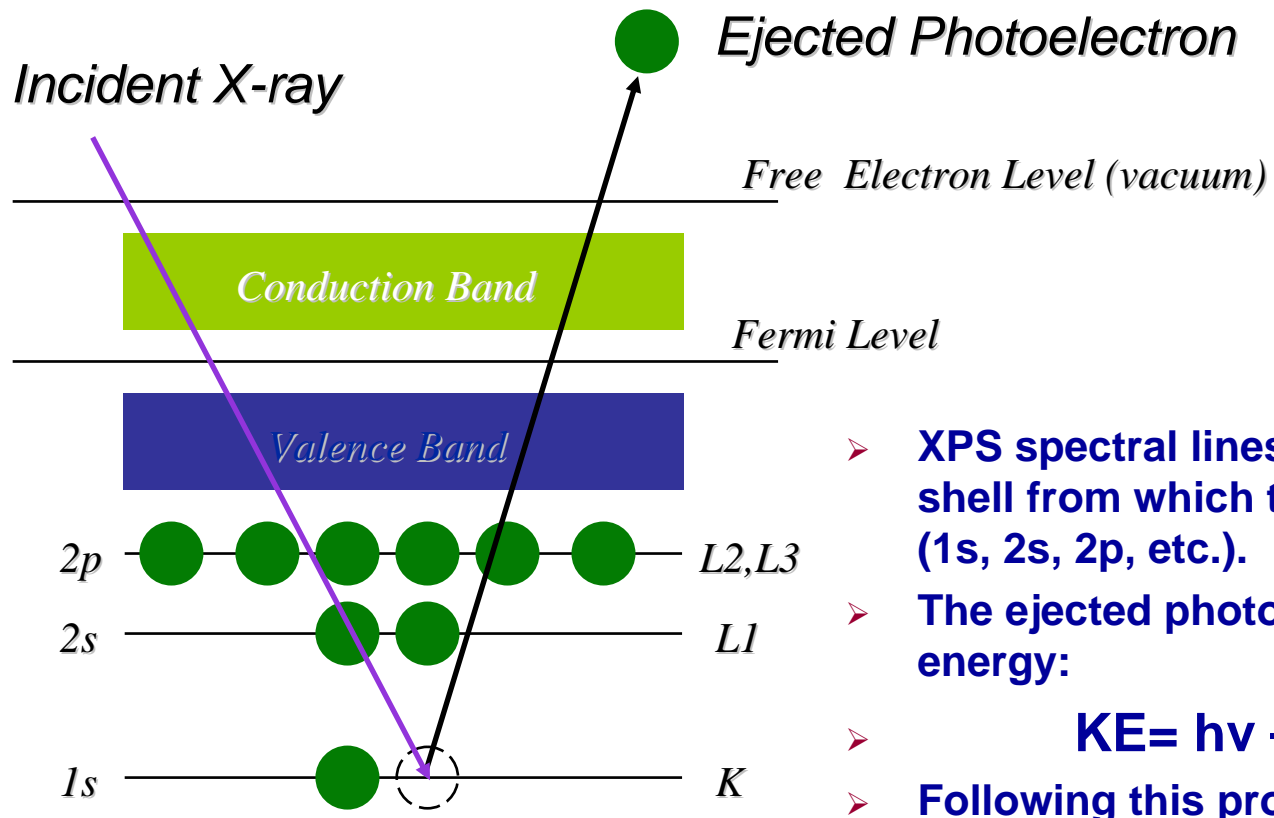# Introduction to
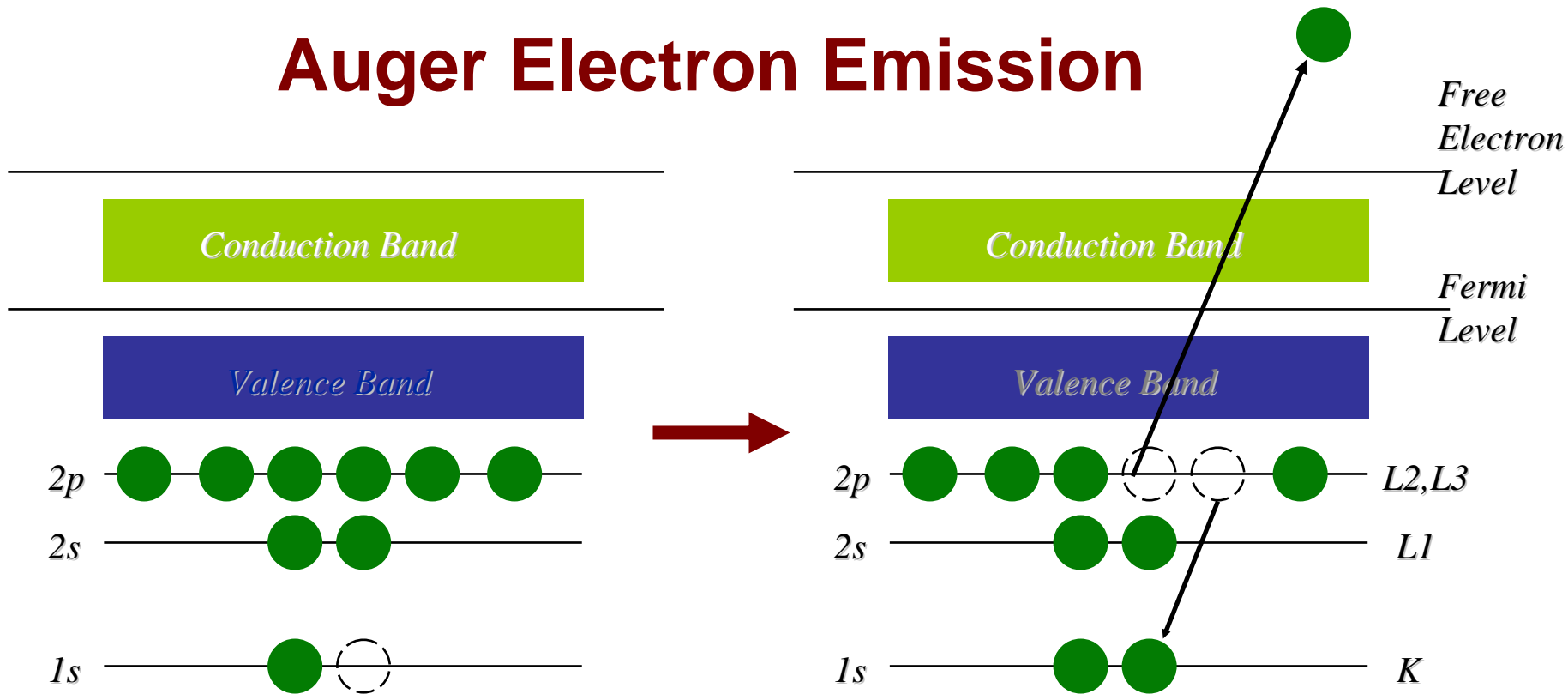# X-ray Photoelectron Spectroscopy (XPS)

- 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.

- XPS which makes use of the photoelectric effect, was developed in the mid-1960's by Kai Siegbahn and his research group at the University of Uppsala, Sweden.

Photoemission of Electrons

Ejected Photoelectron

Incident X-ray

Free Electron Level (vacuum)

Conduction Band

Fermi Level

Valence Band

2p — — — — — — *L2,L3*

2s — — *L1*

1s — *K*

➢ **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= hν – BE - ϕ**

➢ **Following this process, the atom will release energy by the emission of a photon or Auger Electron.**

Auger Electron Emission

Free
Electron
Level

Fermi
Level

Conduction Band		Conduction Band
Valence Band		Valence Band

2p — ⬤ ⬤ ⬤ ⬤ ⬤ ⬤   2p — ⬤ ⬤ ⬤ ◯ ◯ ⬤   L2,L3

2s — ⬤ ⬤   2s — ⬤ ⬤   L1

1s — ⬤ ◯   1s — ⬤ ⬤   K

- ➤ 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 - Binding energy

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

Where: BE= Electron Binding Energy
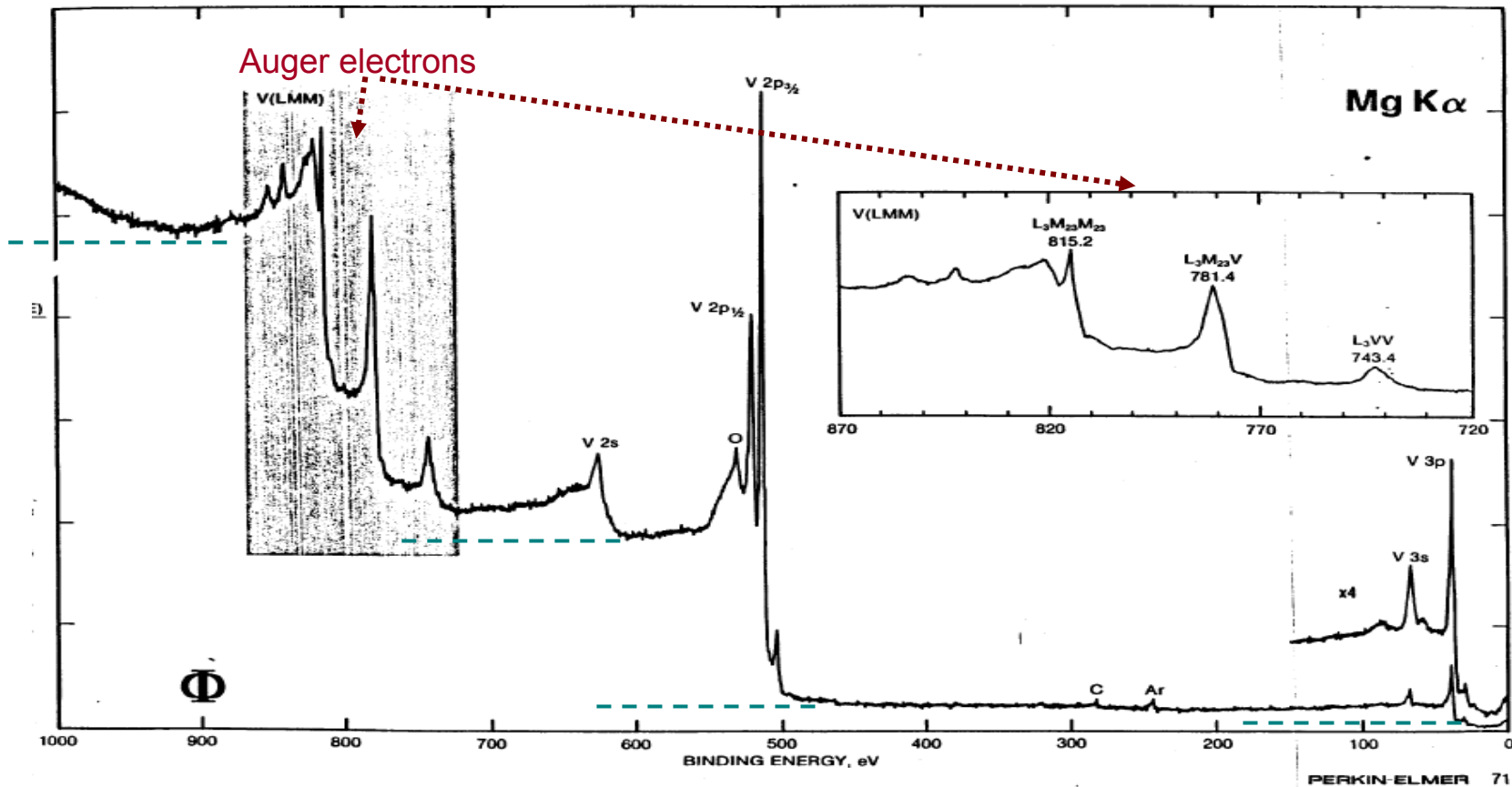
KE= Electron Kinetic Energy

Φ_{spec}= Spectrometer Work Function

Photoelectron line energies: **Not Dependent** on photon energy.

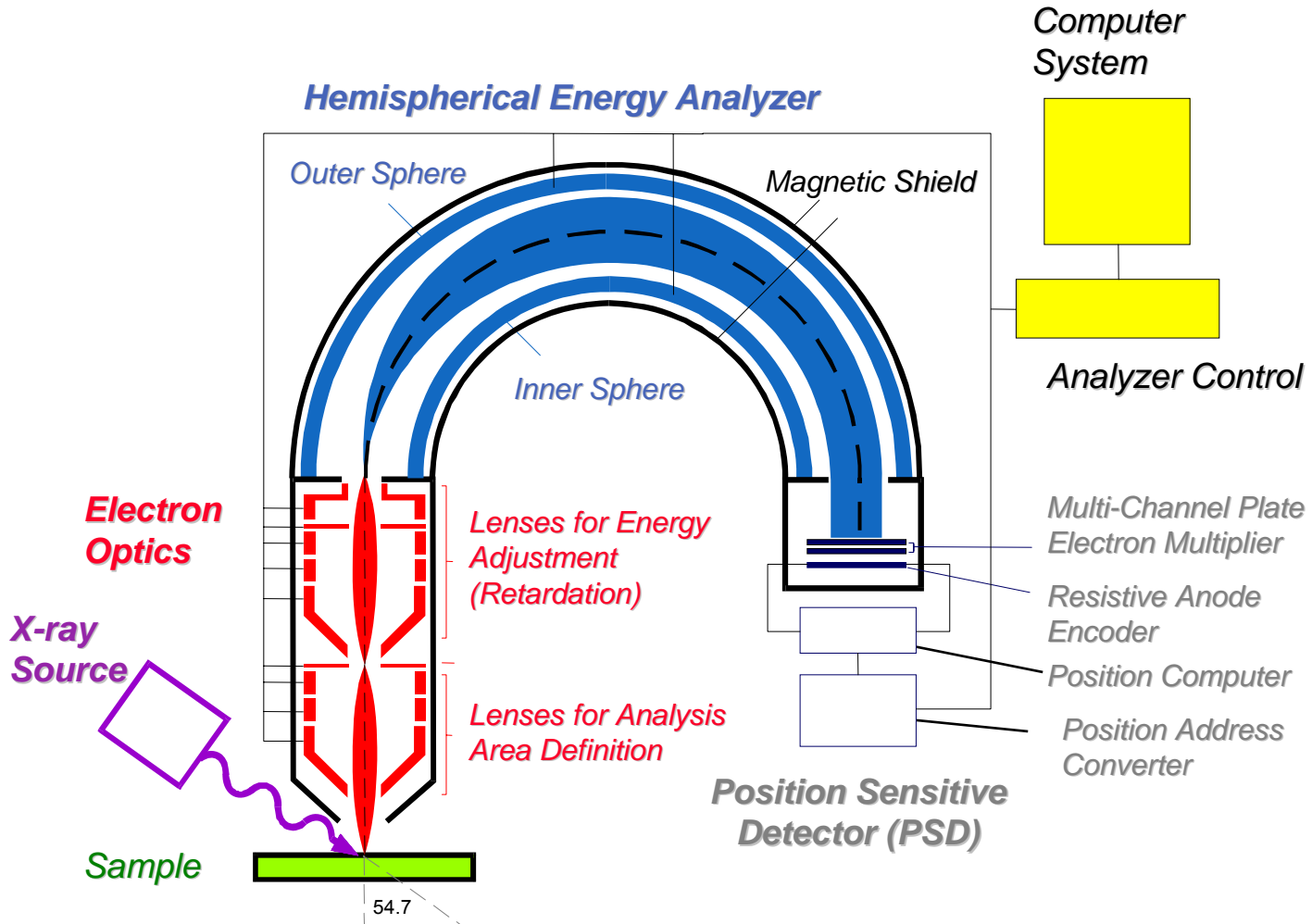Auger electron line energies: **Dependent** on photon energy.
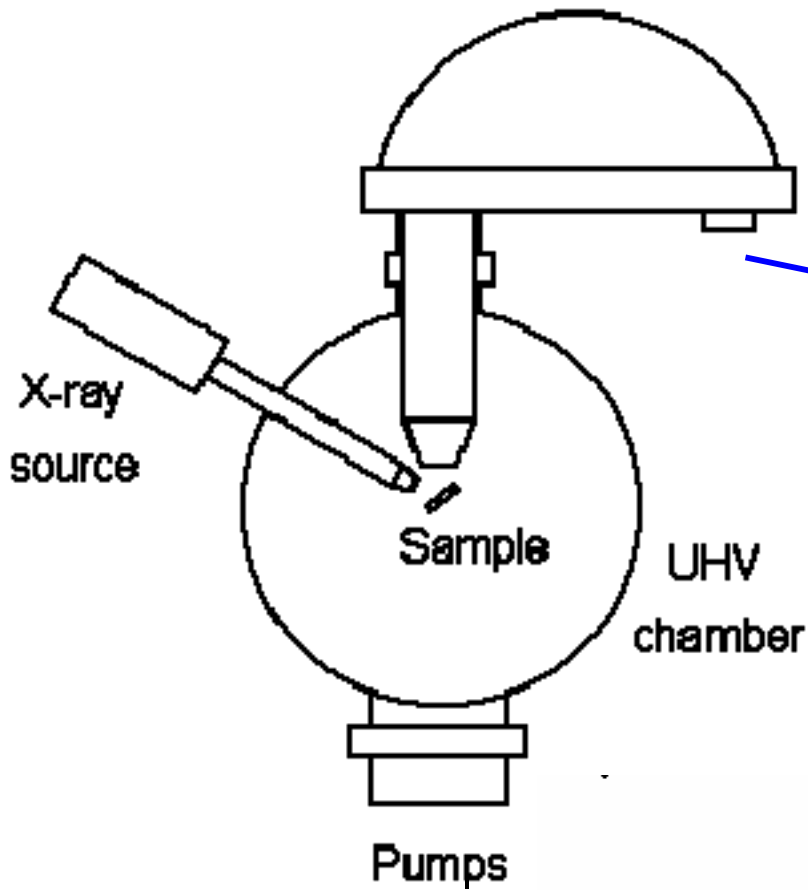
XPS spectrum of Vanadium
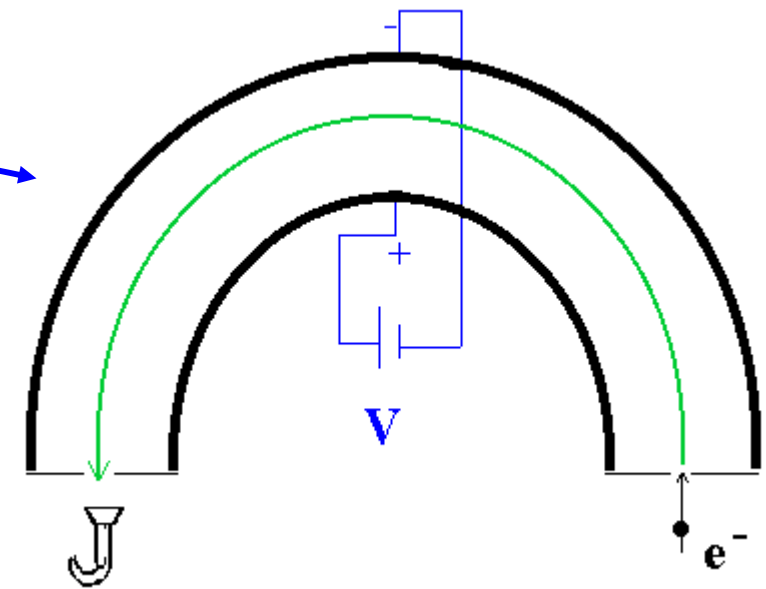

Note the stepped background

- Only electrons close to surface can escape elastically (λ 63%, 3λ 95%))
- Electrons from deeper in sample undergo inelastic collisions while traveling to the surface giving rise to the stepped background
- Empirical models can be used to subtract the backgorund
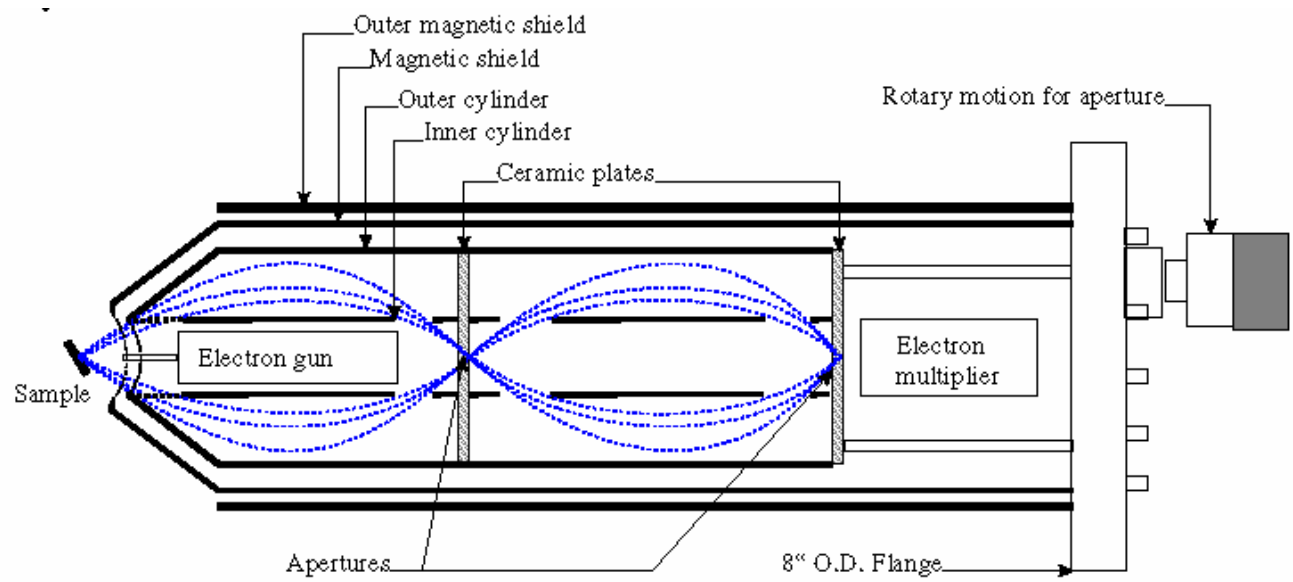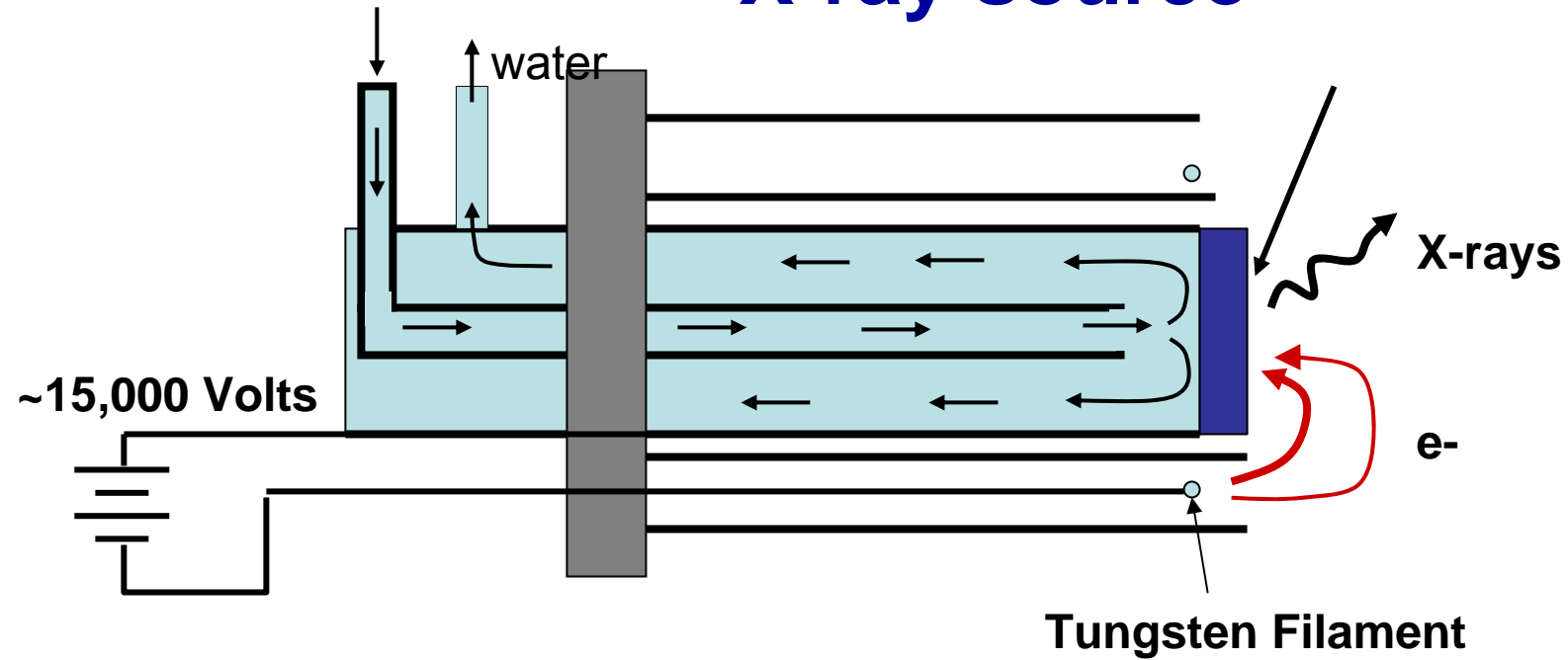
X-ray Photoelectron Spectrometer

Computer System

Hemispherical Energy Analyzer

Outer Sphere

Magnetic Shield

Inner Sphere

Analyzer Control

Electron Optics

Lenses for Energy Adjustment (Retardation)

Multi-Channel Plate Electron Multiplier

Resistive Anode Encoder

X-ray Source

Lenses for Analysis Area Definition

Position Computer

Position Address Converter

Position Sensitive Detector (PSD)

Sample

54.7

X-ray source

Sample

UHV chamber

Pumps

Hemispherical electron energy analyzer

V

e⁻

Cylindrical mirror electron energy analyzer

Outer magnetic shield
Magnetic shield
Outer cylinder
Inner cylinder
Ceramic plates
Rotary motion for aperture

Electron gun

Electron multiplier

Sample

Apertures

8" O.D. Flange

X-ray source

water

~15,000 Volts

X-rays

e-

Tungsten Filament

Mg($K\alpha$) : $h\nu$ = 1253.6 eV
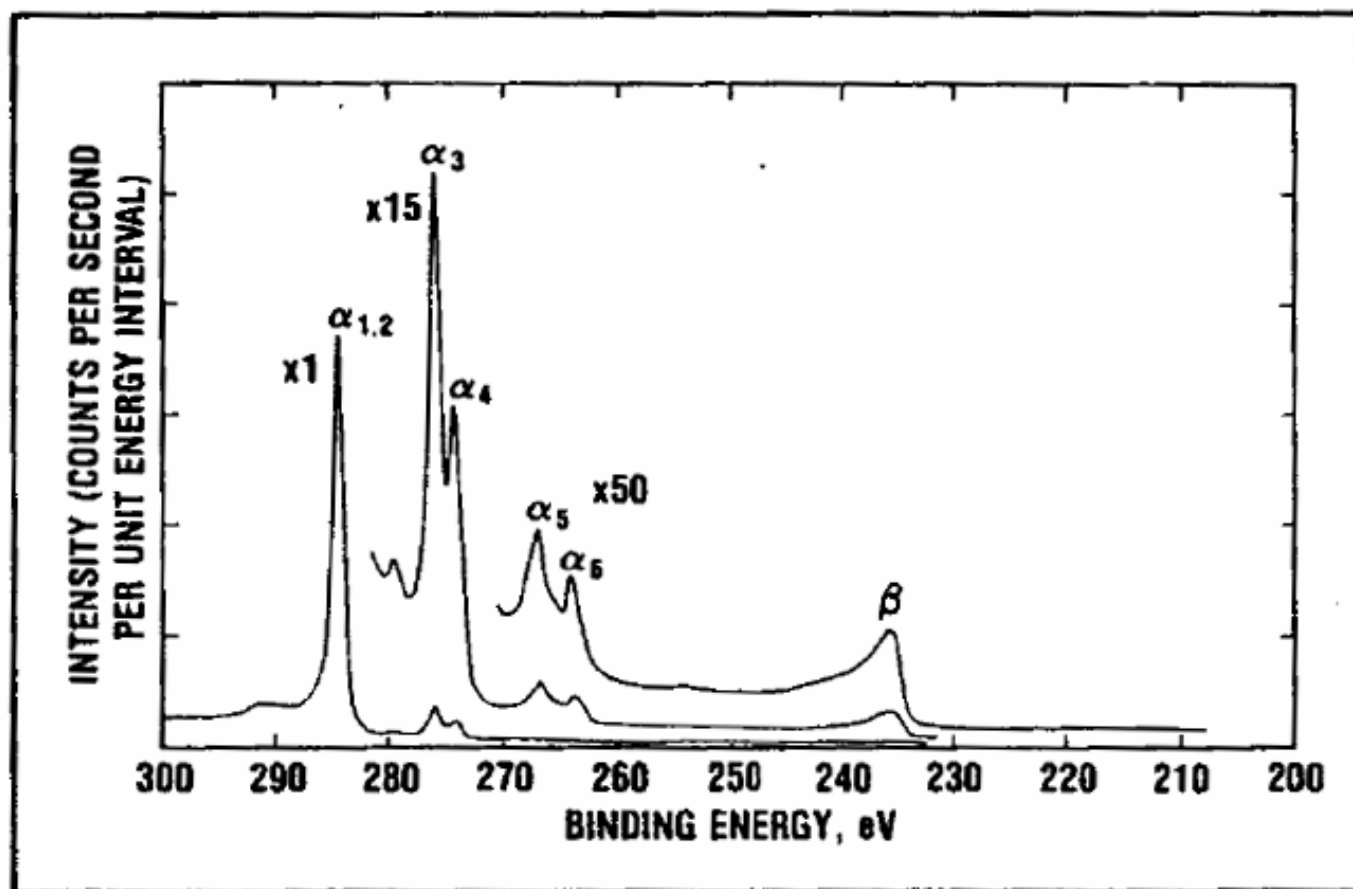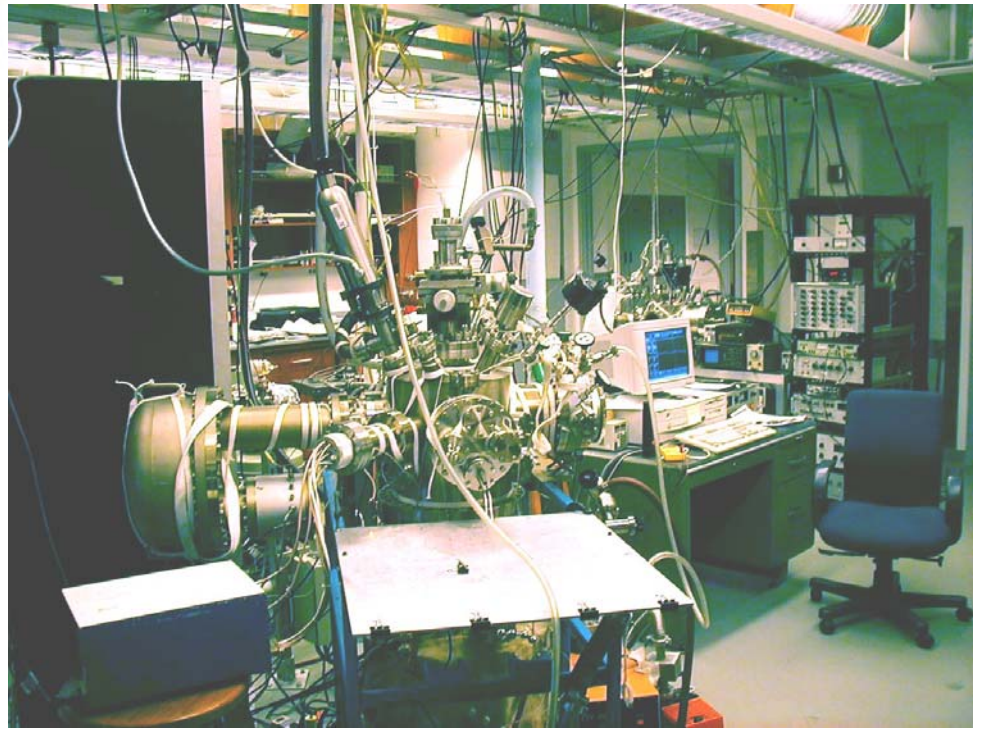
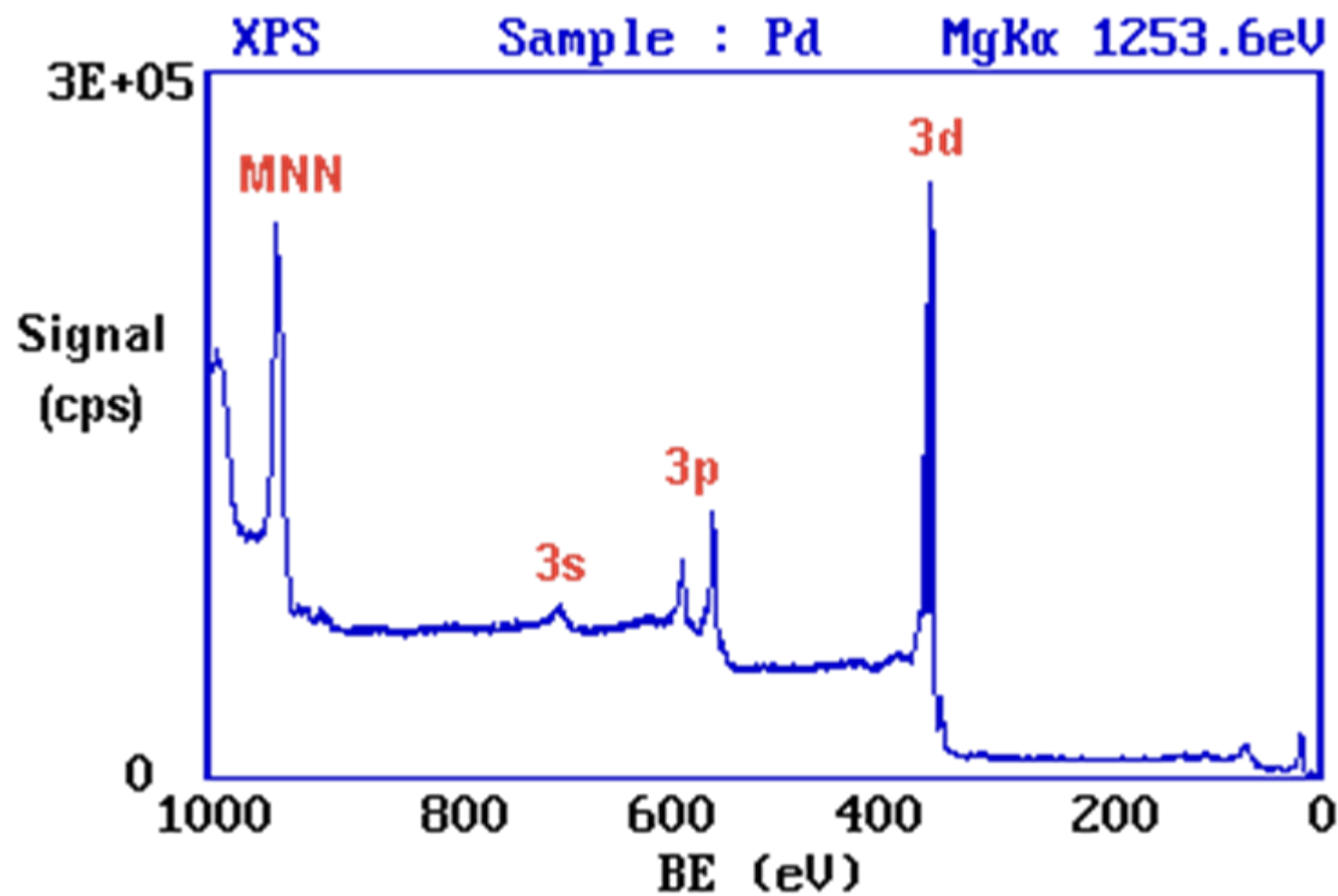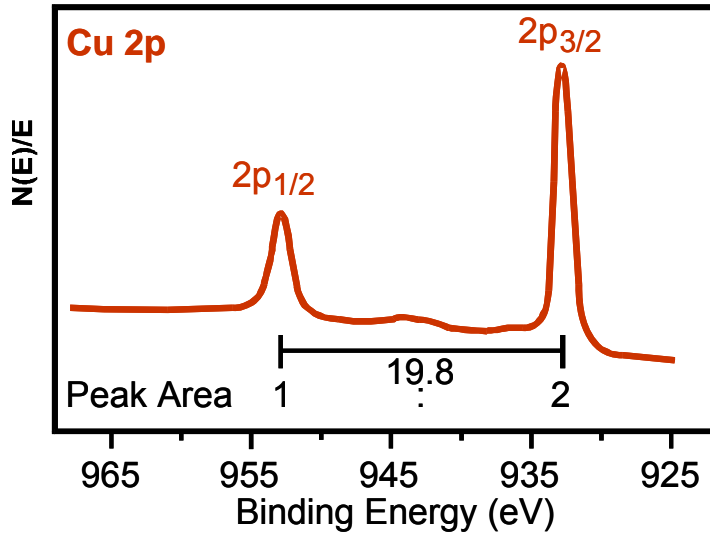Al(Ka) : $h\nu$ = 1486.6 eV

Figure 6.   Mg x-ray satellites (C1s graphite spectrum).

Note that most XPS peaks appear as doublets

A little quantum mechanics is needed to understand why this is the case

Cu 2p

$2p_{3/2}$

$2p_{1/2}$

N(E)/E

19.8

Peak Area   1   :   2

965   955   945   935   925

Binding Energy (eV)

<u>Electron quantum numbers</u>

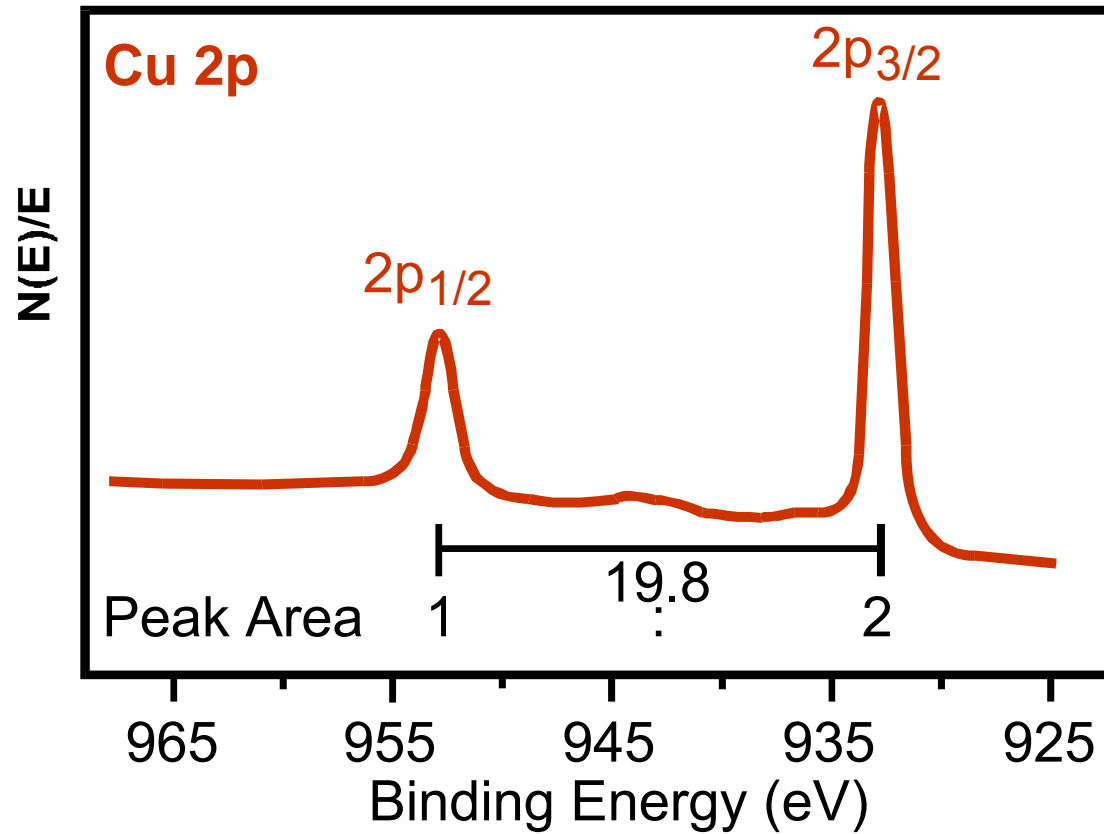orbital momentum: $l = 0,1,2,3$ (s, p, d, and f orbitals)

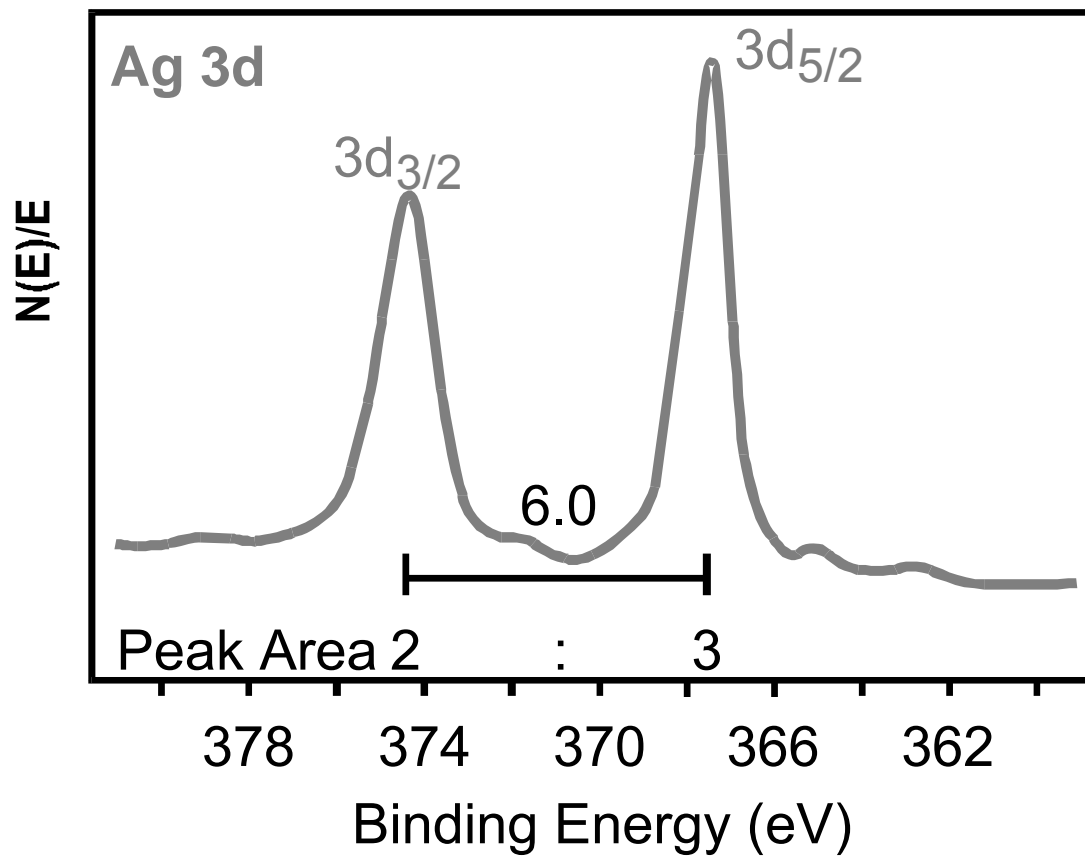spin momentum: $s = +\frac{1}{2}, -\frac{1}{2}$

total momentum: $j = l + s$

Since s can be $+\frac{1}{2}$ or $-\frac{1}{2}$, each level with $l > 0$ is split into two sublevels with an energy difference known as the spin-orbit splitting. The degeneracy of each of these levels is $2j+1$

Orbital	l	j	degeneracy	Electron level
1s	0	1/2	1	1s
2s	0	1/2	1	2s
2p	1	1/2	2	$2p_{1/2}$
2p	1	3/2	4	$2p_{3/2}$
3d	2	3/2	4	$3d_{3/2}$
3d	2	5/2	6	$3d_{5/2}$
4f	3	5/2	6	$4f_{5/2}$
4f	3	7/2	8	$4f_{7/2}$

Orbital	l	j	degeneracy	Electron level
2p	1	1/2	2	$2p_{1/2}$
2p	1	3/2	4	$2p_{3/2}$

Cu 2p

$2p_{3/2}$

$2p_{1/2}$

N(E)/E

19.8

Peak Area   1   :   2

925   935   945   955   965

Binding Energy (eV)

Orbital	l	j	degeneracy	Electron level
3d	2	3/2	4	$3d_{3/2}$
3d	2	5/2	6	$3d_{5/2}$

Ag 3d

$3d_{5/2}$

$3d_{3/2}$

6.0

Peak Area 2   :   3

Binding Energy (eV)

378   374   370   366   362

N(E)/E

Orbital	l	j	degeneracy	Electron level
4f	3	5/2	6	$4f_{5/2}$
4f	3	7/2	8	$4f_{7/2}$

Au 4f

$4f_{5/2}$

$4f_{7/2}$

3.65

Peak Area   3   :   4

N(E)/E

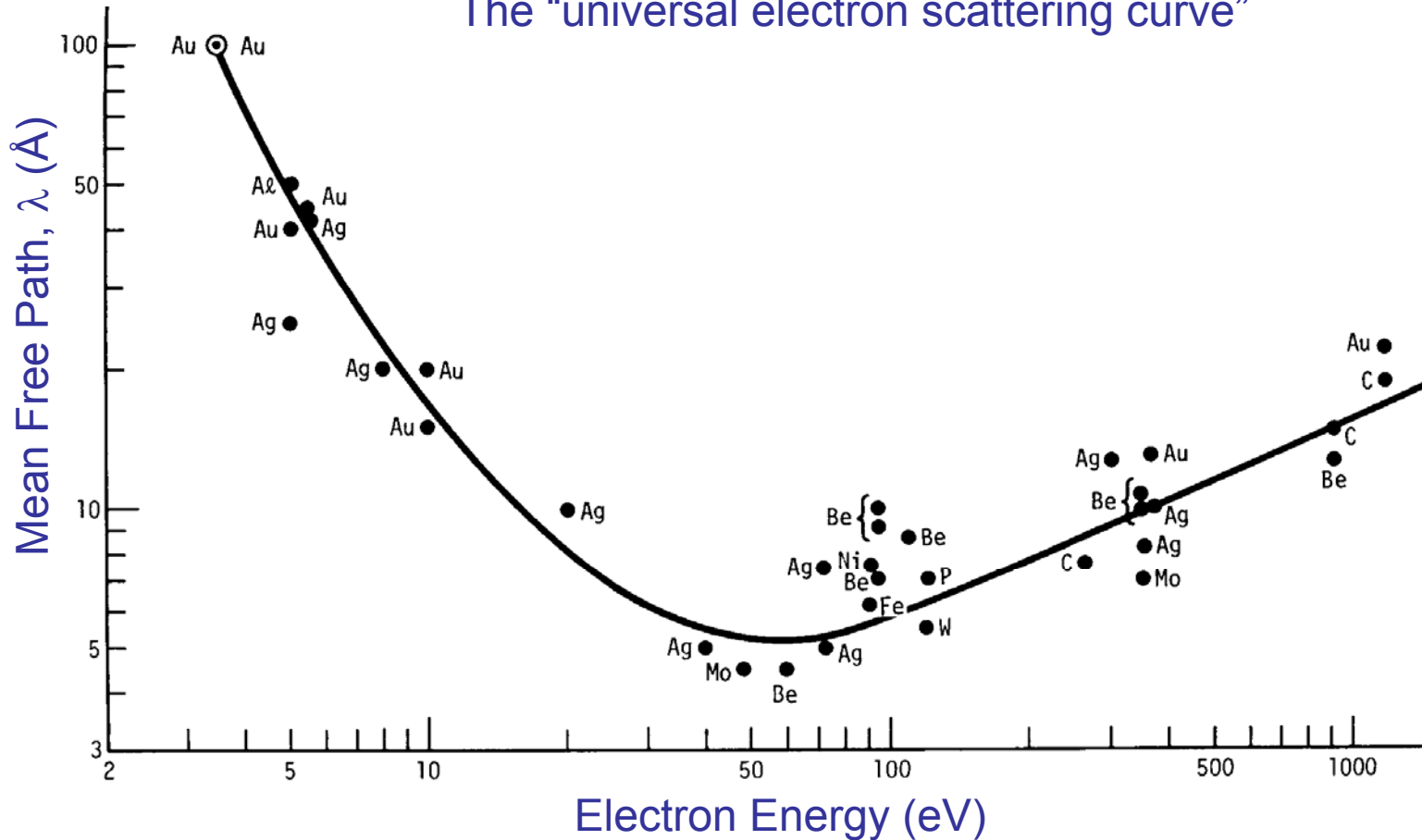91   87   83   79

Binding Energy (eV)
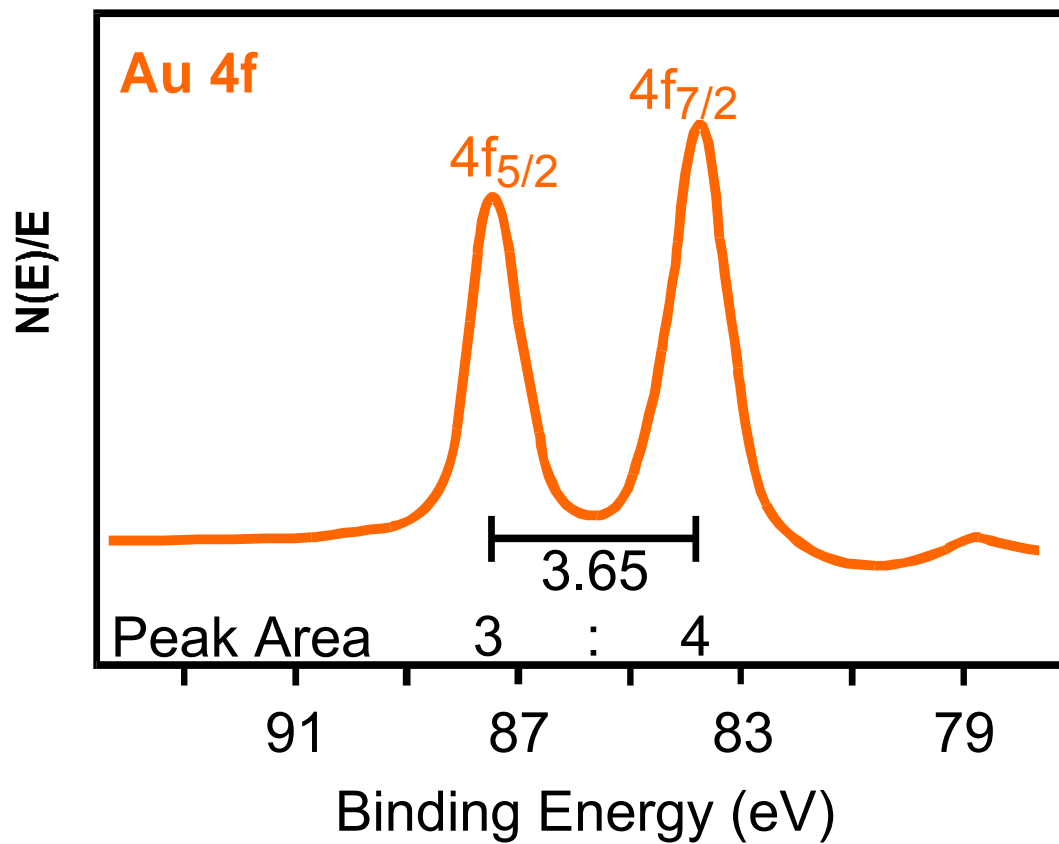
What information can you obtain from XPS?

- **Identification of elements near the surface and surface composition**

- **Local chemical environments**

- **Oxidation states of transition metals**

- **Valence band electronic structure**

- **Morphology of thin films**

Sampling Depth

The "universal electron scattering curve"

- **Electron mean free path is energy dependent**
- **Sampling depth is materials dependent**
- **XPS is surface sensitive but samples more than just the surface**

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 Binding Energies

Chemical Shifts

➢ In addition to the identity of the element and the orbital (s,p, d, f) electron binding energies depend on:

      (1)   the formal oxidation state of the atom
      (2)   the local chemical environment

➢ Both (1) or (2) cause small binding energy shifts (< 5 eV)

➢ An increase in oxidation state causes the binding energy to increase due to a decrease in the screening of the bound electron from the ion core. The ability of XPS to determine oxidation states is used extensively in catalysis research.

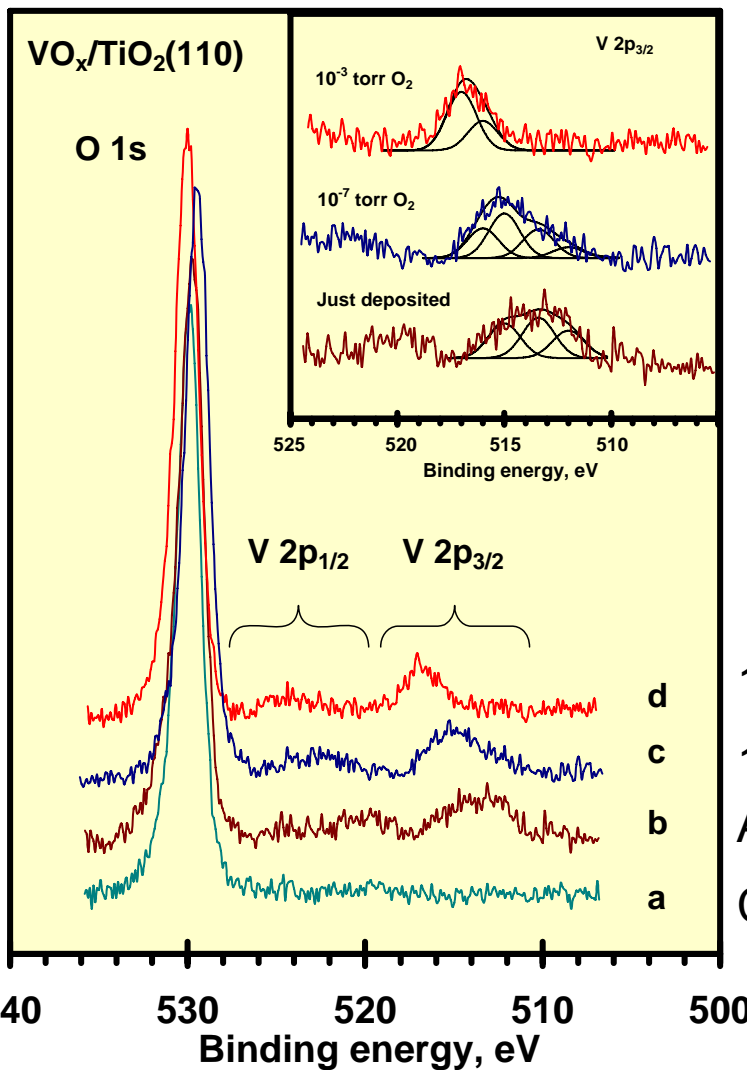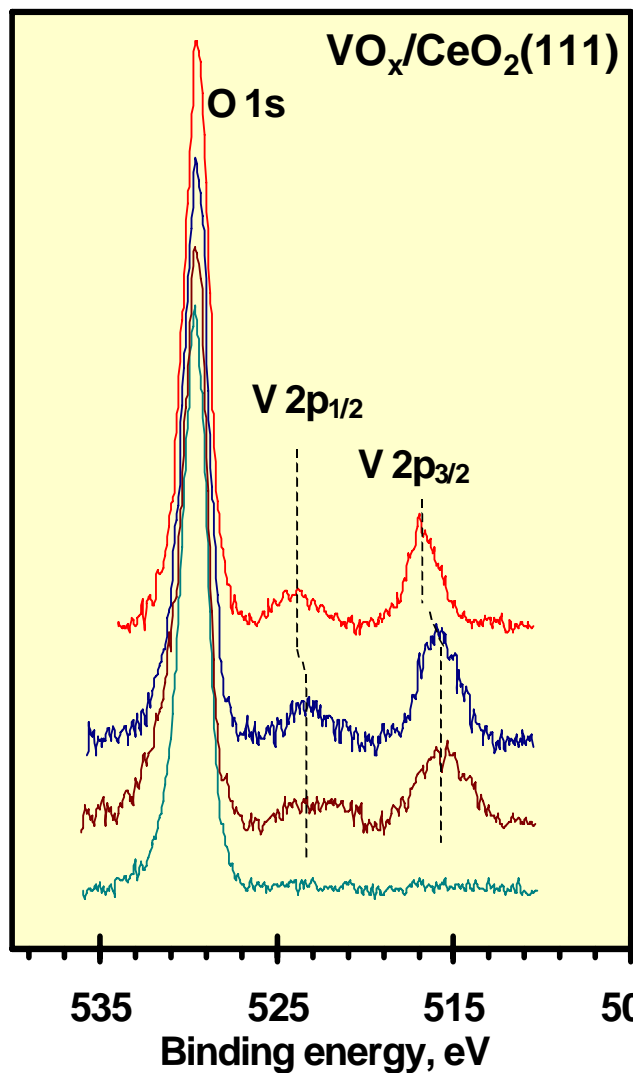# Oxidation States

V(2p$_{3/2}$)

V^0	V^{+5}
511.95 eV	517.45 eV

Vanadium foil

V^0

2p$_{3/2}$
511.95

2p$_{1/2}$

7.7

525   515   505

BINDING ENERGY, eV

COMPOUND	2p$_{3/2}$ BINDING ENERGY, eV	REF.
V		Φ
V		RH2
V		RR
V		LFS
V		NSC
V		GSM
V		FS
V		SA
V		HVB
VB$_2$		MEC
VC		FUM
VS		RH2
VN		RR
VN		STA
(C$_5$H$_5$)$_2$V		BCD
(C$_5$H$_5$)$_2$V		GSM
(C$_5$H$_5$)$_2$VCl		GSM
V acac$_3$		LFS
VO acac$_3$		LFS
VOSO$_4$		LFS
VOCl$_2$		LFS
VO$_2$		SA
VO$_2$		GSM
V$_2$O$_5$		LFS
V$_2$O$_5$		SA
V$_2$O$_5$		NSC
V$_2$O$_5$		Φ
V$_2$O$_5$		NGD

510   515   520

O

(O)

V$_2$O$_5$

V^{5+}

2p$_{3/2}$
517.45

2p$_{1/2}$

O 1s
x-ray
satellite

7.5

533   523   513

BINDING ENERGY, eV

0.5 ML VO$_x$ - XPS

VO$_x$/CeO$_2$(111)

O 1s

V 2p$_{1/2}$

V 2p$_{3/2}$

VO$_x$/TiO$_2$(110)

O 1s

V 2p$_{3/2}$

10^{-3} torr O$_2$

10^{-7} torr O$_2$

Just deposited

Binding energy, eV

V 2p$_{1/2}$ V 2p$_{3/2}$

d

c

b

a

V 2p$_{3/2}$

V^0	512.3 eV
V^{+3}	515.3 eV
V^{+4}	515.7 eV
V^{+5}	516.8 eV

10^{-3} torr O$_2$ 400 K

10^{-7} torr O$_2$ 575 K

As deposited

Clean substrate

535   525   515   505
Binding energy, eV

540   530   520   510   500
Binding energy, eV

Chemical Shifts - Electronegativity Effects

Local chemical environment can also cause small shifts in XPS peak positions

Functional Group		C(1s)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

Electronegative substituents decrease the electron density on the carbon atom causing a small in crease in the C(1s) binding energy

$$\overset{\delta+}{C}-\overset{\delta-}{F}$$

XPS of Polyethylene-terephthalate
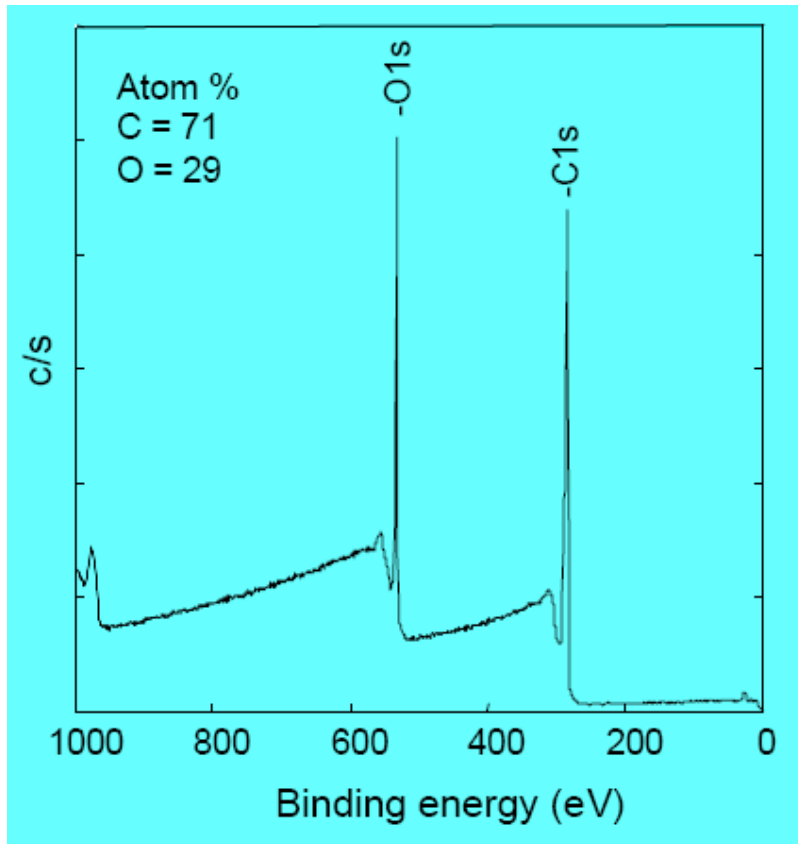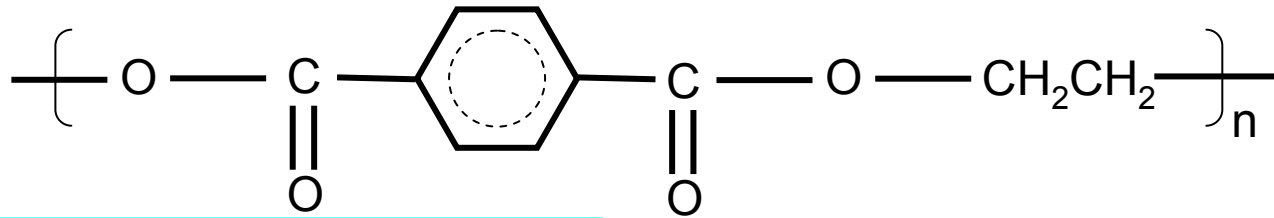
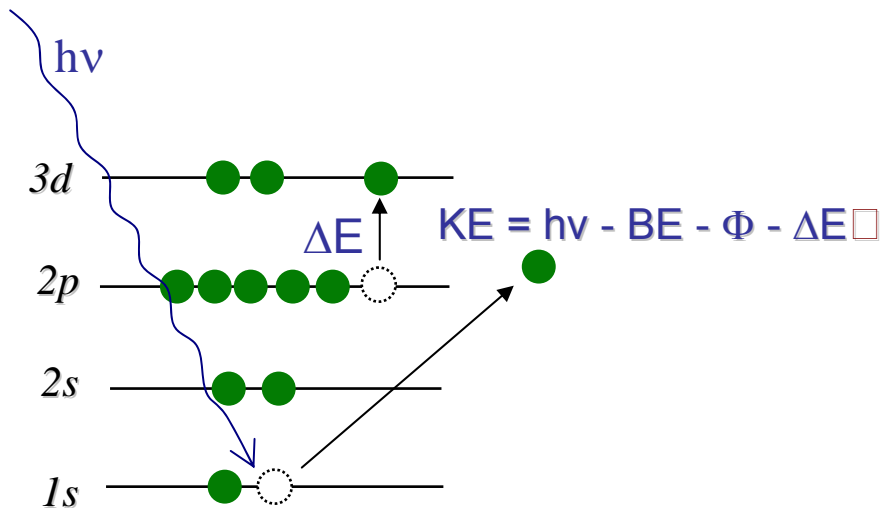Quantitative elemental analysis
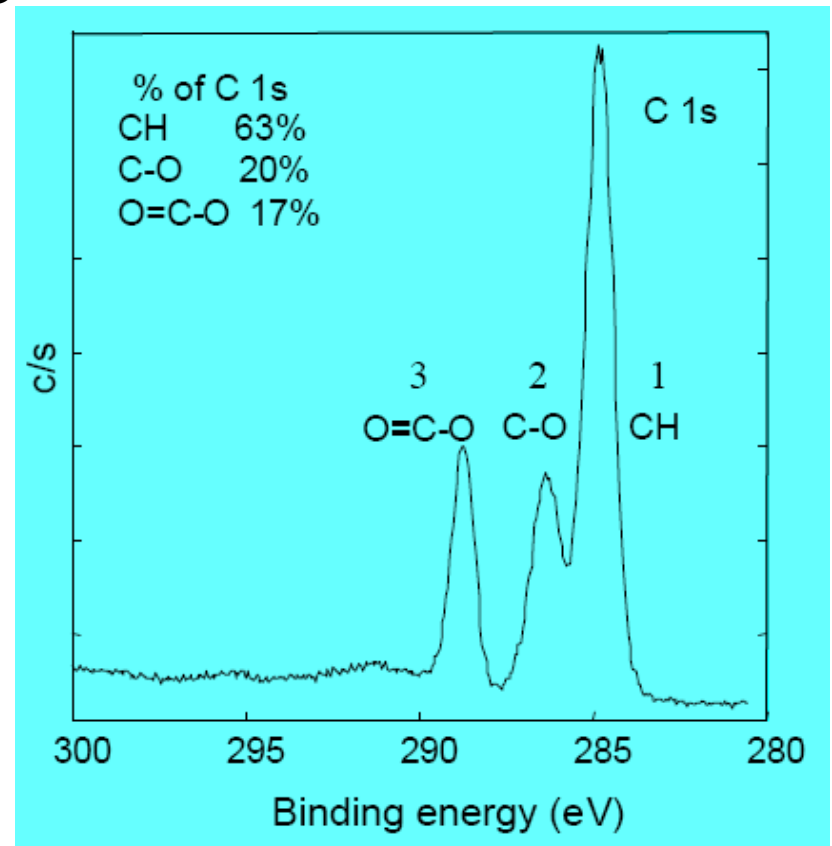
Chemical state analysis

Final State Effects - Shake-up features

Shake-up features occur when additional electron energy level transitions occur during the photoelectron emission process

Primary photoemission

$h\nu$

3d

2p

2s

1s

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

Shake-up process

$h\nu$

3d

2p

2s

1s

ΔE

$KE = h\nu - BE - \Phi - \Delta E$

Ce(3d) - Ce^{+4}

u'''

u

v'''

v

v'' v'

u'' u'

940   920   900   880   860

Binding energy, eV
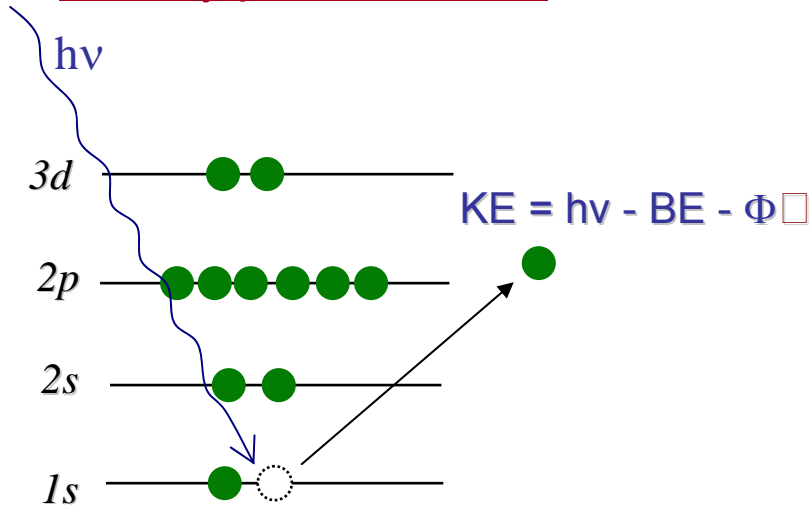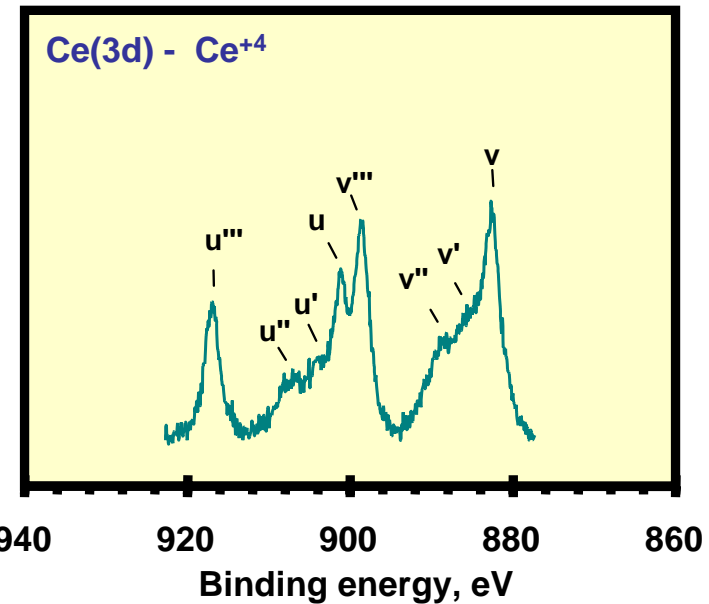
Peaks	Initial State	Final State
Ce^{4+}	v,u	3d^{10}4f^{0}	3d^{9}4f^{2}V^{n-2}
Ce^{4+}	v'',u''	3d^{10}4f^{0}	3d^{9}4f^{1}V^{n-1}
Ce^{4+}	v''',u'''	3d^{10}4f^{0}	3d^{9}4f^{0}V^{n}

Quantitative Analysis of XPS DATA

Element sensitivity factors

Sensitivity factor = $S = f \, \sigma \, D \, \lambda$

f = x-ray flux
s = photoelectron cross-section
D = detector efficiency
λ = electron mean free path

For a homogenous sample:

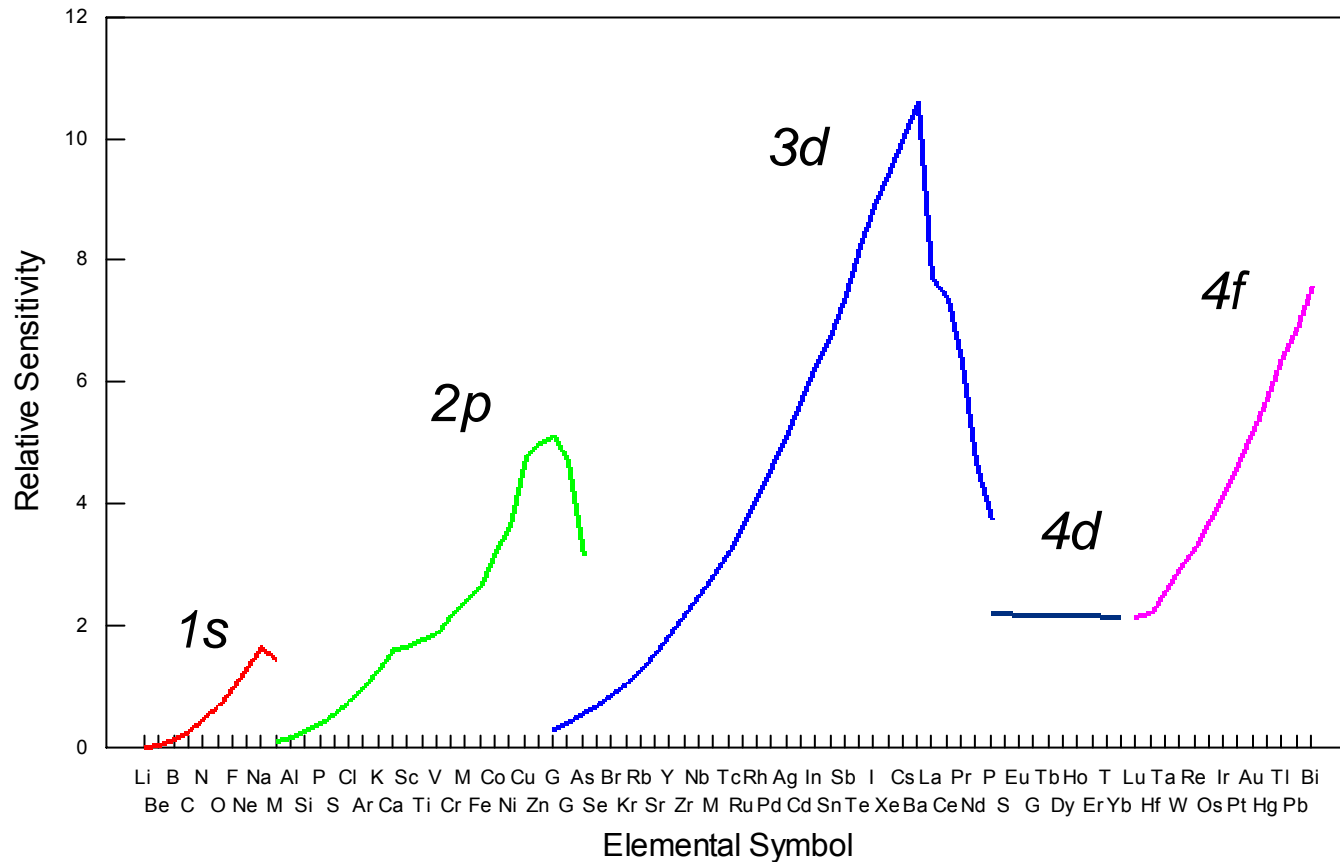$$\frac{n_1}{n_2} = \frac{I_1/S_1}{I_2/S_2}$$

n_i = number of I atoms
I_i = area of I photoemission peak
S = sensitivity factor for i

$$C_x = \frac{n_x}{\sum_i n_i} = \frac{I_x/S_x}{\sum_i I_i/S_i}$$

C_x = concentration of element x

Relative Sensitivities of the Elements

$S(F_{1s}) = 1.0$

Thin Film Morphology

Vanadium Deposition on CeO$_2$(111)

XPS

Ce 3d/ V 2p$_{3/2}$ intensity

ML of vanadium deposited
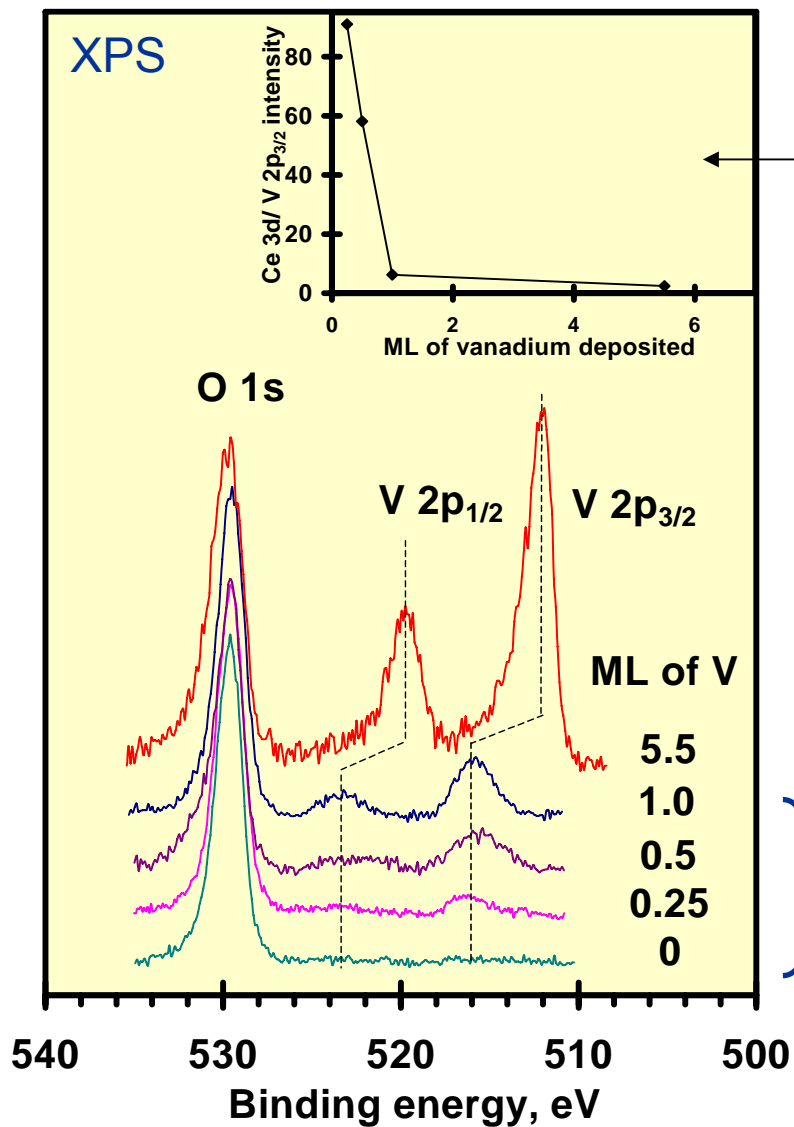
Layer-by-layer film growth

O 1s

V 2p$_{1/2}$ V 2p$_{3/2}$

ML of V

5.5

1.0

0.5

0.25

0

V^{+3}
V 2p$_{3/2}$ = 515.7 eV

CeO$_2$(111)

Binding energy, eV
540   530   520   510   500
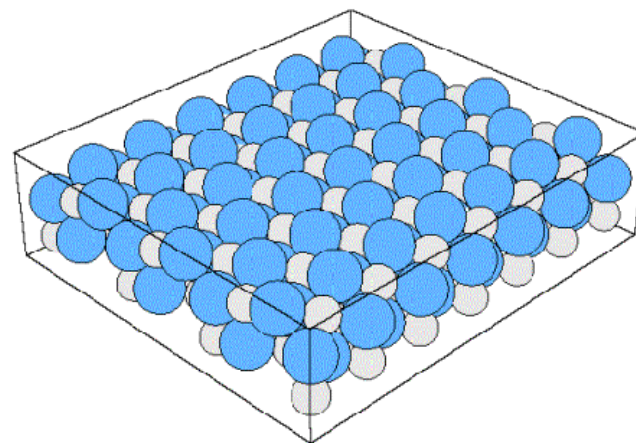
XPS – Depth Profiling

Ar⁺ ion source
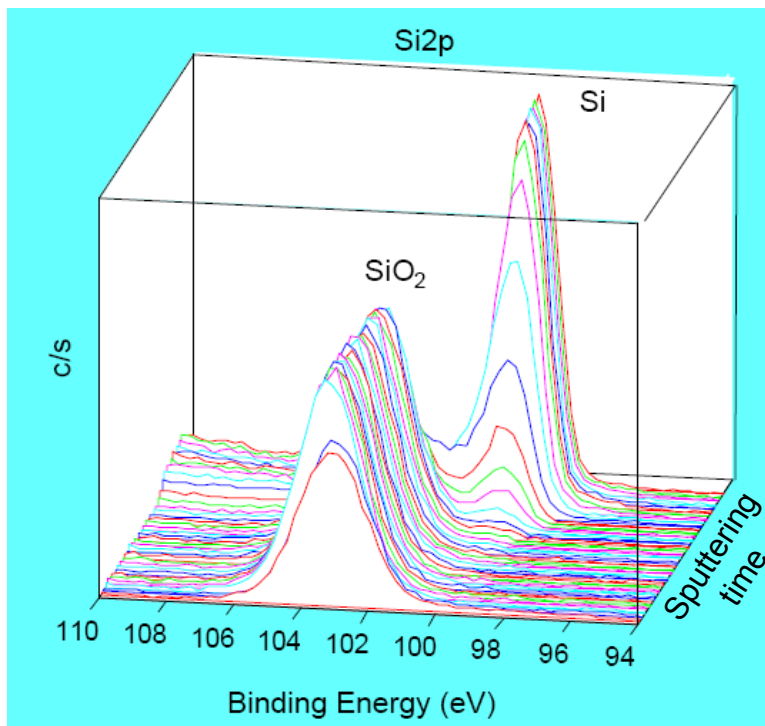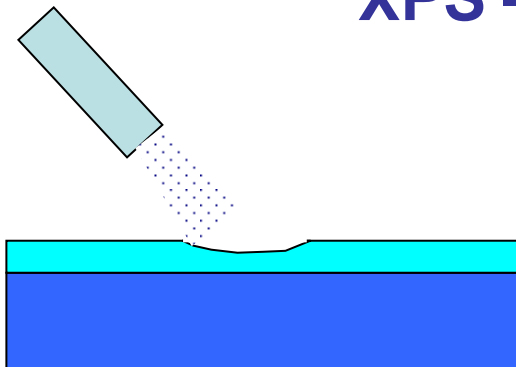
XPS depth profile of SiO_2 layer
on silicon wafer

Si(2p)   - 99.3 eV

Si^{4+}(2p) - 103.3 eV

Scanning XPS

- **Provides elemental and chemical state maps of surfaces**
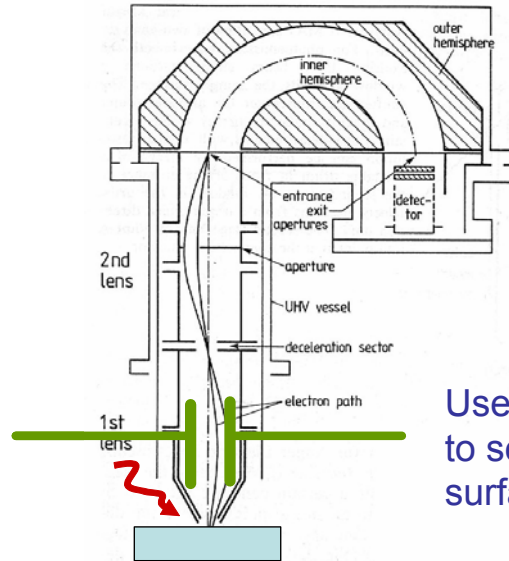
Use electrostatic lenses
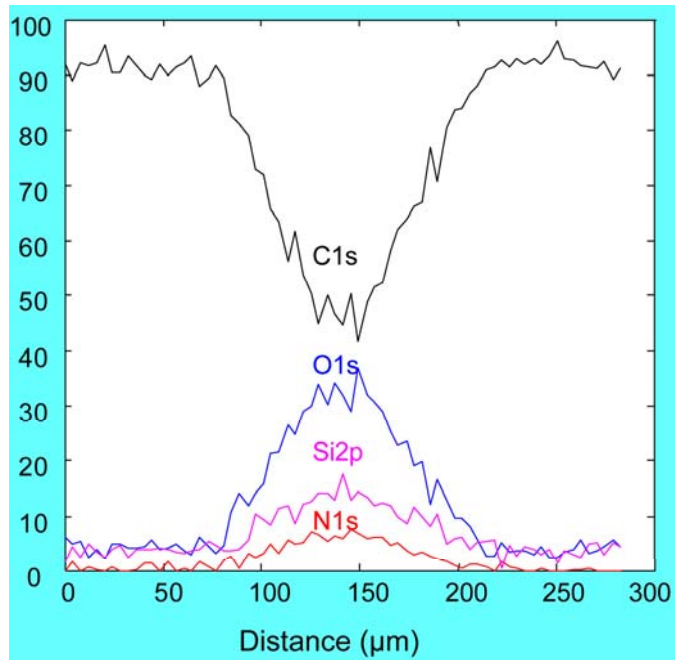to select which are of the
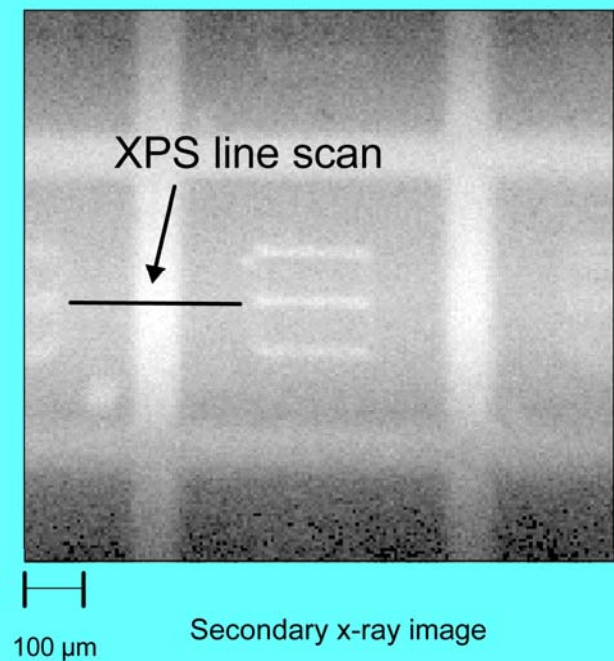surface is analyzed
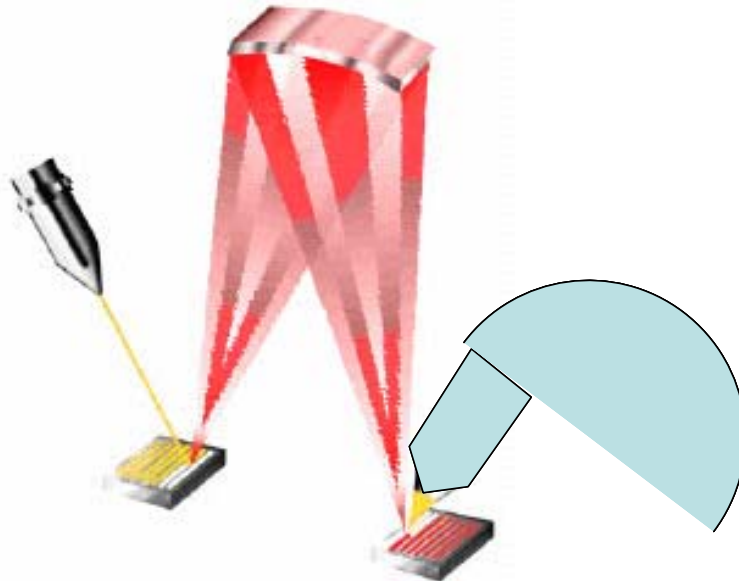
Raster the x-ray beam.

Requires the electron beam in
the x-ray source to be rastered
and a complex quartz crystal lens
to focus the x-rays .
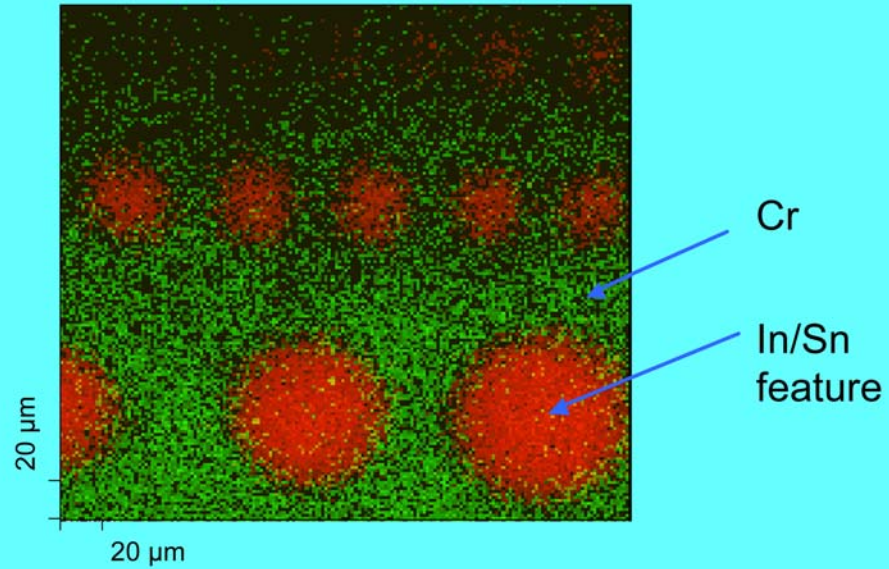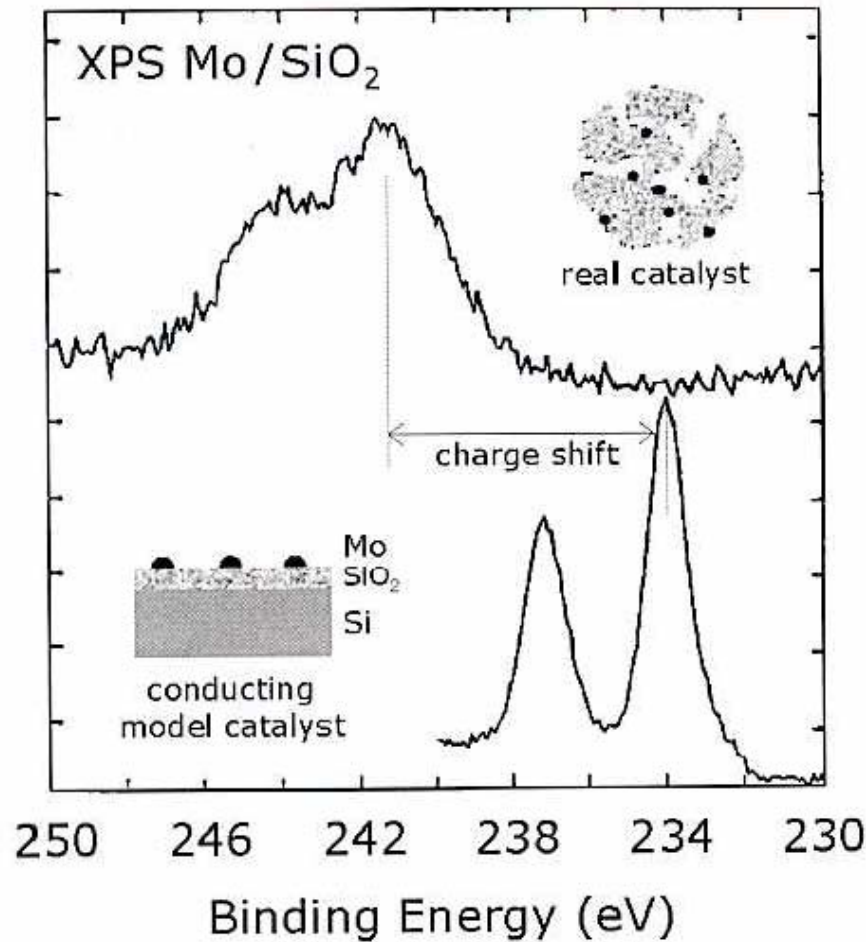
XPS image of a patterned polymer film

line scan

image

Secondary x-ray image

XPS Elemental Map of ITO circular patterns

XPS of Supported Catalysts

XPS Mo/SiO$_2$

real catalyst

charge shift

Mo
SiO$_2$
Si

conducting
model catalyst

250   246   242   238   234   230

Binding Energy (eV)

Issues:

➤ **Sample is not homogenous**

➤ **Only analyze external surface**

➤ **Sample charging**

➤ **Beam damage**

Figure 3.7: Comparison of the monochromatic Mo 3d XPS spectra of MoO$_3$ in an insulating silica-supported catalyst and in a conducting, thin silica film-supported model catalyst, showing the effect of inhomogeneous charge broadening (courtesy of H. Korpik, Eindhoven).

Valence Band Photoelectron Spectroscopy

➤ Density of states near the Fermi level.

➤ Electronic states in the band gap

➤ Binding energies of valance electrons of adsorbates

Need very high energy resolution to obtain useful information. He discharge lamp or synchrotron is typically used as the photon source

If ultraviolet photons (rather than x-rays) are used the technique is called Ultraviolet Photoelectron Spectroscopy (UPS). Other than the photon source instrumentation is identical to that of XPS
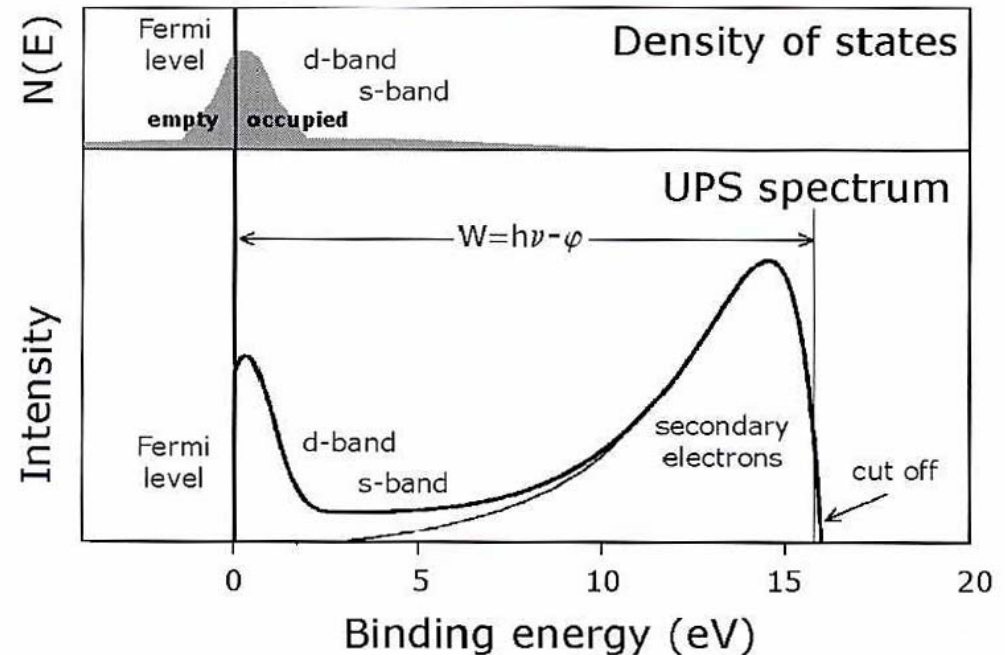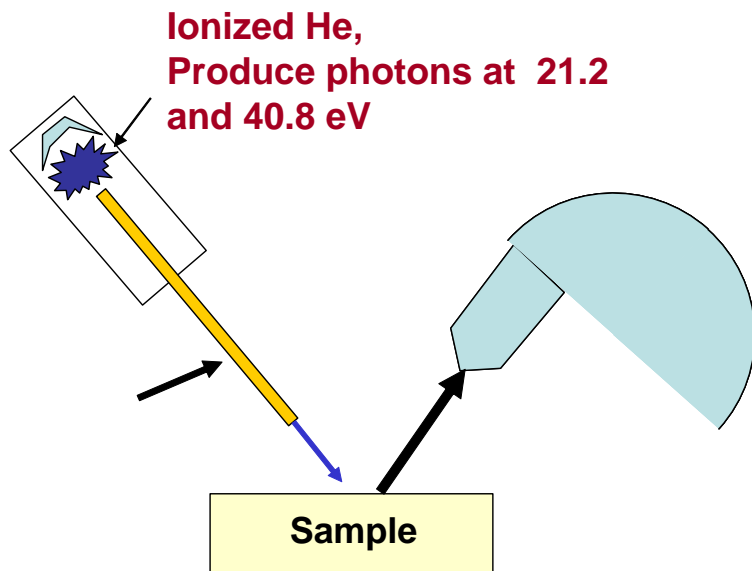
Ionized He, Produce photons at 21.2 and 40.8 eV

Sample

Figure 3.17: Schematic UPS spectrum of a d-metal and the corresponding density of states.

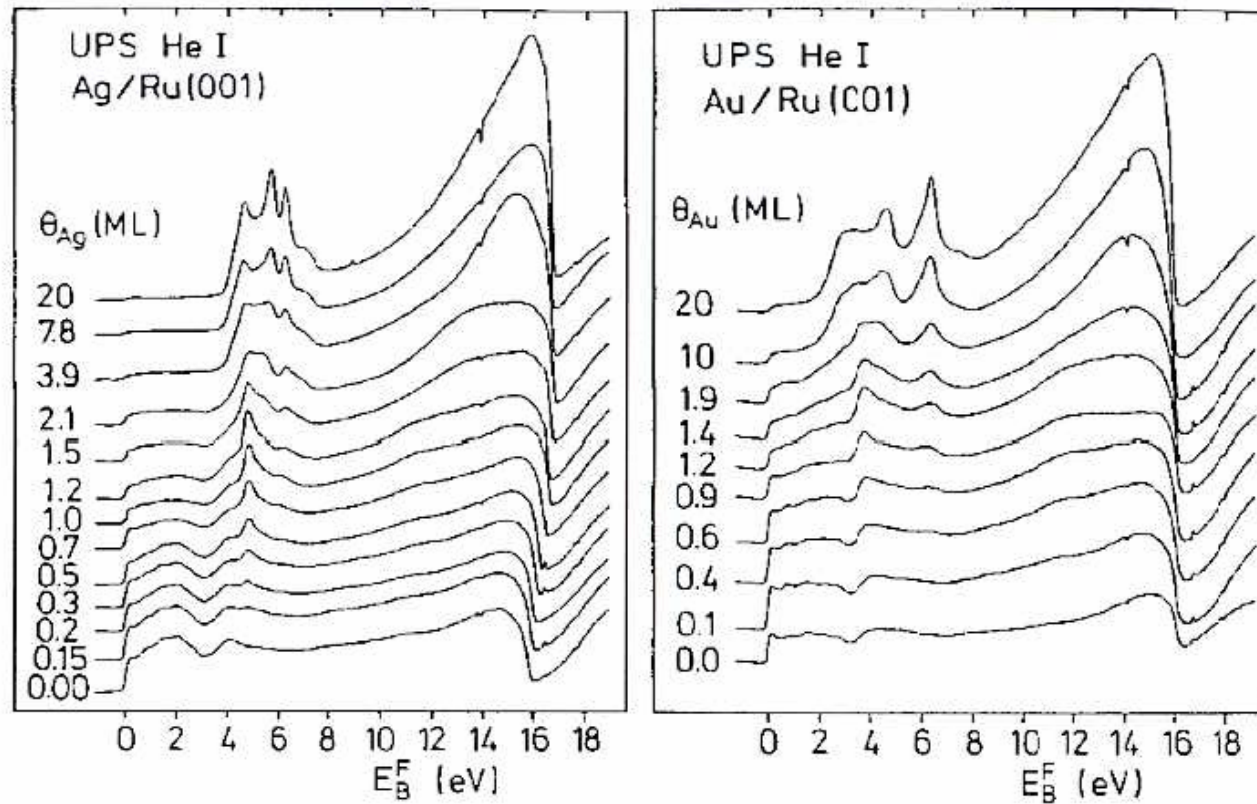# UPS Spectra of Ag/Ru(001) and AuRu(001)

Figure 3.18: UPS spectra of silver and gold layers on a ruthenium (001) substrate show the evolution of the d-band as a function of the silver dimensions. Note also the changes in work function reflected in the width of the spectra of Ag (courtesy of K. Wandelt, Bonn [47]).
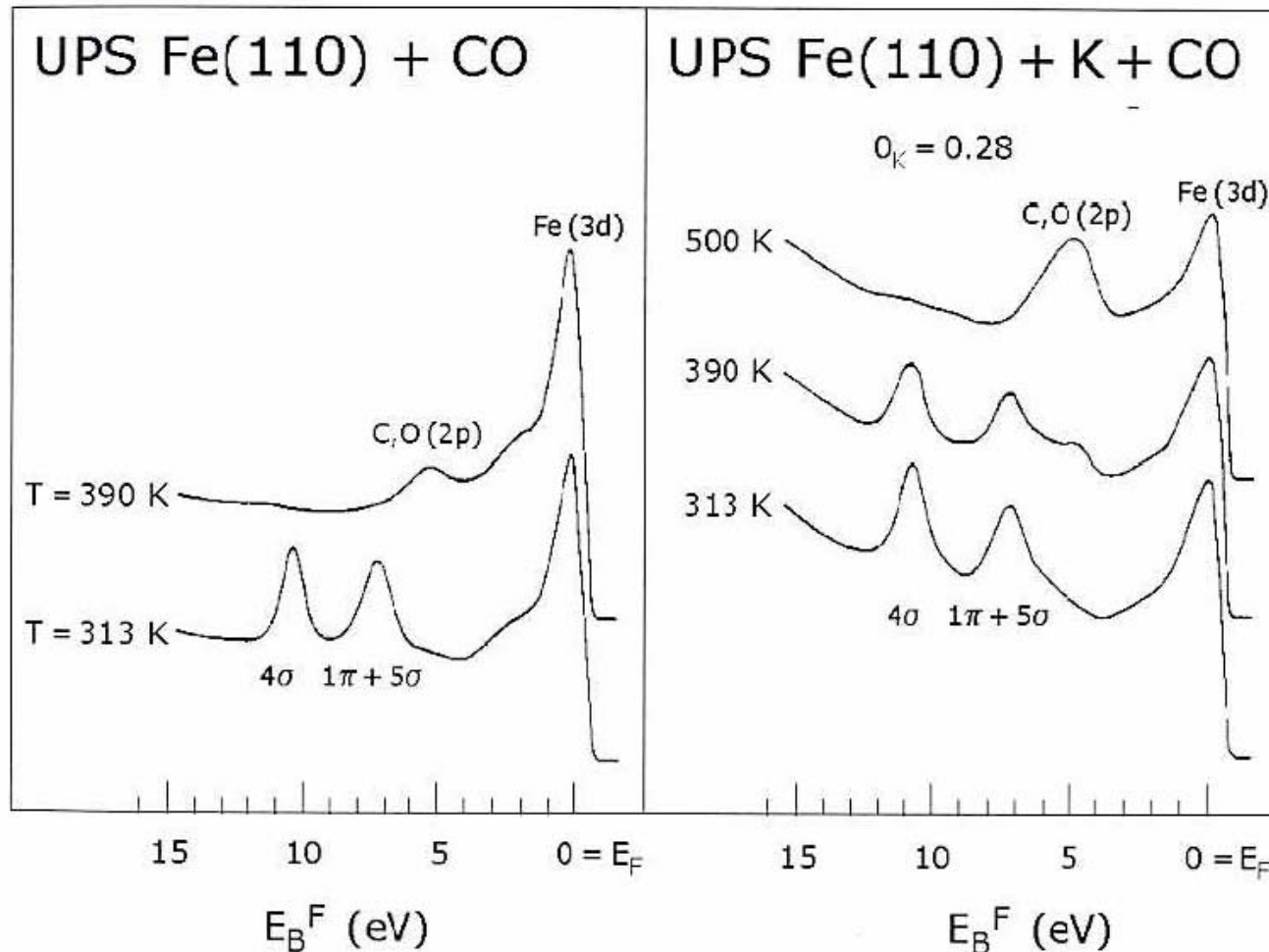
UPS Spectra of Adsorbates

Figure 3.20: UPS spectra of CO chemisorbed on iron show that the 5σ orbital has shifted down to higher binding energy as a result of chemisorption. CO largely desorbs from clean iron upon heating to 390 K. Potassium enhances the bond between CO and the metal and promotes the dissociation of CO at higher temperatures (adapted from Brodén *et al.* [51]).