In Situ Surface Diagnostics during Plasma-Material Interactions

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Outline

• Motivation for studying plasma-materials interactions

• Requirements for in-situ, and ex-situ diagnostics techniques

• Review of selected surface diagnostic methods

• Specific example of applications of the above

• Methods for diagnosing desorbing products and examples

• Pulsed plasmas for surface reaction diagnostics
What type of Plasma-Materials Interactions?

• **Plasma species impinging on surfaces:** *Neutral species* (radicals and stable molecules), *positive ions* and to a lesser extent, *electrons* and *photons*, and perhaps negative ions and *metastable species*.

• **Materials:**
  
  ➢ *Si integrated circuit materials in low-pressure etching processes* (Si, SiO₂, Si₃N₄, photoresist, TiN, Cu, etc.), *reactor materials* (chamber wall coatings, substrate holder, electrodes, etc, - basically any material that comes in contact with the plasma).

  ➢ *Plasma deposition processes, including plasma-assisted atomic layer deposition* (SiO₂, Si₃N₄, several oxide materials deposited on wafer surfaces and reactor walls.

  ➢ *Atmospheric pressure, “cold” plasma* (includes a variety of materials, including biological materials – dominated by neutral radicals).

• Will restrict examples to Si etching
Neutral reactions on surfaces often dominate those in the gas phase, especially at low pressure.

- Recombination of radicals influences etching rates and feature profiles
- Product transport to and deposition on the walls changes the rate of recombination
- Etch product impingement opens up other product channels, forming heterogeneous reactions
Why are Plasma-Wall Interactions Important?

• Modern etching and deposition processes usually consist of a “recipe” containing many steps, e.g., a minute Si etching process may consist of:

1. “Waferless” chamber clean with NF$_3$ plasma.
2. Cl$_2$/Ar plasma etching of Si with substrate rf bias.
3. Cl$_2$/HBr/O$_2$ plasma etching with low substrate bias.

• During this process, the surfaces of the reactor transition from (1) heavily fluorinated to (2) thinly chlorinated to (3) being coated with a thicker SiO$_x$Cl$_y$Br$_z$ film.

• This leads to large changes in heterogeneous rates in <1 min.
Requirements for Plasma-Surface diagnostics

• A method should provide some of the following:
  - chemical identification (elements, bonding, etc.)
  - adsorbate coverages (relative and absolute)
  - sticking coefficients
  - recombination probabilities
  - reaction probabilities
  - activation energies
  - pre-exponential factors
  - reaction orders

• The method should also be:
  - non-perturbing to and by the plasma
  - capable of providing time-dependent measurements
  - easy to interpret
Some Surface Analysis Techniques That Have Been Applied to Plasma-Surface Interactions

• **Ellipsometry (single wavelength and spectroscopic)**
  - Yields n and k, the real and imaginary parts of the complex index of refraction of the film, but no chemical information. Infrared spectroscopy

• **Infrared Absorption Spectroscopy**
  - Measures absorption of infrared light as a function of wavelength due to excitation of vibrations and rotations of species in the beam path.
  - Provides chemical identification.
  - Fourier transformed from the time to frequency domain.
  - This FT-IR signal is very weak for a thin (i.e. ~monolayer) film, hence a multi-pass arrangement is needed, usually with a total internal reflection (TIR), IR–transparent substrate (e.g. GaAs).
Example of SE Probing of Si Etching in a Chlorine Plasma

Spectroscopic Ellipsometry as a Diagnostic Method

• The methods should provide as many as possible of the following:

  - elemental analysis of the near-surface layer: NO
  - chemical identification (bonding, stoichiometry, etc.): NO
  - adsorbate coverages (relative and absolute): YES*
  - sticking coefficients: NO
  - recombination probabilities: NO
  - reaction probabilities: NO
  - branching ratios: NO
  - activation energies: NO
  - pre-exponential factors: NO
  - reaction orders: NO

• The method should also be:

  - non-perturbing: YES
  - not perturbed by the plasma: YES
  - capable of providing time-dependent measurements YES
  - easy to interpret: NO
TIR-FTIR Setup on ICP

Aydil and co-workers\textsuperscript{17, 50, 51, 52}

• Ullal \textit{et al.} used TIR-FTIR to characterize the buildup of SiO and SiOCl groups on GaAs during etching of Si in a chlorine ICP as well as to monitor its removal in a SF6 plasma,\textsuperscript{17, 50, 51} to detect SiHx during plasma-assisted deposition of hydrogenated amorphous Si in SiH4 plasmas.\textsuperscript{52}

TIR-FTIR as a Diagnostic Method

• The methods should provide as many as possible of the following:

  - elemental analysis of the near-surface layer: **YES (but limited)**
  - chemical identification (bonding, stoichiometry, etc.): **YES (but limited)**
  - adsorbate coverages (relative and absolute): **YES**
  - sticking coefficients: **NO**
  - recombination probabilities: **NO**
  - reaction probabilities: **NO**
  - branching ratios: **NO**
  - activation energies: **NO**
  - pre-exponential factors: **NO**
  - reaction orders: **NO**

• The method should also be:

  - non-perturbing: **YES**
  - not perturbed by the plasma: **YES**
  - capable of providing time-dependent measurements **YES (but long times)**
  - easy to interpret: **MAYBE**
Auger Electron Spectroscopy (AES)

- Quantitative detection of all elements except H at sub-monolayer sensitivity.

1) an electron from a high energy beam knocks an electron out of a deep core level (electron #1)

2) an electron from a level farther from the core relaxes into this deep core level (electron #2)

3) electron #3, the “Auger electron” is simultaneously emitted to conserve energy. The energy of this electron is a signature of the atom.

In this example

\[ E_{KL1L2,3} = E_K(Z) - E_{L1}(Z) - E_{L2,3}(Z + 1) - q\phi \]

where \( Z+1 \) indicates that the final state is doubly ionized and \( q\phi \) is the sample work function.

Fig. 10.6 Electronic processes in Auger electron spectroscopy.
X-Ray Photoelectron Spectroscopy (XPS)

- X-rays eject electrons (photoelectrons) from core levels.
- Measure kinetic energy of photoelectrons, get core energy or binding energy, $E_b$ of photoelectron and hence identify element it came from.

$$h \nu = E^F_B (k) + E_{kin} + \phi_{spec}$$

- Quantitative detection of all elements except H at sub-monolayer sensitivity.
- Provides bonding information (i.e. oxidation state).
Challenges with XPS and AES in Plasmas

• XPS and AES are the most general and quantitative surface analysis methods.

• Measuring the energy of electrons emitted from surfaces is a near-impossibility because of:

  1) collisions with the plasma gas
  2) the sheath electric field near the surface accelerates the electrons leaving the surface
  3) magnetic fields increasingly deflect higher energy electrons

• Approaches to work around these limitations...
X-ray photoelectron spectroscopy with vacuum sample transfer

- Transfer sample to XPS analysis chamber after plasma-surface exposure.
XPS with Vacuum Transfer as a Diagnostic Method

• The methods should provide as many as possible of the following:
  
  - elemental analysis of the near-surface layer: YES (only H not detectable)
  - chemical identification (bonding, stoichiometry, etc.): YES
  - adsorbate coverages (relative and absolute): YES
  - sticking coefficients: NO
  - recombination probabilities: NO
  - reaction probabilities: NO
  - branching ratios: NO
  - activation energies: NO
  - pre-exponential factors: NO
  - reaction orders: NO

• The method should also be:

  - non-perturbing: YES
  - not perturbed by the plasma: YES
  - capable of providing time-dependent measurements NO (at t → ∞)
  - easy to interpret: YES
High resolution spectra after Si etching in chlorine ICP
Si(2p 3/2 ) core level spectrum with 2p 1/2 removed

- Strong peak (off scale here) is from underlying Si(100) substrate.

- SiCl, SiCl₂ and SiCl₃ binding energy shifts in excellent agreement with published values.

- A small feature at low binding energy believed to be Si with a dangling bond and 3 Si-Si bonds.
ANGLE-RESOLVED X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

- Some length scales:
  - x-ray penetration: 17,000 Å into Si
  - electron escape depth ($\lambda$): 22 Å for Si

- Angle-resolved measurements provide a depth resolution of ~6Å
Depth Profiles: Silicon Chloride Species

- $\text{SiCl}_x \sim 16 \text{ Å}$
- $\text{SiCl} > \text{SiCl}_2 > \text{SiCl}_3$
- Si$^-$ deep into layer
Spinning Wall Method

• A portion of the plasma wall is rotated so that it is exposed to the plasma and then to an analysis method.

• Auger electron spectroscopy has been used to characterize the surface.

• Mass spectrometry has been used to measure desorption fluxes of species leaving the surface.

• The method currently has been demonstrated with cylindrical substrates and is primarily for studying plasma-wall interactions and not flat substrates such as silicon wafers.
System Configured for Auger Electron Spectroscopy (AES)

Feeding gases into the AES (Staib Ins.) plasma spinning cylinder. The surface exposed to plasma comes from a high-speed motor. The AES e’s and e-beam are directed into the plasma. The plasma is configured for Auger Electron Spectroscopy (AES) or Mass Spec. The AES (Staib Ins.) is shown in the top view with the plasma. The University of Houston is indicated.
AUGER SPECTRA OF REACTOR WALL DURING Cl₂ PLASMAS (ON AND OFF) AT 
\(E_b = 5\) keV

- At \(E_b = 5\) keV, charging of the insulator surface is severe.
- All observed “peaks” are artifacts.

- When the plasma is ON, charging is eliminated, even at \(E_b = 5\) keV.
- Sharp peaks and a smooth baseline are observed.
AUGER SPECTRA OF “SEASONED” REACTOR WALL DURING LONG EXPOSURES TO Cl₂, O₂, OR N₂ PLASMAS

\[ E_b = 5 \text{ keV} \]

\[ \text{AlKLL (0.45)} \]
\[ \text{SiKLL (0.26)} \]
\[ \text{AgMNN (3.3)} \]
\[ \text{OKLL (1.1)} \]
\[ \text{Cl LVV (8.1)} \]
\[ \text{Si LVV (1.5)} \]
\[ N_{KLL} (0.92) \]
\[ \text{N}_2 \text{ plasma} \]
\[ \text{O}_2 \text{ plasma} \]
\[ \text{Cl}_2 \text{ plasma} \]

Anodized Al

10 \mu m

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AUGER ATOMIC CONCENTRATIONS FOR CONDITIONED ANODIZED-Al IN Cl₂, O₂ or N₂ PLASMAS

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>Sensitivity (@E_b=5keV)</th>
<th>mfp (nm)</th>
<th>Cl₂ plasma</th>
<th>O₂ plasma</th>
<th>N₂ plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>8.13</td>
<td>0.89</td>
<td>16.3</td>
<td>0.6</td>
<td>12.7</td>
</tr>
<tr>
<td>Ag</td>
<td>3.27</td>
<td>1.44</td>
<td>1.5</td>
<td>1.8</td>
<td>&lt;2</td>
</tr>
<tr>
<td>N</td>
<td>0.916</td>
<td>1.49</td>
<td>-</td>
<td>-</td>
<td>10.5</td>
</tr>
<tr>
<td>O</td>
<td>1.10</td>
<td>1.86</td>
<td>58.9</td>
<td>70.9</td>
<td>50.0</td>
</tr>
<tr>
<td>Al</td>
<td>0.450</td>
<td>3.79</td>
<td>12.1</td>
<td>17.0</td>
<td>10.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.256</td>
<td>4.21</td>
<td>11.2</td>
<td>9.7</td>
<td>16.7</td>
</tr>
</tbody>
</table>

- Wall is AlₓSiₓO₂ with ~10-20% additional Cl, O, or N in Cl₂, O₂ or N₂ plasmas. *Cl in Cl₂ plasmas corresponds to ~3 x 10¹⁴cm⁻² Cl if uniformly distributed in the near-surface region, or ~8 x 10¹⁴cm⁻² if Cl is just at the surface.*

- Si from erosion of quartz discharge tube; ~1-2 % Ag from Ag-plated gaskets.

- Large amount of Cl in N₂ plasmas, compared to O₂ plasmas.
Pulsed Sputtering: New Method for In-Situ Surface Diagnostics of Chamber Walls During Etching

- Mount small coupon piece on an electrode inserted into the plasma chamber wall.
- Expose coupon to plasma during etching and/or conditioning the chamber.
- Periodically rf bias the electrode in the processing plasma, or in an Ar plasma.
- Detect sputtered species by OES near the surface with and without bias.
- Obtain depth profiles similar to those in Auger Electron Spectroscopy by subtracting no-bias from bias OES signal.
- Studies carried out by Samsung Engineer Junghyun Cho and UH student Priyanka Arora.
Experimental Apparatus

ICP

Matching Network
RF Power (13.56 MHz)

Gas In

RF Power (18 MHz)

Matching Network

Electrode

Optical Fiber

Substrate

To Pump

Spectrometer (HRS-500MS-NI)
Detail of Optical System

- Coupon
- 3/8-24 UNF Thread
- Length 0.21"
- Fiber Optic Feedthrough
- Collimator
- Stainless Optical Cable
- Stainless
- Aluminum
- Ceramic
- 0.08"
- 0.25"
- 0.5"
- 1.5"
- 1.2"
Other Work: New Method for In-Situ Surface Diagnostics of Chamber Walls During Etching

Sputtering of Y$_2$O$_3$ Target: 7 mTorr Ar ICP, Electrode Bias Power of 20 W (-305 Vdc)

- Y lines detected between 407 – 415 nm, only when coupon electrode is biased.
Time-Resolved Si and O Sputtering After Si Etching in Cl₂/Ar/O₂ ICP

- **Si Etching**: Cl₂:Ar:O₂ = 20:2:(0, 1, or 4) sccm, pressure = 20 mTorr, ICP Power = 400 W, Si Substrate Bias Power = 20 W, Run Time = 10 min
- **Sputtering of Y₂O₃ Target**: Ar Flow = 20 sccm, pressure = 9 mTorr, ICP Power = 160 W, Electrode Bias Power = 30 W (-325 Vdc)

- Si and SiCl in film deposited on Y₂O₃ thickest for 5% O₂ and thinnest for 20%O₂.
Other Work: New Method for In-Situ Surface Diagnostics of Chamber Walls During Etching

- Y signal also indicates that the SiOCl-contain film deposited on Y₂O₃ is thickest for 5% O₂ and thinnest for 20%O₂, consistent with the Si and SiCl measurements.
- Interestingly, sputter depth profile for 5% and 20% O₂ are similar, seemingly indicating some penetration of O into Y₂O₃ for the 20% O₂ case.
Detecting Desorbing Species

• Detecting the primary products desorbing from a surface is also challenging.

• Measurements need to occur before many collisions occur.

• Optical spectroscopic analysis (optical emission or absorption spectroscopy, laser-induced fluorescence) should be confined to the near surface region.

• Mass spectrometry needs to be line-of-sight with the substrate with the first sampling orifice close to the substrate.

• Can also use spinning wall method.
- Primary (line-of-sight) products enriched in SiCl₂ and in particular SiCl
Spinning Wall System Configured for Mass Spectrometry (MS)

Feed gases

mass spectrometer

tuning fork chopper

differential pumping

differential pumping

differential pumping

differential pumping

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ATOM RECOMBINATION: Experiment Detects Delayed (L-H) Recombination, not prompt (E-R)
• Plasma-ON signals are a result of desorption of Cl\textsubscript{2} formed by recombination of Cl on the spinning wall surface.

• Plasma-OFF signal is a result of desorption of physisorbed Cl\textsubscript{2}.

J. Guha, V. M. Donnelly, Y-K. Pu, J. Appl. Phys. 103, 013306 (2008);
Extracting Cl L-H Recombination Probabilities

- As desorption rate \( \rightarrow \) rotation rate, mass spec. and \( P_2 \) values \( \rightarrow \) their average values.

- Therefore as \( f \rightarrow \infty \) (i.e. \( t \rightarrow 0 \)) it is as though the sample were continuously exposed to a Cl flux of 1/3 that in the plasma, \( \Gamma_{Cl} \).

- Therefore LH recombination probability,
  \[
  \gamma_{Cl} = \frac{6D_{f \rightarrow \infty}}{\Gamma_{Cl}}
  \]
Cl Atom LH Recombination Probabilities on Anodized Al as a Function of Cl-to-Cl₂ Number Density Ratio

- $\gamma_{\text{Cl}}$ scales with Cl-to-Cl₂ flux ratio.
- Suggests Cl₂ may block sites for Cl adsorption and recombination.
Three Surfaces were Prepared and Reactions Studied:

1. **Lightly oxidized**: Cl₂ ICP, bias on Si substrate, 10 min; then Cl₂ ICP, no bias on Si substrate, 60 min.
2. **Oxidized**: Cl₂/5%O₂ ICP, bias on Si substrate, 10 min; then Cl₂/5%O₂ ICP, no bias on Si substrate, 60 min.
3. **O₂ plasma-treated**: oxidized surface in (2); then O₂ ICP, 60 min; then Cl₂/5%O₂ ICP, no bias on Si substrate, 30 min.

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![Diagram showing AES e's and high-speed motor](image)

![Graph showing E(dI/dE) vs Kinetic Energy (eV) with Cl, O, Si peaks labeled](image)
Cl Langmuir-Hinshelwood Recombination Coefficients and O-atom Near-Surface Concentrations

![Graph showing Cl recombination coefficient versus O surface concentration for different materials: lightly oxidized, O2 plasma-treated, and anodized aluminum.](image)
Why does $\gamma_{\text{Cl}}$ Increase with Increasing O Coverage?

- **O-depleted conditions**: every O bound to 2 Si.

- **O-rich conditions**: occasionally O cannot find a second Si to bond to.

![Chemical Diagram]

$$\text{Si} \quad \text{O} \quad \text{Si} \quad + \text{Cl} \rightarrow \quad \text{Cl}$$

$$\text{Si} \quad \text{O} \quad \text{Si} \quad + \text{Cl} \rightarrow \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Si}$$

$$\text{Si} \quad \text{O} \quad \text{Cl} \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad + \text{Cl}_2(\text{g})$$
Mass Spectra of Products Desorbing from the Spinning Wall in a Cl$_2$ ICP with and without a Si Substrate

Bias = $-108 \text{ V}_{DC}$, Cl$_2$ pressure = 2.5 mTorr, ICP power = 400 W, MS electron energy = 70 eV
Spinning Wall Method

• The methods should provide as many as possible of the following:

  - elemental analysis of the near-surface layer: **YES (only H not detectable)**
  - chemical identification (bonding, stoichiometry, etc.): **SOME (with Auger)**
  - adsorbate coverages (relative and absolute): **YES**
  - sticking coefficients: **NO**
  - recombination probabilities: **YES**
  - reaction probabilities: **YES (but requires other diagnostics)**
  - branching ratios: **YES**
  - activation energies: **SHOULD BE (not done yet)**
  - pre-exponential factors: **MAYBE**
  - reaction orders: **MAYBE**

• The method should also be:

  - non-perturbing: **YES**
  - not perturbed by the plasma: **YES**
  - capable of providing time-dependent measurements **SORE OF (at t > 0.5 ms after plasma exposure)**
  - easy to interpret: **NO**
Pulsed Plasma, Time-Resolved OES Setup

- T-Controlled Jacket
- ICP Coil
- Alumina window
- Chopper Wheel
- Y$_2$O$_3$ Removable liner
- slit
- In out H$_2$O
- Spectrometers
Pulsed Plasma, Time-Resolved OAS Setup
Quantifying these Cl Surface Reactions

• Use pulsed power and time resolved detection of Cl and SiCl$_x$.

• Determine total loss probabilities for Cl at the walls.

• Consider reactions:

1. Cl$_{(g)}$ + Cl$_{(ads)}$ → Cl$_2(g)$
2. Cl$_{(g)}$ + SiCl$_x(ads)$ → SiCl$_{x+1}(g)$
3. Cl$_{(ads)}$ + SiCl$_g(ads)$ → SiCl$_{x+1}(g)$
Time-resolved $n_{Cl}/n_{Xe}$ in Pulsed Cl$_2$ ICP

- Measurements made after Si etching and then conditioning the chamber in the Cl$_2$ plasma without substrate bias.

- **Actinometry**: Cl emission (792.4 nm) divided by Xe emission (828.0 nm) with absolute calibration.

- The lines are $n_{Cl}/n_{Xe}$ simulations from a global model, with the indicated values of $n_e$ and $U$ (ratio of $n_{Cl}$ measured-to- $n_{Cl}$ computed from the model).

- ICP power = 320 W (ON), 0 W (OFF), pressure = 20 mTorr, Cl$_2$:O$_2$:TRG flow rates (sccm) = 20:0:2 or 20:1:2.
Measurements in Pulsed Cl₂ ICP

Time-resolved absorption of (black) Si, (red) SiCl, and (blue) SiCl₂. 500 Hz pulsed plasma with 50% duty cycle. 20 sccm Cl₂/2 sccm Ar at 10 mTorr, 160 W average source power, with -44 V average substrate bias. SiCl₂ number density = 3.1 \times 10^{12} \text{cm}^{-3} at 1000 \mu s.
Cl Recombination Probabilities in Pulsed ICPs

- Recombination coefficients, $\gamma_{Cl}$, and optical emission intensities ratios Cl(792.4 nm) : Xe(828.0 nm), as a function of time for a 70 mins etching period.
- ICP pulse power (frequency = 500 Hz, duty cycle = 50%, ON/OFF = 320/0 W).
- Bias $V_{DC} = 80$ V
- Pressure = 20 mTorr; Cl$_2$/O$_2$/TRG flow rates (sccm) = 20/0/2 or 20/1/2
- Red circles: $n_{Cl}$ at 1000 us, Black triangles: $n_{Cl}$ at 0 µs.
For more details see:


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