Vacuum UV During Plasma Etch and Its Effects on 193 nm PR Roughness

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IMPACT Presentation
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Motivation (1): Courtesy Calvin Gabriel, Spansion

LER/CER history

• Line (and contact) edge roughness (LER/CER) became a major IC industry concern with the use of 193 nm (ArF) resists
• Degrades device performance, leakage, yield and reliability
• Countermeasures
  – Litho/etch process optimization
  – Add pattern transfer layer

As dimensions continue to shrink, even this is not adequate
CER evolution: Dual-damascene via etching

- Resist is heavily distorted by plasma etching
- Dense vias (i.e. overlapping exposure areas) are worse

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Summary

- Line edge roughness is a common and potentially serious problem when patterning 193 nm photoresist
- Both lithography and plasma etching play a role in LER
  - Polymer aggregates in the resist cause it to be susceptible to roughening during both developing and etching
  - Worse as resist is thinner and narrower, or when features are closer together
  - Etching distorts roughness further—ion bombardment, radicals, heat, polymer deposition
  - LER vs. wiggling, and the role of stress
- Modeling of LER/CER will need to account for all of this...
Near-Surface Regions Dramatically Altered by Ions and Reactive Neutrals

Steady state result: Near-surface region shows spontaneous layering; structure propagates down as etch proceeds.

Side view and depth profile of a cell from 5:5:1 C₄F₄/F/ 200 eV Ar⁺ (Si=white, C=grey, F= black).
Plasma-\textit{Polymer} Interactions: Ions and Radicals

1. Ion-surface interactions – ion impact profoundly alters the near-surface polymer region.
   - dramatic example of ion-neutral synergy
   - $\text{Ar}^+/\text{F (H)}$ on polystyrene example

2. Key concept in ‘radiation’ effects in polymers: cross-linking vs. scissioning.

3. How do these effects manifest themselves in plasma-polymer interactions? What relation to PR roughening?
Measured $\text{Ar}^+/\text{Polystyrene}$ Sputter Yield (150 eV)

Drastic drop in yield vs. ion fluence

Polystyrene Starting Cell: MD Model

Top View

Side View

PS monomer
\((C_8H_8)\)
Polystyrene Starting Cell: MD Cell Sideview Post-Thermalization

\( \sim 20 \, \text{Å} \times 28 \, \text{Å} \times 52 \, \text{Å} \)
(depth x width x height)

\( \rho \sim 1 \, \text{g/cm}^3 \)

H:C Ratio = 1
Polystyrene Surface Before and After $10^{17}$ cm$^{-2}$ Ar$^+$ Fluence (100 eV)

Support by XPS/ellipsometry measurements of beam-processed samples (G.S. Oehrlein and R. Bruce, UMd)
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

R.L. Bruce, UMd
Ion Modification of Near-Surface Polymer Region

- Incoming Ions
- Ion Scattering
- C$_x$H$_y$ Products
- Dehydrogenation

Modified Layer:
- Crosslinking
- Sputtering
- Dangling Bond Formation
- Undisturbed Polymer
1. Inert gas ion bombardment initially sputters rapidly, but at some point, crosslinking dominates scissioning and sputter yield drops 2 orders of magnitude.
   - Competition between scissioning and crosslinking that crosslinking eventually wins; even polymers known to be ‘scissioning’ (e.g. PαMS) may also succumb to ion-induced crosslinking near surface.

2. Likely that polymer-based etch masks (e.g. photoresist) must undergo similar near-surface ‘toughening’ to act as etch mask (and deposition often helps).

3. Radicals such as F and H (& Ar+) remove ‘crust’ and sputter yield returns to a high value: more or less ‘conventional’ ion-neutral synergy.
Photoresist Roughening

» Motivation
  • Fundamental etching and roughening mechanisms of photoresist (PR) and polymer masking materials are poorly understood.
  • Particularly a problem with 193 nm photoresist

» Goals
  • Determine plasma species and conditions primarily responsible for PR degradation and roughening, starting with Ar plasmas.

» Approach
  • Find conditions in vacuum beam system that reproduces roughness observed in plasma
  • Vacuum beam system technique:
    • Ar$^+$ ion bombardment
    • Remote Ar or Xe ICP or Xe lamp UV/VUV
    • Temperature-controlled sample stage

We look at the simplest case: Ar plasma only; no FC or other chemistry
Example of Roughening of 193 nm Photoresist

[N. Negishi et al., JVSTB, 23, 217, 2005. (Hitachi)]

How to explain "fettuccini effect"?
Experimental Methods

» Beam system
  • UHV Chamber, Base Pressure: \(~5\times10^{-8}\) Torr pumped with a 2000 L\(\cdot\)s\(^{-1}\) turbo pump, rises to \(~3\times10^{-5}\) Torr when both sources are running
  • Equipped with Commonwealth Ion Source and Oxford Applied Research (OAR) Plasma Source

» Commonwealth Ion Source
  • Normal incidence 150 eV Ar\(^+\)

» OAR ICP Source
  • First source of UV/VUV Radiation from argon or xenon plasma
  • Ions and electrons deflected to walls of differentially pumped region

» Resonance Xenon VUV Line Source
  • Source of 147 nm VUV radiation
  • Flux \(\sim 10^{14}\) cm\(^{-2}\) s\(^{-1}\)

» Results compared to ICP plasma experiments (UMd)
Experimental Methods

» ICP system*: 10 mtorr; $V_{dc} \sim -150$ V; 10% C4F8 ; 90% Ar

- 300 mm wafer
- Blanket 193 nm PR
- Substrate cooling w/10° C cooling liq.

*G.S. Oehrlein et al., UMd
Photoresists

- PMMA-based 193 nm PR (Rohm & Haas; ~250 nm thickness)

- commercial 248 nm PR (~400 nm thickness)

- spin-coated onto Si wafers without the photo-acid generator (PAG) or base quencher
193 nm PR Chemical Structure

- methyl adamantyl methacrylate leaving group
- $\alpha$-gamma butyrolactone methacrylate lactone group
- polar group for adhesion promotion

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193 nm PR Roughness Observed in ICP

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

*G.S. Oehrlein et al., UMd
193 nm PR Roughness Observed in ICP

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

60s $C_4F_8/90\%Ar$ plasma

*G.S. Oehrlein et al., UMd
Ion bombardment only: Not enough roughening

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

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

[Image showing AFM images at different temperatures and PR values]
Remote VUV: bulk modifications

» 193 nm PR exposed to remote VUV (5 min to 11.5 hrs)

» Bulk chemical modifications observed ex-situ with Transmission FTIR

![Chemical structure diagram]
Only (Ar ICP) VUV: surface observation

Surface roughness quantified with 1x1 \(\mu m^2\) AFM images.

<table>
<thead>
<tr>
<th>Time</th>
<th>193 nm PR</th>
<th>248 nm PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td>0.34</td>
<td>5.10</td>
</tr>
<tr>
<td>20 min</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>2.5 hr</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>11.5 hr</td>
<td>0.75</td>
<td>0.26</td>
</tr>
</tbody>
</table>

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

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147 nm VUV radiation: bulk modifications

- 193 nm PR exposed to VUV (1 min to 2 hrs)
- 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
- Much less prevalent with 248 nm PR
Remote VUV Conclusions

» VUV breaks C=O and C-O-C bonds to a depth of ~100 nm as seen in Transmission FTIR.

» This is consistent with previous VUV studies in the literature and plasma experiments, including uv ‘cure.’

» -CH₃ and -CH₂- stretching relatively untouched.

» Relatively large amount of oxygen present in 193 nm PR makes it susceptible to VUV radiation.

» VUV radiation results in smooth surfaces (< 1 nm RMS) compared to argon plasma exposures. Furthermore, elevated temperature (T≤100° C) VUV exposure does not result in roughness.
Simultaneous Ar\(^+\) Bombardment and VUV

**UV/VUV only**
- Minimal surface roughness (<1 nm)

**Ar\(^+\) only**
- Slight surface roughness (a few nm)

**Ar\(^+\) and UV/VUV**
- (VUV at 45° due to geometrical constraints)

VUV Radiation: breaking of C=O and C-O-C bonds to a depth of ~90 nm.

Ion bombardment: highly modified near-surface region.

Experiment designed to achieve 4.0x10\(^{17}\) ion\(\cdot\)cm\(^{-2}\) in 40 min.

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Simultaneous Ar\textsuperscript{+} bombardment and VUV: surface observation

4.0 x 10\textsuperscript{17} ions\textbullet cm\textsuperscript{-2} 150 eV Ar\textsuperscript{+} and 40 min VUV (remote Ar ICP)
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Simultaneous ions &amp; High intensity VUV</th>
<th>Simultaneous ions &amp; Low intensity VUV</th>
<th>Ions only</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>1.523</td>
<td>1.456</td>
<td>1.022</td>
</tr>
<tr>
<td>40°C</td>
<td>2.166</td>
<td>1.437</td>
<td>1.228</td>
</tr>
<tr>
<td>65°C</td>
<td>3.530</td>
<td>2.249</td>
<td>1.318</td>
</tr>
</tbody>
</table>

- **Surface roughness** photon / ion ratio dependent: synergy!!

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Beam and plasma roughness comparison

Ar\(^+\) & VUV (Ar) Beam

- **75° C**: 5.19 nm, 9.80 nm
- **100° C**: 2.30 nm, 1.59 nm

Argon plasma “floating”

- **5.10 nm**, 11.82 nm
- **1.17 nm**, 2.03 nm

248 nm PR

193 nm PR
Lateral scale of features is comparable between plasma and Ar$^+$ + VUV + heating beam experiments.
PMMA-Based 193 nm PR Roughening Mechanism

- *Mechanism* of synergistic effect not clear!
- Ion bombardment alters near-surface (1-2 nm), creating a heavily cross-linked, C-rich region
- VUV photon effects penetrate ~ 50-100 nm, breaking C-O bonds
- Role of heating?
- Energy density? (Engelmann et al.)
- Role of chemistry (e.g. C/F) in plasma?
- Likely that the mechanisms resulting in 193 nm PR roughening are NOT simple!
Spontaneous formation of stable aligned wrinkling patterns

Edwin P. Chan and Alfred J. Crosby*

Received 3rd November 2005, Accepted 19th February 2006
First published as an Advance Article on the web 6th March 2006
DOI: 10.1039/b515628a

We introduce a new methodology to produce aligned, or patterned, surface wrinkles on a soft elastomer sans topography. The surface buckles orient through the manipulation of the local stress distributions, which we control by defining specific regions of local differences in the elastic moduli of the material.
What is happening in plasmas?

To what extent can we relate these beam measurements and associated analysis to actual plasmas?

What are vuv fluxes in ‘realistic’ plasmas?

Are the photon/ion flux ratios we observed in the beam system seen in plasmas?

What exactly are the photons doing in the polymer?
ICP Plasma Measurements*

10-50 mT
20-200 W ICP

VUV Spectrum

Ar 10 mT, 200W

VUV intensity (arb)

Wavelength (nm)
Comparison: Beam Results vs. ICP (UCB; MJ Titus)

Beam and plasma results both show effect scales w/ **fluence**

Ar plasma photon flux estimated;
Exposures: ~10 s-100 s
**VUV Flux Estimates from Literature: $10^{15}$-$10^{16}$ cm$^{-2}$s$^{-1}$**

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**Absolute intensities of the vacuum ultraviolet spectra in oxide etch plasma processing discharges**

J. R. Woodworth, a) M. E. Riley, V. A. Amatucci, T. W. Hamilton, and B. P. Aragon

_Sandia National Laboratories, Albuquerque, New Mexico 87185-1423_

(Received 28 April 2000; accepted 30 October 2000)

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**TABLE V. Comparison of side-view and through-the-wafer-view VUV intensities at the wafer. VUV fluxes are summed over the wavelength intervals listed.**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Flow rate (sccm)</th>
<th>View</th>
<th>VUV fluxes below 130 nm</th>
<th>VUV fluxes 130–140 nm</th>
<th>Total flux 70–140 nm</th>
<th>10$^{14}$ cm$^{-2}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$F$_6$</td>
<td>10</td>
<td>Through wafer</td>
<td>8.3</td>
<td>2.8</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>C$_2$F$_6$</td>
<td>10</td>
<td>Side view</td>
<td>2.5</td>
<td>1.1</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>CHF$_3$</td>
<td>10</td>
<td>Through wafer</td>
<td>27</td>
<td>3.3</td>
<td>30.3</td>
<td></td>
</tr>
<tr>
<td>CHF$_3$</td>
<td>10</td>
<td>Side view</td>
<td>6.8</td>
<td>3</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Ar/C$_2$F$_6$/H$_2$</td>
<td>10/10/10</td>
<td>Through wafer</td>
<td>166</td>
<td>10</td>
<td>176</td>
<td></td>
</tr>
<tr>
<td>Ar/C$_2$F$_6$/H$_2$</td>
<td>10/10/10</td>
<td>Side view</td>
<td>44</td>
<td>6.3</td>
<td>50.3</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>10</td>
<td>Through wafer</td>
<td>350</td>
<td>0.0</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>10</td>
<td>Side view</td>
<td>22</td>
<td>0.0</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>10</td>
<td>Through wafer</td>
<td>13.2</td>
<td>43</td>
<td>56.2</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>10</td>
<td>Side view</td>
<td>4.7</td>
<td>8</td>
<td>12.7</td>
<td></td>
</tr>
</tbody>
</table>
VUV – Polymer Model

\[ J_{hv,0} \quad \frac{dN_i}{dx} = 0 \quad \frac{dN_i}{dx} = 0 \]

\[
\frac{dN_{hv}}{dx} = -\left( \sigma_{ester} N_{ester} + \sigma_{lactone} N_{lactone} + \sigma_{CC} N_{CC,0} \right)
\]

\[
\frac{dN_i}{dt} = -\sigma_i N_i N_{hv} \nu \quad For \ i = \text{ester, lactone}
\]
Simulation Results: Decrease in O concentration with increasing fluence
Model parameters:

\[
\begin{align*}
\sigma_C &= 3 \times 10^{-22} \text{ m}^2 \\
\sigma_O &= 3 \times 10^{-20} \text{ m}^2 \\
n_C &= 1 \times 10^{29} \text{ m}^{-3} \\
n_O &= 2.2 \times 10^{28} \text{ m}^{-3} \\
\lambda (C) &= 33 \text{ nm}
\end{align*}
\]
Examine model at 4 fluences
Model depth profile: fluence 1
Model depth profile: fluence 2
Model depth profile: fluence 3

![Graph showing depth profile with concentration of C & O Species and Photons](image-url)
Model depth profile: fluence 4
Conclusions: PMMA-Based 193 nm PR Roughening (Ar/Xe-Only)

• Ion bombardment, VUV photons, (and substrate heating) act synergistically to give observed “fettucini-like” roughening in beam system

• Recent results suggest electron impact (100’s eV) can affect FTIR similarly; electrons also etch (fast beaming electrons hitting surfaces seen in simulations: e.g. Kawamura & Lieberman IMPACT results)

Effects of electrons and vuv/uv photons may be related to existing tool ‘knobs’;
Can we exploit these effects further??
Next Steps: Study *Patterned* Samples

Samples from Spansion:

300 mm wafers with a dielectric film stack (TEOS on SiN); M1 single damascene trenches.

Immersion ArF resist on SiON on a:C w/ test pattern in resist that includes ~70 nm trenches in the core, pitch ~130 nm.
Preliminary Results on Spansion Sample

- **unprocessed**
  - 0.525
  - 2.5 nm
  - $1 \times 10^{18}$ ions·cm$^{-2}$

- **Heating only 1 hr**
  - 0.458
  - 2.5 nm
  - $2.5 \times 10^{17}$ photons·cm$^{-2}$

- **65°C; non-patterned areas**
  - 0.317
  - 2.5 nm
  - $1 \times 10^{18}$ ions·cm$^{-2}$
  - 2.457
  - 10 nm

$2.5 \times 10^{17}$ photons·cm$^{-2}$ denotes image color scale.