

X-Ray Photoelectron Spectroscopy

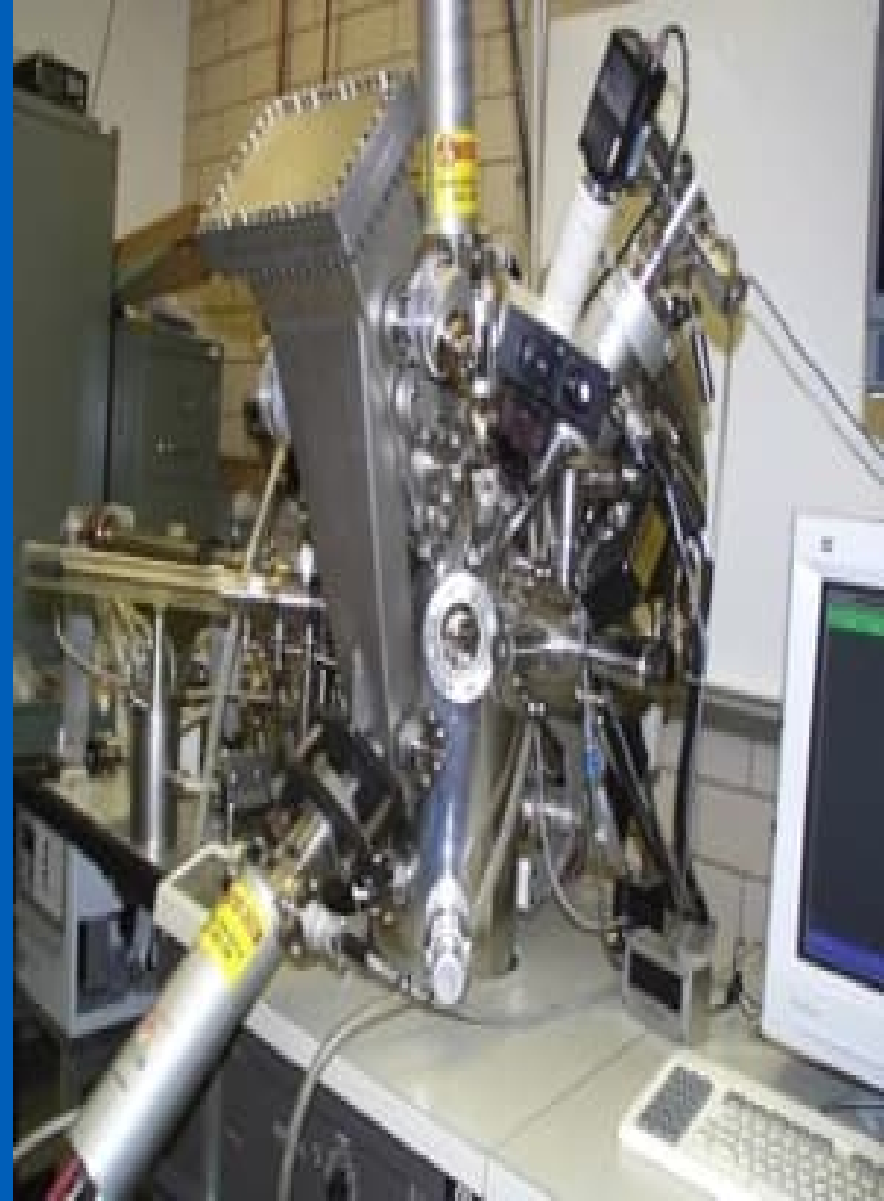
XPS/ESCA

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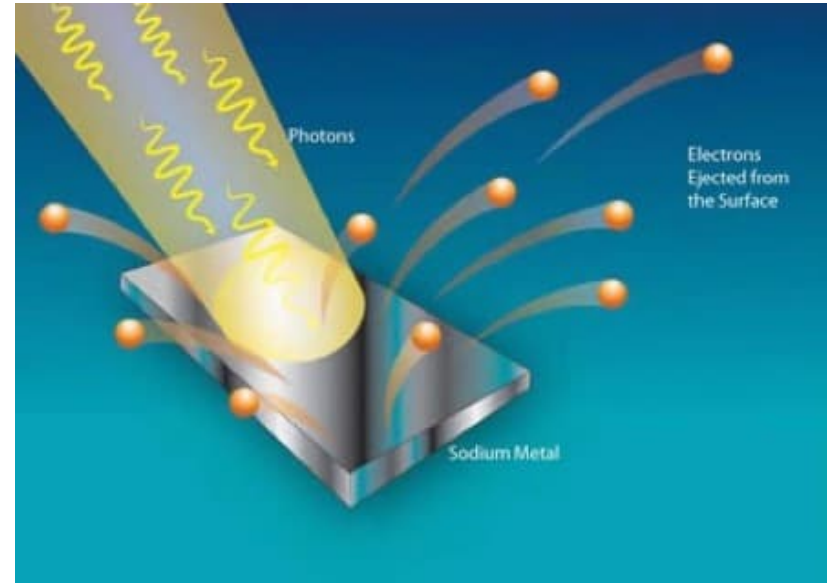


Outline

- **XPS Background**
- **XPS Instrument**
- **How Does XPS Technology Work?**
- **Equation**
- **Spectrum**
- **XPS Applications**
- **Advantages and Limitations**

XPS Background

- In 1905, Elbert Einstein, photoelectric effect
- Electrons gets knocked away from the surface when an electromagnetic radiation with definite $h\nu$ hits the surface
- In 1960, Dr. Siegbahn and his research group, developed the XPS technique and produced the first commercial monochromatic XPS
- 1981, Seighbahn, noble prize

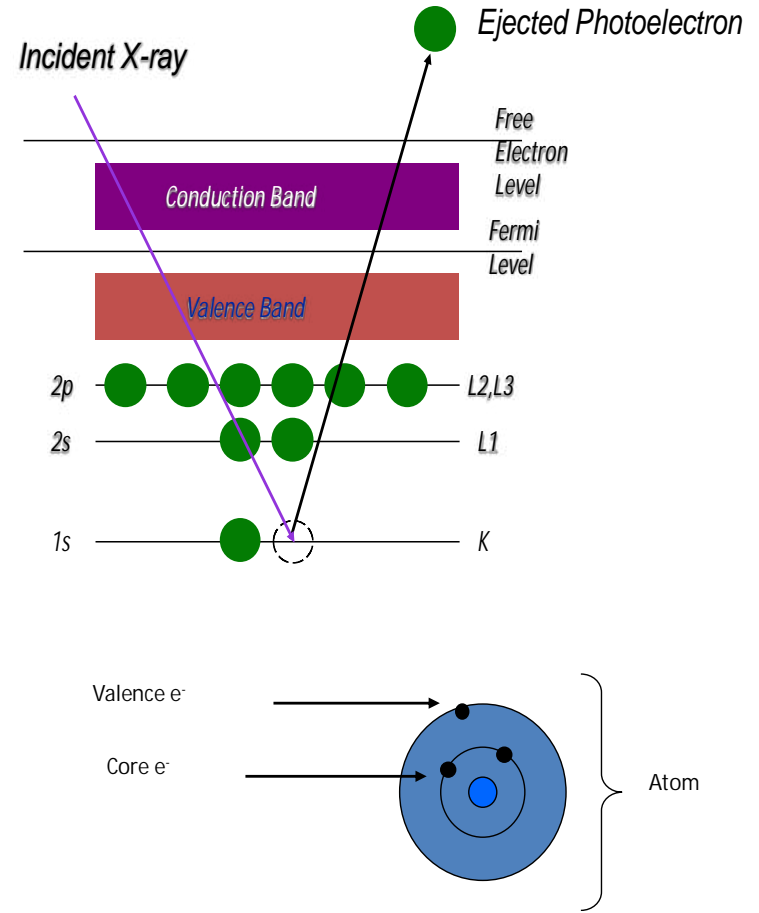


X-Rays

- Irradiate the sample surface, hitting the core electrons (e-) of the atoms.
- The X-Rays penetrate the sample to a depth on the order of a micrometer.
- Useful e- signal is obtained only from a depth 10 to 100 Å on the surface.
- The X-Ray source produces photons with certain energies:
 - MgK α photon with an energy of 1253.6 eV
 - AlK α photon with an energy of 1486.6 eV
- Normally, the sample will be radiated with photons of a single energy (MgK α or AlK α). This is known as a monoenergetic X-Ray beam.

Why the Core Electrons?

- The core e's are local close to the nucleus and have binding energies characteristic of their particular element.
- By using X-rays with energies that match the binding energies of core electrons, XPS can provide detailed information about the chemical composition and electronic structure of a material, making it a valuable tool for surface analysis and materials science.
- Valence electrons, have overlapping energy levels due to the influence of neighboring atoms in the chemical environment, making it difficult to differentiate between elements.
- An electron near the Fermi level is far from the nucleus, moving in different directions all over the place, and will not carry information about any single atom.



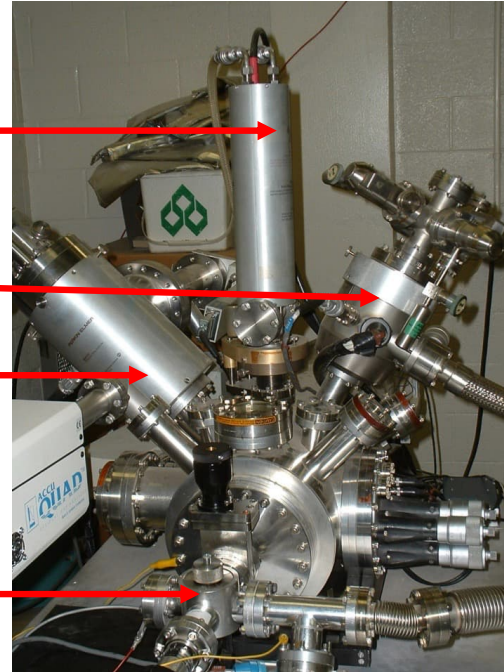
XPS Instrument

X-Ray Source

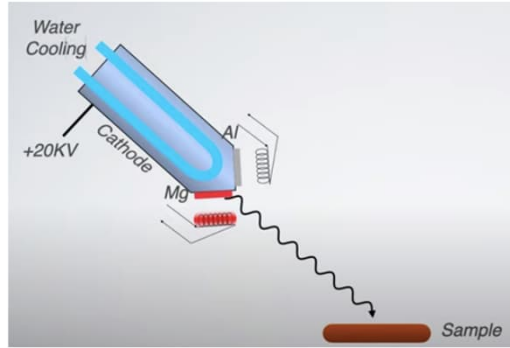
Ion Source

SIMS Analyzer

Sample introduction
Chamber



Schematic Diagram



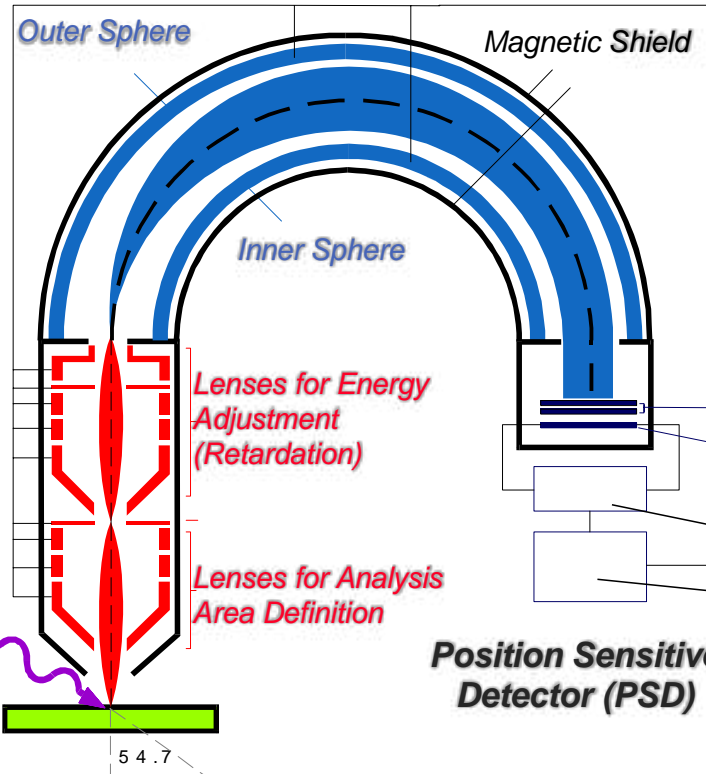
MgK α photon with an energy of 1253.6 eV
AlK α photon with an energy of 1486.6 eV

Electron Optics

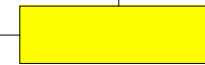
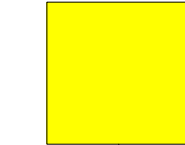
X-ray Source

Sample

Hemispherical Energy Analyzer



Computer System



Analyzer Control

**Multi-Channel Plate
Electron Multiplier**

**Resistive Anode
Encoder**

Position Computer

**Position Address
Converter**

Which materials are analyzed?

- **XPS is routinely used to analyze inorganic compounds, metals, semiconductors, polymers, ceramics, etc.**
- **XPS detects elements with $(Z) > 3$. It cannot detect H ($Z = 1$) or He ($Z = 2$)**
- **Organic chemicals are not routinely analyzed by XPS because they are readily degraded by either the energy of the X-rays or the heat from non-monochromatic X-ray sources**

Equation

$$KE = h\nu - BE - \emptyset$$

KE - Kinetic Energy (measure in the XPS spectrometer)

$h\nu$ - photon energy from the X-Ray source
(controlled)

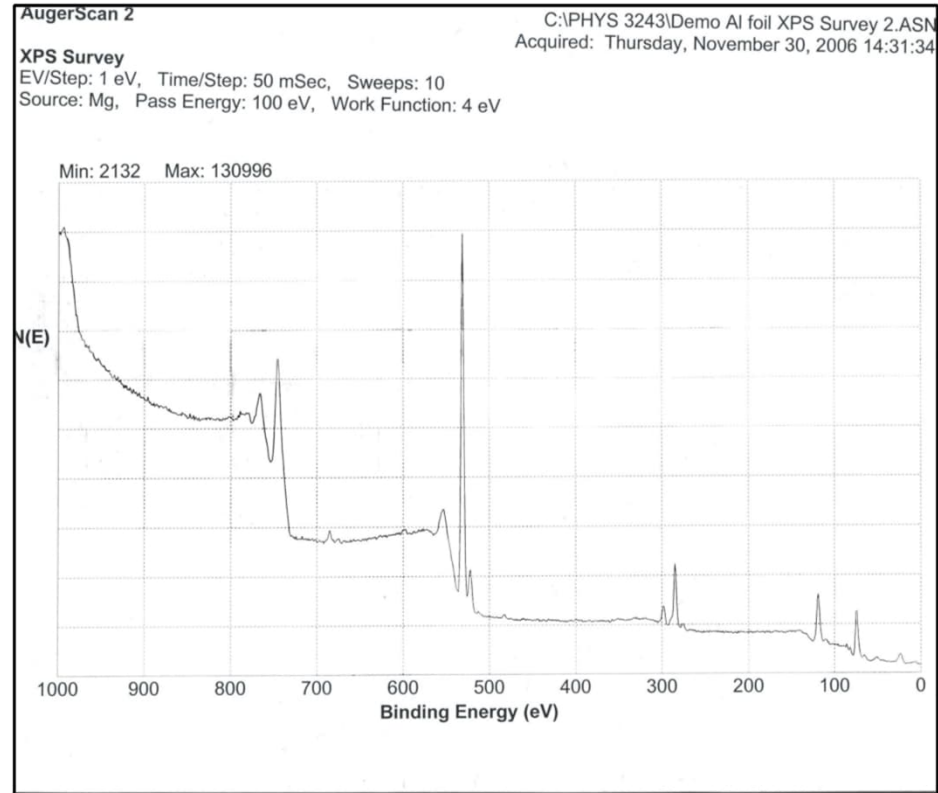
\emptyset - spectrometer work function. It is a few eV, it gets more complicated because the materials in the instrument will affect it. Found by calibration

BE – Binding Energy unknown variable

- The equation will calculate the energy needed to get an e^- out from the surface of the solid.
- Knowing KE, $h\nu$ and \emptyset the BE can be calculated.

XPS Spectrum

- The plot has characteristic peaks for each element found in the surface of the sample.
- There are tables with the KE and BE already assigned to each element.
- After the spectrum is plotted we can look for the designated value of the peak energy from the graph and find the element present on the surface



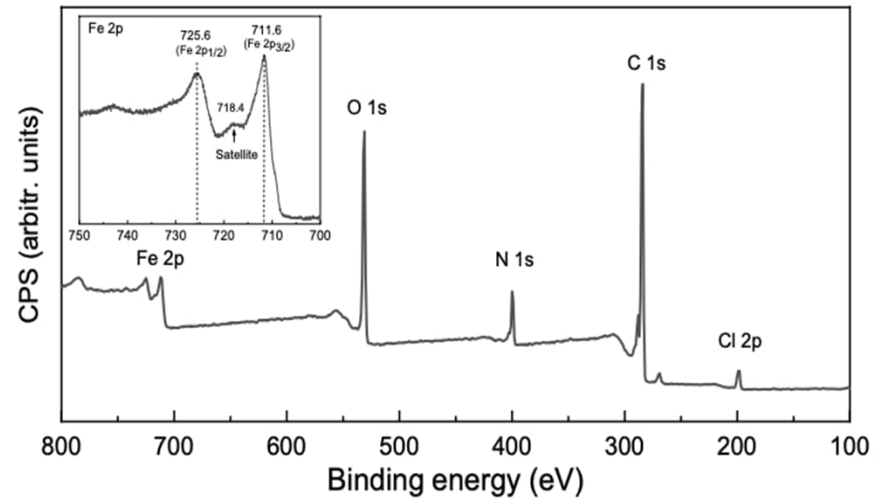
Sample and graphic provided by William Durrer, Ph.D.
Department of Physics at the University of Texas at El Paso

Applications in the industry

- **Semiconductors**
- **Dielectric materials**
- **Electronics packaging**
- **Magnetic media**
- **Thin film coatings**
- **Polymer surface**
- **Catalyst**
- **Corrosion**
- **Adhesion**

Atomic/Molecular Layer Deposited Iron –Azobenzene Framework Thin Films For Stimuli-Induced Gas Captured/Release

- X-ray photoelectron spectroscopy (XPS) was employed to address the elemental composition and the oxidation state of iron in the films.
- The Fe 2p spectrum presents the characteristic Fe peaks at the binding energies of 711.6 eV and 725.6 eV, respectively. Typical for trivalent Fe.
- A distinct satellite peak appears at 718.4 eV, and the distance between the main peak and the satellite, that is, 6.8 eV, is another indication of the trivalent state of iron.
- The wide-scan spectrum, confirms the presence of Fe, C, O, and N.
- The XPS data also reveals Cl contamination which is typical for the ALD/MLD films grown from metal chlorides.



SI Fig. 4. High-resolution XPS spectra for a crystalline film deposited through the FeCl₃+Azobenzene dicarboxylic acid process at 280 °C. Insert shows the Fe 2p XPS spectrum.

Advantages and Limitation

Advantages:

- Elemental specificity: XPS can identify and quantify the elements present on the surface of a material, including those in low concentrations.
- Chemical state information: XPS can provide information on the oxidation state and chemical bonding of the elements present on the surface.
- Depth profiling capability: XPS can be used to analyze the chemical composition of a surface layer as a function of depth, making it useful for studying thin films and multilayered structures.
- Non-destructive: XPS is a non-destructive technique, so it can be used to analyze a material without damaging or altering it.
- High spatial resolution: XPS can provide information on a small area of a sample (typically a few hundred microns), making it useful for analyzing small features or defects.

Limitations:

- Surface sensitivity
- Vacuum requirements
- Limited quantitative analysis
- Limited information on bulk properties.

References

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THANK YOU

Any Questions?