5. Surface Analysis

- **Introduction**

- **Methods:** XPS, AES, RBS

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**Why surface Analysis...?**

**Bulk:**
- structural function
- Electrical/thermal conduction
- Volume increases properties

**Surface:**
- Interface solid-gas: surface chemistry
- (solid-oxide fuel cells, catalysers, corrosion)
- Surface mechanics (solid-solid), tribology
- Functionality: optics, biomaterials, bio-chemistry

1 monolayer = density: $10^{15}$ atoms /cm$^2$
nanotechnology

<table>
<thead>
<tr>
<th>size</th>
<th>0.5nm</th>
<th>1nm</th>
<th>1.5nm</th>
<th>1um</th>
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</thead>
<tbody>
<tr>
<td># volume atoms</td>
<td>1</td>
<td>5</td>
<td>27</td>
<td>2.7 x 10^10</td>
</tr>
<tr>
<td># of surface atoms</td>
<td>8</td>
<td>26</td>
<td>56</td>
<td>5.4 x 10^7</td>
</tr>
<tr>
<td>surface fraction</td>
<td>8</td>
<td>5.2</td>
<td>2.07</td>
<td>0.002</td>
</tr>
</tbody>
</table>

The smaller the particle the more dominant becomes the surface

How analyse a surface...?
methods of surface analysis

- electrons
- Ions (±)
- atoms
- photons (hv)

Scanning probe techniques
force, V

- energy
dose
angle

- electrons
- Ions (±)
- atoms
- molecules
- Photons (hv)

energy dose
Angle
mass
charge
## methods matrix

<table>
<thead>
<tr>
<th>Primary particle</th>
<th>Secondary particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$hv$</td>
<td>electron, ion, atom</td>
</tr>
<tr>
<td>$hv$</td>
<td>ELL, ESR, FITIR, NMR, Raman, XRD, SNOM</td>
</tr>
<tr>
<td></td>
<td>XPS, UPS, XPD</td>
</tr>
<tr>
<td></td>
<td>LAMMA, MALDI</td>
</tr>
<tr>
<td>$e$</td>
<td>EM</td>
</tr>
<tr>
<td></td>
<td>AUGER, EELS, LEED, RHEED, SEM</td>
</tr>
<tr>
<td>$i+/-$</td>
<td>PIXE, GDOES</td>
</tr>
<tr>
<td></td>
<td>GDMS, SIMS, ISS, RBS</td>
</tr>
<tr>
<td>$a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FAB, He Sc</td>
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</table>

### acronyms

- ELL: Ellipsometry
- ESR: Electron Spin Resonance
- FTIR: Fourier Transform Infrared Spectroscopy
- NMR: Nuclear Magnetic Resonance
- Raman Spectroscopy
- XRD: X-ray Diffraction
- XPS: X-ray Photoelectron Spectroscopy
- UPS: Ultraviolet Spectroscopy
- XPD: X-ray Photoelectron Diffraction
- LAMMA: Laser Microprobe Mass Analysis
- MALDI: Matrix Assisted Laser Desorption Ionization
- EL: Electron Microscope
- AES: Auger Electron Spectroscopy
- EELS: Electron Energy Loss Spectroscopy
- LEED: Low Energy Electron Diffraction
- RHEED: Reflection High Energy Electron Diffraction
- SEM: Scanning Electron Microscopy
- PIXE: Proton Induced X-ray Emission
- GDOES: Glow discharge Optical Emission Spectroscopy
- GDMS: Glow Discharge Mass spectroscopy
- SIMS: Secondary Ion Mass Spectroscopy
- ISS: Ion Scattering Spectroscopy
- RBS: Rutherford Back Scattering
- FAB: Fast Atom Bombardment
- He Sc: Helium Scattering
Surface analysis: under vacuum!

- Surface has to remain in the same state during the measurement
  - temperature
  - stability
  - contamination (formation of monolayer $10^{19}$ site/m²)

- Excitation/detection with particles
  $10^{-4}$ mbar or better

- To avoid contaminants:
  $10^{-10}$ mbar

- Exception:
  Photons (optical microscopy)
  Force measurements: AFM
  Liquid-solid interfaces

Common problems and solutions
outgassing, leaks, hydrocarbons
Heating at 150°C, cold traps
UHV systems...

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photon and electron probes
elemental and electronic analysis

- Electron transition between atomic energy levels
  - Core electrons: binding energy depends on the element
  - Excitation/ionisation by a probe particle (photon, electron, ion, ...)
    - Photoelectron
    - After relaxation: X-ray, Auger electron, ...
    - Energy of interaction product is characteristic of the element
photon and electron probes
elemental and electronic analysis

Range of low energy electrons

Electron energy analyser principle

Photoelectron spectroscopy

**Principle**
- Excitation of core or valence electrons
- Energy-dispersive analysis of emitted photoelectrons
- Core levels
  - Binding energy: 200 eV - a few keV
  - Excitation: X-rays (or UV)
  - Set of lines characteristic for each element
- Valence levels
  - Binding energy: a few eV
  - Excitation: UV light
  - Reflects the electronic properties of the surface
Photoelectron spectrum

- Analysis as a function of electron energy
  - Kinetic energy $E_{\text{kin}}$ allows to determine the binding energy $E_B$
    - $E_{\text{kin}} = h\nu - E_B - \phi_s$
  - $\phi_s$: work function
    - In practice, spectrum calibrated with a well-known energy peak (C, O, ...)

Photoelectron spectroscopy

- Kinetic energy $E_{\text{kin}}$ depends on binding energy $E_B$
  - $\text{Atom} + h\nu \rightarrow \text{Atom}^+ + e^-$
  - $E(A) + h\nu = E(A^+) + E_{\text{kin}}(e^-)$
  - $E_{\text{kin}}(e^-) = h\nu - [E(A^+) - E(A)]$
    - $E_{\text{kin}}(e^-)$: kinetic energy of photoelectron
    - $[E(A^+) - E(A)]$: binding energy of electron
  - One-electron process ("photon in - electron out")
Photoelectron spectroscopy
chemical shift

- Shift of peak energy provoked by chemical environment and oxidation state
  - Typ. 0.5-10 eV
- Allows to determine
  - Oxidation state of metallic elements
  - Nature of chemical bond - e.g. for
    - C (C-H, C-O, C-F, ...)
    - O (O^{2-}, OH, ...)
    - Si (metallic, SiO₂, silicones)

Fig. 2.13. Schematic diagram of the type of information obtainable from XPS spectra from an Fe-Cr alloy with oxide film underneath a contaminant film [2.57].

Photoelectron spectroscopy
depth profile

- XPS sensitive to surface (~5 nm)
- Depth profile measurement by sputtering the sample
  - Cycles of ion beam etching (Ar⁺) followed by measurement
- Max. depth: ~1 μm
  - Degradation of sample due to ion bombardment
  - Atomic displacement
  - Surface roughness
  - Variable etching rates
Waves: electrons
AES: Auger electron spectroscopy

- Excitation of core electrons with electrons or X-rays
- Relaxation of an electron
  - X-ray emission
  - Auger emission: energy transfer to a second electron
- Kinetic energy determined by
  - Position of "initial" hole
  - Position of two "final" holes
  - Characteristic for each element
  - Analysis of electron energy

Auger Emission

- Secondary process
  - Competition between X-ray fluorescence and Auger emission
    - Auger emission favoured of shallow core levels: light elements
  - Auger electron XYZ
    - Initial hole: X
    - Relaxation of electron Y
    - Energy transferred to another electron Z that is emitted by the solid:
      - Auger emission
      - For example: (KL_Ls)
  - Energy $E_{\text{kin}}(XYZ)$
    - $E_{\text{kin}}(XYZ) = (E_X - E_Y) - E_z - E_{\text{inter}}$
      - Independent of probe particle energy
      - $E_{\text{inter}}$: interaction energy between holes $L_i$ and $L_j$, relaxation energy, ...
      - $E_{\text{inter}} \ll E_{\text{min}}(XYZ)$ (typ. 1 eV)
Auger spectrum

- Many transitions
- Strong background signal (low energy secondary electrons)
  - Usually, 1st derivative of detected electron current for graphs/analysis
- High surface sensitivity
  - Kinetic energy between 20...1000 eV
    (λ between 2...6 monolayers)
- Mapping by rastering an electron beam
  - Resolution ≈ 50 nm
- Depth concentration profiles by sputtering the surface
- Faster acquisition than XPS
- Quantitative analysis with composition standards
- Chemical effects difficult to interpret

AES examples

- Chemical composition at the surface: FeCr steel in normal and brittle state
- Higher P, Cr and Ni concentration in brittle steel

- Depth profile: thin layers of Al₂O₃-TiN on Si
- After annealing: O diffuses in Ti layer, but not in TiN layer
  - Ti-N: superposition of N and Ti peaks
  - Layer thicknesses: 45 nm of Ti, 55 nm of Al₂O₃
## XPS and AES

<table>
<thead>
<tr>
<th>Infos</th>
<th>XPS</th>
<th>AES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantification</td>
<td>Yes</td>
<td>Yes light elements!</td>
</tr>
<tr>
<td>Chemical bond</td>
<td>Yes</td>
<td>Possible</td>
</tr>
<tr>
<td>Electronic structure</td>
<td>Yes</td>
<td>–</td>
</tr>
<tr>
<td>Mapping</td>
<td>Possible (50 nm?)</td>
<td>SEM (50 nm)</td>
</tr>
<tr>
<td>Depth profiles</td>
<td>Yes (Ar⁺ sputtering)</td>
<td>Yes (Ar⁺ sputtering)</td>
</tr>
<tr>
<td>Surface sensitivity</td>
<td>some nm</td>
<td>some nm</td>
</tr>
<tr>
<td>Detection limit</td>
<td>~%₀₀</td>
<td>~%</td>
</tr>
<tr>
<td>Vacuum</td>
<td>UHV needed</td>
<td>UHV needed</td>
</tr>
</tbody>
</table>

### Particles: Ions

**Rutherford Backscattering Spectroscopy (RBS)**

- **Bombardment of surface with α particles**
- **Analysis of energy of backscattered particles**
- **Thin sample**
  - "Elastic collisions" with atoms of mass $m_2$
  - \[
  \frac{E_1}{E_0} = K \left( \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right)^2
  \]
- **Backscattering geometry ($\theta = 180^\circ$)**
  - \[
  \frac{E_1}{E_0} = \left( \frac{M_1 - M_2}{M_2 + M_1} \right)^2
  \]
- **Maximum sensitivity to chemical composition**
- **Peak at well-defined energy $E_1$**
Particles: Ions
RBS

- Thick sample
  - Inelastic collision before elastic backscattering
  - Continuous spectrum with cut-off energy $E_1$
  - Several elements: superposition of spectra for each element

Example
- Thick film of AlGaN (e.g. blue-emission laser diodes)

Example 1
- Surface impurities on Si
- Isotopes are resolved for light elements
- Area of each peak proportional to concentration and scattering cross-section

Example 2
- Diffusion of As in Si
- Depth resolution of 10 nm
- Ideal cases...
Particles: Ions
RBS

Advantages
- Fast, quantitative method, no need for standards
- Depth profiling possible without ablation
- Good resolution in mass for light elements
- Good sensitivity to heavy elements
- High sensitivity to crystallographic defects

Drawbacks
- Particle accelerator needed
- Irradiation defects ($10^{13}$ He atoms implanted per measurement)