show some initial results and early conclusions

- Many challenges to tackle in future: materials complexity; charging; mask treatment; multiple time scales for reaction and transport
Sub 10-nm Feature Etch

‘C-mask ’ (made separately via C impacts)

Top

Side

Si – White
C – Black

~4.2 nm

Ion and neutral impact
Mask Selectivity is Key

- 4.2 nm opening mask after ~7100 CF$_3^+$ total impacts (~3900 on exposed Si @ 200 eV) ~ $4.3 \times 10^{16}$ cm$^{-2}$

Si – White
Mask C – Black
Incoming C – Red
F – Green
Neutral F (300K) Only

Purely isotropic etch with no ion bombardment

~1.58 \times 10^{18} \text{cm}^{-2} \text{F}
How Do Plasmas *Roughen* (or Smooth) 193 nm Photoresist?

- Dense Features
  - DARC Etch
  - Oxide Etch
  - MSL Etch
  - Oxide Etch
  - Ash

- Isolated Features
  - DARC Etch
  - Oxide Etch
  - MSL Etch
  - Oxide Etch
  - Ash

Source of striations?

Sidewall striations post-etch
Oblique Ion Incidence: Feature ‘Sidewall’

Starting Si Cell

After $5 \times 10^{16}$ cm$^{-2}$ 200 eV CF$_3^+$ Fluence

Végh et al., 2010
View Rotated: Ions Coming Out of Page

Starting Si Cell

After $5 \times 10^{16} \text{ cm}^{-2} 200 \text{ eV CF}_3^+$ Fluence

ions coming out of the page

Striations formed spontaneously; occurs only with FC ions, not Ar
Starting Si Cell

~6.5 nm

After $5 \times 10^{16} \text{ cm}^{-2}$ 200 eV CF$_3^+$ Fluence
Note C concentrates near peaks of ‘ripple’.
1. Plasma influence of *surface texture* generally not well understood but increasingly important as features shrink to nm scale.

2. VUV photons can play key synergistic role at surfaces exposed to plasmas, especially for organic materials.

3. MD simulations of feature profile evolution at nm scale show grazing incidence CF$_x$ ions on Si can create ripple-like structures that form spontaneously. MD may prove a powerful tool for future nm-scale etching.