Methods of Surface Characterization
Application to Plasma-Wall Interaction and Conditioning

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Plasma-Physics-Seminar
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A plan to develop an “in-situ” surface analysis capability in RPPL to characterize materials purity and to study the plasma-wall material interactions in collaboration with Prof. A. Hoffman and his group.

**Concept**

![Diagram of surface analysis methods]

**Surface Analysis Methods**
Challenge

Investigate the various aspects related to plasma-wall interactions, changes in the properties of materials

Develop and characterize new materials

Approaches

Determine the requirements imposed on materials

Systematically produce material samples that are subjected in controlled laboratory experiments

Characterize the material’s structure, composition, and temperature dependent physical properties, both before and after testing
Surface processes on plasma-facing materials

Important issues

- Composition and phase formation through deposition of plasma impurities on wall materials as a result of chemical reactions and transport processes.

- Erosion and implantation of various high-Z material bombarded with ions at elevated temperatures.

- Deposition of hydrogenous carbon layers (such as a-C:H).

- H implantation and inventory in materials as a function of surface contamination layers, such as oxides and carbides.

- New materials and/or material processes that withstand against severe plasma bombardment
Agenda of this talk

• Introduction of various surface analysis

• Principles of surface analytical techniques

• Several examples

• Our plan to set up “in-situ surface spectrometer” in RPPL
### Various surface analysis techniques

![Diagram showing various surface analysis techniques](image)

<table>
<thead>
<tr>
<th>Radiation IN</th>
<th>photon</th>
<th>photon</th>
<th>electron</th>
<th>ion</th>
<th>neutron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation DETECTED</td>
<td>electron</td>
<td>photon</td>
<td>electron</td>
<td>ion</td>
<td>neutron</td>
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</table>

<table>
<thead>
<tr>
<th>SURFACE INFORMATION</th>
<th>ESCA/XPS</th>
<th>EXAFS</th>
<th>EELS</th>
<th>SIMS</th>
<th>INS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical topography</td>
<td>SEM</td>
<td>AFS</td>
<td>LEED</td>
<td>RHEED</td>
<td>ISS</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>STM</td>
<td>IR &amp; SFG</td>
<td>EELS</td>
<td>SIMS</td>
<td>INS</td>
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<tr>
<td>Chemical structure</td>
<td>AES</td>
<td>EXAFS</td>
<td>EELS</td>
<td>SIMS</td>
<td>INS</td>
</tr>
<tr>
<td>Atomic structure</td>
<td>EXAFS</td>
<td>EXAFS</td>
<td>EELS</td>
<td>SIMS</td>
<td>INS</td>
</tr>
<tr>
<td>Adsorbate bonding</td>
<td>EXAFS</td>
<td>EXAFS</td>
<td>EELS</td>
<td>SIMS</td>
<td>INS</td>
</tr>
</tbody>
</table>

**ESCA/XPS** (Electron Spec. for Chemical Analysis/X-ray Photoelectron Spec.)
**AES** (Auger Electron Spectroscopy)
**SIMS** (Secondary Ion Mass Spectroscopy)
**SNMS** (Sputtered Neutral Mass Spectroscopy)
**ISS** (Ion Scattering Spectroscopy)
**EELS** (Electron Energy Loss Spectroscopy)
**EXAFS** (Extended X-ray Absorption Fine Spectra)
**INS** (Ion Neutralization Spectroscopy)
**LEED** (Low Energy Electron Diffraction)
**RHEED** (Reflection High Energy Electron Diffraction)
Incident energies for various surface analysis techniques

- UPS
- ISS
- LEED
- EELS
- XPS
- AES
- SIMS

Energies to be analyzed

- RBS
- PIXE

Electron Energy (eV)

Electron Mean Free Path

- Energy (eV)
- Band Gap
- Elemental Ionization Potential
- Core Binding Energy
- Nuclear Binding Energy

Energy levels for different techniques:
- UPS: 10^0 to 10^10
- ISS: 10^1 to 10^10
- LEED: 10^1 to 10^10
- EELS: 10^2 to 10^12
- XPS: 10^3 to 10^12
- AES: 10^4 to 10^12
- SIMS: 10^5 to 10^12

Electron Mean Free Path vs. Electron Energy (eV)

- Synchrotrons
- Cyclotrons
- FERMI Lab

Incident energies for various surface analysis techniques

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- PIXE

Electron Energy (eV)

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Electron Mean Free Path vs. Electron Energy (eV)

- Synchrotrons
- Cyclotrons
- FERMI Lab
Electron/Ion Beam Analysis of Materials

- ISS, Static-SIMS/SNMS, LEED, UPS
- XPS, AES, Dynamic-SIMS/SNMS
- RBS, NRA, PIXE, EDAX

- ~ 10’s eV ions
- ~ 100’s –1000’s eV ions (Ar⁺)
- ~ 100’s of KeV
- ~ 1-2 MeV He⁺, H⁺, d⁺...

- Deposition
- Sputtering
- Ion Implantation
- Ion Beam Analysis
Comparison of Sensitivities

![Comparison of Sensitivities Diagram](image)

- AES and XPS
- RBS
- PIXE
- SIMS

ATOMIC CONCENTRATION (atomic fraction)

CONCENTRATION (ppm)

0 1 ppm 1% 0.1% 0.01% 0.001% 0.0001% 0.00001% 0.000001% 0.0000001% 0.00000001% 0.000000001% 0.0000000001% 0.00000000001% 0.000000000001% 0.0000000000001% 0.00000000000001% 0.000000000000001% 0.0000000000000001% 0.00000000000000001% 0.000000000000000001% 0.0000000000000000001% 0.00000000000000000001% 0.000000000000000000001% 0.0000000000000000000001% 0.00000000000000000000001% 0.000000000000000000000001% 0.0000000000000000000000001% 0.00000000000000000000000001% 0.000000000000000000000000001% 0.0000000000000000000000000001% 0.00000000000000000000000000001% 0.000000000000000000000000000001% 0.0000000000000000000000000000001% 0.00000000000000000000000000000001% 0.000000000000000000000000000000001% 0.0000000000000000000000000000000001% 0.00000000000000000000000000000000001% 0.000000000000000000000000000000000001% 0.0000000000000000000000000000000000001% 0.00000000000000000000000000000000000001% 0.0000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000000000000000000001% 0.0000000000000000000000000000000000000000000000000000000000000001% 0.00000000000000000000000000000000000000000000000000000000000000001% 0.000000000000000000000000000000000000000000000000000000000000000001%
**Photoelectron Process**  
*Photoelectric Effect*

- \( E_K \) = kinetic energy of ejected photoelectron  
- \( h\frac{\nu}{c} \) = characteristic energy of X-ray photon  
- \( E_B \) = binding energy of core level  
- \( e_F \) = work function term

\[
E_K = h\frac{\nu}{c} - E_B - e_F
\]

**Auger Process**

- \( E_{KLL} \) = \([E_K - E_L] - E_L\)

The relaxation process resulting in the emission of a KLL electron:

**Photoelectron line energies:**  
*Dependent* on incident energy.

**Auger electron line energies:**  
*In-dependent* on incident energy.
XPS
X-ray Photoelectron Spectroscopy

Electrons can be excited in this entire volume, but only escape within the escape depth ~1mm.

X-ray Beam

Electrons are extracted only from a narrow solid angle.

Electron Beam

Raster scan

Electron penetration depth ~10 nm.

AES
Auger Electron Spectroscopy

X-ray Beam

Electron Beam

Electron penetration depth ~10 nm.

Electron excitation area ~1x1 cm². Electrons are emitted from this entire area 1-3 nm

Few mm²

X-ray excitation area ~1x1 cm². Electrons are emitted from this entire area

1-3 nm
Instrumentation for XPS/AES

Essential to use Ultra-high Vacuum (UHV)

- Remove adsorbed gases from the sample.
- Eliminate adsorption of contaminants on the sample.
- Prevent arcing and high voltage breakdown.
- Increase the mean free path for electrons, ions and photons.

<table>
<thead>
<tr>
<th>Degree of Vacuum</th>
<th>Pressure (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Vacuum</td>
<td>$10^{+2}$</td>
</tr>
<tr>
<td>Medium Vacuum</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>High Vacuum</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>Ultra-High Vacuum</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$10^{-11}$</td>
</tr>
</tbody>
</table>
Electron Energy Analyzer

**Cylindrical Mirror (CMA)**
- High throughput
- Co-axial electron source
- Shorter working distance
- Resolution scales with $E_p$

**Hemispherical Sector (HSA)**
- Higher energy resolution
- Angle dependent measurements
- Longer working distance

Single pass CMA (Auger)
Double pass CMA (XPS/UPS)
Complicated mineral

XPS spectra
• Elements present
• Composition
• Chemistry

Simple Cu-Ni Alloy
AES spectra

- Elements present (Li and up)
- Composition (yes)
- Chemistry (not very sensitive, but there)
Quantitative Analysis by XPS and AES

For a Homogeneous sample:

\[ I = N \cdot s \cdot D \cdot J \cdot L \cdot I \cdot A \cdot T \]

\[ N = \frac{I}{sDJLIAT} = \frac{I}{S} \]

Elemental sensitivity factor

Relative concentration of observed elements as a number fraction by:

\[ C_x = \frac{N_x}{S(N)} = \frac{(I_x/S_x)}{S(I_i/S_i)} \]

The values of S are based on empirical data.

Auger- cross section

Photoelectron cross section

\( N = \text{atoms/cm}^3 \)

\( s = \text{photoelectric cross-section} \)

\( D = \text{detector efficiency} \)

\( J = \text{X-ray flux} \)

\( L = \text{orbital symmetry factor} \)

\( I = \text{inelastic electron mean-free path} \)

\( A = \text{analysis area} \)

\( T = \text{analyzer transmission efficiency} \)
Quantitative Analysis: Two examples

Copper-Nickel alloy

<table>
<thead>
<tr>
<th></th>
<th>Peak Area Mct-eV/sec</th>
<th>Rel. Sens.</th>
<th>Atomic Conc %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2.65</td>
<td>4.044</td>
<td>49</td>
</tr>
<tr>
<td>Cu</td>
<td>3.65</td>
<td>5.321</td>
<td>51</td>
</tr>
</tbody>
</table>

Poly(ethylene terephthalate)

\[ \text{\% of C 1s} \]
- CH: 62.7
- C-O: 20.2
- O=C-O: 17.1

Chemical Shift (Binding Energy Shift)
What is Chemical Shift?

Where does the binding energy shifts come from?
How can we identify elements and compounds?

Electron-electron repulsion
Electron-nucleus attraction

Binding Energy

Electron-Nucleus Separation

Fermi Level

M⁻ (more negatively charged)
M
M⁺ (more positively charged)

(1) Electro-negativity effect
(2) Electronic effect: spin-orbit coupling
(3) Final state effect
Electro-Negativity Effect

Poly(ethylene terephthalate)

% of C 1s
CH 62.7
C-O 20.2
O=C-O 17.1

Binding Energy (eV)

Ti and TiO₂

2p₃/₂ = 454.1 eV
Δ = 6.17 eV

2p₃/₂  Ti⁰

5.54 eV

2p₃/₂  Ti⁺⁴

2p₃/₂ = 458.8 eV
Δ = 5.54 eV

Binding Energy (eV)
Ti film exposed to plasma and extracted from plasma chamber

As received
30sec Ar etch
150sec Ar etch
210sec Ar etch
TiO$_2$-SS
210 sec Ar$^+$ etch

C(1s)
from graphitic C

$>$C=O -C-O
C from Ti-C

O(1s)
from lattice oxygen

$\text{-OH}$

Fe from Fe-O
Shake-up
?

Ti(2p$_{3/2}$)
from TiO$_2$

Ti(2p$_{1/2}$)
from TiO$_2$

from Ti-C
ΔG data from *Tables of Physical and Chemical Constants*

<table>
<thead>
<tr>
<th></th>
<th>Atom</th>
<th>Oxide</th>
<th>$-\Delta G$ (kJ mol$^{-1}$)</th>
<th>$-\Delta G/O$ (kJ mol$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td><strong>Low-Z getters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Be</td>
<td>BeO</td>
<td>581</td>
<td>581</td>
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<tr>
<td>5</td>
<td>B</td>
<td>B$_2$O$_3$</td>
<td>1194</td>
<td>397</td>
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<tr>
<td><strong>Medium-Z getters</strong></td>
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<tr>
<td>12</td>
<td>Mg</td>
<td>MgO</td>
<td>569</td>
<td>569</td>
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<tr>
<td>13</td>
<td>Al</td>
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<td>1582</td>
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<tr>
<td>14</td>
<td>Si</td>
<td>SiO$_2$</td>
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<td>428</td>
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<tr>
<td><strong>High-Z getters</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>TiO$_2$</td>
<td>889</td>
<td>444</td>
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<tr>
<td>73</td>
<td>Ta</td>
<td>Ta$_2$O$_5$</td>
<td>1911</td>
<td>352</td>
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<tr>
<td><strong>Bad getters</strong></td>
<td></td>
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<tr>
<td>74</td>
<td>W</td>
<td>WO$_3$</td>
<td>764</td>
<td>254</td>
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<tr>
<td>26</td>
<td>Fe</td>
<td>Fe$_2$O$_3$</td>
<td>742</td>
<td>247</td>
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<tr>
<td>28</td>
<td>Ni</td>
<td>NiO</td>
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<tr>
<td><strong>Reference molecules</strong></td>
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<tr>
<td>1</td>
<td>H</td>
<td>H$_2$O</td>
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<td>228</td>
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<tr>
<td>6</td>
<td>C</td>
<td>CO$_2$</td>
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<td></td>
<td></td>
<td>CO</td>
<td>137</td>
<td>137</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>Li$_2$O</td>
<td>134</td>
<td>134</td>
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</table>
Non-Destructive Depth Profiles
Angle Resolved XPS or AES Measurements

By knowing the escape depth it is possible to use a small acceptance angle to take measurements of signal ratio as a function of angle and relate to a depth profile.

This can be quantified, but often qualitative information is highly useful.
Auger spectra from two areas on a passivated ball surface exhibiting different morphologies. Note chromium enrichment in area 1.
Design concept

1. Be able to extract samples from various positions in the reactor
2. Flexible design of sample extractor
3. Be able to store specimens in UHV for analysis and further treatment
4. Set up flexible surface analysis apparatus in RPPL
5. Be able to do “material preparation” in 4.
6. Be able to transfer the specimen(s) to the analysis facility (other than RPPL)
Sample parking/transfer
Bulk-Schedule

Spring quarter (2004)
Detailed design of the systems, electronics/component repair

Summer quarter (2004)
Design and machining of sample parking/transfer part
Removable sample transfer design, machining, and construction

Fall quarter (2004)
Assembly of the system in Seattle campus
Spectrometer test

Winter quarter (2005)
Spectrometer system set up in RPPL
Test run

Spring quarter (2005)
Preliminary run/test
Simulation experiments

Summer quarter (2005) and up
Experimental runs
Summary

• Various surface analysis methods have been introduced.

• Combination of XPS and AES along with Ion Beam Analysis will provide useful information regarding plasma-surface interactions.

• A versatile design of “in-situ” sample extraction and surface analysis facility has been introduced.

• A system will be set up in RPPL, and will be primarily used to measure the contamination level of plasma through surface analysis.

• The surface analysis facility will be available for other users.
Thank You!!