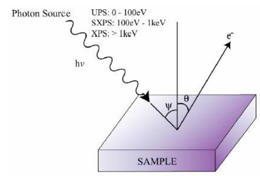
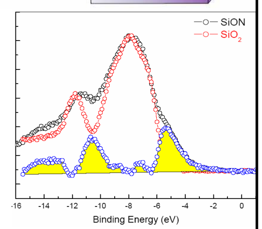
Lecture 5

X-ray Photoemission Spectroscopy (XPS)

5. Photoemission Spectroscopy (XPS)
   - 5.1 Principles
   - 5.2 Interpretation
   - 5.3 Instrumentation
   - 5.4 XPS vs UV Photoelectron Spectroscopy (UPS)
   - 5.5 Auger Electron Spectroscopy (AES)
   - 5.6 Quantitative Analysis

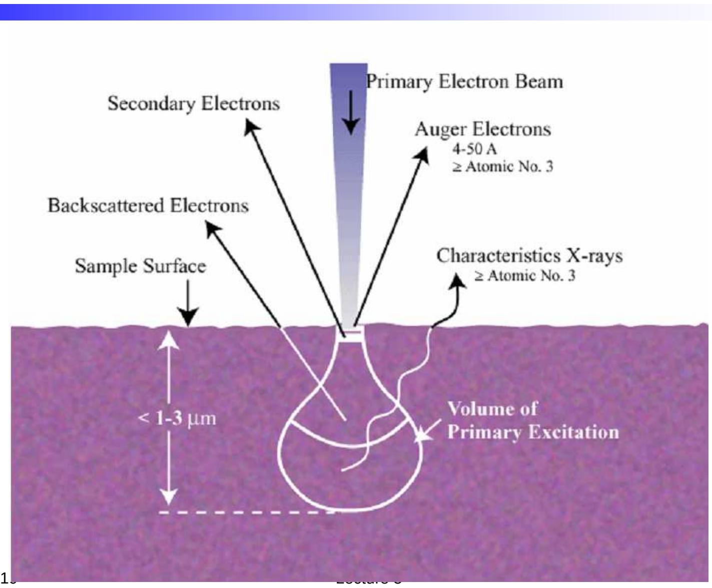




References:

1) Zangwill; Chapter 2, pp. 20-24 and 4
2) Kolasinski, Chapter 2.6
3) Vickerman, Chapter 2 and 3
4) Woodruff, and Delchar, Chapter 3
5) Briggs, Seah, *Practical Surface Analysis*. 1991; Vol. 1.
6) Luth, Chapter 6
7) http://www.phy.cuhk.edu.hk/course/surfacesci/index2.html
8) http://www.chem.qmul.ac.uk/surfaces/scc/
9) http://www.cem.msu.edu/~cem924sg/

Electron beam interactions with the sample



9.1 Electron Scattering

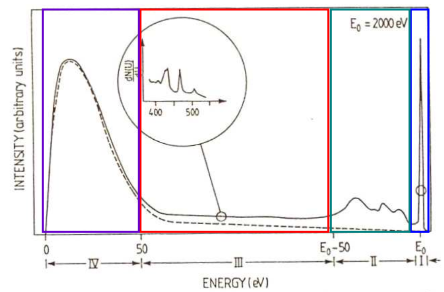
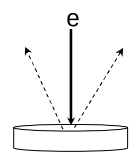


Fig. V.2. Qualitative large-scale overview of the energy distribution of electrons emitted from a surface which is irradiated by an electron beam of primary energy E_0.

Electron diffraction and microscopy:

Elastic backscattered e^-, ~ few % at 100eV

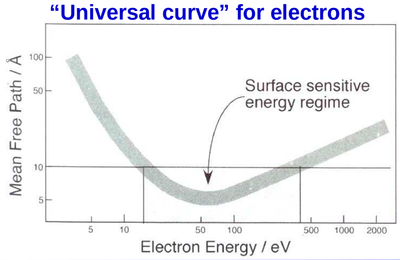


II: Interaction with plasmons

III: Inelastic electrons, Auger

IV: Secondary e^-s, <50eV

"Universal curve" for electrons



Short inelastic mean free path for electrons means that elastic scattering of electrons is <u>**very surface sensitive**</u>

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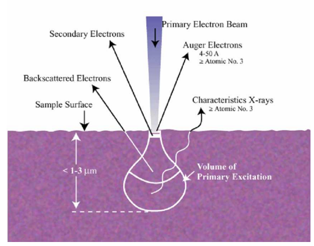
Electron beam-solid interactions

Secondary electrons (SEs): are produced by the interactions between energetic e's and weakly bonded valence e's of the sample



Backscattered electrons (BSEs): are primary e's leaving the specimen after a few large angle elastic scattering events

Auger electron: incident e^- kicks out an inner shell e^-, a vacant e^- state is formed; this inner shell vacant state is then filled by another e^- from a higher shell, and simultaneously the energy is transferred to another e^- that leaves the sample

Characteristic X-rays: emitted when a hole is created in the inner shell of an atom in the specimen due to inelastic e^- scattering, as it can recombine with an outer shell e^- (EDX)

Cathodoluminescene (CL): light emission arising from the recombination of e-h pairs induced by excitation of e's in the valence band during inelastic scattering in a semiconducting sample

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Electron Spectroscopy for Surface Analysis

Spectroscopy	Particles involved	Incident Energy	What you learn
XPS X-ray Photoemission	X-ray in e out	1-4 keV	Chemical state, composition
UPS UV Photoemission	UV photon e out	5-500 eV	Valence band
AES Auger Electron	e in, e out; radiationless process, filling of core hole	1-5 keV	Composition, depth profiling
IPS Inverse Photoemission	e in photon out	8-20eV	Unoccupied states
EELS Electron Energy Loss	e in e out	1-5 eV	Vibrations

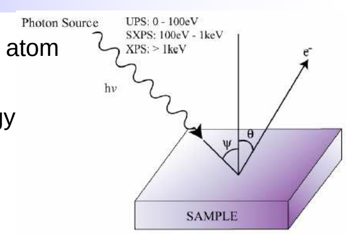
5.1 Photoemission Spectroscopy: Principles

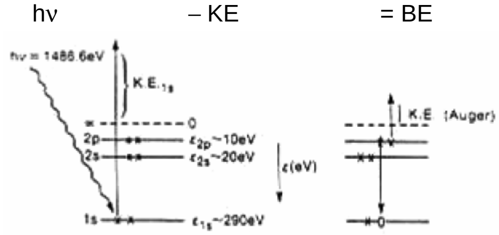
Electrons absorb X-ray photon and are ejected from atom

Energy balance:

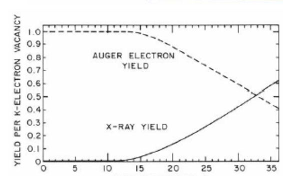
Photon energy – Kinetic Energy = Binding Energy

hν – KE = BE





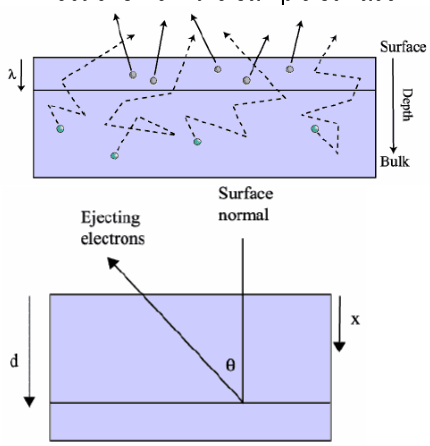
Photoemission Auger Decay



- Spectrum – Kinetic energy distribution of photoemitted electrons
- Different orbitals give different peaks in spectrum
- Peak intensities depend on photoionization cross section (largest for C 1s)
- Extra peak: Auger emission

Photoemission Spectroscopy: Basics

Electrons from the sample surface:



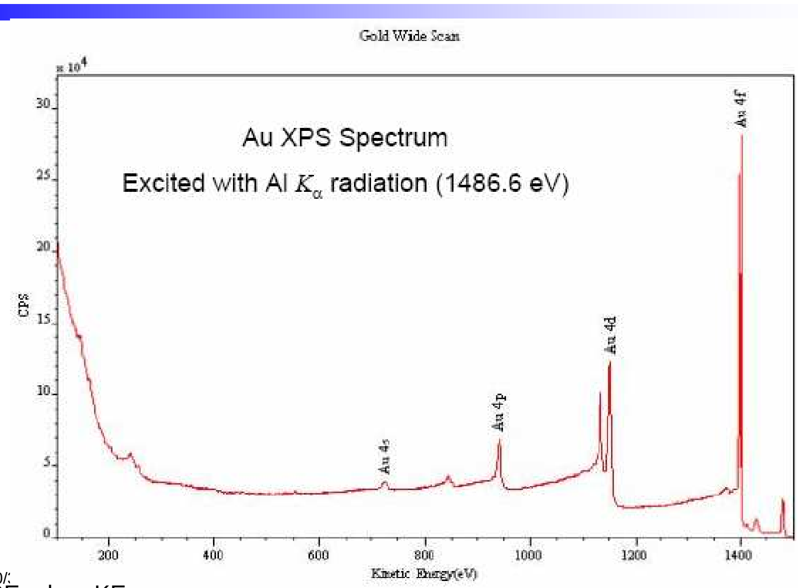
$$I(d) = K\int_0^d \exp\left(\frac{-x}{\lambda\cos\theta}\right)dx$$

Fraction of signal from various depth in term of λ

Depth	Equation	Fraction of signal (θ= 0)
λ	$\frac{I(\lambda)}{I(\infty)} = \frac{\int_0^\lambda \exp\left(\frac{-x}{\lambda\cos\theta}\right)dx}{\int_0^\infty \exp\left(\frac{-x}{\lambda\cos\theta}\right)dx}$	0.63
2λ	$\frac{I(2\lambda)}{I(\infty)} = \frac{\int_0^\lambda \exp\left(\frac{-x}{\lambda\cos\theta}\right)dx}{\int_0^\infty \exp\left(\frac{-x}{\lambda\cos\theta}\right)dx}$	0.86
3λ	$\frac{I(3\lambda)}{I(\infty)} = \frac{\int_0^\lambda \exp\left(\frac{-x}{\lambda\cos\theta}\right)dx}{\int_0^\infty \exp\left(\frac{-x}{\lambda\cos\theta}\right)dx}$	0.95

1. C. J. Powell, A. Jablonski, S. Tanuma, et al. *J. Electron Spectrosc. Relat. Phenom*, 68, P. 605 (1994).
2 D. F. Mitchell, K. B. Clark, W. N. Lennard, et al. , *Surf. Interface Anal.* 21, P. 44 (1994).

5.2 Typical XPS (ESCA) spectrum



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BE = hν - KE

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X-ray and spectroscopic notations

Principle quantum number:
n = 1, 2, 3, …
Orbital quantum number:
l =0, 1, 2, …, (n-1)
Spin quantum number:
s = ± ½
Total angular momentum:
$j = l + s = {}^1/_2, {}^3/_2, {}^5/_2$

Quantum numbers			X-ray suffix	X-ray level	Spectroscopic Level
n	*l*	*j*			
1	0	1/2	1	K	$1s_{1/2}$
2	0	1/2	1	L_1	$2s_{1/2}$
2	1	1/2	2	L_2	$2p_{1/2}$
2	1	3/2	3	L_3	$2p_{3/2}$
3	0	1/2	1	M_1	$3s_{1/2}$
3	1	1/2	2	M_2	$3p_{1/2}$
3	1	3/2	3	M_3	$3p_{3/2}$
3	2	3/2	4	M_4	$3d_{3/2}$
3	2	5/2	5	M_5	$3d_{5/2}$
Etc.			Etc.	Etc.	Etc.

Spin-orbit split doublets

Sub-shell	*j* values	Area ratio
s	1/2	-
p	½; 3/2	1: 2
d	3/2; 5/2	2: 3
f	5/2; 7/2	3: 4

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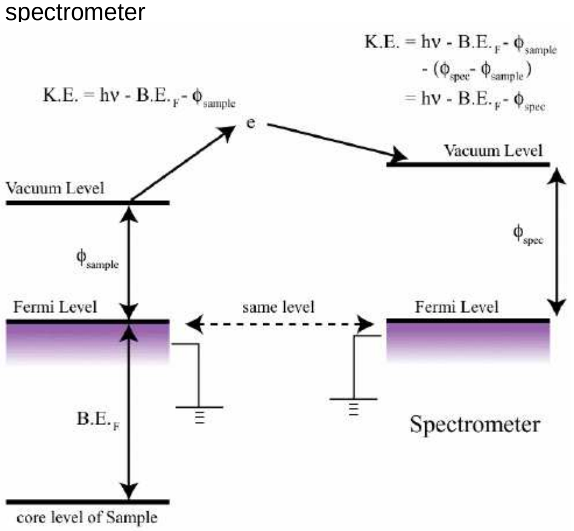
Binding energy reference in XPS

Energy level diagram for an electrically conductive sample grounded to the spectrometer



- common to calibrate the spectrometer by the photoelectron peaks of Au 4f $_{7/2}$, Ag $3d_{5/2}$ or Cu $2p_{3/2}$
- the Fermi levels of the sample and the spectrometer are aligned;
- KE of the photoelectrons is measured from the E_F of the spectrometer.

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Typical spectral features

Associate binding energies with orbital energies, BUT USE CAUTION!

Energy conservation: $E_i(N) + h\nu = E_f(N\text{-}1) + KE$

$\Rightarrow$ $h\nu - KE = E_f(N\text{-}1, k) - E_i(N) = E_B$

Binding energy is more properly associated with ionization energy.

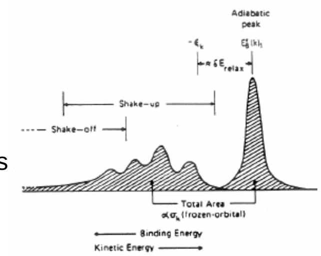
In HF approach, Koopmans' Theorem: $E_B = E_k$ (orbital energy of k^{th} level)

Formally correct within HF. Wrong when correlation effects are included.

ALSO: Photoexcitation is rapid event

$\Rightarrow$ sudden approximation

Gives rise to chemical shifts and plasmon peaks



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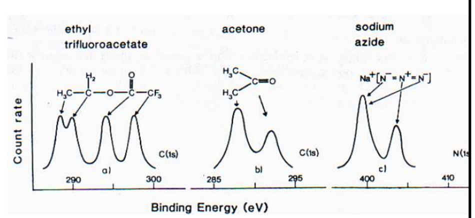
Qualitative results

A: Identify element

B: Chemical shifts of core levels:

Consider core levels of the same element in different chemical states:

$\Delta E_B = E_B(2) - E_B(1) = E_K(2) - E_K(1)$



Often correct to associate ΔE_B with change in local electrostatic potential due to change in electron density associated with chemical bonding ("initial state effects").

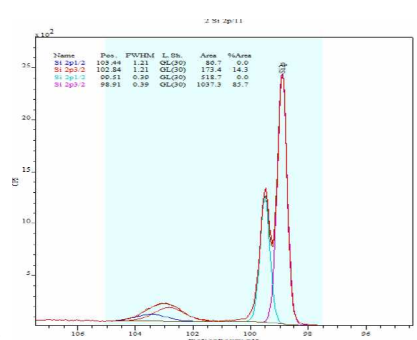
Peak Width:

ΔE measured as FWHM; if assume Gaussian:

$\Delta E = (\Delta E^2_{natural} + \Delta E^2_{photons} + \Delta E^2_{analyzer})^{1/2}$

Lifetime width: $\Gamma = \hbar/\tau$ for $\Gamma \sim 1$ eV, $\tau \sim 10^{-15}$ s

http://www.lasurface.com/database/liaisonxps.php



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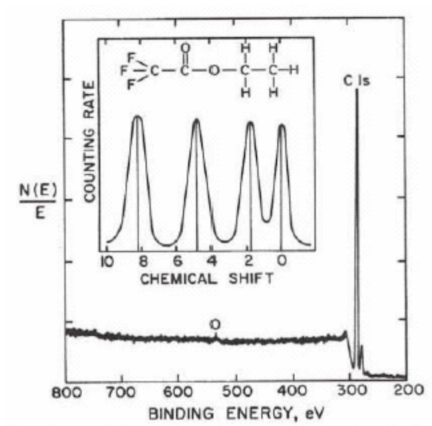
Chemical Shifts



- Carbon 1s chemical shifts in ethyl trifluoroacetate
- The four carbon lines correspond to the four atoms within the molecule

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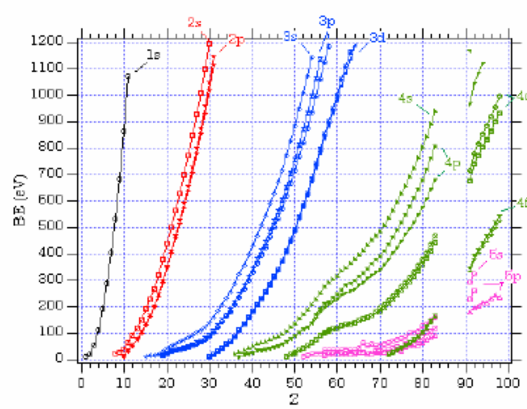
Peak Identification: Core level binding energies

XPS Photoelectron Binding Energies* versus Atomic Number

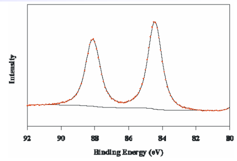
Where the same BE is quoted for different spin-orbit split subshells, the individual subshells are either not resolved or have a complex structure. Spin-orbit coupling: 2p1=$2p_{1/2}$, 2p3=$2p_{3/2}$ etc.

Z	1s	2s	2p1	2p3	3s	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3
1	14																		
2	21																		
3	56																		
4	113																		
5	191																		
6	287																		
7	402																		
8	531	23																	
9	686	30																	
10	863	41	14	14															
11	1072	64	31	31															
12		90	51	51															
13		119	74	74															
14		153	103	102															
15		191	134	133	14														
16		229	166	165	17														
17		270	201	199	17														
18		319	243	241	22														
19		378	296	293	33	17	17												
20		439	350	347	44	25	25												
21		501	407	402	53	31	31												
22		565	464	458	62	37	37												
23		630	523	515	69	40	40												
24		698	586	577	77	46	45												
25		770	652	641	83	49	48												



http://www.lasurface.com/database/elementxps.php

Quantification of XPS



Primary assumption for quantitative analysis: ionization probability (photoemission cross section) of a core level is nearly independent of valence state for a given element

⇒ intensity ∝ number of atoms in detection volume

$$I_A = \sigma_A(\hbar\omega)D(E_A)\int_{\gamma=0}^{\pi}\int_{\varphi=0}^{2\pi} L_A(\gamma)\int_{x,y} J_0(x,y)T(x,y,\gamma,\varphi,E_A)\int_x N_A(x,y,z)\exp\left(\frac{-z}{\lambda\cos\theta}\right)dxdydzd\gamma d\theta$$

where:

σ_A = photoionization cross section

$D(E_A)$ = detection efficiency of spectrometer at E_A

$L_A(\gamma)$ = angular asymmetry of photoemission intensity

γ = angle between incident X-rays and detector

$J_0(x,y)$ = flux of primary photons into surface at point (x,y)

T = analyzer transmission

ϕ = azimuthal angle

$N_A(x,y,z)$ = density of A atoms at (x,y,z)

λ_M = electron attenuation length of e's with energy E_A in matrix M

θ = detection angle (between sample normal and spectrometer)

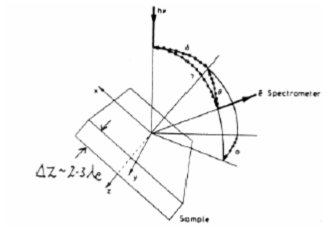


Figure 5.13 Geometry of the XPS analysis configuration

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Quantitative analysis

For small entrance aperture (fixed ϕ, γ) and uniform illuminated sample:

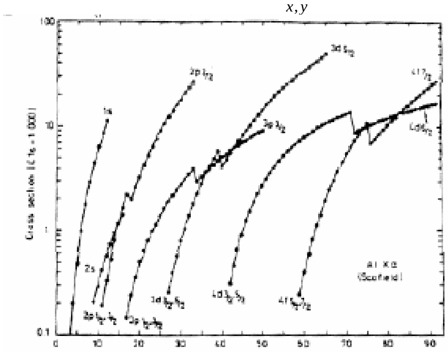
$$I_A = \sigma_A(\hbar\omega)D(E_A)L_A(\gamma_i)J_0 N_A \lambda_M(E_A)\cos\theta_i G(E_A)$$

Angles γ_i and θ_i are fixed by the sample geometry and $G(E_A) = \iint_{x,y} T(x,y,E_A)dxdy$

$G(E_A)$=product of area analyzed and analyzer transmission function

$D(E_A)$=const for spectrometers Operating at fixed pass energy

σ_A: well described by Scofield Calculation of cross-section



5.14 Calculated values of the cross-section $\sigma_A(\hbar\nu)$ for Al Kα radiation in terms of the C 1s cross-section. (After Scofield[16])

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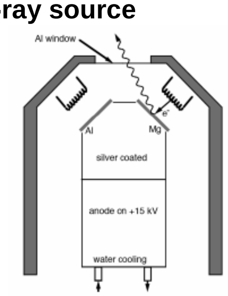
5.3 Photoemission Spectroscopy: Instrumentation

X-ray source

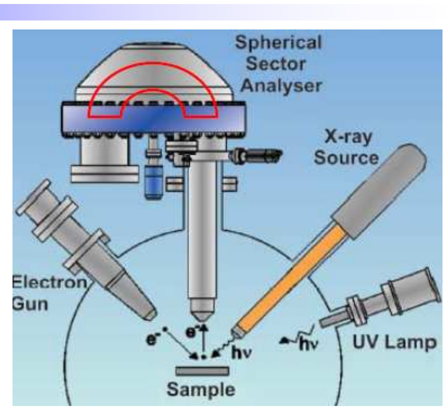


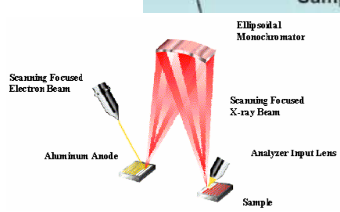
X-ray lines		
Line	Energy, eV	Width, eV
Ti L_α	395.3	3.0
Cu L_α	929.7	3.8
Mg K_α	1253.6	0.7
Al K_α	1486.6	0.85
Ti K_α	4510.0	2.0

How to choose the material for a soft X-ray source:
1. the line width must not limit the energy resolution;
2. the characteristic X-ray energy must be high enough to eject core electrons for an unambiguous analysis;
3. the photoionization cross section of e in different core levels varies with the wavelength of the X-ray, a suitable characteristic X-ray wavelength is crucial to obtain a strong enough photoelectron signal for analysis.

Instrumentation

Essential components:
- Sample: usually 1 cm^2
- X-ray source: Al 1486.6 eV;
  Mg 1256.6 eV
- Electron Energy Analyzer:
  100 mm radius concentric hemispherical analyzer (CHA); vary voltages to vary pass energy.
- Detector: electron multiplier (channeltron)
- Electronics, Computer
- Note: All in ultrahigh vacuum ($<10^{-8}$ Torr) ($<10^{-11}$ atm)
- State-of-the-art small spot ESCA: 5 µm spot size
  Sputtering gun for profiling



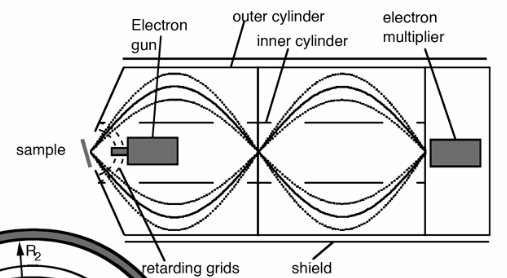


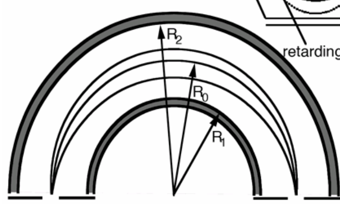
Electron Energy Analyzers

(a) Concentric Hemispherical Analyzer (CHA) and (b) (Double Pass) Cylindrical Mirror Analyser (CMA)

Advantages of CHA: higher resolution than CMA, convenient geometry

Disadvantages: small solid angle





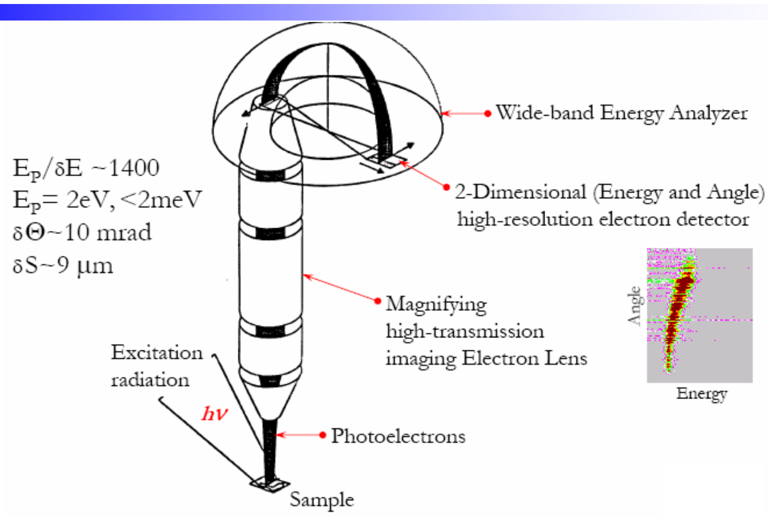
(a.)

Advantages of CMA: very large solid angle

Disadvantages: inconvenient geometry

(b.)

New electron energy analyzers with lens system



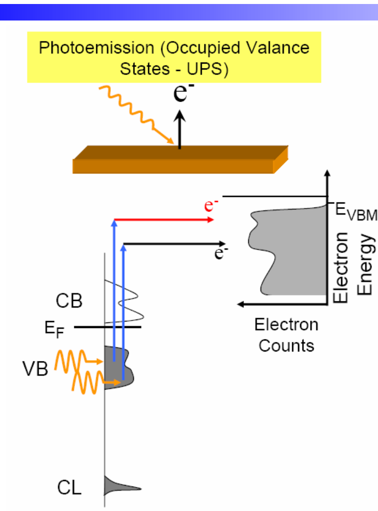
Surface Science Western- XPS

http://www.uwo.ca/ssw/services/xps.html
http://xpsfitting.blogspot.com/
http://www.casaxps.com/
http://www.lasurface.com/database/elementxps.php

Kratos Axis Ultra (left)
Axis Nova (right)

Contact:
Mark Biesinger
biesingr@uwo.ca

5.4 Comparison XPS and UPS



XPS: photon energy hν=200-4000 eV to probe core-levels (to identify elements and their chemical states).

UPS: photon energy hν=10-45 eV to probe filled electron states in **valence band** or adsorbed molecules on metal.

Angle resolved UPS can be used to map band structure (to be discussed later)

UPS source of irradiation: He discharging lamp (two strong lines at 21.2 eV and 42.4 eV, termed He I and He II) with narrow line width and high flux

Synchrotron radiation source

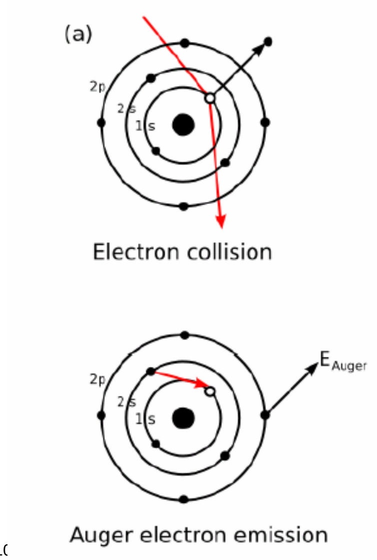
continuously variable phootn energy, can be made vaery narrow, very intense, now widely available, require a monochromator

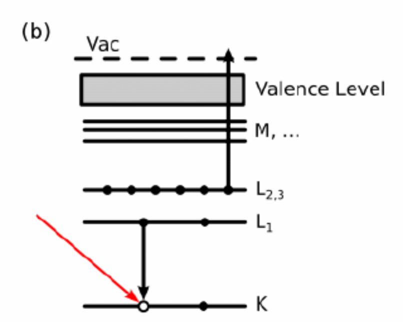
Introduction to Photoemission Spectroscopy in solids, by F. Boscherini
http://amscampus.cib.unibo.it/archive/00002071/01/photoemission_spectroscopy.pdf

Studies with UV Photoemission

- The electronic structure of solids -detailed angle resolved studies permit the complete band structure to be mapped out in *k*-space
- The adsorption of molecules on solids-by comparison of the molecular orbitals of the adsorbed species with those of both the isolated molecule and with calculations.
- The distinction between UPS and XPS is becoming less and less well defined due to the important role now played by synchrotron radiation.

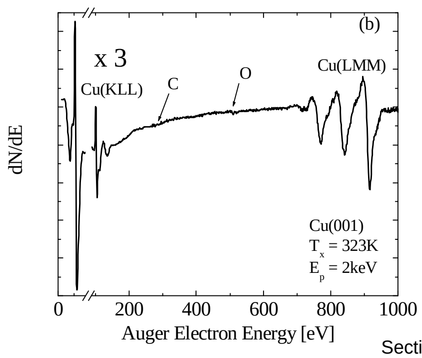
5.5 Auger Electron Spectroscopy (AES)

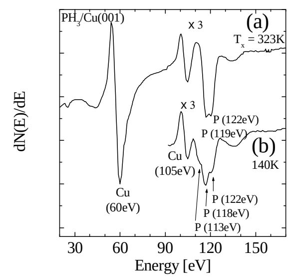




- Steps in Auger deexcitation
- Note: The energy of the Auger electrons do not depend on the energy of the projectile electron in (a)!

Auger spectrum of Cu(001) and CuP





Sections of Auger electron spectra, showing Cu (M2,3VV) and P (L2,3VV) transitions, for a low temperature PH3 overlayer phase at 140K and (b) for a P c (6×8) structure obtained by annealing the surface of (a) to Tx > 450K. Both spectra have been normalized to give the same Cu (60 eV) feature peak height.

Use dN/dE (derivative mode) ⇒ Why?

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Applications of AES

- A means of monitoring surface cleanliness of samples
- High sensitivity (typically ca. 1% monolayer) for all elements except H and He.
- Quantitative compositional analysis of the surface region of specimens, by comparison with standard samples of known composition.
- The basic technique has also been adapted for use in :

  –Auger Depth Profiling : providing quantitative compositional information as a function of depth below the surface (through sputtering)

  –Scanning Auger Microscopy (SAM) : providing spatially-resolved compositional information on heterogeneous samples (by scanning the electron beam over the sample)

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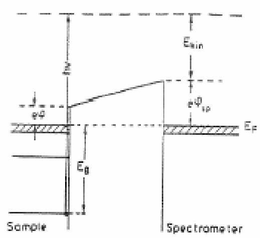
5.6 Quantitative analysis

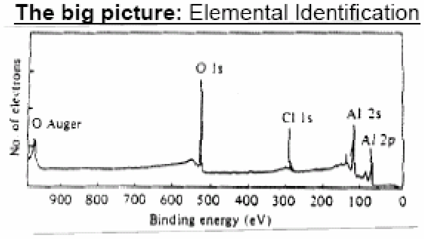


$E_{kin} = h\nu - E_B - e\varphi_{sp}$

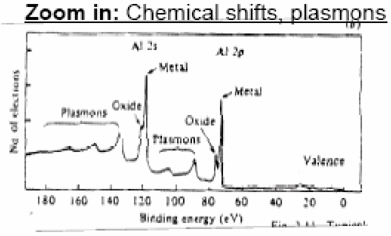
As sample and analyzer are in electrical contact, Fermi levels align.

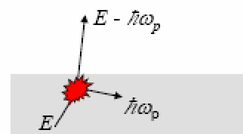
$KE_{PE} + e\phi_{analyzer} = h\upsilon$

The big picture: Elemental Identification



Zoom in: Chemical shifts, plasmons





Quantitative Analysis

- Estimate chemical concentration, chemical state, spatial distribution of surface species
- Simplest approximation is that sample is in single phase

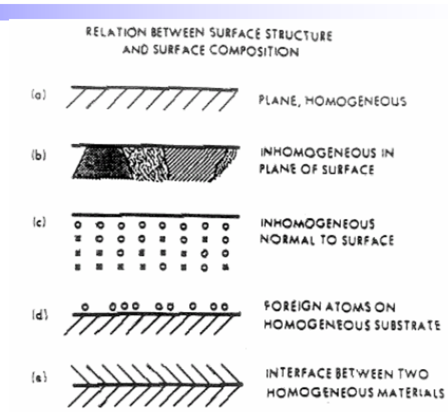


FIG. 1. Idealized surface structures: (a) plane homogeneous surface; (b) a surface with lateral inhomogeneities consisting of several different surface phases; (c) a surface with depth inhomogeneities (the circles and the crosses represent different types of atoms); (d) a surface phase consisting of a submonolayer of foreign atoms on an otherwise homogeneous surface; and (e) an interface between two homogeneous bulk phases (Ref. 1).

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