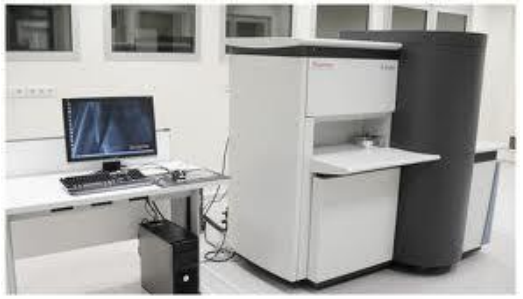
HACETTEPE UNIVERSITY
CHEMICAL ENGINEERING DEPARTMENT

KMU396
MATERIAL SCIENCE AND TECHNOLOGY- I

X-ray Photoelectron Spectroscopy (XPS)



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Outline

- History
- What is XPS?
- Instrumentation
- How XPS Works?
- XPS Spectrum
- Advents and disadvantages of XPS
- Summary
- References

History

- XPS technique is based on the photoelectric effect which was discovered by German physicist G. Hertz in 1887.
- Developed around 1905 by Einstein, A. Ann. Phys. Leipzig.
- Kai Siegbahn and his group in Uppsala (Sweden) developed several significant improvements in the equipment.
- In 1954 recorded the first XPS spectrum.
- In 1981, Siegbahn received Nobel Prize in physics.

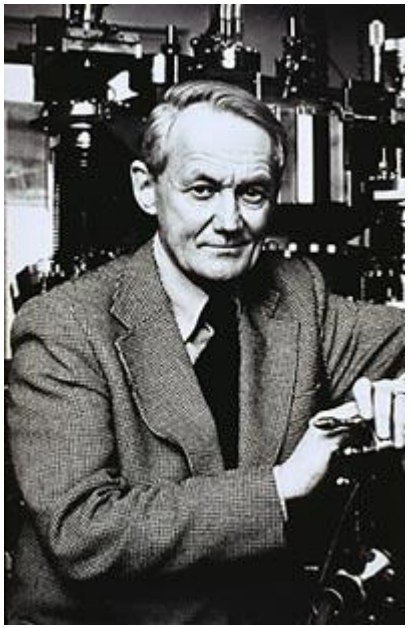


Figure 1: Professor Kai Siegbahn, the founder of x-ray photoelectron
Spectroscopy. *Department of Chemistry, Moscow State University, Vorob'evy gory, Moscow, 119999 Russia*

Journal of Analytical Chemistry, Vol. 60, No. 3, 2005, pp. 297–300. Translated from Zhurnal Analiticheskoi Khimii, Vol. 60, No. 3, 2005, pp. 331–334.

What is XPS?

- X-ray photoelectron spectroscopy (XPS) is used for physical methods of surface analysis.
- XPS is a quantitative spectroscopic technique for solids. Some special design XPS instruments can analyze volatile liquids or gases.
- Measures,
  - elemental composition
  - empirical formula
  - chemical state
  - electronic state

  of the elements that exist within a material.

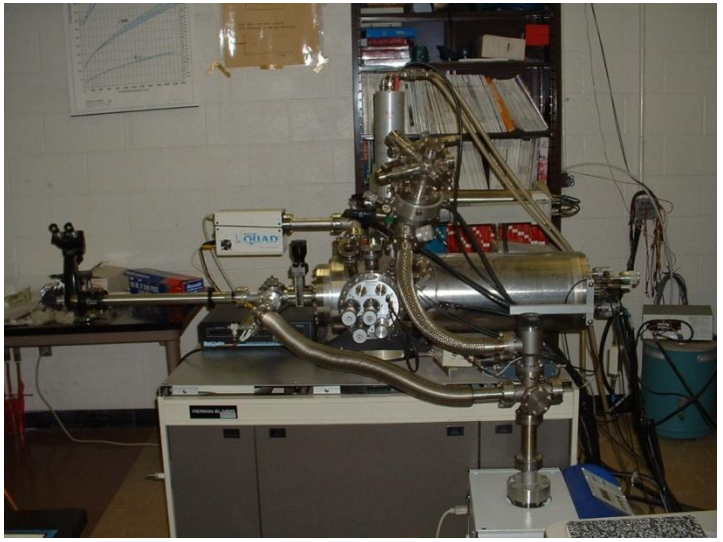


Figure 2: University of Texas at El Paso, Physics Department Side view of the Phi 560 XPS/AES/SIMS UHV System
http://www-group.slac.stanford.edu/sms/xrayspectroscopy.html

Ideal Uses for XPS Analysis

- Surface analysis of organic and inorganic materials, stains, or residues
- Determining composition and chemical state information from surfaces (e.g., polymers, glasses)
- Thin film oxide thickness measurements (SiO_2, Al_2O_3 etc.)
- Corrosion
- Adhesion

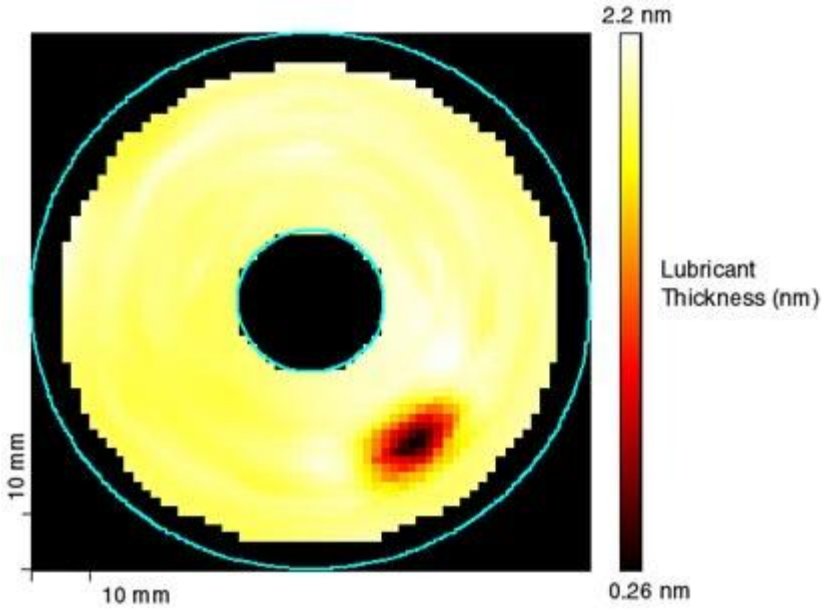


Figure.3. An XPS lubricant thickness map shows the presence of a void in the 2 nm lubricant coating on a 95 mm diameter hard disk media.

http://www.phi.com/surface-analysis-applications/magnetic-media.html

Relevant Industries for XPS Analysis

- Aerospace
- Automotive
- Biomedical/biotechnology
- Compound Semiconductor
- Data Storage Defense
- Displays
- Electronics
- Industrial Products
- Lighting
- Pharmaceutical
- Photonics
- Polymer
- Semiconductor
- Solar Photovoltaics
- Telecommunications

Figure 4: Pharmaceutical Industry
http://www.legaljuice.com/2010/12/salesman_calls_the_cops_after.html

Figure 5: Solar Photovoltaics
http://www.fincher.org/Misc/AlternateEnergy.shtml

Limitations of XPS Analysis

- The smallest analytical area is approximetly 10 nm.
- Limited specific organic information.
- Sample must be compatible with an ultra-high vacuum (UHV) environment (>10-9 Torr).
- Sample size cannot exceed 1 in. (25 mm) in any direction.
- Height should not exceed ½ in. (12 mm).
- Detects all elements with an atomic number of 3 (lithium) and above.

Photoelectric Effect

- Ionization occurs when matter interacts with light of sufficient energy (Heinrich Hertz, 1886)
- Photoelectron spectroscopy is based upon a single photon in/electron out process.

$$E = h\nu$$

h - Planck constant (6.62×10^{-34} J s)

ν - frequency (Hz) of the radiation

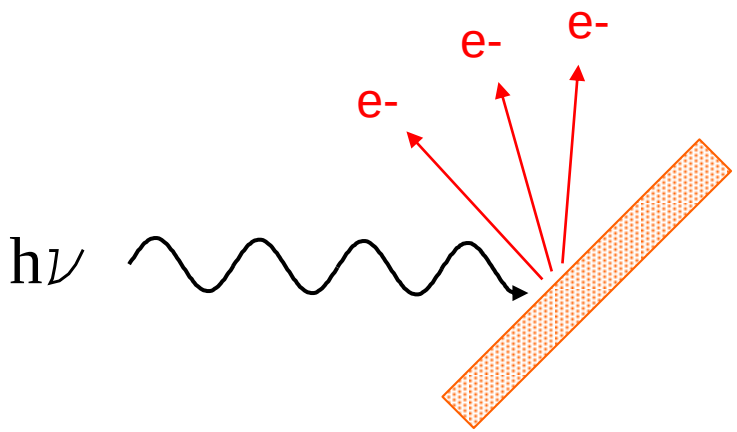


Figure 6: Photoelectron Phenomenon
www.pes.arizona.edu/facility/PES%20lecture1-history.pdf

Photoelectron vs Other Spectroscopies

Photoelectron

- Photon just needs enough energy to eject electron
- Measure kinetic energy of ejected electrons
- Monochromatic photon source

Others

- Photon must be in resonance with transition energy
- Measure absorbance or transmittance of photons
- Scan photon energies

Instrumentation

- X-ray source
- Electron energy analyzer
- An ion gun
- Ultrahigh vacuum system < 10-9 Torr (< 10-7 Pa)
- Electronic controls
- Computer system

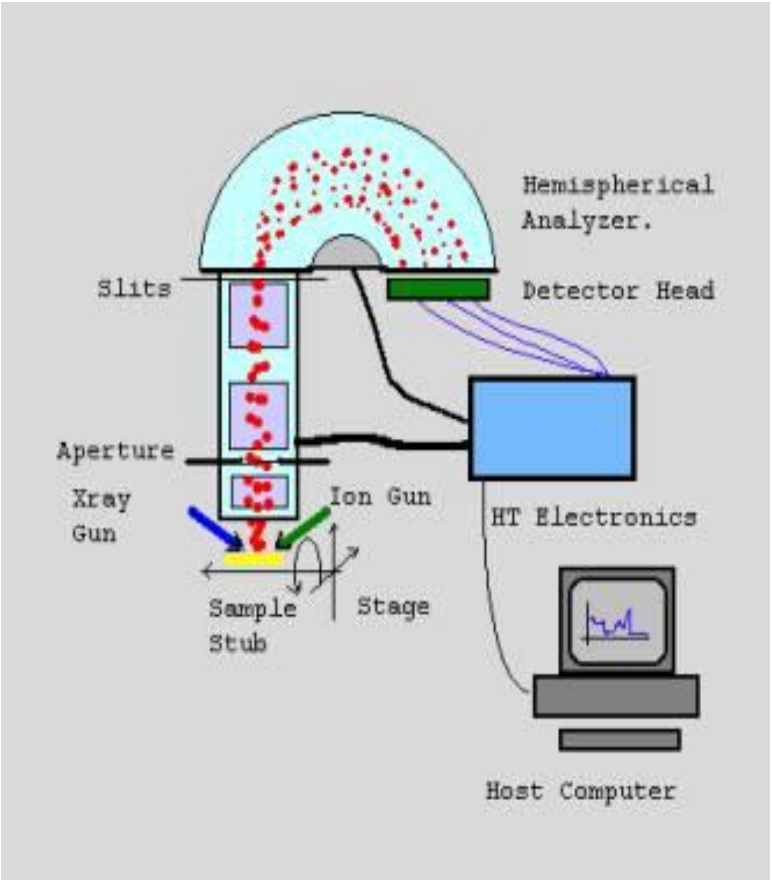


Figure 7:Logical layout for an XPS Instrument. http://www.casaxps.com/help_manual/XPSInformation/XPSInstr.htm

How XPS Works?

- A monoenergetic x-ray beam emits photoelectrons from the surface of the sample.
- UHV environment to eliminate excessive surface contamination
- Electron Energy Analyzer (CHA) measures the KE of emitted e^-s
- The spectrum plotted by the computer from the analyzer signal
- The binding energies can be determined from the peak positions and the elements present in the sample identified.

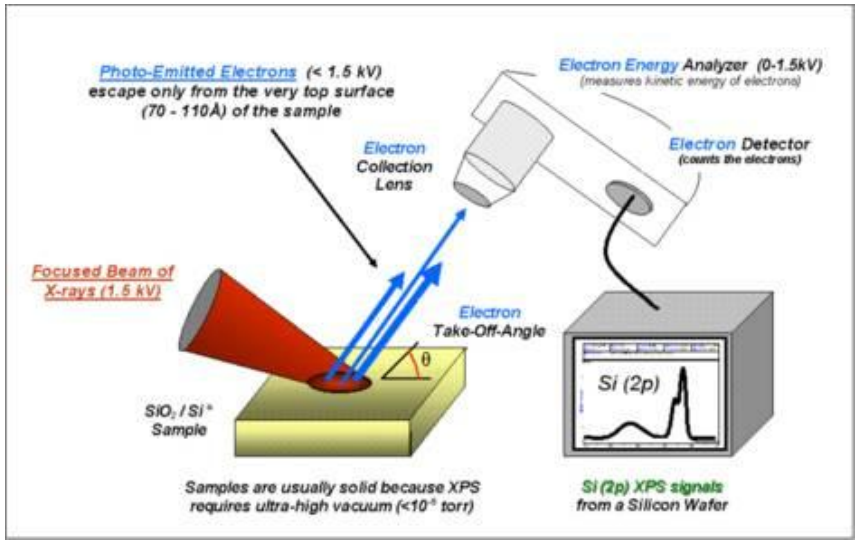


Figure 8: XPS instruments http://wiki.utep.edu/display/~vrrangel/X-ray+Photoelectron+Spectroscopy+%28XPS%29

X-Ray Source

- X-ray hitting the core electrons (e^-) of the atoms.
- e^-s are going to be released giving the Kinetic Energies (KE) characteristic of their elements.

- The most widely used x-ray sources are:

✓ monochromatic aluminium Kα X-rays (AlKα)

✓ polychromatic magnesium Kα X-rays (MgKα).

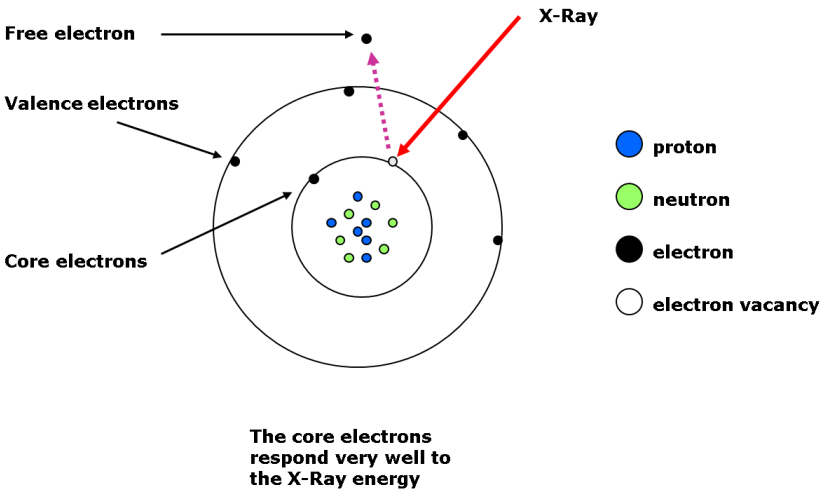


Figure 9: The core electrons respond to X-Ray energy www.casaxps.com/help_manual/XPSInformation/XPSInstr.htm

Binding Energy

- The Binding Energy (BE) is characteristic of the core electrons for each element.
- By measuring the kinetic energy of the emitted electrons ,the binding energy can be determined for the photoelectrons detected.

$E_{h\nu}$ = electron kinetic energy

+ electron binding energy

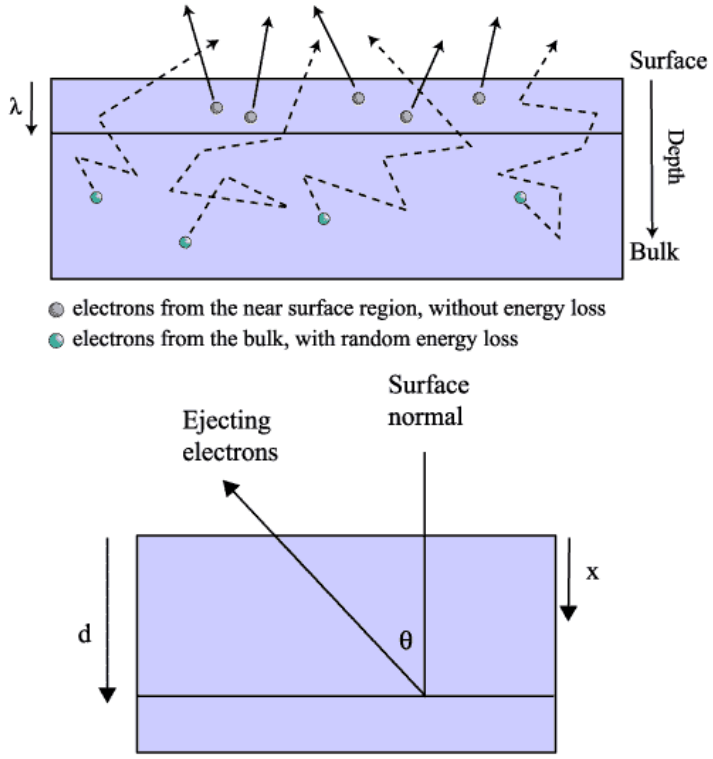


Figure10: Electrons from the sample surface.
http://mee-inc.com/xray-photo.html

Electron Energy Analyzer

Concentric Hemispherical Analyzer (CHA)

- CHA is based on the deflection of charged particles in an electrostatic field according their KE.
- After passing through an energy selecting field only electrons are detected which have a velocity within a certain kinetic energy region (ΔE).
- For the spectrum the energy region is scanned successively with constant ΔE by continuous change of the deflection potentials.

Why Does XPS Need UHV?

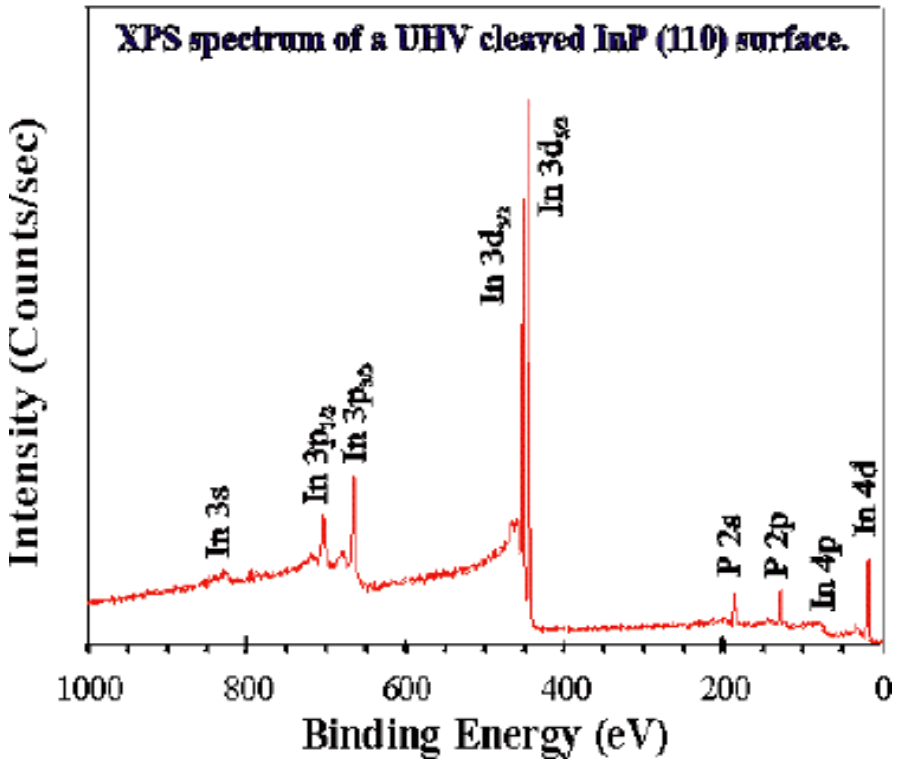
- The pressure of the vacuum system is $\leq 10^{-9}$ Torr

- XPS is a surface sensitive technique

  Contaminates will produce an XPS signal and lead to incorrect analysis of the surface of composition.

- To be analysed without interference from gas phase collisions
- Many vacuum components work with heated filaments and high voltages. Their work free of failure only is warranted under UHV conditions.

XPS Spectrum



- The number of electrons detected vs. the binding energy values.

BE increase from right to left

1000 eV ← → **0 eV**

KE increase from left to right

XPS Spectrum

This spectrum comprises two sets of information:

1. The position of the peaks; Binding energy value of the maximum point of the peak.

2. The shape of each of the peaks determines the concentration of the chemical elements.

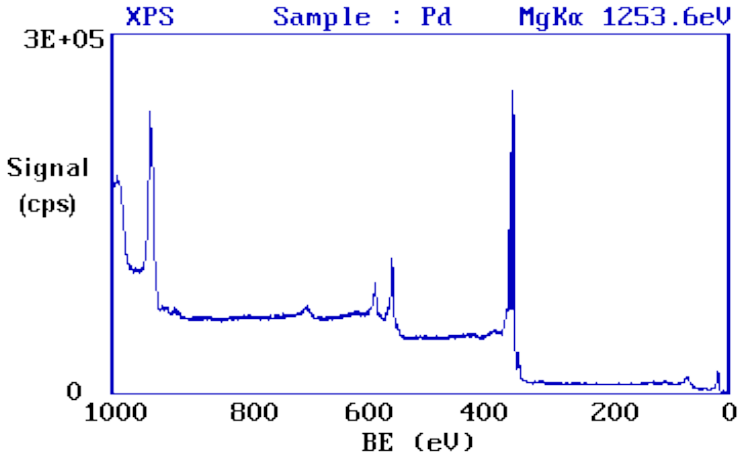


Figure 11: XPS Spectrum of Pd

XPS Spectrum

- There are tables with the KE and BE already assigned to each element.
- The plot has characteristic peaks for each element found in the surface of the sample.
- The intensity of the peaks is related to the concentration.
- The technique provides a quantitative analysis of the surface composition

Advents of XPS

- Chemical state identification on surfaces
- Identification of all elements except for H and He
- Quantitative analysis, including chemical state differences between samples
- Oxide thickness measurements
- Very simple to use and the data is easily analyzed.
- The UHV environment prevents contamination of the surface and aid an accurate analysis of the sample.
- The XPS technique is non-destructive because it produces soft x-rays to induce photoelectron emission from the sample surface

Disadvantages of XPS

- Expensive
- Slow
- Poor spatial resolution
- Requires high vacuum

Summary

- Surface sensitive technique
- Core spectroscopy
- Characterizes solids with a depth 10nm
- Needs UHV environment
- Characteristic binding energy.
- Characteristic set of peaks related KE plotted depending on BE
- The intensity of the peaks is related to the concentration.
- Quantitative technique

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Thank You for Your Attention!