X-ray Photoelectron Spectroscopy (XPS)

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Surface Analysis

The Study of the Outer-Most Layers of Materials (<100 Å).

- ***Electron Spectroscopies***

  XPS: X-ray Photoelectron Spectroscopy

  AES: Auger Electron Spectroscopy

  EELS: Electron Energy Loss Spectroscopy

- ***Ion Spectroscopies***

  SIMS: Secondary Ion Mass Spectrometry

  SNMS: Sputtered Neutral Mass Spectrometry

  ISS: Ion Scattering Spectroscopy

Introduction to X-ray Photoelectron Spectroscopy (XPS)

Introduction to X-ray Photoelectron Spectroscopy (XPS)

- ***What is XPS?- General Theory***
- ***How can we identify elements and compounds?***
- *Instrumentation for XPS*
- *Examples of materials analysis with XPS*

What is XPS?

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces.

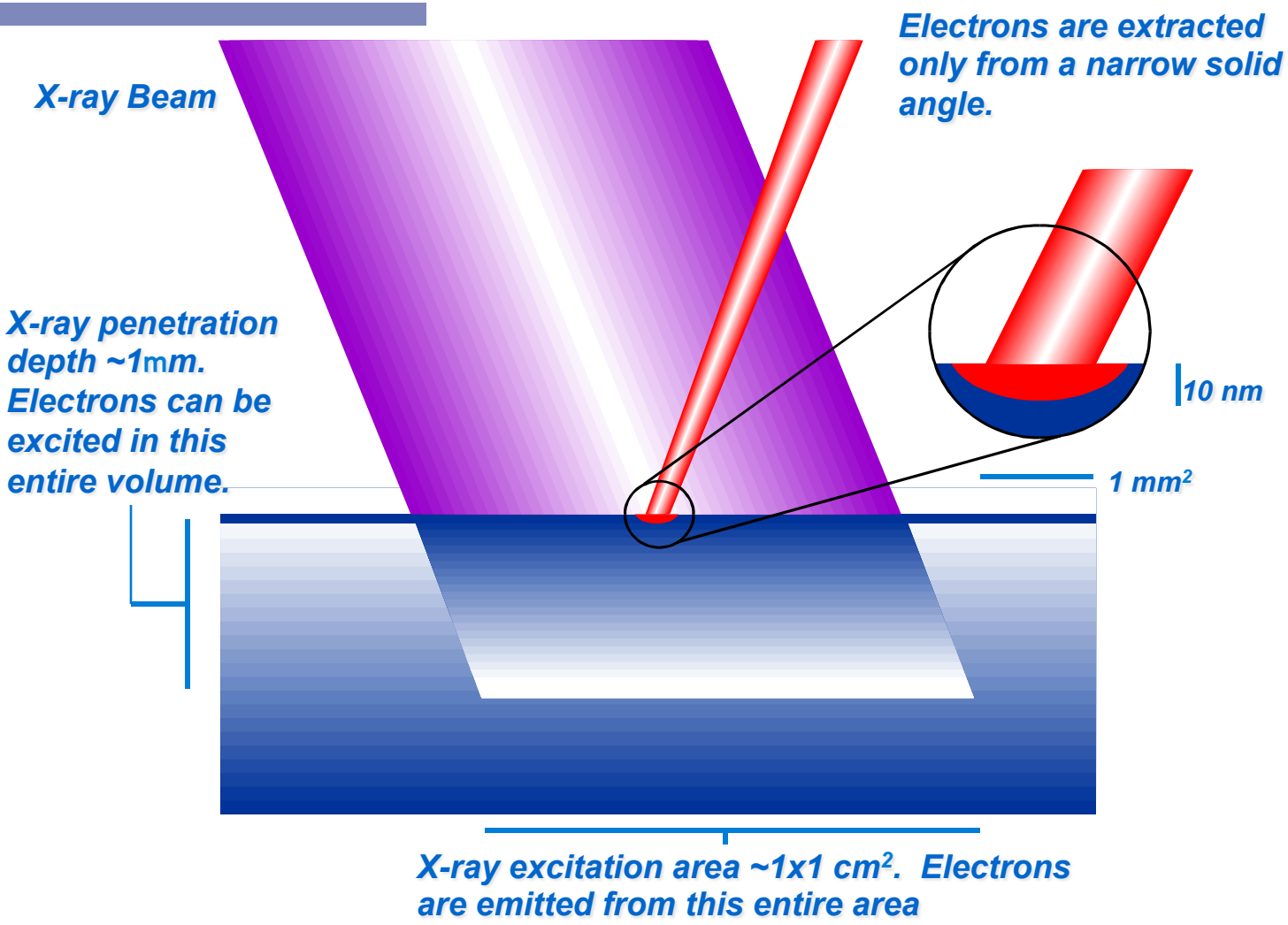
What is XPS?

X-ray Photoelectron spectroscopy, based on the photoelectric effect,[1,2] was developed in the mid-1960's by Kai Siegbahn and his research group at the University of Uppsala, Sweden.[3]

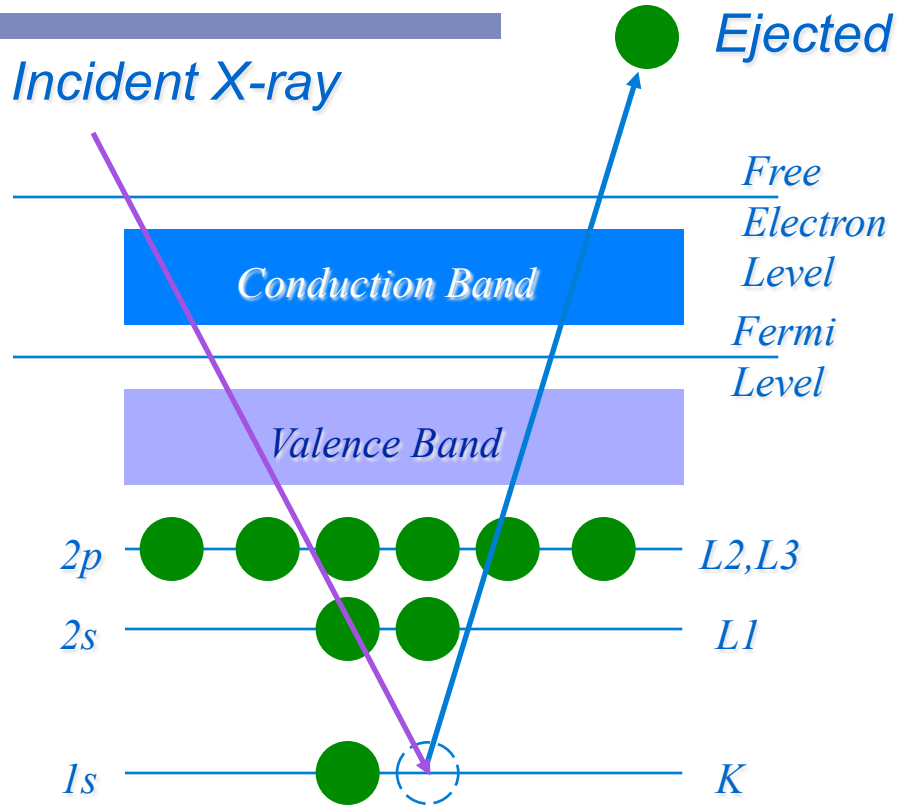
1. H. Hertz, Ann. Physik 31,983 (1887).
2. A. Einstein, Ann. Physik 17,132 (1905). 1921 Nobel Prize in Physics.
3. K. Siegbahn, Et. Al.,Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics.

X-ray Photoelectron Spectroscopy

Small Area Detection



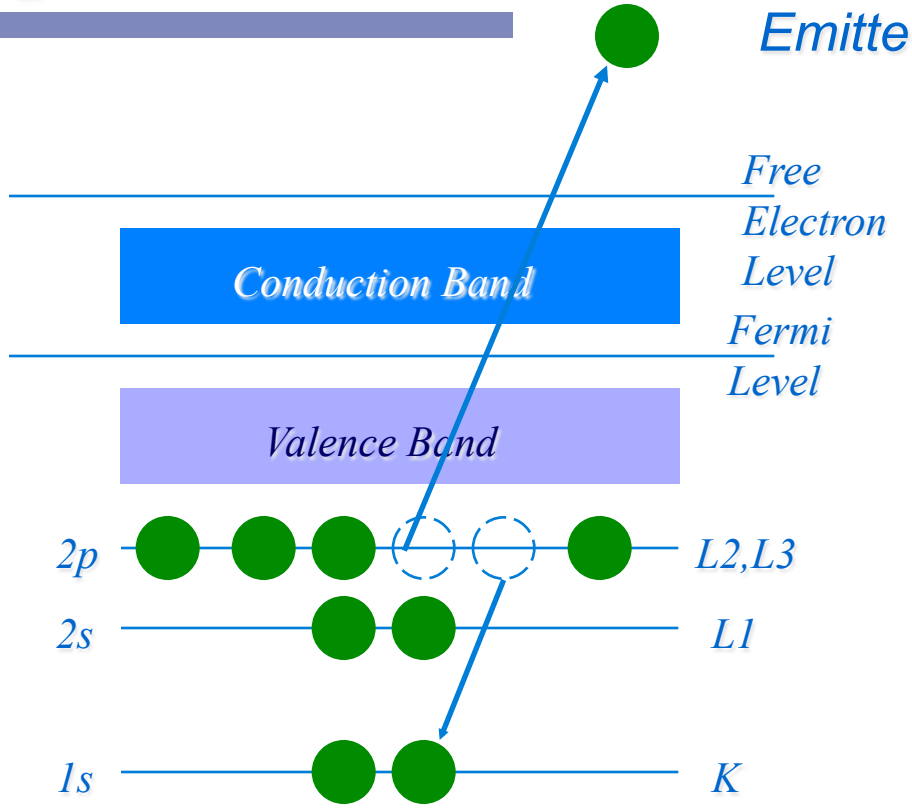
The Photoelectric Process



- *XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).*
- *The ejected photoelectron has kinetic energy:*

  KE=hv-BE-ϕ
- *Following this process, the atom will release energy by the emission of an Auger Electron.*

Auger Relation of Core Hole



- *L electron falls to fill core level vacancy (step 1).*
- *KLL Auger electron emitted to conserve energy released in step 1.*
- *The kinetic energy of the emitted Auger electron is:*

  KE=E(K)-E(L2)-E(L3).

XPS Energy Scale

The XPS instrument measures the kinetic energy of all collected electrons. The electron signal includes contributions from both photoelectron and Auger electron lines.

XPS Energy Scale- Kinetic energy

$$KE = hv - BE - \phi_{spec}$$

Where: *BE= Electron Binding Energy*

KE= Electron Kinetic Energy

ϕ_{spec} *= Spectrometer Work Function*

Photoelectron line energies: Dependent on photon energy.

Auger electron line energies: Not Dependent on photon energy.

If XPS spectra were presented on a kinetic energy scale, one would need to know the X-ray source energy used to collect the data in order to compare the chemical states in the sample with data collected using another source.

XPS Energy Scale- Binding energy

$$BE = hv - KE - \phi_{spec}$$

Where: *BE= Electron Binding Energy*

KE= Electron Kinetic Energy

ϕ_{spec} *= Spectrometer Work Function*

Photoelectron line energies: Not Dependent on photon energy.

Auger electron line energies: Dependent on photon energy.

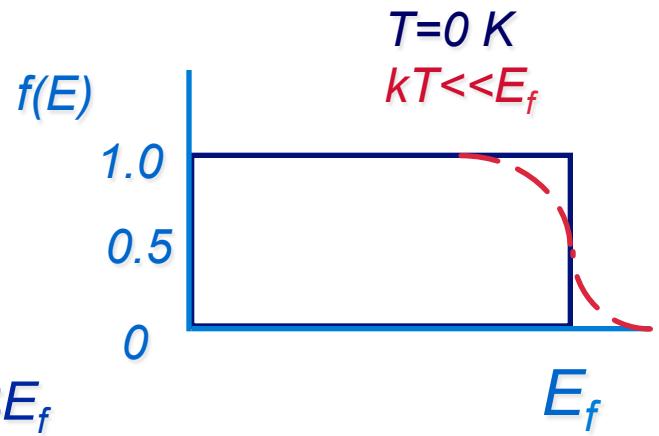
The binding energy scale was derived to make uniform comparisons of chemical states straight forward.

Fermi Level Referencing

Free electrons (those giving rise to conductivity) find an equal potential which is constant throughout the material.

Fermi-Dirac Statistics:

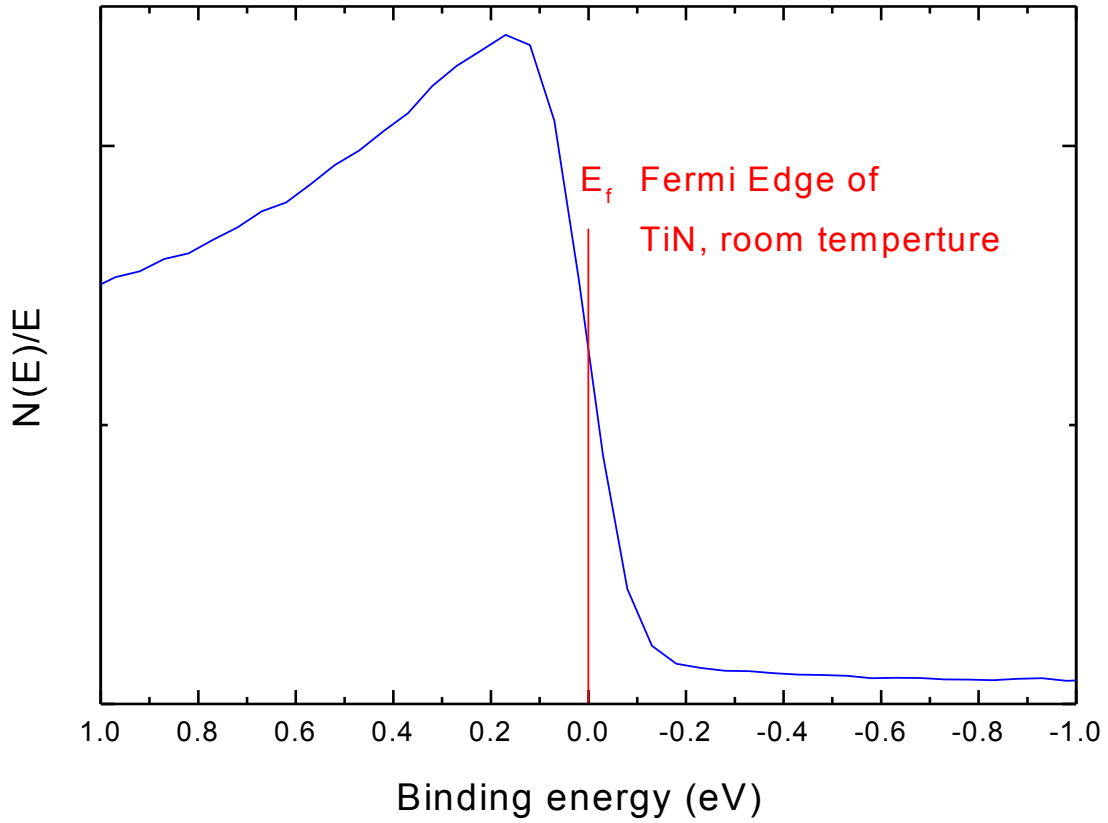
$$f(E) = \frac{1}{\exp[(E-E_f)/kT] + 1}$$



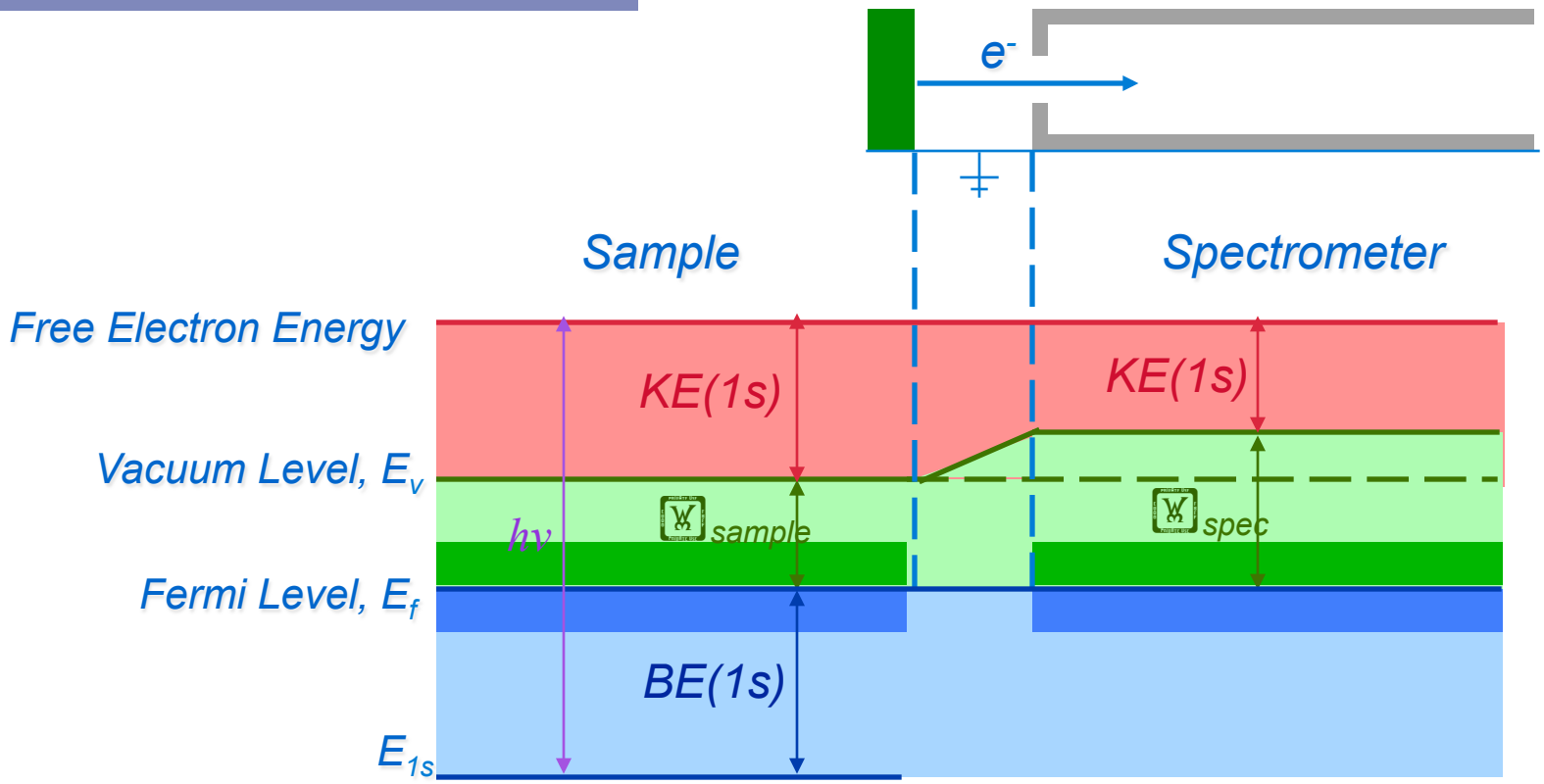
1. *At T=0 K:* $f(E)=1$ *for* $E<E_f$
   $f(E)=0$ *for* $E>E_f$

2. *At* $kT<<E_f$ *(at room temperature kT=0.025 eV)*
   $f(E)=0.5$ *for* $E=E_f$

Fermi Level Referencing

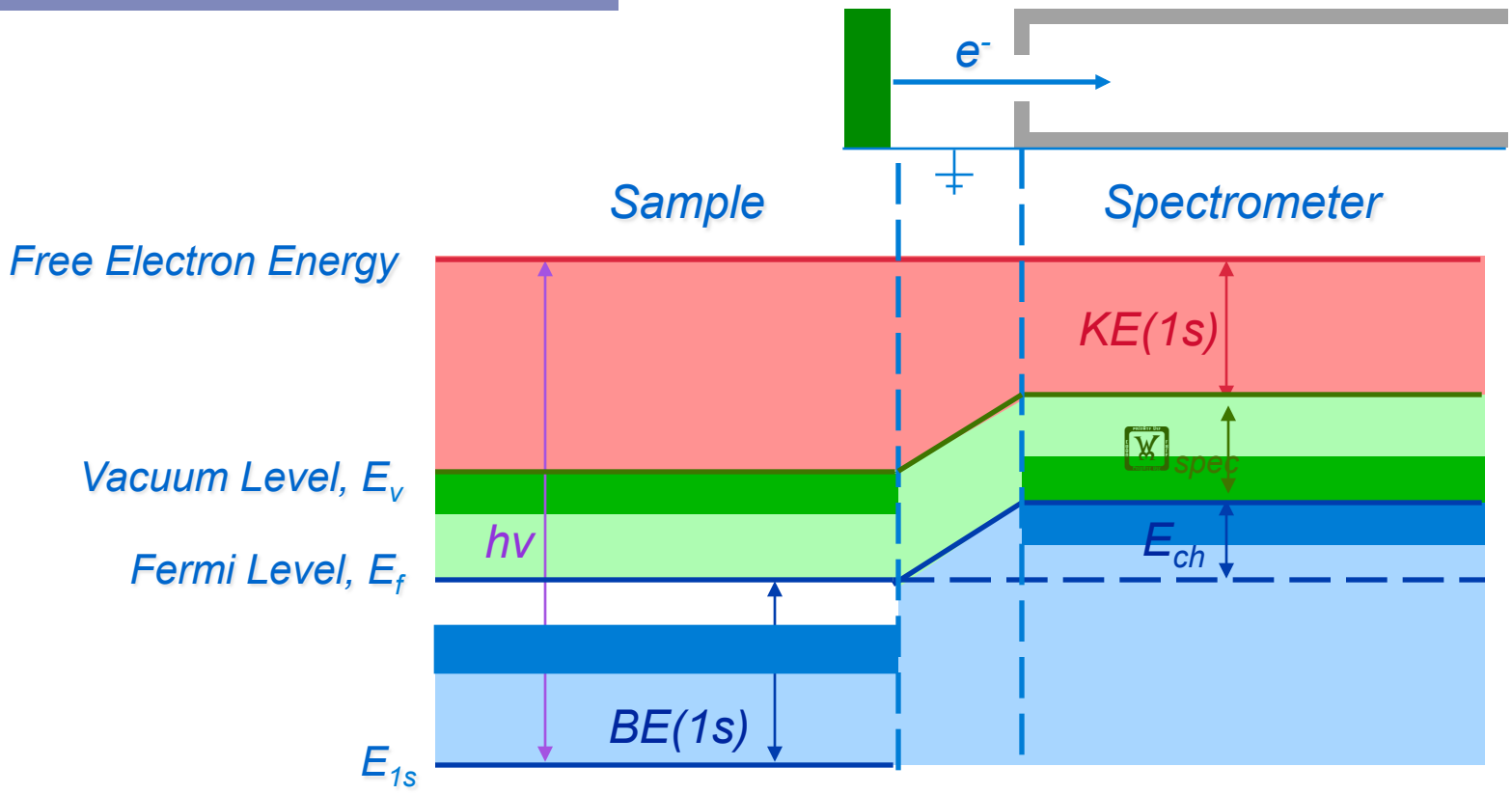


Sample/Spectrometer Energy Level Diagram- Conducting Sample



Because the Fermi levels of the sample and spectrometer are aligned, we only need to know the spectrometer work function, Φ_{spec}, to calculate BE(1s).

Sample/Spectrometer Energy Level Diagram- Insulating Sample



A relative build-up of electrons at the spectrometer raises the Fermi level of the spectrometer relative to the sample. A potential E_{ch} will develop.

Binding Energy Referencing

$$BE = h\nu - KE - \Phi_{spec} - E_{ch}$$

Where: BE= Electron Binding Energy

KE= Electron Kinetic Energy

Φ_{spec}= Spectrometer Work Function

E_{ch}= Surface Charge Energy

E_{ch} can be determined by electrically calibrating the instrument to a spectral feature.

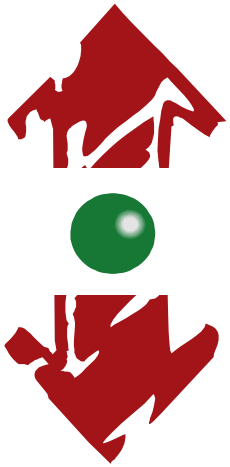
C1s at 285.0 eV

$Au4f_{7/2}$ at 84.0 eV

Where do Binding Energy Shifts Come From?

-or How Can We Identify Elements and Compounds?

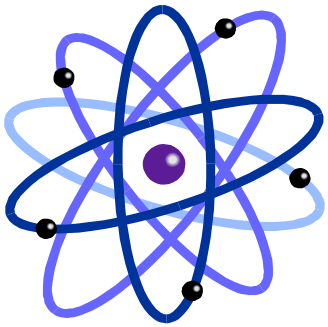
Pure Element



Electron-electron repulsion

Electron

Electron-nucleus attraction



Nucleus

Fermi Level

Binding Energy

Look for changes here by observing electron binding energies

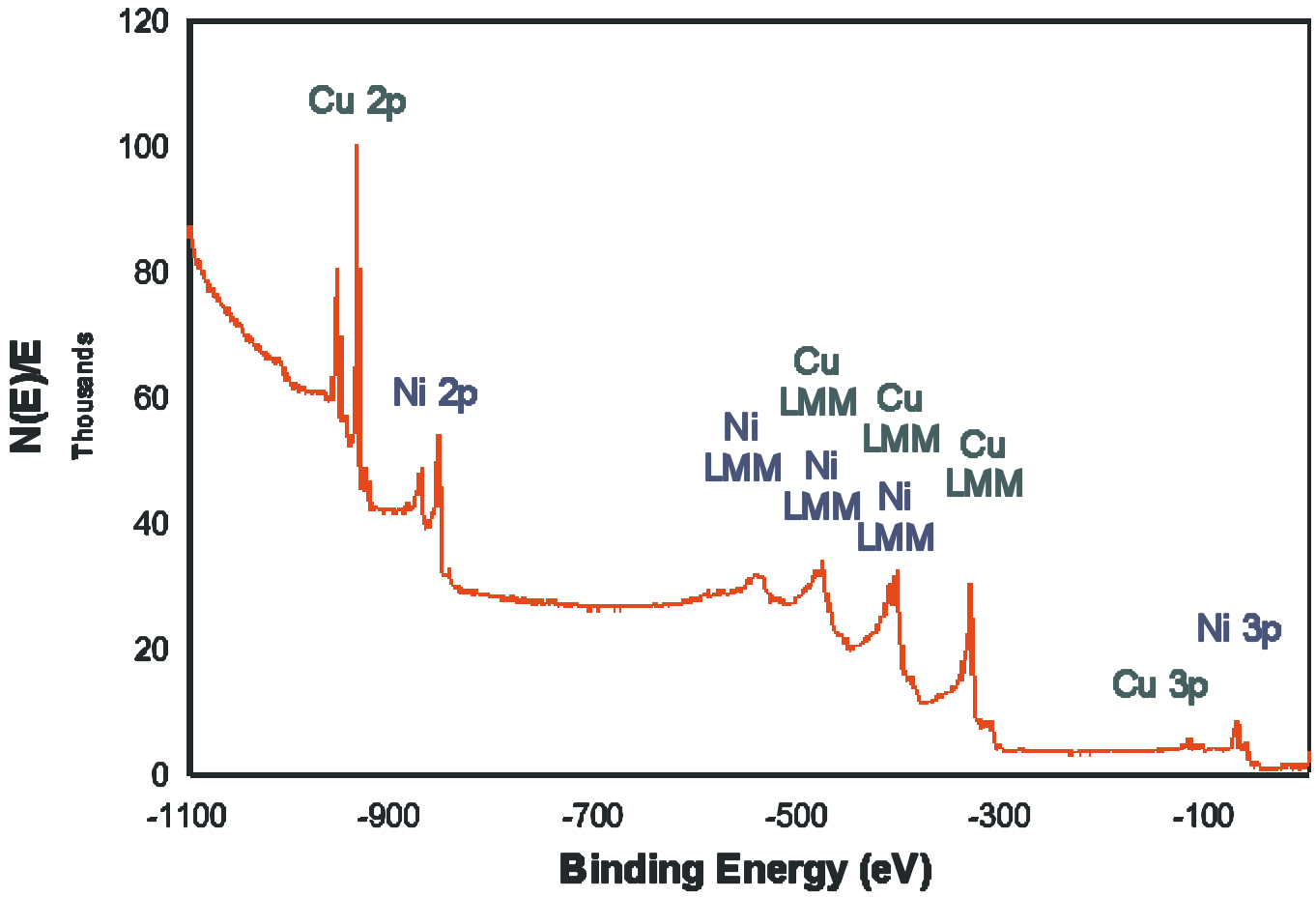
Electron-Nucleus Separation

Elemental Shifts

	Binding Energy (eV)		
Element	***$2p_{3/2}$***	***3p***	***Δ***
Fe	707	53	654
Co	778	60	718
Ni	853	67	786
Cu	933	75	858
Zn	1022	89	933

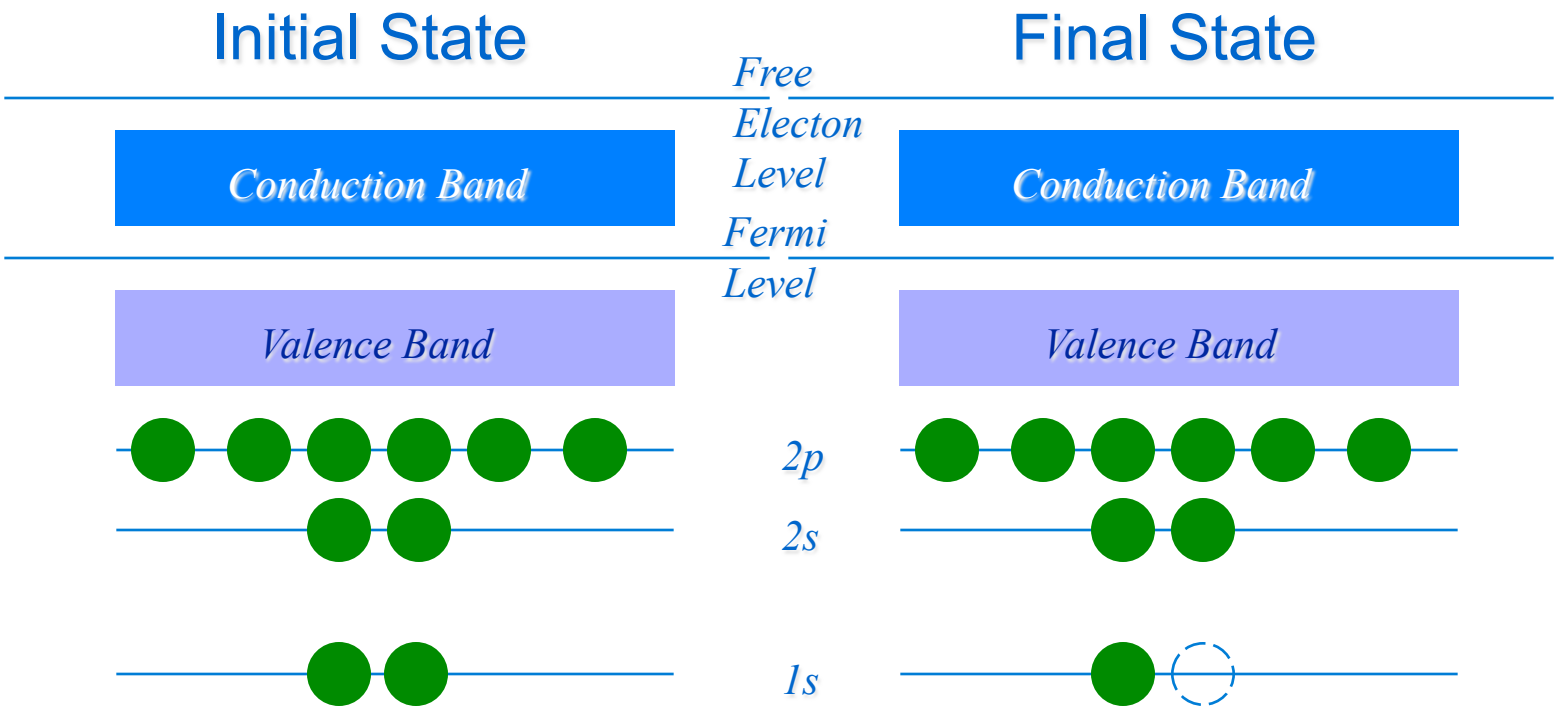
Electron-nucleus attraction helps us identify the elements

Elemental Shifts



Binding Energy Determination

The photoelectron's binding energy will be based on the element's final-state configuration.



The Sudden Approximation

Assumes the remaining orbitals (often called the passive orbitals) are the same in the final state as they were in the initial state (also called the *frozen-orbital approximation*). Under this assumption, the XPS experiment measures the negative Hartree-Fock orbital energy:

Koopman's Binding Energy

$$E_{B,K} = -\varepsilon_{B,K}$$

Actual binding energy will represent the readjustment of the N-1 charges to minimize energy (relaxation):

$$E_B = E_f^{N-1} - E_i^{N}$$

Binding Energy Shifts (Chemical Shifts)

Point Charge Model:

$$E_i = E_i^0 + kq_i + \sum_{j \neq i} q_j / r_{ij}$$

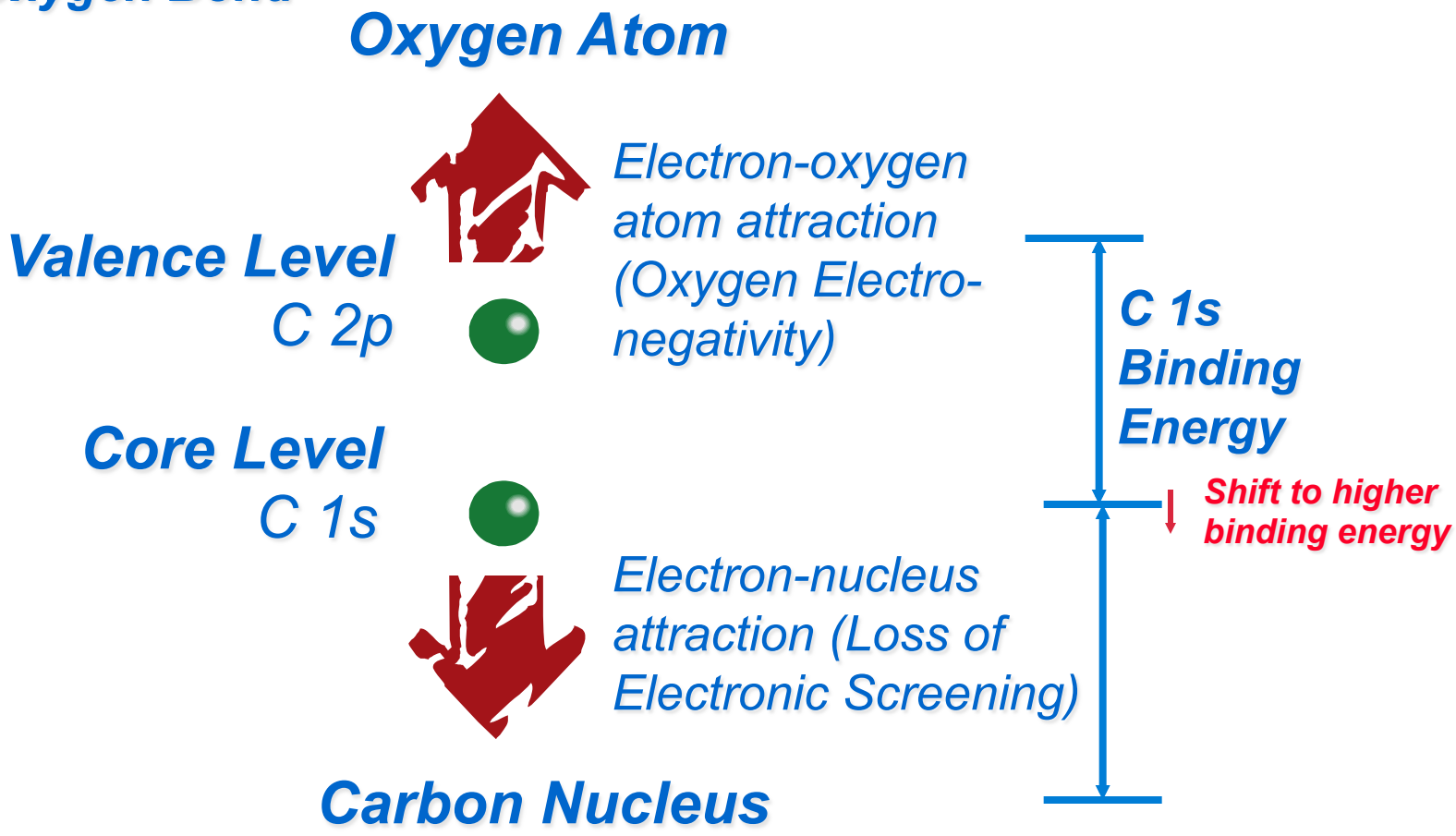
E_B in atom i in given refernce state

Weighted charge of i

Potential at i due to surrounding charges

Chemical Shifts- Electronegativity Effects

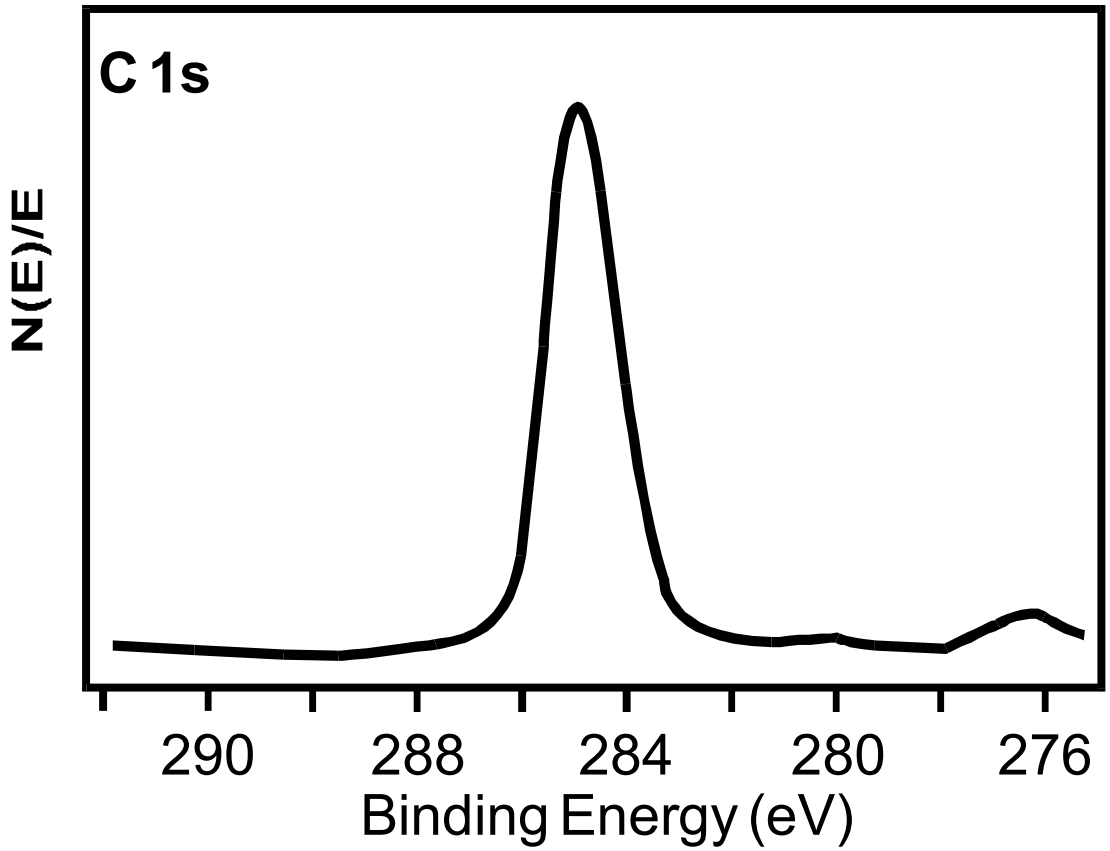
Carbon-Oxygen Bond



Chemical Shifts- Electronegativity Effects

Functional Group		***Binding Energy (eV)***
hydrocarbon	C-H, C-C	285.0
amine	C-N	286.0
alcohol, ether	C-O-H, C-O-C	286.5
Cl bound to C	C-Cl	286.5
F bound to C	C-F	287.8
carbonyl	C=O	288.0

Electronic Effects
Spin-Orbit Coupling



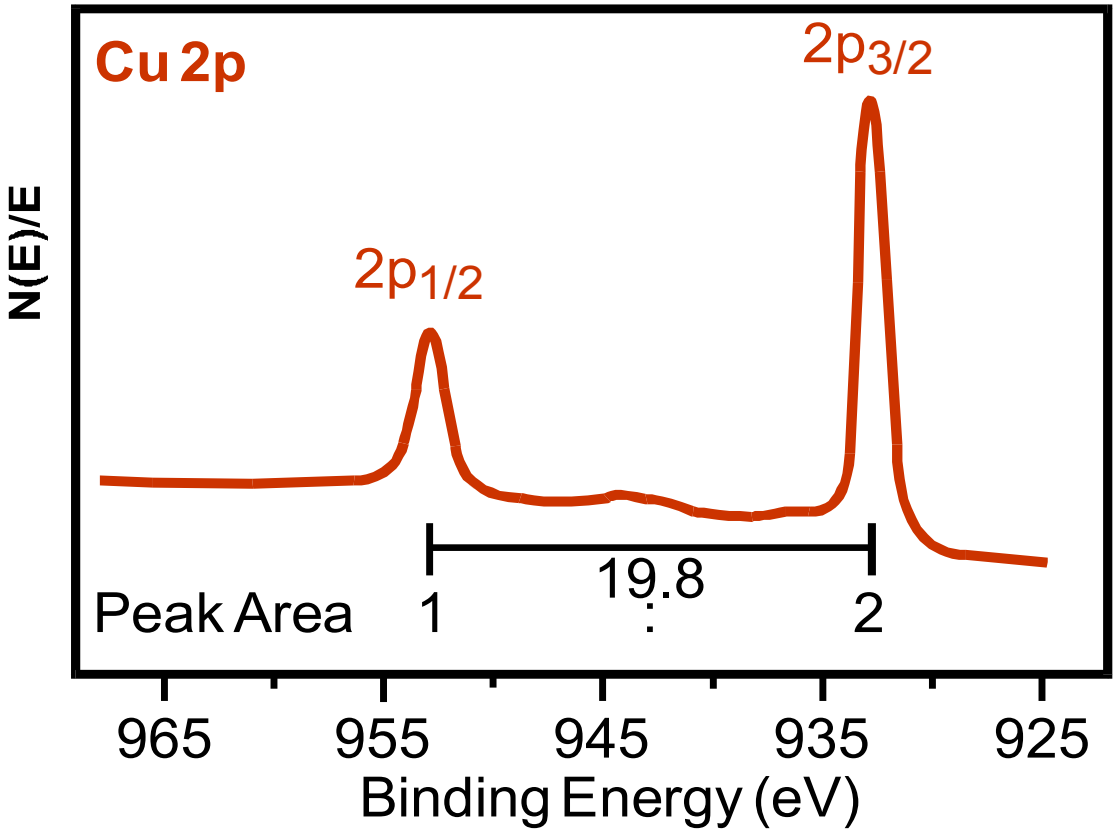
Orbital=s

l=0

s=+/-1/2

ls=1/2

Electronic Effects
Spin-Orbit Coupling



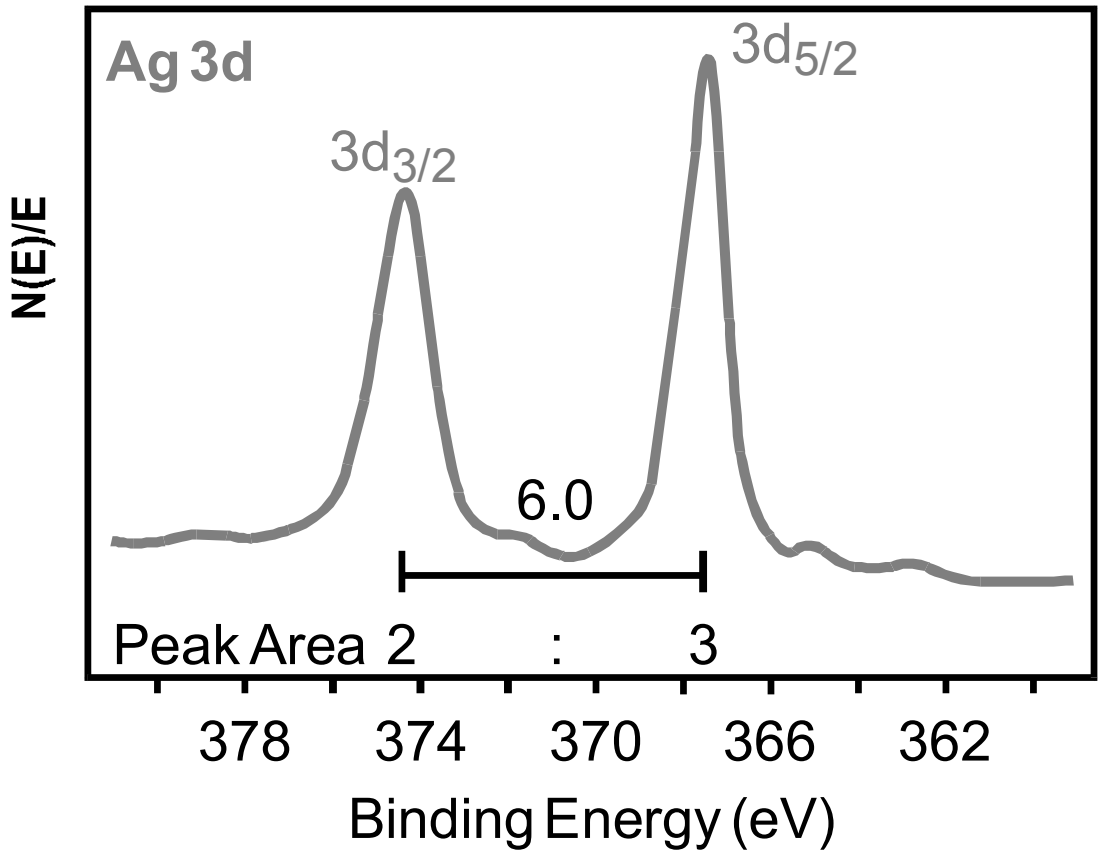
Orbital=p

l=1

s=+/-1/2

ls=1/2,3/2

Electronic Effects
Spin-Orbit Coupling



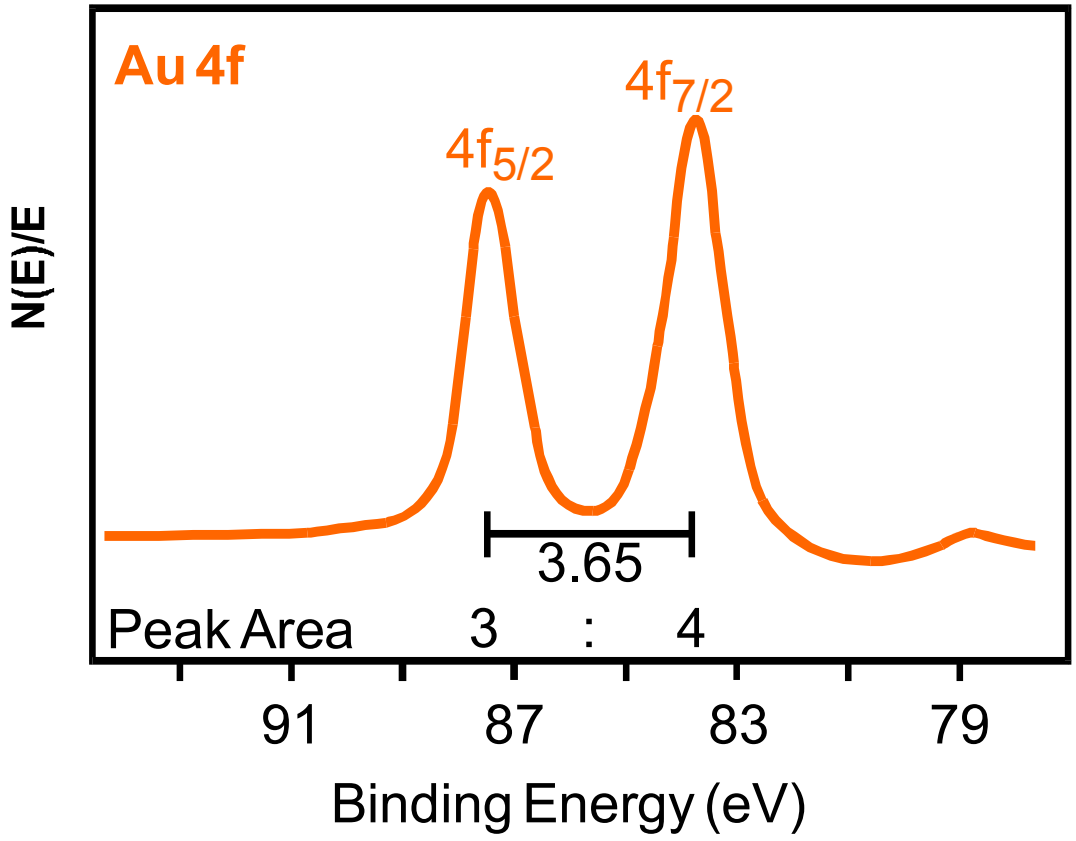
Orbital=d

l=2

s=+/-1/2

ls=3/2,5/2

Electronic Effects
Spin-OrbitCoupling



Orbital=f

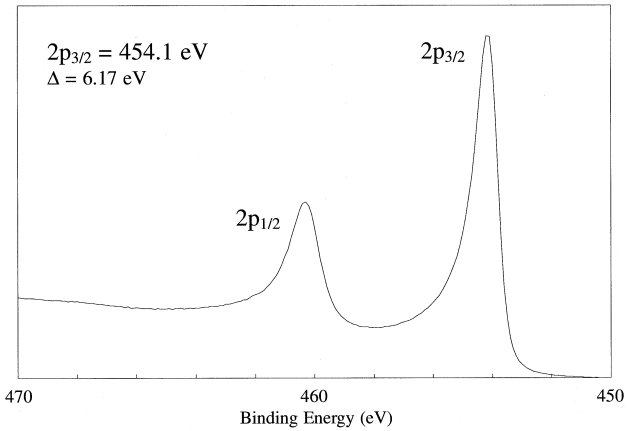
l=3

s=+/-1/2

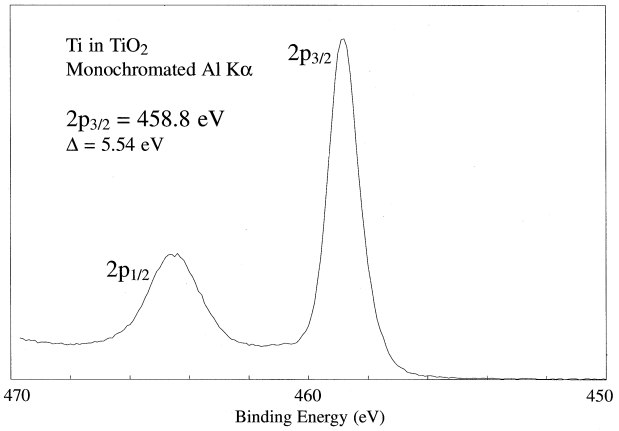
ls=5/2,7/2

Electronic Effects- Spin-Orbit Coupling

Ti Metal



Ti Oxide



Final State Effects- Shake-up/ Shake-off

Results from energy made available in the relaxation of the final state configuration (due to a loss of the screening effect of the core level electron which underwent photoemission).

L(2p) -> Cu(3d)

- *Monopole transition: Only the principle quantum number changes. Spin and angular momentum cannot change.*
- *Shake-up: Relaxation energy used to excite electrons in valence levels to bound states (monopole excitation).*
- *Shake-off: Relaxation energy used to excite electrons in valence levels to unbound states (monopole ionization).*

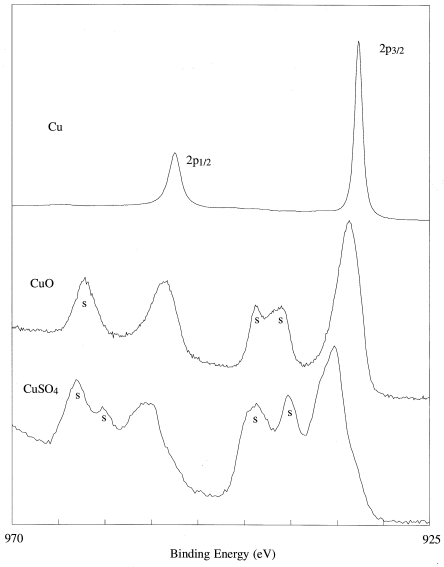
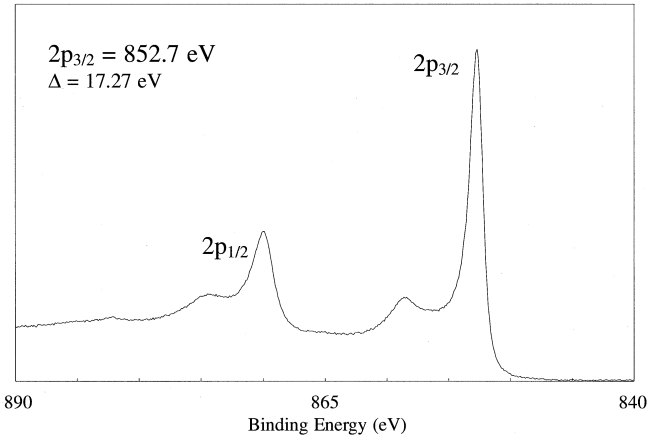


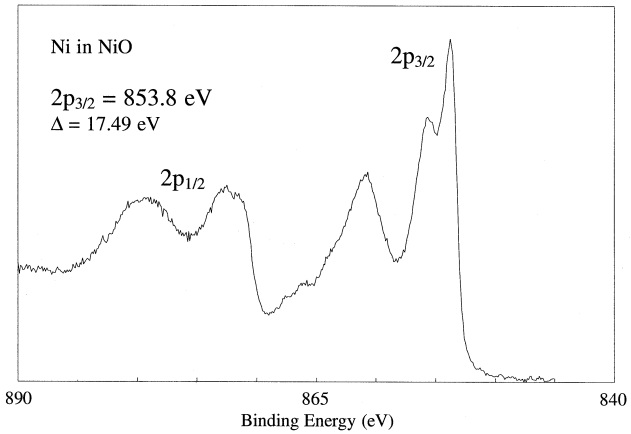
Figure 8. Examples of shake-up lines (s) of the copper 2p observed in copper compounds.

Final State Effects- Shake-up/ Shake-off

Ni Metal



Ni Oxide



Final State Effects- Multiplet Splitting

Following photoelectron emission, the remaining unpaired electron may couple with other unpaired electrons in the atom, resulting in an ion with several possible final state configurations with as many different energies. This produces a line which is split asymmetrically into several components.

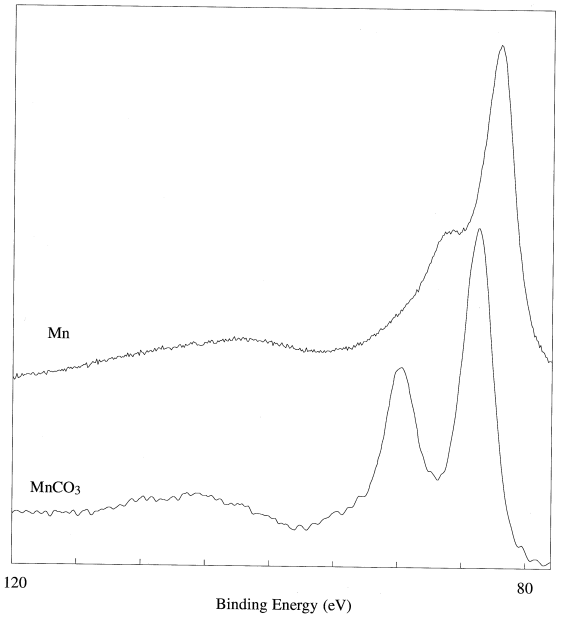


Figure 10. Multiplet splitting of the Mn 3s.

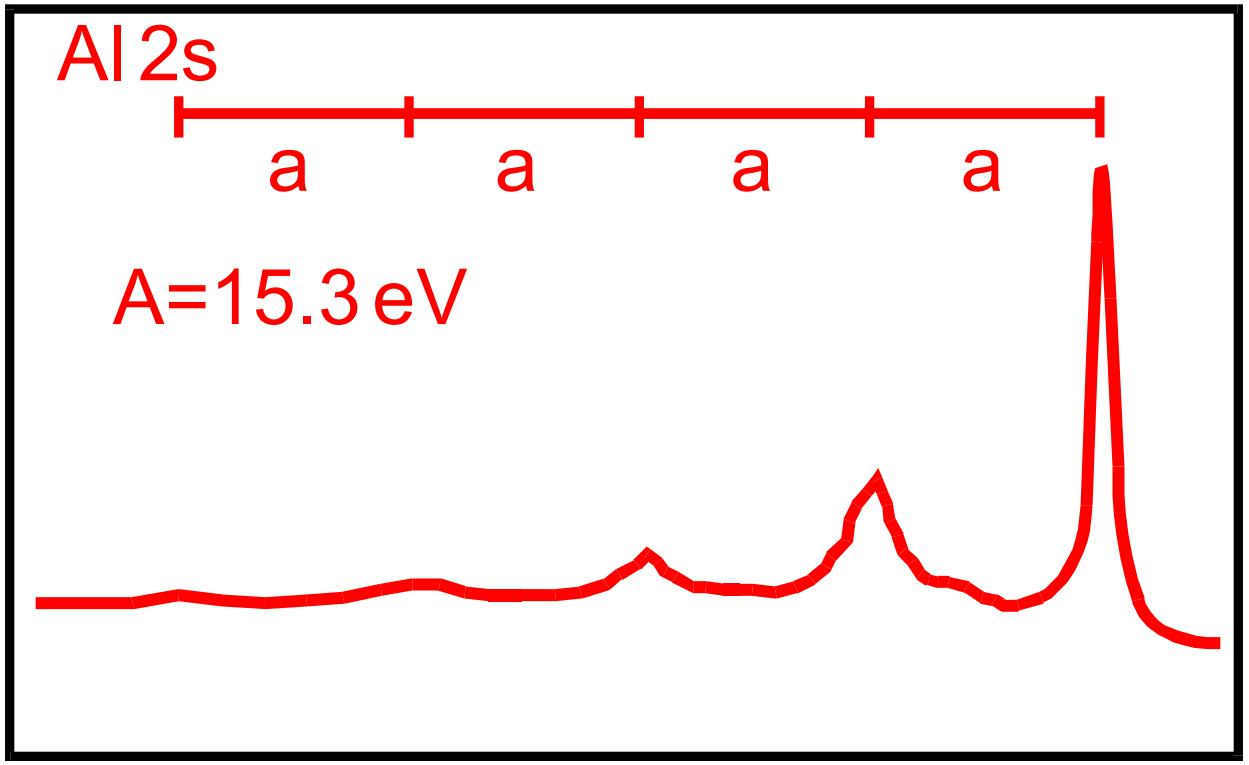
Electron Scattering Effects Energy Loss Peaks

$$e_{ph} + e_{solid} \rightarrow e^{*}_{ph} + e^{**}_{solid}$$

Photoelectrons travelling through the solid can interact with other electrons in the material. These interactions can result in the photoelectron exciting an electronic transition, thus losing some of its energy (inelastic scattering).

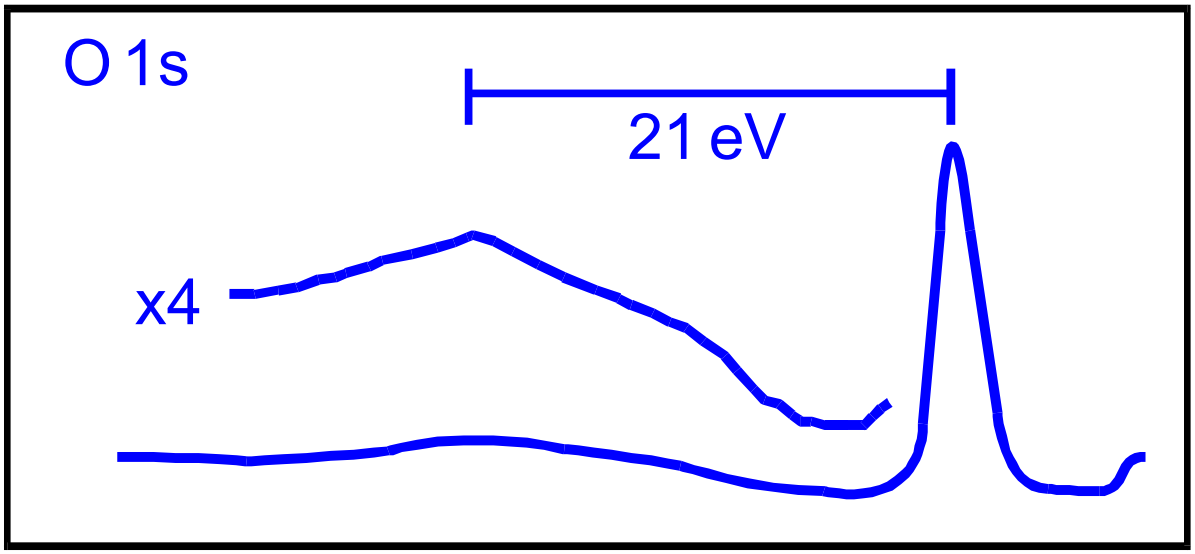
Electron Scattering Effects
Plasmon Loss Peak

Metal



Electron Scattering Effects
Plasmon Loss Peak

Insulating Material



Quantitative Analysis by XPS

For a Homogeneous sample:

$I = N_s DJLIAT$

where: N = atoms/cm^3

s = photoelectric cross-section, cm^2

D = detector efficiency

J = X-ray flux, photon/cm^2-sec

L = orbital symmetry factor

I = inelastic electron mean-free path, cm

A = analysis area, cm^2

T = analyzer transmission efficiency

Quantitative Analysis by XPS

$$N = I/sDJLIAT$$

Let denominator = elemental sensitivity factor, S

$$N = I / S$$

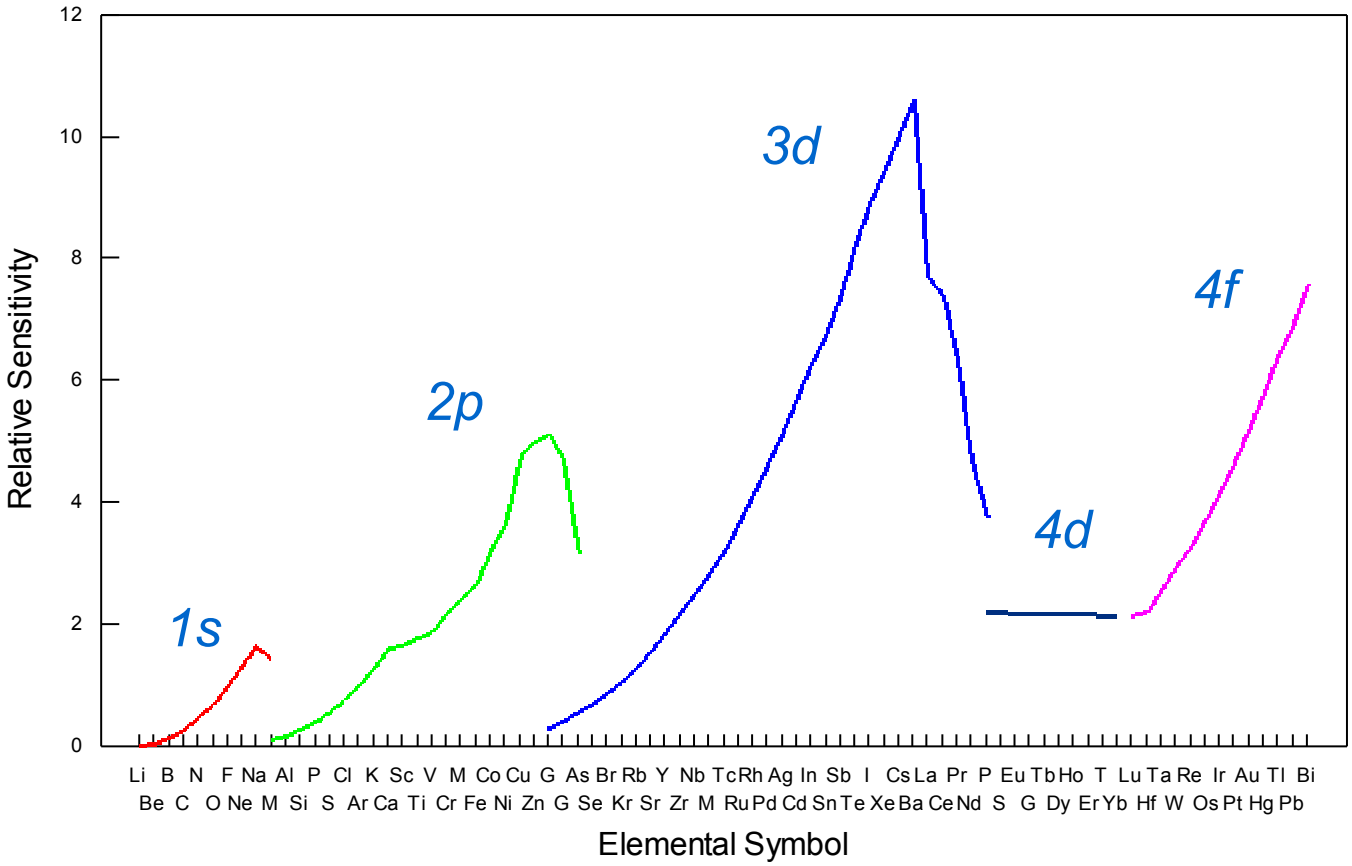
Can describe Relative Concentration of observed elements as a number fraction by:

$$C_x = N_x / \Sigma N_i$$

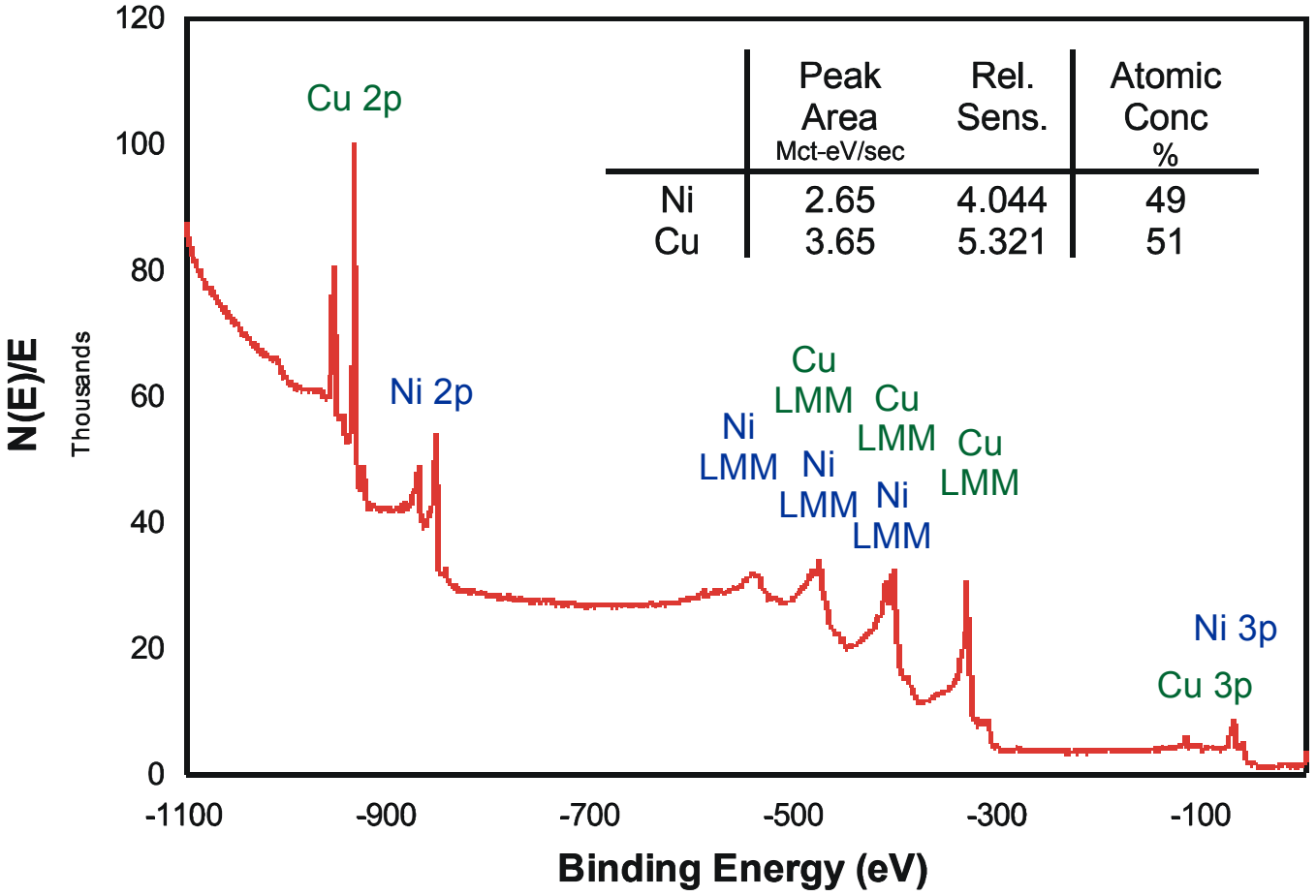
$$C_x = I_x/S_x / \Sigma I_i/S_i$$

The values of S are based on empirical data.

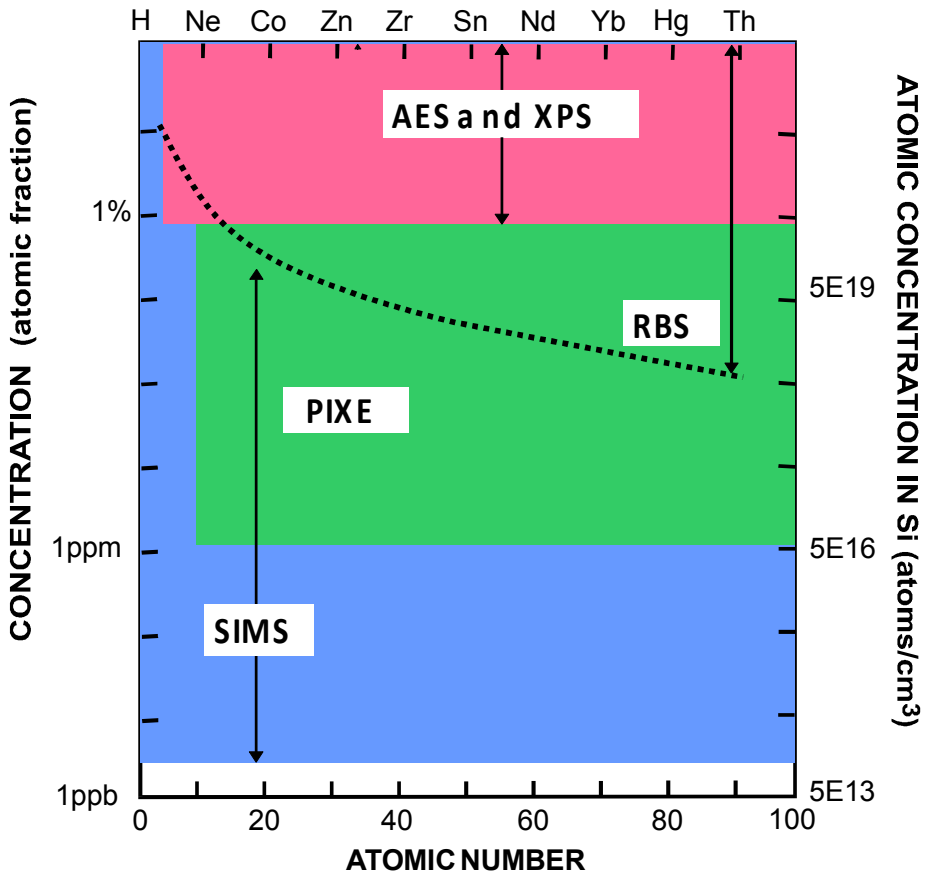
Relative Sensitivities of the Elements



XPS of Copper-Nickel alloy



Comparison of Sensitivities



Instrumentation for X-ray Photoelectron Spectroscopy

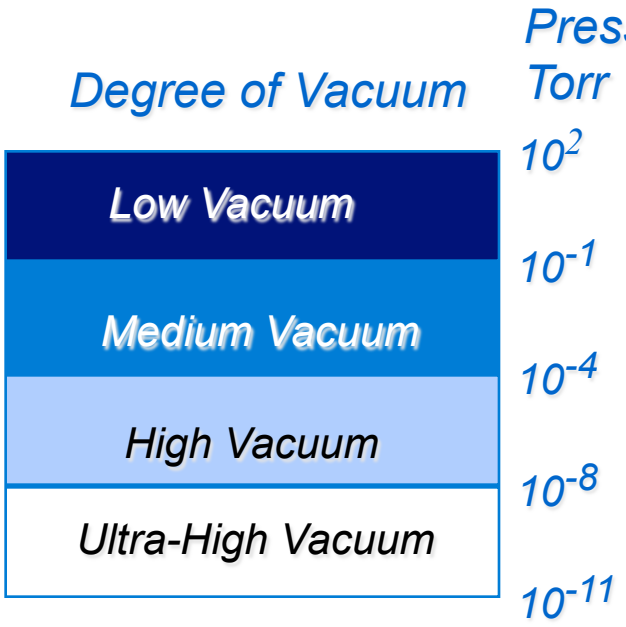
Introduction to X-ray Photoelectron Spectroscopy (XPS)

- *What is XPS?- General Theory*
- *How can we identify elements and compounds?*
- ***Instrumentation for XPS***
- *Examples of materials analysis with XPS*

Instrumentation for XPS

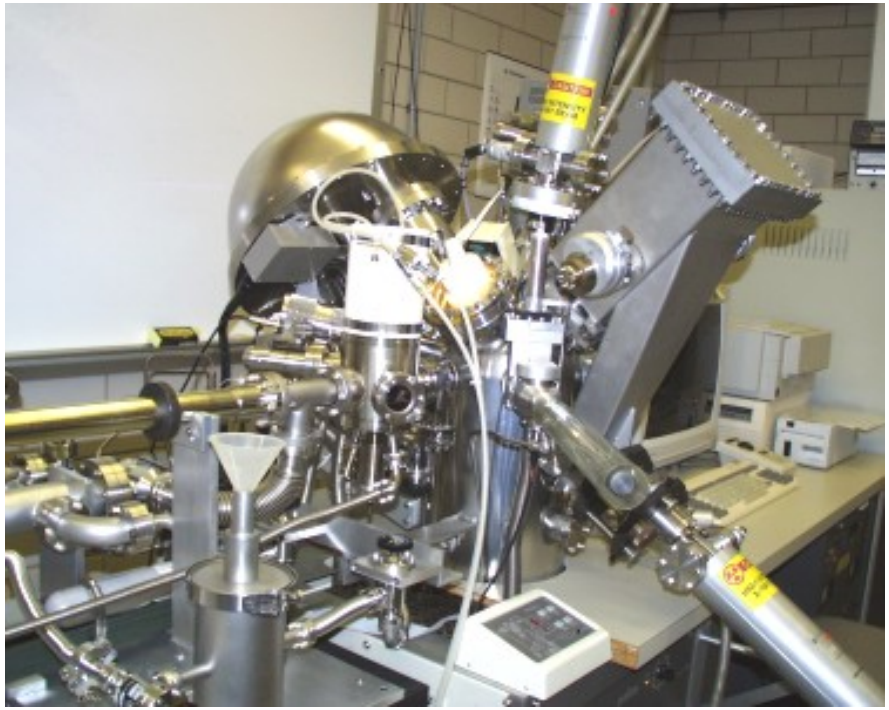
Surface analysis by XPS requires irradiating a solid in an Ultra-high Vacuum (UHV) chamber with monoenergetic soft X-rays and analyzing the energies of the emitted electrons.

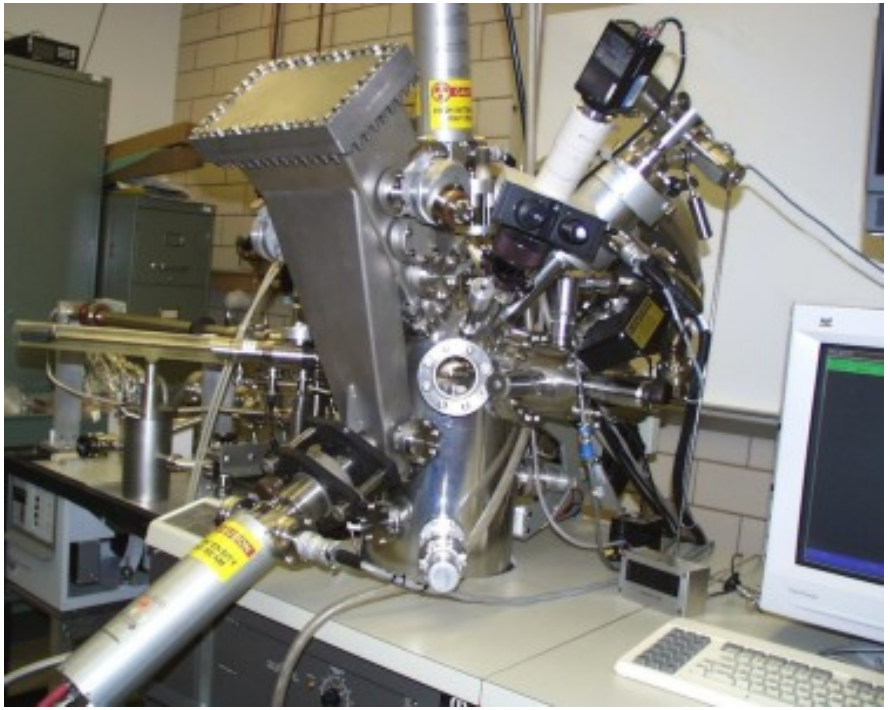
Why UHV for Surface Analysis?



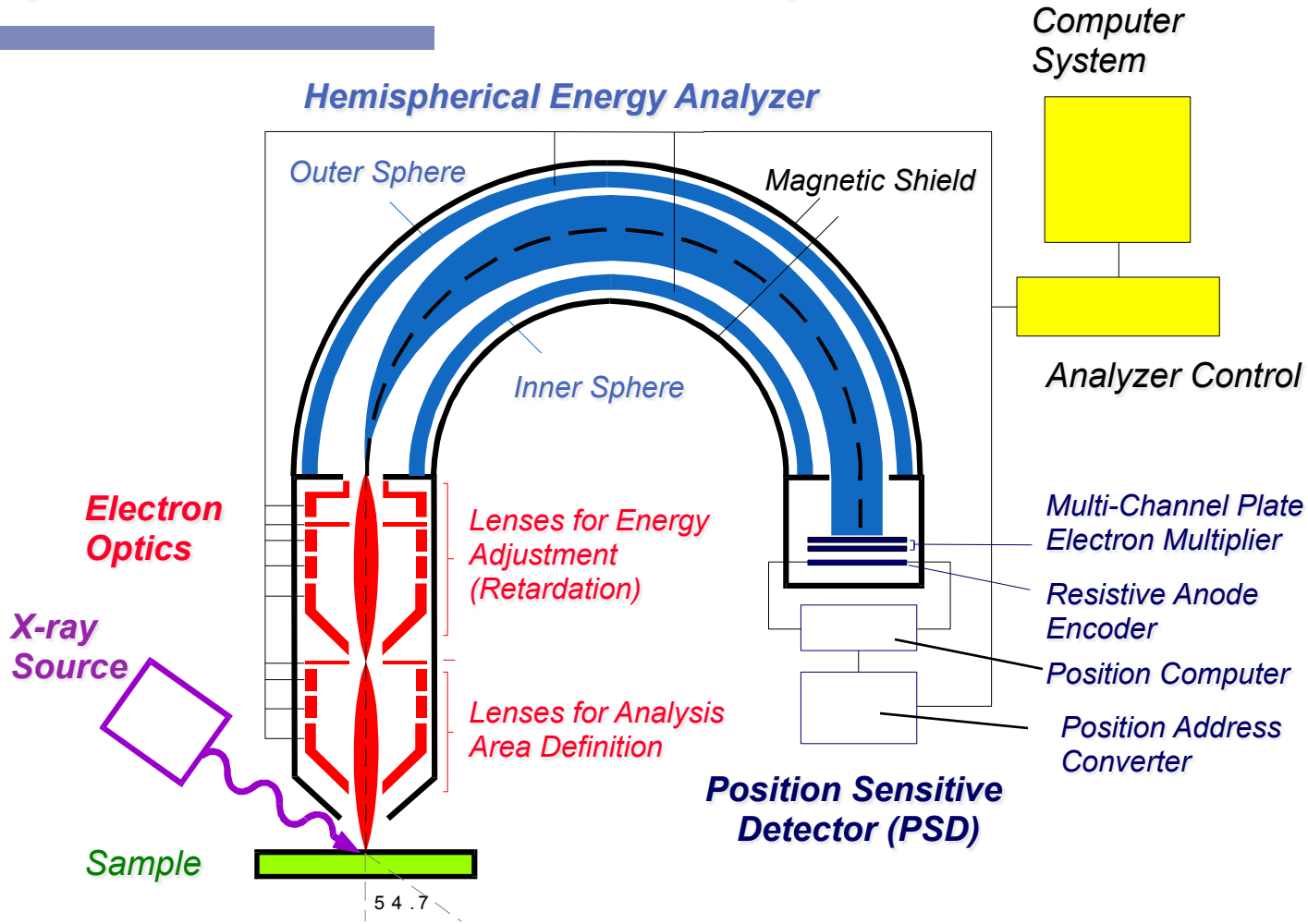
- *Remove adsorbed gases from the sample.*
- *Eliminate adsorption of contaminants on the sample.*
- *Prevent arcing and high voltage breakdown.*
- *Increase the mean free path for electrons, ions and photons.*

X-ray Photoelectron Spectrometer





X-ray Photoelectron Spectrometer



XPS at the ‘Magic Angle’

Orbital Angular Symmetry Factor

$$L_A(\gamma) = 1 + b_A(3\sin^2\gamma/2 - 1)/2$$

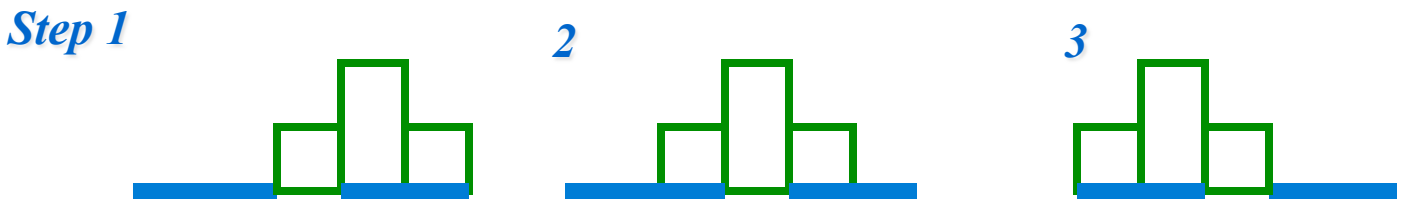
where: γ = source-detector angle
b = constant for a given sub-shell and X-ray photon

At 54.7º the ‘magic angle’

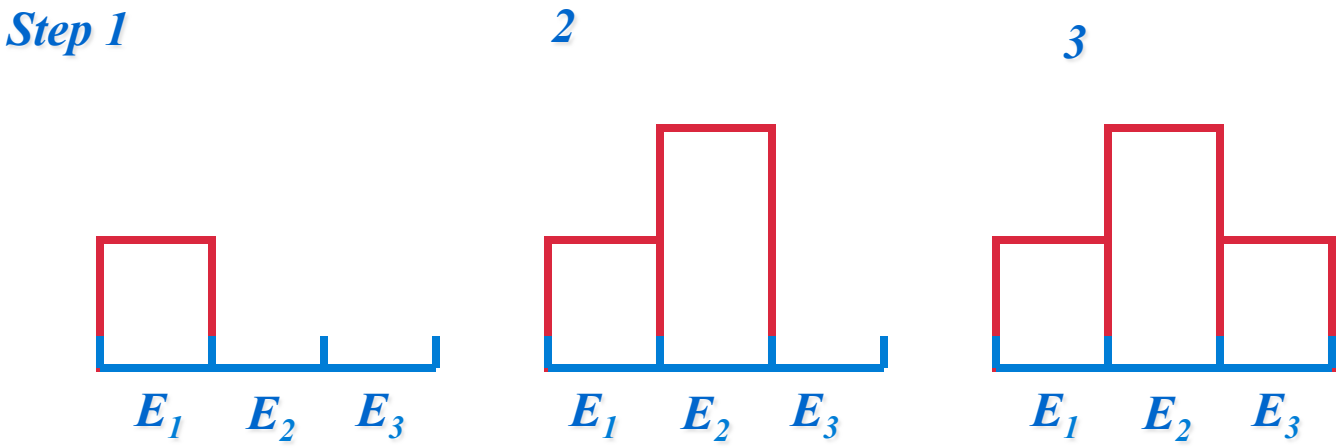
$$L_A = 1$$

Electron Detection

Single Channel Detector



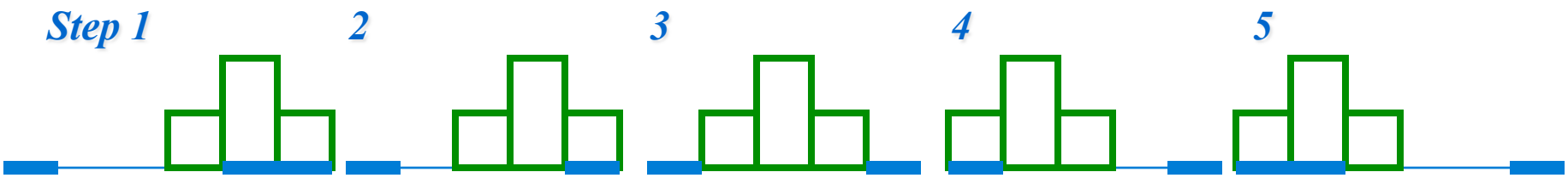
Electron distribution on analyzer detection plane



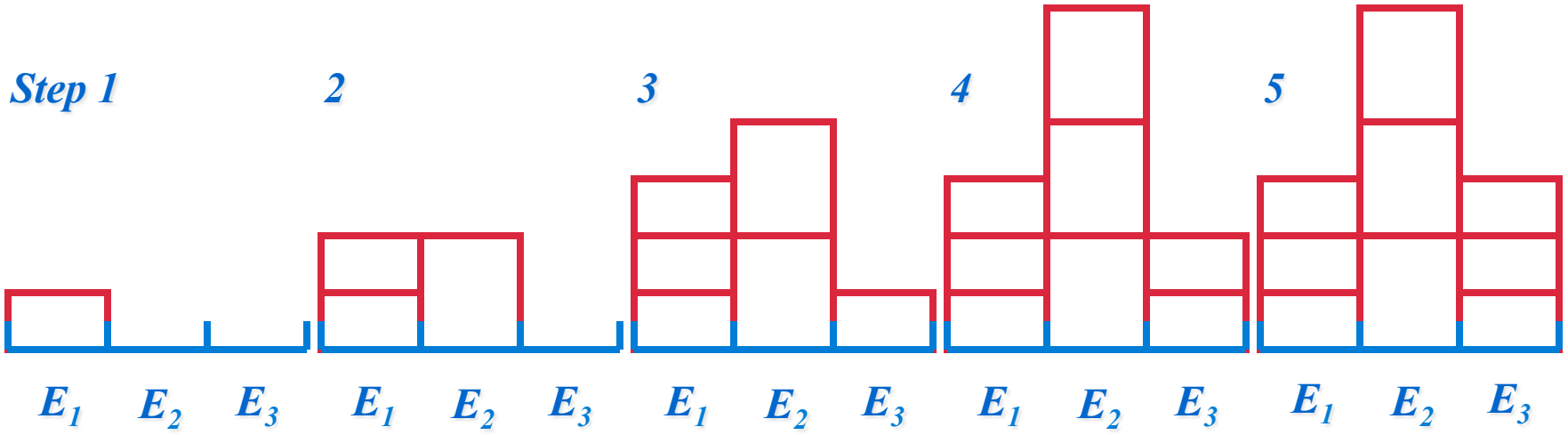
Counts in spectral memory

Electron Detection

Multi-channel Position Sensitive Detector (PSD)

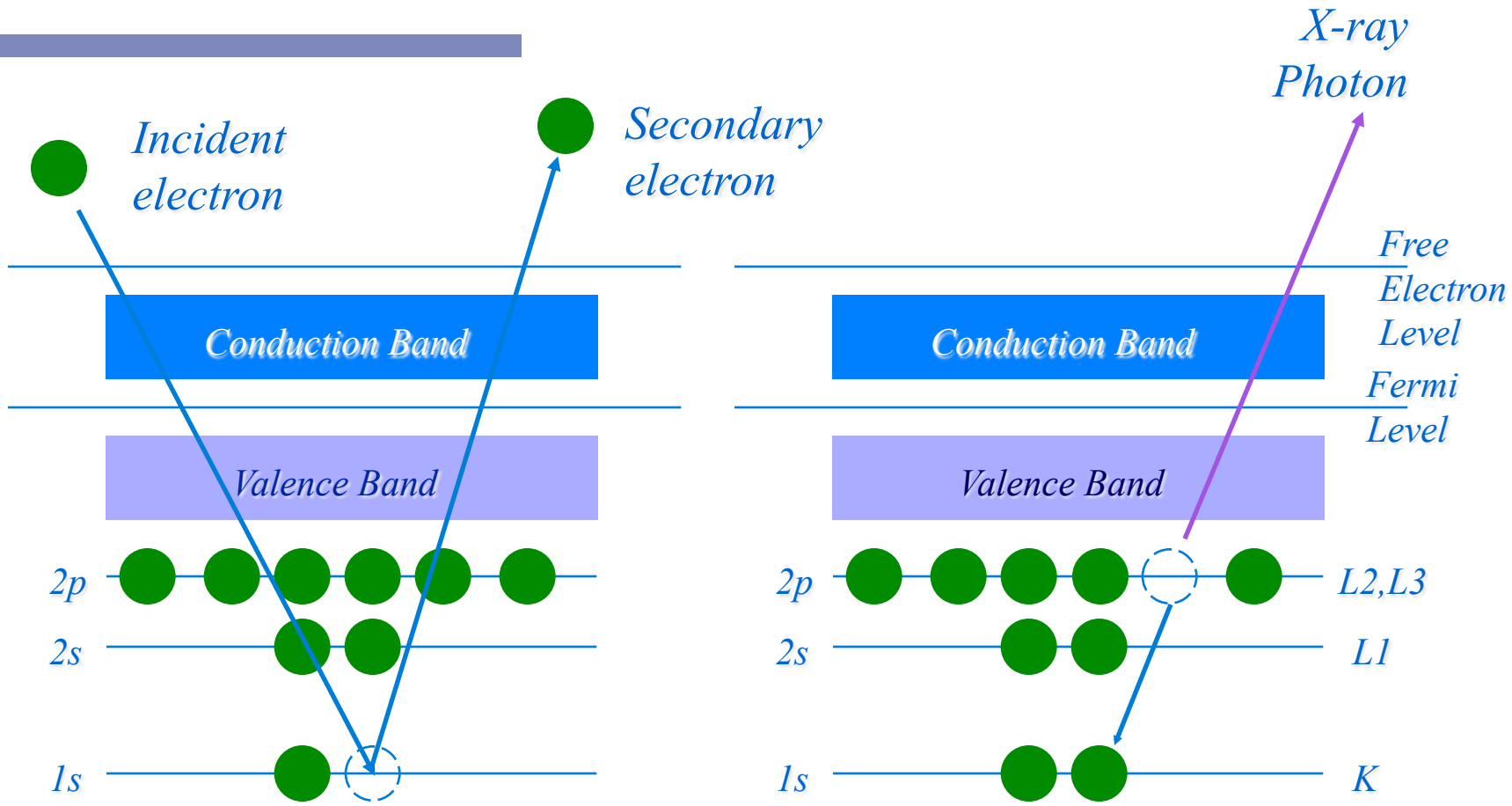


Electron distribution on analyzer detection plane

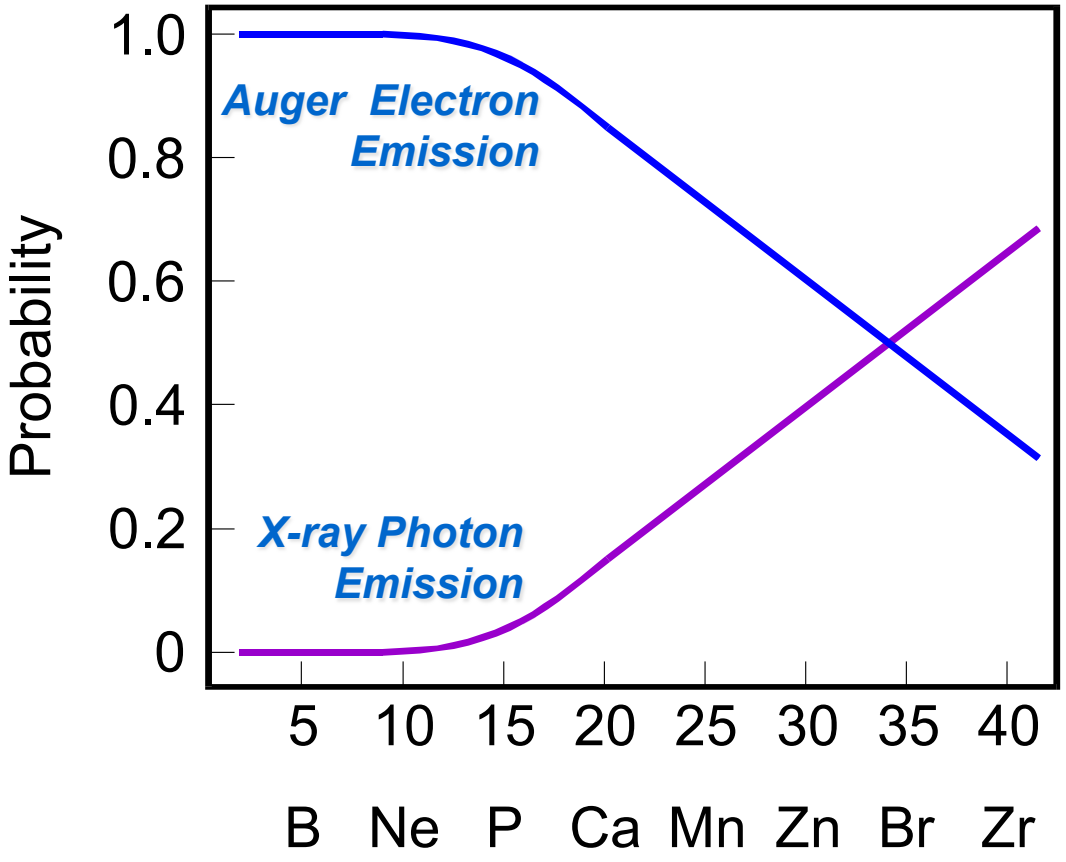


Counts in spectral memory

X-ray Generation

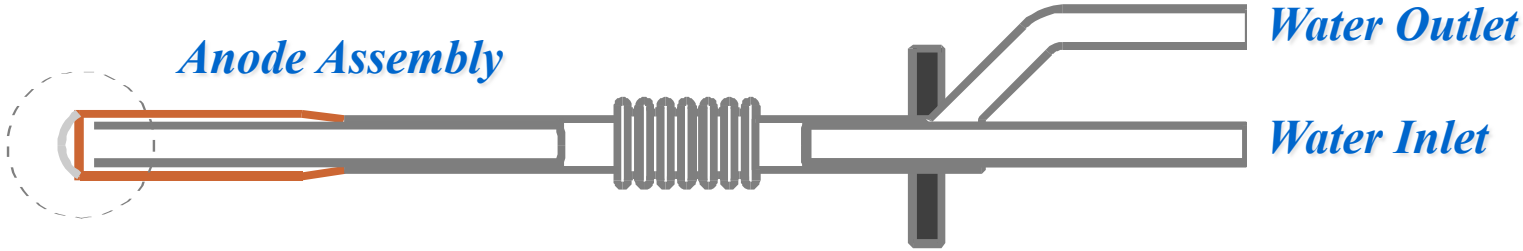


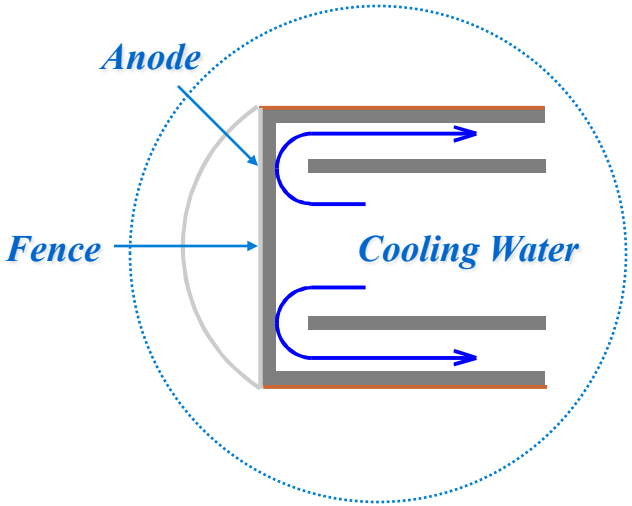
Relative Probabilities of Relaxation of a K Shell Core Hole

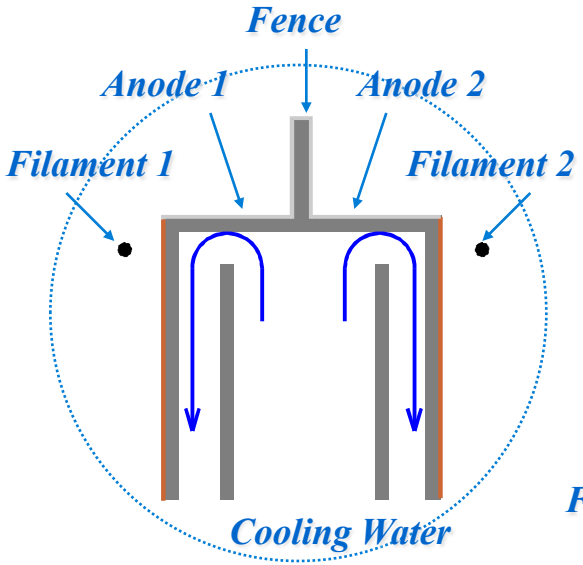


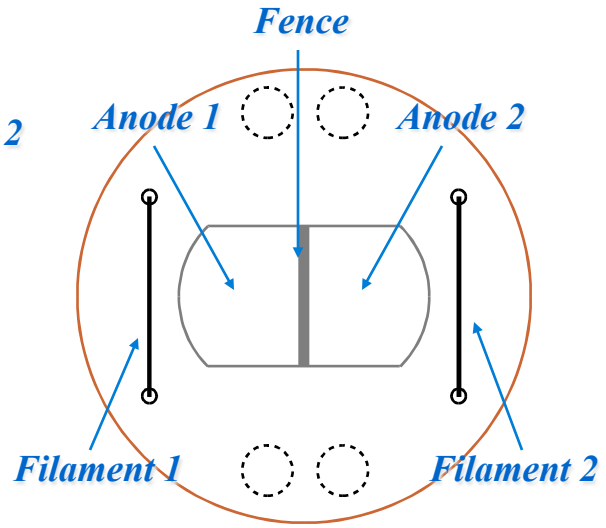
Note: The light elements have a low cross section for X-ray emission.

Schematic of Dual Anode X-ray Source

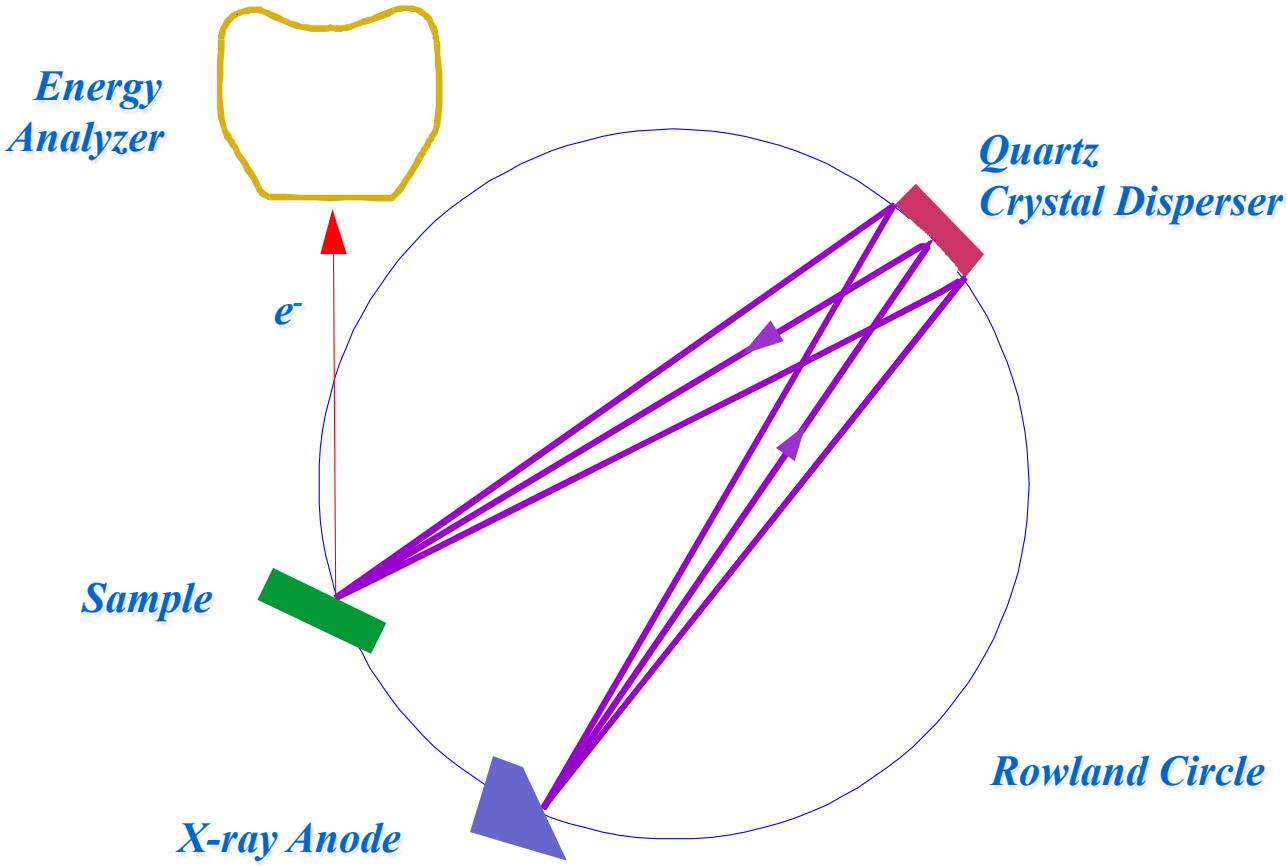








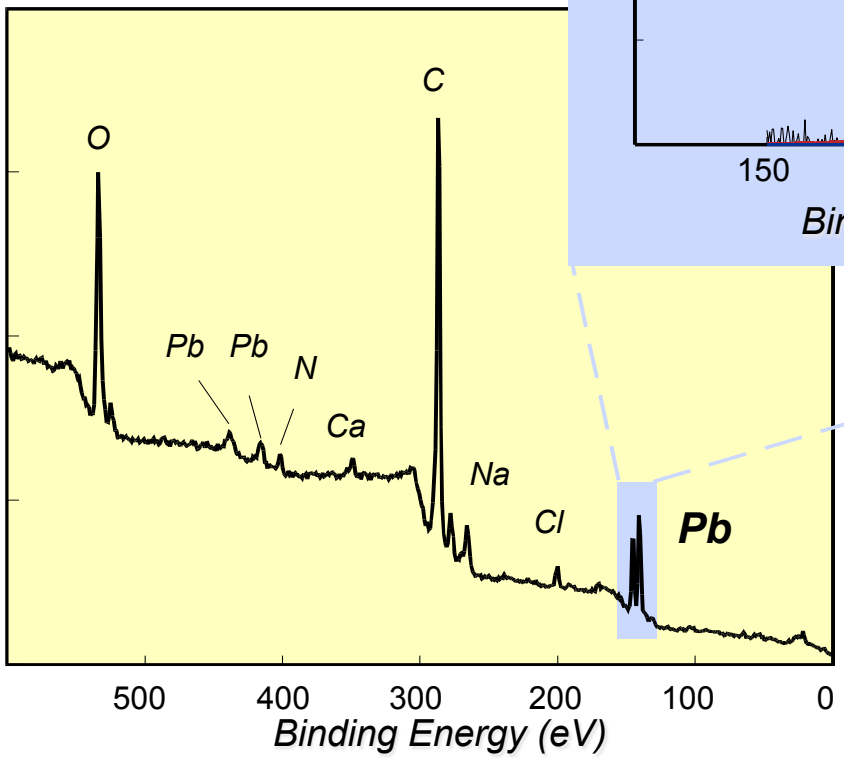
Schematic of X-ray Monochromator

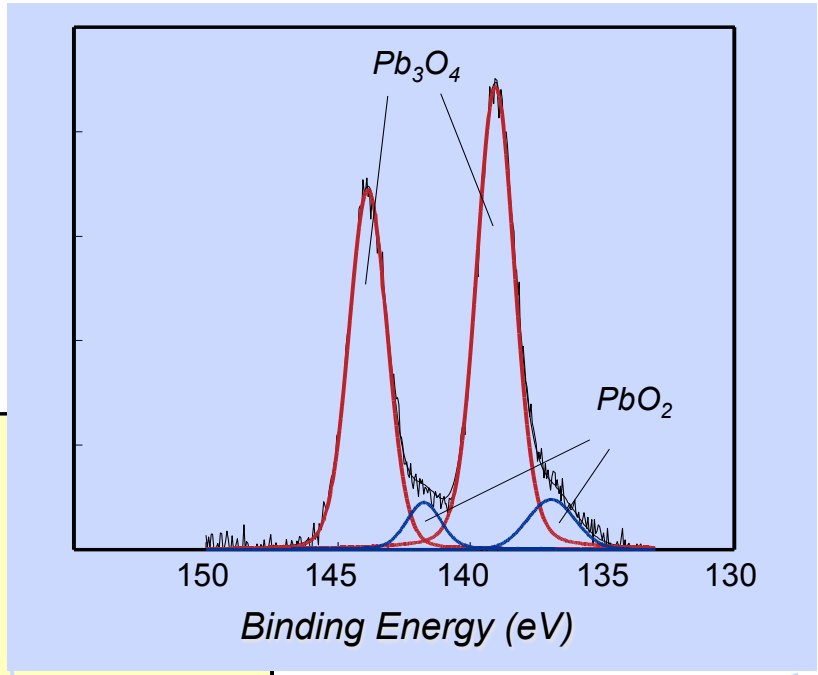


Applications of X-ray Photoelectron Spectroscopy (XPS)

XPS Analysis of Pigment from Mummy Artwork

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



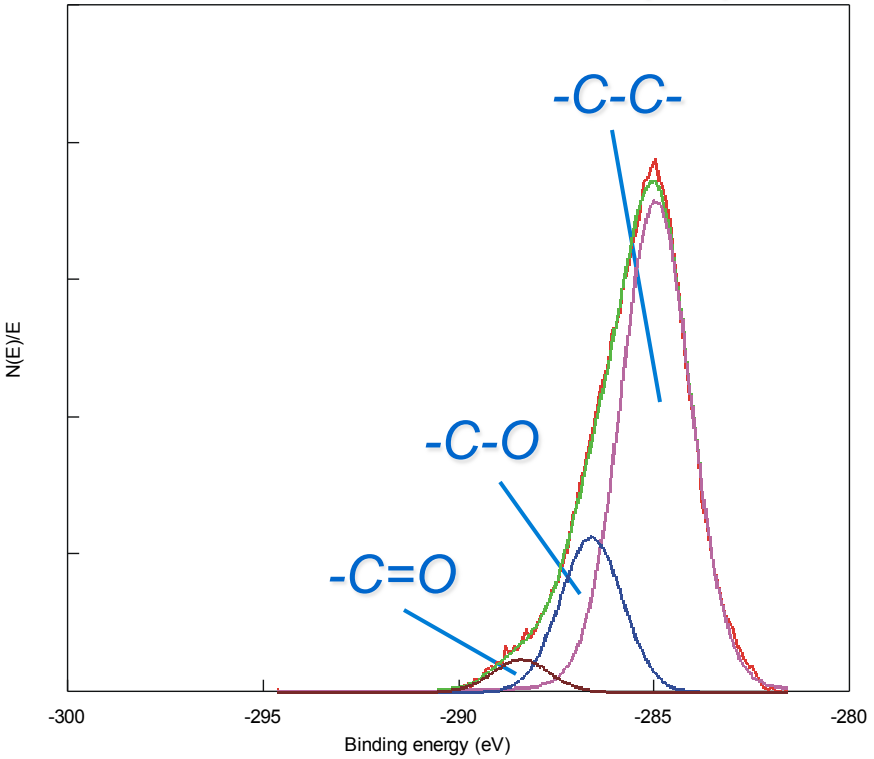


XPS analysis showed that the pigment used on the mummy wrapping was Pb_3O_4 rather than Fe_2O_3

Analysis of Carbon Fiber- Polymer Composite Material by XPS

Woven carbon fiber composite

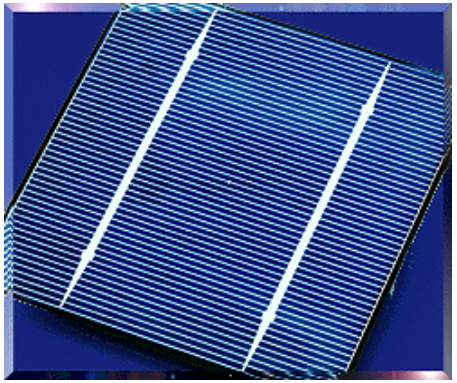
XPS analysis identifies the functional groups present on composite surface. Chemical nature of fiber-polymer interface will influence its properties.



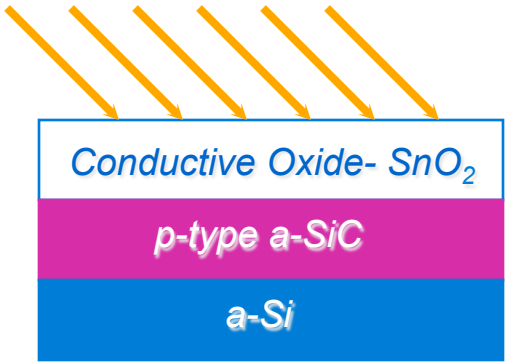
Analysis of Materials for Solar Energy Collection by XPS Depth Profiling-

The amorphous-SiC/SnO_2 Interface

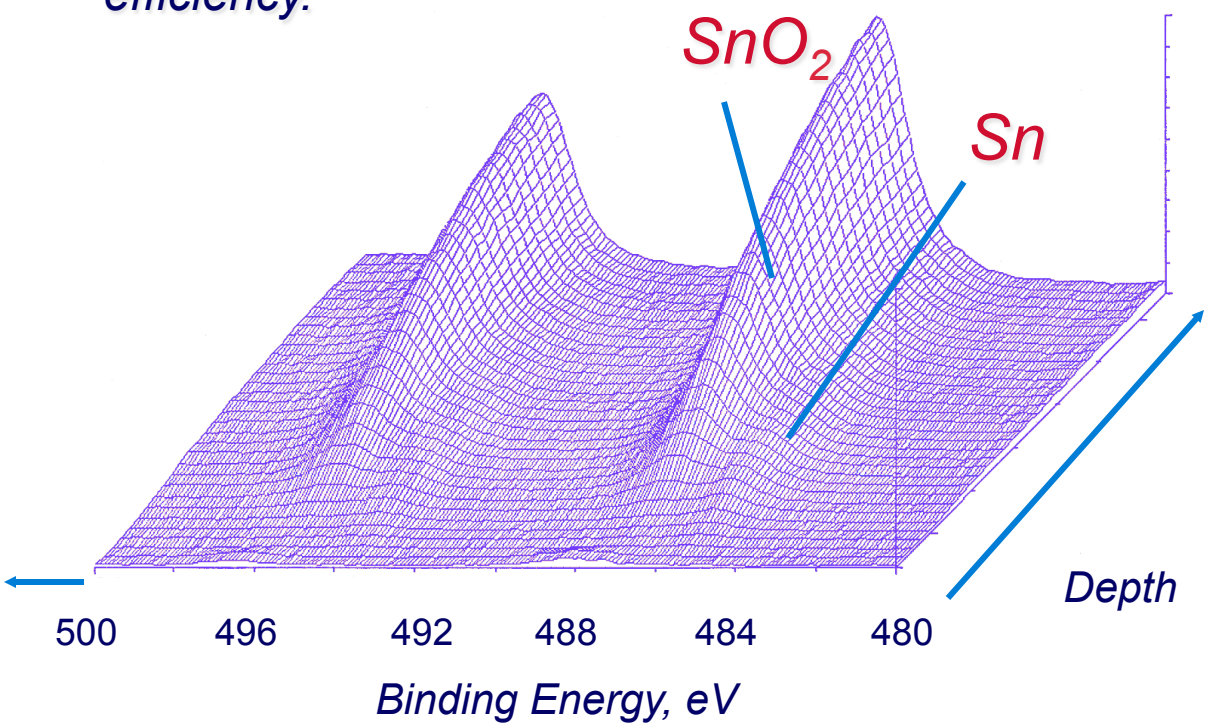
Photo-voltaic Collector



Solar Energy

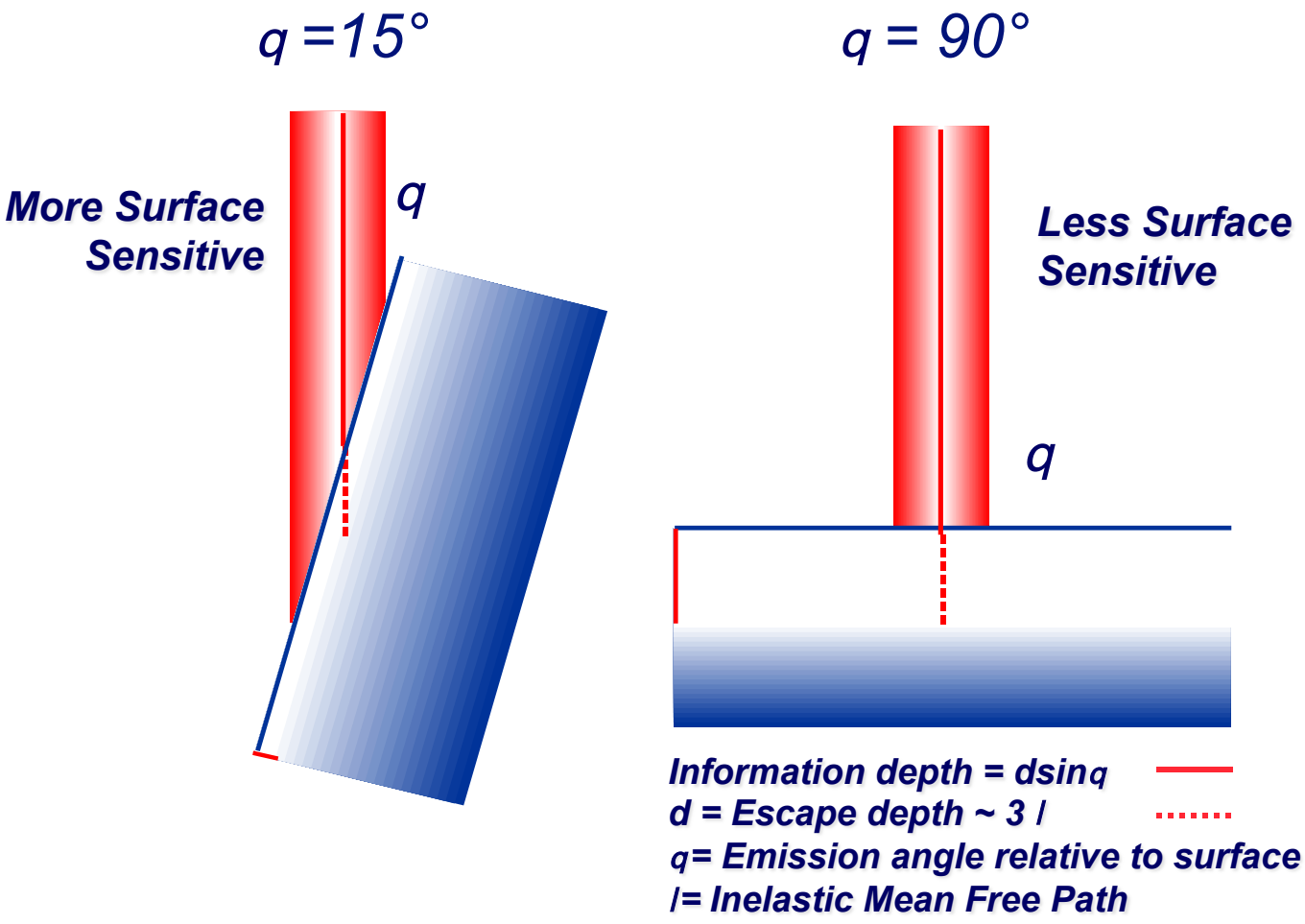


The profile indicates a reduction of the SnO_2 occurred at the interface during deposition. Such a reduction would effect the collector's efficiency.

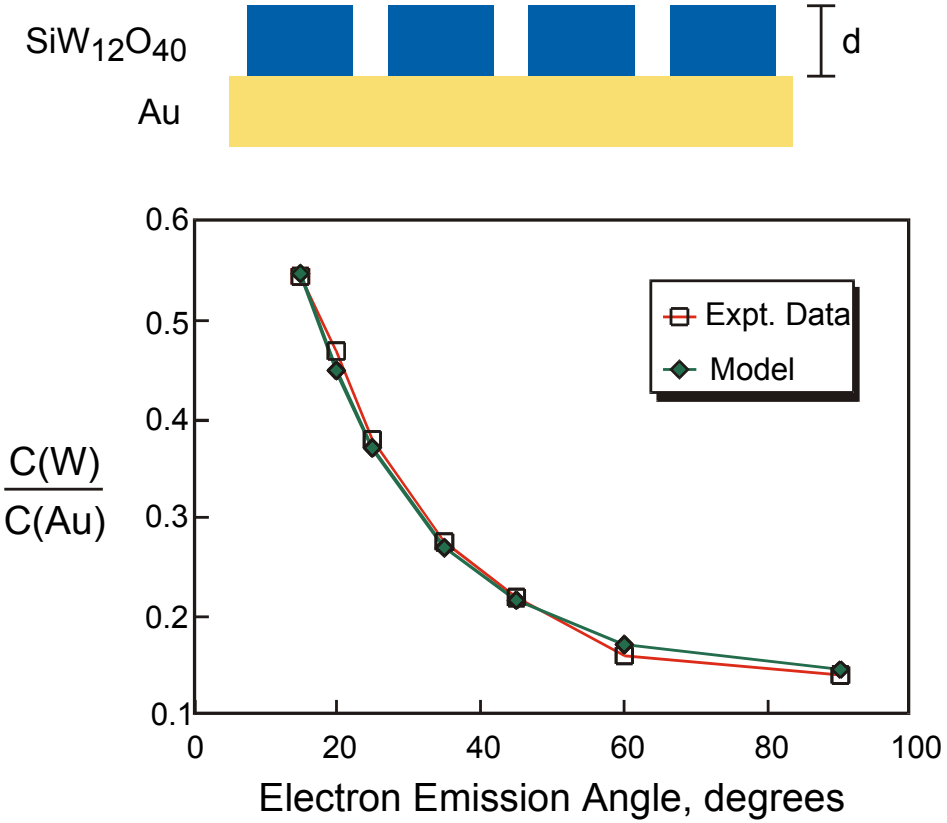


Data courtesy A. Nurrudin and J. Abelson, University of Illinois

Angle-resolved XPS



Angle-resolved XPS Analysis of Self-Assembling Monolayers



Angle Resolved XPS Can Determine

- *Over-layer Thickness*
- *Over-layer Coverage*

Data courtesy L. Ge, R. Haasch and A. Gewirth, University of Illinois