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/cm$^3$
Bottom 2 layers fixed
Surface temperature: 300K

Hard film

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

White: C; Black: H

Original film 50 eV 100 eV 200 eV

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: *Unchanged*

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

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.
C₄F₄/ F/ Ar⁺ on Si

Species Density (arb)

Depth (Å)

0 50 100

0 10 20 30 40 50

C  F  Si

FC  Si-C  Si-F  disordered Si  crystalline Si

FC Film Thickness (Å)

0 5 10 15 20 25 30 35 40 45 50

0 50 100 150 200 250

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

MD Simulation Results

Experimental Results
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

Role of FC clusters in plasma, emitted by surface? Re-deposition of clusters/heavy species?

Incoming Ion
Colored atoms will be etched

~22Å
Examples of Clusters Leaving Surface at Steady State: *Alters Plasma Distribution Functions*
Near-surface alterations consistent with separate XPS and ellipsometry measurements of beam-processed samples
Model 193 nm Photoresist: PMMA Based

Leaving group

$\alpha$-GBLMA

Polar group
193 nm PR Roughness Observed: 

**Ar-only plasma**

» **ICP system**: 10 mtorr; \( V_{dc} \sim -150 \text{ V} \); 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

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FIG. 1. (Color online) LWR variation ($LWR_{\text{final}} - LWR_{\text{initial}}$) 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.
Vacuum Beam Setup

Vacuum Beam (VB) System: Side View

Faraday Cup

Ion Source

VUV Spec.

Sample

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
Simultaneous Ions and Photons: *agreement*!

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

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

Ar 104.8 and 106.7 nm Total VUV Flux

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

To Neutral Mass Spec.

Ion Flux

Ion Current Probe

To Roughing Pump

H\(_2\)O In

H\(_2\)O Out

Load-Lock Port

RF Bias

Ion Energy

Langmuir Probe:
\(n_e, T_e, \Phi_p\)

VUV Spec.

Plasma Stability
Plasma Chemistry

OES

H. Singh, (UC Berkeley, 2000)

(M. Titus et al, 2009)
‘Damaged’ Layer Necessary for Enhanced Roughening: *Energetic Ions + VUV + $T_{\text{elevated}}$*

Beam vs. plasma: remarkable agreement overall
VUV/O₂ and Porous Low K Dielectric Films

Vacuum Beam (VB) System: Side View

Flux = 2.7x10^{14} ions/(cm² s)
150 eV Ar⁺ ions
O₂ in chamber

Flux = 1.3x10^{14} photons/(cm² s)
λ = 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**

![Graph showing absorbance against wavenumber for VUV/O$_2$, O$_2$/VUV turned away, VUV only, and Pristine samples.](image-url)
Synergistic Ion/VUV Effects on 193 nm Photoresist

AFM

2.25

250nm

65°C

Poly (methyl methacrylate)
Carbon  Oxygen  Hydrogen

Pristine photoresist

Species Density (arb)
Roles of Ions, 147 nm VUV Photons and Electrons in 193 nm Photoresist Texture

- **Pristine photoresist**
  - VUV-modified layer
  - Electron-modified layer

- **VUV-modified layer**
  - 2.25 nm
  - 0.28 nm

- **Electron-modified layer**
  - 0.34 nm
  - ~100 nm

- **1 keV Electron**
  - ~55 nm
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

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<th>Fluence (mC/cm$^2$)</th>
<th>Image</th>
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<tbody>
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<tr>
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Ion+VUV

250 nm
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$$^1$**
- **1mC/cm$^2$$^2$**
- **4mC/cm$^2$$^3$**
- **8mC/cm$^2$$^4$**

**Ion+VUV**

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$^\circ$C

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

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Electron-induced scission

Electron-induced cross-linking

250 nm
Vibrational Distributions in Plasmas

Kinetic theory of low-temperature plasmas in molecular gases

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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 $T_u$ 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.