

# *Spectroscopic Surface Methods*

- *Electron Spectroscopies*

*XPS: X-ray Photoelectron Spectroscopy*

*AES: Auger Electron Spectroscopy*

*EELS: Electron Energy Loss Spectroscopy*

- *Ion Spectroscopies*

*SIMS: Secondary Ion Mass Spectrometry*

*LMMS: Laser Microprobe Mass Spectrometry*

*ISS: Ion Scattering and Rutherford Backscattering Spectroscopy*



- **General Information on Electron Spectroscopy:**

- *Electron spectroscopy can be used for the identification of all of the elements in the periodic table except for helium and hydrogen.*
- *The method also permits the determination of the oxidation state of an element and the type of species to which it is bonded.*
- *This technique also provides useful information about the electronic structure of molecules.*

- *The kinetic energy of the emitted electron  $E_k$  is measured in an electron spectrometer. The binding energy of the electron  $E_b$  can be calculated*

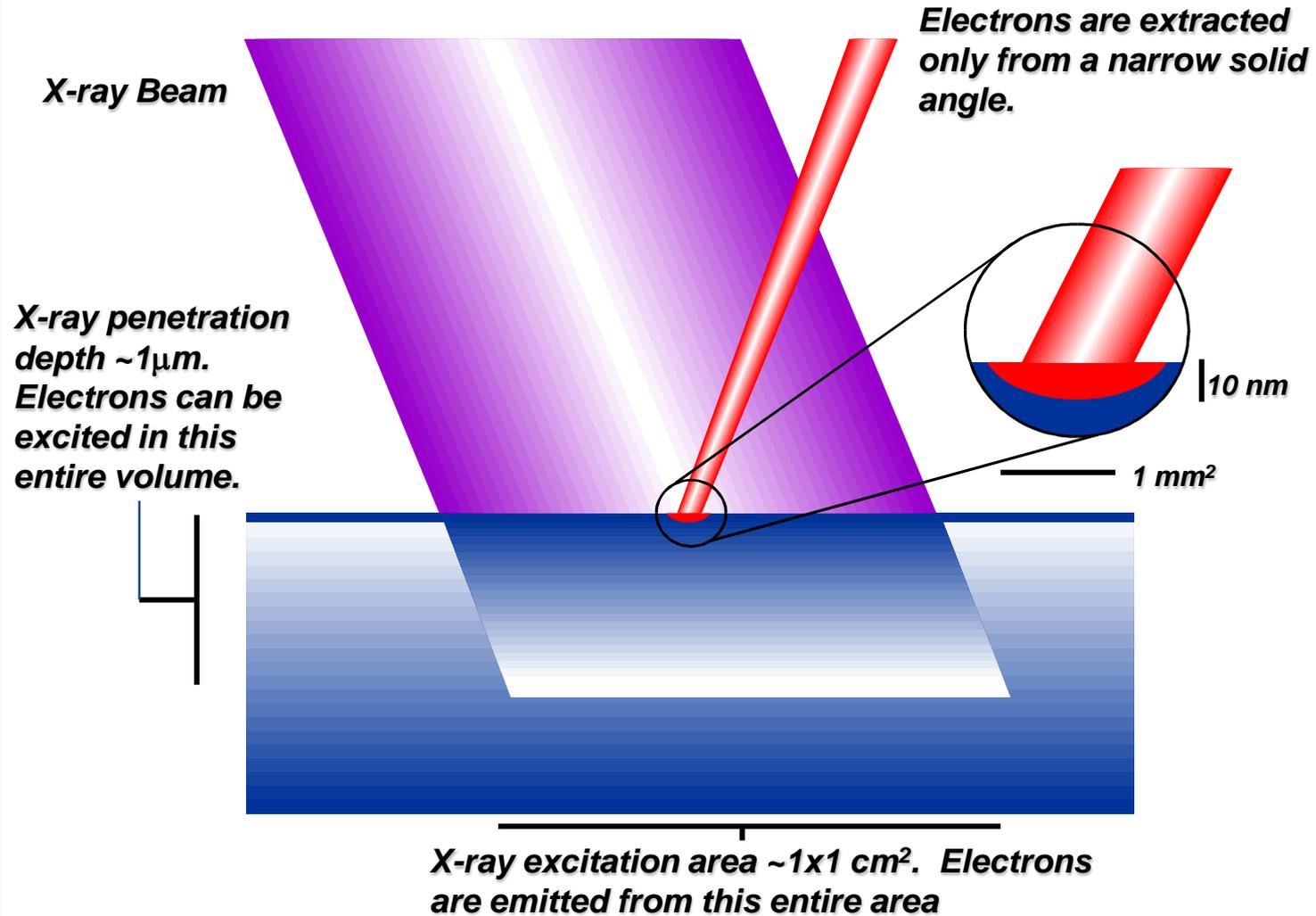
$$E_b = h\nu - E_k - w$$

*where,  $w$  is the work function of the spectrometer, a factor that corrects for the electrostatic environment in which the electron is formed and measured.*

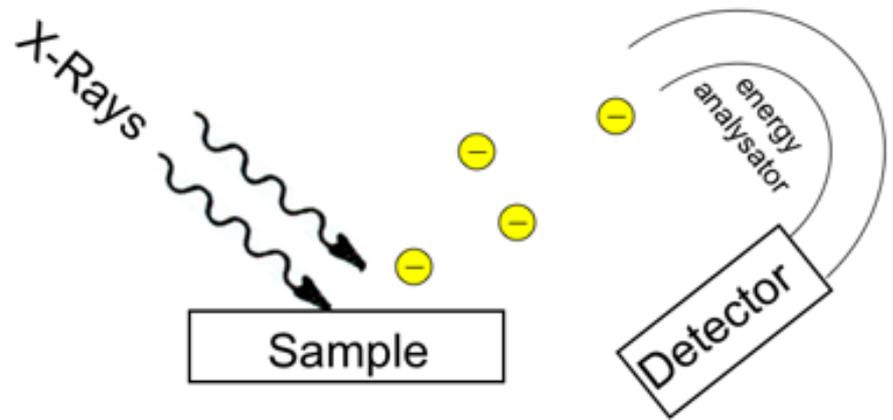
## ***X-ray Photoelectron Spectroscopy (XPS)***

- *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.*
- *X-ray Photoelectron spectroscopy, based on the photoelectric effect was developed in the mid-1960's by Kai Siegbahn and his research group at the University of Uppsala, Sweden.*
- *The advent of commercial manufacturing of surface analysis equipment in the early 1970s enabled the placement of equipment in laboratories throughout the world.*
- *In 1981, Siegbahn was awarded the Nobel Prize for Physics for his work with XPS.*

# X-ray Photoelectron Spectroscopy (XPS)



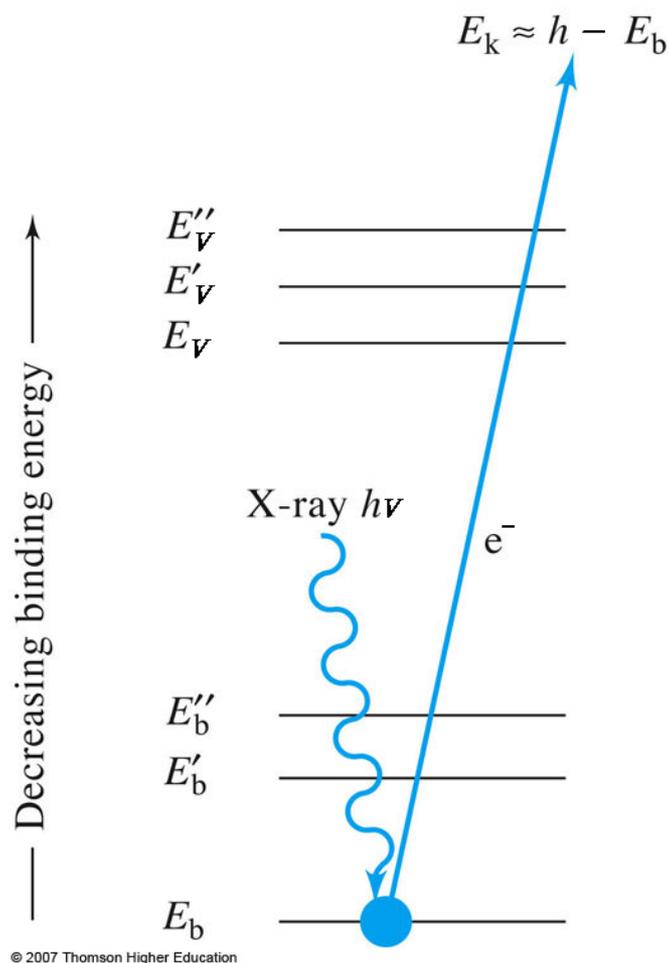
*X-Ray Photoemission spectroscopy (XPS) uses X-ray radiation to probe the binding energy of electrons of the material under study.*



- The incoming light with a fixed photon energy excites electrons from their bound states into free electrons with a kinetic energy that is smaller for formerly stronger bound electrons.*
- With an energy analyzer, electrons of specific kinetic energy can be selected and counted by the detector. Thus the signal is the number of counted electrons over kinetic energy.*

- 
- *X-Ray Photoelectron Spectroscopy (XPS), not only provided information about the atomic composition of the sample, but also information about the structure and oxidation state of the compounds being examined*
  - *An important advantage of XPS is its ability to obtain information on chemical states from the variations in binding energies, or chemical shifts, of the photoelectron lines.*
  - *The relative concentrations of elements can be determined from the photoelectron intensities.*

# The Photoelectric Process



- The incident beam consists of monoenergetic X-rays. The emitted beam is made up of electrons.
- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.)
- The ejected photoelectron has kinetic energy:

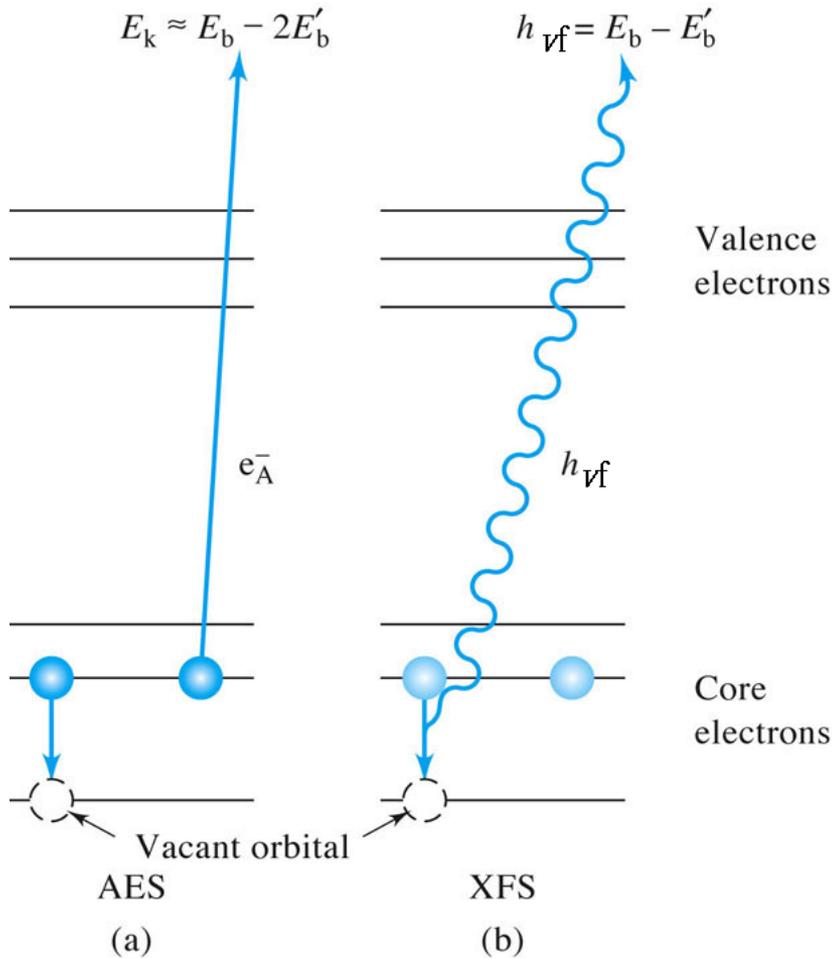
$$KE = h\nu - BE - W$$

W: work function of the spectrometer

- Following this process, the atom will release energy by the emission of an Auger Electron.
- The XPS instrument measures the kinetic energy of all collected electrons. The electron signal includes contributions from both photoelectron and Auger electron lines.

**FIGURE 21-3** Schematic representation of the ESCA process.

# Auger Relation of Core Hole



**FIGURE 21-7** Schematic representation of the source of  
(a) Auger electron emission and  
(b) X-ray fluorescence that competes with Auger emission.

# *Auger Photoelectron Spectroscopy*

- *Auger electron spectroscopy (AES ) is the second type of electron spectroscopy.*
- *Auger spectra are most commonly excited by a beam of electrons, although X-rays are also used.*
- *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.*

## *UV-Photoelectron Spectroscopy*

- *The third type of electron spectroscopy is ultraviolet photoelectron spectroscopy (UPS).*
- *In this method, a monochromatic beam of ultraviolet radiation causes the ejection of electrons from the analyte.*
- *This method is not as common as the first two methods.*

## *Instrumentation for XPS*

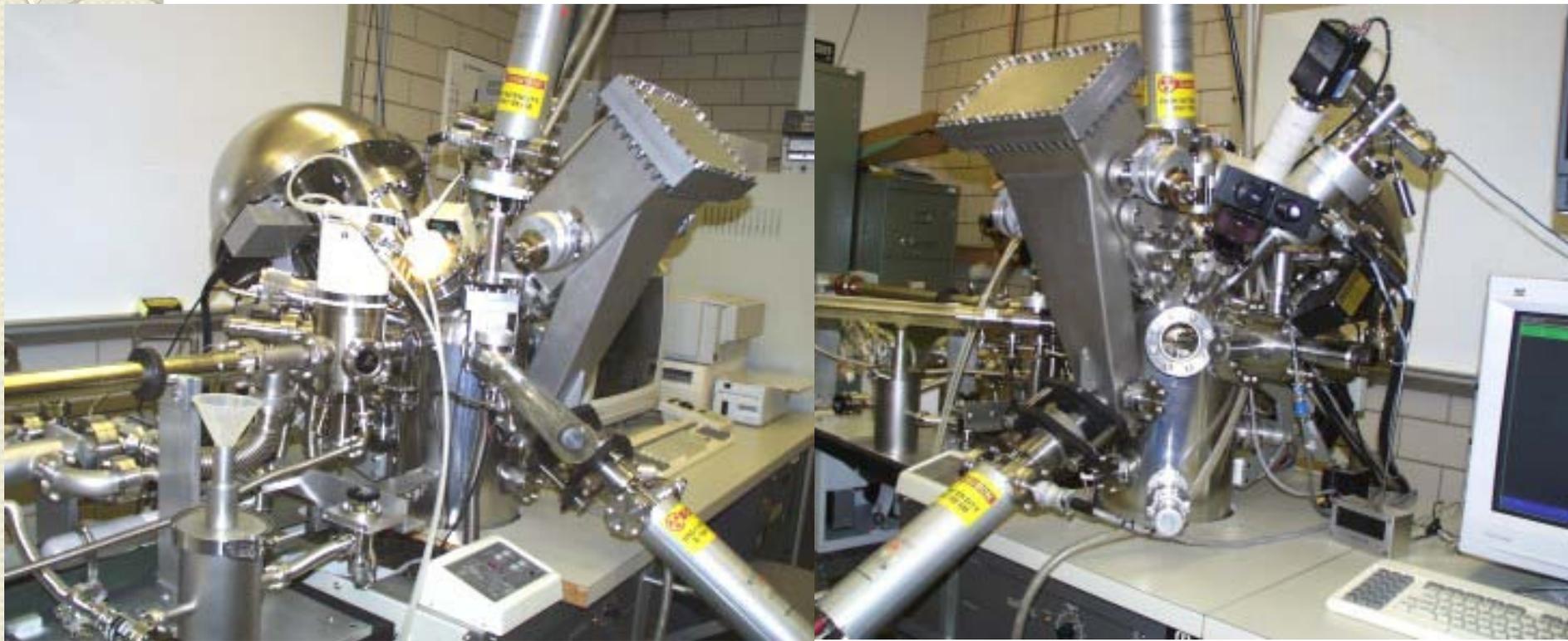
*Surface analysis by XPS requires irradiating a solid in an Ultra-high Vacuum (UHV) chamber with monoenergetic soft X-rays and analyzing the energies of the emitted electrons.*

# Why UHV for Surface Analysis?

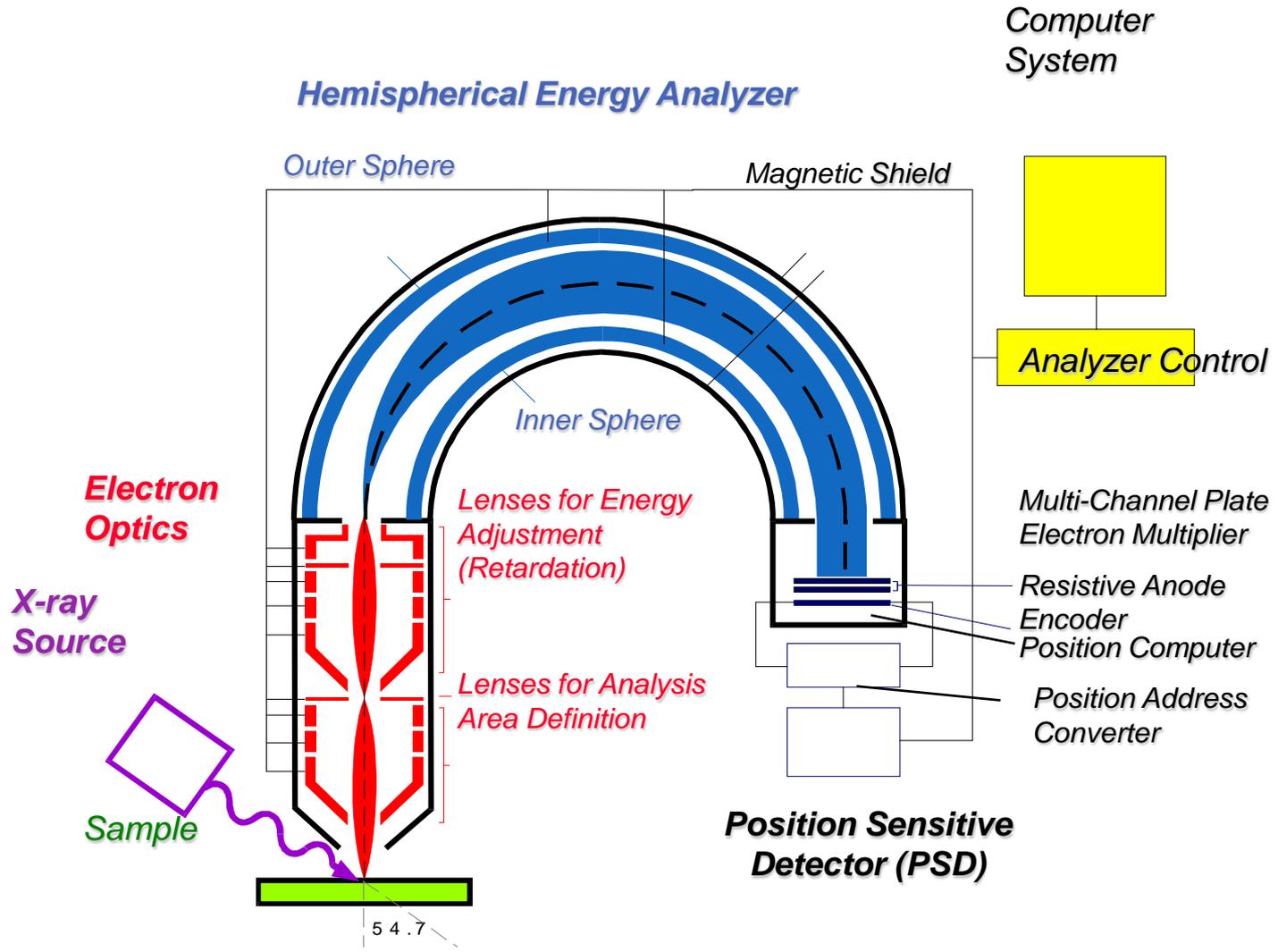
Degree of Vacuum	Pressure Torr
Low Vacuum	$10^2$
Medium Vacuum	$10^{-1}$
High Vacuum	$10^{-4}$
Ultra-High Vacuum	$10^{-8}$
	$10^{-11}$

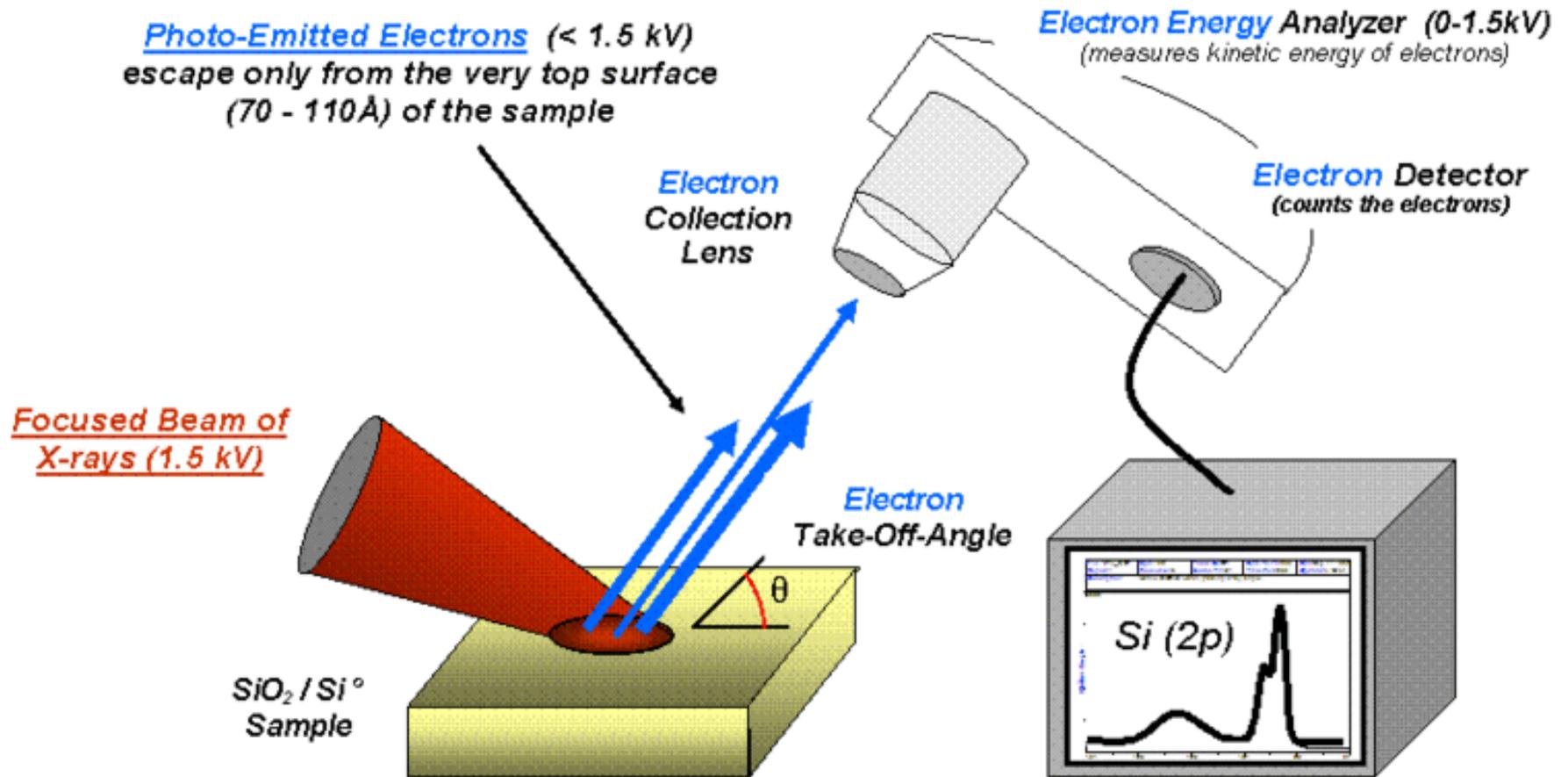
- Remove adsorbed gases from the sample.
- Eliminate adsorption of contaminants on the sample.
- Prevent arcing and high voltage breakdown.
- Increase the mean free path for electrons, ions and photons.

# X-ray Photoelectron Spectrometer



# X-ray Photoelectron Spectrometer





Samples are usually solid because XPS requires ultra-high vacuum ( $<10^{-8}$  torr)

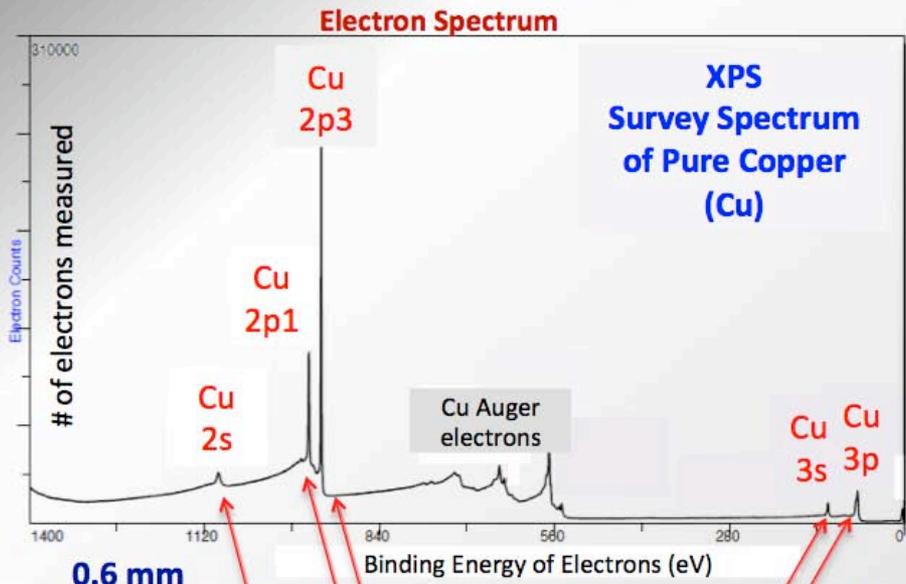
X-ray Gun

Aluminum X-rays (Photons) Energy=1486 eV

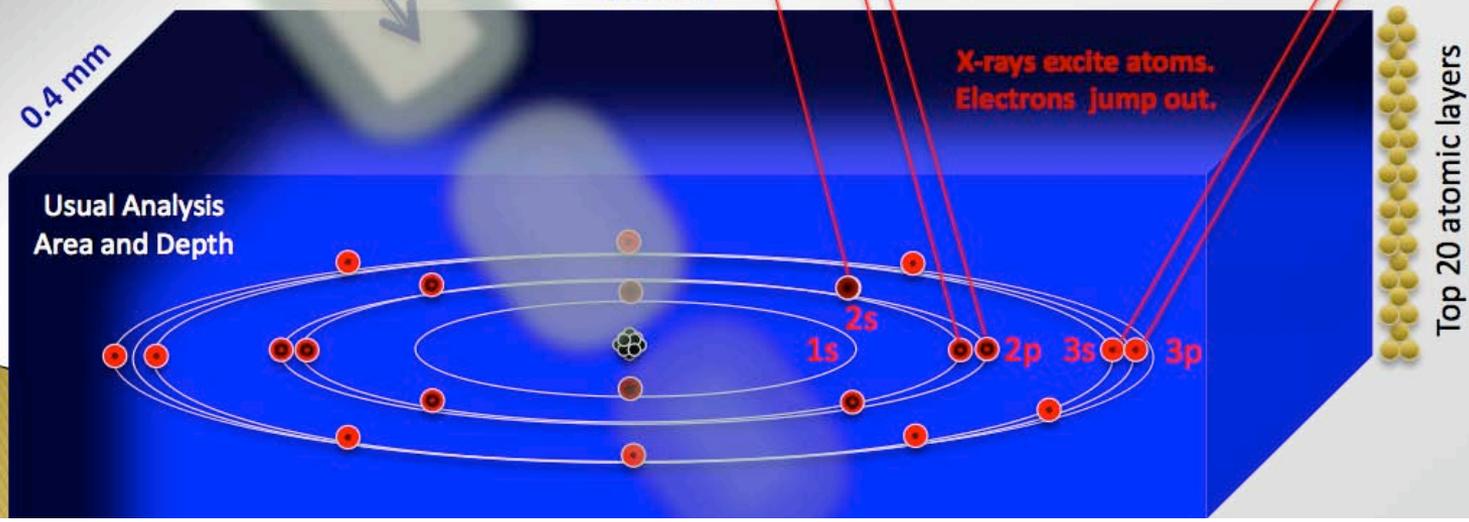
# XPS = X-ray Photo-electron Spectroscopy\*

\*aka ESCA

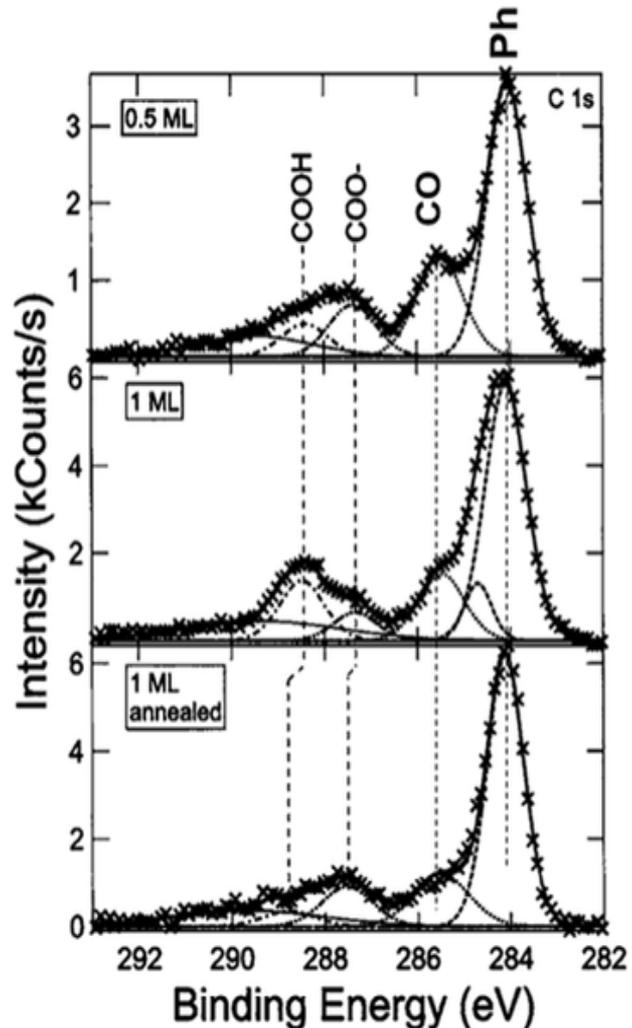
X-rays IN  
Electrons OUT  
Inside Vacuum



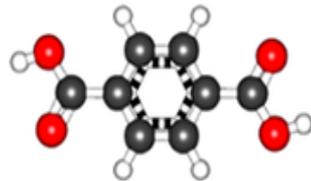
0.6 mm



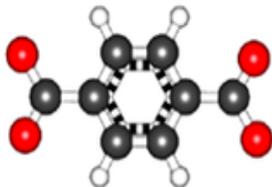
- When we focus on the kinetic energy connected with electrons from a certain state of an element the chemical environment of the element is reflected in small shift of the binding energy of that state.



A hydrogen (white), a carbon (black), and an oxygen (red) atom.



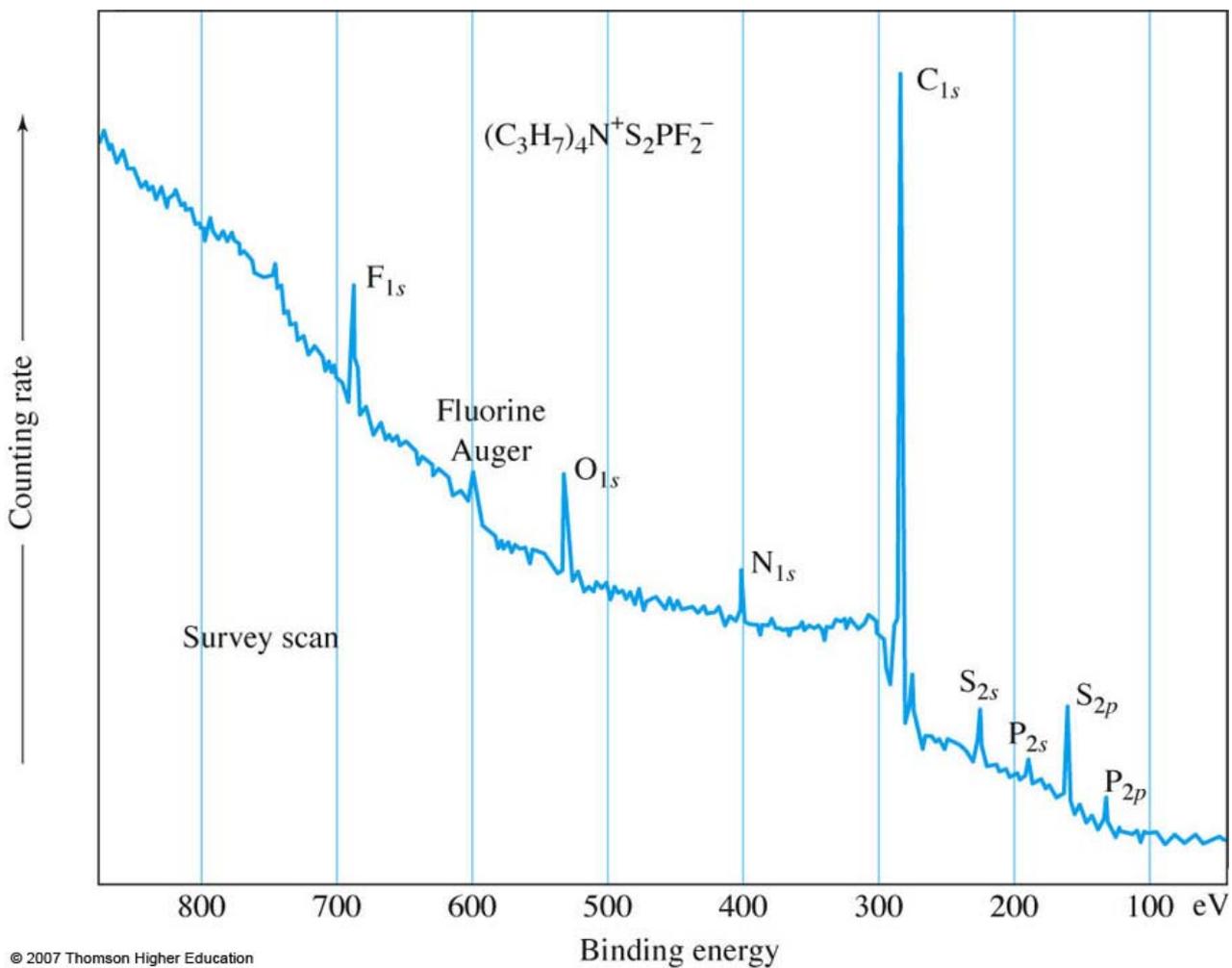
A terephthalic acid molecule featuring a phenyl (C<sub>6</sub>H<sub>4</sub>) and two carboxyl (COOH) units.



Deprotonated variant of the same molecule having two carboxylate (COO<sup>-</sup>) units.

- For example carbon atoms have 1s electron with a binding energy of typically 285 eV.
- If the carbon atoms are connected to other atoms like in phenyl (Ph), carbon monoxide (CO), carboxylate (COO<sup>-</sup>) or carboxyl (COOH) groups, each group exhibits a characteristic binding energy.
- By analyzing peak positions and intensities under different experimental situations one determines the states of the sample.

***Applications of  
X-ray Photoelectron  
Spectroscopy (XPS)***

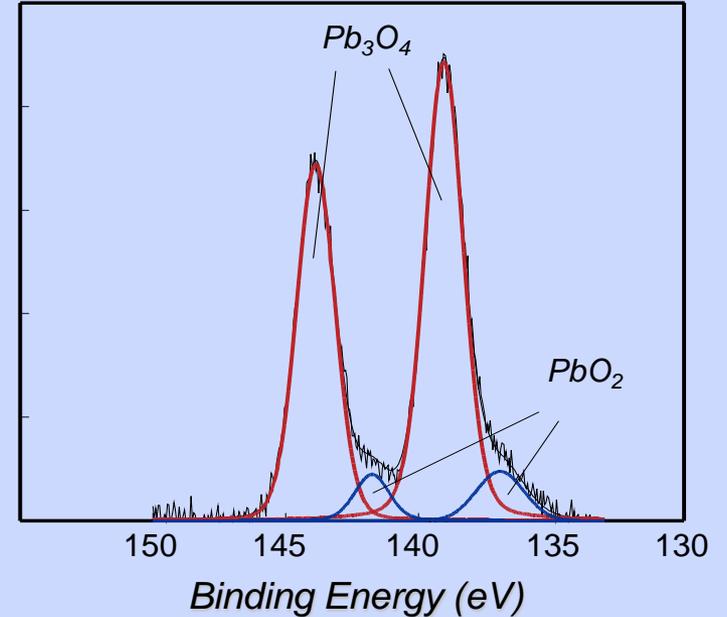
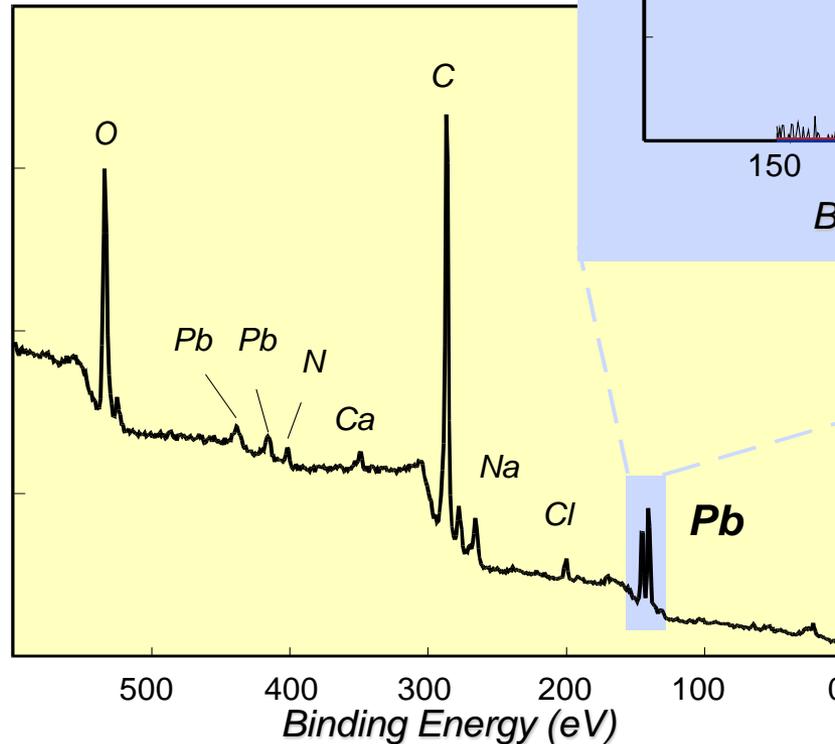


**FIGURE 21-2** X-ray photoelectron spectrum of tetrapropylammonium-difluoridethiophosphate. The peaks are labeled according to the element and orbital from which the emitted electrons originate.

# XPS Analysis of Pigment from Mummy Artwork



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



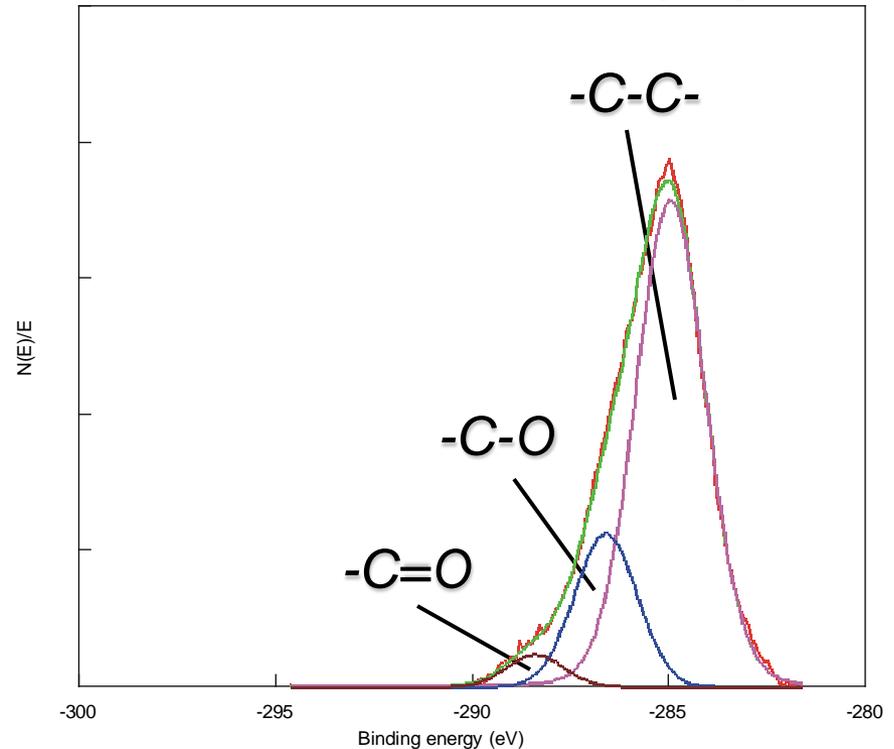
*XPS analysis showed that the pigment used on the mummy wrapping was  $Pb_3O_4$  rather than  $Fe_2O_3$*

# 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.*



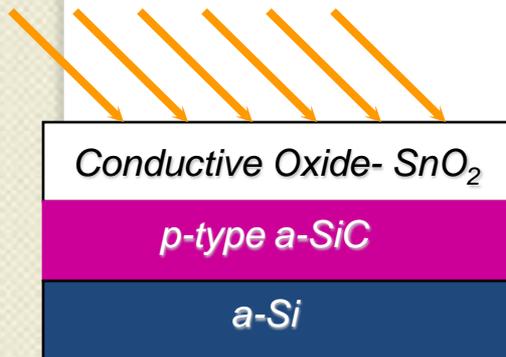
# Analysis of Materials for Solar Energy Collection by XPS Depth Profiling-

## The amorphous-SiC/SnO<sub>2</sub> Interface

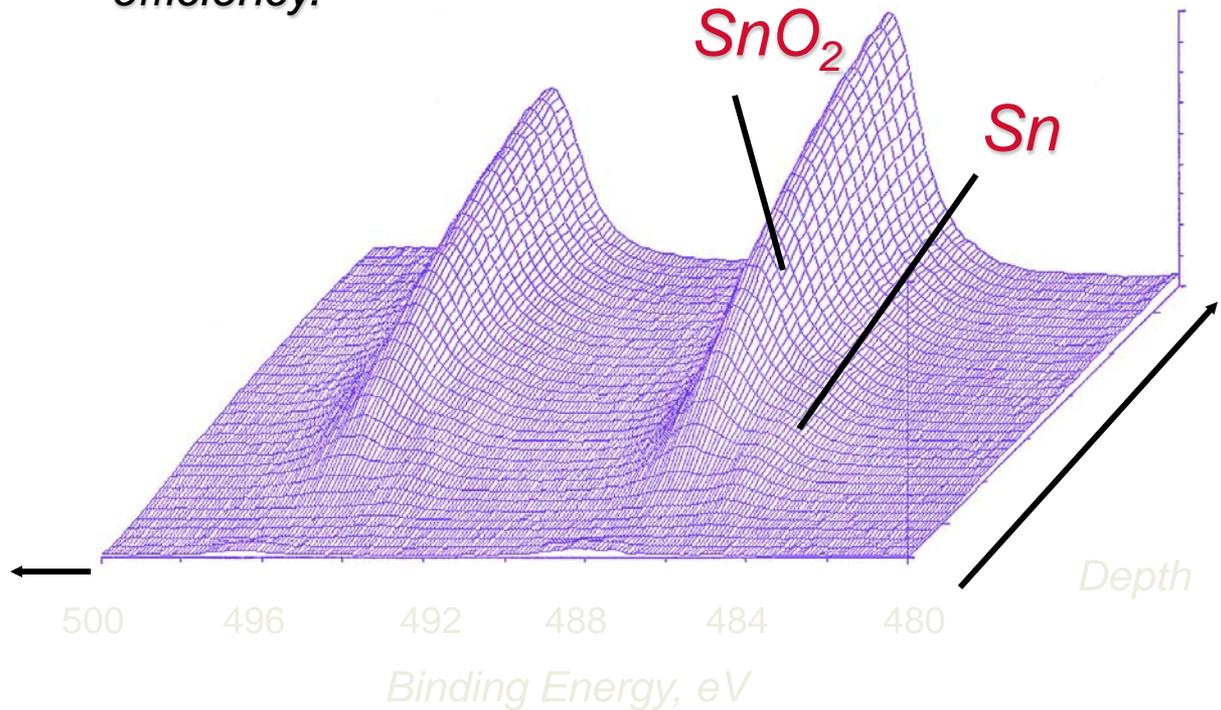
Photo-voltaic Collector



Solar Energy



The profile indicates a reduction of the SnO<sub>2</sub> occurred at the interface during deposition. Such a reduction would effect the collector's efficiency.

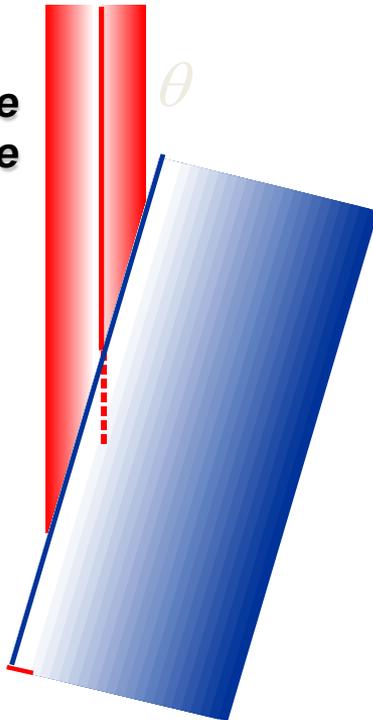


Data courtesy A. Nurrudin and J. Abelson, University of Illinois

# Angle-resolved XPS

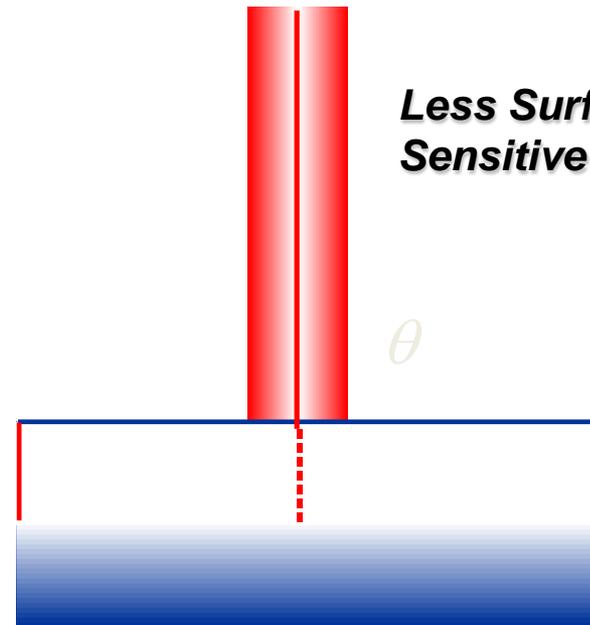
$\theta = 15^\circ$

**More Surface Sensitive**



$\theta = 90^\circ$

**Less Surface Sensitive**



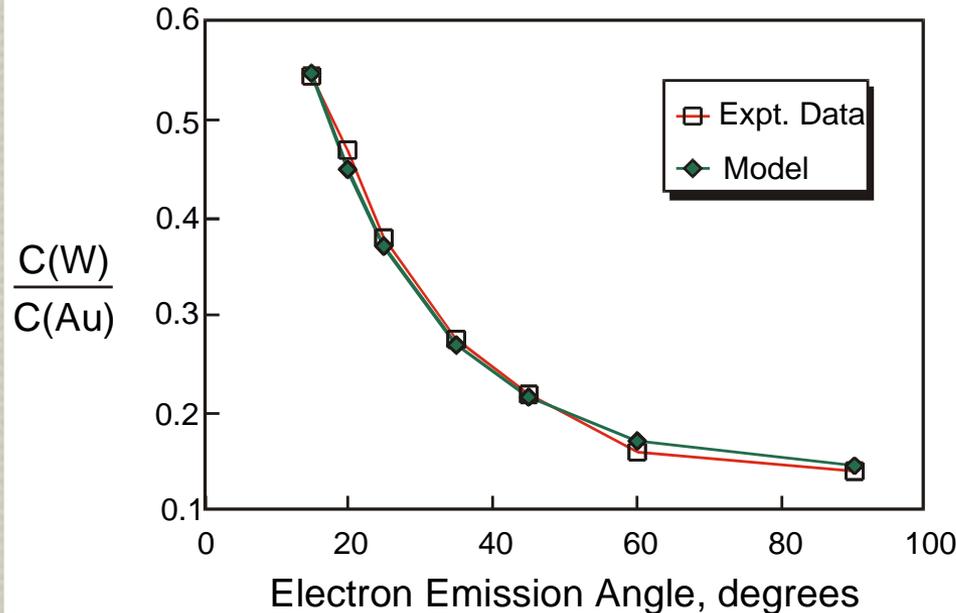
**Information depth =  $d \sin \theta$**  ————  
 **$d =$  Escape depth  $\sim 3 \lambda$**  .....  
 **$\theta =$  Emission angle relative to surface**  
 **$\lambda =$  Inelastic Mean Free Path**

# 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*



*Electron Energy Loss Spectroscopy,  
(EELS) for chemical and  
compositional analysis*

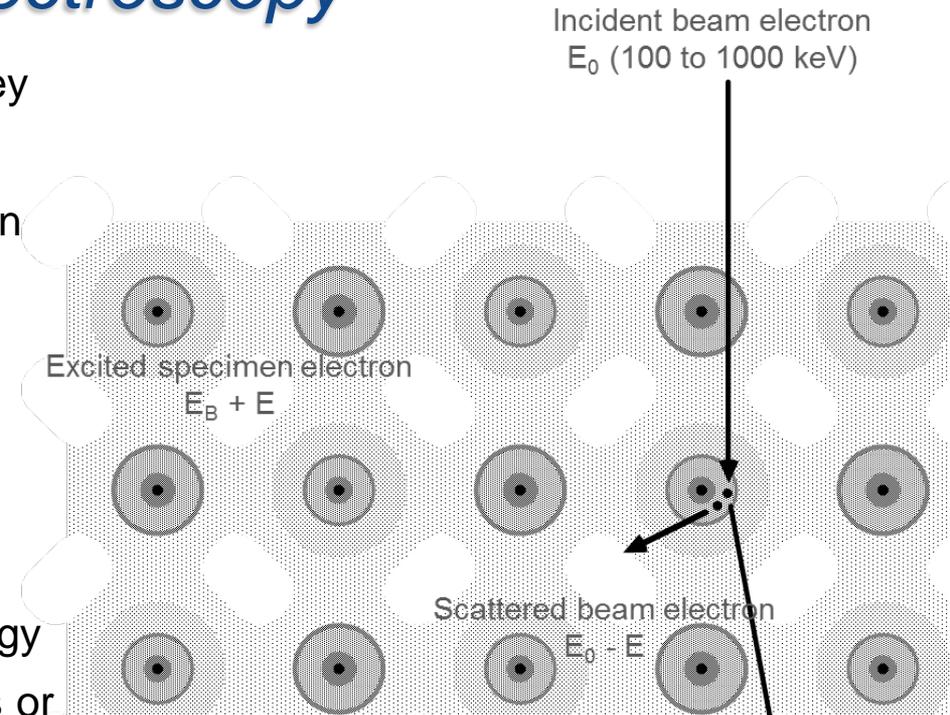


# *What is EELS*

- *Electron energy loss spectroscopy (EELS) is a family of techniques that measure the change in kinetic energy of electrons after they interact with a specimen.*
- *In EELS the energy distribution of electrons that pass through a thin sample is used to analyze the content of the sample and create images with unique contrast effects.*
- *This technique is used to determine the atomic structure and chemical properties of a specimen, including: the type and quantity of atoms present, chemical state of atoms and the collective interactions of atoms with their neighbors.*

# Electron Energy Loss Spectroscopy

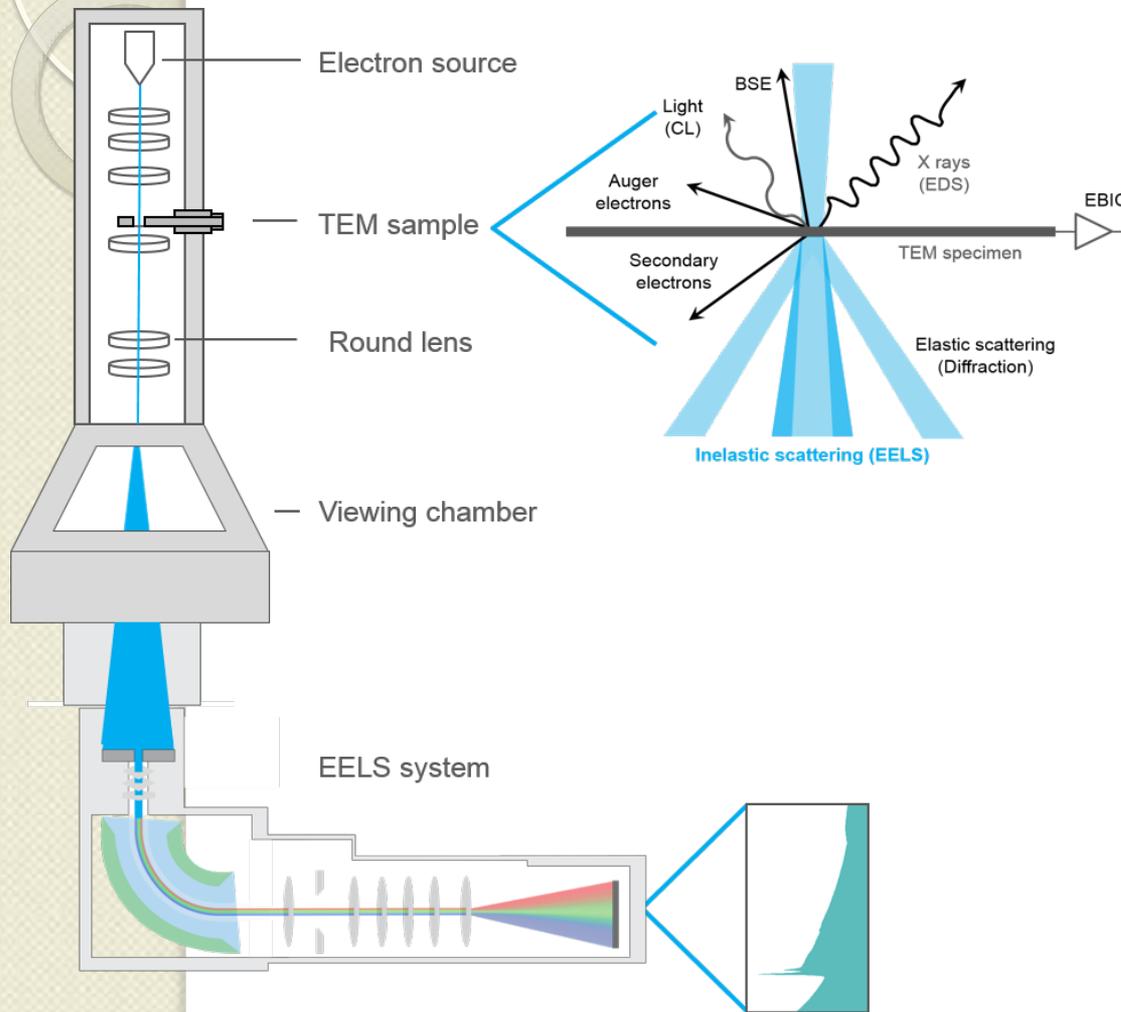
- As electrons pass through a specimen, they interact with atoms of the solid.
- Many of the electrons pass through the thin sample without losing energy.
- A fraction will undergo inelastic scattering and lose energy as they interact with the specimen.
- This leaves the sample in an excited state. The material can de-excite by giving up energy typically in the form of visible photons, x-rays or Auger electrons.



*Atom-scale view of electron energy loss*

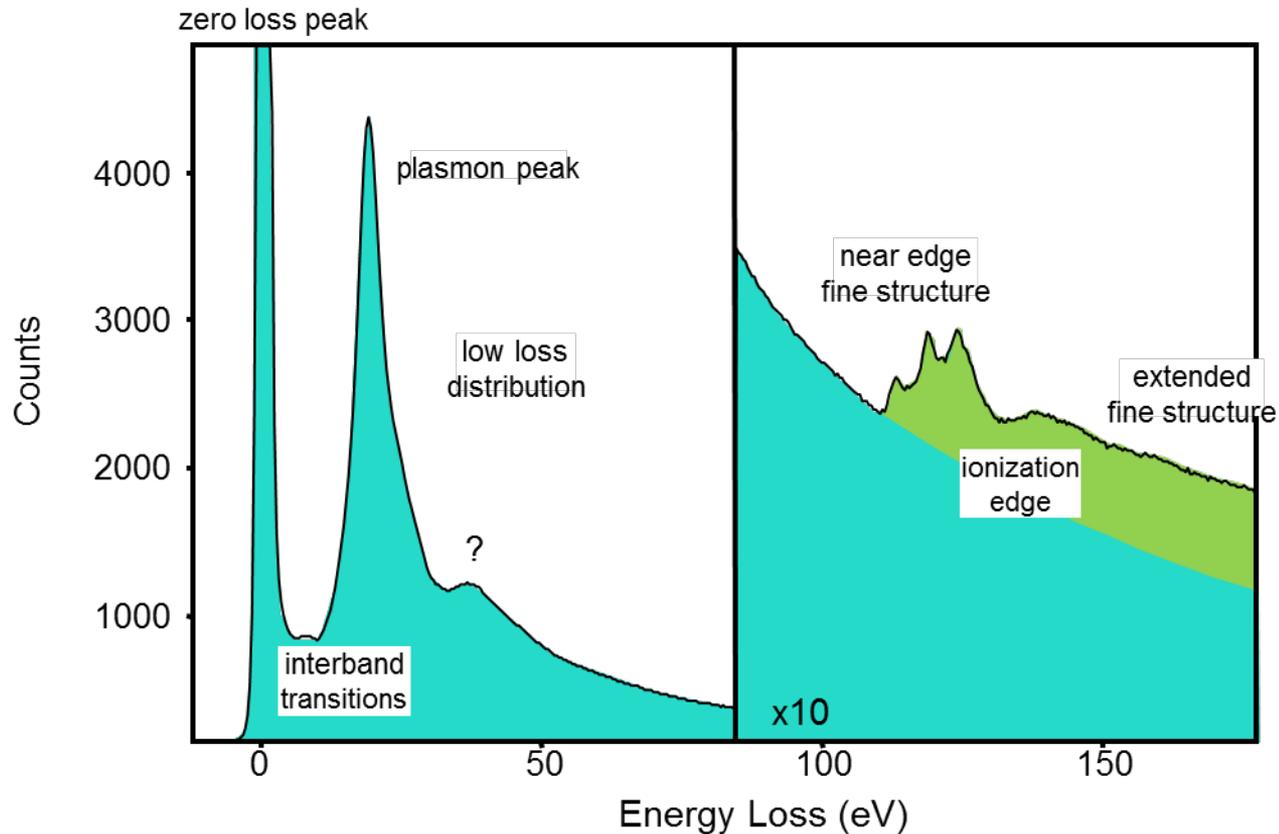
- As the incident electron interacts with the sample, it changes both its energy and momentum.
- You can detect this scattered incident electron in the spectrometer as it gives rise to the electron energy loss signal.
- The sample electron (or collective excitation) carries away this additional energy and momentum

# EELS- Instrumentation



*EELS instrumentation is typically incorporated into a transmission electron microscope (TEM) or a scanning TEM (STEM). These microscope types use high energy electrons (60 – 300 kV typically) to interrogate the sample. As the name implies, the electrons must “transmit” through the sample and thus requires an electron transparent sample. The electrons can interact either elastically (no energy exchange) or inelastically with the sample, and it is these interactions that EELS exploits to extract information about the sample.*

# Specimen information provided by EELS signal



A typical energy loss spectrum. The spectrum has many prominent features and is typically separated into three regions: electrons that have not lost energy (zero-loss peak), electrons that have interacted with the weakly bound electrons in the sample (low-loss distribution), and the electrons that have interacted with the tightly bound core electrons of the atoms (the ionization edges or core-loss region).

➤ *a wealth of information from the sample, including:*

- *Specimen thickness – Zero-loss peak (ZLP) and total spectrum intensity*
- *Valence/conduction electron density – Plasmon peaks*
- *Optical response (complex dielectric function) – Low-loss distribution*
- *Band structure and interband transitions – Near zero-loss features*
- *Elemental composition – Core-loss edges*
- *Bonding and oxidation state (density of unoccupied states) – Near edge fine structure (ELNES)*
- *Distribution of near neighboring atoms (radial distribution function RDF) – Extended energy loss fine structure (ExELFS)*

## *EELS limitations*

➤ The main limitation of the EELS technique is the effect of sample thickness. As the sample thickness increases, the strong interaction of primary electrons within the sample results in the electrons undergoing multiple energy loss events. This tends to reduce the signal-to-background ratio of the EELS edges, reducing the visibility of the edges. However, since the spatial resolution of transmission electron microscope techniques is also reduced as the thickness increases, this loss of the edge visibility is not always the largest impediment to quality data.