Plasma-Surface Interactions and the Control of Plasma Distribution Functions

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Plasma Distribution Functions and Surfaces

- Low temperature plasma distribution functions that characterize non-equilibrium effects encompass *more than just eedfs*

- Ions (IEDFs) play important roles, especially at surfaces

- Photons, especially VUV, and electrons important for organic materials

- Often *synergies* between non-equilibrium effects

- Neutral translational, vibrational and electronic non-equilibrium effects can be important as well
Initial Conditions $\alpha$-C:H MD Calculations

$\alpha$-C:H film
Dimension: 2.8x2.8x7.5 nm
H content: 27%
sp3 bonding: 25.4%
Density: 2.4 g/cm³
Bottom 2 layers fixed
Surface temperature: 300 K

C-H bond 1.04 Angstrom
C-C bond 1.44 Angstrom

Figure 1. Radial distribution function of $\alpha$-C:H film. No evident peaks after 2.65 Angstrom shows that it is an amorphous structure.
Snapshots of a-C:H Film Near Surface Region After Ar⁺ Ion Impacts

Ar⁺ ion energy: 50 – 200 eV

Original film                         50 eV                              100 eV                          200 eV

White: C; Black: H

Snapshot of near-surface-region of a-C:H film before and after 3000 impacts (fluence ~ 3.7e+16 cm⁻²) at various energies.

The Ar ions modify the film by depleting the surface of hydrogen.
Near Surface Region Composition Before and After Ion Impacts

Ar$^+$ ion energy: 200 eV

After 3000 impacts

H/C ratio

Depth, Angstrom

Original film

3.7e+16 cm$^{-2}$ Ion fluence
Composition of H-Free a-C Film Before and After Ion Impacts: \textit{Unchanged}

$\text{H}_2^+$ ion energy: 50eV; No hydrogen in the original film

Ion fluence 0.6e+16 cm$^{-2}$  2e+16 cm$^{-2}$  6e+16 cm$^{-2}$
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.

Silicon etch by fluorocarbon and argon plasmas in the presence of fluorocarbon films

Joseph J. Végh, David Humbird, and David B. Graves
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C₄F₄/ F/ Ar⁺ on Si

Species Density (arb)

Depth (Å)

- C
- F
- Si

FC
Si-C
Si-F
disordered Si
crystalline Si

FC Film Thickness (Å)

Incident 200 eV Ar⁺ (ML)
Si Etch Yield vs. Average FC Film Thickness

MD Simulation Results

Experimental Results

*Oehrlein et al.

Fluorocarbon Film Thickness (nm)

Etch Yield

Etch Yield (SiO$_2$/ion or Si/ion)

600 W Inductive Power
20 mTorr Pressure
Vdc = -100 V

Solid--SiO$_2$ Sample
Open--Si Sample

Varying C$_4$F$_4$/F/Ar+
or CF/F/Ar+
ratios

200 eV Ar+
Relatively Large Products Leave Surface

Si-White, Red
C-Black, Yellow
F- Grey, Green
Ar-Purple

Bottom 2 layers are fixed
Top is open
Periodic BC in lateral dimensions

Incoming Ion

Colored atoms will be etched

Role of FC clusters in plasma, emitted by surface? Re-deposition of clusters/heavy species?
Examples of Clusters Leaving Surface at Steady State: *Alters Plasma Distribution Functions*
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.
Model 193 nm Photoresist: PMMA Based

[Chemical structure diagram]

Leaving group  \( \alpha \)-GBLMA  Polar group
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

What explains this extreme roughness??
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

CNRS/LTM (CEA/LETI-Minatec), 17 Rue des Martyrs, 38054 Grenoble Cedex 09, France

FIG. 1. (Color online) LWR variation (LWR_final − LWR_initial) measured by CD-AFM on isolated patterned resist line after Cl_2/O_2 plasma exposure under LiF, Al_2O_3, and KCl windows as well as when no window is in place.
Vacuum Beam Setup

Vacuum Beam (VB) System: Side View

Base Pressure: $5 \times 10^{-8}$ Torr
Sample Temperature: 20 – 100°C
Ion Source: 150 eV $\text{Ar}^+$ (Commonwealth)
VUV Source: Xe & Ar VUV Source
Simultaneous Ions and Photons: *agreement!*

(D. Nest et al, 2007)

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

<table>
<thead>
<tr>
<th>Temperature</th>
<th>193 nm PR</th>
<th>248 nm PR</th>
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<tbody>
<tr>
<td>75°C</td>
<td>5.19 nm</td>
<td>2.30 nm</td>
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<tr>
<td>100°C</td>
<td>9.80 nm</td>
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Argon plasma

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<tr>
<td>75°C</td>
<td>5.10 nm</td>
<td>1.17 nm</td>
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<tr>
<td>100°C</td>
<td>11.82 nm</td>
<td>2.03 nm</td>
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</table>
Ar ICP Comparison

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

(M. Titus et al, 2009)

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.

Ion Flux
Ion Current Probe

To Ion Mass Spec.

Ion Composition ~ Products

OES

Langmuir Probe:
$n_e, T_e, \Phi_p$

To Roughing Pump

H$_2$O In

Load-Lock Port

H$_2$O Out

RF Bias

Ion Energy

H. Singh, (UC Berkeley, 2000)
‘Damaged’ Layer Necessary for Enhanced Roughening: *Energetic Ions + VUV + T*$_{\text{elevated}}$

Beam vs. plasma: remarkable agreement overall

\[ J_+ t \sim 10^{17} \text{ cm}^{-2} \]
\[ J_{hn} t \sim 10^{17} \text{ cm}^{-2} \]
\[ T \sim 60^\circ \text{C} \]
**VUV/O₂ and Porous Low K Dielectric Films**

Vacuum Beam (VB) System: Side View

- **Flux** = \(2.7 \times 10^{14}\) ions/(cm\(^2\) s)
- **150 eV Ar\(^+\) ions**
- **O₂ in chamber**

- **Flux** = \(1.3 \times 10^{14}\) photons/(cm\(^2\) s)
- \(\lambda = 147\) nm
- **Xe excimer lamp**

- **5 x 10^{-8} Torr base pressure**
- **Sample temperature: 20 – 100°C**
- **150 eV Ar\(^+\) (Commonwealth)**
- **Xe VUV Source**

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

Joe Lee, 2009
VUV/O$_2$: Synergistic Effects
Synergistic Ion/VUV Effects on 193 nm Photoresist

AFM

Pristine photoresist

65°C

Ar

Poly (methyl methacrylate)
Carbon Oxygen Hydrogen

Species Density (arb)

Distance from Top (nm)

C
O
H

250nm

2.25
Roles of Ions, 147 nm VUV Photons and Electrons in 193 nm Photoresist Texture

Pristine photoresist

VUV-modified layer

Electron-modified layer

~ 2nm

~ 100nm

1 keV Electron

~ 55nm

Pristine photoresist
Surface roughness – Ion/VUV/ Electron

Ion fluence: $1 \times 10^{18}$ ions/cm$^2$, 147 nm photon fluence: $4.8 \times 10^{17}$ photons/cm$^2$

Substrate temperature: 65°C

The surface morphology and roughness changes dramatically with electron dose or fluence

Electron Fluence

| Fluence (mC/cm$^2$) | Image
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0 mC/cm$^2$</td>
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</tr>
<tr>
<td>1 mC/cm$^2$</td>
<td><img src="image2.png" alt="Image" /> 5.46</td>
</tr>
<tr>
<td>4 mC/cm$^2$</td>
<td><img src="image3.png" alt="Image" /> 6.87</td>
</tr>
<tr>
<td>8 mC/cm$^2$</td>
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Electron-induced scission
Surface roughness – Ion/VUV/ Electron

Ion fluence: $1 \times 10^{18}$ ions/cm$^2$, 147nm photon fluence: $4.8 \times 10^{17}$ photons/cm$^2$
Substrate temperature: 65°C

*The surface morphology and roughness changes dramatically with electron dose or fluence*

Electron Fluence

- 0mC/cm$^2$
- 1mC/cm$^2$
- 4mC/cm$^2$
- 8mC/cm$^2$

Ion+VUV

- 4.00
- 5.46
- 6.87
- 2.01

Electron-induced scission
Electron-induced cross-linking
Vibrational Distributions in Plasmas

Kinetic theory of low-temperature plasmas in molecular gases

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‡ Lebedev Physical Institute of the Russian Academy of Sciences, Moscow, Russia


Coupling eedf and molecular vibrational energy distributions: neutral chemistry effects
Coupled EEDF and $N_2$ Vibrational Levels

**Figure 2.** Electron energy distribution functions in $N_2$ for $E/N = 10^{-15}$ V cm$^2$ and the following values of $T_e$ in K: 2000 (A); 3000 (B); 4000 (C); 6000 (D).

**Figure 3.** Vibrational distribution function of $N_2(X, v)$ for the same conditions as in figure 2.
Concluding Remarks

1. Importance of controlling various plasma DFs at surfaces is clear: surface effects are generally sensitive to a variety of DFs.

2. Ion, electron and photon energy distributions often have direct surface effects; synergies are common.

3. Surface processes alter plasma DFs through emission and alteration of plasma chemistry.

4. Neutral DFs – vibrational and electronic especially – can also play dominant roles at surfaces.