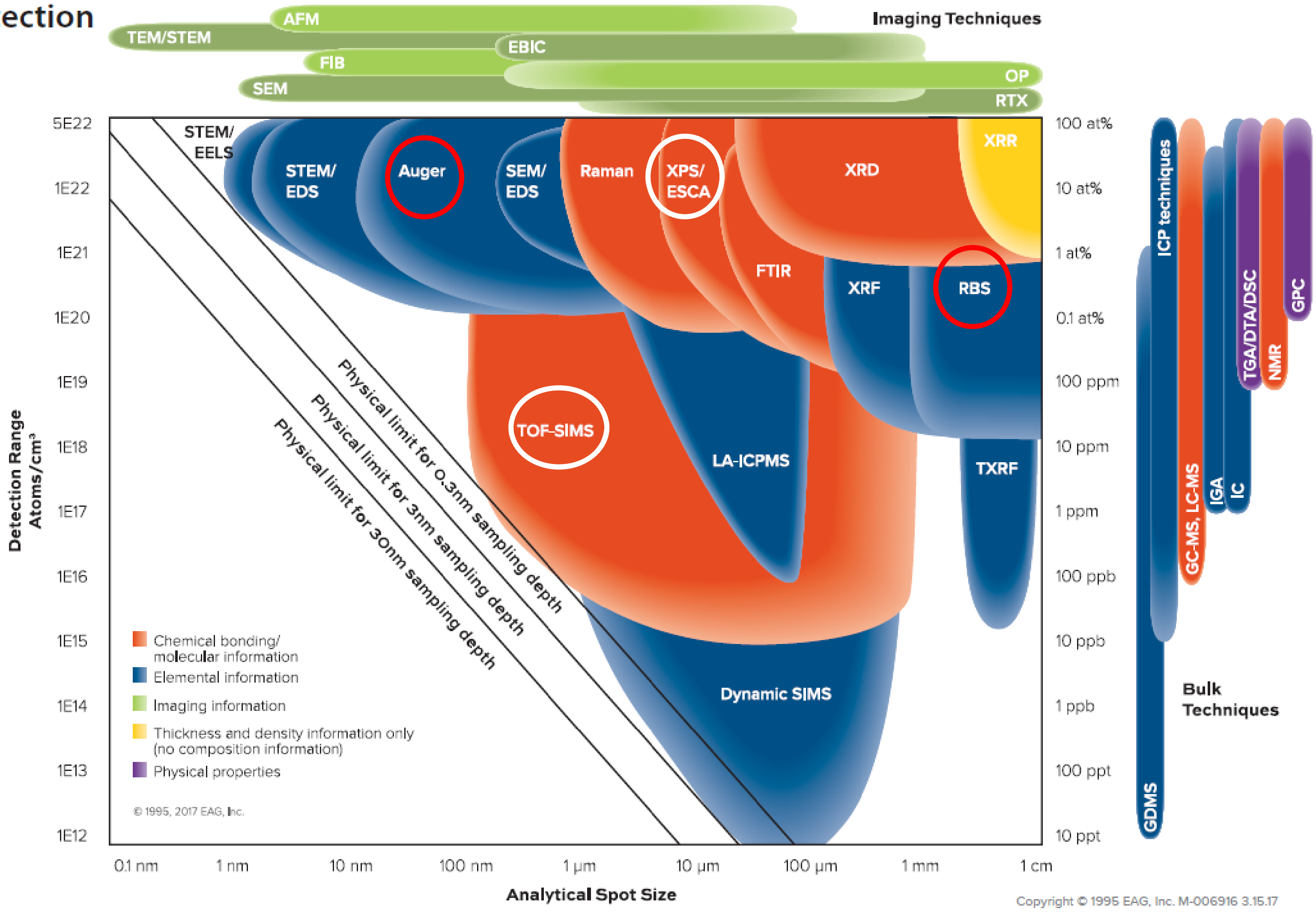
Surface Analytical Techniques (XPS, Auger, SIMS and RBS)

Jerry Hunter, Ph. D.

Analytical Methods

Analytical Resolution vs. Detection Limit



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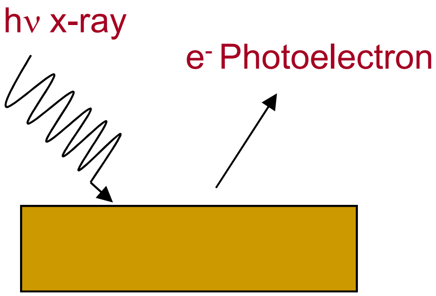
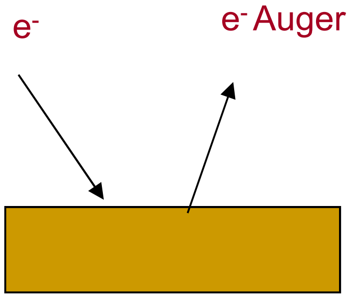
Electron Spectroscopy



XPS/ESCA
1981 Nobel Prize
Siegbahn + 1921 Einstein



Auger

XPS Key ideas to take away

- XPS provides detection limits to ~0.1% atomic
- XPS is very surface sensitive (top <10 nm)
- XPS gives chemical bonding information
- XPS is useful for surveys of unknown contamination
- Can combine with ion sputtering to perform compositional depth profiling

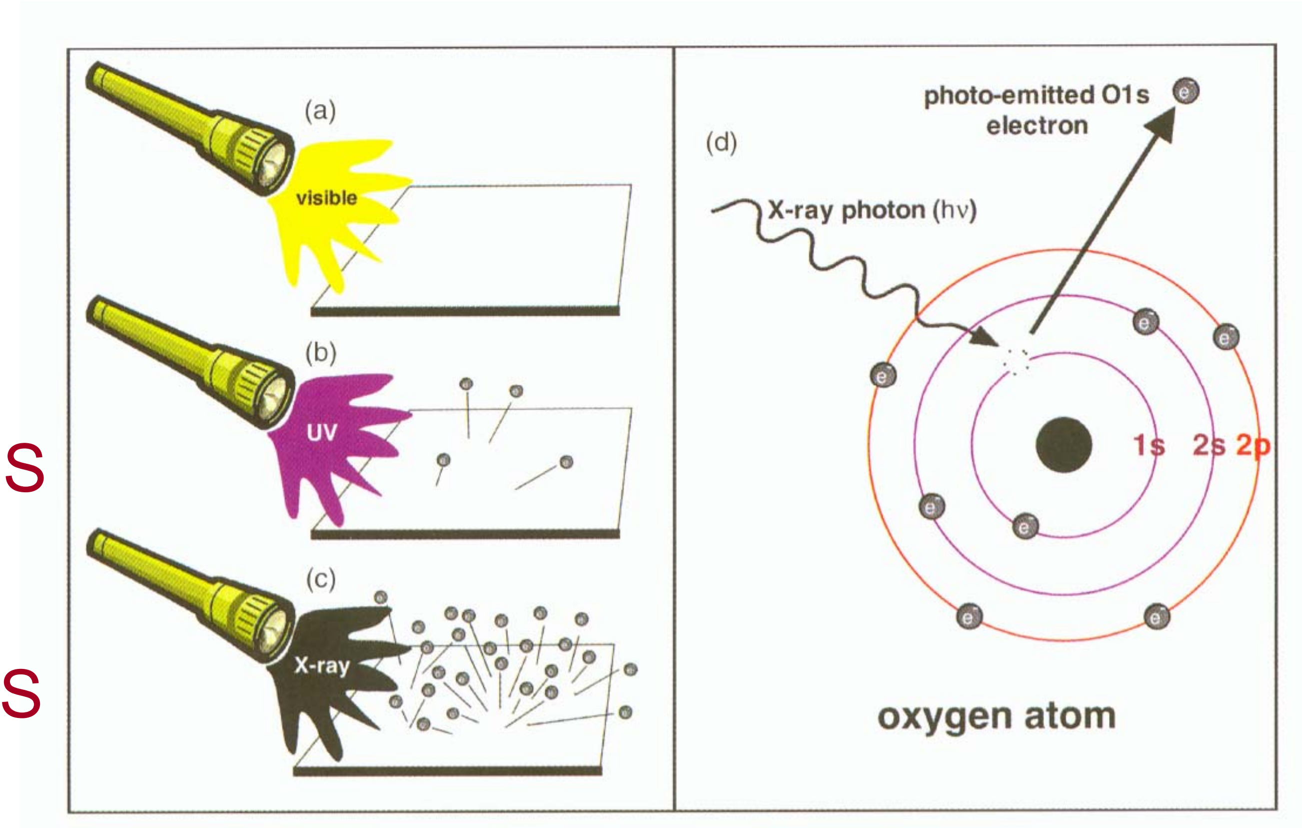
X-ray Photoelectron Spectroscopy (XPS)

- X-ray beam irradiates a sample surface resulting in the ejection of photoelectrons from the core level of the atoms present in the sample
- Photoelectrons are extracted and filtered with respect to their energy (energy is representative of the elements in the sample)
- Can be combined with sputtering to do depth profiling

X-ray Photoelectron Spectroscopy (XPS)

- Signal detected: Photoelectrons from near surface atoms
- Elements detected: Li – U, Chemical bonding
- Detection limit: 0.1 – 1% atomic
- Imaging: Yes
- Lateral Resolution: 9um – 2mm

Photoelectric Effect

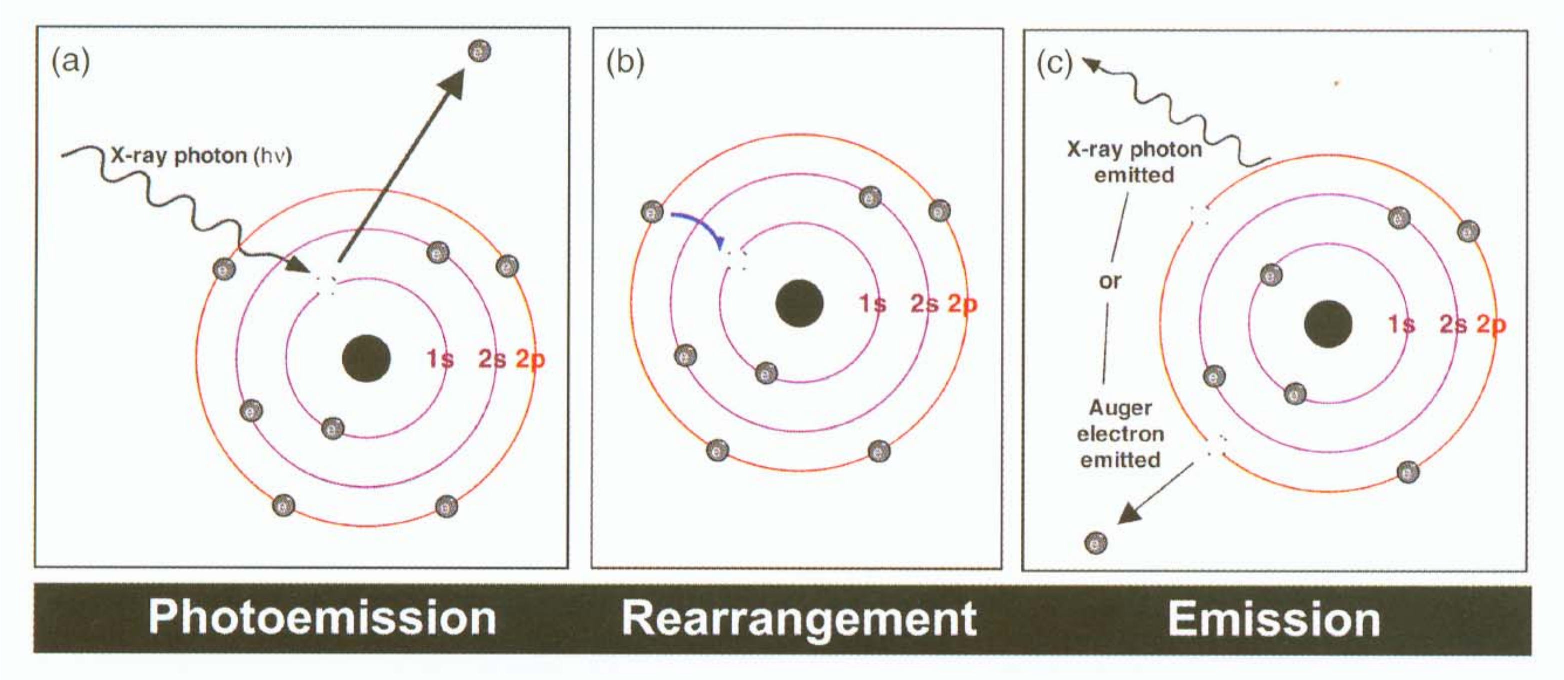


UPS

XPS

Vickerman

Photoemission Process



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X-ray photoelectron spectroscopy, XPS
(a.k.a. Electron Spectroscopy for Chemical Analysis, ESCA)

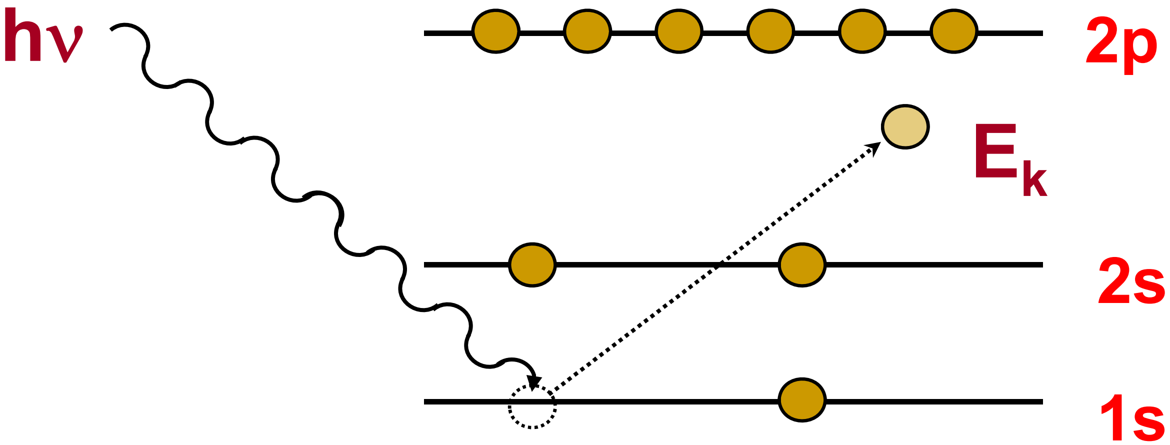
Photoelectric effect:

Photon of energy, $h\nu$, bombards a material and is absorbed by an electron with binding energy E_b which then is ejected into the vacuum with kinetic energy,

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

where,

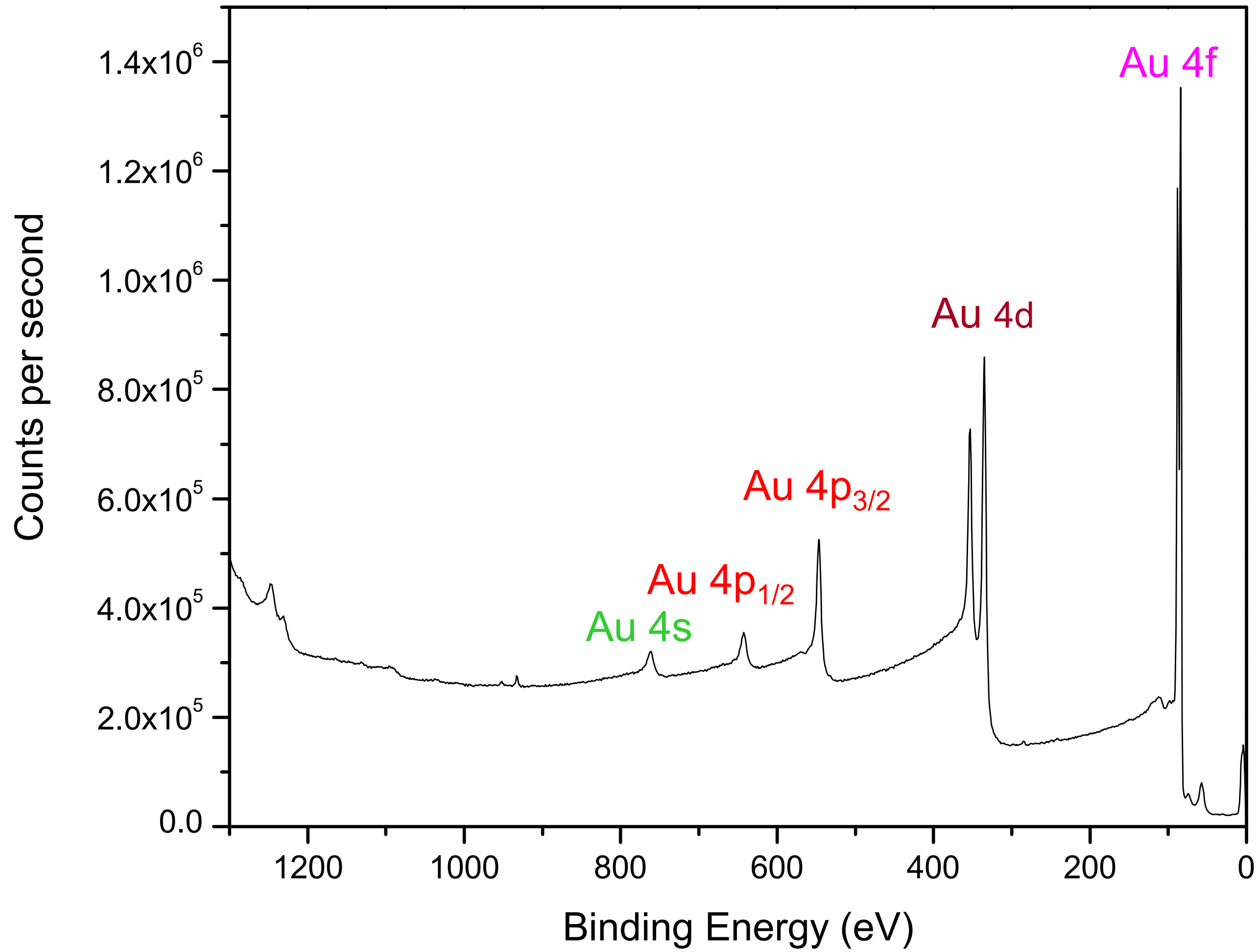
ϕ = work function to remove the electron from the surface



Courtesy of J. Shallenberger

XPS Survey Spectra of Gold foil

note peaks have discrete, well defined energies



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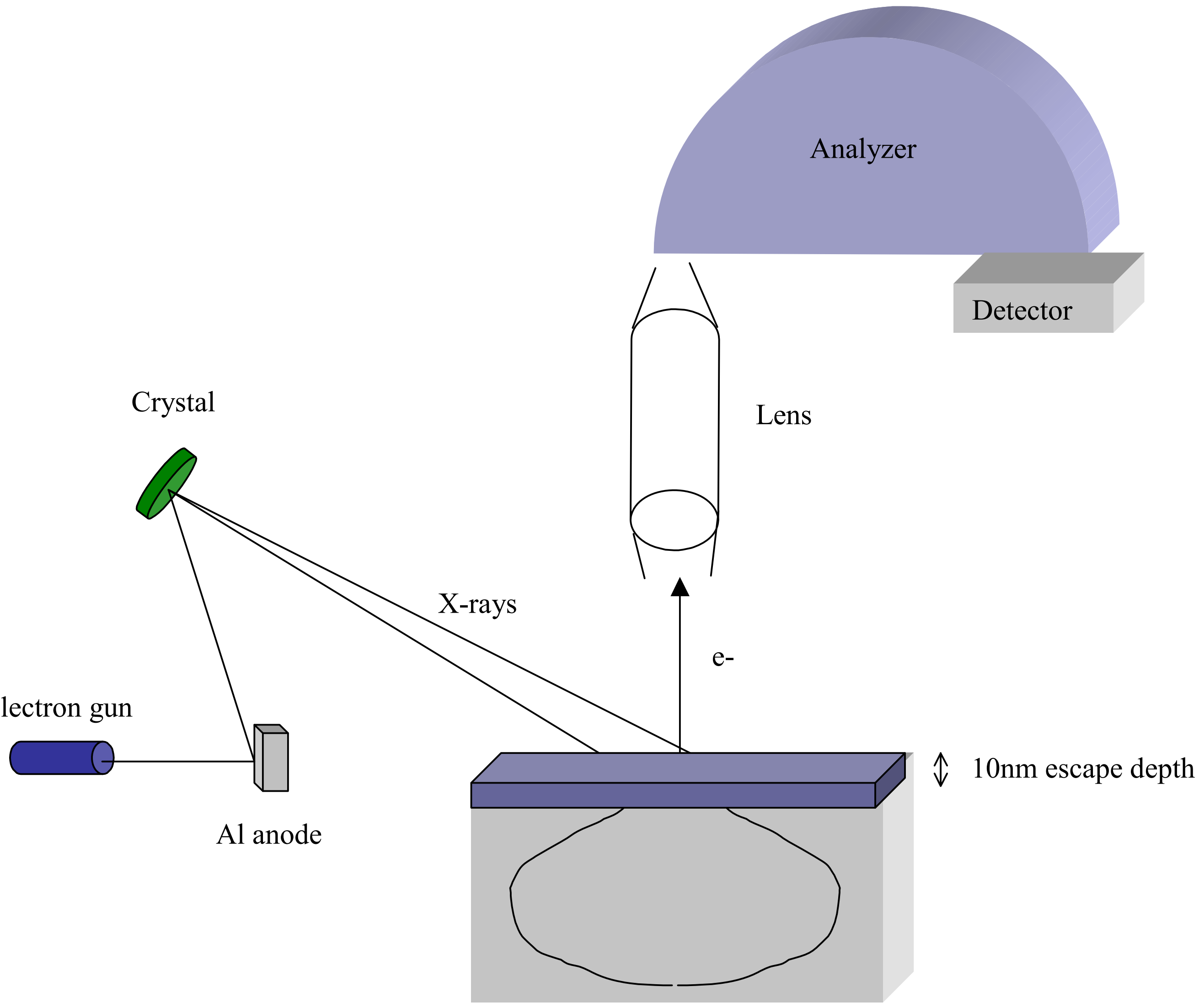
XPS Strengths and Limitations

- Strengths
  - Can detect Li-U
  - Surface sensitive (1-10nm sampling depth)
  - Sensitive to differences in chemical environment
  - Quantitative without standards
  - Works well on insulating materials
- Limitations
  - Poor lateral resolution (~10 μm)
  - Surface sensitive
  - Detection limit ~0.1% atomic
  - Cannot detect H

Courtesy of J. Shallenberger

The XPS Experiment

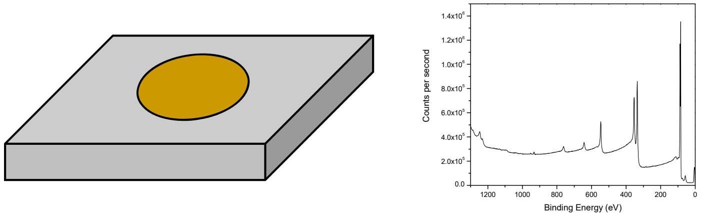


Types of XPS data

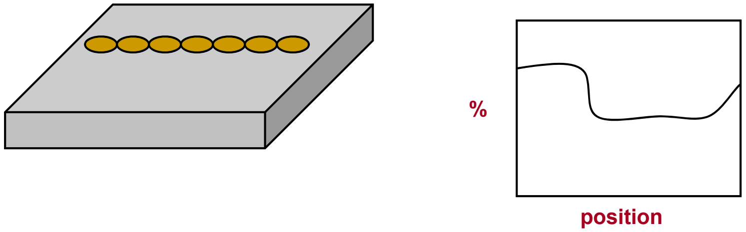
- Spectra
  - Survey – a wide energy scan to see all elemental lines
  - High resolution scans – narrow energy scans to look at chemical bonding for specific elemental lines
- Depth profiles
  - Sputter depth profiles for composition vs. depth up to a few μm
- XPS maps
  - Elemental or bonding information images with ~10 μm resolution

Modes of data acquisition

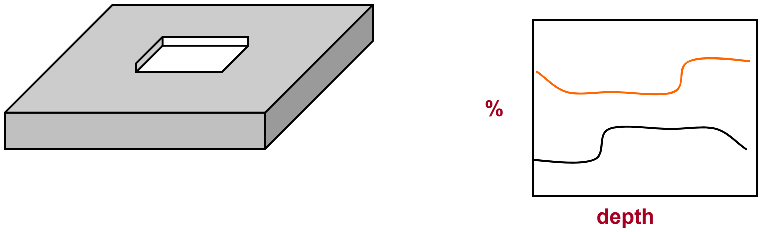
Point mode (spectra)
Most common analysis approach;
variable analysis size



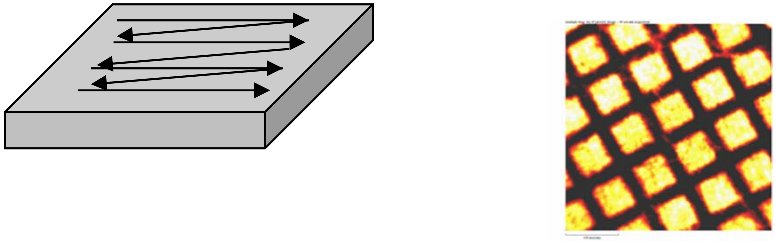
Line scan (1-D surface scan)



Depth Profile

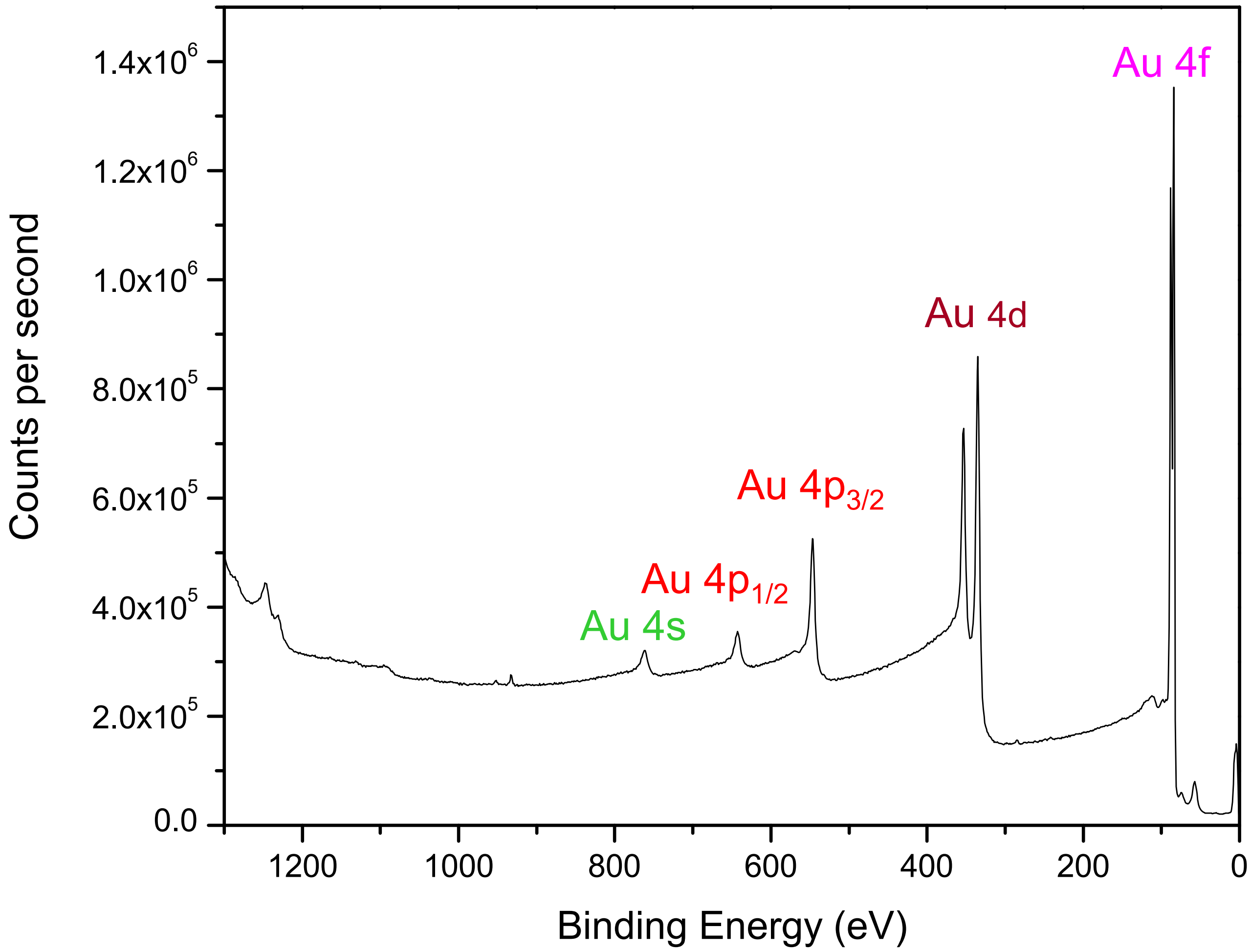


Mapping (2-D surface image)



XPS Survey Spectra of Gold foil

note peaks have discrete, well defined energies



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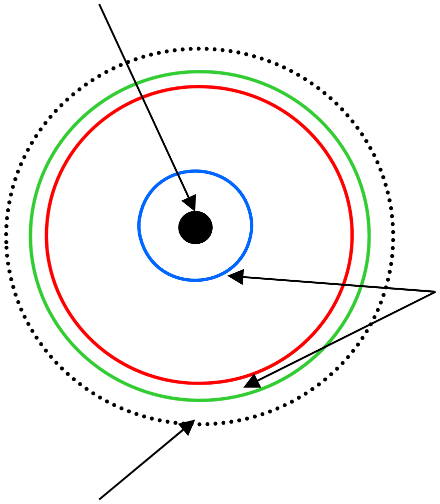
Gold electronic structure

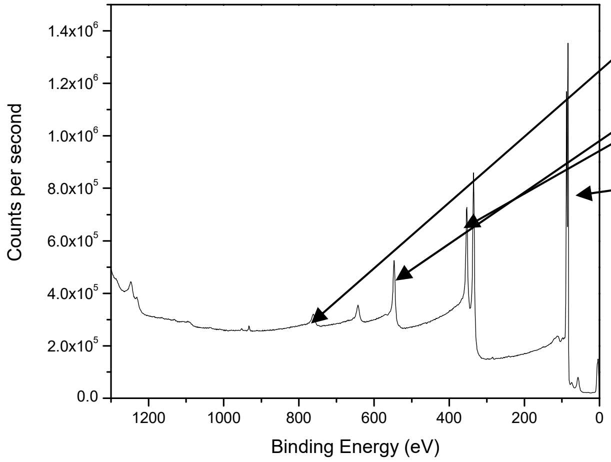


nucleus

core electrons

valence electrons

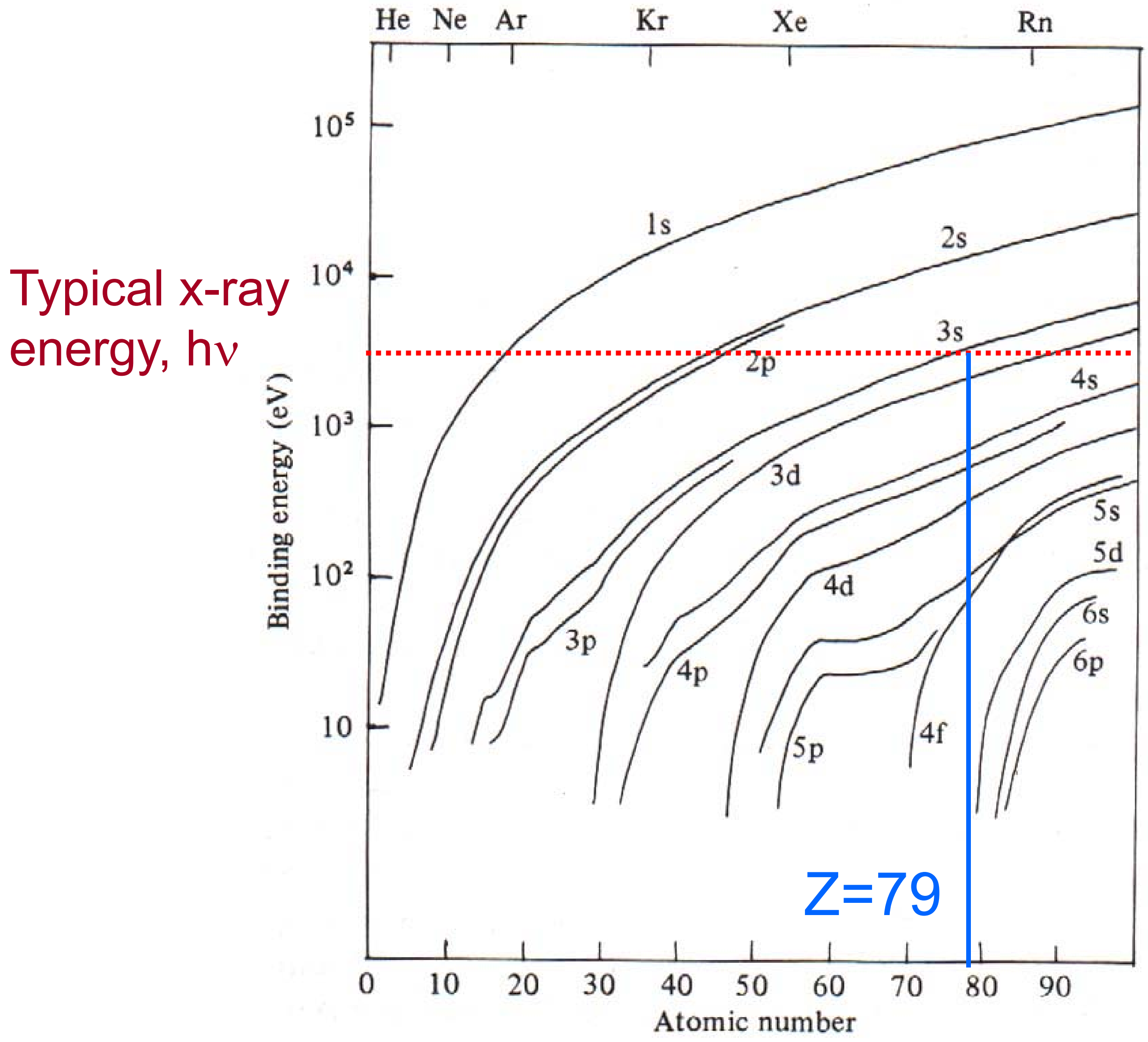
$$\mathrm{Au} = [\mathrm{Ar}]\ 3d^{10}4s^{2}4p^{4}4d^{10}5s^{2}5p^{4}4f^{14}5d^{10}6s^{1}$$



Orbital	Binding energy
$3d_{3/2}$	2291
$3d_{5/2}$	2206
4s	762
$4p_{1/2}$	643
$4p_{3/2}$	546
$4d_{3/2}$	353
$4d_{1/2}$	335
5s	107
$4f_{5/2}$	88
$4f_{7/2}$	84
$5p_{1/2}$	74
$5p_{3/2}$	57

Courtesy of J. Shallenberger

XPS capable of identifying Li-U



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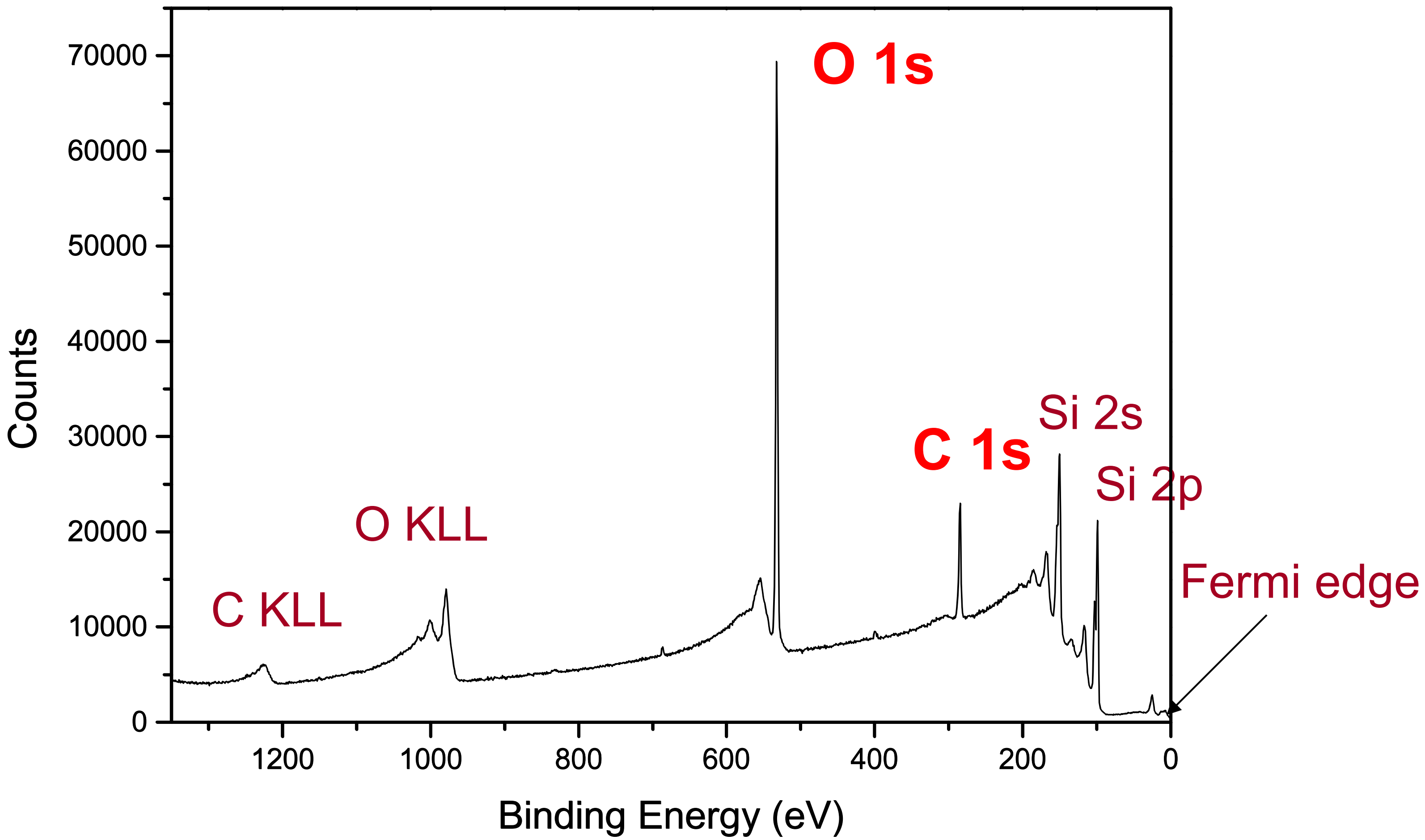
Photoelectron spectrum of silicon wafer

Photoelectron spectrum of silicon wafer



Always see C and O, due to high surface sensitivity

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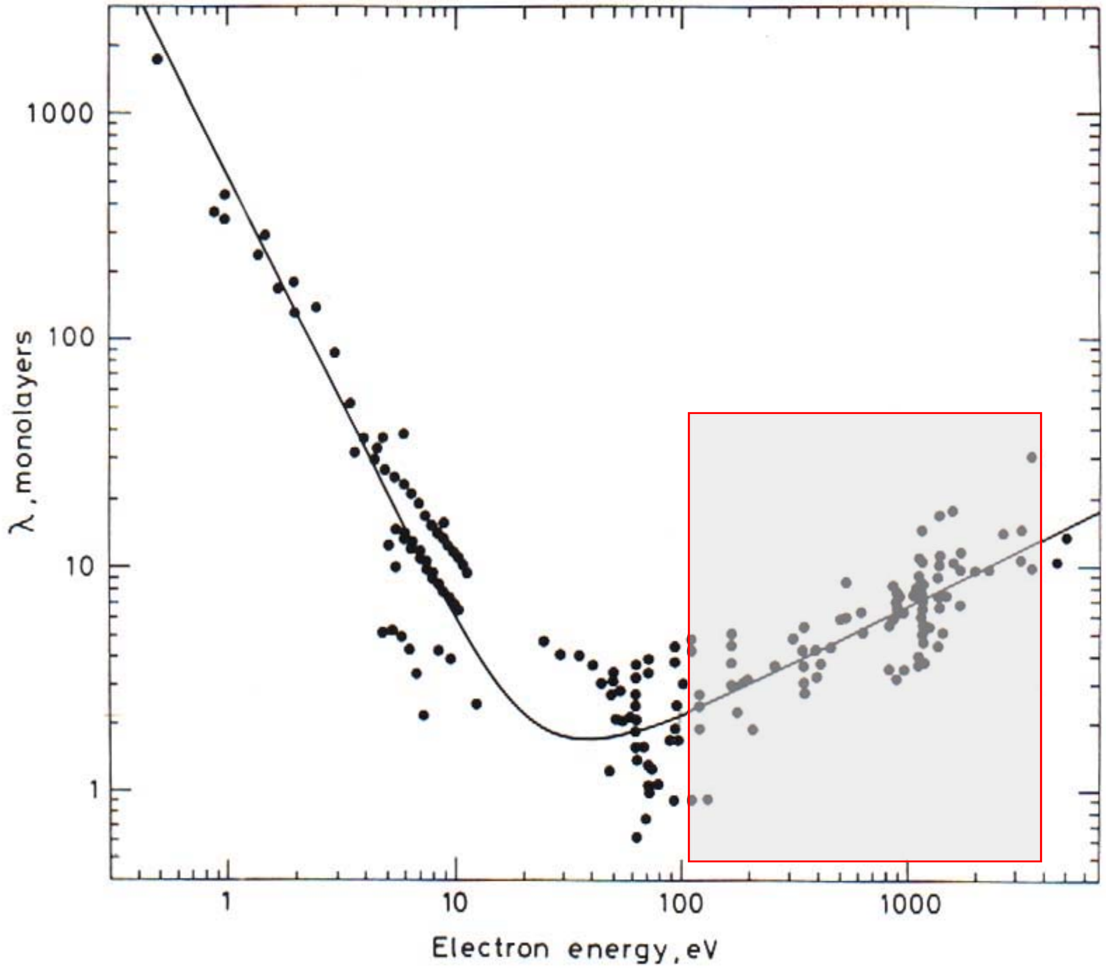
Surface Sensitivity

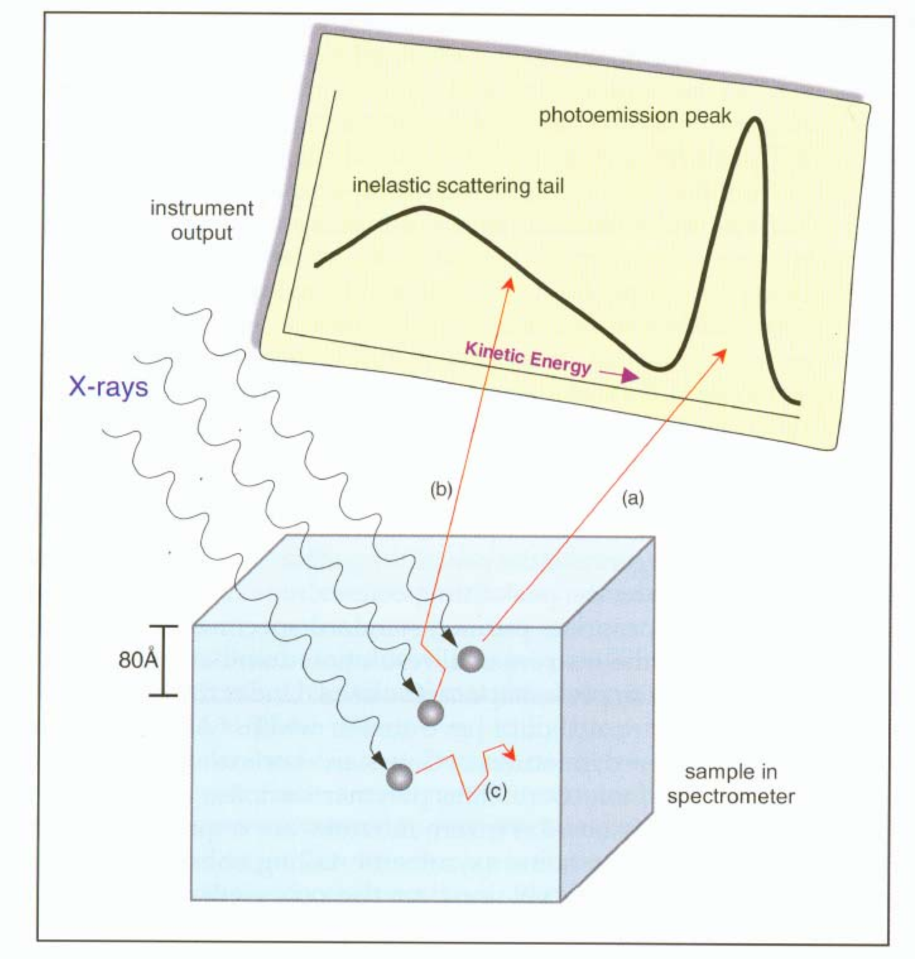


- XPS is surface sensitive because an electron with kinetic energy < 1,500 eV will NOT travel very far through a solid

from Briggs and Seah, Practical Surface Analysis 2nd Edition John Wiley & Sons (Chichester) 1990, p. 207.

Courtesy of J. Shallenberger

Surface Sensitivity



- X-rays penetrate deeply into sample causing electron emission
- Only electrons emitted near the surface that have escaped with no energy loss will contribute to the photoemission peak
- Some electrons have experienced inelastic collisions prior to escaping the sample surface and will present as a background in the spectrum
- Electrons that are too deep have insufficient energy to escape the surface
- Analytical depth is determined by the distance a photoelectron can travel without the loss of energy

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Chemical Shift

- Binding energy of core electrons can change when the chemical environment changes
- Generally, the binding energies of core levels increase when valence electrons are removed from an atom
- Binding energies of core levels decrease when valence electrons are added to an atom

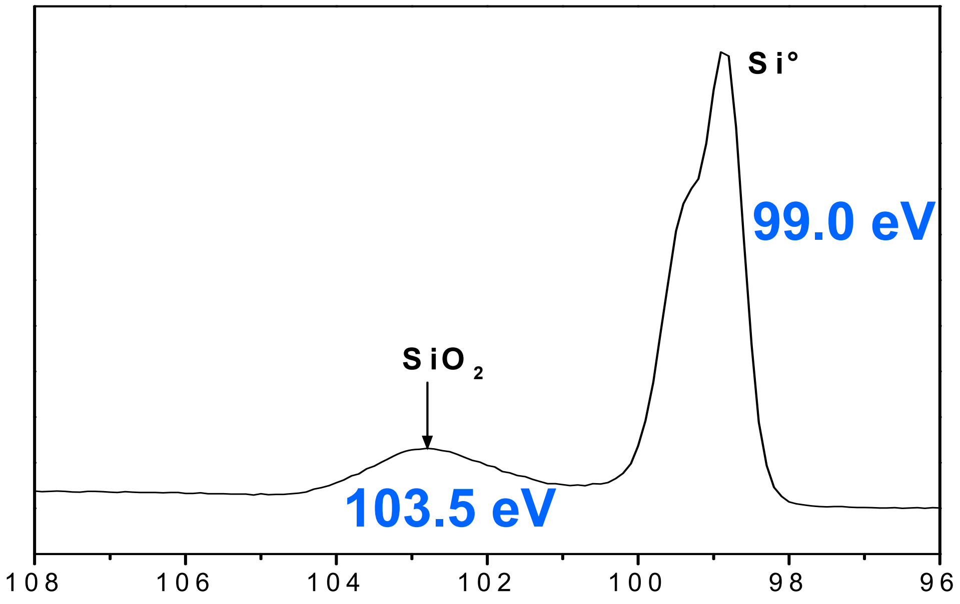
From: U. Dayton J. Grant XPS short course

General observations in chemical shifts

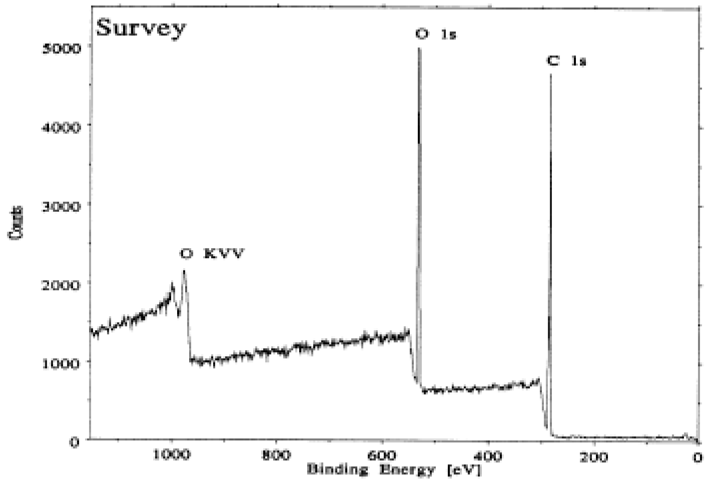
(1) higher valence oxidation state species has electrons bound with higher energy compared with more reduced state

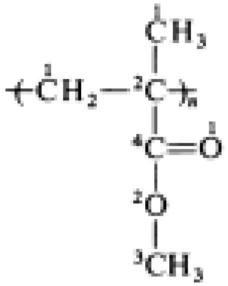
(2) In atoms with same formal valence state, BE increases with electronegativity of neighboring atoms

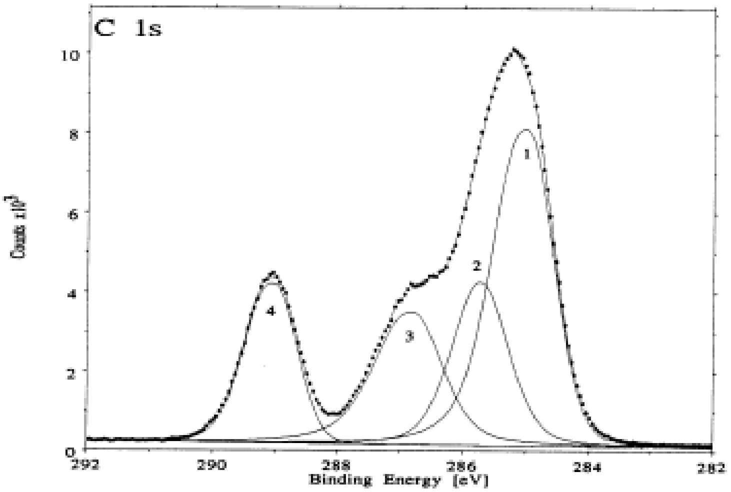
High resolution spectrum

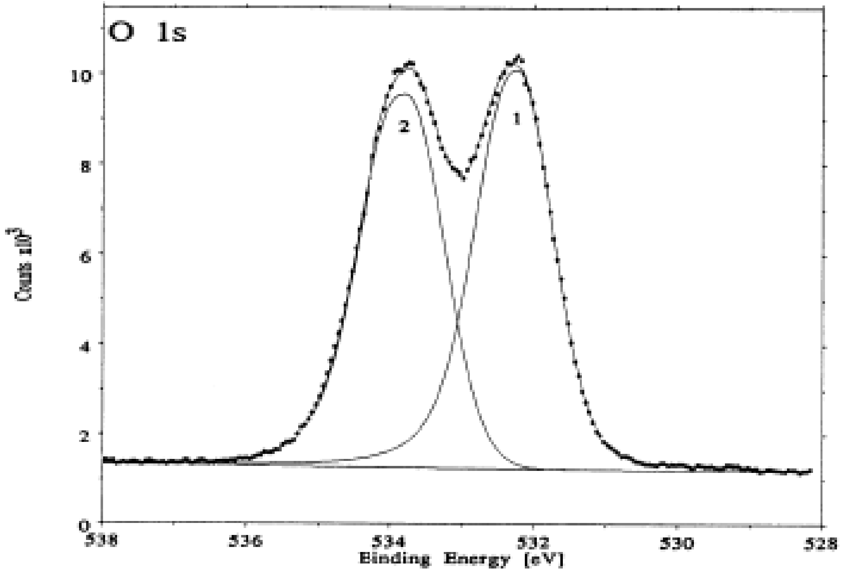


XPS of Poly (methyl methacrylate) PMMA





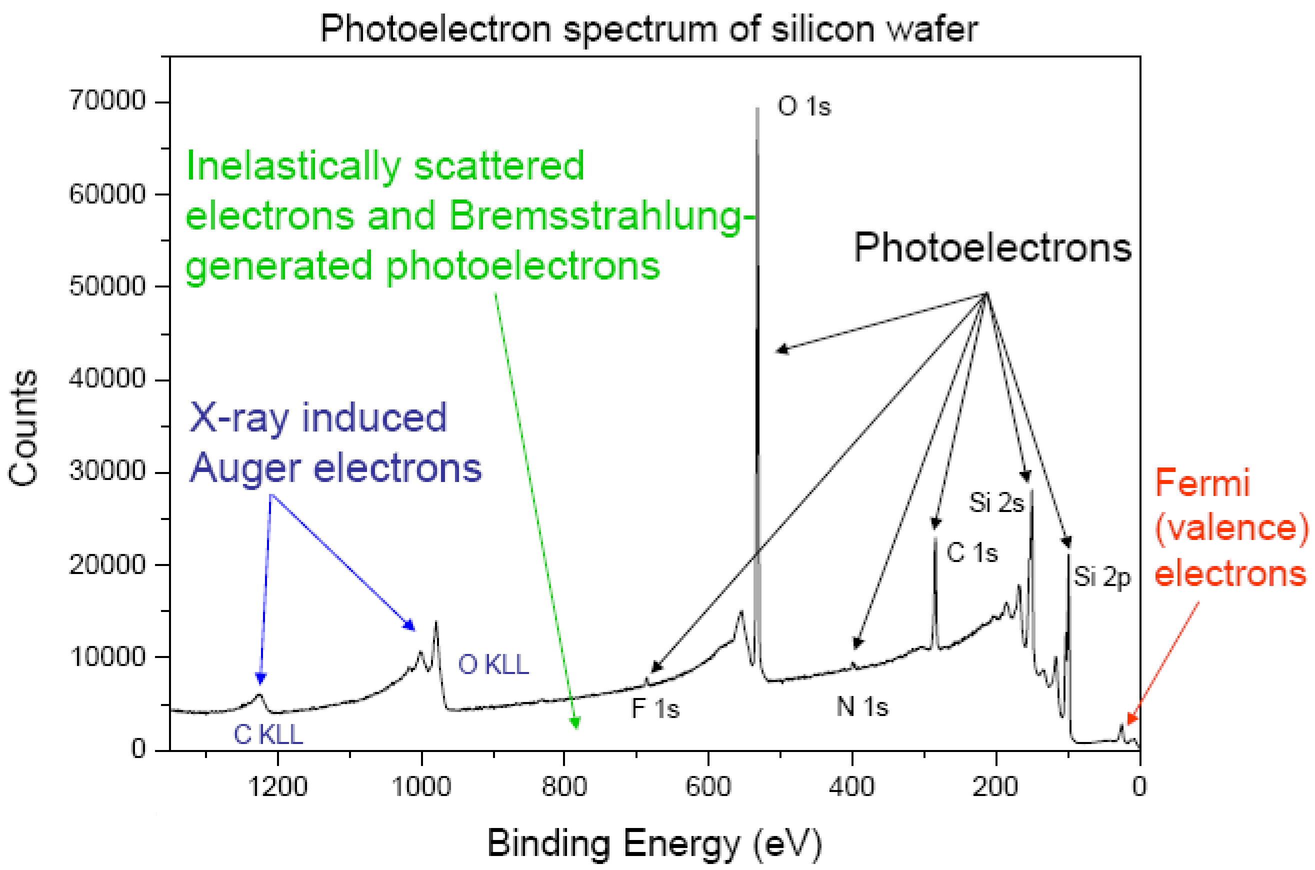




XPS of Polymers Database ed: G. Beamson and D. Briggs

Spectral Features in XPS

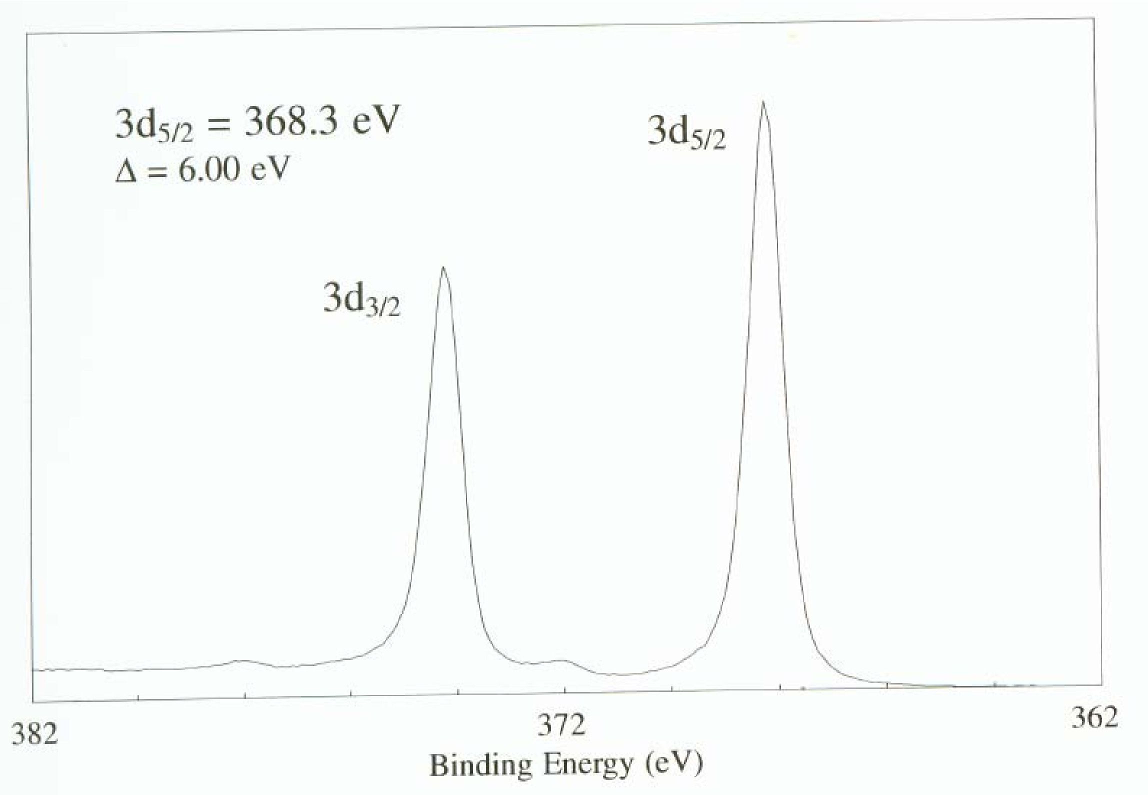
XPS Spectral Features



1-5% of detected electrons are photoelectrons with no loss of energy

Courtesy of J. Shallenberger

Spin orbit splittings: Ag 3d peak

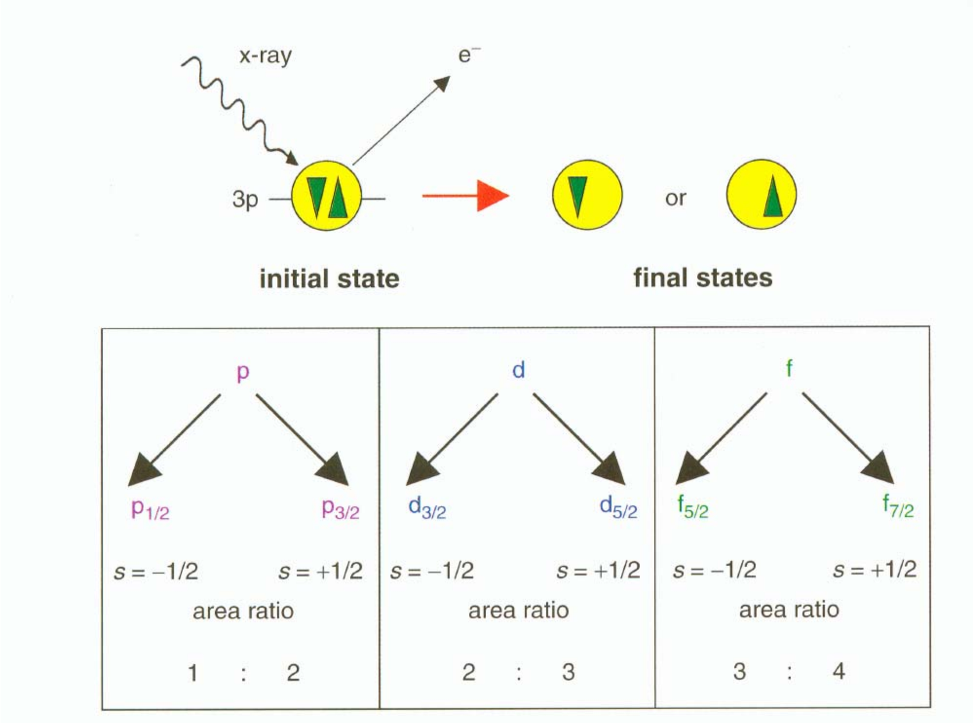


Subshell	***j* value**	**Area ratio**
s	½	-
p	½, 3/2	1:2
d	3/2, 5/2	2:3
f	5/2, 7/2	3:4

Peak ratios given by: 2j+1

Physical Electronics Handbook of X-ray Photoelectron Spectroscopy

Spin-Orbit Splitting



- After electron emission from a 3p orbital subshell, remaining electron can have either spin-up or spin-down state
- Magnetic interaction between these electrons and the orbital angular momentum leads to spin-orbit splitting

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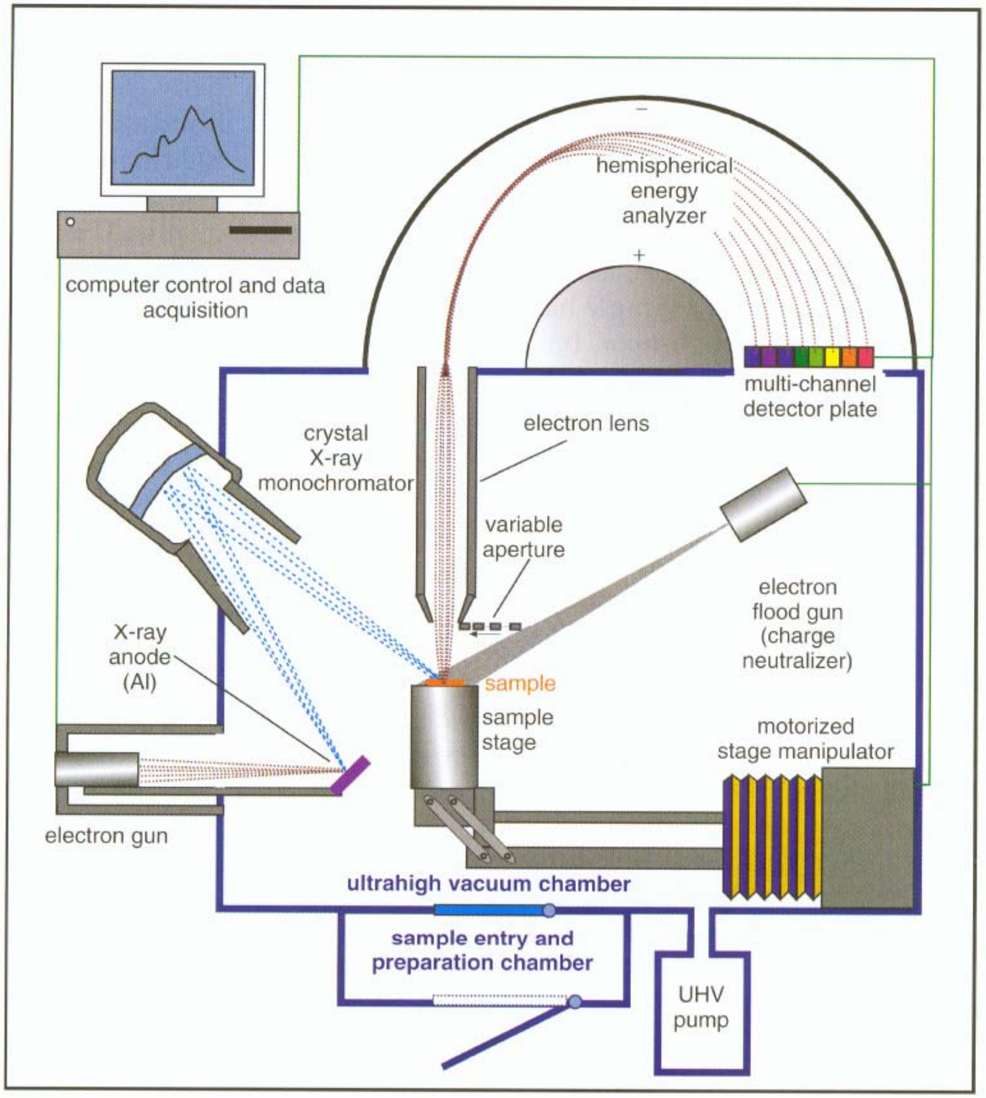
XPS instrumentation



Vickerman, chapter 3

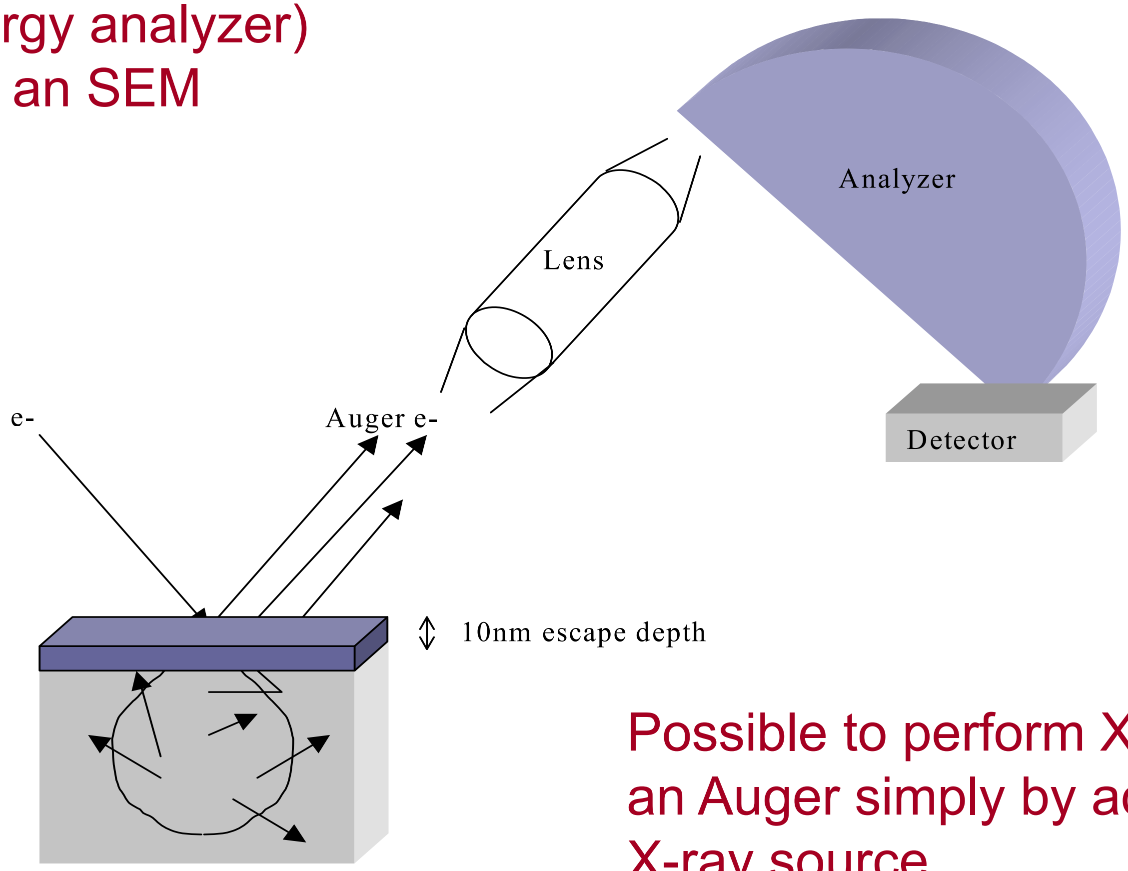
XPS Summary

- Elemental sensitivity
  - Range Li – U
  - Excellent specificity
  - Detection limits 0.1 – 1 atomic %
- Spatial resolution
  - Few μm for commercial systems
- Analysis depth
  - Depends on material and photoelectron energy
  - Can sputter depth profile for larger depths
- Quantitative
  - Homogeneous samples easier
  - Need reliable sensitivity factors
- Chemical information
  - Chemical shift can give bonding information

From: U. Dayton J. Grant XPS short course

The Auger Experiment

Auger is essentially an XPS (electron energy analyzer) hooked up to an SEM



Possible to perform XPS on an Auger simply by adding an X-ray source

Auger Process

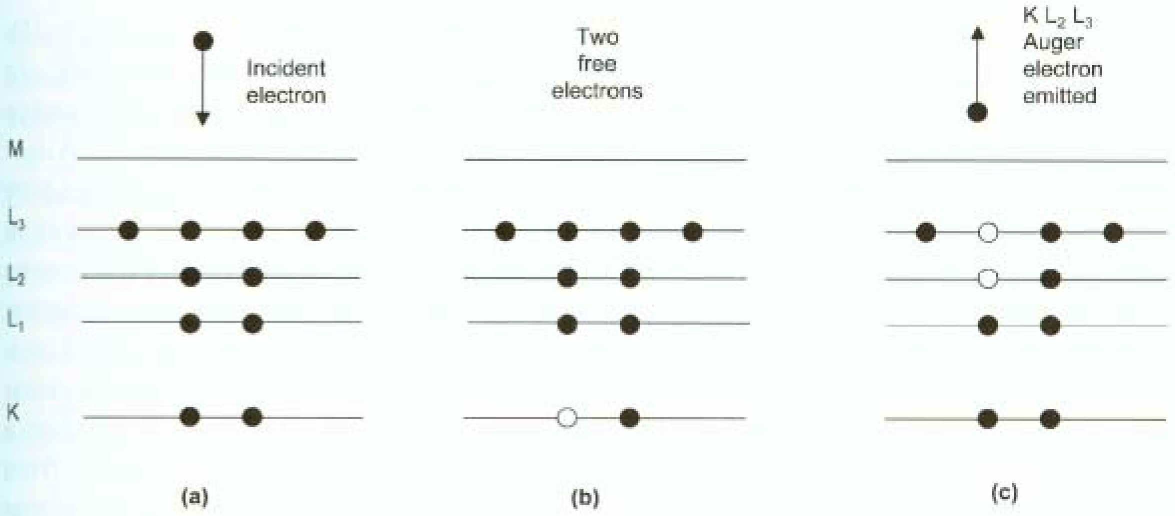


Figure 1. Illustration of the KL_2L_3 Auger process: (a) atom showing electrons present in filled K and L levels before an electron is removed from the K level, (b) after removal of an electron from the K level and (c) following the Auger process where a KL_2L_3 Auger electron is emitted. In (c) one L level electron fills the K vacancy and the other L level electron is ejected due to the energy available on filling the K level.

Auger Summary

- Elemental sensitivity
  - Range Li – U
  - Excellent specificity
  - Sensitivity factor variation is ~100
  - Detection limits 0.1 – 1 atomic %
- Spatial resolution
  - 10-20 nm for commercial systems
- Analysis depth
  - Depends on material and Auger electron energy
  - Can sputter depth profile for larger depths
- Quantitative
  - Not as straightforward as XPS
  - Need reliable sensitivity factors
- Chemical information
  - Chemical shift in some cases
- Beam damage
  - More significant problem vs. XPS
- Sample charging is an issue

From: U. Dayton J. Grant XPS short course

Auger vs. XPS

- XPS better able to analyze insulating materials
- Spot size is orders of magnitude smaller with AES allowing chemical analysis of nm size spots
- Narrow XPS peaks allow chemical analysis
- High resolution elemental maps possible with AES
- Both capable of elemental depth profiling

Courtesy of J. Shallenberger

Auger and XPS

- Similar
  - Surface sensitivity (all of the discussion about IMFP, mean escape depth, etc. holds for the Auger electrons
  - Kinetic energies are typically 100ev – 2kV
  - Cost of instrument ($500K - $1M)
  - Typically same type of analyzer
  - Detection limits
  - Elements detected (Li-U)
  - Depth profiling by sputtering
- Different
  - Excitation source is electrons
  - Multi-electron process
  - Much higher lateral resolution (10nm vs. 10,000 nm)
  - Much higher background
  - More typically used for elemental information
  - Higher likelihood of beam damage from e-beam

Electron Spectroscopy = Surface Analysis

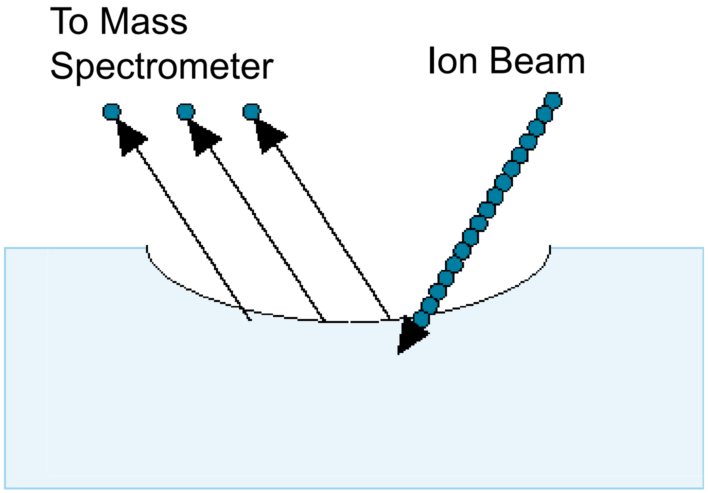
- Identification of elements present at the surface – qualitative analysis
- Quantitative analysis of elements at the surface
- Chemical bonding information
- Distribution of elements across the surface – elemental image or map
- Change in composition with depth – depth profile

Electron Spectroscopy Key ideas to take away

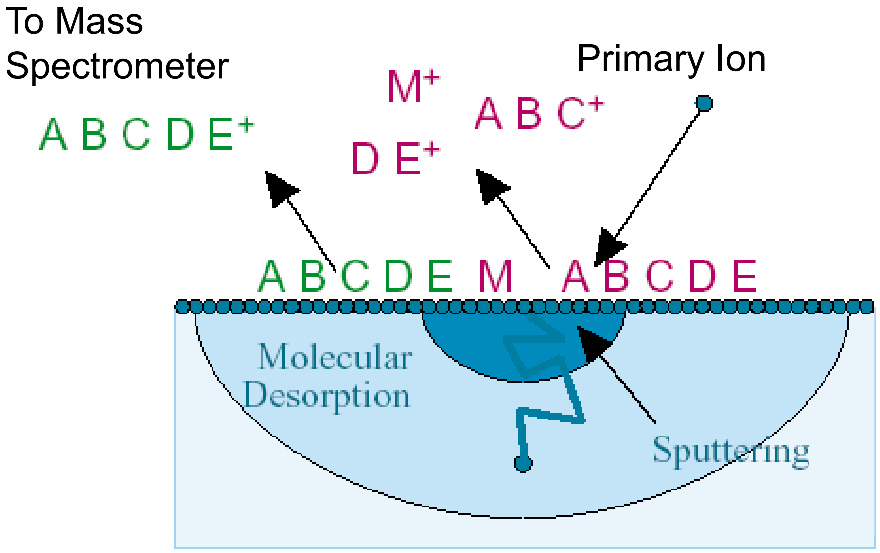
- Electron spectroscopy provides detection limits to ~0.1% atomic
- Both XPS and Auger are very surface sensitive (top <10 nm)
- Auger has much better (~10nm) lateral resolution than XPS (1 – 10 um)
- XPS gives chemical bonding information
- Auger and XPS are useful for surveys of unknown contamination
- When combined with ion sputtering can perform compositional depth profiling

Dynamic and Static Modes of Operation

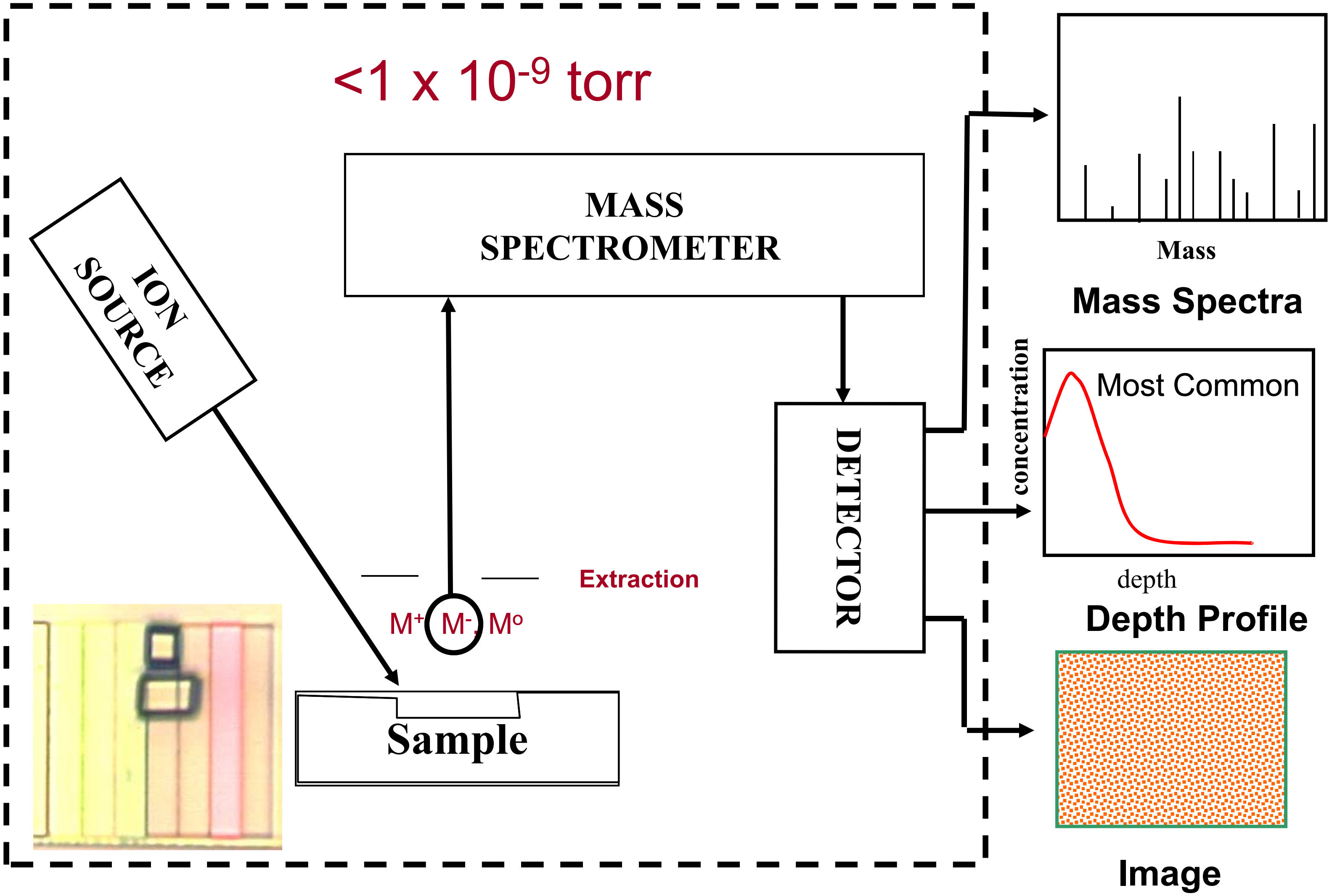
Dynamic SIMS



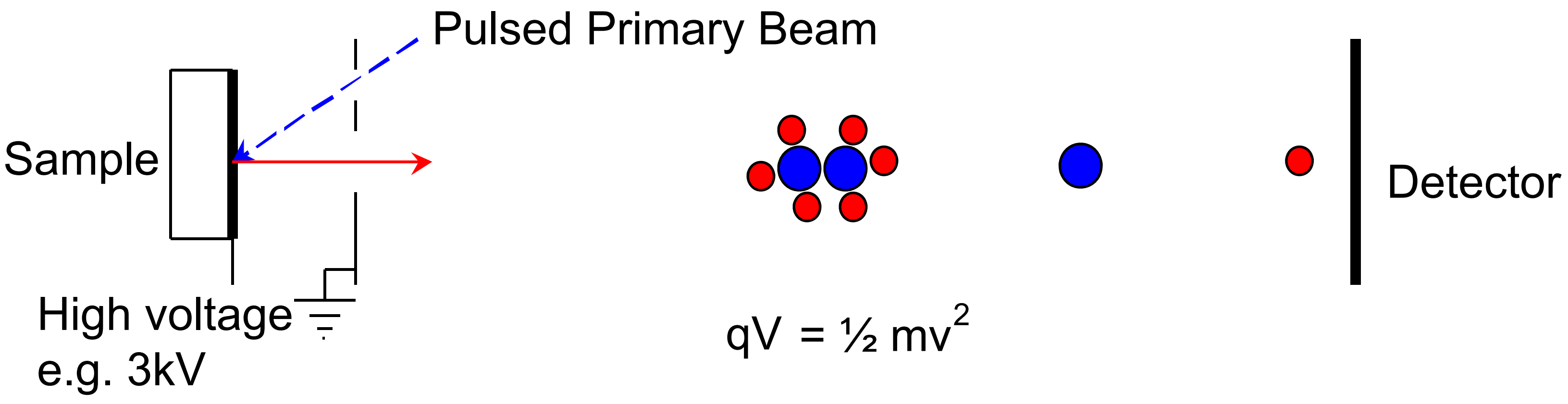
Static SIMS



SIMS Technique



Time-of-Flight SIMS: Basic Principles



$qV = \frac{1}{2} mv^2$

Flight time of each ion is recorded: $t = k(m)^{1/2}$

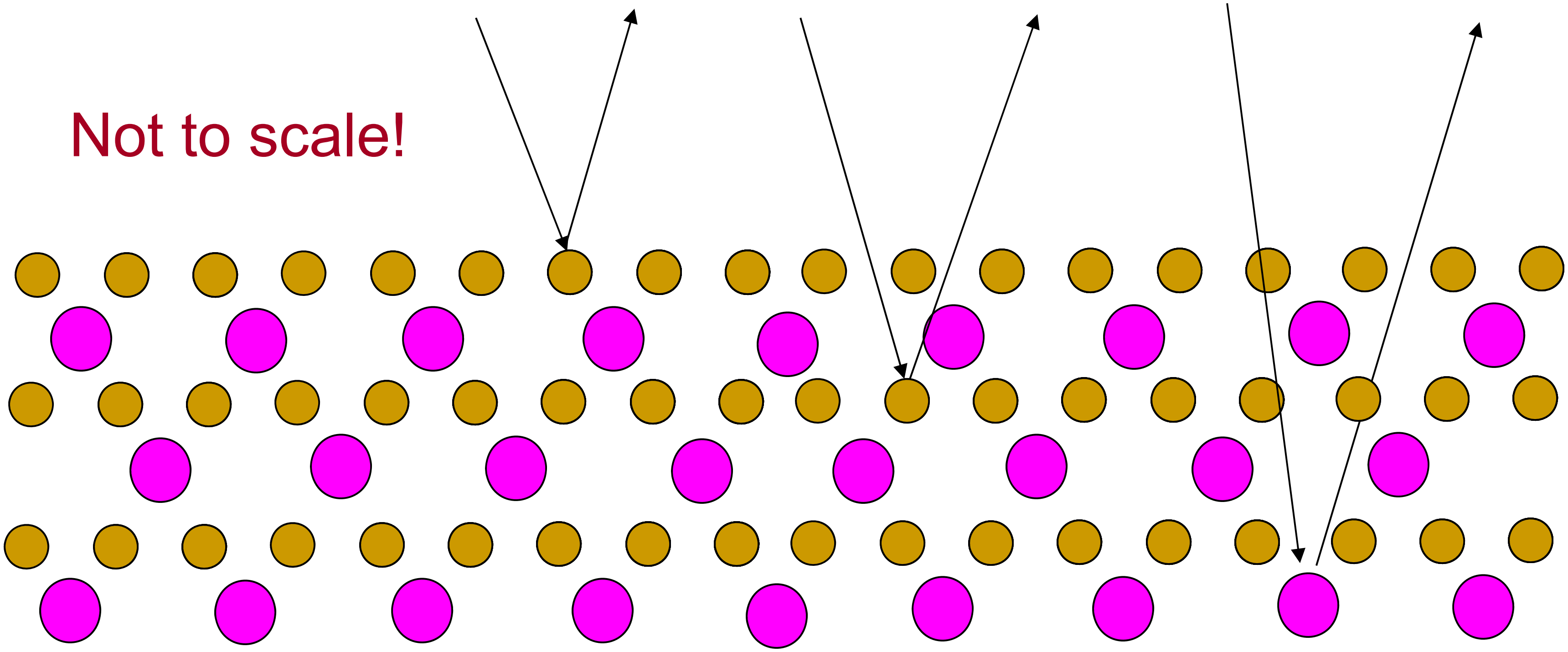
Convert time axis to mass by rearrangement: $m = at^2 + b$

- Quasi-parallel detection of entire mass spectrum
- Unlimited mass range

Courtesy of EAG

Scattering Methods

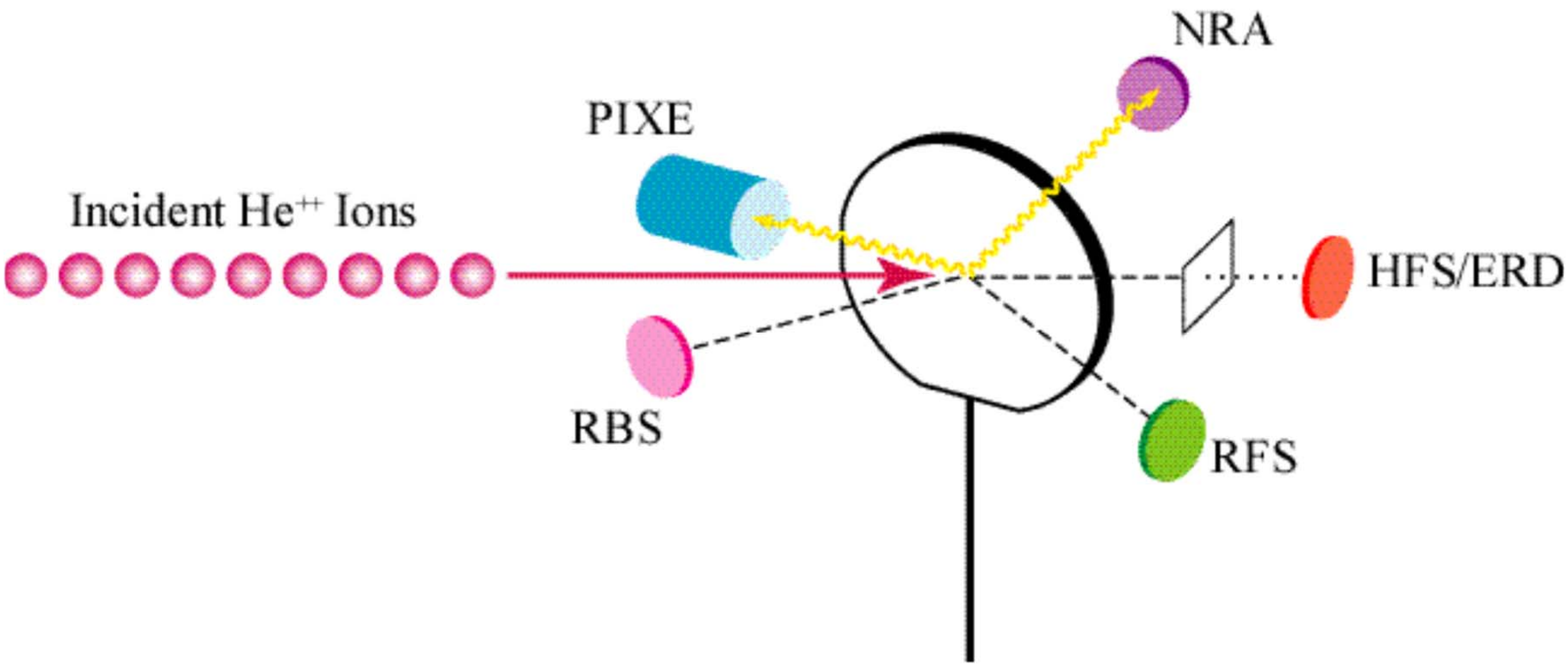
Technique	ISS/LEIS	MEIS	RBS
Ions	1-2kV He^+ or Ne^+	50-500kV H^+ or He^+	1-3MeV H^+ or He^+
Depth resolution	Top surface	0.3-1nm	5-50nm
Maximum depth	Surface	Surface-50nm	2-20μm



Not to scale!

MeV Ion Beam Processes

Techniques



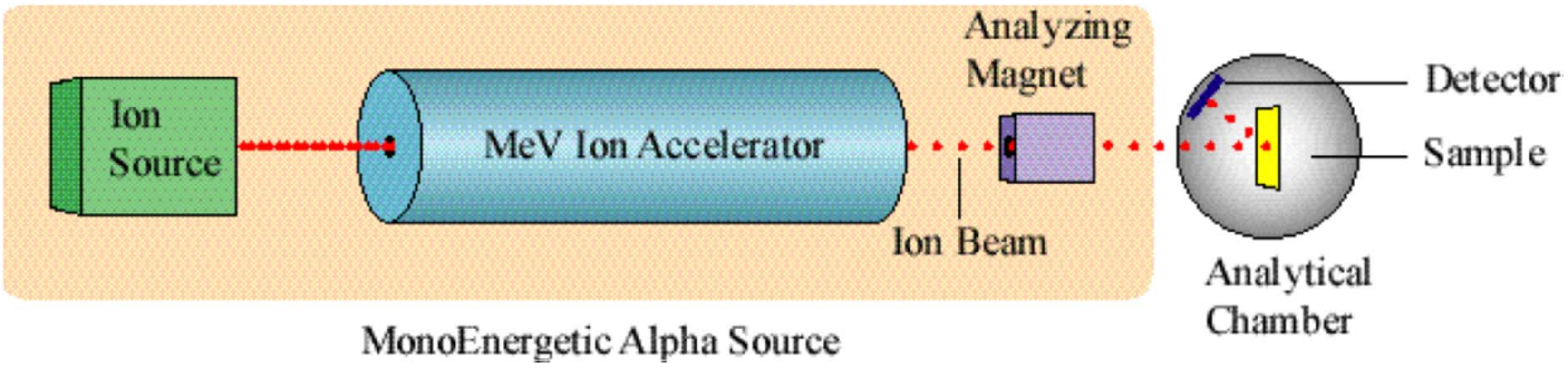
Courtesy of EAG

RBS Accelerator System

MODEL 5SDH-4 PELLETRON ACCELERATOR

Instrument Configuration

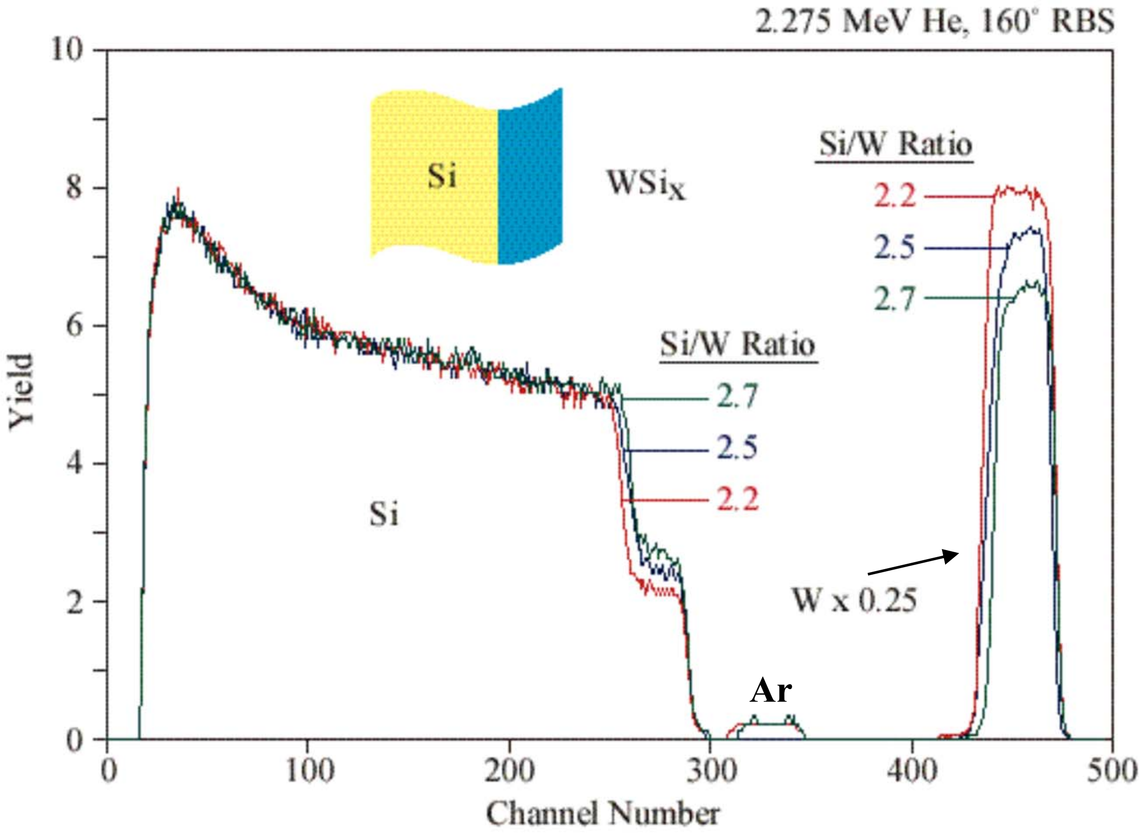
- MeV ions from an electrostatic accelerator are focused on a sample in a vacuum chamber for analysis.
- Typically, 2 MeV He^{++} ions are used.



Courtesy of EAG

Analysis of Tungsten Silicide

Comparison of Three WSi_x Films



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