X-ray photoelectron spectroscopy - An introduction

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Material Characterisation Methods

- Thin Film X-Ray Diffraction
- Reflection High Energy Electron Diffraction
- Low Energy Electron Diffraction
- Scanning Tunnelling Microscopy
- Transmission Electron Microscopy
- Electron Diffraction
- X-Ray Diffraction
- Extended X-ray Absorption Fine Structure
- Surface EXAFS
- Extended Electron Energy Loss Fine Structure
- Electron Energy Loss Spectroscopy
- X-ray Photo-electron Spectroscopy
- Static Secondary Ion Spectroscopy
- Dynamic SIMS
- Imaging SIMS
- Small Area XPS
- Time-of-Flight (Imaging) SIMS
- Scanning Auger electron Microscopy
- Fourier Transform Infra-Red Spectroscopy
- Scanning Electron Microscopy
- Energy Dispersive X-ray Analysis
- Nuclear Magnetic Resonance
- Mass Spectroscopy Gas Chromatography
What is surface?

- What happens at surfaces is extremely important in a vast range of applications from environmental corrosion to medical implants.
- A surface is really the interface between different phases (solid, liquid or gas).
- We can think of the surface as the top layer of atoms but in reality the state of this layer is very much influenced by the 2 – 10 atomic layers below it (~0.5 – 3 nm).
- Surface modification treatments are often in the range of 10 – 100 nm thick. >100 nm can be thought of as the bulk.
- Surface analysis encompasses techniques which probe the properties in all these ranges.

*God made solids, but surfaces were the work of the devil*  
------Wolfgang Pauli
Surface Analysis - Techniques Available

- Properties and reactivity of the surface will depend on:
  - bonding geometry of molecules to the surface
  - physical topography
  - chemical composition
  - chemical structure
  - atomic structure
  - electronic state

No one technique can provide all these pieces of information. However, to solve a specific problem it is seldom necessary to use every technique available.
XPS-Basic Principle

Excitation

\[ E_{\text{kin}} = \hbar \nu - E_B - \omega \]

De-excitation

\[ E_{KL2,3L2,3}(Z) = E_K(Z) - [E_{L2,3}(Z) + E_{L2,3}(Z + 1)] \]
Auger electron vs x-ray emission yield

Auger Electron Emission

X-ray Photon Emission

Probability

5 10 15 20 25 30 35 40
B Ne P Ca Mn Zn Br Zr

Atomic Number

Elemental Symbol
XPS spectrum ITO

Auger peaks
Sn MNN
In MNN
O KLL

Photoelectron peaks
Sn 3d
O 1s
In 3d
Sn 3p
In 3p
In 3s
Sn 3s
In/Sn 4s
In/Sn 4p
C 1s
In/Sn 4p

CPS

Binding Energy (eV)

x $10^4$
Peak width ($\Delta E$)

$$\Delta E = (\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2)^{1/2}$$

- Gaussian broadening:
- Instrumental:
  There is no perfectly resolving spectrometer nor a perfectly monochromatic X-ray source.
- Sample
  For semiconductor surfaces in particular, variations in the defect density across the surface will lead to variations in the band bending and, thus, the work function will vary from point to point. This variation in surface potential produces a broadening of the XPS peaks.
- Excitation process such as the shake-up/shake-off processes or vibrational broadening.

- Lorentzian broadening.

The core-hole that the incident photon creates has a particular lifetime ($\tau$) which is dependent on how quickly the hole is filled by an electron from another shell. From Heisenberg’s uncertainty principle, the finite lifetime will produce a broadening of the peak.

$$\Gamma = \frac{\hbar}{\tau}$$

Intrinsic width of the same energy level should increase with increasing atomic number.
Examples of XPS spectrometers
Schematic of an XPS spectrometer

Number of emitted electrons measured as function of their kinetic energy
Instrument: Kratos Axis Ultra$^{DLD}$ at MiNaLab
The new XPS instrument-Theta Probe

- Spectroscopy
  - Source-defined small area XPS
    - 15 µm to 400 µm
- Snapshot spectrum acquisition
  - Up to 112 channels
  - Faster serial mapping
  - Faster profiling
- Unique parallel ARXPS with up to 96 channels
- Large samples (70 mm x 70 mm x 25 mm)
- Sputter profiles
- Mapping possible up to full size of sample holder
- ISS included

Target applications
- Thickness measurements
- Surface modification, plasma & chemical
- Self assembly
- Nanotechnology
- Ultra thin film technologies
- Shallow interfaces
Sample requirements

- Has to withstand high vacuum (≤ 10^-7 Torr).
- Has to withstand irradiation by X-rays
- Sample surface must be clean!
- Reasonably sized.
The probability that a photoelectron will escape from the sample without losing energy is regulated by the Beer-Lambert law:

\[ e^{-\frac{z}{\lambda_e(E)\cos\theta}} \]

Where \( \lambda_e \) is the photoelectron inelastic mean free path.

Attenuation length (\( \lambda \)) \( \approx 0.9 \) IMFP

IMFP: The average distance an electron with a given energy travels between successive inelastic collisions
Features of the XPS spectrum

- **Primary structure**
  - Core level photoelectron peaks (atom excitation)
  - Valence band spectra
  - CCC, CCV, CVV Auger peaks (atom de-excitation)

- **Secondary structure**
  - X-ray satellites and ghosts
  - Shake up and shake off satellites
  - Plasmon loss features
  - Background (slope)
Quantification

Unlike AES, SIMS, EDX, WDX there are little in the way of matrix effects to worry about in XPS. We can use either theoretical or empirical cross sections, corrected for transmission function of the analyser. In principle the following equation can be used:

\[ I = J \rho \sigma K \lambda \]

- \( I \) is the electron intensity
- \( J \) is the photon flux,
- \( \rho \) is the concentration of the atom or ion in the solid,
- \( \sigma \) is the cross-section for photoelectron production (which depends on the element and energy being considered),
- \( K \) is a term which covers instrumental factors,
- \( \lambda \) is the electron attenuation length.

In practice atomic sensitivity factors (F) are often used:

\[ [A] \text{ atomic } \% = \frac{(I_A/F_A) \sum (I/F)}{\sum I/F} \]

Various compilations are available.
Koopmans Theorem

Koopman's Theorem:
The BE of an electron is simply difference between:
  initial state (atom with \( n \) electrons) and
  final state (atom with \( n-1 \) electrons (ion) + free photoelectron)

\[
BE = E_{\text{final} \ (n-1)} - E_{\text{initial} \ (n)}
\]

If no relaxation followed photoemission, \( BE = -\varepsilon \)
\( \varepsilon \) = orbital energy which can be calculated from Hartree-Fock method
Koopmans Theorem-deviation

Measured BE's and calculated orbital energies different by 10-30 eV because of:
- electron rearrangement to shield core hole - the frozen orbital approximation is not accurate
- electron correlation & relativistic effects

Both initial state effects and final state effects affect measured BE

Comparison of experimental XPS C 1s binding energies with those calculated via Koopman's theorem for C in a range of molecules. Although experimental and theoretical values differ by 15 eV (associated with relaxation effects) the systematic comparison is excellent as indicated by the straight line of unity gradient (after Shirley, 1973).
Chemical shift

\[ \Delta E_{(i)} = k \Delta q + \Delta V_M - \Delta R \]

- \( \Delta q \): changes in valence charge
- \( \Delta V_M \): Coulomb interaction between the photoelectron (i) and the surrounding charged atoms.
- \( \Delta R \): relaxation energy change arising from the response of the atomic environment (local electronic structure) to the screening of the core hole.
Chemical shift - Growth of ITO on p c-Si

Intensity arbitrary units

Si 2p

SiOₓ

1.5 nm

0.5 nm

BHF 15 sec + 500°C

Binding Energy (eV)

Si

In oxide

In 3d

3/2

5/2

In

Sn oxide

Sn 3d

3/2

5/2

Sn

3.0 nm

1.5 nm

0.5 nm
Chemical shift

![Graph showing chemical shifts for different TFAA samples.](image)

- **TFAA 5**: 
- **TFAA 4**: 
- **TFAA 3**: 
- **TFAA 2**: 
- **TFAA 1**: 

![Graph showing Ti 2p binding energy for different stages of sputtering.](image)

- **2p3/2 oxide**
- **2p3/2 metal**
- **2p1/2 oxide**
- **Outermost surface**
- **After 40 mins sputtering**
- **After 30 mins sputtering**
Shake-up satellites in Cu 2p

![Graph showing shake-up satellites in Cu 2p binding energy range from 970 to 930 eV]

- **Shake-up satellites** indicated.
- **Cu**, **CuO**, and **CuSO₄** binding energy peaks highlighted.

<table>
<thead>
<tr>
<th>Binding energy (eV)</th>
<th>Cu</th>
<th>CuO</th>
<th>CuSO₄</th>
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<tbody>
<tr>
<td>970</td>
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Plasmons

- They describe the interaction (inelastic scattering) of the PE with the plasma oscillation of the outer shell (valence band) electrons.
- Plasmons in their quantum mechanical description are pseudoparticles with energy $E_p = \hbar \omega$.
- $\omega = \left(\frac{ne^2}{\varepsilon_0 m}\right)^{1/2}/2\pi$  
  $n =$valence electron density,  
  $e, m =$ electron charge and mass  
  $\varepsilon_0 =$dielectric constant of vacuum.

Pure elements

Mo-Si-Al Compound
Peak asymmetry in metals caused by small energy electron-hole excitations near $E_F$ of metal
Depth profile with ion sputtering

- Use of an ion gun to erode the sample surface and re-analyse
- Enables layered structures to be investigated
- Investigations of interfaces
- Depth resolution improved by:
  - Low beam energies
  - Small ion beam sizes
  - Sample rotation
Angle Resolved XPS (ARXPS) for non-destructive depth profile

$$I_{(d)} = I_o * \exp(-d/\lambda)$$

$$I_{(d)} = I_o * \exp(-d/\lambda \cos \theta)$$

$$\lambda = \text{attenuation length} \quad (\lambda \approx 0.9 \text{ IMFP})$$

$$\lambda = 538\alpha_A / E_A^2 + 0.41\alpha_A (\alpha_A E_A)^{0.5}$$

($$\alpha_A^3$$ volume of atom, $$E_A$$ electron energy)
XPS-Check list

- Depth of analysis ~ 5nm
- All elements except H and He
- Readily quantified (limit ca. 0.1 at%) 
- All materials (vacuum compatible) 
- Chemical/electronic state information
  - Identification of chemical states
  - Reflection of electronic changes to the atomic potential
- Compositional depth profiling by
  - ARXPS (ultra thin film <10 nm),
  - change of the excitation energy
  - choose of different spectral areas
  - sputtering
- Ultra thin film thickness measurement
- Analysis area mm² to 10 micrometres