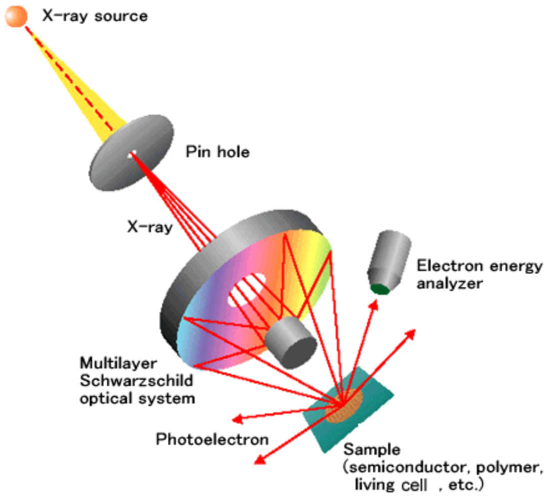
CHE680
Advanced Analytical Chemistry
Lecture 6

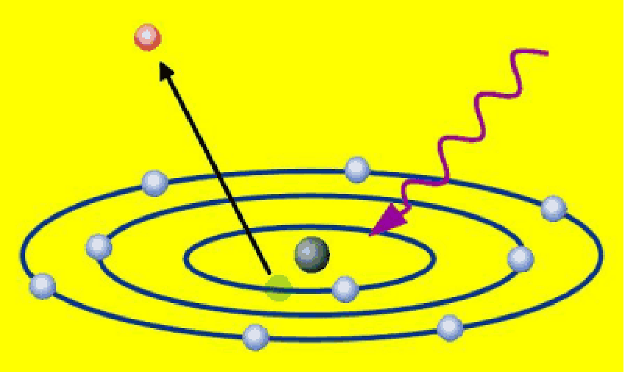
Buffalo State
State University of New York

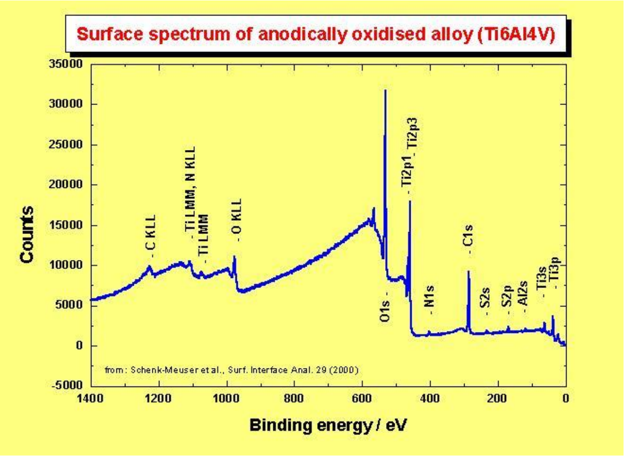
Jamie Kim
Department of Chemistry
Buffalo State College

1. Basic Principles
2. Experimental Condition
3. Generation of X-rays
4. Detectors
5. Applications

X-ray Photoelectron Spectroscopy (XPS)







http://www.chem.qmul.ac.uk/surfaces/scc/scat5_3.htm
http://www.jhu.edu/~chem/fairbr/surfacelab/xps.html

X-ray Photoelectron Spectroscopy (XPS)

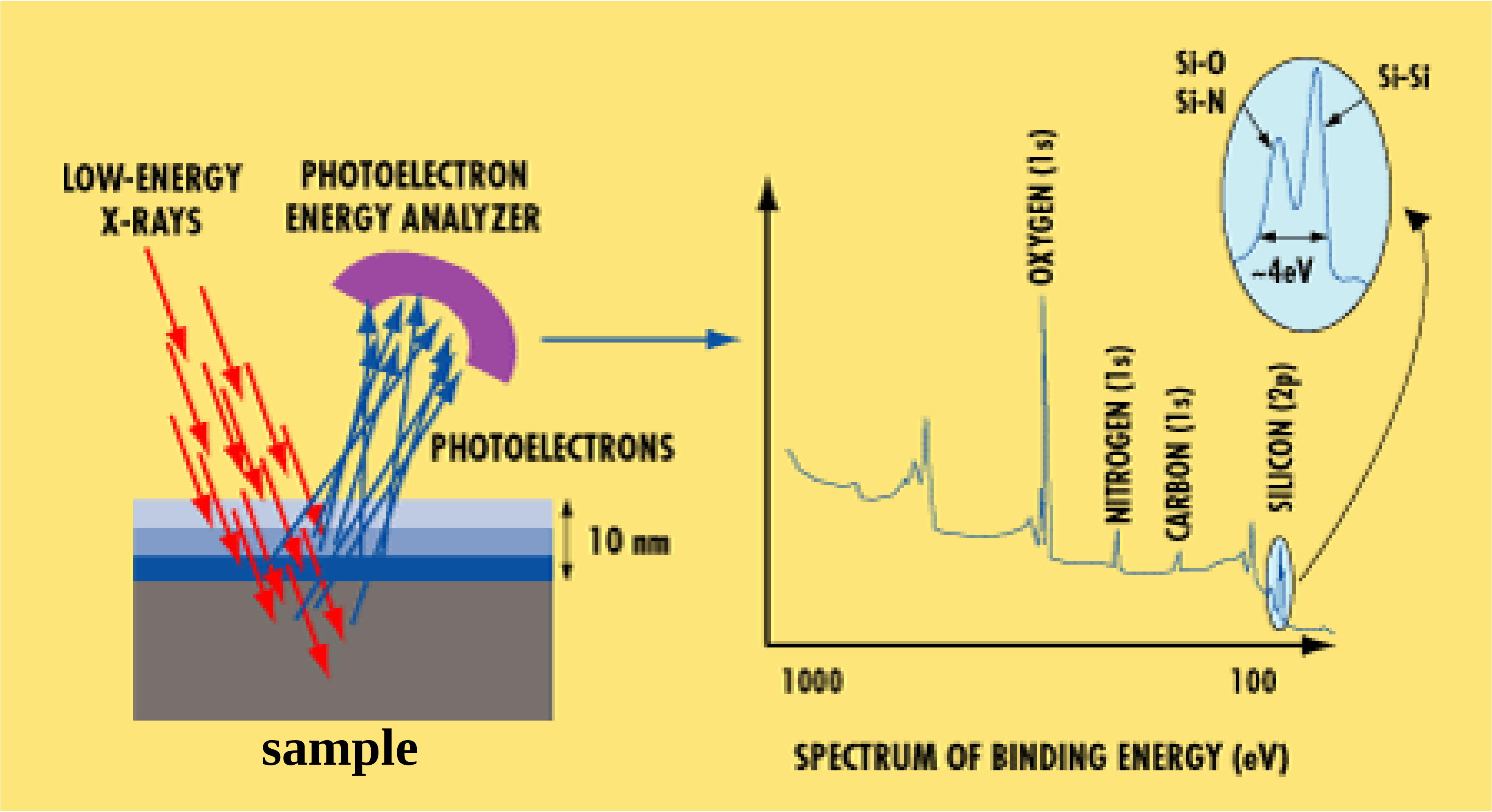
XPS also referred to as *Electron Spectroscopy for Chemical Analysis (ESCA)*, identifies elements by analyzing energies of photoelectrons ejected by monochromatic X-rays.

The energy of each photoelectron is directly related to the atom from which it was removed; therefore *identifying elements on a sample surface* is possible.

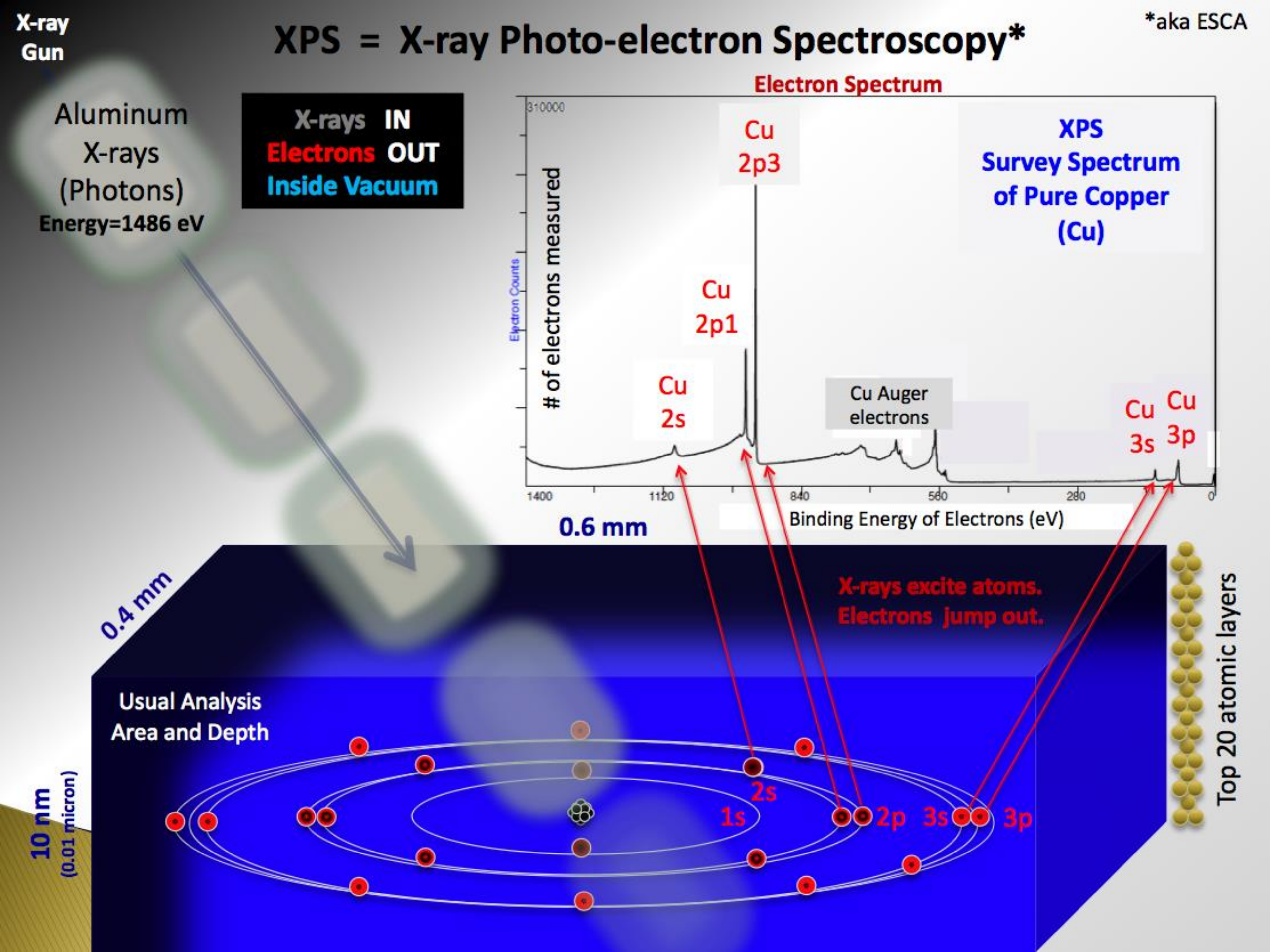
A high-resolution spectrometer sums the number of ejected photoelectrons at specific levels of energy, and these sums are converted into elemental compositions.

In many cases, valence state(s) or chemical bonding environment(s) are also identifiable from these sums.

Overview of XPS



qualitative (peak positions) and quantitative (peak intensities) surface analysis

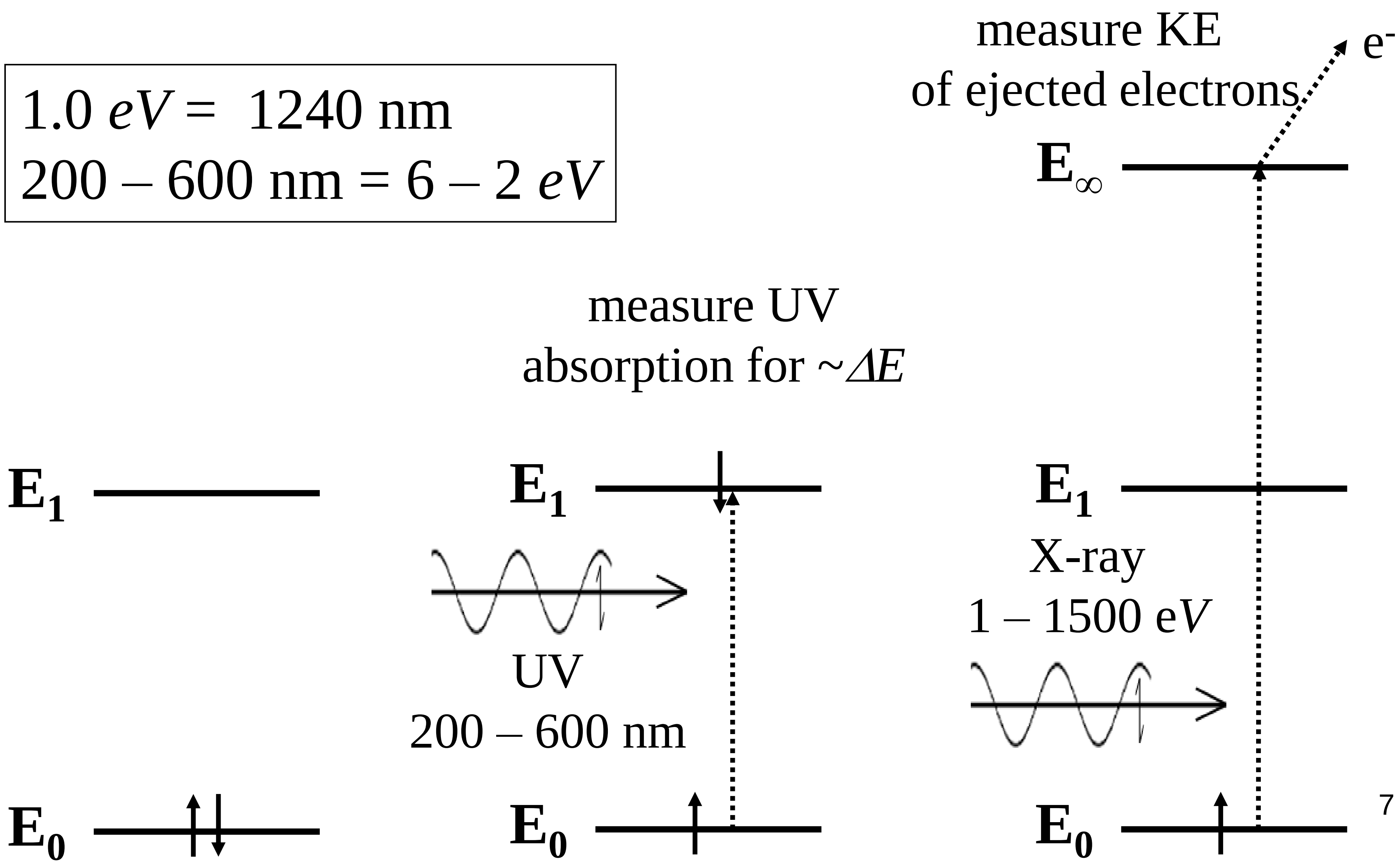


X-ray Gun
XPS = X-ray Photo-electron Spectroscopy*
*aka ESCA
Aluminum X-rays (Photons)
Energy=1486 eV
X-rays IN
Electrons OUT
Inside Vacuum
Electron Spectrum
310000
Electron Counts
# of electrons measured
Cu 2p3
Cu 2p1
Cu 2s
Cu Auger electrons
Cu 3s
Cu 3p
XPS Survey Spectrum of Pure Copper (Cu)
1400
1120
840
560
280
0
Binding Energy of Electrons (eV)
0.6 mm
0.4 mm
X-rays excite atoms.
Electrons jump out.
Top 20 atomic layers
Usual Analysis Area and Depth
10 nm
(0.01 micron)
1s
2s
2p
3s
3p

XPS vs. UV/Vis: What's the Extreme Electronic Transition?

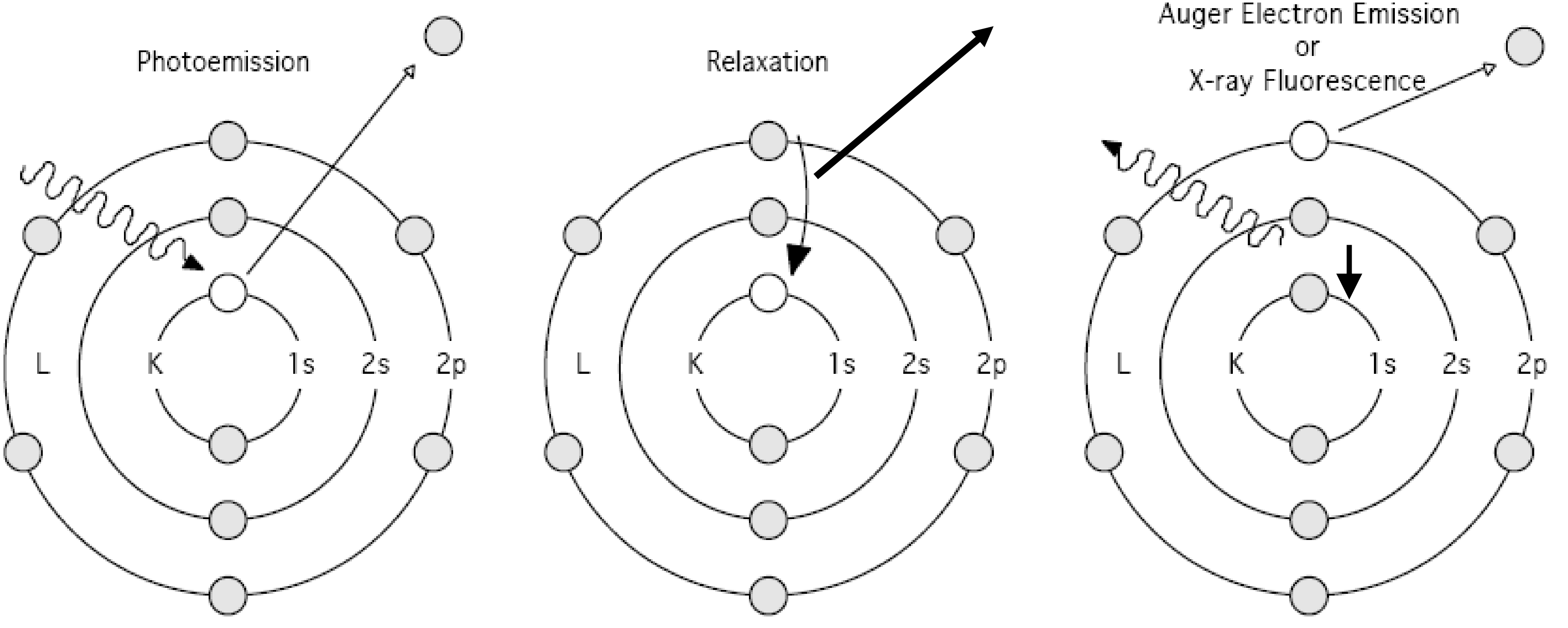
1.0 *eV* = 1240 nm

200 – 600 nm = 6 – 2 *eV*



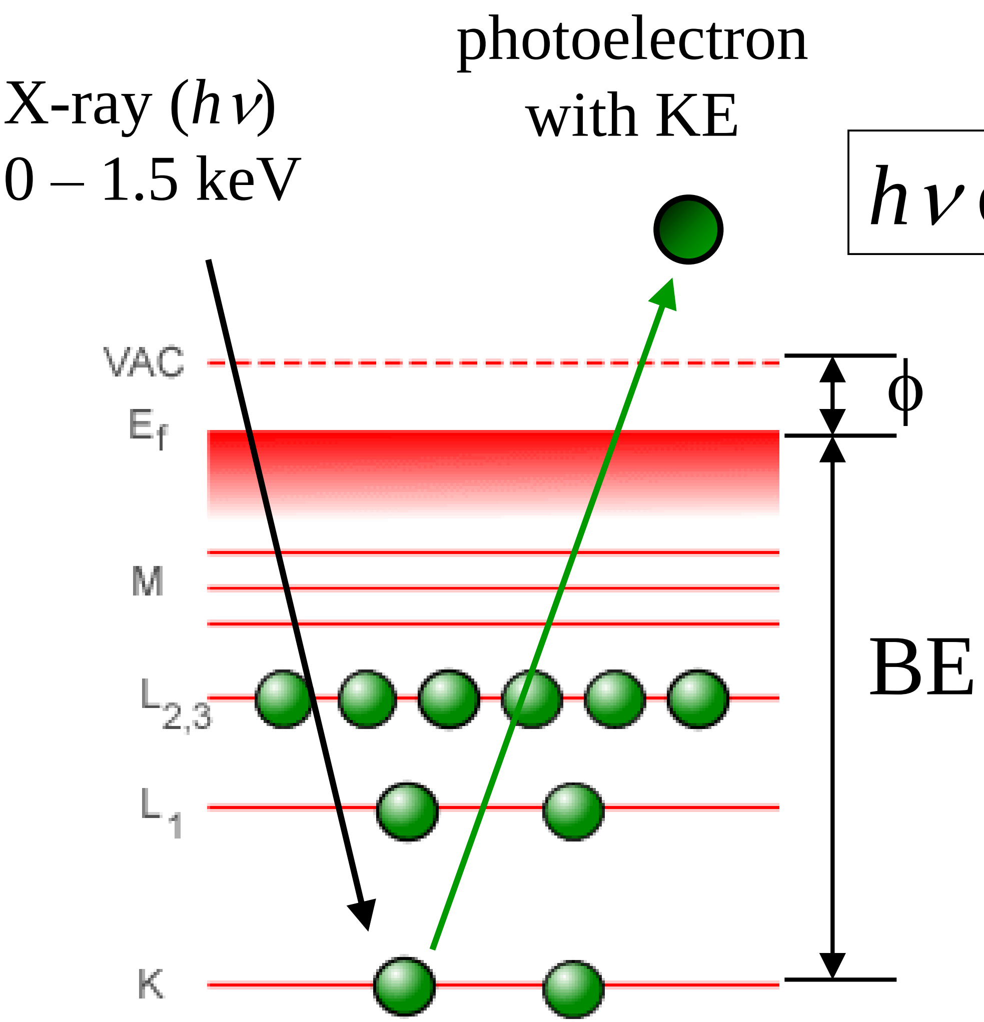
Fate of Core Holes

X-ray generation



Auger electron spectroscopy

Principles of (XPS)

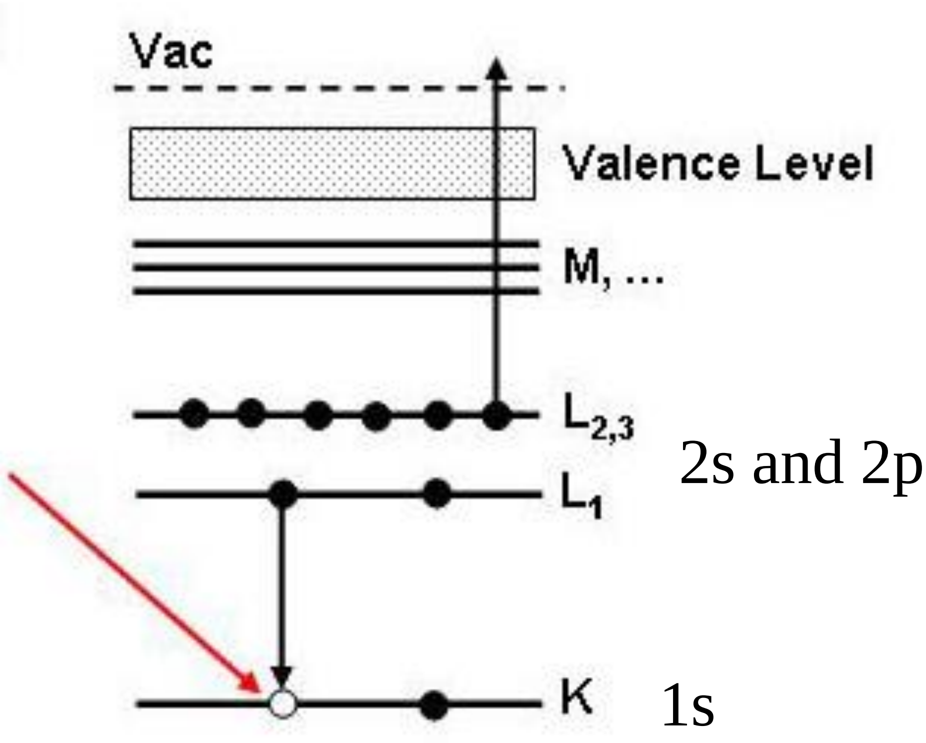


$$h\nu \text{ of X-ray} = BE + KE + \phi$$

BE: binding energy
KE: kinetic energy
ϕ: work function

KE is measured
BE depends on the valence state(s) or chemical bonding environment(s)

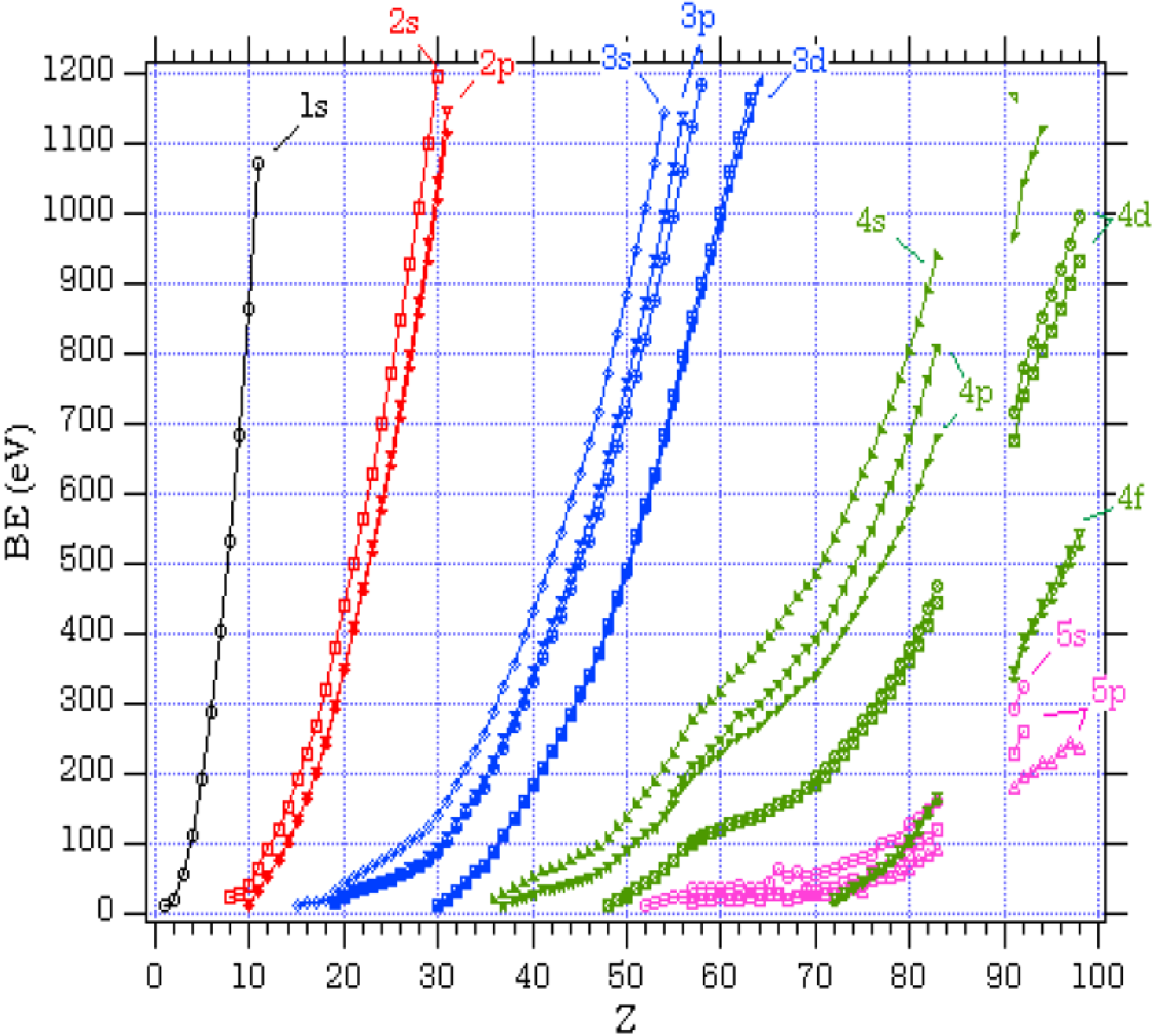
Auger Electron Spectroscopy (AES)



$KL_1L_{2,3}$ transition
= (KLL)

1. An electron in K shell (1s orbital) is removed by x-ray.
2. For a $KL_1L_{2,3}$ transition, K (the core level hole,) L_1 (the relaxing electron's initial state), and $L_{2,3}$ (the emitted electron's initial energy state).
3. Similarly, there are LMM, MNN types of transitions in an Auger spectra.

BE (Binding Energy)



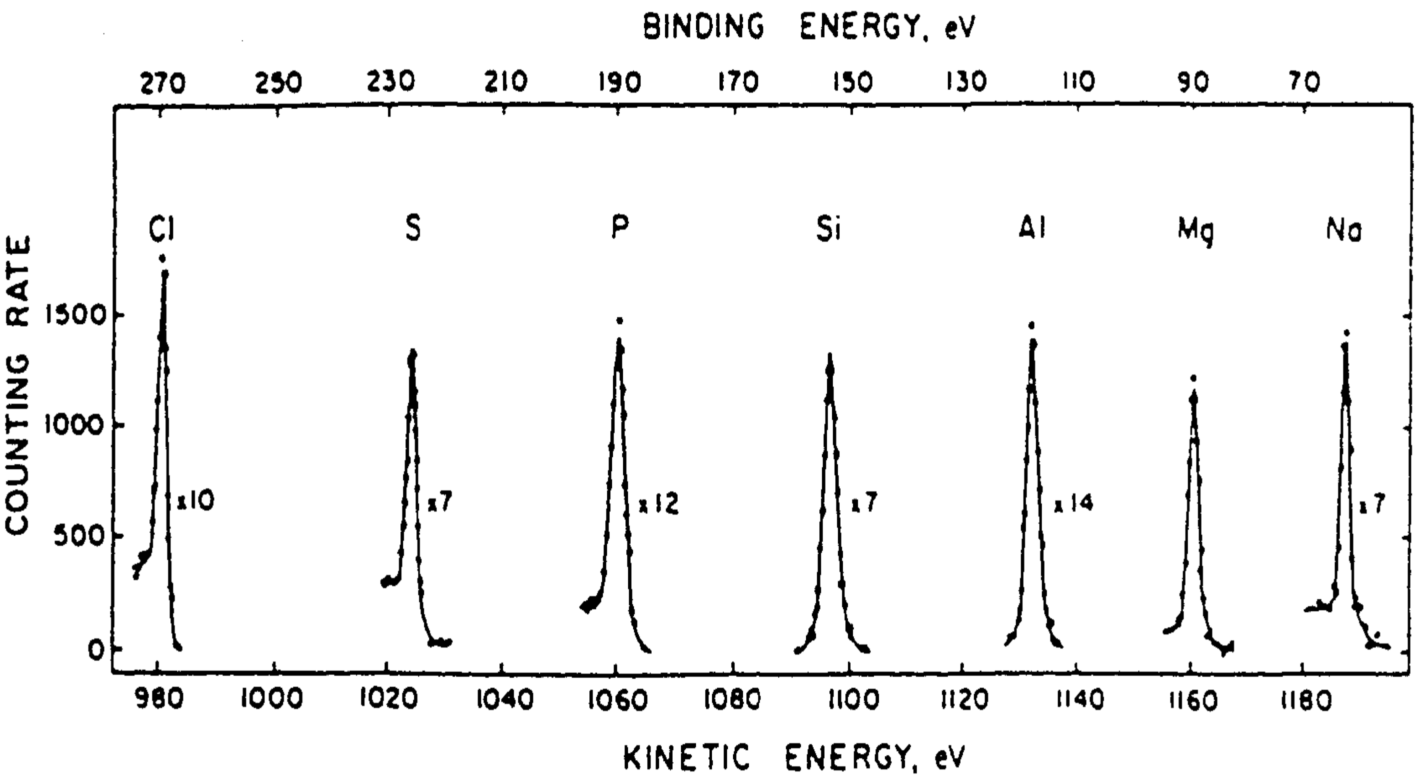
BE (Binding Energy)

Energy of levels :

BE(1s) > BE(2s) > BE(2p) > BE(3s)…

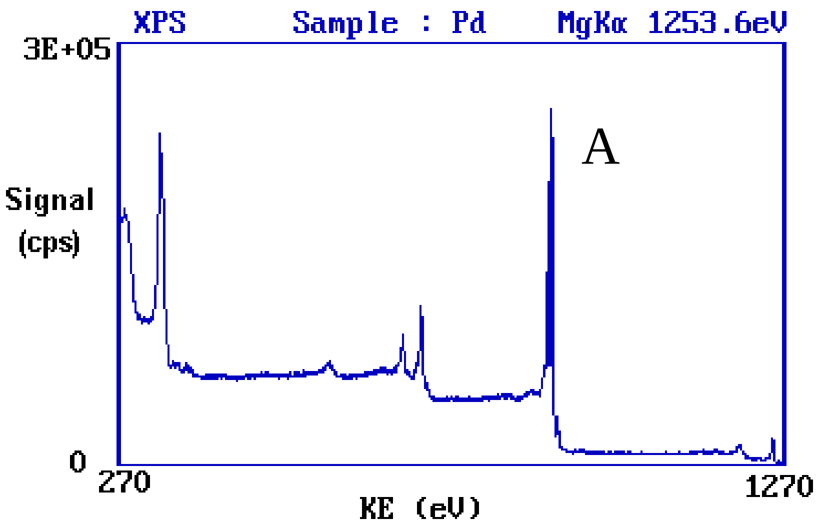
Atomic number (Z):

BE(Na 1s) < BE(Mg 1s) < BE(Al 1s)…



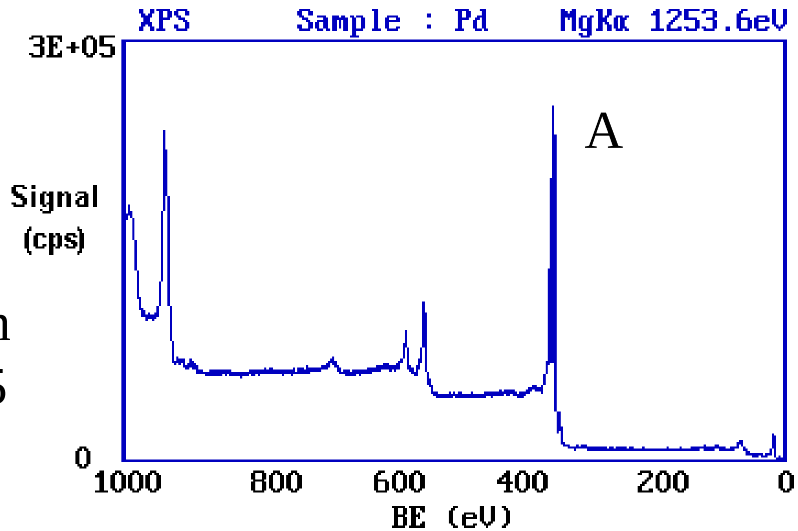
How Does It Work?

XPS spectrum from a Pd metal sample using Mg K_α radiation



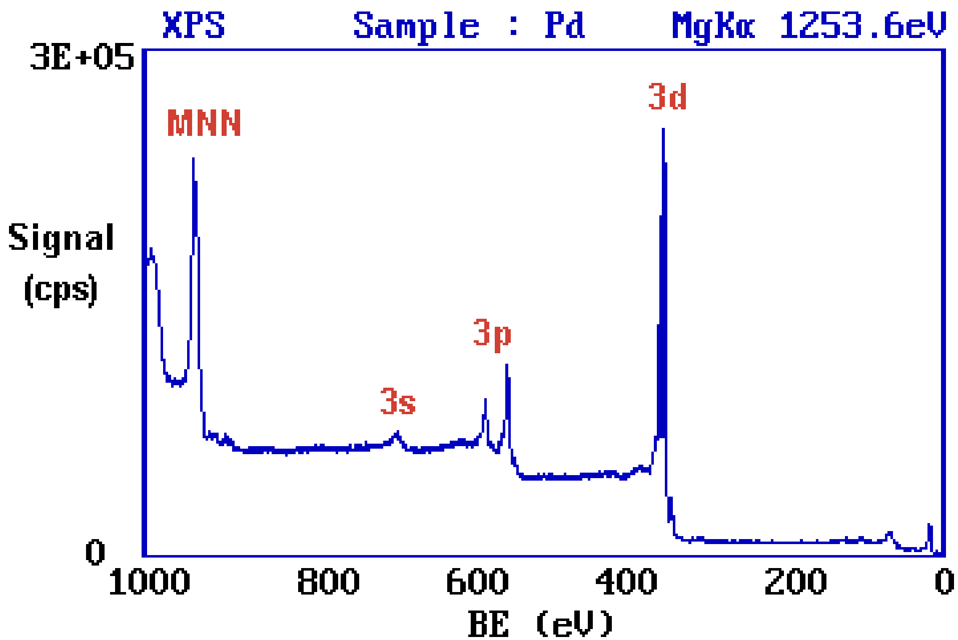
the main peaks occur at kinetic energies of ca. 330, 690, 720, 910 and 920 eV.

Plotting against BE as opposed to KE.



The most intense peak (A) is now seen to occur at a binding energy of ca. 335 eV

Chemical and Structural Information

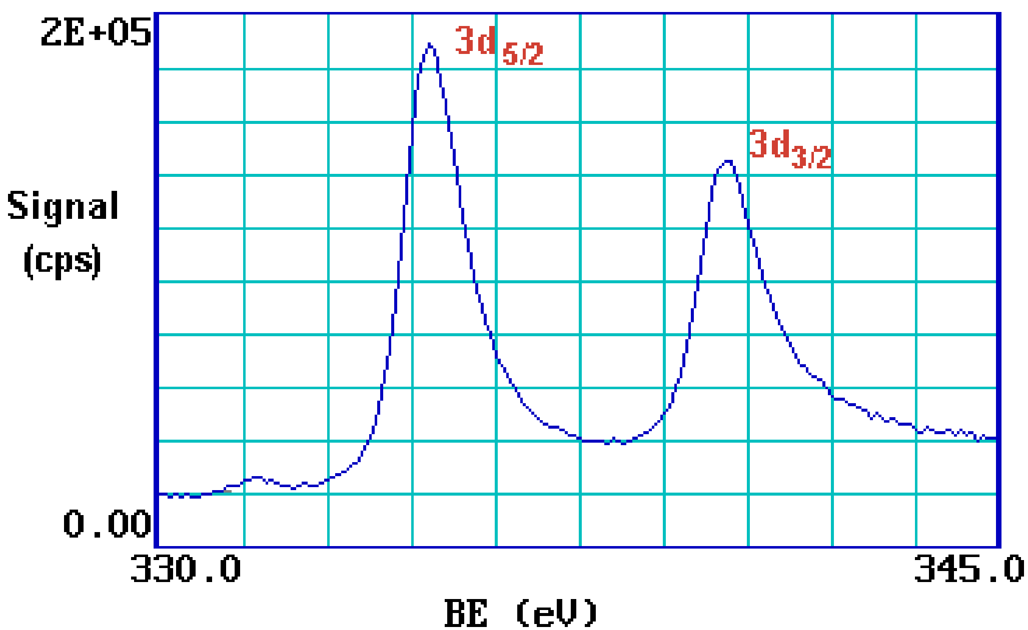


1. the valence band (4*d*,5*s*) emission occurs: ca. 0 - 8 eV (measured with respect to the Fermi level, or alternatively at ca. 4 - 12 eV if measured with respect to the vacuum level).
2. the 4*p* and 4*s*: 54 and 88 eV, respectively
3. the 3d/sp/3s: ca. 335, ca. 534/561, and 673 eV respectively.
4. the remaining peak is not an XPS peak at all ! - it is an Auger peak arising from x-ray induced *Auger emission*. It occurs at a kinetic energy of ca. 330 eV.

Complexity of XPS Spectra I: Spin-Orbit Splitting

Closer inspection of the spectrum shows that emission from some levels (most obviously 3*p* and 3*d*) produces a closely spaced doublet. Why?

For d electron in d^9 system, l–s coupling produces j =5/2 and 3/2 (for d electron, l = 2 and s = ½, j = l + s … l – s).

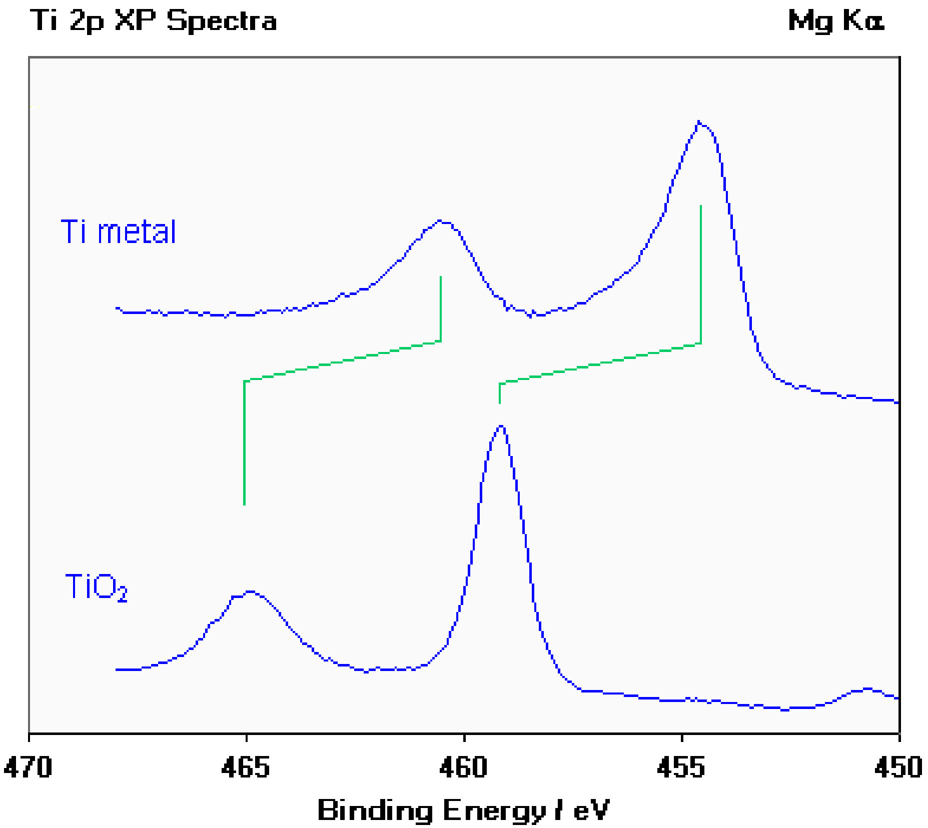


Complexity of XPS Spectra II: Chemical Shift

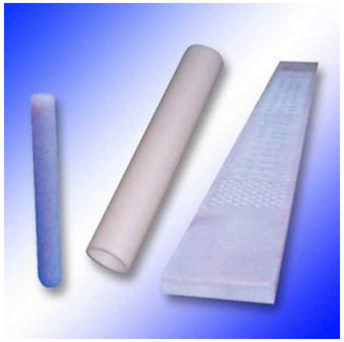
The exact binding energy of an electron also depends on:

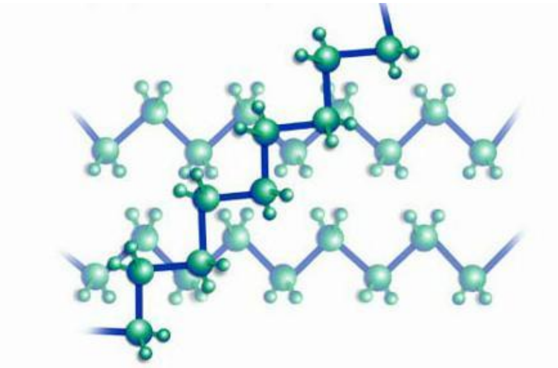
1. the formal oxidation state of the atom
2. the local chemical and physical environment

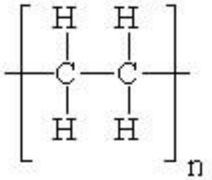
Changes in either (1) or (2) give rise to small shifts in the peak positions in the spectrum - so-called *chemical shifts* .



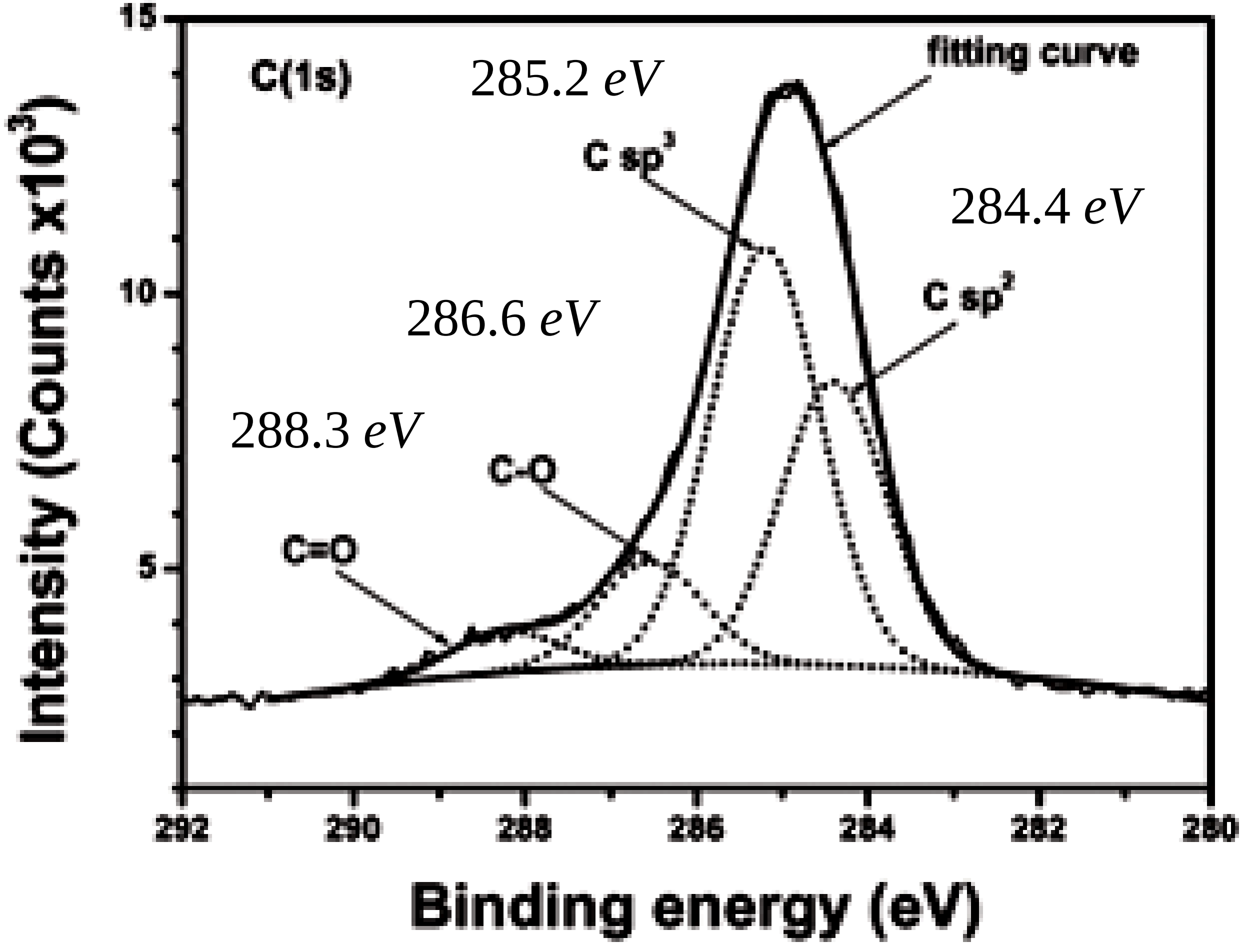
Actual XPS Peak Analysis by Fitting



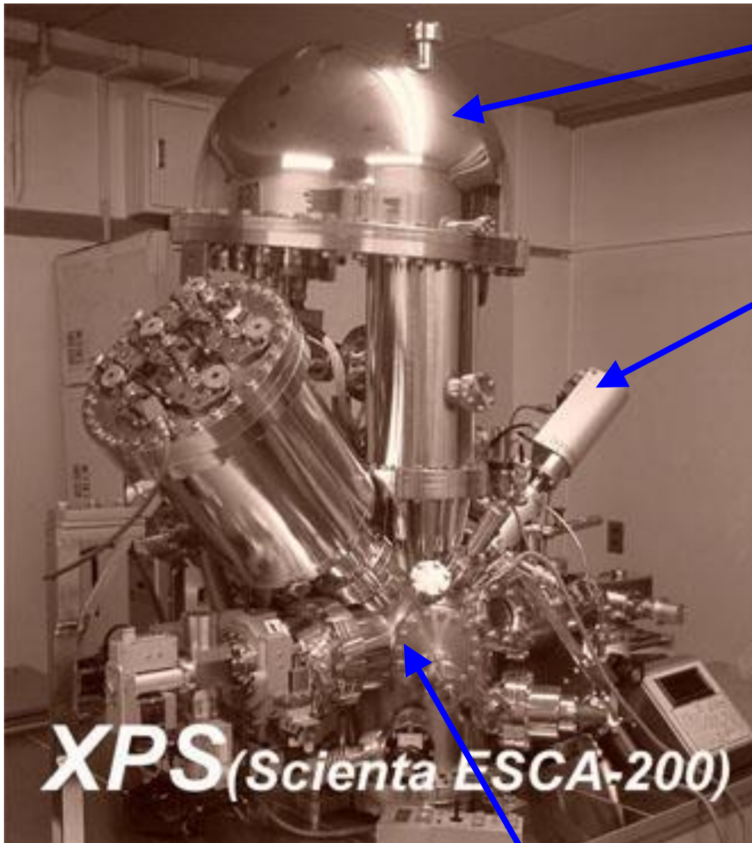




XPS spectrun of carbon atoms in ultra-high molecular weight polyethylene (UHMWPE) after surface oxidation



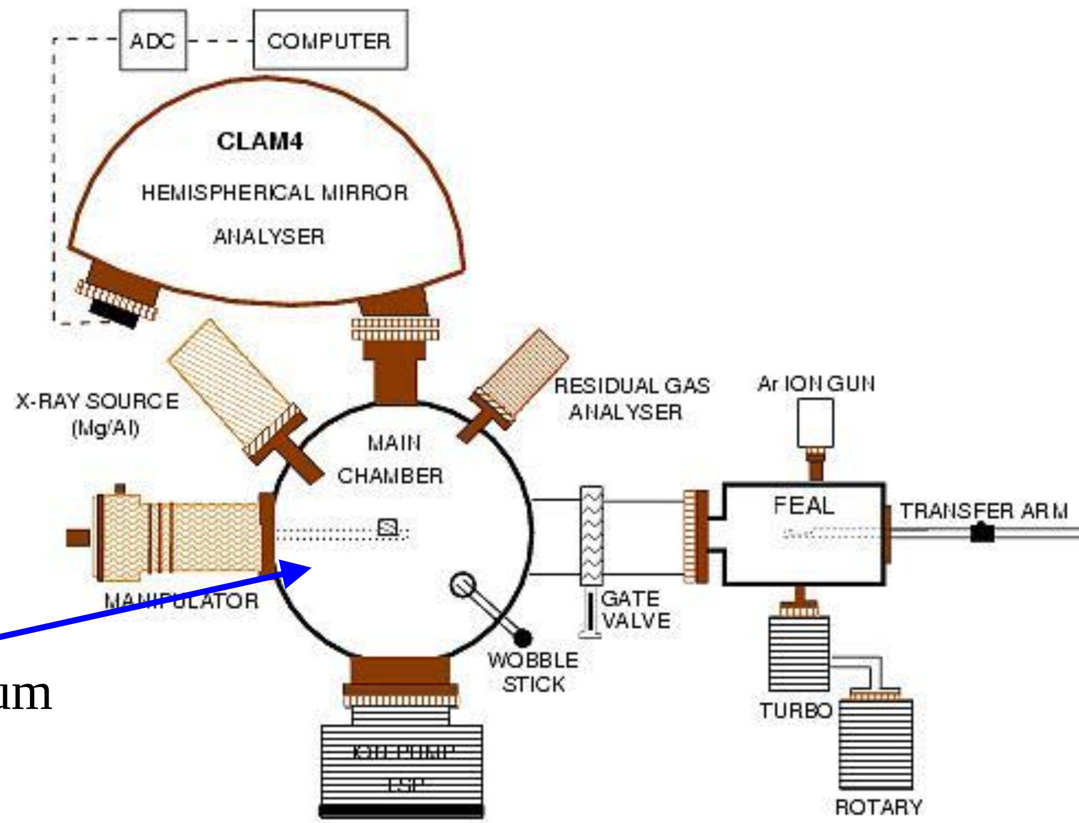
Instrumentation



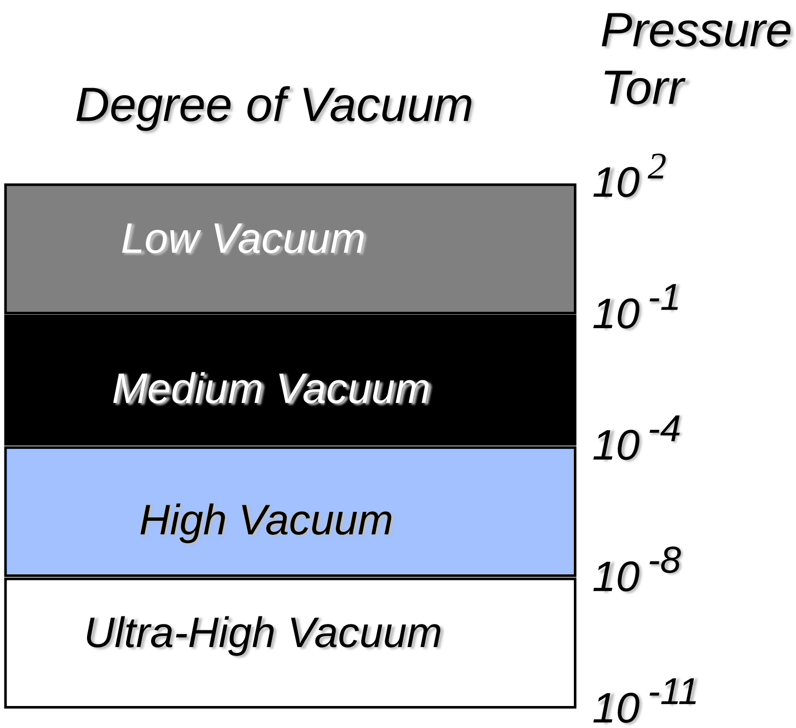
electron analyzer
(detector)

X-ray source

Ultra-high vacuum
(UHV)



Why UHV for Surface Analysis?



- 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.

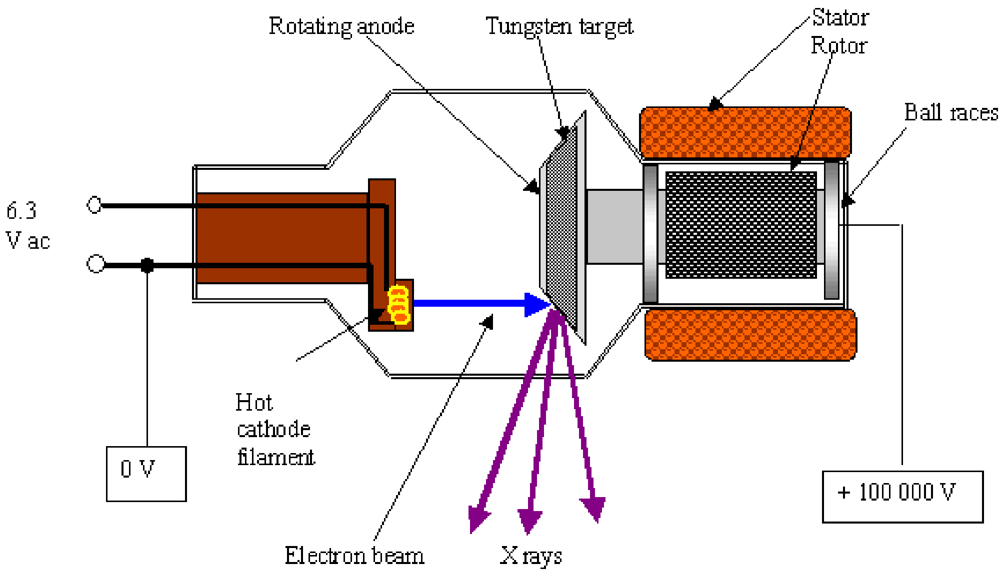
X-ray Source

The most commonly employed x-ray sources are those giving rise to:

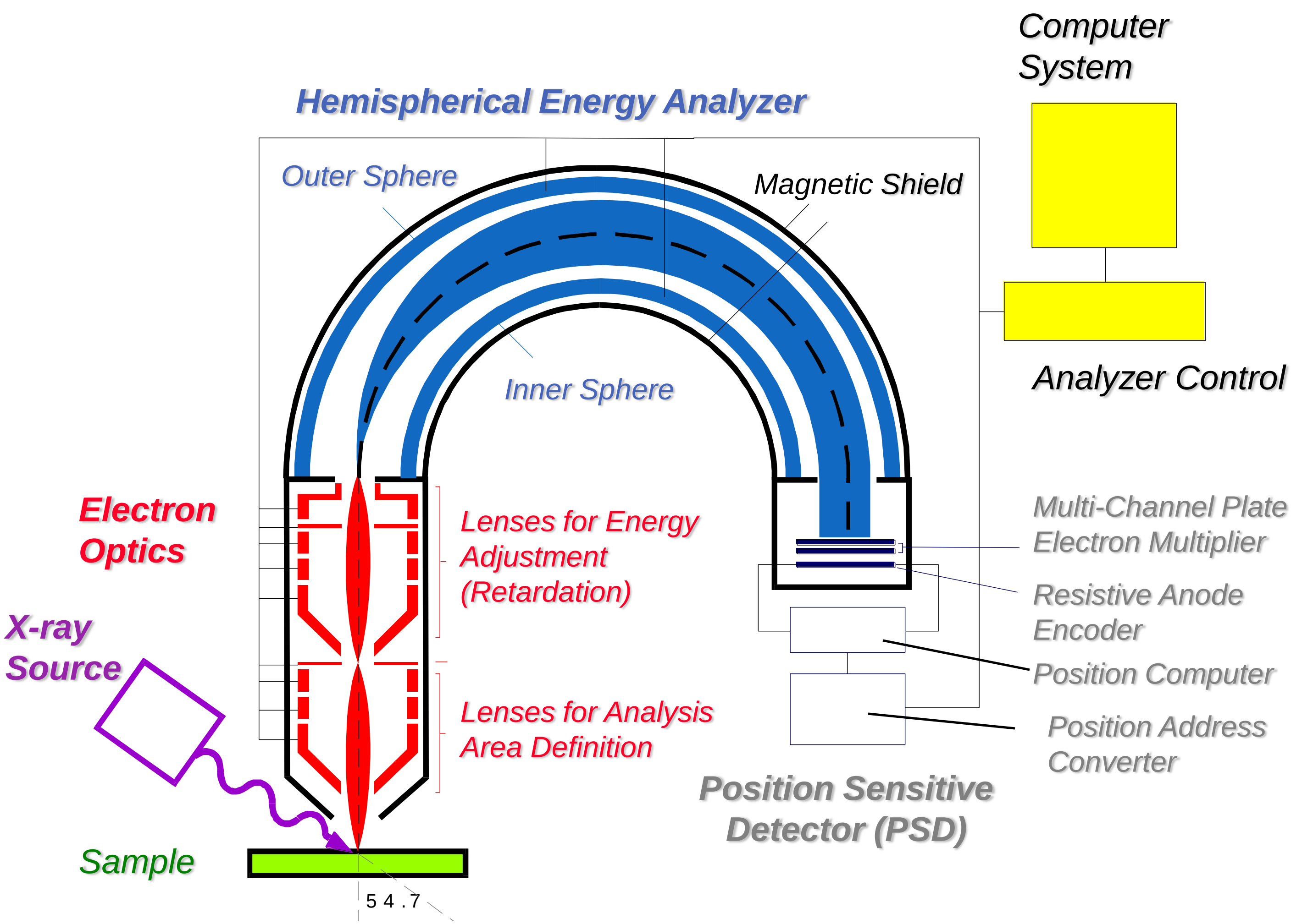
Mg K_α radiation : $h\nu$ = 1253.6 eV
Al K_α radiation : $h\nu$ = 1486.6 eV

$$eV = \tfrac{1}{2}mv^2 = h\nu_{max}$$

Twin Anode X-Ray Source for XPS

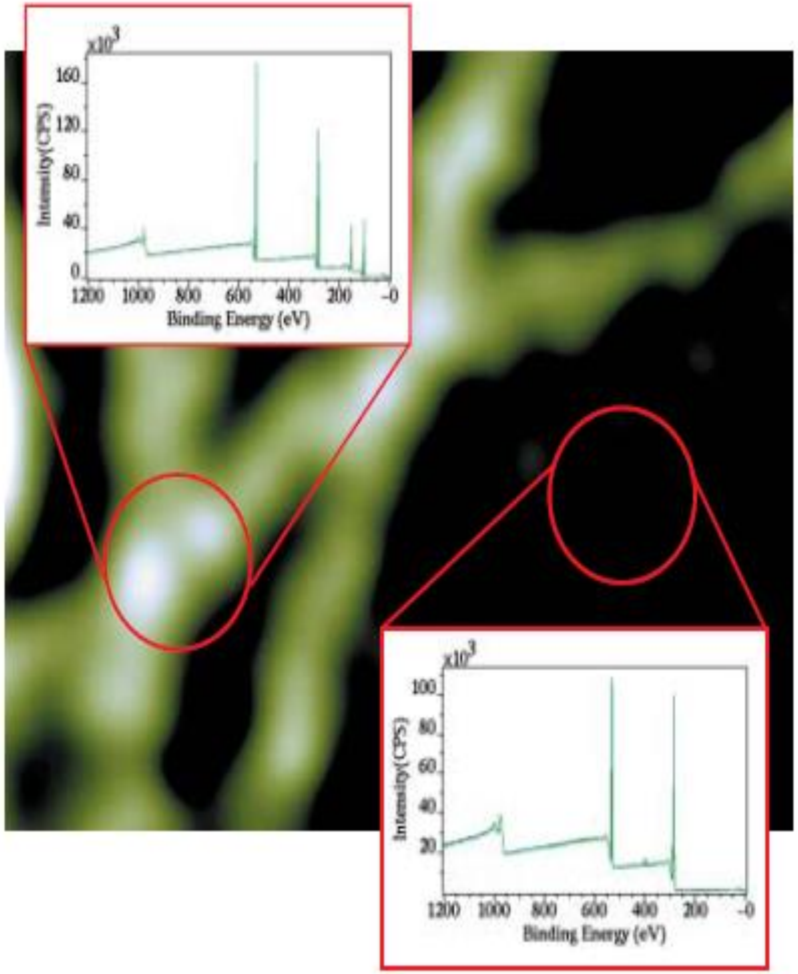


Detector: Electron Analyzer



Applications of XPS

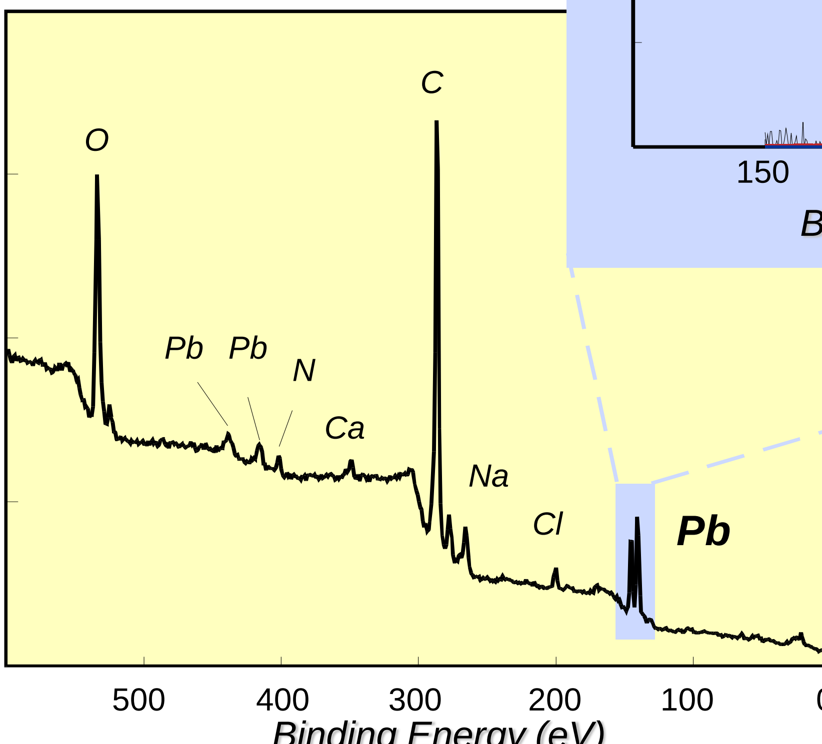
- Characterization of reactive interactions at interfaces
- Analysis of concentrations of chemical substances at interfaces
- Detection of impurities on material surfaces (failure analysis)
- Studying gas-solid reactions at surfaces (catalysis)
- Investigation of solid-solid reactions when there is reactive frictional wear
- Analysis of surface pretreatment/treatment, e.g. using plasma techniques

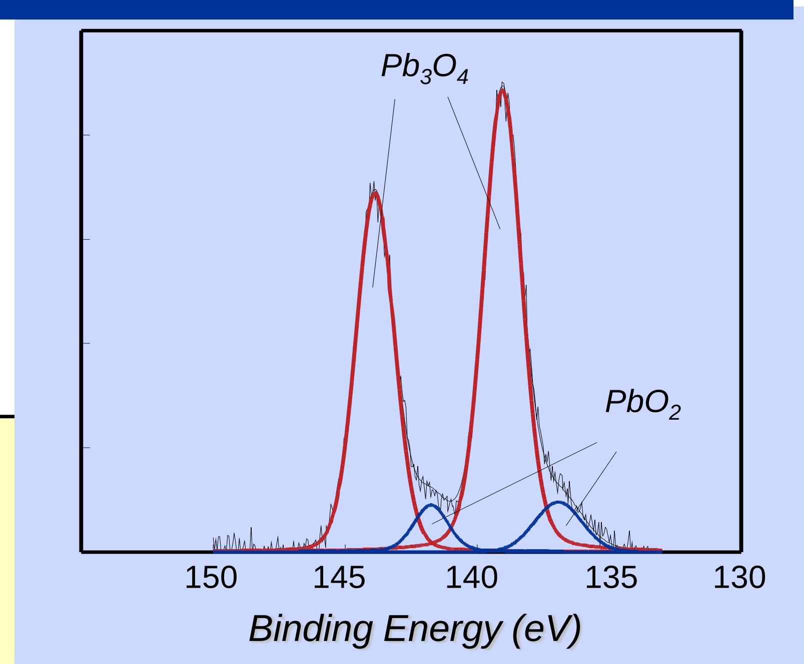


Silicon distribution in silicone-coated polyamide fibres (Ø = 12 µm) on a pressure sensitive adhesive tape (Section: 350x350 µm)

XPS Analysis of Pigment from Mummy Artwork

Egyptian Mummy
2nd Century AD
World Heritage Museum
University of Illinois





XPS analysis showed that the pigment used on the mummy wrapping was Pb_3O_4 rather than Fe_2O_3

Analysis of Carbon Fiber- Polymer Composite Material by XPS

XPS analysis identifies the functional groups present on composite surface. Chemical nature of fiber-polymer interface will influence its properties.

Woven carbon fiber composite