Probing beam	Technique	Types of information
Photons	X-ray photoelectron spectroscopy (XPS)	Surface composition (Li and heavier), surface chemical state
	X-ray diffraction (XRD)	Film crystal structure and phase
	X-ray reflectance (XRR)	Film thickness and interface roughness
	Laser Raman	Molecular structure
	Fourier transform infrared spectroscopy (FTIR)	Molecular structure
	Ellipsometry	Film thickness
	Photoluminescence spectroscopy	Luminescence properties
Ions	Rutherford backscattering spectrometry	Film composition, film thickness, elemental profiles, information about interface
	Nuclear reaction analysis	Specific isotope composition and distribution
	Ion channeling	Crystalline quality and defect (impurity) locations, information about interface
	Elastic recoil detection analysis	Light element concentration and depth distribution
	SIMS/Nano-SIMS/TOF-SIMS	Molecular and elemental species
	Low-energy ion scattering	Outer surface composition, surface structure
	Glow discharge mass spectrometry	Depth profile
	Focused ion beam	Ion-induced EDS, secondary ion microscopy, ion-induced secondary electron microscopy, nanolithography (site specific cross-sections), film surface cleaning
Electrons	Auger electron spectroscopy	Surface elemental (and chemical state) composition
	Scanning electron microscopy	Surface topography, film thickness?
	Transmission electron microscopy	Microstructure, chemical information, film thickness?
	Low-energy electron diffraction	Surface structure
	Energy-dispersive X-ray spectroscopy	Composition and composition distribution
Other Methods	Scanning probe methods (STM, AFM, etc.)	Topography, electronic structure, site-specific information
	Atom probe microscopy	Atom

X-Ray Photoelectron Spectroscopy (XPS)

- Electron Spectroscopy for Chemical Analysis (ESCA)
  - Noble prize of 1981
  - Compositional and Chemical state analysis
  - Quantitative Analysis that can detect all elements
  - Detection of Binding Energies of photoelectrons
  - Monoenergetic X-ray photon

Mg Kα(1253.6 eV)

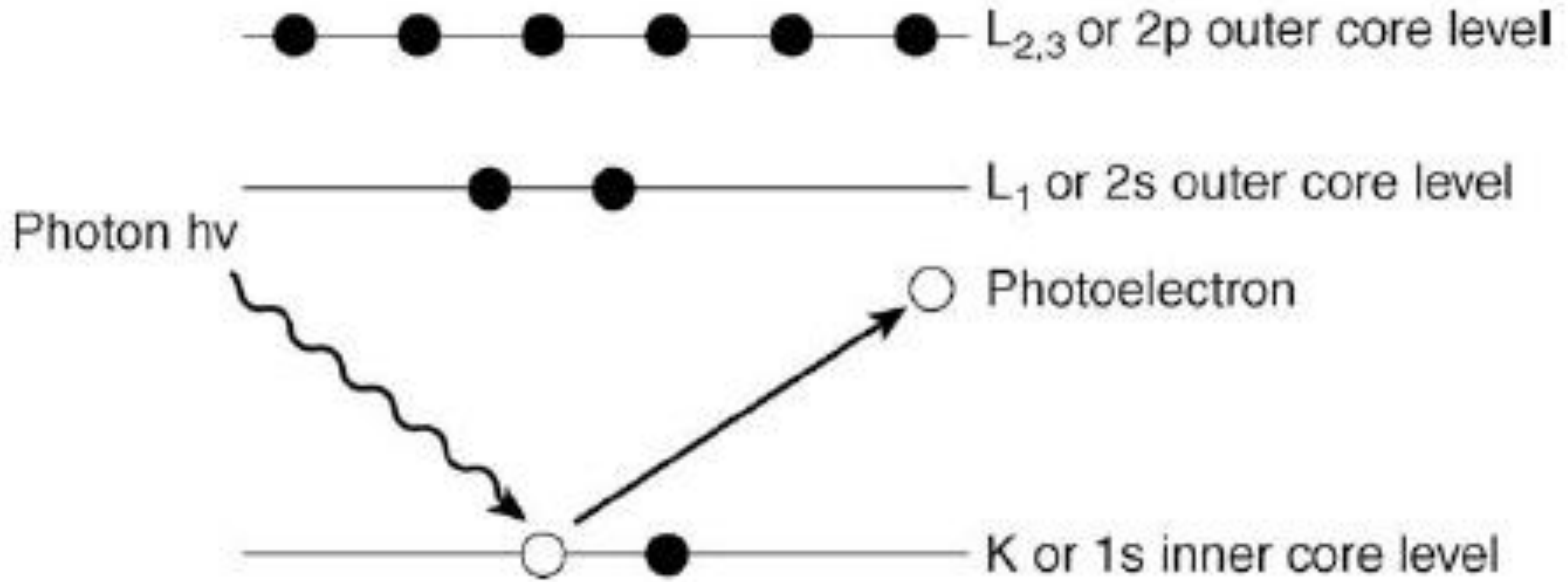
Al Kα(1486.6 eV)

K.E. 300-1500 eV

Short Range = 0.5-3 nm (IMFP)

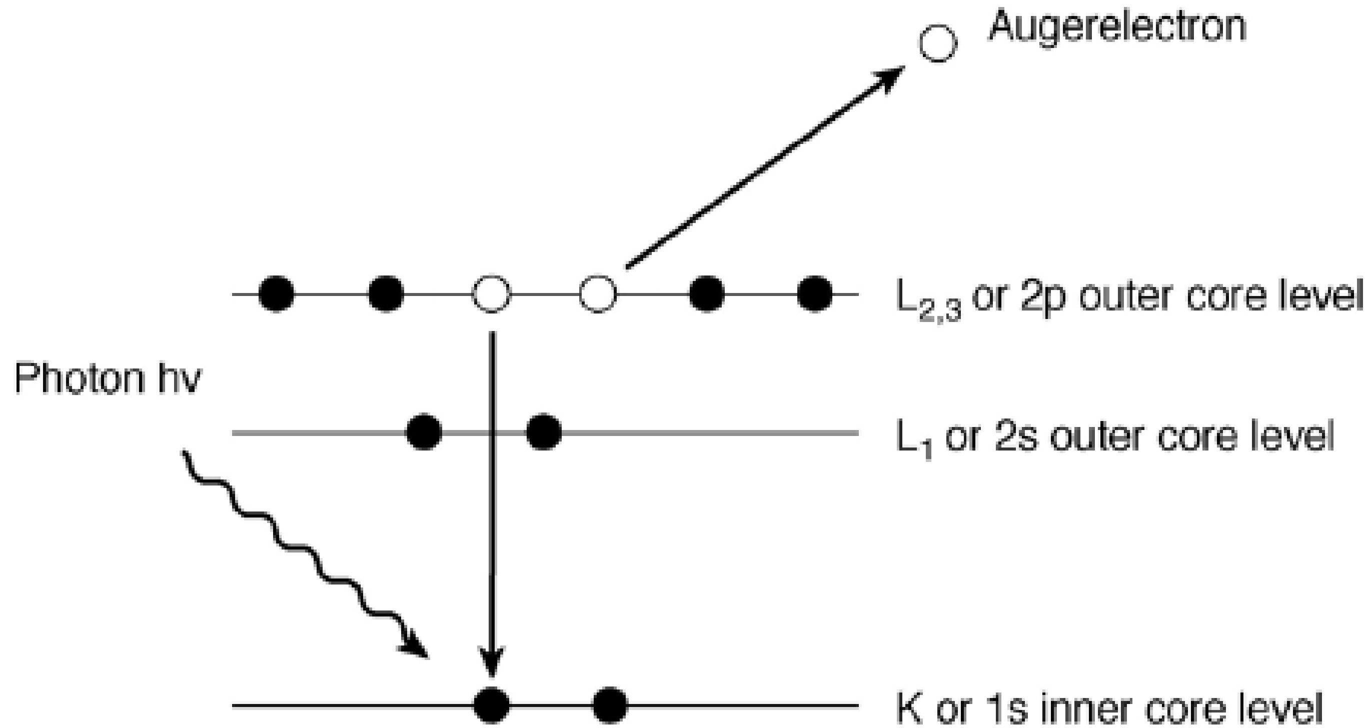
Dr. Bilal Rasul Warraich, The University of Sargodha

X-Ray Photoelectron Spectroscopy (XPS)



$$K.E. = h\upsilon - BE - \Phi_s$$

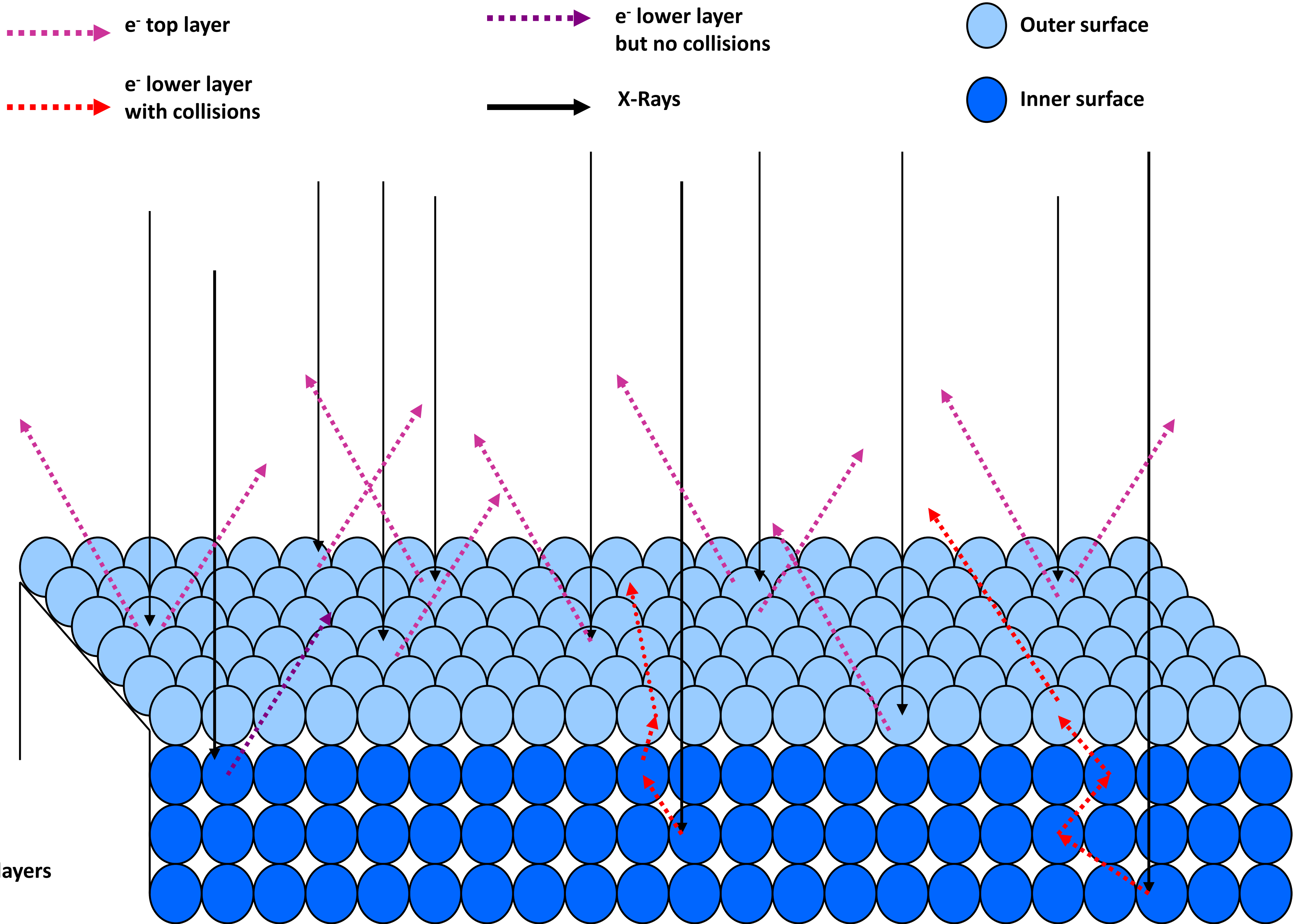
X-Ray Photoelectron Spectroscopy(XPS)



- Core level vacancy is filled with an e^- from higher level shell and a 3rd e^- is emitted to conserve energy

$$E_{KLL} = E_K - E_L - E_L$$

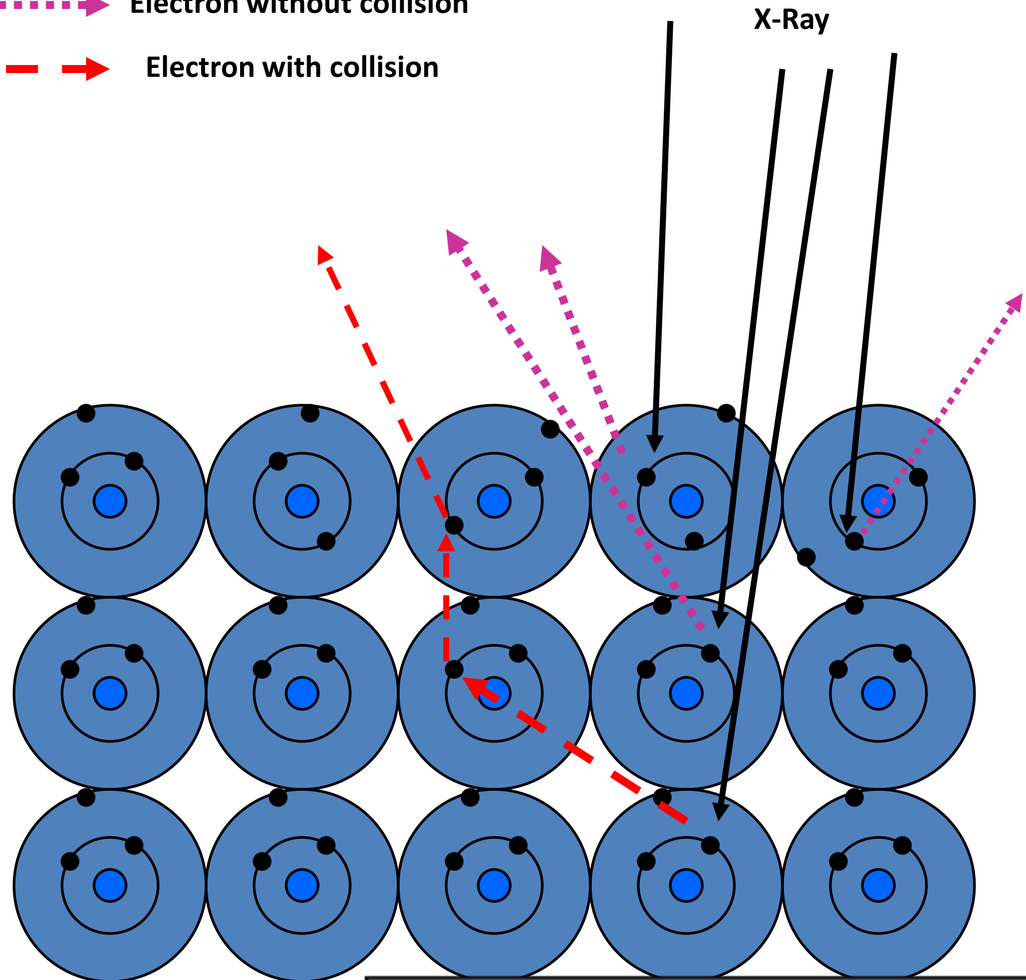
- KE of photoelectron increases as BE decreases
- intensity of photoemission a intensity of photons
- need monochromatic (x-ray) incident beam
- a range of KE's can be produced if valence band is broad
- BE follows energy of levels: BE(1s) > BE(2s) > BE(2p) > BE(3s)...
- BE of orbital increases with Z: BE(Na 1s) < BE(Mg 1s) < BE(Al 1s)...
- BE of orbital not affected by isotopes: BE(7 Li 1s) = BE(6 Li 1s)



e⁻ top layer
e⁻ lower layer but no collisions
Outer surface
e⁻ lower layer with collisions
X-Rays
Inner surface
Atoms layers

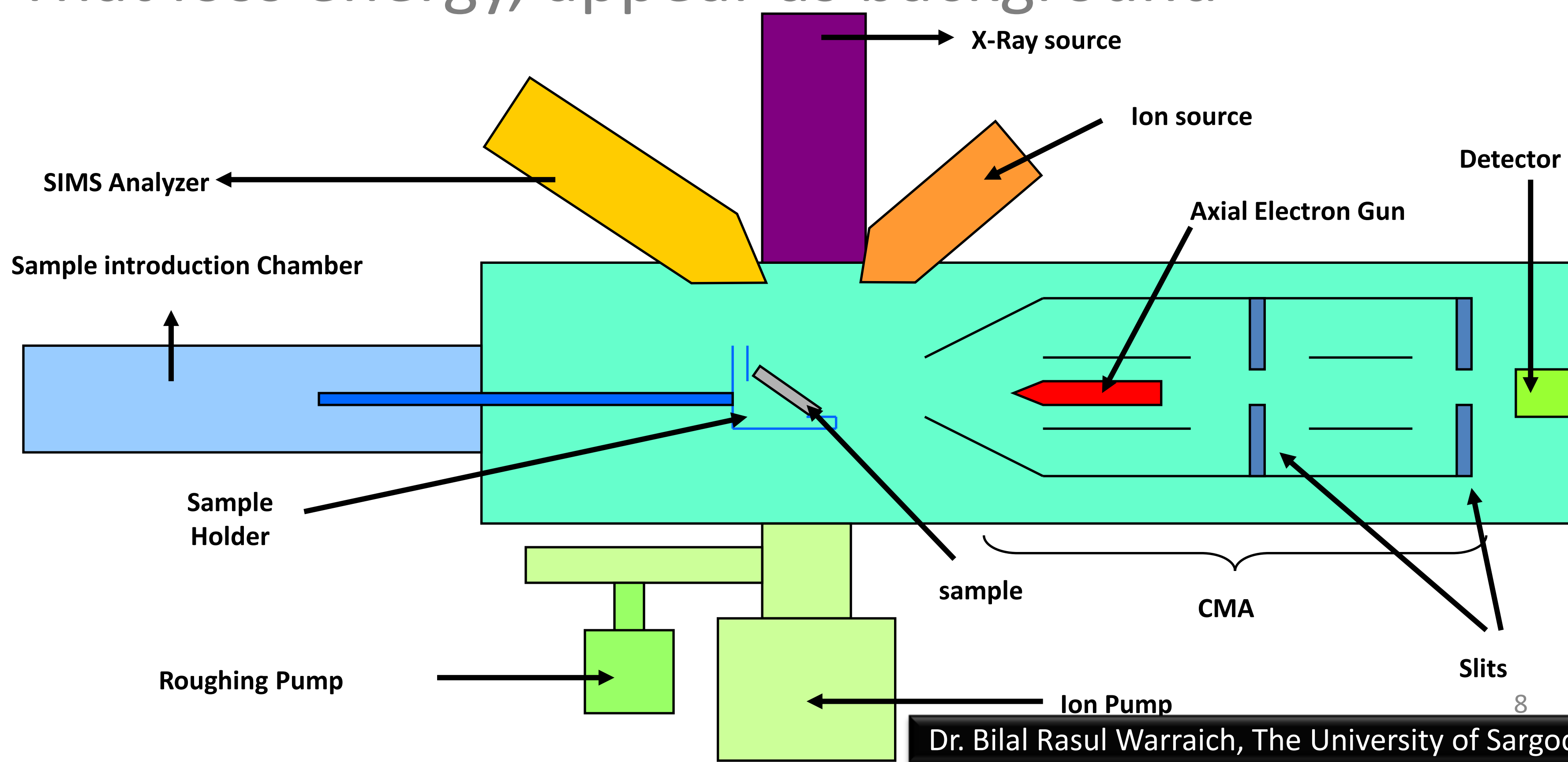
X-Ray Photoelectron Spectroscopy(XPS)
X-Rays and the Electrons

The noise signal comes from the electrons that collide with other electrons of different layers. The collisions cause a decrease in energy of the electron and it no longer will contribute to the characteristic energy of the element.



X-Ray Photoelectron Spectroscopy (XPS)

- Electrons emitted without inelastic energy loss appear as spectral peaks as a function of binding energy
- That loss energy, appear as background



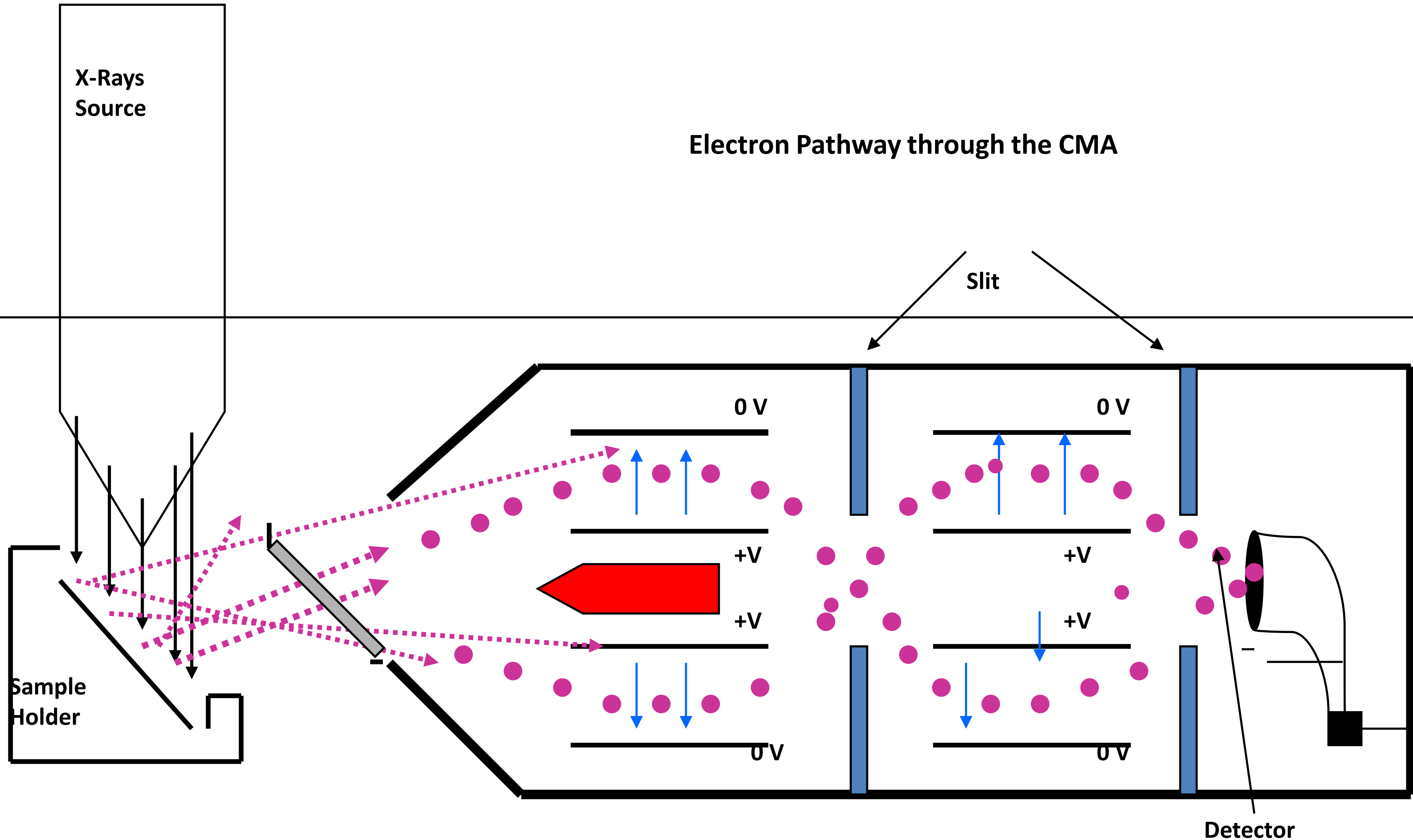
X-Ray Photoelectron Spectroscopy(XPS)
Cylindrical Mirror Analyzer (CMA)

- The electrons ejected will pass through a device called a CMA.
- The CMA has two concentric metal cylinders at different voltages.
- One of the metal cylinders will have a positive voltage and the other will have a 0 voltage. This will create an electric field between the two cylinders.
- The voltages on the CMA for XPS and Auger e^-s are different.

X-Ray Photoelectron Spectroscopy(XPS) Cylindrical Mirror Analyzer (CMA)

- When the e^-s pass through the metal cylinders, they will collide with one of the cylinders or they will just pass through.
  - If the e^-'s velocity is too high it will collide with the outer cylinder
  - If is going too slow then will collide with the inner cylinder.
  - Only the e^- with the right velocity will go through the cylinders to reach the detector.
- With a change in cylinder voltage the acceptable kinetic energy will change and then you can count how many e^-s have that KE to reach the detector.

X-Ray Photoelectron Spectroscopy(XPS)
Cylindrical Mirror Analyzer (CMA)



X-Ray Photoelectron Spectroscopy(XPS) Cylindrical Mirror Analyzer (CMA)

Equation

$$KE = h\nu - BE - Ø$$

KE--------Kinetic Energy (measure in the XPS spectrometer)

hv --------photon energy from the X-Ray source (controlled)

Ø ---------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--------is the unknown variable

The equation will calculate the energy needed to get an e^- out from the surface of the solid.

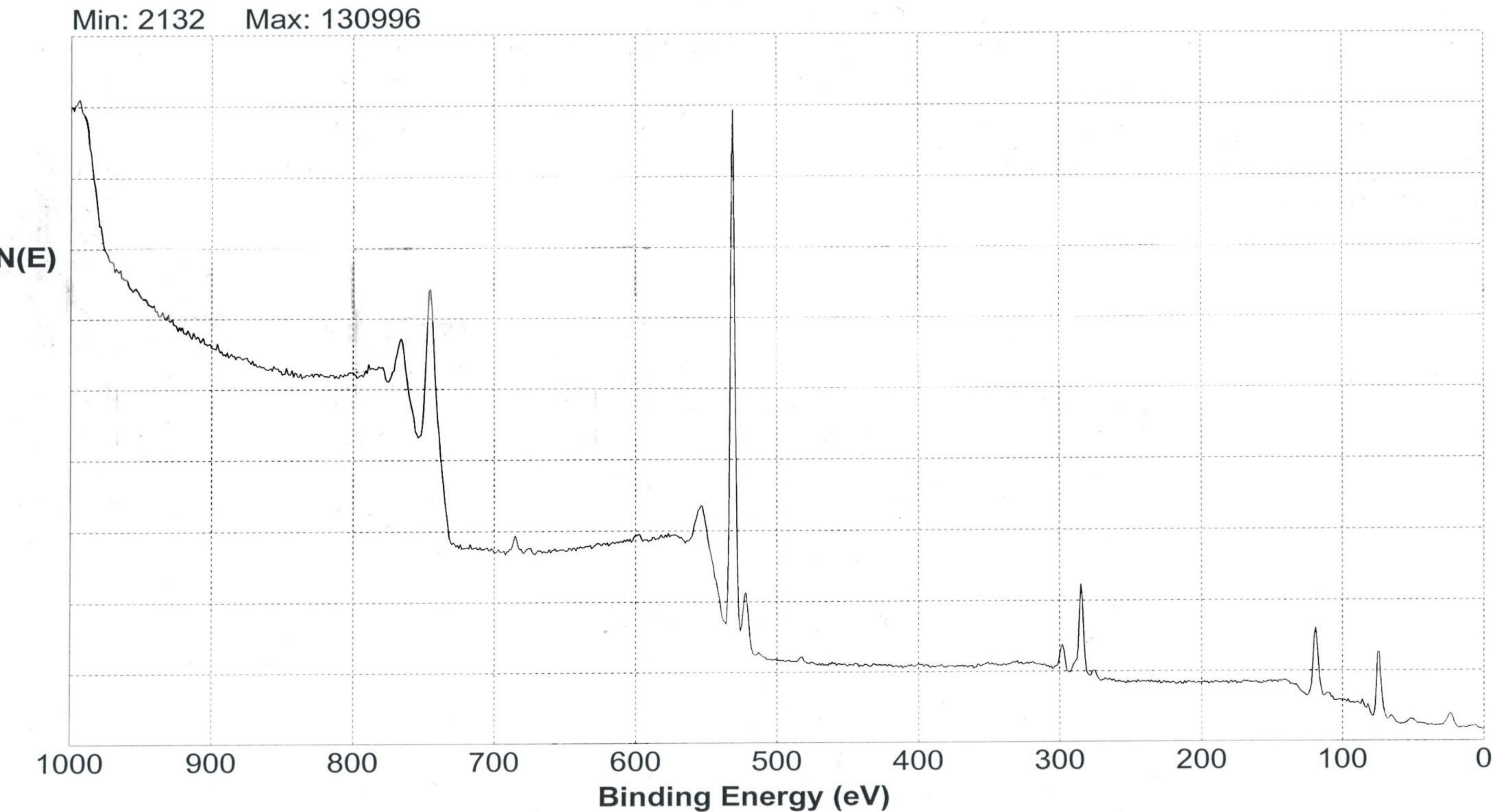
Knowing KE, hv and Ø the BE can be calculated.

AugerScan 2

C:\PHYS 3243\Demo Al foil XPS Survey 2.ASN
Acquired: Thursday, November 30, 2006 14:31:34

XPS Survey

EV/Step: 1 eV, Time/Step: 50 mSec, Sweeps: 10
Source: Mg, Pass Energy: 100 eV, Work Function: 4 eV



X-Ray Photoelectron Spectroscopy(XPS) Data collection

- The XPS peaks are sharp.
- In a XPS graph it is possible to see Auger electron peaks.
- The Auger peaks are usually wider peaks in a XPS spectrum.

X-Ray Photoelectron Spectroscopy(XPS)

- Data collection: Wide Scan(Survey Spectra)1000 eV, surface composition

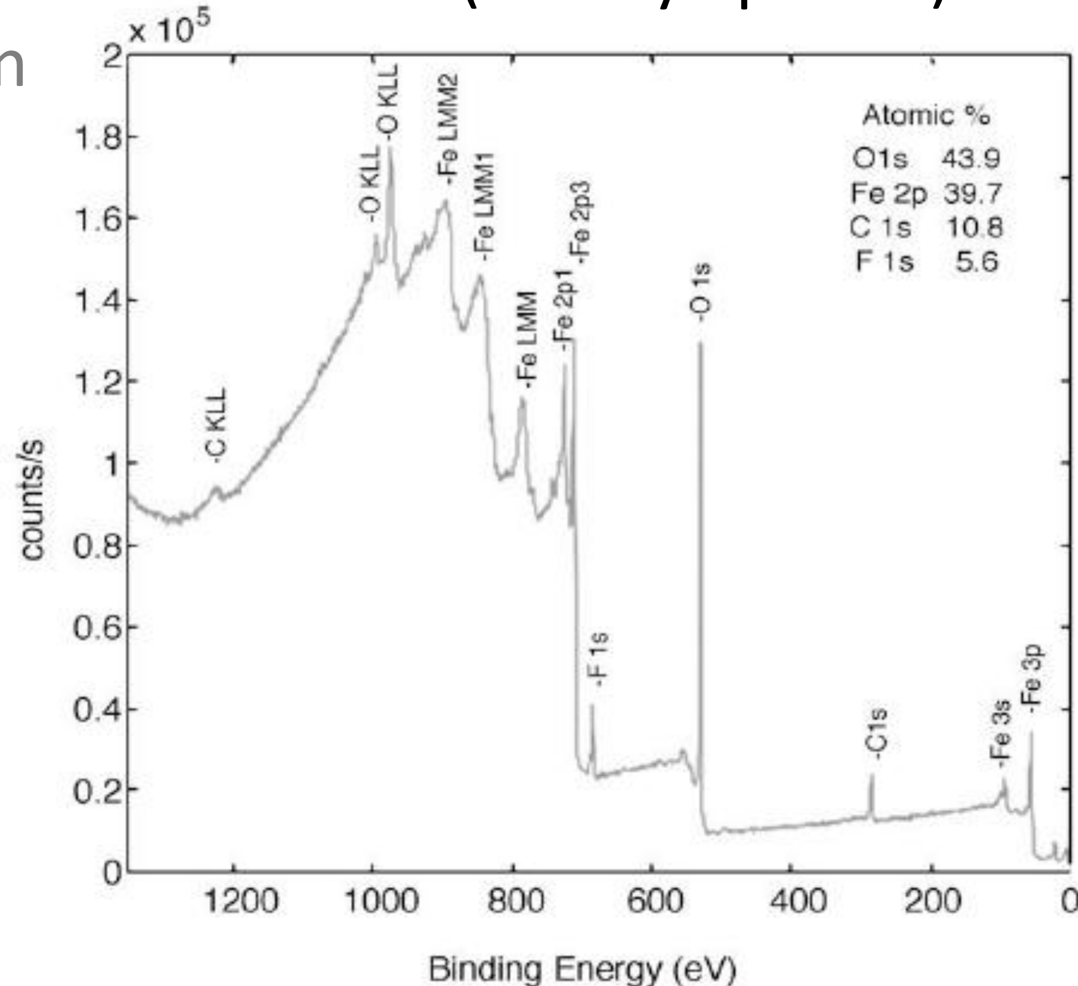


Figure 16.5: XPS survey scan of an iron oxide grown on a silicon wafer. In addition to Fe 2p and O 1s photoelectron peaks, O KLL and Fe LMM Auger peaks are observed. Also present are C and F peaks from surface contamination.

X-Ray Photoelectron Spectroscopy(XPS)

Data collection

- Narrow Scan
  - High resolution
  - Smaller energy window
  - Chemical state of Specific elements

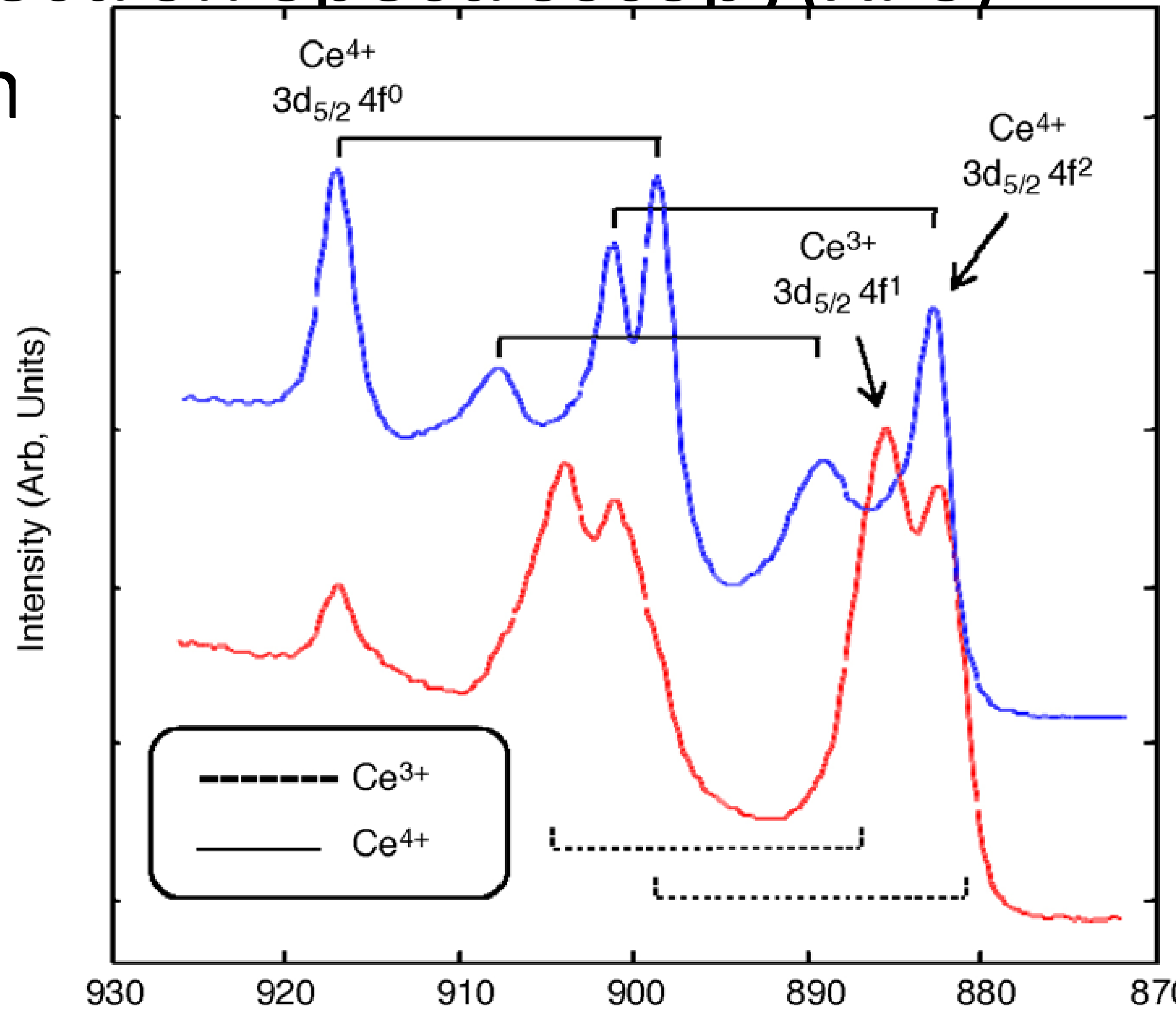


Figure 16.6: Narrow scans of Ce 3d photoelectron peaks from a ceria (CeO_2) film which contains mostly Ce^{4+} (top) and the film after a reduction process which introduces a significant amount of Ce^{3+} (bottom). High-resolution narrow scans for particular core levels provide useful information about the chemical state information.

X-Ray Photoelectron Spectroscopy(XPS)

- Depth profiling
  - Ar and Xe ions for etching used to determine the elemental and chemical profiles. C_{60} ions-damage is lesser
  - Use of energetic ions may chemically degrade sensitive materials Angle-Resolved X-Ray Photoelectron Spectroscopy(ARXPS)
    - Photoemission Angle θ-75°
- Quantification
  - No. of e^-s from an element is signature of its concentration
  - $C_x = (I_x/S_x)/(\Sigma I_i/S_i)$, C_x is atomic concentration the element x, I_x=measured intensity of photoelectron peak and S_x is Sensitivity Factor

X-Ray Photoelectron Spectroscopy(XPS)

- Strengths
  - Measures surface elemental composition
  - Identification of all elements except H and He
  - Non-destructive depth information
  - Thickness measurement
- Limitations
  - Require ultrahigh vacuum
  - Smallest analytical area 1-10 micron
  - Preferential sputtering is challenge during quantitative analysis